EU-NORM
1st International Symposium

5-8 June 2012
Tallinn, Estonia

PROCEEDINGS

KESKKONNAMINISTEERIUM

ENVIRONMENTAL BOARD

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Opening Address

Andres Onemar
Director General
Environmental Board

It is a great honour for me to write the opening address to the book First European International Symposium on Naturally Occurring Radioactive Material on behalf of the Environmental Board. I would like to thank the steering committee for choosing Tallinn to celebrate this scientific event and giving to the Environmental Board the opportunity to organize it.

The Environmental Board, established in 2009, is relatively young institution. The evergrowing role we play is determined, on the one hand, by the areas of governance appointed to us. We deal with people, plants, animals and their living environments in terms of the four basic elements-on land, in water, in fire and in the air.

The Environmental Board today is a collective of leading environmental specialists who were previously scattered throughout other organisations. One of the key concepts for the Environmental Board is balance: we seek to preserve (and where necessary create) a realistic balance between the use and protection of natural resources; we work with Estonia's residents, state agencies, companies and organisations and those of the European Union in a balanced way; and we are achieving balanced development within our organisation in terms of both competence and regional coverage.

The Environmental Board's logo is a flower whose petals are marked with the signs of the four elements-earth, air, fire and water. It represents the way the world works, and the way it has always worked, as a balance between these ancient elements. This balance expresses the values we hold dear and the goals we set ourselves in what we do. We strive to foster human development whilst protecting the diversity and vitality of our natural environment.

Anything to do with radiation and radioactive materials strikes fear into the hearts of many people, since they tend to be couched in terms of something abnormal and life-threatening. In fact, as we all know, radiation is as much a part of nature as we ourselves are, and enjoys extensive use in medicine, science and industry.

Natural mineral resources like some ores contain naturally occurring radioactive materials (NORM). Ores are widely used in industry for production of fuel, metals, energy, etc. The by-product of industrial production is residue and waste which could have significant level of concentration of radionuclides. As the population is constantly growing, so is growing the industry to answer the constantly increasing demand. This means that the amount of NORM created in industries is getting bigger year by year and so are the problems with NORM. Therefore more attention need to be turned to regulation of the use of NORM containing material as well as to exposure that both the public and industry workers receive in production cycle and waste management.

This scientific event, First European International Symposium on Naturally Occurring Radioactive Material, should have the added value of identifying common interests which can be used to establish collaborative scientific projects from the discussions and debates developed in its sessions.

We are delighted to host NORM-society here in Estonia which brings the valued knowledge to our doorstep. The information and experiences gathered from the event will be good basis to update our knowledge and skills to find possible solutions in everyday worklife.

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Miscellaneous

EU Regulatory Framework for Naturally Occurring Radioactive Materials (NORM)

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Abstract

In 1996, natural radiation sources were already mentioned in standards established by Euratom as well as those established by the IAEA. Since then, the European Commission has moved ahead publishing, on a regular basis, technical support guidance and recommendations on NORM issues. In 1997 for instance, recommendations were published to help dealing with "significant increase in exposure due to natural radiations". In 1999 the European Commission published radiological protection principles concerning the natural radioactivity of building materials and reference levels for workplaces processing materials with enhanced levels of naturally occurring radionuclides. Lastly, in 2001 the European Commission published recommendations dealing with exemption and clearance levels for NORM residues. All these recommendations have provided member states with criteria and a sound technical framework to help establish national regulations for NORM and NORM residues. Several EU States have already included all or parts of these recommendations in their regulatory framework. From now on, the Commission wishes to harmonize, promote and consolidate these recommendations, writing them down in the new EU-BSS version. All current updated BSS parts, regarding NORM issues, are hereby presented with comments and explanations.

1. INTRODUCTION

Many industrial activities, other than those concerned by the nuclear fuel cycle, need to be monitored and regulated regarding protection against ionising radiations, inter alia:

- Underground water industrial treatments for water consumption which may concentrate natural radioactive materials in filters or related industrial equipment;
- Hydropathical establishments;
- Low Specific Activity (LSA) Scales from gas, oil or coal extraction;
- Certain specific coal-fired power plant works;
- The uses or treatment of ores, products or derived products such as: tin, lead, copper, alumina (bauxite or corundum), titan, niobium/tantalum, bismuth, thorium, zircon (or badalleyite), phosphogypsum as well as rare earths may contain significant concentration of NORM.
- The production of Thorium compounds and manufacture of thorium-containing products which may lead to high occupational doses.
- Other industrial processes which may accumulate natural radioactive materials within some manufactured materials or within related industrial process residues [1].

The following table figures out some examples of natural radioactive sources classified by activity levels. Corresponding occupational doses encountered in these industries are also indicated. Most references in this table come from French surveys[1] and publications presented in previous EAN-NORM workshops.

Bq/g			Natural Radioactive Materials [1], [3]	Occupational doses in practice
<0.05	0.05 0.005	^{238}U ^{232}Th	Kaolin; hard coal mining; lead, Zinc.	negligible
<0.5	0.15-0.5 0.3-0.5 0.1-0.4 0.2	^{238}U ^{232}Th ^{235}U ^{40}K	Bauxite & red sludge; **N.B.:** Studies about red sludge recycling possibilities to make construction materials [16] shows doses going up to 0.75 mSv/ year to potential inhabitants.	10 µSv to 0.75 mSv per year
< 2	0.4-1.7 0.03-1 0.45 1	^{238}U ^{232}Th ^{40}K* ^{210}Pb*	Phosphorite, raw phosphate, phosphate Fertilizers, phosphoric acid production, gypsum from phosphorite production, rutile, ilmenite. ("radiation spots" up to 30-40 µSv/h) [5], [6], [13], [15] Carbon combustion in power plants (Ashes may contain from 0.1 to 0.3 Bq/g of ^{238}U; 0.05 Bq/g of ^{235}U; 0.05 of ^{232}Th; about 0.45 Bq/g of ^{40}K and about 1 Bq/g of ^{210}Pb)	10 µSv to 1 mSv per year
< 5	0.01-4 0.8 0.01-4	^{238}U ^{232}Th ^{235}U ^{40}K	Industries dealing with refractory ceramic manufacturing, glassworks, foundry, steel or metallurgy processes. International literature shows activities reaching 10 Bq/g and yearly doses between 10 and 140 µSv. However, exceptions might occur with zircon durst exposure where doses may exceed 1 mSv a year.	10 µSv to 1 mSv per year
	5 0.5 ? ?	^{238}U ^{232}Th ^{210}Pb ^{210}Po	Zircon [1], [10], [12] **NB.:** ^{210}Pb, ^{210}Po could be also inhaled and increase doses.	200 µSv to 1 mSv per year
< 50	17 1.3 0.28 7.1 32	^{238}U ^{235}U ^{232}Th ^{210}Pb ^{226}Ra	Tin-Tantalum	Poor statistics
< 150	20-100 80-150	^{238}U ^{232}Th	Low Specific Activity (LSA) scales from gas, petrol, coal extraction and geothermic installations Oil industry radiation spots may vary from 1 to 100 Bq/g. Literature shows records of 4000 Bq/g - [3], [14]) Monazite (poor statistics)	Poor statistics
< 500	494 37 250 250	^{232}Th ^{210}Pb ^{214}Pb ^{226}Ra	LSA scales from Ti ore treatment	Doses vary from 0.5 to 20 µSv/h
> 500		^{232}Th	Thorium used as raw material to manufacture electrodes or specific equipments, see [7].	> 80 mSv/year! for 500 hours of thorium tool manufacturing in a French factory [1]

2. EUROPEAN REGULATORY APPROACH FOR NORM

2.1 General approach

The EURATOM Basic Safety Standards (for the protection of the health of workers and the general public against the dangers arising from ionizing radiation or EU-BSS) provides Member States with a sound European regulatory framework in radiation protection. EU member states have to transpose these European requirements into their national legislation.

The EU-BSS is currently being consolidated, merging 5 existing directives in a same document[20], clarifying some parts and adding existing EU recommendations dealing with natural radiation sources.

Article 2 of the new EU-BSS states that all practices involving radiation sources are to be regulated including *"practices which involve the presence of natural radiation sources that lead to a significant increase in the exposure of workers or members of the public, in particular the activities in industries processing materials with naturally occurring radionuclides, or activities related to such processing."*

It is also required (article 24) **to identify** *"practices"* defined as *"any activity that involves the operation or introduction of radiation sources or which alters exposure pathways and is managed as a planned exposure situation"*. Henceforth, industries dealing with NORM will need **to be identified** by the national regulatory authority and to comply with the following requirements for all planned exposure situations.

