Naturally Occurring Radioactive Material (NORM V)

Proceedings
of an international symposium
Seville, Spain, 19–22 March 2007

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NATURALLY OCCURRING RADIOACTIVE MATERIAL
(NORM V)

PROCEEDINGS SERIES

NATURALLY OCCURRING RADIOACTIVE MATERIAL (NORM V)

PROCEEDINGS OF THE
FIFTH INTERNATIONAL SYMPOSIUM ON
NATURALLY OCCURRING RADIOACTIVE MATERIAL
ORGANIZED BY
THE UNIVERSITY OF SEVILLE
IN COOPERATION WITH
THE INTERNATIONAL ATOMIC ENERGY AGENCY,
THE SPANISH NUCLEAR SAFETY COUNCIL
AND THE UNIVERSITY OF HUELVA
AND HELD IN SEVILLE, 19–22 MARCH 2007

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FOREWORD

All minerals and raw materials contain radionuclides of natural origin, of which the most important for the purposes of radiation protection are the radionuclides in the ^{238}U and ^{232}Th decay series and ^{40}K. For most human activities involving minerals and raw materials, the levels of exposure to these radionuclides are not significantly greater than normal background levels. Such exposures, while having been the subject of much research, are not of concern for radiation protection. However, certain activities can give rise to significantly enhanced exposures that may need to be controlled by regulation. Material giving rise to these enhanced exposures has become known as naturally occurring radioactive material (NORM).

Historically, most regulatory attention has been focused on the mining and processing of uranium ore, because such activities are a direct consequence of the radioactivity in the ore and form part of the nuclear fuel cycle. Over the past decade or two, however, more and more countries have introduced measures to regulate exposures arising from a wider range of natural sources, in particular minerals and raw materials other than those associated with the extraction of uranium. Two important developments in this regard were the publication of the International Basic Safety Standards for Protection against Ionizing Radiation and for the Safety of Radiation Sources (issued in 1996 as IAEA Safety Series No. 115) and the European Council Directive 96/29/Euratom of 13 May 1996, both of which contained provisions for protective measures against significantly increased exposures of workers and members of the public to natural sources.

As a direct consequence of the Euratom Directive and its possible implications for non-nuclear industries in Europe, a symposium on NORM, the first in the current series, was held in Amsterdam in 1997. The second in the series (NORM II) was held in 1998 in Krefeld, Germany, the third (NORM III) in Brussels in 2001 and the fourth (NORM IV) in Szczyrk, Poland in 2004. In addition, a symposium on Technologically Enhanced Natural Radiation was held in Rio de Janeiro in 1999, reflecting the growing interest within regions beyond Europe in the management of exposure to NORM. The close involvement of the IAEA in most of these symposia is reflected in the fact that the proceedings of the Rio de Janeiro and Szczyrk symposia have been published as IAEA-TECDOC-1271 and IAEA-TECDOC-1472, respectively. This involvement has been significantly expanded in the case of NORM V. The IAEA entered into a formal cooperation arrangement with the organizing body, the University of Seville, in terms of which the IAEA, in addition to publishing these proceedings, served on the steering committee and scientific committee of the symposium and provided financial support to several participants from Member States eligible to receive assistance under the IAEA Technical Cooperation Programme. These activities were undertaken as part of the IAEA's programme to promote the application of the safety standards, in this case with particular reference to natural sources of radiation, and to provide for the dissemination of information among Member States.

The NORM V symposium, which was attended by 200 participants from 40 countries, was held exactly one decade after the first symposium in the series and provided an important opportunity to review the many developments that had taken place over this period. It also coincided with various current initiatives to review and revise international recommendations and standards on radiation protection and safety. The proceedings contain all 37 oral presentations and four rapporteur reports, as well as a summary that concludes with the main findings of the symposium. Text versions of 46 poster presentations are provided on a CD-ROM which accompanies these proceedings.

The IAEA, on behalf of the organizer, the University of Seville, gratefully acknowledges the cooperation and support of all the organizations and individuals that have contributed to the success of this symposium.

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SUMMARY

1. BACKGROUND TO THE SYMPOSIUM

1.1. Objectives

Many technical and regulatory developments concerning exposure to naturally occurring radioactive material (NORM) have occurred during the ten years since the organization of the first in this series of symposia. This symposium, the fifth in the series, provided an important opportunity to review those developments, particularly the progress made in identifying, quantifying and managing the radiological risks associated with industrial processes involving NORM. It also provided a forum for discussing the way forward towards the achievement of a much needed internationally harmonized regulatory approach. This was particularly important in the light of current initiatives to revise the following major texts dealing with radiation protection and safety:

(a) The 1990 Recommendations of the International Commission on Radiological Protection (ICRP), published in 1991 as ICRP Publication 60;
(b) The International Basic Safety Standards for Protection against Ionizing Radiation and for the Safety of Radiation Sources (the BSS), published in 1996 as IAEA Safety Series No. 115;
(c) The European Council Directive 96/29/Euratom of 13 May 1996, laying down basic safety standards for the protection of the health of workers and the general public against the dangers arising from ionizing radiation.

The technical programme was well subscribed and comprised 37 oral and 50 poster presentations. To help realize the objectives of the symposium, arrangements were made in the programme for each day's presentations and discussions to be reviewed and summed up by a rapporteur. On the final day, the rapporteur's report included a review of the entire symposium and of the extent to which the objectives of the symposium had been met.

1.2. International aspects

The first NORM symposium, held in Amsterdam, Netherlands in 1997, had been organized in response to concerns within the non-nuclear industry in the European Union (EU) that the implementation of the Council Directive

96/29/Euratom would place unreasonable and unwarranted legal obligations on many industrial enterprises that handled and processed material containing low levels of radionuclides of natural origin. Subsequently, as new regulations for the control of exposure to NORM became established in EU Member States and as knowledge about the levels of exposure improved, those concerns diminished to some extent, although the definition of the scope of regulation remains controversial. Furthermore, it became apparent that this was becoming more of a global issue because of the increasingly international profile of the mining and minerals processing industry, with large quantities of minerals being mined and beneficiated in countries remote from Europe and shipped to other countries — often over vast distances — for further processing. In line with this trend, successive NORM symposia began to take on a more international flavour and the involvement of the IAEA became progressively greater.

Given this background, specific steps were taken during the planning of the NORM V symposium to encourage stronger participation from countries outside the EU:

(a) The steering committee arranged for broad international representation on the scientific committee of the symposium and encouraged the members of that committee to actively promote participation in the symposium from within their own geographic regions;
(b) The IAEA provided financial support to nine participants from Member States eligible to receive assistance under the IAEA technical cooperation programme.

These efforts were evidently successful in that the symposium attracted some 200 participants from 40 countries, far outstripping — in both respects — the participation in any of the previous symposia.

2. HARMONIZATION OF RADIATION PROTECTION STANDARDS AND REGULATORY APPROACHES

2.1. Key concerns

The keynote address delivered during the opening session of the symposium focused attention on the need for moving towards a harmonized approach to the management of exposure to NORM, especially given that minerals and raw materials are traded internationally on a very large scale and bearing in mind the opportunity provided by the current initiatives to revise international recommendations and standards. While there had been some progress towards harmonization at the international level, the question remained as to whether consensus on this matter was really being achieved. Even the definition of NORM itself was not universally agreed upon and there were different interpretations as to which exposures to NORM should be subject to the requirements for practices and which should be subject to the requirements for intervention.

Of particular concern were the numerous and significant inconsistencies between countries in the application of regulatory control measures. Instances were mentioned of countries extending the scope of regulation down to values of activity concentration that were five or ten times lower than those agreed upon in international forums. Several examples were quoted of severe disruption to international trade because of these inconsistencies, including some instances of imports of minerals being prohibited, even though their activity concentrations were sometimes well within the range for normal rocks and soil. It was also pointed out that a significant factor in all of this was the heavy reliance on modelling using hypothetical exposure scenarios to assess the exposures of workers and members of the public. Depending on the degree of conservatism adopted, these modelling assessments gave results that could differ by more than two orders of magnitude, leading to the possibility of false conclusions being drawn on the need for regulation. However, it was recognized that in the ten years that had elapsed since the first NORM symposium in this series, considerable progress had been made in improving the reliability of exposure assessments through the increasing use of facility specific measurements. It was hoped that this positive development would now lead to a more common understanding of the radiological risks involved and thus to a more harmonized regulatory approach.

2.2. The definition of NORM

Since all materials contain radionuclides of natural origin it was emphasized by several speakers that there is a need to distinguish between the few that require regulatory attention and the vast majority that do not. The fact that NORM is an acronym for ‘naturally occurring radioactive material’ had led to a tendency in some quarters for all minerals to be regarded as NORM, with the erroneous implication that they were therefore all radiologically hazardous and in need of regulatory control. One attempt to distinguish those materials that needed to be regulated had been to introduce the term TENORM, an acronym for technologically enhanced NORM, but it was pointed out on more than one occasion that this did not solve the problem and was potentially confusing because there was no direct correlation between the need for regulation and the application of any industrial process. The IAEA had addressed the issue by adopting only the term NORM in its safety standards while restricting the definition of this term to include only material that was radioactive in the regulatory sense (i.e. material that was subject to regulation because of its radioactivity) and not to include other material that was radioactive only in the scientific sense.

2.3. Practice or intervention?

The recommendations in ICRP Publication 60 utilize the concepts of practices and interventions for the purposes of defining the approach to radiation protection and, accordingly, the BSS is based firmly on these two concepts. However, for exposure to natural sources, the distinction between the two concepts has not always been clear, particularly where there are elements of both practices and intervention at the same site. This was the situation described in a paper from Nigeria relating to the assessment of exposures from tailings generated by the mining and processing of heavy mineral deposits. The need for remedial action was identified in order to reduce doses to the local population from residues from past, unregulated activities, while at the same time there was a need to establish appropriate levels of protection for ongoing operations, implying a need to achieve compliance with the 1 mSv dose limit for members of the public. The situation was further complicated by the fact that the local population was, on an informal basis and to an increasing extent, excavating the ore using simple tools and processing it in their backyards, raising the question of whether these individuals should be regarded as workers or members of the public for the purpose of radiation protection. It was stated in the presentation that the implementation of remedial measures (in accordance with the requirements for intervention) would be followed by full or partial implementation of radiation protection measures for practices.

A further example of the ‘grey’ area between practices and intervention was illustrated in a paper from the European Commission. The European Council Directive 96/29/Euratom requires that work activities involving the (unintended) presence of natural sources and leading to significantly increased exposures are subject to all or part of the requirements for both practices and interventions, as necessary. This was reported to have led to different regulatory approaches in different European Member States. As a consequence, in the revision of the Euratom Directive, consideration was being given to defining more precisely those NORM activities that should be regulated as practices, with the regulatory requirements for such activities then being essentially the same as those for practices involving exposure to radionuclides of artificial origin. A so-called ‘positive list’ of work activities involving NORM was being proposed, specifying those work activities that require the attention of the regulatory body. If a NORM activity was not on the list the regulatory body would not need to be notified. This list was very similar to a list in IAEA Safety Reports Series No. 49, Assessing the Need for Radiation Protection Measures in Work Involving Minerals and Raw Materials, which specified the industry sectors most likely to require some form of regulatory consideration. The similarity between these lists was an example of how an improved understanding of the radiological risks from NORM had led to a convergence of views on where regulatory attention should be focused.

During the keynote address, attention was drawn to the approach adopted in the BSS whereby exposures to natural sources are generally subject to the requirements for intervention but that certain exposures are, by exception, subject to the requirements for practices. These exceptions are listed in the BSS as public exposures to discharges and radioactive waste arising from practices involving natural sources, certain occupational exposures to radon, and any other occupational exposures specified by the regulatory body. Although the last mentioned exception involves judgement by the regulatory body, attention was drawn to the guidance provided in a related IAEA Safety Guide, which states that it is usually unnecessary to regulate (as a practice) material in which the activity concentrations are below 1 Bq/g for uranium and thorium series radionuclides and 10 Bq/g for ^{40}K. It was reported that, in accordance with General Conference Resolution GC(48)/RES/10 of September 2004, these activity concentration criteria are now being proposed for inclusion in the revised version of the BSS as ‘entry levels’ for the application of the requirements for practices.

It was emphasized that the activity concentration criteria of 1 and 10 Bq/g are order of magnitude values (in line with the approach taken already for exemption values in the BSS and the Euratom Directive) and are not based on dose considerations, but rather on the upper bound of activity concentrations in the natural environment, as reported by the United Nations Scientific Committee on the Effects of Atomic Radiation (UNSCEAR). The values are intended to be used either to define the scope of national regulations or to define what should be regarded as radioactive material for the purpose of such regulations. In addition, they can be used to determine whether material from within a practice can be released from regulatory control. In the presentation from the European Commission, it was reported that the same criteria were being considered for adoption into the revised Euratom Directive. In the final rapporteur presentation of the symposium, it was concluded that these criteria were becoming increasingly supported, albeit with a few reservations for specific exposure situations, and that their adoption was the most viable way forward towards a harmonized regulatory approach.

It was also pointed out that the transport of radioactive material, including NORM, is a practice that is subject to the requirements of the Regulations for the Safe Transport of Radioactive Material (IAEA Safety Standards Series No. TS-R-1), commonly referred to as the Transport Regulations. However, in the case of "natural material and ores containing naturally occurring radionuclides that are either in their natural state, or have been processed only for purposes other than for the extraction of the radionuclides, and that are not intended to be processed for use of these radionuclides", these regulations do not apply unless the radionuclide activities or activity concentrations exceed certain values specified in the regulations. For ^{238}U and ^{232}Th in equilibrium with their progeny the applicable value of activity concentration is 10 Bq/g. However, there was a lack of clarity on what exactly was meant by the term 'natural material' and this was raised as a concern on more than one occasion. For instance, a zirconia refractory is a product, for industrial use, manufactured from zirconia raw material — was this product a natural material or not? The symposium concluded that, for the purpose of safety in transport, there was no sense in differentiating between raw materials and those same materials after they had been processed into 'objects', but the Transport Regulations could be interpreted as meaning that the latter no longer fell within the definition of natural material. Consequently, a strong plea was made for the standards to be clarified accordingly.

2.4. Criteria for exemption

As mentioned in Section 2.2, for the purposes of international standards the IAEA had chosen to define NORM as material containing radionuclides of natural origin at levels that require it to be subject to regulatory control. Except for certain commodities (e.g. foodstuffs, drinking water and building materials) and residues in the environment, this regulatory control would be implemented in accordance with the requirements for practices. However, it was emphasized on several occasions that for NORM it was especially important to apply a graded approach to the regulation of practices because the radiological risks vary over a wide range, depending on the type of practice, and are often very low. The first level of this graded approach was a regulatory decision that the optimum regulatory option was not to apply regulatory requirements to the legal person responsible for the material, i.e. to grant an exemption. It was encouraging to note from the presentations and discussion that there now seemed to be unanimous recognition that the so-called 10 μSv criterion for exemption (the criterion of 'trivial dose') was not appropriate for activities involving NORM and that a value of the order of 1 mSv in a year was more likely to be consistent with the optimum use of regulatory resources. Many countries mentioned, either directly or by implication, that the value of 1 mSv was indeed being used as an exemption level and in the final rapporteur presentation it was concluded that this was now commonplace as a de facto NORM standard. For example, it was reported that in Germany, “Control of residues [from industrial processes with enhanced natural radioactivity] is required if the processing or disposal of these residues could result in the reference effective dose of 1 mSv in a calendar year being exceeded”. The European Commission reported that exemption criteria of 1 mSv in a year for occupational exposure and 0.3 mSv in a year for public exposure were being considered for adoption into the revised Euratom Directive.

The European Commission also reported on a proposal to incorporate into the revised Euratom Directive certain criteria for radionuclides of natural origin in building materials. These criteria, which are currently published only as guidance, are expressed in terms of incremental dose from gamma radiation. Building material giving rise to a dose not exceeding 0.3 mSv per year would be exempt from all restrictions. In connection with this, the concept of an activity index based on the activity concentrations of ^{226}Ra, ^{232}Th and ^{40}K was proposed as a screening tool for identifying materials that might be of concern.

It was mentioned on more than one occasion that there were currently no universal exemption criteria expressed in terms of activity per unit surface area. This was an issue affecting decisions on the removal from regulatory control of items whose surfaces were contaminated by NORM, for example pipes and other equipment from the oil and gas industry. One presentation highlighted the fact that not only were there differences in numerical values between countries, but also differences in the choice of parameter, e.g. beta activity concentration, alpha activity concentration, a combination of beta and alpha activity concentrations, or the activity concentrations of individual radionuclides. It remains to be seen whether it would be feasible to develop universally applicable exemption/clearance levels for surface contamination with respect to NORM.

3. INDUSTRIAL PROCESSES INVOLVING NORM

The scope of the symposium was intended to be focused on important NORM industry sectors (other than the mining and extraction of uranium) that had received less attention in the past or that were associated with issues of particular topical interest. Consequently, dedicated sessions were organized for the following six industry sectors:

(1) Thorium and its industrial applications;
(2) Processing and use of zircon and zirconia;
(3) Production of titanium dioxide pigments;
(4) Monazite and the extraction of rare earths;
(5) Extraction, processing and use of phosphate minerals;
(6) Scrap recycling and waste management.

Except for the session on thorium, each session started with an invited overview paper in order to set the scene. The papers were delivered by experts from India, South Africa, Spain, the United Kingdom and the United States of America. Information was presented on industrial processes, exposure levels and radiation protection measures, as follows:

(a) The presentations dealing with the zircon/zirconia, titanium dioxide and phosphate industry sectors provided summaries of information that is currently being incorporated into IAEA safety reports. In the case of zircon/zirconia and titanium dioxide, this information represents the first comprehensive review of the radiological aspects of these industry sectors.
(b) The phosphate industry is a much broader topic, and the radiological aspects of the main processes have been studied in some detail over many years. Consequently, the presentation on the phosphate industry focused only on the wet acid processing route, which is the dominant production mode for phosphoric acid and its derivative fertilizers. Using inhalation dose characterization as an example, it highlighted the need for a global initiative to establish benchmark data that would lead to greater reliability in estimating radiological hazards and thus reducing the tendency for over-regulation. For instance, personal monitoring programmes persist at facilities throughout the world despite the fact that in many cases they achieve no practical benefit and the facilities would qualify for the lowest level of the graded approach, i.e. no regulation necessary.
(c) The presentation on monazite and the extraction of rare earths was of particular interest because this industry sector is characterized by exposure levels that are generally higher than those found elsewhere, the chemical extraction processes are rather specialized and consequently not widely understood, and significant quantities of waste with relatively high activity concentrations are generated and have to be managed accordingly.
(d) The presentation on scrap recycling described a voluntary protocol that had been established in Spain through cooperation between representa-

tives from government and industry and that had now been in operation for eight years. The success of the protocol was demonstrated by the fact that, through this constructive and cooperative approach, Spain had now achieved international prominence in the control of radioactive materials (including NORM) in scrap.

In addition to these dedicated sessions, two ‘miscellaneous’ sessions were organized, in which other NORM industry sectors such as the production of iron and steel, the extraction of oil and gas, the processing of bauxite, and the mining of copper were covered.

4. DOSE ASSESSMENTS AND THEIR LIMITATIONS

4.1. Doses received by workers

Comparisons of the results of various dose assessments for workers were highlighted in the symposium. These comparisons revealed large discrepancies due to differences in parameter values used in the calculations. Facility specific measurements were replacing generic assumptions to an increasing extent, leading to a better appreciation of the overestimation that could result from the use of unrealistic assumptions. Such overestimation could in turn lead to false conclusions being drawn on the need for and extent of regulation. The following examples were mentioned during the keynote address:

(a) Processing of phosphates: doses overestimated by up to 86 times;
(b) Processing and use of zircon/zirconia: doses overestimated by up to 2000 times;
(c) Extraction of rare earths from monazite: doses overestimated by up to 1200 times;
(d) Production of titanium dioxide pigments: doses overestimated by up to 1500 times.

Further examples came to light during other presentations. Assessments reported from Germany and Spain, based on the assumption of a 2000 h annual exposure period, gave the following comparisons with assesments reported elsewhere based on actual exposure periods:

(1) External gamma doses in zircon storage facilities: 1.0–3.3 mSv/a (2000 h) compared with 0.25–0.28 mSv/a (actual);

(2) Dust inhalation in zircon milling operations: 0.5–2 mSv/a (2000 h) compared with 0–0.7 mSv/a (actual).

In the presentation from the USA on wet acid phosphate processing, it was reported that earlier estimates of worker inhalation doses based on assumed dust parameter values (activity mean aerodynamic diameter, activity concentration and particle solubility in lung fluid) gave annual doses of 2.85–5.60 mSv, whereas more recent calculations based on measured values of these parameters gave doses “well below 1 mSv/a”, even for phosphate rock with activity concentrations at the upper end of the range of activity concentrations found in commercially exploited material.

The results of various dose assessments reported during the course of the symposium are summarized in Table 1 and provide further confirmation of the general conclusions from previous work involving occupational exposure to NORM. For most of the industrial processes concerned, worker doses were generally too low to warrant regulatory control, especially when taking into account the effects of normal occupational health and safety measures such as respiratory protection in dusty areas. One notable exception was the industry sector dealing with monazite and extraction of rare earths, where significant doses could be received by workers as a result of the high thorium content of monazite and the nature of the processes involved.

The production of thorium-containing gas mantles was also identified as potentially giving rise to exposures of regulatory concern, although it was pointed out that the use of thorium in most industrial applications, including gas mantles, was being phased out as substitutes became available. Thorium was still regarded as essential for the production of high intensity discharge lamps and, to some extent, of TIG welding rods, but the doses associated with these applications were too low to be of regulatory concern. In the case of TIG welding rods, some substitution for thorium was already occurring and the Swedish authorities were reported to be considering steps to encourage a more rapid change to new materials.

4.2. Doses received by members of the public

Several presenters reported on the results of public exposure assessments. A summary of these results is given in Table 2. The assessments were generally regarded as conservative; nevertheless, the doses were in most cases found to be only a small fraction of a millisievert. The highest doses were those calculated for the future use of landfill disposal sites, either in controlled situations (authorized industrial use) or uncontrolled situations (intrusion), but even in these situations the doses were significantly below 1 mSv.

TABLE 1. SUMMARY OF WORKER DOSES REPORTED IN THE SYMPOSIUM

	Annual effective dose (mSv)		
	Minimum	Typical	Maximum
Production of gas mantles	~1		~10
Gas lantern maintenance		~0.2	
Storage of TIG welding rods		~0.002	
Manual TIG welding			0.15
Robotic TIG welding		Negligible	
Thorium-containing lamps		Negligible	
Recycling of thorium electrodes (TIG welding and lamps)			0.3
Bulk storage of zircon	0.25		0.28
Zircon milling		0.8[a]	
Production of zirconia by thermal processing of zircon	0.7		3.1
Production of zirconia, zirconium chemicals and zirconium metal by chemical processing of zircon	0.5		1
Manufacture of ceramics containing zircon or zirconia	0.01		1
Manufacture of refractories containing zircon or zirconia	0.05		0.8
Use of zircon in foundries			0.5
Manufacture of cathode ray tubes containing zircon			0.4
Manufacture of zirconia-containing abrasives			1
Bulk storage of ilmenite	0.03		0.08
Manufacture of titanium dioxide pigments			1[b]
Separation of heavy minerals from monazite-containing ores[c]	~1		7
Chemical extraction of rare earths from monazite	3		9
Manufacture of phosphate fertilizer, wet acid process (dust)	0.02		0.8
Manufacture of phosphate fertilizer, wet acid process (gamma)			0.8

TABLE 1. SUMMARY OF WORKER DOSES REPORTED IN THE SYMPOSIUM (cont.)

	Annual effective dose (mSv)		
	Minimum	Typical	Maximum
Elemental phosphorus production		1	
Refurbishment of oil extraction equipment	0		0.93
Melting of thorium-containing scrap metal			0.3
Separation and fractionation of natural gas	0		0.02
Production of ethylene and polyethylene from natural gas	0		1.6

[a] Higher doses, up to 3.3 mSv, were reported but were based on an assumed annual occupancy of 2000 h rather than the actual occupancy (see comments in the text).

[b] For the sulphate process, the annual dose in the hydrolysis and Moores filtration areas could be up to 6 mSv in the absence of controls.

[c] In addition, worker doses estimated using conservative assumptions to be potentially in the range 8–125 mSv/a were reported for a heavy minerals separation plant in Brazil, principally due to dust inhalation, but these estimates were made prior to the implementation of actions that significantly reduced exposures.

As in the case of occupational exposures reported in Section 4.1, these results provide further confirmation of the general conclusions from previous work involving exposure to NORM. Furthermore, some presenters again drew attention to discrepancies in the results of dose calculations due to differences in the assumptions used in various dose calculations, as illustrated by the following examples:

(a) A presentation from South Africa reported on the results of a public dose assessment conducted for a large mining and minerals processing complex. Dose contributions from inhalation (dust, radon and thoron) and ingestion (foodstuffs and drinking water) were calculated for groups of individuals at nine locations in the vicinity of the complex. The results of an initial, conservative assessment indicated that the annual doses received by individuals in these groups varied from 0.058 to 0.254 mSv. Although these doses were already rather low, the assessment was repeated using more realistic assumptions regarding airborne dust levels, amounts of local food consumed, the agricultural use of the land and the extent of groundwater utilization. For three of the nine groups the doses remained the same, but for the remaining six groups the doses were found to be substantially reduced — in some cases more than 90% lower.

TABLE 2. SUMMARY OF PUBLIC DOSES REPORTED IN THE SYMPOSIUM

	Annual effective dose (mSv)		
	Minimum	Typical	Maximum
Zircon milling	0.00001		0.32
Production of zirconia by thermal processing of zircon		0.037	
Chemical processing of zircon		Negligible	
Stack emissions from a ceramic tile plant (per caput)			0.0001
Use of glazed tiles containing zircon	0.009		0.113
Stack emissions from a zircon refractories plant			0.0001
Zirconia in cathode ray tubes		Negligible	
Titanium dioxide pigment manufacture		Negligible	
Mining and beneficiation of phosphate rock	0.017		0.021
Thermal phosphorus production		0.001	
Use of phosphorus slag for road construction	0.001		0.06
Mining and beneficiation of copper ore and phosphate rock			0.2
Disposal of red mud from bauxite processing		0.01	
Landfill, off-site resident			
Disposal of zircon foundry sand		0.0006	
Landfill, use of land for industrial purposes			
Use of tin slag for land reclamation			0.45[a]
Landfill, intrusion following loss of control			
Disposal of used zircon foundry sand	0.002		0.13
Disposal of zircon fusion dust		0.0045	
Disposal of zircon chemical processing waste		0.75	
Disposal of zircon refractories plant waste	~0.001		~0.01

[a] Maximum dose received by workers on the reclaimed site.

(b) During the keynote address, attention was drawn to an issue of public exposure in connection with the 1 Bq/g activity concentration criterion for uranium and thorium series radionuclides in materials, below which it was generally considered unnecessary to regulate (see Section 2.3). Although this criterion had not been derived using a dosimetric approach, it had nevertheless been accepted at the time of adoption that it was generally consistent with a maximum dose of about 1 mSv except, possibly, where the material was used for construction of dwellings. This was now being questioned in the light of modelling results reported from Germany, which predicted that an adult residing next to a mine residue deposit with an activity concentration of 1 Bq/g could receive an annual dose via the drinking water pathway of nearly 6 mSv, while for a child of 1–2 years the dose would be more than 10 mSv. However, a similar modelling exercise based on more realistic assumptions supported by measured data predicted annual doses of only 0.05–0.1 mSv for both adults and children. This large discrepancy underlines the need for caution when using modelling predictions as the basis for determining the need for regulation.

5. DISCHARGES TO THE ENVIRONMENT

Several presentations reported on liquid and aqueous discharges from mining and mineral processing operations, including data from various environmental measurements made in the vicinity of specific industrial facilities. In every case, the radiological impact was reported as being insignificant or zero. It was clear from the presentations that environmental regulations played a major role in ensuring that pollutants, including radionuclides, were to a large extent removed before discharge. The increased recycling of water and/or the use of various effluent treatment techniques such as neutralization, settling and precipitation were mentioned in connection with a wide range of industrial facilities, including the mining of copper, the chemical processing of zircon, the production of titanium dioxide pigments, the extraction of rare earths from monazite and the production of iron and steel. In many cases, the radionuclide content of the discharged water was similar to local environmental levels. At a mineral sands processing plant in Brazil, it was reported that the radionuclide concentrations in the liquid effluent from the hydrogravimetric concentration process were actually lower than those found upstream of the discharge point.

The overview paper on monazite and the extraction of rare earths provided information from India on the discharges associated with the chemical extraction process. This information was of particular interest because the radionuclide activity concentrations in various process materials are unusually high throughout the extraction process and the quantities of liquid effluent produced are large (15 m^3 per tonne of monazite processed). It was reported that before treatment the acidic and alkaline effluent streams contain ^{228}Ra at concentrations of several hundreds of becquerels per litre. Following the treatment and mixing of these streams, the radionuclides are co-precipitated with calcium phosphate. Discharge of the supernatant liquid to a river is then carried out in compliance with authorized discharge limits. As a result of improved effluent management at one plant over the past 20 years, the activity in the water and sediment had shown a reduction of 3–4 times and the dose received by a member of the public via the fish consumption pathway was negligible. It was also reported that gaseous and airborne particulate emissions from the plant were well below the applicable discharge limits and the environmental impact of these emissions was insignificant.

Treated water discharged from a copper mining operation in Zambia was reported to have very low radium activity concentrations (from <0.03 to about 0.04 Bq/L). The radium concentrations in the suspended solids were also very low at about 0.06–0.08 Bq/g. In view of these results, it was interesting to learn that unacceptable pollution was nevertheless considered to be taking place because the Zambian legal limit for discharge of radioactivity to the environment was zero.

Protection of the environment was the subject of a paper from Norway, which described a project being undertaken to establish safe limits for the discharge of formation water from oil and gas facilities in the North Sea. This water contains enhanced concentrations of ^{226}Ra, ^{228}Ra and other radionuclides of natural origin. The discharge limits are to be established on the basis of doses received by marine biota as well as humans. Reference organisms have been chosen for this geographical area for the purpose of modelling activity concentrations in sea water and biota and calculating doses. A conceptual model of radiological responses of organisms, populations and ecosystems has been proposed. It was suggested that the discharge limit should be based on an absorbed dose to biota of 5 mGy/h.

6. USE, REUSE AND RECYCLING OF NORM RESIDUES AND NORM CONTAMINATED ITEMS

6.1. Regulatory approach

Several presentations referred to options for use, reuse and recycling as a means for reducing the quantities of material that need to be disposed of as NORM waste. In Europe in particular, this was starting to be reflected in standards and regulations. It was reported from the European Commission that a proposal had been made to incorporate into the revised Euratom Directive specific provisions for the reuse and recycling of residues, including provision for authorizing their dilution with non-radioactive material where this was identified as the optimum option. It was reported from the Netherlands that the option of recycling or recovery is explicitly mentioned in Dutch regulations and that the general approach was to give priority to identifying by-products that could be safely developed out of NORM residues using the principle of dilution with non-radioactive material where necessary.

In a presentation on the international project Stack Free by 53? Beneficial Uses of Phosphogypsum, it was pointed out that since 1992, the United States Environmental Protection Agency (EPA), concerned about potential risks from the radioactivity in phosphogypsum, has defined this material as a toxic waste, with containment in stacks as the only acceptable management and disposal method for most of the material, despite the fact that large quantities of phosphogypsum can be safely put to beneficial use. This decision by the EPA was reported to have had a strong impact on the rest of the world's perceptions of phosphogypsum and its regulatory regimen. One case in point highlighted in the presentation was the suspension of the traditional practice in Spain of spreading phosphogypsum on local soils both for reclamation and as a fertilizer, as a result of an injunction sought by local environmental groups. The case was based partly on invocation of EPA standards. It was reported that the local farmers challenged the injunction and were granted relief, enabling the practice to resume on condition that close monitoring of potential environmental impacts and plant take-up was maintained. The monitoring results have demonstrated that the use of phosphogypsum in this way is safe and beneficial, with the result that it is now registered under Spanish law as a fertilizer. A further benefit is that a former phosphogypsum stack has now been reclaimed for a public park in a densely populated area..

6.2. Uses of phosphogypsum as a co-product of phosphate fertilizer production

It was reported that one outcome of the work undertaken so far in connection with the 'Stack Free' project mentioned in Section 6.1 was that more than 50 beneficial uses of phosphogypsum had been identified, of which the top four with respect to potential volumes of use are agriculture, construction materials, landfill management and roads. The scale of potential use could result in a significant reduction of new phosphogypsum tonnage and even, in suitable settings, the removal of stacks altogether. Symposium participants were informed that the activities under this project and the activities of the IAEA in developing and implementing international safety standards are now being coordinated and combined, with one important aim being to generate the following sequence of tiered publications designed to negotiate the basis for a transparent, safe practice of phosphogypsum use:

(a) A Safety Report on radiation protection and NORM residue management in the phosphate industry;
(b) A 'white paper' on good phosphogypsum management practices;
(c) A set of manuals, with associated management aids and decision support tools, that will address to a level of operational detail topics such as phosphogypsum in road beds and, where possible, will be coupled with training and support systems that effect and support knowledge transfer.

A presentation by the University of Seville described work carried out to assess the agricultural use of phosphogypsum as a calcium amendment in reclaimed salt marsh soils in south-western Spain. The work investigated the concentrations of radionuclides and heavy metals in phosphogypsum, their effect on soils and drainage waters and their transfer from soil to plants. The results showed that, although some of the environmental impacts of radionuclides and heavy metals in the phosphogypsum were measurable:

(1) Radon exhalation rates remained within the range of reference values for typical agricultural soils;
(2) Concentrations of radionuclides and heavy metals in the soil remained within the range of typical environmental values;
(3) Radionuclide concentrations in drainage waters remained close to the standards for drinking water;
(4) The contamination of foodstuffs by radionuclides and heavy metals was inconsequential.

It was concluded that the beneficial use of phosphogypsum as a soil amendment, which has been practised for the last 30 years in the area concerned, could continue safely for several decades in compliance with current safety regulations.

6.3. Uses of NORM residues as filling materials for construction

In a presentation from Sweden it was reported that blast furnace slag from the steel industry, with a ^{226}Ra concentration of 0.25 Bq/g, is used as a filling material for construction of roads and buildings, although in the case of the latter, preventive measures are recommended to ensure that indoor radon concentrations do not exceed 200 Bq/m^3. In addition, burnt alum shale, found in former alum shale mining areas in Sweden, has been extensively used as a filling material for construction of tennis courts and sports grounds, while its use as filling material for housing construction had proved unsuitable due to high indoor radon concentrations. In Malaysia, the use of 85 000 t of tin slag with a ^{226}Ra concentration of more than 4 Bq/g was reported to have been approved for reclaiming a swampy area for light industrial use on the basis of a dose assessment that predicted, conservatively, a maximum annual effective dose of 0.45 mSv to a worker on the site.

6.4. Use of red mud as a building material component

It was reported from Germany that efforts to identify industrial uses for red mud — a bulk residue from bauxite processing — had not produced any positive results. However, in a paper from Hungary it was reported that, from the point of view of gamma radiation, red mud would be considered acceptable for use as a component of building material, for instance bricks, if used as an additive (maximum 20 wt%) to other materials. In most manufacturing processes these materials would include, in addition to clay, components such as sawdust and polypropylene pellets to improve the porosity, strength and thermal insulation. It was shown that by increasing the firing temperature to above 800°C and optimizing the use of additional materials, for instance adding sawdust at 15–25 wt%, the radon emanation coefficient could be reduced by up to 80%.

6.5. Recycling and reuse of NORM contaminated materials and equipment

Several presentations referred to the recycling of equipment from the oil and gas industry, where metal items such as pipes, vessels, pumps and valves become contaminated with scale containing radium, sometimes at high concentrations. Two basic recycling options were mentioned:

(1) Melting of the contaminated items at a dedicated recycling facility;
(2) Decontamination of the items by washing and/or mechanical techniques to render them suitable for reuse or for recycling in a conventional melting facility.

The first option was addressed in a paper from Germany, which described the radiological conditions in a dedicated melting facility for contaminated metal scrap. It was pointed out that the nature of the contamination of oil and gas industry equipment could be both radioactive (up to about 1000 Bq/g ^{226}Ra) and chemical (mostly mercury) and that only about 50% of the scrap was radioactively contaminated. The German facility was also used for melting scrapped welding electrodes and lighting elements containing ^{232}Th at activity concentrations of 12–15 Bq/g. As reported in Table 1, annual effective doses received by workers in the facility did not exceed 0.3 mSv.

With regard to the second option, decontamination of oil industry equipment contaminated with scale with ^{226}Ra and ^{228}Ra activity concentrations of up to 1670 Bq/g was addressed in a paper from Argentina. As reported in Table 1, annual effective doses received by workers at the facilities concerned were estimated to be less than 1 mSv.

The invited paper from India on mineral sands separation and chemical extraction of rare earths made reference to contaminated materials and equipment arising from the decommissioning of extraction facilities. As mentioned in Section 3, the relatively high concentrations of thorium decay series radionuclides in the monazite feedstock leads to similarly high concentrations in other materials throughout the process, implying that the recycling and reuse of materials and equipment needs to be approached with care. It was reported that large surface contaminated items such as tanks were decontaminated so that they could be recycled in conventional melting facilities. Filters, electrical fittings and pipes were also decontaminated (by washing) and then recycled in conventional melting facilities or reused. Contaminated structural material and floor and wall cement plaster chippings were not recycled however — they were instead disposed of as NORM waste either in earthen trenches or engineered cells, depending on the degree of contamination.

The invited paper from Spain on scrap metal recycling (see Section 3) highlighted some important realities with regard to the control of radioactive contamination in the recycling of scrap metal at conventional melting facilities. Because of the serious consequences of radioactive sources such as ^{137}Cs being inadvertently melted, a high degree of public and political sensitivity had been generated on the issue of radioactivity in scrap. This sensitivity could be expected to apply equally to radioactivity introduced through NORM contamination. Since the implementation of a control protocol in Spain, it had been found that 43% of all radioactivity detections at the entrances to scrap recycling facilities were due to NORM. In what would appear to be a practicable and effective approach to the implementation of the protocol, the action taken in response to a detection was determined in the first instance on the basis of dose rate measurements, irrespective of whether the radionuclide concerned was of artificial or natural origin. For NORM, this should ensure that highly active contaminants such as pipe scales are identified and dealt with appropriately.

7. CONDITIONING, STORAGE AND DISPOSAL OF NORM WASTE

7.1. Bulk mining and mineral processing waste

Several references were made to the large quantities of low activity tailings produced in various types of mining and beneficiation operations and the need for their containment. A presentation from South Africa referred to the radiological impacts on the public of mine residue deposits from a copper and phosphate mining and beneficiation complex (see Section 4.2). Another presentation referred to tailings from mineral sands separation in India, most of which have activity concentrations below 1 Bq/g and are returned to the dredged area and used as backfill.

Even for countries with little or no mining activity, examples were given of the need to dispose of large quantities of low activity residues from mineral processing operations. It was reported from the Netherlands that bulk mineral residues containing low concentrations of radionuclides of natural origin are disposed of in existing hazardous waste repositories (surface containments) with only minor additional measures being needed to take care of the radiological aspects. Several papers referred to the disposal of bulk quantities of red mud (e.g. 900 000 t/a in Germany). The residue was described as chemically stable and non-toxic, with radionuclide activity concentrations well below 1 Bq/g. It was reported from Germany that red mud is disposed of in special fenced off areas in accordance with national disposal regulations. Investigations at a large disposal site revealed negligible impact on surface water and groundwater. Internal exposure of members of the public via dust inhalation was also found to be trivial. A modelling exercise based on the results of leachability measurements was applied to a red mud disposal site in Eastern Europe. It was concluded that the migration of radionuclides is restricted to the immediate vicinity of the disposal site and that there is little or no impact on groundwater or agricultural products. Similar results were obtained for bulk residues from coal mining and coal fired power generation facilities in the same region. The hazard from heavy metals and organic compounds was stated to be greater than that from radioactivity.

Although the radiological impact of these bulk wastes has repeatedly been shown to be very low when they are suitably contained, it was pointed out in a presentation on phosphogypsum residues that the huge volumes of phosphogypsum already contained in stacks (and still being generated) could have very significant cost implications at the time of final closure, particularly for older designs of containment. Aside from the aspects of financial liability, it was also pointed out that there is growing concern that, even in terms of safety and environmental legacy, the stacking of phosphogypsum may not be the best long term solution when, as an alternative, phosphogypsum can be put to various uses as a by-product.

7.2. Waste designated for disposal in landfill facilities

Several references were made during the course of the symposium to the use of landfill facilities for the disposal of NORM waste containing moderately elevated levels of uranium and thorium series radionuclides. Examples quoted in connection with the processing and use of zircon and zirconia include the following:

(a) Waste zircon sand;
(b) Precipitates from liquid effluent treatment in the chemical processing of zircon;
(c) Waste refractory materials containing zircon or zirconia;
(d) Used investment casting shells, cathode ray tubes, oxygen sensors, abrasive products.

Examples quoted from the titanium dioxide pigment industry include neutralized metal chloride impurities from the chloride process and digester residue from the ilmenite based sulphate process.

Generally, the landfill sites concerned were facilities for conventional (i.e. non-radioactive) industrial waste and subject to normal waste disposal controls. It was noted that in some cases the presence of other harmful contaminants in the waste (for example heavy metals in some used refractory linings) require the site to be specially designated for hazardous waste.

7.3. Scales and sludges

It was reported that scales and sludges from certain mineral processing operations exhibit radium activity concentrations of up to several thousand becquerels per gram. The management of these wastes in the Netherlands was described. Filter bags containing the scales and sludges are sent to a dedicated waste storage facility where they are compacted by shredding and immobilized with cement before being stored in 100 L drums. At that same facility, sludges from the oil and gas industry containing mercury and organic compounds are subjected to a specialized drying operation to evaporate the water and separate mercury, following which the material undergoes further treatment before being packaged for storage in drums. Scales and sludges arising from processes other than oil and gas extraction were mentioned during the course of the symposium. These included:

(a) Scale from the chemical processing of zircon (^{226}Ra up to 5000 Bq/g);
(b) Radium rich sludges from the production of zirconium metal;
(c) Scale from the sulphate process for titanium dioxide pigment production;
(d) Scale rich in ^{228}Ra from the chemical extraction of rare earths from monazite;
(e) Pipe scale from paper manufacturing facilities;
(f) Used filters from the treatment of drinking water.

It was evident that in many countries suitable regulations and disposal facilities for these types of waste had not yet been established.

7.4. Solid wastes from rare earth extraction

Monazite, a major source of rare earths, contains characteristically high concentrations of thorium series radionuclides. The solid wastes arising from the chemical processing of monazite contain correspondingly high concentrations of these radionuclides, and their disposal has to be controlled accordingly. In the presentation from India on monazite and rare earth extraction, the following information on solid wastes was provided:

(a) Approximately 80–100 kg of insoluble unreacted monazite is produced per tonne of monazite processed. The ^{228}Ra activity concentration is 400–1000 Bq/g. The waste, in the form of a sludge, is neutralized and filtered and the filter cake is disposed of at engineered storage facilities consisting of trenches covered with a concrete slab and meeting specific shielding requirements.

(b) Approximately 60–100 kg of mixed cake of PbS and $Ba(Ra)SO_4$ is produced per tonne of monazite processed. The ^{228}Ra activity concentration is about 2000–5000 Bq/g (dry). The cake is filtered and disposed of at engineered facilities similar to those described in (a).

(c) About 100 kg of phosphate sludge from the neutralization and calcium phosphate precipitation of acidic and alkaline effluents is produced per tonne of monazite processed. The ^{228}Ra activity concentration is 25–100 Bq/g. This waste is disposed of in earthen trenches with a soil topping of 0.5–1 m. The disposal site is demarcated, fenced and identified with caution signs.

(d) Nearly 250 kg of thorium hydroxide cake is produced per tonne of monazite processed. This material gives rise to gamma dose rates similar to those in (a). It is disposed of at engineered facilities in the form of silos meeting specific shielding requirements.

7.5. Furnace dust

This type of waste was mentioned in several presentations. It originates from certain mineral processing operations involving high temperatures — high enough to cause the volatilization of ^{210}Pb and ^{210}Po. These radionuclides become selectively concentrated in the furnace dust, which is emitted to the atmosphere and/or precipitated and removed as waste. Precipitator dust from a thermal phosphorus facility in the Netherlands was described as a stable solid material that, while not requiring any conditioning or treatment, has to be stored in polyethylene lined containers at a dedicated waste storage facility in view of the particularly high concentrations of ^{210}Pb and ^{210}Po. After 150 years it will have decayed to below clearance levels, allowing it to be disposed of as conventional waste. In other presentations, mention was made of furnace dust from facilities for the manufacture of ceramic tiles and refractories and for the production of iron and steel. These furnace dusts contain lesser concentrations of ^{210}Pb and ^{210}Po such that decay storage is not necessary and immediate disposal in landfill facilities is possible. In the case of furnace dust from a steelworks, mention was made of further studies to confirm its leaching behaviour at the disposal site.

8. MAIN FINDINGS OF THE SYMPOSIUM

8.1. Regulatory aspects

(a) Considerable progress has been made in the last ten years towards the harmonization of standards and regulatory approaches. However, the issue of harmonization remains a prospect rather than a reality and continues to be the subject of much debate. In the meantime, severe disruptions in international trade are being experienced to an increasing extent. A determined effort is therefore needed at the national and international level to achieve a common and coherent approach to the regulation of NORM.

(b) The activity concentration criteria of 1 Bq/g for uranium and thorium series radionuclides and 10 Bq/g for ^{40}K are, despite some reservations, generally accepted as the most practicable way forward in determining which materials should be considered for regulation in terms of the requirements for practices.

(c) The IAEA Transport Regulations are not entirely clear regarding the definition of 'natural material'. For material which has been processed, this leads to some confusion in determining the criterion for inclusion in the Transport Regulations.

(d) A dose criterion of the order of 1 mSv per year is now commonplace as a de facto standard for exemption of NORM from the regulatory requirements for practices.

8.2. The expanding knowledge base on exposures to NORM

(a) Some industrial applications of thorium have been shown to give rise to significant worker exposures, but these applications are now disappearing as non-radioactive substitutes become available. This appears to leave work involving monazite and rare earth extraction as being the only major area outside of the uranium industry where worker doses are likely to reach a substantial fraction of the dose limit. In other industrial activities involving NORM there is growing evidence that the enforcement of normal occupational health and safety measures would most likely be sufficient to ensure that annual effective doses received by workers do not significantly exceed 1 mSv, and therefore do not require the implementation of specific radiation protection measures.

(b) The information now available on public exposure to NORM suggests that the annual effective doses received by members of the public are likely to always be below 1 mSv, provided that present day environmental protection measures (such as the treatment of effluent streams) are applied. Indeed, the only evidence of doses even approaching 1 mSv relates to exposures arising from the occupancy of former landfill sites containing NORM.

(c) With the increasing use of facility specific data for worker and public dose assessments it is becoming ever more clear that the use of unrealistic assumptions to characterize exposure situations can give rise to very large overestimates of dose. These overestimates can in turn lead to false conclusions being drawn on the need for, or extent of, regulation. More attention therefore needs to be focused on the use of site specific measurements for dose assessment.

8.3. Options for minimizing NORM waste

(a) The use, reuse and recycling of NORM residues and NORM contaminated items — including, where appropriate, the dilution of NORM residues to reduce the activity concentration — is now starting to be recognized as a legitimate and desirable option for minimizing the quantities of NORM that need to be disposed of as waste. In particular, the beneficial (and safe) uses of phosphogypsum as a co-product of fertilizer production are now very much in the spotlight and, in some countries at least, there is already evidence of a shift in regulatory attitude towards this approach. However, when considering the use of NORM residues in the construction of dwellings, as a component of either landfill material or construction material, the possibility of increased radon exposure needs to be carefully taken into account.

(b) It has been demonstrated that NORM contaminated metal scrap can be safely recycled in a suitably controlled melting facility and this recycling option now seems to be gaining greater acceptance by the general steel industry.

(c) A protocol developed in Spain for controlling the inadvertent introduction of radioactively contaminated scrap into conventional scrap processing facilities, based on voluntary cooperation between all the concerned parties, is now gaining acceptance at the international level as a model for dealing with this problem. The protocol, while originally having been designed to prevent the inadvertent melting of radiation sources, is equally effective in dealing with scrap with unacceptable levels of NORM contamination.

8.4. Management of NORM residues designated as waste

(a) Despite the many opportunities for use, reuse and recycling, there are still many NORM residues that will ultimately have to be disposed of as waste. There is now a considerable body of knowledge on appropriate methods for conditioning, storage and disposal of the various types of NORM waste, but the necessary facilities and regulatory provisions are in many cases not yet in place.

(b) There is growing evidence to suggest that bulk wastes contained in properly engineered surface impoundments have very low radiological impacts. However, their environmental, safety and financial liability implications can be seriously underestimated. This has been demonstrated in the case of phosphogypsum stacks, where recent developments have suggested that the stacking option is not optimal and that more attention should be given to beneficial uses of the material.

(c) Landfill disposal has been demonstrated as being an appropriate option for dealing with many types of NORM residue for which the quantities and activity concentrations are moderate, including most types of furnace dust with enhanced concentrations of ^{210}Pb and ^{210}Po. Normal landfill facilities are generally suitable, but the presence of non-radiological contaminants such as heavy metals may require the use of landfill sites specially designated for hazardous waste.

(d) Scales and sludges, which are generated in small volumes but which may have activity concentrations reaching very high levels, such as those originating from the oil and gas industry, usually have to be held in storage pending the establishment of suitable disposal facilities. Suitable techniques exist for conditioning (e.g. separation of mercury) and long term storage.

NORM residues from the chemical extraction of rare earths from monazite are produced in significant quantities and have characteristically high activity concentrations. It has been demonstrated that such wastes can be suitably disposed of either in earthen trenches or in engineered cells, depending on the activity concentration.

OPENING SESSION

Chairpersons

L. RAMOS
Spain

T. LUDWIG
Germany

OPENING ADDRESS

M.A. Castro Arroyo
University of Seville,
Seville, Spain

It is a great honour for me to participate in this official inauguration on behalf of the University of Seville. I welcome you here to attend the Fifth International Symposium on Naturally Occurring Radioactive Material and I wish you a happy and comfortable stay in our town.

I would like to thank the organizing committee for choosing Seville to celebrate this scientific event. This fact should be considered as a consequence of the tradition and experience that several research groups of our university have in the study of naturally occurring radioactive material.

The University of Seville is the second largest institution devoted to higher education in our country. It has more than 70 000 students, more than 4000 lecturers and fellows and an annual budget of around €400 million. From its founding five centuries ago, the University of Seville has played a relevant role in the development and transformation of our region. As head of General Services for Research in this university, I would like to emphasize the special effort and the economic assistance that our university has offered during the last decades to the improvement of our instrument and scientific facilities.

In the context of the topics covered in this symposium, I should mention the modern and sophisticated capabilities available both in the radioisotope laboratories located at the Centre for Research, Technology and Innovation (CITIUS) and at the National Centre for Accelerators at Isla de la Cartuja, recently recognized by the European Union as a singular research facility. This scientific event should have the added value of identifying new common interests which can be used as starting points to establish new collaborative scientific projects from the discussions and debates developed in its sessions.

The ancient city of Seville has been greatly transformed since the sixteenth century, when Miguel de Cervantes called it “triumphant Rome in spirit and richness”. After several centuries of decay, Seville is now suffering a sort of ‘big bang’ that affects not only the numerous construction sites you can see in our streets (I apologize for them) but also the composition and character of its people. Seville is now an open town that combines a long history, a set of modern structures and an open and flexible atmosphere which invites you to the discussion and criticism of ideas.

It is here that I officially declare the Fifth International Symposium on Naturally Occurring Radioactive Material to be open.

KEYNOTE ADDRESS

MANAGING EXPOSURE TO NORM — CONSENSUS OR CHAOS?

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Abstract

Ten years after the first in this series of international symposia on NORM was held in Amsterdam, exposure to natural sources has continued to have a high profile in most parts of the world and has evoked a considerable degree of controversy. The paper looks at the progress made in identifying and quantifying the radiological risks to exposed individuals and putting in place, at the national level, additional or revised legislative and regulatory measures for the mitigation of these risks. The current direction in which the approach to managing exposure to NORM is moving, especially in the light of the revised recommendations proposed by the ICRP, is also examined. The achievement of a harmonized approach to the management of exposure to NORM is clearly an important goal, especially given that minerals and raw materials are traded internationally on a very large scale. It would appear that shortcomings in the regulatory approach in certain countries may be hampering the achievement of this much needed internationally harmonized approach and creating a situation in international trade that some might describe as 'chaotic'. The development of standards and regulations continues to depend quite heavily on dose modelling assessments where adequate facility specific data are not yet available. The paper demonstrates by way of two examples — exposure of workers in mineral processing industries and exposure of members of the public to drinking water contaminated by mine residues — why great caution is required in the dose modelling approach.

1. INTRODUCTION

It is now exactly a decade since the first in this series of international symposia on NORM was held in Amsterdam. This event came six years after the publication of the current version of the basic recommendations of the International Commission on Radiological Protection (ICRP) in the form of ICRP Publication 60 [1], and just one year after the publication by the International Atomic Energy Agency of the current version of the International Basic

Safety Standards for Protection against Ionizing Radiation and for the Safety of Radiation Sources (the BSS), jointly sponsored by four organizations within the United Nations and by two other international bodies [2]. These two publications marked the first real steps taken at the international level to deal with protection against exposure to natural sources of radiation. They set in motion a series of developments around the world to focus regulatory attention on this area, one notable example being the publication, in 1996, of Directive 96/29/Euratom of the Council of the European Union [3], which placed specific legal requirements on European Member States for the control of work activities involving a significant increase in exposure to natural sources.

Considerable effort has now been devoted worldwide to identifying and quantifying the radiological risks to exposed individuals and putting in place, at the national level, additional or revised legislative and regulatory measures for the control of these risks. Indeed, the whole topic of exposure to natural sources has attained a high profile in most parts of the world and has also evoked a fair degree of controversy. The achievement of a harmonized approach to the management of exposure to NORM is clearly an important goal, especially given that minerals and raw materials are traded internationally on a very large scale. However, there are signs that such a harmonized approach is still proving to be elusive.

All three of the above mentioned international publications — ICRP Publication 60, the BSS and the European Council Directive — are now undergoing revision, so it is particularly opportune at this time to examine the progress made, to determine the direction in which our radiation protection philosophy is moving and to evaluate our success (or lack thereof) in achieving an internationally harmonized approach to protection against exposure to natural sources including, in particular, exposure to naturally occurring radioactive material (NORM).

2. WHAT IS NORM?

Opinions differ on what exactly is meant by the term NORM. Reports of the occurrence of significant concentrations of radionuclides of natural origin in the oil and gas industry go back to 1904 [4] and it seems that the term NORM was first coined by this industry in the late 1980s when referring to the radium rich scales deposited inside well tubulars, surface piping, vessels, pumps and other production and processing equipment. Since then the term has become widely adopted beyond the oil and gas industry and now tends to be associated with almost any type of mineral or mineral processing activity where the presence of radionuclides of natural origin is of interest.

The term NORM has become firmly entrenched in our technical vocabulary, but as an acronym for ‘naturally occurring radioactive material’ it is actually a misnomer — the descriptor ‘naturally occurring’ refers to the radionuclides in the material and not necessarily to the material itself, which may well be a product of a physical, chemical or thermal industrial process. Furthermore, because radionuclides of natural origin are ubiquitous in our environment, it could be argued that all materials are effectively NORM — not only minerals (rocks and soil) of all types, but also all vegetable and animal matter including the food we eat, the water we drink and even our own bodies. Clearly, there is a need to single out only those few materials of potential radiological concern.

One attempt to do this has been through the introduction of a new term — TENORM (‘technologically enhanced naturally occurring radioactive material’). However, this approach does not solve the problem and, indeed, can be misleading because it implies that the materials of concern are limited to those in which the radionuclides have become concentrated as a result of an industrial process. This is often the case, but not always. For instance, it is estimated that a smelting plant worker exposed to furnace fume and precipitator dust with a highly enhanced ^{210}Pb concentration of, say, 200 Bq/g could receive an annual dose of about 120 μSv, whereas a titanium dioxide production worker exposed to ilmenite feedstock with an unenhanced ^{232}Th activity concentration of, say, 2 Bq/g could receive an annual dose of 800 μSv, nearly seven times higher.[1] Materials in their natural state are in principle no less important to consider than materials with activity concentrations enhanced by some form of processing and any distinction between the two for the purposes of radiation protection is artificial and without any scientific foundation.

The approach adopted by the IAEA for the purposes of international radiation protection standards is to use only the term NORM, regardless of the origin of the material, while defining ‘radioactive material’ more narrowly as “material that is designated in national law or by a regulatory body as being subject to regulatory control because of its radioactivity” [6]. NORM is then a particular form of radioactive material (defined in the narrower sense) where the radioactivity in question is associated with radionuclides of natural origin. This approach solves the problem of how to single out only those materials of radiological concern, while avoiding the need for any additional and potentially misleading terms such as TENORM, the use of which is therefore discouraged.

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[1] The basis for the derivation of these doses is given in Ref. [5].

Uranium ore, of course, falls within the definition of NORM but is a special case because the mining and processing of this material form part of the nuclear fuel cycle and have therefore long been subject to stringent regulatory control. This has led to a situation where the ‘nuclear style’ standards applied to these operations are in some respects inconsistent with the standards now being established for other NORM related activities. Nevertheless, the nature of the radiological hazards associated with uranium mining and processing is such that a significant level of regulatory control will always be required.

3. PERSPECTIVES ON THE FIVE NORM SYMPOSIA TO DATE

3.1. Topics of major interest

Looking at the subject matter presented at the five NORM symposia spanning the last decade, some interesting observations can be made. While the categorization of presentations into specific topics is rather subjective and complicated by the fact that some presentations covered more than one topic, a general picture does seem to emerge, as shown in Fig. 1. (The mining and processing of uranium ore is not included in the analysis because it received relatively little coverage, having long been the subject of attention elsewhere.) About 20% of the subject matter relates to the establishment of standards and regulations and to the identification of the main types of industrial activities of concern, reflecting the considerable progress made in this area during the ten year period, particularly in Europe. However, a greater proportion of the

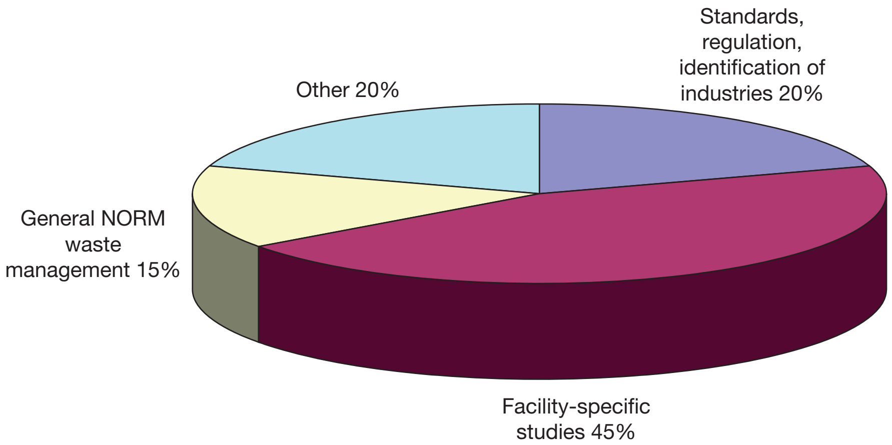

FIG. 1. Subject matter presented at NORM I to NORM V.

subject matter — nearly half — has been devoted to studies conducted in particular industrial facilities or types of facility. This is encouraging, because without this detailed facility specific information it is difficult to imagine how sensible steps can be taken towards identifying what needs to be controlled and how.

3.2. Scope of regulation — the key issue

The question of how to define the scope of regulation of NORM activities (other than the mining and processing of uranium ore) in terms of the concepts of exclusion, exemption and clearance has been the main area of concern from the very beginning — the opening remarks made at the first NORM symposium in Amsterdam [7] were devoted almost entirely to this issue. Despite the fact that significant progress has since been made towards achieving international consensus, as described later in the paper, some issues remain unresolved and the issue of defining the scope of regulatory control continues to dominate discussion. Consequently, the implementation of an internationally harmonized approach to deciding what should be included within the scope of regulation is still far from being achieved.

3.3. Principal NORM industries of interest

The 'facility specific studies' category shown in Fig. 1 is broken down in Fig. 2 to indicate the principal NORM industries of interest and the relative coverage given to those industries during the five NORM symposia. Analysis

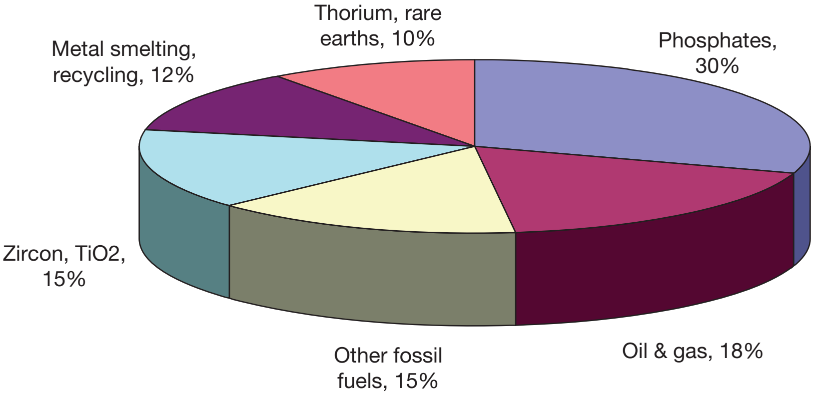

FIG. 2. Facility specific studies presented at NORM I to NORM V

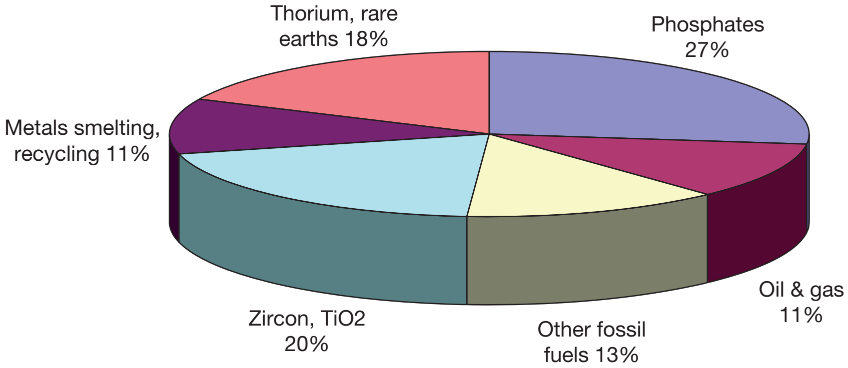

FIG. 3. Breakdown of the IAEA literature database on NORM.

of an IAEA database of more than 700 literature sources on exposure to NORM (other than exposures in uranium ore mining and processing), shown in Fig. 3, gives much the same result. Although there has been fairly uniform coverage of the main industries of concern, it seems that the phosphate industry has been the subject of the most attention, as would have been expected given the widespread nature of this industry, the variety of processes involved and the existence of very large quantities of NORM residue in the form of phosphogypsum.

The industries identified in Figs 2 and 3 have been broken down into more detail in a recent IAEA Safety Report [5] to generate the following list, roughly in descending order of radiological priority:

(1) Extraction of rare earth elements;
(2) Production and use of thorium and its compounds;
(3) Production of niobium and ferro-niobium;
(4) Mining of ores other than uranium ore;
(5) Production of oil and gas;
(6) Manufacture of titanium dioxide pigments;
(7) The phosphate industry;
(8) The zircon and zirconia industries;
(9) Production of tin, copper, aluminium, iron and steel, zinc and lead;
(10) Combustion of coal;
(11) Water treatment.

The categories ‘mining of ores other than uranium ore’ and ‘water treatment’ are included particularly because of the potential for exposure to high concentrations of radon in underground workplaces, although there may also be concerns about the buildup of radionuclides in effluents and residues.

A working party on NORM established by the European Commission Article 31 Group of Experts to assist in the revision of the Directive 96/29/ Euratom has recently proposed an almost identical list of NORM industries that may in future become automatically required to submit notification to the relevant national regulatory body.

The IAEA is currently engaged in the development of a suite of publications in its Safety Reports Series to provide detailed information for regulatory bodies and operators involved in some of the industries listed above. Safety Reports have been completed for the oil and gas and the zircon and zirconia industries [8, 9] and further reports dealing with the phosphate industry, the titanium dioxide pigment industry and the extraction and use of thorium are in preparation.

4. PROGRESS IN THE DEVELOPMENT OF REGULATORY STANDARDS

The recommendations in ICRP Publication 60, together with additional guidance on radon in ICRP Publication 65 [10], have provided the basis for the international standards on exposure to natural sources contained in the BSS [2] and supporting Safety Guides. The standards make an important differentiation between exposures subject to the requirements for intervention and those subject to the requirements for practices.

4.1. Exposures subject to the requirements for intervention

4.1.1. General requirements

Paragraph 2.5 of the BSS states that “Exposure to natural sources shall normally be considered as a chronic exposure situation and, if necessary, shall be subject to the requirements for intervention…”, meaning that in such circumstances:

(a) The exposure does not fall within the scope of regulation in terms of the requirements for practices;
(b) Remedial action has to be undertaken to reduce or avert the exposure whenever such action is justified (usually, this means when a specified action level is exceeded);

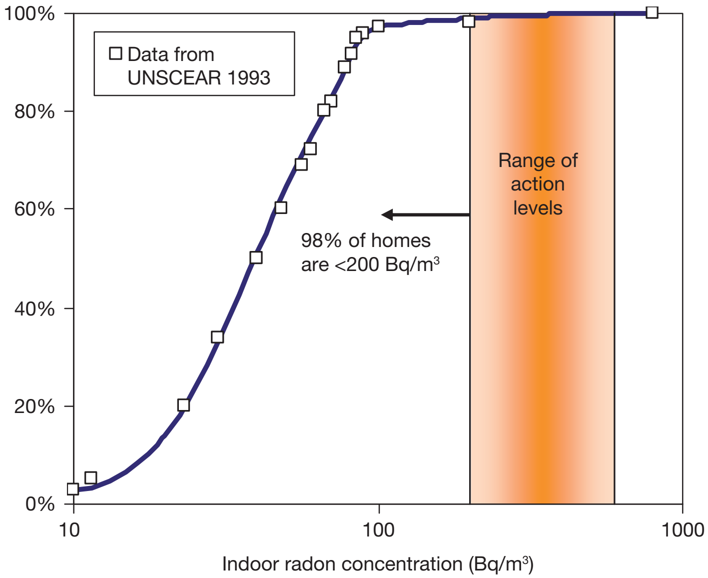

FIG. 4. Action levels for radon concentrations in dwellings in relation to the cumulative worldwide distribution.

(c) The form, scale and duration of any such remedial action has to be optimized so as to produce the maximum net benefit, understood in a broad sense, under the prevailing social and economic circumstances (usually this entails the selection of an optimized level of remediation for inclusion in the remedial action plan).

4.1.2. Specific requirements for radon[2]

A chronic exposure situation addressed specifically in the BSS [2] is exposure to radon. The requirements for radon are no different from those for any other chronic exposure situation, but more detailed guidance is provided for radon in the BSS in accordance with the recommendations contained in ICRP Publication 65 [10]. For dwellings, the expected range of action levels for remedial action is an annual average of 200–600 Bq/m^3. Figure 4 illustrates the situation in the context of worldwide indoor radon concentration data from the

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[2] In this paper, the use of the term ‘radon’ is generally taken to include not only the parent radionuclide ^{222}Rn but also its short lived progeny. However, the term ‘radon concentration’ refers to the concentration in air of the parent radionuclide ^{222}Rn alone.

1993 UNSCEAR report [11] — these data suggest a population weighted average radon concentration of 40 Bq/m^3, although national averages may depart significantly from this value. The adoption of a range of action levels therefore reflects the recognition that "…the best choice of an action level may well be that level which defines a significant, but not unmanageable, number of houses in need of remedial work", and that "It is then not expected that the same action level will be appropriate in all countries" [1]. The lower bound of the range of action levels (200 Bq/m^3) corresponds to the 98th percentile of the worldwide radon concentration distribution.

It is important to note that the choice of radon action level for dwellings is based not only on dose considerations, but also on the practicalities of remedial action (i.e. the percentage of homes to be remediated). For a typical exposure situation, conversion from indoor radon concentration to annual effective dose can be made quite readily because the conversion involves relatively few assumptions (mainly assumptions about occupancy and radon progeny equilibrium factor). Assuming an annual occupancy of 7000 h and an equilibrium factor of 0.4, action levels in the range of 200–600 Bq/m^3 correspond to annual effective doses in the range 3–10 mSv. This provides a logical basis for the determination of action levels for workplaces because, as stated in ICRP Publication 65 [10], "Workers who are not regarded as being occupationally exposed to radiation are usually treated in the same way as members of the public. It is… logical to adopt an action level for intervention in workplaces at the same level of effective dose as the action level for dwellings." The resulting range (rounded) quoted in Ref. [10], taking into account the occupancy and dose coefficients for workers, is 500–1500 Bq/m^3. In the BSS [2], the mid-point of this range, 1000 Bq/m^3, has been adopted by international consensus as a guideline action level for remedial action in workplaces.

4.2. Exposures subject to the requirements for practices

4.2.1. Which exposures are involved?

Certain human activities giving rise to exposure to natural sources have the characteristics of practices and some form of control in accordance with the requirements for practices, rather than an intervention approach, may be appropriate. The following three situations are addressed in the international standards:

(1) In workplaces where radon is not incidental to the work (e.g. uranium mines) or in other workplaces where a reduction in radon concentrations to below the action level cannot reasonably be achieved, exposure to

radon is treated as occupational exposure and subject to the requirements for practices.

(2) Paragraph 2.1 of the BSS states that "The practices to which the Standards apply include… practices involving exposure to natural sources specified by the Regulatory Authority as requiring control…". Paragraph 2.5(a) of the BSS goes on to say that the exposure associated with such practices includes "…public exposure delivered by effluent discharges or the disposal of radioactive waste…unless the exposure is excluded or the practice or the source is exempted…".

(3) The transport of radioactive material, including NORM, is regarded as a practice. However, if the material has not been, or is not intended to be, processed for purposes of extraction and use of the contained radionuclides, the requirements of the Regulations for the Safe Transport of Radioactive Material (the Transport Regulations) [12] apply only if the total activity concentration of the material exceeds 10 times the 'activity concentration for exempt material' defined in the Transport Regulations. For a material in which the uranium and thorium decay chains are deemed to be in equilibrium, this condition can be expressed mathematically as:

$$x(^{238}U) + x(^{232}Th) + 0.01\ x(^{40}K) > 10$$

where $x(i)$ is the activity concentration of radionuclide i.

4.2.2. 'Entry' criteria for regulation of materials in accordance with the requirements for practices

In terms of item (2) in Section 4.2.1, it is the responsibility of the regulatory body to specify which exposures to natural sources require control, but no further guidance on this existed at the time of publication of the BSS. Some countries had introduced numerical criteria in one form or another, but there were very large variations between countries, with arguments that some criteria were too strict and others were too permissive. Following many years of international debate, a major step forward was achieved with the publication in 2004 of IAEA Safety Standards Series No. RS-G-1.7 on Application of the Concepts of Exclusion, Exemption and Clearance [13]. That publication advises that "It is usually unnecessary to regulate…" material containing radionuclides of natural origin at activity concentrations below 1 Bq/g for radionuclides in the uranium and thorium decay series and below 10 Bq/g for ^{40}K. The Safety Guide adds, however, that "… there are some situations (such as the use of some building materials containing natural radionuclides) for which exposures from materials due to radionuclides with activity concentrations below [these values] would necessitate consideration by the regulatory body for some types of regulatory control". This is discussed further in Section 8.1.2. IAEA Safety Standards Series No. RS-G-1.7 states that the aforementioned values may be used:

(a) In the definition of the scope of national regulations;
(b) To define radioactive material for the purpose of such regulations;
(c) To determine whether material within a practice can be released from regulatory control.

The values for radionuclides of both natural and artificial origin are expressed as orders of magnitude only, on the basis that the uncertainties in their derivation do not support a greater level of precision. This approach is identical to that adopted for the derivation of exemption values for limited quantities of material in Schedule I of the BSS.[3]

In September 2004, the Board of Governors of the IAEA approved the use of these radiological criteria for radionuclides in commodities in the application of the BSS and this decision was reported to the IAEA General Conference at its 48th regular session. The General Conference, in Resolution GC(48)/RES/10, welcomed the decision, encouraged IAEA Member States "…to make use of the criteria, for example to facilitate trade…", and further encouraged the IAEA Secretariat "…to take account of the criteria in the forthcoming review and revision of the BSS".

The approach taken for radionuclides of natural origin in Ref. [13] was based on the realization that the derivation of activity concentration values on the basis of the same radiological criteria as those used for artificial radionuclides would produce values that in many cases would be lower than concentrations occurring in material in the natural environment. Thus many human activities previously unregulated from a radiological standpoint, such as the construction of houses from natural building material or even the use of land in many areas, could become subject to regulation. Establishing levels for radionuclides of natural origin that entailed such widespread regulatory consideration, in circumstances where in many cases it was unlikely to achieve any improvement in protection, was not considered to be an optimum use of regulatory resources. Therefore, the derivation of activity concentration values for radionuclides of natural origin other than radon was not based on a

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[3] These exemption values also appear in Annex I of the European Council Directive 96/29/Euratom [3].

dosimetric approach but on a methodology that placed greater emphasis on optimization of protection, including optimization of regulatory resources.

This methodology followed an approach similar to that used for deriving radon action levels and involved the selection of activity concentration values that took into consideration the worldwide distribution of concentrations of radionuclides of natural origin in soil given in the 2000 UNSCEAR Report [14]. The worldwide distribution for ^{238}U and ^{232}Th series radionuclides is shown in Fig. 5, together with data for various commercially exploited minerals with elevated concentrations of these radionuclides. These data clearly demonstrate the rationale for selecting an activity concentration criterion of 1 Bq/g. The worldwide distribution for ^{40}K in soil extends up to 3.2 Bq/g, which is compatible with the activity concentration criterion of 10 Bq/g for this radionuclide.

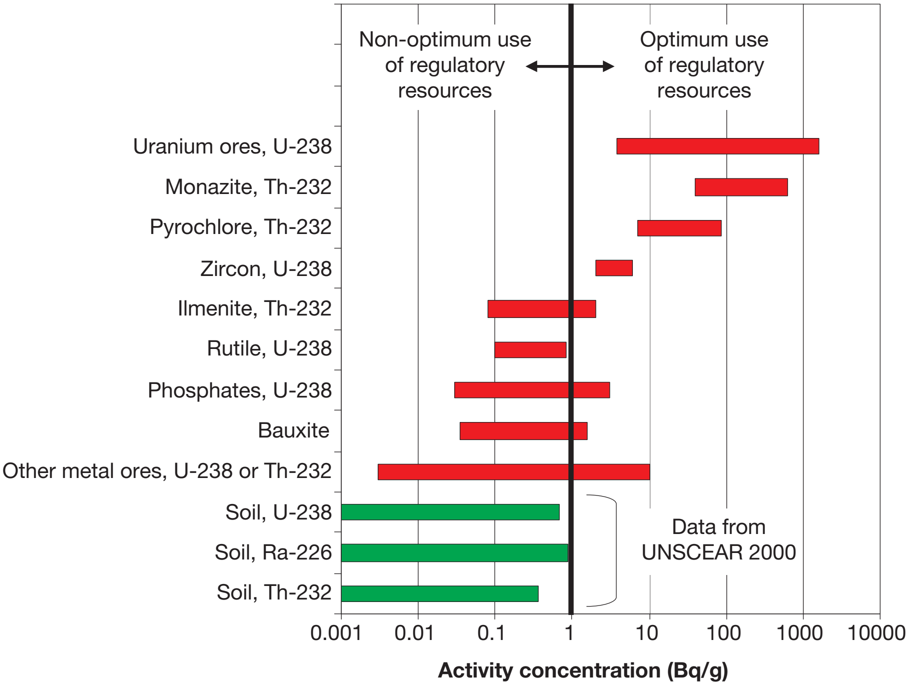

FIG. 5. Concentration ranges of uranium and thorium series radionuclides in minerals.

4.2.3. Exemption — the first step in the graded approach to regulation

Unlike the situation with radon, in which there is a reasonably identifiable relationship between radon concentration and annual dose, the activity concentrations of radionuclides in NORM do not give a clear indication of the dose that is likely to be received by an exposed worker or member of the public unless there is a reasonable amount of additional information on the exposure scenario involved and the type of NORM giving rise to the exposure. Thus, even if the activity concentration value of 1 Bq/g for uranium and thorium series radionuclides is significantly exceeded, the dose received by an exposed individual may still be such that the optimum regulatory option is not to apply any regulatory requirements, in other words to grant an exemption. This can be regarded as the first step in a 'graded approach to regulation'. In the event that exemption is not the optimum option, the next steps to be considered in the graded approach are, in ascending order of stringency of control, the requirements for notification, registration and licensing. These requirements are in principle no different from those applicable to exposures to artificial sources of radiation. Further information on the application of the graded approach to the regulation of exposures to NORM is provided in Ref. [5].

Criteria for exemption, without further consideration, of substances containing radionuclides of artificial origin are based on the premise that exemption will be the optimum option when the dose incurred by an individual is of the order of 10 μSv or less in a year [2]. For NORM, the situation is quite different. Owing to the existence of significant and highly variable levels of background exposure to radionuclides of natural origin, exemption is likely to be the optimum option over a much wider range of doses, typically doses of the order of 1 mSv or less in a year. For situations where occupational exposure to gamma radiation and radionuclides in dust is the principal exposure of concern, as is likely to be the case in most NORM industries [5], it is recommended in Refs [15, 16] that "…regulatory agencies choose activity concentrations of parent nuclides within the range of 1–10 Bq g^{-1} to determine whether the exposures from these materials should be regarded as occupational" while noting that, on the basis of pessimistic assumptions, activity concentrations in this range "…will lead to an effective dose of about 1–2 mSv in a year", i.e. up to about 10% of the annual dose limit for workers. This is borne out by the results of calculations described in Ref. [5], based on a variety of exposure situations in NORM industries (see Section 5.2).

5. OCCUPATIONAL EXPOSURE TO NORM

5.1. Dose assessment by modelling and its limitations

Many assessments of doses received by workers have been heavily based on exposure scenario modelling. Caution is required in any modelling assessment because the extent to which a model simulates the true exposure situation is critically dependent on the assumptions used. A modelling study conducted for the European Commission [17] was intended to provide a basis for the establishment of specific guidance on the regulatory control of workplaces where materials containing naturally occurring radionuclides were of concern. However, because of the very broad range of assumptions considered, this study came up with widely varying predictions of annual worker doses that extended up to hundreds or even thousands of millisieverts. The regulatory and public perception implications of these unrealistic predictions naturally caused consternation among many NORM industries.

The IAEA subsequently conducted modelling assessments for a similar range of exposure situations, but using more realistic assumptions [5]. One major difference from the European study was the assumption that radon in the workplace would be at a concentration below the relevant action level (after remedial action, where necessary) and would not therefore be treated as a source of occupational exposure — evidence suggests that this will generally be the case, especially for above ground workplaces. The results, expressed in terms of dose per unit activity concentration, are shown in Table 1, noting that the term ‘activity concentration’ here means the highest individual radionuclide activity concentration in the material concerned. The activity concentration values in the last column of Table 1 represent the levels at which the range of effective doses expected to be received by a worker starts to extend beyond about 10% of the 20 mSv occupational dose limit and thus into an area where the need for radiation protection measures becomes more certain. It can easily be deduced from Table 1 that:

(a) A worker exposed to a large stockpile of material with an activity concentration of 5 Bq/g would be expected to receive an annual dose in the range 0.1–2 mSv (the exact value depends mainly on the type of material involved);
(b) A worker exposed to a small quantity of material (~1 m^3) with an activity concentration of 50 Bq/g would be expected to receive an annual dose in the range 0.4–2 mSv;
(c) A worker exposed to furnace fume and precipitator dust with an activity concentration of 500 Bq/g would be expected to receive an annual dose in the range 0.3–1.5 mSv.

TABLE 1. RELATIONSHIP BETWEEN DOSE AND ACTIVITY CONCENTRATION FOR EXPOSURE OF WORKERS TO NORM [5]

Category of material	Broad estimate of annual effective dose per unit activity concentration (mSv/a per Bq/g)		Individual radionuclide activity concentration above which the expected dose may exceed 10% of the dose limit (Bq/g)
	Minimum	Maximum	
Large quantity, e.g. orebody, large stockpile	0.02	0.4	5
Small quantity, e.g. mineral concentrate, scale, sludge	0.008	0.04	50
Volatilized: furnace fume and precipitator dust	0.0006	0.003	500[a]

[a] This value refers to the activity concentration in the precipitator dust, with exposure to fume having been accounted for by assuming an equivalent dust loading of 1 mg/m^3 at the same activity concentration (i.e. a concentration of 0.5 Bq/m^3 in fume) and an activity median aerodynamic diameter of 1 μm.

As pointed out in Ref. [5], these results can be very useful in prioritizing in advance the types of industrial process most likely to need radiation protection measures, since such prioritization only requires knowledge of the activity concentrations of the process materials concerned and assignment of such materials to one of three simple categories.

5.2. Comparison of modelling results with the results of facility specific assessments

The IAEA is gathering and documenting radiological data on several important NORM industries, including data on worker doses assessed to the extent possible on the basis of facility specific measurements. This is making it possible to obtain rather more reliable indications of the doses likely to be received by workers. Table 2 shows, for a selection of NORM industries, a comparison of dose information determined from modelling with broad assumptions [17], from modelling with more realistic assumptions [5] and from assessments based to a greater extent on facility specific measurements. This comparison illustrates how the use of unrealistic modelling assumptions can generate very misleading results, particularly if an attempt is made to include

TABLE 2. ASSESSMENTS OF WORKER DOSES IN A SELECTION OF NORM INDUSTRIES

	Annual effective dose (mSv)			
	Based on modelling using broad assumptions [17]		Based on modelling using realistic assumptions [5]	Based on facility specific measurements
	Radon included	Radon excluded		
Bulk phosphate ore in a warehouse	0.2–69	0.02–11	0.01–0.8	0.8 (general plant worker)[a] [18]
Thermal phosphorus plant				
Removal of precipitator dust	0.1–10	0.1–10	0.8 (general plant worker)[b]	1 (general plant worker) [19]
Exposure to fume near a furnace	0.02–0.9	0.02–0.9		
Bulk pyrochlore feedstock in a warehouse	132–635	11–121	23	Up to 20[c]
Bulk zircon sand in a warehouse	0.8–583	0.4–286	0.5–0.9	0.25–0.28 [9]
Fabrication of zircon refractory products	0.001–58	—[d]	0.01–0.04	0.05–0.2 [9]
Rare earths extraction				
Bulk monazite sand in a warehouse	13.5–9763	—	10–152	Average 1–8 (general plant worker) [20]
Removal of residue	0.2–184	<0.2–101	0.2–36	
Bulk ilmenite feedstock in a warehouse	0.2–119	0.02–24	0.0004–0.9	0.03–0.08
TiO_2 production: removal of scale	50–342	Similar to ‘radon included’	<0.01–20	<1–6
Oil and gas extraction: removal of scale	0.00003–243	Similar to ‘radon included’	0.002–33	<1 to a few mSv [5]

[a] Dose from gamma radiation only — dust inhalation was not considered.

[b] It was assumed that the activity concentration of ^{210}Po was 10% of that of ^{210}Pb, in line with observations.

[c] Data not yet available but considered by experts to have the potential for approaching 20 mSv.

[d] —: The contribution of radon could not be established from the data.

exposure to radon when in most situations this exposure is expected to be moderate and should not be treated as occupational. On the other hand, modelling can give reasonably reliable results provided that realistic assumptions are made.

5.3. The special case of materials rich in potassium

The natural abundance of ^{40}K in potassium is 0.0117%. The specific activity of ^{40}K, calculated from its 1.265×10^9 year half-life, is 2.617×10^5 Bq/g. Thus, pure potassium contains ^{40}K at an activity concentration of 30.6 Bq/g. Materials rich in potassium, such as some fertilizers, contain ^{40}K at concentrations above background values but clearly these concentrations are always less than 30.6 Bq/g. Intakes of ^{40}K are excluded from the international standards because they are controlled homeostatically and not amenable to further control. Therefore, exposure to ^{40}K is an issue only for external exposure. Calculations of the dose per unit activity concentration of ^{40}K likely to be received by a worker exposed to three types of potassium fertilizer — K, PK and NPK — are reported in Ref. [5] and the results are summarized in Table 3. These results show that the total annual effective dose per unit activity concentration is rather insensitive to the type of fertilizer. The annual effective doses derived from these results, shown also in Table 3, are in the range 0.15–0.18 mSv. Even if a ^{40}K activity concentration of 30.6 Bq/g for pure potassium were to be assumed (an extreme worst case assumption), the annual effective dose would still be only 0.6–0.9 mSv. It can be concluded, therefore, that the exposure of a worker to bulk quantities of potassium rich materials such as fertilizers is most unlikely to warrant regulatory control.

TABLE 3. DOSE RECEIVED BY A WORKER EXPOSED TO A LARGE STOCKPILE OF POTASSIUM RICH FERTILIZER

	Highest reported ^{40}K activity concentration (Bq/g) [17]	Effective dose per unit ^{40}K activity concentration (mSv/a per Bq/g) [5]			Annual effective dose (mSv)
		Gamma radiation	Dust inhalation[a]	Total	
K fertilizer	9.63	0.016	0.002	0.018	0.17
PK fertilizer	6.16	0.020	0.004	0.024	0.15
NPK fertilizer	5.90	0.024	0.006	0.030	0.18

[a] Dose calculated for ^{238}U and ^{232}Th series radionuclides only.

6. PUBLIC EXPOSURE TO NORM

Public exposure attributable to industrial activities involving NORM is still an area in which dependable information is lacking because the doses are difficult to quantify reliably and their assessment is heavily dependent on modelling with its associated drawbacks. A review of information on doses received by members of the public from NORM industries is given in the 2000 UNSCEAR report [14], which states that “Although exposure rates of the order of 100 (μSv a^{-1} could be received by a few local residents, levels of 1–10 μSv a^{-1} would be more common”. Data being gathered by the IAEA on NORM industries is generally in line with the figures quoted by UNSCEAR, although higher doses have been indicated for exposure scenarios involving the uncontrolled use (residential/intrusion) of landfill disposal sites. Examples of the results of dose assessments are given in Table 4.

7. POSSIBLE IMPLICATIONS OF THE REVISED ICRP RECOMMENDATIONS AND THE LIKELY TRENDS IN SAFETY STANDARDS

On 12 January 2007 the ICRP posted on its web site the final draft of its revised recommendations, which were intended to supersede the 1990 Recommendations [1] during the course of 2007. These draft recommendations represent more of an update than a fundamental change, but the ICRP has decided to move away from the previous process based system of practices and interventions to an approach that emphasizes the similarity of protective actions taken, regardless of the exposure situation. Since the current approach to protection against exposure to natural sources differentiates quite explicitly between practices and interventions, the implications of the revised ICRP recommendations need to be examined carefully.

In terms of the revised approach to protection, the ICRP now refers to exposure situations rather than types of human activity. Two types of exposure situation are applicable to exposure to natural sources — planned exposure situations and existing exposure situations. It seems that these situations correspond more or less to those that until now have been subject to control in accordance with the requirements for practices and intervention, respectively.

The revised recommendations, as they apply to what are currently referred to as practices, may end up having little impact on international standards. For what has until now been categorized as intervention, it is the opinion of the ICRP that the revised recommendations will lead to an improvement in the level of protection, but how this will be reflected in future

TABLE 4. DOSE RECEIVED BY A MEMBER OF THE PUBLIC: SOME RESULTS OF MODELLING ASSESSMENTS

	Exposed individual	Estimated annual effective dose (μSv)
Zircon and zirconia industries [9]		
Landfill disposal, waste zircon sand	Resident	0.6
Landfill disposal, waste zircon sand	Intruder (trespasser or resident)	2–130
Zircon milling	Nearby resident	0.01–32
Zircon milling	Worker, adjacent industrial facility	200–320
Use of glazed tiles containing zircon	Building occupant	9–113
Production of fused zirconia	Nearby resident	37
Landfill disposal, zircon fusion furnace dust	Intruder (resident)	4.5
Chemical processing of zircon	Nearby resident	Negligible
Landfill disposal, zircon chemical process waste	Intruder (resident)	750
Landfill disposal, refractory plant waste	Intruder (resident)	A few μSv
Phosphate industry		
Phosphate mining and beneficiation	Nearby resident	17–21
Thermal phosphorus production	Nearby resident	1
Road construction using phosphorus slag	Road user	1–60
Titanium dioxide pigment industry		
Sulphate production process	Nearby resident	Insignificant

international standards is presently unclear. The use of the term ‘existing exposure’ in place of ‘chronic exposure’ would seem to be a simple change in terminology, as would the replacement of the term ‘critical group’ by the term ‘representative person’. The principle of justification (of action to reduce doses) still applies as before, but the ICRP no longer uses the concept of an action level to define the level above which remedial action is deemed to be justified (and, conversely, below which such action is not justified). Instead, the ICRP now proposes the concept of a ‘reference level’ that, for existing exposure situations, is a level of individual dose above which one should plan not to stay, and below which one strives to reduce all actual doses, with all exposures above or below this level of individual dose being subject to optimization of protection.

It would appear from the above that for chronic (existing) exposure situations the basic principles of justification and optimization remain as the cornerstones of the protection approach, but with increased emphasis on optimization. In that sense, there may be no need to make significant changes to the standards. However, the proposed new concept of reference levels would need to be considered carefully — is such a level in effect simply an upper bound on the range of appropriate action levels that may be considered? Judging from the revised recommendations for indoor radon, this would seem to be the case — the recommended upper bounds for reference levels for radon in homes and workplaces are 600 and 1500 Bq/m^3, respectively, identical to the existing global upper bounds for action levels, with the reference level in a particular country being set somewhere within this bound by the national authority, taking into account the prevailing economic and societal circumstances. It should be noted also that there are now no values specified as being the equivalents of the existing lower bounds of the radon action levels (200 and 500 Bq/m^3 for homes and workplaces, respectively), although the option of such a value being set at a national level for homes is still open, as implied by the statement that "… in addition to reference levels, national authorities may also wish to specify levels at which protection against radon-222 can be considered optimised, i.e. where no further action is needed".

8. CONCLUSION — WHAT REMAINS TO BE DONE?

8.1. Further standards development

8.1.1. Revision of the BSS and other IAEA standards

In 2006, ten years after publication of the BSS, a review was carried out to determine whether a revision of the BSS was warranted. It was concluded that, while there was no major issue requiring urgent revision, there was a case to be made for a general revision of the BSS in order to take account of the many improvements that had been suggested. The revision process started towards the end of 2006 and will continue over the next few years. This in turn will require a review and revision of at least some of the supporting Safety Guides.

Now that there is some clarity regarding the ICRP's revised recommendations, it is possible to anticipate the way in which international standards are likely to develop over the next few years. IAEA Member States have repeatedly appealed for stability in the standards and, as far as exposure to natural sources is concerned, there is as yet no strong case for significant change. One important task is to take account of the radiological criteria for radionuclides in commodities in the revision of the BSS, in accordance with General Conference Resolution GC(48)/RES/10 (see Section 4.2.2). For exposure to NORM, this would entail considering the incorporation into the requirements of the activity concentration values of 1 Bq/g for uranium and thorium series radionuclides and 10 Bq/g for ^{40}K — these values are already included in the standards, but only as guidance at present. The question has also arisen as to whether exposure to natural sources should be dealt with in the BSS as part of the overall requirements or as a separate section (as is currently the situation in the European Directive 96/29/Euratom). The present state of agreement on the structure of a revised BSS favours integration into the overall requirements, on the grounds that the radiation safety approach with respect to exposure to natural sources is in principle no different from that for other types of exposure. There are indications that the European Commission may also be considering adopting this integrated approach in its current work to revise the European Directive.

8.1.2. Public exposure to NORM residues

There is one important gap at the Safety Guide level that has not yet been fully addressed. There are a few situations where it may be found necessary to regulate materials at activity concentrations below the values quoted in Ref. [13] (i.e. below 1 Bq/g for uranium and thorium series radionuclides), for example the use of some building materials containing residues from mineral processing industries and possibly the contamination of some drinking water aquifers by mine residue deposits. More work needs to be done to establish quantitative guidance for these situations; this should include a consideration of the dose implications, although a dosimetric approach on its own is unlikely to lead to guidance that truly reflects an optimum use of regulatory resources. As illustrated in Section 8.1.3, the dose implications need to be established with care and circumspection, because of the considerable uncertainties associated with exposure modelling and the need to ensure that the conservatism associated with low probability scenarios is not compounded such that the overall result is unrealistic.

8.1.3. An example of problems with the modelling of doses from mine residue deposits

Modelling has been carried out to estimate, for the groundwater drinking water pathway, the dose received by a person residing within the immediate zone of influence of a mine residue deposit. Contamination of a drinking water aquifer in this manner was one of the exposure scenarios considered in Ref. [21] in the derivation of the internationally agreed activity concentration values below which regulation was to be considered unnecessary [13]. As explained in Section 4.2.2, this dosimetric approach was used only for radionuclides of artificial origin, but it is a simple process to repeat the calculation for radionuclides in the uranium decay series. Preliminary results of such an exercise, together with results from a similar exercise carried out independently using different assumptions, are summarized in Table 5 and are further discussed below:

(a) Using the modelling parameters in Ref. [21], an estimation for a mine residue deposit containing 20 million m^3 of material indicated a leach rate of about 0.0001 a^{-1} and a ^{238}U drinking water contamination level of about 2.8 Bq/L per unit activity concentration (in Bq/g) in the residue deposit. This resulted in an annual ingestion dose received by an adult of about 0.1 mSv per unit activity concentration. A child of age 1–2 years was estimated to receive a similar dose. Using instead a predetermined leach rate of 0.001 a^{-1} (as was assumed in the alternative modelling exercise), the corresponding dose estimates were about 1 mSv.

(b) Extensive analyses of radionuclides in groundwater around the perimeters of gold mine tailings dams in South Africa (comprising a total of 6 billion t of material at an average ^{238}U concentration of almost exactly 1 Bq/g) gave a 90th percentile ^{238}U concentration of 2.78 Bq/g and a mean value of 1.22 Bq/L [22]. The 90th percentile value is essentially the same as that predicted by the model described in Ref. [21], giving the same dose per unit activity concentration (0.1 mSv) as that reported in (a). When the mean concentration was used, the dose per unit activity concentration was 0.05 mSv.

(c) Another modelling exercise carried out for a residue pile of the same dimensions [23] was based on rather different input parameters, which were considered to be ‘conservative but not unrealistic’. The annual ingestion dose received by an adult was estimated to be more than 5 mSv per unit activity concentration, while the corresponding dose for a 1–2 year old child was more than 10 mSv.

TABLE 5. DOSE MODELLING PREDICTIONS FOR INGESTION OF GROUNDWATER CONTAMINATED BY A MINE RESIDUE DEPOSIT

	Activity concentration of ^{238}U in groundwater per unit activity concentration in the residue (Bq/L per Bq/g)	Committed effective dose in a year per unit activity concentration in the residue (mSv per Bq/g)	
		Adult	Child, 1–2 years
IAEA model [21]			
Based on modelled groundwater contamination, including a modelled leach rate of 0.000111 a^{-1}	2.75	0.12	0.11
Based on modelled groundwater contamination, but with a predetermined leach rate of 0.001 a^{-1} as was assumed in Ref. [23]	24.83	1.06	1.01
Based on measured groundwater contamination (90th percentile) [22]	2.78	0.12	0.11
Based on measured groundwater contamination (mean) [22]	1.22	0.05	0.05
Alternative model of groundwater contamination and ingestion dose, with an assumed leach rate of 0.001 a^{-1} [23]	Not reported	5.683	10.269

The question as to which set of assumptions is the more appropriate is a matter of debate. The main purpose of this example is simply to demonstrate that the choice of modelling assumptions can have a critical influence on the result, and that it is always preferable to make the greatest possible use of measured data. It also raises some other questions, for instance:

(1) Is it reasonable to characterize the ‘representative person’ as a person belonging to any particular age group (e.g. 1–2 years as in the results presented above), or is it more appropriate to consider only an adult or

perhaps a combination of age groups weighted according to the number of years spent in each age group?

(2) Is it reasonable to assume that residents will choose (or will be permitted) to obtain their regular drinking water supply from a contaminated well next to a mine residue deposit when such water is likely to be unfit for drinking purposes due to contaminants such as dissolved salts and heavy metals?

8.2. Harmonization of standards and regulatory approaches at the national level

Despite having achieved a considerable degree of consensus in the development of international standards for NORM, the standards and regulatory approaches being adopted at the national level are still far from being harmonized. With minerals being traded worldwide on a very large scale, this is resulting in a situation that some might describe as ‘chaotic’, with severe disruptions in the movement of goods from one country to another and unnecessary interference in normal trade. In addition, scarce regulatory resources, especially in developing countries, are probably not being used in an optimum fashion, leading to the possibility that more pressing radiological issues are not receiving an appropriate level of attention. The problem is illustrated by the following anecdotal reports:

(i) Consignments of imported zircon and zirconia are reported to have been rejected and returned to the exporting country because their activity concentrations exceeded ‘local background’ by more than a predetermined factor ranging up to a value of ten.

(ii) It has been reported from another country that the criterion for regulation of materials containing radionuclides of natural origin has been set at 0.1 Bq/g, ten times lower than recommended in the international standards.

(iii) The import of certain fertilizers, phosphate ores and zirconium containing products has reportedly been prohibited because of elevated levels of radionuclides of natural origin. It seems that the authorities applied a limit on activity concentration of 0.15 Bq/g, above which the material is rejected. This has had a discriminatory effect on some potential trading partners whose products do not meet this criterion.

Clearly there is a need to move towards a more harmonized approach in order to minimize problems like this that appear to be occurring on an ever increasing basis.

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THORIUM AND ITS INDUSTRIAL APPLICATIONS

(Topical Session 1)

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THORIUM APPLICATIONS IN SPAIN

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Abstract

The Spanish Regulatory Authority — the Nuclear Safety Council — following the recommendations of European Directive 96/29 embarked on studies to assess the risk associated with non-nuclear applications of thorium in Spain. The work presented in this paper reflects preliminary results of a study aimed at checking the traditional applications of thorium that are still in use and assessing the radiological impact of each one of them and the environmental impact of waste disposal. In this regard, several applications have been tracked through the Spanish market. The most important result obtained from the analysis of all these applications is that the vast majority of them have been abandoned as a result of the replacement of thorium by other elements, mainly yttrium, cerium and lanthanum. Nowadays the most important application is the manufacture and use of thoriated electrodes for tungsten inert gas welding. This is followed by the application in lighting, where thorium is used to coat tungsten electrodes in high intensity discharge lamps. The market for thoriated tungsten electrodes for welding involves 300 000–400 000 units per year, all of which are imported, mainly from China, so there is no manufacturing of thoriated electrodes in Spain. The life of one of these electrodes has been tracked from its arrival in Spain to the disposal of the pieces remaining after use, assessing the radiological impact of storage, welding, sharpening and disposal as waste. Some of these tasks have been completed and some are still in progress.

1. INTRODUCTION

Following the recommendations of European Directive 96/29 [1], the Spanish Regulatory Authority — the Nuclear Safety Council (Consejo de

Seguridad Nuclear) — embarked on studies to assess the risk associated with non-nuclear applications of several types of naturally occurring radioactive material (NORM) used mainly in industry. In particular, the study of thorium applications in Spain was entrusted to a cooperative research team from the University of the Basque Country and the University of Zaragoza.

The work presented in this paper reflects preliminary results of this study, aimed at checking which of the traditional applications of thorium still remain in use and finding out whether new applications have been developed, as well as assessing the radiological impact of each one of them and the environmental impact of waste disposal. In this regard, the uses reported in the European Commission reports Radiation Protection 95 [2] and Radiation Protection 107 [3], as well as in US Nuclear Regulatory Commission report NUREG-1717 [4], have been sought in the Spanish industry. It has been concluded that only the following applications should be tracked through the Spanish market: incandescent gas mantles, welding electrodes, lamps, aeronautical and aerospace thoriated alloys, vacuum tubes and optical lenses. The most important result obtained from the analysis of all these applications is that the vast majority of them have been abandoned as a result of thorium having been replaced by other elements, mainly yttrium, lanthanum and cerium.

Nowadays, the most important application is the manufacture and use of thoriated electrodes for tungsten inert gas (TIG) welding, followed by the application in lighting, where thorium is used to coat tungsten electrodes in high intensity discharge (HID) lamps. Aeronautical and aerospace thoriated alloys are used in aircraft engine parts, but only to a limited extent, if at all. The market for vacuum tubes is dominated by magnetrons for microwave ovens, but the activity content is only one hundredth of that of one welding rod and consequently the dose can be neglected. In optical lenses, thorium was added to some optical glasses to improve their optical properties. It seems that safety and environmental concerns, plus the availability of better optical manufacturing methods, led to the decline in the use of thorium, with production virtually stopping in the 1980s.

While external exposure is easily monitored, the radiation hazard arising from inhalation and ingestion of thorium or thorium contaminated dust during the various production operations such as the use of welding rods in many industries and the equivalent (but smaller scale) deployment in lamp technology requires a more elaborate assessment. In Spain there are no processes of sintering or pressing tungsten electrodes in the welding rod industry.

2. THORIUM CHARACTERISTICS

Naturally occurring thorium is mainly the single isotope ^{232}Th, a radioactive alpha emitter with a half-life of 1.405 × 10^{10} a. The long radioactive decay chain headed by ^{232}Th contains another thorium isotope, ^{228}Th, with a half-life of only 1.9116 a. If radioactive equilibrium is achieved, both radioisotopes have the same activity. More information on the complete decay chain can be found in Table 1.

Natural thorium can be found in several minerals; nowadays thorium is recovered commercially from the mineral monazite that contains 3–9% ThO_2 along with rare earth minerals. Thorium was discovered by Berzelius in 1828 who named it after Thor, the Scandinavian god of war. Its main properties are [6]: atomic weight 232.0381; atomic number Z = 90; melting point 1750ºC; boiling point 4788ºC; specific gravity 11.72. Pure thorium is soft and very ductile and can be cold rolled, swaged and drawn, but is difficult to find — usually it is contaminated with oxide. When contaminated with the oxide, thorium slowly tarnishes in air, becoming grey and finally black Thorium oxide has the highest melting point of all oxides and is the chemical compound used in industrial applications of thorium. Its characteristics are: white odourless solid, molecular weight 264.04 g/mol, melting point 3220ºC, boiling point 4400ºC; specific gravity 9.86. Thorium oxide is alloyed with tungsten, which has a higher melting point of 3422ºC, to improve some of the properties of pure tungsten.

TABLE 1. MAIN CHARACTERISTICS OF THE ^{232}Th DECAY CHAIN [5]

Primary chain			Secondary chain		
Isotope	Half-life	Main decay	Isotope	Half-life	Main decay
^{232}Th	1.40 × 10^{10} a	Alpha			
^{228}Ra	5.75 a	Beta			
^{228}Ac	6.15 h	Beta			
^{228}Th	1.9116 a	Alpha			
^{224}Ra	3.66 d	Alpha			
^{220}Rn	55.6 s	Alpha			
^{216}Po	0.145 s	Alpha			
^{212}Pb	10.64 h	Beta			
^{212}Bi	60.55 m	Beta 64%	^{212}Bi	60.55m	Alpha 36%
^{212}Po	0.299 μs	Alpha	^{208}Tl	3.053m	Beta
^{208}Pb	Stable		^{208}Pb	Stable	

3. INCANDESCENT GAS MANTLES

Incandescent gas mantles, also known as Welsbach mantles, were the main application of ThO_2 up to the invention of TIG welding. They have been used for more than 100 years since their invention by Baron Carl Auer von Welsbach in 1885. Thorium containing mantles were available in a variety of designs and sizes, each intended to fit into one of the many different lighting devices in use. To function, the mantle must be heated to a temperature of 1870–2370ºC, which causes the thorium oxide in the mantle to incandesce. This is achieved by placing the mantle over, in or near a gas or kerosene flame that burns during the operation of the device. The greatest incandescence is obtained with mantles that consist of 99% thorium oxide plus 1% cerium oxide after pre-burning. The heat energy accumulates in thorium oxide and then the absorbed energy is transferred to cerium oxide, which emits strong visible light [7]. Without thorium oxide, the heat energy absorbed by cerium oxide is released mainly as infrared radiation. In view of the potential risks, the use of radioactive mantles cannot be justified and nowadays they have been substituted with non-radioactive mantles that contain yttrium instead of thorium to produce incandescence. Thorium is not an essential element of gas mantles because non-radioactive mantles are as bright as radioactive ones.

The main problem with radioactive mantles is that they, and many other radioactive consumer products, are sold without any information concerning radioactivity, which is essential for consumers to be able to decide whether to purchase them. Furthermore, the general public should be educated so that they can understand the information concerning radioactivity. There is not much quantitative information about the thorium content of mantles. Nevertheless, in NUREG-1717 [4] it was assumed that a typical mantle contained 250 mg (1 kBq) for the purpose of dose calculations. They noted that some mantles contained up to 400 mg. In Europe there is no longer any fabrication of radioactive gas mantles and it is almost impossible to find them on the market. But it seems that some manufacturing still exists in the USA. Radioactive mantles could not be found in Spain.

4. WELDING ELECTRODES

Metallurgical industries present a high potential risk for workers due to the radioactivity of thorium, as thoriated welding rods probably represent the most extensive use of thorium among the non-nuclear industrial applications of this isotope. Thoriated welding rods used in TIG welding are tungsten electrodes with a 1–4% thorium oxide (ThO_2) content. This type of welding is used in industry for aluminium, stainless steel, thin sheets of metal and wherever a very good and reliable weld is required. TIG welding can be performed in any position, particularly in inverted and vertical positions. Thoriated TIG electrodes are 15 cm long, with a diameter of 1–4.8 mm. The role of the rod is to provide a high temperature plasma in a gas atmosphere, usually argon, produced by a continuous gas flow. The arc is about 1–2 cm long and thorium is added to the tungsten rods because it helps to strike the arc and maintain a better arc stability, avoiding fluctuations in the flame. Manufacturers have tried to substitute the thorium with other non-radioactive elements with similar electrical, metallurgical and thermal properties, such as lanthanum and cerium, but performance is not improved and the producers of tungsten electrodes for inert gas welding rely largely on thorium as the most effective additive. Sometimes thorium is also added to the alumina grinding discs used for sharpening the tungsten electrodes.

In Spain the most widely used thoriated welding rods are those containing 2% ThO_2 and having a diameter of 1.6, 2.0 or 2.4 mm. Sometimes, 1 and 4 mm diameters are used. Measurements were performed on different rods from two large suppliers of welding electrodes in Spain. The Spanish market for thoriated electrodes involves 300 000–400 000 electrodes per year, almost all of which are manufactured in China.

4.1. Storage

Storage in warehouses of electrodes from different importers was considered and the radiation field was simulated using the computational code MCNP-4C [8]. The modelled scenario consisted of a set of shelves 2 m high, 2 m wide and 1 m deep, storing 2% ThO_2 welding rods 1.6, 2.0 and 2.4 mm in diameter. The rods were usually in PVC or polyethylene boxes containing 10 units. The exposure scenario is summarized in Table 2.

TABLE 2. EXPOSURE SCENARIO FOR THE STORAGE SIMULATION

Rod diameter (mm)	Boxes					Total mass (kg)
	Quantity	Width (cm)	Length (cm)	Height (cm)	Volume (cm^3)	
1.6	850	4	18	0.5	36	64.5
2.0	300	4	18	0.5	36	37.5
2.4	850	6	18	0.8	86.4	153.5

In order to standardize and avoid different criteria on the distribution of boxes in the shelves, a unique density of 2.22 g/cm^3 (1.75 g/cm^3 due to the welding rods) and a unique geometric distribution of boxes were assumed. The photon energies considered were those of all X ray and gamma emissions in the decay chain with an emission frequency higher than 0.1% [5], grouped in 30 keV intervals. In this way, the total final probability accounted for was 99.02% with a mean energy of 594 keV. Radiation doses were calculated at distances of 20 and 60 cm from the shelf.

The results for the central part of the front face of the shelf are summarized in Table 3 and illustrated in Fig. 1. The dose rates obtained in the adjacent corridor, 60 cm from the shelf and 1 m above the floor, are shown in Fig. 2. Considering now that a warehouse worker walks at a speed of 3 km/h along the corridor, the dose received by the worker would be 3.39×10^{-4} μSv. Assuming that the worker is exposed once per hour, the annual dose would be 1.97 μSv for a working year of 1700 h. Secular equilibrium in the decay chain is assumed — it is shown later in the paper that this assumption leads to an overestimation of the dose.

4.2. Distribution of ThO_2 in the rods

Electrodes are made by sintering and eventually pressing a mixture of tungsten and ThO_2 powder. The homogeneity of the distribution of thorium in the rods was studied by measuring the activity of different segments by gamma and alpha spectroscopy and also by electron microscope analysis of the surface

TABLE 3. DOSE RATES CALCULATED AT THE CENTRE OF THE FRONT FACE OF A SET OF SHELVES ON WHICH THORIATED WELDING RODS ARE STORED

Height from floor (cm)	Dose rate (μSv/h)	
	20 cm from shelf	60 cm from shelf
5	2.11	1.16
40	2.89	1.56
70	2.69	1.45
105	3.13	1.72
135	2.71	1.48
170	2.97	1.62
200	2.27	1.25

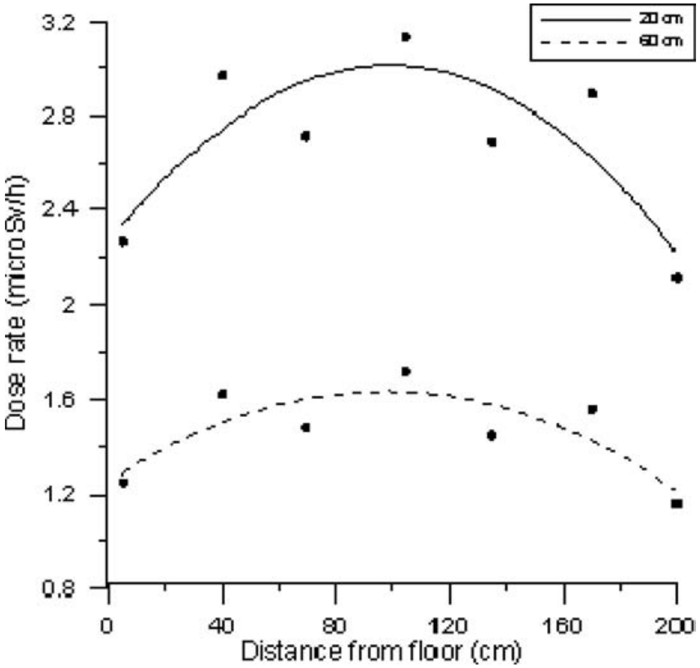

FIG. 1. Dose rate distribution beside a set of shelves storing thoriated electrodes

and of different cuts made at different places along the electrode perpendicularly to its axis. The results show that the ThO_2 particles are more or less homogeneously distributed both along the electrodes and in the radial direction, so it was concluded that the distribution could be considered homogeneous. The sharp end of the electrode where the electric arc is produced was the subject of particular study. Electron microscope photographs showed that fusion and sublimation of ThO_2 takes place at the surface, with the ThO_2 grains being almost absent from the external surface of the sharp end of the electrode after 1 h of continuous use.

4.3. Radioactive equilibrium of the ^{232}Th chain

To establish the equilibrium status of the different radioisotopes in the ^{232}Th chain, a quantitative determination of the thorium content was performed by alpha and gamma spectrometry. The aim was to define with some precision the source term of the radiation field and to know the radionuclide content generated in the diverse stages of the use of the electrodes as well as of the residues. The analysis of radionuclides was carried out by using intrinsic

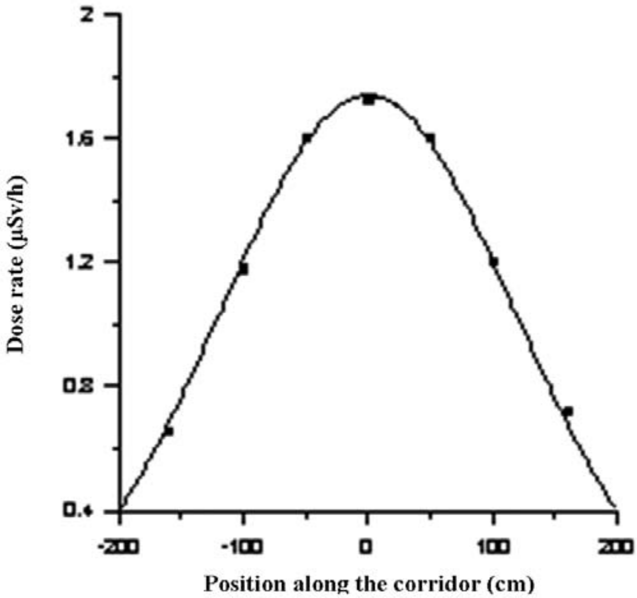

FIG. 2. Dose rate distribution along the adjacent corridor

germanium low background reverse Canberra detectors GX4018 with 40% efficiency and, for the alpha spectroscopic analysis, Canberra passivated implanted planar (PIP) silicon detectors with 450 mm^2 of active area.

The electrodes studied had a ThO_2 content in the range 1.7–2.2%. Measurements of the content of ^{232}Th and its decay product ^{228}Th are summarized in Table 4, along with similar measurements conducted on lanthanated and ceriated electrodes for comparison. The uncertainty of the measurements is about 1% (k = 1). The theoretical activity concentrations of ^{232}Th are 61.16 Bq/g for 1.7% ThO_2, 71.8 Bq/g for 2.0% ThO_2 and 79.22 Bq/g for 2.2% ThO_2.

If equilibrium conditions prevail, the activities of ^{232}Th and ^{228}Th will be the same. Extraction of thorium will cause the equilibrium to be broken and the parent isotope will start the reconstruction of the equilibrium. Then the ratio $^{228}Th/^{232}Th$, initially with a value of unity, should diminish with time to a minimum of 0.422 after 39 855 h or 4.55 a. Should the ratio be below this number then at least a second thorium extraction has occurred. If this new extraction is performed precisely at the moment of the minimum, the new minimum ^{228}Th/^{232}Th ratio will fall to a value 0.178. The decay equations give the following expression for the ratio ^{228}Th/^{232}Th:

$$\frac{A\left({}^{228}Th\right)}{A\left({}^{232}Th\right)} = 1 + \left[\frac{\lambda_4}{\left(\lambda_2 - \lambda_4\right)} e^{-\lambda_2 t}\right] + \left[1 + \frac{\lambda_2}{\left(\lambda_4 - \lambda_2\right)} e^{-\lambda_4 t}\right]$$

$$\cong 1 + 1.4980 \quad \left[e^{-\lambda_4 t} - e^{-\lambda_2 t}\right]$$

The results in Table 4 suggest that at least two separations of thorium have been made, one of them is obvious — it was when thorium was extracted from the mineral — but a second one has been performed in the course of fabrication of the welding rods as the value of the thorium ratio is around 0.3, below the minimum value of 0.422 that would be obtained with only one extraction.

4.4. Radioactivity of airborne particulate and dust while welding

The workplace thorium air concentration was measured by taking samples of airborne particulate and dust components. To simulate the breathing conditions of workers in a representative way, low volume samplers were used [9]. Both the welding and the grinding operations were monitored, as well as the environmental radioactivity in the workplace. The welding

TABLE 4. ^{232}Th AND ^{228}Th CONTENT OF THORIATED, LANTHANATED AND CERIATED ELECTRODES.

Type of electrode	Diameter	Weight (g)	Activity concentration		
			^{232}Th (Bq/g)	^{228}Th (Bq/g)	Ratio ^{228}Th/^{232}Th
2% ThO_2 (brand 1)	1	0.1431	78.23	20.95	0.268
	2.4	0.8652	64.40	20.40	0.317
	4	2.5675	60.53	18.46	0.305
2% ThO_2 (brand 2)	1	0.1169	51.40	19.17	0.373
	2.4	0.4521	63.00	24.29	0.386
	4	2.2371	62.86	23.74	0.378
2% La O_2	2	0.2452	0.45	0.13	0.289
2% CeO_2	2	0.2209	0.20	0.06	0.30

intensities were 80–90 A for manual welding and 140 A for an automatic robot welding machine. Airborne particulate and dust samples were collected at a welding school run by a major Spanish welding electrode manufacturer. Nitrocellulose filters 47 mm in diameter with a nominal pore size of 0.8 μm were used. Samples were collected at the working point while welding both manually and with an automatic robot welding machine. Also, samples of environmental airborne particulate were collected in the welding hall. The air flow rate was set at 30 L/min in order to simulate the normal breathing of a person. Some of the results are summarized in Table 5. Thorium-230 belongs to the ^{238}U family and was detected in manual welding, probably coming from the material being welded. Measurements conducted on deposits on hands while welding gave a negligible activity.

4.5. Radioactivity of airborne particulate and dust while sharpening the welding rods

Samples of airborne particulate were collected while performing the grinding operation on the electrodes. The sharpening operation of one electrode takes about 1–2 minutes and generally is performed manually, usually after having accumulated many electrodes, which are then sharpened together. Samples of dust deposited onto the hands (usually gloves have to be worn) and airborne particulate from the nose position of the worker were also collected. The activity collected on the filters was very low. Taking into account the short duration of the exposure, even when several electrodes are accumulated, a negligible dose can be assumed. The deposition on the hands, mainly on the left hand (for a right handed person) could be more important if the obligatory gloves are not worn. The airborne particulate and dust, as well as the deposition on the hand while sharpening thoriated electrodes and pure tungsten electrodes, was measured. In one trial, involving a surface area sample of 31.5 cm^2, the activity concentrations were 6.00×10^{-3} Bq/cm^2 for ^{232}Th, 2.13 ×

TABLE 5. ACTIVITY OF AIRBORNE PARTICULATE AND DUST WHILE WELDING

	Volume of air sample (m^3)	Mass of deposit (mg)	Activity concentration (Bq/m^3)		
			^{232}Th	^{228}Th	^{230}Th
Robot trial 1	2.25	1.5	8.80×10^{-4}	2.77×10^{-4}	Not detected
Robot trial 2	3.96	4.6	3.65×10^{-4}	Not detected	Not detected
Manual Welding	2.272	4.8	3.00×10^{-3}	1.35×10^{-3}	4.27×10^{-4}

10^{-3} Bq/cm^2 for ^{228}Th and 1.08 × 10^{-3} Bq/cm^2 for ^{230}Th. Thorium-230 probably comes from the alumina grinding discs used for sharpening the rods.

5. LAMPS

A variety of electric lamps used for illumination may contain thorium. In the past, thoriated tungsten filaments were used extensively in incandescent lamps intended for general lighting purposes. However, most such lamps now use rhenium–tungsten filaments. Thorium has also been widely used in lamps requiring high electrode emissivity, in lamps that emit intense light such as lamps used in vehicles and in lamps emitting light with specific spectra. The most common type of outdoor and industrial lamps containing thorium appears to be HID lamps, including mercury vapour, metal halide, and mercury–xenon arc lamps. These lamps are constructed with thick walled glass or quartz envelopes designed to withstand considerable temperature variations and rough use. In addition to general outdoor or industrial lighting, HID lamps are used for roadway lighting and for lighting in large indoor structures. The lamps are in different external forms but essentially all of them contain a quartz capsule about 1.5 cm in diameter and about 2.5–3 cm long. Electrodes coated or containing ThO_2 are located at both extremes of the central axis. Two electrodes in the form of rods, each with a total mass of 0.1083 g, were measured. The activity of these lamp electrodes is only 2 × 10^{-3} times the activity of a single 2.4 mm diameter thoriated TIG electrode. In addition, the ThO_2 part of the lamp electrodes are encapsulated and so there is no ^{220}Rn emission and only gamma rays would need to be considered in any future dose estimation. The conclusion is that the dose contribution of lamps can be ignored.

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RADIATION EXPOSURE IN THE PRODUCTION AND USE OF THORIATED GAS MANTLES

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Abstract

Even today, thoriated gas mantles are quite often used in Germany, mainly for street lighting, lighting of railway points and nautical lighting. During production, maintenance and repair of these gas illumination devices, thorium can be released in inhalable form as dust, leading to internal contamination. Analyses of workplaces where workers change the gas mantles, clean the lights and do other maintenance work outside show incorporation of radioactivity due to working conditions. During maintenance of street lighting in workshops there is a risk of workplace contamination, not only in the workshop itself but also in the maintenance van. Results of a measurement campaign are shown in the paper. A few months ago, the production of thoriated gas ended in Germany. The radiation exposure during the production process has been investigated very comprehensively and it has been shown that there had been relatively high exposures in the past. The lifetime doses of two workers producing gas mantles may exceed the limit of 400 mSv if the range of errors in estimation is taken into account. The main part of these doses results from incorporation rather than from external exposure, although in some cases external exposure may be fairly high. The paper describes the materials and methods used in assessing the doses and presents the results of workplace related analyses and internal dose assessments for the production, storage and use of thoriated gas mantles.

1. INTRODUCTION

1.1. Reasons for using thorium in gas mantles and frequency of use

Thorium oxide is the main component of gas mantles as it raises their light emitting efficiency. There have been several attempts to replace thorium with other rare earth metals, but up to now the light emitting efficiency and the mechanical stability are unsatisfactory. The total activity of a single gas mantle can vary from a few becquerels up to 17 kBq [1].

The principal use of these gas mantles in Germany is for gas light in some larger cities, for example Dresden, Düsseldorf, Frankfurt and Berlin. There are as many as 20 000 gas lanterns with 10 gas mantles each in one single city. In Germany there are approximately 10 000 nautical lighting devices and 100 000 railway points (switches) equipped with gas mantles. Furthermore, thoriated gas mantles are used in camping lights and other private applications. About 1.5 million gas mantles are sold annually in Germany. These public and railway lighting devices have to be maintained and repaired. It has been estimated that more than 250 people are occupationally involved with thoriated gas mantles in Germany.

1.2. Hazards while using thorium as an unsealed source

Two main exposure pathways are distinguishable: internal exposure through inhalation of thorium-containing dust and external exposure when higher activities are handled. Normally the dose from external exposure is less than the dose from internal exposure, but it cannot be neglected. There are a few workplaces, especially those where gas mantles are produced, where the external exposure could contribute of the order of some millisieverts per year.

During the production and use of thorium containing gas mantles, internal exposures cannot be totally avoided. Therefore a monitoring programme has to be established to protect the exposed workers. The main procedures are the analysis of 24 h urine samples or the sampling and analysis of individual air monitoring samples. Interpretation of the analysis results is difficult because of biased views with respect to naturally occurring radionuclides.

2. MATERIALS AND METHODS

2.1. Reference nuclide

The use of thoriated gas mantles may result in exposure to ^{232}Th, ^{230}Th and their radioactive progeny. Out of this mixture of radionuclides only the three isotopes ^{232}Th, ^{230}Th and ^{228}Th are radiologically relevant, as a comparison of the dose coefficients shows [2]. None of the other daughter radionuclides make a significant contribution to the overall dose. The radionuclide composition of a gas mantle depends on the time elapsed after chemical separation of the thorium. The activity of ^{228}Th could, at most, be the same as that of ^{232}Th. The activity of ^{230}Th could be of the same order of magnitude as that of ^{232}Th as a worst case, depending on the origin of the raw material. So an upper bound on the estimation will be obtained if — as a first order simplification — the activity of all three thorium nuclides is set to be equal. The actual dose would not be underestimated with this assumption. The advantage of this approach is that one can focus the analysis on the activity of one reference nuclide, namely ^{232}Th.

2.2. Air monitoring

The workers were equipped with personal breathing zone air samplers during their normal work (see Fig. 1). The inhalable dust [3] was collected on type

FIG. 1. Personal air monitoring during maintenance of gas lanterns.

BIA MF 11301 (pore size 8 μm, 37 mm diameter) membrane filters by using a sampling unit with an electronically controlled volume airflow of 0.21 m^3/h.

2.3. Urine samples

In the case of workers who maintain gas lanterns, 24 h urine samples were collected. Second samples were taken two months later. Those workers employed in the production of thoriated gas mantles have been regularly monitored with 24 h urine samples for a long time [4].

2.4. Smear samples

Smear tests were taken with type Pedi AG, Zürich, Nr. 100829 smears. Several work sites were smeared with a surface area of 100 cm^2. A removal factor of 10% was assumed. All smears were analysed for ^{232}Th activity.

2.5. Analysis

For the determination of ^{232}Th it was decided to use a high resolution inductively coupled plasma mass spectrometer (ICP-MS) [5]. Filter materials and smears were ashed and dissolved in nitric acid. Urine samples were directly measured after addition of nitric acid. The detection limit of this method is 0.001 μg/sample or, for ^{232}Th, 0.01 mBq/sample.

3. THORIUM EXCRETION RATES DUE TO NON-OCCUPATIONAL INGESTION

Within the framework of a project supported by the German Federal Office for Radiation Protection, individuals who were not occupationally exposed to thorium were chosen as volunteers for a broad investigation of naturally induced thorium excretion rates in urine. The persons lived in different regions of Germany with a wide spectrum of naturally occurring radionuclides in the soil. This is reflected in the results of thorium in urine for these individuals, which span many orders of magnitude. In total, 306 urine samples were measured. The minimum value was lower than the detection limit of 0.001 μg/d and the maximum value was 2.024 μg/d. The median was 0.012 μg/d, equivalent to 0.05 mBq/d ^{232}Th. This median value is a reference value for the evaluation of the excretion rate of ^{232}Th.

4. EXPOSURE ESTIMATION FOR PRODUCTION OF GAS MANTLES

For almost a decade, the exposure of workers at a gas mantle production facility in Germany was investigated. Many urine samples were collected and air monitoring measurements were made. The first measurements — ten years ago — showed a high activity concentration in the workplace. Step by step, radiation protection measures were installed, for example the enclosure of machinery and installation of air extraction systems. The average air activity concentration of ^{232}Th for the highest exposed procedure (cutting) decreased in the course of these measures from nearly 200 mBq/m^3 to 10 mBq/m^3.

4.1. Production steps

Gas mantles are manufactured in several production steps. The basic material is a cotton hose in the form of a coil. This is soaked in thorium nitrate solution and treated with liquid ammonia. The soaked coils are centrifuged, uncoiled, and hung up to dry. The next step entails cutting them into smaller pieces of fabric which are then pressed into the required form and attached to a mounting. The overlapping tissue is cut, after which these intermediate products are burnt. During the later steps, the thorium is in dioxide form. The cotton fabric is totally burnt away, leaving only the thorium dioxide mantles. To stabilize these fragile gas mantles for transport they are dipped in varnish. The last step is the packaging. Additional operations involving thorium exposure are the testing of selected gas mantles, the cleaning of the work sites and the maintenance and repair of the machinery. During all of these operations, thorium may be inhaled, first in nitrate form and later in dioxide form.

FIG. 2. Personal air monitoring during the drying of coils.

4.2. Results of the urine samples

More than 200 urine samples from the 10 workers involved were analysed — one urine sample per year up to 1994 and four samples per year since 1995. Most of the results were below the detection limit, which varied over the period of the investigation from 0.2 to 1.5 mBq/d ^{232}Th. However, for nearly every worker there were some results above the detection limit. The maximum value was 2.8 mBq/d. A comparison with the median value of the non-occupationally induced excretion rate of 0.05 mBq/d ^{232}Th (see Section 3) indicated an occupationally induced incorporation among the workers investigated.

The measurements were interpreted in accordance with the ICRP human respiratory tract model [6] and the dose coefficients for intakes of radionuclides by workers [7]. A chronic incorporation and an AMAD of 5 μm were assumed, as well as a mixed chemical form of the inhaled thorium in the ratio of nitrate to dioxide appropriate for the worker concerned. As an example, the maximum rate of thorium excretion corresponded to an annual uptake of about 2600 Bq.

4.3. Results of air monitoring

Between 1995 and 2003 many personal and stationary air monitoring samples were collected. Separate measurements were carried our for the workplaces where thorium nitrate was handled and those where thorium dioxide was used, in order to distinguish between the two inhalation classes and production steps. The results were expressed as uptake per working hour. A working matrix was determined for every worker, showing the relative periods involved in the different production steps over the course of a year. The total annual uptake was calculated by multiplying the time spent at each workplace by the uptake per working hour at that workplace and then summing over the whole year. The highest annual uptake was about 900 Bq for dioxide and about 90 Bq for nitrate.

4.4. Dose estimation for workers in a gas mantle production facility

The external dose, measured with approved dose meters, also had to be taken into account. The annual external doses varied between zero and 6.8 mSv, depending on the operations performed by the worker. The highest external doses were found to be associated with working with the barrels in which the thorium nitrate was delivered, mixing of the soak solution and handling of the soaked coils.

For each monitored worker, the assessed values resulting from the urine measurements were compared with those resulting from the air monitoring measurement. The accumulated dose was expressed for each worker as a range of doses over the worker's lifetime, to account for errors in estimation. Based on the reference nuclide, all relevant nuclides were considered in this assessment. The lowest lifetime dose range for an individual worker was 23–84 mSv and the highest was 134–483 mSv. For two of the workers, the error bars extended beyond the limit on lifetime dose applied in Germany of 400 mSv.

5. EXPOSURE ESTIMATION FOR USE OF GAS MANTLES

An investigation was performed to estimate the intake of thorium by maintenance workers of a lighting supplier company.

5.1. Work steps

When only cleaning and changing of gas mantles is requested, maintenance of the lantern heads is done at their location. Workers go to the location in service vans and reach the lantern heads by ladder. The vans are equipped for minor repair work inside them. If a lantern needs more extensive repair, the head is removed and brought to a workshop where it is completely disassembled and reassembled. Leak tests of gas tubes and gas mantles are done in a separate room next to the main workshop. According to the work records, five workers were identified as having mostly done outside maintenance work and were therefore suitable for participation in the project. Of those employees who had done workshop and final checking work, only one could be persuaded to take part in the project. Samples were taken from the participants, as described in Sections 2.2 and 2.3, and smear test samples were taken from inside the workshops, from inside the vans and from inside the lanterns when they were opened for cleaning and changing of the gas mantles.

5.2. Results of the urine samples

Ten urine samples of five workers who maintained gas lanterns were analysed to determine the excretion rates. All the results were above the detection limit of the analytical method. Six of the results fell below the median value of 0.05 mBq/d for natural radioactivity of ^{232}Th as described in Section 3. Four values were in the range of 0.1–0.3 mBq/d ^{232}Th. The precise maximum value was 0.32 mBq/d.

5.3. Results of the air monitoring

For two days three workers were equipped with personal breathing zone air samplers (see Section 2.2) during their normal maintenance work. The exposure time was from 1 h to about 6 h. The results of the filter analysis were in the range of 1.28–0.02 mBq per filter. The highest value was associated with an exposure time of 1.5 h.

5.4. Results of the smear samples

Eighteen smear test samples were taken. Only the ^{232}Th activity was determined. This activity was in the range of 5–900 mBq per sample. For the ^{232}Th activity alone, a third of the samples exceeded the maximum value of 100 mBq/cm^2 permitted in Germany. If the other relevant nuclides are taken into account, this value would be exceeded for most of the other workplaces.

5.5. Dose estimation for workers using gas mantles

The excretion rates of ^{232}Th in urine are of the same magnitude as the excretion rates attributable to natural uptake. Therefore, incorporation attributable to occupational exposure is not evident from these measurements. Nevertheless, it might be interesting to evaluate the dose of the most highly exposed individuals in this investigation. Under the assumptions described briefly in Section 2.1, a rough and conservative estimate could be made, taking into account the dose coefficients for inhalation and the retention values for urine excretion. This results in a dose of 0.16 mSv for air monitoring measurements and 0.27 mSv for urine measurements. This difference can be deemed to be acceptable when considering the possible sources of errors in the different methods used.

6. SUMMARY

According to legislation, the authorities do not need to be notified of maintenance to the gas lanterns investigated in this study. The maximum dose of these workers is far below an annual effective dose of 6 mSv, and even far below the average dose of about 2.1 mSv per year received by the citizens of Germany from natural sources [8].

The smear measurements require that the stationary workshop and the workshop vans be professionally decontaminated, because most of the surface contamination exceeds the permitted limit of 100 mBq/cm^2.

The comprehensive investigation conducted at a gas mantle factory has shown that workers could receive relatively high doses. The introduction of radiation protection measures has resulted in a clear reduction in the dose received by these workers.

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THORIUM AND URANIUM BIOACCUMULATION IN WHEAT AND RYE PLANTS

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Abstract

Greenhouse pot experiments were carried out to study the mobility of U and Th in soil and the bioavailability of these radionuclides to two widely cultivated plants (wheat and rye). The purpose of this research was to estimate an ability of the crops to accumulate U and Th, thus removing these metals from contaminated soil. Rye and wheat grown in radionuclide enriched soils demonstrated a significant increase in concentrations of U and Th in the roots of both these plants. Th was less available for plant uptake than U. The ratios of radionuclide concentrations in roots of the plants grown in contaminated soil to those in roots of the control plants were 45 (U) and 25 (Th). Despite such a significant increase of radionuclide concentrations in the plants, the U content in the soils decreased by only two times, and the Th concentration in the contaminated soils remained unchanged. No transfer of U and Th to plant leaves was detected in any of the plants. As a result of soil contamination at trace levels, wheat and rye were able to accumulate U and Th in the roots but were unable to translocate these radionuclides to leaves at measurable concentrations.

1. INTRODUCTION

Environmental pollution is a global problem resulting from mining, industrial, agricultural and military activities. Radioactive contamination is among the main sources of environmental pollution, which can seriously threaten human health. The restoration of contaminated soils is difficult and expensive. Phytoremediation is a promising in situ technology, where plants are used to facilitate removal of metals from contaminated soils [1]. The plant root system induces a gradient of water flow through soil toward the plant root surface. This flow of water can remove a portion of metals from the soil. Then metals may be taken up by roots and transferred to the upper parts of the plant. The removal of radionuclides from soils is an area in which phytoremediation may have a particular impact due to the lack of alternative effective technologies.

Uranium and thorium are common natural radioelements. These radionuclides are present in soil in varying concentrations related to the nature of the parent rocks during soil genesis. Uranium is naturally present at low concentrations in the global environment, but is generally more abundant than metals such as Sn, Cd, Hg and Pb. Thorium is surprisingly abundant in the Earth's crust, being almost as abundant as Pb and three times more abundant than U. The data on distribution of U and Th in plants have been demonstrated in many scientific publications [2–6]. These long lived naturally occurring radionuclides may be transferred to plants along with the nutrients during mineral uptake and then may be accumulated in different plant parts, thus removing these metals from contaminated soil. Although under normal environmental conditions levels of U and Th concentrations in native plants are generally very low, there are numerous reported data on increased uptake of U and Th by plants growing in contaminated soils [7–9]. This work was undertaken to study the mobility of U and Th in soil and their bioavailability to two widely cultivated *Porceae* plants (wheat and rye). The purposes of the research were (1) to estimate an ability of the crops to accumulate U and Th, thus removing these radionuclides from contaminated soil and (2) to determine the effects of radionuclide bioaccumulation on uptake of other nutrients and trace elements by the plants.

2. MATERIALS AND METHODS

Greenhouse pot experiments were carried out in October 2005. Wheat (*Triticum aestivum* L.) and rye (*Secale cerealeis* L.) seeds were obtained from the Microbiology Department of St. Petersburg Technical University. Seeds were germinated for five days on moist filter paper. Five day old seedlings were transferred to large ceramic pots filled with soil. Before sowing, the soil in the pots was watered with 500 mL of four different water solutions: 1: $Th(NO_3)_4$, 2: $(UO_2)(NO_3)_2$, 3: a mixture of nitrates of U and Th (concentrations of U and Th in the solutions were 50 mg/L^{-1}) and 4: control. Each test was performed in triplicate. Initial soil samples were taken for analysis just after watering, before seedlings were transferred to soil. During the experiment, plants were watered every day with tap water. Plants and soil (from the root surface) were collected three times: within 3, 7 and 11 days after sowing. At the end of the experiment, soil from the bottom of all pots was also collected to estimate possible leaching of U and Th to deeper soil layers. Just after sampling, while the plants maintained turgor pressure, the plants were carefully washed until they were free of any visible soil particles**.** The plant and soil samples were then air dried at room temperature to a constant weight and analysed by instrumental neutron activation analysis. The samples were irradiated for 18 h (soils) and 24 h (plants) in a thermal neutron flux of 1×10^{14} $n\cdot cm^{-2}\cdot s^{-1}$ in the FRM-II reactor of Munich Technical University. The k0 method was used to calculate the concentrations of elements [10]. A statistical treatment of experimental data (the program Statistica for Windows 5.5) was used to estimate the mean concentrations of elements and differences between groups of samples. A cluster analysis was applied to assess the effects of the treatments on element behaviour in the plants.

3. RESULTS AND DISCUSSION

The mean concentrations of elements in rye and wheat roots and leaves are presented in Tables 1 and 2. Although rye is botanically related to wheat (both belong to the *Hordeae* tribe), these two plants differ markedly in concentrations of many elements. Wheat has higher amounts of many elements than rye. This is typical for both the roots and leaves of the plants. The only exception is Na. Its concentration in rye leaves is higher than in wheat leaves ($P < 0.05$). In rye and wheat roots the concentration of Na is very similar. The concentrations of many elements (As, Co, Eu, Fe, Na, Sc, Ta, U and Zn) in roots of both these plants are higher than in leaves. This indicates that roots prevent the penetration of large amounts of different elements to the upper plant parts. Plants have evolved highly specific mechanisms to take up, translocate and store various elements. The uptake mechanism is selective; plants preferentially acquire some elements over others. For example, the concentrations of essential plant nutrients such as K (and Rb, the chemical analogue of K) and Sr in rye and wheat leaves are higher than in roots. This means that the plants use the mechanism of active transport of these elements from roots to leaves. It was surprising to find that the concentration of Sb in rye and wheat leaves was higher than in roots — Sb is not an essential plant nutrient and this finding cannot be explained at the moment.

As might be expected, after adding U and Th to the soil the concentration of these radionuclides in the soil increased significantly. Compared with the control, the U concentration was 6 times higher after treatment with U and 3 times higher after treatment with U + Th. The Th concentration was 5 times higher after treatment with Th and 3 times higher after treatment with U + Th.

TABLE 1. MEAN CONCENTRATIONS OF ELEMENTS IN RYE
(mg/kg except where indicated otherwise)

	Control		Soil with added U		Soil with added Th		Soil with added U + Th	
	Roots	Leaves	Roots	Leaves	Roots	Leaves	Roots	Leaves
As	0.43±0.11	<0.4	0.57±0.06	<0.4	0.45±0.23	<0.4	0.46±0.14	<0.4
Au	0.09±0.02*	0.19±0.11	0.12±0.03	0.16±0.10	0.16±0.12	0.13±0.12	0.14±0.02◆	0.19±0.07
Ba	25.3±3.0[a]	35.1±0.5	20.5±7.4	28.8±12.2	33.9±8.0	34.9±8.9	18.8±2.0◆	38.0±8.5
Br	18.9±18.2[a]	4.84±1.58	7.12±1.84	3.15±0.31	14.9±10.4	3.56±0.43	12.5±10.7	3.33±1.19
Ca,%	0.49±0.03[a]	0.78±0.24	0.56±0.27	0.84±0.27	0.43±0.05	0.78±0.20	0.46±0.13	0.72±0.33
Ce	1.71±0.49	1.72±0.37	<5	1.82±0.70	2.21±1.69	2.10±0.82	3.01±1.99	1.60±0.63
Co	0.31±0.01[a]*	0.08±0.01*	0.45±0.06◆	0.09±0.01	0.42±0.09	0.10±0.01	0.37±0.08	0.08±0.04
Cr	8.66±2.23	6.16±0.63	22.0±16.7	6.88±1.63	12.8±8.5	6.16±1.23	15.3±8.4	5.76±2.11
Cs	1.50±1.08	1.43±0.91	0.96±0.10	1.26±0.83	3.09±1.76	0.53±0.13	1.27±0.65	2.07±1.66
Eu	0.08±0.02[a]*	0.03±0.01*	0.12±0.01◆	0.03±0.02	0.13±0.10	0.03±0.03	0.35±0.42	0.03±0.01
Fe	610±109[a]*	317±86	855±160	319±88	779±14	304±29	628±179	287±122
Hf	1.16±0.40	0.94±0.19*	1.70±0.49	1.08±0.35	1.62±1.05	0.90±0.29	1.38±0.04	0.94±0.41
K,%	1.92±0.78[a]	5.09±2.16	2.45±1.16	5.63±2.89	2.13±0.69	5.75±1.72	2.00±0.97	5.68±1.75
La	0.59±0.05	0.72±0.17*	<1	0.77±0.21	0.79±0.61	0.82±0.26	0.35±0.23	0.67±0.22
Lu	0.02±0.01[a]*	0.05±0.01	0.05±0.01◆	0.05±0.02	0.04±0.03	0.04±0.02	0.04±0.01◆	0.04±0.01
Na,%	0.83±0.21[a]	0.13±0.02*	0.82±0.03	0.13±0.01	1.04±0.36	0.12±0.01	0.94±0.32	0.13±0.03
Rb	22.3±3.6[a]	36.4±14.0	25.6±6.63	38.4±17.8	23.7±4.6	38.3±10.4	19.6±6.4	36.9±8.9

TABLE 1. MEAN CONCENTRATIONS OF ELEMENTS IN RYE (cont.)
(mg/kg except where indicated otherwise)

	Control		Soil with added U		Soil with added Th		Soil with added U + Th	
	Roots	Leaves	Roots	Leaves	Roots	Leaves	Roots	Leaves
Sb	0.73±0.05[a]	1.83±0.97*	1.20±0.57	2.08±1.69	1.94±1.31	3.01±3.27	0.84±0.42	4.44±3.13
Sc	0.11±0.03[a]*	0.03±0.01*	0.17±0.06	0.04±0.01	0.15±0.01	0.03±0.01	0.12±0.03	0.03±0.01
Sm	0.07±0.02*	0.08±0.02*	0.99±0.38◆	0.11±0.03	0.13±0.02◆	0.09±0.03	0.60±0.35	0.07±0.03
Sr	<25	16.6±5.7	<36	60.5±42.8	<21	80.2±55.3	<21	124±7
Ta	0.06±0.03	<0.05	0.14±0.09	<0.05	0.09±0.03	<0.05	0.08±0.03	<0.05
Th	0.21±0.02*	0.18±0.01	0.32±0.06◆	0.19±0.06	9.56±2.30◆	0.22±0.06	5.68±2.67◆	0.27±0.09
U	0.77±0.37	<0.40	34.2±13.8◆	0.35±0.05	1.26±0.10	0.42±0.08	17.5±12.3	0.45±0.23
Yb	0.12±0.05	0.18±0.03*	0.20±0.07	0.21±0.08	0.19±0.10	0.19±0.06	0.14±0.04	0.20±0.09
Zn	171±63[a]	68.2±8.6	179±46	65.8±3.1	181±54	71.4±15.4	148±51	71.9±12.3

◆ Differences between the control and different treatments are statistically significant ($P < 0.05$).

[a] Differences between roots and leaves of control plants are statistically significant ($P < 0.05$).

* Differences between rye and wheat are statistically significant ($P < 0.05$).

TABLE 2. MEAN CONCENTRATIONS OF ELEMENTS IN WHEAT
(mg/kg except where indicated otherwise)

	Control		Soil with added U		Soil with added Th		Soil with added U + Th	
	Roots	Leaves	Roots	Leaves	Roots	Leaves	Roots	Leaves
As	0.86±0.09	<0.4	0.75±0.26	<0.4	0.71±0.15	<0.4	0.45±0.07	<0.4
Au	0.31±0.03	0.21±0.16	0.19±0.10	0.17±0.09	0.20±0.07	0.28±0.11	0.29±0.13	0.20±0.15
Ba	27.3±3.2	32.7±15.1	19.7±3.9	30.7±9.8	29.6±16.9	32.3±19.6	32.2±15.8	33.5±13.3
Br	18.7±6.5 [a]	7.52±1.99	10.5±5.5	5.98±1.46	24.6±20.0	5.92±1.77	18.6±13.0	5.51±1.77
Ca,%	0.66±0.37	0.82±0.22	0.70±0.04	0.88±0.26	0.91±0.17	0.85±0.51	0.79±.022	0.88±0.40
Ce	2.30±1.17	2.42±0.67	3.01±2.63	2.42±0.78	2.03±0.66	3.23±0.42	3.84±1.67	2.24±0.39
Co	0.47±0.01 [a]	0.14±0.04	0.43±0.04	0.13±0.02	0.51±0.02	0.13±0.02	0.41±0.04	0.14±0.02
Cr	29.9±23.0 [a]	9.56±2.68	15.8±0.4	8.67±2.42	22.7±10.5	10.9±2.9	25.7±19.8	8.47±1.01
Cs	1.23±0.93	1.53±1.09	0.82±0.35	1.63±1.34	1.73±0.21	0.91±0.07	1.98±1.50	1.22±0.39
Eu	0.15±0.01 [a]	0.05±0.01	0.17±0.05	0.04±0.01	0.21±0.08	0.07±0.06	0.14±0.01	0.04±0.01
Fe	978±9 [a]	409±120	625±209	364±87	915±304	429±101	614±63 [◆]	355±66
Hf	2.06±0.52	1.66±0.40	1.85±0.40	1.59±0.47	2.87±1.45	1.96±0.59	3.37±2.68	1.37±0.18
K,%	2.19±0.75 [a]	6.23±0.34	2.80±0.98	6.47±2.19	3.23±1.02	6.63±1.35	3.24±1.22	7.39±2.32
La	0.94±0.20	1.22±0.24	0.95±0.05	1.11±0.24	0.95±0.30	1.39±0.60	0.44±0.59	1.09±0.18
Lu	0.05±0.01	0.08±0.03	0.09±0.03	0.08±0.02	0.08±0.04	0.10±0.03	0.09±0.07	0.07±0.01
Na,%	0.80±0.14 [a]	0.06±0.01	0.54±0.13	0.06±0.01	0.91±0.42	0.06±0.01	0.83±0.15	0.05±0.01
Rb	28.8±3.5 [a]	40.1±3.7	30.6±11.1	40.8±18.8	37.2±12.4	40.3±10.1	33.9±14.5	45.9±13.8

TABLE 2. MEAN CONCENTRATIONS OF ELEMENTS IN WHEAT (cont.)
(mg/kg except where indicated otherwise)

	Control		Soil with added U		Soil with added Th		Soil with added U + Th	
	Roots	Leaves	Roots	Leaves	Roots	Leaves	Roots	Leaves
Sb	0.82±0.45 [a]	4.13±0.62	0.85±0.34	4.64±3.50	1.99±1.29	2.68±2.18	1.51±0.48	1.17±0.60
Sc	0.20±0.01 [a]	0.05±0.01	0.13±0.05	0.04±0.01	0.18±0.08	0.08±0.03	0.11±0.05	0.04±0.01
Sm	0.14±0.02	0.15±0.02	0.76±0.10[◆]	0.15±0.03	0.16±0.05	0.19±0.06	0.56±0.28	0.13±0.01
Sr	<40	15.0±5.0	<32	27.6±15.2	<19	28.9±12.1	<25	24.7±10.0
Ta	0.10±0.01	<0.05	0.09±0.02	<0.05	0.13±0.06	<0.05	0.14±0.10	<0.05
Th	0.32±0.04	0.28±0.09	0.26±0.04	0.24±0.09	8.59±3.90[◆]	0.79±0.46	9.92±12.1	0.32±0.04
U	0.91±0.04 [a]	0.25±0.10	23.2±3.9[◆]	0.32±0.13	1.06±0.47	0.32±0.13	11.6±2.9[◆]	0.21±0.06
Yb	0.25±0.07	0.35±0.07	0.37±0.30	0.30±0.09	0.29±0.15	0.44±0.13	0.39±0.38	0.29±0.06
Zn	170±2 [a]	87.6±11.9	195±87	83.2±8.8	163±17	82.3±4.3	147±50	76.9±0.8

[◆] Differences between control and different treatments are statistically significant ($P < 0.05$).

[a] Differences between roots and leaves of control plants are statistically significant ($P < 0.05$).

There was no leaching of these metals to deeper soil layers. The concentrations of Th and U in the bottoms of all pots were approximately the same, regardless of the treatments.

Rye and wheat grown in the pots with radionuclide enriched soils demonstrated significant increases in the concentration of Th and especially U in the roots of both plants. After addition of the mixture of U and Th to the soil, the concentrations of U and Th in the plant roots were also increased. However, this increase was less marked than in the experiments where U and Th were added to soil as single elements, probably because of competition between these metals during the uptake process. It is significant that the concentrations of U and Th in the leaves remained unchanged. This means that the transfer of these radionuclides from soil to leaves via root uptake was minimal.

The ratios of the U and Th concentrations in the roots of wheat and rye to the concentrations of these elements in the soil where the plants were grown are shown in Fig. 1. The ratios are higher for U than for Th for all the treatments

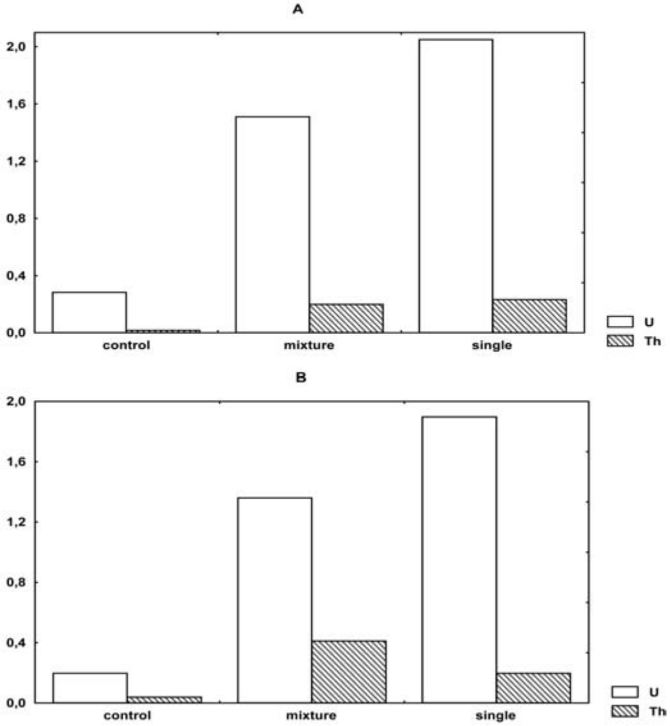

FIG. 1. Ratios of U and Th concentrations in rye (A) and wheat (B) roots grown in control and contaminated soils to the U and Th concentrations in the control soil and in the soil where U or Th (singly) or U + Th (mixture) were added.

and for both plant species. It has been reported that the mobility of uranium in soil is higher than the thorium mobility, regardless of the soil type [11, 12]. Th^{4+} is readily soluble, but at the same time it may be quickly adsorbed or precipitated as hydrolysate. It has been suggested [13] that the manner of migration in soil may be different for Th than for U, with Th migrating either as a negatively charged particle or as an anionic complex with organic matter. Since soil metal mobility correlates with the bioavailability of the metal to the plant, certain differences in the bioavailability of U and Th can be expected.

Calculation of the soil to plant concentration ratios showed that the $U_{[root]}/U_{[soil]}$ ratios in experiments with U and U + Th are greater than unity. One might expect that such a significant uptake of U by plants could result in a decrease of U concentration in the rhizosphere soil. As an example, Fig. 2 (A) illustrates the dynamics of U in the soil where rye was grown (for the control, after adding U and after adding U + Th). With time, the soil U concentration decreased slightly in the experiment with the mixture of U and Th and decreased rather significantly in the experiment where only U was added to

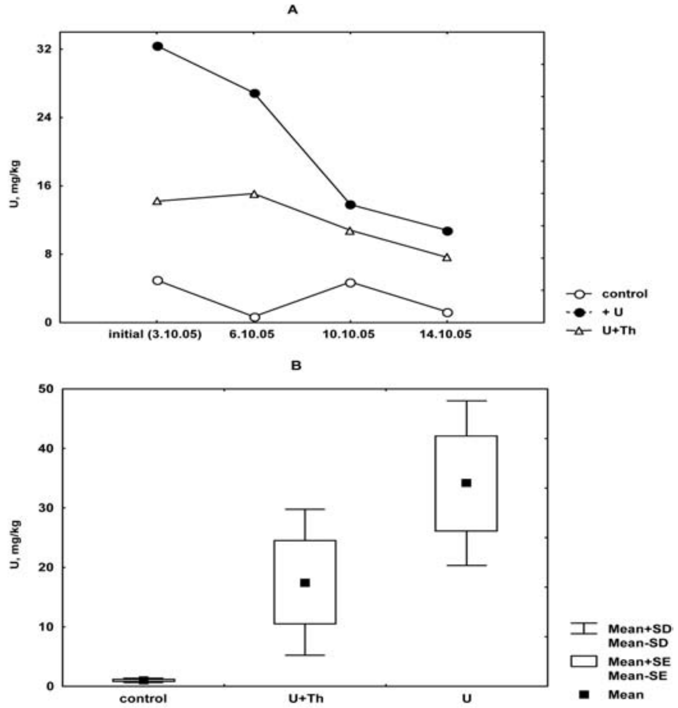

FIG. 2. Dynamics of U in soil (A) and mean concentrations of U in rye roots grown in control soil and in soil to which U and U + Th were added (B).

soil. As seen from Fig. 2 (B), such a decrease in the soil U concentration resulted from uptake of U by the plant roots. The decrease was lower in the experiment with U + Th because the plants could take up less U than in the experiment with U alone.

The ratios of radionuclide concentrations in the roots of the plants grown in contaminated soil to those in the roots of the control plants are about 45 (U) and 25 (Th). This confirms that Th is less available than U for plant uptake. Despite such a significant increase of U and Th concentrations in the plants, the U content in the contaminated soils decreased only by a factor of two and the Th concentration remained unchanged. Moreover, U was not transferred from roots to leaves and therefore it was not actually removed from the contaminated soil. The main conclusions from these observations are: (1) the biomass of the young seedlings was probably too small to clean up the large mass of contaminated soil and (2) due to the higher mobility of U in soil and, as a result, the higher level of bioavailability of this metal to plants, U may be more easily removed from soil than Th.

Bioaccumulation of any metal in a plant can result in certain variations in concentrations of some other elements in the plant. In the experiments, wheat roots were less affected than rye roots. Compared with the control, there was a statistically significant increase in the concentration of Sm in the roots of the wheat grown in U contaminated soil, while in the roots of the wheat grown in soil where U and Th were both added the concentration of Fe was lower ($P < 0.01$). In rye roots more variations in element concentrations were observed after treatment of soil with U. In this case, there were statistically significant increases in the concentrations of Co, Eu, Lu, Sm, and Th over those in the control plants. The concentration of Sm in the roots of the rye grown in Th enriched soil was higher ($P < 0.05$) than the Sm content in roots of the control plants. In the roots of rye grown in the soil treated with both U and Th, the concentrations of Au and Lu increased and the Ba content decreased. The elemental composition of the leaves of the rye and wheat seedlings remained rather stable for all the treatments.

Fig. 3 illustrates the results of a cluster analysis of the leaves of rye and wheat (control plants and plants grown in U contaminated soil). The leaves of the control plants are well divided into two groups, rye and wheat. We could expect such a division; it was due to differences in the concentrations of several elements in the leaves of wheat and rye (Table 1). However, there is no such good distinction for plants grown in contaminated soil. Considering the fact that the concentrations of elements in the leaves of the plants grown in control and contaminated soils are similar, these variations are probably explained by certain changes in the relationships between elements in the plants grown in contaminated soils. Exactly the same situation is observed in the plant roots.

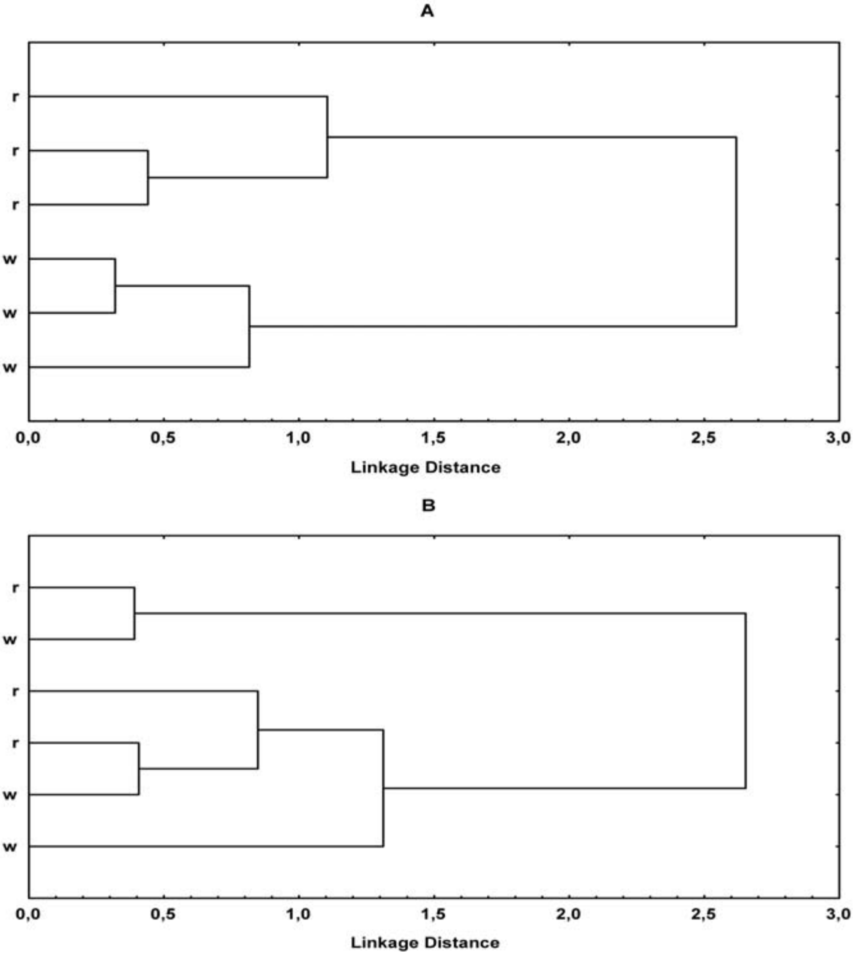

FIG. 3. Cluster analysis (Ward's method) of rye leaves (r) and wheat leaves (w) grown in control soil (A) and in soil enriched with U (B).

ACKNOWLEDGEMENT

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PROCESSING AND USE OF ZIRCON AND ZIRCONIA

(Topical Session 2)

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Invited Paper

THE INDUSTRIAL USES OF ZIRCON AND ZIRCONIA AND THE RADIOLOGICAL CONSEQUENCES OF THESE USES[*]

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Abstract

The paper reviews the industrial uses of the natural mineral zircon and the zirconia derived from it. Brief reference is made to the natural mineral baddeleyite, but since it is a minor source of zirconium it is not discussed at length. The annual world market for zircon is around 1 million tonnes and its main uses are in ceramics, refractories, foundry materials, chemicals and abrasives. More specialized uses are in glass, electronics, pigments and catalysts and for the production of zirconium metal. The paper reviews the processes used in these industry sectors and the products made from each of them. In each case the radiation exposures to workers and the public from these industrial processes are considered. The potential exposure to workers and the public from the products of each of these industrial sectors is discussed, together with a positioning of this exposure in terms of international regulatory standards. In order to do this, a review of the current status of international standards, as applicable to zircon and zirconia, is included. The paper also covers the more generic issues such as milling, transportation and waste disposal, as applied to these industries. The paper shows that 23% of zircon and zirconia users should be outside the scope of regulation and that the radiological impact associated with a further 54% is sufficiently low to allow such users to be exempted from regulation. The remaining 23% of users could become subject to some level of regulatory control.

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[*] Information included in this paper was used in the development of the IAEA Safety Report on Radiation Protection and NORM Residue Management in the Zircon and Zirconia Industries [1].

1. INTRODUCTION

This paper presents an overview of the zircon and zirconia industries, including the raw materials and the product uses. The legislation which appears to be relevant for these industry sectors is reviewed and, for the purposes of this paper, summarized into a set of simplified guidelines. The remainder of the paper reviews the preparation of milled zircon and zirconia, an overview of the main uses of zircon and zirconia and a consideration of the transport issues around these materials. During the review of the uses, emphasis is placed on the process for manufacturing specific products, the exposure pathways and doses anticipated from those pathways, a consideration of the waste disposal issues and, using the simplified guidelines, the likely degree of regulation that may be required in each industry sector.

2. OVERVIEW OF THE INDUSTRY

2.1. Zircon

Zircon occurs most commonly around the globe in beach placers or dune deposits. The distribution of the reserves of zircon is shown in Table 1, which shows that the known reserves have increased from 37 million t in 2002 to 54 million t in 2005. Most of these reserves are in Australia and southern Africa. Table 2 shows the global production of zircon, again comparing the years 2002 and 2005. Global production of zircon is around 1.1 million t/a, largely from Australia and South Africa. In contrast, Table 3 shows the main consumer countries of zircon and it is apparent that the bulk of the mineral is used in Europe and the Far East. Consequently, transport becomes an essential element in this global resource market and is dealt with separately later in the paper. Of note is the significant increase in Chinese consumption of zircon, a pattern which is repeated across many other commodity groups. Table 4 shows that the most important use of zircon is in the ceramics industry. Within this industry the production of ceramic tiles and sanitary ware is the main growth area. There have been changes in the usage pattern between 2002 and 2005, with a decrease in foundry and refractory uses and an increase in the production of zirconia, zirconium chemicals and ceramics.

2.1.1. Zircon and radioactivity

All zircon contains uranium and thorium in the crystal lattice. These primordial radionuclides were added to the zircon structure during the crystal-

TABLE 1. RESOURCES OF ZIRCON BY COUNTRY (courtesy: TZ Minerals International, 2005)

	Resources (million t)	
	2002	2005
South Africa	14	11
Australia	9.1	20
Ukraine	4	5
United States of America	3.4	6
India	3.4	3
Mozambique	—	6
Madagascar	—	3
Rest of the world	3.6	—
Total	37	54

TABLE 2. PRODUCTION OF ZIRCON BY COUNTRY (courtesy: TZ Minerals International, 2006)

	Production (kt)	
	2002	2005
Australia	438	437
South Africa	420	398
USA	70	164
Ukraine	35	32
India	18	23
Brazil	18	26
China	—	35
Rest of the world	134	70
Total	1132	1185

TABLE 3. CONSUMPTION OF ZIRCON BY REGION
(courtesy: TZ Minerals International, 2006)

	Relative consumption	
	2002	2005
Europe	36%	35%
China	20%	26%
North America	14%	13%
Asia–Pacific	14%	15%
Japan	7%	5%
Rest of the world	9%	6%

TABLE 4. COMMERCIAL USES OF ZIRCON
(courtesy: TZ Minerals International, 2006)

	Relative consumption	
	2002	2005
Ceramics	49%	54%
Refractories	16%	14%
Foundry sands and mould washes	17%	13%
Chemicals and zirconia	9%	12%
Television glass	8%	4%
Other	1%	3%

lization of the zircon in molten rock. Being a very stable mineral, zircon is used as a 'geothermometer' and it has been shown that many commercial zircons are of great geological age — of the order of 500–1000 million years. The radionuclides added during crystallization have decayed over time to their current levels, which for most commercial zircons would be about 250–350 ppm uranium, and about 100–200 ppm thorium. Some zircons contain higher levels of thorium but these are often due to the presence of separate grains of the thorium-bearing mineral monazite. The stability of the zircon structure has been demonstrated by the low values of radon emanation fraction measured and the ability of zircon to retain ^{210}Po within its structure up to temperatures of about 1200°C. The crystal structure of zircon can be destroyed by very high temperatures and chemical attack. Once the structure is destroyed the contained radionuclides are liberated and their subsequent distribution depends on the processes being used. Generally the decay chains in most zircons are in secular equilibrium.

2.2. Zirconia

Naturally occurring zirconia is called baddeleyite and occurs in igneous rocks such as carbonatite. South Africa was the largest producer of baddeleyite until 2002, but these production facilities have now closed down and the only commercial source of this mineral is the Kola Peninsula region of the Russian Federation. Most of the zirconia now available is manufactured from zircon (34 000 t/a), with the natural supply from the Russian Federation being relatively small (6000 t/a). Table 5 shows the uses of zirconia — the main uses are in refractories and ceramic pigments, with the ceramic pigment sector having shown a significant increase between 2002 and 2005.

2.2.1. Zirconia and radioactivity

In a similar manner to zircon, the baddeleyite received its content of radionuclides during crystallization from the molten rock. Unlike zircon, however, the baddeleyite may not be in secular equilibrium owing to modifica-

TABLE 5. COMMERCIAL USES OF ZIRCONIA
(courtesy: TZ Minerals International, 2006)

	Relative consumption	
	2002	2005
Refractories	42%	39%
Ceramic pigments	22%	33%
Advanced ceramics and catalysts	6%	12%
Abrasives	10%	6%
Electronics	6%	6%
Oxygen sensors	2%	2%
Glass and gemstones	2%	1%
Other	10%	1%

tions occurring in the geological environment. The activity concentrations of ^{238}U and ^{232}Th in baddeleyite formerly originating from South Africa were each about 9–10 Bq/g. In contrast, the activity concentration of ^{238}U in baddeleyite originating from the Russian Federation is about 3 Bq/g.

3. SIMPLIFIED GUIDELINES FOR EVALUATING THE REGULATORY IMPLICATIONS FOR THE ZIRCON AND ZIRCONIA INDUSTRIES

There is a considerable degree of variability in national regulatory standards affecting NORM. This causes some confusion for the operators and traders in this industry. In order to conduct this review, national regulatory standards have not been considered, but rather the standards established by the International Atomic Energy Agency (IAEA) and the European Union (EU):

(a) The IAEA International Basic Safety Standards [2];
(b) The IAEA Transport Regulations [3];
(c) IAEA Safety Standards Series on exemption, exclusion and clearance [4];
(d) EU Report Radiation Protection 122, Practical Use of the Concepts of Clearance and Exemption and Clearance to Natural Radiation Sources [5].

Based on these documents, the following simplified guidelines have been formulated for the purpose of establishing, later in the paper, the likely regulatory implications for the zircon and zirconia industries:

(1) An occupationally exposed worker is one who receives an annual effective dose exceeding 1 mSv;
(2) A supervised area is one in which a worker may receive an annual effective dose not exceeding 6 mSv;
(3) A controlled area is one in which a worker may receive an annual effective dose exceeding 6 mSv;
(4) The action level for radon in workplaces is 500 Bq/m^3;
(5) The action level for radon in homes is 200 Bq/m^3;
(6) The dose limit for a member of the public is 1 mSv from all sources;
(7) The dose constraint for a member of the public is 0.3 mSv from a single source;
(8) The regulator must be notified if the activity concentration of any material exceeds 1 Bq/g;

(9) The exemption and clearance level for NORM is an annual effective dose of 0.3 mSv;

(10) For NORM to be exempt from the Transport Regulations, the sum of the ^{238}U and ^{232}Th activity concentrations must be less than 10 Bq/g.

In order to review the possible regulatory impacts of the different zircon and zirconia uses, the concept of the graded approach to regulation, as established in the IAEA standards, was used as the basis for formulating the following simplified guidelines on levels of regulation:

(i) Notification is assumed to be required if the activity concentration of any ^{238}U or ^{232}Th series radionuclide in material is above 1 Bq/g;

(ii) Exemption is assumed to be the regulatory option if the annual effective dose is less than 1 mSv for workers and 0.3 mSv for members of the public;

(iii) Registration of a work activity is assumed to be required if the annual effective dose received by a worker exceeds 1 mSv;

(iv) Licensing of a work activity is assumed to be required if the annual effective dose received by a worker exceeds 6 mSv.

The development of these simplified guidelines allows the uses of zircon and zirconia to be reviewed against a consistent benchmark. The actual situation may vary depending on regulatory preferences, etc.

4. PROCESSING OF MATERIALS

4.1. Milling of zircon

This processing step is used by more than 70% of zircon users, which means that more than 700 000 t of zircon are milled each year in preparation for other processing steps. There are 3 forms of milled zircon in common use, each defined by the particle size. Zircon flour occurs as a 95% ‘minus 75 µm’ product or a 95% ‘minus 45 µm’ product. Micronized zircon is generally a 95% ‘minus 5 µm’ product. The flour products are commonly prepared by the use of air swept ball mills fitted with classifiers and baghouses for dust collection. In contrast, micronized zircon is made by a wet milling process using vibro energy or stirred ball mills. The main exposure pathways from this process are external exposures from storage of raw materials and products, inhalation exposures from plant leaks, bagging operations and process cleanups. Radon exposure is not generally significant as long as storage areas are well ventilated. Typical annual effective doses received by workers in milling plants are approximately 300 μSv from external radiation and 500 μSv from dust inhalation, giving a total of less than 1 mSv. This, however, is dependent on good operation of the facility to ensure that dust control is maintained. Waste disposal issues are minimized by the high value of the product, which encourages recycling. Any waste that cannot be recycled is mixed with damp sand or concrete prior to disposal in a landfill facility. The annual effective dose received by a member of the public from milling operations is unlikely to exceed about 250 μSv if dust control is responsibly managed.

The regulatory implications of zircon milling, therefore, would be the submission of a notification to the regulatory body. Well managed operations could be exempted, but because of the possibility of poor management, registration may be appropriate.

4.2. Manufacture of zirconia

Zirconia has three crystal structures with different temperature stability ranges. The monoclinic phase is stable up to 1200°C, at which point it changes to the tetragonal phase and then at 2300°C to the cubic phase. Dissociation occurs at 2680°C. This change in phase causes volume changes which diminish the usefulness of zirconia in high temperature applications. However, the crystal structure can be stabilized by the addition of oxides of elements such as magnesium, calcium or yttrium. The degree of stabilization can also be varied to produce partially or fully stabilized zirconia. There are two process routes to make zirconia — the thermal process and the chemical process.

4.2.1. Thermal process

In this process zircon is melted with coke at 2800°C in an electric arc furnace. The carbon reduces the zircon to zirconia and silicon monoxide. Silicon monoxide, being unstable, is rapidly oxidized to silica, which comes off the process as a silica fume. Stabilizing elements are added to the melt to produce the desired composition. The molten product is tapped from the furnace, cast into blocks and crushed to the desired particle size range.

Typical radionuclide activity concentrations in this process are 3–4.5 Bq/g for ^{238}U in the raw zircon, 4.5–6.8 Bq/g for ^{238}U in the zirconia and about 6 Bq/g for ^{226}Ra in the silica fume. The high temperatures used in this process destroy the crystal structure and allow the more volatile elements to be partially removed into the silica fume. Consequently the fume may be enriched in ^{226}Ra, ^{210}Po and ^{210}Pb. The zirconia phase retains the high boiling point elements such as uranium and thorium. Exposure pathways in this process are therefore

(a) external radiation from the raw material, from product storage and from maintenance of the silica fume collector systems and (b) inhalation exposure from silica fume and zirconia dust during the milling and bagging operations. Radon exposure is usually insignificant with well ventilated storage. Typical annual effective doses received by workers in a thermal zirconia plant are 70–260 μSv from external exposure and 600–3000 μSv from dust inhalation, giving a total annual effective dose of 700–3100 μSv.

Waste disposal issues in these plants are related to the silica fume, if not used as a by-product, and contaminated scrap from fume collection systems. Most internally generated wastes related to zircon or zirconia are recycled internally.

The operators of thermal zirconia plants should notify their regulatory bodies since both the product and the raw material are above 1 Bq/g. Since the annual effective dose received by a worker can exceed 1 mSv, the thermal zirconia process will probably require registration.

4.2.2. Chemical process

There are three possible chemical process routes to zirconia. These may be subdivided into two broad groups — those that require dissociation of the zircon and those that do not. The route not requiring dissociation entails caustic soda fusion of zircon at 700°C, producing sodium zirconate. The zirconate is then dissolved in hydrochloric acid to form zirconium oxychloride, better known as ZOC. The ZOC may be converted into zirconia by calcination or by dissolution and hydroxide precipitation. Zircon dissociates into ZrO_2 and SiO_2 at temperatures above 1800°C. Following this step, the dissociated material may be treated with either caustic soda or acid. The alkali route dissolves the silica, leaving zirconia which is then calcined, while the acid route produces a soluble zirconium salt which is later precipitated with alkali to obtain the oxide.

The chemical process also destroys the zircon crystal structure and liberates the radionuclides. The pathway followed by these radionuclides depends on which process is used, but generally the zirconia produced from these processes is greatly reduced in radioactivity. The radionuclides removed from the zircon or zirconia are contained in the process effluents which are usually neutralized and disposed of at a controlled site. The activity concentration of ^{238}U is 3–4.5 Bq/g in the raw material, <0.1 Bq/g in the zirconia, 1–2 Bq/g in the process waste streams and up to 5000 Bq/g in tank residues. Since the processing is carried out in the liquid phase, the presence of radioactive scale is a risk. Exposure pathways for the process are external exposures from raw materials, pipe scales, tank residues and effluent streams.

Typical annual effective doses received by workers in a chemical zirconia plant are 500–1000 μSv.

The main area of focus for this process route to zirconia is waste disposal, since most of the radionuclides are removed from the process in the effluents. Liquid effluents are neutralized and the precipitate is placed with any solid process wastes in a disposal dam. Authorization is needed for these disposal dams. The need for contaminated scrap to be controlled is also an issue.

The annual effective dose received by a worker in the chemical zirconia process is usually less than 1 mSv. However, because of the possibility of reaching the 1 mSv level and also because of the potential public exposure from radionuclide containing wastes, it is likely that these plants would require registration.

5. INDUSTRIAL USES OF ZIRCON AND ZIRCONIA

5.1. Ceramics

The ceramics field is very diverse and includes such products as glazed tiles, porcelain tiles, sanitary ware such as baths and wash basins, frits, ceramic pigments and engineering ceramics. The main application in the ceramics field is in glazed tiles and sanitary ware. In this application the ceramic has a two piece body — a clay based ceramic body is covered with a silicate/borate glaze to provide waterproofing, durability and decoration. Zircon is added to the glaze for opacification and to provide a white colour. The zircon may be added in the milled form as micronized zircon or as a frit. The concentration of milled zircon in the glaze is up to 20%.

Frits are ceramic glasses containing silica and boric acid and are manufactured by melting all constituents together and then quenching in water, followed by milling. The composition of the frit is controlled to the needs of the application but the use of a frit allows a water soluble constituent to be added to the glaze and converted into an insoluble form. The frit composition is set so as to control the vitrification point of the glaze. By adding the zircon in a frit form the eventual particle size of the zircon crystallites in the final glaze is controlled to the optimum for light reflection and maximum opacification. The zircon content of frits is usually 10–20%. The firing temperature for glazed ceramics is of about 1100–1270°C.

In contrast to the glazed ceramics, porcelains have a one piece ceramic body; however, they may also be glazed for decorative purposes. Porcelain ceramic tiles are more resistant to wear than the glazed variety and they are composed of clays, quartz, feldspars and nepheline syenite together with zircon. In this application the zircon is used in the milled form at concentrations of up to 15%.

Ceramic pigments are manufactured by mixing zirconia, quartz, sodium fluoride and an appropriate cation. The mixture is fired, with a controlled ramp-up of temperature to 900°C, followed by a soak time. After firing, the product is milled. The colours available vary with the cation added, with iron producing pink, vanadium 4+ producing blue and vanadium 3+ producing yellow.

There are many 'high tech' uses for zirconia in the engineering field such as coatings, grinding media and cutting tools. Zirconia coatings are applied by plasma spraying, while grinding media are manufactured by high pressure forming and sintering. Zirconia contents are 60–95%. Cutting tools are made by fusion of zirconia with alumina, with a ZrO_2 content of 5–10%.

The exposure pathways are very similar for all of the above applications in the ceramics field. The clays and zircon contribute ^{238}U, while the feldspars and syenites contribute ^{40}K. External exposure may arise from raw material storage and materials handling, while inhalation exposure may arise from mixing and blending, or from firing of products. For occupational exposure, the manufacture of ceramics leads to an annual effective dose of 30–200 µSv from external radiation and 10–400 µSv from inhalation, with a total annual effective dose of 10–500 µSv. Public exposure pathways occur with glazed and porcelain ceramics where the dominant pathway is external exposure. Radon in homes is also a possible pathway for these applications. The typical annual effective dose received by a member of the public from glazed ceramics amounts to 7–50 µSv from external radiation, together with an increase of 3–5 Bq/m^3 in indoor radon concentration. In contrast, porcelain tiles give rise to an annual effective dose of 3–150 µSv from external radiation and an increase in radon concentration of 10–46 Bq/m^3. Frits, ceramic pigments and engineering ceramics are used only in industrial applications, so do not result in any significant public exposure pathways.

Wastes related to raw materials are recycled internally and a typical waste from a ceramic plant has an activity concentration of about 0.6 Bq/g, while waste glaze slurry has an activity concentration of less than 2 Bq/g. There are no processes in the ceramics industries for enhancing the radionuclide levels above the natural levels in the zircon or the zirconia.

The ceramics industry could be a candidate for a generic exemption from regulation since the annual effective dose received by a worker is less than 1 mSv and that received by a member of the public from the use of the products is of the order of 100 µSv.

5.2. Refractories

Refractories are materials that are designed to maintain strength, dimensional stability and chemical resistance at high temperature. They are manufactured in the form of bricks, fibres, nozzles, slide gates, valves and grouts. One of the largest uses of zircon and zirconia in refractories is in the glass industry, where the linings of glass furnaces are made from a combination of zircon and zirconia bricks. The zircon bricks for glass furnaces typically contain 30–40% zircon. Zirconia is commonly used for nozzles, slide gates, filters, and ceramic linings, where the zirconia content approaches 94%. Refractories are typically made from alumina, magnesia, clays, binders and zircon or zirconia. There are two methods of fabrication: (a) mixing of the ingredients, pressing into the desired shapes, drying and kiln firing and (b) mixing of ingredients, melting in a furnace and casting the molten mass into the desired shapes.

The exposure pathways in such industries are external exposure from raw materials and products, inhalation exposure from mixing and blending of components and final shaping of products, especially where this is done by grinding. Inhalation exposure can also occur from furnace dusts where enrichment in polonium and lead can occur to levels of 20–30 Bq/g. The activity concentration of ^{238}U in refractory products ranges from about 2.5 Bq/g for glass refractories to about 5 Bq/g for the more specialized zirconia products. This can result in external exposure pathways during the use of these products, plus a potential for inhalation exposure during the demolition of furnaces. Annual effective doses received by workers during the manufacture of refractories have been assessed to be less than 600 μSv from external radiation and 10–200 μSv from inhalation of dust, with a total annual effective dose of less than 800 μSv. The use of the refractory products also needs attention as dust control is needed. The type of dust control that would be required for normal occupational health protection in such work should be sufficient. The restriction of dust exposures to normal permitted levels will also keep inhalation of radionuclides under control.

Most wastes arising from the manufacture of refractories are recycled internally, but waste refractories themselves are usually buried in landfill facilities. Used refractory bricks may be contaminated with non-radioactive substances such as heavy metals, and the disposal of these bricks is governed more by these substances than by the radionuclide content. Depending on the furnace application, used refractory bricks may have to be sent to a hazardous waste site. Annual effective doses arising from the burial of waste refractories at landfill sites have been assessed at a few microsieverts.

Refractory manufacturers should notify their regulatory bodies as the activity concentration in their raw material is above 1 Bq/g. The annual effective dose received by a worker is generally less than 1 mSv and the dose received by a member of the public is insignificant because refractory items are for industrial use only. The refractory industry could be a case for exemption from regulation, but the regulatory body would probably need to be convinced on a case by case basis.

5.3. Foundry uses

Zircon is used in the preparation of moulds for the casting of metals. These moulds are generally made of quartz sand and lined with zircon sand. The refractory nature of the zircon provides temperature resistance and the ability to make more precise castings. In this application the zircon content of a sand mould would be 10–30%. A related application uses a mould wash consisting of a slurry of various minerals including zircon, where the ingredients are milled prior to slurrying. The sand moulds are sprayed with the mould wash to impart a refractory surface layer to the mould. In this form the content of zircon in the mould wash would be in the range of 60–70%. The most precise form of metal casting is achieved by the investment casting process where a wax replica is made of the article to be cast. This wax replica is coated with a slurry containing zircon in the milled form. After several applications of the slurry with drying of each individual coat, the wax replica becomes covered with a shell of refractory material. Firing of the shell hardens the shell and removes the wax. These shells contain 30–50% zircon.

The main exposure pathways in a foundry are external exposure during handling and storage of the raw material and during handling of the used moulds, and inhalation exposure during the mixing and blending operations and during the mould removal operation. The typical annual effective dose received by a worker in a foundry operation is less than 200 μSv from external exposure and less than 300 μSv from inhalation, with a total annual effective dose of less than 500 μSv.

Used moulding sands are generally recycled within the foundry or reused in the construction industry. Used shells from investment casting are generally disposed of in landfill facilities. The ^{238}U activity concentration in the wastes from foundries is in the range of 0.9–1.3 Bq/g. The annual effective dose received by a member of the public from such disposal activities has been estimated to be about 100 μSv.

Foundry operators should notify their regulatory bodies because of the activity of the raw materials, but the foundry operations could receive a generic exemption due to the low doses received in this industry sector and the low potential exposures to the public from disposal operations.

5.4. The glass industry

Zircon is added to the glass used in the face plates of cathode ray tubes used in televisions and computer monitors. The purpose of this addition is to absorb the X rays emitted by the electron gun in the tube and to increase the refractive index of the glass. The zircon content is in the range of 3–5%. Zircon is also added to the glass used in LCD and plasma displays but at a concentration of 1–2%. The zircon is added in the flour form to the glass making ingredients.

The exposure pathways in this industry are external exposures from raw material storage and inhalation exposure from handling of zircon flour. The annual effective dose received by a worker in a CRT manufacturing facility is less than 300 μSv from external exposure and less than 100 μSv from the inhalation of dust. The increase in radon concentration is insignificant and the total annual effective dose is less than 400 μSv. In terms of doses received by the public from the use of such equipment, the exposure pathways would be by external exposure from the face plates of the displays. Since the ^{238}U activity concentration in a CRT face plate is less than 0.2 Bq/g, the dose received by a member of the public will be insignificant.

Recycling is common in the manufacturing part of the glass industry, but post-use recycling is not practised due to the lack of quality control that this introduces to the product. However, owing to the very low activity concentration, the product would be suitable for disposal in a landfill facility if no other route could be found. The WEEE Directive in Europe may have an influence on the disposal of such equipment.

Operators in this field should notify the regulatory body because the activity concentration in the raw material is above 1 Bq/g, but since the annual effective dose received by a worker is well below 1 mSv and since there are no significant pathways for public exposure, a generic exemption could be considered for this application.

5.5. Zirconium chemicals and zirconium metal

Zirconium chemicals are used mainly in paint driers, paper coatings and antiperspirants. They are also used in a diversity of other applications such as leather tanning, fungicides, grain refiners and flame proofing.

Zirconium chemicals are commonly produced from the oxychloride (ZOC). This intermediate product may either be produced at the site of the chemicals manufacture or the producer may purchase the ZOC directly. The manufacturing process of ZOC is described in Section 4.2.2.

Zirconium metal is used in the nuclear industry as the containment for nuclear fuel rods. It is produced from zircon by a carbo-chlorination process at 2000°C, where zirconium tetrachloride is produced. This material is reduced using metallic magnesium to obtain the zirconium metal. The use of zirconium in the fuel cycle also requires the removal of hafnium, which is an inherent contaminant of zircon.

The exposure pathways in chemical manufacturing depend on whether the operator produces ZOC on-site or purchases it. In the case of ZOC production on-site, the pathways are the same as described in Section 4.2.2. If the operator has purchased the ZOC there are no significant pathways for exposure as the starting material has insignificant levels of radionuclides. The exposure pathways for metal manufacturing would also be similar to those described in Section 4.2.2, but metal plants may produce radium bearing sludges which can result in public exposure.

Operators in the ZOC production process and the metal producers would be required to notify the regulatory body owing to the activity of the raw materials, but chemical producers starting with purchased ZOC would probably not be required to notify the regulatory body because the activity of the raw material is less than 1 Bq/g.

5.6. Zirconia catalysts

Zirconia is used as a physical support for other catalysts and as a catalyst in its own right. This application of zirconia requires ultra pure material and the starting material is one of the zirconium chemicals. The zirconia is precipitated from a solution under carefully controlled conditions and the product is calcined. The properties of the product are controlled by the manner of preparation. Since the activity concentrations in the starting materials are less than 1 Bq/g and no enrichment takes place, the activity concentrations in the catalyst materials are also less than 1 Bq/g. Under these conditions it is unlikely that a catalyst producer would need to notify the regulatory body.

5.7. Electronics and solid electrolyte devices

High purity zirconia is used for specialized electronic applications such as insulators, piezoelectrics, fibre optics and microwave systems. Because of the purity required, this zirconia is prepared by precipitation from solutions, so is extremely low in radionuclide content and will contain well below 1 Bq/g of radionuclides. Another important use of zirconia utilizes its ability to be an electrolyte in the solid phase. This property is used in the manufacture of oxygen sensors commonly used in the control of combustion equipment, in particular the control of internal combustion engines. The zirconia used for this application is often produced using the thermal route for zirconia production and as a result may contain more than 1 Bq/g of ^{238}U.

No significant exposure pathways are associated with electronics production. The manufacture of oxygen sensors will involve an external exposure pathway, but these sensors are small and may be exempted from regulatory control on the basis of the total contained activity, in accordance with the exemption levels specified in Ref. [2]. These oxygen sensors may have a waste disposal issue in that they may be sufficiently active to trigger a gate monitor. However the total level of contained activity in such devices is very low and burial in a landfill facility is an appropriate method of disposal. Education of waste site operators would be required to avoid unnecessary checking. Manufacturers of oxygen sensors may be required to notify the regulatory body, but exemption should be possible for the manufacture of both electronic and solid electrolyte devices.

5.8. Specialized products

High purity zirconia is used for hip joints, bone replacements, dental ceramics, gemstones and lasers. The zirconia used in these applications is produced by precipitation from solutions and has a ^{238}U activity concentration of less than 0.1 Bq/g. No enrichment processes occur in this manufacturing sector and notification should not be required.

5.9. Zirconia abrasives

Zirconia is used in the manufacturing of abrasives. These abrasive materials may be used in grinding wheels, sharpening stones and abrasive papers. Abrasives are made by dissolving zirconia in molten alumina. The product is solidified, crushed and sized. The zirconia content of abrasives is typically 25–40%.

The activity concentration in the raw material for this industry will be 4–6 Bq/g, as thermally derived zirconia is usually used in this application. The activity concentration in the abrasive product is 1–2 Bq/g. Exposure pathways will be external from raw material storage and handling, inhalation from the crushing and sizing operations and further inhalation pathways from the use of the grinding wheels. The annual effective dose received by a worker in an abrasive manufacturing facility has been assessed to be less than 1 mSv.

Raw materials from manufacturing are usually recycled and other waste disposed from this industry is usually buried in a landfill facility, as the materials have low external exposure potential and no dust generating properties.

The potential for inhalation of dust during the use of such products requires good dust control systems. Since the use of this type of abrasive is usually industrial, the maintenance of normal occupational hygiene control is sufficient to keep dust exposure to low levels. However, the abrasive manufacturers should notify the regulatory body, owing to the activity concentration in their raw material being above 1 Bq/g. Exemption may be possible for this sector after a risk assessment has confirmed good management practices.

6. TRANSPORT OF ZIRCON, ZIRCONIA AND THEIR PRODUCTS

The transport of radioactive materials is subject to the requirements of the IAEA Transport Regulations [3]. Materials do not fall within the scope of these regulations if they are natural materials or ores containing naturally occurring radionuclides which are not intended to be processed for the use of these radionuclides, provided that the total activity concentration of ^{238}U and ^{232}Th (with their decay products in equilibrium) does not exceed 10 Bq/g. All zircon sands and flours are therefore exempt from the Transport Regulations. Dose assessments have been carried out to support this exempt status and the results are shown in Table 6. Most baddeleyite is also exempt, although some of this natural zirconia is above 10 Bq/g and secular equilibrium cannot be assumed. However, baddeleyite from the Russian Federation is usually exempt from the Transport Regulations.

All zircon and zirconia products contain less than 10 Bq/g total activity, but in the strict sense they are not naturally occurring materials. They are, however, manufactured from NORM. For the purposes of this paper it is assumed that the exemption provided for in the Transport Regulations also

TABLE 6. DOSES ATTRIBUTABLE TO THE TRANSPORT OF ZIRCON

	Annual effective dose (μSv)	
	Worker	Members of the public
Zircon sand in bulk	150	10
Zircon flour in bags	500	110

covers products made from NORM, and under these conditions all zircon and zirconia products are exempt. This point is not made entirely clear in the Transport Regulations.

7. CONCLUSIONS

In analyzing the information collated above for all the industrial uses of zircon and zirconia, it is apparent that 77% of current operators would need to notify their regulatory bodies because the activity concentrations in their raw materials exceeds 1 Bq/g. Conversely, 23% of operators would not need to notify the regulatory body of their activities. The 77% for whom notification is required can be further split into 54% of operators that should be eligible for exemption and 23% that will probably need to be registered. It is of note that, from the above analysis, no operator should require licensing.

A more in-depth look at the industry sectors requiring registration shows that they consist of the following:

(a) The zircon millers who annually process some 700 000 t of zircon and whose operations involve a potential inhalation hazard to workers;
(b) The zirconia producers who annually treat about 50 000 t of zircon and whose operations involve a potential external radiation and inhalation hazard to workers, as well as a potential for public exposure;
(c) The zirconium metal producers who annually process about 20 000 t of zircon and whose operations involve a potential inhalation hazard to workers, as well as a potential for public exposure.

To put these industries into perspective, it is useful to compare their exposures, as shown in Table 7. While the annual effective doses received by workers in these industries can exceed the threshold level of 1 mSv for treating the exposure as occupational, the amount by which the threshold is exceeded is marginal. Furthermore, the doses do not approach levels where licensing would be required.

It can be concluded that, while low levels of radiation exposure are potentially associated with the zircon and zirconia industries, the high price of the materials provides a financial incentive for the operators to maintain good control. Around 80% of the industry sectors are amenable to exemption from regulatory control while the other 20%, with good management practices, should require minimal regulatory control.

TABLE 7. DOSES RECEIVED BY WORKERS IN INDUSTRY SECTORS THAT MAY REQUIRE REGISTRATION

	Material handled (t)	Occupational exposure: annual effective dose (mSv)	Public exposure
Zircon milling	700 000	~1	—
Thermal zirconia production	50 000 (thermal + chemical)	~3	—
Chemical zirconia production		~1	Potential from waste disposal
Zirconium metal production	20 000	~1	Potential from waste disposal

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RADIOLOGICAL ASSESSMENT OF ZIRCON PROCESSING IN NIGERIA

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Abstract

Processing of zircon along with monazite, ilmenite and magnetite as a by-product of the mining and processing of cassiterite and columbite have been taking place in the Jos Plateau area, Nigeria, for several decades. The processing in a typical mill involves dry mill separation of the heavy mineral concentrate won from alluvial deposits into cassiterite, columbite, zircon, monazite, ilmenite, magnetite and unsorted tailings after going through a combination of magnetic (low and high intensity) and electrostatic separators. The zircon product is important because of the radiological hazard it poses, with average ThO_2 and U_3O_8 concentrations of 8 wt% and 0.50 wt% respectively, and radiation dose levels of 70–100 μSv/h. Radiological assessments of the processing sites and activities were carried out to justify remedial action, with the justification criterion based on regulations of the Nigerian Nuclear Regulatory Authority (NNRA).

1. INTRODUCTION

Alkaline rocks or the so-called Younger Granites occur in central Nigeria as ring structures with a sequence of volcanic phase followed by a series of granitic intrusions. These rocks are the source of commercial quantities of cassiterite, columbite, zircon, monazite, thorite, molybdenite and pyrochlore. Cassiterite and columbite mining, mostly from alluvial deposits, and processing of the ores, have been taking place for over a hundred years, mostly centred on the Jos Plateau in central Nigeria. Associated with this activity are extensive mine tailings that have been generated over the years and these tailings are left either unsorted or separated into zircon, monazite and ilmenite.

The wide dispersal of the alluvial deposits containing the ores favoured exploitation by a large number of operators, ranging from small scale miners to those that are large and highly mechanized. Dredging and gravel pump methods are applied in the mechanized mining of cassiterite and associated minerals, including zircon, in the Jos plateau area of Nigeria. Dredging involves spreading the ore containing material on revolving or oscillating screens and disaggregating using high pressure water jets. The undersize portions, which contain the heavy minerals, are separated after passing through jigs. The concentrates are then taken to processing mills where the ores are separated from the tailings through the use of shaking tables, magnetic and electrostatic separators. A typical processing mill occupies an area of about 1000 m^2 with an office block and the mill shade housing separating tables, magnetic and electrostatic separators. With increasing depletion of the soft ore containing materials there was an increasing use of simple tools by the local population to dig out the ores in hand dug pits and use panning methods to recover the ores. The processing activities for the recovery of the concentrates take place in their households and backyards. All the separation processes obviously lead to increases in the specific activity of the source material.

Over the years there has been growing concern about the radiological impact of the tailings from the processing and mining activities from both the large and small scale operators since it has been established that these tailings are rich in zircon, monazite, xenotime and thorite. The radiation levels have long been considered to be much higher than the annual dose limit for members of the public [1–3] and the radiological impact is not only arising from the enhanced radiation levels from the processing of the ores but also from the haphazard disposal of the tailings in the affected areas. This work reports the radiological assessment of zircon, the mineral with the reported highest radioactivity levels, from the mineral processing activities in the Jos area, central Nigeria.

2. RADIOLOGICAL ASSESSMENT OF MINING AND PROCESSING SITES

Radiation monitoring was carried out in some selected mining and processing sites and settlements. These comprise four processing mills and five mining and processing community settlements. All the sites are located near Jos, central Nigeria.

An external dose rate (μSv/h) survey was performed with a calibrated portable survey meter manufactured by RADOS© (RDS-120 Universal). The instrument has a scintillation probe in addition to two external probes, a GM probe and an alpha pancake probe. Ten measurements were averaged at each site. The five community settlements covered by the survey are Shafa, Litiya, Fahapa, Rayfield and Bisichi. Most of the measurements were taken from tailings piles that can be found all around these settlements. Background values were in the range of 5–8 μSv/h, while the tailings piles exhibited dose rates in the range of 10–30 μSv/h. For the processing mills, measurements were made at James Dung, Dadin Kowa and two mills belonging to the former Amalgamated Tin Mines. The process lines at each of the mills were followed in the course of the survey and the dose rate values were found to be in the range of 10–80 μSv/h. The highest values were for the heaps of processed zircon.

The average dose rate of 25 μSv/h for most of the tailings piles corresponded to an annual dose of about 50 mSv for people in the vicinity, assuming a 2000 hour working year. This by far exceeds the 1 mSv dose limit for members of the public [4]. This was cause for alarm since the tailings are not well managed or contained.

3. INTERVENTION AND REMEDIATION MEASURES

In general, exposure to NORM in the environment is not regarded as being subject to the requirements for practices. The concept of intervention is now largely accepted in addressing this radiological hazard. Interventions are human activities that seek to reduce existing radiation exposure, or the existing likelihood of incurring exposure. A three step system can be adopted in addressing the radiological hazard arising from the processing of zircon in the Jos area after identifying work activities that may lead to increases in exposure. The first is monitoring of the work areas and worker exposures, the second is implementing corrective measures as needed and the third step is full or partial implementation of radiation protection measures for practices.

Towards achieving these measures the Nigerian Nuclear Regulatory Authority (NNRA) now has a regulation governing TE-NORM which is backed by government policy and strategy for radioactive waste management. The programme of action for intervention includes an awareness campaign, radiation survey and monitoring, sample collection and analysis and some remediation action based on the results of the survey and the analysis of collected material.

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RADIOLOGICAL IMPACTS ASSOCIATED WITH A ZIRCON SAND PROCESSING PLANT IN BRAZIL

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Abstract

Aimed at assessing radiological impacts of zircon sands processing in Brazil, a survey of zircon sand and flour production and of the ceramic and porcelain industries has been performed in order to identify the most important industries that should be investigated. As a starting point, an important processing plant located in a coastal area of Rio de Janeiro State has been investigated. Mining and milling of heavy mineral sands are performed in the plant to produce zirconite, ilmenite and rutile. The zirconite fraction is then sent to milling companies involved in zircon silicate flour production, which will be used in the ceramics and porcelain industries. The contents of natural radionuclides in raw materials, residues and the end products of the plant milling were measured by gamma spectrometry. The radionuclide flux in the process showed the highest concentrations of ^{238}U and ^{232}Th in the monazite fraction, respectively, 7300 and 44 500 Bq/kg, followed by zirconite (2300 and 500 Bq/kg), rutile (1240 and 1600 Bq/kg) and ilmenite (130 and 620 Bq/kg). The only discharge to the environment is a liquid effluent, which exhibited concentrations of U and Th of the order of 1%, and no environmental impact was observed. Previous studies pointed out that individuals are occupationally exposed to uranium via inhalation and estimated an effective dose due to uranium of 0.4 mSv/a. Regarding inhalation exposure, the results indicated the existence of operational areas with dose values above the maximum recommended limits. The bioassay monitoring data indicated that the implemented actions have decreased the dose to workers dose significantly. The paper presents an overview of previous studies that were carried out in order to evaluate radiological impacts associated with zircon sand processing plants in Brazil.

1. INTRODUCTION

Brazilian monazite sand is composed of four minerals: ilmenite ($FeTiO_3$); zirconite ($ZrSiO_4$); rutile (TiO_2) and monazite, an orthophosphate of rare earths containing up to 6% ThO_2 and 0.3% U_3O_8. The most important deposits of monazite sand in Brazil are located on the Atlantic coast of the country, in the northern part of the State of Rio de Janeiro.

Buena, a small village in this region, is the place where an important processing plant has been in operation for more than 25 years. The only industrial activity of the region is the mining and milling of the heavy mineral sand and many Buena inhabitants work at the mill (Buena Unit). An important characteristic of the people living in this area is their low mobility. Most of the people have been living in Buena and its surroundings for more than 40 years [1]. The food consumed by the population is mainly composed of local products [2].

Because of the levels of thorium, monazite was considered as a strategic mineral and the Buena Unit was classified as a nuclear facility according to Brazilian standards [3]. Thus for years it has been occupationally and environmentally monitored. As the mill´s process area was classified as a controlled area, access to the area is restricted, the workers are continuously monitored by EPIs and they use overalls, boots, gloves, hardhats and masks for protection. Over time, and according to the surveys and studies conducted in the area, new control methods have been introduced.

The process begins with the concentration of the minerals by a hydrogravimetric process. After the separation, the ore concentrate is sent to the mill and the sterile material (sand) is then returned to the pit. The heavy mineral content in the sand and concentrate are shown in Table 1. It can be observed that the minerals in the ore are around ten times more concentrated than in the original sand. In the mill, the heavy minerals are separated by dry separation (physical separation through electrostatic, magnetic and gravimetric processes). The industrial process is described in the simplified flow chart in Fig. 1.

TABLE 1. CHARACTERISTICS OF THE HEAVY MINERAL SAND AND CONCENTRATE [4]

	Content (%)	
	Heavy mineral sand	Concentrate
Ilmenite	3.9–4.3	39.1–43.0
Zirconite	2.3	23.3–23.6
Monazite	0.28–0.65	2.8–6.5
Rutile	0.18–0.30	1.8–3.0
Silica	60–85	6.0–8.5
Other	2.1–2.5	20.5–25.0

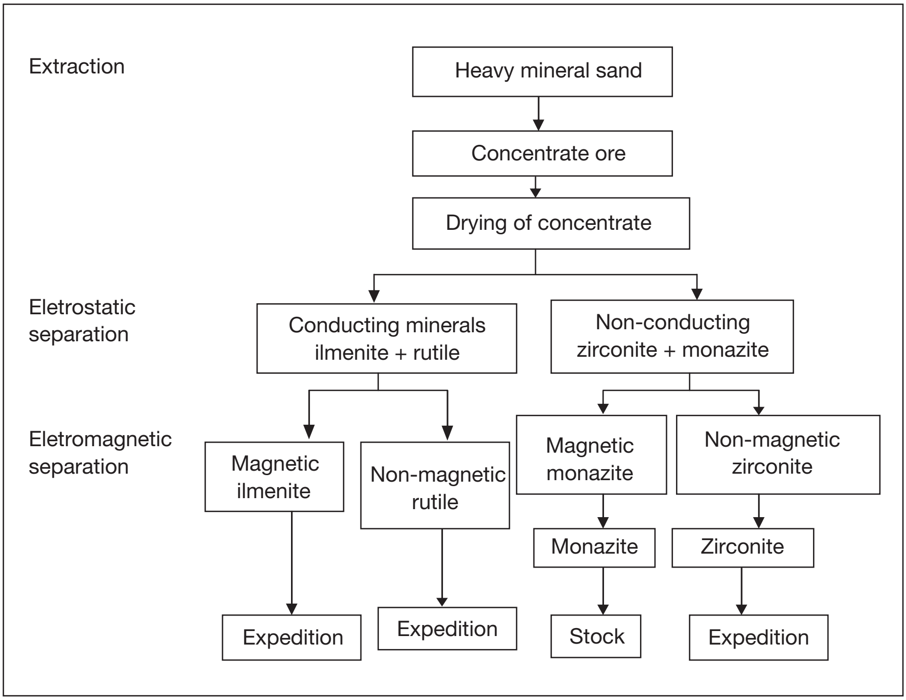

FIG. 1. Simplified flow chart of the mineral separation process.

The final phase of the dry separation process produces zirconite (zirconium silicate), ilmenite (iron titanate) and rutile (titanium dioxide) that are sold directly from the mill. Nowadays, monazite is being stored for a new future process which is in development.

The zirconite fraction is then sent to milling companies for the production of zircon flour to be used in the ceramics and porcelain industries. The radiological impacts associated with these industries will be assessed in the near future.

The former chemical processing of monazite concentrate was performed in other plants and produces rare earth chlorides. The process generated two by-products: mesothorium cake and thorium concentrate cake, both of which contain most of the initial thorium and uranium of the monazite concentrate. The radioecological questions concerning the monazite sand cycle waste in Brazil have been addressed in other publications [5, 6].

2. METHODOLOGY

A summary of the main results of previous studies and surveys carried out in the Buena region aimed at assessing the radiological impacts associated with a zircon sand processing plant in Brazil are presented below. These studies have included public and occupational exposures to uranium and thorium due to operation of the processing plant.

3. RESULTS

3.1. Public exposure

The contents of natural radionuclides in raw materials, residues and the end products of the plant milling were measured by gamma spectrometry and are presented in Table 2. These results are part of the environmental radiological programme that was carried out by the Institute of Radiation Protection and Dosimetry/IRD/CNEN from 1996 to 2002.

The radionuclide flux in the process showed the highest concentrations of ^{238}U and ^{232}Th in the monazite fraction, followed by zirconite, rutile and ilmenite. The only discharge to the environment is a liquid effluent from the hydrogravimetric process. Water used in the process is pumped from a local lagoon and after its utilization in the hydrogravimetric process it is returned to the lagoon. The data from the liquid effluent monitoring programme showed

TABLE 2. RADIONUCLIDE CONCENTRATIONS IN RAW MATERIALS, RESIDUES AND END PRODUCTS OF THE MILLING PLANT

	Radionuclide activity concentration (Bq/kg)[a]	
	^{238}U	^{232}Th
Heavy mineral sand	99	520
Heavy mineral concentrate	2 100	7 580
Monazite fraction	7 300	44 500
Zirconite	2 300	500
Rutile	1 240	1 600
Ilmenite	130	620
Silica (sand)	10	44
Overflow (waste)	1 350	2 090

[a] Secular equilibrium assumed.

concentrations of U, Th, ^{226}Ra and ^{228}Ra of the order of 10^{-3}, 10^{-2}, 10^{-2} and 10^{-1} Bq/L, respectively. It is interesting to observe that higher radionuclide concentrations in the water of the lagoon were found upstream instead of downstream of the effluent discharge point [7]. This unexpected result led to research that concluded that the radionuclide concentrations originated naturally from springs at the lagoon head area. Curiously, the levels of radionuclides in the mill effluent were lower than the levels of this natural environment and no environmental impact was observed due to the effluent discharge of the mill.

Significant concentrations of thorium, uranium and other nuclides from the respective radioactive series have been reported in the standard diet consumed by the inhabitants of Buena village [2]. The results indicated that the major route of intake of ^{226}Ra and ^{210}Pb by workers and inhabitants is ingestion (alimentary diet and water).

Characterization of the airborne particle aerosol and the origin of the aerosol source were performed in samples collected in the vicinity of the mill [8, 9]. The airborne particle characterization has suggested that the inhabitants of Buena were exposed to mineral sands particulate (mainly from the mineral sands processing plant and a natural deposit of mineral sands located in the village), marine aerosols and particles from anthropogenic sources in the respirable fraction of the aerosols [8]. Thus, as the inhabitants of Buena are also exposed to aerosols containing natural sources, no direct impact of the aerosols from the mill could be quantified.

3.2. Occupational exposure

The main radiological problem in this mill concerns the dust generation during the gravitational separation steps of the process (vibrating tables are used to sieve the minerals and the products are handled and bagged in the area). The main studies and surveys performed in the mill concern a survey of the potential exposure of the workers and studies of radionuclides incorporated by them.

3.2.1. Occupational measurements

In a study of the potential occupational exposure, a survey was carried out at five different locations within the mill, relating to different steps of the process, by aerosol sampling with AGF followed by gross alpha counting [10]. Evaluating the ^{232}Th activity by the long lived alpha emitters, the ^{232}Th concentration in the fine fraction of the aerosols (2.5–10 μm) was 0.026–0.26 Bq/m^3, while the finest fraction of the aerosols (below 2 μm) had a ^{232}Th concentration of 0.0016–0.00076 Bq/m^3. Thus, using the data of the respirable fraction of aerosol, the assessed value of the inhalation dose ranged from 8 to 125 mSv/a.

Regarding external occupational exposure, which was estimated by thermoluminescent dosimeters, (TLDs) during one year using 17 workers, an average of 2.7 ± 0.3 mSv/a was observed [10]. Additionally, gamma radiation dose rates were measured at the five different points of the mill. The value of the dose rate was 0.07–1.90 μSv/h (0.1–3.4 mSv/a). Considering the external and inhalation dose, the total dose was estimated to be 8–128 mSv/a. The highest value was found in the drying area, while the smallest value was found in the magnetic separation of the non-magnetic minerals area.

3.2.2. Bioassay monitoring

Because of Buena's location in a high background radiation area (HBRA) the workers of the mill are exposed to radiation as inhabitants of a HBRA and as workers in a NORM facility. The evaluation of occupational radiological exposures is not straightforward, especially considering all the uncertainties involved in measurements, models, in vivo samples and so on. Aiming to discriminate the background internal contamination (Buena) from the mill contribution from the mill, research has been carried out taking into account data of excreta samples from the mill workers and from the Buena inhabitants [11, 12].