An indicative list of concerned types of industry is attached to the new EU-BSS. This list, called "positive list", covers known industrial activities which may require regulatory control; each Member State will have to establish its own "positive list". Secondary processes are also to be taken into account when considering these types of industries:

(1) extraction of rare earths from monazite;
(2) production of thorium compounds and manufacture of thorium-containing products;
(3) processing of niobium/tantalum ore;
(4) oil and gas production;
(5) geothermal energy production;
(6) TiO_2 pigment production;
(7) thermal phosphorus production;
(8) zircon and zirconium industry;
(9) production of phosphate fertilisers;
(10) cement production, maintenance of clinker ovens;
(11) coal-fired power plants, maintenance of boilers;
(12) phosphoric acid production;
(13) primary iron production;
(14) tin/lead/copper smelting;
(15) ground water filtration facilities;
(16) mining of ores other than uranium ore.

Following this identification process, some of these identified practices may be exempted according to values (Art. 25.1) set out below (BSS/annex VI, Table A, Part2):

Radionuclides	Activity concentration
Natural radionuclides from the ^{238}U	1000 Bq/kg
Natural radionuclides from the ^{232}Th	1000 Bq/kg
^{40}K	10 000 Bq/kg

Unless exempted, they shall be **notified** to the regulatory authority. Following this notification, a **regulatory decision** will have to be taken whether **to exempt** (art. 26.2) **or authorise** (art. 26.4), under certain conditions, such activities. The new EU-BSS has added that activities liable to lead to an affective dose to *"a member of the public"* exceeding **0.3 mSv/year** shall imply **an authorisation** (27.3.f). According to the EU-BSS definition an "authorisation" could be either a registration or a licence (the latter implying a dedicated licensing process (art.28)).

It is added that if these practices are liable to significantly affect drinking water quality or any other exposure pathway, whether below exempted activity concentrations or not, a notification has to be issued anyway to the regulatory authority (25.4) and likewise, a regulatory decision will have to be taken (art.26.2 and 26.4).

2.2 Building materials

Many existing building materials contain significant quantities of NORM which may lead to doses exceeding 1 mSv/year. Nevertheless, the production of building materials containing natural radioactive materials may remain justified because of their interesting chemical, mechanical or physical properties regarding construction aspects. It was then agreed to establish the following regulatory approach for building materials so that the legislation guarantees not to exceed, in practice, a reference level of 1 mSv a year for a member of the public.

The "*undertaking*" who is, in our case, the person or organisation responsible for introducing NORM residues in building materials has henceforth **to notify** this practice (art. 25.3) if the following index is liable to exceed 1:

$$I = C_{^{226}Ra}/300 + C_{^{232}Th}/200 + C_{^{40}K}/3000, \text{ with } C \text{ in Bq/kg.}$$

In addition to the **regulatory notification** mentioned above and prior placing these products on the market, the *undertaking* shall also **inform the users** of the residues and their activity concentrations (art. 25.3). The production of building materials, whether from natural materials or using recycled residues is not regulated as a practice. Nevertheless, the *"undertaking"* has to ensure that activity concentrations are measured and made available prior to their placing on the market as well as the activity concentration index and corresponding classification (art. 75.6). The classification is defined as follow in the annex VII of the EU-BSS:

Uses	Categories	
	A ≤ 1mSv	**B>1mSv**
Bulk materials (1)	I≤1 (Type A1)	I>1 (Type B1)
Superficial materials with restricted uses (2)	I≤6 (Type A2)	I>6 (Type B2)

The definition of uses (1) and (2) should be established in national building codes.

The index calculation and related notification to the authority will become a real stake for certain industries since it determines whether or not to be regulated (art.26), may restrict product distribution or uses in the EU market and may impose constraining labelling on the products (articles 25.3 and 75).

The concentration activity determination of ^{226}Ra, ^{232}Th and ^{40}K varies from one laboratory to another depending on protocols and methodologies in place so the European Commission mandated the CEN/CENELEC under the Council directive 89/106/EEC of December 21, 1988 concerning construction products so as to help standardize and harmonize activity concentration measurement and test standards.

This regulatory Index was thought to be a good screening test for building materials but in-depth investigation has revealed some difficulties.

In gamma-spectrometry, the ^{232}Th gamma emission detection is not easy to perform out of the noise made by ^{234}Th (direct progeny of ^{238}U). So decisions are to be made **on which progenies** of the ^{232}Th to be considered for measurement and on which methodology to be established **to allow proper estimate of the ^{232}Th activity concentration.**

It should be added that the cascade of progenies derived from ^{232}Th is rarely in secular equilibrium in building material. Indeed, the ^{228}Ra (direct progeny) is often naturally washed out, with time, by circulating water in soil, before the raw material extraction. Radium may also be washed out again during industrial processes. ^{232}Th activity concentration may then become predominant compared to its progenies (^{228}Ra and derived progenies) and this may wrongly reduce the estimate of the regulatory index.

Art.75.4 specifies that identified types of building materials which are not liable to give doses exceeding the reference level of 1 mSv/year for indoor external exposure from building materials, in excess of prevailing outdoor external exposure shall be exempted from any requirements at national level. In addition to this regulatory index to estimate, the same article allows A1 and A2 products to be exempted from any market restriction.
Nevertheless, B1 and B2 products may be acceptable for certain constructions depending on building uses and activity background. Such considerations shall be decided by national authorities as appropriate following the index calculation. Specific dose modelling could then be performed depending on activity background and projected use of these product categories. A CEN/CENELEC working group is also mandated by the European Commission to work on dose modelling harmonization.

A list of building materials will be specified by member states in their regulatory framework based on the following indicative list which is included in the Annex XI of the new EU-BSS:

- Natural materials
  - Alum-shale.
  - Building materials or additives of natural igneous origin, such as: granite, gneiss, porphyries, syenite, basalt, tuff, pozzolana and lava.

- Materials incorporating residues from industries processing NORM such as: fly ash; phosphogypsum; phosphorus slag; tin slag; copper slag; red mud (residue from aluminium production) and residues from steel production.

3. Radiation protection overview

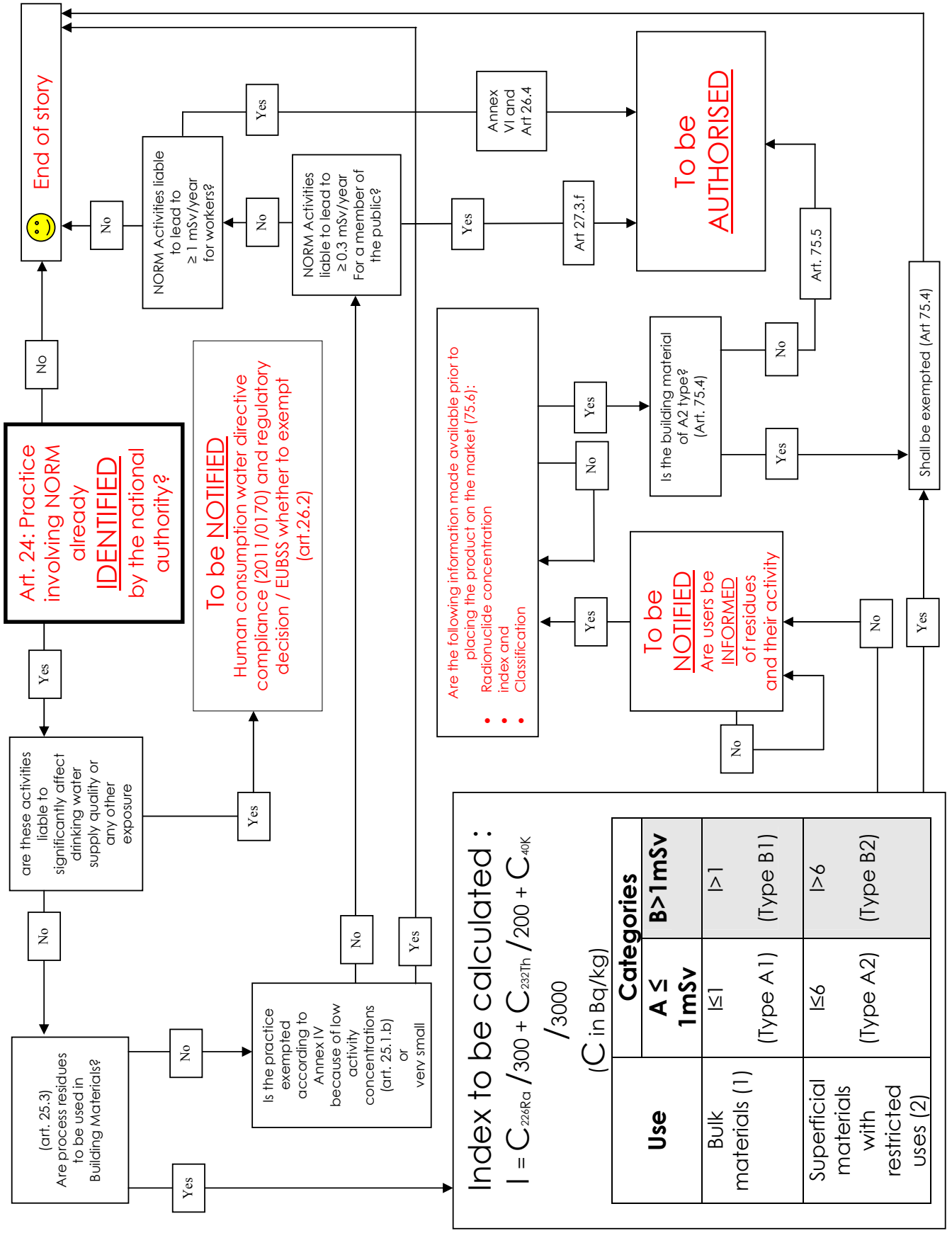
The notification process is robust enough to ensure declaration of NORM radiation protection issues to be looked at within the regulatory authority. As regards building materials, concerned products will go through a screening process with an index to be estimated; regulatory restrictions depending on this index will then be established, as appropriate, when exceeding the reference level of 1 mSv/year for a member of the public.