Regarding ^{232}Th internal contamination, excreta samples of 29 workers in the mill and 21 inhabitants of Buena, where most of workers live, were collected and analysed [6]. The average ^{232}Th concentration in faeces of the unexposed Buena population (6.7 ± 5.9 mBq/g_{ash}) was about one third of the average ^{232}Th concentration in faeces samples from workers (25.9 ± 18.4 mBq/g_{ash}) and twice the average concentration in faeces from inhabitants of the city of Rio de Janeiro (2.3 ± 1.5 mBq/g_{ash}), the control group. The results have shown the higher intake of ^{232}Th by the workers than their wives, which can be caused by dust ingestion. It is suggested that measures to decrease dust ingestion in the mill should be reinforced. Besides, the results pointed out the importance in characterizing the region where workers live when occupational control is carried out [1].

Concerning occupational exposure to uranium, the intake of radionuclides by the workers and the inhabitants of the mill's vicinity was studied by excreta sample analysis. The results indicated that workers might be exposed to compounds of uranium type S by inhalation, with an AMAD of 1 or 5 μm and exposed by ingestion to compounds of uranium type M. A value of effective dose due to uranium inhalation of 0.4 mSv/a was estimated [12].

Only one of the sixty mill workers monitored in the whole-body counter for measurements related to intakes of long lived nuclides showed activity in the lung slightly above the detection limit [1].

4. CONCLUSIONS

(a) The highest concentrations of ^{238}U and ^{232}Th were observed in the monazite fraction, followed by zirconite, rutile and ilmenite.

(b) The liquid effluent discharge of the plant to the environment exhibited a concentration of radionuclides of the order of 1%, which is below the radionuclide levels found in the water from the region, and no environmental impact was observed due to liquid discharge.

(c) The airborne particle characterization has suggested that the inhabitants of Buena village can be slightly exposed to mineral sands particulate from the mineral sands process. However, other natural sources can have a greater influence than the mill for this exposure route. In conclusion, no environmental impact from the mill process could be observed.

(d) Significant concentrations of thorium, uranium and other nuclides from the respective radioactive series in the standard diet consumed by the inhabitants of the village of Buena were reported. Thus, to evaluate the internal contamination of the workers, the intake of radionuclides by food consumption has to be taken into account.

(e) Concerning bioassay monitoring, an effective dose of 0.4 mSv/a due to inhalation of uranium was estimated and the concentrations of ^{232}Th in workers' faeces were three times higher than those for their wives.

(f) Regarding occupational exposure measurements, the results indicated the existence of operational areas where effective doses were above the maximum recommended limits. The results showed that these areas have to be continuously monitored in order not to allow unnecessary exposure of the workers.

(g) The comparison of the potential exposure data by occupational measurements and the bioassay monitoring data indicated that the implemented actions to decrease the dose (such as the use of EPIs and masks) had significantly contributed to the reduction of the dose to the workers.

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RADIOACTIVITY MEASUREMENTS IN CERAMICS INDUSTRIES: RESULTS AND COMMENTS[*]

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Abstract

As part of the NORM evaluation programme launched by the Spanish Nuclear Safety Council, a radiological study of the ceramics industry was carried out by the Environmental Radioactivity Laboratory of the Universidad Politécnica de Valencia. The study covered three types of plant: zircon sand milling, ceramic frit production and ceramic tile production, all of which use zircon as a raw material. In accordance with European Directive 96/29/Euratom, these types of plant are of radiological interest because of the presence of ^{238}U and to a lesser extent ^{232}Th, together with their progeny. The first step in the study was to collect information on materials and processes used in the different types of factory, after which a radiological characterization of the materials, including dust from the indoor environment, was performed. Gamma spectrometry analysis was carried out using a Ge(HP) detector. The second step was to identify the areas in which radioactive materials and workers were present. Direct measurements were carried out in different factory areas, which were radiologically characterized using a portable radiation monitor and thermoluminescent dosimeters. Finally, the external and internal radiation doses received by workers were estimated, on the basis of the aforementioned measurements.

1. INTRODUCTION

The use of naturally occurring radioactive material (NORM) is widespread in Spain, but was not subject to official regulation until the issue of the Real Decreto 783/2001 [1]. This decree specifies the Regulation on Health Protection against Ionizing Radiations as a result of the implementation of

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[*] Research sponsored by the Spanish Nuclear Safety Council as part of its NORM evaluation programme.

European Council Directive 96/29 Euratom [2]. This regulation indicates, in Section VII, Natural Sources of Radiation, Article 62, the need to study those activities in which workers or members of the public could be exposed to significant doses of radiation.

These industrial activities include those that use zircon (zirconium silicate) sand as a raw material [3]. This sand is milled for use directly by the ceramics industry or as an intermediate step for producing milled frits that are also used in the production of ceramics (see Fig. 1).

Zircon occurs naturally in association with quartz and other minerals such as rutile (TiO_2), ilmenite ($FeTiO_3$) and monazite (a phosphate of rare earth elements). The presence of ^{238}U and to a lesser extent ^{232}Th, together with their progeny, in the crystalline structure of zircon is the reason for the risk of exposure to radiation. In this paper, the methodology used for the radiological study of the zircon processing plants is described and the measurements recorded during the radiological characterization of the workplaces involved are presented. Finally, an estimate of the radiation doses received by workers is given, together with conclusions and comments.

2. MATERIALS AND METHODS

2.1. Milling of zircon

The plant studied has two milling lines, corresponding to dry and wet milling processes. The dry process consists of a ball mill (silex or alumina balls) and a dynamic classification system that feeds back the largest particles and produces ‘zircon flour’. The wet process also consists of a ball mill, followed by a dynamic size classifier and a dryer at the end of the process that produces ‘micronized zircon’. A schematic representation of the processes is shown in Fig. 2. The following plant zones were studied: the raw material store, dry milling, wet milling, settling tanks, micronized zircon bagging area and end product store.

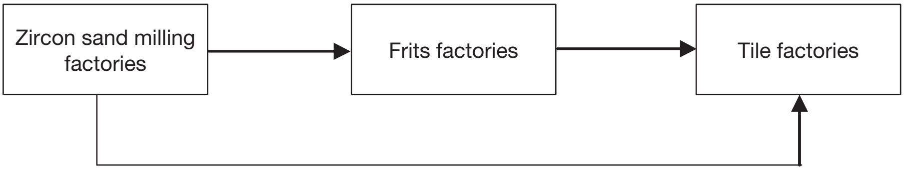

FIG. 1. Manufacturing processes using zircon sand.

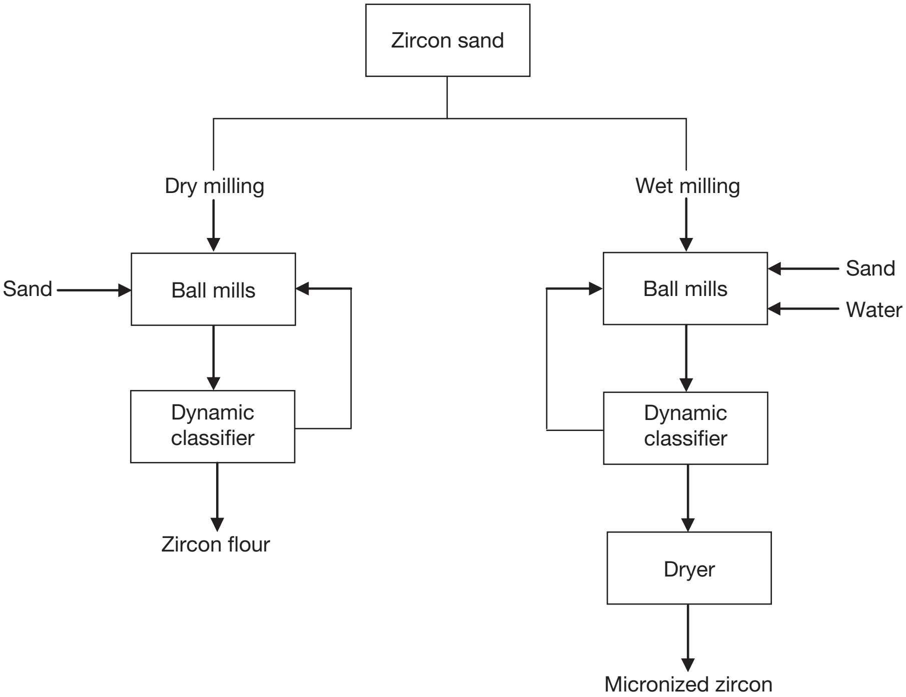

FIG. 2. The dry and wet milling processes.

2.2. Manufacture of frits

Frits are intermediate materials for use in other factories producing end products. They comprise a wide variety of raw materials, of which only zircon is of radiological interest. The raw material mixes are prepared according to customer needs. Most of the formulations do not contain zircon, but when they do the ZrO_2 content rarely exceeds 18%. This type of plant therefore generally represents no significant radiological risk, either for the employees or for the environment. The radiological study was carried out in the areas shown in Fig. 3.

FIG. 3. Production line at a frits factory.

2.3. Manufacture of ceramic tiles

This type of plant includes a great variety of processes due to the enormous amount of different end products. The radiological study therefore focused only on those manufacturing lines in the factory that used zircon. Figure 4 shows a simplified schematic representation of one of these lines. The radiological measurements were taken in places assigned to these functions.

2.4. Experimental

The zircon milling plant operates with zircon sand having a particle diameter of 100–200 μm, usually imported from Australia or South Africa. The dry milling process produces zircon flour, which has a particle size of ≤50 μm. The wet milling process produces micronized zircon, which has an even smaller particle size of ≤5 μm. Samples of zircon sand and end products were provided by the factory. The frits plant supplied three different formulations for radiological analysis containing, respectively, 0%, 4.6% and 18% ZrO_2. From the tile factory, three samples were taken: micronized zircon as the raw material and two porcelain tiles, one of them superwhite, as the end products. All samples were dried in powder form at 100°C to a constant weight and then sieved (0.5 mm mesh size) and placed in a 190 mL cylindrical beaker for gamma isotopic analysis.

Airborne dust sampling was conducted using a mobile low volume air sampler with an adjustable sampling gooseneck (F & J, model DF-14ME) and supplied with nitrocellulose filters with a pore size of 0.8 μm. Sample collection was made at a flow rate of approximately 30 L/min with a collection period of 3–24 h in the milling plant and 7 d in the frit and tile factories, depending upon the dust concentration. Radon monitoring was performed, even though there was good natural ventilation in all the factories. Activated charcoal type EPA canisters were placed at different points of the plant for a period of 3 d. External gamma dose rate levels were measured using a portable radiation monitor (Berthold LB 133) in different zones of the factory. Thermoluminescent dosimeters (TLDs) of the type LiF: TLD-100 were also used to evaluate the integrated gamma dose. The TLDs were exposed for one month in zones where direct measurements were made.

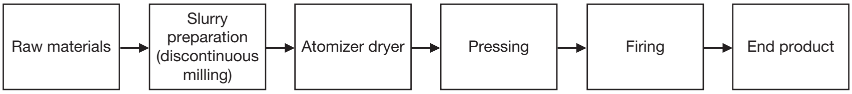

FIG. 4. Production line at a tile factory.

All measurements of gamma ray emitting nuclides were performed with an ORTEC 919E multichannel analyser containing a type GMX Ge(HP) detector. The activity of ^{238}U was quantified by the main peaks of ^{214}Bi and ^{214}Pb. The activity of ^{232}Th was determined from the ^{228}Ac peaks. Radioactive equilibrium was assumed in both of the natural decay series [4–6]. The ^{40}K activity was determined from the 1460.75 keV photon energy peak. Radon was evaluated by measuring every canister using a type GEM Ge(HP) detector. A Harshaw 4000A reader was used to read the dosimeter cards.

3. RESULTS AND COMMENTS

3.1. Measurements

Table 1 shows the ^{238}U, ^{232}Th and ^{40}K activity concentrations for each sample analysed. In the zircon milling plant, concentration values for U and Th in zircon sand were similar in all cases, falling within the ranges 2681–3615 and 592–714 Bq/kg, respectively. These activity concentrations agree with values reported in the literature [5, 7]. The U and Th activity concentrations measured in the end products (zircon flour and micronized zircon) showed values similar to those of the raw material. This means that the milling process does not significantly modify the assumed secular equilibrium of the natural decay chain. The activity concentration of ^{40}K was below the detection level in all these samples. The measured activity concentrations are much higher than the corresponding worldwide average values for soils, which are reported to be 35 and 30 Bq/kg for ^{238}U and ^{232}Th, respectively [8].

The ^{238}U and ^{232}Th activity concentrations measured in the samples of frits were in accordance with the ZrO_2 concentrations corresponding to the different formulations, the highest values being 901 and 230 Bq/kg, respectively. Owing to the presence of potassium compounds in the formulations, ^{40}K was detected in these samples. The micronized zircon coming from the tile factory showed a value in accordance with that measured in the milling plant. The values for porcelain products were much lower than those of the raw material because of their low overall zircon content.

The dust concentrations in the air of the milling plant ranged from 0.56 mg/m^3 in the end product store to 4.64 mg/m^3 in the area designated as ‘dry milling 1’. The concentrations in the frit factory ranged from 0.129 mg/m^3 in the zircon silo area to 0.234 mg/m^3 in the mixer area. The concentrations in the tile factory ranged from 0.04 mg/m^3 in the end product store to 1.81 mg/m^3 in the area of the discontinuous mill. Values for radon measurements were 6–34 Bq/m^3, similar to those generally found indoors in the Valencia region.

TABLE 1. RADIOACTIVITY IN RAW MATERIALS AND END PRODUCTS

	Activity concentration (Bq/kg)		
	^{238}U	^{232}Th	^{40}K
Zircon milling sand			
South African zircon sand	3615 ± 124	604 ± 33	<74
Australian zircon sand 1	2681 ± 93	597 ± 5	<69
Australian zircon sand 2	3159 ± 108	714 ± 37	<71
Zircon flour	3134 ± 104	592 ± 37	<110
Micronized zircon	2908 ± 101	607 ± 34	<99
Frits			
0% ZrO_2	11.6 ± 2.7	10.4 ± 7.7	1090 ± 63
4.6% ZrO_2	275 ± 12	53.6 ± 8.9	1973 ± 93
18.5% ZrO_2	901 ± 32	230 ± 17	339 ± 51
Tiles			
Micronized zircon raw material	3346 ± 111	719 ± 43	<117
Porcelain tiles	75 ± 6	68 ± 12	507 ± 58
Superwhite porcelain tiles	191 ± 11	76 ± 14	490 ± 6

3.2. Dose assessment

An estimate of the effective dose (E) received by workers was performed in accordance with the European Council Directive 96/29 [2]. The effective dose was obtained from the following equation:

$$E = E_{external} + \sum_j h(g)_{j,inh} \cdot J_{j,inh} \quad (1)$$

where

$E_{external}$ is the effective dose from external exposure during a year,

$\sum_j h(g)_{j,inh} \cdot J_{j,inh}$ is the committed effective dose for inhalation from intakes during a year,

$h(g)_{j,inh}$ is the committed effective dose per unit intake for inhaled radionuclide j (Sv/Bq) by an individual in age group g,

$J_{j,inh}$ is the relevant intake via inhalation of the radionuclide j in a year (Bq).

Other intake paths were ignored.

3.3. External dose

External exposure is caused mainly by gamma radiation from radionuclides in the ^{238}U and ^{232}Th decay series. As already mentioned, TLDs and a portable radiation monitor (LB 133) were used to detect and measure external radiation exposures in several work areas at the plant. The results of these measurements are shown in Table 2. The annual effective dose corresponding to a total of 2000 working hours (8 h/d × 250 d/a) is included in the table.

TABLE 2. DOSE ATTRIBUTABLE TO EXTERNAL RADIATION

	Dose rate (μSv/h)		Annual effective dose (mSv)	
	LB 133	TLD	LB 133	TLD
Zircon milling sands				
Raw material store[a]	1.66	Not available	3.32	Not available
Dry milling 1	0.12 ± 0.04	0.16 ± 0.05	0.24 ± 0.08	0.32 ± 0.10
Dry milling 2	0.19 ± 0.06	0.14 ± 0.11	0.38 ± 0.12	0.28 ± 0.22
Wet milling	0.15 ± 0.07	0.09 ± 0.06	0.30 ± 0.14	0.18 ± 0.12
Settling tanks	0.39 ± 0.09	0.41 ± 0.15	0.78 ± 0.18	0.82 ± 0.30
Product bagging	0.24 ± 0.11	0.22 ± 0.05	0.48 ± 0.22	0.44 ± 0.10
End product store	0.017 ± 0.015	0.20 ± 0.18	0.034 ± 0.030	0.40 ± 0.36
Frits				
Raw material store (zircon silo)	0.68	0.45	1.36	0.9
Tiles				
Zircon silo	0.28	0.5	0.56	1

[a] Measured at 1 m distance.

3.4. Internal dose

In accordance with Eq. (1), the internal committed effective dose due to inhalation of dust particles was calculated as:

$$\sum_j h(g)_{j,inh} \cdot J_{j,inh} \tag{2}$$

The conversion factors $h(g)_{j,inh}$ were obtained from Annex III of the European Directive [2], using the values for members of the public over the age of 17. The intake ($J_{j,inh}$) was calculated as the product of the dust mass inhaled and its activity concentration:

(a) The total dust mass inhaled by a worker was estimated from the dust concentration in air (mg/m^3), an annual exposure period of 2000 h, and an inhalation rate of 1.25 m^3/h. In order not to underestimate the dose, the inhalable fraction of the dust was set to unity.
(b) It was assumed that the activity concentration of each dust sample was the same as that in the materials present in the area in which the sample was collected.

Different values were found in the same area for different measurements, indicating a variability in the dust concentration and justifying a conservative approach to the dose calculations.

3.5. Total effective dose

The estimated dose contributions from external exposure and inhalation of dust particles are shown in Table 3. The total annual effective dose was calculated as the sum of the external and internal doses. The results for all the factories studied showed an annual external dose in the zircon storage areas sometimes greater than 1 mSv (3.32 mSv in the milling plant) or otherwise around 1 mSv (1.36 and 1 mSv for the manufacture of frits and tiles, respectively). The annual internal dose was above 1 mSv only in some areas of the zircon milling plants, i.e. the dry milling and product bagging areas, with values of 2.04 and 1.13 mSv, respectively. In the rest of the factories these values are practically zero, with an appreciable value (0.32 mSv) only occurring close to the zircon silos at the tile factory, owing to the higher activity of the materials

TABLE 3. ESTIMATED WORKER DOSES

	Annual effective dose (mSv)		
	External	Internal[b]	Total
Zircon milling sands			
Raw material store	3.32	Not available	3.32
Dry milling 1[a]	0.32	2.04	2.36
Dry milling 2	0.38	0.54	0.92
		1.00	1.38
Wet milling	0.30	0.59	0.89
		0.83	1.13
Settling tanks	0.82	Not available	0.82
Product bagging	0.78	1.11	1.89
		1.13	1.91
End product store	0.40	0.25	0.65
Frits			
Raw material store (zircon)	1.36	0.05	1.41
Raw material store (no zircon)	0	<0.01	0
Mixing	0.04	0.03	0.07
Distributor	0	0.02	0.02
Tiles			
Zircon silo	1.00	0.32	1.32
Discontinuous milling	0.06	0.08	0.14
Atomizer	0.02	0.07	0.09
End product store	0.14	<0.01	0.14

[a] Internal dose corresponding to samples taken near the area of unloading of raw material.

[b] Where two values are given, the first corresponds to the lowest dust concentration and the second to the highest.

and the dust present in the area. All these values are consistent with those found elsewhere in the literature [5, 6] and with those considered by the European Commission in its publication on the establishment of reference levels for regulatory control of workplaces [9].

It should be noted that doses have been calculated assuming an annual exposure of 2000 h for each of the areas studied. Consideration was not given to the fact that the plant concerned has introduced rotating shift work, moving workers periodically through every working area.

4. CONCLUSIONS

Some values of total annual effective dose exceed the annual dose limit of 1 mSv for members of the public, mainly in the milling plants, indicating that this type of industry needs to be carefully monitored. Some areas show quite high external dose values. Therefore, shielding walls are recommended and workers' occupancy of these areas needs to be controlled. Also, the internal dose makes an important contribution to the total dose, so it is very important to set up a highly efficient air cleaning system. Factories manufacturing frits and tiles show lower values of total effective dose — in both cases, only the zircon silo gives an effective dose exceeding 1 mSv, mainly due to external exposure. It should be borne in mind that the dose values obtained are conservative due to the fact that the occupancies assumed in the dose calculations are much higher than actual values.

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NORM IN THE ITALIAN TILE AND REFRACTORY INDUSTRIES

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Abstract

In recent years, the Regional Agency for the Environmental Protection of Veneto (ARPAV) has carried out surveys in the refractory and tile industries investigating, in particular, the natural radioactivity levels of residues and dusts. Elevated activity concentrations have been recorded for ^{210}Pb and ^{210}Po (21 000 and 35 000 Bq/kg, respectively) in dust generated in a refractory fusion furnace. In addition, high values of ^{210}Po (up to 46 000 Bq/kg) have occurred in the hydrated lime used for trapping dust in the tile firing process. Doses to the public as a result of airborne dust emissions from these two processes are estimated using a comprehensive prediction model (PC Cream) for refractories and a simplified model for tiles. In both cases, individual effective doses appear to be less than 1 μSv/a while collective doses are slightly more than 1 man mSv/a. The PC Cream simulation data were obtained in the course of collaboration between ARPAV and the Catholic University of Brescia.

1. INTRODUCTION

Zircon sand is known to exhibit non-negligible levels of natural radioactivity. Zircon sand and zircon flour (a product of sand milling) are used in the manufacture of refractory materials and in the tile industry, both sectors being of considerable importance for the Italian economy. Depending on the process, radionuclides of natural origin occur in products, by-products, residues and wastes [1].

2. TILE INDUSTRY

2.1. General manufacturing aspects

Italy is one of the world's main tile producers, supplying 13% of the total world market. Several hundred factories form this sector, 80% of which are located in the ceramic tile industry zone in the provinces of Modena and Reggio Emilia [2]. Zircon flour and, on occasion, zircon sand are used in the glaze applied to the tiles and sometimes in the tile mixture itself (the 'biscuit'), as is the case for white porcelain stoneware. The standard production process involves firing at 1000–1200°C for both glazed tiles (using a single or double firing process) and unglazed tiles. To precipitate dusts released during the firing process, lime is commonly used — this becomes hydrated lime after the dust extraction process. Radionuclides of natural origin are contained in non-negligible amounts in zircon sand and flour and, apart from ^{210}Po, are found diluted in the finished products. The ^{210}Po volatilizes in the firing process and concentrates in dusts, some of which escape to the atmosphere and some of which are precipitated in the hydrated lime.

2.2. Survey data and estimated dose

In 2005, ARPAV carried out a survey in some relevant tile manufacturing factories to assess the activity concentrations in residues and dusts for the complete process [3]. The highest activity concentrations found in hydrated lime were used as input data for estimating the collective effective dose[1] received by the population living near the plant and attributable to the emission of dusts from the firing process stack. The estimate was based on the simplified model given in Annex C (para. 1B) of the 1982 UNSCEAR Report [4]. The model considers two stages of exposure: (1) direct inhalation during the passage of the cloud and (2) intakes (ingestion of contaminated food and inhalation of resuspended material) and external radiation after deposition. The activity released from the stack was calculated by multiplying the dust activity concentrations (assumed to be the same as those in the hydrated lime) by the dust emitted per year through the stack (261 kg/a).[2] The dust activity

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[1] All doses mentioned in this paper are committed doses.

[2] The use of hydrated lime data instead of dust specific data could lead to an underestimate of the dust activity concentration, and consequently of the dose, due to the addition of the lime matrix.

concentrations in the hydrated lime and the estimated radionuclide activities released from the stack are shown in Table 1.

In the first stage of exposure considered in the model, the inhalation dose for the population living in the plant area was calculated from the time integrated activity concentrations in that area arising from the whole radionuclide release. For ^{222}Rn, the dose added by the plant release was calculated by comparison with the inhalation dose due to natural emanation from soil: all radon contained in the processed zircon sand and flour (2976 t/a) was assumed to be released into the air. Some parameters were updated with respect to the 1982 UNSCEAR Report — the age weighted inhalation effective dose coefficients and breathing rates were taken from Annex B (Table 17 and para.153) of the 2000 UNSCEAR Report [5].

In the second stage of exposure considered in the model, the dose arising from the deposited activity was calculated by comparison with doses resulting from the natural presence of radionuclides in soil. Apart from some fixed parameters [4], the key data used in the calculation were taken from Ref. [5] as follows:

(a) Natural soil concentrations of 35, 30 and 400 Bq/kg for radionuclides in the ^{238}U and ^{232}Th decay chains and for ^{40}K, respectively;

(b) Age weighted effective doses for inhalation and ingestion of various naturally occurring radionuclides as specified in Annex B (Tables 17, 18) of Ref. [5];

TABLE 1. STACK EMISSIONS FROM A TILE MANUFACTURING PLANT

	Maximum activity concentration in the hydrated lime (Bq/kg)		Estimated activity released from the stack (Bq/a)
	Value	Uncertainty[a]	
^{238}U	9	21%	2 349
^{226}Ra	10	7%	2 610
^{210}Pb	425	4%	110 925
^{210}Po	46 100	6%	12 032 100
^{235}U	—	—	235
^{232}Th	3	9%	783
^{40}K	369	5%	96 309

[a] 68% confidence interval.

(c) Age weighted external radiation dose rates due to the natural levels in soil of the radionuclides in the ^{238}U and ^{232}Th decay chains and of ^{40}K as specified in Annex B (Table 6) of Ref. [5];

(d) An individual effective dose of 470 μSv/a for inhalation of natural levels of ^{222}Rn.

The results of the model estimates are shown in Table 2 and Fig. 1. The total collective effective dose arising from the plant emissions was about 1.4 man mSv in a year. Taking the ratio of the collective dose to the population living in the local municipality gave an effective dose per caput of less than 0.1 μSv/a. This is negligible compared with the action level of 300 μSv/a indicated by Italian law (Legislative Decree No. 241/00). The most significant exposure pathway was the ingestion of contaminated food after deposition. The radionuclide that contributed most was ^{210}Po, followed by ^{222}Rn (see Fig. 1). When site and plant technical data become available, a more accurate

TABLE 2. COLLECTIVE DOSE ARISING FROM EMISSIONS FROM A TILE MANUFACTURING PLANT

	Collective effective dose in a year (man-Sv)				
	Passage of the cloud	Deposition			Total
		Ingestion	Inhalation	External radiation	
U-238	2.75E-08	5.70E-10	4.79E-11	2.33E-07	8.65E-08
U-234	3.31E-08	6.39E-10	5.93E-11		9.22E-08
Th-230	1.24E-07	1.32E-09	1.10E-10		1.84E-07
Ra-226	3.70E-08	2.03E-08	6.59E-11		1.16E-07
Rn-222	2.19E-04		1.19E-06		2.20E-04
Pb-210	4.92E-07	3.02E-06	4.31E-07		3.94E-06
Po-210	1.61E-04	9.94E-04	1.40E-05		1.17E-03
Th-232	7.17E-08	3.19E-10	7.45E-11	1.02E-07	1.06E-07
Ra-228	9.02E-09	1.86E-08	1.86E-11		6.17E-08
Th-228	1.26E-07	2.22E-10	2.57E-10		1.61E-07
Rn-220			3.11E-08		3.11E-08
U-235	2.95E-09	5.46E-11	4.96E-12		3.01E-09
K-40				8.90E-07	8.90E-07
Total	3.81E-04	9.97E-04	1.57E-05	1.23E-06	1.39E-03

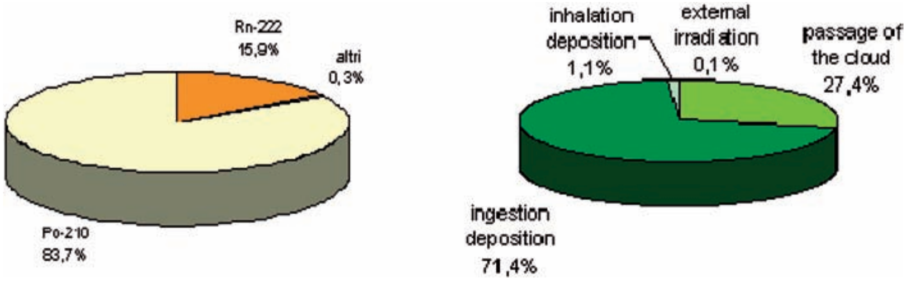

FIG. 1. Contributions of radionuclides and exposure pathways to the collective dose.

prediction model will be used, as has been described later in the paper for the refractory industry.

3. REFRACTORY INDUSTRY

3.1. General manufacturing aspects

The Italian refractory industry comprises about 40 companies, several of which use zircon sand or other zircon based components as raw materials [2]. In the standard process, this material is melted in an electric furnace with alumina and silica after preparation, and the resulting moulded components are sent for finishing or, if not to standard, recycled to the manufacturing process. Radionuclides of natural origin are contained in non-negligible amounts in the raw materials and, apart from ^{210}Pb and ^{210}Po, are found diluted in the finished products. The ^{210}Pb and ^{210}Po volatilize in the fusion process and concentrate in the furnace dust.

3.2. Survey data and estimated dose

A few years ago, ARPAV carried out a radiological survey at the premises of a company in northern Italy (one of the main users of zircon sand). The activity concentrations measured in dust from the fusion stack (Stack 1) and the scraps grinding stack (Stack 2), as reported in Ref. [6], were used as input data for a dose modelling assessment to determine the impact of dust emission into the atmosphere.

To estimate the doses delivered to the population as a consequence of the release of radioactivity from the stacks into air, the PC Cream simulation code developed by the UK Health Protection Agency was used. The code is based on the methodology described in Ref. [7]. The exposure pathways considered were as follows:

(a) Inhalation of radionuclides in the plume;
(b) External radiation from radionuclides in the plume;
(c) External radiation from radionuclides deposited on the ground;
(d) Inhalation of radionuclides resuspended from ground deposits;
(e) Ingestion of food grown on contaminated land.

The model assumes continuous release conditions and a Gaussian dispersion of the plume. The activity concentrations measured in the two stacks were used as input data, along with the total amount of emitted dust per year, namely 191 and 198 kg for stacks 1 and 2, respectively. It was assumed that all the ^{222}Rn in the processed zircon sand was released into the air. The dust activity concentrations and estimated activity releases are shown in Table 3. Taking into account the continued vertical rise of the plume due to initial buoyancy and momentum of the flue gases, the effective stack release height was taken to be 70 m. Local meteorological data, averaged over a year, were used as inputs to the model. Individual effective doses were calculated for the critical group living close to the factory in the prevailing wind direction. Individuals in the critical group were assumed to belong to three different age groups (infants, children and adults), to stay indoors 80% of the time and to eat only food of local origin according to the standard diet of north-eastern Italy [8]. The collective effective dose was calculated for the whole EU population.

TABLE 3. STACK EMISSIONS FROM A REFRACTORY PLANT

	Dust activity concentration (Bq/kg)				Estimated activity released from the stack (Bq/a)	
	Stack 1		Stack 2			
	Value	Uncertainty[a]	Value	Uncertainty[a]	Stack 1	Stack 2
^{238}U	358.5	18%	1191	22%	6.86E+04	2.36E+05
^{226}Ra	147	6%	1046	6%	2.81E+04	2.07E+05
^{210}Pb	21 050	19%	1033	4%	4.02E+06	2.05E+05
^{210}Po	35 000	5.7%	1239	12%	6.69E+06	2.56E+05
^{235}U	20	10%	59	9%	3.82E+03	1.17E+05
^{232}Th	27	6%	178	6%	5.16E+03	3.52E+04
^{40}K	10	17%	255	6%	1.91E+03	5.05E+04

[a] 68% confidence interval.

TABLE 4. DOSES TO INDIVIDUALS IN THE CRITICAL GROUP, ARISING FROM EMISSIONS FROM A REFRACTORY PLANT

Age group	Annual effective dose (μSv)
Infant	7.8E-02
Child	4.5E-02
Adult	2.4E-02

The individual effective doses calculated for the worst case exposure scenario are shown in Table 4. The doses are less than 0.1 μSv/a — far below the action level of 300 μSv/a defined by Italian law (Legislative Decree No. 241/00). For all three age groups, the radionuclides contributing most to the dose were ^{210}Po, ^{210}Pb and ^{222}Rn, and the most significant exposure pathway was the ingestion of contaminated food. Details for the adult age group are shown in Fig. 2.

The collective effective dose was determined to be 3 man mSv in a year. This value is close to the estimate of 1.2 man mSv reported in Ref. [6], which was determined using the simplified model reported by UNSCEAR [4, 5] as used for the tile industry dose assessment described earlier in the paper. Again, the most significant radionuclides were ^{210}Po, ^{210}Pb and ^{222}Rn, while the main exposure pathway was the direct inhalation of radionuclides in the plume.

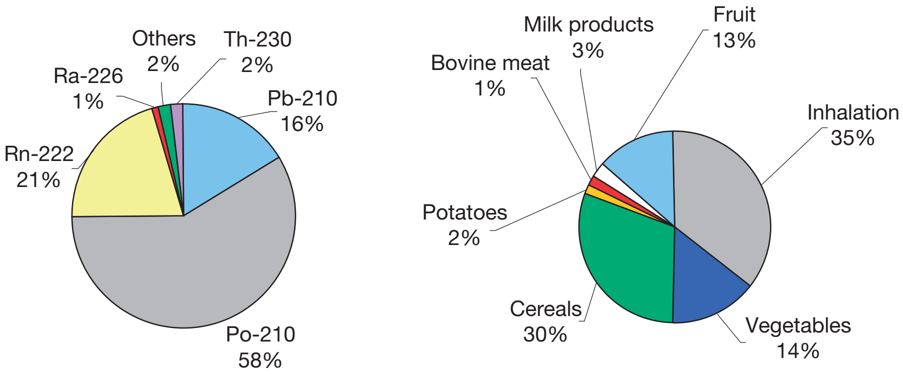

FIG. 2. Contributions of radionuclides and exposure pathways to the dose received by adults.

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DETERMINATION OF RADON SPECIFIC EXHALATION RATE FROM ITALIAN CERAMIC TILES

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Abstract

Porcelain tiles commonly manufactured in Italy have been studied for both natural radionuclide content and radon emanation using high resolution gamma spectroscopy and the E-PERM electret ion chamber, respectively. The measured activity concentrations were 33–257 Bq/kg for ^{238}U, 33–197 Bq/kg for ^{226}Ra and 39–76 Bq/kg for ^{232}Th; the radon exhalation rates were found to be at or below the lower limit of detection (0.0004 $\mathrm{Bq \cdot kg^{-1} \cdot h^{-1}}$). While previous work on the raw materials for porcelain tiles, such as quartz and zircon sand, showed measurable radon exhalation rates, our results on the end products showed extremely low rates. This observation suggests that it is highly probable for radon present in the tile to be released during the manufacturing process (vitrification); conversely, the radon produced through the decay of radium after the vitrification process remains locked up in the glass-like matrix. Additional measurements are needed to confirm that radon exhalation from porcelain tiles is negligible in terms of the inhalation dose rate.

1. INTRODUCTION

The study focuses on the determination of the radon specific exhalation rate from Italian ceramic tiles. It is well known that glazed and porcelain tiles can contain significant levels of natural radioactivity due to the presence of zircon sand used as a raw material. A previous study, focusing on the determination of natural radioactivity concentrations in several zircon sands commonly used in Italian ceramic industries [1], showed that the activity concentrations of ^{238}U and ^{232}Th were 1800–3150 and 360–1100 Bq/kg, respectively. These concentrations are significantly higher than the world average for soils, rocks and the Earth's crust and confirm the results obtained by other authors [2–6]; on the hand, the activity concentrations of ^{40}K were very low (30–90 Bq/kg).

Zircon sands have a high temperature resistance with a melting point of 2000–2500°C, acid corrosion resistance, high heat conductivity and low thermal expansion. These properties make zircon materials particularly suitable as opacifers in the preparation of ceramic glazes.

The samples analysed in this study are different kinds of Italian porcelain tiles. The main characteristics of these products are an extremely compact body, high density, low porosity and very strong intercrystalline coherence, and these properties provide the porcelain tiles with improved resistance to corrosion and erosion, high surface hardness, excellent tensile strength, and abrasion, chemical and stain resistance. According to the current international standard ISO 13006, porcelain tiles are classified as a material with porosity lower than 0.5% in terms of water absorption, whereas the commercial products generally have 0.1% porosity, far lower than the ISO standards values.

The raw materials making up the porcelain tile body can be divided into two groups: the clayey materials (e.g. sedimentary clays, schistose clay, loamy clay, marl), which serve as plasticizers; and non-plastic materials including feldspar, talc and quartz used to confer a strong structure. Sometimes zircon sand is used to obtain a super white body porcelain tile. The chemical compositions of four types of porcelain tile are reported in Table 1.

The ultimate product characteristics are influenced not only by the raw materials but also by the production processes applied (batching, grinding, pressing, drying and firing). In general, the ceramic and porcelain tile manufacturing process consists of a series of successive stages, which can be summarized as shown in Fig. 1. For many ceramic products, the body composition depends on the amount and type of raw materials, which are formulated to give the desired properties. Once the ingredients are weighed, they are combined in a mixer (depending on the ceramic sector, mixing may range from large scale continuous operations to carefully controlled small scale batch mixing); sometimes it is necessary to add water to achieve fine grinding. If wet milling is used, the excess water is usually removed via spray drying, which involves pumping the slurry to an atomizer consisting of a rapidly rotating disc. In this study, twelve samples of porcelain tiles were analysed to determine the natural radioactivity concentration and radon exhalation rate.

TABLE 1. CHEMICAL COMPOSITION OF PORCELAIN TILES [7]

	Composition (%)			
	Type 1 (base body)	Type 2 (base body)	Type 3 (super white body)	Type 4 (super white body)
SiO_2	67	71	68	64
Al_2O_3	21	18	18	21
K_2O	1.7	1.8	1.4	2.9
Na_2O	4.5	4.0	3.5	3.9
CaO+MgO	0.8	0.9	0.7	0.7
Fe_2O_3+TiO_2	0.8	0.9	0.6	0.1
ZrO_2	—	—	4.4	3.1
Remainder	4.2	3.4	3.4	3.4

2. MATERIALS AND METHODS

2.1. Sample collection and preparation

Porcelain tile samples were collected from major local manufacturers in the Emilia-Romagna region (Table 2). All porcelain tile samples were cut

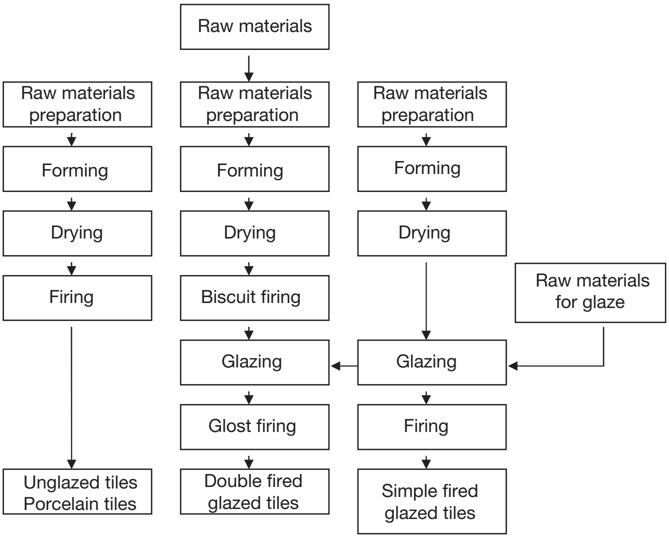

FIG. 1. General production process for ceramic tiles.

TABLE 2. SAMPLES ANALYSED IN THE STUDY

Code	Sample	Original size (cm)
01	Grey porcelain tile	33 × 33
02	Grey light porcelain tile	45.2 × 45.2
03	White porcelain tile	30 × 40
04	Porcelain tile	45 × 45
05	Beige porcelain tile	34 × 34
06	Beige porcelain tile	30 × 30
07	White porcelain tile	32.5 × 32.5
08	Porcelain tile	45 × 45
09	Light oak porcelain tile	60 × 15
10	Light porcelain tile	11.5 × 11.5
11	White and grey porcelain tile	30 × 30
12	White porcelain tile	30 × 60

into smaller pieces with an average dimension of about 5 × 5 cm, and a mass of 30–60 g (Fig. 2).

2.2. Gamma ray spectrometry measurements

The natural activity concentrations were determined by high resolution γ ray spectroscopy. The system consists of an HPGe coaxial high purity germanium detector of 22.6% nominal relative efficiency and with a resolution

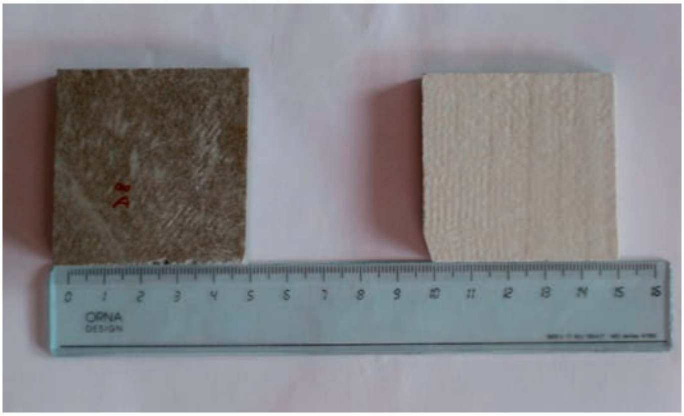

FIG. 2. *Example of porcelain tiles analyzed in the study.*

of 1.9 keV at 1.33 MeV (^{60}Co). The samples were contained in 450 mL Marinelli beakers and kept for about three weeks before measurement, in order to achieve radioactive equilibrium between ^{226}Ra, radon and its short lived decay products. Short lived daughters with more easily measured gamma ray emissions such as ^{234}Pa^{m}, ^{214}Pb, ^{214}Bi, ^{228}Ac and ^{212}Pb were used for proxy determinations of the activity concentrations of their respective parents ^{238}U, ^{226}Ra and ^{232}Th. Gamma ray peaks of 1001.03 (^{234}Pa^{m}), 609.32 and 1120.28 keV (^{214}Bi), 295.21 and 351.92 keV (^{214}Pb), 338.40, 911.07 and 968.90 keV (^{228}Ac) and 238.63 keV (^{212}Pb) were used. The counting time was 60 000 s. The measurement times were sufficiently long to ensure that the overall uncertainty was generally less than 10% at a 95% confidence interval.

2.3. Radon exhalation rate measurements

The radon exhalation rate was measured by hermetically closing the sample in a container and monitoring the radon activity concentration as a function of time. The system consisted of an E-PERM® electret ion chamber measuring the ^{222}Rn activity concentration accumulated in a glass jar (Fig. 3), which is a component part of the E-PERM® radon-in-water measurement test kit [8, 9]. The accumulation measurements were performed with screw capped and casketed glass jars, the chamber configuration was SST (chamber ‘S’, short-term electret), and the total accumulation volume after subtracting the

FIG. 3. *Electret ion chamber and glass jar of the E-PERM® system.*

excluded volume for the E-PERM® chamber was 3.6 L. The accumulation time was set at 20 d. Triplicate measurements were carried out for each sample to take into account the natural variability of radon emanation. More details are given in Ref. [10].

The radon activity concentration growth, C_v (in Bq/m^3) is given by:

$$C_v = \frac{E(1-e^{-\lambda t})}{V_c \lambda} + C_0 e^{-\lambda t}$$

where:

E is the radon exhalation rate (Bq/h) from the sample;
V_c is the volume of the container (m^3);
λ is the radon decay constant (7.56×10^{-3} h^{-1});
t is the accumulation time (h);
C_0 is the ^{222}Rn activity concentration (Bq/m^3) in the accumulation vessel at the start of the accumulation time ($t = 0$).

2.4. Emanation coefficient measurements

The radon emanation coefficient representing the ratio of the amount of ^{222}Rn released to the total amount of radon produced was calculated by the following equation [11]:

$$\eta = \frac{E}{C_{Ra}\ \lambda_{Rn}}$$

where:

E is the measured specific exhalation rate of the sample (Bq·kg^{-1}·h^{-1});
C_{Ra} is the ^{226}Ra content (Bq/kg);
λ_{Rn} is the radon decay constant (7.56×10^{-3} h^{-1}).

3. RESULTS AND DISCUSSION

Table 3 shows the activity concentrations of the naturally occurring radionuclides ^{238}U, ^{226}Ra and ^{232}Th, the radon exhalation rate and the radon emanation coefficient in the ceramic tiles examined. The radon exhalation rate

TABLE 3. ACTIVITY CONCENTRATION, RADON EXHALATION RATE AND RADON EMANATION COEFFICIENT FOR PORCELAIN TILES

Code	Activity concentration (Bq/kg)			Specific exhalation rate ($Bq \cdot kg^{-1} \cdot h^{-1}$)	Radon emanation coefficient (%)
	^{238}U	^{226}Ra	^{232}Th		
01	126	114	52	<0.0004	
02	130	111	55	0.0016	0.2
03	217	197	62	<0.0004	
04	204	153	47	<0.0004	
05	115	113	76	0.0016	0.2
06	257	186	48	<0.0004	
07	94	46	39	<0.0004	
08	46	33	42	0.0010	0.4
09	47	46	43	<0.0004	
10	41	48	41	<0.0004	
11	33	36	40	<0.0004	
12	41	37	40	<0.0004	

is given in $Bq \cdot kg^{-1} \cdot h^{-1}$. The activity concentrations were 33–257 Bq/kg for ^{238}U, 33–197 Bq/kg for ^{226}Ra and 39–76 Bq/kg for ^{232}Th. As shown in Table 3, nine of the twelve samples exhibited an exhalation rate lower than the LLD of 0.0004 $Bq \cdot kg^{-1} \cdot h^{-1}$ and the other three a very low rate (0.0010–0.0016 $Bq \cdot kg^{-1} \cdot h^{-1}$). These results are consistent with the results observed in a previous study [10]. That study focused on the radon exhalation in building materials used in Italian dwellings and also analysed four samples of ceramic tiles (two glazed tiles and two porcelain tiles). All four samples showed exhalation rates below the detection limit (0.0015 Bq/h for an exposure time of 240 h). Many authors [11–15] have reported radon exhalation rates higher than those reported for porcelain tiles in this work and in Ref. [10], although the ^{226}Ra and ^{238}U activity concentrations of their materials were similar or lower than those shown in Table 1. This observation is in agreement with the findings of a survey of radionuclide content and radon emanation rate in building materials used in the United States of America [15], where it was noted that the uranium content of a material alone cannot be used to predict how much radon is emanated.

As explained in Section 1, porcelain stoneware is made from mixtures of kaolin, white firing plastic clays, feldspars, quartz sands, alumina and zircon sands. Radon exhalation from clay and clay bricks has been observed in Refs [11, 16–20], the radon emanation coefficient in quartz sands has been determined in Ref. [21] and the radon emanation rate and emanation coefficient of mineral zircon have been measured in Refs [10, 22]. Thus, while porcelain tile raw materials show measurable radon exhalation rates, the exhalation rate in the end products appears to be close to the detection limit. From these considerations it seems highly probable that the manufacturing process makes it extremely difficult for radon to be released from tiles.

A likely explanation for this effect could be the high density and low porosity (<0.5%) obtained by the pressing process and firing, as it is well known that a dense material with low porosity does not allow radon to diffuse through it quickly [23, 24]. In fact, firing aims to achieve vitrification of the mass that depends on the reactivity of the clayey components and the synergistic vitrification action developed by the feldspars. It is recognized that vitrification chemically binds the contaminants in a glass-like matrix that significantly reduces contaminant mobility [25]. Therefore, it is highly probable that radon present in the tile is released during vitrification, whereas the radon produced through the decay of radium after the vitrification process remains locked up in the glass-like matrix.

In summary, the dose from the inhalation of radon emanating from these building materials was found to be extremely low. In addition, ceramic floor and wall coverings could act as a barrier that inhibits the migration of radon from structural building materials (bricks and cement) to indoor air. Nevertheless, additional measurements are needed to confirm that radon exhalation from porcelain tiles is a negligible problem.

4. CONCLUSIONS

In this study, the natural radionuclide content, radon exhalation rate and emanation fraction of twelve porcelain tiles commonly manufactured in Italian ceramics industries were determined. The activity concentrations were 33–257 Bq/kg for ^{238}U, 33–197 Bq/kg for ^{226}Ra and 39–76 Bq/kg for ^{232}Th. Nine of the twelve samples exhibited an exhalation rate lower than the LLD (0.0004 $\text{Bq}\cdot\text{kg}^{-1}\cdot\text{h}^{-1}$) and the other three a rate of 0.0010–0.0016 $\text{Bq}\cdot\text{kg}^{-1}\cdot\text{h}^{-1}$. Such low rates could be the result of the manufacturing process, which makes it extremely difficult for radon to be released from tiles; in fact, the main characteristics of these products are an extremely compact body, high density, low porosity and very strong intercrystalline coherence obtained by the pressing and firing processes. However, it is well known that vitrification chemically binds the contaminants in a glass-like matrix that significantly reduces contaminant mobility. To sum up, it is highly probable that the radon present in the tile is released during vitrification, whereas the radon produced through the decay of radium after the vitrification process remains locked up in the glass-like matrix.

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RAPPORTEUR SUMMARY OF OPENING SESSION AND TOPICAL SESSIONS 1 AND 2

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1. INTRODUCTION

This report attempts to place the issues raised in these sessions within the broader context of international NORM regulatory initiatives as they are currently evolving. The opening session highlighted the knowledge gained over the ten years since the first NORM symposium was held in Amsterdam. A significant amount of work has been done during this time, particularly in Europe, with respect to identifying industries, developing standards and performing facility specific studies. With this increased knowledge came a growing understanding that NORM regulatory programmes may over-regulate industrial activities and valuable commodities as a result of excessively conservative modelling assumptions and an incomplete understanding of actual industrial operations. The unfortunate result has been non-uniformity of NORM regulations which may erect an unintended technical barrier to international trade. It is hoped that the issues identified in NORM V will enable regulatory bodies to move towards international harmonization of NORM regulation. It is clear, however, that such harmonization will not be possible until there is international agreement on the following:

(a) The regulatory definition of NORM;
(b) A standard defining the scope of regulation, exemption and exclusion;
(c) A graded approach to regulating NORM based on a realistic evaluation of materials and processes.

2. THE REGULATORY DEFINITION OF NORM

All materials of geological origin contain radionuclides of natural origin (e.g. petroleum, natural gas, phosphate rock, coal, drinking water) and the radionuclide activity concentration may vary over several orders of magnitude, depending on geological factors or processing history. While a material may contain radionuclides of natural origin, it is not necessarily itself a radioactive material in the regulatory sense. Limiting the definition of NORM to include only material that needs to be regulated because of its natural radionuclide content would promote regulatory efficiency.

TENORM is a misleading term and should be avoided. The term TENORM (technologically enhanced NORM) is sometimes used to describe NORM that has become concentrated through anthropogenic influence. The term misleadingly suggests that TENORM is a distinct class of NORM that, because human activity has elevated its radionuclide content, should be the exclusive focus of regulatory control. Such a view distracts from the principal purpose of NORM regulation: controlling exposures to natural sources of radiation that are significant enough to be of regulatory concern.

3. THE SCOPE OF NORM REGULATION

Given that radionuclides of natural origin are ubiquitous in the environment, the question was raised: what should be the starting point for regulation? Should the threshold for regulation be the activity concentration in a given material or the dose received by workers and the public? For material containing radionuclides of natural origin, the relationship between radionuclide concentration and annual dose cannot be ascertained with certainty from activity concentration alone without accurate information on exposure scenarios and physical characteristics of the material (e.g. solubility, particle size distribution, radon emanation coefficient).

The distinction between practices involving natural sources and interventions is predicated in ICRP Publication 60 and described in the IAEA Basic Safety Standards (BSS), along with supporting Safety Guides. Exposure to natural sources is normally subject to the requirements of intervention, where remedial action must be justified. Certain activities giving rise to exposure, however, may be deemed to have the characteristics of practices requiring some form of control. Until recently, guidance on deciding which exposures to natural sources should be regulated has been minimal.

IAEA Safety Standards Series No. RS-G-1.7 provides guidance, reflecting international consensus, which may be used in establishing the scope of NORM regulations based on practical application of the concepts of exclusion, exemption and clearance. With regard to radionuclides of natural origin, RS-G-1.7 considered the worldwide distribution of activity concentrations and recommends a value of 1 Bq/g as the starting point for establishing the scope of regulatory control:

- <1 Bq/g: regulation is not optimal;
- >1 Bq/g: regulation may be required.

IAEA Safety Standards Series No. RS-G-1.7 further explains a dose based graded approach to controlling exposures to NORM in which the radionuclide concentration exceeds 1 Bq/g, with the objective of optimizing regulatory resources.

4. DOSE MODELLING

Recent material specific and facility specific studies have shown that a cautious approach is needed in modelling worker and public exposures to NORM to avoid significantly overestimating dose. Studies involving phosphate, zircon, rare earths and titanium industries show that modelling worker annual effective dose based on facility specific measurements yields dose estimates significantly lower than modelling based on broad assumptions. Moreover, it is often the selection of the model that determines the outcome, because some models are inherently more conservative than others. Knowledge of industrial processes, therefore, is essential to accurate dose modelling. Accurate material specific information is equally important. For example, particle size distribution is extremely critical for the accurate estimation of inhalation dose from ^{238}U and ^{232}Th series radionuclides.

5. UNRESOLVED NORM ISSUES

5.1. Revision of the BSS

A general revision of the BSS will take place over the next few years to take into account many suggested improvements along with the ICRP 2007 recommendations. An important task is to incorporate criteria for radionuclides of natural origin in commodities, consistent with the current guidance.

5.2. Public exposure to NORM

There may be some situations where regulation of materials containing uranium and thorium series radionuclides at concentrations below 1 Bq/g may be necessary. One such situation is suspected to be the use of building materials in residential construction. Just as for occupational exposure to NORM, accurate material specific data and realistic exposure scenarios are required to avoid overestimating the dose.

5.3. Transport of NORM

While the transport of radioactive materials, including NORM, is considered to be a practice, the IAEA Transport Regulations (IAEA Safety Standards Series No. TS-R-1) establish a 1 Bq/g exemption value and exclude from the scope of the regulations ‘natural materials and ores’ having an activity concentration up to ten times this exemption value (i.e. up to 10 Bq/g for uranium or thorium series radionuclides), provided such materials are not intended to be processed for their radionuclide content. Natural materials are not defined in the regulations or guidance and whether NORM having a radionuclide activity concentration in the range of 1 to 10 Bq/g is considered natural will determine its regulatory status. Materials considered to be TENORM are occasionally deemed to be not natural and therefore outside the exclusion. Such determination may result in denial of shipment by transport carriers. A more serious consequence could be the erection of a technical barrier to international trade in certain commodities. Clarification is therefore needed that NORM regulatory decisions should not be based on whether a material is ‘technologically enhanced’ and that the term natural materials includes any material containing radionuclides of natural origin.

6. EUROPEAN ALARA NETWORK FOR NORM

A newly created European ALARA network for NORM ($\mathrm{EAN_{NORM}}$) may serve as a potential starting point for harmonization of NORM regulations. In 1996 the European Commission created a European ALARA network to identify European research topics regarding optimization of occupational exposure to ionizing radiation and to serve as a conduit for information for information exchange in the European nuclear industry and research organizations. The $\mathrm{EAN_{NORM}}$ is currently under development with the objective of interconnecting groups of experts and sharing experience gained in implementing the ALARA principle into European NORM industries. The $\mathrm{EAN_{NORM}}$ intends to develop Codes of Practice for NORM industry managers and promote good radiation protection practice. It also intends to improve and support appropriate radiation protection training, to identify problems to be solved and to propose solutions. The first $\mathrm{EAN_{NORM}}$ Workshop is scheduled for 20–22 November 2007 in Dresden, Germany (see www.ean-norm.net for further information).

7. PROCESSING AND USE OF THORIUM

Two papers addressed the current uses of thorium in commercial products: its use in thoriated tungsten electrodes in tungsten inert gas (TIG) welding applications in Spain and its use in incandescent gas lantern mantles in Germany. Thoriated TIG electrodes typically contain 2% thorium and are used in large quantities (300 000 to 400 000 electrodes per year in Spain). Occupational exposure was assessed under conditions of storage of bulk quantities and use. Storage of bulk quantities of thoriated electrodes was simulated under different configurations of containers holding from 64.5 to 153.5 kg. Applying realistic modelling of occupational exposure, it was determined that occupational exposure from storage was not expected to exceed a few microsieverts per year. The use of thoriated tungsten electrodes includes welding using automated welding machinery, manual welding, and manual sharpening of electrodes using an abrasive wheel. Airborne dust measurements during welding showed ^{232}Th concentrations ranging from 0.88 to 3.0 mBq/m^3. Exposure to airborne ^{232}Th during electrode grinding is considered negligible. Overall, it appears that even though thoriated electrodes in Spain are a high volume and fairly high activity concentration material, occupational exposure to ^{232}Th is anticipated to be below 1 mSv per year.

The use of thorium oxide to improve the luminosity of gas lantern mantles has long been known. In Germany, lantern mantles are no longer manufactured but are still in widespread use in street lighting and for other illumination purposes. This study reviewed data obtained in former manufacturing operations from 1995 to 2003 and concluded that manufacturing lantern mantles could give rise to occupational lifetime doses ranging from 23 to over 400 mSv. The study also investigated thorium exposure of gas lantern maintenance workers and concluded that this source of occupational exposure does not require notification under national law. The maximum annual worker dose was concluded to be far below 6 mSv and probably well below 1 mSv.

An additional paper investigated the mobility of uranium and thorium in soil and the uptake of these radionuclides by wheat and rye. It was determined that although bioavailability of uranium exceeded that of thorium, bioaccumulation was mainly in plant roots and no transfer to plant leaves was detected.

8. PROCESSING AND USE OF ZIRCON AND ZIRCONIA

An invited paper on this topic presented a comprehensive investigation of how various operations and uses of zircon (zirconium silicate) and zirconia (zirconium oxide) fall within a graded approach to regulation, as envisioned by

IAEA and European regulations and guidance. Zircon and zirconia are minerals of international significance to a broad array of industries, including ceramics, foundry, glass, abrasives, electronics and pigments. Zirconia may be naturally occurring or produced by treating zircon to remove silicon dioxide. Zircon and zirconia contain radionuclides of natural origin and have been scrutinized for regulation as NORM. As highlighted in the opening session, there is no uniform regulatory approach to deciding whether zircon and zirconia should be regulated as NORM and what level of control is required for using these materials. The regulatory analysis presented in the paper offers a resolution to this situation based on internationally accepted regulations and guidance.

Based on a consultation of the IAEA BSS, the IAEA Transport Regulations and IAEA Safety Standards Series No. RS-G-1.7, considered in conjunction with the European Commission report Radiation Protection 122, the following stylized regulatory framework of analysis was derived for the purpose of the paper:

(a) Notification was assumed to be required if the activity concentration of a material exceeded 1 Bq/g;
(b) Exemption was assumed to be the regulatory option if the annual occupational dose did not exceed 1 mSv and the public dose did not exceed 0.3 mSv;
(c) Registration of a work activity was assumed to be required if the annual occupational dose exceeded 1 mSv;
(d) Licensing of a work activity was assumed to be required if the annual occupational dose exceeded 6 mSv.

After analysing information collected for a broad array of industrial uses of zircon and zirconia covering virtually all known applications, it was concluded that 77% of current operations would require notification because the activity concentration exceeded 1 Bq/g and 23% of operations would not require notification. Of those operations requiring notification, over half (54%) should be eligible for exemption and 23% would probably require registration. No operation using zircon or zirconia would require licensing.

These findings were broadly in line with results presented in the same session on studies conducted in Spain and Italy.

In considering worker exposures to ionizing radiation, it is important to acknowledge that normal industrial hygiene practices, unrelated to radiation protection (e.g. dust controls) have a substantial benefit in reducing the occupational dose.

The importance of distinguishing between zircon use in industrial operations and the influence of higher activity concentration accessory minerals (monazite) in processing mineral concentrates containing zircon, monazite and titanium values (ilmenite, rutile) cannot be overemphasized. The influence of dose from higher activity monazite components in zircon ore concentrates was reported in papers investigating zircon processing in Nigeria and Brazil. In particular, the Brazilian study was done in an area of high natural background radiation where the population intake of NORM was higher than that of the control group located outside the high background area. Under these circumstances, interpretation of bioassay data was difficult.

PRODUCTION OF TITANIUM DIOXIDE

(Topical Session 3)

Chairpersons

A. FAHLI
Morocco

J.L. MARTÍN-MATARRANZ
Spain

Invited Paper

PRODUCTION OF TITANIUM DIOXIDE

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Abstract

Titanium dioxide pigments provide whiteness and opacity to a vast range of everyday products from coatings and plastics to inks and even cosmetics and food. Manufacturing takes place using two different processes — the so called 'sulphate' and 'chloride' routes — to produce more than 4.5 million t per year worldwide. Both routes start from impure TiO_2 based feedstocks containing moderately enhanced concentrations of radionuclides of natural origin. Experts from the TiO_2 production industry and feedstock suppliers are assisting the IAEA in the development of a Safety Report concerning exposure to NORM within the TiO_2 industry. The data assessment shows that, for both process routes, most of the radioactivity reports to the solid process wastes and there are no areas of concern related to products, co-products or liquid or gaseous effluents for production units operating to current environmental standards. Risk assessments for the landfill disposal of solid process waste similarly did not indicate any areas of concern where current waste management practices were followed. Process deposits, typically scale material, can exhibit enhanced activity concentrations of radium. Specific management practices such as controlled vessel entry to restrict worker exposure to these materials may be necessary. With such measures, it is considered unlikely that a worker would receive an annual effective dose exceeding 1 mSv.

1. INTRODUCTION

Titanium dioxide is a simple inorganic compound produced as a pure white powder. It is commonly available in two main crystal forms, anatase and rutile, and is typically supplied to the market in a range of package sizes or in bulk. Sales as water based slurry are also common in the USA. The properties and uses of TiO_2 make it an interesting and valuable chemical and these properties overshadow its rather mundane appearance. It has a very high refractive index of about 2.7, which compares with values of only 2.0 and 1.6 for zinc oxide and china clay, respectively. This high refractive index gives the potential for producing a high level of opacity or hiding power, making TiO_2 a much better pigment than the other chemicals mentioned. While TiO_2 is the best white pigment available, this does not restrict its use to anything that is white. The opacity is also used in combination with coloured pigments to give them the required hiding power. The crystal size of the TiO_2 needs to be optimized to maximize its effectiveness as a pigment, with the optimum for light scattering being around 0.2 μm. These properties give a highly versatile product with worldwide sales of around 4.5 million t. The main uses are in coatings such as paints, followed by plastics, high grade papers and printing inks (see Fig. 1). There is also a wide range of minor uses that are important in total volume terms, including uses as pharmaceuticals, foodstuffs and cosmetics.

2. IAEA SAFETY REPORT

The TiO_2 industry is a NORM industry, in that it uses feedstocks based on minerals that contain moderately elevated concentrations of radionuclides of natural origin. Information exists in the public domain relating to the impact of this usage, but much of it is inaccurate or out of date. Therefore, when the IAEA embarked upon the development of a Safety Report on TiO_2 production, this was strongly supported by the industry.[1] The scope of the Safety Report includes the production of TiO_2 feedstocks, TiO_2 pigments and $TiCl_4$.

3. TITANIUM DIOXIDE MANUFACTURE

The overall process of manufacture is to take an impure TiO_2 feedstock and to convert this into the pure white TiO_2 pigment. The process sounds very simple, but to achieve the required level of purity it is necessary to chemically convert the impure TiO_2 into another chemical, to separate out the impurities and then to convert back to pure TiO_2 — in effect a chemical purification. There are two commercial processes used to achieve this, the so called ‘chloride’ and ‘sulphate’ process routes.

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[1] The Safety Report is being developed with the direct involvement of Huntsman Pigments/Tioxide Europe Ltd, Lyondell/Millenium, Rio Tinto, Tronox, Dupont, Iluka and ANSTO and with the indirect involvement of other titanium dioxide manufacturers — Kemira, Sachtleben, Cinkarna and Precheza — through CEFIC, a trade association of European chemical manufacturers.

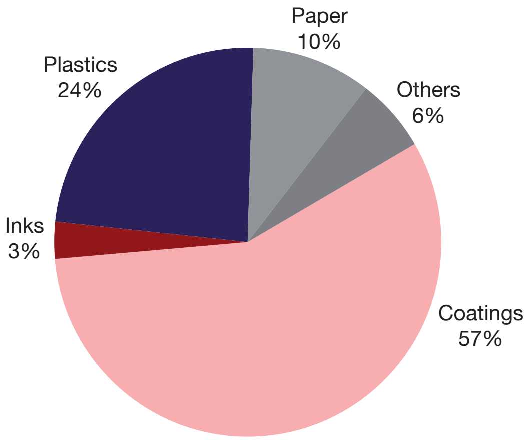

FIG. 1. Market segments for TiO_2.

3.1. The chloride process route

The overall chemistry of this process can be represented as:

$$TiO_2 + C + 2Cl_2 \rightarrow TiCl_4 + CO + CO_2$$

$$TiCl_4 + O_2 \rightarrow TiO_2 + 2Cl_2$$

The chlorine released when the TiO_2 is re-formed is recycled back to the beginning of the process such that the only chlorine consumed is that which reacts with impurities. The unit operations involved in the process are shown in Fig. 2.

Chlorination is carried out at a temperature of about 1000°C in a fluidized bed reactor in the presence of coke. The resulting gas stream contains $TiCl_4$, oxides of carbon and all the impurity metals from the feedstock in the form of metal chlorides. The gas stream is contacted with recycled liquid $TiCl_4$, which cools it to a level at which the other metal chlorides separate out as solids. The $TiCl_4$ goes forward with further cooling to be condensed as a liquid and is then fed to a high temperature oxidation reactor where it is reacted with oxygen in a plasma reactor or toluene burner to re-form TiO_2 and release the chlorine which is recycled back to the beginning of the reaction. This pure TiO_2 is subjected to a range of chemical surface treatments and milling and drying operations to give a range of products with particular properties in terms of dispersion and durability, suitable for various end use applications. The metal

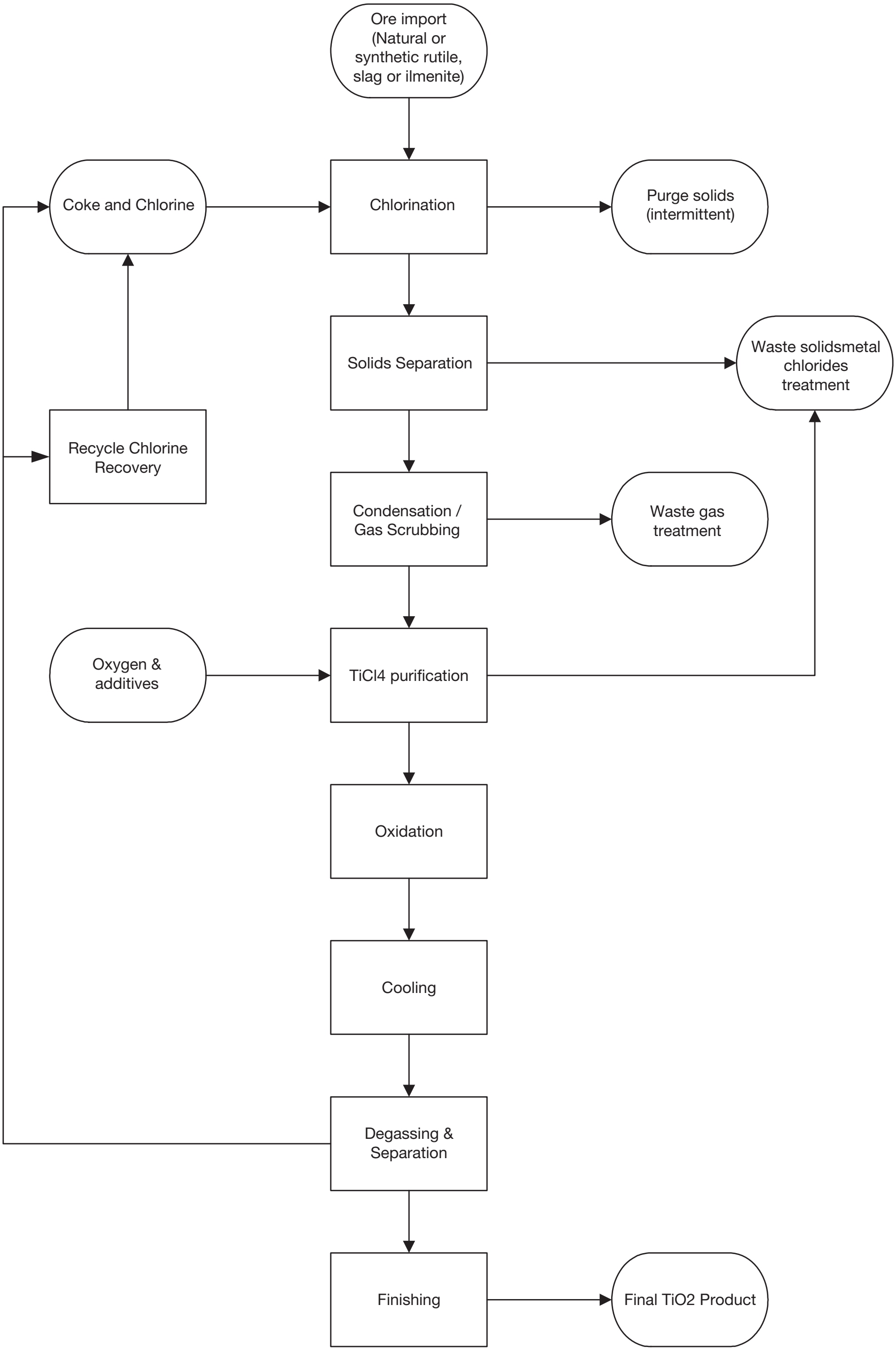

FIG. 2. The chloride process TiO_2 production route.

chloride impurities that are removed by the processing are typically neutralized with lime or limestone and sent for disposal at a landfill site.

3.2. The sulphate process route

The sulphate process is more complicated in terms of the number of unit operations involved. These are detailed in Fig. 3. The overall chemistry of the process can be represented as:

$$FeTiO_3 + 2H_2SO_4 \rightarrow TiOSO_4 + FeSO_4 + H_2O$$

$$TiOSO_4 + H_2O \rightarrow TiO_2 \cdot nH2O + H_2SO_4$$

$$TiO_2 \cdot nH_2O \rightarrow TiO_2 + nH_2O$$

The feedstock is first digested in strong sulphuric acid which converts the titanium components into titanyl sulphate and the iron into sulphates. Where the feedstock used is ilmenite based, a reduction step is required in which iron is added to convert any ferric iron to the ferrous form to aid separation later in the process. This is followed by a clarification step to remove any undigested material from the liquor. For an ilmenite process, crystallization typically follows, which separates out the co-product ferrous sulphate heptahydrate (copperas), though it is also possible to extract copperas later in the process. Copperas is sold for a range of applications including water treatment, agriculture and use in cement. The liquor passes forward to a hydrolysis stage in which the oxysulphate is reacted with water to produce a hydrated titanium dioxide product and releases sulphuric acid. The hydrated TiO_2 passes forward to a rotary kiln where it is calcined to produce the anhydrous titanium dioxide product. Further processing (finishing), is then analogous to the chloride process involving chemical surface treatments (coating) and milling and drying operations. The acid that is released at hydrolysis is not strong enough to be used directly in the digestion step, so it is subject to one of two processes, either acid concentration or neutralization (to produce gypsum). In the former, the acid is typically subjected to a number of heating, concentration and filtration cycles to increase the strength of the acid to a level allowing reuse in the process or sale. The process also concentrates residual iron that is separated as a ferrous sulphate monohydrate co-product. The alternative process, involving gypsum production, treats the acid with a calcium salt to give gypsum, which is used in plasterboard manufacture, agriculture and cement.

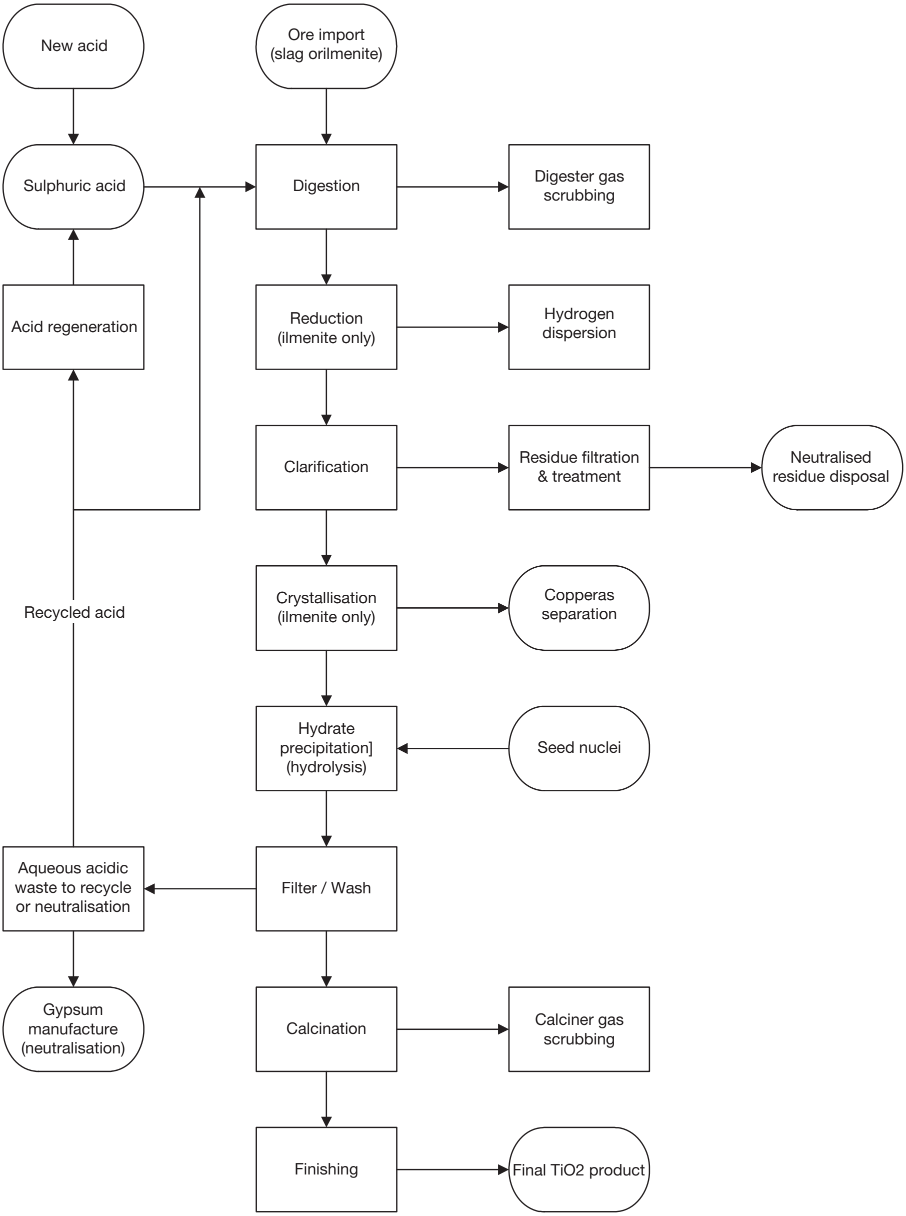

FIG. 3. The sulphate process TiO_2 production route.

3.3. Feedstocks

The compositions of the main feedstocks used within the industry are detailed in Table 1. Rutile, synthetic rutile and chloride slag are the feedstocks most commonly used in the chloride process, while sulphate slag and ilmenite are the feedstocks most commonly used in the sulphate process. However, one major manufacturer uses ilmenite in the chloride process. In general, the higher grade feedstocks (in terms of percentage TiO_2) are used for the chloride process rather than for the sulphate process. The upper activity concentrations detailed for each feedstock represent the highest values known to be used within the industry. However, producers invariably operate with a blend of feedstocks, so these upper activity concentrations represent the highest values that might be used within a blend rather than the highest overall feedstock values.

Rutile is a natural high grade TiO_2 mineral. Synthetic rutile is produced by reducing the iron oxide in ilmenite to metallic iron using carbon monoxide, followed by reoxidation and separation from the TiO_2 rich fraction (the Becher process) or leaching with hydrochloric acid (the Benelite process). Slag feedstocks are produced by the smelting of ilmenites with coal at high temperature. The process is adjusted to produce the required particle sizes for use in the sulphate or chloride processes. Ilmenite is a naturally occurring titanium/iron oxide found either in rock form or as a heavy mineral sand.

The choice of feedstock depends on how the plant has been configured at the design stage, on environmental, health and safety (EHS) requirements and on the overall processing costs. The overall costs will relate to the feedstock purchase price, its TiO_2 content, the cost of dealing with wastes arising and any EHS requirements which will include consideration of radiological implications and effluent discharge requirements. Particularly for sulphate route

TABLE 1. FEEDSTOCK COMPOSITIONS

	TiO_2 (%)	Uranium		Thorium	
		U (ppm)	^{238}U (Bq/g)	Th (ppm)	^{232}Th (Bq/g)
Rutile	93–96.5	10–60	0.1–0.74	20–90	0.08–0.36
Synthetic rutile	88–95.5	3–60	0.04–0.80	35–480	0.14–1.9
Chloride slag	85–86	0.2–6	0.002–0.08	0.2–30	0.001–0.12
Sulphate slag	79–86	0.2–6	0.002–0.08	0.2–30	0.001–0.12
Ilmenite	45–65	6–80	0.1–1.0	20–500	0.08–2.0

production plants, co-product production will be an integral part of the process, so the choice between using ilmenite or slag will have been made at the design stage.

3.3.1. Choice of feedstock — chloride process

Ilmenites are only used by one chloride route producer — relative to other feedstocks, ilmenites are of low cost and have a low TiO_2 content, which leads to high chlorine losses and high volumes of waste products. Slags have low activity concentrations and relatively low TiO_2 contents and give a high volume of waste products. Synthetic rutiles have higher activity concentrations and higher TiO_2 contents and give an intermediate level of waste products. Natural rutiles have intermediate activity concentrations and the highest TiO_2 content — they give the lowest waste volumes but have the highest purchase price.

3.3.2. Choice of feedstock — sulphate process

In relative terms, ilmenites for the sulphate process have high activity concentrations, low cost and low TiO_2 content and generate a high volume of co-products or wastes. Slag based feedstocks have low activity concentrations and a high TiO_2 content — they produce lower co-product or waste volumes but have a higher purchase price. Rutile feedstocks cannot be digested in sulphuric acid, so they can only be used for the chloride process.

4. RADIOLOGICAL ASPECTS OF THE SULPHATE PROCESS

4.1. Activity concentrations within the process and in wastes and products

Clearly, activity concentrations will depend on the feedstocks used. In general, activity concentrations when using slag based feedstocks will be low throughout the process, whereas when ilmenites are used, some concentration will take place within the process. There are three types of process change that influence the distribution and impact of radionuclides within the process:

(a) Selectivity of different radioelements within the natural decay chains due to the chemistry involved;
(b) Concentration or dilution due to volume change within the process;
(c) Deposition or precipitation of radioelements due to changes in physical conditions within the process.

4.2. Digestion

A key step as far as the process is concerned and in terms of its impact on the distribution of activity is the digestion step. All the feedstock is digested with sulphuric acid which results in some disequilibrium:

(a) U — the majority is expected to pass forward in the liquor;
(b) Th — as for U;
(c) Ra — low solubility, evidence suggests 75–95% not digested;
(d) Pb — low solubility, expect majority to remain;
(e) Bi — chemistry predicts the majority will pass forward, evidence suggests 40–75%.

After digestion, the solid volume is reduced by a factor of 5–6 and the overall impact is an increased activity concentration in the remaining digester residue that is separated after the reduction stage.

The activity concentration for digester residue from an ilmenite feedstock is typically:

(1) ^{238}U series: 0.6–1.0 Bq/g (maximum, some disequilibrium) compared with 0.1–0.2 in the feedstock;
(2) ^{232}Th series: 1.2–2.5 Bq/g compared with 0.4–0.5 in the feedstock.

4.3. Post-digestion

Following the digestion operation, the majority of the radionuclides would be expected to remain in solution when the titanyl sulphate ($TiOSO_4$) is hydrolysed and separated out as a solid from the liquor. The main product TiO_2 which is produced via hydrolysis of the titanyl sulphate stream therefore does not contain any appreciable activity. Ferrous sulphate heptahydrate ($FeSO_4.7H_2O$ — copperas), which is extracted from the liquor either prior to or after hydrolysis of the titanyl sulphate, also does not contain appreciable activity. The radionuclides remain in the acidic liquor until this is treated, typically either via an acid reconcentration process, or by neutralization to produce gypsum.

4.4. Gypsum production and neutralization

The acidic liquor comprises mainly sulphuric acid and iron sulphate and this is typically neutralized by lime or limestone to produce gypsum and iron hydroxides.

$$H_2SO_4 + Ca(OH)_2 \rightarrow CaSO_4{\cdot}2H_2O$$

$$FeSO_4 + Ca(OH)_2 \rightarrow Fe(OH)_2 + CaSO_4$$

The effective volume dilution factor if all of the acid is neutralized to make gypsum is approximately a value of 4 when compared to the feedstock, but this will depend on the level of neutralization, the efficiency of copperas/ferrous sulphate extraction (if employed) and the feedstock used. The end result is that the activity level of gypsum is low and of no concern, whether used as a product or disposed of as a waste.

4.5. Acid concentration

The other option for treatment of the acid liquor is acid concentration. The acid released when titanyl sulphate is hydrolysed cannot be reused directly in the process as it is not strong enough. If the acid concentration option is chosen, then the acid can be reused in the process or sold. This process also concentrates residual iron salts to produce an iron sulphate monohydrate co-product.

The process is one of sequential heating, concentration and precipitation stages and the radionuclides that pass forward can end up either in the concentrated acid or the iron salt. The overall maximum activity concentrations here are likely to be similar to those in the starting feedstock.

An overview of activity concentrations within the process, based on the processes described, is shown in Fig. 4. The representation is based on three activity concentration bands: <1 Bq/g, 1–10 Bq/g and >10 Bq/g. The lower band was based on the recommended exclusion level specified in the IAEA Safety Standards [1].

4.6. Concentration of radionuclides within the process

The activity of the main process materials does not give the full story in terms of the distribution of radionuclides. Where physical and chemical changes take place, radionuclides may be deposited, particularly those of marginal solubility such as radium. This leads to deposits of increased activity concentration that may build up with time in the form of material referred to as process scale. These deposits are of low volume but considerably more active than the main input or output flows to or from the system. In practice, the radium scale is often associated with barium sulphate and particular areas

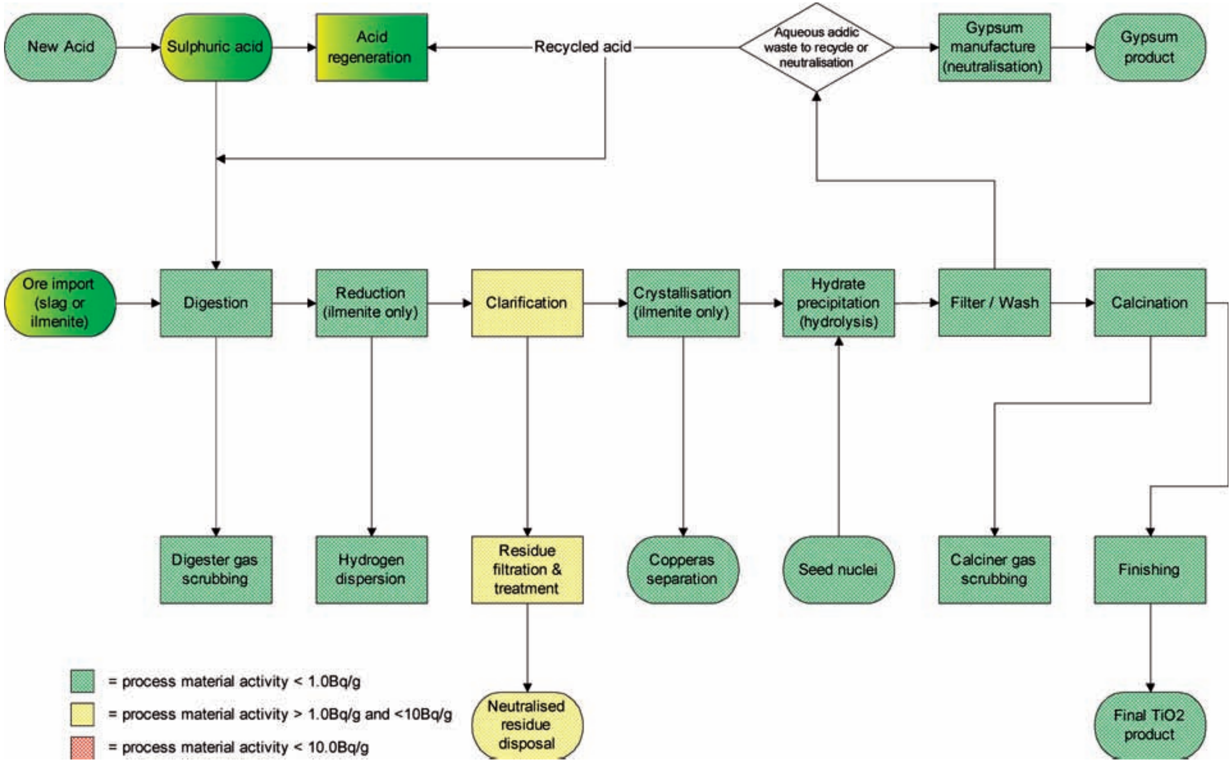

FIG. 4. Activity concentrations of process materials within the sulphate process.

where it is found are at the copperas crystallizers, in the hydrolysis area and in the Moores filtration area. The former is where the acid stream is concentrated and cooled to precipitate out iron salts, hydrolysis is where titanyl sulphate product is converted to hydrated TiO_2 and the latter where this precipitated material is separated from the acidic liquor. Areas within the process where this concentration of radionuclides takes place are shown Fig. 5.

4.7. Occupational exposures and doses

Measured instantaneous dose rates and calculated occupational exposures for sulphate process workers are summarized in Table 2. These reflect the low activity concentrations of the process materials and the low occupancy for many process activities. In general, the effective dose received by workers is much less than 1 mSv/a and could not approach the international 20 mSv/a limit for workers.

Some form of control may be required for work involving exposure to the buildup of process scale, such as entry into copperas crystalliser vessels, hydrolysis tanks, Moores tanks and acid stock tanks and decontamination of equipment removed from these areas of the process. In practice, these activities would be managed to restrict doses to 1 mSv/a or less.

5. RADIOLOGICAL ASPECTS OF THE CHLORIDE PROCESS

5.1. Activity concentrations within the process and in wastes and products

As for the sulphate process, the activity concentrations within the process will depend on the feedstock used, selectivity of radioelements due to the chemistry, concentration due to volume change and deposition/precipitation of radioelements due to changes in physical conditions within the process. The chloride process is simpler in terms of the number of unit operations involved. There are consequently less changes in physical conditions for the chloride process.

5.2. Chlorination

The principal reaction in this process is chlorination at approximately 1000°C under reducing conditions. The following chemistry is anticipated:

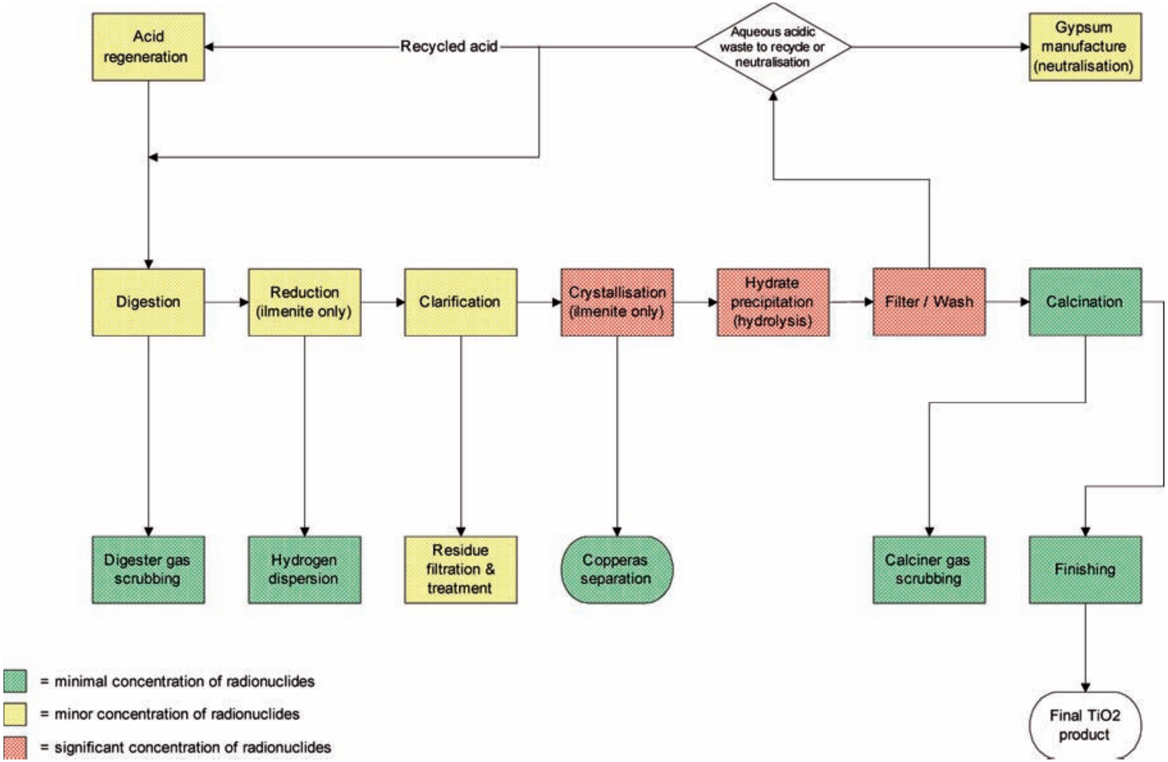

FIG. 5. Concentration and deposition of radionuclides within the sulphate process.

TABLE 2. WORKER EXPOSURES — SULPHATE PROCESS

	Instantaneous dose rate (μSv/h)	Annual effective dose (mSv)	Comment	Measures to minimize dose
Feedstock handling	0.05–0.3	<1	High specific gravity	Minimize dust, supervised areas, respiratory protection
Digester residue operations	0.2–1.5	<1	Material normally damp	
Digester residue landfill disposal	0.16–0.5	0.4–1.1	Overestimate due to capping of material	Minimize drying out and dust formation
Copperas crstallizers	0.2–10	<1	High dose rate relates to vessel entry, low occupancy	Restricted access
Hydrolysis area	0.2–50	<1–6	Highest dose rate measured at piece of equipment. Highest general dose rate 12 μSv/h	Consider need for restricted access, supervised area, logging of hours
Moores filtration area	1–21	<1–6	Highest dose rates for vessel entry	
Weak acid stock tanks	10	<1	Vessel entry, low occupancy	Restricted access
Decontamination of equipment	Equipment dependent	<1	Removal of scale, check activity, defined actions	Controlled area or personal dosimetry, process operational measures to minimize buildup, chemical treatment required, e.g. neutralization

(a) U — will chlorinate and pass forward in the gas stream;
(b) Th — the vast majority will pass forward (boiling point 940°C);
(c) Ra — $RaCl_2$ only melts at 1000°C so there is a possibility of some retention within the chlorinator;
(d) Pb — the vast majority will pass forward (boiling point 950°C);
(e) Bi — will chlorinate and pass forward in the gas stream;
(f) Rn — will remain in the gas phase.

There is a possibility of some absorption of volatile chlorides into the chlorinator refractory lining.

5.3. Quench/solids separation

The gas stream produced in the chlorinator, comprising $TiCl_4$, CO, CO_2 and metal chlorides, passes forward and is quenched with recycled liquid $TiCl_4$, lowering the temperature and condensing out metal chloride solids. These solids contain the vast majority of the radionuclides. Some polonium may stay with the $TiCl_4$ that goes forward in the process but will be returned as part of a recycle stream when the $TiCl_4$ is distilled.

The separated metal chloride solids are slurried in water and neutralized typically with lime. Neutralization will precipitate essentially all the radionuclides. The level of neutralization will determine losses to the liquid effluent. For full neutralization, everything will go to the solid waste.

5.4. Solid wastes

Apart from some loss of Rn, which will be highly dispersed, all radionuclides will remain within the chlorination solids handling areas. Comparing a damp neutralized waste solid with the starting feedstock, the volume is likely to have reduced, with the radionuclides becoming concentrated by a factor of about 1–2.5, depending on the type of feedstock used. Some buildup of activity within the chlorinator bed over a period of time is also likely, but the activity concentration when the material is removed will be a function of operating regime. Higher temperatures and higher flow rates will lead to lower activity buildup within the chlorinator. An overview of activity concentrations within the chloride process, based on the processes described, is presented in Fig. 6.

5.5. Concentration of radionuclides within the process

The chloride route is a continuous process, unlike the batch process associated with the sulphate route, and involves much fewer unit operations. Consequently, there is less opportunity for the buildup of radionuclides within the process. Figure 7, which shows these areas, is therefore similar to Fig. 6.

5.6. Occupational exposures and doses

Measured instantaneous dose rates and calculated occupational exposures for chloride process workers are summarized in Table 3. These

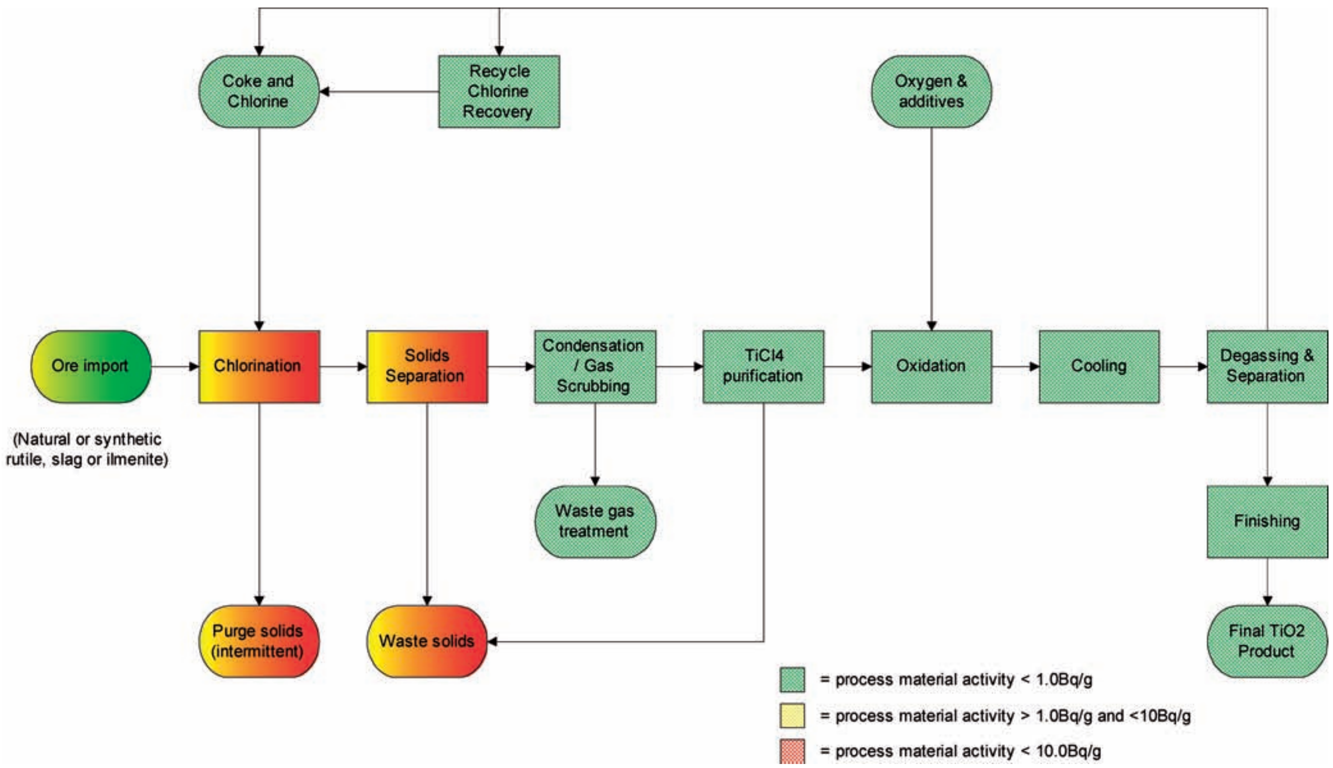

FIG. 6. Activity concentrations of process materials within the chloride process.

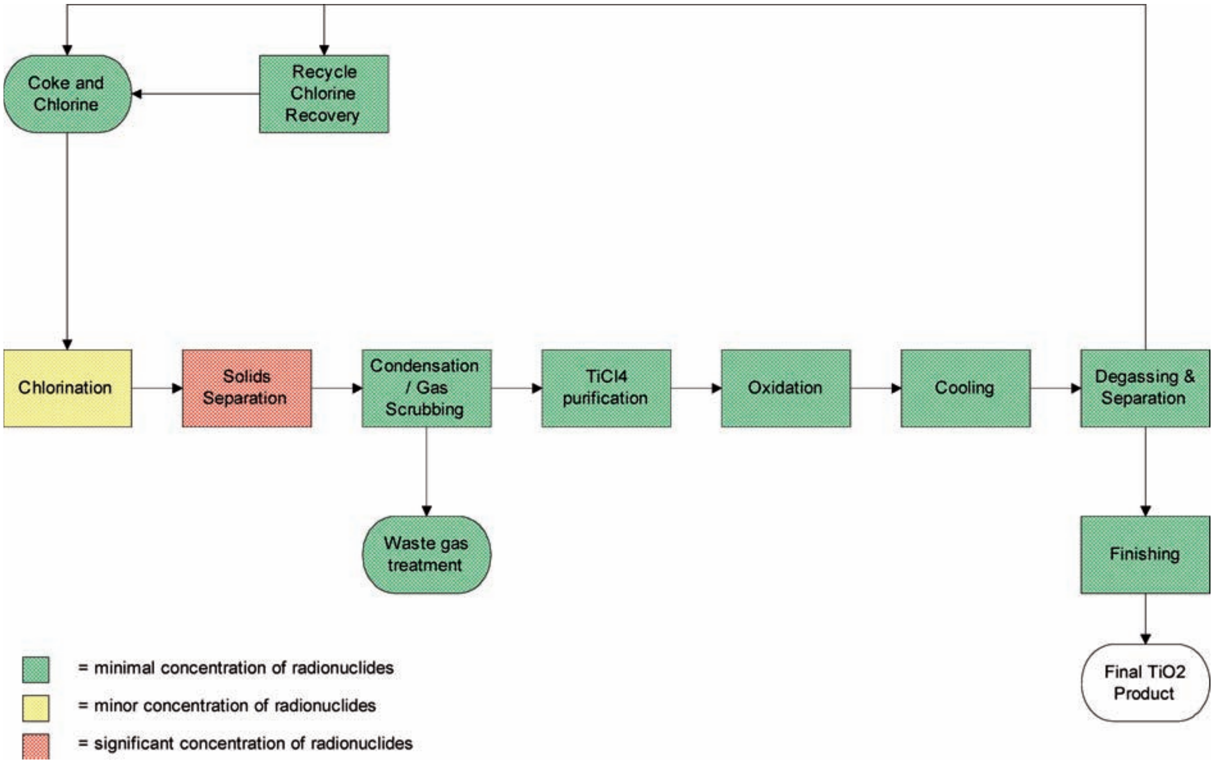

FIG. 7. Concentration and deposition of radionuclides within the chloride process.

TABLE 3. WORKER EXPOSURES — CHLORIDE PROCESS

	Instantaneous dose rate (μSv/h)	Annual effective dose (mSv)	Comment	Measures to minimize doses
Feedstock handling	0.1–0.15	<1	Minimize losses and dust generation	Respiratory protection for dust is adequate for radiation protection
Inside chlorinator	2.5	<1	Access during refurbishment	Respiratory protection, systems of work that minimize internal access
Bed purging		<1	Limited occupancy (high temperature hazard), infrequent operation	
Neutralization area	10	<1	Filter maintenance	Manage exposure time
	35	<1	Tank entry	Consider need to classify as controlled area, restrict access, respiratory protection, disposable clothing and equipment washdown
	50–90	<1	Internal tank descaling	
	2.7	<1	Working in area	Limited time close to equipment
Landfill operation	0.5	<1	Limited occupancy	Shielding by cover materials
Process scale, rubber linings	15		Removed from process equipment	Segregation of equipment, restricted access
Co-product processing	0.3–0.35	<1	Dependent on co-product and feedstock, numbers represent maximum values	

reflect the low activity concentrations of the process materials and low occupancy for many process activities. In general, the effective dose received by workers is much less than 1 mSv/a.

The areas where some form of control is required relate particularly to vessel entry into areas with potential for the buildup of process scale, e.g. the neutralization area and areas or activities where dust levels may be high. In practice, these activities would be managed to restrict doses to 1 mSv/a or less.

6. ENVIRONMENTAL IMPACTS AND PUBLIC EXPOSURE

In accordance with European Directive 92/112/EEC on Procedures for the Reduction and Eventual Elimination of Pollution Caused by Waste from the Titanium Dioxide Industry, in Europe and with environmental requirements in other parts of the world, discharges of waste to the aquatic environment from TiO_2 production have been significantly reduced or stopped entirely. Essentially all radioactivity is returned to the solid phase either as a waste or co-product. There are no problems associated with the activity concentrations of co-products and good waste management practices related to disposal ensure that risks are well controlled and low.

This has been confirmed by work carried out to assess the environmental impacts of a production site and a waste landfill. A radiological assessment of a sulphate route ilmenite based production site was carried out, involving sampling within and beyond the site boundary. A comparison of the following operational and pre-operational measurements showed no detectable differences:

(a) Dose rates at five external stations;
(b) Radon/thoron progeny;
(c) Radium concentrations in airborne particulates;
(d) Radium concentrations in groundwater;
(e) Radium concentrations in soil and seawater.

It was concluded that there was no additional dose to members of the public from operation of the process.

The landfill operation for one producer involving disposal of ilmenite based sulphate process digester residue was subject to a radiological risk assessment. The assessment concluded that the techniques employed reduced external dose rates to background levels and that risks were reduced to trivial levels. This assessment was carried out on a landfill prior to the introduction of enhanced waste disposal requirements under the EU landfill Directive so it would be expected that risk levels would have now reduced further.

The other possible route of public exposure relates to transport of feedstock. Typically, this may involve movement of bulk cargo in ships with transfer to truck, rail or conveyor at the destination port. This material is of high value, leading to a desire to minimize losses, and shipping and dockside transfer would normally be operations that would not be accessible to members of the public. Practices used to minimize risk could include, as necessary, interruption of transfer activities in windy conditions, covering of loads on trucks and use of protective respiratory equipment by workers should there be a risk of significant exposure to dust.

7. CONCLUSIONS

Titanium dioxide is manufactured via two process routes from feedstocks containing low concentrations of radionuclides of natural origin. None of the input activity is transferred to the TiO_2 products. For the co-products generated, there is either minimal transfer or the level in the co-product can be disregarded on the basis of exclusion principles. The majority of the input activity is transferred to process wastes, which are disposed of in landfill facilites. However in both processes there is a potential for generating process scale deposits which contain enhanced radionuclide concentrations. Where appropriate, management practices are implemented to limit worker exposures to these materials.

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RADIOLOGICAL IMPLICATIONS DUE TO THORIUM IN TITANIUM MINERAL SEPARATION AND CHEMICAL PROCESSING

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Abstract

This study gives the results of measurements of thorium and its progeny in titanium minerals and an assessment of NORM related radiological issues in mineral separation and chemical processing plants in India. The concentrations of ^{232}Th and ^{228}Ra in titanium minerals and titanium dioxide are presented. External gamma exposure rates and airborne thorium concentrations in plants processing such minerals are studied. The radionuclide concentrations in liquid effluent and solid wastes are analysed and disequilibrium with respect to ^{228}Ra is observed.