For occupational practices involving NORM, from now on, if effective dose to workers is liable to exceed 6mSv/year, the EU-BSS requirements for the protection of workers, apprentices and students shall apply. Under 6 mSv per year, the undertaking shall, at least, keep exposures under review according to the article 33.2.

Regarding clearance aspects for NORM, the EU-BSS has fixed 300μSv/year for members of the public and 1 mSv for workers. For residues or effluents from NORM industries: 0.3 mSv/year above prevailing background activity will remain the main criterion under which no restrictions are to be established. In comparison, the criterion for artificial radionuclides is more constraining with 10 μSv/year as a reference level (annex VI EU-BSS). Additionally, drinking water supply and any other potential contamination pathways need to be kept monitored against contamination and assessed against drinking water standards[21] and national regulations as appropriate.

These new regulatory features regarding NORM and building materials represent a breakthrough regarding EU natural radiation source regulation; these regulatory features need to be considered by stakeholders along with EU regulations regarding health risks from Radon.

Stéphane Calpéna
NORM reg.
Flowchart
Draft BSS 2011



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A Protocol For Radiological Evaluation of NORM Industries

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Abstract

The experience gained performing detailed radiological studies on several chemical industries located at the South-western Spain has conducted to the construction of a general protocol suitable to evaluate the radiological impact of any NORM industry. This protocol is formed by two sections devoted to the occupational and environmental radiological evaluation in each industry, respectively, while each section is formed by different phases in such a way that the protocol has to be applied in a sequential form, being not necessary the application of all the phases in all cases. In the great majority of NORM industries will be enough with the application of the first phases if the conclusions derived from their application is that occupational effective doses are clearly lower than 1 mSv/year, and the environmental radiological impact is quite limited. Only in specific cases, where the application of the first phases conduit to the possibility of occupational and/or environmental doses near or even higher than 1 mSv/y, the final phases of the protocol with a detailed radiological evaluation should be applied. With this "graded approach" the efforts are optimized and the economic impact of these studies for the industries is minimized.

The practical implementation of this protocol has been performed in two typical NORM industries located in the South-west of Spain; the first one is devoted to the production of phosphoric acid from phosphate rock of sedimentary origin, and the second one is devoted to the manufacture of titanium dioxide pigments using a heavy mineral (illmenite) as a raw material. The conclusions obtained after the application of the different phases of the protocol in these industries are shown and discussed also in this work.

I. Introduction

The Applied Nuclear Physics Research group from the University of Sevilla and the Radiation Physics Group of the University of Huelva, under the joint supervision of the authors of this paper, developed since 2005 until 2008 the I+D Project entitled "Evaluation of the radiological impact associated to the activities of several non-nuclear industries located at the South-West of Spain" with the financial support of the Spanish Nuclear Security Council (CSN). In this project, detailed pilot studies about the occupational and public radiological impact of two specific industries devoted to the production of P_2O_5 and TiO_2 were performed.

These evaluations were intimately related to the application of Title VII of the Euratom Council Directive concerning significant increase in exposure due to natural radiation sources, surpassed obviously to the Spanish legislation (Council Directive, 1996). This Title requires carrying out studies and evaluations in some working activities with the objective of determining if there exist significant increments in the exposure either to workers or members of the public which cannot be considered negligible from the radiological protection point of view. The industries "affected" by this Title VII are commonly known as NORM industries (NORM, acronym in English of *Naturally Occurring Radioactive Materials*).
With basis in the knowledge generated in the implementation of the mentioned I+D project, as well as in previous studies performed jointly for both research groups, it was concluded that a protocol for

the radiological evaluation of the chemical industries involved in the Title VII of the European BSS for the Health Protection of the General Public and Workers against Dangers of Ionizing Radiation can be designed. This protocol was developed with basis in the results obtained in the study of two paradigmatic NORM industries; the first one devoted to the production of phosphoric acid by the "wet acid" method by treating sedimentary phosphate rock, and the second one devoted to the production of the titanium dioxide pigments by the "sulphate" method by treating illmenite mineral as a raw material.

The proposed radiological evaluations (in its occupational and environmental sections) are formed by different phases or steps, which should be applied in a sequential form in such a way that as we advance in the application of higher phases, more detailed should be the radiological evaluations performed. No all the phases should be applied in the study of a determined NORM industry. Only it will necessary to apply a posterior phase or step of the protocol if the conclusions obtained after the implementation of the previous phases induce to that. In this way, we have tried to adapt the exhaustivity of the evaluation to the real dimensions of the radiological impact under evaluation (IAEA, 2007).

This paper has two main chapters, where will be detailed the main phases proposed for the radiological evaluation of chemical NORM industries. Chapter 2 will be devoted to the protocol in its occupational side, while Chapter 3 will be devoted to the protocol in its environmental/public side. Both sides are included in a general protocol and can be considered as twins in its philosophy, but cannot be considered independent because in some phases one side can feed from the results obtained from the other. This inter-relation between the two sides of the constructed protocol will be particularly highlighted in this paper.

II. OCCUPATIONAL PROTOCOL

The protocol in its occupational side is formed by three different phases to be applied in a sequential form, if its needed, being a priori only obligatory the application of the first one in all the chemical industries that can be considered affected by the Title VII of the European BSS for the Health Protection of the General Public and Workers against Dangers of Ionizing Radiation. In the following paragraphs are detailed the several works and actions to be carried out in the three phases, indicating at the same time the main conclusions to be obtained from each one.

II.1. First Phase

The application of the first step of the protocol in its occupational side, requires to carry out the following tasks

a) Identification of the different materials involved in the production process of the industry under evaluation
   Raw materials
   Intermediate products
   Commercial final products, co-products and valorized residues
   Wastes

b) Detailed information about the management processes applied to the raw materials, final products, co-products and residues.

c) Detailed design of a flux diagram reflecting the production process of the industry under evaluation with the objective of analyzing the steps of the production process where accumulation/ concentration of radionuclides can occur.

d) Precise quantification of the amounts of materials involved in the production process including those amounts which can be negligible from the industrial point of view as scales, sludges, etc., that generally "appears" during the maintenance of the production process.

e) Identification of the places inside the industry where the raw materials, co-products, final products and wastes are stored, and evaluation of the possible places where the inhalation can play an important role as an exposure route, including the ^{222}Rn.

f) Sampling of representative aliquots of the raw materials and determination in them of the activity concentrations of the radionuclides of interest: These radionuclides of interest are compiled in the appendix of this paper.

g) Classification, or not, of the industry as a NORM activity.

h) If the industry is not classified as NORM, then the protocol can be considered finished. If is classified as NORM, then the next step of the protocol should be applied.

With basis in the radiometric determinations performed in the raw materials and in the analysis by an expert in radiological protection of the production and management processes of products and wastes, an evaluation will be performed with the objective of concluding if the industry under study can be considered as an industry which can be qualified as a NORM or not. If the answer is no, this protocol in its occupational side can be considered finished in this phase. If the industry, on the contrary, can be qualified as NORM industry, it is necessary to continue applying then the second phase.