1. INTRODUCTION

The titanium minerals ilmenite and rutile are present in the beach sands of coastal India in varying concentrations, along with other minerals such as zircon, monazite and garnet. These heavy minerals are recovered by surface/dredge mining and are separated by standard mineral separation techniques based mainly on the conductive, magnetic and gravimetric properties of the different minerals. The major constituent among the heavy minerals is ilmenite ($FeO{\cdot}TiO_2$). Ilmenite and rutile contain low levels of natural radioactivity due to the presence of thorium and uranium series radionuclides. Very few data are available [1, 2] on the radiological aspects in industries processing these minerals and their derived products. This study gives the results of measurements of thorium and its progeny in titanium minerals and an assessment of NORM related radiological issues in mineral separation and chemical processing plants in Kerala, India.

2. METHODOLOGY

Ilmenite and rutile samples from mineral separation plants at Chavara in Kerala were obtained and counted in a gamma spectrometer (4″ × 3″ NaI(Tl) detector coupled to a 4K MCA, HPD, BARC Model) after equilibrium ingrowths of the progeny of radon and thoron. The external gamma exposure rates at different locations (1 m above ground) where workers are normally deployed were measured using a Geiger–Müller survey meter and a scintillometer (Electronics Corporation of India Ltd, Models MR121D and SM141D). Over a period of two years, 85 air samples were collected on a monthly basis from processing plants with reference to ilmenite and rutile streams. The samples were collected on GFA filter papers representing breathing zones and were analysed for thorium and thoron progeny by a programmed alpha counting method described elsewhere [3]. A few air samples were also collected from TiO_2 pigment plants where the pigments are manufactured from ilmenite by the chloride process. The likely occupational inhalation exposures were estimated using ICRP dose conversion factors. In order to assess the radiological impact due to waste tailings, samples of liquid effluent and solid tailings were collected and activity concentrations were analysed by gross alpha counting (using an ECIL Model SP-647 ZnS(Ag) counter having a counting efficiency of 25% and a detection surface diameter of 4.5 cm), gross beta (using an ECIL GM counter having an efficiency of 15%) and gamma spectrometric methods.

3. RESULTS AND DISCUSSION

The activity concentrations of ^{232}Th and ^{228}Ra in the titanium minerals ilmenite and rutile are given in Table 1. The ^{232}Th concentration in ilmenite samples varied typically in the range of 0.23–0.86 Bq/g with an average activity of 0.57 Bq/g. The ^{228}Ra concentrations in the samples were also of the same order, with a mean of 0.51 Bq/g, indicating secular equilibrium conditions. Rutile mineral samples showed a ^{232}Th concentration of 0.08–0.15 Bq/g with a mean of 0.1 Bq/g. Data with respect to two derived products, synthetic rutile and TiO_2, are also given in the table. These derived products are manufactured by HCl leaching, followed by chlorination and oxidation. In the case of synthetic rutile, the activity concentration was 0.11–0.23 Bq/g. In TiO_2 finished pigment powder the ^{232}Th concentration was in the range of 0.09–0.22 Bq/g with a mean of 0.13 Bq/g. In freshly prepared pigment samples the ^{228}Ra activity was found to be lower than ^{232}Th, with a mean value of 0.04 Bq/g, indicating significant disequilibrium with respect to the parent nuclide. The

TABLE 1. ACTIVITY CONCENTRATIONS IN ILMENITE AND DERIVED PRODUCTS

	No. of samples in composite	Activity concentration (Bq/g)			
		^{232}Th		^{228}Ra	
		Range	Mean ± SD	Range	Mean ± SD
Ilmenite	3	0.23–0.86	0.57 ± 0.25	0.21–0.69	0.51 ± 0.21
Rutile	3	0.08–0.15	0.10 ± 0.03	0.08–0.14	0.10 ± 0.04
Synthetic rutile	4	0.11–0.23	0.19 ± 0.06	0.08–0.15	0.09 ± 0.03
TiO_2 pigment powder	4	0.09–0.22	0.13 ± 0.05	0.02–0.13	0.04 ± 0.05

TABLE 2. EXTERNAL GAMMA DOSE RATES IN TITANIUM MINERALS PROCESSING

	Radiation field (μGy/h)
Mineral concentrate storage area	2.0–5.0[a]
Concentration upgrading plant	0.6–1.0
High tension separators area	2.0–2.5
Magnetic separators area	1.1–1.8
Ilmenite initial separation	1.7–2.8
Rutile section	0.8–1.5
Ilmenite final product section	0.5–1.5
General background	0.5–1.0

[a] Higher fields are due to the presence of monazite mineral containing nearly 8% ThO_2.

disequilibrium observed in these cases could be due to the solubilization of some part of the radium during the removal of iron from the ore.

The external gamma dose rates measured at different locations in the ilmenite separation plants are given in Table 2. Since the mineral separation plants are situated in areas of high natural background radiation (due to the presence of monazite sand), the observed radiation fields in ilmenite and rutile process areas were comparable with the general radiation background in the area. The radiation field in the ilmenite section was 0.5–1.5 μGy/h. The estimated occupational external exposure was 1 mSv/a, assuming an incremental elevated gamma exposure level of 0.5 μGy/h above background and an occupancy period of 2000 h.

Table 3 gives the airborne activity due to thorium in ilmenite separation and TiO_2 production plants. Airborne ^{232}Th in the plants with particular reference to the ilmenite and rutile separation area was observed to be in the range of 0.003–0.04 Bq/m^3 with a mean of 0.008 Bq/m^3. Only limited numbers of samples were taken in TiO_2 pigment production plants and the average ^{232}Th concentration observed at different spots was 0.005 Bq/m^3. From the data, assuming a breathing rate of 1.2 m^3/h for 2000 working hours per year, the likely annual inhalation dose was calculated to be 0.7 mSv. For the purpose of dose estimation, the material was assumed to be of lung absorption class S (insoluble mineral) and to have a particle size of 7 μm [3] in deriving dose coefficients in accordance with international standards [4]. The thoron progeny measurements in the process locations showed insignificant potential alpha energy concentrations in the range 1–5 mWL.

The radionuclide concentrations in different solid wastes and the liquid effluent generated during the mineral separation and chemical processing of the mineral are given in Tables 4 and 5. The mean concentrations of gross alpha and beta activities in the wet mill liquid effluent were 0.05 and 0.08 Bq/L, respectively. The ^{228}Ra values in the effluent were in the range of 0.01–0.048 Bq/L, with a mean value of 0.03 Bq/L. The wet mill solid tailings showed nearly 4 Bq/g of ^{232}Th activity. Solid wastes generated during chemical processing of the titanium mineral, including the iron oxide waste produced during acid regeneration, indicated ^{232}Th concentrations of 0.6–3.4 Bq/g. Significant disequilibrium was observed with respect to ^{228}Ra in these solid wastes. The study indicates that constant monitoring and appropriate protection measures are required to control possible leach-out and groundwater contamination in the disposal environment.

TABLE 3. AIRBORNE ACTIVITY (^{232}Th) CONCENTRATIONS IN ILMENITE SEPARATION PLANTS

	No. of samples	^{232}Th activity concentration (Bq/m^3)	
		Range	Mean ± SD
Ilmenite separation area	50	0.003–0.029	0.006 ± 0.003
Rutile separation area	35	0.003–0.041	0.010 ± 0.004
TiO_2 pigment plant	4	0.001–0.008	0.005 ± 0.003

TABLE 4. RADIOACTIVITY IN TAILINGS AND EFFLUENT FROM MINERAL SEPARATION PLANTS

		Activity concentration		
		Gross alpha	Gross beta	^{228}Ra
Wet mill liquid effluent (Bq/L)	Range	0.03–0.08	0.04–0.16	0.01–0.048
	Mean ± SD	0.05 ± 0.002	0.08 ± 0.027	0.03 ± 0.012
Solid tailings (Bq/g)	Range	15.2–27.6	11.3–21.0	2.3–5.4
	Mean ± SD	22.4 ± 4.5	16.5 ± 3.1	3.9 ± 1.1

TABLE 5. RADIOACTIVITY IN TAILINGS FROM THE CHEMICAL PROCESSING OF TITANIUM MINERAL

	Activity concentration (Bq/g)			
	^{232}Th		^{228}Ra	
	Range	Mean ± SD	Range	Mean ± SD
Solid waste after settling neutralized effluent (1)	1.76–3.45	2.75 ± 0.72	0.14–0.39	0.24 ± 0.10
Solid waste after settling effluent (2)	0.61–3.0	1.58 ± 1.01	0.05–0.46	0.30 ± 0.18
Iron oxide waste	0.75–1.20	1.02 ± 0.19	0.40–0.71	0.58 ± 0.13

4. CONCLUSIONS

The typical ^{232}Th activity concentration in ilmenite, the major titanium mineral, was 0.6 Bq/g and its progeny ^{228}Ra was in secular equilibrium. Lower concentrations were observed in other forms such as rutile and TiO_2 pigment. Thorium series radionuclide concentrations in titanium minerals are lower than the exemption level of 1 Bq/g specified in the IAEA Basic Safety Standards [5]. The study indicated the possibility of external gamma exposure of 1 mSv and an inhalation dose of 0.7 mSv annually, due to the presence of NORM in those industries processing titanium minerals. Exposure to thoron progeny was insignificant in these process plants. The activity concentrations of ^{232}Th and ^{228}Ra in solid waste samples were higher than those in the minerals and significant disequilibrium with respect to ^{228}Ra was observed in such samples. The activity concentrations in the solid wastes may be of concern in certain cases. Further studies are required to assess the water dissolution characteristics of these solid wastes. The study indicates that regular monitoring and appropriate engineered protection measures are required to control long term impacts on the disposal environment.

ACKNOWLEDGEMENT

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MONAZITE AND THE EXTRACTION OF RARE EARTHS

(Topical Session 4)

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Invited Paper

NATURALLY OCCURRING RADIOACTIVE MATERIAL (NORM) IN THE EXTRACTION AND PROCESSING OF RARE EARTHS

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Abstract

The presence of NORM in rare earth minerals in varying concentrations is quite often significant enough to result in occupational and environmental radiation exposures during their mining, milling and chemical processing for the extraction of the rare earth elements and compounds. Depending on the monazite concentration in the raw sand, radiation exposures of the order of 0.13–1.00 man mSv per tonne are involved in the mining and separation of monazite. The chemical extraction of rare earths from monazite involves occupational radiation exposures in the range of 0.30–1.00 (mean: 0.64 ± 0.19) man mSv per tonne of rare earth concentrate. The paper discusses comprehensively the various resources of rare earths and the different processes adopted in the industry. The influence of NORM on the radiation backgrounds, radiation fields encountered in processes, radiation exposures, generation of radioactive wastes and the environmental impact of the mining and milling of rare earth minerals and chemical extraction of rare earths are also discussed.

1. INTRODUCTION

The term ‘rare earths’ (REs) refers to a group of fifteen elements including those with atomic numbers 57 (La) to 71 (Lu), as well as yttrium (39) and scandium (21). These elements have varied applications in products of everyday use, and also in advanced scientific research. REs in commercially exploitable quantities are found in minerals such as monazite, bastnaesite, cerites, xenotime, gadolinite, fergusonite, allanite and samarskite. Most of these minerals contain some thorium or uranium, or both. The presence of NORM in the RE minerals in varying concentrations is quite often significant enough to result in occupational and environmental radiation exposures during their mining, milling and chemical processing for the extraction of the RE elements and compounds. These exposures require careful evaluation and analysis to assist in decision making regarding the extent and applicability of regulatory standards.

The presence of thorium and uranium and their decay products in the mineral result in enhanced natural background radiation fields in their areas of occurrence, and these deposit areas have come to be widely known as natural high background radiation areas (NHBRAs). Most of the mineral recovery plants are situated in these NHBRAs. The mining of the ores and further processing results in concentration/redistribution of the NORM in the process streams, product intermediaries, products and effluents. This paper attempts to present an overview of the resources, processes for RE extraction, the concentrations of NORM encountered at various levels, the impact on the occupational and environmental radiation exposures, and their significance with respect to regulation and control.

2. RARE EARTH MINERALS AND NORM

Monazite contains 0.2–0.4% uranium as U_3O_8 and 4.5–9.5% thorium as ThO_2, depending on the region of origin/occurrence. Bastnaesite contains 0.1–0.2% thorium as ThO_2 and negligible concentrations of uranium. Xenotime contains almost equal percentages of uranium and thorium, 0.81% U_3O_8 and 0.83% ThO_2 respectively. Table 1 gives typical concentrations of RE oxides and radionuclides in some common RE ores [1]. Monazite is widely distributed and many countries such as Australia, Brazil, China, Egypt, India, Malaysia, South Africa, Sri Lanka, Taiwan (China) and the United States of America are engaged in its production.

Until recently, monazite was the most important resource for REs. Of late, the mineral bastnaesite is getting an edge over monazite as a resource for RE production. Large deposits of this mineral at Mountain Pass, California and the Bayan Obo deposits in China constitute the most important sources of REs in the world today [1, 2]. Some other countries which have bastnaesite deposits are Brazil, Burundi, the Democratic Republic of the Congo, Madagascar, and countries of the former Soviet Union.

TABLE 1. TYPICAL COMPOSITION OF SOME RE MINERALS

	Composition (%)			
	TREO[a]	U_3O_8	ThO_2	P_2O_5
Monazite, Australia	61.33	0.34	6.55	26.28
Monazite, India	59.68 (60)	0.37 (0.35)	9.58 (8.0)	26.23 (27)
Monazite, Malaysia	59.65	0.24	5.90	25.70
Monazite, Thailand	60.20	0.44	5.76	26.52
Monazite, Rep. of Korea	60.20	0.45	5.76	26.52
Monazite, DPRK	42.65	0.18	4.57	18.44
Bastaesite	58–74	—	0.11–0.20	0.64–0.94
Xenotime, Malaysia	54.00	0.81	0.83	26.20
Gadolinite	32–46	—	up to 2	—

[a] Total RE oxides.

3. RADIOLOGICAL PROPERTIES OF THE THORIUM AND URANIUM DECAY CHAINS

In the decay scheme of naturally occurring thorium, one atom of ^{232}Th emits six alpha particles, four beta rays and several gamma rays before becoming the stable end product ^{208}Pb. The alpha energies range from 4.0 to 8.78 MeV. The chain also shows high energy beta and gamma rays of 2.26 and 2.61 MeV, respectively. Each atom of ^{238}U in natural uranium decays to stable lead through the emission of eight alpha particles and six beta rays along with accompanying gamma rays. The maximum energies of emissions are 7.69, 3.26 and 1.76 MeV for alpha, beta and gamma, respectively [3].

3.1. Concept of secular equilibrium

Aged natural thorium/uranium does not exhibit any appreciable change in activity concentration with respect to time, as the parent nuclide is very long lived. The entire chain, which consists of several short lived daughter products, shows the characteristic decay of the parent nuclide. Such a situation is known as secular equilibrium. Under these conditions, the activity of the daughter nuclide will be equal to the activity of the parent. Equilibrium gets disturbed due to chemical separation. In the case of thorium, its immediate daughter product ^{228}Ra gets separated easily. Thus an initially pure sample of thorium will show the activity associated with ^{232}Th and ^{228}Th. The separated ^{228}Ra will decay according to its half-life of 5.8 years. With a half-life of 1.9 years, ^{228}Th will also decay initially, but the daughter nuclides will slowly build up by the decay of the parent ^{232}Th and hence secular equilibrium will be re-established in a period of about 50 years. Since thorium based activity is predominant in the RE industry, the discussions in this paper will be mostly concerned with thorium chain nuclides.

3.2. Radiological hazards of thorium

The hazards from thorium can be from both external and internal sources. External hazards are due to high energy beta and gamma rays, while internal hazards are mainly due to alpha emitting radionuclides deposited inside the body. The internal hazard is mainly by way of inhalation of thorium bearing dust and short lived decay products of thoron gas (^{220}Rn). Inhaled thorium bearing dust is deposited in different regions of the respiratory tract, depending on the particle size. The probability of deposition in different regions of the respiratory tract depends on the activity median aerodynamic diameter (AMAD) [4]. A fraction of deposited activity becomes solubilized and/or transported to various body tissues through body fluids.

Thorium is almost always associated with its immediate daughter product ^{228}Ra, which is chemically much more mobile. Radium is easily leached from the site of deposition and is translocated to different organs. The most important site of deposition of radium is bone, where it becomes uniformly distributed. Ingestion by way of food and drinking water is another possible route of entry of thorium and daughter products into the human system.

3.2.1. The concept of working level (WL) for thoron daughters [5]

For inhalation of thoron and daughter products, the organ at risk is the lung. The energy imparted by a known amount of inhaled activity in the lung is therefore a measure of radiation exposure by that activity. One WL corresponds to the potential alpha energy concentration of short lived ^{220}Rn daughters (thoron daughters) in radioactive equilibrium with a ^{220}Rn concentration of 275 Bq/m^3. In terms of potential alpha energy concentration, any mixture of the daughter products of radon (thoron) which on ultimate decay dissipate an energy of 2.08×10^{-5} J/m^3 (1.3×10^5 MeV/L) constitute one WL. Lead-212 (ThB) accounts for more than 90% of the potential alpha energy. Hence exposure to thoron daughters is practically that due to ThB only.

4. MINING, MINERAL SEPARATION AND CONCENTRATION OF RE ORES

4.1. Monazite

The southwest and southeast coastal regions of India have rich deposits of heavy minerals, the major constituents being ilmenite, zircon, rutile, garnet, monazite and sillimanite. The monazite content of the beach sands generally varies from <0.1 to 2%. Monazite of Indian origin contains approximately 9% Th as ThO_2 and 0.35% U as U_3O_8. Table 2 gives the typical thorium and uranium radioactivity content of the raw sand and monazite.

Surface mining, collection of beach washings and dredge mining are the mining methods adopted. The mineral separation plants (MSPs) make use of the differences in the electrical and magnetic properties and differences in specific gravity of the constituent minerals to separate them. The dredged sand is concentrated by slurrying in water and passing down through spirals. The dried concentrate is passed through a series of high tension electric separators and magnetic separators of varying intensities. Wet tabling and froth flotation effect fine separation of some minerals. During the final stages of monazite separation, air tabling also is adopted [6]. The process is essentially the same in all MSPs. A typical flow sheet for separation of monazite is given in Fig. 1. Some other countries having sizable monazite resources (which are being exploited or are under various stages of being exploited) are Australia, Brazil, Burundi, Democratic Republic of the Congo, Egypt, Madagascar, Malaysia, South Africa, Sri Lanka, Vietnam, Taiwan (China) and the USA [1].

TABLE 2. TYPICAL RADIOACTIVITY CONTENT OF BEACH SANDS AND MONAZITE IN INDIA

	Activity concentration (Bq/g)		Radiation field, infinite spread (μGy/h)
	^{232}Th	^{238}U	
Raw sand	0.32–6.44 (78.5–1570 ppm Th)	0.04–0.74 (2.9–58.8 ppm U)	0.5–5.0
Monazite	322 (78 543 ppm Th)	37 (2942 ppm U)	180–250

Note: Th chain activity (equilibrium) = 10 × ^{232}Th activity. U chain activity (equilibrium) = 14 × ^{238}U activity.

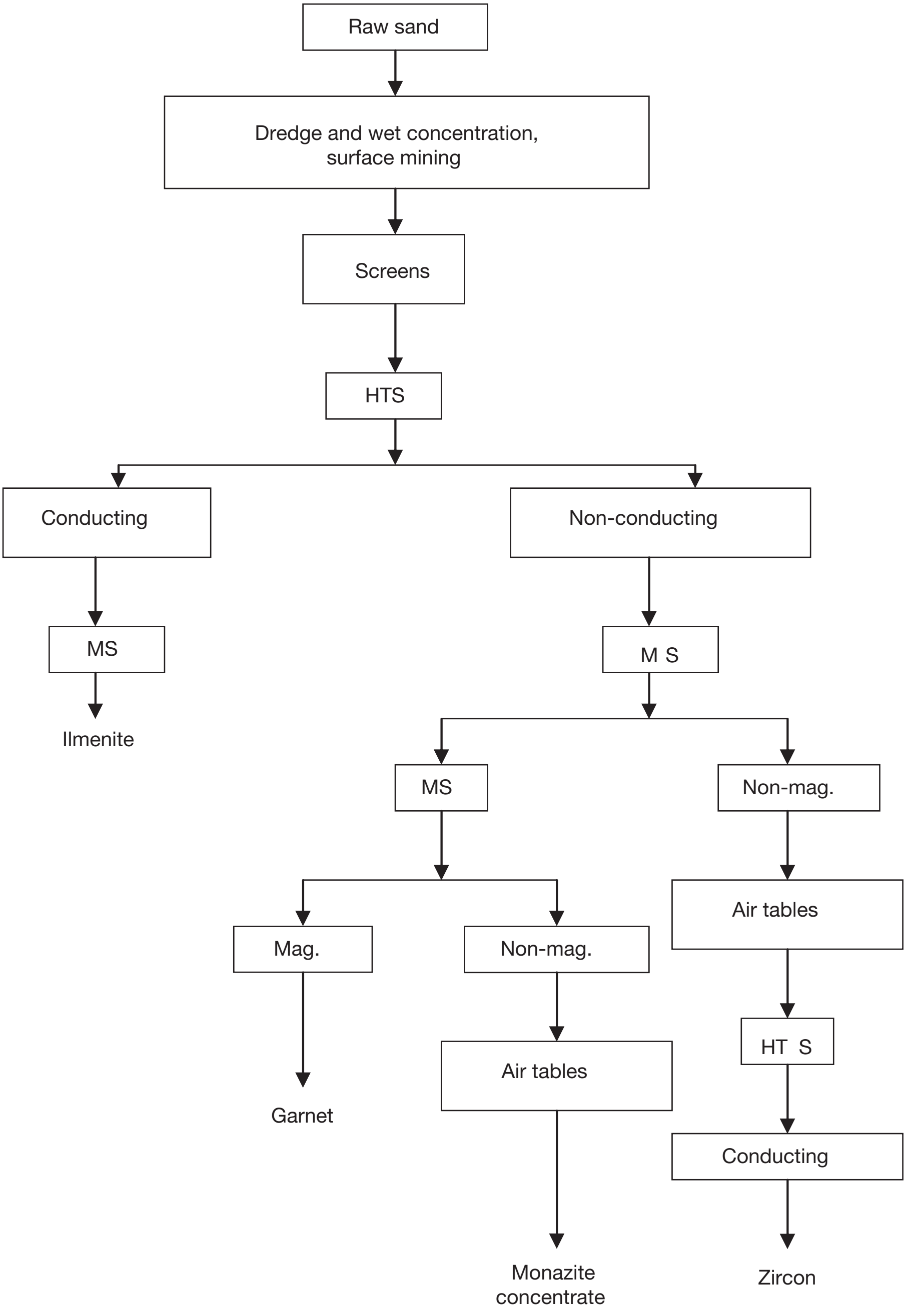

FIG. 1. Simplified process flow sheet for monazite separation.

4.2. Bastnaesite

Bastnaesite deposits (Mountain Pass, California) contain nearly 10% bastnaesite along with calcite, barite, strontianite, silica and small amounts of apatite. The minerals are exploited by open pit mining. The major operations involved in the mining and concentration are blasting of the ore, crushing/ grinding, flotation, acid leach and drying [1]. Major deposits are found in the USA and China and these are the countries mainly involved in exploiting this mineral.

4.3. Complex ores — China

RE ores from the dolomite mines in the Inner Mongolia region of China consist of iron–dolomite and RE minerals (with various types of niobium, as well as bastnaesite and monazite). Excavated ore contains nearly 30% iron and 5% RE oxides. The iron content of the blasted ore is upgraded by ball milling, grading and magnetic drum separation (primary iron concentrate). The secondary iron concentrate by flotation and concentration results in REs of 10–15% concentration in the froth part. Table separation and further flotation increases the concentration to 60% [1].

5. RARE EARTH EXTRACTION PROCESSES

5.1. Processing of monazite.

Brazil, India and Malaysia are the major producers of RE concentrates from monazite. Production of REs from black monazite by Pacific Ocean Rare Earths in Taiwan (China) has also been reported. Malaysian tin ore, ‘amang’, contains other minerals along with monazite and xenotime. The Malaysian Rare Earth Corporation (xenotime producer) and Asian Rare Earth Sdn started working in 1982 for production of $RECl_3$. China is known to be producing REs from monazite from Hunan province since 1977 [2].

5.1.1. Sulphuric acid decomposition of monazite [7]

Several variations of the sulphuric acid digestion of the mineral concentrate were in vogue during the early years of processing of monazite. Essentially the process consisted of digestion of the ground (ball milled) mineral using fuming H_2SO_4 at 200–220°C in a cast iron or silicon iron or glass lined reactor. The mineral is decomposed exothermically, forming a pasty mixture of sulphates and acid sulphates suspended in phosphoric acid and excess sulphuric acid. This is further treated with cold water to form a stable solution of sulphates of RE, Th and U. The residue contains unreacted monazite, silica and other impurity minerals. Neutralization causes precipitation of thorium phosphate and leaves most of the REs and uranium in the solution. Various processes had been developed for the production of individual REs and concentrates. However, extensive purification of the RE fraction was required for removing the thorium, a significant portion of which precipitate with the RE double sulphate. This process has been now replaced with alkali digestion.

5.1.2. Alkali digestion of monazite and selective acid extraction of REs

Chemical processing of monazite, an orthophosphate of Th and the RE elements, is done by alkali digestion and selective extraction with hydrochloric acid. Figure 2 shows a simplified process flow sheet of the process [8, 9]. Monazite is finely ground in a ball mill and mixed with caustic soda in reaction vessels known as attack tanks. The reacted mass, which contains the trisodium phosphate and hydroxides of thorium, uranium and REs along with unreacted monazite, is leached with water. Trisodium phosphate is dissolved, leaving behind the hydroxides. These are subsequently leached with dilute hydrochloric acid. The RE fraction goes into solution leaving behind the insoluble hydroxides. The reactions can be represented as follows:

$$\mathrm{RE(PO_4) + 3NaOH \rightarrow RE\ (OH)_3 + Na_3PO_4}$$

$$\mathrm{Th_3(PO_4)_4 + 12NaOH \rightarrow 3Th(OH)_4 + 4Na_3PO_4}$$

$$\mathrm{RE(OH)_3 + 3HCl \rightarrow RECl_3 + 3H_2O.}$$

The trisodium phosphate (TSP) by-product is converted into crystals, packed and sold. Thorium hydroxide is stored as such or the crude thorium hydroxide from the extraction stage is dissolved in concentrated HCl. The unattacked sand is separated by filtration and thorium is converted to thorium oxalate and stored. During the above process the radium (^{228}Ra) and lead present in the monazite appear in the RE composite chloride ($RECl_3$) fraction. These are removed from the product by a process known as 'deactivation' with 'lead elimination'. Radium present in the RE is carried down by barium sulphate by precipitating barium chloride with sodium sulphate. Lead is eliminated by sodium sulphide. The solid waste obtained from the deactivation with lead elimination, referred to as 'mixed cake', is suitably contained and

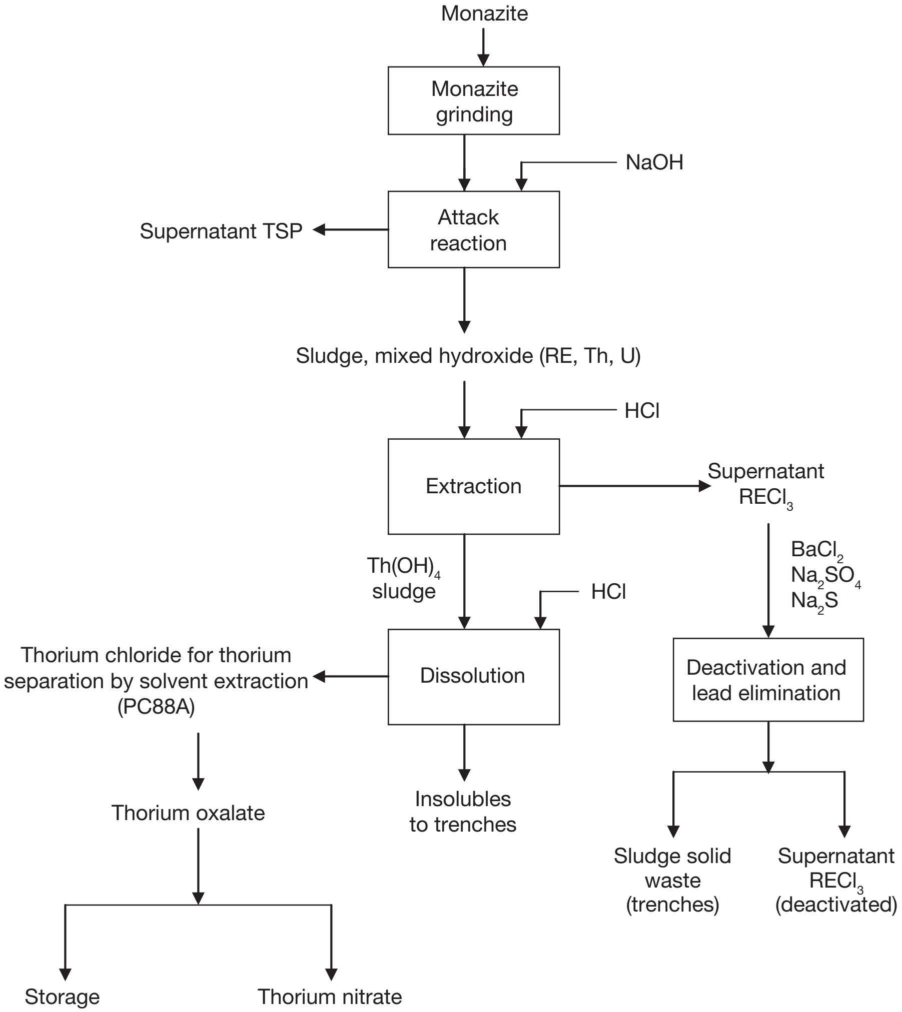

FIG. 2. Simplified process flow sheet for monazite processing.

disposed of as radioactive waste. The deactivated and lead free composite RE chloride is evaporated and made into flakes and marketed. For the separation of individual REs, a solvent extraction process is employed.

Monazite is chemically processed at the Rare Earth Division plant of Indian Rare Earths Ltd (IREL) at Udyogamandal in India for recovery of REs. The plant processes 3000–4000 t of monazite per year. The diversified products include oxides, fluorides and carbonates of composite REs, cerium compounds and salts of the heavy REs Sm, Gd, Eu and Y and compounds of the light REs Nd and Pr.

5.1.3. Processing of bastnaesite and other ores

The crude bastnaesite ore (Mountain Pass, California) is crushed and ground and subjected to multistage flotation to obtain a concentrate of 60% RE oxide. This concentrate is leached with hydrochloric acid to produce 70% RE oxide concentrate, leaving behind the $CaCl_2$ in solution. This concentrate is dried, roasted and again treated with HCl to produce an RE chloride. A large amount of Th-containing waste and wastewater not meeting the effluent standards is generated in the process [2, 10, 11].

At present, mixed bastnaesite–monazite concentrate is industrially treated using a high temperature sulphuric acid process at about 800°C, followed by solvent extraction. This process leads to a large amount of HF-containing waste gas and a slag-to-concentrate weight ratio of up to 0.66, annually yielding tens of thousands of tonnes of slag containing 0.2 wt% thorium. This has to be stored as radioactive waste. The recent development of the stepwise carbo-chlorination–chemical vapour transport (SC-CVT) process for RE extraction from bastnaesite and mixed bastnaesite–monazite concentrate of Chinese origin is reported in Ref. [12]. This process is claimed to be more environmentally friendly and energy saving.

RE present in the phosphoric acid produced during the processing of rock phosphate is recovered by solvent extraction and oxalate precipitation after the uranium fraction is separated from the solution containing RE–U concentrate. The uranium bearing fraction is disposed of as radioactive waste or recovered [10].

6. OCCUPATIONAL EXPOSURES

Radiological safety in the different stages of the RE industry (monazite based) is ensured through compliance with the relevant IAEA standards, as well as national regulations [13–15].

6.1. Mineral separation plants

Typical radiation fields observed at various stages of the operations are given in Table 3. The background radiation fields in the plants range from 1 to 100 μGy/h. The mineral separation plants are situated at the natural high background areas and radiation fields in the range of 1–3 μGy/h are typically the background in the area. Mineral processing, especially dry milling, gives rise to dust which contains radioactive particles due to finer grains of monazite which become airborne in the process. Since the activity involved is long lived

TABLE 3. TYPICAL RADIATION FIELDS ASSOCIATED WITH MINERAL SEPARATION

	Radiation field (μGy/h)
Mining areas	1–4
Raw sand	1–4
Concentration plant	1–1.5
Sand concentrate (dump yard)	4–15
Sand concentrate in storage	5–20
Screens	2
Primary high tension separators	4
Monazite high tension separators	6
Magnetic separators	2–4
Monazite air tables	8–20
Monazite wet circuit	5–30
Monazite bags	200
Zircon	2–4
Ilmenite, rutile, garnet	2
General background	1–3

(Th-nat), this gives rise to a committed dose. The airborne activity concentrations of Th encountered in these plants are of the order of less than one twentieth of the corresponding derived air concentration (DAC) [16, 17]. The internal dose attributable to thoron and thoron daughters is not significant in the mineral separation plants, owing to very low emanation of thoron from the mineral [6].

In the case of mining and separation of monazite the radiation doses incurred varied widely, depending on the concentration of monazite in the raw sand. The doses were also highly dependent on the operations. In the earlier stages of the mineral industry most of the operations, such as sand collection, sun drying, feeding and product handling, were conducted manually. Technological improvement and mechanization of mining and processing operations have resulted in lesser exposures in recent times. The individual annual exposures in a minerals plant handling raw sand of low monazite content (approximately 0.5%) varied from 1.5 to 2.5 mSv (mean: 1.98, standard deviation: 0.41 mSv). For a minerals plant that processed raw sand richer in monazite content (2% monazite feed concentration) the individual annual exposures were about 4.2–7.0 mSv (mean: 4.91, standard deviation: 0.81 mSv). Operations such as dry screening, air tabling and wind tabling result in airborne dust and radioactivity, which in turn contribute to internal exposures. The introduction of wet operations and covered air tables with air extractors has helped greatly in reducing the airborne activity concentrations in recent times. For sand containing higher concentrations of monazite, the representative radiation exposures were in the range of 0.50–1.00 mSv (mean: 0.68, standard deviation: 0.11 mSv) per tonne of monazite. For lower monazite content the exposures were in the range of 0.13–0.65 mSv (mean: 0.38, standard deviation: 0.19 mSv) per tonne [18].

6.2. Chemical processing of monazite [18, 19]

Radioactive equilibrium of the Th chain is broken at the acid extraction stage. Thereafter the buildup and decay of activity at different stages follow separate routes. The activity inventory at various stages is marked by disequilibria and the activity at each stage has to be accounted for by taking the material balance, fractionation and buildup/decay. Typical radiation fields observed at different stages of monazite processing are given in Table 4. The fields in the normally occupied areas range from 0.5 to 8 μGy/h. Radiation fields up to 1500 μGy/h are observed on some of the deactivation tanks due to the buildup of ^{228}Ra activity on the rubber lining of these tanks. Occupancy in such areas is controlled by standard radiation protection practices.

Apart from external exposure, chemical processing involves significant internal exposure, mainly due to the inhalation of airborne long lived activity due to thorium and short lived activity due to thoron and daughter products. High emanation of thoron is observed from surfaces contaminated by spillages and from thorium concentrate. The thoron daughter concentrations in the plants generally are in the range of 25–200 mWL (compared with a DAC of 1000 mWL). However, these levels could be as high as 1–3 WL in contaminated areas and bulk storage areas to which entry is restricted, prohibited or permitted only with respiratory protection and which are under constant surveillance. Inhalation of thorium bearing dust is possible in the case of releases from ball milling, drying, etc. By engineered and operational controls, airborne activity levels of less than one twentieth of the DAC are achieved in these plants. Typically, external and internal exposures contribute equally to the total exposure in a monazite processing plant [6]. In the case of a plant processing 3000–4000 t/a of monazite, the individual annual exposures for the past 25 years were in the range of 3–9 mSv. The representative exposures for RE production are in the range of 0.3–1 man mSv (mean: 0.64, standard deviation 0.19 man mSv) per tonne of RE concentrate produced by the

TABLE 4. TYPICAL RADIATION FIELDS ASSOCIATED WITH MONAZITE PROCESSING

	Radiation field (μGy/h)
Caustic soda digestion plant:	
General background	0.5–2
Ball milling	1–5
Ball mill	15–20
Monazite bag, 50 kg	200
Digestion area	2–5
Digestion tanks	10–15
RE extraction plant:	
General background	1–8
Mixed hydroxide filters	15–20
RE extraction area	2–5
Extraction tanks	20–25
Thorium concentrate filtration	10–35
Thorium concentration filter	30–35
Deactivation area	15–40
Deactivation tanks	300–1000
RE chloride evaporation area	1–2
RE chloride drums	1–2
Diversified RE products plant	<0.5–1.5
Heavy RE plant	<0.5
Nd–Pr concentrate plant	<0.5
Product handling area/store	<0.5–2
Active wastes:	
Mixed cake (solid waste)	400–600
Thorium concentrates (wet)	60–70
Thorium oxalate	200
Aged thorium concentrates	500–600
Insoluble waste (unreacted monazite)	30–100
Effluent plant cake	2

chemical processing of monazite. The wide range in these exposures was due to factors such as the plant conditions prevalent from time to time, modifications and control measures. Table 5 gives the occupational exposure history in the Indian RE industry for the past few years [18, 19].

TABLE 5. EXPOSURES IN THE INDIAN RARE EARTHS INDUSTRY, 1995–2003 [6, 18, 19]

	Minerals plant I, low monazite content	Minerals plant II, higher monazite content	RE plant
Range of average per capita annual doses (mSv)	1.5–2.5	4.2–7	3–9
Range of collective doses in a year (man Sv)	0.13–0.70	1.3–2.6	2.3–3.9

6.3. Radioactivity concentrations in RE concentrates and compounds

The deactivated lead free RE chloride concentrate contains ^{228}Ra in the range of 0.5–1.5 Bq/g. The cerium hydrate and Nd–Pr carbonate contain ^{228}Ra of the same order, 4–5 Bq/g. The Sm–Gd concentrate has a very low content of ^{228}Ra, approximately 0.2 Bq/g. These are all below the exemption level specified in the IAEA Basic Safety Standards [16]. The ^{228}Ra concentrations in the RE chloride concentrate before deactivation vary from 200 to 300 Bq/g.

7. WASTE MANAGEMENT AND ENVIRONMENTAL IMPACT

Wastes from the mining and processing of radioactive ores are potential sources of radiological impact, both for those working in the industry and for members of the public who may be exposed if wastes are dispersed in the environment. These wastes are characterized by large volumes and low activity concentrations of radionuclides with very long half-lives. These may also produce radioactive waste containing much higher levels of radioactivity than exemption levels. However, in the case of mining and mineral separation, the concentrations are for most of the time below the exemption levels, although the disposal of large quantities may exceed the exemption levels for total activity [16, 20].

The principal dose limit for members of the public is 1 mSv in a year. The radiation detriment due to a source relates to all human radiation exposures, both present and future, caused by the source during its lifetime. In the case of mining and milling wastes, there is also a need to consider exposures due, for example, to human intrusion into the waste at some future time. Mining and mineral processing tailings will continue to present a potential hazard to human health, even after closure, and therefore additional measures may be needed to provide for the protection of future generations. Recent reports on the legacy of monazite processing in Brazil, which discuss the cycle of monazite processing in that country and its consequences in terms of site remediation, amounts of wastes and residues generated and stored at an urban site and soil contamination at a rural site, are a pointer to this issue [21, 22].

7.1. Generation, treatment and disposal of radioactive waste

7.1.1. Mining and mineral separation

Solid waste

Surface mining of beach washings and inland placers, as well as dredge mining, generate large volumes of overburden which include topsoil, clay, silica sand, slime, peat, organic waste (e.g. vegetation, trees, roots), screen-overs and shells. The volume of waste generated depends on the heavy mineral concentration in the mined raw sand and the recovery achieved in the processes. Typically 600–700 kg of tailings are generated per tonne of raw sand mined and are used as backfill. The mineral free tailings from the pre-concentration stages, mainly containing silica, are used for refilling the dredged area. The tailings sand generated in the dry mill typically vary from 70 to 100 kg per tonne of concentrated feed sand processed. The tailings, which contain unrecovered monazite and other minerals, are recycled along with fresh feed to the dry mill. The dry and wet solid tailings are transported by mechanized means such as pumping, conveyors, covered trucks and dump trucks/bins to the disposal site. The water used for wet concentration of minerals also carries solid tailings. The crude monazite concentrate also requires appropriate management. For long term storage, the monazite rich fraction of the processed mineral sand or monazite bearing waste is segregated, appropriately transported and stored in earthen trenches. The crude monazite concentrate slurried in water is directly pumped into the trench and periodically topped up with about 1 m of mineral free sand to reduce the radiation fields to natural levels encountered in the area (NHBRA levels). These trenches are in controlled areas located away from normally occupied areas, well demarcated with boundary fencing/walls and identifiable with prominent caution signs. Table 6 gives typical radioactivity levels associated with solid waste from mining and mineral separation. The mined and refilled areas are replanted and rehabilitated. There is a continuous reforestation programme for restoring the ecological balance to the maximum extent possible [23].

TABLE 6. TYPICAL RADIOACTIVITY LEVELS IN SOLID WASTE FROM MINING AND MINERAL SEPARATION

	Activity concentration (Bq/g)		Radiation field (μGy/h)
	Gross alpha	Gross beta	
Mine tailings	0.3–0.5	1.6–4.6	0.3–0.5
Pre-concentration tailings	0.3–0.8	1.7–3.8	0.3–0.4
Mineral separation tailings	50–80	250–350	30–50

Liquid effluents

The tailings water released after mining, pre-concentration and separation of minerals contains radioactivity levels comparable with levels normally encountered at the NHBRAs. Typical activity concentrations are given in Table 7. The water is recycled into the process after adequate settling.

TABLE 7. TYPICAL RADIOACTIVITY LEVELS IN WATER FROM MINING AND MINERAL SEPARATION

	Activity concentration (Bq/L)	
	Gross alpha	Gross beta
Mining	0.04	0.04
Pre-concentration	0.01	0.03
Mineral separation	0.05	0.09

Gaseous effluents

The gaseous releases are mainly the exhausts from the driers, the contents of which may include solid particulate material and SO_2. The release of radioactivity through the exhaust air during the mineral separation process is negligible.

7.1.2. Chemical processing of monazite

Solid waste:

Chemical processing of monazite results in the following solid wastes:

(a) Unreacted monazite (insoluble)

In addition to unreacted monazite from the monazite caustic soda reaction, this waste also contains traces of RE, Th, Ra and U and is acidic in nature. The insoluble waste separates out during the recovery of thorium hydroxide and its conversion to thorium oxalate by the solvent extraction process. Otherwise, this waste usually goes along with the thorium hydroxide cake. Approximately 80–100 kg of insoluble waste is produced per tonne of monazite processed.

The waste sludge is neutralized and filtered by mechanically (hydraulic or otherwise) operated filters and the filtered cake is disposed of in engineered storage facilities (‘RCC trenches’) The design of the structure takes into consideration the local conditions (such as rainfall, acidity, water table, flooding and earthquakes) and radiation shielding requirements to meet regulatory requirements. The trenches are provided with a top concrete slab after filling.

The main radionuclide in the waste is ^{228}Ra, with an activity concentration of 400–1000 Bq/g. The radiation field on contact with the insoluble waste is around 30–100 μGy/h and the radiation field over the sealed trenches is 2–4 μGy/h [6].

(b) PbS–Ba(Ra)SO_4 mixed cake

The mixed cake of PbS and Ba(Ra)SO_4 results from the deactivation and lead elimination of RE chloride. The $BaSO_4$ carries along with it ^{228}Ra as $RaSO_4$. This waste contains traces of U, Th and RE. Between 60 and 100 kg of this cake is generated per tonne of monazite processed. The cake, filtered in mechanically operated filters, is disposed of in RCC trenches, the design of which takes into consideration the local geological and meteorological conditions and radiation shielding requirements to meet the regulatory requirements. The trenches are provided with a top concrete slab after filling.

The activity concentration of ^{228}Ra was of the order of 10 000 Bq/g (dry) in early years but this has declined to about 2000–5000 Bq/g (dry) in recent years due to process changes entailing repeated deactivation. The radiation field on contact with the cake is around 400–600 μGy/h. Presently the cake is directly pumped to FRP lined RCC trenches, which results in reduced radiation exposure of workers. These trenches are sealed when full and the radiation field over the sealed trenches is about 3–5 μGy/h [6].

(c) Solid waste from effluent treatment plant (ETP) cake

Phosphate sludge results from the neutralization and calcium phosphate precipitation of acidic and alkaline effluents generated during the processing of monazite. The ETP cake mainly contains phosphate and carries low levels of radioactivity (mainly ^{228}Ra at an activity concentration of 25–100 Bq/g). The quantity of this waste is up to about 100 kg per tonne of monazite processed. This waste is disposed of in a controlled area in earthen trenches. The earthen trenches are provided with a 0.5–1 m thick soil topping. The disposal site is well demarcated, fenced and identified with suitable caution signs. The radiation field in contact with the cake is less than 2 μGy/h. The radiation field above the soil topped area is comparable to the natural background prevailing in the area [6].

(d) Thorium concentrate

Thorium hydroxide cake produced during the extraction of REs from monazite contains the uranium fraction as well as the unreacted monazite. The radiation fields on contact with this wet cake range from 60 to 70 μGy/h. Aged thorium concentrate gives a radiation field of 500–700 μGy/h. The radiation fields in contact with bags filled with thorium oxalate vary from 200 to 220 μGy/h. The quantity generated amounts to nearly 250 kg per tonne of monazite processed. This sludge is disposed of in engineered RCC silos. These are provided with adequate shielding to ensure that there is no enhancement of the external radiation background in public areas. The thoron and thoron daughters that are produced decay inside the silos themselves, as these are closed structures.

(e) Contaminated scrap

Surface contaminated scrap material (including metallic, non-metallic and flammable material) is generated during operations such as routine maintenance and modifications.

Table 8 gives the radioactivity levels usually observed in solid wastes produced during the chemical processing of monazite.

TABLE 8. TYPICAL RADIOACTIVITY LEVELS IN SOLID WASTE FROM THE CHEMICAL PROCESSING OF MONAZITE

	Activity concentration (Bq/g)			Radiation field (μGy/h)
	Gross alpha	Gross beta	^{228}Ra	
Monazite, insoluble	800–2500	800–3000	400–1000	30–100
Mixed cake	2000–4000	3000–7000	2000–5000	400–600
ETP cake	75–100	300–600	25–100	2–3
Thorium oxalate	8000	—	—	200–220

Liquid effluents

Acidic and alkaline effluents from the processing plants and water and chemicals used for decontamination constitute the liquid effluents in monazite processing. Nearly 15 m^3 of effluents are generated per tonne of monazite processed. The characteristics of the liquid effluents are given in Table 9. Acidic effluents and alkaline effluents after adequate settling are treated at the ETP to remove the activity content. The two streams are mixed in a flash mixer, followed by calcium phosphate precipitation by the addition of calcium chloride. The major pollutants in the effluents are phosphate, fluoride and radionuclides (mainly ^{228}Ra). The radionuclides are co-precipitated with calcium phosphate, which also removes most of the phosphate and fluoride ions in the effluent. After addition of a suitable flocculating agent, the slurry flows into a clariflocculator and is allowed to settle. The supernatant liquid is collected in a post-treatment tank for monitoring and discharge to a river. The sludge is filtered in a rotary drum filter and collected in HDPE laminated bags and disposed of. The discharges were within the prescribed discharge limits for liquid effluents for the plant of M/s Indian Rare Earths Ltd [24, 25].

Gaseous effluents

During the various chemical processing stages, gaseous and particulate emissions take place. The radionuclides of concern in the emission are thoron daughters (^{212}Pb, ^{212}Bi) and Th (^{232}Th, ^{228}Th). The major sources of thoron daughters are the thorium storage silos. However, since the silos are sealed structures most of the thoron gas and daughters decay inside the silos. The release of airborne activity takes place mainly from processing plants and the effluents are discharged through stacks. The stack heights are set on the basis of

TABLE 9. TYPICAL PRE-TREATMENT LEVELS IN LIQUID EFFLUENTS FROM THE PROCESSING OF MONAZITE,

	pH	Activity concentration (Bq/L)			F (ppm)	PO_4 (ppm)
		Gross alpha	Gross beta	^{228}Ra		
Acidic effluent	1.6–2.0	100–300	400–600	150–200	70	—
Alkaline effluent	12–13	600–900	900–1000	300–400	—	3000

the local meteorological parameters and the permitted ground level concentrations of the discharged pollutants.

The releases are much below the authorized discharge limits [25]. Gaseous effluents such as HCl, Cl_2 and H_2S are also released during normal operations. Sodium hydroxide scrubbers in the ventilation system effectively control the releases, which conform to the limits set by the national authorities. The environmental impact of airborne releases from mining, mineral separation and chemical processing of monazite is insignificant [6].

7.1.3. Decommissioning waste [26]

Solid waste

The solid wastes resulting from decommissioning of mining and mineral separation plants are inactive. A considerable quantity of solid waste such as radioactive sludge (accumulated in tanks, surface contaminated equipment, tanks, filters, motors, pumps and pipelines), electrical fittings, contaminated structural materials, wall cement plaster and floor/wall chippings are generated during the decontamination of chemical processing plants. These wastes are classified into various categories based on the radionuclide content and on contamination levels and the wastes are disposed of in accordance with approved waste disposal practices.

Surface contaminated equipment such as large tanks are decontaminated and the contamination free material is disposed of as inactive scrap. Other contaminated equipment such as filters, electrical fittings and pipelines is decontaminated by washing and is reused or disposed of. Contaminated structural parts and floor/wall cement plaster chippings are disposed of in RCC trenches or earthen trenches, depending on the radionuclides, their activity concentrations and the radiation fields.

Liquid waste

The liquid waste generated during decommissioning of mining and mineral separation facilities consists mainly of water used for washing and contains activity concentrations usually encountered in NHBRAs; hence it is disposed of as inactive water. The liquid waste generated during the decommissioning of chemical plants consists of decants from sludge tanks, wash water and water used for decontamination of equipment. The wastes are segregated into different streams, depending on their acidity/alkalinity and radioactivity content. All the effluents are treated to scavenge the radionuclides and other pollutants. The treated effluents are discharged to the water body after ensuring compliance with the stipulated limits.

Gaseous wastes

There are no gaseous releases during decommissioning of mining and mineral separation plants. The gaseous releases encountered during the decommissioning of chemical plants are insignificant.

7.2. Environmental impact

7.2.1. Mining and mineral separation

The radiation fields, airborne activity concentrations, groundwater and soil are regularly monitored within the environment surrounding the mineral separation and chemical processing plants. The mined areas that have been refilled with mineral free sand exhibit external radiation fields in the range of 0.3–0.5 μGy/h, an order of magnitude lower than the respective original levels. The emanation of thoron from monazite mineral is only about 0.1% and the operations do not give rise to enhanced levels of thoron or thoron daughters in the vicinity of the MSPs. Environmental air monitoring shows that the long lived alpha activity and thoron daughter concentrations in air near the MSPs are within the range of natural variations observed at the HBRAs. The mining and mineral separation activities result in a net reduction of the notional individual exposures by factors ranging from 2 to 5 [6, 23].

7.2.2. Chemical processing of monazite (RE extraction)

The radiation exposures in locations adjacent to the waste disposal area are comparable to the natural background radiation exposures. The levels of radionuclides in the air contribute only about 5% of the dose limits for members of the public, as prescribed by competent authority [15, 25].

Monitoring wells are provided around the RCC trenches and thorium silos to monitor the groundwater for any seepage of radioactivity. The results obtained for the last decade on the samples collected and analyzed routinely did not reveal any enhancement in activity over the period, indicating the integrity of the trenches and thorium silos.

Extensive studies were carried out in the Periyar River in the south of India, which is the recipient of treated effluent discharges from the monazite plant along with a host of other industries situated in the area [27, 28]. The activity in the water and sediment showed a reduction by a factor of 3–4 compared with values observed prior to 1980, due to better effluent management at the monazite processing plant. The annual per capita radiation dose received by a member of the public resulting from the liquid effluent discharge via the water–fish–human route is estimated to be less than 10 μSv.

8. CONCLUSIONS

The mining of beach sands, mineral separation and chemical processing of monazite for the recovery of REs involve occupational radiation hazards of varying magnitudes. The average per capita occupational exposures range from 1 to 9 mSv per year. Internal exposure contributes to nearly half of the exposure, which is unique to this industry. Mechanization of the operations, process modifications, administrative controls and constant surveillance have over the years helped to reduce the exposures and to maintain them at levels as low as reasonably achievable (ALARA). Production of REs from monazite involves occupational exposure, typically 0.64 ± 0.19 man mSv per tonne of RE concentrate. RE extraction from sources other than monazite, especially bastnaesite, involve radiological safety problems of much lower magnitude.

Wastes from the mining and processing of radioactive ores are potential sources of radiological impact, both for those working in the industry and for members of the public who may be exposed if wastes are dispersed in the environment. These wastes are characterized by large volumes and low activity concentrations of materials containing radionuclides with very long half-lives. Engineering and administrative controls ensure that exposures of the public resulting from the releases from mining, mineral separation and monazite processing are insignificant. However, there is also a need to consider other exposures, for example those due to human intrusion into the waste at some future time. Mining and mineral processing tailings will continue to present a potential hazard to human health even after closure, and therefore additional measures may be needed to provide for the protection of future generations.

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DEPORTMENT OF NORM IN THE PROCESSING OF A PHOSPHATE ORE CONTAINING RARE EARTHS

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Abstract

The Nolans Bore deposit, located in central Northern Territory, Australia, contains naturally occurring radioactivity. The deportment of NORM radionuclides in any chemical treatment process is determined by the minerals hosting uranium and thorium and by the processing conditions. The Nolans Bore ore contains apatite, which usually hosts most of the uranium decay chain activity, and 'monazite type' family minerals, which usually host most of the thorium decay chain activity. The management of ^{238}U and ^{232}Th decay chain radioactivity is required in the processing of phosphate ores that contain NORM, for the recovery of rare earths and phosphate. From a regulatory perspective, management is required to protect the workforce and the public by minimizing their exposure to radioactivity and to protect the environment by appropriate management of processing wastes. Several processing options to separate phosphate and rare earth elements were assessed in preliminary studies and the distribution of the uranium and thorium and other radionuclides were tracked. Some separation of uranium and thorium from the valuable components was achieved.

1. INTRODUCTION

Rare earths (REs) are often found in association with phosphate rocks. The concentration of the rare earths in these deposits tends to be low, and therefore their recovery has been reported as a by-product of wet phosphoric acid production or as a by-product of fertilizer production via the nitrophosphoric acid route. There is considerable literature available on the presence of radioactivity in phosphate ores [1, 2] and the association of NORM radioactivity with rare earths [3–5]. In particular, uranium is often associated with apatite deposits, with the uranium content typically ranging from 5 to 300 ppm U. In the past, uranium has been recovered as a by-product of wet phosphoric acid production, using solvent extraction technology. Under some circumstances, the radioactivity concentration in process wastes has been a major determinant of the viability of a project.

The Nolans Bore deposit, located in the Northern Territory in Australia, contains considerably higher concentrations of rare earths when compared to most phosphate rock deposits. However, the radioactivity content of the ore, including uranium, is also relatively high. The nature of the mineralogy requires that a process be developed specifically tailored to take into account the ore mineralogy. The objective of the current study was to examine the distribution of various radionuclides at an early stage of process development, in order to ensure appropriate management of the contained radioactivity in accordance with best practice.

2. RADIOACTIVITY IN THE ORE

The Nolans Bore ore contains 250 to 500 ppm U and 5000 to 9000 ppm Th, depending on the location of the ore in the deposit. These concentrations correspond to 3.1–6.2 Bq/g ^{238}U and 20.4–36.7 Bq/g ^{232}Th, respectively. These concentrations of radioactivity in the ore have required that a radiation management plan is in place during exploratory drilling, and will require that any proposed mine, plant and waste disposal facilities have a radiation management plan in place before commencement. The ore is classified radioactive for transport purposes.

The major potential pathways to radiation exposure include external gamma rays and dust inhalation. As is frequently observed with NORM, the NORM host minerals report preferentially to the finest particle size fractions when milled. This has particular implications with regard to exposure from dust inhalation and the need for dust suppression during drilling, ore handling and comminution. For one Nolans Bore ore sample containing on average 4.2 Bq/g U and 21.6 Bq/g Th, the finest, <45 μm fraction from milling contained 5.1 and 24 Bq/g of the two radionuclides, respectively. Finer, respirable particle sizes may contain still more enhanced concentrations of radioactivity and, as a proactive measure, exploration personnel are currently monitored for exposure to dust.

The U and Th are, to a large extent, hosted by different minerals. The two main economic minerals in the Nolans bore ore are:

— Fluorapatite	$Ca_5(PO_4)_3(F,OH)$
— Cheralite	$(LREE,Ca,Th)PO_4{\cdot}H_2O$.

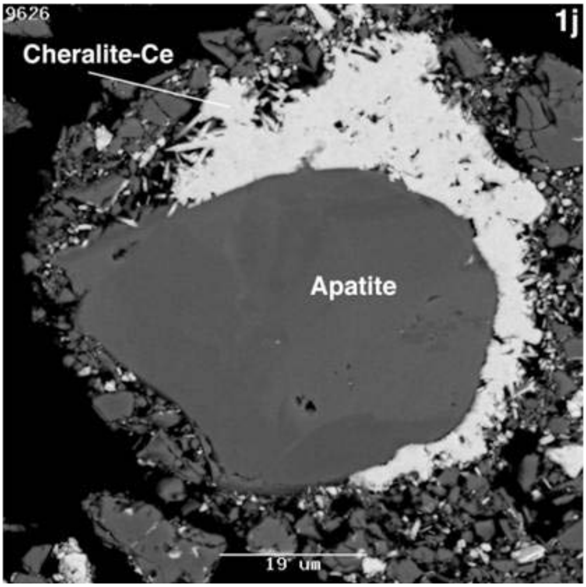

FIG. 1. Rare earth host mineral association.

Because of the complex mineralogy and fine mineral grain size, as shown in Fig. 1, the potential for mineral processing to a concentrate before chemical processing was considered unlikely to be successful, but examination of mineral processing options is the subject of a current study.

Apatite is more readily dissolved in acid than the more refractory cheralite. Most apatite ores are low in Th (5–40 ppm). The uranium content of Nolans Bore ore is high in comparison with other ‘apatite’ ores. The majority of the Th is present in the chemically more refractory phosphate ‘monazite type’ minerals, together with the major fraction of the rare earths. This is an important issue for the separation of a higher grade RE intermediate and the production of phosphate and REs containing low concentrations of radioactive impurities. The Th/RE ratio in Nolans Bore ore is high and the thorium concentrations are comparable to those in other monazites [6].

3. THE DEPORTMENT OF RADIOACTIVITY DURING PROCESSING

Process development was primarily driven by the need to achieve effective separation of phosphate and rare earths. Because of the high concentrations of radioactivity and their occupational health and product quality

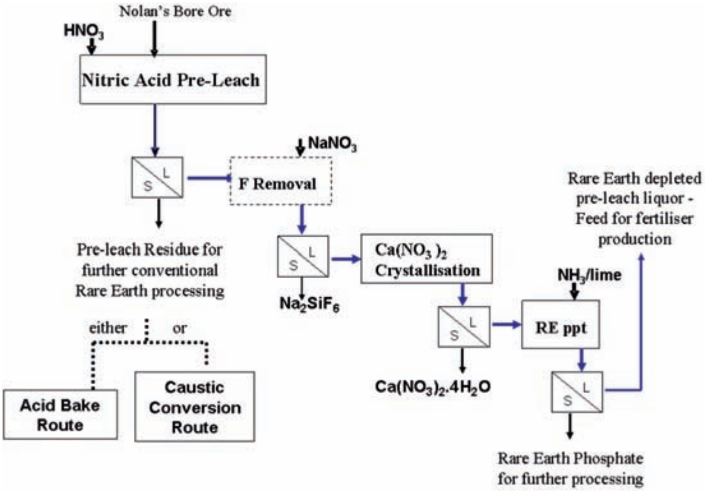

FIG. 2. Conceptual treatment of Nolans Bore ore using nitric acid.

implications, the behaviour of radioactivity was monitored during the early stages of a process options study. The analysis of solids was carried out using neutron activation analysis (NAA) for thorium, gamma spectrometry for ^{232}Th and ^{238}U decay chain progeny and XRF for uranium. Solutions were analysed using gamma spectrometry and ICP MS.

In the early stages of development, a broad framework for processing Nolans Bore ore was defined. This was based on an acid pre-leach process to remove the apatite, followed by conventional rare earth processing to recover the rare earth values from the pre-leach residue. Conventional rare earth technology considered included a sulphuric acid roast followed by water leaching or caustic conversion followed by acid leaching.

Both nitric acid and hydrochloric acid were considered for the pre-leach. Sulphuric acid leaching is inappropriate in this case, due to gypsum formation, resulting from the presence of high concentrations of calcium. It has been reported that, under the more aggressive sulphuric acid digestion conditions typical of wet phosphoric acid processing, the rare earths report with the solid gypsum.

The conceptual process flowsheets considered in this study are shown in Figs 2 and 3. Process conditions in the nitric acid pre-leach were optimized to

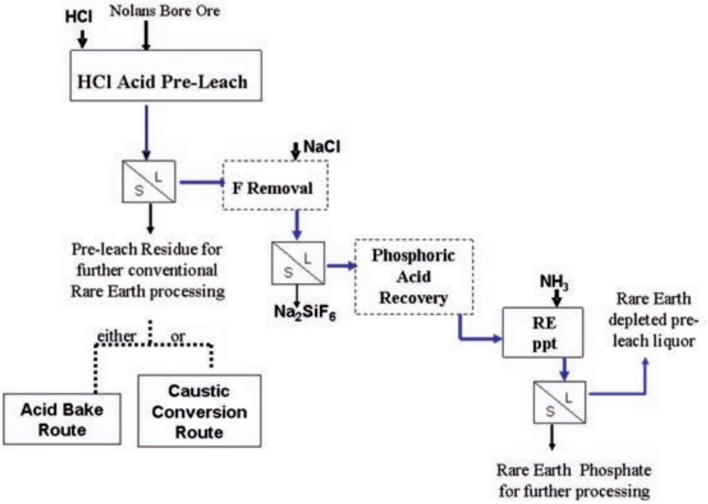

FIG. 3. Conceptual treatment of Nolans Bore ore using hydrochloric acid.

maximize calcium and phosphate dissolution and minimize rare earth dissolution. Treatment of the pre-leach liquor follows the conventional nitrophosphate route for NPK fertilizer production, incorporating a rare earth recovery step. The second option involves a hydrochloric acid pre-leach step, followed by phosphoric acid recovery by solvent extraction [7].

The concentrations of radionuclides in these processes are given in Tables 1 and 2. The concentration of radioactivity in process solid phases increased through the process flowsheet, as the relative mass of solids flow in the process stream decreased. Preliminary results, not reported here, indicated that, with further processing to recover the rare earths, the total radioactivity concentrations in downstream process solids will be still higher. Based on the relative mass flows, the distribution of long lived radionuclides was determined and is also presented in Tables 1 and 2.

For convenience, the indicated total activity concentrations were estimated based on the assumption that shorter half-life radionuclides will grow back into equilibrium with their longer half-life parents (U, Th, Ra and Pb radionuclides) within a few weeks. This assumption is valid for radioactivity in waste and product streams, but not when considering occupational health and safety (OHS) effects from dynamic processes in an operating plant.

The results indicate that a nitric acid pre-leach extracted approximately 50% of the radionuclides from both the ^{238}U and ^{232}Th decay chains. A hydrochloric acid pre-leach extracted a significantly lower portion of the activity, approximately 30%, contained in the ore. With HCl there was a greater variability in the extraction of various radionuclides. The 30% extraction corresponds approximately to the indicated weight per cent of apatite in the ore. The more aggressive nitric acid leach appears to attack some of the more refractory minerals (including some RE minerals) to a greater extent. It is likely that a radium separation process will be required for the treatment of recycled pre-leach process solutions.

For both process options, a fraction of the rare earths in the ore was leached during the pre-leaching step, but can be recovered from the pre-leach solution by precipitation. These rare earth precipitates contained significant radioactivity concentrations, 1000–1500 Bq/g total activity, as shown in Tables 1 and 2. Varying fractions of the decay chain radionuclides co-precipitate with the RE from the pre-leach solutions.

The separation of voluminous crystalline calcium nitrate from the nitric acid pre-leach solution did not result in significant radioactivity separation (<2% of the activity in the ore), and the nitrate product would not be considered to be radioactive from a regulatory perspective. Remaining traces of contained radioactivity are likely to be further removed by improved product washing or liquor separation conditions.

The rare earths present in the cheralite need to be converted to a soluble form for subsequent rare earth extraction. The preleached solids can be treated using various processes, such as caustic conversion or sulphation roasting, before the treated solids are leached to extract the rare earths. These processes for treating the pre-leach residue must enhance rare earth extraction, and at the same time enable some separation of impurities, including radionuclides. This is the subject of current studies.

Uranium extraction during pre-leach was higher using nitric acid (51%) compared with hydrochloric acid (39%). There is some experience [1, 2, 8] with the recovery of uranium from these types of acidic phosphate solutions and this is a subject of the current study. Very little uranium is separated during rare earth precipitation from the pre-leach solutions (approximately 2% of the uranium in the ore).

Although the present work gives a picture of the deportment/distribution of radioactivity for various process options, relatively small quantities of radionuclides can also accumulate in small masses of process streams in the form of scales and/or dusts, which can become significant OHS and waste disposal issues. Similarly, small quantities of radionuclides can contaminate process

TABLE 1. RADIOACTIVITY CONCENTRATIONS AND DISTRIBUTIONS IN NITRIC ACID PRE-LEACH PROCESS STREAMS

	Chemical assays (ppm)		Radionuclide assays (Bq/g)								Total estimated activity (Bq/g)
			^{232}Th decay chain			^{238}U decay chain				^{235}U	
	Th	U	^{232}Th	^{228}Ra	^{224}Ra	^{238}U	^{234}Th	^{226}Ra	^{210}Pb		
Nitric acid pre-leach: ore	5 300	490	22	22	22	6.1	5.9	5.0	5.0	0.4	291
HNO_3 pre-leach residue	9 900	830	40	29	37	10	11	8.5	8.8	0.7	499
Calcium nitrate	250	20	1.0	0.3	0.3	0.25	0.07	0.03	0.2	DL	6
RE precipitate from HNO_3 pre-leach	38 000	200	155	64	140	2.5	DL	9.4	44	1.7	1491
			Relative percentage distributions of radionuclides (%)								
Estimated dissolution in pre-leach relative to the ore			46	62	50	51	49	51	49	52	51
Radioactivity in calcium nitrate solid relative to the ore			4.1	1.3	1.0			0.5	3.5		1.7
Radioactivity in rare earth precipitate relative to the ore			43	18	39	2.4		11	53		31

TABLE 2. RADIOACTIVITY CONCENTRATIONS AND DISTRIBUTIONS IN HYDROCHLORIC ACID PRE-LEACH PROCESS STREAMS

	Chemical assays (ppm or mg/L)		Radionuclide assays (Bq/g or Bq/L)								Total estimated activity (Bq/g or Bq/L)
			^{232}Th decay chain			^{238}U decay chain				^{235}U	
	Th	U	^{232}Th	^{228}Ra	^{224}Ra	^{238}U	^{234}Th	^{226}Ra	^{210}Pb		
Hydrochloric acid pre-leach: ore	5 300	490	22	22	22	6.1	5.9	5.0	5.0	0.4	291
HCl pre-leach residue	12 800	930	52	39	46	12	13	9	10	0.4	605
HCl pre-leach liquor	400	80	1628	838	2096	988	838	170	1035	67	26 860
RE precipitate from HCl pre-leach liquor	26 500	200	108	38	114	2.5	8.4	7.4	DL	1.8	1 046
			Relative percentage distributions of radionuclides (%)								
Estimated dissolution in pre-leach relative to the ore			22	42	32	39	31	42	38	66	33
Radioactivity in rare earth precipitate relative to the ore			19	7	20	2	5	6		16	14

equipment, which then requires particular measures to be taken in regard to plant maintenance and the final disposal of equipment.

The leach residues from downstream rare earth processing (sulphation roasting and leach or caustic conversion and leach) are the main process wastes and may be combined with process solution purification and waste water treatment residues for waste management. Careful attention to the analysis of these residues will reveal whether or not all the radionuclides have been accounted for in the overall process.

With regard to waste management and product quality, the deportment of radioactivity is determined primarily by the behaviour of the parent radionuclides and the decay chain progeny, which have comparatively long half-lives.

4. SUMMARY

The use of a new approach/process has required the monitoring of radionuclides to ensure that OHS issues can be appropriately managed and that product quality specifications are met. Pre-leaching the Nolans Bore ore has achieved an effective separation of phosphorous from the ore, and upgraded the rare earth content of leached ore solids. Significant radioactivity (30–50%) also leaches during this process; however, processes are available to separate impurity radionuclides and to recover uranium. The distribution of radioactivity in various process options for further rare processing, such as acid roasting and caustic conversion, is currently being investigated.

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LUNG TYPES OF THORON DAUGHTERS IN A MONAZITE STORAGE FACILITY

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Abstract

The dissolution of thoron daughters, sampled in the workplace of a monazite storage facility, in simulated body fluid is studied. The dissolution of real ^{212}Pb aerosols can be described by the superposition of two exponential dependencies, with the rate of fast dissolution: $\lambda_f = 145$ d^{-1}, rate of slow dissolution: $\lambda_s = 2$ d^{-1} and the part of the activity with a fast rate of dissolution: k = 0.3. The estimated values of dose conversion factor from thoron daughter exposure to effective dose — 80–150 nSv per Bq·h·m^{-3} considerably (at least 3–5 times) exceeds the DCF values recommended by UNSCEAR. It is shown that the most appropriate monitoring method for inhalation intake of ^{212}Pb aerosols is the direct measurement of whole body nuclide activity.

1. INTRODUCTION

Traditionally in radon exposure investigations, attention is generally paid to exposure to ^{222}Rn and its daughters. Considerably less attention is paid to the other radon isotope ^{220}Rn, and usually it is presumed that the thoron daughter contribution to public and worker exposures is practically negligible. Nevertheless, in some specific situations the inhalation of thoron daughters (especially the most long lived nuclide ^{212}Pb) can be the dominant source of internal exposure in workplaces.

An example of such a workplace is the monazite storage facility situated in the south-east part of the Sverdlovsk region of Russia. Monazite contains 5–10% ThO_2 (sometimes up to 30%) and 0.2% U_3O_8. Since 1960, more than 82 000 t of monazite concentrate have been stored at this facility in 19 wooden warehouses (former granaries) and 4 hangars [1]. The warehouses were built in

1940 and most of them are in need of significant repair now. The very high values of thoron volume activity and thoron equivalent equilibrium concentration (EEC) do not permit the use of the standard techniques of radon and radon daughter measurement. Specially designed nuclear track detectors were used for monitoring of radon and thoron volume activity. The thoron EEC was measured by grab sampling of radioactive aerosols on filter. The monazite dust concentration in air also was measured by air sampling on the filter.

2. METHOD AND RESULTS

The main sources of radiation exposure of storage facility workers are external gamma radiation (~0.15 mSv/h inside the warehouse, 0.07 mSv/h on the outside wall and 0.012 mSv/h at a distance of 10 m from the warehouse), inhalation of radon and thoron daughters (EEC_{Rn} = 45–250 Bq/m^3; EEC_{Tn} = 60–700 Bq/m^3), direct inhalation of thoron gas (thoron activity concentration 1600–14 000 Bq/m^3) and inhalation of monazite dust.

TLD and electronic direct reading alarm detectors are used for the monitoring of external exposure. At the same time, monitoring for internal exposure is considerably more complicated. The problem of internal exposure monitoring is especially important considering the perspectives of reconstruction of the storage facility and the processing of the monazite concentrate for thorium and rare earth extraction.

At present, the values of dose conversion factor (DCF) from thoron EEC exposure to effective dose, as recommended by UNSCEAR, are in the range of 32–40 nSv per Bq·h·m^{-3} [2, 3]. In general, such a DCF value corresponds to Type F materials according to their rates of absorption from the respiratory tract to body fluids [1]. It was shown that DCF value is considerably dependent on absorption rate (type F or type M) of thoron daughters [1]. Also, it was stressed that experimental data on the actual lung type of thoron daughters (especially ^{212}Pb) in workplaces are needed.

In the assessment of dissolution rate of radioactive aerosols it is very important to provide a correspondence between the chemical properties of the aerosol in the experiment to the properties of the aerosol in real workplaces. Aerosol sampling in closed laboratory boxes is not suitable for practical assessment of aerosol types. On the other hand, thoron daughter concentrations in ordinary workplaces or dwellings are too small for experimental purposes.

The presence of the unique monazite storage facility allows estimation of the aerosol type of ^{212}Pb for real aerosols sampled in a workplace. The aerosol sampling was conducted for 3 h in the monazite warehouse. Due to the need for sample transportation, the time interval between the finishing of the sampling and the beginning of measurement was approximately 3 h. To estimate the type of ^{212}Pb aerosols, their dissolution from the aerosol filter in simulated body fluid was studied. The filter was placed in Ringer solution at 37°C for some time. Then the filter was rinsed with clean Ringer solution at the same temperature and its activity was determined by gamma spectrometer. After the activity measurements the filter again was placed in solution and the cycles of dissolution and activity measurements were continued. It was found that the decrease of ^{212}Pb activity on the filter can be described by superposition of two exponential dependencies:

$$\frac{A(t)}{A_0} = k \cdot \exp[-(\lambda_0 + \lambda_f)] + (1-k) \cdot \exp[-(\lambda_0 + \lambda_s)] \tag{1}$$

where

A_0	is the initial filter activity,
A(t)	is the filter activity after dissolution during time t,
λ_0	is the ^{212}Pb decay constant,
λ_f	is the rate of fast dissolution,
λ_s	is the rate of slow dissolution,
k	is the part of the activity with a fast rate of dissolution.

The parameters of the dissolution kinetics are shown in Table 1. The ICRP model of nuclide transfer from the respiratory tract to body fluids is shown in Fig. 1 [4]. It was presumed that the kinetics of ^{212}Pb absorption from the respiratory tract to body fluids can be described by the same mechanism as ^{212}Pb dissolution from the aerosol filter to the Ringer solution. So for the calculations of the ^{212}Pb dynamics in the respiratory tract, the values $f_r = k = 0.3$; $s_r = \lambda_f = 145\ d^{-1}$; $s_s = \lambda_s = 2\ d^{-1}$ were assumed. The dependence of the aerosol deposition in the respiratory tract on the AMAD, the type of breathing (nose or mouth breather) and the intensity of work was taken from ICRP tables [4]. The nuclide dynamics and the absorbed and equivalent doses in organs and tissues were calculated using standard WinAct and DCAL 8.4 software. The estimated values of dose coefficients (Sv/Bq) for inhalation intake of ^{212}Pb aerosols are given in Tables 2–4. The estimated values of dose coefficients for real ^{212}Pb aerosols are between the reference values for Type F and Type M materials [5].

TABLE 1. PARAMETERS OF ^{212}PB AEROSOL DISSOLUTION FROM FILTER IN RINGER SOLUTION AT 37°C (8 SAMPLES)

Parameter	Average	Minimum	Maximum	Standard deviation
λ_f, (d^{-1})	145	79	278	60
λ_s, (d^{-1})	2.0	1.1	3.9	1.0
k	0.30	0.21	0.45	0.08

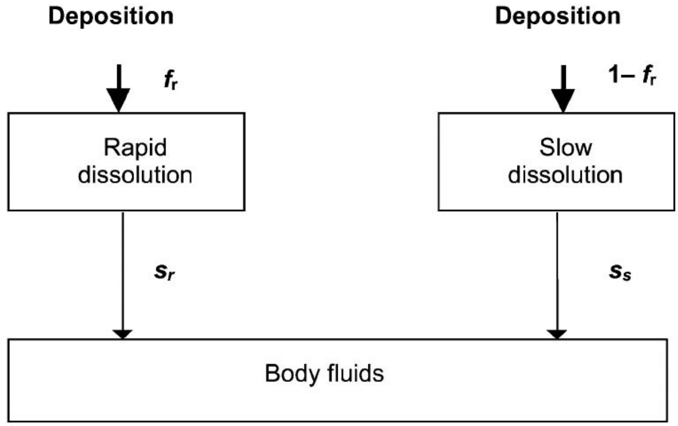

FIG. 1. ICRP model of nuclide transfer from the respiratory tract to body fluids [4].

TABLE 2. DOSE COEFFICIENTS FOR INHALATION INTAKE OF REAL ^{212}Pb AEROSOLS, AMAD = 0.3 μm (Sv/Bq)

Organs and tissues	Heavy work		Light work	
	Mouth breathing	Nose breathing	Mouth breathing	Nose breathing
Stomach wall	1.87E-09	1.91E-09	1.90E-09	2.04E-09
Small intestine wall	1.94E-09	2.06E-09	1.97E-09	2.19E-09
Upper large intestine	2.32E-09	2.78E-09	2.35E-09	2.93E-09
Lower large intestine	2.38E-09	2.92E-09	2.41E-09	3.07E-09
Kidneys	4.29E-08	4.25E-08	4.35E-08	4.55E-08
Liver	1.19E-08	1.19E-08	1.20E-08	1.27E-08
Extra thoracic region ET1	4.07E-05	1.51E-04	4.36E-05	1.60E-04
Extra thoracic region ET2	1.24E-08	1.89E-08	1.28E-08	1.96E-08

TABLE 2. DOSE COEFFICIENTS FOR INHALATION INTAKE OF REAL ^{212}Pb AEROSOLS, AMAD = 0.3 μm (Sv/Bq) (cont.)

Organs and tissues	Heavy work		Light work	
	Mouth breathing	Nose breathing	Mouth breathing	Nose breathing
Lymph nodes extra thoracic	1.99E-09	2.44E-09	2.03E-09	2.60E-09
Bronchial region (basal)	5.16E-07	4.43E-07	4.85E-07	4.21E-07
Bronchial region (secretory)	9.49E-07	8.15E-07	8.95E-07	7.77E-07
Bronchiolar region	7.42E-07	6.89E-07	8.45E-07	7.93E-07
Alveolar region	5.47E-08	5.12E-08	5.47E-08	5.48E-08
Lymph nodes thoracic	1.88E-09	1.88E-09	1.91E-09	2.01E-09
Lungs at whole	5.09E-07	4.56E-07	5.29E-07	4.82E-07
Bone Surfaces	4.47E-08	4.47E-08	4.54E-08	4.78E-08
Red Marrow	5.68E-09	5.68E-09	5.76E-09	6.08E-09
Effective dose	6.42E-08	5.90E-08	6.66E-08	6.24E-08

TABLE 3. DOSE COEFFICIENTS FOR INHALATION INTAKE OF REAL ^{212}Pb AEROSOLS, AMAD = 1 μm (Sv/Bq)

Organs and tissues	Heavy work		Light work	
	Mouth breathing	Nose breathing	Mouth breathing	Nose breathing
Stomach wall	2.38E-09	2.26E-09	2.38E-09	2.30E-09
Small intestine wall	2.61E-09	2.76E-09	2.60E-09	2.79E-09
Upper large intestine	3.74E-09	5.02E-09	3.65E-09	5.03E-09
Lower large intestine	3.96E-09	5.50E-09	3.86E-09	5.51E-09
Kidneys	5.18E-08	4.47E-08	5.22E-08	4.57E-08
Liver	2.95E-08	1.29E-08	1.47E-08	1.32E-08
Extra thoracic region ET1	1.28E-04	4.65E-04	1.37E-04	4.94E-04
Extra thoracic region ET2	3.32E-08	4.59E-08	3.00E-08	4.93E-08
Lymph nodes extra thoracic	2.76E-09	3.88E-09	2.81E-09	4.04E-09
Bronchial region (basal)	1.74E-06	9.86E-07	1.28E-06	6.14E-07
Bronchial region (secretory)	3.19E-06	1.80E-06	2.34E-06	1.12E-06
Bronchiolar region	6.25E-07	4.15E-07	6.78E-07	4.39E-07
Alveolar region	5.51E-08	3.72E-08	5.87E-08	4.08E-08
Lymph nodes thoracic	2.31E-09	2.03E-09	2.32E-09	2.07E-09

TABLE 3. DOSE COEFFICIENTS FOR INHALATION INTAKE OF REAL ^{212}Pb AEROSOLS, AMAD = 1 µm (Sv/Bq) (cont.)

Organs and tissues	Heavy work		Light work	
	Mouth breathing	Nose breathing	Mouth breathing	Nose breathing
Lungs at whole	1.05E-06	6.15E-07	8.49E-07	4.49E-07
Bone surfaces	5.49E-08	4.89E-08	5.52E-08	4.99E-08
Red marrow	6.97E-09	6.21E-09	7.01E-09	6.32E-09
Effective dose	1.31E-07	8.12E-08	1.07E-07	6.15E-08

TABLE 4. DOSE COEFFICIENTS FOR INHALATION INTAKE OF REAL ^{212}Pb AEROSOLS, AMAD = 5 µm (Sv/Bq)

Organs and tissues	Heavy work		Light work	
	Mouth breathing	Nose breathing	Mouth breathing	Nose breathing
Stomach wall	3.91E-09	2.78E-09	3.77E-09	2.63E-09
Small intestine wall	4.81E-09	3.74E-09	4.61E-09	3.57E-09
Upper large intestine	8.89E-09	7.99E-09	8.41E-09	7.73E-09
Lower large intestine	9.75E-09	8.91E-09	9.21E-09	8.63E-09
Kidneys	7.58E-08	4.92E-08	7.37E-08	4.62E-08
Liver	2.21E-08	1.48E-08	2.14E-08	1.39E-08
Extra thoracic region ET1	3.20E-04	9.88E-04	3.49E-04	9.88E-04
Extra thoracic region ET2	1.12E-07	9.60E-08	1.03E-07	8.93E-08
Lymph nodes extra thoracic	4.71E-09	6.29E-09	4.73E-09	6.15E-09
Bronchial region (basal)	3.46E-06	1.35E-06	2.75E-06	6.76E-07
Bronchial region (secretory)	6.34E-06	2.46E-06	5.05E-06	1.24E-06
Bronchiolar region	8.63E-07	3.08E-07	9.01E-07	2.77E-07
Alveolar region	4.57E-08	2.03E-08	4.91E-08	2.08E-08
Lymph nodes thoracic	3.52E-09	2.32E-09	3.40E-09	2.17E-09
Lungs at whole	1.93E-06	7.44E-07	1.62E-06	4.18E-07
Bone surfaces	8.37E-08	5.61E-08	8.11E-08	5.28E-08
Red marrow	1.06E-08	7.12E-09	1.03E-08	6.70E-09
Effective dose	2.41E-07	1.01E-07	2.03E-07	8.13E-08

The possible distributions of dose coefficient values for the respiratory tract due to uncertainties in the dissolution parameters were calculated by the Monte Carlo method using specially developed software. Two kinds of parameter distribution were considered, uniform distribution and normal distribution. For parameter λ_s the bounded normal distribution was used, so only positive values of the parameter were considered. The results are shown in Fig. 2.

The dependences of the DCF values (converting thoron daughter exposure to effective dose) on the air exchange rate λ_υ and attachment rate of free atoms to aerosols λ_χ were calculated by the method described in Ref. [1]. The dependences of DCF for adult workers as a function of air exchange rate λ_υ attachment rate of free atoms to aerosols λ_χ and lung type ^{212}Bi aerosols are shown in Fig. 3. It should be noted that the DCF values, based on the experimental assessment of ^{212}Pb absorption from the respiratory tract to body fluids, considerably exceed the range of 32–40 nSv per Bq·h·m^{-3} recommended by UNSCEAR [2, 3]. Taking into account the re-evaluated DCF values, the internal exposure due to inhalation of thoron daughters in the monazite storage facility is comparable with external exposure. In this case, a very important problem of radiological protection of workers is the individual monitoring of internal exposure due to the inhalation intake of thoron daughters (especially ^{212}Pb). The typical techniques of individual monitoring of internal exposure are the estimation of nuclide inhalation intake by its retention (in lungs or whole body) or excretion (faecal or urine) [6].

The estimated value of ^{212}Pb inhalation intake during the working shift in the monazite storage facility is nearly 1000 Bq. The half-life of ^{212}Pb ($T_{1/2}$ = 10.6 h) is comparable with the working shift duration. So the traditional calculation of nuclide dynamics for a single intake is not suitable for internal monitoring programme purposes. All calculations of the nuclide dynamics for the estimated ^{212}Pb absorption rate from the respiratory tract to body fluids were performed for uniform inhalation intake during a 6 h working shift. During the calculations the following factors were considered:

- The aerosol dispersion: AMAD 0.3 (AMTD 0.19), 1 and 5 μm;
- The type of breathing: nose and mouth breather;
- The intensity of work: light exercise (breathing rate 1.2 m^3/h) and heavy exercise (breathing rate 1.7 m^3/h).

The system of differential equations describing the nuclide dynamics in the respiratory and gastro-intestinal tracts, organs and tissues of the body [4, 7, 8] was solved. The samples of nuclide retention as well as faecal and urine

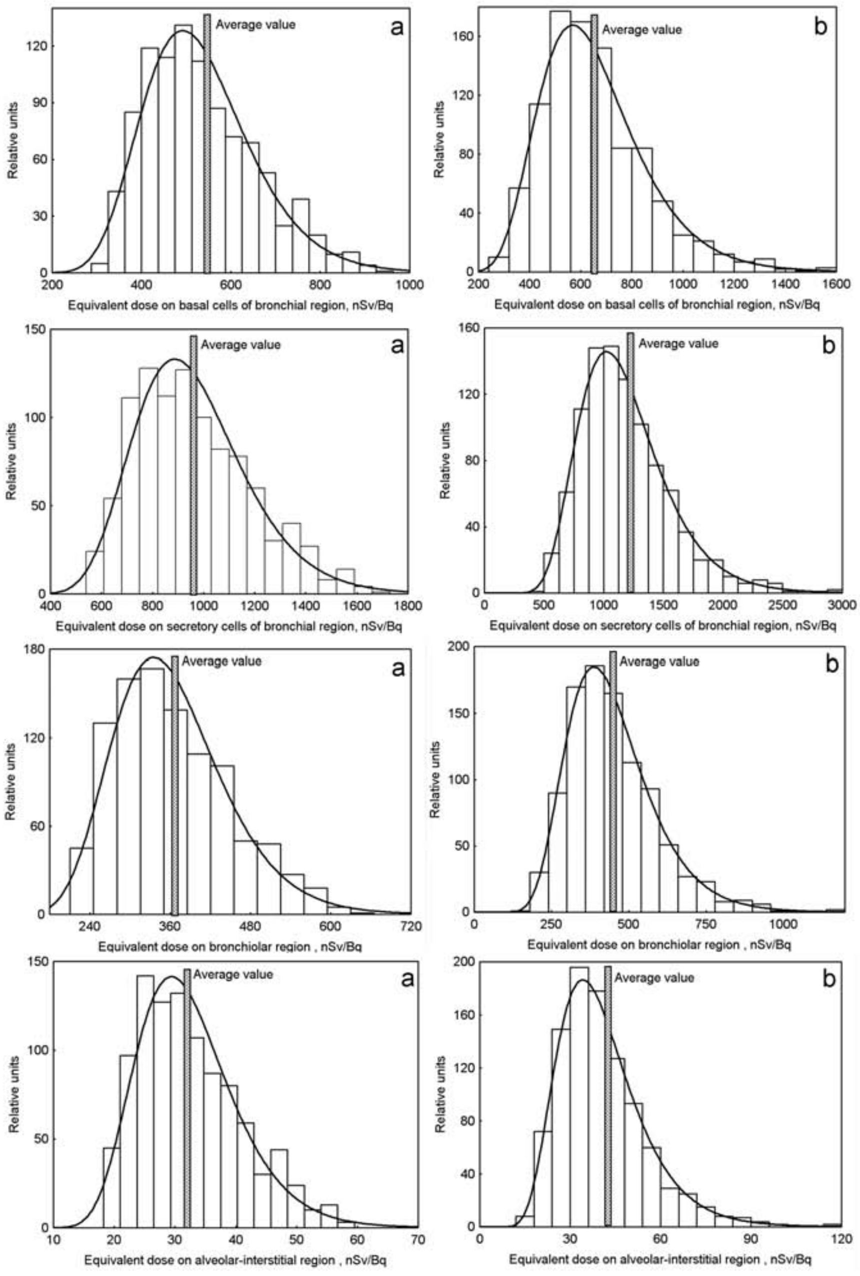

FIG. 2. Distributions of dose coefficients for respiratory tract due to uncertainties of ^{212}*Pb dissolution parameters (AMAD = 1 μm, nose breather, light work); a — uniform distribution of parameters, b — normal distribution of parameters.*

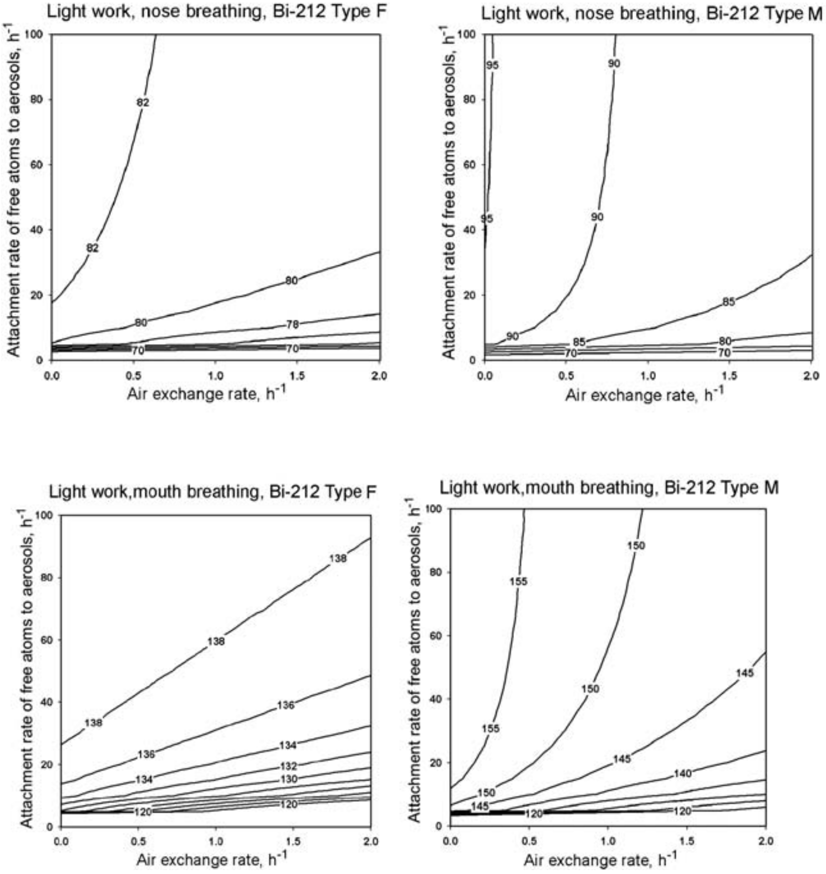

FIG. 3. The dependences of DCF (thoron daughter exposure to effective dose) for adult workers as a function of air exchange rate λ_υ and attachment rate of free atoms to aerosols λ_χ, nSv per Bq·h·m^{-3} (AMAD = 1 μm)

excretion dynamics are shown in Fig. 4 and Table 5. The calculation results are presented as a part of the total uniform intake during a 6 h working shift. The beginning of the time period corresponds to the beginning of a working shift.

3. CONCLUSIONS

(a) The dissolution of real ^{212}Pb aerosols in simulated body fluid can be described by superposition of two exponential dependencies with a rate of fast dissolution of $\lambda_f = 145$ d^{-1}, a rate of slow dissolution of $\lambda_s = 2$ d^{-1} and the part of the activity with a fast rate of dissolution k = 0.3.

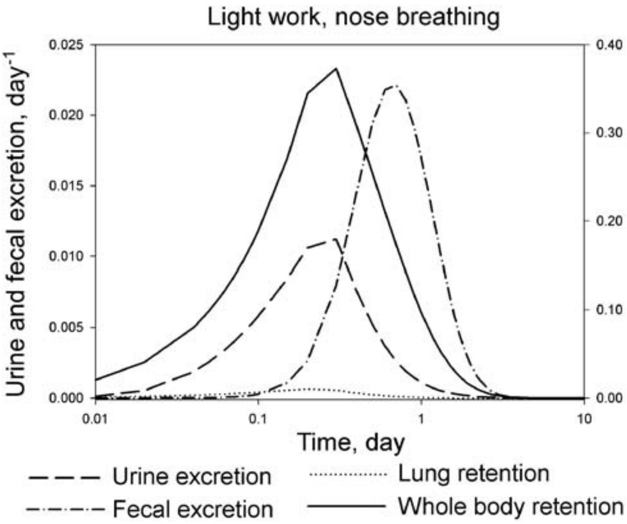

FIG. 4. Dynamics of ^{212}Pb whole body and lung retention and faecal and urine excretion for estimated nuclide absorption rate from the respiratory tract to body fluids (AMAD = 1 μm)

TABLE 5. FRACTION OF ^{212}Pb INTAKE (TAKING RADIOACTIVE DECAY INTO ACCOUNT) RETAINED IN THE BODY AND TRANSFERRED TO URINE AND FAECES DURING THE SAMPLING PERIOD τ

AMAD (μm)	Exercise	Breathing type	Whole body retention		Urinary excretion			Faecal excretion
			$\tau = 12$ h	$\tau = 24$ h	$\tau = 8$ h	$\tau = 12$ h	$\tau = 24$ h	$\tau = 24$ h
0.3	Heavy	Mouth	0.121	0.052	0.0017	0.0022	0.0017	0.0014
		Nose	0.147	0.060	0.0017	0.0022	0.0017	0.0028
	Light	Mouth	0.123	0.053	0.0017	0.0022	0.0017	0.0014
		Nose	0.156	0.064	0.0018	0.0024	0.0018	0.0029
1.0	Heavy	Mouth	0.164	0.069	0.0021	0.0027	0.0021	0.0030
		Nose	0.249	0.095	0.0021	0.0027	0.0019	0.0093
	Light	Mouth	0.180	0.075	0.0021	0.0028	0.0021	0.0042
		Nose	0.255	0.097	0.0021	0.0027	0.0020	0.0092
5.0	Heavy	Mouth	0.404	0.162	0.0048	0.0058	0.0040	0.0168
		Nose	0.401	0.145	0.0027	0.0033	0.0023	0.0176
	Light	Mouth	0.358	0.142	0.0035	0.0045	0.0032	0.0156
		Nose	0.391	0.141	0.0025	0.0032	0.0022	0.0172

(b) The estimated values of DCF (thoron daughter exposure to effective dose) are in the range of 80–150 nSv per Bq/h·m^{-3}, at least 3–5 times greater than the DCF values recommended by UNSCEAR.

(c) The most appropriate monitoring method for inhalation intake of ^{212}Pb aerosols is the direct measurement of whole body activity. The assessment of ^{212}Pb inhalation intake by urinary excretion is possible for a sample collection time of 8–12 h. Even in this case, the total activity of the sample will be in the range of 1.5–3 Bq for a total intake during the working shift of about 1000 Bq. The estimation of the inhalation intake of ^{212}Pb aerosols by measurement of faecal excretion can be efficient and non-dependent on the type of breathing and intensity of work only for coarse aerosols (AMAD ≈5 μm).

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EXTRACTION, PROCESSING AND USE OF PHOSPHATE MINERALS

(Topical Session 5)

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Invited Paper

INHALATION DOSES AND REGULATORY POLICY IN WET ACID PROCESSING OF SEDIMENTARY PHOSPHATE ROCK

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Abstract

The wet acid method of phosphoric acid and fertilizer production exposes workers to both mists and dusts containing NORM. The relative contributions of the uranium and thorium series and activity concentrations of their members depend primarily upon the source of the processed ore. The wet acid process is the prevalent method used by the industry and varies little worldwide. Consequently, similar facilities can and perhaps should compare monitoring results by scaling to the activity concentrations of the processed ores. A global effort to characterize and benchmark activity concentrations in ores, products and by-products would be extremely advantageous in fostering good management practices for the phosphate industry. Early studies focused on external doses to workers involved in phosphoric acid filtration and maintenance of the filtration assemblies. As more comprehensive dose assessments emerged, the inhalation component was examined using high volume samplers, gross activity counting methods and a simple model of the respiratory tract for dose conversion. Inhalation doses came under more scrutiny with the advent of the revised human respiratory tract and model computer programs for its implementation (LUDEP and IMBA), improved air sampling techniques and an emphasis on scenario based probabilistic dose assessments. Without adequate parameter data, probabilistic dose assessments can generate possible, although not probable, doses that approach or exceed some regulatory limits. These recent developments highlight the importance of determining the sensitivity of inhalation dose estimates to the model parameters, such as airborne particle size distributions and their solubilities in lung fluid. It is also important to carefully consider these data during ALARA review and when forming regulatory policies regarding the need for respiratory protection programmes and administrative or engineering controls, thus lowering the risk of over-regulation.

1. INTRODUCTION

Phosphate rock processing is a broad subject and a full discussion of the industry is beyond the scope of this paper. Thermal processing, processing of igneous rock, and the lesser applied technologies, such as digestion of rock with nitric acid, will not be discussed. Wet acid processing of sedimentary phosphate rock using the dihydrate method is the dominant production mode for phosphoric acid and its derivative fertilizers. Sulphuric acid is reacted with phosphate rock concentrate slurry to produce phosphoric acid and phosphogypsum according to the reaction:

$$Ca_3(PO_4)_2 + 3H_2SO_4 + 6H_2O \rightarrow 3CaSO_4{\cdot}2H_2O + H_3PO_4$$

Sedimentary phosphate rock contains radionuclides of the uranium, thorium and actinium series. The activity concentrations of the members of these series vary with the source of the ore. The rock itself also varies in mineral structure and constituents. There are, however, some identifiable trends in the distribution of radionuclides during processing.

1.1. Distribution of radionuclides

A proper inhalation dose assessment requires knowledge of the distribution of radionuclides through the process that converts phosphate rock to phosphoric acid and dry fertilizer products. If only gross activity measurements are taken, knowledge of the process radiochemistry reduces assumptions that must be employed, and thereby reduces conservatism in the final dose estimate. Some of the more important elements are discussed below.

(a) Uranium — It has been known for decades that most of the uranium goes with the phosphoric acid as soluble salts. Phosphoric acid is produced when concentrated phosphate rock slurry is mixed with sulphuric acid. The efficiency of the acid digestion depends on the rock surface area available for attack, the residence time in the attack tank, mixing and other factors. Consequently, a small amount of rock will pass through undigested along with the uranium it contains. This uranium goes into the phosphogypsum by-product. Many factors such as oxidizing conditions and overall P_2O_5 recovery are involved in uranium partitioning, so there is no definitive correlation between rock content and acid and phosphogypsum contents.

(b) Radium — Most of the radium goes with the phosphogypsum (primarily $CaSO_4$), since radium is a divalent cation like calcium. A small fraction of phosphogypsum and other impurities gets through the filtration process and into the phosphoric acid product. The acid is clarified in large settling tanks to remove much of these contaminants.

(c) Lead — There are contradictory statements in the published literature. Some report that all lead goes with the phosphogypsum, while one reports that most ^{210}Pb goes with the acid [1]. If the latter is correct, the activity concentration of ^{210}Pb in phosphogypsum is determined by ingrowth from ^{222}Rn. That is not likely. It would take considerable time (about 100 years) to establish a ^{226}Ra/^{210}Pb ratio of unity, which can be found in fresh gypsum [2]. Also, a TVA-TFI study [3] showed that most of the lead goes with the gypsum, probably as lead sulphate. $PbSO_4$ is quite insoluble.

(d) Polonium — One study indicated that over 99% of ^{210}Po goes with the phosphogypsum [4]. This is also supported by isotopic ratios in the phosphogypsum [2]. Mazzilli et al. [5] reported that 78% of the ^{210}Po goes to the phosphogypsum in Brazilian wet acid facilities.

(e) Thorium — Thorium forms sparingly soluble salts with hydroxides, fluoride, and phosphate. Sulphate compounds are relatively soluble. Complexes with phosphate, sulphate, and fluoride should dominate. Partitioning is variable as with uranium, but most of the thorium goes with the acid [2]. These authors were surprised to find that only 25% of the thorium reports to the gypsum. Other authors [5] reported higher than expected thorium fractionation to gypsum (80%) and attribute thorium distribution to variability in chemical processes.

1.2. Phosphoric acid and phosphogypsum by-product

Dissolved uranium is carried by the phosphoric acid as uranyl phosphate, sulphate and fluoride complexes. Uranium has tetravalent and hexavalent forms. The tetravalent form in the rock feed is oxidized to U^{6+} and the uranyl ions mainly complex with phosphates. Research funded by the Florida Institute of Phosphate Research has shown that solids suspended in collected samples and sediments produced during storage contained gypsum, the alkali fluosilicates Na_2SiF_6 and $NaKSiF_6$, chukhrovite ($Ca_4SO_4SiAlF_{13}\cdot nH_2O$) and the complex iron phosphate $Fe_3(NH_4,K,H)H_8(PO_4)_6\cdot 6H_2O$. Data evaluations suggested that the last of these compounds was mostly but not exclusively present in the ammonium form. There is a long list of other possible compounds [6]. All of these, especially gypsum, can be expected to have radionuclide substitutions. The primary ones to be expected are radium sulphate, lead sulphate, lead disulphate, polonium disulphate and thorium disulphate.

Also, chukhrovite is notorious for having a high radium content as radium substitutes for the four calcium ions.

The radionuclides known or suspected to go with the gypsum can form fluorides, oxides, hydrides and sulphides. Sulphides are not a problem when processing Florida rock because they are precipitated by arsenic. Rock from other sources, e.g. North Carolina, will give a sulphide smell. For examples of other compounds, consider polonium and radium. Since the reaction takes place in air, there will be some polonium dioxide. There may even be some fluorides of polonium (likely to be volatile and decompose rapidly). There can also be various less common combinations of ions. Since fluorine is present, there could be a small amount of radium fluoride. Some phosphate makes it through the digestion process, so there may also be $Ra_3(PO_4)_2$.

There was at least one attempt to separate radioactive materials from the phosphogypsum using a cyclone. A higher proportion of the radioactivity is found in the fine fraction. This makes sense because the radium and calcium do not actually co-crystallize due to differences in solubility of the sulphates (calcium sulphate is soluble and radium sulphate is highly insoluble), difference in ionic radii between Ca and Ra and differences in the crystalline structures of the sulphates [7]. That means that the radium in phosphogypsum should be in the form of small crystals of radium sulphate, not bound to other crystals. The coarse fraction is gypsum mixed with some undigested rock, also containing radioactivity including radium from the rock, but the overall mixture should have a lower activity concentration than the fine fraction. The main problem is that not enough radioactive material can be removed to make a meaningful difference.