Obviously, all chemical industries qualifies as a no NORM industries, should be prepared, to repeat the application of the first phase of the protocol in its occupational side every time that the production process experiment significant changes and every time that the origin and main characteristics of the raw materials change.

What would be the main output of applying this first phase of the protocol (in its occupational side) in the industries located at the South-West of Spain, and devoted to the production of phosphoric acid, and titanium dioxide pigments, respectively? In both cases, the conclusion is clear. They should be considered as NORM industries, being essential in both applying the following phase of the occupational protocol. The phosphate rock used as main raw material for the production of phosphoric acid contains 1.5 Bq/g of ^{238}U (Bolívar and García-Tenorio, 1996), with all the daughters in secular equilibrium, and in opinion of the authors of this work with basis in the previous experience in this type of studies, all the industries using raw materials with activity concentrations for the components of the uranium and thorium series higher than 1 Bq/g should be evaluated radiologically with high detail.

In the case of the TiO_2 industry, the raw material used contains quite moderate concentrations of U, Th and daughters, being the levels clearly lower than 1 Bq/g. But in the TiO_2 industrial process there exist a series of processes (digestion of the raw material with sulphuric acid, filtration of lixiviated materials, etc) where easily can be generated by-products or residues clearly more enriched in some natural radionuclides, will all the dosimetric implications associated (Bolivar et al., 2011). The application of the second phase of the occupational protocol is then needed.

It can be considered surprising that the first step of the occupational phase is based simply in a detailed knowledge of the industrial process and in the measurement of the radioactive content of the raw materials. However, this information can be more than enough to evaluate as NORM or no the industry under analysis. For example, all the industries devoted to the production of phosphoric acid using as raw

material phosphate rock of igneous origin (radioactive content quite moderated) and applying an industrial process similar to the analyzed in detail by the authors in Huelva (with sedimentary phosphate rock) they would not need to apply additional phases to the first one of the occupational protocol (in order to verify the similarity between its industrial process and the analyzed in the pilot study and to check the moderate concentrations of natural radionuclides in the raw material). If the industrial process under analysis is quite different to the applied one in the known pilot studies, avoiding possible comparisons or if the raw material contains no moderate amounts of natural radionuclides, it will be imperative the application to the industrial process under analysis of at least the second phase of the protocol in its occupational side.

II.2. Second Phase

If the industry under analysis, as a conclusion of the study performed in the first phase of the occupational protocol, is qualified as a NORM industry, it should perform in the second phase the following studies:

a) Collection of representative aliquots of the sample types detailed in the point a) of the first phase of the protocol (raw materials, intermediate products, commercial final products, co-products and valorized residues wastes, residues,...) and determination of the activity concentrations of the radionuclides reflected in the appendix of this paper.

b) If in the industrial process is generated fine material susceptible to be inhaled, design of an aerosol sampling campaign (with sampling times equal or higher than 48 hours) in strategic locations of the factory (in the dustiest places, in the neighboring of gaseous emissions, etc). In the collected aerosols should be determined the activity concentrations (massic and volumetric concentrations) of the radionuclides of interest, which are the ones complied in the appendix of this paper. In the case of the industries devoted to the production of phosphoric acid and to the production of titanium dioxide pigments, the aerosol samplings and analyses would be centered in the milling zones as well as in the areas where the generated residues are temporally accumulated and/or stored

c) Measurements of the ^{222}Rn concentrations with active systems during at least one week in areas of the industries where radon can experiment accumulation (closed warehouses, digestion area, etc.), and where the working time expended by the workers cannot be evaluated as negligible. This imply the need to perform also ^{222}Rn determinations in the areas where the generated residues are temporally accumulated and/or stored

d) Localization along the industrial process, if exists, of points where superficial scales can be formed or where sludge can be deposited (pipes, filters, heat exchangers, etc.). If theses scales or sludge are localized, the total amount should be determined, and representative aliquots should be analyzed.

e) To measure the external effective doses in the points where scales were detected.

Then, with basis in the information and results obtained, the second phase of the occupational protocol should finish with an estimation of the effective doses received by the workers in the industry under analysis. If the estimation shows that via external radiation and via inhalation the total effective doses are clearly lower than 1 mSv/y, and at the same time the activity concentrations of ^{222}Rn along the industry are clearly lower than 400 Bq/m^3, the protocol in its occupational side could be considered as closed, because it would not be necessary the adoption of corrective actions in order to decrease the exposures of the workers, and it would not be necessary to take radiological protection measurements. If it is not the case, it will be imperative to continue with the application of the occupational protocol, entering in the development of the third and final phase.

What would be the conclusion obtained after the application of this second phase to the industries devoted to the production of phosphoric acid and to the production of titanium dioxide pigments? In both cases the occupational doses inside the industries and in the management of residues are clearly lower than 1 mSv/y (Bolívar and García-Tenorio 2005; Bolivar et al., 2011). And the ^{222}Rn concentrations inside the plants and warehouses of both industries are clearly lower than 400 Bq/m^3. It is not necessary then, to adopt correction measures, and the application of the occupational protocol can be considered as finished.

The action plan proposed in the second phase of the occupational protocol is centered in radiometric determinations of materials, fact which can be considered as surprising if we have in consideration that the main objective is to know if the workers have received a significant increment in their exposures. The only precise way to determine the effective doses received by the workers is through the implementation of a detailed "in-situ" (in the working place) dosimetric program, taking into account all possible routes of exposition (external radiation, inhalation, ingestion, etc.). However, if the dominant exposure routes are the direct radiation and the inhalation (which is the case in the great majority of chemical NORM industries) the occupational effective doses will be very much dependent of the radionuclides activity concentrations in the materials involved in the industrial process under evaluation and in the suspended aerosols. In fact, *we can indicate that it is possible to perform an estimation of the effective doses received by the workers if there is an adequate knowledge of the radioactive characteristics of the materials involved in the industrial process under evaluation and of the working conditions in which these materials are used or generated.*

The occupational effective dose estimations with basis in the mentioned radiometric determinations can be carried out in a straightforward way, following official documents of several agencies or applying physic-mathematical models supported by independent international organisms (IAEA, 2007).

In addition, external radiation measurements can be essential at this phase at places where can be formed scales (filters, pipes, deposit walls) or where sludge could be accumulated, if the previous radiometric determinations performed in scales and sludge give very high concentrations for one or several natural radionuclides (Bolívar et al., 2009). In this way, the performed dosimetric estimation could be refined for the general workers, at the same time that can be evaluated more precisely for the workers in charge of the cleaning and maintenance operations in the industry (operators in charge of the removal of scales in the pipes, operators in charge of the removal of sludge from the bottom of deposits, etc.)

II.3. Third phase

If via external radiation and via inhalation the total effective dose estimated for the workers is not clearly lower than 1 mSv/y, or exists some doubts if the value of 1 mSv/y can be approached, it is necessary the performance of the following additional studies in the third and last phase of the occupational protocol.

a) Construction of a detailed dosimetric map of the external dose rates measured "in-situ" in all the places of the industry under evaluation. Special resolution will have this dosimetric map in the areas where is known the possible presence of enriched amounts of natural radionuclides (areas of scales formation, areas of sludge accumulation, filtration areas, etc,).

b) To perform a more detailed sampling campaign (in locations and in time) of aerosols, with the posterior determination of their radioactive content, as a basis for a more refined estimation of the committed effective doses by inhalation received by the workers. The aerosol samplings will be now not restricted to the milling area and to the zone where the residues are stored, being performed also in other areas of the industry and during a time interval of at least one month (several samplings of at least 48 hours of duration distributed during one month).

c) To carry out a study with very high resolution of the ^{222}Rn activity concentrations inside the industry under evaluation, if in the previous studies in the second phase, these activity concentrations were not clearly lower than 400 Bq/m^3. It is recommended to perform these studies with passive detectors, in order to extend the sampling period during at least three months for obtaining representative values. The ^{222}Rn measurements should be done in the places of the industry where the rate of ventilation are lower, as well as in the area where the residues are stored or piled temporally inside the industry.

The analysis and evaluation of the results obtained in this third phase will allow taking in consideration the need or not of adopting radiological protection countermeasures. The justification and explanation of the possible countermeasures, main output of the occupational protocol application in the more conflictive cases, does not constitute the objective of this paper, and for that reason will be not detailed and justified. However, and with basis in our previous experience in the field, we can indicate that in many cases the adoption of very simple and economic countermeasures can produce an appreciable decrease in the exposures received by the workers (use of protective masks in dusty places, temporal permanence restrictions to the workers in particular areas of the production process, etc).

The third phase of the occupational protocol does not need to be applied in the industries devoted to the production of phosphoric acid and to the production of titanium dioxide pigments, described previously in this paper, because the conclusions obtained after the application of the second phase allow the closing of the radiological evaluation in both industries without to entry in the application of the third phase. In its occupational side, no radiological protection countermeasures should be taken in the P_2O_5 and the TiO_2 industries in order to decrease the worker exposures.

III. ENVIRONMENTAL PROTOCOL

The environmental protocol is formed by two phases: a first phase, which can be considered as exploratory and relatively easy to apply after the application of the occupational protocol, and a second phase divided in two parts which are centered in the atmospheric and terrestrial-aquatic compartments, respectively. It is understood that the environmental protocol is applied after the whole implementation of the occupational protocol, because in some points the actions to be taken in the environmental protocol will be based in the results obtained in the occupational one.

The application of the protocol in its environmental side needs the fulfillment of a clear requirement: the industry to be evaluated by the application of the environmental protocol should be considered as a NORM industry after the application of the previous occupational protocol. If after the implementation of the occupational protocol, the industry under evaluation has not been qualified as a NORM industry, the application of the environmental protocol is not needed, because the environmental (and public) radiological impact of this industry can be evaluated a priori as negligible.

In the following paragraphs are detailed the different studies and actions to be applied/taken, if are needed; in each one of the two phases that form the environmental protocol.

III.1. First Phase or Exploratory Phase

Having in consideration that the first phase of the environmental protocol will be applied only in those industries where at least the second phase of the occupational protocol has been previously implemented, this environmental first phase will be formed by the following studies/actions:

a) With basis in the determinations performed in the second phase of the occupational protocol in wastes and effluents, and with basis also in the data about the fluxes of materials compiled in the first phase of the occupational protocol, to estimate the radioactive fluxes to the environment, with origin in the industrial process. In addition, if possible, it is important to identify radioactive markers (for example isotopic ratios) in the liquid, solids or gaseous effluents of the industry characterized by values very much different those found in the environmental compartments under evaluation before starting the industrial activity. These radioactive markers can be used to identify and evaluate the impact of the emissions in the different environmental compartments (Landa, 2007).

b) To obtain a detail information about the natural ecosystems that could be affected by the wastes releases of the industry under evaluation (estuaries, rivers, neighboring soils, aquifers, etc.).

With basis in the determined radioactive fluxes, as well as in the characteristics of the "affected" ecosystems, if the radioactive environmental impact can be qualified a priori as negligible, we can finish the implementation of this phase (and of this protocol in its environmental side). If the impact is not evaluated as negligible (IAEA, 2001) the second phase of the protocol should be applied.

What would be the conclusions obtained as a result of implementing this first exploratory phase to the two industrial activities that we are taking as examples? In the case of the industry devoted to the production of titanium dioxide pigments, the conclusion is that it is not necessary the application of the posterior phase. The implementation of the environmental protocol can be closed after finishing the first phase because the environmental radiological impact produced by this industrial activity can be considered as negligible (García-Tenorio and Bolívar, 2011). No countermeasures are needed.

In the analyzed TiO_2 industry is produced a first residue in the digestion process of the raw material, known as un-attacked mud, which can contain high activity concentrations of radium (up to 2.5-3 Bq/g of ^{228}Ra and 1.0 Bq/g of ^{226}Ra in dry form). This residue is produced at a rate of 25 thousand tons per year containing about 40% of water, and in its wet form are transported from the industry to a management residue plant, where are treated. This waste does not produce any radiological environmental impact, being necessary only the application of the occupational protocol to the management plant where are treated and stored. Additionally, the TiO_2 industry in Huelva releases waters to the Huelva estuary. These waters result of the implementation of a neutralization process where waters coming from the production process lose their acidity as well as their heavy metal and radionuclide content. These treated waters, due to its origin, contain then activity concentrations of natural radionuclides lower that the found ones in the natural waters of the estuary, causing for that reason a null radiological environmental impact (García-Tenorio and Bolívar, 2011).

A quite different conclusion is approached if the industrial process under evaluation is the devoted to the production of phosphoric acid, by treating sedimentary phosphate rock. In this industry, and as a by-product of the production process, are generated annually about 2 million of phosphogypsum (PG), containing 0.6-0.8 Bq/g of ^{226}Ra, ^{210}Pb y ^{210}Pb (Mas et al., 2006; Abril et al., 2009).

These phosphogypsum have been at Huelva (Spain) historically stored since 1968 in big piles located in the vicinity of the industry (even until 1998, 20% of the PG produced was released directly to a neighboring estuary) and although during the last years the piling is being carried out trying a minimum interaction with the surrounding estuarine compartment, this interaction has occurred historically, and can continue now in a less extent (Hierro et al., 2012). The existence of a possible environmental radioactive impact implies the need of applying the second phase of this protocol in its environmental side, as it will be detailed in the following section of the paper.

By analyzing the main characteristics of the PG and of the lixiviates that PG piles generate, we can indicate that both are characterized for presenting values for the isotopic ratios $^{226}Ra/^{228}Ra$ y $^{230}Th/^{232}Th$, clearly higher than one, and clearly higher than the typical values which can be found in not anthropogenically affected environmental compartments (soils, sediments, plants). For that reason, the isotopic ratios $^{226}Ra/^{228}Ra$ and $^{230}Th/^{232}Th$ can be considered as excellent markers of the impact caused for the working activity under evaluation in the natural receptor media (San Miguel et al., 2003; Aguado et al., 2005).

III.2. Second Phase or Detailed Phase

This second phase is formed by two parts that, if it is necessary, would be implemented independently. Each part has the following steps:

Second Phase: Part 1

a) If the working activity under evaluation produces atmospheric emissions with no negligible radioactive content, compilation of all the relevant information concerning the most predominant wind regimes along the different seasons of the year, and posterior implementation of the steps b), c) and d). If do no exists radioactive atmospheric emissions, the Part 1 of this second phase will be closed.

b) With basis in the information compiled in the previous step, design of a sampling campaign in the surroundings of the industry for the collection of aerosols, if they exist particulate atmospheric emissions with radioactive content.

c) Measurements of the radionuclides indicated in the appendix of this paper, in the aerosols previously collected, looking with special interest to the possible radioactive markers characteristics of the emissions of the industry under analysis. With basis in the obtained results, a radiological evaluation associated to the possible increments in radioactivity, should be performed.

d) If the atmospheric emissions of the industry or from the residue piles can be enriched in ^{222}Rn, to proceed to its experimental determination, as well as to the posterior radiological evaluation associated to the possible increments observed.

The aerosols and ^{222}Rn sampling campaigns should have a temporal duration enough to obtain statistically supported conclusions, and should be performed looking the season of the year less favorable from the inmission point of view, in order to consider the obtained information as representative of the impact caused by the industry under evaluation (the aerosol sampling campaign should be extended for at least one month, while the ^{222}Rn sampling campaign should be extended for at least 3 months).

The second phase, in its part 1, does not need to be implemented in the industry devoted to the production of titanium dioxide pigments that we are considering, being supported this conclusion in the results obtained in the application of the first phase. Indeed, in the first phase it was indicated that the atmospheric emissions of the TiO_2 plant contain a practically null content of natural radionuclides, as it was deduced from the detailed study of the industrial process, and at the same time this industrial activity does not generate any residue producing during its management the incorporation of particulate matter of ^{222}Rn to the atmosphere. The only residue generated (undissolved mud) in its transport to the treatment and storage plant cannot produce the incorporation of particulate matter to the atmosphere because its transported as produced in wet form.

On the contrary, in the industry devoted to the production of phosphoric acid, the second phase in its part 1, should be implemented in a selective way, because although its atmospheric emissions does not contain appreciable amounts of natural radionuclides, as it was deduced from the detailed study of the industrial process and the application of the protocol in its occupational side, the phosphogypsum piles where this by-product is stored can be a source of particulate matter enriched in natural radionuclide to the neighboring environment (Borrego et al., 2007).

Then, it is needed in this part of the second phase of the environmental protocol to proceed to the collection of aerosols in the surroundings of the PG piles and to evaluate their radiological implications, The PG piles can be also a source of ^{222}Rn, being also necessary to perform ^{222}Rn determinations in the vicinity of the piles (essentially in the populated areas, if exist) and evaluate the radiological impact.