Uranium is present in phosphate rock primarily as U^{4+} (40–91%, mean: 65%) presumed to be followed by U^{6+} as the remainder [8]. It is also assumed that U^{4+} substitutes for Ca^{2+} in the apatite structure because of their nearly identical ionic radii. However, there are very few U atoms available for substitution (1 U: >25 000 Ca) and there are other more plentiful substitute ions available, e.g. sodium and magnesium. During acidulation, ferrous iron readily reduces U^{6+} to U^{4+}. The reduction is also catalyzed by fluoride ion from the rock [4]. A small amount of U^{4+} reports to phosphogypsum for three major reasons: (a) phosphogypsum coats unreacted rock particles containing uranium, (b) due to some substitution of uranium in the crystal lattice of the phosphogypsum, and (c) acid losses containing uranium phosphate to the phosphogypsum. Small amounts of uranium may be present in phosphogypsum in the form of the uranyl ion (UO_2^{2+}) contained within the residual phosphoric acid which remains after filtration and transport to the stack. U^{4+} may adsorb on the surface of phosphogypsum as UO_2HPO_4, or UO_2^{2+} may substitute for two Ca^{2+} ions on the surface of the crystal lattice [9].

1.3. Reaction of phosphoric acid with ammonia

Diammonium phosphate (DAP) and monoammonium phosphate (MAP) are the major granulated products formed by the reaction of ammonium hydroxide with phosphoric acid. The chemical formula for DAP is $(NH_4)_2HPO_4$. Certainly, one would expect the oxides of uranium to form. There are many possibilities with uranium, and with plenty of phosphate ions available combinations of the two should be plentiful. One could speculate that uranium diphosphate would be the dominant species, but a literature search did not reveal an answer.

With granulated triple superphosphate the situation is even more complex. In that case, the rock concentrate is reacted with phosphoric acid to yield the original beneficiated mineral (e.g. francolite) with more uranium added in and a multitude of possible chemical combinations.

2. GLOBAL RADIOACTIVITY DATABASE

The wet acid process is used throughout the world with only minor variations of any consequence for radionuclide distributions. This means that one could roughly scale the expected activity concentrations and inhalation hazards to the input rock source. This would save significant resources that may be unnecessarily devoted to monitoring programmes, to respiratory protection programmes with dubious benefits and to unwarranted regulatory restrictions.

Published data on the radionuclide and metals contents of worldwide phosphate rock, wet acid process products and phosphogypsum are highly variable in time of sampling, analysis methods and parameters chosen for analysis. At best, the existing data can yield only a partial picture of the current international market. In order to establish a concurrent, coordinated and consistent database, an internationally funded programme would obtain samples of rock from currently active mining sites and products and phosphogypsum from active processing sites. Rock samples would be correlated to the processing sites where they are used. A model structure for such a programme already exists. Rothamsted Research (UK) has been collecting, storing and analyzing soil, fertilizer and crop samples from their experimental plots for one and a half centuries. Not only have these samples served their original purposes, but also have revealed trends, e.g. pollution and radioactive fallout, unforeseen by the scientists who collected them so long ago. Nevertheless, they had the foresight to realize that other uses for the samples would develop.

The phosphate industry and regulators should follow their lead. Essentially, use a well vetted sampling protocol, use the best analysis equipment available, follow rigorous QA/QC and store the samples for future research. For the first time, all major global rock production and processing sites would be analysed for a comprehensive set of radionuclides, metals and other parameters of interest according to a rigorous set of protocols. In this way, the data set will be complete and uncertainties stemming from differences in analytical techniques and sample handling will be avoided. All laboratories will use the same set of handling protocols and analysis techniques. Quality assurance and quality control will be maintained using chain of custody and cross-checking with standards and a statistically reliable subset of samples. Both the database and the analytical protocols used in its development will become the new benchmark for the twenty-first century global phosphate industry and samples will be stored and categorized as in the Rothamsted model.

3. INHALATION DOSE CHARACTERIZATION

Once benchmark data are in place, whether making a rough estimate of projected doses or a rigorous site specific inhalation dose assessment, certain parameters must be known or assumed (with justification). Inhalation dose assessment techniques have greatly improved over the last half century. In past decades, phosphate industry inhalation dose assessments were conducted by taking high volume air samples in the workplace that were analysed for gross activity. Many assumptions were applied to estimate doses to workers. With the advent of cascade impactor sampling, high resolution spectroscopy, the revised human respiratory tract model and computer applications, inhalation doses can be estimated with fewer conservative assumptions and less uncertainty. Consequently, inhalation dose estimates tend to be lower using the newer techniques and measurements of sensitive parameters.

Radioactive materials have been assessed in the workplace using Ge(Li) gamma spectroscopy and alpha spectroscopy (for ^{238}U and ^{210}Po only) [10]. The most important radionuclides, as ranked by the annual limit on intake (ALI) for all three natural decay series, were considered for the phosphate dust inhalation assessment. Unpublished data (using unknown methodology) gave a mean particle diameter of 1.6 μm, so a default AMAD of 1 μm was used for all particles. The range of dust loading was reported as 3.0–13.5 mg/m^3. Activity concentrations of dust samples were not measured, and were estimated based on raw materials. The committed effective doses due to phosphate dust inhalation were 2.85–5.60 mSv/a. The lack of sufficient data for sensitive inhalation dose parameters required application of conservative assumptions and probably resulted in the overestimation of dose. This conclusion was also expressed by the author of the study.

The equipment and techniques necessary to gather data on the missing parameters are expensive and complex. Other investigators experienced the same difficulties and also used a default AMAD, made radionuclide activity concentration estimates based on gross activity collected on filters in conjunction with bulk material measurements and made conservative assumptions about particle solubilities in lung fluids [11]. Results were published as dose distributions. The most probable doses for individual workers were:

(a) <0.05 mSv/a for those moving rock concentrate;
(b) <0.02 mSv/a in phosphoric acid production;
(c) <0.05 mSv/a in dry product areas;
(d) <0.8 mSv/a in product shipping and storage.

Use of uncertainty analysis techniques invariably compounds individual parameter uncertainties on occasion to produce very high potential doses, which are nevertheless highly unlikely in reality. For that reason, the displayed range of possible doses for workers who move dry materials in shipping and storage areas was up to 3.5 mSv/a. These authors also recognized that the inhalation doses were very likely to be overestimated and recommended a more targeted follow-up study to gather data on the unknown parameters.

The first follow-up study was completed in 2005 [13], accompanied by four related publications [12, 14–16]. Measured parameters included airborne particle size distributions, particle densities, particle shapes, particle chemistries and radionuclide activity concentrations. The solubility of particles in lung fluid was not examined during the first follow-up study pending the outcome of a sensitivity analysis for that parameter. The sensitivity analysis proved that the inhalation dose is extremely sensitive to this parameter, so further studies were conducted [17–18].

Dust samples were collected in areas identified in the first comprehensive study [11]. These areas included the granulation area for dry products, the dry products storage warehouse and shipping operations. An example of the dry products storage area is shown in Fig. 1. The particle mass concentration was found to increase with increasing particle size at the majority of the plants and operational areas.

Sampled aerosol particles appear as spheroids or rough spherical fragments under scanning electron microscopy using samples from all seven cascade impactor stages. The main elemental components of large sized and medium sized particles are similar to those in bulk dry product. For small sized

FIG. 1. Dry products storage area.

particles, the fraction of phosphorus is small in comparison to elemental impurities such as silicon and sulphur. The density of products and particles are 1.6–1.7 g/cm^3. The ^{238}U, ^{226}Ra and ^{210}Pb activity concentrations in bulk dry product and settled dust from central Florida are in the ranges of 2.33–4.15 Bq/g, 0.0296–0.0555 Bq/g and 0.248–0.333 Bq/g, respectively. No significant differences in the concentrations of ^{238}U and ^{226}Ra were found between dry product, settled dust and airborne particles. Lead-210 is, however, highly concentrated in airborne particles up to 3.2 Bq/g, probably due to the attachment of ambient airborne radon decay products on workplace airborne particles.

Under the least conservative assumptions of blood absorption rates, all worker exposures are less than 1 mSv/a. In contrast, the most conservative assumptions yield worker effective doses in excess of 1 mSv/a for some 44%, 31% and 15% of individual effective dose assessments in the granulator, storage and shipping areas, respectively. The study thus demonstrates the importance of facility and area specific particle solubility data in effective dose assessments.

The lung fluid solubility of uranium, thorium and lead in phosphate product particles was determined using an in vitro dissolution test using serum ultrafiltrate (SUF) lung fluid simulant [19] at the physiological pH of 7.2–7.4,

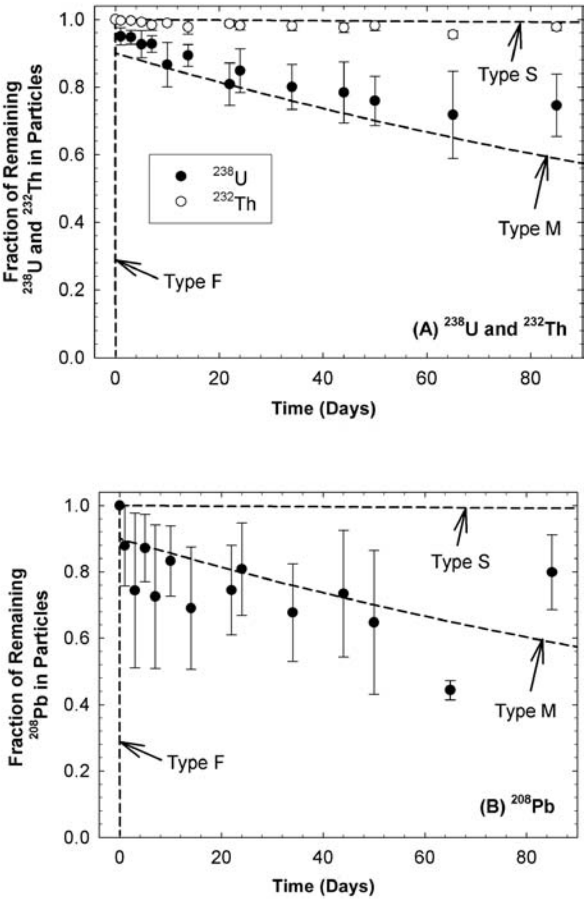

FIG. 2. Fraction of remaining ^{238}U, ^{232}Th and ^{208}Pb in particles as a function of time in serum ultrafiltrate (SUF): (A) ^{238}U and ^{232}Th and (B) ^{208}Pb. Retentions of default absorption type materials in ICRP 66 HRTM are depicted for comparison

consistent with lung lining extracellular fluid. The solubility data and other aerosol information were then used for individualized effective dose assessments at six phosphate facilities. Dissolution testing showed that the majority of phosphate, the main component of the inhaled aerosol particle, was dissolved rapidly in the lung fluids. However, uranium, thorium and lead did not dissolve as rapidly as the surrounding matrix (Fig. 2). Between 3 and 14% of the ^{238}U in NORM aerosols dissolves rapidly in the lung fluid, while the remaining fraction dissolves with a half-time of 91–315 d. The dissolution kinetics for ^{238}U in phosphate processing NORM aerosols were noted to be close to but slightly slower than that of type M materials in the ICRP 66 clearance model. For ^{232}Th, less than 1.4% of the radioactivity is dissolved rapidly in the lung fluids, while the remaining fraction dissolves with a half-time of more than 866 d. Selection of type S is thus recommended for dose assessments in radiation protection. Lung fluid solubility data for ^{208}Pb displayed a wide sample to sample variation. Of the ^{208}Pb, 3–41% is dissolved rapidly, while the remainder dissolves more slowly, with a half-time of 38–866 d. No noticeable correlations were found between radionuclide solubility and the product type or particle size. The data support the selections of ICRP 66 (1994) type M for uranium and lead and type S for thorium as adequate for the purpose of effective dose assessment to workers in these phosphate processing facilities. Inhalation effective doses were calculated using the most current human respiratory tract model (HRTM).

4. REGULATORY POLICY

The IAEA Basic Safety Standards [20] provides the framework for the protection of NORM industry workers. In conjunction with published scientific articles, IAEA Safety Reports describing processes and good practices, some basic site specific data, and a ‘graded approach’ [21] to regulation, worker protection is ensured without undue expense on the part of industry. The BSS is in place and some NORM issues will be readdressed in the next version, important inhalation dose parameters have been recently measured and published as discussed herein. The main missing components for effective and harmonized worldwide regulation are the global radioactivity database described in this paper and the political will to cooperate.

At least three quarters of the sedimentary phosphate rock mined in the world today contains less than 2 Bq/g of the individual members of the uranium and thorium series and much of it contains less than 1 Bq/g. Even at levels approaching 2 Bq/g, the resulting inhalation doses are well below 1 mSv/a. Personal monitoring programmes persist at facilities throughout the world despite the fact that in many cases they achieve no practical benefit and would qualify for the lowest level of the graded approach, i.e. no regulation necessary.

It is important to carefully consider these data during ALARA review and when forming regulatory policies regarding the need for respiratory protection programmes and administrative or engineering controls, thus lowering the risk of over-regulation.

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RADIOACTIVITY IN THE PHOSPHATE FIELD: ACTIONS UNDERTAKEN BY IMPHOS

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Abstract

In order to prevent a potentially negative impact on the phosphate industry of the European Council Directive 96/29/Euratom, IMPHOS participated in several events where discussions were held on the issue of NORM and the consequences of the application of the Directive for the non-nuclear industries, including all the NORM symposia from September 1997 to May 2004. In addition, IMPHOS has undertaken actions to establish an ad hoc committee with members designated by member companies and to initiate a desktop study conducted by CEPN to review the implications of applying the Directive for the phosphate industry. This study is an important collection of data on radiological protection, including doses expected to be received by exposed individuals and monitoring considerations. The main conclusions of these actions are that the radioactivity in the phosphate industry is relatively insignificant, with the total annual exposure of a phosphate worker being less than three thousandths of the limit recommended by the ICRP.

1. INTRODUCTION

All raw materials contain traces of natural radioactivity. The main contributions to human exposure to ionizing radiation arise from natural sources, cosmic rays, the radionuclides in the Earth's crust and the natural radioactivity of the human body. The science of radiological protection and of national and international regulatory regimes have evolved to ensure safety in the use of these sources of exposure.

In May 1996, The European Union issued Council Directive 96/29/Euratom that set limits on radioactivity concentration in naturally occurring radioactive material (NORM). In order to monitor the impact of the Directive on the phosphate sector, IMPHOS commissioned the Centre d'Etude sur l'Evaluation de la Protection dans le Domaine Nucléaire (CEPN), France, to undertake a study and participated in several events where discussions were held on the issue of NORM and the consequences of the application of the European Directive for the non-nuclear industries.

2. RADIOACTIVITY IN PHOSPHATE ROCK AND DERIVATIVES

Rock phosphate and its derivatives contain a number of elements, including impurities such as Cd, Ni, Cr and the radioactive elements U, Th and their decay products. Rock phosphates are chemically processed more and more in the producer countries and directly exported as 54% P_2O_5 phosphoric acid to produce intermediate products, such as triple super phosphate and ammonium phosphates. Different processes are needed because of different rocks and gypsum disposal systems. The chemical reaction by the wet process is:

$$Ca_3(PO_4)_2 + 3H_2SO_4 \leftrightarrow 2H_3PO_4 + 3CaSO_4$$

The insoluble calcium sulphate (phosphogypsum) is then separated from the phosphoric acid, usually by filtration.

Phosphate fertilizers vary considerably from one product to another with regard to their radioactivity content, ranging over an order of magnitude (30–300 ppm weight). Table 1 illustrates some typical values of naturally occurring radioactivity in some phosphate rock. About 80% of the ^{226}Ra, 30% of the ^{232}Th and 14% of the ^{238}U is left in the gypsum.

3. ACTIONS UNDERTAKEN BY IMPHOS

Radioactivity in phosphates has attracted much interest, particularly when recovery of U from phosphates has an added value. IMPHOS has addressed the issue of phosphate radioactivity since its creation. It has sponsored research on U recovery by ionic flotation at the University of Nancy. The research work was recognized by a granted patent. In order to survey the

TABLE 1. TYPICAL RADIOACTIVITY LEVELS IN PHOSPHATE ROCK

Origin	Activity concentration (Bq/kg)		
	^{238}U	^{226}Ra	^{232}Th
Florida	1500	1600	16
South Carolina	4800	4800	78
Morocco	1700	1700	30
China	150	150	25

application of the new European Directive, IMPHOS contracted CEPN, France, to conduct a study on radioactivity issues in phosphate products and participated in several events where discussions were held on the issue of NORM and the consequences of the application of the European Directive for the non-nuclear industries.

3.1. Assessing radioactivity in phosphate mining and processing

Because of possible concerns over the radiation exposure that could result from the handling of radioactive materials and from the use or disposal of their wastes, the European Commission has supported a programme of work in this area over a number of years and has assembled a substantial body of information by means of contracts and contributions from experts. As protection against the effects of ionizing radiation, the Member States of the EU were previously subject to two Directives: 80/936/Euratom of July 1980 and 84/467/Euratom of September 1984. The new European Directive 96/29/ Euratom, which was implemented in May 2000, is more restrictive than the previous Directives and provides a regulatory control system for the protection of the workers and the public from sources of ionizing radiation. However it does not necessarily apply to the exposure to natural radiation sources

In order to provide more background on the EU objectives, the underlying principles and scope of application of the planned Directive, and a detailed method for the initial evaluation of the degree of annual exposure of workers from different phosphate industry activities, IMPHOS commissioned the CEPN, France, to undertake some work on Modalities of Application of Title VII of the Directive 96/29 EURATOM to the Phosphate Industry: Analysis of the European Regulation and Presentation of a Method of Evaluation of Exposure. The report constituted an important collection of data and information on the radiological protection system, with quantitative data on the range of doses that can be received by a person or by certain organs and tissues in particular, the permissible limits for certain exposed workers and the public, the classification of workplaces and work conditions, the monitoring of individuals who can be subject to internal radiation and the monitoring of exposure to contamination through skin. The study also provided updated information on the application of the Directive in each EU Member State and the sectors of the industry to be considered in this application, with particular attention to the phosphate industry.

During the introduction of the broad guidelines and major conclusions contained in the report, the author underlined the need for the phosphate industry to undertake specific communication campaigns in order to provide relevant and credible data and information on the subject and to avoid as much as possible any misunderstandings and confusion, and thus any negative reactions and attitudes of the general public.

3.2. Symposia and meetings

IMPHOS participated in several events where discussions were held on the issue of NORM, extending from NORM I held in 1997 to NORM IV in 2004.

NORM I

The NORM I symposium was held in Amsterdam from 8–10 September 1997 and covered the following topics: the phosphate industry; metal production; the refractories, abrasives and ceramics industry; the TiO_2 pigment industry; the oil and gas industry and the coal and fly-ash industry.

In the phosphate industry, radioactivity is particularly located in phosphogypsum, dust (phosphate rock or fertilizers), sludge and scales. The concentrations of natural radionuclides in phosphate ore vary from 100 to about 5000 Bq/kg and are dominated by the contribution of the ^{238}U decay series. Igneous phosphate rock contains much less uranium but higher concentrations of ^{232}Th. Phosphoric acid produced from rock phosphate via the wet process retains roughly 60% of the most highly soluble radionuclides (U, Th). Indeed, 80% of the radium existing in phosphate rock is retained by the phosphogypsum, with a ^{226}Ra activity concentration of 900–1300 Bq/kg.

In the thermal process, phosphate ore is crushed, mixed with silica and coke and calcined at a temperature of up to 1500°C in an electric arc furnace to produce elemental phosphorus. Because of the high temperature of the process, about 95% of the relatively volatile radionuclides are released to the process air, giving typical concentrations of 50–500 Bq/g of ^{210}Pb and ^{210}Po in dusts.

The concentrations of radionuclides in fertilizers vary widely, in part due to the different chemical compositions of fertilizers and also due to the raw materials used in their production.

NORM II

IMPHOS participated in the International NORM II Symposium held in Germany from 10–13 November 1998. The symposium was organized in five sessions. Each one of the sessions dealt with a specific aspect of NORM: measurement and monitoring, exposure of workers and the public, experience of the industry, waste management, and legislative and regulatory aspects. The conclusions and recommendations of the symposium can be summarized as follows:

(a) The intended mode of application of the European standard remains ambiguous and requires the EU to establish guidelines for the application of the standard at the level of each Member State of the EU in the shortest time;
(b) In collaboration with scientists and legislators, the industry should assume leadership in the discussion of the Directive with the EU;
(c) The application of the new Directive should necessarily take into account the additional cost associated with decontamination;
(d) Methods of determination of radioactivity were not well defined and no consensus was reached on the meaning of 'natural' radioactivity in the current clearance criteria;
(e) The term radioactivity is rather ambiguous and needs to be better clarified;
(f) Often, the dose rate calculations are based on conservative assumptions that lead to unrealistically high results;
(g) The industry fears that if regulations are passed they will increase the production costs, which might lead to a loss of competitiveness regarding other countries;
(h) There is a need for clear international harmonized policy on how to process the large volumes of contaminated industrial waste and scrap;
(i) There is a need for developing guidelines by the EU on the adoption of the Directive into national laws.

NORM III

IMPHOS participated in a meeting of the scientific committee connected with the third NORM symposium held in Brussels in May 2001. IMPHOS was part of the committee that selected the papers to be presented or submitted as papers or posters. The selected papers for presentation were scheduled in the different sessions, and figured under the eight different topics of the symposium, which were as follows: regulatory aspects, mineral processing, the mineral salts, coal, radon in the work place, wastes, the environment, and the scrap and construction material industry. As a result, the phosphate industry does not figure among the industries on the list. In fact, only one Greek paper dealt directly with the phosphate industry. It was a paper from the University of Thessalonika that looked at the atmospheric fallout from a phosphate processing plant and its impact on the surrounding environment.

NORM IV

IMPHOS participated in the NORM IV symposium held in Poland in May 2004. With regard to phosphates, the symposium included coverage of igneous rock phosphate (of volcanic origin), which is more radioactive than sedimentary phosphate — this is due to the elevated level of ^{232}Th in the igneous rock — and discussed the possible uses and management of phosphogypsum and the scaling found in different parts of a phosphoric acid plant. The discussions during the previous NORM symposia show that the radioactivity of phosphate rock and phosphate fertilizers would seem to pose no risk to the environment.

IAEA meeting in Vienna in May, 2002

IMPHOS participated in a meeting held at the IAEA, Vienna in May 2002 on The Extent of Environmental Contamination by Naturally Occurring Radioactive Material (NORM) and Relevant Abatement Measures. The IAEA prepared a technical document (IAEA-TECDOC) that reviews all the sources of naturally occurring radioactivity. On phosphates, the input from IMPHOS was particularly to provide relevant information about radioactivity in phosphates and phosphate fertilizers.

International consultation meeting in Florida

IMPHOS attended an international consultation meeting on the future of phosphate and phosphate related products, held at the conference centre of the Florida Institute of Phosphate Research (FIPR) in Bartow, Florida on October 3–4, 2006. This meeting was organized in association with the IAEA, the OECD Nuclear Energy Agency and other partners. A major focus of the meeting was on safety and risk assessment. The meeting discussed the fundamental changes occurring in the phosphate industry that are being driven by structural transformations in the world economy, changing attitudes to risk, renewed concerns about strategic raw materials and increased concern for the environment and waste reduction. The meeting also explored options for responding to the likely consequences of these changes, including possible collaborative work plans. During this event, it was noted that phosphate is a limited resource that cannot be synthetically produced. It was also noted that phosphogypsum is a co-product of phosphoric acid production that has some unique properties and advantages over other forms of gypsum and can be used as a fertilizer, a soil conditioner, backfill for road construction, a construction material for the production of plasterboard and cement aggregate.

4. SOME DEVELOPMENTS AND CONSIDERATIONS ON THE ISSUE OF RADIOACTIVITY IN PHOSPHATES.

The solutions ensuing from the studies, symposia and meetings to overcome the radioactivity problem of NORM are the following:

(a) NORM wastes should be, in this way, diluted in the liquid ecosystem. Thus, from a radioactivity viewpoint it is more appropriate to dilute NORM waste than to dispose of it in piles.
(b) Spreading of NORM waste with a relatively low activity concentration over the land may not, or may only with a low percentage, increase the original radiation field. Phosphogypsum can be widely used as a beneficial soil amendment. Uptake of crops grown on such amended soils is still acceptable.
(c) Some PK fertilizers which contain radioactive materials slightly above the exemption levels do not affect the natural radioactivity at soil level when spread all over.
(d) There is a tendency to reuse naturally occurring radioactive materials as a way to decrease the volume of waste. Phosphogypsum and sludge from the phosphate industry are widely used for road construction and wall board plaster.

Radioactivity in phosphate mining and processing is found mainly in:

(1) Phosphate ore dust emission during mining, beneficiation, chemical processing, handling, and storage;
(2) Management of wastes, in particular phosphogypsum, which concentrates radium;
(3) Sludge and scaling in equipment used in wet process phosphoric acid production.

In order to prevent problems with radioactivity in phosphate industries, IMPHOS is called upon to take a pragmatic strategy. Hence, the following plan was proposed:

(i) To undertake a campaign of information about the impact of radioactivity from the phosphate industry towards member companies;
(ii) To institute a think tank with member companies’ participation in order to lay down an ‘IMPHOS position’, which can be promoted by the IMPHOS Secretariat at regional level (EU), to the International Commission on Radiological Protection (ICPR), to institutions that

develop regulatory standards, as well as other involved institutions such as EFMA, IFA and PPI;

(iii) To follow up news pertaining to the matter at hand by developing an information network involving EU and international bodies such as ICRP, directly concerned with their research activities or decision making;

(iv) To carry out a self audit of radioactivity levels in member companies' facilities according to a pre-agreed programme based on conventional tests and procedures.

With respect to phosphogypsum, which receives on average 40% of the radionuclides present in the phosphate rock — a percentage that involves particularly the less soluble portion of radionuclides, i.e. radium and polonium — the problem of radioactivity increases particularly from the exhalation of ^{222}Rn that has a relatively short half-life and does not pose a significant health hazard.

Finally, regarding phosphate fertilizers, the problem of radioactivity is raised at two levels:

- At the storage level where fertilizers continue to exhale ^{222}Rn in the surrounding atmosphere. A sufficient means to reduce the effect of ^{222}Rn is to practice adequate ventilation in warehouses.
- At the level of fertilizer use where radioactive elements are thought to get into plants, and at the current level of knowledge it seems that there is little evidence to show that the passage of radionuclides in the food chain starts with phosphate fertilizer use even if P were to be applied at a high rate.

5. CONCLUSIONS

The main conclusions and recommendations are:

(a) The natural radioactivity of phosphate rock is still lower than that of some soil and radioactive material in the atmosphere;

(b) The total annual exposure of phosphate workers to radioactive material in a closed workspace is lower than three thousandths of the admissible threshold recommended by the ICRP;

(c) Several studies have shown that, in general, the radioactivity in the phosphate industry is insignificant compared with other industry sectors;

(d) This is why the scientific community pays less and less attention to the phosphate industry;

(e) The nuclear scientific community estimates that the issue of hazards due to NORM and particularly phosphate rock is considered as not important enough to warrant undertaking any efforts to solve it.

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PUBLIC EXPOSURE FROM MINES OPERATING ON AN IGNEOUS OREBODY

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Abstract

The impact on members of the public from the extraction and beneficiation of naturally occurring radioactive materials is of primary concern for responsible operators. In Phalaborwa, South Africa, two companies mine and beneficiate an igneous orebody in close proximity to the community. The unique features of this community allow an integrated look into the radiological impact of these activities. It is shown that the doses received by members of the public in the surrounding community are far below the public dose limit and similar to or less than the statistical variation in natural background.

1. INTRODUCTION

The object of the paper is to provide an integrated look at the Phalaborwa region of South Africa and the impact on members of the public of the mining of an igneous orebody, taking cognisance of primary and secondary exposure pathways. It is based on public safety assessments conducted in accordance with the nuclear authorizations of two mining operations in the region and provides some views on the results obtained by the author in his capacity as radiation protection specialist for those operations [1–4].

1.1. The Phalaborwa igneous complex

The Phalaborwa Igneous Complex is situated in the Limpopo Province of South Africa (see Fig. 1). One of the unique features of this town is that it is in a fairly pristine environment compared with more urban societies.

The situation in Phalaborwa is unique, with three communities in close proximity to a single source, the igneous mineral deposit, which created both primary extraction and some form of beneficiation. The two major facilities are Palabora Mining Company (PMC), comprising a copper mine and smelter, and Foskor Limited, comprising a phosphate mine and ore beneficiation plant.

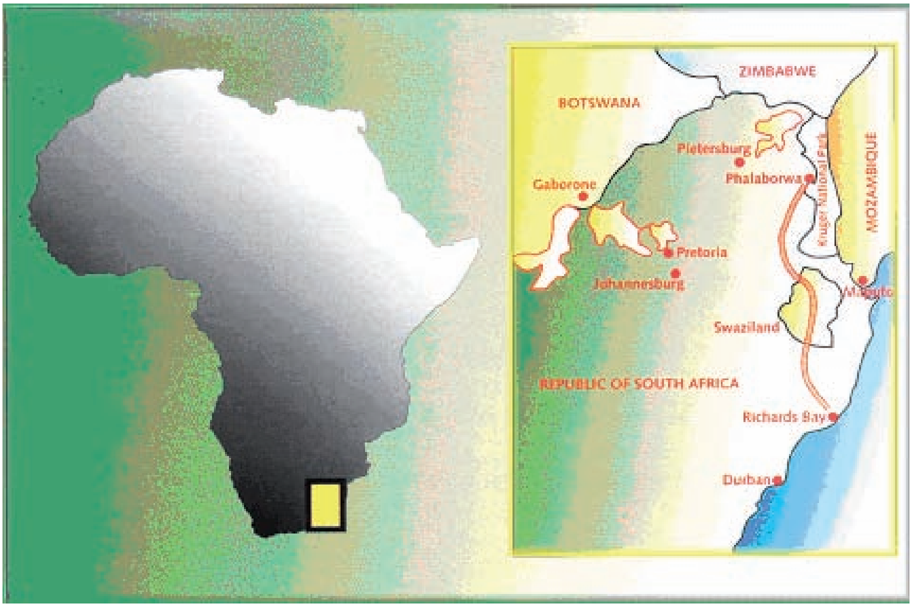

FIG. 1. Location of Phalaborwa.

There is also a phosphoric acid plant but this is relatively minor in terms of source size when compared to the sum of PMC and Foskor. To the immediate east of the igneous formation is the Kruger National Park, while the two mines are located next to one another from east to west. The town of Phalaborwa, meaning ‘better than the south’, is located to the north of the mining complex, while smallholdings and game farms, with another town, Namakgale, are located further to the west and north-west.

1.2. Geology of the igneous orebody

The dominant rock type in the Phalaborwa area, older than 3000 million years, is granite–gneiss of the Archaic Complex. Intrusive in this are younger rock types of the Phalaborwa Igneous Complex. Inclusions of serpentine, talc and amphibole schist are found in the granite–gneiss and igneous rock. The major mineral content of the ore is as follows:

- Apatite: $Ca_2 (PO_4)_3F$;
- Magnetite: Fe_3O_3;
- Phlogopite: $KMg_3 (AlSi_3O_{10}) (FOH)_2$;

— Copper sulphide: CuS;
— Baddeleyite: ZrO_2.

Table 1 summarizes the typical radionuclide activity concentrations associated with mining operations at the complex, presented as an average of various samples analysed by the South African Nuclear Energy Corporation on behalf of the companies involved. A unique feature of this complex is the predominance of thorium decay series radionuclides.

1.3. Mining operations

1.3.1. PMC

The ore was initially removed from an open pit, once the largest in the world. Currently the orebody lies below the open pit and is mined by the block caving method. The main process is the mining and beneficiation of copper. The process is shown in Fig. 2.

1.3.2. Foskor Limited

Foskor is primarily a phosphate mine and beneficiation plant. The mining method is typical of opencast hard rock mining. Drilling of 250 mm blast holes is accomplished using electrically driven rotary drills. Explosives are then used to loosen the 12–15 m high benches. After blasting, an electrically driven loading shovel loads rock onto 100–180 t diesel-electric trucks that transport it to the primary crusher or the waste dumps. Rocks that are too big for the shovel are pushed to one side and crushed by mechanical impact or explosives.

TABLE 1. TYPICAL ACTIVITY CONCENTRATIONS

	Activity concentration (Bq/g)				
	Phosphate rock	Phosphate tailings	Copper concentrate	Magnetite	Copper extraction tailings
^{238}U	0.14	0.26	1.43	0.14	3.52
^{226}Ra	0.14	0.27	1.14	0.14	1.81
^{210}Pb	0.12	—	0.56	0.08	8.84
^{232}Th	0.47	0.31	0.56	0.11	2.09
^{228}Ra	0.55	0.33	1.04	0.16	1.60
^{228}Th, ^{224}Ra	0.55	0.35	1.04	0.16	1.60

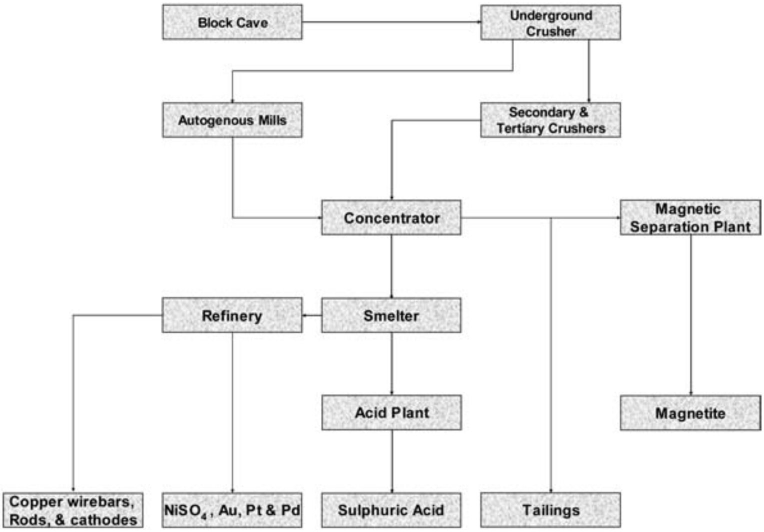

FIG. 2. PMC mining and beneficiation process.

From the primary crushers, the rock passes through secondary and tertiary crushers before entering the milling section where the ore is ground to a fine pulp. The pulp is put through a flotation and filtration process to extract the phosphate rock and, depending on the ore stream, then put through a magnetic separation and secondary flotation process to extract magnetite and copper concentrate. The final product is stockpiled and dried before loading it onto rail cars for delivery. The tailings are pumped to two tailings dams for final disposal.

2. PUBLIC SAFETY ASSESSMENT

2.1. Methodology

Empirical equations were used for activity concentration points along the secondary pathways where actual measurements were not available. Generally, average radionuclide concentrations in air, food and water were combined with the annual rates of intake to obtain an estimate of the total radionuclide intake during that year.

2.2. Critical groups

A critical group is defined as a group of members of the public which is reasonably homogenous with respect to its exposure for a given radiation source and given exposure pathway and is typical of individuals receiving the highest dose by the given exposure pathway from the given source. For the purpose of this assessment, several actual and hypothetical groups were considered to ensure an appropriate estimate of the incremental public dose as a result of the mining activities in the complex. All age groups were assumed to be present in the critical group of each scenario, with homogeneous exposure from the applicable sources. A clear distinction needs to be made between the actual and hypothetical groups. The focus of the current monitoring programme was on the actual critical groups and compliance with dose limitation requirements was determined annually for these groups. Hypothetical critical groups are seen as possible future variations that might need consideration in any future planning, especially the planning for mine closure and town development. The following critical groups were considered:

Exposure primarily from the phosphate mine

(a) Actual critical group north of the site, on the site border; includes a family living in Phalaborwa;
(b) Actual critical group represented by a family living in Namakgale, approximately 10 km north-west of the site;
(c) Actual critical group living on the south-east border of the Selati tailings dam;
(d) Actual critical group situated on smallholdings to the west and north-west of the Selati tailings dam, between the tailings dam and the critical group described in (b) above;
(e) Disruptive or unplanned flood event.

Exposure primarily from the copper mine

(a) Actual critical group north of the site, on the site border; includes a family living in Phalaborwa;
(b) Actual critical group represented by a family living in Namakgale, approximately 10 km north-west of the site;
(c) Hypothetical group represented by a small farm community located to the south-east on the banks of the Selati river, utilizing river water;
(d) Hypothetical group represented by a small farm community located to the south-east on the banks of the Selati river, utilizing groundwater;

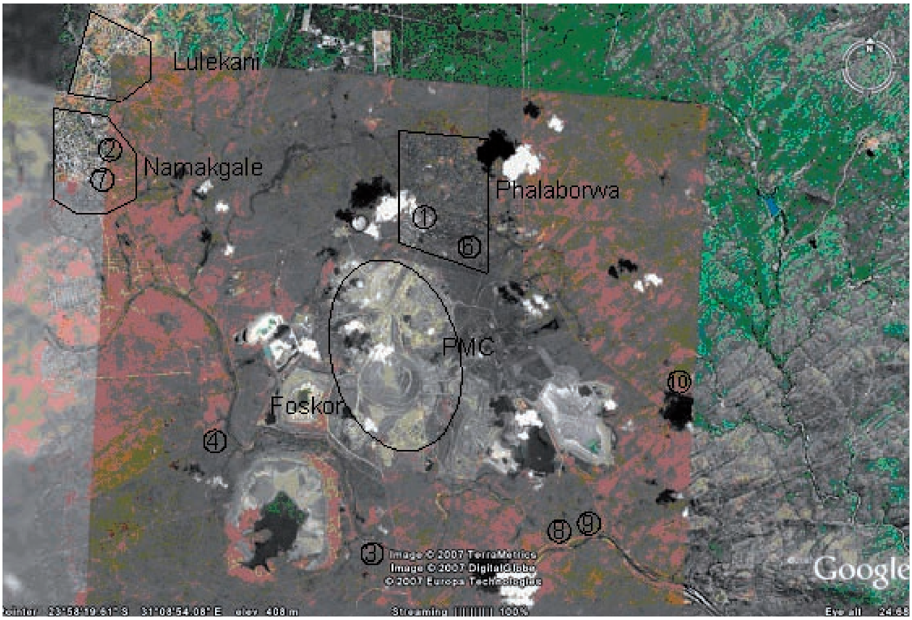

FIG. 3. Locations of critical groups.

(e) Hypothetical group representing a small farm community located to the east, utilizing different boreholes from those included in (9) above;

(f) Hypothetical event, e.g. an abnormal rainfall event equal to a 1 in 100 years flood.

The locations of the critical groups are shown on the satellite photograph in Fig. 3.

2.3. Exposure pathways

The principal exposure pathways considered for most of the critical groups listed in Section 2.2 are shown in Table 2.

2.4. Wind direction and water flow

The wind direction at Phalaborwa is represented by the wind rose shown in Fig. 4. The wind blows from a south-easterly direction for approximately 70% of the time.

A major difference between the PMC risk assessment and the Foskor risk assessment was that actual receptor fallout dust measurements were not available for the former. It was therefore assumed for the PMC assessment that

TABLE 2. EXPOSURE PATHWAYS

Critical group	Exposure pathway		
	External radiation	Inhalation	Ingestion
1	Soil, plume immersion	Dust, radon, thoron	Fish, leafy vegetables, root vegetables, fruit
2	Soil, plume immersion	Dust, radon, thoron	Fish, leafy vegetables, root vegetables, maize, cereal, poultry, eggs, meat, milk
3	Soil, plume immersion	Dust, radon, thoron	Fish, leafy vegetables, root vegetables, maize, cereal, poultry, eggs, meat, milk
4	Soil, plume immersion	Dust, radon, thoron	Fish, leafy vegetables, root vegetables, maize, cereal, poultry, eggs, meat, milk
6	Soil, plume immersion	Dust, radon	Fish, leafy vegetables, root vegetables, fruit
7	Soil, plume immersion	Dust, radon	Fish, leafy vegetables, root vegetables, maize, cereal, poultry, eggs, meat, milk
8	—	Radon	Surface water, leafy vegetables, root vegetables, maize, cereal, poultry, eggs, meat, milk
9	—	Radon	Groundwater, leafy vegetables, root vegetables, maize, cereal, poultry, eggs, meat, milk
10	Soil, plume immersion	Dust, radon	Groundwater, leafy vegetables, root vegetables, maize, cereal, poultry, eggs, meat, milk

the concentration at source equalled the concentration at the receptor (i.e. no resuspension of dust) and that the wind direction was the only factor determining the concentration at the receptor.

The direction of surface water flow is opposite to the predominant wind direction, away from the site and into the neighbouring national park. The surface water thus affects only the hypothetical critical groups in terms of drinking water and irrigation. However, the actual critical groups were affected by the uptake of radionuclides in fish. Groundwater also flows away from the community, through the mine sites towards the Selati river and therefore only affects the hypothetical critical groups.

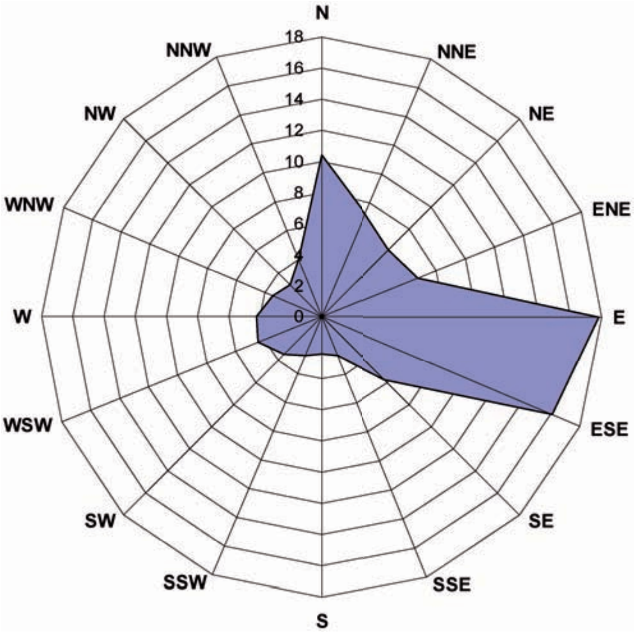

FIG. 4. Wind rose for Phalaborwa.

3. RESULTS OF INITIAL ASSESSMENT

The results of the initial public safety assessment are summarized in Table 3.

4. DISCUSSION OF RESULTS AND REVISED ASSESSMENT

Owing to the proximity of the mines to three communities, it is necessary to fully quantify the impacts on these communities, actual and potential, to ensure responsible management. This assessment was very conservative in its approach, in that it assumed that a critical group received all of its consumables from a potentially affected area, but this is very unlikely in the Phalaborwa region. The shallow soils and low crop potential prevent any extensive agricultural use and farming consists mainly of game and cattle farming. In addition, the areas available for growing crops are limited, with only one smallholding producing leafy or root vegetables in marketable quantities. This smallholding does not have cattle to provide meat and milk, nor does it produce cereals and

TABLE 3. RESULTS OF THE INITIAL ASSESSMENT

Critical group	Annual effective dose, by age group (μSv)					Exposure pathway	
	0–2 a	2–7 a	7–12 a	12–17 a	>17 a	Primary contribution	Secondary contribution
1	52.4	112	147	122	144	Ingestion: fish	Ingestion: leafy vegetables
2	43.7	105	138	108	137	Ingestion: fish	Ingestion: leafy vegetables
3	242	271	355	481	254	Ingestion: leafy vegetables	Ingestion: fish
4	60.0	118	153	131	146	Ingestion: fish	Ingestion: leafy vegetables
5	Similar to (3) which is already conservative and the most restrictive, hence no further calculations made						
6	72.7	65.8	73.7	97.9	73.0	Inhalation	Ingestion: leafy vegetables
7	126	111	132	195	107	Inhalation	Ingestion: leafy vegetables
8	60.6	56.1	61.9	98.9	58.3	Ingestion, water	Meat, milk for infants
9	431	292	233	256	181	Ingestion: water	Meat, milk for infants
10	136	111	109	140	99.4	Ingestion: water	Meat, milk for infants
11	Similar to (8) which is already conservative and the most restrictive, hence no further calculations made						

maize in addition to vegetables. However, for the purpose of the initial assessment, it was assumed that large scale farming was possible, hence the inclusion of the various pathways.

The initial assessments for both facilities utilized measured data, and only reverted to conservative assumptions where such data were not available. A good example is the inhalation dose at the receptor locations. Foskor's programme was structured around its impact on air quality, a primary concern for the company, and radionuclide specific airborne dust measurements were therefore available. However, PMC was more concerned with its impacts on surface water and groundwater, so more emphasis was placed on gaining a good understanding of these impacts. In the case of PMC, therefore, airborne dust measurements at receptor locations were not made. Instead, it was conservatively assumed that the air concentration at source was not reduced over time and distance and only the wind direction accounted for any reduction in exposure at the receptor location compared with that at the source. It should be noted that physical location and other physical parameters played an important part in the difference in focus by the two companies.

For Foskor, the initial assessment indicated that critical group 3 received the highest dose, but further investigations showed that the occupants do not use the land for any type of farming, thus removing ingestion as a possible pathway. Broadly the same principal applied to critical group 9 (of concern for PMC), for whom the primary dose contribution in the initial assessment was from the use of borehole water for drinking purposes. In this instance, the effect of the poor groundwater quality was recognized. The groundwater in the Phalaborwa region is not suitable for human consumption and should thus be excluded for the second iteration of the assessment.

It should also be noted that the airborne dust activity concentration measured by Foskor in Phalaborwa and Namakgale includes not only the impact of Foskor but also the contribution from PMC. It should thus be seen as the total impact of both facilities on Phalaborwa and Namakgale. The impacts from each facility could have been assessed separately, but this would have required the same comprehensive airborne dispersion model, using the same assumptions, to be applied to each facility and the results used to determine the relative dose contributions. Since the impact determined for critical groups 1 and 2 was small (<200 μSv/a), it was not considered necessary to proceed along this line. However, it is important to note that a significant amount of conservatism was introduced by assuming that the activity concentrations at the receptor and source were the same.

A revised impact assessment was therefore made, in order to take account of the following:

(a) Dust sampling in Phalaborwa and Namakgale represents the combined impact of PMC and Foskor (the difference between the two is that Foskor allows fishing in the company dams and such fish may therefore be consumed);
(b) Ingestion does not contribute to the dose received by critical group 3;
(c) Fish consumption does not contribute to the dose received by critical group 4, as these individuals do not fish on the Foskor site;
(d) Groundwater does not contribute to the doses received by critical groups 9 and 10.

The results of this revised assessment are shown in Table 4. It is clear from these results that the doses received by all critical groups are significantly less than the 1 mSv limit on annual dose for members of the public and, moreover, are less than or close to the statistical variation (about 100 μSv) in the natural background in South Africa. This implies that public exposure is not a factor in determining whether the operations should be subject to regulatory control.

An interesting aspect of the responsible management approach to radiation protection by both companies was an initial community belief that the ambient radiation level was caused by the mines and that this had caused an increased cancer rate amongst the local population. Notwithstanding almost constant communication with the community through different forums to

TABLE 4. RESULTS OF THE REVISED ASSESSMENT

Critical group	Annual effective dose, by age group (μSv)				
	0–2 a	2–7 a	7–12 a	12–17 a	>17 a
1	52.4	112	147	122	144
2	43.7	105	138	108	137
3	70.1	134	173	153	189
4	20.6	16.6	19.4	30.1	11.8
6	30.0	28.1	30.2	37.4	26.7
7	8.26	7.77	8.50	1.07	7.27
8	60.6	56.1	61.9	98.9	58.3
9	156	128	108	96.5	68.8
10	72.2	70.0	75.5	93.9	60.7

alleviate this anxiety, one person did attempt to utilize the 'radiation coming from the mines' as an argument in a court action claim. It was realized that it is very important not to resort to generic assumptions, but to be realistic, using scenarios and parameters to which the community can relate. A shortcoming is also that the radiation protection process remains somewhat unfamiliar and that a common denominator, such as a management system similar to ISO 9001 or ISO 14001, could be helpful in convincing the public that an authorized facility is responsible in terms of its management of this particular risk.

5. CONCLUSIONS

(a) The annual effective dose received by the various critical groups, attributable to the mining operations, is significantly below the limit of 1 mSv that is applicable in terms of international standards.
(b) The radiological impact is generally less than or marginally above the statistical variation in natural background.

Based on experience in Phalaborwa, it is advisable to present the radiation protection management system in the same terms as ISO 14001, a system known to the general public.

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TOWARDS A MANAGEMENT AND REGULATORY STRATEGY FOR PHOSPHORIC ACID AND PHOSPHOGYPSUM AS CO-PRODUCTS[*]

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Abstract

Since 1946, the USA, to date global leader in diammonium phosphate (DAP) production, has in the same process generated billions of tonnes of phosphogypsum (PG) — some five tonnes of PG for every tonne of phosphoric acid. Most US PG is stored in 20 huge 'stacks' in central and north Florida, with significant holdings in other states. Since 1992 USEPA, concerned about potential risks from its radioactivity, has defined PG as a "waste by-product [… of] limited economic or environmental value". In consequence, the mandatory stacking regime imposed has had a strong impact both on the rest of the world's perceptions of PG and its regulatory regimen. PG is classed as a toxic waste, with containment as the only acceptable management and disposal method. In that there are many highly beneficial uses for PG, to predefine it as a waste is incorrect: a product is only a waste when it has no foreseen or foreseeable use. Large quantities of PG can be safely used in agriculture, construction, road building and landfill management. PG is a beneficial soil amendment, which has recently been shown by the University of Seville's Huelva study to yield agricultural and environmental benefits. Given that at least 50 countries in the world already have PG stacks, and that globally some 150 million tonnes, and rising, are produced each year, increasingly in the emerging economies of Brazil, China and India, it is perhaps time to re-examine PG as a developmental resource not a waste, reclassifying it, as it once was, as a co-product of wet process phosphoric acid production. This will have far reaching benefits for perception, regulation and exploitation of PG worldwide and may reduce or eliminate the unnecessary and expensive risk of PG ending as a very costly 'negative externality' of fertilizer production.

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1. INTRODUCTION: TOWARDS A WORLD WITHOUT STACKS OF PHOSPHOGYPSUM?

When in the early 1960s President John F. Kennedy (JFK) mandated NASA to send a man to the moon and back safely by the end of the decade [1], the management technique he invoked was to make the outcome of his instruction non-negotiable, but the means of delivery wholly open to discussion. After initially responding that it could not be done, to which JFK simply said: “But if I were to say, my fellow citizens, that we shall send to the moon, … a giant rocket more than 300 feet tall … then return it safely to earth, … and do it first before this decade is out — then we must be bold” [2], NASA changed tack and successfully set about executing the mission. The structured negotiation technique is one that John Nash describes in his Nobel prize winning work as ‘The Bargaining Problem’ [3], where the overall objective is changing the point of equilibrium [4] in an apparently intractable situation [5].

The project Stack Free by 53? Beneficial Uses of Phosphogypsum (‘Stack Free?’) (see www.stackfree.com) has followed this Kennedy/Nash method: as a ‘thought experiment’, it posits a non-negotiable outcome — a world by 2053 in which stacks, or piles, of phosphogypsum (PG) no longer exist, other than as holding piles for future use — whether in road building, construction, agriculture or the potentially hundreds of other applications that continue to be proposed for PG use. It then ‘reverse engineers’ a pathway to achieve that goal, taking into account, in sequence, the four main critical success factors for arriving at the end point. These are:

(1) Technical feasibility;
(2) Regulatory acceptability;
(3) Commercial sustainability;
(4) Political will.

Only if all four conditions can be met simultaneously will the Stack Free? proposition stand and a new ‘point of equilibrium’ be established. The methodology is shown schematically in Fig. 1.

The whole Stack Free? project derives much of its initial momentum from the seminal paper of 1998 by A. Davister, Phosphogypsum: A Waste (More or Less Harmful) or a Resource? [6].

1.1. What is phosphogypsum and how is it made?

Phosphoric acid (P_2O_5) and phosphogypsum (PG) are the twin products of the ‘wet process’ method for making phosphoric acid, in which phosphate

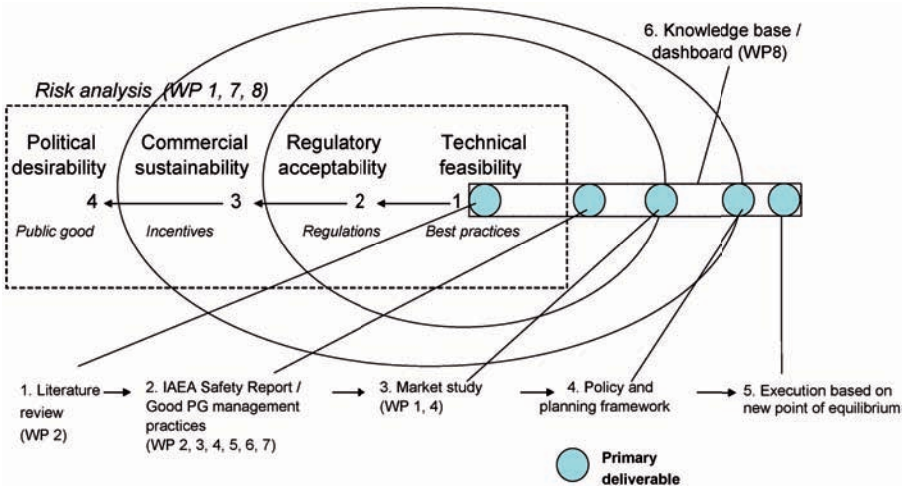

FIG. 1. Stack Free by 53? The onion ring methodology.

rock is digested with acid, most commonly sulphuric. For every tonne of P_2O_5 processed there are five of PG. This simple 1:5 ratio is at the heart of the PG problem — the sheer quantity produced in order to meet demand for P_2O_5. The basic chemistry of the wet process 'is exceedingly simple' [7].

(a) The tricalcium phosphate in the phosphate rock is converted by reaction with concentrated sulphuric acid into phosphoric acid and the insoluble salt calcium sulphate.

$$Ca_3(PO_4)_2 + 3H_2SO_4 \rightarrow 2H_3PO_4 + 3CaSO_4$$

(b) The insoluble calcium sulphate is then separated from the phosphoric acid, most usually by filtration. The reaction between phosphate rock and sulphuric acid is self limiting because an insoluble layer of calcium sulphate forms on the surface of the particles of the rock. This problem is kept to a minimum by initially keeping the rock in contact with recirculated phosphoric acid to convert it as far as possible to the soluble monocalcium phosphate and then precipitating calcium sulphate with sulphuric acid.

$$Ca_3(PO_4)_2 + 4H_3PO_4 \rightarrow 3Ca(H_2PO_4)_2$$

$$Ca(H_2PO_4)_2 + 3H_2SO_4 \rightarrow 3CaSO_4 + 6H_3PO_4$$

FIG. 2. Central Florida PG stack.

(c) Calcium sulphate exists in a number of different crystal forms, depending particularly on the prevailing conditions of temperature, P_2O_5 concentration and free sulphate content [8].

As shown in Fig. 2, stacks may be several square kilometres in size, and up to 100 m high.

Current PG capacity is approximately 150 million t per year [9], scheduled to increase by one-third in the coming ten years as new capacity, for example in Ma'aden, Saudi Arabia, comes on stream. The consequence [10] is that in the absence of a solution being found to using PG as a resource, PG tonnages stored worldwide will double some time between 2025 and 2040, the earlier date being increasingly more likely, especially if Morocco stops its current practice of ocean disposal.

1.2. Looking backwards and forwards

The issue is driven by a combination of retrospection and forward planning. On the retrospective side there are the twin challenges, first, in the USA of closing old style stacks at very high cost (up to US $500 million per

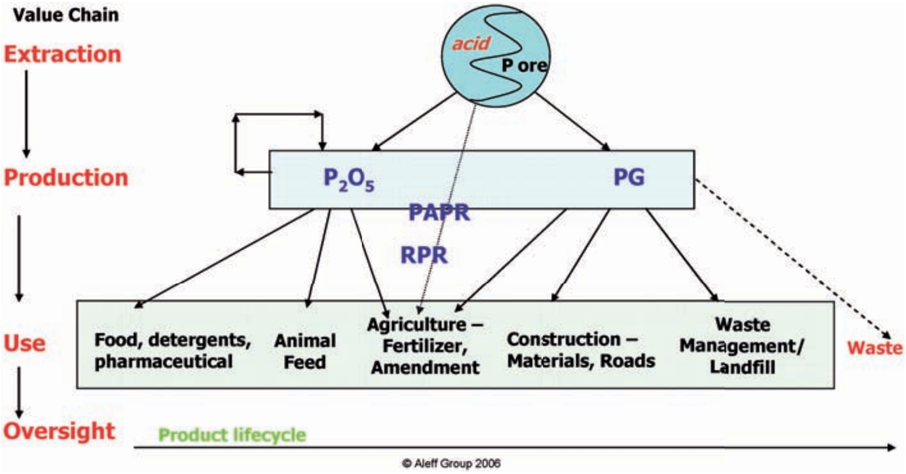

FIG. 3. Phosphate rock, phosphoric acid and PG — high level co-product model, 'end to end'.

stack) and secondly, of making good use of current global holdings in 50 or more countries. On the planning side, there is the challenge of preventing a possible doubling of current tonnages in stacks as (a) global production increases overall and (b) the practice of ocean disposal still practised in some producing environments winds down or is banned. Such a planned approach opens the prospect of an integrated management system for both phosphoric acid and PG, as co-products of the same process of reacting phosphate rock with sulphuric acid, in which the full life cycle of production and consumption is planned from the outset with a 'minimum legacy' objective in mind, including mining, use and eventual managed disposal of necessary waste (see Fig. 3).

The timing of such a change is perhaps as good as it is likely to be for decades to come, in that the industry is currently showing a significant trend towards relocating the production presently based in developed countries (notably USA and Europe) to the east and south, in or closer to the emerging economies, notably Brazil, China, India and the Middle East. Therefore, whatever solution is found to the PG challenge is likely to be in place for a long time hence.

2. 'NEGATIVE EXTERNALITY'

The theory of externality examines the impact of activities when these 'spillover' onto third parties [11]. When the result is a cost that is imposed on third parties, it is called a negative externality. When third parties benefit from an activity in which they are not directly involved, the benefit is deemed positive. Economists frequently cite pollution as an example of negative externality; a necessary process — industrial manufacture — has pollution as a side-effect. As is now vigorously under debate regarding CO_2 emissions, this externality may reach such a level that it defeats the benefits of the causative process. This tipping point has seemingly been reached in the USA for older design PG stacks, notably in central Florida [12]. In 2001, a medium sized production company in Florida, Mulberry Phosphates Inc., went bankrupt, leading to the abandonment of its two stack and pond water systems, one of which, Piney Point is in a highly sensitive area right next to Tampa Bay. This site also contained some 1.0–1.5 billion gallons (3.8–5.7 billion L) of acidic water requiring treatment. For two years immediately following the bankruptcy, there was little intervention to maintain the integrity of the stack and Florida at that point had enjoyed a number of years of moderate to low hurricane activity. In 2003 the situation changed, and by midyear was at emergency point. Both State and federal authorities were forced to intervene, at very high cost. By late 2006 the site, now largely remediated, was sold out of receivership into private hands, but at a very high cost.

The evidence from the Piney Point stack closure process has led to provisional figures of up to US $500 million per stack being identified as the likely level of liability that will be required in financial reports to shareholders and stakeholders under Sarbanes–Oxley reporting rules [13]. If such liabilities are unresolved there is a significant possibility that the losses of the phosphate industry will exceed total profits to date, effectively putting the industry at risk worldwide. Leaving aside the aspect of financial liability, there is also growing concern that even in terms of safety and environmental legacy, stacks may not be the best long term solution [14].

2.1. Current state

According to the onion ring model shown in Fig. 1, Stack Free? had methodologically satisfied the conditions for progressing from activity 1 (technical feasibility) to activity 2 (regulatory acceptability) by mid 2006.

2.1.1. Critical success factor 1 — technical feasibility

Technical feasibility has been established in two primary ways: (1) the assembly of a ‘blue ribbon’ team of production experts from both industry and academia to conduct an ongoing peer review and (2) a literature review.

Blue ribbon team

The blue ribbon team meets regularly and is progressively extending its membership as more and more examples of good practice become known to it. It now includes members from around the world, and is in the process of building an information exchange network based on the project web site.

Literature review

A literature review, focused to date on English language publications but now extending to other key sources in Spanish, Portuguese, Russian and other languages, has reviewed some 1900 publications from more than 50 countries which are now assembled into a database. The database currently:

(a) Contains peer reviewed literature from 58 countries, with India, Poland and the USA being the top three sources, accounting for 53% of titles;
(b) Identifies and classifies more than 50 beneficial uses of PG that have been researched, of which the top 4 in respect of potential volume of use are:
  — Agriculture;
  — Construction materials;
  — Landfill/waste;
  — Roads.

While PG research in the USA has slowed since the 1989 promulgation of the ‘Phosphogypsum Rule’, it is still increasing in the world at large, as seen in Fig. 4 [15].

Based on the literature review to date, it has been broadly concluded that beneficial use is technically feasible, even desirable, in domains such as agriculture and construction. The scale of potential use could result in a significant reduction of new phosphogypsum tonnage and even, in suitable settings, to the removal of stacks altogether.

2.1.2. Critical success factor 2 — regulatory acceptability

By 2007, the premise of acceptability, while still not fully resolved, is sufficiently robust that the boundary condition between regulatory acceptability and commercial sustainability is now being explored, for example through an analysis of global PG market potential. There are perhaps two touchstone aspects to the current regulatory debate surrounding PG; the first is definitional, the other numerical.

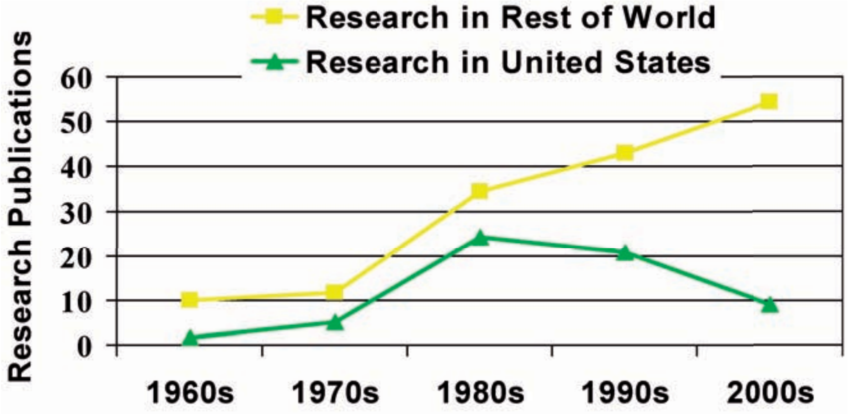

FIG. 4. PG research publications per year.

Definitional

In definitional terms, the creative tension that characterizes the most recent EU legislation [16] is indicative of the global debate as to how to define waste. For, while from a strict definitional point of view: "…..'waste' shall mean any substance or object in the categories set out in Annex I which the holder discards or intends or is required to discard" [17], the framing condition within which this definition is set is: "The recovery of waste and the use of recovered materials as raw materials should be encouraged in order to conserve natural resources. It may be necessary to adopt specific rules for reusable waste" [18]. PG sits nicely caught between these two statements, in that in some jurisdictions it is required to be 'discarded' (stacked in the USA) but at the same time other authorities are trying to promote the use of such residues, both in general and also specifically for PG.

Numerical

From a numerical point of view the debate is in some respects more precise [19]. On the one hand USEPA (and Canada) define the activity concentration threshold above which PG is sufficiently radioactive to be a potential danger as 0.37 Bq/g [20], while the IAEA regards material with activity concentration levels below 1 Bq/g as 'not requiring regulatory attention' [21] and material with levels above 1 Bq/g as candidates for exemption on a case by case basis. The great bulk of PG 'reserves' worldwide sit between these two values, so the consequence of USEPA agreeing to abide by, or at least accept under strict conditions, the IAEA criterion would be to release a very large quantity of PG into potential use.

2.1.3. A publication pathway

Stack Free? proposes as a practical way of resolving this debate a sequence of tiered publications as follows, designed to negotiate the basis for a transparent, safe practice of PG use.

A culture of safety: IAEA

Independently of the Stack Free? project, the IAEA had, in 2002, embarked on the development of a Safety Report on radiological issues in the phosphate industry and how these are being addressed to achieve compliance with the IAEA Safety Standards. A fruit of the European ALARA Network Workshop in Augsburg, Germany in October 2005 and of subsequent consultative meetings with the IAEA in February and October 2006 was the decision to collaborate on the background research and drafting that would be necessary to complete the development of such a report. The drafting process at the time of preparation of this paper is well advanced and, when published, the IAEA Safety Report on radiation protection and NORM residue management in the phosphate industry may give encouragement to the 'public good' perspective on PG regulation, while at the same time emphasizing the need to see it as a recoverable resource (co-product), not a waste.

Good PG management practice

While the emphasis of the IAEA publication will be worker, public and environmental safety, a closely allied publication, currently in development by the Stack Free? expert team consists of a White Paper on Good Phosphogypsum Management Practices (GPGMP). The alignment to Good Practice standards such as Good Clinical Practice (GCP), Good Laboratory Practice (GLP) and Good Manufacturing Practice (GMP) by design sets the prospective regulatory environment for PG in the context of well established 'good practice' methods of addressing risk management and best practices within a single, globally accepted standard. The 'GXP' process has also, by tradition and practice, brought together major stakeholders, such as government, industry, academia (centres of excellence) and international organizations in a consensus building approach to the management of processes that, while inherently risky, are of existential significance to the world as a whole — whether for the production of safe wholesome food, or safe, efficacious drugs. In particular, the International Conference on Harmonisation (ICH) [22] managed to develop and have implemented worldwide a global GCP standard [23] that both significantly reduced the negative externality of drug development (focusing on patient benefit and risk avoidance, allowing mutual acceptance of data across major markets, eliminating duplicate and repeat trials) but also demonstrated that a global standard (or protocol) could be achieved. The implementation process itself is arranged in five steps, and continues to respect local and regional differences within the global standard. This is significant in view of the need in PG regulation to preserve the concept and practice of regionality, as detailed below.

Manuals

One of the lessons learned, rather ruefully, from the literature review is the extent to which known solutions to problems have been ignored, overlooked or are simply not available. Stack Free? proposes to develop manuals, with associated management aids and decision support tools — probably on-line — to enable a better informed approach to PG management. The manuals will address to a level of operational detail topics such as PG in road beds and, where possible, will be coupled with training and support systems that effect and support knowledge transfer.

3. THE CASE FOR CHANGE

At its simplest PG is a direct consequence of the global production of food, and the case for a change of approach to PG, towards a proactive culture of safe use, is nowhere more evident than in agriculture and food production. The University of Seville, supported by the Government of Andalucia, Spain, has recently completed a case study of the progressive removal of a major stack in the estuary mouth town of Huelva [24] for use by local farmers. As is evident from Fig. 5, the town of Huelva, once remote from its PG stack, is now within 200 m of it, a process mirrored in central Florida, where once isolated stacks are now encroached upon by residential and commercial development. As a result of an injunction on PG use sought by local Andalusian environmental groups, a case based partly on their invocation of USEPA standards, the traditional practice of spreading PG on local soils (dating back to the 1950s) was suspended.

FIG. 5. Huelva PG stack and reclaimed park.

The Huelva farmers challenged the injunction and were granted relief, enabling the practice to resume. As a condition of the resumption however, the Government of Andalucia required, under court supervision, the close monitoring of phosphogypsum use in local agriculture, both for reclamation and as fertilizer, including potential environmental impact and residue take-up into crops and on into the food chain. The methodology used by Professors Abril and Tenorio and their team, whose results have demonstrated that phosphogypsum is safe and beneficial, has led to its registration under Spanish law as a fertilizer, subject of course to authorized, ‘on label’ application [25]. In addition to the benefits restored to the farmers and the local economy, Huelva also demonstrates a significant reversal of the externality effect, from negative, to positive; for in this case a former stack site has also been reclaimed for a public park, which in a densely populated area such as Huelva is of very considerable interest to the local community. While this paper is too brief to detail the principle fully, it is clear that the Huelva example shows how a regional approach to problem solving, within a framework on international standards and best practices, can achieve Nash’s goal of a redefined point of equilibrium.

The regional solution [26] has the following outline characteristics, which may form the basis for a revised regulatory approach, based on a 'regionality' principle:

(a) Transparency;
(b) Consistent global regulatory and safety standards for evidence based decision making processes, leading to local, and locally accountable, solutions;
(c) Cooperation between:
  — Local/regional government,
  — Centres of excellence, local and international,
  — Industry — producers and customers,
  — Community;
(d) Common policy objectives;
(e) Complementary, mutually reinforcing, stakeholder reasons for change;
(f) Inclusivity in decision making, but not rights of veto;
(g) Clear communications with all stakeholders;
(h) Ongoing monitoring and surveillance.

4. AN INTEGRATED, SAFE, TRANSPARENTLY REGULATED SYSTEM, BASED ON 'REGIONALITY'

Huelva demonstrates a way in which the risk of what Nash calls the 'non-cooperative game' model which has blighted US approaches to PG since 1992, can be managed into a cooperative process. This cooperative process begins with the recognition of PG as a co-product of phosphoric acid, in and of itself a 'cooperative game' tactic [27]. Inherently, the radiation safety case made against PG is inconsistent and seemingly arbitrary since, typically, there is as much radioactivity in phosphoric acid as there is in PG [28]. And at the point where the assessment of the relative risks and benefits of PG use as opposed to storage (a) affects livelihoods and (b) impacts public amenities such as parks, decision makers have a wider framework of reference to work within than the relative abstractions of numerical thresholds of activity concentration or legal definitions of waste.

In that there is a risk of regulatory 'spillover' from the USA to other countries, it is crucial that the cooperative approach prevails over the non-cooperative one. In such a cooperative mode, as ICH GCP has shown, it is possible to promulgate and support global standards and procedures without violating local accountability and adaptability to local requirements and perceptions. This is in no way to argue for a deregulation of PG, or a 'blank

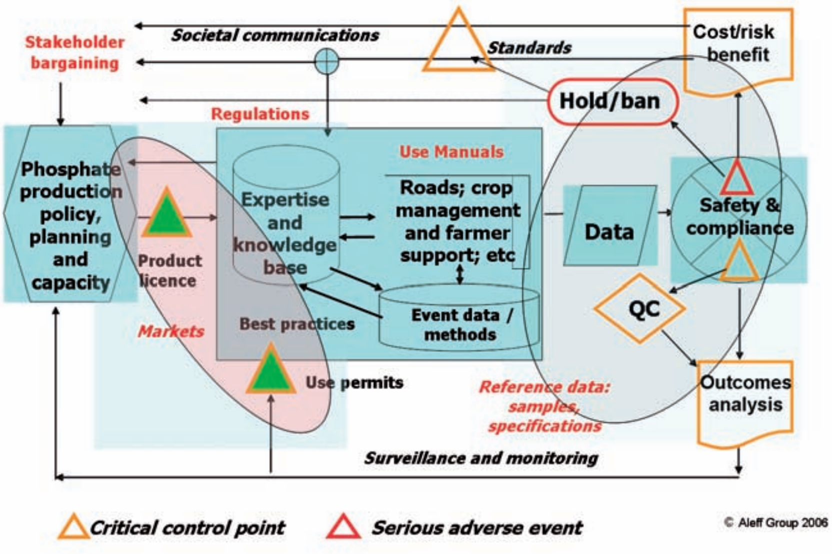

FIG. 6. Safety and public good: a cooperative bargaining solution for co-product P/PG in use.

cheque' for use. In fact, the appropriate type of regulatory regime for PG, as has been achieved in Spain, can be the basis for sustainable success.

As a contribution to the transition to a cooperative mode, the schematic diagram shown in Fig. 6 is offered as an attempt to embed Nash's methods into the regulatory process, very much in the spirit of GCP. There are risks in any process but, when well managed and independently monitored these risks are outbalanced by benefit to a sufficient extent that even in a risk vs. risk model, the risk of use is substantially lower than the risk of containment.

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RADIOLOGICAL ASSESSMENT OF THE AGRICULTURAL USE OF PHOSPHOGYPSUM IN SOUTH-WEST SPAIN: RESULTS OF A THREE-YEAR FIELD EXPERIMENT[1]

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Abstract

Phosphogypsum (PG) is a NORM material generated as a by-product of the phosphate fertilizer industries. Some 3000 t of PG are generated annually in south-west Spain. Since the 1970s, PG has been used as a Ca amendment for sodic soils in the Guadalquivir river area. Agricultural use of PG has been explicitly allowed in recent Spanish regulations. Nevertheless, attention should be paid in order to ensure radiological safety and acceptable levels of heavy metals (e.g. Cd) in agricultural products. A three year field experiment has been conducted on a 6 ha farm in the area of Marismas de Lebrija. The farm has been divided into 12 elemental plots of 0.5 ha each (20 m × 250 m). Two treatments (control and 25 t/ha PG repeated every two years) have been applied in triplicate. Tile drains are placed at 1 m below the soil horizon, longitudinally distributed and spaced every 5 m. The following potential effects of PG have been studied: ^{222}Rn exhalation in soils, ^{226}Ra and U isotope losses in drainage waters, ^{226}Ra in aerosols following PG application, ^{226}Ra, U isotopes and ^{210}Po activity profiles in soil, and soil to plant transfer of radionuclides. ^{222}Rn exhalation (measured by the charcoal canister method) showed averaged values of 30 ± 5 Bq·h^{-1}·m^{-2}, with slightly higher means and dispersions for PG plots. No significant differences between treatments could be found in ^{226}Ra and ^{238}U concentrations in drainage waters, with typical concentrations around 5 and 200 mBq/L for Ra and U, respectively. ^{226}Ra activities found in aerosols resulted in negligible doses for exposed workers. Radionuclide profiles in soils showed a relative enrichment of concentrations in the surface horizon (0–30 cm) for ^{226}Ra, U isotopes and ^{210}Po in the plots treated with PG. Finally, preliminary studies on soil to plant transfer showed

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^{226}Ra and ^{238}U concentrations under the minimum detection level in tomatoes produced in the zone.

1. INTRODUCTION

FERTIBERIA, a fertilizer factory located in Huelva (south-west Spain) owns a non-active phosphogypsum (PG) stack lying on the right bank of the Tinto river. From this PG stack, about 1 km^2 and 8–10 m deep, PG could be extracted for agricultural uses.

PG has being traditionally used since the late 1970s as a Ca amendment for the reclaimed soils from the salt marsh area of the Guadalquivir river. Recent Spanish regulations (R.D. 824/2005, from July 2005) explicitly allow the use of PG as a soil amendment. European regulations (CE 466/2001) establish upper limits for concentrations of some heavy metals (Hg, Cd and Pb) in food. The USEPA has a specific regulation for the agricultural use of PG (64 FR 5574), allowing such use if the ^{226}Ra concentration is below 370 Bq/kg. Consequently, attention should be paid in order to ensure radiological safety and acceptable levels of heavy metals (e.g. Cd) in agricultural products.

The main goal of this work is the radiological and alimentary assessment of the agricultural use of PG, a by-product of the fertilizer industry, as a Ca amendment in reclaimed salt marsh soils in south-west Spain. The work plan included: PG characterization (concentrations of radionuclide and heavy metals), experimental field studies to investigate the effect of PG in agricultural soils and drainage waters, and the soil to plant transfer of radionuclides and heavy metals.

2. MATERIALS AND METHODS

The experimental site is located in Marismas de Lebrija (see Fig. 1) where marsh soils were reclaimed from the estuarine region of the Guadalquivir river, south-west Spain (36º56’N, 6º7’W). A tile drain system was installed in 1977. After reclamation, these marsh soils were classified as Aeric Endoaquepts. In the 6 ha experimental farm, six rectangular (250 m × 20 m) plots were established. These plots were crossed lengthwise with ceramic drainage lines 250 m long and spaced 5 m apart. These tiles were placed at a depth of 1 m. The experimental design consists of two treatments: PG (25 t/ha) and control, with three replicates each, randomly distributed. PG was first applied in March 2003 and repeated in September 2004. In normal practice, PG is applied over a

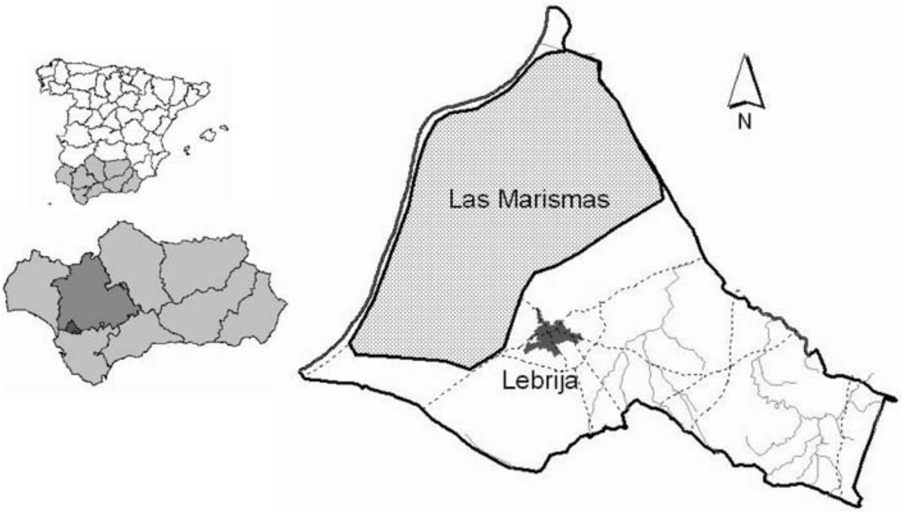

FIG. 1. *Location of 'Las Marísmas de Lebrija' in south-west Spain.*

previously tilled soil, with additional deep tillage immediately after PG application.

^{222}Rn exhalation was measured, using a total of 78 charcoal canisters, sampled in four campaigns (September and October 2004, February 2005 and February 2006), with 3 canisters per sampling point (at the centre of each control and PG amended plots) and some additional quality controls.

Studies of ^{222}Rn exhalation from PG stacks and PG characterization for radionuclides and heavy metals content are presented in a separate paper [1]. Radium-226 was measured by liquid scintillation, providing activity concentrations of 720 ± 260 Bq/kg. Lead-210 and ^{238}U activity concentrations (measured by alpha spectrometry) resulted in 660 ± 160 Bq/kg and 170 ± 110 Bq/kg, respectively. Cd concentrations (measured by ICP-MS) were 2.0 μg/g. For the rest of the elements considered in the USEPA 200.8 method, concentrations were not much higher than the corresponding ones for soils (Hg was not measured).

Soil in the experimental site was sampled at three different depths (0–30, 30–60 and 60–90 cm), with three sampling points for each plot. Sampling campaigns were carried out in March 2003, September and October 2004 and January 2006.

Soil samples were characterized for several agronomical parameters: humidity, pH, EC, cations (Na, Ca, Mg and K), P-Olsen, RAS and different forms of N. Radionuclides were measured in soil samples by gamma spectrometry (^{226}Ra, ^{40}K and ^{228}Ac) and alpha spectrometry (U isotopes and

^{210}Po). Multi-elemental analyses of soils were carried out by ICP-MS following the EPA method 200.8 and after pseudo total acid digestion.

Instantaneous fluxes of drainage waters were monitored using a simply designed recording meter based on the ultrasonic measurement of water levels in a slotted U pipe [2]. Samples of drainage water were collected following irrigation episodes in 2003 (furrow irrigated cotton crop), 2004 (sprinkled irrigated sugar beet crop) and 2005 (furrow irrigated cotton crop). Na and Ca concentrations were measured in these drainage waters (by atomic absorption spectrometry). Multi-elemental analyses of dissolved metals were carried out by ICP-MS following the EPA 200.8 method. Composite water samples from 2005 were analysed for ^{226}Ra content.

Industrial tomatoes and surface soils were sampled from several farms in the area of Marismas de Lebrija for analyses (radionuclides and heavy metals). Additional tomato samples were taken from a market survey covering different origins of production in Spain.

Soil to plant transfer experiments were conducted at greenhouse level using soils from the control plots and PG from the FERTIBERIA stack, and growing industrial tomatoes, reported elsewhere [3].

3. RESULTS AND DISCUSSION.

3.1. Radon-222 exhalation

The results are summarized in Table 1. The ^{222}Ra exhalation showed high spatial and temporal variability, with higher average values for the PG amended plots (34 $\mathrm{Bq \cdot h^{-1} \cdot m^{-2}}$ compared with 24 $\mathrm{Bq \cdot h^{-1} \cdot m^{-2}}$ for the control plots), but differences were not statistically significant due to the high dispersion. In all cases, the ^{222}Rn exhalation decreased after deep tillage (applied at the end of September 2004). The highest exhalation rate, found in September 2004, was 55 ± 19 $\mathrm{Bq \cdot h^{-1} \cdot m^{-2}}$ (PG plots). In all the cases, they are within the range of reference values for typical agricultural soils (40–200 $\mathrm{Bq \cdot h^{-1} \cdot m^{-2}}$) [4].

3.2. Soil analysis

3.2.1. Agronomical parameters

Humidity increased with depth from 13–15% in the 0–30 cm horizon up to 20–28% in the 60–90 cm depth interval. The pH was quite uniform, with a mean value of 8.4. The EC increased with depth due to the saline water table.

TABLE 1. RADON-222 EXHALATION FOR CONTROL AND PG AMENDED PLOTS

	^{222}Rn exhalation (Bq·h^{-1}·m^{-2})[a]	
	Control plots	PG amended plots
September 2004	39 ± 13	55 ± 19
October 2004	23 ± 7	30 ± 7
February 2005	13 ± 7	28 ± 29
February 2006	21 ± 8	26 ± 8

[a] Mean and standard deviation of 9 canisters (3 canister per sampling point at the centre of each plot, with 3 plots per treatment).

The concentrations of Na and Mg increased strongly with depth, while K concentrations did not show any significant variation. In PG amended plots, the Ca concentration increased in the 0–30 cm soil horizon. Differences in P-Olsen and RAS among control and PG amended plots were not statistically significant.

3.2.2. Radionuclide and Cd concentrations

The results are summarized in Table 2 for soils sampled in January 2006. The short term effect of two consecutive PG applications (April 2003 and September 2004) cannot be statistically solved (p_1) from the concentrations in surface soils (0–30 cm) for control versus PG plots. Nevertheless, activity concentrations for the elements from the ^{238}U series are quite far away from the situation of secular equilibrium, and the upper soil horizon (0–30 cm) is enriched in these radionuclides with respect to deeper layers. Both results are congruent with the cumulative effect of the historical applications of PG carried out in the area. It has to be taken into account that radionuclides from the ^{238}U series are in secular equilibrium in the phosphate ore rock, but 90% of the ^{226}Ra remains in the PG while about 85% of the ^{238}U is separated with the phosphoric acid [5]. Thus, in 2006, ^{226}Ra and ^{210}Po activity concentrations in soils (0–30 cm) were around 38 and 23 Bq/kg, respectively, compared with 13 Bq/kg for ^{238}U. The corresponding activity concentrations at the sub-surface level (30–90 cm) were 26, 23 and 10 Bq/kg for ^{226}Ra, ^{210}Po and ^{238}U, respectively. The input of radionuclides associated with PG is primarily associated with the 0–30 cm soil horizon, from where they subsequently progress to deeper layers.

Although the cumulative effect of PG can be recognized in these agricultural soils, actual levels of activity concentrations are within the range of

TABLE 2. ACTIVITY CONCENTRATIONS AND Cd CONTENT IN JANUARY 2006 SOIL SAMPLES

Sample	Activity concentration (Bq/kg)					
	^{226}Ra (γ, ^{214}Bi)	^{210}Po (α)	^{228}Th (γ, ^{228}Ac)	^{238}U (α)	^{40}K (γ)	Cd content (μg/g)
C1 (0–30 cm)	37.6 ± 1.3	22.9 ± 0.6	30 ± 2	13.1 ± 0.3	590 ± 12	0.19 ± 0.02
C2 (0–30 cm)	34.5 ± 0.6	24.8 ± 0.7	29.9 ± 1.0	11.5 ± 0.3	630 ± 13	0.21 ± 0.02
C2 (30–60 cm)	28.7 ± 0.7	17.7 ± 0.5	35.8 ± 1.1	8.5 ± 0.2	680 ± 15	0.13 ± 0.01
C2 (60–90 cm)	22.8 ± 0.8	32.8 ± 0.8	33.9 ± 1.3	9.1 ± 0.3	622 ± 8	0.09 ± 0.01
C3 (0–30 cm)	36.1 ± 0.9	36.1 ± 0.9	29.9 ± 1.1	11.5 ± 0.3	640 ± 8	0.21± 0.02
PG1 (0–30 cm)	33.9 ± 1.0	36.1 ± 0.9	30.7 ± 0.7	14.8 ± 0.3	607 ± 9	0.20 ± 0.02
PG2 (0–30 cm)	41.7 ± 0.9	32.9 ± 0.9	31.6 ± 1.3	13.2 ± 0.4	648 ± 7	0.14 ± 0.01
PG2 (30–60 cm)	29.1 ± 0.9	22.8 ± 1.4	33.5 ± 1.2	10.9 ± 0.3	670 ± 8	0.09 ± 0.01
PG2 (60–90 cm)	24.0 ± 0.9	16.8 ± 0.4	36.8 ± 1.4	9.9 ± 0.2	663 ± 7	0.07 ± 0.01
PG3 (0–30 cm)	41.7 ± 0.9	24.1 ± 0.6	36.2 ± 1.0	13.2 ± 0.3	681 ± 7	0.22 ± 0.02

Note: ^{226}Ra was measured by γ spectrometry through the 609.4 keV γ emission from ^{214}Bi, assuming secular equilibrium in sealed samples after one month of storage. (α) denotes measurements by a spectroscopy. Cd was measured by ICP-MS. Measurements were carried out by the Central Research Facilities of the University of Seville (CITIUS) and reported with 1σ analytical uncertainties.

environmental reference values for the ^{238}U series (up to 70 Bq/kg with most frequent values ranging from 20 to 40 Bq/kg).

Results for Cd are in good agreement with the above mentioned situation for ^{238}U and its daughters. Thus the concentration in the arable layer (0–30 cm) was 0.2 μg/g, twice the value for deeper layers. The remaining elements included in the EPA 200.8 method (results not shown here) have concentrations with a practically uniform distribution in depth, except for Sr and Ni with decreasing and increasing concentrations with depth, respectively.

In terms of legal reference levels for some hazardous metals for considering an agricultural soil to be polluted [6], actual measured levels for Pb, Zn, Cu, Cd, Tl and Co are an order of magnitude below such limits. Measured concentrations for As, Cr and Ni were five times lower than the respective limit concentrations and only the concentrations for V were a factor of 2 below such a limit. Considering the most restrictive concept of PNEC (predicted non-effect concentration) for Cd in soil (1 ppm), the actual levels are still a factor of 5 below this limit.

3.3. Drainage waters

Measurements of Na and Ca concentrations in irrigation and drainage waters (by AA), along with the corresponding hydrograph, allowed the estimation of net losses. Thus, net Na losses for a furrow irrigated cotton crop during the whole irrigation period in 2005 were 400 ± 50 kg/ha and 500 ± 200 kg/ha for the control and PG amended plots, respectively.

Cd was below the minimum detection level (MDL) of 0.2–0.4 ppb in most of the cases, with maximum measured concentrations below 2 ppb. For the rest of the elements included in the EPA 200.8 method for which concentrations were over their respective MDLs, concentrations were generally within the EPA standards for drinking water. Concentrations generally decreased with increasing drainage flows (note that the total volume of drainage decreased during the irrigation season as a consequence of the progressive closure of big cracks, governing the preferential flow).

The dispersion of data did not enable any statistically significant difference to be distinguished between treatments (PG and control) in drainage waters for 2003 and 2004. In 2005 (after two PG amendments), the concentrations in the drainage waters for Fe, Co, Ni, Sr and U (this last shown in Fig. 2) were significantly higher in the PG amended plots in most of the irrigation episodes. Finally, the measurement of ^{226}Ra concentration in drainage waters (sampling campaign of 2005, shown in Fig. 2) revealed non-significant differences between treatments (PG and control) and averaged values around 4 mBq/L, the same level as in unperturbed natural aquatic ecosystems. Water applied for irrigation was analysed by ICP-MS (5 independent samples). Cd was below the MDL in all the cases, while ^{238}U concentration was 1.51 ± 0.09 ppb.

3.4. Radium-226 in aerosols following PG application

During the application of PG (in March 2003), aerosol samples were taken at different points in the farm and analysed for ^{226}Ra. The results showed activity concentrations of up to 3.80×10^{-4} Bq/m^3. Doses from the inhalation and ingestion of aerosols were estimated for a worker spending 8 h per working day and 100 working days per year under these conditions. The resulting maximum doses were 11×10^{-5} mSv/a, a negligible fraction of the public dose limit of 1 mSv/a.

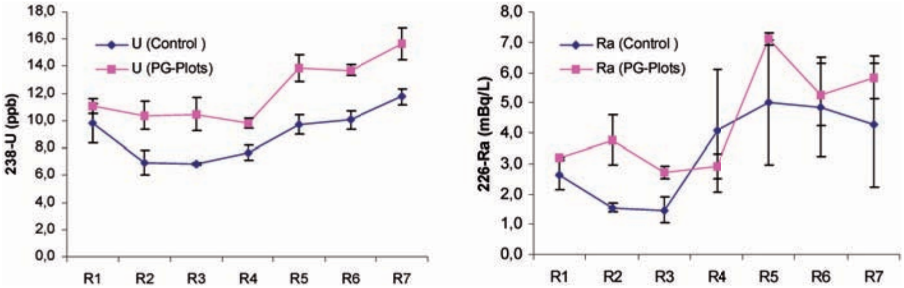

FIG. 2. ^{238}U and ^{226}Ra concentrations in composite samples of drainage waters for the seven irrigation episodes corresponding to the summer of 2005 (furrow irrigated cotton crop). Results show averaged concentrations for each treatment (3 replicates) with the corresponding standard deviations.

3.5. Soil to plant transfer

Industrial tomatoes were sampled from several farms in the area for analysis. The ^{238}U concentrations were below the MDL in all the cases. Cd concentrations ranged from 6 to 14 ppb (on a fresh weight basis). These concentrations were similar to those found in the plant plot experiments [3] and were below the threshold limit of 50 ppb. Cd concentrations in fruit were positively correlated with ^{226}Ra concentrations in soil (and thus, with the accumulated application of PG), as shown in Fig. 3.

Additional tomato samples were taken from a market survey covering different origins of production in Spain. Cd concentrations in tomatoes from the market were in the range of 0.014–0.058 ppm (dry weight), one order of magnitude lower than the industrial tomatoes from Lebrija. The concentration of ^{238}U was below the MDL.

3.6. Radiological and alimentary assessment

An estimate was made of the contribution of the radionuclides from the ^{238}U series to the radioactive doses by ingestion of food. The control group was defined as consuming 80.5 kg/a of vegetable and fruit (the average value for Spain), but produced exclusively in the area. The activity concentrations found in tomatoes (or the corresponding MDLs) were assumed to be representative of mean activity concentrations. The resulting annual doses were 9.6 μSv/a. The consumption of red crabs (potentially living in the drainage canals) was considered as the critical pathway for the contribution to the radioactive doses.

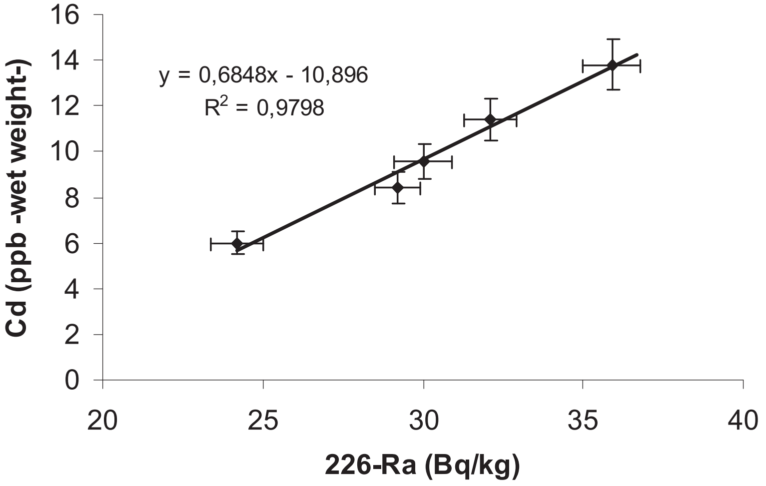

FIG. 3. Cd concentration in tomato samples from several farms in Marismas de Lebrija versus ^{226}Ra activity concentration in surface soils.

Assuming a consumption of 20 kg/a (4 times the average consumption of molluscs and crustaceans in south-west Spain), the dose received was 0.04 mSv/a (from the contribution of ^{226}Ra and U isotopes).

To evaluate potential future risks, a scenario was defined in which PG was repeatedly applied at the usual rates of 20 t/ha every two years over a period of 100 years. As a conservative hypothesis, the associated inputs of radionuclides and Cd were considered to be homogenized in the 0–30 cm soil horizon. Assuming the ^{222}Rn exhalation rate to be proportional to the ^{226}Ra concentration in this soil layer, the expected exhalation rate was 160 $Bq{\cdot}h^{-1}{\cdot}m^{-2}$, still within the range of reference environmental values (the contribution to dose was not evaluated since this depends on the ^{222}Rn concentration in air, which is defined by factors on a geological scale more than by local exhalation rates). The estimated contribution to radioactive dose by ingestion of food from vegetable origin (by using the concentration factors found in this work) increased to 0.15 mSv/a. Finally, the Cd concentration in tomatoes was close to the upper limit of 50 ppb (fresh weight).

4. CONCLUSIONS

This work proved that the actual ^{222}Rn exhalation rates in agricultural soils (average values of 34 and 24 $Bq{\cdot}h^{-1}{\cdot}m^{-2}$ for PG amended and control plots, respectively) are relatively low compared with reference values for soils.

Actual levels of activity concentrations in soils for radionuclides from the ^{238}U series are in the range of typical environmental values. The same is true for Cd concentrations in soil. The ^{238}U activity concentrations in drainage waters are close to the standards for drinking waters, but they are relatively high compared with typical values for natural non-perturbed aquatic ecosystems.

The Cd concentration in tomatoes produced in the area are within the standards of EC rules, but were higher than in market tomatoes originating from elsewhere.

As a final conclusion, PG produced in Huelva has been used in the area during the last 30 years as a Ca amendment in the agricultural soils of this area. All the experimental evidence indicates that current practice could still continue safely for several decades in compliance with current safety regulations.

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REDISSOLUTION OF ^{226}Ra FROM SEDIMENTS IN A SPANISH ESTUARY AFFECTED BY THE PHOSPHATE INDUSTRY: MODEL COMPARISONS IN THE FRAMEWORK OF THE IAEA EMRAS PROJECT[1]

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Abstract

The Huelva estuary (south-west Spain), a fully mixed tidal estuary, consists of two rivers: Odiel and Tinto. A phosphate fertilizer processing complex has been releasing NORM radionuclides directly into the Odiel river over several decades. As a consequence, high levels of ^{226}Ra, U and Th isotopes and other radionuclides have been measured in water, suspended matter and bed sediments of the estuary. Nevertheless, direct releases stopped in 1998 due to new regulations from the EU and, since then, a self cleaning process has been observed. It consists of a continuous decrease in activity concentrations in water and bed sediments. The study by means of numerical models of the ^{226}Ra self cleaning process observed in the estuary has been proposed as an EMRAS project task. A model has been proposed by each institute participating in the exercise. Models have different configurations and temporal and spatial resolutions. Some processes, for instance tides or uptake/release of radionuclides between water and sediments, are described in different ways. However, all are started from the same initial conditions, provided by the University of Seville model. The endpoint of the simulations

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[1] Work carried out in the framework of the EMRAS (Environmental Modelling for Radiation Safety) project of the International Atomic Energy Agency.

is to give the temporal evolution of the total ^{226}Ra inventory in the bed sediments of the estuary and to estimate from it the sediment halving time. A brief description of the main features of each model is provided and the results are compared and analysed.

1. INTRODUCTION

During the last few decades, a number of projects have been launched to validate models for predicting the behaviour of radioactive substances in the environment. Such projects took advantage of the great deal of experimental data gathered, following the accidental introduction of radionuclides into the environment, to assess the contamination levels of components of the ecosystem and of the human food chain. For instance, the BIOMOVS and VAMP projects stimulated intensive efforts for improving the reliability of the models aimed at predicting the migration of ^{137}Cs in lakes and of ^{137}Cs and ^{90}Sr in rivers. Similar co-operative studies for model validation were not done for other important systems such as coastal waters and drainage areas. Moreover, apart from Cs and Sr, other long lived radionuclides that may be of importance for the medium and long term effects related to environmental contamination were not the object of equally extensive validation exercises.

The activities of the working group WG-4 (Aquatic Working Group) of the EMRAS project are aimed at filling some of the above gaps. Several priorities were selected for the new intercomparison exercises to be carried out in the framework of EMRAS: radionuclides other than Cs and Sr, extreme events, physical factors dealing with remobilization and modelling of radionuclide behaviour in coastal areas. The Huelva estuary is a scenario suitable for this study in the framework of the EMRAS project.

The estuary is located in the south-west of Spain. It consists of a tidal, fully mixed estuary formed by the Odiel and Tinto rivers, which surround the town of Huelva (Fig. 1). The rivers join at the Punta del Sebo. From this point, they flow together through the same channel towards the Atlantic ocean. An industrial area, including a complex dedicated to the production of phosphoric acid and phosphate fertilizers, is located next to the Odiel river. The fertilizer plants have been the main source of natural radionuclides in the estuary — it is well known that the phosphate rock used as raw material by this industry contains significant amounts of natural radionuclides, mostly U, Th and Ra. The industrial processing of the phosphate rock leads to a redistribution of radioactivity. For instance, during the wet process for phosphoric acid production, 86% of U and 70% of Th present in the rock are transferred to the phosphoric acid itself, while 80% of the Ra content follows the so-called phosphogypsum path. This is a form of impure calcium sulphate removed as a

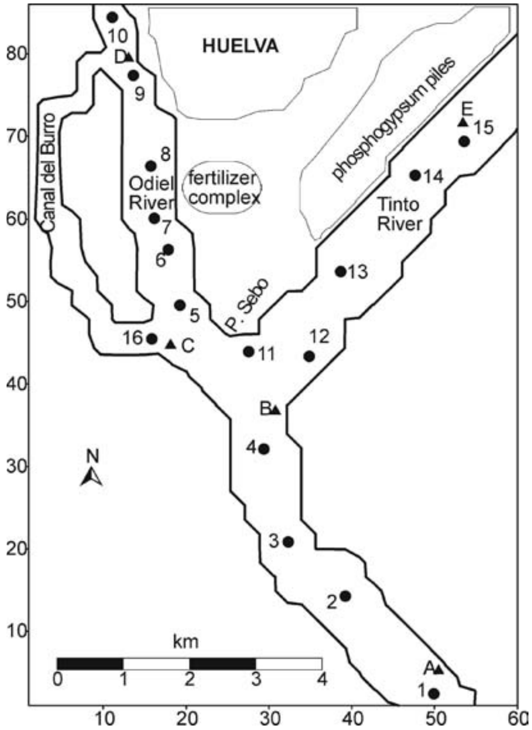

FIG. 1. The Huelva estuary showing points where samples were collected (circles) and points where current measurements are available (triangles). The location of the fertilizer complex and of the phosphogypsum piles is also shown. The Atlantic ocean is approximately 1 km to the south of point 1. Each unit in the axis corresponds to 125 m.

precipitate during the process. Phosphogypsum is usually disposed of into open air piles or discharged into rivers or estuaries, giving rise to a local radioactive impact. During 1990, for instance, 2×10^6 t of rock were processed and 3×10^6 t of phosphogypsum were produced [1]. These wastes were partially released directly into the Odiel river (20%) or conveyed with water through a pipeline to phosphogypsum piles (the remaining 80%) located by the Tinto river (see Fig. 1), where such material is stored in the open air. The gypsum piles cover some 12 km^2 of the Tinto river bank. Since 1998, phosphogypsum has not been released directly into the Odiel river owing to new EU regulations, although phosphogypsum is still being disposed of in the piles by the Tinto river. These new piles, however, are surrounded by dykes to prevent leaching to the river.

The time evolution of ^{226}Ra activities in water and sediments during 1999–2002 has been studied [1]. Results indicated that a self cleaning process was taking place in the estuary as a consequence of the new waste policy, since a systematic and continuous decrease in activity conentration was found in the water column and in bed sediments. The objective of this work consists of studying by means of different models the self cleaning process that has been observed in the Huelva estuary. A general description of the scenario is given in the following section. Next, models used in the exercise are briefly presented and finally results are discussed.

2. GENERAL DESCRIPTION OF THE SCENARIO

The estuary is very shallow (maximum depth about 19 m) and well mixed vertically due to the strong tidal currents, of the order of 1 m/s. The tidal range is about 2 m for the main tide M_2. Moreover, the stream flows of the rivers are very low (ranging from 0.5 to 70 m^3/s in usual conditions in the case of the Odiel river and even lower values for the Tinto river) and a fast dispersion of fresh water into a much larger volume of salt water occurs [2]. This mixing takes place upstream of the studied area and water salinity along the estuary may be considered constant and typical of seawater. Residual currents, due to the river discharges, are of the order of 1 cm/s over the estuary. The concentrations of suspended sediments in the estuary depend on the tidal state. Thus, minimum concentrations are expected during high and low water due to sedimentation during slack water periods. During ebb and flood periods, higher currents produce some erosion of the bed sediment. Seasonal variations must be expected as well. Nevertheless, net sedimentation rates are small and these processes have been neglected in previous modelling studies. Indeed, suspended matter concentrations of the order of a few milligrams per litre have been measured along the estuary.

The information provided with the scenario is the following:

(a) Water depths with a resolution of 125 m.

(b) Initial conditions of the simulation. These are concentrations of ^{226}Ra in the bed sediment and in the water column over the estuary. These concentrations have been obtained from a run of a model developed at the University of Seville and correspond to concentrations at the moment when direct releases from the fertilizer complex were stopped. Initial conditions also provide the partition of Ra in the bed sediment between a fast and slow exchangeable phase.

(c) Boundary conditions. These are provided in order to solve the hydrodynamics of the estuary (tidal amplitudes and phases at the estuary entrance) and radionuclide dispersion. These last conditions consist of measured concentrations at the three open boundaries of the domain.

(d) Physical characteristics of the estuary: monthly averaged river flows, sediment characteristics and suspended matter concentrations. Limited information is available on the bottom sediment characteristics. In some of the sampling points indicated in Fig. 1, the bulk density, organic matter content and fraction of muds (particles <63 μm) were measured for samples collected in 1991.

(e) Kinetic rates for radium exchange (obtained from laboratory experiments) and average distribution coefficient in the estuary. Thus the modeller may decide between using a distribution coefficient or a kinetic model for describing the interactions between the dissolved and solid phase.

The endpoint of the exercise consists of providing the time evolution of the total ^{226}Ra inventory in the bed sediment and the time evolution of the mean radionuclide concentration in the water column. Models are started from the initial conditions and the system evolves without any external source of radionuclides. Thus, it may be determined whether a self cleaning process of the system is actually predicted by the model. The timescale at which this process occurs is also of interest. Data files and a detailed scenario description may be downloaded from the EMRAS web site [3].

3. MAIN CHARACTERISTICS OF THE MODELS

A brief description of the models that have been used in the exercise is given below. The models range from box models, in which the full estuary is divided into a small number of boxes, to high resolution hydrodynamic and advection/diffusion models.

MASCARET (EDF R&D, France)

This is a 1-D hydrodynamic system for simulating hydrodynamic flows, water quality and sediment transport [4]. In the present application the hydrodynamic and pollutant transport modules of the model have been used. The interactions of dissolved radionuclides with the bed sediments have been described by means of two different approaches: a k_d based model and a kinetic model consisting of two consecutive reversible reactions [5]. The hydrodynamic module solves the shallow water equations on a looped and branched network [6]. Equations are solved using implicit finite differences. The estuary geometry was described by means of 42 profiles extracted from the provided bathymetry. The model contains 250 sections of 50 m length in the Odiel and Tinto rivers and 150 m in the common channel. The monthly water flows were imposed at both the Odiel and Tinto rivers and water elevation was defined at the entrance of the estuary from the data provided for tides. The main M_2 and S_2 tides are considered. The 1-D advection–diffusion equation in its conservative form is solved together with the hydrodynamics. The time step for calculations is 60 s.

COASTOX (IMMSP, Ukraine)

This is a 2-D depth averaged model [7]. As in MASCARET, the hydrodynamics, including tides, and dispersion modules are solved on-line (simultaneously). To diminish the computational time (the calculation time step was on the scale of minutes) the simulation was provided for periods of 10–12 days for some values of the river discharges and then the hydrodynamics were replicated for other periods with a similar magnitude of river discharges.

The interaction of dissolved radionuclides with the bed sediment is described by means of a desorption coefficient and an adsorption coefficient, which is deduced from k_d and the desorption coefficient. Thus, it is a kinetic model consisting of a single reversible reaction. The spatial resolution of the model is 125 m.

USEV (University of Seville, Spain)

The University of Seville model (2-D depth averaged) is described in Ref. [8]. Dispersion and hydrodynamics are solved off-line and standard tidal analysis is used to calculate tidal constants (amplitudes and phases) over the domain. These constants are stored and later read by the dispersion module for a fast computation of tidal currents. Thus, one year of dispersion calculations with a temporal resolution of 60 s takes a few minutes on an up to date PC. The interactions of dissolved radionuclides with the bed sediments are described through a kinetic model consisting of two consecutive reversible reactions [5]. The spatial resolution is 125 m.

ENEA model (ENEA, Italy)

The ENEA model is a box model based on quantitative evaluations and the balance of radionuclide contents in the water system components (surface water, deep water, bottom sediment) accounting for the fluxes among these. The model structure is conceptually similar to the one adopted for the submodel MARTE (model for assessing radionuclide transport and countermeasure effects in complex catchments) [9] implemented in the computerised decision support systems MOIRA [10]. The water body is divided into three sectors. Each sector is subdivided into three compartments: surface water, deep water and bottom sediment. A fourth compartment, representing the sediment interface between bottom sediment and water, is considered to simulate the quick interaction processes of radionuclides with particulate matter. The first order differential equations of the model were obtained by calculating the radionuclide budget in the system compartments from the balance between the input and output radionuclide fluxes. These are assumed to be proportional to the amount of radionuclides in the respective 'source' compartment. Eddy diffusion (horizontal, between sectors and vertical between surface and deep waters) is simulated by two way fluxes that are calculated from the difference between radionuclide concentrations in two contiguous sectors. The radionuclide absorption by suspended matter and by the sediment interface layer is modelled according to the well known k_d concept. The model is aimed at evaluating the radionuclide concentrations in the abiotic components of the water body averaged over approximately one month. Consequently, the effects due to the tidal cycle are described as an average exchange of radionuclides between the sea and the estuary water. The simulation time step is one day.

4. RESULTS AND DISCUSSION

The time evolution of the computed ^{226}Ra inventory in the sediments of the complete estuary and the mean concentration in the water column obtained with the different models are shown in Fig. 2.

All the models predict a decrease of activity in both phases. Different behaviours may be observed for the sediment phase between models that use two step kinetics (USEV and MASCARET 2-reaction) and models that use a single reaction or a distribution coefficient. In the former case, the first rapid reaction followed by a slower redissolution is clearly seen. In the second case, a continuous reduction in the inventory is obtained. A detailed view of the initial phase of the process is presented in Fig. 3, as well as the time evolution of the bed inventory after this initial phase.

It is worth commenting that there is a slight difference in the initial inventory in the bed sediment between MASCARET and the other models. This is due to the fact that MASCARET is a 1-D model, thus ^{226}Ra concentrations in the bed provided in the scenario as 2-D data had to be converted into a 1-D structure and some activity was missing in the process. From measurements in the estuary, it has been found [1] that the sediment half-time (the time in which the ^{226}Ra sediment inventory decreases by a factor of 2) is 630 d. The values of this half-time obtained with the different models may be seen in

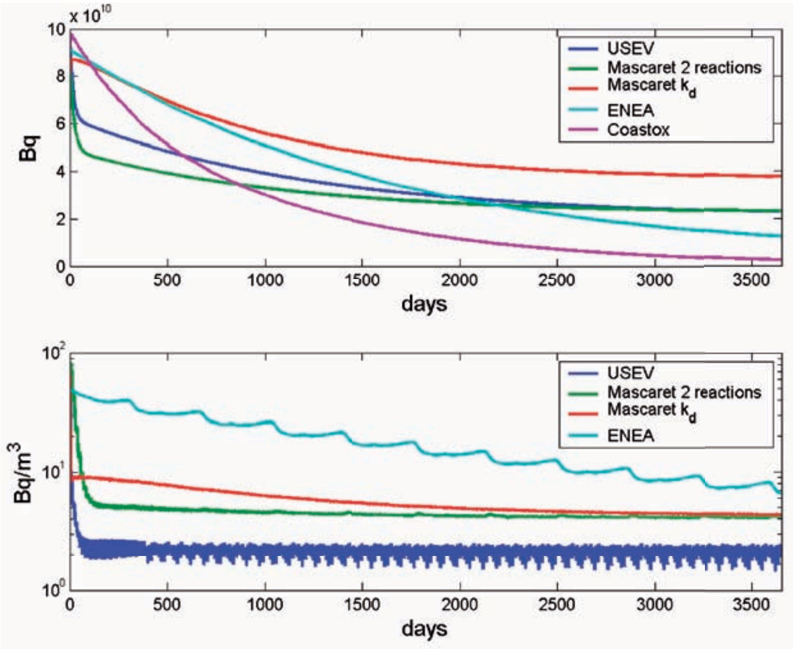

FIG. 2. Computed evolution of total ^{226}Ra inventory in bed sediments (upper) and average concentration in the water column (lower).

Table 1. Computed half-times range between some 400 and 1400 d, thus all models predict that a self cleaning process of the estuary is occurring, and the order of magnitude of the process timescale is correctly estimated as well. Nevertheless, it seems that the main differences between the models appear in the initial stages of the process. Due to the difficulty in simulating this initial phase, strongly dependent on the kind of model adopted to describe water–sediment interactions, the trends shown in Fig. 3 (lower) have been fitted to exponential decay curves and the corresponding half-times derived from them are also presented in Table 1. Thus, model behaviours after the initial phase may be compared. It must be pointed out that the first halving times are deduced from the full simulation for each model (t = 0–3650 d, looking simply at the time when the total inventory in the bed is reduced by a factor of 2) while the second ones (in the third column in Table 1) are obtained for each model after the initial dissolution phase (t = 200–3650 d, after numerical fitting to an exponential curve). It can be observed that all models give very similar results at a longer timescale, if the initial phase of redissolution is not considered, with halving times ranging from 617 to 844 d.

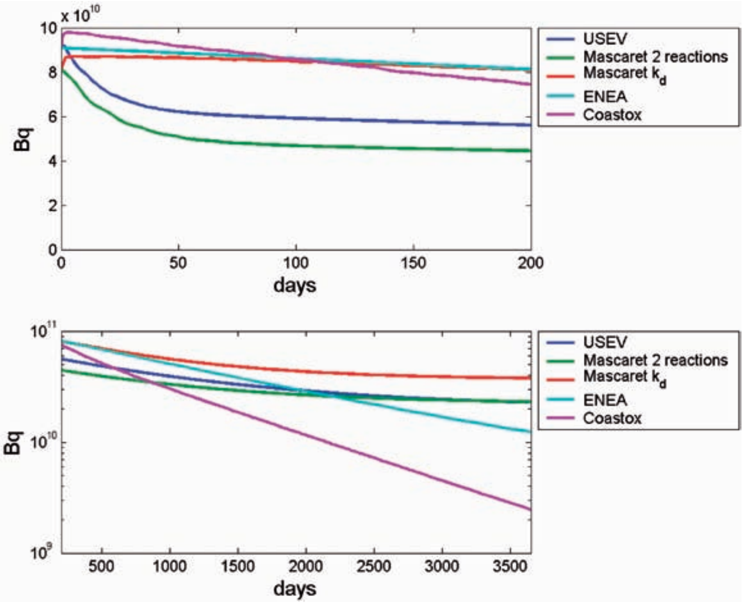

FIG. 3. Time evolution of computed inventories in the bed sediment at different timescales.

TABLE 1. COMPUTED SEDIMENT HALF-TIMES OBTAINED FROM THE FULL SIMULATIONS (t = 0–3650 d) AND AFTER THE INITIAL DISSOLUTION PHASE (t = 200–3650 d).

	Half-time (d)	
	Full simulation	After initial phase
Coastox	597	632
USEV	510	758
MASCARET 2 reactions	405	617
MASCARET k_d	1405	629
ENEA	1186	844

It may be questioned which is the most suitable water–sediment interaction description. Recent experimental [5] and modelling [11] evidence suggests that a 2 reaction kinetic model is more appropriate than a k_d or a one reaction model to describe both radionuclide uptake and release from contaminated sediments since the latter produces dissolution rates that are faster than

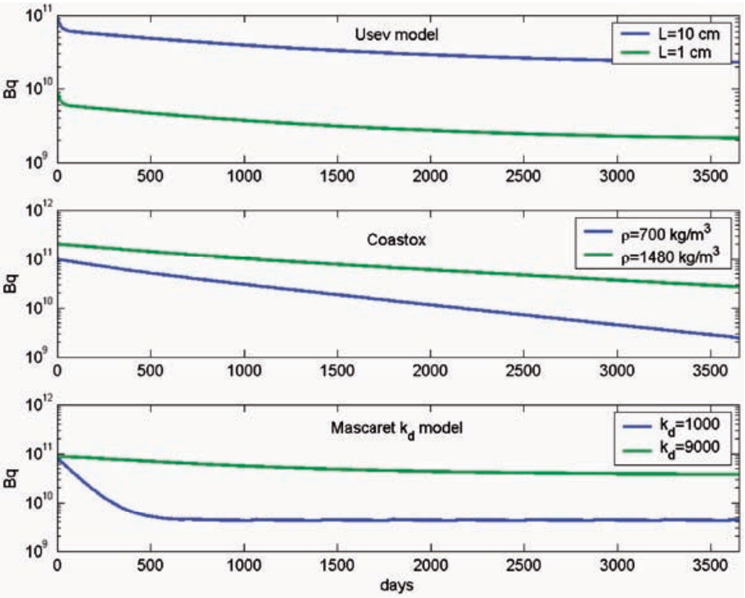

FIG. 4. Sensitivity of models to several parameters. The time evolution of the total ^{226}*Ra inventory in the bed sediment is shown. Upper: sensitivity to the sediment mixing depth. Middle: sensitivity to the sediment bulk density. Lower: sensitivity to the distribution coefficient.*

those deduced from experiments and field measurements. However, no clear conclusion can be derived from this work. Indeed, all models produce acceptable values for the sediment half-time. The main differences between models appear in the initial stages of the redissolution process, but no experimental data are available to test which ones are giving a more realistic answer.

Sensitivity tests have been carried out to study the model response to changes in some of the parameters involved. A summary is presented in Fig. 4 for several parameters and models. One of the parameters is the sediment mixing depth (the sediment depth that interacts with the dissolved phase). Since the ^{226}Ra concentrations in the surface sediment at the initial time are provided with the scenario description, reducing the mixing depth to 1 cm from the nominal value of 10 cm clearly implies a reduction of the inventory in the initial time by a factor 10. Nevertheless the model output remains essentially the same, showing a self cleaning process occurring at the same rate (results for the USEV model are shown). The COASTOX model has been tested with the nominal average sediment bulk density provided with the scenario (700 kg/m^3 from measurements) and a more standard value (1480 kg/m^3). Apart from the obvious change in the initial inventory, a similar cleaning process is obtained for both model runs. Finally, the MASCARET model has been tested with two k_d values. The mean value of the ^{226}Ra k_d measured in the estuary (36 samples), and provided with the scenario, is 9×10^3. The model has also been tested with a k_d of 1×10^3, which is closer to the value recommended by the IAEA [12] based upon a 20% fraction of exchangeable Ra in coastal sediments (0.7×10^3). A reduction of the distribution coefficient makes the radionuclide more soluble and as a consequence there is a faster self cleaning process over the first hundreds of days.

5. CONCLUSIONS

Different models have been applied to simulate the self cleaning process that has been observed in an estuary formerly affected by ^{226}Ra releases from a fertilizer complex. Models are very different in structure and resolution, from box models in which the complete estuary is divided into 3 compartments, to high resolution two dimensional models that explicitly solve tidal circulation. Water–sediment interactions are also described in different ways: distribution coefficients and kinetic models are used. In spite of these differences, all models predict that a self cleaning process occurs and that the timescale of the process ranges between some 400 and 1400 d, i.e. a few years. The main differences between models appear during the initial phase of the cleaning process. A very good agreement between models is obtained if halving times are calculated after such an initial phase. In this case they range from 617 to 844 d. This exercise also shows, as already stated [13], that a multi-model approach can be useful for the management of complex environmental assessment problems. The multi-model approach identifies those conclusions that receive the largest consensus among modellers and those that should be carefully handled.

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RAPPORTEUR SUMMARY OF TOPICAL SESSIONS 3, 4 AND 5

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1. TITANIUM DIOXIDE PRODUCTION

The uses of titanium dioxide were presented in a pie chart, which showed that coatings accounted for more than half of the total production. Information on activity concentrations was presented for the various titanium dioxide feedstocks, showing that the ^{232}Th series radionuclides were usually at higher concentrations than those of the ^{238}U series. The sulphate and chloride chemical processes, through which titanium dioxide pigments are produced, were described by means of the chemical reactions involved and the process flow charts.

Occupational exposures in the sulphate process were generally considered to give rise to doses of less than 1 mSv/a, although without proper management measures such as restricted access, supervision and logging of time they could be as high as 6 mSv/a in the hydrolysis and Moores filtration areas because of the buildup of scale. In the chloride process the effective doses received by workers were always less than 1 mSv/a. As far as environmental impacts and public exposures were concerned, no additional doses were received by members of the public from the operation of the process.

Here I am taking the liberty of reproducing the guideline of OSHA (Occupational Safety & Health Administration of the US Department of Labor):

> “Safety glasses, goggles, or faceshields should be worn during operations in which titanium dioxide might contact the eyes (e.g. through dust particles). Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with titanium dioxide. Contact lenses should not be worn if the potential exists for titanium dioxide exposure.”

Is ^{232}Th the reason for this OSHA guideline? Apparently, it is not. The concentrations of ^{232}Th and its progeny are negligible in TiO_2 pigment. There are reported to be cases of a rare liver disease afflicting persons working with titanium oxide pigments and having weak immune systems.

There was a statement that the radionuclide concentration in gypsum derived from the sulphate process was low and of no concern, whether used as a product or disposed of as waste.

2. EXTRACTION AND PROCESSING OF RARE EARTHS

It was reported that monazite, until recently the most important resource for rare earths, has a total rare earth oxide content of 42–61%, a uranium oxide content of 0.18–0.45%, a thorium oxide content of 4.6–9.6% and a phosphate content of 18–27%. It was pointed out that this was one NORM industry where inhalation of thoron (^{220}Rn) could be a significant radiological hazard.

Information on the separation and chemical processing of monazite was presented. Mill tailings from the monazite separation process, which contain unrecovered monazite and have a gross alpha activity concentration of 50–80 Bq/g, a gross beta activity concentration of 250–300 Bq/g and a radiation field of 30–50 μGy/h, are recycled to the mill. Typical gross alpha and beta activity concentrations in solid wastes from the chemical process can be up to several thousands of becquerels per gram and typical radiation fields can be up to several hundred microgray per hour. Nearly 250 kg of thorium concentrate (thorium hydroxide cake) is produced per tonne of monazite processed, and has to be disposed of in engineered silos.

It is significant to note that the occupational exposure in the production of rare earths from monazite gives rise to a typical collective dose of about 0.6 man mSv per tonne of rare earths concentrate produced. In a plant processing 3000–4000 t of monazite annually, the individual worker doses over the past 25 years have been in the range of 3–9 mSv/a. This is quite a high annual dose compared with those received by workers in most other NORM industries.

In an investigation of the processing of a phosphate ore containing rare earths it was reported that, with regard to waste management and product quality, the deportment of radioactivity is determined primarily by the behaviour of the parent radionuclides and the decay chain progeny, which have comparatively long half-lives. The results indicated differences in behaviour between uranium and radium. What about the surface-to-volume ratio which is remarkably increased after grinding and flotation?

In another paper, thoron daughter concentrations in a monazite storage facility in the Urals were measured and discussed. The equivalent equilibrium concentration for thoron (EEC_{Tn}) was 60–700 Bq/m^3, giving rise to the inhalation by storage facility workers of thoron gas with an activity concentration of 1600–14 000 Bq/m^3, as well as monazite dust.

Using the ICRP model of radionuclide transfer from the respiratory tract to body fluids, dose coefficients for inhalation of ^{212}Pb aerosols were estimated. An important conclusion from this work is that the dissolution of ^{212}Pb aerosols in body fluids can be described by the superposition of two exponential dependencies, with the rate of fast dissolution being $\lambda_f = 145$ d^{-1}, the rate of slow dissolution being $\lambda_s = 2$ d^{-1} and the part of the activity with the fast rate of dissolution being k = 0.3. Furthermore, the most appropriate monitoring method for inhalation intake of ^{212}Pb aerosols is the direct measurement of whole body activity. The assessment of ^{212}Pb inhalation intake by urinary excretion is possible for a sample collection time of 8–12 h, but the total activity of the sample will be only 1.5–3 Bq for a total intake during the working shift of about 1000 Bq. This new information should be brought to the attention of UNSCEAR.

3. EXTRACTION, PROCESSING AND USE OF PHOSPHATE MINERALS

It has been pointed out that published data on the radionuclide and metals contents of worldwide phosphate rock, wet acid process products and phosphogypsum (PG) are highly variable in time of sampling, analysis methods and parameters chosen for analysis. Thus, a ‘global radioactivity database’ to characterize and benchmark activity concentrations in the various process materials is proposed, in order to foster good management practices for the phosphate industry.

Inhalation dose characterization suggests that the most probable doses for individual workers in phosphate processing are less than 0.05 mSv/a in all situations except for product shipping and storage (up to 0.8 mSv/a). It was pointed out that inhalation doses were very likely to be overestimated.

It was observed that the International Basic Safety Standards (BSS) provide standards for protection applicable to NORM, and that further consideration of some NORM issues will take place during the current revision process for the BSS. Important inhalation dose parameters have recently been measured and published, and an IAEA Safety Report for the phosphate industry is in draft. Most sedimentary phosphate rock has a radionuclide concentration of less than 2 Bq/g and much of this is at a level of less than 1 Bq/g. Inhalation doses are well below 1 mSv/a, even for the more highly active phosphate rock. In many cases, personal monitoring achieves no practical benefit and no regulation is necessary. It is important to carefully consider these data when forming regulatory policies in order to avoid over-regulation.

The Institut Mondial du Phosphate (IMPHOS) has commissioned experts to investigate the implications of applying the requirements of Euratom Directive 96/29 to the phosphate industry, and has taken account of new developments reported in all the previous NORM symposia. It has concluded that the natural radioactivity levels in phosphate rock are not much different from normal levels in soil and that the exposure of workers in the industry is insignificant.

A study carried out in South Africa to determine the radiological impact on members of the public of two companies that mine and beneficiate an igneous ore body — a copper mine and a phosphate plant — has concluded that the radiological impact is generally less than or marginally above the statistical variation in natural background. Estimated doses were far below 1 mSv/a. Nevertheless, problems had been experienced in dealing with concerns from the surrounding community. It was recommended that the radiation protection management system should be presented in the same terms as ISO 14001, a system known to the general public.

In a presentation on the management and regulatory strategy for phosphoric acid and PG as co-products, it was mentioned that the regulatory approach in the USA had been driven by a concern about the potential risks from the radioactivity in PG. It was mentioned that in the USA, PG production is approximately 150 million t/a, and that worlwide production was set to increase significantly in the future. If a solution was not found soon to overcome the acceptability problem of using PG as a resource in agriculture, construction materials, landfill/waste and roads, the PG tonnages stored worldwide could be expected to double by 2025–2040.

It was interesting to note the yearly evolution of PG research publications, had been decreasing in the USA (the world's largest PG producer) since the 1980s, while continuing to increase in the rest of the world.

The current situation was summarized in terms of developments within the IAEA, which had recognized the need to consider PG as a resource and was currently developing a Safety Report on the phosphate industry, and within the 'Stack Free' international research initiative, which was working towards the development of a white paper on good PG management practice and detailed manuals at the operational level to promote a better informed approach to PG management.

Considerations in the agricultural use of PG were discussed, taking into account ^{222}Rn exhalation from soils, ^{226}Ra and U isotopes in drainage waters and ^{226}Ra in aerosols. In an investigation in Spain, it was found that ^{222}Rn exhalation rates in agricultural soils are only moderately increased, and that the radionuclide activity concentrations (as well as the Cd concentrations) in the soil remained within the normal range of environmental values. The Cd concentration in tomatoes produced in the area are within standards, but were higher than in market tomatoes originating from elsewhere. PG produced in Huelva has been used in the area during the last 30 years as a Ca amendment in agricultural soils. All the experimental evidence indicates that current practice could still continue safely for several decades in compliance with current safety regulations.

A comparison of environmental models in the framework of the IAEA Environmental Modelling for Radiation Safety (EMRAS) project was presented for the Huelva estuary in Spain. This estuary had previously been subject to radiological impact by a fertilizer plant and PG piles and was currently undergoing a self cleaning process. The time evolution of the computed ^{226}Ra inventory in the sediments and water was obtained from full simulations and after an initial dissolution phase. The main differences between the models appeared during the initial phase of the cleaning process. A very good agreement between models was obtained when halving times were calculated after this initial phase. In this case they ranged from 617 to 844 days.

SCRAP RECYCLING AND WASTE MANAGEMENT

(Topical Session 6)

Chairpersons

U. QUADE
Germany

A.J. VAN DER WESTHUIZEN
South Africa

Invited Paper

RADIOLOGICAL CONTROL OF METAL SCRAP: THE 'SPANISH PROTOCOL'[1]

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Abstract.

In 1998 an orphan ^{137}Cs source was accidentally melted in a steel plant located in the south of Spain. This source was introduced in the recycling process after being mixed inadvertently with a large quantity of metal scrap, provoking enormous public commotion. The national authorities, before implementing any legislation, and in a decision that can be considered as revolutionary, decided to bring to the table all the main actors that could be involved in the problem. These included representatives from different administrative organs and from the different industrial sectors involved in the problem, creating a working group which produced, after long negotiations and open discussions, the Voluntary Protocol for Radiological Surveillance of Metallic Materials. This protocol, based on the principle of collaboration, is now commonly known internationally as the Spanish Protocol and, after eight years of implementation, has drastically transformed the Spanish situation regarding the control of sources and NORM materials associated with metal scrap. In fact, this protocol has resulted in Spain achieving international prominence in the control of radioactive materials with respect to metal recycling. The details of the protocol (how it works), the positive aspects associated with its implementation and an evaluation of the main results and outputs obtained after the passing of around eight years since its launching are summarized in this paper.

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[1] Further information can be obtained from the following websites: www.mityc.es/Nuclear/Seccion/Vigilancia/; www.recuperacion.org; www.bir.org; www.unesid.org; www.csn.es; www.enresa.es.

1. ORIGIN AND MAIN CHARACTERISTICS OF THE PROTOCOL

In June 1998 a highly radioactive ^{137}Cs source was accidentally melted in the Acerinox steel plant in Cadiz, southern Spain. This source was introduced into the recycling process after inadvertently being mixed with a large quantity of metal scrap. Part of the radioactive content of the source was released to the environment and dispersed by the prevailing winds, mainly towards the Mediterranean Sea. Minute traces of ^{137}Cs originating from this accident were even detected by sensitive monitoring systems in northern Italy and Switzerland. The accident caused adverse national and international publicity, affecting the industrial sector involved with the recycling of metal scrap, as well as the Spanish public bodies and institutions involved in the control, regulation and surveillance of radioactive materials.

As a consequence of this accident, the Spanish Parliament required the national regulatory body to adopt the necessary measures for the control and proper management of metal scrap circulating within the country to address the risk of accidental incorporation of radioactive sources or NORM. However, before implementing any legislation, and in a decision that can be considered as revolutionary, the Spanish government decided to create a forum for dialogue between the different public and private stakeholders in order to analyse the problems and seek possible solutions. Over a period of 18 months, this group discussed different alternatives in an open atmosphere. The final result was the signing, on 2 November 1999, of the Spanish Protocol on Radiological Surveillance of Metal Recycling (the ‘protocol’).

This protocol was initially signed by the following institutions of the Spanish administration: the Ministry of Industry and Energy (MINER), the Ministry of Infrastructure, the Spanish Nuclear Security Council (CSN) and ENRESA (a public company undertaking the management of radioactive waste generated in Spain), and by the following associations of the industrial sector: the Steel Utilities Association (UNESID) and the Metal Recovering Association (FER). At a later stage, the protocol was also signed by the following metals related industrial associations: the Aluminium Utilities Association (ASERAL), the Lead Utilities Association (UNIPLOM) and the Copper Utilities Association (UNICOBRE), as well as by the main Spanish unions: the Unión General de Trabajadores (UGT) and the Comisiones Obreras (CCOO). The signed protocol was the final output after very long and detailed negotiations and is based on the following main points:

(a) It is voluntary.

(b) It promotes, as an essential step, a common knowledge of the problem and the search for possible solutions through continuous training. (All working and administration levels are involved in this point.)

(c) It recognizes the recovery plants and smelters as ‘collaborators in the system’ and not as ‘criminals who have to be prosecuted’. In other words, the protocol can be characterized by the label “the polluter pays, not the finder”.

(d) It includes different mechanisms for its revision where necessary, on the basis that “we should learn from our mistakes”.

(e) It provides for free and continuous training of workers in the metals and scrap industries, because experience shows that it is not enough to have very good equipment if the workers that use it do not know how to operate it and what the data mean.

(f) It works on the basis of sharing of costs by all the agents involved in the chain (authorities, scrap and steel companies and radioactive waste managers). The objective is not to find ‘a head to be cut’ but rather to find a solution to the problem.

A highlight of the protocol is that every signatory gives and receives something and its innovative approaches have been recognized internationally. The protocol has provided the basis for a European Council recommendation and is now being used by the United Nations as a basis for guidance on the radiological control of metal scrap.

2. COMMITMENTS OF THE PARTIES TO THE PROTOCOL

One of the positive aspects of the protocol is that it defines in a clear and unambiguous way the commitments of the various parties to it, in order to facilitate smooth and proper implementation. The most important commitments of the main signatories are:

(a) MINER:

- To create and continuously update a Register of Collaborators of the Protocol communicating, at the same time, new registrations to the various signatories;
- To grant a generic transfer authorization of detected radioactive material from the relevant facility to ENRESA;
- To govern special interventions in case of serious accidents giving rise to radioactive contamination;

(b) Ministry of Infrastructures:
- To require radiation monitoring certification from the metal scrap importers, as a mandatory step before authorizing the unloading of scrap at Spanish harbours;
- To inform the CSN in case of any radiological event related to the entry of foreign scrap at Spanish harbours or land frontiers;

(c) CSN:
- To issue safety guidance to the parties involved in the protocol, in a generic manner as well as case by case;
- To inspect periodically the monitoring systems of metal recycling and melting facilities;
- To set up radiological criteria and particularly to fix investigation levels (NI) and exemption (NE) levels;
- To inform the industrial sector and ENRESA about the applicability of the protocol;
- To promote training activities;
- To direct interventions when such actions are needed;

(d) ENRESA:
- To manage the disposal of radioactive material detected by the recycling and melting facilities;
- To collaborate in the re-export of radioactive material detected in scrap of foreign origin;
- To give technical advice to the industrial sector;
- To collaborate in training activities;
- To sign a specific agreement with each facility included in the protocol for the management of the radioactive material detected in their installations;

(e) Scrap recovery and melting facilities:
- To install, maintain and operate an appropriate monitoring system in each facility;
- To completely control the radiation levels in all scrap and materials processed in their facilities;
- To take all the necessary and appropriate measurements for avoiding radiological risks;
- To require radiological monitoring certification from the suppliers of foreign scrap and/or material to be processed;
- To inform the CSN of each relevant event involving the detection of radioactivity;
- To sign a specific agreement with ENRESA for removal and proper management of radioactive sources or NORM detected in their facilities;

— To collaborate in training activities, contributing in the formation of its personnel in radiological protection issues.

With these very well defined commitments, the protocol is applied in the manner explained in the following section.

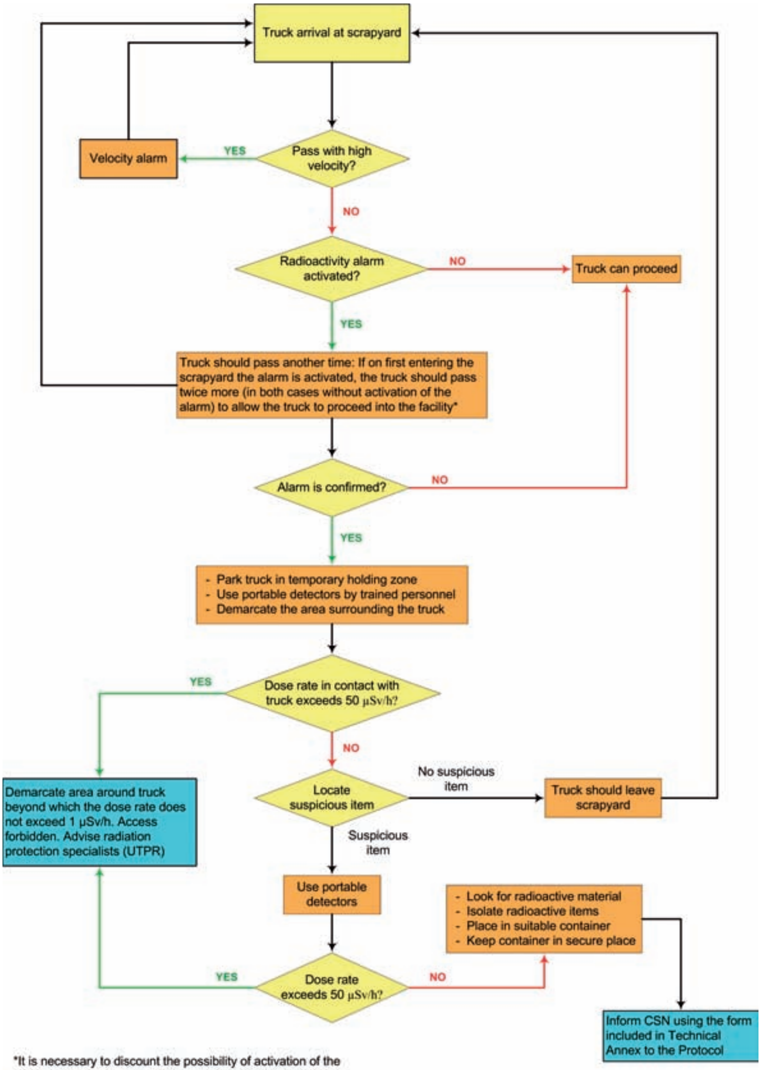
3. THE PROTOCOL: HOW IT WORKS

The working procedure of the protocol, reflecting its appropriate execution, is illustrated in Fig. 1. The flow diagram shows in a clear and unambiguous way the steps to be followed for appropriate control of all the metal scrap and materials processed in Spanish metal recovery and melting plants. The working procedure is based on full monitoring, using calibrated monitoring systems at scrap yards, of the scrap and processed materials entering the facilities. If during one of these surveys the investigation level fixed by the CSN is exceeded (i.e. the alarm of the scrap yard is triggered), the consignment concerned is halted and an immediate investigation is carried out. After checking that the alarm was not triggered as a result of medical radiation treatment of the truck driver or accompanying person, the dose rate is measured using portable instruments in contact with the truck.

If the dose rate exceeds 50 μSv/h (case A), a zone around the affected consignment should be marked such that at the perimeter of the zone the dose rate does not exceed 1 μSv/h. In addition, access to the zone should be immediately prevented, the services of a radiation protection technical unit (UTPR) should be brought in and the CSN should be immediately advised.

If the dose rate does not exceed 50 μSv/h (case B), the radioactive material causing the alarm to trigger should be located and identified. If the dose rate measured in contact with the identified material exceeds 50 μSv/h, the same measures as for case A should be taken. However, if this dose rate is not exceeded (case C), the procedure is still not complete — the identified radioactive material should be first segregated, characterized and isolated (see Fig. 2), and then guarded safely in proper containers until ENRESA removes it and proceeds with its management and disposal. In addition, the affected facility should inform the CSN of the event. This notification should be performed by completing a standard form, which has been agreed upon by the signatory parties and included in the protocol as a technical annex.

Finally, it is necessary to highlight the essential role of ENRESA in managing the detected radioactive material with known foreign origin. This management includes the re-export of the material when applicable.



*It is necessary to discount the possibility of activation of the alarm due to medical treatment of truck drivers with radiation

FIG. 1. Flow diagram of the working procedure reflected in the protocol

FIG. 2. Pieces containing radioactive material identified in a Spanish metal recycling facility by applying the working procedure of the protocol.

4. THE PROTOCOL: EIGHT YEARS OF EXPERIENCE

With eight years now having passed since the launching of the protocol, it is now possible to perform a critical evaluation, highlighting the principal strong points of the protocol and main results of its implementation. There has been a steady and uninterrupted growth in the number of signatories to the protocol — 109 Spanish facilities having now signed up, comprising 79 recycling companies, 26 iron and steel industries, 2 melting companies and 2 aluminium refining companies. The current signatories include all the steel melting plants, most of the shredding plants and some other scrap yards, and these are soon to be joined by other non-ferrous plants. In these facilities, 14 million t of material are checked radiologically at least once per year.

Thanks to the work and investments made by the signatory companies, it can be stated with confidence that there is now a radiological control net of scrap material in place with appropriate and improved monitoring systems. As a result, radioactive materials are being removed under proper control and at the same time the number of detections is increasing, as evident from the data shown in Fig. 3. The numbers of notifications per year are shown in Table 1.

The increase in the number of detections is obviously related to the increase in the number of signatories, although indirectly it is also related to the improvement in the quality and effectiveness of the monitoring systems and the improved awareness of the workers involved in the control of the scrap metal. The effectiveness of the protocol in the control of radioactive material mixed or associated with metal scrap can also be deduced by examining the data

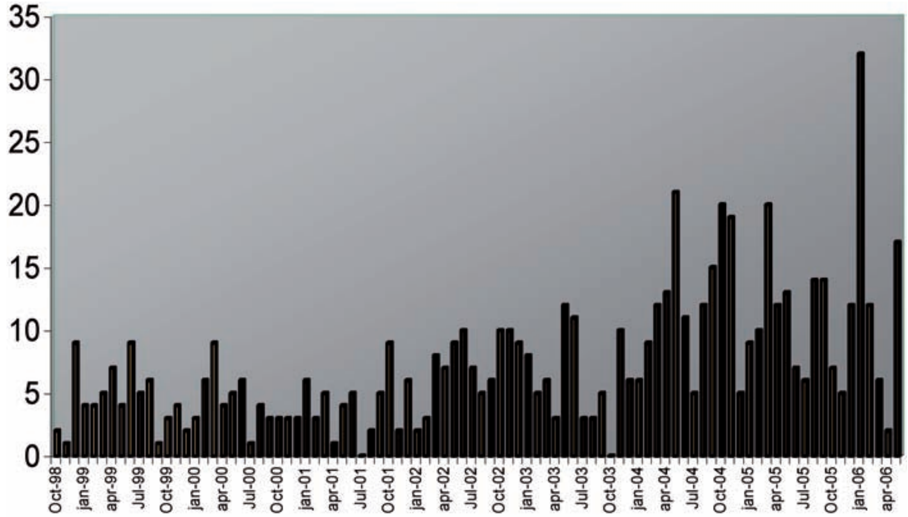


FIG. 3. Evolution in the number of detections of radioactive material per month performed by the signatory companies to the protocol.

presented in Fig. 4, which shows that 31% of detections worldwide in 2005 occurred in Spain, a much greater percentage than the size of the Spanish metal recycling and smelting sector relative to the rest of the world. This high percentage of detections in international terms is the clearest and most reliable indicator of the success of the protocol, and should not be misinterpreted as suggesting a ‘poorer’ quality of scrap metal treated in Spanish facilities or a lower level or absence of radiological control by the scrap suppliers.

TABLE 1. DETECTION OF RADIOACTIVE MATERIAL IN SCRAP

Year	Notifications
1999	54
2000	50
2001	47
2002	86
2003	72
2004	141
2005	129

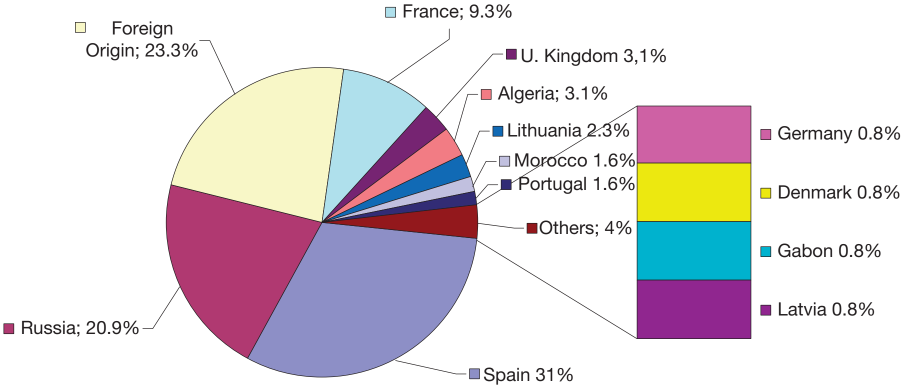


FIG. 4. Relative numbers of radioactive material detections in metal recycling and melting facilities during 2005, by country.

Important additional information can be obtained from the database of radioactive material detections in Spanish facilities reported since the launch of the protocol. First, it can be seen from Fig. 5 that various radionuclides are involved. Although there are significant detections of radionuclides generally associated with orphan sources, such as ^{137}Cs, ^{60}Co and ^{241}Am (22%, 11% and 4% of notifications, respectively), the radionuclide most often detected (60% of notifications) is the natural radionuclide ^{226}Ra, a member of the ^{238}U decay series.

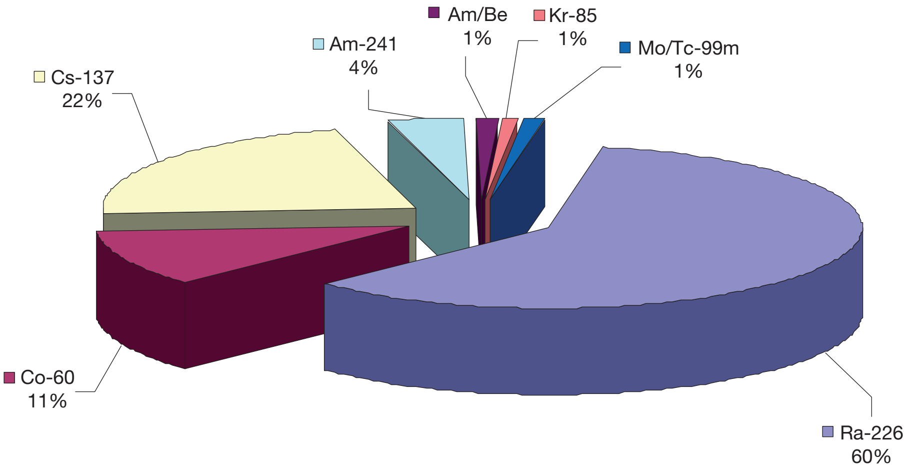


FIG. 5. Main radionuclides detected in Spanish metal recycling and melting facilities in terms of the protocol.

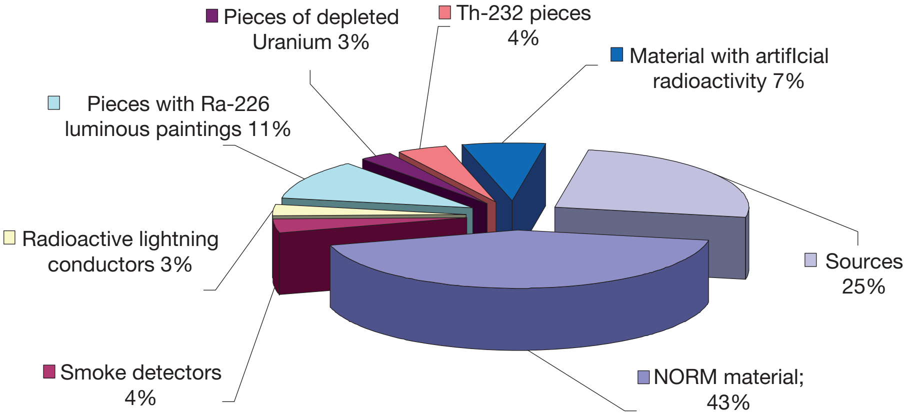


FIG. 6. Average distribution of the different types of radioactive materials detected in Spanish metal recycling and melting facilities.

Figure 6 shows that typical orphan sources represent only 25% of the radioactive materials detected and, from rough estimates, only about of 10% of these were considered to have significant radiological implications. NORM accounted for the largest percentage of materials detected (43%), consistent with the finding that ^{226}Ra was the most frequently detected radionuclide. The NORM originates from pipes and other equipment in which scales are present, heavily enriched in radium isotopes and adhering tightly to the inner surfaces. These scales are basically formed by precipitates of barium and strontium sulphates and calcium carbonates and are caused by solubility changes associated with temperature variations, pressure changes, etc. The scales can contain ^{226}Ra at concentrations of up to several thousand bequerels per gram and, as reported in several other papers at this symposium, are typically found associated with pipes and equipment of companies involved in the extraction of oil and gas. However, radium scales can also be found in other, quite different NORM industries, such as the production of phosphoric acid and phosphate fertilizers using sedimentary phosphate rock as raw material and the production of titanium dioxide using ilmenite as a feedstock.

5. CONCLUSIONS

The protocol is the result of the joint efforts of a group of individuals over a period of almost two years. The key point of this joint work is that all the members of the working group came to an understanding of the position of the rest of the group. Only with this effort has it been possible for the representatives of the scrap metals industry to understand how important is to be able to control a piece of scrap no bigger than a pea and for the representatives of the radiation protection bodies to understand why it may be impossible to know the origin of every small piece of scrap.

The protocol works because:

(a) It is voluntary;
(b) There are no guilty people but, instead, collaborators in the system;
(c) There are shared costs between all the members: the scrap industry, the steel industry, the government, etc.

To implement a solution on a global basis, a broader understanding of the real dimensions and possibilities of the model for the protocol is needed. If governments are just looking at saving money in the short term and trying to find some ‘heads to cut’, more and more orphan sources and NORM will continue to be melted with disastrous consequences.

The problem needs to be analysed from a broader perspective, looking for long term solutions. The steel and the scrap sector are not the problem, they are the solution, the only solution.

ACKNOWLEDGEMENT

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ESTIMATION OF PERSONAL DOSE WHILE PROCESSING NORM CONTAMINATED METAL SCRAP

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Abstract

In 1998 Siempelkamp Nukleartechnik started to operate a special melting shop at the Krefeld site. Contaminated metal scrap resulting from decommissioning of natural oil and gas production plants, the mining industry, fertilizer production and groundwater extraction is melted in order to transfer the contamination such as mercury and NORM into the slag and the dust, enabling the decontaminated metal to be recycled. Usually, NORM contamination results from the radium decay chain ^{226}Ra and/or from the thorium decay chain. According to the German radiation protection ordinance, based on the Euratom radiation protection recommendations, an observation of the working areas is necessary if the dose caused by NORM during the total disposal process exceeds 1 mSv/a. To determine the worker doses, measurements were made in 2005 in various ways. Besides long term TLD dose measurements, workplaces were measured with electronic dosimeters for 24 h periods. Additionally, the workers wore personal dosimeters during their working time. The working time at each workplace was documented to be able to weight the daily dose for the specific workplace. Contrary to the dose from external radiation, a former study has shown that incorporation of radionuclides into the body is negligible. Due to the possible mercury concentration in the air, all of the workers wear breathing apparatus with a filtration factor of 99.997%. No radioactivity has been detected by urine analyses. The resulting personal doses calculated from the measurements are approximately 0.08–0.3 mSv/a, which is in the range of previous results, ascertained only by TLD dose measurements.

1. INTRODUCTION

In a special melting plant at the Siempelkamp site in Krefeld called GERTA, which started operation in 1998, contaminated metal scrap is treated to remove chemical or radioactive contamination. The material mainly comes from decommissioning in the oil and gas production industries [1, 2] (see Fig. 1). The chemical as well as the radioactive contamination appears in the scale inside pressure pipes, where the predominant process is the precipitation of the radioactive isotope ^{226}Ra. After a short period, about a month, the daughter nuclides ^{218}Po, ^{214}Bi and ^{214}Pb are found to be nearly in equilibrium with ^{226}Ra. The activity concentration found in the pipe scale is up to 1000 Bq/g. Given that the scale represents 0.5–5% of the total amount of material, this gives a maximum overall activity concentration of 50 Bq/g.

Another kind of material has its origin in the production of tungsten welding electrodes and lighting filaments. Thorium at 2–4% is added to the tungsten to improve its thermal and luminous efficiency. The resulting activity concentration of ^{232}Th is found to be in the range 12–15 Bq/g. The treatment of these materials and the generated waste leads to an exposure of workers, which needs to be examined in relation to the dose limits given in Refs [3, 4].

2. MOTIVATION FOR THIS STUDY

About 50% of the incoming scrap is contaminated only with chemical substances. The other 50% is also (or only) contaminated with NORM. The Euratom radiation protection recommendations [3] and the German Radiation Protection Directive [4] require the monitoring of radiation doses if the dose, during handling of the waste, is likely to be more than 1 mSv/a for any person. To ascertain whether this limit is exceeded in the melting shop, various dose measurements were necessary.

FIG. 1. Examples of contaminated pressure pipes from the oil and gas industry and waste material from the tungsten welding electrode industry.

3. MEASUREMENTS

Most of the measurements were carried out in 2005 during industrial training at Siempelkamp Nukleartechnik [5]. To get an overall view of the exposure conditions, this investigation was aimed at estimating workplace exposure levels and not the dose actually received by workers. First the exposure conditions and the exposure time were determined for each workplace. Next, exposure measurements were carried out in different ways to get an average exposure for each workplace. In particular, stationary measurements with thermoluminescent dosimeters (TLDs) and electronic personal dosimeters (EPDs) (see Fig. 2) were carried out, as well as direct dose rate measurements and measurements of personal dose.

3.1. Stationary dose measurements

To obtain an accurate stationary reading during melting and dismantling operations in the GERTA plant, nine dosimeters were positioned and monitored on a daily basis during each of the melting and dismantling operations. The workplace EPD provided the most complete data set for a daily resolution of the workplace dose. The EPDs were placed in the following locations:

(a) Outdoor storage;
(b) Thermal cutting room;
(c) Shear control balcony;
(d) Shear bin (exit materials);

FIG. 2. Measuring equipment: EPD, TLD (installed at shear exit) and area dose rate meter.

(e) Intermediate storage;
(f) Melting oven console;
(g) Furnace control room;
(h) Pouring/slag removal;
(i) Filter dust (outdoors).

TLDs are routinely placed in five locations throughout the GERTA facility and are replaced approximately every three months. These dosimeters provide accurate data over the three month period. For this investigation, these data are the most accurate for calculating the annual dose, as they are obtained over a longer time frame. The TLDs are positioned in the following locations:

(1) Melting oven, furnace control desk;
(2) Intermediate storage;
(3) Shear control balcony;
(4) Thermal cutting room;
(5) Shear exit bin.

3.2. Direct dose rate measurements

Direct dose rate measurements were made for all critical work areas during a dormant period, when neither dismantling nor melting was occurring. These dose rate measurements were made during a period of approximately 1 h, giving the average dose rate in this time period, which could be regarded as representative of the total background dose for the GERTA facility. Direct dose rate measurements were made in the following work areas:

(a) Shear/thermal cutting room;
(b) Melting hall;
(c) Pouring and slag removal;
(d) Outdoor storage.

The measurements show for most of the areas monitored a natural background dose rate for the Siempelkamp site in Krefeld of about 0.10–0.11 μSv/h, which leads to a daily dose of approximately 2.5 μSv. This background dose rate was subtracted from the TLD and EPD dose rate measurements. Data were not gathered at the site of the filtration system since previous studies had shown the dose rate in this location to be negligible and undetectable, because the filtration system mainly contains lead and polonium isotopes such as ^{210}Pb and ^{210}Po.

3.3. Personal dose measurements

In addition to stationary EPDs, the workers were instructed to wear dosimeters during their shift work while dismantling and melting NORM materials. In addition to EPD dose monitoring, the workers recorded approximately how much time they spent in each of the primary working areas.

4. MEASUREMENT RESULTS

Data were recorded for two measurement campaigns involving dismantling and melting of NORM materials. The third measurement campaign involved only the dismantling of NORM materials over a two week period. From the different sources of data, the dose rate was calculated for each of the work areas or activities in the GERTA plant. Each method gave a different result because each was only accurate for the given time frame and some methods often did not provide information for the full working area for GERTA.

4.1. Results of stationary dose measurements

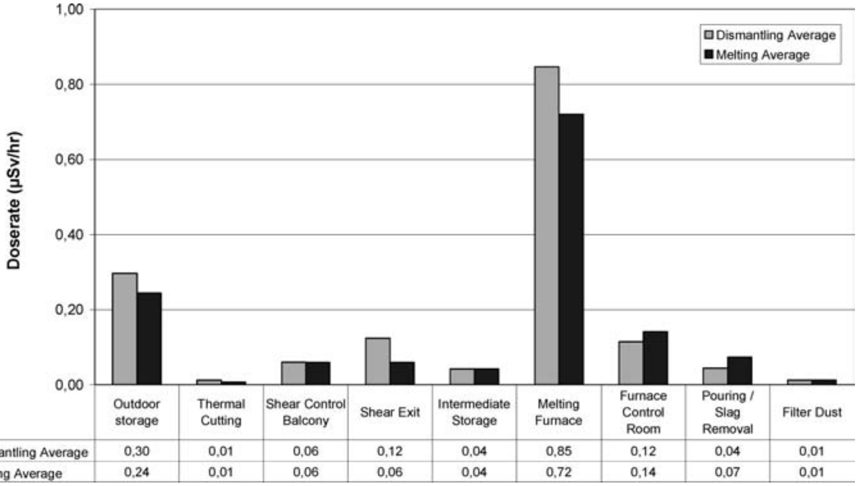
The data from the workplace EPDs were recorded on a daily basis to determine the dose rate, but a weighted average was used over the accumulated time frame for the melting or dismantling campaign. Therefore, in determining the overall average for the dose rate of a certain work area, the campaign with the longest duration of exposure gave a greater accuracy than those with shorter recording periods.

During dismantling, the primary work areas were the outdoor storage, thermal cutting, shear control balcony and shear exit. The remaining workplaces were not used since melting was not occurring during this time. For the work areas where dismantling occurred, the outdoor storage yielded the highest dose rate of 0.30 μSv/h, followed by the shear exit bin (from which all the dismantled materials exit) at 0.12 μSv/h. The dose rate in the thermal cutting room was at background level.

Melting activities are conducted primarily in the furnace hall, the outdoor filtration area, the pouring and slag removal area and the outdoor storage area. Following the trend of the dismantling data, the furnace hall had the highest average dose rate of 0.72 μSv/h. The outdoor storage area had the next highest dose, similar to the dismantling data trend. This knowledge is rather trivial, because the primarily dose rate is not produced by the handled material, but much more by the stored waste. The high dose in the outdoor storage does not merit concern for the workers, since the time they spend doing outdoor work is significantly less compared with their other activities within the GERTA plant. The location where pouring and slag removal takes place gave an average dose rate of 0.07 μSv/h and the location where the filter dust is packed contributed a negligible dose rate, since the bulk of the active material is deslagged.

For the workplace EPDs, the comparison between melting and dismantling is shown in Fig. 3. Although, in terms of dose rate, only the outdoor storage, intermediate storage and furnace control room are independent of the melting and dismantling processes, the thermal cutting room, shear control balcony, intermediate storage and filter dust locations also appear to be equal in dose rate to one another, regardless of the radioactivity. During dismantling, the shear exit has a higher dose rate than when not in use during melting. It is interesting that the furnace area was slightly lower during melting than while not in use during dismantling. The reason for this was the presence of drums with floor sweepings with higher activity, i.e. residues from the shear and the thermal cutting, stored in the furnace room during the dismantling campaign — they raised the dose rate. Also, the furnace control/computer room was close to the floor sweepings and the dose rate here was higher than during normal conditions when such materials were absent.

Radiation measurement using TLDs is a regular practice at GERTA. Over the past six years, TLD reports have been analysed to get a weighted average (dependent on exposure time) for each of the five areas (see Section 3.1). They



	Outdoor storage	Thermal Cutting	Shear Control Balcony	Shear Exit	Intermediate Storage	Melting Furnace	Furnace Control Room	Pouring / Slag Removal	Filter Dust
□ Dismantling Average	0,30	0,01	0,06	0,12	0,04	0,85	0,12	0,04	0,01
■ Melting Average	0,24	0,01	0,06	0,06	0,04	0,72	0,14	0,07	0,01

FIG. 3. Comparison of workplace dose rates measured by EPDs for melting and dismantling.

give a comprehensive, and perhaps the best estimate of, the dose rate for GERTA over a longer time period, in this case three months. To be able to calculate the workplace dose from the TLD dose, the average exposure time for the workplace is needed. Therefore the workers note the time for each activity in which they were involved in an exposure area. From these notes, an average time spent was calculated and allocated to this special workplace. Figure 4 shows the percentage of the time spent in the melting and the dismantling areas.

Figure 5 shows a comparison between the measured area dose and the time weighted area dose. As expected, the working area around the furnace

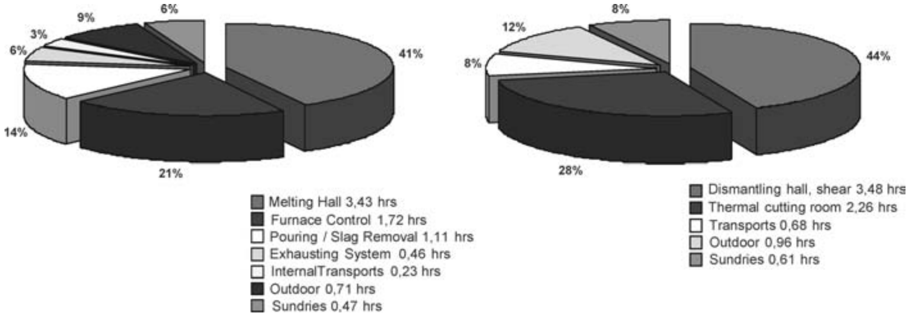


FIG. 4. Time spent for various activities in the melting area (left) and the dismantling area (right).

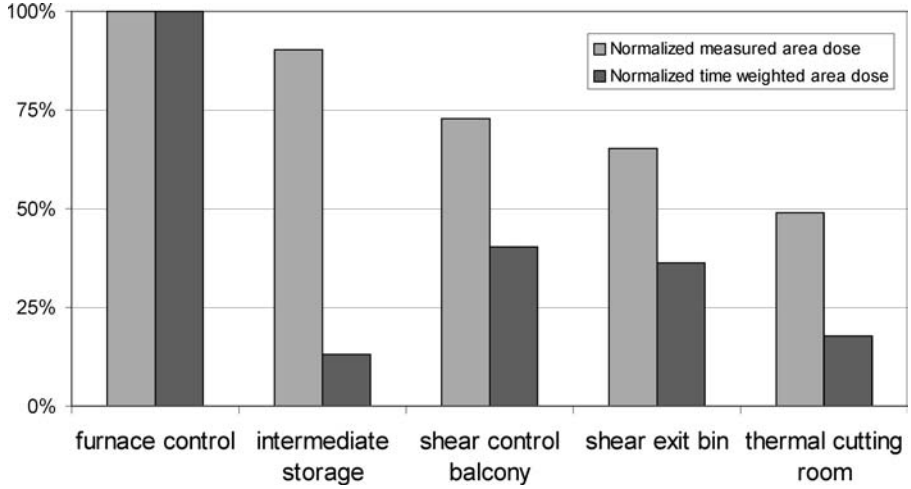


FIG. 5. Comparison of weighted and unweighted normalized area doses for different workplaces.

control gave the highest correlation. This is because the distance from the TLD to the contaminated material is similar to the distance in the real workplace. For the workers at the furnace control, pouring and deslagging, the working distance is less than while dismantling at the shear. Although the measured dose is nearly as high as at the furnace, the time weighting leads to the lowest workplace dose because the time spent at the intermediate storage is very short.

Figure 6 shows the dose timeline for the two main working areas: the furnace operation platform and the shear. As can be seen from the fitted curves in the diagram, the dose rate of the melting process follows the dismantling process with a time gap. Additionally, the dose near the furnace is much higher than during dismantling. This can be explained by two effects. One is that the worker is closer to the contaminated material during slag removal and slag packaging than during dismantling. On the other hand the activity concentration associated with the melting process is much higher in the slag than in the incoming and dismantled material. Note that the dose rate in Fig. 6 consists of raw data from the TLDs and is only qualitative. The data are not corrected for background or work time.

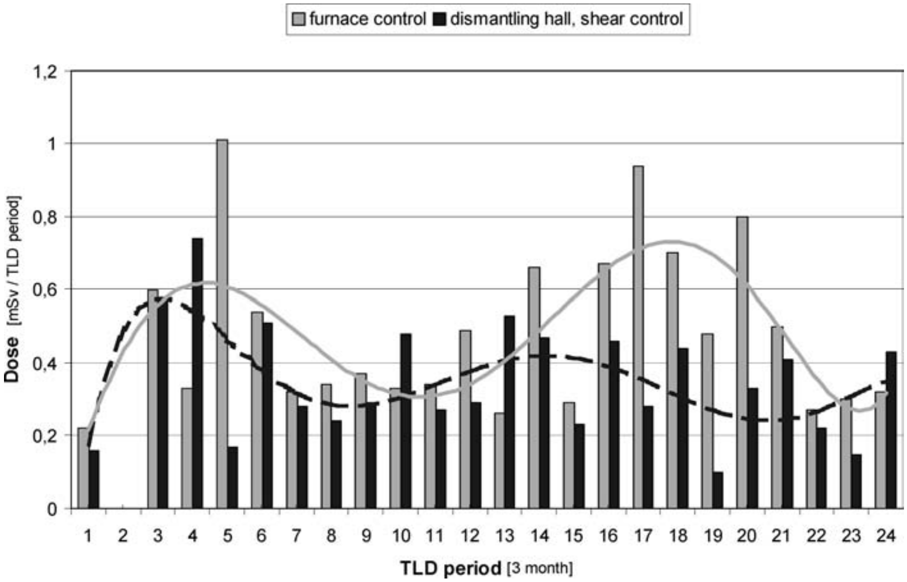


FIG. 6. Comparison of melting and dismantling over a period of 6 years. This is TLD raw data not background corrected and not corrected for one shift.

4.2. Results of personal dose measurements

From the worker notes, the dose per shift and the average time spent on each activity for dismantling and melting as mentioned above was provided for the duration of the three campaigns. From these notes, the overall average dose for dismantling was 2 μSv per shift or 0.25 μSv/h. The overall average dose for melting was 4 μSv per shift or 0.5 μSv/h. Assuming alternating melting and dismantling campaigns of equal time segments, an average dose rate for the GERTA plant is calculated to be 0.38 μSv/h. However the doses recorded for dismantling were averaged over a shorter period, and hence a smaller amount of data contributed to the accuracy of the dismantling compared with the doses recorded for melting.

In the same way that TLD work time was weighted, the workers' directly measured doses were also weighted by the approximate time spent at each activity. The breakdown of their work schedules per shift, on average, is shown in Fig. 4 for dismantling and melting. Dismantling activities are dominated by work at the guillotine shear and thermal cutting hall, whereas the melting activities are dominated by work in the furnace room and the furnace control panel.

The dose rates were statistically extrapolated from the workers' EPDs. This method was a crude method as it assumed that the dose for a single worker per shift was the same for each activity. By averaging the dose rate with the time spent for a specific activity in that shift, and then averaging the data over all shifts, a very crude dose rate for each work activity was obtained. Compared to the workplace EPDs, direct dose measurements and TLDs, this method is a statistical extrapolation and its values are rather inaccurate in conveying the dose rate in the GERTA facility. However, since it is not possible to determine exactly what fraction of the recorded dose was due to any specific activity during the shift, the dose was multiplied with the fraction of the shift spent at a specific activity in order to obtain the dose rate.

5. COMPARISON OF THE DIFFERENT METHODS OF DATA ACQUISITION

It is possible that the different methods of measuring workplace doses lead to different results. Workplace EPDs and TLDs are fixed in position, whereas the workers' EPDs during the working time are at various distances to the contaminated material. As an example, Fig. 7 shows a comparison of three workplaces during dismantling. The doses for the shear and the intermediate storage are all in a small range, with a maximum deviation of 25%. The discrepancy of the measured doses in the thermal cutting room shows very clearly the result of significant variations in distance to the contaminated material.

6. CONCLUSIONS

Approximately half of the activities in GERTA are spent handling NORM, the other half dealing with toxic contaminants, primarily mercury. Based on these annual time statistics, and the average percentage of time spent at each activity (recorded from the worker notes), in addition to the dose rates acquired from the direct dosimeter readings, workplace EPDs and TLDs, the annual dose per worker can be calculated (Table 1). Except in the melting area, the TLDs gave the highest calculated annual dose. It is interesting that the TLD measurements give nearly double the doses given by the personal EPDs, which should give the most precise total dose.

From this point of view, the TLDs gave a sufficiently conservative dose with a maximum dose of approximately 0.3 mSv/a for the working areas in GERTA. Assuming they can be positioned in a practical way according to the working conditions, for instance a measuring point at an average working

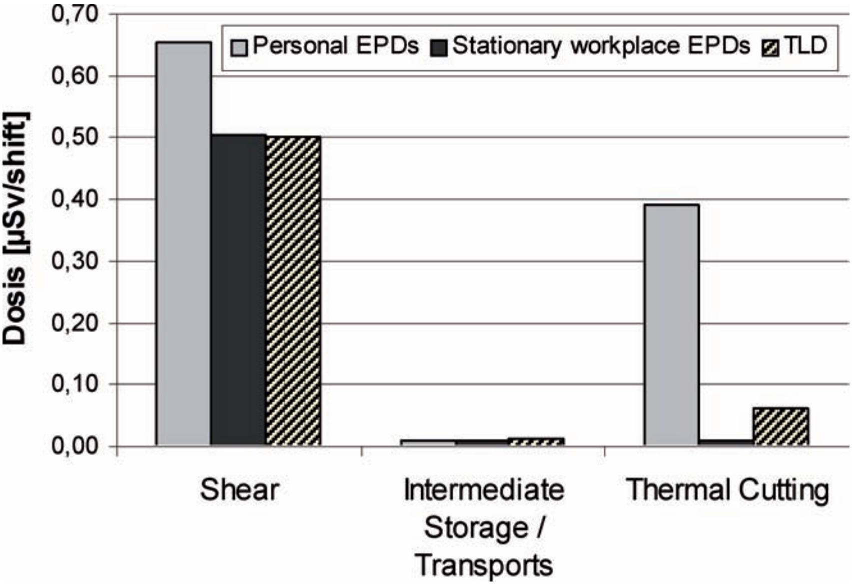


FIG. 7. Comparison between the different measuring methods.

TABLE 1. DOSES ASSOCIATED WITH THE DISMANTLING AND MELTING AREA

Measuring method	Anual effective dose (mSv)		
	Dismantling	Melting	Total
Personal EPD	0.04	0.10	0.14
Stationary EPD	0.03	0.26	0.29
TLD	0.07	0.21	0.28

distance to the contaminated material, TLD measurements are easy to carry out and give a good conservative estimate for the real working situation.

All the calculated doses in Table 1 are specified without any value of uncertainty. The reason is that there are many different sources of uncertainty in the various measuring methods, besides those associated with the measurements themselves, and they are not clearly defined up to now. In detail they are:

(a) The frequent changing of workplaces when the dose rate is very low makes it difficult to assign a dose for a single workplace;
(b) As mentioned before, it is not correct to assume that the dose for a single worker per shift is the same for each activity;
(c) Averaging the dose of the workplace EPDs, and more especially the TLDs, and weighting by the working time reduces the effective dose (this effect was already taken into account);
(d) Storage of floor sweepings in the furnace hall led to an overestimation of the workplace dose for this area.

Nevertheless, the results gained up to now show that the NORM processing activities in the GERTA plant result in doses to workers well below 1 mSv/a. The investigation will be continued during further NORM campaigns in GERTA.

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A STUDY CONCERNING NORM IN INTEGRATED STEELWORKS

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Abstract

Integrated steelworks are significant as far as NORM is concerned, as confirmed by literature data indicating enrichment in natural radionuclides during some steps of steel production. A study concerning an integrated steelworks was performed by the Regional Agency for the Environmental Protection of Veneto (ARPAV), together with the National Agency for the Environmental Protection and for Technical Services (APAT). The main steps of the standard working cycle for integrated steelworks are described. Natural radionuclide activity concentration measurements were carried out in samples from two integrated steelworks (coke production residues, blast furnace dust and sinter dust). Enhanced levels of ^{210}Pb and ^{210}Po are recorded for some dust and residue samples; elevated values of these nuclides (more than 40 Bq/g) are shown in sinter dusts, suggesting the development of estimates of the dose delivered to population in their environmental path.

1. STEEL PRODUCTION IN INTEGRATED STEELWORKS

Iron and steel production from iron ore is well known: ores, coke and melting materials are fused at 2000°C in a blast furnace to give pig iron, which is further converted into steel; coke is prepared through coal distillation at 900°C; iron ores are usually subject to sintering before use in the blast furnace, a thermal process (1400 °C) aimed at obtaining adequate size and physical resistance.

Dust is generated in thermal processes (coke distillation, sintering, blast furnace fusion) and is partly precipitated and partly emitted in air. Water and tar are formed as residues of coke production. These dusts and residues may have a natural radioactivity content, transferred from iron ores, that could be of some interest from the radiological point of view. In the literature, elevated values of ^{210}Pb and ^{210}Po are reported in dust from sinter and blast furnace processes as a result of enrichment following volatilization [1]. Similar cases occur in other high temperature treatments such as zircon sand fusion for refractory material production [2].

In Italy, only four integrated steelworks still operate [3]. ARPAV carried out a small survey on two of these in 2004–2005, collecting samples of dust and residues of the kind just mentioned. The assessments of radioactivity content are presented. It should be noted that the sintering process was active in one plant only (plant 1).

2. SAMPLING AND ANALYTICAL METHODS

Samples of various materials were collected in the two plants, in 2004 for plant 1 and in 2005 for plant 2. Details of the materials are given in Tables 1 and 2. ARPAV analysed the samples for ^{238}U, ^{226}Ra, ^{235}U, ^{232}Th and ^{40}K by gamma spectrometry, while APAT produced estimates of the ^{210}Pb and ^{210}Po content through radiochemical analysis. Uranium-238 was assessed through its decay product ^{234m}Pa. Radium-226 was assessed through its decay products ^{214}Pb and ^{214}Bi, with secular equilibrium being restored by keeping the samples in a sealed aluminium beaker for a month. Thorium-232 was assessed through its gamma emitting decay products. As far as gamma spectrometry is concerned, the coincidence summing, in particular for ^{214}Bi, and self-attenuation effects have been corrected through GESPECOR software. The radioanalytical methods for the determination of ^{210}Pb and ^{210}Po activity concentrations were based on (a) sample pretreatment, (b) radionuclide separation, and (c) source preparation. Finally ^{210}Po was counted by α spectrometry and ^{210}Pb by a low background beta counter.

3. RESULTS AND DISCUSSION

The activity concentrations for all samples are shown in Tables 1 and 2. The data refer to the year of measurement (2005 for plant 1 and 2006 for plant 2).

TABLE 1. ACTIVITY CONCENTRATIONS IN MATERIALS FROM PLANT 1

	Activity concentration (Bq/kg)						
	^{238}U	^{226}Ra	^{210}Pb	^{210}Po	^{235}U	^{232}Th	^{40}K
Tar (coke production)	3 (24)	<0.3	181 (10)	177 (10)	<0.7	1 (19)	<3.0
Blast furnace dust (sample 1)	18 (22)	26 (7)	665 (10)	632 (10)	<1.0	11 (7)	83 (6)
Blast furnace dust (sample 2)	20 (22)	22 (7)	1583 (10)	1544 (10)	6 (34)	11 (8)	242 (6)
Sintering dust (common electrostatic precipitator)	27 (22)	32 (6)	1167 (10)	1058 (10)	2 (27)	5 (11)	180 (6)
Sintering dust (weep electrostatic precipitator)	<15	24 (7)	47 243 (10)	42 867 (10)	<4,0	7 (19)	6219 (5)

TABLE 2. ACTIVITY CONCENTRATIONS IN MATERIALS FROM PLANT 2

	Activity concentration (Bq/kg)						
	^{238}U	^{226}Ra	^{210}Pb	^{210}Po	^{235}U	^{232}Th	^{40}K
Coke quenching water	<5.0	<0.3	13 (30)	7 (20)	<0.8	0.3 (16)	3 (11)
Coke oven take out dusts	21 (23)	15 (8)	14 (20)	2 (15)	6 (32)	10 (9)	30 (9)
Blast furnace dust (secondary off-gas at filterpress)	17 (23)	15 (7)	1461 (15)	1146 (10)	<1.1	5 (9)	30 (8)
Blast furnace dust (primary off-gas at APO)	8 (24)	13 (8)	324 (15)	296 (10)	<1.2	6 (9)	67 (7)

For plant 1, enhanced concentrations of ^{210}Pb and ^{210}Po are shown in all samples, reaching particularly high levels in dust from the sintering process (weep precipitator). All other nuclides of natural origin are at moderate or low concentrations. In plant 2, where the sintering process is not present, an increase of ^{210}Pb and ^{210}Po in blast furnace dust is observed, similar to that occurring in plant 1 (and again no anomalies appear for the remaining radionuclides). Generally, the high values in dust of ^{210}Pb and ^{210}Po depend on the enrichment due to volatilization in the high temperature processes.

These results indicate that care is need when dealing with residues from thermal processes of integrated steelworks, both for dust emitted into the atmosphere from the stacks and those destined for disposal as solid waste. This is particularly true for dust produced in the sintering process.

The dose received by the local and global population for releases into the air and for leaching at disposal sites is being calculated using specific modelling codes.

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RADIOLOGICAL IMPACT ASSESSMENT FOR LANDFILL DISPOSAL OF NORM WASTES IN MALAYSIA

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Abstract

In Malaysia, a radiological impact assessment (RIA) report has to be compiled in order to comply with the Atomic Energy Licensing Act 1984, Act 304 and the Guidelines LEM/TEK/30 SEM.2, September 1996 for activity related to the landfill disposal of NORM wastes. Most of the NORM problems in Malaysia are associated with tin mining, mineral sands processing and oil production activities. The Malaysian Nuclear Agency has experience in conducting the RIAs for the disposal of NORM wastes by landfill. This paper describes an example of RIAs to dispose of tin slag at a specified site in the northern region of Malaysia.

1. INTRODUCTION

Tin was at one time the primary export commodity for Malaysia. Nowadays, only a handful of facilities are still operational and in active business owing to a decrease in demand and rising operating costs. Given the current climate, methods and ways are being sought to overcome the problems related to the future disposal of the waste.

In Malaysia, any practice that involves the use of radioactive materials is governed by the Atomic Energy Licensing Act 1984 [1] and its subsidiary legislation. Guidelines LEM/TEK/30 SEM.2, September 1996 [2] were introduced by the Atomic Energy Licensing Board (AELB) addressing issues and activities involving NORM produced by the oil and gas industries. At present, this is the only guideline available for addressing issues related to disposal of NORM wastes. According to the guidelines, for disposal purposes the operator is required to carry out a radiological impact assessment (RIA) for all proposed disposals to demonstrate that no member of the public will be exposed to more than 1 mSv/a from all activities/sources.

The Malaysian Nuclear Agency (Nuclear Malaysia) has been engaged by a local company to do an RIA study on the use of tin slag as fill material for reclamation works at a specified site in the northern region of Malaysia. Since land is scarce in this part of the northern region, the company decided to make full use of the land by reclaiming it and converting its status to a light industrial area. The tin slag was chosen because 85 000 t were already available at the site, resulting from approval by the AELB as a temporary storage site. The tin slag was produced by a smelting company and has been found to contain slightly higher amounts of NORM as a result of the direct physical separation process of the tin ore (the feed material) during downstream processing. The area of concern was about 27.4 acres of swampy land with fully grown small trees and bushes. Before the reclamation work there were no human activities in the areas around the site [3].

2. METHODOLOGY

This study analysed and assessed the possible radiological impact on identified critical groups of the population working on the proposed disposal site. The study was carried out by:

(a) Determining the source term of the NORM present in the tin slag involved;
(b) Referring to the radiological criteria set by AELB;
(c) Identifying the critical group or groups of the population affected directly or indirectly by the radiological exposure from the site;
(d) Identifying the critical pathways that allowed the radionuclides identified in the source term to reach the critical group(s) and eventually give rise to the maximum radiation dose.

The expected annual dose results were compared with the permissible levels adopted as a guide, i.e. 1 mSv/a for individual members of the public and 1 man Sv in a year for the collective dose of the overall population.

3. SOURCE TERM

Tin slag is the residue produced during the smelting of tin ores. The concentrations of radionuclides in the tin slag were found to be 0.95 Bq/g ^{238}U, 0.42 Bq/g ^{232}Th, 4.57 Bq/g ^{226}Ra and 1.11 Bq/g ^{228}Ra [3].

4. EXPOSURE SCENARIO AND CRITICAL GROUP

The exposure scenario considered in this assessment covered only the potential impact on the individuals working on the site (i.e. in the warehouse), in other words an industrial use scenario. In this scenario, the potential exposures considered were those for individuals working in a building (warehouse) constructed over the disposal site. No occurrence of erosion was considered, as a result of assuming that the integrity of the contaminated zone area (tin slag layer of thickness 0.5 m) and the building foundation would be maintained. Various depths of clean soil cover were analysed and a soil cover of 1.2 m was chosen for the optimum estimated dose and viability of the reclamation project. The warehouse workers were assumed to be the critical group in this assessment. The workers were assumed to work on-site for 8 h per day, 5 days per week. The exposure time was assumed to consist of 8 h indoors and 1 h outdoors on-site. The exposure pathways evaluated included external, dust inhalation and radon inhalation. The water supply was assumed to come from an unaffected off-site source. Four hundred and sixty four individuals were assumed to work on-site corresponding to the affected area considered in the assessment.

5. MODELLING AND ANALYSIS

Dosimetric models were established based on the public and exposure scenarios identified. The radiological impact on the critical group working on-site as a result of slag disposal was analysed using models using the RESRAD 6.3 computer code [4]. Inputs to the code were mostly based on the site specific data. They were obtained from the measurements made by Nuclear Malaysia and from the reports made available to Nuclear Malaysia by other relevant government agencies. Any unavailable local data were adopted from default figures recommended by RESRAD, which in most cases were found to be very conservative [5]. Default or estimated values were used in cases where no site specific input parameter values were available. Uncertainty in the values of these parameters introduces an uncertainty in the overall dose estimates. Therefore, in order to evaluate the potential effects of such uncertainty in the critical parameters, a limited sensitivity analysis was performed. These default values were assessed and chosen to be the most realistic for the conditions on-site. However, as a normal practice in any impact assessment, the values were chosen in such a way that use of these values in any situation would not result in underestimation of the dose (slightly conservative).

6. RESULTS OF ANALYSIS

The results of the analysis and the graphic presentation for the industrial scenario are shown in Table 1 and Fig. 1, respectively. It is clear from these results that the maximum total dose expected to be received by members of the critical group working on the proposed site (in warehouses) as a result of the disposal of the tin slag is 0.45 mSv/a. The estimated annual doses are found to be below the dose limit of 1 mSv/a. From Fig. 1 it can be seen that the radionuclide which gives the most significant contribution to the total dose is ^{226}Ra. The dose decreases with time due to the leaching process taking place. Owing to close proximity of the site to the sea, dilution of radionuclides was expected. Based on the projected size of the workforce on the site, i.e. assuming 464 individuals (industrial use scenario), the collective dose received by this group was estimated to be 0.21 man Sv. As with the individual doses, this estimated dose also falls within the acceptable collective dose limit criterion, namely 1 man Sv.

7. CONCLUSIONS

Based on the RIA study conducted, the site chosen was approved by the AELB for disposal of tin slag and for reclamation of the land for construction of warehouses (i.e. industrial use). All future developments and new projects (if they exist) other than those described above for the reclaimed land should be subject to the submission of a new RIA report.

TABLE 1. DOSE CALCULATED FOR THE INDUSTRIAL USE SCENARIO

Elapsed time (years)	Total annual effective dose (mSv)
1	0.444
3	0.227
10	0.0215
30	2.78×10^{-5}
100	2.39×10^{-6}
300	4.54×10^{-6}
1000	5.53×10^{-5}
100 000	2.22×10^{-11}

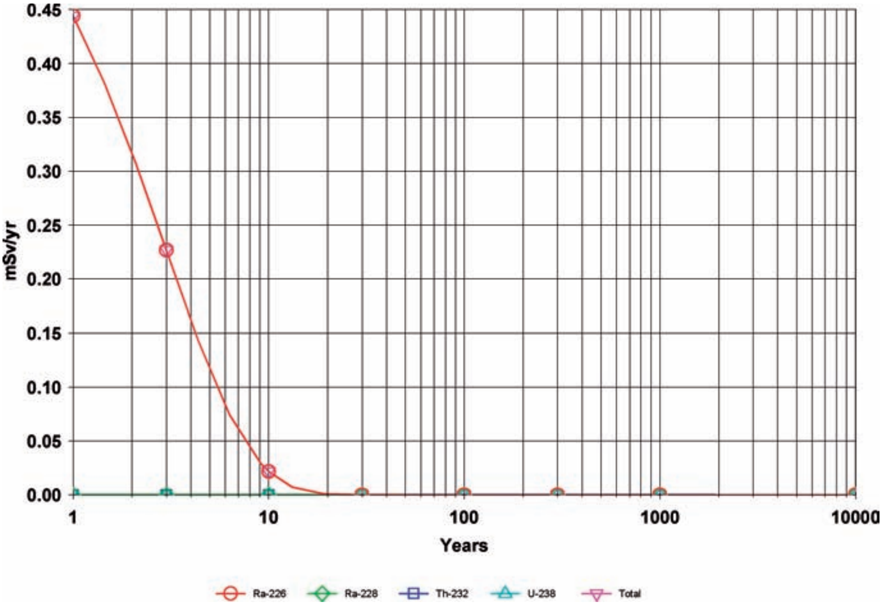

FIG. 1. Total annual effective dose calculated for the industrial use scenario.

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TREATMENT OF NORM RESIDUES IN THE NETHERLANDS

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Abstract

In the Netherlands, different types of NORM coming from the various industries are produced. These materials are partly waste and partly suitable for recycling. If the NORM is considered waste, there are two options available: treatment and storage as radioactive waste or disposal as a hazardous substance. If recycling is foreseen, there are specific demands on the process and use. A summary of the current types and amounts of NORM wastes and recyclable materials is given. The relevant legislation and the opportunities for the NORM industry are discussed and treatment options that COVRA has developed for conditioning prior to long term storage are shown. An overview of the conditions under which the hazardous waste depositories are allowed to process specific NORM wastes is given.

1. INTRODUCTION

As in many other countries, in the Netherlands, a wide variety of NORM materials is generated by industries. Some of these materials are considered waste and are intended for disposal, while some of these materials are suitable for recycling or recovery. As far as NORM is considered waste, two options are available: treatment and storage by the Central Organisation for Radioactive Waste (COVRA) or by a specified waste depository for hazardous wastes. In this paper a short overview of the current situation concerning types and amounts of NORM wastes is described. The recovery of materials and treatment processes are presented. Furthermore, the relevant legislation and opportunities for the NORM industry are discussed. Specific attention is given to the treatment options COVRA has developed for the conditioning of NORM prior to long term storage. An overview of the conditions under which the hazardous waste depositories are allowed to process specific NORM wastes is also given. Last but not least, some alternative options which are available and/or under development for the recovery of NORM are dealt with.

2. DESCRIPTION OF SCENARIOS

2.1. Recycling and recovery

The option of recycling or recovery is explicitly mentioned in regulations, and as far as the application in infrastructural works is concerned there is a specific demand that NORM residue is diluted to such a level that the produced material is no longer considered radioactive. The general approach for this option is first to see whether a product can be developed out of NORM residue (considering technical, economic and environmental aspects). Second, an overall safety assessment of the radiological implications for a given process and application is developed to see whether any major threats could occur. Potential threats do occur during processing of the residue and during the life cycle of the product. In the latter case, the leachability of radionuclides and subsequent dose limits and contamination levels are aspects which have to be taken into consideration. In case both criteria are met, the technical development and processing of NORM can proceed.

As far as marketing aspects are considered, the NORM requirements are just one set of aspects determining the feasibility of recycling or recovery. Other aspects including economics, market principles and customer perception are far more restrictive and the most appropriate way to ensure that the product is no longer NORM is paramount (even for those applications where it is not formally required).

An example of recycling or recovery of NORM in infrastructural works is the development of a granulate on the basis of mixing the NORM sludge with binders. This process of granulation by a rotating disc technology seems to be most promising for large quantities of low level NORM.

A special option is given by the treatment of NORM contaminated steel scrap which can either be cleaned (in case recovery is considered and cleaning is possible) or recycled by melting at the Siempelkamp facility in Germany.

2.2. Waste treatment and storage at COVRA

The statutory task of COVRA is to take care of all the radioactive waste produced. COVRA collects and transports the waste from the producers to its facilities, where it is treated if necessary and deposited in storage buildings (Fig. 1).

COVRA has a monopoly position: in the Netherlands, work involving radioactive substances is only allowed when licensed under the Nuclear Energy Act. This act stipulates that a licensee can only dispose of radioactive waste (including NORM waste) by handing it over to an authorized organization. As far as high(er) level waste is concerned, only COVRA is authorized. Although COVRA is also authorized to accept low level wastes there is an alternative option formed by specific hazardous waste repositories. All activities with radioactive substances, excluding shipments, have to comply with the rules laid down in the Radiation Protection Decree, which is part of the Nuclear Energy Act. In the decree, a definition is given for radioactive waste: “Radioactive waste: a substance can be considered to be waste, if for this substance no use, reuse or recycling is foreseen, and the substance is not to be discharged”. In the decree, limits are also given for exemption and clearance of radioactive materials. The limits are based on Council Directive 96/26 of the European Commission. In the Netherlands, the choice has been made to use the same levels for exemption and clearance. However, for work activities up to a tenfold higher level, a notification procedure is required instead of a licensing procedure.

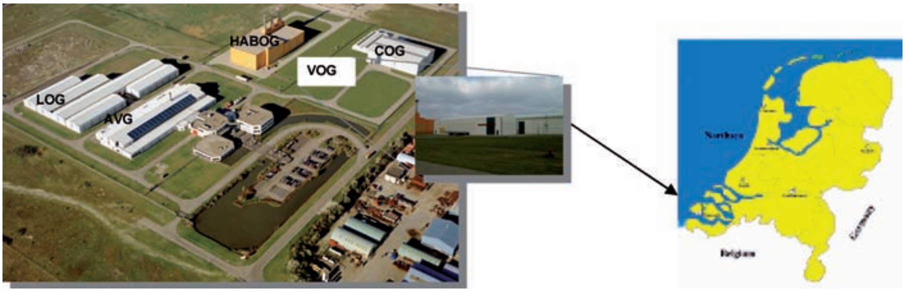

FIG. 1. The COVRA site: location in the Netherlands and aerial view showing buildings for the treatment of low and medium level waste (AVG) and storage buildings for conditioned low and medium level waste (LOG), high level waste (HABOG), low level NORM waste from the mineral processing industry (COG) and low level NORM from the uranium enrichment industry (VOG).

Complications for the safe and cost-effective processing and storage of the radioactive waste are:

(a) Heterogeneous waste supply: In the Netherlands, there are some 200 producers of radioactive waste, varying from nuclear power plants and research establishments to various industries and hospitals. Most of them generate only small volumes of low and medium level waste. Some nuclear processing industries generate large volumes of solid, low level NORM waste. Some processing industries generate larger volumes of solid, very low level NORM waste. Nuclear power plant(s) and research reactors produce waste with a high level of activity, but only in small volumes.

(b) Single final product: It is estimated that roughly two-thirds of the waste stored at the COVRA site will be disposed of in a geological repository. This implies that the wide range of wastes must be processed into a single (or a few) final product(s), compatible with the specifications of the envisaged repository, and easy to handle and maintain.

(c) Predictability of costs: Radioactive waste must be isolated from the environment, controlled and monitored over very long periods of time. The ‘polluter pays’ principle is a leading principle in waste management. According to this principle, the fees levied when the waste is collected must cover all costs of treatment, storage and final disposal. Once the waste is accepted, all liabilities are taken over by COVRA, which takes full title because some wastes may have to be managed over longer periods of time than the periods for which the waste producers exist. Consequently, the fee must cover all present costs and the discounted value of all future costs.

(d) Industrial activity: Radioactive waste treatment and storage are considered normal industrial activities. As a consequence, COVRA is located in an industrial area in the south-west corner of the Netherlands, close to the Borssele nuclear power plant (NPP) (see Fig. 1). This puts additional demands on safety compared to dedicated sites in more secluded surroundings.

This explains why simple processing, versatile production equipment and passive safety are central in the design and operation of the COVRA facilities. For example, all storage buildings are modular, which provides flexibility to adapt to changes in waste supply. The radioactive waste is immobilized in a form that is physically and chemically stable and stored in a way that minimizes the need for control and safety systems, maintenance, monitoring and human intervention.

The waste is stored in discrete packages that are resistant to degradation and hazards and can be inspected and retrieved for final disposal. Finally, application of passive safety principles also leads to more predictable costs because it minimizes the need for control and safety systems, maintenance, monitoring and human intervention — the costs are largely determined by capital investment such as equipment and buildings. In the sections below, this approach is explained in more detail for the different types of waste processed and stored at the COVRA site.

2.2.1. Low and intermediate level radioactive waste

The Dutch hospitals, research industry and NPP produce approximately 200 t of solid, low and medium level waste (LLW) per year as well as 1000 t of NORM coming from a wide range of industries. A few industries, such as the phosphate and titanium dioxide pigment industries, produce large quantities of very low level waste (VLLW) — up to 10 000 t or more per year. These quantities are too large to be handled by COVRA. Hence, an alternative was developed by which, under certain conditions, repositories for hazardous waste are allowed to accept these types of NORM wastes. As a result, the small amounts of NORM wastes (e.g. scales, insulation wool and filters) are treated using the same technologies as for LLW.

Treatment of this type of waste by supercompaction starts in 100 L drums. This requires that the wastes are dry and sludges have to be dried or stabilized (by the addition of cement, for instance). As the cost of the disposal is dependent on the volume, the main object of the waste treatment is to reduce the size of the drum needed (supercompaction by a 1500 t press is shown in Fig. 2). Subsequently, all supercompacted waste is conditioned with cement in relatively small drums. Cement is a very stable product and creates an alkaline environment for the waste materials. This will prevent or slow down the degradation of the waste materials. Producing relatively small units of 200 or 1000 L makes it easy to handle the units for repair. In order to keep the dose rate in the storage areas low, the 200 L drums with conditioned waste and having a surface dose rate exceeding 0.2 mSv/h are put in 1000 L shielding containers. The shielding is removed once the dose rate has decreased.

In a storage building (Fig. 3), conditioned waste packages are placed in blocks that leave open corridors for inspection. Lower dose rate packages are stored along the outer walls of the modules, and on the top layers in order to provide additional shielding for higher dose rate packages at the interior. The storage buildings are of a modular design. At the moment, COVRA operates three storage units. Each unit has a capacity for approximately 5000 m^3 of

FIG. 2. Treatment of LLW (AVG).

conditioned waste. A reception bay connects the three storage units. A fourth unit will be built in 2007 and connected to the central reception bay. In total, 16 storage units can be constructed at the site. The storage building is a simple concrete building with no mechanical ventilation. Humidity in the building is kept at a low level (50% on average) using mobile equipment (construction dryers), in order to prevent condensation of moisture from the air on the packages and subsequent corrosion. All waste in the storage building is well contained. The storage area is a contamination free area.

FIG. 3. Storage building for LLW (LOG).

2.2.2. Calcinate from thermal phosphorus production

Waste from thermal phosphorus production is produced in larger quantities and generally as a stable and solid product (calcinate). For this NORM waste, containing ^{210}Pb, ^{210}Po and ^{210}Bi, a tailor-made solution was developed. The calcinate resulting as waste from the production of phosphorus in a dry, high temperature process is a stable product that does not need to be conditioned to ensure safe storage. Any additional conditioning would most likely enlarge the volume and would certainly add to the cost of storage. Moreover, as the activity decays to concentrations below clearance levels in about 150 years, conditioning is also undesirable because it would increase the cost of disposing of the waste as conventional waste. The calcinate produced at the phosphorus plant is dried at the plant and collected in a specially designed ‘20 foot’ container. The container has the dimensions and properties of a standardized ISO container (ISO-668 type 1CC). There are no doors in the container but there are three filling positions in the roof of the container that can be closed with a lid. A large polyethylene bag serves as a liner. The inside and outside of the container are preserved with high quality paint. The container can be filled with 30 t of material. This higher payload required re-certification of the container. These containers are stacked four high in the container storage building (Fig. 4). The containers are stored in blocks comprising two rows, which leave open corridors for inspection. The container storage building is a steel construction frame with insulation panels. High quality criteria were set for the construction and for the materials used in order to achieve at least a

FIG. 4. Storage building for calcinate (COG).

100 year lifetime with practical maintenance (the half-life of ^{210}Pb is 22.3 a). Technical provisions in the building are minimal. There is no mechanical ventilation and the concrete floors are provided with a fluid tight top layer of epoxy. The average air humidity in the storage building is kept below 50% using mobile equipment, in order to prevent condensation of moisture from the air on the packages and subsequent corrosion.

2.2.3. Depleted uranium oxide (DUO)

For DUO tails, a solution similar to that for calcinate has been chosen, namely storage of this unconditioned NORM in larger containers (3.5 m^3 boxes). The DUO originates from UF_6. Since UF_6 is not a stable product suitable for long term storage, it is converted into the very stable U_3O_8. This is done in the uranium conversion plant of AREVA (France). Recovery of DUO for economic reasons (as a feed for enrichment) is possible at any time. Construction of the first storage building (one storage unit and a reception bay) started in 2003. The building was finished in March 2004 and became operational in August 2004. Five more modules are permitted in COVRA's licence and two modules will be constructed in 2008. The containers with DUO are stacked three high in the container storage building (see Fig. 5). The containers are stored in blocks, which leave open corridors for inspection. The building, which has a concrete structure, can be expanded modularly and an overhead crane is provided for each storage module. There is no mechanical ventilation. The concrete floors are provided with a fluid-tight top layer. The

FIG. 5. Storage building for depleted uranium tails (VOG).

average air humidity in the storage building is kept below 50% using mobile equipment in order to prevent condensation of air moisture in the packages and subsequent corrosion.

2.2.4. Filter bags from dewatering of sludges

Another source of NORM waste is the enrichment of radionuclides in the processing of all kinds of ores. In several cases the enrichment takes place in the waste stream in which all impurities of the ores are concentrated. Depending on the processes used, this can generate scales in certain parts of the installation or form solid waste (e.g. sludges) which has to be treated and can be processed (depending on its radionuclide content) by COVRA or other specified repositories. NORM is also collected in filter bags used in the treatment of sludges (e.g. dewatering). Because sludge contains precipitates of radium (and in some cases thorium) the filter bags will be contaminated with those scales and become a NORM waste once they are exchanged (removed) from the filter press. Because they contain relatively high amounts of radionuclides (up to several thousands of becquerels per gram) they are not allowed to be treated by the hazardous waste depositories and therefore have to be treated by COVRA, which has developed a method for processing these filter bags into the system as described above (compaction, immobilization and storage). This treatment consists of the use of two shredders placed at an angle of 90° to each other in order to process these filter bags into small flakes with the size of a few centimetres (see Fig. 6). This approach reduces the exposure

FIG. 6. Shredding of filters in the AVG.

during handling of the filter bags in order to make them fit for 100 L drums by avoiding the need for manual folding and cutting. In addition, it reduces the storage cost by better utilization of the volume of the drum.

2.2.5. Sludges from the oil and gas industry

In some cases, sludges contain levels of radionuclides that are too high to be accepted by the hazardous waste repositories. The sludges from the oil and gas industry not only contain large amounts of water but also mercury and organic compounds. These components make drying and/or stabilization of the sludge with cement very difficult. Therefore, an alternative treatment path was developed by the supplier in cooperation with COVRA. This treatment involves a drying operation in a dedicated installation, by which not only the water is evaporated but also certain quantities of mercury are collected. The dried material, containing all the radionuclides, can then be treated according to one of the available routes at the COVRA facility. One complicating factor in this treatment route is that the intermediate treatment takes place in Germany, which involves significant additional legislative and regulatory requirements. Packaging of sludges is shown in Fig. 7.

2.3. Disposal of bulk NORM waste at hazardous waste repositories

As already mentioned, COVRA cannot supply a solution for large quantities of very low level NORM wastes. For this reason, repositories that are

FIG. 7. Packaging of sludges.

allowed to process hazardous chemical waste may accept these NORM wastes on condition that they make a radiological assessment of the processing of the NORM wastes. Subsequently, they have to inform the authorities and implement the basic requirements as given in the legislation, as well as customized measures based on additional legal requirements and radiological assessment. Based on initial experience, it seems that the additional measures for the processing of NORM wastes can be limited to minor adjustments. The measures taken in order to process hazardous wastes are already providing a high standard of protection for both workers and the public. Just a basic adjustment of the waste administration, informing the workers and employing a specialized health physics specialist, is enough to transform a 'conventional' hazardous waste repository into a NORM waste repository (see Fig. 8).

3. CONCLUSIONS

Some NORM wastes are produced in quantities too large to allow processing through the standard radioactive waste routes at COVRA (due to the available processing capacity and costs of processing) or have an activity too low to justify these routes. In the Netherlands, legislation allows the development of tailor made solutions for all kinds of NORM residues. Alternative routes at COVRA were developed for bulk calcinate and uranium oxide, as well as various options for the treatment of sludges and filters. For NORM immobilized by calcination or converted into a chemically stable oxide, an ordinary container is sufficient to prevent any non-controllable release of

FIG. 8. Disposal of large quantities of NORM.

radioactivity. To prevent corrosion of the container, a storage building with humidity control is used. Corridors between the blocks of containers allow for inspection of degradation and other hazards. For large quantities of VLLW, disposal at a hazardous waste repository is allowed after a safety assessment and subsequent minor adjustments to existing measures.

As a result of cooperation between COVRA and NORM waste generators, cost optimized solutions are being developed. Treatment of the waste outside the country (e.g. in Germany or France) is being arranged under the restriction that as far as radioactive waste is concerned (according to national legislation) this radioactive waste has to be returned to COVRA.

Finally, application of passive safety principles also leads to more predictable costs: because it minimizes the need for control and safety systems, maintenance, monitoring and human intervention. The costs are largely determined by capital investments (e.g. equipment and buildings).

As a result there are no NORM residues which cannot be dealt with in the Netherlands.

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MISCELLANEOUS TOPICS (1)

(Topical Session 7)

Chairpersons

S. CHAŁUPNIK

Poland

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NORM MEASUREMENTS IN THE OIL AND GAS INDUSTRY IN ARGENTINA

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Abstract

The oil and gas industry, which is especially significant in Argentina, is one industry that concentrates natural radionuclides during its processes. The Nuclear Regulatory Authority of Argentina (ARN) carried out a project with the objective of evaluating NORM, mainly in this type of industry. Seven facilities were characterized, three of them related to the gas industry and four related to the oil industry. In all cases, facility specific dose rates were measured. First, background measurements were made and then a screening survey was carried out to detect values above background. Of the values obtained, 57% were in the background range, 19% were below 2 μSv/h, 15% were in the range of 2–10 μSv/h and 9% were above 10 μSv/h. Some values were as high as 400 μSv/h. The annual effective doses were estimated to be in the range of 0.02–1.6 mSv/a, far below the dose limit for workers (20 mSv/a), but in some cases above the dose limit for the public (1 mSv/a). The radon gas concentration was also measured in gas facilities. The values obtained showed that radon concentrates in the ethane and propane flows. In addition, samples were taken and later analysed by gamma spectrometry, liquid scintillation and fluorimetry in the ARN laboratories. It was confirmed that the main radionuclides involved are ^{226}Ra and ^{228}Ra and that uranium does not migrate into the oil and gas extraction processes. The radium isotope concentrations measured in some samples were above the exemption values established by IAEA Safety Series No. 115. Finally, protective measures to reduce occupational doses in the cleaning and maintenance processes were suggested, as well as for storage of NORM contaminated items.

1. INTRODUCTION

Radioactive materials containing radionuclides of natural origin are known as NORM (naturally occurring radioactive material). Some minerals have significant levels of natural radionuclides that are extracted and processed with other elements. Some industries involve processes that concentrate natural radionuclides and then may cause some risk to people if the exposures are not under control. These naturally radioactive materials that are concentrated by some industries are known as TENORM (technologically enhanced naturally occurring radioactive material). Although there is a conceptual difference between NORM and TENORM, sometimes the term NORM is used to refer to TENORM. TENORM is found in some effluent flows and wastes from some non-nuclear industries, for example in metal residues, scales, sludges and fluids. These materials, the by-products and the final products from processes may enhance the exposure of workers and members of the public. The most important radioactivity source in TENORM is due to the presence of isotope products of the uranium and thorium decay chains [1–3].

The presence of radioactive materials of natural origin in geological formations is well known. The materials containing natural radionuclides found in oilfields are typically located in subsurface formations of oil and gas reservoirs created in the Jurassic period. In the oil and gas industry, the techniques used in forcing the oil to the surface include recirculation of produced water, which is extracted with the final products. The NORM materials are transported to the surface with this water. A decrease in pressure and temperature results in sulphate and carbonate precipitation inside the pipelines and in the internal surfaces of the equipment. The similar chemical behaviour of radium and barium produces selective co-precipitation of both elements in scales. Other products of the uranium and thorium decay chains can also be found. The naturally radioactive material which is not present in scales appears in the vessels with the drained water or in sludges. Other radionuclides of interest, particularly in gas equipment, are radon gas and ^{210}Pb, which usually forms a thin cap in the internal surface of processing equipment [4, 5].

From the occupational point of view, the main aspects of radiological protection related to scales and sludges are gamma irradiation and internal contamination of workers arising from the maintenance of equipment containing NORM. The Nuclear Regulatory Authority of Argentina (ARN) carried out a project whose objective was the evaluation of NORM, mainly in this type of industry. For this purpose, seven facilities were characterized, three of them related to the gas industry and four to the oil industry. In this paper, the results obtained within the companies surveyed are presented, with the aim of evaluating the presence of NORM and the exposure of workers.

2. DESCRIPTION OF FACILITIES

2.1. Oil facilities

2.1.1. Facility A

The company provides pumping systems for oil and gas extraction processes. This facility performs the assembling of equipment with new or recovered items. The equipment for recycling arrives at a sector called ‘discharging’ and from there goes to the ‘disassembling’ sector, where the components are washed, recovered and refurbished. The rejected components are returned to the discharging sector to await disposal as waste or sale as scrap.

2.1.2. Facilities B, C and D

These facilities perform services of cleaning, maintenance and inspection of tubing. They are different bases of the same company. In Argentina, the company has seven bases. The tubes arrive and are classified and stored in the storage area until the washing process begins in the washing area. The wastes from the washing process are temporarily stored until they are removed by the service companies. All processes are performed in well ventilated areas. The washing process is carried out in two steps: first the tubes are introduced to a washing container with a mix of water and gasoline at 90°C for 10–15 min. Then an internal and external manual washing with pressurized water is carried out. The water is collected in vessels called APIs. In some facilities, mechanical equipment is also used to remove scales. The solid wastes from the process are collected in two containers located at both ends of the pipe. These wastes are then manually carried to a large container where they are temporarily stored.

2.2. Gas facilities

2.2.1. Facility E

The company separates and fractionates the heavy components of natural gas (LGN) in two facilities: a separation plant and fractionation plant. In the separation plant, the natural gas is received and dried. Then the heavy components are sent in the liquid state via a 600 km pipeline to the fractionation plant, were ethane, propane, butane and gasoline are separated. In the fractionation plant there are five main areas: reception of the rich component mix, separation of the rich components, ethane reconditioning, storage areas, dispatch and services. The measurements were performed in the final area.

The distillation process is performed in three continuous stages:

(a) A de-ethanizing tower retains ethane at the top;
(b) A depropanizing tower retains propane at the top;
(c) A third tower retains butane at the top and gasoline at the bottom.

Ethane is then purified and dispatched, while propane, butane and gasoline are stored.

2.2.2. Facilities F and G

These two facilities produce ethylene and polyethylene. The ethylene is obtained from ethane. The polyethylene is produced from ethylene. Facility F has been in operation since 1981 and facility G since 2001.

3. MEASUREMENTS

To determine whether there were areas or equipment contaminated with NORM, various locations were surveyed. The survey locations were selected on the basis of the processes performed in each place, taking into account the origin, function and visual inspection of the different items. In situ dose measurements were performed and samples were taken for analysis at the ARN laboratories.

3.1. In situ measurements

Dose rate measurements were carried out in predetermined areas. The equipment used was:

(a) Scintillation detector (INa)Tl IDENTIFINDER 1.2" × 1.5";
(b) Geiger-Müller detector AUTOMESS 2174.

First, background measurements were performed in the surroundings of each facility. Then, in facilities A, E, F and G, measurements were performed in contact, with the locations being selected on the basis of the origin, function (information given by the facility staff) and visual inspection of the elements (sludge presence). If possible, the internal surfaces of the items were also measured (with a probe). The results are summarized in Table 1, while values above 10 μSv/h found in facility F are presented separately in Table 2.

TABLE 1. DOSE RATES MEASURED IN CONTACT AT FACILITIES A, E, F AND G

	Background (μSv/h)	At facility	
		Range (μSv/h)	Number of measurements in range
Facility A	0.20 ± 0.02	Background	9
		<2	5
		2–10	9
		10–20	2
		>20 (28.2 and 30)	2
Facility E	0.10 ± 0.02	Background	7
		<1	6
Facility F	0.15 ± 0.04	Background	9
		<2	11
		2–10	5
		>10	5
Facility G	0.12 ± 0.03	Background	19
		<1	11
		1–3	16

TABLE 2. DOSE RATES EXCEEDING 10 μSv/h AT FACILITY F

	Dose rate at various distances from the surface (μSv/h)		
	Contact	1 m	3 m
P5601 pump	400	20	2
P5601 suction pump	320	20	—
Pipes at 1 m from P5601 pump	110	—	—
Pipes at 2 m from P5601 pump	30	—	—
5601 pipe	22	5.5	—

In facilities B, C and D, dose rate screening was performed in each area with the objective of detecting dose rate values above background. After that, detailed measurements were performed at those points where values above background were found. The results are summarized in Table 3, while more detailed results for the washing area of facility D are presented in Table 4.