Second Phase: Part 2

With total independence of the actions taken in relation with the possible atmospheric emissions, in some working activities under evaluation will be necessary the application of the second phase, in its Part 2 of the environmental protocol. This second phase, part 2, will have the following steps:

a) If there are liquid or solid releases with a significant radioactive content, a sampling campaign should be performed in the environmental receptor media (lithosphere, hydrosphere) looking for the collection of good environmental indicators of possible radioactive impacts (sediments, algae, suspended matter in waters, etc). Afterwards, the steps b) and c) should be applied. In the case that the industry under evaluation has not liquid or solid releases, the second phase of the environmental protocol in its part 2 can be considered closed.

b) Determination of the radioactive content (measurement of the radionuclides indicated in the appendix of this paper) in the collected samples, looking with special emphasis to the radioactive markers previously identified, if they exist.

c) If from the performance of point b), the existence of a significant radioactive environmental impact is concluded, evaluation of the radiological implications through the trophic chain

Once the second phase of the environmental protocol, in its atmospheric and terrestrial versions, has been applied in all the industries not exempt after the application of the exploratory phase, it will be adopted all the radiological protection countermeasures considered as necessary by the competent organism. These countermeasures can even imply a change in the management policy of residues and effluents by the industry under evaluation.

The second phase, in its Part 2, should not be applied in the case of the industry devoted to the production of titanium dioxide pigments, with basis in the results and conclusions obtained in the application of the environmental protocol in is phase 1, because no solid releases exist and the liquid effluents have a content in natural radionuclides lower than the waters of the estuary where are released. On the contrary, the second phase, in its Part 2, should be applied fully in the case of the industry devoted to the production of phosphoric acid, because, historically PG releases to the estuary of Huelva had occurred, and, nowadays, they are liquid releases from the leaching occurring in the un-restored piles. The impact of these releases in waters and sediments, as well as in plants and biota in general, from the neighboring estuary have been deeply studied by the research groups leaded by the authors of this paper, following these studies the philosophy of this protocol (see for example Hierro et al., 2012). The results obtained in the evaluation of the radioactive and radiological impact produced by the releases originated directly or indirectly by the P_2O_5 industry are not presented and discussed , because are out of the scope of this paper.

CONCLUSIONS

Through its practical implementation in two paradigmatic NORM industries located at the South-West of Spain, and devoted to the production of phosphoric acid and titanium dioxide pigments, respectively, it has been show the goodness of the protocol designed by the authors for the occupational and environmental radiological evaluation of NORM chemical industries.

The protocol has been constructed, trying to adapt the evaluation to the characteristics of the industry under consideration, depending the depth and extension of the evaluation of the results which are being obtained gradually in its application. In this way the human resources and the economical costs associated to its implementation are adapted to the dimension of the possible radiological problem under evaluation.

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APPENDIX

The radioactive characterization of the samples of this protocol should cover the determination of the activity concentrations of the following radionuclides:

Uranium isotopes: ^{238}**U,** ^{234}**U**
Thorium isotopes: ^{232}**Th,** ^{230}**Th,** ^{228}**Th**
Radium isotopes: ^{226}**Ra,** ^{228}**Ra**
Lead isotope: ^{210}**Pb**
Polonium isotope: ^{210}**Po**
Potassium isotope: ^{40}**K**

Activity concentrations should be expressed in Bq kg^{-1}, being essential to include information about the sampling procedures applied, about the radiochemical procedures and about the radiometric techniques used for each of the previously mentioned isotopes. The collection and measurement procedures should allow obtaining the LIDs lower than: 10 Bq/kg in the case of solid samples, 10 Bq/m^3 for liquid samples, and 10 μBq/m^3 for gaseous samples.

For possible dosimetric calculations, in the great majority of cases, it would be possible to consider secular equilibrium between the radionuclides belonging to the natural series and with a half-life lower than 1 year. In addition, the ^{235}U concentration in a sample can be estimated from the value determined for ^{238}U, assuming that the Uranium present is natural uranium.

The Swedish Radiation Safety Authority's regulations on exemption and clearance of NORM

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Abstract

Naturally Occurring Radioactive Material, NORM, has been under the authority's radiation protection regulation causing some natural activities to be regulated overly strict in some aspects. The presented regulations present appropriate levels of specific activities both for exemption of NORM and for specific clearance. Sweden has no industries with extensive use of NORM, which appears mainly in discussion about its proper management in connection with disposal or possible recycling.
The regulations define exemption levels for NORM, in line with the ideas for the expected next version of the BSS presented by the European Commission. For example, the exemption level is simply 1 Bq/g for any nuclide in the U-238 or Th-232 series, which is also the clearance level for bulk material. The regulations contain a restriction of < 100 ton peat ash per year, above which special regulations will be in force for management of ash from peat energy production facilities.
For disposal on municipal landfill and similar disposal sites, specific clearance levels are ten times higher than the exemption values in BSS, i.e. 10 Bq/g for nuclides in the U-238 series. Also certain products relating to alum shale, such as the shale itself and alum shale based concrete from demolished buildings, known not to exceed 3 Bq/g is allowed for certain construction purposes other than for buildings, such as road construction.

INTRODUCTION

When the EURATOM Basic Safety Standard, BSS, was implemented by amending the Radiation Protection Act in 2000, some practices required a licence although they represented very small radiation risks. Such extensive administration cannot be justified from the standpoint of radiation protection and the regulations, especially for NORM, have therefore been in need of simplification. Regulations on exemption and clearance of NORM up to a certain specific activity have been developed and entered into force in January 2012 (SSMFS 2011:4). These regulations are aiming at simplifying the management of NORM that is enforced according to the Environmental regulations. NORM is defined as "material containing naturally occurring radionuclides and which is in its natural state or has solely been processed or enriched for purposes other than for extraction of radionuclides and which is also not intended for processing in order to make use of the material's radioactivity".

NORM IN SWEDEN

The draft version of the next BSS, expected to be in force in a few years, offers a list of NORM practices with possible radiation protection concerns. A review of such activities was carried out in Sweden between 2006 and 2007 (SSI ref. no. 2006/880-40) pursuant to the BSS Directive. There are few industries in Sweden giving rise to NORM, and, as a rule, the amount is very small or the specific activity in the material is low. A few examples are given below. The main NORM relates to *drinking water filtration*. Both the National Food Administration and the National Board of Health and Welfare recommend that the uranium content in drinking water should be below 15 µg/l and water filtration systems are becoming increasingly common for small single family water production and large municipal drinking water

production plants. These filters, containing uranium, may eventually need to be discarded. There is no large industries producing large amount of *scale* and it remains unnoticed until the time the metal is discarded and arrives at scrapyards, where sensitive dose meters are triggered. Peat enhances NORM and a concentration occurs in *peat ash*. Separate regulations are being drafted by the Authority for peat burning installations consuming large quantities of peat and generating more than 100 tonnes of ash per year. The slag produced in *steel industry* does not contain activity concentrations that cause any need for protective measures. The situation is similar for NORM residues from mining, even though it is known that the specific activity might exceed 1 Bq/g for smaller amounts of residues.

There are larger quantities of NORM from activities in the past, including the phosphate industry that has produced *phosphogypsum* as well as practices going back several centuries, including residues from alum shale exploitation. The largest deposit of alum shale residue lies near the hamlet of Kvarntorp, containing 40 million m^3 of *burned alum shale*. Alum shale may have uranium content up to 3.7 Bq/g. Also, about 20 million m^3 of alum shale-based lightweight *concrete* has been manufactured in Sweden. When old dwellings built using this concrete between the 1930s and 1970s fall into disuse and are demolished, large quantities of NORM are foreseen. The specific activity in the concrete varies from only 0.6 to 2.4 Bq/g. Naturally occurring radioactive material can be in the form of *bore cores and drill cuttings* taken from bedrock as a result of drilling and rock sampling. Other examples include construction and agricultural work involving handling of excavated material containing naturally occurring radionuclides with a relatively high specific activity.

EXEMPTION AND CLEARANCE

Exemption

Radioactive sources which occur in a licensed practice may be exempted from reporting, or exempted from regulation altogether, if the source has a low specific or total activity. For exemption based mainly on specific or total activity, a reference is used called 'exemption level'. Exemption levels to be used in the European Union are provided in an annex to the BSS and have been implemented in Swedish legislation. Sometimes a practice may be exempted due to the inherent safety condition of the practice, even if the sources used might exceed the exemption levels. Exemption always refers to human activities; the expression "a source is exempted" simply means that all activity in connection with such source is exempted.

Exemption of NORM

For NORM arising in practices exemption will depend on the specific activity of the material. NORM is exempted when the specific activity is lower than 1 Bq/g per nuclide in the uranium or thorium series, and 10 Bq/g for potassium-40. The activity in slag from steel production is below 1 Bq/g and the material can be handled without any restrictions in the Radiation Protection Act. NORM is also exempted when it has been removed, deposited or reused in a manner as described in the regulations and discussed later in this paper.

When the specific activity in the material is above 1 Bq/g but below 10 Bq/g per nuclide in the uranium or thorium series or above 10 Bq/g but below 100 Bq/g for potassium-40, the Radiation Protection Act is in force and the general responsibilities remains, but no licence is required. This is also the situation for ceramic household products, water treatment filters in private households, decorative or utility good and single unprocessed samples of rocks or minerals which are part of a geological collection. Licencing of the NORM practice is required when the specific activity is above 10 Bq/g per nuclide in the uranium or thorium series or above 100 Bq/g for potassium-40. By this, as can be anticipated now, only a few water treatment plants, scrap yards storing scale and uranium prospecting will require licencing.

Clearance

The term *clearance* is associated with a process in which a source previously subject to regulation may be exempted, i.e. taken out of the regulatory regime, for example due to radioactive decay. Another example is a certain part of a source, such as part of a wall from a nuclear installation, fulfilling the clearance criteria. Clearance levels must be lower than, or at least as low as, levels for general exemption. Otherwise, the source would enter into the regulatory regime again, after clearance. In the case of NORM, the regulations state that the clearance and exemption values are the same.

The Radiation Protection Act, exemption and clearance

After a source has been subject to clearance, the Swedish Radiation Protection Act is exempted completely. The same is not necessarily true for exemption. The Act has a requirement contained in Section 6, which stipulates that all aspects of a practice must be carried out in a safe manner in terms of radiation protection.

Directed or specific clearance

Sometimes a regulator can accept that a source exceeding the clearance level still may be subject to clearance for a certain waste stream, for instance if the source is disposed of at a disposal site. This is called *specific*, or sometimes *conditional* or *directed* clearance. In such a case, regulatory requirements may remain in effect until the source has been disposed of at a final disposal site. It should be mentioned that other legislation, such as the Swedish Environmental Code, applies to disposal in landfills. A meaningful specific clearance for a certain waste component therefore assumes that the suggested waste stream can be implemented without being blocked by other legislation. The waste may need to be stored until such assurances have been obtained.

Specific clearance of NORM

NORM having an specific activity of no more than ten times the concentration stated for exemption and generated from practices may be delivered to a waste deposit site without taking account of the material's radioactive properties. This type of waste deposit site shall be arranged so that it gives at least the same level of protection as a waste deposit site for non-hazardous waste in accordance with the Landfill Ordinance (2001:512). Disused water treatment filters, zirconium sand and some scale can be disposed of this way.

Certain types of NORM such as building materials, burned alum shale, soil and rocks may be deposited or reused for road constructions. Waste from mineral prospecting should be managed in accordance with regulations on waste from extraction of minerals in Utvinningsförordningen (2008:722), which is based on the EU directive on the management of waste from extractive industries (2006/21/EC).

Table 1. The regulations' requirements for different levels of specific activity.

Specific activity for nuclides in the uranium- and thorium series.	Activities in connection with disposal of NORM	Radiation protection requirements after disposal
specific activity > 10 Bq/g	Licence required	Licence required for the disposal site (Alternatively: exemption after individual regulatory review)
1 Bq/g < specific activity < 10 Bq/g	No licence required but the general responsibilities in the Act (Section 6) remain	
specific activity < 1 Bq/g	General exemption from the Radiation Protection Act	

DILUTION

In practices using licensed sources, the rules normally imply that dilution is not acceptable.
If an installation is dismantled in connection with decommissioning and a source is dropped into a container of scrap metal by mistake, it is necessary to recover the source for continued management according to the licence conditions. It is not acceptable to make a new calculation of the total specific activity of the container's scrap metal in order to determine whether the container's total content can be subject to clearance.

In the case of NORM, the situation is somewhat different. It is more natural to consider mean specific activity levels. If soil masses that partly consist of alum shale are transported in construction work, or if drilling for a drinking well removes a mixture of mainly inactive soil mixed with alum shale, it is not self-evident that the uranium-richer material must be separated from other material. When formulating the rule, the Authority has already considered that specific radioactive concentration of alum shale is only moderately higher than the clearance value. For disposal of NORM, averaging is accepted for one truckload or for one occasion of disposal, e.g. at a disposal facility.

For naturally occurring radioactive material with an unevenly distributed specific activity, an average value may be estimated for the activity in terms of the total quantity of material generated by the work, for example per transport or per deposit.

WASTE MANAGEMENT ACCORDING TO ENVIRONMENTAL LEGISLATION

NORM is material that, when exempted from the radiation protection act, will be managed as waste according to the Environmental Code. The NORM regulation is aiming at simplifying the management of NORM and legalise the management of the material that already exist.

A person who generates waste must ensure that it is managed in accordance with the applicable Environmental regulations. This requirement applies equally to householders and industrial operators. For the householder it means sorting their waste and delivering it to the appropriate place. The owner of waste is responsible for its treatment as well. This however does not apply to household waste, which falls

under the local government authorities. The local municipality is responsible for the collection, handling and treatment of household waste, except waste covered by producer responsibility obligations. When NORM will be exempted from the Radiation Protection Act, materials owned by private persons such as building material and water filters will be managed this way.

OTHER REGULATION

In addition to the Swedish Radiation Safety Authority's regulations concerning handling of naturally occurring radioactive material, other authorities may have rules or regulations having an impact on handling and use of such material. For instance, the Swedish National Board of Housing, Building and Planning have regulations concerning limits for radon and gamma radiation in new buildings. The National Food Administration has regulations concerning drinking water from major water-works, and the National Board of Health and Welfare has general recommendations concerning drinking water from private wells as well as concerning radon in indoor air. The Swedish Work Environment Authority has regulations concerning radon in occupational environments. Material that is recycled should not be used as filler material on land where buildings may be constructed in the future.

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Application of the ICRP Recommendations in Existing Exposures Situations such as NORM Activities

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Abstract

After the publication of its general recommendations on radiological protection in 2007 (Publication 103), the International Commission on Radiological Protection (ICRP) is now preparing a series of publications dedicated to different types of existing exposure situations such as radon exposure, cosmic exposure in aviation or NORM activities. The future publication related to NORM activities is not yet ready for public consultation. It will however be developed in line with, in particular, the draft publication related to radon exposure already on the ICRP website for consultation.

1. Introduction

The International Commission on Radiological Protection (ICRP) is developing a series of publications aiming at provide advice on the implementation of its new general recommendations (ICRP, 2006, 2007) in existing exposure situations. The Publication 111 on the application of the Commission's recommendations to the protection of people living in long-term contaminated areas after a nuclear accident (ICRP, 2009) has been recently published. A draft publication related to the radiological protection against radon exposure is currently on the ICRP website for public consultation. Two other publications are in progress, on the protection against cosmic exposure in aviation and on the protection against the enhanced exposures from industrial processes using naturally occurring radioactive material (NORM).

Along these publications, ICRP is developing a coherent approach for the application of its recommendations in existing exposure situations. Such an approach, graded, pragmatic, flexible and ambitious, is mainly based on the application of the principle of optimization of the protection below appropriate reference levels. The structure and the provisions of these publications will be very similar.

The draft report on the protection against the enhanced exposures from industrial processes using NORM would be in a few months sufficiently elaborated to be proposed for public consultation. The ICRP will focus its recommendations on exposures to naturally occurring radionuclides where human activities have enhanced the potential for exposure by either increasing the exposure to naturally elevated levels of radionuclides or where the concentrations of radionuclides have been enhanced in materials. Here are the main issues which would be developed.

2. Characteristics of exposures

Exposure in various types of existing exposure situations has similar characteristics. The first one is the ubiquity and variability of the radiation exposure. NORM are ubiquitous and are present in almost all materials on earth. Almost all human activities have the potential to either increase or decrease exposures to these materials.

Existing exposure situations are exposure situations that already exist when a decision on control has to be taken. As a consequence, the control of the situation is exercised by controlling the pathways rather than the source itself (which cannot be modified or which is not easy to control). This characteristic is frequent in NORM activities.

Another characteristic of existing exposure situations is the large distribution of individual exposures. There are a large number of industries processing large volumes of material. There is a wide range of activity concentrations that may result within these industries and the potential for significantly different exposures of the public or workers from these situations. These facts result in a very heterogeneous distribution of individual exposures arising from NORM activities.