3.2. Laboratory analysis

Samples of scales, sludges and washing effluents at facilities A, B, C and D were analysed at the ARN laboratory. The scales and sludge samples were obtained from items exhibiting dose rates above background. First, the samples were analysed by gamma spectrometry using a Canberra GeHp detector, model GX2518, with 30% efficiency. Then ^{226}Ra analysis was performed using a radiochemical method based on the co-precipitation of radium with $BaSO_4$

TABLE 3. DOSE RATES MEASURED IN CONTACT AT FACILITIES E, F AND G

	Background dose rate (μSv/h)	Number of measurements above background	Dose rate in contact (μSv/h)
Facility B	0.09 ± 0.01	1	2.2
Facility C	0.11 ± 0.01	0	—
Facility D, store area	0.13 ± 0.01	1	2.8
Facility D, washing area	0.13 ± 0.01	3	1–10
		1	10–20

TABLE 4. MEASUREMENTS IN THE WASHING AREA AT FACILITY D

	Dose rate at various distances from the surface (μSv/h)		
	Contact	1 m	3 m
Washing container	1.0	—	—
Large container	10.0–18.5	3.0	0.90
Waste container 1	1.0–2.8	—	—
Waste container 2	3.8	0.80	—-
API vessel	0.10–0.13	—	—

and the measurement of radon gas by liquid scintillation. The uranium concentration was measured by fluorimetry using Jarrel Ash equipment. The results are summarized in Table 5. At facilities E, F and G, radon gas measurements were performed by the Lucas cell method, in which radon samples were collected in cells coated with SZn(Ag) and then measured using a Ludlum 2200 alpha counter. The results are shown in Table 6.

4. RESULTS

4.1. External exposure

Dose rates above background were detected in tubing containing scale, in miscellaneous items, in containers for material from washing and maintenance processes and in ethane and propane flows. It was found that 57% of the dose

TABLE 5. URANIUM AND RADIUM CONCENTRATIONS IN SAMPLES FROM FACILITIES A, B, C AND D

	Uranium concentration (μg/g)		Radium activity concentration (Bq/g)			
			^{226}Ra		^{228}Ra	
	Minimum	Maximum	Minimum	Maximum	Minimum	Maximum
Facility A	<0.4	1.9 ± 0.8	<0.1	1270 ± 130	115 ± 11	1670 ± 17
Facility B	<10.0	33.0 ± 9.8	<0.0017	26.8 ± 2.7	<0.0011	9.6 ± 0.9
Facility C	<10.0	1.5 ± 0.7	<0.00014	0.07 ± 0.01	<0.00096	0.1 ± 0.01
Facility D	<0.4	<0.7	0.0019 ± 0.0004	18.7 ± 1.8	0.0021 ± 0.0004	65.4 ± 6.5

TABLE 6. RADON CONCENTRATIONS IN GAS STREAMS AT FACILITIES E, F AND G

	Radon gas concentration (Bq/m^3)
Facility E, ethane + CO_2	1841 ± 300
Facility F, tower top (propane 18%, propylene 75%)	337 773 ± 30 000
Facility G, tower top (propane 18%, propylene 75%)	62 572 ± 5000

rates were at background levels, 19% were below 2 (μSv/h, 15% were in the range of 2–10 μSv/h and 9% were above 10 μSv/h.

In order to assess the maximum occupational dose that a worker might receive in these facilities, conservative scenarios were established. Occupancies were calculated on the basis of information provided by the facility staff. Homogeneous whole body irradiation was assumed. The maximum dose rates, occupancies and calculated annual effective doses are shown in Table 7.

4.2. Internal contamination

Inhalation and ingestion of radioactive material are exposure pathways that become important during the cleaning and maintenance processes, in which workers may be in contact with particulate material, wastes, etc. These pathways will be evaluated in the next stage of the investigations.

TABLE 7. RESULTS OF EXTERNAL EXPOSURE ASSESSMENTS

	Items giving rise to dose rates above background	Maximum dose rate (μSv/h)	Annual occupancy (h)	Annual effective dose (mSv)
Facility A	Miscellaneous items, pipes	30	20 (5 min/d, 240 d/a)	0.6
Facility B	Pipes	2.2	25 (5 min/d, 300 d/a)	0.05
Facility C	None	—	—	—
Facility D[a]	Pipes	2.8	25 (5 min/d, 300 d/a)	0.07
	Container with scales, at 1 m	0.8	320	0.26
	Large container, in contact	18.5	25 (5 min/ d, 300 d/a)	0.45
	Large container, at 1 m	3	50 (10 min/ d, 300 d/a)	0.15
Facility E	Depropanizer pump	0.9	20 (5 min/ d, 240 d/a)	0.02
Facility F	Pump 5601	400	4	1.6
Facility G	Pump P93	3.0	4	0.01

[a] It was assumed that the worker was exposed to all sources and therefore received a total annual effective dose of 0.93 mSv.

4.3. Radon gas concentration

It was confirmed from the measurements performed in the gas facilities that radon is concentrated in ethane and propane flows. This is a result of radon having a condensation point between those of propane and ethane and thus following these products in the distillation and cracking flows.

4.4. Sample analyses

The analyses performed by fluorimetry showed that uranium is not concentrated in scales. This reflects the fact that uranium is not mobilized in the oil extraction process. The analyses performed by gamma spectrometry confirmed that the radionuclides involved come from the decay chains of ^{238}U and ^{232}Th. The radionuclides that mainly concentrate in these processes are ^{226}Ra and ^{228}Ra. Some of the radium concentrations measured in scale samples are above the exemption values established in IAEA Safety Series No. 115 [6], namely 10 Bq/g for ^{226}Ra and ^{228}Ra.

5. CONCLUSIONS

The dose rates measured at most facility locations were within normal background levels. Some instances of dose rates above background included tubing contaminated with NORM (facilities A, B and D) and the washing area in facility D. The wastes arising from the washing area are stored in each facility until removal by service companies. It is reported that this material may be used in road construction. In the gas facilities E, F and G, some dose rates were above background in the ethane and propane flows.

In oil facilities an annual effective dose of 0.6 mSv was conservatively estimated from the highest dose rate measured in tubing. In facility D, assuming that a worker may be exposed to additional scenarios, including duties not only in the storage area but also in the washing area, the annual effective dose calculated in a conservative way was 0.93 mSv. It is suggested that the doses received by the workers in these areas be optimized by examining the possibilities for reducing the occupancy periods.

With regard to gas facilities, the values measured in facility F were higher than those measured in facility G, owing to greater accumulations of radionuclides in the older facility. The annual effective dose calculated in a conservative way from the highest value measured was 1.6 mSv. Although the time spent by workers in the areas of highest dose rate is short, it is suggested that the presence of workers in these areas be justified and that their doses be optimized by examining the possibilities for reducing the occupancy times.

The results obtained from this investigation may not agree with the results of future investigations, owing to the fact that the contamination of tubing and various other equipment may vary over time. All the annual effective doses are very low in comparison with the dose limit established in the ARN Standards for workers (20 mSv). In the case of facility F, the value exceeded the limit for members of the public (1 mSv) [6]. In order to improve the dose assessment for workers, it would be advisable to perform TLD measurements over a period of three months and to evaluate the inhalation and ingestion pathways, especially during inspection, repair or maintenance activities because of the possibility of aerosol generation.

For those items giving rise to dose rates above background levels it would be important to define suitable storage methods. As some items are sold as scrap, it is advisable to first clean them to reduce the dose rate. In this respect, protective measures to reduce occupational doses in the cleaning and maintenance processes, as well as in the storage of NORM contaminated items, have been proposed, based on international practice [7, 8].

This work has confirmed that the main radionuclides found in this type of industry are ^{226}Ra and ^{228}Ra, members of the ^{238}U and ^{232}Th decay chains, respectively. In some cases, the radium activity concentrations measured in scale samples were above the exemption values established in international standards. This work has also confirmed that uranium is not mobilized in the oil extraction process. On the basis of radon gas concentrations measured in gas facilities, this work has confirmed that radon concentrates in ethane and propane flows. The possibility of gas inhalation should be taken into account during inspection, repair or maintenance activities — in normal operations, the gas is confined within the pipes and vessels with no risk to workers. Finally, it is suggested that the facilities be re-evaluated to determine the buildup of NORM contamination over time.

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RADIOACTIVITY IN PRODUCED WATER FROM OIL AND GAS INSTALLATIONS — DOSES TO BIOTA AND HUMANS[1]

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Abstract

Substantial amounts of produced water containing elevated levels of ^{226}Ra and ^{228}Ra are discharged into the sea as a result of oil and gas production on the Norwegian continental shelf. The average concentration in the discharges is 3.3 and 2.8 Bq/L of ^{226}Ra and ^{228}Ra, respectively. The main objective of the project described in the paper is to establish radiological safe discharge limits for radium, lead and polonium in produced water produced by oil and gas installations on the Norwegian continental shelf. One of the objectives of the study is to provide information to enable risk assessment based on doses from ionizing radiation to marine biota and man. Reference organisms for the North Sea area have been chosen for calculation of absorbed dose to biota. The dose calculations rely on specific knowledge of activity concentration in the reference organism, activity concentration in seawater and sediments, dose conversion factors and

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time spent at different locations relative to the point of discharge. Based on the calculated doses to marine biota, ‘potential no effect concentrations’ are recommended.

1. INTRODUCTION

Substantial amounts of produced water, about 143 million m^3 in 2004, are discharged to the marine environment in connection with oil and gas production on the Norwegian continental shelf. One potential problem with this release of produced water, also referred to as formation water or brine, is that it contains elevated levels of ^{226}Ra and ^{228}Ra. A systematic survey of the levels of ^{226}Ra, ^{228}Ra and ^{210}Pb was conducted in 2003 in produced water from all 42 Norwegian platforms discharging produced water. The concentrations of ^{226}Ra and ^{228}Ra varied between the detection limit (1 Bq/L) to 16 and 21 Bq/L, respectively. For ^{210}Pb the levels were below the detection limit. On the basis of these results, annual discharges of 440 GBq ^{226}Ra and 380 GBq ^{228}Ra were calculated. These correspond to average discharges of 3.3 and 2.8 Bq/L of ^{226}Ra and ^{228}Ra, respectively [1].

The two platforms discharging most of the ^{226}Ra and ^{228}Ra are Troll B and C. In total these two platforms discharged approximately 190 GBq ^{226}Ra and 155 GBq ^{228}Ra in 2003. The average ^{226}Ra and ^{228}Ra concentrations in produced water from these platforms are approximately 9 and 8 Bq/L, respectively. In comparison, the levels of ^{226}Ra in North Sea water is approximately 1–2 mBq/L.

It is generally assumed that when produced water rich in barium and poor in sulphate is brought into contact with seawater, which is rich in sulphate, radium will co-precipitate with $BaSO_4$. Depending on the size of these particles they will either be transported with the water masses, settle more or less immediately or attach to other organic or inorganic particles and sequentially settle to the seafloor. Owing to the chemical similarities of barium and radium, the fate of radium is determined by the speciation of the macro amounts of barium. Data on the speciation of radium and barium and the effect of components in produced water on the speciation of radium and barium are sparse however.

In today’s oil production, several chemicals are added, e.g. scale and corrosion inhibitors, emulsion breakers and surfactants, and sulphide removers. These chemicals are usually organic compounds comprising functional groups, which may also interact with cations such as Ra^{2+} and Ba^{2+}. Thus radium may exist in compounds more easily accessible for uptake in biota than the inorganic aqueous or food borne form. An understanding of how different compounds in produced water affect the mobility, bioavailability and sedimentation of radium is essential to determine the fate and effects of radium discharges. Consequently, sediment dwelling organisms may be an important group of marine organisms that might be exposed to radionuclides. Once taken up by sediment dwelling invertebrates, the nuclides can be transferred to a higher level of the marine food chain (fish), ultimately forming a potential risk for human consumption. In addition to the food borne route of exposure, water borne exposure would be expected to form an alternative route by which fish can be contaminated. The relative uptake from the different exposure routes, as well as the effect of chemicals on the bioavailability of radionuclides, is of great importance when assessing possible consequences for animal welfare and food safety. For evaluation purposes, the behaviour of produced water radium must be compared to radium already present naturally in seawater [2, 3].

The main objective of the PROOF programme is to establish radiological safe discharge limits for radium, lead and polonium associated with other components in produced water from oil and gas installations on the Norwegian continental shelf. The oil and gas production industry refers to such a limit as ‘potential no effect concentration’ (PNEC).

2. SUB-OBJECTIVES OF THE PROJECT

The project has been divided into six work packages:

WP 1: Background and sources

Natural background levels of the relevant radionuclides (^{226}Ra and ^{228}Ra) in seawater have been established. A few seawater samples from the North Sea have earlier been analysed for ^{226}Ra. These results indicate that the concentration level is 1–2 mBq/L. Surface water samples from 10 locations, of which 3 include depth profiles, have recently been sent for analysis. The analysis is in progress.

WP 2: Speciation, mobility and sedimentation mechanisms

The study will determine the levels and distribution of relevant radionuclides in produced water. Furthermore, mobility and sedimentation mechanisms of the radionuclides for different discharge scenarios are to be studied.

WP 3: Bioavailability

The study will assess bioavailability and bioaccumulation of radium in biota following exposure through water and through the diet. The effect of organic complexing agents on these processes is also to be studied.

WP 4: Biological effects

The study will assess effects of ionizing radiation on bottom dwelling marine organisms and in vitro fish models.

WP 5: Modelling with the DREAM model

The task of this work package is modelling of the concentration of the radionuclides in seawater and biota using the DREAM model. The model is extended to include adsorption and sedimentation. The amount of water released per day is 35 000 m^3, corresponding to the release from the Troll B or C installations. The calculations show a dilution of 1 in 100 after 80 s, corresponding to a horizontal distance of 30 m from the point of discharge.

WP 6: Risk assessments

The total absorbed dose and dose rates are to be calculated for selected organisms living in the discharge areas. The calculations will take into account the external dose arising from the radionuclide concentration in the seawater and the internal dose from uptake by the organisms themselves.

3. PNEC IN THE CONTEXT OF DOSES FROM IONIZING RADIATION

The current system of radiation protection of humans is based on the linear non-threshold model stating that even very low doses give rise to an increase in risk for stochastic effects. One must, however, keep in mind that the risk from very low doses is very low and will often be unobservable. Recently, the International Commission on Radiological Protection summarized the effects of doses to humans, stating that a total effective dose of less than 10 mSv will lead to an extremely small additional cancer risk and will not be observable even in a large exposed group [4]. On this background, an annual effective dose limit in the range of 1–100 μSv to the most exposed individuals from consumption of seafood will be proposed. This dose limit will be one of the factors to be taken into account in the proposed PNEC.

Regarding the absorbed dose and dose rate to biota, a conceptual mode of responses of organisms, populations and ecosystems to ionizing radiation in the environment has been proposed [5]. The model considers 5 zones of exposure:

1.	Uncertainty, below background	<10–40 μGy/h
2.	Radiation well-being	40 μGy/h–5 mGy/h
3.	Physiological masking	5–50 mGy/h
4.	Ecological masking	50 mGy/h–4Gy/h
5.	Obvious action	4– >3000 Gy/h

A dose limit ensuring that exposure to biota is within zone 1 or 2, i.e. below 5 mGy/h, is suggested for incorporation into the PNEC value for releases of produced water.

4. STRATEGY FOR DOSE CALCULATIONS

4.1. Dose to humans from dietary intake

The route of intake chosen is the consumption of fish from the affected areas. The committed effective dose to the most exposed individuals will be calculated using a methodology for assessing the radiological consequences of routine releases of radionuclides to the environment [6].

4.2. Dose to biota

Reference organisms have been chosen using the selection criteria outlined in the EPIC project [7]. Factors taken into account are ecological niche, radiosensitivity, radioecological sensitivity, geographic location and usability in research and surveillance. Pelagic fish represented by Atlantic cod (Gadus morhua) and bottom feeders represented by European plaice (Pleuronectes platessa) are considered to be the most relevant target species.

The total absorbed dose rate, in units of gray per hour, is used as a measure for exposure to ionizing radiation. For the external component, the results of the model calculations of ambient water concentrations and sediment concentrations performed in WP5 are used. In the calculation of the internal dose from uptake, the influence of other chemical components present in the produced water is taken into account using the results from WP2 and WP3.

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INVESTIGATION OF NORM ACTIVITIES IN SWEDEN

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Abstract

Work activities where workers and the public may be exposed to naturally occurring radioactivity have been investigated in Sweden by the Swedish Radiation Protection Authority (SSI). Investigations were made as a summary of earlier measurements in Sweden and in other countries, inspections and measurements, as well as interviews. Sweden has few sites for production of material containing naturally occurring radioactive substances, but such material occurs in many workplaces. The steel industry is the main activity where raw material is used in production. The concentration of radioactive substances in the raw material is, however, low. SSI found that for the majority of activities, doses to workers and the public are low as long as regulations from the Swedish Work Environment Authority regarding dust, ventilation and welding are followed. Two fields will need further actions though peat ash and filters from drinking water treatment. For peat ash, the next step is to look at the possibilities of regulating peat mining to avoid high concentrations of uranium in ash. For deposits of naturally occurring radionuclides in pipes and discarded filters from drinking water treatment, handling and disposal procedures, regulations, criteria and routines still have to be developed.

1. BACKGROUND

In 1999, 15 environmental quality objectives were adopted by the Swedish Parliament. Another objective, on biodiversity, was adopted in November 2005. These objectives describe what quality and state of the environment are sustainable in the long term and provide a coherent framework for environmental programmes and initiatives at the national, regional and local levels. SSI is responsible for the objective of ‘a safe radiation environment’. The objective has three interim targets, of which one concerns ionizing radiation; by 2010 environmental concentrations of radioactive substances emitted from all human activities will be low enough not to represent a threat to human health or biological diversity. Radiation doses will be limited as far as reasonably possible. The maximum radiation exposure to the public (absorbed dose) due to human activities will not exceed 1 mSv per person and year. The additional individual dose to members of the public will be lower than 0.01 mSv per person and year from each individual activity.

The reason for the investigation made by SSI is the European Council Directive 96/29/Euratom for the health protection of the general public and workers against dangers of ionizing radiation — the concept of ‘work activities’ has been integrated into the scope of this Directive. Member States must identify work activities where exposure to natural radiation may arise. The Member States can then decide about which work activities should be subject to national control.

In 2003 the Swedish Government Committee on Management of Non-nuclear Radioactive Waste proposed regulations regarding NORM to be included in the Swedish Radiation Protection legislation. Previously, the production, handling and waste management, including final disposal, of such products, had not been subject to legal regulations. The Committee proposed that the producer that utilizes raw material containing naturally occurring radioactive substances must have the full financial responsibility for future depositing of the waste. The government accepted this proposal, which is reflected in the Government Bill on Nuclear Safety and Radiation Protection of 2006. The Bill states that this kind of material must be regulated by the Radiation Protection Act, which has been the case since July 2006. The Bill also states that in cases where a work activity gives rise to wastes containing concentrations of natural radionuclides above levels of clearance/exemption, the company responsible for the activity is identified as the responsible ‘producer’. The financial responsibility for the waste management of course lies with the producer. The main problem to solve at the moment is how to dispose of the NORM waste in a correct way, from a radiation protection point of view.

2. WORK ACTIVITIES

2.1. Ash

In 2005, SSI issued regulations and general advice on the handling of wood fuel ash contaminated by ^{137}Cs. The use of peat in the production of energy may also produce ash with enhanced concentrations of naturally occurring radionuclides. Peat mining is today authorized by the Swedish Geological Survey — the Act on Nuclear Activities specifies a limit on the handling of materials containing uranium for nuclear fuel. The limit is 200 ppm uranium, equivalent to 2470 Bq/kg of ^{238}U. This regulation is applied for limiting mining from a radiological point of view. As this is not a judicially sound basis for the regulation, SSI is planning to investigate whether a regulation could be introduced based on the Radiation Protection Ordinance. So far SSI has assessed the doses that might be caused by different exposure pathways. Discussion will take place on whether to regulate peat mining or the handling of the ash. The decision will be based on an optimization between costs and dose averted.

2.2. NORM residues

The Swedish drinking water regulations include action levels for radon in drinking water at 100 and 1000 Bq/L and a recommendation for uranium in drinking water at 15 μg/L. Some of the equipment for drinking water treatment available on the market, such as filters of different kinds, may be enriched with radionuclides in such a concentration that the used equipment needs to be handled and disposed of with care from a radiological point of view. The volume of enriched used water treatment filters is growing and several issues have to be solved — handling and disposal procedures, regulations, criteria and routines still have to be developed. This is the case for all NORM waste, but is particularly important when it comes to filters from water treatment, be it filters from drinking water treatment plants or filters from drilled wells for households. SSI will further investigate how a final repository for used filters and deposits containing enhanced concentrations of naturally occurring radioactive nuclides will be arranged.

It is known that industries using large amounts of water may have problems with deposits of naturally occurring radionuclides in pipes. This has been found in pipes from paper industries in Sweden. Deposits are usually found when pipes are transported to scrap metal yards.

The iron and steel industry uses raw material from mines in two plants in Sweden. The concentrations of naturally occurring radionuclides are low in the raw material, but blast furnace slag contains enriched concentrations of these radionuclides. The gamma dose rate on the surface of the slag is up to 0.4 μSv/h and the concentration of ^{226}Ra is 250 Bq/kg. The slag is reused as filling material for road construction and also for buildings. Preventive measures to avoid radon concentrations above the action level of 200 Bq/m^3 for indoor air should be taken when slag is used for building construction. Liquid discharges have not been investigated but since water treatment exists due to environmental regulations the discharges are considered low. Atmospheric discharges of ^{210}Po and ^{210}Pb from off-gas and treatment systems are also considered to be very low. Soil sample analyses from around one of the steel industry areas did not show any increase in the environmental concentration of these radionuclides.

2.3. Thoriated welding electrodes

Thoriated tungsten welding electrodes are used by both professional welders and hobby welders. Different studies on exposure from thoriated electrodes show that both the welding as well as the grinding of the electrodes may give rise to an exposure from thorium and its decay products. According to the Swedish Welding Commission there is knowledge about the risk from thoriated welding electrodes among welders. Work environmental regulations state that separate ventilation must be used when welding but not for grinding. Wet grinding equipment that reduces the dispersion of dust and particles is available on the market. New environmentally friendly electrodes without thorium are available on the market and a slow change to these electrodes is in progress. Still, thoriated electrodes are used slightly more often than the environmentally friendly electrodes, according to the major retailers of welding equipment in Sweden. SSI might consider encouraging a faster change to new electrodes on the market.

2.4. Zircon sand

Zircon sand is used for its high temperature properties in iron and steel foundries and in fine ceramics. Zircon is neither mined nor milled in Sweden. The exposure from the use and storage of zircon has been investigated and is considered low. The gamma dose rate from a bag of sand is up to 3 μSv/h, but the time spent close to the bag is short. The use of zircon in industries may volatilize ^{210}Po and ^{210}Pb and dust can be inhaled. It was observed that industries that use zircon sand have an interest in avoiding dusty environments due to other health aspects. As long as the Work Environment regulations for dust are followed, the risk from naturally occurring radioactive nuclides is low.

2.5. Historic waste

Historic waste from industry processes is found in several places in Sweden. Large amounts of burned alum shale are found in piles in areas where alum shale mining has occurred. The red coloured material is widely used as filling material on tennis courts and sports grounds. Before awareness of the hazards with radon emanation from the material had been raised, houses were built upon the material, with high radon concentrations indoors as a result. Residues from mining and the steel industry can also be found, as well as phosphogypsum from the phosphate industry. This material can be used for road construction but should be avoided as building material for house construction. The untouched historical waste is not considered hazardous from a radiological point of view.

2.6. Radon in workplaces

Radon in indoor air is the most common exposure to naturally occurring radionuclides in Swedish workplaces. Since 1997, an action level for workplaces above ground of 400 Bq/m^3 has been in place. Radon in mines has been controlled since 1972 and today there is an action level for radon progeny of 2.5 MBq·h·m^{-3} in a year (equivalent to a radon concentration of about 1500 Bq/m^3 for a 1600 h annual exposure time). Radon in mines is measured continuously and reported to the Work Environment Authority. If the radon exposure in a mine is found to be too high, a change in tasks by the mine workers is required for a certain period.

A random selection of workplaces above ground was measured for radon during 2005 and 2006. The mean concentration of 209 measurements in 85 work places was 82 Bq/m^3. Two per cent of the measurements showed radon concentrations above the action level, all in basements or on the ground floors. A separate study is ongoing for radon in schools and pre-schools. The action level for schools is 200 Bq/m^3 according to General Advice from the National Board of Health and Welfare. Preliminary results show that about 10% of schools and pre-schools are estimated to have radon concentrations above 200 Bq/m^3. A summary of measurements made in schools and pre-schools until 1999 estimated that 16% of the schools had radon concentrations above 200 Bq/m^3. In earlier studies, enhanced radon concentrations were found in water treatment plants and churches.

2.7. Aircrews

SSI is actively working in the area of protection of aircrews from cosmic radiation. SSI has initiated plans to regulate the situation for aircrew members from a radiological point of view. The estimated doses to Swedish aircrew are comparable to doses to workers at nuclear power plants.

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EXPOSURE AND RADIATION PROTECTION FOR WORK AREAS WITH ENHANCED NATURAL RADIOACTIVITY

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Abstract

Work activities with materials containing an enhanced content of natural radioactivity may lead to increased exposures of workers or members of the public. Thus they are subject to radiation protection regulations if reference levels are exceeded as described in the German Radiation Protection Ordinance which has been in force since July 2001. To optimize monitoring and/or possible radiation protection measures, reliable methods for measurements and exposure assessments have to be developed, taking into account material matrices, radionuclides involved, workplace conditions and exposure pathways. In this context, case studies have been carried out for both radiation exposure of workers at several work places and exposure of members of the public due to the disposal of industrial residues. In the paper, practical results and conclusions are summarized for two cases: (i) exposure of workers during handling and/or milling of zircon sand and (ii) exposure of members of the public who live close to a red mud disposal site of an aluminium oxide production plant.

1. INTRODUCTION

In Part 3 of the German Radiation Protection Ordinance (RPO) [1], work activities are described as operations involving the (unintended) presence or increase of natural radiation sources leading to a significant radiation exposure of workers or members of the public and/or to radioactive contamination. Work activities which may lead to elevated exposures of workers are given in Appendix XI of the RPO. Elevated exposures of members of the public may result from the use or disposal of residues from industrial processes with enhanced natural radioactivity as listed in Appendix XII. Both work activities and the disposal of the listed residues are subject to radiation protection regulations if reference levels are exceeded. These levels are dose limits that apply to workers involved in work activities. Control of residues is required if the processing or disposal of these residues could result in the reference effective dose (Richtwert) of 1 mSv in a calendar year being exceeded. Based on this reference effective dose, a list of residues to be considered is given in Appendix XII, and appropriate action levels in terms of specific activities of natural radionuclides in the residues have been deduced. Furthermore, the authorities can prescribe protective measures for unlisted materials or residues in cases of elevated exposures to workers or members of the public that cannot be disregarded from the viewpoint of radiation protection.

Practically, protective measures should be implemented only after a careful assessment of the radiological situation. Specific measurements have to be carried out to assess whether the reference levels of the RPO are exceeded. Contrary to the monitoring of workers in the field of practices, generally applicable methods for measurements and assessments are not yet available for work activities and industrial residues containing enhanced natural radioactivity. Therefore, a Coordinating Office has been established at the Federal Office for Radiation Protection to investigate typical work activities and industrial residues, with the objective of developing optimized methods for measurements and exposure assessments, and to provide guidance for practical solutions [2]. In this context, a study of the exposure pathways of workers and members of the public during the disposal of residues (sludges) from pig iron production was carried out previously [3]. In the present paper, the possible exposure of members of the public from red mud of an aluminium oxide production plant, which is explicitly listed in Appendix XII of the RPO, is discussed. Furthermore, results of a zircon sand study are presented. This material is known to have enhanced natural radioactivity [4–6] but is not listed in the RPO since a previous estimate using a generic model [7] did not indicate a significant exposure to workers. To verify this exclusion, practical measurements have been carried out in cooperation with a zircon milling company in Germany.

2. EXPOSURE OF WORKERS DURING HANDLING AND/OR MILLING OF ZIRCON SAND

For different kinds of industrial applications, for example for the production of zircon based opacifiers used in the ceramics industry (glazes of tiles and sanitary ware), fine and dry flour of iron free zircon sand is needed as an ingredient. Zircon sand is used also to an increasing extent for the production of iron free grinding balls, cylinders, bricks for linings of mills, funnels and special parts exposed to abrasion. It is well known that zircon sand has an approximate chemical composition of ZrO_2 (66%), SiO_2 (33%), Al_2O_3 (≤0.2%) and TiO_2 (≤0.2%) and contains small amounts of enhanced natural radioactivity, i.e. the radionuclides of the ^{238}U and ^{232}Th decay chains [4–6]. Work activities related to zircon sand handling or milling, as well as the raw zircon sand, the products or components containing such sand and the production residues, are not included in Appendices XI and XII of the German RPO. The omission of zircon sand residues is due to an earlier estimate based on a generic model [7] that the airborne zircon dust in a foundry may lead to an internal exposure of workers of only up to 0.5 mSv/a. To verify this estimate, a case study has been initiated together with a zircon sand milling company in Germany. Thus an assessment of the possible exposure pathways (external exposure, finger exposure and internal exposure due to inhalation of dust) of workers handling zircon sand was carried out to evaluate the radiological situation. The measurements are specific to the work areas considered.

Different kinds of sample materials were analysed in the laboratory using gamma ray spectrometry. The samples originated from different places around the world and reflect the most commonly used raw materials in Germany. About 500 g of sample material was put into gas-tight containers to keep the radon and its decay products inside the sample container. After waiting for almost three weeks to reach the equilibrium between them, the emitted gamma radiation was measured with an n-type high purity Ge detector (GMX detector, 40% relative efficiency) placed inside lead shielding. The GMX detector provides high detection efficiency also at low gamma ray energies such as the 46.54 keV gamma ray originating from ^{210}Pb decay and the 63.28 keV gamma ray from ^{234}Th decay, which have, in addition, low emission probabilities of 4.25% and 4.1%, respectively. A systematic study was performed to deduce correction factors for the self-absorption of these gamma rays in the zircon sand samples. Selected results are listed in Table 1. The highest ^{238}U activity concentration of about 3700 Bq/kg was found in a sample from South Africa.

TABLE 1. ACTIVITY AND MASS CONCENTRATIONS IN ZIRCON SAND (2-sigma uncertainties are displayed in parentheses)

Origin	Density (g/cm^3)	Activity concentration (Bq/kg)			Mass concentration (μg/g)	
		^{238}U	^{226}Ra	^{232}Th	U_{nat}	Th_{nat}
South Africa	2.7	3700 (700)	3500 (700)	645 (130)	300 (6)	160 (30)
USA	2.7	1320 (260)	1500 (300)	190 (40)	107 (21)	47 (9)
Australia	2.85	2300 (450)	2300 (450)	530 (110)	185 (40)	130 (25)

Ambient dose rate measurements were performed at several working places in the milling plant, where the mobile dose rate meters were placed on a tripod about 1 m above ground. Enhanced values were measured, for example, in the storage and milling rooms. A pile of several thousand tons of zircon sand generated an ambient dose rate $\dot{H}^*(10)$ of about 0.9 μSv/h, measured in front of the pile. The highest values measured were about 1.5 μSv/h, in fair agreement with published values of 1.7 μSv/h [4]. Assuming 2000 hours of working time per year in the storage or milling rooms, which is a conservative assumption, an effective dose of about 3 mSv would be delivered to the workers. This estimate is based on a conversion factor of 1 between the measured ambient dose and the effective dose according to the recommendations given in Appendix D of the Guidelines [2]. It should be noted that for workers (>17 years of age) in opencast mining areas, a conversion factor of 0.6 is recommended [8] for the estimate of the effective dose which would result in an effective dose of 1.8 mSv/a.

Usually the zircon sand is milled according to the specifications of the user, and a grain size down to 1 μm is achievable. In the milling room, airborne dust is unavoidable and may be inhaled by the workers. Thus, the size distribution of the dust grains in the breathing air was measured using a Berner impactor placed on a tripod. The maximum of the distribution was found for a grain size between 3 and 6 μm, and for the range from 0.3 to 3 μm the dust contained the highest alpha activity. In particular the small grain size fraction of the dust may be deposited in the lung, causing internal exposure. Therefore, the exposure pathway due to the inhalation of dust was investigated in more detail.

The dust measurements were carried out during the milling of a large amount of zircon sand using two standard air sampler systems (GSA-GSP). The two dust samplers were placed in the milling room with the air sucking heads positioned about 1 m above ground. The amount of dust deposited on a filter placed into the air stream was measured over a period of about 8 h. An average dust concentration in air of about 3.2 mg/m^3 was estimated. The alpha activity of the dust collected by the filter was measured using a commercially available and calibrated gross alpha counter. As a result, an alpha activity in air of 29 mBq/m^3 was determined. Using the conservative assumption of 2000 working hours per year at this place, a standard breathing rate of 1.2 m^3/h and an effective dose coefficient of 8.0 μSv/Bq, a lung dose of about 0.65 mSv per year can be calculated due to this alpha activity. The effective dose coefficient has been deduced from a weighted average (according to the amounts of U_{nat} and Th_{nat}, see Table 1) of the dose coefficients given for inhalation of uranium and thorium and their decay products in Appendix C of Ref. [2].

The milling process and the partitioning of the product are only partly remotely controlled. Thus there are situations where the workers have to perform some tasks by hand and have contact with zircon sand, zircon flour or zircon dust layers, i.e. the hands and fingers may get contaminated. Therefore, measurements of the exposure of the fingers of workers handling the zircon sand and/or operating the milling machines were carried out using authorized finger dose meters containing thin thermoluminescent detectors on the basis of ^{7}Li:Mg,Cu,P (TLD-700). These detectors are sensitive to beta and gamma radiation. Six detectors were used for a relatively short period, about ten working days. On these days, standard working tasks were performed by the workers. Using the assumption of 2000 h of working time (which is a quite conservative assumption), $H_p(0.07)$ dose values between 0.3 and 9 mSv have been estimated for the fingers. These values need to be verified by additional measurements over a longer period of time to improve the statistical significance of the results; however, they are far below the organ dose limit (500 mSv for fingers) specified in the RPO.

In conclusion, possible exposure paths were identified and studied during the handling and/or milling of zircon sand. The estimated effective doses do not exceed the reference level of the RPO regulation (6 mSv/a for workers). Thus the omission of these work activities from Appendix XI of the RPO is justified and authorities do not need to intervene. Dedicated measures to improve the radiation protection of workers are not necessary. The implementation of working conditions and general safety standards according to the guidelines of the professional organizations and associations of the mineral industry also contributes, in this particular case, to the compliance with the radiation protection regulations.

3. EXPOSURE OF WORKERS AND/OR MEMBERS OF THE PUBLIC FROM DEPOSITED RED MUD

Bauxite is the raw material for the production of aluminium oxide. Nowadays, the raw material is imported in large amounts into Germany. The material contains, besides aluminium, many compounds of medium and heavy elements as well as natural radionuclides in low concentrations. In the primary production process, the aluminium is extracted as aluminium hydroxide via a chemical method. The bauxite is washed, ground and dissolved in sodium hydroxide at high pressure and temperature (Bayer process, 1887). The resulting liquor contains, besides aluminium compounds, undissolved bauxite residues containing Fe_2O_3 (30–60%), SiO_2 (3–50%), Na_2O (2–10%) and TiO_2 (Trace–10%) [9, 10] — the so-called red mud. About 900 000 t of red mud are produced every year in Germany [11]. The colour reflects the high amount of iron hydroxide in the red mud. It has been subjected to sodium hydroxide treatment, i.e. red mud is highly caustic with pH values in excess of 13, but chemically stable and non-toxic. Despite many efforts, red mud is not used for any important industrial processes and thus is disposed of in special areas according to the German disposal regulations. The areas are usually fenced and closed to the public. Red mud is explicitly listed in the RPO, Appendix XII, due to the occurrence of enhanced natural radioactivity. Thus, a possible exposure of members of the public has to be assessed.

At the beginning of the study of a large disposal site in Germany, the possible exposure of workers through external gamma radiation was estimated. The dose rate $\dot{H}_x$ was measured at several places on the fenced disposal area with a mobile dose rate meter positioned about 1 m above the ground. Values between 180 and 275 nSv/h were obtained. The contribution from the background, measured outside the area, was about 50 nSv/h. Since the annual amount of working hours directly on the deposit is low, of the order of 100 h, the exposure of workers is not significant and can be neglected.

The activity concentrations of natural radionuclides in bauxite and red mud samples were determined in the laboratory using gamma ray spectrometry. The bauxite samples were milled to a grain size of <2 mm using a laboratory mill to obtain homogeneous samples. Subsequently, the sample material was filled into gas-tight containers. After a waiting period of about three weeks, as was done for the zircon sand samples, the gamma rays were measured with the GMX detector setup. Typical results are given in Table 2.

The activity concentrations in the bauxite samples are relatively low and the radionuclides ^{238}U and ^{226}Ra are found to be in radioactive equilibrium (within uncertainties). For the red mud, the measured activity concentrations are generally higher compared with the values for the bauxite samples. Furthermore, the activity concentrations of ^{228}Ra and ^{228}Th (radionuclides in the ^{232}Th decay chain) are about twice as high as the values for ^{238}U and ^{226}Ra of the ^{238}U decay chain.

TABLE 2. ACTIVITY CONCENTRATIONS IN BAUXITE AND RED MUD (2-sigma uncertainties are given in parentheses)

	Activity concentration in dry mass (Bq/kg)					
	^{40}K	^{228}Ra	^{228}Th	^{226}Ra	^{238}U	^{210}Pb
Gove-bauxite	<20	140 (20)	140 (40)	95 (15)	93 (18)	80 (15)
Boke-bauxite	<20	135 (20)	135 (40)	65 (10)	65 (13)	62 (12)
Red mud	<30	370 (50)	380 (50)	190 (30)	190 (40)	150 (30)

The enhanced activity concentrations in bauxite and red mud samples found in the investigation are in agreement with previous work [9]. Since red mud is listed in Appendix XII of the RPO, it has to be assessed and handled according to the regulations. The total activity concentration in the red mud sample was deduced to be 0.19 Bq/g (^{238}U decay chain) + 0.38 Bq/g (^{232}Th decay chain) = 0.57 Bq/g according to the sum rule given in Appendix XII where the representatively determined highest activity concentrations of any member of the decay chains of ^{238}U and ^{232}Th are added. Subsequently, this value is compared with a control limit which depends on the groundwater conditions and on the amount of residues to be deposited. In this particular case, the deduced value of 0.57 Bq/g is lower than the control limit of 1.0 Bq/g as given in the regulations for a disposal site outside the catchment area of an exploitable groundwater reservoir. Thus, the disposal of red mud on this site is not subject to regulations. However, a reduced control limit of 0.5 Bq/g has to be applied if more than 5000 t of residues are deposited in an area of exploitable groundwater. In any case, a detailed analysis of the groundwater conditions is required, which is, however, outside the scope of the present study.

The red mud disposal site investigated in this case had been established many years ago at an area with a thick clay (waterlogged soils) basement and sidewalls which provide a natural shield against water flow due to their low permeability. Surface water and groundwater samples were taken at several control points and analysed. For this purpose, the water samples were treated in the radiochemical laboratory according to specific procedures [12], and subsequently the alpha and beta activities were measured. Some typical results are given in Table 3. The measured activity concentrations are very low and close to the upper end of the natural background concentrations measured for undisturbed groundwater in Germany.

Another possible scenario would be the internal exposure of members of the public due to inhalation of airborne dust generated from the surface of the

TABLE 3. ACTIVITY CONCENTRATIONS IN GROUNDWATER AND SURFACE WATER (2-sigma uncertainties are given in parentheses)

	Activity concentration (mBq/L)				
	^{210}Pb	^{210}Po	^{226}Ra	^{228}Ra	^{238}U
Groundwater 4	2.5 (1.1)	2.8 (0.6)	59 (7)	14.0 (3.8)	<0.7
Groundwater 6	3.4 (1.2)	2.9 (0.6)	11.0 (1.9)	12.0 (3.5)	<0.7
Well A (surface)	4.5 (1.2)	4.6 (0.8)	5.3 (1.8)	15 (4)	2.8 (0.8)

red mud deposit. During the production of aluminium hydroxide, the continuously generated red mud is suspended in process water and pumped through long pipes to the disposal site. Subsequently it precipitates and part of the water is recycled. On sunny days, parts of the surface are not covered by water so that airborne dust could be produced and transported to the population living in the neighbourhood. To estimate the possible internal exposure of members of the public due to inhalation, the model developed for uranium mining sites has been applied [8]. Based on the activity concentrations given for red mud in Table 2, and assuming radioactive equilibrium in each decay chain, a dust concentration of 50 $\mu g/m^3$ and occupancies of 2000 h outdoors and 7000 h indoors, an effective dose of about 10 μSv/a has been estimated for a person of age >17 years. Similar values have been obtained for children. Hence, this exposure path is not significant and can be neglected.

In summary, based on the measurements and exposure assessments, the red mud disposal site is in compliance with the German regulations as outlined in the RPO. No additional radiation protection measures have to be implemented.

Since July 2001 Germany has had in place, for the first time, dedicated regulations to enforce radiation protection measures for workers and members of the public to limit exposure to natural radiation sources. The regulations are based on generic model considerations and partly on measurements and encompass specified work activities as well as a detailed list of industrial residues. The results of the present study confirm the validity and omission of these regulations for the bauxite residue and zircon sand milling, respectively.

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STATUS OF NATURALLY OCCURRING RADIONUCLIDES IN COPPER MINE WASTEWATER IN ZAMBIA

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Abstract

For over half a century, the Zambian economy has been relying on copper and cobalt minerals from granitic rocks of the Katanga Basin. Geologically, granites tend to be good host rocks for uranium minerals. This general observation is in addition to the well known fact that the Katanga Basin is a relatively uraniferous area. Copper mine wastewater may contain a number of alpha and beta emitters and routine control of the mine wastewater requires the measurement of mixtures of naturally occurring radionuclides. In 1993, a zero radioactivity limit value (no discharge accepted) for any radioactive material was adopted into Zambian law (Environmental and Pollution Control Act of 1993). The main objective of this study was to assess the level of naturally occurring radionuclides in mine wastewater and tailings sludge discharged to the environment from a copper mine where by-product uranium was mined and processed between 1957 and 1960. The results of this ongoing survey indicate that the radioactivity content of mine wastewater and tailings sediments exceeds the zero limit stipulated under Zambian law but are within the 'non-action level' in other countries like Poland, Portugal and South Africa. The maximum dissolved ^{226}Ra measured was 0.230 Bq/L in water discharged to surface streams and 0.176 Bq/L in the slurry discharged to tailings facilities, while ^{228}Ra was below 0.03 Bq/L in both cases. In sediments, the maximum values were 104 Bq/kg (^{226}Ra), 80.8 Bq/kg (^{228}Ra), 66.1 Bq/kg (^{224}Ra), and 1720 Bq/kg (^{40}K) discharged to tailings facilities and 56.8 Bq/kg (^{226}Ra), 47.3 Bq/kg (^{228}Ra), 56.8 Bq/kg (^{224}Ra) and 1595 Bq/kg (^{40}K) discharged to surface streams.

1. INTRODUCTION

The Zambian copper belt is one of the major mining districts of the world. It extends about 480 km north-west from Luanshya town in Zambia into the Katanga region of the Democratic Republic of Congo (see Fig. 1). Mining activities in Zambia started in the late 1920s. The mining industry was initially privately owned until the 1980s when the mines were consolidated into one company, the Zambia Consolidated Copper Mines (ZCCM), owned by the government of Zambia. The advent of privatization in 2000 resulted in ZCCM being privatized again, paving the way for two major mining companies to come on board, Konkola Copper Mines (KCM) and Mopani Copper Mines (MCM). This study of naturally occurring radionuclides in mine wastewaters was done at Nkana mine of MCM, where uranium was once mined and processed between 1957 and 1960.

The Nkana orebody at MCM consists of mineralized beds within the sedimentary sequence of quartzite/sandstone, black shale, dolomite and argillites. The main copper ore minerals are chalcopyrite and bornite, with subordinate chalcocite and oxides occurring at the North Shaft. Minor oxide copper minerals are associated with localized leach zones. Carrolite and cobal-

FIG. 1. Map of Zambia showing the copper belt region.

tiferous pyrite are the major cobalt bearing minerals, with minor amounts of cattierite.

Members of the general public in Zambia usually treat exposure to ionizing radiation as a phenomenon related to nuclear power plants and/or disasters in nuclear installations. The best example is the zero radioactivity limit for radioactive materials to be discharged to the environment in terms of the Environmental Council of Zambia wastewater guidelines, compared with ‘non-action’ levels in other countries such as Poland, Portugal and South Africa [1, 2].

Lately, more attention is being paid to radiation exposure caused by naturally occurring radionuclides. In Zambia, investigations in this field are connected only with radon exposure in underground mines but there is also a potential external gamma radiation hazard at workplaces, as well as a hazard to the natural environment receiving mine wastewater as the radium precipitates from the water.

This survey of naturally occurring radionuclides in mine wastewater and sediments was done at Nkana mine of MCM, where radon gas measurements in the underground mine [3] showed that the radon levels were over 1000 Bq/m^3 [4]. It was therefore expected that the radioactivity due to radium isotopes would be enhanced. Radium is often considered to be the most important decay product of ^{238}U. Not only does it have a high radiotoxicity but it also decays to radon, a radioactive gas whose decay products can cause lung cancer. When ingested, radium absorption from the gastrointestinal tract into blood and soft tissue is significant, with eventual deposition in bones.

The main objective of the study was to assess the levels of naturally occurring radionuclides in mine wastewater and sediments being discharged to the environment to ascertain whether pollution is taking place in the context of Zambian law.

Previous uranium exploitation at Nkana mine and the associated radioactive tailings deposition at the Amco tailings pile were focused on a small uranium deposit exploited at the Mindola No. 4 shaft in 1957–1960. Uranium occurred in the primary minerals pitchblende/uraninite and approximately 120 000 kg of U_3O_8 were recovered from the ore with an average grade of 0.25% U_3O_8. Uranium occurs in a similar manner, but at much lower levels, in most of the copper belt mines in Zambia [5].

Investigations at gold and copper mines in Cuba [6] have indicated that ^{226}Ra concentrations range between 53 and 7216 Bq/kg in various minerals and residues. Water samples had a ^{226}Ra concentration of between 4 and 160 Bq/L. A study of NORM in the copper industry in Arizona [7] reported that groundwater from six mines had ^{226}Ra concentrations ranging from undetectable levels to 4.81 Bq/L, ^{228}Ra concentrations ranging from undetectable levels to 4.51 Bq/L and total uranium concentrations ranging from undetectable levels to 7.73 Bq/L.

In the United States of America, the present drinking water standard is 0.18 Bq/L for ^{226}Ra as a maximum contaminant level (MCL) and the Environmental Protection Agency has established MCLs for alpha emitters of 0.1 Bq/L for ^{226}Ra, 0.2 Bq/L for combined ^{226}Ra and ^{228}Ra and 0.6 Bq/L for gross alpha activity [8].

In Poland, wastewater from coal mines in which the content of ^{226}Ra was more than 0.7 Bq/L had to be treated as a waste material with enhanced radioactivity [9]. Unfortunately, after Poland joined the European Union, such a requirement was cancelled due to the need for unification with European law, in terms of which there are no limitations on radium in wastewater. In South Africa, there is also no limitation of radium concentration in wastewater but the provisions of the Regulations of the 1993 Nuclear Energy Act applied to radioactive material in which the activity concentration of any radionuclide was 0.2 Bq/g or more [1].

This paper highlights the status of naturally occurring radionuclides in mine wastewater and sediments at one of the Zambian copper mines where uranium was formerly mined and processed. At this mine, wastewater from cobalt and copper beneficiation is discharged to surface water courses and tailings facilities. The treatment is generally restricted to sludge settlement and lime dosing.

This is the first attempt to sample and measure naturally occurring radionuclides in mine wastewater and sediments discharged to the environment in Zambia. The survey needs to be extended to other mines in Zambia to generate a complete picture of the status of NORM in uraniferous mines in Zambia.

2. METHODS AND INSTRUMENTATION

Three sampling campaigns were conducted between September 2005 and October 2006. Sampling for both wastewater and sediments was done in the latter half of each year when production was at a maximum to meet the annual production target. In 2005, sampling was done in September and November. In 2006, sampling was done in August. Sediment sampling was not done in November 2005 due to logistical problems. The sampling sites for both wastewater and sediments were the tailings thickener feed (mine wastewater), tailings thickener overflow (after settling) to the stream and the tailings thickener underflow (sludge) to the tailings facilities. These samples were analysed for dissolved and total radionuclides at the Central Mining Institute, Laboratory of Radiometry, Katowice, Poland.

Radioactivity in copper mine wastewater is mostly from ^{226}Ra from the ^{238}U series and ^{228}Ra from the ^{232}Th series. An existing method of chemical separation of radium [10] was modified for liquid scintillation counting [11]. Radium is co-precipitated with barium in the form of sulphates and this precipitate is mixed with liquid gelling scintillator. The prepared samples were measured by a low background liquid scintillation spectrometer (Quantulus, Wallac Oy, Finland). This counter was equipped with alpha–beta separation and an anti-coincidence shield, which enabled measurements of ^{226}Ra concentration above 0.003 Bq/L to be made simultaneously with measurements of ^{228}Ra (LLD = 0.03 Bq/L) and ^{224}Ra (LLD = 0.05 Bq/L). In addition, the procedure enabled the simultaneous determination of ^{210}Pb.

Sediments were analyzed quantitatively using a high resolution gamma spectroscopy system equipped with an HPGe semiconductor detector. Samples of sediments were dried at 105°C until reaching a stable mass. Radium-226 was measured directly by the 186 keV energy peak (^{226}Ra) or by its progeny after equilibrium had been reached — by ^{210}Pb at 295 and 351 keV and by ^{214}Bi at 609 keV. Radium-228 was determined by ^{228}Ac at 338 and 911 keV, while ^{224}Ra was determined by ^{212}Pb at 238 keV and by ^{208}TI at 583 keV. The detection limit was less than 1 Bq/kg for each radionuclide. The results are expressed in units of becquerel per kilogram dry mass and the uncertainty was quoted in terms of one standard deviation.

3. RESULTS AND DISCUSSION

The results of the analyses based on liquid scintillation spectroscopy measurements for dissolved ^{226}Ra and ^{228}Ra are given in Table 1. The measured concentrations of radium isotopes in the samples showed remarkably enhanced concentrations of dissolved ^{226}Ra in the tailings discharge and little ^{228}Ra in water discharged to the stream. This was expected, considering the high sulphate content of the ore (chalcopyrite) with the presence of barium ions which co-precipitate with ^{226}Ra and settle out as sediment in the tailings discharge.

In sediments, enhancements of radionuclides discharged to the environment were found to be negligible, as shown in Table 2. The concentrations of the radionuclides generated during beneficiation of copper and cobalt are almost the same as those in the discharge to the tailings facilities, with little reduction in concentration in the discharge to the streams. This can be attributed to the alkaline nature of the mine wastewater, which does not

TABLE 1. DISSOLVED RADIONUCLIDES IN WASTEWATER

	Activity concentration (Bq/L)					
	Tailings thickener feed		Tailings thickener overflow		Tailings thickener underflow	
	^{226}Ra	^{228}Ra	^{226}Ra	^{228}Ra	^{226}Ra	^{228}Ra
September 2005	0.097 ± 0.011	0.18 ± 0.06	0.043 ± 0.007	<0.03	0.176 ± 0.019	0.08 ± 0.07
November 2005	0.115 ± 0.011	<0.03	0.041 ± 0.006	0.11 ± 0.04	0.212 ± 0.018	0.10 ± 0.03
August 2006	0.065 ± 0.010	<0.03	0.037 ± 0.005	<0.03	0.230 ± 0.021	<0.03

TABLE 2. RADIONUCLIDES IN SEDIMENTS

	Activity concentration (Bq/kg)			
	^{226}Ra	^{228}Ra	^{224}Ra	^{40}K
Tailings thickener feed				
September 2005	78.4 ± 6.1	60.1 ± 3.3	54.8 ± 3.1	1621 ± 88
August 2006	80.25 ± 3.75	73.9 ± 4.6	66.1 ± 5.75	1720 ± 69
Tailings thickener underflow				
September 2005	80.6 ± 4.3	53.5 ± 3.7	50.7 ± 3.6	1424 ± 58
August 2006	104.0 ± 4.5	80.8 ± 5.1	69.8 ± 4.7	451 ± 29
Tailings thickener overflow				
September 2005	50.17 ± 4.3	39.7 ± 3.7	35.7 ± 3.3	81 ± 58
August 2006	56.85 ± 3.65	41.9 ± 4.5	38.6 ± 4.7	96 ± 18

support dissolution of ^{226}Ra. Therefore, the suspended radionuclides generated from mining activities end up in sediments at tailings facilities.

The average concentrations for dissolved radionuclides in mine wastewater and suspended radionuclides in sediments before and after treatment are shown in Figs 2–6.

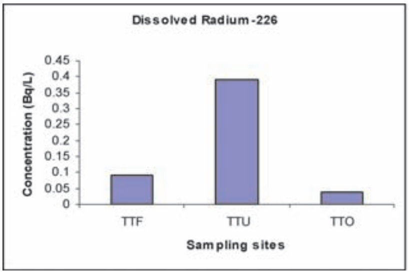

FIG. 2. Dissolved ^{226}Ra in wastewater.

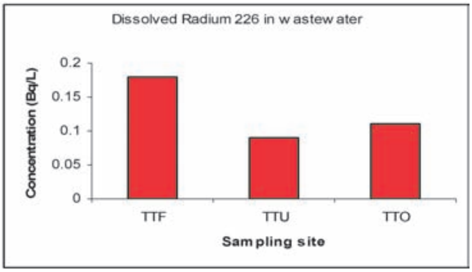

FIG. 3. Dissolved ^{228}Ra in wastewater.

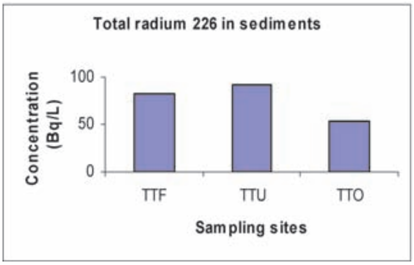

FIG. 4. Total ^{226}Ra in sediments.

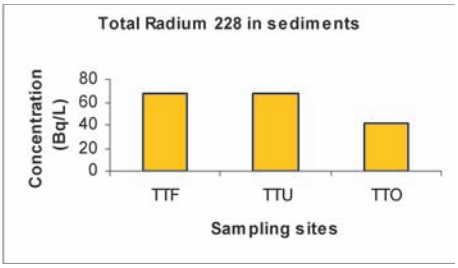

FIG. 5. Total ^{228}Ra in sediments.

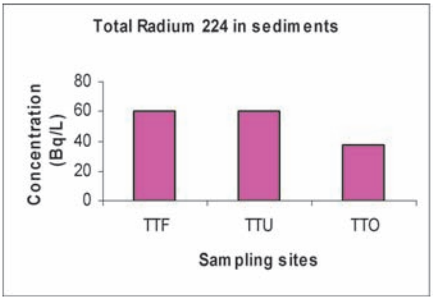

FIG. 6. Total ^{224}Ra in sediments.

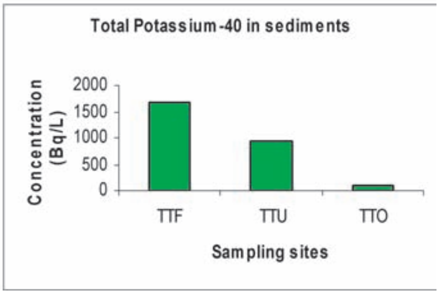

FIG. 7. Total ^{40}K in sediments.

Note to Figs 2–7: TTF: Tailings thickener feed (mine wastewater)
TTU: Tailings thickener underflow (to tailing facilities)
TTO: Tailings thickener overflow (to the stream).

4. CONCLUSIONS

From the preliminary survey with a limited number of sample measurements it can be concluded that the current treatment strategy of lime dosing and sludge settling enhances the dissolved ^{226}Ra concentration in the tailings thickener underflow discharged to the tailing facilities and little is discharged to the streams. It can also be concluded that this treatment strategy has little or no effect on the suspended radionuclides in the sediments — almost all the radioactivity associated with copper and cobalt beneficiation ends up in the tailings facilities. Therefore, under the Zambian legal limit of zero radionuclide discharges into the environment, pollution in the form of naturally occurring radionuclides can be said to be taking place.

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REVISION OF THE EURATOM BASIC SAFETY STANDARDS WITH REGARD TO NATURAL RADIATION SOURCES

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Abstract

The current Basic Safety Standards Directive 96/29/Euratom includes natural radiation sources in a specific Title VII, which covers NORM industries, radon in workplaces, and the exposure of aircrews. The Commission and the Group of Experts established under Article 31 of the Euratom Treaty have undertaken a revision of the Directive amongst others to strengthen the requirements on natural radiation sources in view of further harmonization. The revision will also allow for the new Recommendations of ICRP and similar developments for the Inter-Agency Basic Safety Standards. A provisional outline of the new requirements, in particular with regard to NORM industries, is presented. The prospect for incorporating NORM industries in an overall graded approach to regulatory control and radiation protection for any type of practice is discussed, as well as the link with other EC legislation and guidance on the quality of drinking water and on construction materials.

1. THE EURATOM BASIC SAFETY STANDARDS OF TODAY

The Euratom Basic Safety Standards (EU BSS) for the protection of the health of workers and the general public against the dangers arising from ionizing radiation (Directive 96/29/Euratom) [1] set out the framework for radiation protection within the European Union and Member States are obliged to transpose them into national legislation. When the present EU BSS were issued in 1996 they included for the first time special provisions concerning exposure to natural radiation sources (Title VII of the Directive). Some exposures to natural sources were, however, excluded from the scope of the Directive, such as exposure to radon in dwellings and the natural level of radiation, i.e. to radionuclides contained in the human body, to cosmic radiation at ground level or to above ground exposure to radionuclides in the undisturbed earth crust.

Title VII addresses the concept of a ‘significant increase in exposure due to natural radiation sources’. There are no defined activity concentrations or doses above which exposures are regarded to be of regulatory concern. Instead, title VII introduces a stepwise system where the Member States are required to identify work activities of concern and set up appropriate means for monitoring exposures in these work activities and as necessary apply radiation protection measures to reduce exposures (articles 40 and 41). Title VII also introduces requirements on the protection of aircrews (article 42). The work activities indicated in Title VII are specified as:

> “a. work activities where workers and, where appropriate, members of the public are exposed to thoron or radon decay products or gamma radiation or any other exposure to radiation in workplaces such as spas, caves, mines underground workplaces and above ground workplaces in identified areas;
> b. work activities involving operations with, and storage of, materials, not usually regarded as radioactive but which contain naturally occurring radionuclides, causing a significant increase in the exposure of workers and, where appropriate, members of the public;
> c. work activities which lead to the production of residues not usually regarded as radioactive but which contain naturally occurring radionuclides, causing a significant increase in the exposure of members of the public and, where appropriate, workers;
> d. aircraft operation.”

2. GUIDANCE TO MEMBER STATES

In order to clarify the intentions behind Title VII of the Euratom BSS and to offer guidance to national authorities in regulating natural radiation sources, the European Commission has published several reports, most of them endorsed by the Article 31 Group of Experts. The guidance given in these reports is also intended to stimulate harmonization between Member States and can be downloaded from the European Commission web site.[1] Of

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[1] http://ec.europa.eu/energy/nuclear/radioprotection/index_en.htm

particular relevance to NORM are the recommendations for the implementation of Title VII of the EU BSS (RP 88) [2], reference levels for workplaces processing NORM contaminated materials (RP 95) [3], guidance for natural radioactivity of building materials (RP 112) [4] and for applying the concepts of exemption and clearance to natural radiation sources (RP 122) [5]. The Commission has also published screening levels for discharges of effluents containing NORM (RP 135) [6]. Here follows a brief overview of the content of these reports.

Radiation Protection 88 [2] is technical guidance on the identification of work activities that might be of concern for the protection of workers and of related protection measures. It deals with radon in workplaces, exposure to aircrews and industrial processes involving natural radionuclides other than radon. A framework for the control of exposure to workers is introduced, indicating that a level of 1 mSv/a could be of relevance when assessing where precautions are required and 6 mSv/a could be of relevance where further protective measures would be needed.

Radiation Protection 95 [3] provides reference levels for identifying industries where workers' exposure should require regulatory control. The reference levels are specified in terms of activity concentrations of the input material. The exposure scenarios are based on a review of relevant industries within the EU and consider normal and unlikely, or extreme, situations. The reference levels have been defined in relation to 'marker points' in terms of annual effective dose (1 and 6 mSv/a).

Radiation Protection 112 [4] provides guidance for controlling the radioactivity of building materials (defined as "any material which is produced for incorporation in a permanent manner in buildings"). Controls on the radioactivity of building materials are based on the following criteria and principles:

"a) …Within the European Union, doses exceeding 1 mSv a^{-1} should be taken into account from the radiation protection point of view. Higher doses should be accepted only in some very exceptional cases where materials are used locally… ;

b) …Building materials should be exempted from all restrictions concerning their radioactivity if the excess gamma radiation originating from them increases the annual effective dose of a member of the public by 0.3 mSv at the most… ".

In order to identify whether the dose criterion is met, Radiation Protection 112 derives an activity concentration index[2] using well established results of room models.

Radiation Protection 122, Part II [5] gives guidance on the concepts of exemption and clearance for natural radiation sources for materials arising from industries that mine or process ores or other materials for which the presence of naturally occurring radionuclides is of concern. It proposes to set the criteria for exemption and clearance for such work activities at an annual effective dose increment of the order of 0.3 mSv, in addition to background exposure from natural radiation sources. As the NORM industries normally process and release large volumes of materials, one single set of levels for exemption and clearance is used. Based on this, exemption/clearance levels for NORM were calculated with different scenarios (transport, storage, disposal on a heap, etc.). Levels are rounded to 0.5 Bq/g for uranium and thorium in secular equilibrium on the basis that "…this is in the upper range of concentrations usually found in ores and thus ensures that regulatory control is practicable".

Radiation Protection 135 [6] analyses NORM discharges to sea, air and river and proposes screening levels as amounts of gigabecquerels per year. The screening levels correspond to dose criteria of 10, 100 and 300 μSv/a. The report also includes a study of the regulatory situation in the Member States with regard to NORM. Although all Member States have acknowledged the issue of 'work activities' within their regulatory structure, it was clear from a benchmark exercise that the national approaches to topics such as discharge limits differed.

3. REASONS FOR A REVISION OF TITLE VII

When adopting the present EU BSS, the European Union opted for a flexible approach to natural sources, thus leaving considerable room for interpretation. This has led to different approaches in different Member States. Although there exists guidance on, for instance, exemption and clearance levels, Member States have come to different conclusions on which materials should be subject to regulatory control. Some of the products including NORM or residues from NORM industries intended for recycling are subject to trade

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[2] $I = C_{Ra}/300 + C_{Th}/200 + C_K/3000$, where C_{Ra}, C_{Th} and C_K are the radium, thorium and potassium activity concentrations (in Bq/kg) in the building material.

between Member States. Therefore, harmonization is also needed from a trade and economic point of view.

Since 1996, the Member States have gained considerable knowledge on NORM issues, by national studies, inventories and assessments. The international knowledge has improved with a number of conferences on this topic and case studies with real dose assessments. Guidance material has been published by international organizations and bodies such as the IAEA. International consensus on the concepts of exclusion, exemption and clearance has also been achieved [7].

The knowledge gained will, along with new recommendations from the ICRP, provide a firm basis for introducing more binding requirements on NORM. A revision of the EU BSS is also timely from the perspective that the IAEA has recently started a revision of the Inter-Agency Basic Safety Standards (IA BSS), something which may further improve international harmonization in this field.

4. REVISION PROCESS

In 2005, the Article 31 Group of Experts set up a number of working parties with the task of analysing the need for a revision of the EU BSS and proposing changes to the Directive. The Working Party: Natural Sources has presented a report on NORM industries to the Article 31 Group of Experts and during 2007 focused on radon (workplaces as well as dwellings). A provisional timetable has been set up, where the aim is to propose a new EU BSS Directive before the end of 2008. If so, adoption by the European Council would be possible during 2010.

Radon in dwellings and in drinking water are two issues not mentioned in this paper, but both are part of the scope of the revision. In both areas, European Commission recommendations exist [8, 9] and, if possible, the content will be incorporated into the Directive. The possibility of explicitly addressing radon and introducing a regulatory framework in the Directive is at present analysed by the Working Party: Natural Sources.

5. CHALLENGES

A revision of the EU BSS is always a challenge for the European Commission and the Article 31 Group of Experts, in particular the quest for integrating natural sources further in the general radiation protection scheme. But the experience from the present directive shows that Member States interpret Title VII in different ways, thus leading to different approaches to natural sources in different Member States.

The revision of the EU BSS will aim at strengthening existing legislation, incorporating other Directives and, if possible, also parts of what is now in guidance reports and Recommendations. Efforts will also be made to link the regulatory approach for natural sources as closely as possible to the regulatory approach for artificial radionuclides, although it may be difficult to achieve this completely because natural sources differ in a number of ways to artificial sources. Natural radioactivity is often involved in work activities or processes well known to mankind and these industries do not exploit the material for its radioactive properties. The safety risks differ significantly, as natural sources can never result in health effects of the kind high activity sources or the use of nuclear energy may cause in accidental situations.

Taking such differences into account, a regulatory approach which is similar for both categories could be helpful, not only for the regulator but also for industries which treat both types of material, in particular waste treatment facilities, which may handle both nuclear waste and spent sources along with material being contaminated with natural radionuclides, e.g. pipes from oil and gas industries or groundwater treatment facilities. A common regulatory approach may also enhance the public's perception of the radiation protection framework.

One of the issues discussed is whether NORM should be regulated as before by a separate Title or whether it can be covered by the general regulatory requirements on planned exposure situations. Whether this will be possible or even suitable will depend on the revision of the EU BSS as a whole. Nevertheless, certain areas have been identified where the regulatory framework with regard to NORM can be improved. The following section describes some of the ideas and proposals discussed by the Working Party: Natural Sources.

6. OUTLINE FOR A REVISED EURATOM DIRECTIVE WITH REGARD TO NORM INDUSTRIES

6.1. Work activities

As previously mentioned, the present Title VII requires Member States to ensure the identification of work activities which may be of concern, leaving the Member State to decide what is considered of concern. For clarification, but also as a step towards harmonization of the regulatory framework for NORM, the Working Party has proposed to introduce in the EU BSS a specific list of work activities of concern. The list covers work activities known to require regulatory consideration [10] and is to a large extent similar to the work activities listed by the IAEA as requiring regulatory consideration [11].

The proposed list of work activities is a so-called positive list specifying what work activities are to be regulated. If a NORM industry is not on the list the idea is that it does not have to be regulated. However, the Working Party has suggested that a new EU BSS should be constructed in such a way as to enable Member States to add work activities to the list if the national authorities identify other activities requiring regulatory attention.

6.2. Materials of concern

As a starting point, the Working Party has proposed the following dose criteria for the exemption of NORM industries from regulatory control: 1 mSv/a for workers and 0.3 mSv/a for members of the public. Above these values, optimization should apply and protective actions should be considered to reduce the doses.

Assessing doses from NORM activities can be complicated, in particular doses to members of the public. The Working Party has therefore proposed operational levels based on activity concentrations (see Table 1). According to UNSCEAR 2000 [12] and ICRP Publication 75 [13], workers or members of the public will generally not receive doses higher than 1 or 0.3 mSv/a, respectively, if the activity concentrations are lower than the values in Table 1, except for particular situations such as exposure due to building materials containing natural radionuclides or to drinking water contaminated by wastes from mining.

Some individual elements in the decay chain, e.g. Po-210 or Pb-210, may warrant the use of values significantly higher than those in Table 1, by up to two orders of magnitude. Numerical values for segments of the decay chain can be found in Radiation Protection 122, part II [5].

TABLE 1. VALUES FOR DEFINING THE SCOPE OF REGULATORY CONTROL FOR NORM INDUSTRIES

	Activity concentration (Bq/g)
Natural radionuclides from the U-238 series	1
Natural radionuclides from the Th-232 series	1
K-40	10

6.3. A graded approach to occupational exposure

The system of protection of workers exposed to NORM should essentially be the same as for workers exposed in other practices. In the case of NORM, however, it is most unlikely that severe radiological accidents can occur and the existence of other industrial hygiene regulatory controls should be taken into account for purposes such as dose assessments and classification of workers. When discussing the regulatory requirements for NORM industries, a graded approach for the protection of workers was considered a suitable way to proceed. Reference was made to the graded approach suggested by Radiation Protection 88 [2].

If, at any time in the industrial process, the activity concentration exceeds the values shown in Table 1, the Working Party proposes that the regulatory authorities should be notified by the undertaking. The notification should include information on the materials processed, radionuclide concentrations, products, by-products and residues. Based on this information the authorities can impose requirements for the initial assessment of the exposure of workers. When the assessed exposure of workers is expected to be less than 1 mSv/a, the work activity may be exempted from further regulatory control. If the assessed exposure of workers in a group of identical industrial processes is consistently less than 1 mSv/a, these processes could be exempted on a generic basis.

If the exposure of workers can exceed 1 mSv/a but is less than 6 mSv/a the Working Party has proposed that Member States shall require the employers to regularly assess whether doses could effectively be further reduced and whether there is a potential for doses to increase over time or as a result of changes in the work practices. Where appropriate, the authorities shall request a formal implementation of the principle of optimization as it would for any other practice. Subsequent controls on monitoring occupational doses shall be commensurate with the magnitude of the exposures. Furthermore, designated members of the staff should be trained in radiation protection. For this purpose, the competence and human resources of a health and safety department within the undertaking can be used. Where appropriate, a qualified expert in radiation protection should be responsible for the training.

When the exposure of workers to NORM exceeds or is likely to exceed 6 mSv/a, Member States shall require the application of the principle of optimization and of the control measures as laid down in Title VI of the EU BSS for practices. Depending on the required level of control, this may take the form of a registration with only limited obligations on the undertaking to achieve the aimed level of protection, or a licence with detailed and enforced exposure control measures.

6.4. Control of public exposure from discharges and disposal of waste and residues

Doses to members of the public from industrial facilities discharging liquid and gaseous effluents containing NORM are generally below 0.3 mSv/a (see Section 6.2). Operational values in terms of becquerels per year could also be used (see for example Radiation Protection 135 [6]).

In particular situations, such as when drinking water resources are likely to be affected by discharges from NORM industries, authorization should be required. The authorization may include discharge limits and requirements on monitoring discharges. The authorization should be based on an optimization approach and of the assessment of doses to the public achieved by the undertaking.

For reuse and recycling of residues, the Working Party proposes that, in addition to the proposed reporting for NORM industries, handling material with concentrations above the values indicated in Table 1, the undertaking should also report about the foreseeable reuse and recycling of the residues. If the results of the dose assessment to members of the public indicate exposures that exceed 0.3 mSv/a, an authorization should be needed. The recycling of residues for the manufacture of building materials may warrant lower values than those proposed in Table 1.

The controversial subject of dilution has been discussed from the point of view that, for some residues from NORM industries, the optimized solution may be to dilute the residues with other materials. The Working Party, however, points out that dilution of residues from NORM industries should require, where appropriate, the review and approval of the competent authority.

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RAPPORTEUR SUMMARY OF TOPICAL SESSIONS 6 AND 7

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1. INTRODUCTION

In my summary I do not want to engage myself in reporting on the details of the presentations; rather I want to evaluate their contribution to answering some of the basic questions that were raised by D.G. Wymer in his opening presentation of this symposium. In his overview on the developments over the last ten years in the identification of the magnitude of the NORM problem, he challenged the participants to answer the question whether we are reaching consensus on the management of exposure to NORM, or whether we are still in a state of chaos. He concluded that the basic question is to reach consensus on the scope of regulatory control of NORM.

2. SCOPE OF REGULATORY CONTROL

The selection of appropriate criteria for defining the scope of regulatory control is a critical issue for NORM. Although in some cases the radiological hazards can be significant, the number of industries potentially subject to regulatory control is very large and inappropriate selection of criteria could result in many industries being regulated without any net benefit in terms of risk reduction. For this reason, the concepts of exclusion, exemption and clearance are of the utmost importance in defining the scope of regulatory control of NORM. The range of doses resulting from terrestrial radiation (excluding radon) lies between a few hundred microsieverts and a few millisieverts per year. The corresponding activity concentrations vary from a few hundredths to a few becquerels per gram.

Whereas the exemption levels for artificial sources are based on the concept of triviality of risk, associated with a dose of 10 μSv in a year, this is an impractical basis for the derivation of exemption levels for natural radionuclides. If one would impose a restriction of 10 μSv for NORM activities, it would in general not be practicable to implement a control scheme for such a small increment to the natural radiation background, which is in fact below the natural variability. Many human activities previously unregulated could then be subject to regulation. Establishing levels for natural radionuclides that invoke such widespread regulatory consideration, in circumstances where in many cases it is unlikely to achieve any improvement in protection, is not an optimum use of regulatory resources. Therefore, derivation of exemption levels for naturally occurring radionuclides should be based on a methodology that places greater emphasis on optimization of protection, including optimization of regulatory resources. ICRP Publication 60 refers to a second basis for exemption, other than exemption on the basis of trivial dose, namely that "no reasonable control procedures can achieve significant reduction in individual and collective doses". This basis for exemption is more appropriate for NORM activities than the 'trivial dose' basis.

IAEA Safety Series No. RS-G-1.7 recommends the application of the concepts of exclusion, exemption and clearance for NORM at the level of 1 Bq/g for ^{238}U, ^{232}Th and ^{226}Ra, and 10 Bq/g for ^{40}K. According to this Safety Guide, it is unlikely that individual dose due to the exposure up to these levels will exceed 1 mSv/a, except for specific situations such as building materials. Member States may consider lower activity concentrations for such situations. On the other hand, exposure to materials with activity concentrations exceeding 1 Bq/g may still lead to doses below 1 mSv/a. Such practices may then be exempted on a case by case basis. In all cases, when a NORM practice cannot be exempted, a graded approach to regulatory control should be established in which the regulatory body should define what is necessary and sufficient for an optimal level of radiation protection.

3. NORM RESIDUES

NORM industries generally produce large volumes of residues, of the order of 10^4–10^6 t/a. This necessitates a different, pragmatic approach from normal radioactive waste management, for which the principle of concentration and containment is used. For most NORM residues containment is not possible, and in many cases it is not waste but a useful recyclable residue. Therefore, for NORM residues the principle of dilution and dispersion should be preferred wherever possible. It saves resources of other materials and it reduces waste volumes. Furthermore, one should keep in mind that concentration/containment and dilution/dispersion are complementary concepts, not contradictory concepts.

4. RECYCLING OF CONTAMINATED SCRAP

Contaminated scrap is being detected in increasing amounts when entering a country, such as in harbours, and at the entrances of scrap yards and steel melting plants. The portal monitors used for the detection do not discriminate between artificial and natural sources and the alarm is set at a certain level above background. Therefore, clearance levels for metal scrap do not work in these cases. The invited lecture dealt with the Spanish protocol for controlling contaminated scrap, which was developed after the incident of the melting of a ^{137}Cs source in 1998 in the south of Spain. The protocol has been accepted as a sort of international standard and is based on voluntary cooperation of the concerned parties. It regulates the financial and waste management aspects of the detected scrap, depending on the origin of the scrap and whether it is detected before or after processing.

Much of the contaminated scrap originates from NORM industries and specific melting installations, such as at Siempelkamp in Germany, can deal with this type of contamination. The natural radionuclides go to the slag, which can be reused for instance for road construction, and the steel ingots are free of radioactivity. A German study showed that the doses to workers are below 0.3 mSv/a. From the discussion it became clear also that the general steel industry seems to be inclined towards accepting this type of contaminated scrap, which would be a major step forward for the management of NORM contaminated metal scrap.

5. WASTE MANAGEMENT

An Italian study showed enrichment of volatile radionuclides such as ^{210}Pb and ^{210}Po in fly ash in the steel industry, which is a usual feature in high temperature industrial processes. The concentrations were moderate, up to 50 Bq/g. Additional investigations are needed to define if the management of this type of waste needs further regulatory control according to Italian regulations.

In a study from Malaysia, the use of tin slag (activity concentrations 1 Bq/g ^{238}U, 0.4 Bq/g ^{232}Th and 4.5 Bq/g ^{226}Ra) as a fill in land reclamation for an industrial area was investigated. The results showed that future workers in the industrial area would not be exposed to doses exceeding 0.45 mSv/a. It was questioned during the discussion if such a dose is acceptable, as it exceeds the public dose constraint of 0.3 mSv/a, but apparently the Malaysian authorities considered this as the optimal solution for this type of waste and approved the reuse of the residue for this application.

A Dutch presentation dealt with the general principles for managing NORM contaminated residues. The approach was very pragmatic, showing that the primary aim is to recycle the residues. If this cannot be done, the waste is disposed of in a hazardous waste disposal site, stored for an interim period for decay (for ^{210}Pb containing waste) or for future reuse (depleted uranium), or disposed of as radioactive waste if the activity concentration is very high (more than 1000 Bq/g).

6. OIL AND GAS INDUSTRY

An Argentinian contribution confirmed that the doses received by workers in the oil and gas industry are generally below 1 mSv/a. Dose rates at most facility locations are within normal background levels. Older facilities show in general a higher level of contamination, and therefore periodic control of activity levels may be required. It was shown that in ethane and propane flows of gas facilities, radon can accumulate to very high activity concentrations, exceeding 300 000 Bq/m^3, which needs specific consideration when maintenance work is being carried out.

A second contribution on NORM in the oil and gas industry came from Norway, in which the environmental aspects of discharges of produced water have been investigated. Model calculations showed that the dilution of natural radionuclides in sea water occurs very rapidly. Based on the dose to certain biota and subsequent ingestion doses for the public, ‘potential no-effect concentrations’ can be calculated. The importance of this work is that it may show that considerable amounts of natural radionuclides might be discharged in the north-west Atlantic Ocean without environmental effect.

7. INVESTIGATIONS TO IDENTIFY THE NEED FOR REGULATORY CONTROL

As a consequence of the implementation of the European Basic Safety Standards in the national legislation of the European Union Member States, a number of investigations have been carried out in the last decade to identify NORM industries that cannot be ignored from a radiation protection point of view. The contributions from Sweden and Germany should be regarded in the light of this obligation. It shows that regulatory concern is necessary only in a few cases, such as the use of peat ash and the management of filters from the drinking water industry. The latter has also been the subject of a few posters and confirmed that radionuclides can accumulate to high levels in filters and sludge from water treatment plants and need regulatory control. In Sweden, special attention is paid to identify workplaces with high radon concentrations.

8. STANDARDS

A special case of non-compliance with national standards was reported from Zambia. The general public in Zambia usually treat exposure to ionizing radiation as a phenomenon related to nuclear power plants and/or disasters in nuclear installations. This has led to the adoption of a zero radioactivity limit for radioactive materials to be discharged to the environment. The contribution showed that, as a result of this extreme policy, disposal of wastewater from a copper mine is not in compliance with the regulations, even though it is treated to promote sedimentation of the natural radionuclides in a tailings pond. Other countries with a more pragmatic policy would not have a problem with such discharges.

The contribution from the European Commission showed the intentions to revise the Euratom Directive 96/29/Euratom with respect to natural sources. The revised Directive will have more binding requirements on natural sources in order to harmonize the way the various Member States have implemented Directive 96/29/Euratom. It will also promote a graded approach to regulatory control. The Commission has identified about the same list of industries of concern as the IAEA and it considers adopting the IAEA levels for defining exemption and clearance. However, lower levels may be chosen by individual Member States if appropriate. Consideration is given to specific situations, such as building materials, which may probably be regulated in a more binding way then has been done up to now. For discharges and waste, a public dose of 0.3 mSv/a is being considered as a constraint. Recycling of residues may be promoted, as well as dilution for the purpose of recycling, when this is considered to be the optimal solution.

9. CONCLUSIONS — CONSENSUS OR CHAOS?

It seems that international consensus on standards is emerging. A dose criterion of 1 mSv/a for workers is being used in many countries as a level at which to start regulatory control of NORM activities. The corresponding level of activity concentrations of 1 Bq/g for the uranium and thorium decay chain and 10 Bq/g for ^{40}K in solid materials in the NORM industry, as used by the IAEA, is being considered for adoption also by the European Commission in its revised Euratom Directive. The cooperation of the Commission and the

IAEA in the revision process of both the international BSS and the Euratom Directive is a major step forward in reaching a harmonized approach on an international level.

The investigations presented show that on many occasions the doses to workers and the public are below 1 mSv and need no further regulatory control, or else only notification. There are, however, situations that may need a more stringent control. The European Commission's initiative to establish a NORM-ALARA Network, which should lead to information exchange between operators and regulators, may also contribute to define where and how regulatory control of NORM should be exercised.

It is recognized that waste management for NORM activities needs a pragmatic approach and cannot be handled in the same way as radioactive waste with artificial radionuclides. Reuse of NORM residues is being practiced in several countries, thereby applying the D&D principle as the optimal solution.

The presentations and discussions in these two sessions contributed mainly to reaching consensus, but one can conclude that inconsistencies still exist.

MISCELLANEOUS TOPICS (2)

(Topical Session 8)

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TRADE IN RADIOACTIVE MATERIALS — POTENTIAL PROBLEMS AND POSSIBLE SOLUTIONS

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Abstract

The strengthening of radiation protection regulations (including border controls) in consumer countries may potentially lead to the partial or complete loss of market for some mineral producers, and the resulting economic and logistical constraints have become a serious consideration for individual industries. The IAEA Regulations for the Safe Transport of Radioactive Material (IAEA Safety Standards Series No. TS-R-1) and Advisory Material (IAEA Safety Standards Series No. TS-G-1.1) provide detailed instructions on the transport of material with elevated concentrations of natural radionuclides. However, these documents are somewhat complex for a common user and this paper presents an overview of a simplified step by step guideline developed for both the minerals industry and the appropriate regulatory authorities. Also presented are considerations for the regulatory control of natural radioactivity in international transport and trade and the potential radiation protection and regulatory problems that may arise during transport and at international border crossings. Solutions for these problems are offered in the conclusion.

1. INTRODUCTION

An analysis of the suitability of Ref. [1] for NORM was made in 1999 [2, 3] and followed up in 2000 [4]. The strengthening of radiation protection regulations (including border controls) in consumer countries may potentially lead to the partial or complete loss of market for some mineral producers, and the resulting economic and logistical constraints have become a serious consideration for individual industries in countries such as Brazil, South Africa and Australia. The Natural Materials Radiation Control Initiative group was formed [4] and, after two workshops in South Africa, the work is now continuing at the IAEA where several publications addressing radiation protection issues in different industries are currently being prepared.

2. GUIDELINE FOR THE TRANSPORT OF MINERAL CONCENTRATES CONTAINING NORM

While the control of NORM in the processing/storage environment and the disposal of the generated wastes are well covered in international guidelines, the transport of potentially radioactive ores and concentrates does not receive sufficient attention. References [6–8] provide instructions on the transport of material with elevated concentrations of natural radionuclides, but these documents are somewhat complex for a common user and are easily misunderstood. Therefore, a simplified guideline has been developed for both the minerals industry and appropriate regulatory authorities [9]. The guideline takes into account the fact that in different jurisdictions, different regulations may apply to the transport of minerals containing NORM. In some States/countries, the IAEA's 2005 regulations [7] are (or shortly will be) in force; in others the 1996 regulations [6] apply; in rare cases a special amendment was made to the exemption clause for NORM prior to the adoption of international regulations [10]. In case of any doubt, a user of the guideline is directed to an appropriate regulatory authority for additional consultation.

The guideline contains firstly (Part 1) a description of the criteria for the application of transport regulations, depending on where the materials are being transported. Part 2 deals in detail with determination of activity concentration in the transported material and the applicability of exemption criteria. Different scenarios are considered and practical calculation examples are presented for cases of (a) material that has not been subject to chemical or thermal processing, and (b) material for which such processing took place. Also, in the case where secular equilibrium in the material is disrupted, two different examples of calculations are given and discussed in detail — depending on the availability of the 'full chain' analysis. If it is determined that a specific material is subject to regulation, four requirements that must be followed are summarized. Part 3 deals with the classification of materials. The transport index, category and specific activity categorization are discussed. Parts 4–7 describe in depth the conditions under which a material can be transported as an excepted package, placarding requirements, advantages and disadvantages of having material transported in the vehicle under exclusive use and the need for the covering of the material that is being transported. Part 8 describes the possibilities of blending materials with different specific activities prior to transport and Part 9 provides a detailed explanation of the requirements for the assessment of surface contamination with regard to NORM. There is no specific exemption provision for 'natural material' in the international regulations with regard to surface contamination, which may present significant problems, particularly during the decommissioning of plant equipment and the transport of scrap metal resulting from this decommissioning. This guideline [9] is available for download from http://calytrix.biz/radlinks/tenorm/.

3. INTERNATIONAL TRADE IN COMMODITIES CONTAINING NORM

In recent years there have been numerous calls for the standardization of international exemption levels applicable to materials containing naturally occurring radionuclides. It has been pointed out, for example in Ref. [11], that "guidance is lacking on how to deal with inconsistencies in classification and transport of NORM residues that have been released from regulatory control". Another document [12] specifies that "guidance should be prepared on how to assess the levels of natural radionuclides in an effective and economic way for the purpose of clearance". Further confusion may arise due to the fact that in some countries different methods of activity calculations and different limits apply to the release of a material from regulations and its transport [11].

It appears that potential problems may be easily eliminated by adopting Title VII of the European Council Directive 96/29/Euratom [13]. It must be noted, however, that this Directive contains the principle that the work activities of concern are those that cause a significant increase in the exposure of workers or members of the public, without a reference to any numerical value. A follow-up document from the European Commission [14] also did not provide any guidance on what 'a significant increase' actually is. It was left to appropriate regulatory authorities in different countries to determine what to regulate and what not to regulate, resulting in additional confusion. Numerous technical documents supplementary to the European Council Directive have been provided in recent years, but it is still unclear how the transfer of a material containing naturally occurring radionuclides from one country to another should be handled — particularly in a case where these two countries have different regulatory approaches. The situation becomes even more complex when different regulations apply within the same country due to the federal system of government, for example in Australia and the USA.

A big step forward was the publication of IAEA Safety Standards Series No. RG-S-1.7 [15] in 2004, which was followed by the publication of the associated Safety Report in 2005 [16]. Any considerations with regard to the transport of materials are, however, omitted and it is noted that activity concentrations as limits for material in transport are established in the Transport Regulations [6, 7]. The Safety Guide [15] establishes an exclusion value of activity concentration for all radionuclides of natural origin at 1 Bq/g (except ^{40}K, for which the value is 10 Bq/g), which is consistent with Ref. [1]. It must be noted that this value was set on the basis of consideration of the worldwide distribution of activity concentrations of these radionuclides, instead of a very complicated (and probably unnecessary) modelling of exposure to NORM.

The Safety Guide [15] contains a specific part on ‘trade’, which is of particular interest, as it proposes that “…the regulatory bodies concerned should co-ordinate their activities and share their concerns… to facilitate the movement of materials” and “…to avoid unnecessary hindrances to trade at boundary transfer points, States should co-ordinate their regulatory strategies and their implementation”.

Currently, it is not entirely clear how IAEA Safety Standards Series No. RS-G-1.7 [14] will apply to international trade in minerals that contain natural radionuclides in concentrations that are exempted under the international transport regulations [6, 7] but are above those specified in the Guide (NORM ‘in the bracket’ between 1 and 10 Bq/g). Basically, it is suggested that “…authorities in exporting States should ensure that systems are in place to prevent unrestricted trade in material with higher activity concentrations. In general, it should not be necessary for each importing State to set up its own routine measurement programme solely for the purpose of monitoring commodities, particularly if there is confidence in the controls exercised by the exporting State”.

It is important to ensure that controls over commodities containing NORM are established in the exporting country and communicated to the appropriate authority in the importing country — prior to an exporter company encountering problems at a port or a border crossing, due to the lack of proper documentation or because of a simple misunderstanding [17].

Reference [15] also establishes the concept of a ‘graded approach’ that contains a suggestion for a regulatory body for a case when activity concentrations in NORM exceed the specified value (1 Bq/g) “by several times (e.g. up to ten times)”. It may be possible not to apply regulatory requirements to a material, thus providing an exemption on a case by case basis. It would, however, be hard to come across the case when a particular material containing naturally occurring radionuclides with activity concentrations just below 10 Bq/g may be exempted from regulations with regard to storage and processing. For example, the gamma dose rate in air from a mineral concentrate containing 9 Bq/g of ^{232}Th will be of the order of 5.5 μGy/h [18], which is above the typical level of background radiation by about two orders of magnitude [18]. The suggestions on the practical application of ‘graded approach’ are provided at the end of the paper (Suggestion 2.1).

The main reason for the ‘10 times’ exemption for natural materials in transport regulations is that the possible radiation exposure of workers and the general public during transport is likely to be too low to require regulation. Essentially, a shipment of NORM can be transported between countries without having to comply with transport regulations, but will need to be considered by the appropriate regulatory authority for possible control (or exemption) because it is above typical background. This is likely to occur not when a mineral reaches its destination, but at a border crossing point, typically in an international port. It is quite impractical to place a radiation protection specialist at every border crossing, so the authority to conduct measurements and make assessments of materials crossing the border must stay with personnel who are in charge of the situation in the first place — customs officers.

The complexities of regulations dealing with the transport of potentially radioactive materials and minuscule differences that may qualify a mineral concentrate for exemption are typically hard to understand — even for a ‘regulator’ — without a prior (and quite extensive) study of the issue. A full understanding of the regulations can hardly be expected from a customs official, who normally deals with many other (and very different) matters on a day to day basis, and a situation at a border crossing may become rather difficult. A customs officer will definitely require a detailed guideline from his/her country’s appropriate authority on how to use particular radiation monitoring equipment and how to handle a material that looks a bit ‘hot’. It is, therefore, suggested that a company in any country planning to export material containing naturally occurring radionuclides to a specific country contacts an appropriate authority in this ‘importing’ country and enquires about possible requirements for a particular material (Suggestion 1.1).

Several quite comprehensive documents describing NORM in detail may be of help for appropriate regulatory authorities [19–21], but it is unlikely that an average customs officer will be familiar with all aspects of a particular NORM — therefore, a comprehensive guideline is essential. The only known standard of this type (specifically addressing the inspection of the radioactivity content in the process of minerals’ import) was developed in China in 2005 [22]. The procedure suggested in this document is based on the comparison of background radiation level and the radiation emitted from a particular material.

4. CONTROL OF NORM AT INTERNATIONAL BORDERS

Three guidelines of special importance were published in September 2002 by the IAEA. To prevent incidents and to harmonize policies and procedures, the IAEA issued publications, co-sponsored by the World Customs Organization, Europol and Interpol, on the inadvertent movement and illicit trafficking of radioactive material [23–25]. These publications are supported by a reference manual on equipment specifications and test procedures [26].

The second publication [24] is of particular interest and needs to be discussed in detail, together with the reference manual [26]. The IAEA-TECDOC [23] provides detailed information on the process of detection, selection of instruments, investigation levels, alarm settings and their verification, localization and verification of the presence of radioactive material. The reference manual [26] contains technical data for border monitoring equipment, test procedures and many practical examples.

The majority of actual alarms at borders will be innocent ones, resulting from the presence of medical radionuclides administered to patients, NORM, and legal shipments of radioactive materials. Such alarms cause significant operational issues as all activations of portal monitor alarms should be fully investigated. After a shipment of NORM has caused an alarm and relevant radionuclides have been identified, interviews with the personnel involved and an examination of all relevant documentation are the complementary activities that will be part of the investigation. Suggestions for a NORM exporter on what documentation must be provided and what information it must contain is provided at the end of the paper (Suggestions 1.2 and 1.3).

In Ref. [24] the information on radionuclides typically present in NORM is provided and reference is made to Annex I, but Table II of this Annex gives information with regard to radionuclides in NORM that is (a) incomplete, and (b) in some cases, incorrect. Whilst the completeness of the list of substances can be debated, an example of information provided for 'monazite sand' calls for the table to be revised. The data in Ref. [24] specify that this material contains 0.03–1.0 Bq/g of ^{226}Ra and 0.05–3.0 Bq/g of ^{232}Th; while another IAEA publication states that monazite sand contains 6–20 Bq/g of ^{238}U (^{226}Ra) and 160–170 Bq/g of ^{232}Th [20]. In practice, the material may contain 30 Bq/g of ^{238}U (^{226}Ra) and 250–270 Bq/g of ^{232}Th.

An updated table containing approximate activity concentrations for materials that could be encountered at international borders is provided in the appendix to this paper. The information in this table will be expanded and regularly updated in the online version of the paper on the web site mentioned in Ref. [9].

5. CONCLUSIONS — PRACTICAL SUGGESTIONS

Suggestion 1.1

A company in any country planning to export NORM to a specific country needs to contact an appropriate authority in this 'importing' country and enquire about possible requirements for a particular material [23]. This contact can be made via the company that imports the material, directly — using a radiation protection adviser with the detailed knowledge of all relevant regulations, or via the appropriate regulatory authority in the exporting country.

Suggestion 1.2

The transport documentation for a particular material needs to contain detailed information about the concentrations of naturally occurring radionuclides in this material. As the requirements for documentation will differ from country to country, all necessary information may be provided in the document that typically accompanies every material shipment — Material Safety Data Sheet (MSDS). It is suggested that all relevant companies review their MSDSs to ensure that all of them contain not only detailed information on concentrations of naturally occurring radionuclides but also an example of gamma spectra for a particular material (in the form of either a table or a chart). While not absolutely necessary, this information would help in the process of clearing a particular NORM through the radiation detection equipment at international border crossings.

Suggestion 1.3

It may be that NORM is transported as an 'excepted package' due to either blending of radioactive material with an 'inert' one or due to the fact that bags/drums with the material are placed in the middle of a sea container with ballast/shielding material around them. In this case, in addition to the information provided as per suggestion 1.2 above, supplementary documentation that may be required:

(a) In the case of blending: information on radioactivity content of blended materials and a certificate from an appropriate regulatory authority to confirm that this authority has approved the blending. Reference [15] clearly states that "deliberate dilution of material… to meet the values of activity concentration… should not be permitted without the prior approval of the regulatory body”.

(b) In the case of several bags/drums in the middle of a sea container, detailed data on the material and its packaging, and a drawing specifying the location of the package inside and provisions for its stability in the centre of this container in case of an accident.

Suggestion 2.1

Reference [15] suggests that a ‘graded approach’ can be used when the activity concentration exceeds the relevant values by several times; and it is also suggested that this should be consistent with the magnitude and likelihood of radiation exposure. A factory processing NORM would need to submit a radiation management plan to a regulatory authority. Upon receiving this plan, an appropriate authority may apply the graded approach to possible occupational exposures in NORM processing as follows:

(1) 0–0.1 mSv/a: no regulation will be necessary.
(2) 0.1–1 mSv/a: a brief justification statement is to be prepared for the review by an appropriate regulatory authority. A licence/authorization may then be issued.
(3) 1–6 mSv/a: a comprehensive management plan is prepared for the review by the appropriate regulatory authority. After it has been established that the best practicable technology is used in the processing of NORM and doses are as low as reasonably achievable a licence/authorization could be issued and appropriate monitoring and reporting requirements would be established.
(4) An all-inclusive periodic review of working practices will be required and strict controls placed on a processing company if occupational exposure could result in a dose exceeding 6 mSv/a.

A separate (but similar) process must be followed to ensure that any possibility of the exposure of members of the public, contamination of the environment and radiation exposure of the biota is minimized. As the processing of NORM typically involves chemical and thermal treatment of the material and many hazardous substances may be used in the process, all approvals are typically obtained via an environmental protection authority, with radiation protection being only a part of an overall environmental impact assessment.

It is suggested that the decision to allow the importation of a particular NORM into the country should be based on information described above, and not on a simple comparison of numerical data, such as concentrations of radionuclides. For example, milling of a mineral containing 4 Bq/g of ^{232}Th in a facility with an appropriate dust control system will result in the radiation exposure of a plant operator that may be significantly less than in the case of milling similar material containing 2 Bq/g of ^{232}Th in a factory with no provisions for dust suppression. It is, therefore, important to ensure that an appropriate regulatory authority has all necessary information before the decision about a particular shipment of a particular material is made. The graded approach can then be applied to relevant work practices and to the use or disposal of residues generated by these practices, and specific exemptions could then be issued for the information of customs officers with regard to particular material shipments.

Suggestion 2.2

Reference [15] suggests that "…the regulatory bodies concerned should co-ordinate their activities and share their concerns…to facilitate the movement of materials and …to avoid unnecessary hindrances to trade at boundary transfer points, States should co-ordinate their regulatory strategies and their implementation". As suggested in 1.3 above, it is likely that appropriate regulatory authorities in exporting countries will be approached by companies exporting NORM and asked for assistance in contacting authorities in importing countries. It is expected that, in accordance with the IAEA Safety Guide [15], controls over the export of NORM will need to be established [17] and communicated to appropriate authorities in importing countries.

Suggestion 2.3

Appropriate regulatory authorities in importing countries must provide comprehensive guidelines on the detection of radioactive material at international borders to the law enforcement personnel such as customs officers and police. It is expected that appropriate monitoring equipment in accordance with the technical reference manual [26] will be provided, and the suggestions from three international guidelines [23–25] are included in relevant procedure manuals.

Suggestion 3 — training and education

Government: Appropriate regulatory authorities must be fully familiar with NORM processes in their State/country to ensure that correct advice is given to other government departments, to the users of NORM and to the general public. As is correctly stated in the report of the European Committee on Radiation Risk: “in areas of complex scientific issues where there may be low probability, high impact risks, proper scientific advice is crucial” [27]. It is also important that a border monitoring guideline described in 2.3 above is supplemented by appropriate training of all relevant personnel.

Industries producing/using NORM: Training programmes for all workers dealing with NORM are essential; all employees must clearly understand the risks of radiation exposure and the need for radiation monitoring. It is also important to ensure that the results of any monitoring and/or assessments are communicated and explained to every worker involved in the monitoring programme. It is also necessary that the management of a company dealing with NORM has access to qualified radiation protection advice and is aware of any current and future legislation that is potentially applicable to a company’s products or imported materials in all States/countries where this company operates.

Shipping/transport industry: The importance of training for relevant personnel cannot be understated. The fear of radiation has been described in detail in the full text of the paper [2] and, unfortunately, it still prevails when a shipping company does not wish to transport any substance that is labelled ‘radioactive’. Whilst the transport of the material as an ‘excepted package’ [9] may provide some answers, the fact that the sign ‘radioactive’ must be visible when the package/container is opened may create an unwarranted panic in case of an accident.

One recent court case in the USA [28] indicates that a person could sustain ‘compensable injury’ simply from fear of radiation. This particular case was a result of a truck driver’s contact with a leaking container that was mistakenly labelled as radioactive waste. Although the driver suffered no physical injuries and was not actually exposed to radiation, the court determined that the driver’s post traumatic stress disorder, depression, fatigue and anxiety were rationally connected to his contact with the hazardous material and were therefore compensable under Tennessee law.

A complete training programme for all workers involved in loading, transporting and unloading NORM must be designed and carried out by a qualified radiation protection adviser, with the approval of an appropriate regulatory authority. Monitoring of radiation exposure of certain transport occupations and communication of data obtained to relevant personnel is also essential. This exposure is typically very low and in most cases can only be modelled theoretically, due to the fact that measured levels are often less than the minimum detection limit of the equipment in use.

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Appendix

ACTIVITY CONCENTRATIONS FOR MATERIALS THAT COULD BE ENCOUNTERED AT INTERNATIONAL BORDERS

Information was collected from several publications [18, 19, 30–34], proceedings of conferences mentioned in Refs [2, 4, 5, 11, 35] and from other papers referenced on the Internet [9] and is shown in Table 1. The information in Table 1 will be expanded and regularly updated in the online version of the paper at http://calytrix.biz/radlinks/tenorm/.

TABLE 1. ACTIVITY CONCENTRATIONS IN MATERIALS

	Approximate activity concentration (Bq/g)		
	^{40}K	^{226}Ra (^{238}U)	^{232}Th
Mining and minerals processing			
Bauxite (aluminium production)	0.01–0.60	0.1–9.0	0.03–2.3
Spodumen (beryllium ore)	n/a	0.59	0.022
Coal (Brazil)	n/a	0.359	0.033
Coal (China)	0.104	0.036	0.030
Coal (EU)	0.001–0.3	0.007–0.185	0.003–0.022
Coal (Hungary)	n/a	0.3–0.9	n/a
Coal (Japan/Australia)	0.010–0.500	0.005–0.050	0.005–0.070
Coal (Poland)	0.785	n/a	0.159
Columbite (columbium production)	n/a	n/a	up to 50.0
Copper ore	0.466	0.03–100.0	0.02–0.11
Gold ore concentrate (Brazil)	n/a	0.114	0.049
Gold ore concentrate (Finland)	n/a	up to 54.0	n/a

TABLE 1. ACTIVITY CONCENTRATIONS IN MATERIALS (cont.)

	Approximate activity concentration (Bq/g)		
	^{40}K	^{226}Ra (^{238}U)	^{232}Th
Iron ore	n/a	0.005–0.245	0.005
Iron slag	0.035	0.12–0.15	0.15–0.23
Pyrochlore (niobium production)	n/a	6.0–10.0	7.0–80.0
Niobium ore (Brazil)	n/a	0.93–4.55	0.904–6.390
Nb/Ta concentrate (niobium production)	n/a	up to 70.0	up to 8.0
Phosphate ore (Brazil)	n/a	0.11–0.88	0.204–0.753
Phosphate ore (China)	n/a	0.15	0.025
Phosphate ore (Christmas Island)	n/a	0.30	0.007
Phosphate ore (Cuba)	0.027–0.238	0.09–2.70	0.003–0.039
Phosphate ore (Israel/Jordan)	n/a	1.30–1.85	n/a
Phosphate ore (Morocco/Tunisia)	n/a	0.59–1.70	0.010–0.200
Phosphate ore (Nauru)	n/a	0.85	n/a
Phosphate ore (Senegal/Togo)	n/a	1.3–2.3	0.07–1.00
Phosphate ore (South Africa)	n/a	0.14	0.47
Phosphate ore (United Republic of Tanzania)	0.28	5.76	0.35
Phosphate ore (former USSR)	0.037	0.04–0.39	0.04–0.23
Phosphate ore (USA)	n/a	0.15–4.80	0.01–0.08
Rare earth concentrate	n/a	1.0	6.0–1.0
Rare earth concentrate (monazite)	n/a	1.0–30.0	3.0–270.0
Ta/Nb concentrate (tantalum production)	n/a	up to 70.0	up to 8.0
Tantalum ore	n/a	0.06	0.005
Tin ore	n/a	1.0–2.0	0.3
Tin slag for tantalum production	n/a	4.0	11.0
Tin by-product (amang)	n/a	2.0–17.8	3.0–326.7
Titanium heavy sands concentrate	n/a	0.2–1.7	0.6–6.6
Rutile – natural and synthetic (titanium production)	n/a	0.2–0.5	0.2–2.9

TABLE 1. ACTIVITY CONCENTRATIONS IN MATERIALS (cont.)

	Approximate activity concentration (Bq/g)		
	^{40}K	^{226}Ra (^{238}U)	^{232}Th
Ilmenite (titanium production)	0.005	0–1.0	0–4.1
Cassiterite (zinc production)	0.065	0.001	0.021–0.300
Baddeleyite (zirconium production)	n/a	7.0	0.3
Zircon sand (zirconium production)	0	3.7–16.0	0.3–13.0
Building materials			
Bricks	0–0.981	0.014–2.893	0–0.648
Cement	n/a	0.04–0.20	0.03–0.20
Cement with 20% fly ash	0.18	0.055	0.040
Cement with 20% blast furnace slag	0.219	0.02	0.038
Clay	0.5	0.04	0.02
Concrete	0.15–1.60	0.04–2.2	0.04–0.20
Concrete with 20% copper slag	n/a	0.14	0.035
Coal ash (brick and concrete production)	0.44	0.1–0.3	0.10–0.12
Gypsum (natural)	0.008–0.4	0.007–0.02	0.001–0.01
Granite	0.6–4.0	0.03–0.5	0.04–0.36
Phosphogypsum (for plasterboard)	up to 0.12	up to 1.0	up to 0.3
Sand and gravel	n/a	0.015	0.02
Sandstone	0.04–1.00	0.02–0.07	0.02–0.07
Slate	0.5–1.0	0.03–0.07	0.04–0.07
Tiles (floor and wall)	0.19–0.27	0.028–0.096	0.014–0.083
Tuff	0.9–2.0	0.11–0.26	0.19–0.35
Wall board (from natural gypsum)	0–0.19	0.02	0.01
Wall board (from phosphogypsum)	n/a	0–0.452	0–0.02
Other materials			
Phosphoric acid	n/a	1.2–1.5	n/a

TABLE 1. ACTIVITY CONCENTRATIONS IN MATERIALS (cont.)

	Approximate activity concentration (Bq/g)		
	^{40}K	^{226}Ra (^{238}U)	^{232}Th
Mono-ammonium phosphate (MAP), Morocco	0.028	2.741	0.009
Mono-ammonium phosphate (MAP), Russia	0.037	0.041	0.014
Di-ammonium phosphate	n/a	2.3	0.015
Di-calcium phosphate	n/a	0.74	0.037
Triple superphosphate	0.092	0.080–2.160	0.007–0.048
Bony superphosphate	0.045	0.057	0.004
Normal superphosphate	n/a	0.52–1.1	0.015–0.044
PK (phosphate/potassium)	n/a	0.41	0.015
NPK (nitrogen/phosphate/ potassium)	n/a	0.44–0.47	0.015
Alumina	n/a	0.3–0.6	0.5–1.2
Glazes (zirconium)	n/a	1.0	0.4
Scrap metal from oil & gas (scale & sludge)	n/a	1–100 (up to 4000)	0–0.5
Refractory brick	n/a	4.0–10.0	0.2–10.0
Slag wool (old insulation doors & bakery ovens)	n/a	3.0–5.0	10.0–15.0
Zirconia	n/a	7.0	0.3–1.0

Note: Material containing more than 10 Bq/g of ^{232}Th will be subject to international transport regulations [6, 7]. If it is known that ^{226}Ra is in equilibrium with its parent ^{238}U, the same 10 Bq/g activity concentration limit appears to be applicable. If, however, ^{238}U has been removed (or not present, as in oil and gas sludge), the limit for ^{226}Ra will be 100 Bq/g (assuming that an exemption from para 107(e) of the regulations [6, 7] is applicable to a particular material). The data on the materials containing naturally occurring radionuclides in very low concentrations has also been provided for reference. For example, it is very unlikely that a container with natural gypsum would trigger an alarm. If, however, an alarm is triggered, the data in Table 1 would indicate that either the material in question is not what is stated in the transport documents, or some other substance/object is present in this particular container.

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MEASUREMENT OF SURFACE CONTAMINATION ACCORDING TO LEGAL REQUIREMENTS

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Abstract

The measurement of radioactive contamination of metal surfaces is a common issue in NORM industries, e.g. because of scale deposition in pipes and other equipment in oil and gas production facilities. Regulatory requirements for measurements may address radiological assessments aimed at occupational radiation protection or may be aimed at confirming compliance with surface contamination limits for the release of scrap from the dismantling of installations for recycling. Such requirements may apply to different parameters, for instance the alpha or beta activity per unit surface area or to summation formulas for the activities of relevant long lived radionuclides per unit surface area, and differ from country to country. The measurement of surface contamination levels in large scrap volumes requires a method that is applicable in a straightforward way under field conditions with minimum expenditure of time. These objectives can be accomplished by means of beta contamination measurements combined with gamma spectrometric sample analyses for the calibration according to the activity ratios of the long lived radionuclides. A calibration of beta contamination measurements was performed by numerical calculations using a well known Monte Carlo particle transport model. Apart from the detector sensitivity, the detector response is dominated by the mass per unit area of the contaminated layer and by the activity ratios of the relevant long lived radionuclides. The calibration has been validated for surface contamination of different types and origins, comprising the radium isotopes ^{226}Ra, ^{228}Ra and their daughter radionuclides. The comparison with measurements of scratch samples shows good agreement. Therefore, it may be concluded that the use of the Monte Carlo particle transport model calculation represents a cost effective and very adaptive method for the calibration of surface contamination measurements.

1. INTRODUCTION

Surface contamination of pipes and other components by naturally occurring radionuclides of the decay chains of ^{238}U and ^{232}Th is a common issue in NORM industries. In the present paper, the measurement of radioactive surface contamination is considered by way of example for oil and gas production facilities, but the method applies similarly to other NORM industries.

The parent radionuclides ^{238}U and ^{232}Th have very long half-lives and are ubiquitous in the Earth's crust, with activity concentrations that depend on the type of rock. Their decay produces chains of daughter radionuclides of different physical characteristics with respect to mobility, half-lives, decay modes and energies of emitted radiation. Concerning the radioactive contamination of oil and gas production facilities, it should be mentioned that the reservoir water contains Group II (Periodic Table) cations of calcium, strontium, barium and radium dissolved from the reservoir rock. As a consequence, the produced water contains the long lived radium isotopes ^{226}Ra from the ^{238}U series and ^{228}Ra from the ^{232}Th series, whereas their parent nuclides are not mobilized with the formation water. Depending on the operational history, pipes, valves and other components of the production facilities are contaminated with ^{226}Ra and ^{228}Ra and their daughter radionuclides to a varying extent. It should be mentioned that in some oil and gas fields, ^{210}Pb occurs in considerable amounts from the outset in the produced water, which may cause a relatively high surface contamination with ^{210}Pb. An elevated surface contamination with ^{210}Pb may also be caused by the decay of ^{222}Rn. The radioactive decay chains of the radium isotopes ^{226}Ra and ^{228}Ra, which are the leading radionuclides contained in NORM in the oil and gas industry, are shown in Fig. 1.

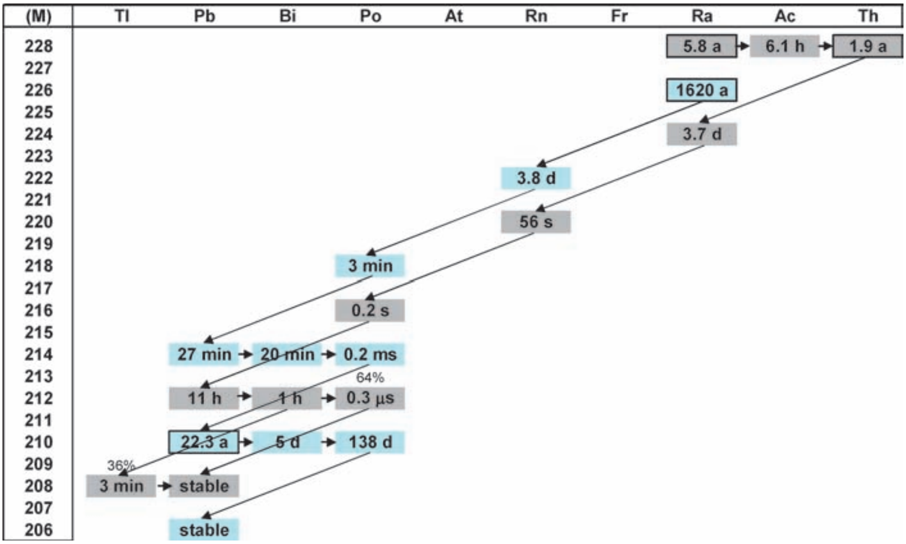

FIG. 1. Radioactive decay of Ra-226 and Ra-228 (half-life indicated for each radionuclide).

The radiological assessment of contaminated pipes or other components requires knowledge of the activities of the long lived radionuclides per unit surface area (the short lived radionuclides are in radioactive equilibrium with their long lived parent radionuclides). Taking into account that, for the given circumstances, ^{210}Po may be considered as short lived, the relevant long lived radionuclides, which in general will have different activity concentrations, are ^{226}Ra, ^{210}Pb, ^{228}Ra and ^{228}Th. The alpha and beta emitting radionuclides of the sub-chains, which comprise the long lived (leading) parent radionuclide and its short lived daughter radionuclides up to the next long lived radionuclide are summarized in Table 1.

2. REGULATORY REQUIREMENTS

Regulatory requirements for the release of pipes and other components as ‘uncontaminated’ for unrestricted reuse, and/or for the clearance of scrap for smelting, deal with at least two issues: the definition of the radiological parameter that has to be applied for the decision and the definition of a limit for this parameter below which the treatment of contaminated pieces according to a certain licensing regime is not required. For limiting surface contamination, different radiological parameters may be used, e.g. the beta activity per unit surface area, S_β or the alpha activity per unit surface area, S_α. Sometimes, regulatory bodies combine limitations of the kind $S_\beta \leq L_\beta$ and/or $S_\alpha \leq L_\alpha$, where L_β and L_α are the limiting values of beta and alpha activity per unit surface area, respectively. In this case, the more restrictive condition has to be applied.

TABLE 1. ALPHA AND BETA EMITTERS IN THE SUB-CHAINS OF THE RELEVANT LONG LIVED RADIONUCLIDES

	Alpha emitters		Beta emitters	
	Radionuclides	Total number	Radionuclides	Total number
^{226}Ra+	^{226}Ra, ^{222}Rn, ^{218}Po, ^{214}Po	4	^{214}Pb, ^{214}Bi	2
^{210}Pb+	^{210}Po	1	^{210}Pb, ^{210}Bi	2
^{228}Ra+	—	0	^{228}Ra, ^{228}Ac	2
^{228}Th+	^{228}Th, ^{224}Ra, ^{220}Rn, ^{216}Po, ^{212}Bi (36%), ^{212}Po (64%)	5	^{212}Pb, ^{212}Bi (64%), ^{208}Tl (36%)	2

The radiation protection ordinance of the Netherlands MR-NABIS [1] defines, for instance, the presence of NORM with an average mass per unit surface area of less than 1 g/cm^2 on non-radioactive solids as 'surface contamination' and requires measurements of the beta activity per unit surface area on surfaces of non-radioactive materials. The regulations [1] require a treatment of contaminated parts according to the licensing regime if the beta activity per unit area, S_β, of accessible surfaces is above the limit, L_β, of 4 Bq/cm^2.

Combined limitations are applied, for instance, in the Libyan 'NORM Management Manual' [2] that defines radioactive surface contamination as the presence of radioactivity on a surface in excess of $L_\beta = 3.0$ Bq/cm^2 or $L_\alpha = 0.3$ Bq/cm^2, and these limits as action levels for radiological control in the workplace.

International regulations for the safe transport of radioactive material are set out in the IAEA Safety Standards [3] defining radioactive contamination as the presence of a radioactive substance on a surface in excess of 0.4 Bq/cm^2 for beta and gamma emitters and low toxic alpha emitters or of 0.04 Bq/cm^2 for all other alpha emitters (in the present case this concerns ^{226}Ra). If the activity per unit surface area S_r of radionuclide *r* is above its so-called exemption level (L_r), the object is regarded as a 'surface contaminated object'.

An alternative approach is recommended by the European Commission for the recycling of metals from the dismantling of nuclear installations [4]. Based on the assessment of exposure scenarios, a limiting activity per unit surface area, L_r, corresponding to a maximum individual dose of about 10 μSv/a, was derived for each long lived radionuclide *r*. For the radionuclides relevant in scales from oil and gas production facilities, the following clearance levels are listed in Table 7–1 of Ref. [4]: $L_{\text{Ra-226}} = 0.3$ Bq/cm^2; $L_{\text{Pb-210}} = 0.58$ Bq/cm^2; $L_{\text{Ra-228}} = 0.39$ Bq/cm^2 and $L_{\text{Th-228}} = 0.097$ Bq/cm^2. For the clearance of scrap the so-called summation formula

$$\sum_r \frac{S_r}{L_r} \leq 1$$

has to be applied.

For a given type of radioactive contamination with known activity ratios between the relevant long lived radionuclides, the above mentioned requirements can be transformed into each other. Therefore the compliance with any exemption or clearance levels defined by a regulatory body for surface contamination may be proven, for instance, by measurement of the beta activity per unit surface area S_β.

Denoting by A_r (in Bq/g) the activity per unit mass of contamination for radionuclide r and by μ (in g/cm^2) the mass per unit surface area, the activity per unit surface area, S_r, (in Bq/cm^2) is determined by

$$S_r = A_r \times \mu \tag{1}$$

In the following, ^{226}Ra is selected as the 'reference nuclide' and the activity ratio is defined as

$$R_r = A_r/A_{Ra-226} \tag{2}$$

Using the numbers of alpha and beta emitters listed in Table 1, a limit L_α can be transformed, for instance, into a derived limit for S_β:

$$L_\beta(L_\alpha) = L_\alpha \times \frac{2\times(1+R_{Pb-210}+R_{Ra-228}+R_{Th-228})}{4+R_{Pb-210}+5\times R_{Th-228}} \tag{3}$$

The derived limit for the beta activity per unit surface area, S_β, which corresponds to the summation formula in Ref. [4], is given by the following equation:

$$L_\beta(L_r) = \frac{2\times(1+R_{Pb-210}+R_{Ra-228}+R_{Th-228})}{\sum\limits_r R_r/L_r} \tag{4}$$

Example: For scale from contaminated pipes of a former flare line of an oil and gas production facility in the Libyan Arab Jamahiriya, by means of gamma spectrometric measurements of scratch samples the following activity ratios were established: $R_{Pb-210} = 0.7$; $R_{Ra-228} = 0.5$ and $R_{Th-228} = 0.7$. From Eq. (3), the limit of $L_\alpha = 0.3$ Bq/cm^2 defined in Ref. [2] is equivalent to a derived limit of $L_\beta(L_\alpha) = 0.21$ Bq/cm^2 for beta activity per unit surface area . A derived limit of $L_\beta(L_r) = 0.44$ Bq/cm^2 resulting from Eq. (4) would have to be applied in terms of Ref. [4]. The exemption level $L_{Ra-226} = 0.04$ Bq/cm^2, which is valid according to Ref. [3], yields a derived limit of $L_\beta(L_{Ra-226}) = 0.23$ Bq/cm^2. The limit of $L_\beta = 4$ Bq/cm^2 defined in Ref. [1] is about one order of magnitude above the previously mentioned derived limits. From the radiological point of view it presents, however, a reasonable limit, which corresponds, according to Ref. [4], to a maximum individual dose of approximately 0.1 mSv/a.

3. MEASUREMENT OF RADIOACTIVE SURFACE CONTAMINATION

3.1. General comments

If a scale sample can be scratched from the surface of a contaminated piece, direct measurement of the surface contamination is possible by measuring the mass per unit surface area μ, and the activity per unit mass of contamination, A_r, of each relevant long lived radionuclide r. The activity per unit surface area S_r of each relevant radionuclide r is then determined by Eq. (1) and the beta activity per unit surface area, S_β, is calculated by

$$S_\beta = 2 \times \left(S_{\mathrm{Ra-226}} + S_{\mathrm{Pb-210}} + S_{\mathrm{Ra-228}} + S_{\mathrm{Th-228}} \right) \tag{5}$$

However, disadvantages of this approach are the exhausting and time consuming extraction of scratch samples and the relatively high expense of the gamma spectrometric measurements of A_r. In many cases it is impossible to obtain sufficient sample mass. The contaminated surface layer is frequently so thin that a scratch sample cannot be taken at all. Therefore, an alternative method for measuring the surface contamination will be necessary, especially in the case of low levels of contamination that have to be checked against exemption or clearance levels.

The measurement of surface contamination in large scrap volumes or in complex production facilities requires a method that is applicable in a straightforward way under field conditions with a minimum expenditure of time. These objectives can be accomplished by means of beta contamination measurements. They have to be combined with gamma spectrometric analyses of a few scratch samples, as the calibration has to take into account the existing activity ratios of the relevant long lived radionuclides. This is necessary because of the radionuclide specific energy spectra of the emitted beta particles, which influence the detector response. The calibration also has to take into account the mass per unit area μ of the contaminated surface layer, as it influences the self absorption of emitted beta particles within the scale layer.

3.2. Application of a beta sensitive surface contamination probe

By means of a beta sensitive surface contamination probe that has been calibrated for the given conditions (i.e. the activity ratios between the relevant long lived radionuclides and the mass per unit surface area), sufficiently accurate, or at least conservative, measurements of S_β are possible. The surface contamination probes are in general sensitive for beta particles as well as for gamma rays. Therefore, in addition to the counts C_β in cps (counts per second) resulting from the required beta activity per unit surface area measured, S_β, counts $C_{\gamma,\mathrm{area}}$ due to gamma emissions originating from the contamination of this area and counts $C_{\gamma,\mathrm{surr}}$ originating from gamma emissions from the surrounding contaminated surface and from other pieces also contribute to the total count rate C_{total} of the measurement device:

$$C_{\mathrm{total}} = C_\beta + C_\gamma \text{ with } C_\gamma = C_{\gamma;\mathrm{area}} + C_{\gamma;\mathrm{surr}} \tag{6}$$

To determine the beta count rate, C_β, in addition to the measurement of the total count rate, C_{total}, the gamma count rate C_γ has to be measured at the same position by shielding the detector against beta particles by a 3 mm thick aluminium plate. After this, C_β is calculated according to Eq. (6).

3.3. Calibration of a beta sensitive surface contamination probe

The determination of the beta activity per unit surface area S_β from a measured beta count rate C_β requires the calibration of the measurement device. The detector response depends on the activity per unit mass of contamination A_r of each relevant long lived radionuclide r and on the mass per unit surface area μ of the contaminated layer. The calibration may be performed experimentally or by means of Monte Carlo particle transport calculations for the detector used, yielding for each relevant radionuclide r a detector response function $D_r(\mu)$ in units of cps per becquerel per square centimetre. Given an activity per unit surface area S_r of the radionuclide r (r = ^{226}Ra, ^{210}Pb, ^{228}Ra or ^{228}Th), the detector response, D_r, defines the count rate, $C_{\beta;r}$, (in cps) for beta particles emitted by radionuclide r and its short lived daughters:

$$C_{\beta;r} = n_r \times D_r \times S_r \tag{7}$$

where n_r denotes the number of beta particles emitted per decay of radionuclide *r* by this radionuclide and/or its short lived daughters (for the four subchains ^{226}Ra+, ^{210}Pb+, ^{228}Ra+ and ^{228}Th+ the value of n_r is 2, see Table 1). The ratio between the activity per unit surface area, S_β, and the beta count rate C_β:

$$C_\beta = \sum_r C_{\beta;r} \tag{8}$$

resulting from the combination of Eqs (1), (5) and (7) is:

$$\frac{S_\beta}{C_\beta} = \frac{2 \times \mu \times \sum_r A_r}{2 \times \mu \times \sum_r D_r \times A_r}. \tag{9}$$

Using the activity ratios R_r defined in Eq. (2), the beta activity per unit surface area, S_β, is determined by the measured beta count rate, C_β, via:

$$S_\beta = C_\beta / D_\beta(\mu) \quad \text{and} \tag{10}$$

$$D_\beta(\mu) = \frac{\sum_r D_r(\mu) \times R_r}{\sum_r R_r}. \tag{11}$$

$D_\beta(\mu)$ denotes the effective detector response for beta emissions. It depends on the given ratios of the activity conentrations of the long lived radionuclides and on the mass per unit area, μ.

The radionuclide specific detector response functions, $D_r(\mu)$, were calculated for the beta sensitive surface contamination probe 'NORM1' (RADOS GmbH), which is a plastic scintillation detector with a window size of 17.1 cm × 4.4 cm $\cong$ 75 cm^2. The geometrical dimensions of the probe (28.2 cm long × 6.2 cm wide × 3.8 cm high) are suited for measuring surface contamination also in pipes with inner diameters of ≥3 inches (75 mm) (taking into account the 3 mm thickness of the aluminium plate that has to be used for the shielding of beta particles for the measurement of C_γ).

The detector response functions $D_r(\mu)$ were calculated with version 4C of the Monte-Carlo N-Particle transport code MCNP (developed by the Los Alamos National Laboratory and distributed by bodies such as the OECD/NEA [5]). The results are shown in Fig. 2.

The detector response functions for the sub-chains ^{210}Pb+ and ^{228}Ra+ are relatively small compared with those for ^{226}Ra+ and ^{228}Th+. This is due to the low energy of each beta particle emitted by these sub-chains: decay of ^{210}Pb with $E_{\beta;max}$ = 63 keV and of ^{228}Ra with $E_{\beta;max}$ = 39 keV.

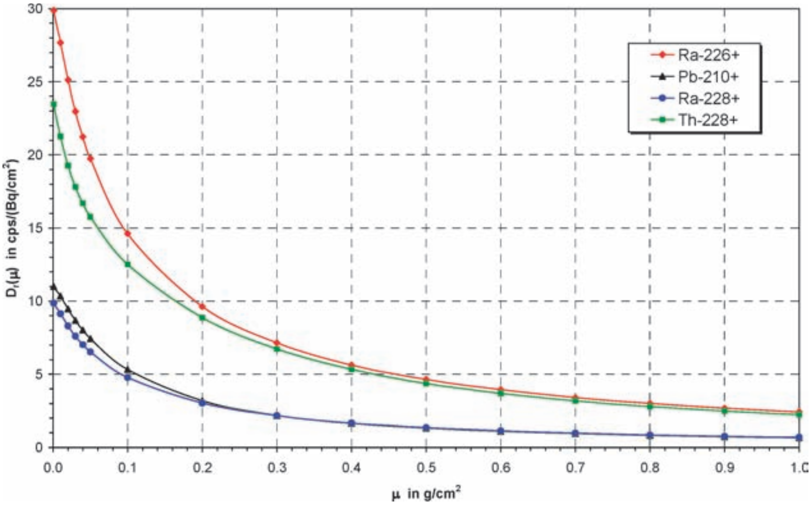

FIG. 2. Detector response functions $D_r(\mu)$ for sub-chains of relevant radionuclides.

The calculated detector response functions are validated by means of experimental calibration data for different types of NORM layers with known specific activities of ^{226}Ra, ^{210}Pb, ^{228}Ra and ^{228}Th and with varying layer thicknesses. With respect to field conditions, beta activities per unit surface area S_β directly measured by gamma spectrometry on the basis of scratch samples taken from layers of different scale types have been compared with surface contamination measurements performed with the NORM1 probe using the calibration given in Eqs (10) and (11). The comparison shown in Fig. 3 confirms a good agreement. It may be concluded that the use of Monte Carlo particle transport model calculations represents a cost effective and very adaptive method for the calibration of surface contamination measurements.

3.4. Proof of compliance with surface contamination limits

A direct measurement of the mass per unit surface area μ, which has to be known for calculating the detector response function, cannot be realized in some cases, for instance in the case of a very thin scale contamination that may remain after pipe cleaning. To overcome this difficulty, an alternative approach for the determination of μ can be applied if the beta activity per unit mass, A_β, of this scale type is known from former measurements ($A_\beta = \Sigma\, n_r \cdot A_r = S_\beta/\mu$). It can be assumed that A_β is a relatively constant parameter. On this basis, the mass per unit surface area μ can be estimated for each measurement point from

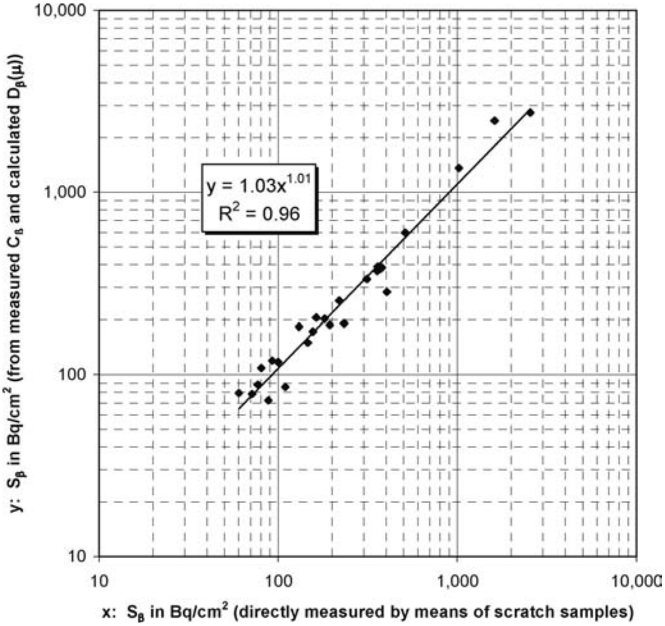

FIG. 3. Comparison of beta activity per unit surface area, S_β determined directly by measurements of scratch samples and estimated alternatively from measured beta count rates C_β with calculated detector response functions $D_\beta(\mu)$ via Eq. (10); 26 scale samples of six different types (activity ratios) and mass per unit surface area μ from 0.05 to 1.5 g/cm^2

the measured beta count rate, C_β, by solving the following equation, which results from Eqs (1) and (10), with respect to μ:

$$\frac{C_\beta}{\mu \times D_\beta(\mu)} = A_\beta \cong \text{const} \qquad (12)$$

As the detector response function, $D_\beta(\mu)$, tends to its asymptote (~1/μ) with increasing mass per unit surface area μ because of self-absorption, this approach cannot be applied for very thick scale layers. However, for the masses per unit surface area of the types of contamination that are relevant for proof of compliance with regulatory limits, this approach can be used for the calculation of derived limits LC_β for the measured beta count rate corresponding to a contamination limit L_β. As shown by way of example in Fig. 4 for the scale type that is characterized by the activity ratios R_r considered in the

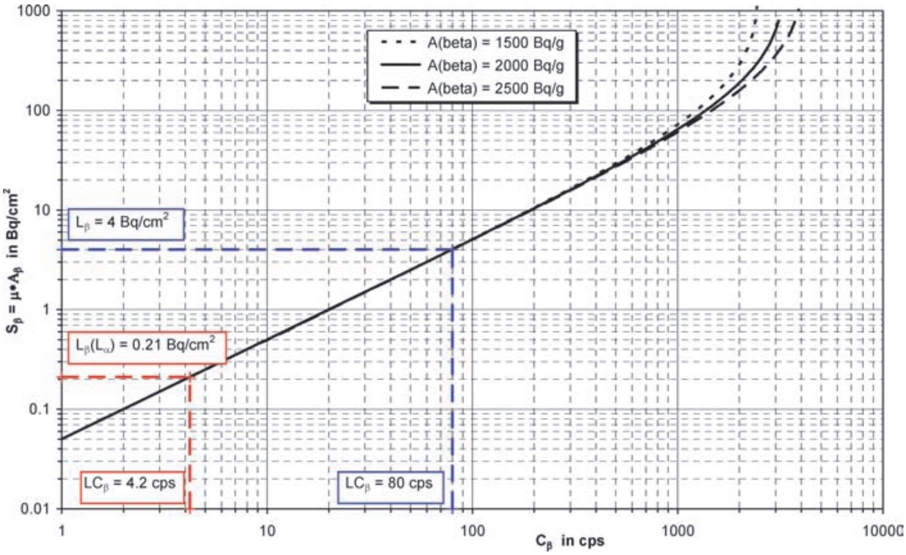

FIG. 4. Derived limits LC_β for beta count rates C_β for the scale type considered in the example given in Section 2 with a specific beta activity of $A_\beta \cong (2000 \pm 500)$ Bq/g, which correspond to the limits $L_\alpha = 0.3$ Bq/cm² ($L_\beta(L_\alpha) = 0.21$ Bq/cm²) and $L_\beta = 4$ Bq/cm², respectively.

example of Section 2, the calculation of derived limits LC_β is not affected by uncertainties concerning the beta activity per unit surface area, A_β, in the relevant region of beta count rates.

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ENVIRONMENTAL IMPACT OF RADIOACTIVITY IN WASTE FROM THE COAL AND ALUMINIUM INDUSTRIES IN WESTERN BALKAN COUNTRIES

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Abstract

The paper deals with industrial tailings resulting from the use of coal and bauxite, assessing the impact on the population and the environment in the western Balkan countries (WBC). It considers the direct hazard resulting from the wastes on their immediate neighbourhood and the radionuclide dispersal in the environment through surface and groundwater. The selected test sites have been investigated by different methods assessing the presence and type of radionuclides in the primary and waste products, analysing and identifying the pathways for dispersion of radionuclides in the waste surroundings, and defining the impact of the waste on the ecosystem. The processes of leachability and fractionation of the various radionuclides have been studied also. The transport of radionuclides in groundwater has been studied by 3-D groundwater flow and solute transport modelling. The following parameters have been assessed: (1) gamma dose rate levels, (2) radon in soil gas, (3) radon exhalation, (4) indoor and outdoor radon, (5) radionuclide activity in soil and in waste material, (6) radionuclides in surface water and groundwater, and (7) radionuclides in biota. Several

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case studies highlight the transfer of the radionuclides to plants and animal consumption products. The radionuclide concentrations in the waste and in the surroundings range over three orders of magnitude. The radionuclide concentrations in groundwater surrounding the waste are low and have a lower variability than in the wastes. The radon concentrations above the tailings are increased with respect to the surroundings. The transfer factors in the soil–plant–animal system indicate low bioavailability of the radionuclides investigated. A preliminary dose assessment shows that the highest contributions to dose are from external and radon exposure. On the basis of the results obtained by using transport model simulation and considering the high Kd values and low concentration of radium, radionuclide transport in groundwater is slow and limited to a restricted area around the tailings sites.

1. INTRODUCTION

The EC (6th Framework) International Cooperation (INCO) project 509214 Assessment of Environmental Risk of Radioactively Contaminated Industrial Tailings (INTAILRISK) investigates waste containing NORM material from coal burning power plants (CBPP) and the aluminium industry in western Balkan countries (WBC). The objectives of the project are to assess the possible hazards to the public and the environment arising from radionuclides in the wastes studied (tailings and derived products). The project investigates the risk from the waste itself, the dispersion of radionuclides from the waste to the environment and the possible effects from the secondary (derived) products. In the framework of the project, the possible hazards associated with the leaching of radionuclides from the waste and contaminating groundwater, surface water, soil and agricultural products have been studied at different test sites, selected on the basis of specific characteristics such as age, remediation actions, climate, subsurface characteristics and distance to living areas. The test sites in the various participating countries have been characterized in detail in terms of radionuclide type, distribution and dispersion. The current paper focuses on the results of the uptake of radionuclides in biota and on the results of the contaminant transport model.

2. METHODOLOGY

2.1. Site characterization

The test sites, including the tailings ponds, their surroundings up to nearby living areas and sometimes the industrial facilities and the raw materials, have been characterized by (1) gamma dose rate measurements, (2) radon in soil gas, (3) radon exhalation, (4) indoor and outdoor radon concentration, (5) radionuclide activity concentration in soil and waste material, (6) radionuclides in surface water and groundwater, and (7) radionuclide concentrations in biota. A description of the various test sites studied and the methodology applied can be found at the project web site www.ibes.be/intailrisk.

2.2. Leachability study

Speciation studies of radionuclides and trace elements involve sequential or parallel leaching experiments using selective reagents to extract radionuclides associated with particular phases of the investigated materials. Literature data indicate that the parallel extraction method has been proved useful in investigating the main differences in solid speciation of radionuclides in agricultural soils, particularly when taken in conjunction with the results of an ultra-filtration study.

The methods used most frequently for speciation studies of natural radionuclides (^{238}U and ^{232}Th series) are Tessier's method, Schultz's method and a standardized 3 step sequential extraction technique developed by a European working group coordinated and supported by the Bureau Commun de Reference, known as the BCR technique. Previous studies have not provided statistically significant quantification of leachability and bioavailability of radionuclides, which can be widely used in environmental assessment models. Therefore, some of the participating laboratories have developed their own methods based on the above mentioned methods. The results obtained by those techniques have been compared to the BCR method. Despite that fact, it was necessary to perform a leachability study to improve the knowledge of the capability of radionuclides for migration processes.

2.3. Contaminant transport modelling

3-D reactive and non-reactive transport models of contaminants in groundwater have been studied using the MODFLOW and MT3D codes. MODFLOW solves the partial differential 3-D flow equation by using a finite differences method:

$$\frac{\partial}{\partial x_i}\left(K_{ij}\frac{\partial h}{\partial x_j}\right)=S_s\frac{\partial h}{\partial x}+Q$$

where:

S_s is the specific storage coefficient,

h is the hydraulic head,

K_{ij} is the hydraulic conductivity,

Q is the recharge,

i,j are the 1, 2, 3 main directions

A numerical model implemented in Visual MODFLOW requires:

(1) The horizontal and vertical discreetization of the domain in cells. The solution is assigned to the node located at the centre of the cells;
(2) The type of simulation (steady state or transient) and initial conditions;
(3) The main hydrogeological parameters for each cell: hydraulic conductivity, porosity and storage coefficient;
(4) The boundary conditions (i.e. assigned hydraulic head: h = cost, assigned flux to a cell: q = cost for pumping wells, recharge, inactive cells indicating no flux condition; variable flux that depends on the hydraulic head in the cell);
(5) The model calibration that uses the parameters estimation procedure (PEST):

$$\underbrace{\frac{\partial c}{\partial t}}_{I}+\underbrace{\frac{(1-n)}{n}\rho_s\frac{\partial c_a}{\partial t}}_{IV}=-\underbrace{\frac{\partial}{\partial x_i}\left(v_i c\right)}_{II}+\underbrace{\frac{\partial}{\partial x_i}\left(D_{ij}\frac{\partial c}{\partial x_i}\right)}_{III}-\underbrace{\lambda c}_{V}-\underbrace{\sum Qc_{in}}_{VI}$$

MT3D solves in 3-D the advection–dispersion equation of a contaminant in the aquifer. Different terms indicate: I: initial concentration, II: advection, III: dispersion, IV: adsorption, V: decay, VI: recharge or loss. MT3D automatically uses MODFLOW results to solve the transport equation. It needs the horizontal and vertical dispersivity coefficients as input parameters, the definition of the initial concentration (at time t = 0); the definition of the boundary conditions (presence of source with constant concentrations, inactive cells and cells with variable concentrations). The model was constructed using geological, hydrogeological and hydrochemical data from wells located in the source area (TENT B thermo-power plant, Obrenovac, Serbia and Montenegro) as well as its surroundings. The transport model was implemented by using reactive, soluble sulphates in combination with radium as a passive contaminant.

3. RESULTS

3.1. Dispersion of radionuclides around the waste

As a general observation, the distribution of radionuclides in soil around the investigated tailings is limited to the close vicinity of the tailings and does not extend beyond about 100 m. Figure 1 shows an example of the gamma dose rate distribution around the tailings area of the Kakanj CBPP (Bosnia).

Another example (Fig. 2) shows that the radon exhalation rate remains small, and is elevated only in the tailings area.

3.2. Radionuclide leaching to the groundwater

At the test site Kansk Achinsk of the Siberian research group, joined to the project, the radionuclide distribution in depth soil profiles highlight disequilibrium between ^{238}U and Ra/Pb, with relative depletion of the former radionuclide. This indicates the possible migration of U to deeper levels or leaching to the groundwater. Figure 3 illustrates this type of disequilibrium on the test site of Kansk Achinsk in Siberia.

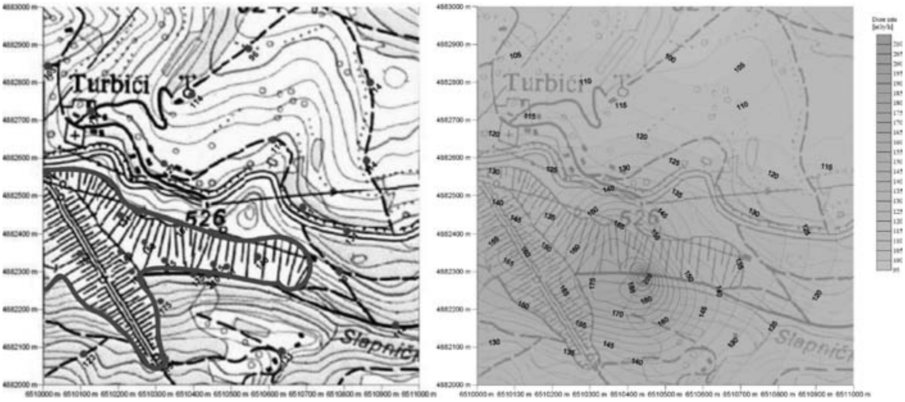

FIG. 1. Dose rate map of the Kakanj CBPP repository (Bosnia). The tailings area is outlined in grey on the left hand image.

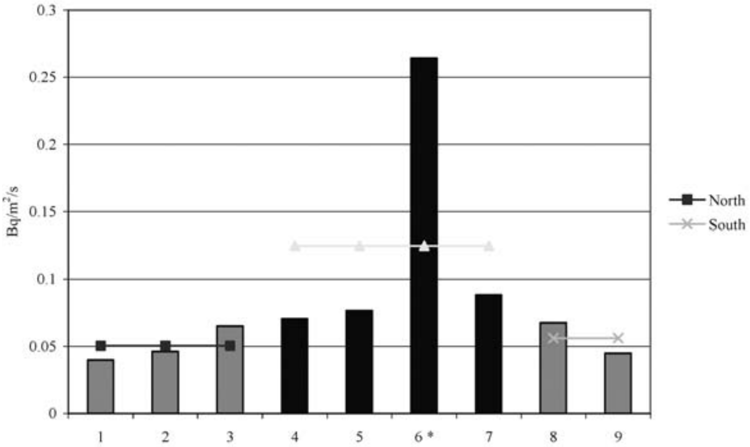

FIG. 2. Radon exhalation rate on and around the waste repository of the Kocevje coal mine (Slovenia). Black bars — on the repository. Grey bars — outside the repository.

3.3. Radionuclide uptake in biota (agricultural products)

Sampling was performed at two different locations in Bosnia and Herzegovina. Sampling point A was located in the vicinity of the Kakanj coal burning power plant in the central part of Bosnia and Herzegovina, while sampling point B was located in the vicinity of the Tusnica-Livno coal mine in the southwestern part of Bosnia and Herzegovina. The main soil parameters are shown in Table 1.

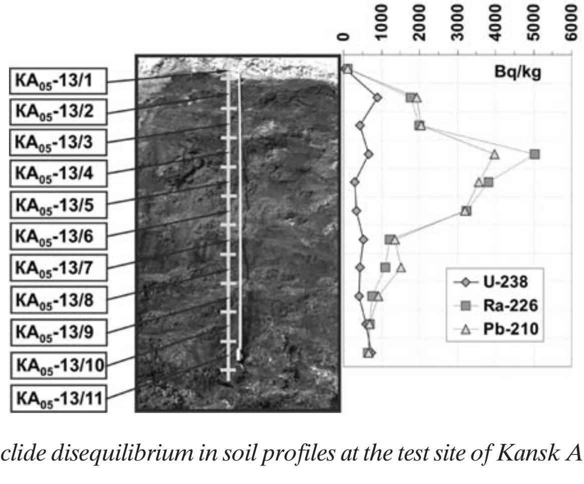

FIG. 3. Radionuclide disequilibrium in soil profiles at the test site of Kansk Achinsk (Siberia).

TABLE 1. SOIL PARAMETERS AT INVESTIGATED POINTS

	pH	Humus (%)	Humidity (%)	Minerals (%)	Organic matter (%)	Type of soil
Point A, Kakanj	7.63	3.9	2.16	89.54	8.3	Loamy
Point B, Tusnica-Livno	7.77	6.1	4.87	76.67	18.46	Loamy

The radioactivity concentrations in the agricultural products analysed (Table 2) did not indicate any significant contamination of the agricultural products. Transfer factors obtained for point A were generally higher than those recorded at point B, despite the fact that the radioactivity concentrations of ^{238}U and ^{226}Ra in the soil at point B were significantly higher owing to the use of coal ash for fertilization of the agricultural land.

The differences between points A and B could be explained by the fact that point A was in the vicinity of a coal burning power plant and was therefore affected by the fly ash from the facility as well as by ash from the waste disposal site (dry type). As a result, higher percentages of ash for unwashed samples of grass, hay and corn stalk from point A were recorded, compared with the same samples from point B. That finding indicated the possibility of surface contamination of the green vegetables in the case of a significantly increased radioactivity concentration in the fly ash from the coal burning power plants. Additionally, the soil type and soil parameters at point B (loamy soil, high content of organic matter 18.5%) indicated a lower migration potential of natural radionuclides. Generally it is reported that the uranium transfer factor decreases from sandy to clayey soils [1, 2]. The presence of organic matter generally decreases the uranium transfer factor [1, 3, 4].

The transfer factors obtained are in good agreement with literature data, considering that transfer factors usually vary over a wide range and, for natural radionuclides, are generally low for agricultural products. There are several reports that among agricultural products, leafy vegetables generally show higher transfer factors, followed by root, fruit and grain crops [1, 5, 6].

According to the transfer factors obtained in the soil–plant system, the transfer of ^{238}U, ^{232}Th and ^{226}Ra to biota is limited. The dose by ingestion of the agricultural products, therefore, would not significantly contribute to the total dose in the case of acceptable levels of these radionuclides in the waste and soil. The risk from ingestion of the agricultural products would be higher in the case of significantly increased levels of natural radionuclides in waste as well as in areas with a high natural background.

TABLE 2. RADIOACTIVITY CONCENTRATIONS AND TRANSFER FACTORS (dry weight)

		^{238}U		^{232}Th		^{226}Ra	
	Point	Activity concentration (Bq/kg)	Transfer factor (kg plant per kg soil)	Activity concentration (Bq/kg)	Transfer factor (kg plant per kg soil)	Activity concentration (Bq/kg)	Transfer factor (kg plant per kg soil)
Soil 0–15 cm	A	41.12 ± 4.40		31.39 ± 1.3		26.60 ± 1.11	
	B	141.50 ± 10.80		39.53 ± 1.3		196.90 ± 1.90	
Grass	A	2.09 ± 0.41	0.0508 ± 0.0113	0.36 ± 0.05	0.0114 ± 0.0017	3.20 ± 0.31	0.1204 ± 0.0125
	B	4.39 ± 0.71	0.0310 ± 0.0055	0.33 ± 0.05	0.0084 ± 0.0012	7.17 ± 0.66	0.0364 ± 0.0034
Hay	A	1.53 ± 0.22	0.0371 ± 0.0067	0.19 ± 0.02	0.0061 ± 0.0008	1.93 ± 0.18	0.0098 ± 0.0009
	B	2.62 ± 0.34	0.0185 ± 0.0028	0.21 ± 0.02	0.0052 ± 0.0006	4.86 ± 0.41	0.0247 ± 0.0021
Corn stalk	A	0.82 ± 0.15	0.0200 ± 0.0041	0.13 ± 0.02	0.0040 ± 0.0008	1.19 ± 0.12	0.0449 ± 0.005
	B	1.58 ± 0.28	0.0112 ± 0.0021	0.14 ± 0.03	0.0035 ± 0.0007	1.80 ± 0.19	0.0091 ± 0.0009
Corn	A	0.10 ± 0.04	0.0025 ± 0.0010	< 0.02		0.18 ± 0.02	0.0009 ± 0.0001
	B	0.13 ± 0.05	0.0009 ± 0.0003	0.05 ± 0.02	0.0012 ± 0.0004	0.27 ± 0.03	0.0014 ± 0.0001
Bean	A	0.07 ± 0.02	0.0017 ± 0.0006	0.04 ± 0.01	0.0011 ± 0.0004	0.08 ± 0.01	0.0031 ± 0.0005
	B	0.20 ± 0.06	0.0014 ± 0.0004	0.05 ± 0.01	0.0012 ± 0.0003	0.32 ± 0.04	0.0016 ± 0.0002
Potato	A	0.42 ± 0.14	0.0103 ± 0.0036	0.28 ± 0.05	0.0090 ± 0.0015	0.19 ± 0.05	0.0071 ± 0.0018
	B	0.67 ± 0.20	0.0047 ± 0.0014	0.27 ± 0.04	0.0070 ± 0.0010	0.67 ± 0.08	0.0034 ± 0.0004
Turnip	A	0.29 ± 0.15	0.0070 ± 0.0036	< 0.02		0.36 ± 0.07	0.0138 ± 0.0028
	B	0.66 ± 0.25	0.0046 ± 0.0018	< 0.02		1.07 ± 0.16	0.0054 ± 0.0008

3.4. Radionuclide contaminant transport model

Considering the fly ash deposits (6 km^2) in the TENT B area as the possible source of groundwater contamination, the radium content (about 0.8 Bq/L) in surface waters and groundwater was treated as a passive contaminant (i.e. non-reactive); on the other hand, the sulphate content (400 mg/L) measured in the wells of the deposits was treated as a reactive contaminant (i.e. a soluble compound with natural retardation). In order to model the worst scenario for radium transport, only the advection term (i.e. transport of the contaminant at the same velocity as the groundwater flow) and the dispersion term of the advection–dispersion equation of a contaminant transport in the aquifer was considered. In the case of sulphates, a further transport term was included: the retardation (i.e. transport delay caused by the soil–water partitioning of the contaminant). The constant partition coefficient, Kd, a function of the contaminant, was tuned in the range of 0–1000 mg/L.

The maps in Figs 4 and 5 show the results of the simulation of radium particle migration and of sulphates from the deposit considering the advection

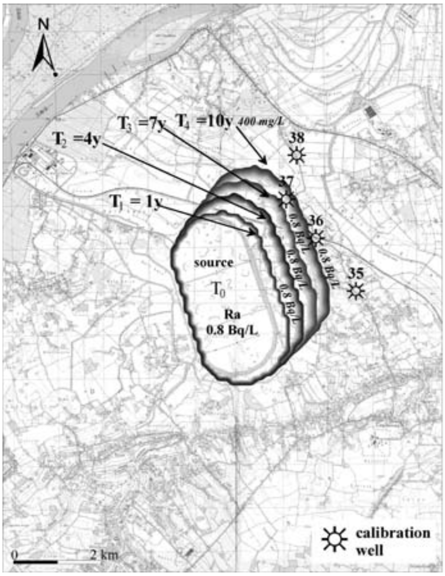

FIG. 4. *Ra contaminant transport modelling results. Isolines represent the simulation of the source concentrations at various times up to 10 years. The symbols indicate some sampled wells used as calibration points.*

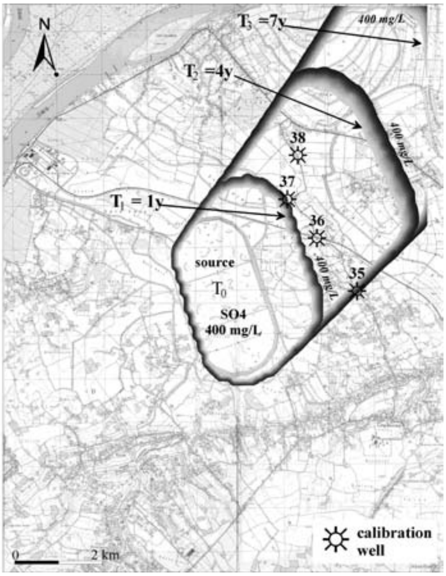

FIG. 5. *Sulphate transport modelling results considered as soluble compound. Isolines represent the simulation of the source concentrations at various times up to 10 years. The symbols indicate some sampled wells used as calibration points.*

and dispersion terms of the equation, as well as the effect of an increasing Kd on the plume extent for the sulphate. The simulation time was 10 years. For the studied test site, in casu tailings of 'TENT B' CBPP in Serbia, the simulation results show the absence of any significant Ra migration around the confined repository.

Furthermore, in order to highlight how the plume concentration changes over time down-gradient from the initial source area, a monitoring well with a known concentration of sulphates is added. This monitoring well is used to assess the plume concentration at this point by displaying a concentration vs. time breakthrough curve. Considering for sulphates a value of Kd = 0.2 mL/g (the most realistic situation), after 10 years the concentration at the monitoring wells is of the same order of magnitude of the measured concentration (Fig. 6).

4. DISCUSSION AND CONCLUSIONS

The impact of radionuclides from tailings from the coal and aluminium industry studied on several relevant and specific test sites by different teams of the project consortium are qualitatively summarized in Table 3.

It can be generally stated that the surface contamination by radionuclides in the studied sites remains limited to the close periphery of the waste sites themselves. The groundwater downstream of the waste facilities is not, or only weakly, affected by the radionuclides.

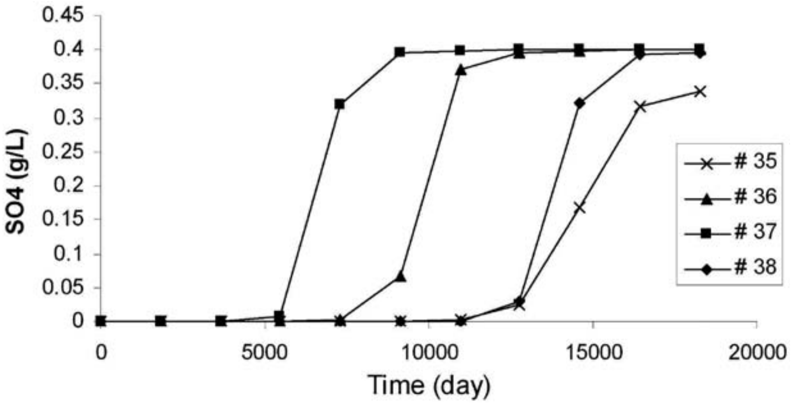

FIG 6. Calibration curves of the sulphates (Kd = 0.2 mL/g) calculated for some sampled wells located in the western side of the studied area. In general, the source concentration is reached in the various wells within 8000–10 000 d.

TABLE 3. OVERVIEW OF PARAMETERS STUDIED IN AND AROUND CBPP AND ALUMINIUM INDUSTRIAL TAILINGS AND THEIR GENERALIZED QUALITATIVE IMPACT

Studied parameter	Generalized observed impact
Gamma exposure	Limited to the close vicinity of the tailings
Radon in soil	Limited to the close vicinity of the tailings
Radon exhalation	Limited to the close vicinity of the tailings
Radon in indoor and outdoor air	Sometimes increased in settlements close to tailings
Radionuclides in soil	Limited to the close vicinity of the tailings
Radionuclides in water	Low to moderate concentrations
Radionuclides in biota	Low to moderate concentrations

On the basis of the recorded radioactivity concentrations in agricultural products and calculated transfer factors in the soil–plant system, it can be stated that bioavailability of the observed radionuclides is generally low, and hence the radiation risk coming from the ingestion of agricultural products is limited.

The main (but limited) contribution to the dose received by the surrounding population comes from (indoor) radon.

Contaminant transport modelling indicates a limited radionuclide contamination and dispersion in groundwater. Greater hazards arise from heavy metals and organic pollutants.

ACKNOWLEDGEMENT

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DEPENDENCE OF RADON EMANATION FROM RED MUD ON HEAT TREATMENT

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Abstract

The radionuclide concentration in red mud was examined from the aspect of its availability for use in the building industry. It turned out from the preliminary examination that the concentration of radionuclides of natural origin is higher in red mud than in the bauxite raw material. Activity concentrations of ^{226}Ra and ^{232}Th measured in these red mud samples were about 10 times higher than the concentrations in common soils. It was found that red mud is not suitable for direct use as a building material according to the European Union classification concerning building materials, but using the following mixing ratio: maximum 20% red mud, minimum 80% clay, these requirements are met. The radon emanation experiments were also conducted. The aim was to examine the dependence of emanation factor on different parameters (e.g. firing temperature). This procedure was carried out in two different ways: first without any additional material and then adding a known amount of sawdust (5–35 wt%) and firing at a given temperature (400–1000°C). During the examination of emanation factors it appeared that a significant decrease can be obtained through control of the firing temperature. The average emanation factor of the untreated dry red mud was 20%; it decreased by about 5% during the heat treatment. Lower values were found when using a reducing atmosphere. In order to find the reason for the decreased emanation, measurements of specific surface and pore volume were carried out. A correlation was determined between these factors.

1. INTRODUCTION

Interest has recently been focused on the elimination of the environmental damage caused by industrial by-products containing elevated concentrations of natural radionuclides, and the utilization of such materials instead. One example is red mud, which originates from bauxite processing. NORM contains radionuclides found in nature, i.e. thorium, uranium and their progeny. Once NORM becomes concentrated through human activity such as mineral extraction it may become a radioactive contamination hazard.

The use of industrial by-products (e.g. slag, fly ash and red mud) is widespread in the building industry, and they are primarily used as additives to concrete [1–4]. In buildings where materials with a high ^{226}Ra concentration are used, the gamma dose rate increases owing to the presence of radium and its daughter elements, which cause a higher external radiation dose [5–6]. Radon-222 possibly emanates from red mud and accumulates in closed rooms; therefore, the increase of internal radiation dose must be taken into account with the inhalation of ^{222}Rn and its decay products [7–8]. Several authors [9–14] have pointed out that the emanation coefficient can be significantly influenced by many parameters such as pore size, specific surface, grain size distribution, density of the grains, homogeneity of ^{226}Ra within the grain and humidity. For this purpose it is necessary to examine the role of these parameters.

The main goal of the work was to establish the possibilities for utilization of bauxite wastes in the building industry, taking radiological factors into account. The European Union index classification concerning building materials was applied [15]. The activity concentrations of ^{226}Ra, ^{40}K and ^{232}Th and the radon emanation coefficient of red mud were determined under different conditions.

If red mud is applied as a component of building material, not only the gamma dose but also the radon emanation may have radiological consequences. That is the reason for firing ‘pure’ red mud samples and red mud mixed with sawdust, in the hope of obtaining a decreased emanation coefficient. The thermal dependence of the emanation coefficient was found to be in the range of 300–1000°C in the case of ‘pure’ red mud samples and also in the presence of additional material (sawdust) in some cases.

2. MATERIALS AND METHODS

2.1. Sampling

Red mud samples were collected from the deposition ponds of two alumina plants in Hungary, located as shown in Fig. 1 (the Almásfüzitő plant

FIG. 1. Origins of red mud samples (1. Almásfüzitő, 2. Ajka).

was closed several years ago, but the Ajka plant is still working). Samples were dried at a temperature of 105 ± 0.5°C to a constant weight and then the fractions were sieved according to grain size using an Edmund Bühler KS 15-B type shaker. These samples were measured by gamma ray spectroscopy and also for radon emanation.

2.2. Determination of ^{226}Ra and ^{232}Th

The dried bauxite and red mud samples were stored for 30 d in airtight aluminium Marinelli beakers with a volume of 600 cm^3 in order to attain radioactive equilibrium of ^{226}Ra with its progeny. The concentrations of naturally occurring radionuclides were determined by high resolution gamma ray spectrometry, using a Eurisys EGNC 20-190-R n type HPGe detector with an efficiency of 20% and with an energy resolution of 1.8 keV at the energy peak of 1333 keV of the ^{60}Co isotope. The gamma spectra were recorded by a Tennelec PCA-MR 8192 multichannel analyser. The data collection time was in the range of 15 000–40 000 s. The system was calibrated using an etalon certified by the Hungarian National Authority of Measures. The ^{226}Ra concentrations were determined by measuring the activities of its decay products ^{214}Pb (295 and 352 keV) and ^{214}Bi (609 and 1120 keV) that were in secular equilibrium with ^{226}Ra following the 30 d storage. The activity of ^{40}K was measured by the 1461 keV gamma ray, and that of ^{232}Th by the 911 keV gamma ray of ^{228}Ac and the 2614 keV gamma ray of ^{208}Tl [16].

2.3. Measurements of ^{222}Rn emanation

A precise weight of dried red mud sample (about 10 g) was put into a 50 cm^3 glass ampoule and was dried in a vacuum dryer chamber for 3 h at 60°C before sealing. After a 30 d storage period, the ampoule was broken in a special metal receptacle. The radon gas was pressed through a filter by N_2 into a 1 L Lucas cell. The method was repeated with another Lucas cell, so the efficiency of transport was higher than 99.7%. After 3 h — in order to have time to reach the equilibrium of radon with its progeny having short half-lives [17] — measurements were performed twice with an EMI photomultiplier for 1000 s. The Lucas cells were calibrated by a PYLON RN 2000A type passive radon source, with an activity of 105.7 ± 0.4% kBq in a Genitron EV 03209 calibration chamber of volume 210.5 L. The emanation coefficient, ε, was determined as a quotient of the activity of the radon sucked from the ampoule and the activity of ^{226}Ra of red mud in the ampoule. The overall relative standard uncertainty was less than 12%.

2.4. Specific surface, pore volume measurements

A Micrometics ASAP 2000 device was used to measure the pores smaller than 100 nm. Samples of mass 1–2 g of different granulation were put into a vacuum (pressure <100 Pa) at 100°C to remove gases linked to the surface. Then adsorption and desorption isotherms for nitrogen gas were measured at the temperature of liquid nitrogen. The specific surface was calculated according to the BET theory.

Pores larger than 100 nm were measured by an SMH6 type mercury poremeter device. Samples of mass 1–5 g were put into a vacuum (pressure <0.1 mm Hg) at room temperature, after which the measuring receptacle was filled with mercury and the change of Hg level in the capillary versus pressure (0–1000 bar) was recorded. The distribution of pore volume was calculated by using the above mentioned results.

3. CHARACTERIZATION OF SAMPLES FOR USE AS CONSTRUCTION MATERIALS

Two major problems arise in the course of utilization of red mud in the building industry. The first is the internal gamma dose and the other is the radon problem due to the relatively high ^{226}Ra and ^{232}Th activity concentrations. The estimation of potential risk associated with ^{222}Rn is based on the activity concentration of ^{226}Ra and the emanation power.

The radiological testing of construction materials is based on the ^{226}Ra, ^{232}Th and ^{40}K concentrations. The value recommended for the maximum allowable activity concentration index by the European Union (and some individual countries such as Finland and Norway) [15] is:

$$I = \frac{C_{Ra}}{300 Bq/kg} + \frac{C_{Th}}{200 Bq/kg} + \frac{C_K}{3000 Bq/kg}$$

where:

I is the activity concentration index
C_x is the measured activity concentration of the radioisotope x (Bq/kg).

The values recommended by the EU were taken into account in the course of the qualification (see Table 1).

4. RESULTS

The activity concentrations of different isotopes in the samples are shown in Table 2. It can be clearly seen that the measured activities in the samples are higher than the world average ^{226}Ra and ^{232}Th activity concentrations of building materials. The activity concentrations of these samples (e.g. ^{226}Ra: 105–700 Bq/kg) are between 2 and 14 times higher than the world average radionuclide concentration of clays (^{226}Ra: 50 Bq/kg, ^{226}Th: 50 Bq/kg, ^{40}K: 670 Bq/kg) [5]. The activity index was calculated from the above mentioned values and is shown in Table 3.

TABLE 1. ACTIVITY CONCENTRATION INDEX

	Activity concentration index for two dose criteria	
	0.3 mSv/a	1 mSv/a
Materials used in bulk amounts, e.g. concrete	≤ 0.5	≤ 1
Superficial and other materials with restricted use, e.g. tiles, boards	≤ 2	≤ 6

TABLE 2. ACTIVITY CONCENTRATIONS IN THE SAMPLES [18]

	Average radionuclide concentrations, range in parentheses (Bq/kg)		
	^{40}K	^{232}Th	^{226}Ra
Sample from Ajka	48 (5–101)	292 (285–380)	360 (150–700)
Sample from Almásfüzitő	102 (50–207)	232 (92–545)	298 (105–498)
World average for clay	670	50	50

TABLE 3. ACTIVITY CONCENTRATION INDEX OF THE SAMPLES

	Activity concentration index		
	Average	Minimum	Maximum
Ajka (100%)	2.58	2.09	3.85
Almásfüzitő (100%)	2.08	1.06	4.42
Ajka (20%)	1.04	0.75	1.27
Almásfüzit? (20%)	0.89	0.68	1.35

On the basis of the activity concentration index, samples of red mud of different origins could be used with restrictions, for example as an additional material in a maximum mixing ratio of 20%.

The radon emanation coefficient ε was determined in some cases and was found to be in the range of 6–22%, with an average value of about 10–20%, as shown in Table 4. The emanation coefficient depends on the material, grain size, moisture and origin of sample.

In most manufacturing processes, additional materials (sawdust and polypropylene pellets) are used in various mixing ratios (5–40%) to improve the quality (porosity, strength and thermal insulation) of bricks. Therefore, red

TABLE 4. AVERAGE EMANATION COEFFICIENT OF THE SAMPLES

	Average emanation coefficient, range in parentheses (%)
Sample from Ajka	18.5 (12–22)
Sample from Almásfüzitő	12 (6–14)

mud samples were mixed with sawdust in different ratios and fired in the temperature range of 300–1000°C. The variation of emanation coefficient as a function of additional material and burning temperature is shown in Fig. 2.

Temperature can be seen to have an effect on the emanation coefficient. The effects of changing pore volume and specific surface on emanation coefficient were examined. The results are shown in Figs 3, 4. Raising the amount of sawdust and the firing temperature decreases the emanation coefficient. The specific surface is inversely proportional to the firing temperature. The pore volume changes proportionally with the amount of additional

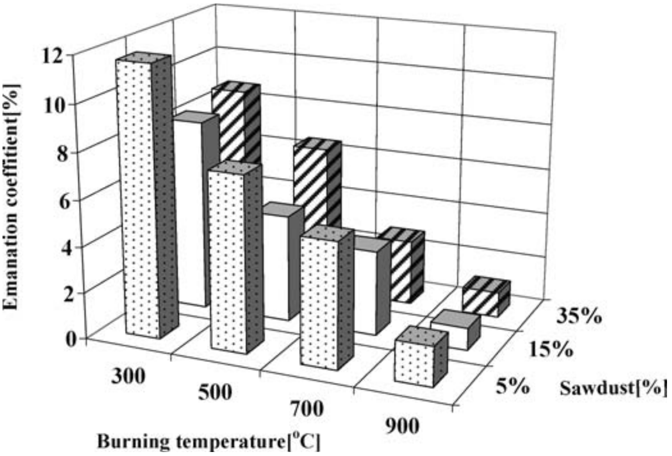

FIG. 2. Variation of emanation coefficient at different firing temperatures and mixing ratios.

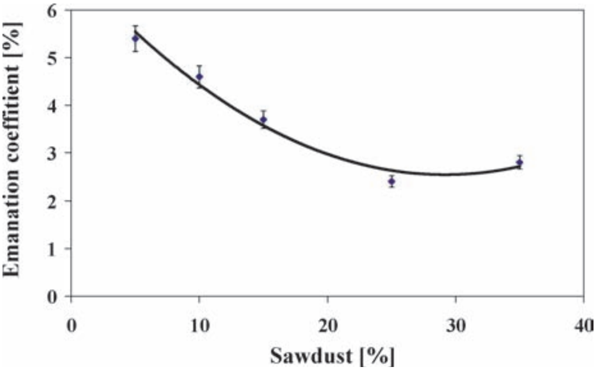

FIG. 3. Correlation between emanation coefficient and amount of sawdust (700°C).

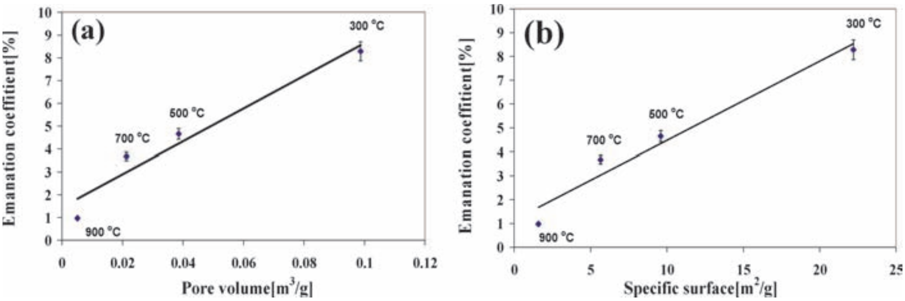

FIG. 4. Dependence of emanation coefficient on (a) pore volume, (b) specific surface (15% sawdust).

material and the emanation coefficient changes in accordance with this tendency. It is evident that a change of pore volume and specific surface may have a considerable effect on the emanation coefficient. It can be very important from the point of view of radiation protection in possible future applications.

5. CONCLUSIONS

In the samples investigated, the activity concentrations of radionuclides of natural origin are higher than the world average values for rocks. Hungarian red mud is suitable for use with restrictions as an additive (maximum 20 wt%) according to EU recommendations. However, on the basis of emanation measurements, increased radiation exposure could be expected in dwellings. Examining the emanation factors, it has been found that the emanation coefficient of red mud can be decreased significantly (perhaps by up to 80%) by:

(a) Increasing the firing temperature to above 800°C;
(b) Optimizing the use of additional materials (e.g. sawdust at 15–25 wt%);
(c) The emanation coefficient decreases linearly with specific surface and pore volume;
(d) Radiological factors must be taken into account when constructing buildings using red mud.

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CHEMICAL TYPES OF BONDING OF NATURAL RADIONUCLIDES IN TECHNOLOGICALLY ENHANCED NATURALLY OCCURRING RADIOACTIVE MATERIAL (TENORM)

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Abstract

TENORM (technologically enhanced naturally occurring radioactive material) is an acronym for solid material containing human made elevated concentrations of naturally occurring radioactive elements. In this study, an enhancement is given if at least one radionuclide exceeds 200 Bq/kg. Raw materials, wastes and products were taken from the following types of industry: aluminium production, refractory industry, fertilizer production, hard coal mining and crude oil exploitation, as well as Th contaminated soils. In order to estimate their environmental hazard dimensions, the availability and mobilization potential of the natural radionuclides stored in those materials were investigated. For this purpose, the 3 step extraction procedure proposed by the European Bureau Communautaire de Référence was applied as well as the German extraction procedures DIN 19730 and 38414-S4. The reagents obtained represent the water soluble, easily exchangeable, plant available, reducible and oxidizable level. These extraction solutions were then measured by gamma spectrometry for determining the activity concentrations of the following radionuclides: ^{238}U, ^{226}Ra, ^{210}Pb, ^{228}Ra and ^{228}Th. By doing so, the chemical types of bonding of these radionuclides can be evaluated. The measuring geometry for gamma spectrometry strongly depends on the reagent volumes resulting from the extraction procedures, which are about 200 mL. Therefore, a special calibration was introduced by using reference water of known radionuclide content from the German Federal Office for Radiation Protection. In order to verify the reliability of

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that calibration standard containing low, medium and high activity concentrations, a measurement comparison was undertaken in a second, independent laboratory, which confirmed the results. The described analytical procedures provide information about potential migration pathways of the natural radionuclides contained in TENORM, as well as the radiological risks for workers dealing with TENORM and members of the public who may be affected (e.g. by dump sites, secondary use as building material).

1. INTRODUCTION

Within the framework of the EU project TENORMHARM, carried out from 1 November 2001 to 31 December 2004 under Contract No. FIGM-CT-2001-00174, samples of technologically enhanced naturally occurring radioactive material (TENORM) were delivered from a Romanian aluminium production plant and a Belgian fertilizer facility. In Germany, solids were provided by a refractory production plant and crude oil exploitation company, sediments were taken from river banks affected by pit waters from hard coal mining and some soils contaminated especially by ^{232}Th progeny. The analyses of those materials by the three extraction procedures (BCR, DIN 19730 and DIN 38414-S4) and the determination of the reagents' activity concentrations were undertaken in the Geology Laboratory of the University of Duisburg–Essen.

2. INVESTIGATION METHODS

All the sample materials were dried for 24 h at 105°C and then homogenized by sieving for the grain size fraction <2 mm. An aliquot was separated from that to be measured by gamma spectrometry for its initial radionuclide content. Then the amounts needed for each of the three extraction procedures were weighed precisely and transferred to acid cleaned 250 mL propylene (PP) centrifugal cups. By the successive adding of several reagents, the radionuclides of different types of bonding were dissolved in those liquids. For the preparation of the chemical solutions needed, bi-distilled water and chemical solutions of the purification degree 'p.a.' were used. All three procedures require extraction shaking, which was done by an overhead shaker at 50 rpm in accordance with the time limits mentioned in the respective standard instruction. After each step, the suspension in the PP cup was centrifuged at 4500 rpm for 5 min; in some cases the centrifuging time was extended to 20 min if the suspension was not fixed on the bottom of the cup before. The separated extraction liquid was then decanted by a 45 µm membrane filter and transferred into an acid cleaned polyethylene (PE) storage cup of 250 mL volume. In terms of the sequential BCR procedure, the reagent of the next step was filled in the same PP cup, which contained the remaining solid material on the bottom from the extraction step before.

2.1. Extraction procedures

The three extraction procedures applied require different amounts of starting materials and different handling schemes, as shown in Table 1. The sequential extraction as proposed by the BCR was carried out according to Ref. [1]; the references for those DIN procedures are Refs [2, 3], as given by the German Institute of Standardization.

In summary, five liquid fractions were obtained as representatives of the easily exchangeable (F1), reducible (F2), oxidizable (F3), plant available (F4) and water soluble (F5) level.

2.2. Gamma spectrometry

The set-up of the high resolution gamma spectrometry method comprises an n type HPGe detector of quasi-coaxial shape, equipped additionally with a beryllium window for including also gamma energies lower than 100 keV. This

TABLE 1. THE THREE EXTRACTION PROCEDURES APPLIED

Fraction	Procedure
BCR (starting material volume 5 g)	
F1 (easily exchangeable)	200 mL of 0.11 mol/L CH_3COOH, shaking time 16 h
F2 (reducible)	200 mL of 0.1 mol/L H_3NOHCl, pH 2, shaking time 16 h
F3 (oxidizable)	a) 2 × 50 mL 35 % H_2O_2, each heated up to near dryness b) 250 mL of 1 mol/L CH_3COONH_4, pH 2, shaking time 16 h
DIN 19730 (starting material volume: 80 g)	
F4 (plant available)	200 mL of 1 mol/L NH_4NO_3, shaking time 2 h
DIN 38414-S4 (starting material volume: 20 g)	
F5 (water soluble)	200 mL of bi-distilled H_2O, shaking time 24 h

system is controlled by InterWinner 5.0 software made by ORTEC and calibrated with GENITRON standards in different volumes for the relevant radionuclides of the ^{238}U decay series (Series-Nr. 92-M-134) and ^{232}Th decay series (Series-Nr. 92-M-112). The radionuclide detection procedures as presented in Table 2 require radon dense measuring boxes to allow radioactive equilibrium to be established. The boxes were therefore sealed by radon rejecting tape. In order to evaluate the initial activity concentrations of those radionuclides in the materials, the grain size fraction <2 mm was measured for 24 h in a 60 mL cylindrical box. This measuring geometry also enables ^{234}Th and ^{210}Pb corrections for self-absorption, as proposed in Ref. [4]. For the gamma spectrometric measurement of the extraction liquids, a special geometry based on 250 mL Marinelli beakers was introduced by using waste water, which bears several artificial radionuclides covering the energy range of 59–1332 keV. It was provided by the German Federal Office for Radiation Protection (BfS) and has been validated by more than 280 intercomparison measurements. A control measurement of the prepared calibration standard was undertaken successfully with a second gamma spectrometry system located at the Laboratorium Radiometrii of the Polish Central Mining Institute (GIG), Katowice.

The detection limit of the gamma spectrometry calibrated in this way is 0.5 Bq/L for ^{226}Ra and slightly higher for other radionuclides. However, before the gamma spectrometric measurements were started, all the extraction reagents as well as the calibration standard were solidified in order to avoid precipitation of particles on the Marinelli beaker bottom. After exact determination of the liquid volume, the solidification was done by adding Agar-Agar into the liquid heated to about 80°C. The Marinelli beaker was then put into boiling water for at least 10 min. Subsequently, it was allowed to cool down slowly.

TABLE 2. RELEVANT RADIONUCLIDES OF THE ^{238}U AND ^{232}Th DECAY SERIES

Radionuclide	Measured via	Gamma line(s)
^{238}U	^{234}Th after storage for 80 d	63.3 keV
^{226}Ra	^{214}Pb	295 and 351 keV
	^{214}Bi after storage for 3 weeks	609 and 1120 keV
^{210}Pb	Directly	46.5 keV
^{228}Ra	^{228}Ac after storage for 36 h	911 and 969 keV
^{228}Th	^{208}Tl to be multiplied by 3 after storage for 3 weeks	583 and 860 keV

In order to determine the radionuclide activity concentrations dissolved in each extractant as a proportion of the starting solid material, it was necessary to calculate the volume activity concentration of the extraction liquids in relation to the activity concentration in the dry mass. That was possible because the amount of starting material was weighed carefully before the extraction was undertaken. Therefore, the activity concentration of each extraction liquid represented a percentage of the dry mass activity concentration of the starting material. The relationship between the activity concentration of the liquid (i.e. $\text{activity}_{\text{liquid}}$) and that of the dry mass (i.e. $\text{activity}_{\text{solid}}$) is given by the following equation:

$$\text{activity}_{\text{solid}}[\text{Bq/kg}] = \frac{1000}{\dfrac{1000}{\text{vol}_{\text{liquid}}[\text{mL}]} \cdot \text{weight}_{\text{materialextracted}}[\text{g}]} \cdot \text{activity}_{\text{liquid}}[\text{Bq/L}] \qquad (1)$$

Factor for correlation of extraction liquid given in millilitres related to 1 L

Factor for correlation of volume extraction liquid up to weighed amount of material given in grams filled in centrifugal cups and related to 1 kg

The residuals from the extraction procedures were discarded due to the fact that their volumes, especially of the BCR scheme, were much too small for reliable gamma spectrometric measurements. Therefore, the radionuclide concentrations remaining in those residuals were calculated by subtracting the total sum of the activities stored in the extraction reagents from the initial radionuclide content.

3. MANUFACTURING PROCESSES AND INITIAL RADIONUCLIDE CONCENTRATIONS

3.1. Aluminium production

The raw material for aluminium production is bauxite and that for the Romanian processing plant (located close to the eastern city Tulcea) comes from the Brazilian Trombeta zone and the Boke deposit in Guinea Bissau [5]. The aluminium oxides in the bauxite are extracted according to the so-called

Bayer process, which generates huge amounts of red sludge as the remaining waste from thickening of the aluminium hydroxides. The Boke bauxite contains ^{226}Ra at 230 Bq/kg and ^{210}Pb at 420 Bq/kg; the bauxite from the Trombeta zone contains ^{226}Ra at 2000 Bq/kg and ^{210}Pb at 4000 Bq/kg. The Tulcea red sludge was found to contain ^{226}Ra at 190 Bq/kg and ^{210}Pb at 330 Bq/kg.

3.2. Refractory industry

One important refractory product is mullite, for which the manufacturing process starts with a mixture of either alumina and silica or bauxite and kaolin to be loaded into an electric arc furnace with temperatures exceeding 2000°C [6]. There the materials are calcined and transformed into a liquid state by fusion processes. The initial chemical combination Al_2SiO_5 is no longer available to be converted into unbound Al_2O_3 and free silica, and the result is mullite ($3Al_2O_3{\cdot}2SiO_2$). In order to further increase the hardness of mullite, zircon sand is also added to the arc furnace. The resulting product is then called fused zirconia–mullite (FZM). During the melting in the furnace a large amount of dust is generated, which is collected by air filters. The raw material zircon sand contains 2750 Bq/kg ^{226}Ra, the FZM product 1600 Bq/kg ^{226}Ra and 1000 Bq/kg ^{210}Pb, whereas the filter dust sample is exclusively contaminated by 162 000 Bq/kg ^{210}Pb.

3.3. Fertilizer production

As the raw material for Belgian fertilizer production, one of the types of phosphate ore used is imported from Morocco, which is of sedimentary origin and contains ^{238}U at 1200 Bq/kg, ^{226}Ra at 1500 Bq/kg and ^{210}Pb at 1600 Bq/kg. In terms of the wet production process for multi-nutrient (MN) fertilizers, the phosphate rock is mixed with sulphuric acid (H_2SO_4) for converting the insoluble phosphate portion into soluble phosphoric acid (H_3PO_4), which also produces 5 t of phosphogypsum waste per tonne of phosphoric acid [7]. The by-product is single superphosphate (SSP), which is a starting material for the MN fertilizers or further processed for triple superphosphate (TSP), also needed for that fertilizer type. The investigated fertilizer of PK type (representative of MN fertilizers) generally contains more than 750 Bq/kg ^{238}U and about 160 Bq/kg of ^{226}Ra and ^{210}Pb, whereas the phosphogypsum sample is proven for all the relevant radionuclides of both decay series not to exceed 200 Bq/kg.

3.4. Hard coal mining

In terms of underground hard coal mining activities, it is usually necessary to pump groundwater to the surface. Depending on the geological background, these waters can be strongly enriched in radium isotopes [8]. Once on the surface, the presence of barium in river water into which pit water is discharged can result in radium precipitation along the river under oxidizing conditions forming a solid called radiobarite, $Ba(Ra)SO_4$. This phenomenon is also known from discharged radium bearing waste waters of phosphate fertilizer production [9]. The sediments collected from a sewer in the northern Ruhr district contain only ^{226}Ra (sediment 1: 540 Bq/kg; sediment 2: 1300 Bq/kg; sediment 3: 1250 Bq/kg) and ^{210}Pb growing again (sediment 1: 330 Bq/kg; sediment 2: 650 Bq/kg; sediment 3: 520 Bq/kg); ^{228}Ra is never detected.

3.5. Thorium contaminated soils

In Germany, two special sites are known to have been contaminated by ^{232}Th progeny, which are now decontaminated [10]. At one location, residues of thorium–cobalt catalysts, which had formerly been used in connection with the so-called Fischer–Tropsch process for producing synthetic fuels by hydrogenation of coal, were disposed of. The second site became contaminated by thorium bearing dust when a thorium processing gas mantle plant was destroyed by an air raid at the end of World War Two and the dust was widely spread in the vicinity of the factory. Soil 1 contaminated by the residue was found to contain ^{238}U at 10 000 Bq/kg, ^{226}Ra at 1000 Bq/kg, ^{228}Ra at 501 000 Bq/kg and ^{228}Th at 420 000 Bq/kg. Both the other soils are derived from the former gas mantle factory — soil 2 contains ^{238}U at 2200 Bq/kg, ^{226}Ra at 1200 Bq/kg, ^{210}Pb at 2000 Bq/kg, ^{228}Ra at 11 000 Bq/kg and ^{228}Th at 9300 Bq/kg, and soil 3 contains ^{238}U at 1600 Bq/kg, ^{226}Ra at 880 Bq/kg, ^{210}Pb at 1600 Bq/kg, ^{228}Ra at 8900 Bq/kg and ^{228}Th at 7600 Bq/kg.

3.6. Crude oil exploitation

The exploitation of crude oil and natural gas are very often connected with strong enhancements, especially of radium isotopes ^{210}Pb and ^{228}Th [11]. Two different types of TENORM are typically generated during those exploitation processes: if barium is dissolved in the produced brines, it precipitates inside the pipeline walls and other installations as scale due to pressure and temperature changes and radium isotopes are then co-precipitated as radiobarite ($Ba(Ra)SO_4$). The much higher ^{210}Pb concentrations are caused by exhaled radon from oily materials in volatile dense areas (e.g. pipelines, vessels or storage tanks). Contaminated sludge results from the drilling process itself or is left behind in the sumps of separation vessels. The scale sample analysed was found to contain ^{226}Ra at 9200 Bq/kg, ^{210}Pb at 45 600 Bq/kg, ^{228}Ra at 1400 Bq/kg and ^{228}Th at 1800 Bq/kg. The sludge contains ^{226}Ra at 48 100 Bq/kg, ^{210}Pb at 46 100 Bq/kg, ^{228}Ra at 12 800 Bq/kg and ^{228}Th at 13 000 Bq/kg.

4. RESULTS AND CONCLUSIONS

All the radionuclide portions dissolved per extraction fraction are presented in Fig. 1.

(a) Aluminium production:
Both the raw materials contain enhanced radionuclide concentrations and show comparable leaching behaviour. The Trombeta bauxite in particular provides ^{226}Ra and ^{210}Pb for the easily exchangeable fraction of 55% and 20%, respectively, being roughly equivalent to 900 Bq/kg each. In addition, ^{226}Ra is also determined to be available for plants by 40%, corresponding to 800 Bq/kg. Forty per cent of the ^{226}Ra, i.e. 80 Bq/kg, is both water soluble and also easily exchangeable from the Tulcea red sludge. Due to the relatively low radionuclide concentrations in that waste, the transfer seems to be diluted during the aluminium production process.

(b) Refractory industry:
From the additive zircon sand, only small amounts of ^{226}Ra are dissolved within the whole BCR procedure (10%) due to the strong fixation of radionuclides in the zircon crystal lattice. Concerning the product FZM, 20% of the initial ^{226}Ra is bound to the oxidizable fraction, while lead is left in the residue. Since the fusion process raises the temperature to levels at which ^{210}Pb (besides ^{222}Rn and ^{210}Po) is removed from the production process, the filter dust generated in the process contains ^{210}Pb at an activity concentration of more than 160 000 Bq/kg, from which 10% is bound to iron and manganese oxides and 30% is fixed on sulphides.

(c) Fertilizer production:
The Moroccan phosphate ore is characterized by ^{226}Ra mostly (50%) bound to organic matter and sulphides, which are the main rock components due to the phosphorite forming by animal particles. The most strongly enhanced uranium of the PK fertilizer product is plant available by 45% and water soluble as well (30%), which is to be expected for a fertilizer. Its uranium concentration is caused by the phosphoric acid associated with the wet process, because it leaches almost all the uranium

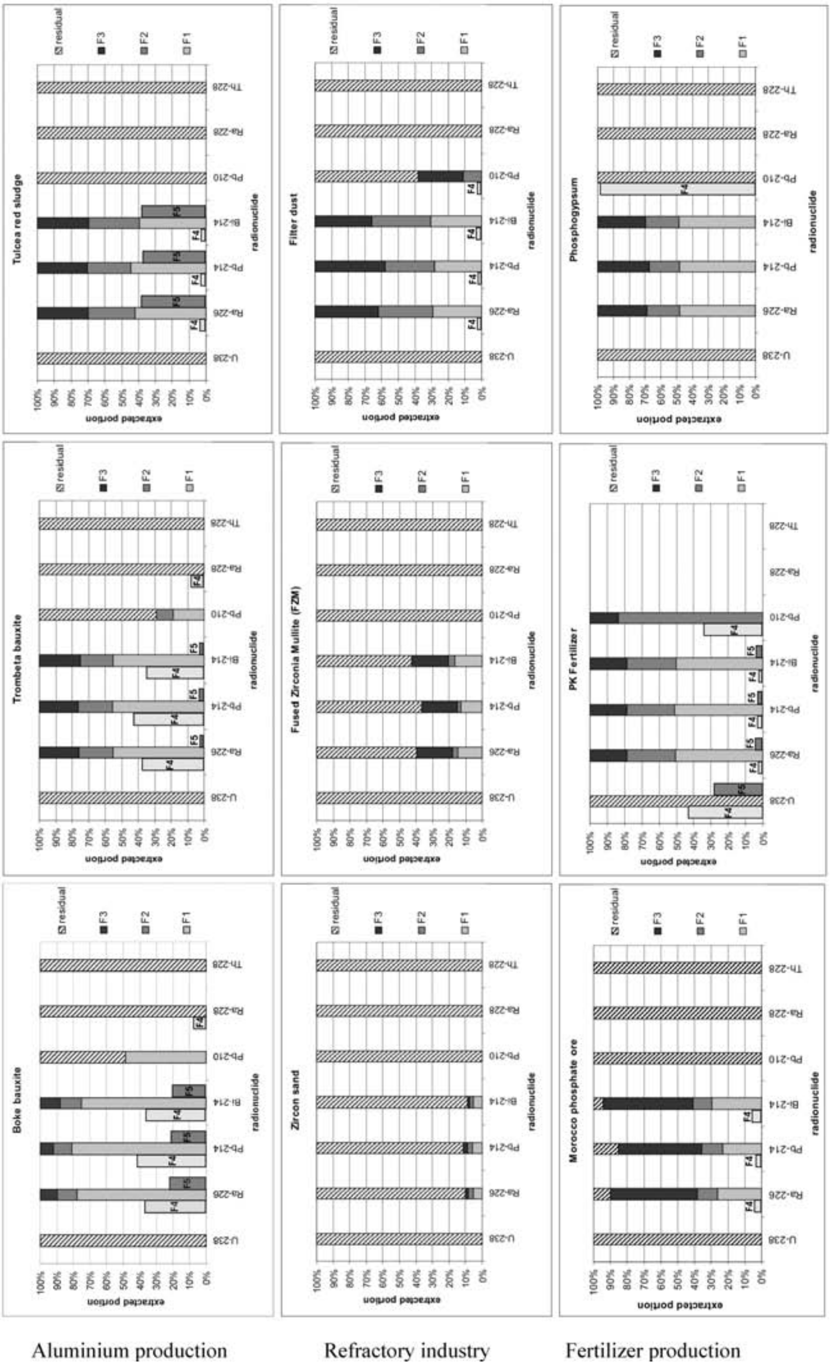

FIG. 1. Dissolved radionuclide fractions from raw materials, products and wastes.

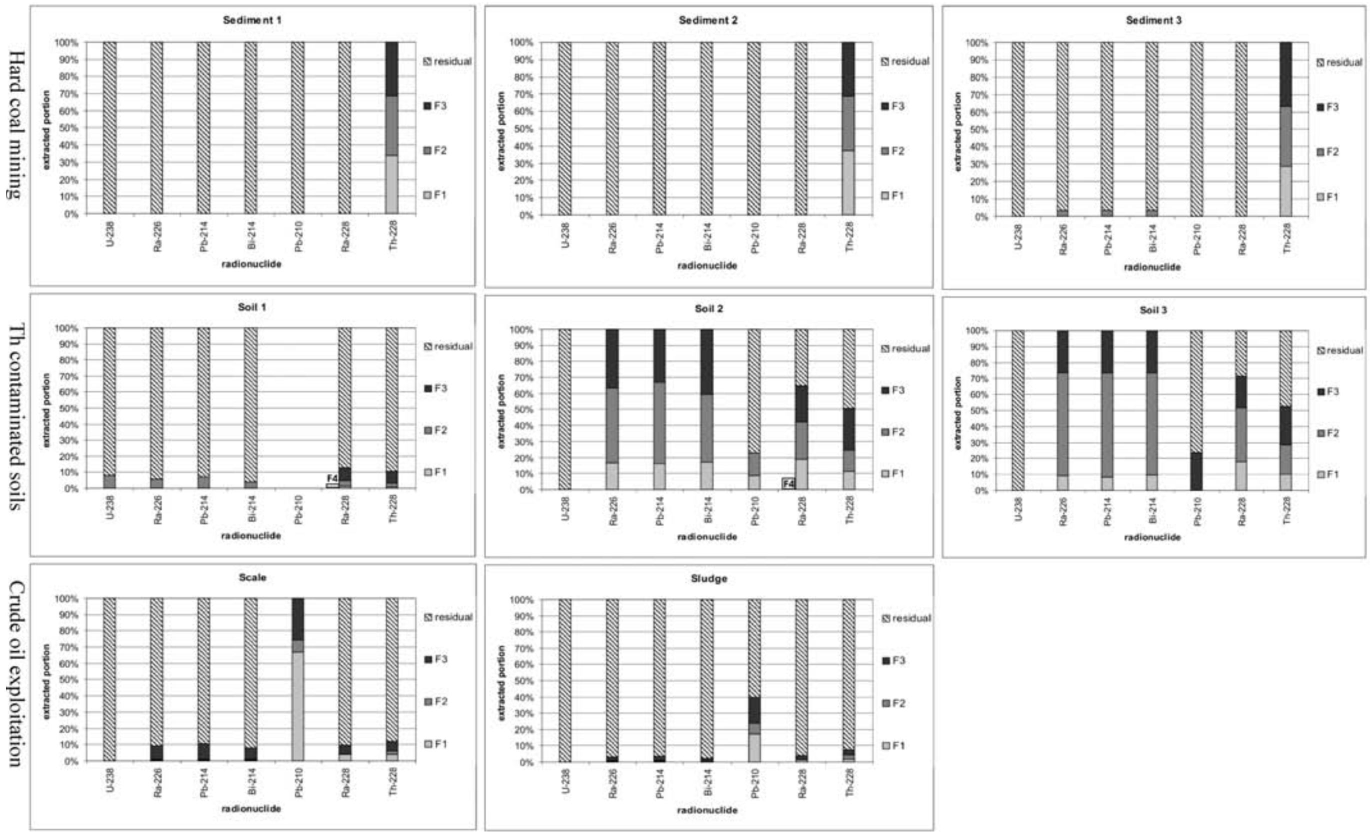

FIG. 1. *Dissolved radionuclide fractions from raw materials, products and wastes (cont.).*

from the initial rock and transfers it into the product. By definition, the waste material phosphogypsum is not TENORM, but provides almost all the initial lead content (45 Bq/kg) for plants. Its generally low activity concentrations can be explained by the unbalanced ratio (5:1) of huge phosphogypsum amounts compared with the produced phosphoric acid volume.

(d) Hard coal mining:
The contaminated sediments were found not to exhibit any enrichment of ^{226}Ra and lead radionuclides under any of the investigated chemical conditions. This can be explained by the very stable crystalline structure of the radiobarite in which they are fixed, such that the solutions used are not sufficiently aggressive to disrupt and remove the compounds. This result is in good accordance with Ref. [12]. The closely corresponding amounts of ^{228}Th present in all three BCR fractions of all sediments can be neglected due to the very low initial activity concentrations (<200 Bq/kg).

(e) Thorium contaminated soils:
By far the highest activity concentrations are found in the thorium contaminated soils. The low leaching coefficients for ^{228}Ra and ^{228}Th of soil 1 are put into perspective by their extremely high initial concentrations, so 2% of each is fixed in the reducible fraction (10 000 Bq/kg) and 8% in the oxidizable one (40 000 Bq/kg), 2% of the ^{228}Ra is also plant available. In soil 2, roughly 20% of ^{228}Ra (2200 Bq/kg) can be found in each of the BCR fractions and 8% (900 Bq/kg) is plant available, 12% of ^{228}Th is easily exchangeable and reducible respectively, 25% is bound to organic matter and sulphides. Soil 3, taken at the same site, shows similar types of radionuclide bonding, just the initial activity concentrations, which are also of the same ratios, are slightly lower.

(f) Crude oil exploitation:
All the ^{210}Pb concentration contained in the scale is completely leached in terms of the BCR procedure, 65% (almost 30 000 Bq/kg) is easily exchangeable, 10% (4700 Bq/kg) is bound to iron and manganese oxides and 25% (12 000 Bq/kg) is fixed on organic matter and sulphides. The sludge sample is determined for a similar initial ^{210}Pb and also ^{226}Ra concentration, but most is left in the residue; 18% of the lead is easily exchangeable (8300 Bq/kg), 6% (2800 Bq/kg) is fixed in the reducible fraction and 18% in the oxidizable one. The ^{226}Ra mentioned above is only detected in the last BCR fraction by 3%, which means 1400 Bq/kg.

(g) Procedure:
As the analyses show, the measuring procedure developed is reliable and leads to comparable and reproducible results, i.e. samples from the same sources are determined for the same types of radionuclide bonding. This

is proven by all the extraction liquids of the three sediments from the environment influenced by hard coal mining and by the leaching coefficients of the highly thorium contaminated soils 2 and 3 as well.

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RAPPORTEUR SUMMARY OF TOPICAL SESSION 8 AND OVERALL CONCLUSIONS

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1. INTRODUCTION

As the final rapporteur I was asked to give an overview of the whole conference rather than just a straight summary of the final sessions. In particular, I was asked to try and take a step back from the individual presentations and consider what overall themes and conclusions could be taken away from NORM V.

The first clear conclusion is the high quality of the symposium itself. The structure, content, organization and implementation were all to be commended, and sincere thanks are given to the Spanish sponsors, the local organizers and the IAEA. Specific mention is made of R. García-Tenorio, G. Manjón and D.G. Wymer, whose efforts played a large part in the success of the event.

The symposium contained oral and poster presentations which collectively covered the wide range of NORM issues in a very effective manner. Plenary presentations at the start of each session provided an excellent overview of the issues in different sectors and laid the groundwork for subsequent presentations and discussions. From all of these, certain themes emerged, and I have attempted to summarize these below.

2. NORM INFORMATION AND NETWORKS

The symposium demonstrated the large variety of expertise that is drawn together within the subject of NORM. It is truly a multi-disciplinary area, with contributions from the fields of geology, chemistry, engineering and biology, as well as radiation protection. The latter calls upon expertise in instrumentation and analysis, environmental modelling, as well as health physics.

Research into NORM has expanded significantly over the last ten years and a very substantial amount of work on the subject has been published. This work is produced from all over the globe, and from many different sources. Some organizations and associations have begun to compile their own databases of papers, and it is considered that the development of a wider database of NORM related information would be extremely useful. To obtain real value from such a database it is important that mechanisms for providing, accessing and sharing information are developed at the same time. A European NORM network to promote information sharing on-line is being developed and it is hoped that this concept might be taken up on a wider international basis.

Despite the large quantity of work already done, NORM is still an evolving subject and in some areas information remains quite scarce. One such area is residues from the treatment of groundwater — some information was provided at this symposium but it is felt that the issue is worthy of further work. Again, the development of databases and networks could assist in establishing the scale of the problem.

3. REGULATORY STANDARDS AND HARMONIZATION

The need to establish standards, especially for the scope of regulatory control, is a recurring theme. Most NORM industries are international and there are clear benefits to be derived from the harmonization of standards. Much progress has been made, both nationally and internationally, since the first NORM symposium in 1997. However, the issue of harmonization remains a prospect rather than a reality and remains the subject of much debate.

In terms of specific issues, the use of the 1 Bq/g criterion, as proposed by the IAEA for determining the scope of regulation is increasingly supported, although it is clear that some reservations remain in respect of specific exposure situations. It is suggested that this criterion (with some caveats) does represent the most viable way forward if harmonization is to be seriously pursued. In doing this, it is important that the meaning and purpose of this criterion remain clearly understood. A number of times during the symposium, 1 Bq/g was referred to as a ‘limit’, which it clearly is not.

The adoption of a 1 mSv/a (worker dose) criterion for the application of regulatory controls is now commonplace and it is suggested that it has now become a de facto NORM standard. There is, however, still a need for more guidance on how this might be applied to real workplaces, for example where there are large differences between potential and actual dose distributions.

The above criteria provide the starting point for establishing a graded approach to regulation, within which the concepts of exemption, notification, registration and licensing are introduced according to the significance of the radiological hazard. This approach enjoys broad support, although it is felt that it would now be useful to consider the details of how it should be applied to different NORM industries in practice.

4. ASSESSING DOSES TO WORKERS AND THE PUBLIC

Systems for applying regulatory controls depend significantly on the individual doses that are received, and the symposium contained a great deal of information on how such doses might be assessed. Exposure models clearly must be used with care, since the results are greatly dependent on the reliability of any assumptions made. In terms of public exposures (e.g. due to waste disposal activities), dose modelling is inevitable and many excellent examples of this approach were presented. In terms of worker exposures, the emphasis is clearly now on the use of workplace and individual monitoring data to ensure that dose estimates are realistic.

The symposium highlighted some issues that still remain in respect of the basic dosimetric data (dose coefficients and dose conversion factors) and the methods used to estimate internal doses from NORM. It is evident that data derived from an artificial radionuclide perspective may not always be directly applicable to NORM, or at the very least such data require careful selection if dose estimates are to be accurate.

5. INTERNATIONAL ISSUES

The international nature of NORM has already been highlighted, and the value of international symposia cannot be underestimated. About 200 participants were present at this symposium, representing 40 different countries, and the important role of the IAEA Technical Cooperation Programme in sponsoring a number of participants is very much appreciated. However, some key NORM producing/processing countries were not represented (e.g. China, which was identified as a major NORM industry base in a number of presentations). Further efforts to encourage the involvement of such countries (for example at NORM VI in Morocco, 2010) are needed.

A number of presentations highlighted issues associated with the transportation and monitoring of NORM, either as a planned shipment of material, or as a residue in the metal recycling industry. This adds a further international dimension, since it may involve locations far removed from the NORM industries themselves. The detection of NORM and the resulting actions (often the refusal of materials) are increasingly causing problems. Harmonization is again a key factor, as is the training of monitoring personnel.

6. CONTROL OF OCCUPATIONAL DOSES

Much of the debate on NORM has focused on the scope of regulation and whether the low doses associated with many NORM industries warrant any control. However, in some industries, such as the extraction and processing of rare earths, significant doses are received and controls are clearly required. Unfortunately there was little information presented on the methods used in practice to restrict exposures in such workplaces. More information on practical protection methods (i.e. engineering controls, working procedures and personal protective equipment) and their efficacy in different work environments would be welcome.

One interesting issue to emerge was related to the planning of new NORM extraction/processing facilities. Traditionally, controls have been considered in terms of their application to an existing operation. However, a lesson from the wider radiological protection community is that controls at the design stage are usually the most effective option. This applies equally well to new NORM facilities, in which a proactive approach to the choice of materials, process or plant may yield benefits in terms of the control of NORM arising during the subsequent operational and decommissioning phases.

7. THE ROLE OF NORM INDUSTRIES

Decisions on the regulation of NORM can potentially have a severe impact on the industries concerned, and it was encouraging to see so many industry participants and presenters at the symposium. The active participation of industry in the debate is extremely important and the involvement of industry in the drafting of IAEA Safety Reports has been of significant assistance in this respect.

8. NORM AND THE PUBLIC

The use of a 0.3 mSv/a dose constraint for public exposure from a single source is increasingly being applied, although there are still some differences at a national level. Some excellent examples of the assessment of public doses from the use and disposal of NORM were presented, with the majority indicating that exposures were often very low. There was, however, little mention of involving and communicating with the public, and what their stakeholder role might be. This was particularly noticeable in the debate on the treatment of the residues from the phosphate industry. A range of options exist, including use in building materials and application to agricultural land. The symposium illustrated the important work that has been done to assess the potential radiological impact of these options. However, the wider social impact — whether the addition of NORM into homes or the food chain is acceptable to the public — has yet to be considered.

9. NORM AND THE ENVIRONMENT

It was interesting to see a number of presentations considering the protection of other species in the environment. This is one of the cutting edge topics in radiation protection and it is encouraging to see it appear on the NORM agenda. NORM radionuclides already exist throughout the biosphere, and this at least provides some benchmark against which the exposure tolerance of different species might be evaluated.

The work presented at the symposium suggested that radiation doses to other species were unlikely to exceed the variation observed in the natural background, although it must be accepted that relatively few studies have been undertaken so far. One important factor is that radioactivity is only one component, often a very minor one, of the materials released into the environment. There are often much more severe environmental challenges, e.g. due to chemical toxicity, or simply the sheer physical quantities of materials involved.

10. MANAGEMENT OF NORM RESIDUES

This is a major challenge for a number of NORM industries and was addressed by a number of presentations in which a range of problems, and some local solutions, were laid out. The main theme to emerge was that these problems were best resolved through an integrated strategy for the management of residues which, in turn, includes practical provisions for the disposal of waste. As indicated by a number of presentations, options for use, reuse and recycling of residues do exist and should be explored. Some of these options may subsequently lead to the production of NORM waste, and this should be considered as part of the integrated strategy.

Also to emerge was the realization that some residues will almost certainly require disposal as waste. Again, a range of disposal options was presented, including dilution and dispersion, a strategy that may well be the optimum solution for some NORM wastes. For other types of waste, especially where activity concentrations are very high, the disposal of waste to specially engineered repositories may be preferred. However, the lack of such facilities is a major barrier to the pursuit of this option.

11. CLOSING THOUGHTS

D.G. Wymer (IAEA), in his opening presentation asked whether there was chaos or consensus in relation to NORM. My impression from this symposium is that there is a great deal of consensus but also still some chaos. It should be acknowledged that a great deal of progress has been made, nationally and internationally, in identifying the problems associated with NORM and in identifying a practical way forward.

There has been a great deal of debate on the scope of regulatory controls, and the criteria proposed by the IAEA (and endorsed by ICRP) have gained substantial support. This support is not universal and harmonization may be thought of as an opportunity rather than a reality at present. The question now is how far we are prepared to compromise in seeking a truly harmonized approach. Whatever the case, it is clear that in many cases the time has come to move from discussion to implementation. In doing so, we need now to consider the implementation of specific regulatory controls in practice. At the same time, the challenge of establishing an integrated and coherent strategy for the management of NORM residues needs urgent consideration.

Finally, I would say again how valuable NORM V was, and pass my compliments to the organizers, presenters and all those who participated in the discussions.

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	N. TSURIKOV	Australia
Topical Sessions 3 and 4	A. FAHLI	Morocco
	J.L. MARTÍN-MATARRANZ	Spain
Topical Session 5	J. WELBERGEN	Netherlands
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Topical Session 7	S. CHAŁUPNIK	Poland
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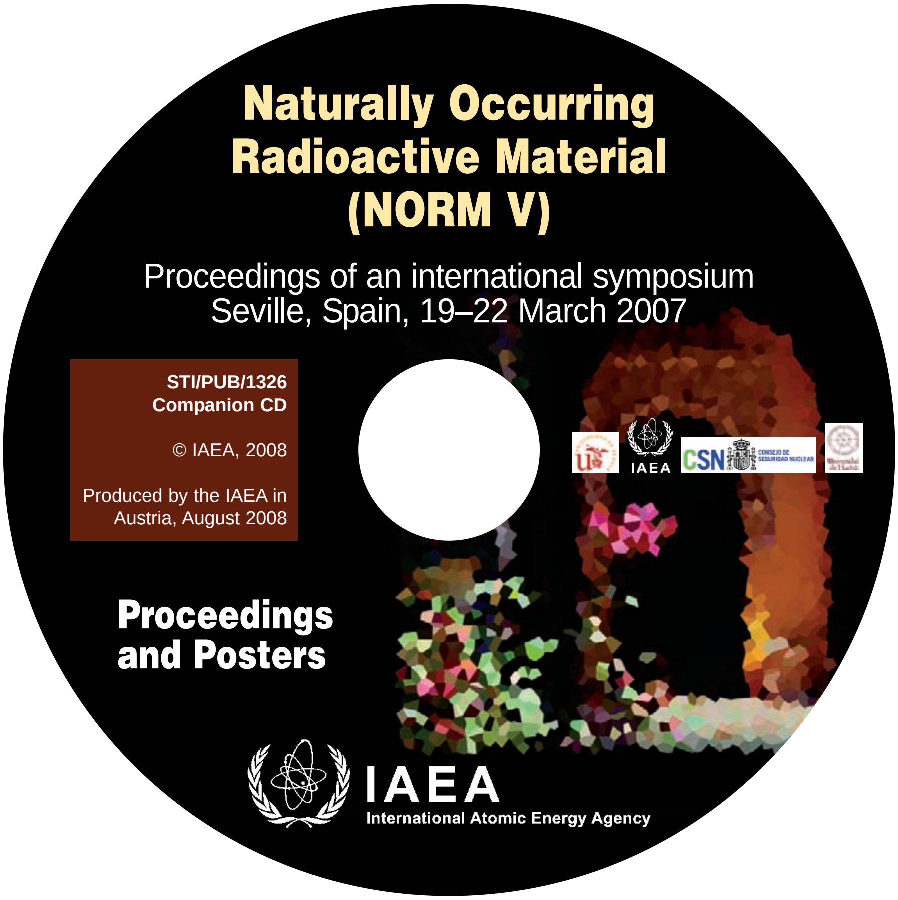

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All minerals and raw materials contain radionuclides of natural origin, of which the most important for the purposes of radiation protection are the radionuclides in the ^{238}U and ^{232}Th decay series and ^{40}K. For most human activities involving minerals and raw materials, the levels of exposure to these radionuclides are not significantly greater than normal background levels. Such exposures, while having been the subject of much research, are not of concern for radiation protection. However, certain work activities can give rise to significantly enhanced exposures that may need to be controlled by regulation. Material giving rise to these enhanced exposures has become known as naturally occurring radioactive material (NORM). The NORM V symposium, which was attended by 200 participants from 40 countries, was held exactly one decade after the first symposium in the series and provided an important opportunity to review the many developments that had taken place over this period. It also coincided with various current initiatives to review and revise international recommendations and standards on radiation protection and safety. The Proceedings contain all 37 oral presentations and four rapporteur reports, as well as a summary that concludes with the main findings of the symposium. Text versions of 46 poster presentations are provided on a CD-ROM, which accompanies these Proceedings.

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