In several existing exposure situations, the exposure of workers may be adventitious. It is the case when the exposure of workers cannot reasonably be regarded as being the responsibility of the operating management. It may be the case in some NORM industries.

The lack of awareness of the concerned parties, including exposed individuals as well as responsible persons, about the radiation risk, is also a key feature of existing exposure situations. Many NORM activities are industries where the concentration of radionuclides in product, by-product or waste material is consequential and unintended in relation to the primary activity of the industry. In many cases there is a lack of awareness of the presence of radioactive material in these products.

Several NORM activities should be managed by professionals well informed and trained vis-à-vis the radiological risk, with the involvement of relevant stakeholders. However, in many cases there is a need to develop a radiation protection culture aiming at raising the awareness and scaling of the risks to create a questioning and proactive attitude. In several situations, the persistence or reduction of the risk is mainly dependant on individual behaviour so that the role of self-help protective actions is crucial.

Finally, the fact that, to be efficient, the protection strategy should be implemented on a long term perspective, with little chance to totally eliminate the exposure, is a characteristic of several existing exposure situations including NORM activities.

3. Types of exposure situations and categories of exposure

The Commission's system of radiological protection of humans is described in *Publication 103* (ICRP, 2007). According to paragraph 44, it "applies to all radiation exposures from any source, regardless of its size and origin." In particular, according to paragraph 45, "the Commission's Recommendations cover exposures to both natural and man-made sources. The Recommendations can apply in their entirety only to situations in which either the source of exposure or the pathways leading to the doses received by individuals can be controlled by some reasonable means. Sources in such situations are called controllable sources."

In the past most exposures to natural radiation sources were deemed to be outside the system of radiological protection as being essentially not amenable to control by any reasonable means. However, NORM activities are human activities enhancing exposures either due to the actions of people in placing themselves in situations where exposures are higher or due to enhancing concentrations in products or wastes which then come into contact with workers and the public in their everyday life. Then, if the source itself (naturally radioactive materials extracted from the earth crust) is not always directly controllable, the pathways from the source to the exposed individuals are.

3.1. Types of exposure situations

The ICRP recommendations apply to all sources and to individuals exposed to radiation in the following three types of exposure situations which address all conceivable circumstances.

- • *Planned exposure situations* are situations involving the deliberate introduction and operation of sources. Planned exposure situations may give rise both to exposures that are anticipated to occur (normal exposures) and to exposures that are not anticipated to occur (potential exposures).
- • *Emergency exposure situations* are situations that may occur during the operation of a planned situation, or from a malicious act, or from any other unexpected situation, and require urgent action in order to avoid or reduce undesirable consequences.
- • *Existing exposure situations* are exposure situations that already exist when a decision on control has to be taken, including prolonged exposure situations after emergencies.

NORM exposure situations have the characteristics of existing exposure situations since the primary source is concentrations of ubiquitous natural activity in material from the earth's crust. Human activities may create or alter pathways modifying concentrations. These pathways can be controlled by preventive and corrective actions. In most cases, the source itself, already exists when a decision of control has to be taken. NORM are mentioned as examples of existing exposure situations in paragraph 284 of *Publication 103* (ICRP, 2007). Such a consideration is *a priori* still valid.

However, in some cases, the existing source is removed and noticeably modified with the objective to use it as a radiation source. In such a case, the situation should be managed as a planned exposure situation. It is for national authorities to decide which workplace situations are to be regarded from the outset as planned exposure situations.

When natural radionuclides are used as radioactive sources, the corresponding practices may give rise to emergency exposure situations when the control of the source is lost. In the majority of cases, however, because of the processes implemented, NORM activities are very unlikely to give rise to an emergency exposure situation even though the discovery of very high concentrations in a place may require the prompt implementation of protective actions.

The philosophy of *Publication 103* (ICRP, 2007) compared to *Publication 60* (ICRP, 1991) is to recommend a consistent approach for the management of all types of exposure situations. This approach is based on the application of the optimisation process below appropriate dose constraints or reference levels.

3.2. Categories of exposures

The Commission distinguishes between three categories of exposures: occupational exposures, public exposures, and medical exposures of patients.

Occupational exposure is defined by the Commission as all radiation exposure of workers incurred as a result of their work in the paragraph 178 of *Publication 103* (ICRP, 2007). The Commission has noted the conventional definition of occupational exposure to any hazardous agent as including all exposures at work, regardless of their source. However, because of the ubiquity of radiation, the direct application of this definition to radiation would mean that all workers should be subject to a regime of radiological protection. Then the paragraph 178 of *Publication 103* specifies that "the Commission therefore limits its use of 'occupational exposures' to radiation exposures incurred at work as a result of situations that can reasonably be regarded as being the responsibility of the operating management".

Publication 65 (ICRP, 1993) indicates in its paragraph 86 that "workers who are not regarded as being

occupationally exposed to radiation are usually treated in the same way as members of the public". This provision set for radon exposure is applicable to other sources of exposure, keeping in mind that the health and safety of the workers remains under the responsibility of their employer.

According to the paragraph 180 of *Publication 103* (ICRP, 2007), "*public exposure* encompasses all exposures of the public other than occupational exposures and medical exposures of patients. It is incurred as a result of a range of radiation sources. The component of public exposure due to natural sources is by far the largest, but this provides no justification for reducing the attention paid to smaller, but more readily controllable, exposures to man-made sources. (…)" It means that NORM activities lead to public exposure. People concerned are both members of the public and workers when their exposure cannot reasonably be regarded as being the responsibility of the operating management.

Medical exposures are mainly radiation exposures of patients. Such exposures occur in diagnostic, interventional, and therapeutic procedures. The exposure is intentional and for the direct benefit of the patient. Natural radionuclides are no longer used in medicine so that a priori no medical practice can be seen as a NORM activity. If it is ever the case, the corresponding situation should be controlled using the relevant requirement.

The Commission also aims to protect the environment however relevant recommendations are not yet established. The Commission's aim is to prevent or reduce the frequency of deleterious radiation effects to a level where they would have a negligible impact on the maintenance of biological diversity, the conservation of species, or the health and status of natural habitats, communities and ecosystems.

4. Application of the principles

4.1. Justification of protection strategies

In the ICRP system of protection, the principle of justification is one of the two source-related fundamental principles (see ICRP, 2007; paragraph 203). In application of this principle, any decision that alters the radiation exposure situation should do more good than harm. This means that, by introducing a new radiation source, by reducing existing exposure, or by reducing the risk of potential exposure, one should achieve sufficient individual or societal benefit to offset the detriment it causes.

In most cases, exposure from NORM activities can be controlled mainly by action modifying the pathways of exposure and in some cases by acting directly on the source. Corresponding protection strategies are deemed to be justified from the Commission point of view. The justification of the reuse or the recycling of residues, for example in consumer products or building materials, should be carefully considered.

4.2. Optimisation

Optimisation is the second fundamental principle of radiological protection, and is central to the system of protection. It is source-related like the principle of justification and applies to all three exposure situations: planned exposure situations, emergency exposure situations, and existing exposure situations. According to the principle of optimisation, the likelihood of incurring exposures, the number of people exposed, and the magnitude of their individual doses should all be kept as low as reasonably achievable, taking into account economic and societal factors. This means that the level of protection should be the best under the prevailing circumstances, maximising the margin of benefit over harm. In order to avoid severely inequitable outcomes of this optimisation procedure, there should be restrictions on the doses or risks to individuals from a particular source (dose or risk constraints and reference levels) (see ICRP, 2007; paragraphs 203 and 211).

Implementation of the optimisation principle of protection is a process that is at the heart of a successful radiological protection programme. It must be framed carefully to take into account the relevant attributes of the exposure situation. Furthermore, it should include, as appropriate to the exposure situation, the involvement of the relevant stakeholders. These two elements are considered by the Commission as important components of the optimisation process (see ICRP, 2006; paragraph 23).

4.2.1. Dose restriction

According to paragraph 225 of *Publication 103* (ICRP; 2007), "the concepts of dose constraint and reference level are used in conjunction with the optimisation of protection to restrict individual doses. A level of individual dose, either as a dose constraint or a reference level, always needs to be defined. The initial intention would be to not exceed, or to remain at, these levels, and the ambition is to reduce all doses to levels that are as low as reasonably achievable, economic and societal factors being taken into account."

The Commission retains the term 'dose constraint' for this level of dose in planned exposure situations (with the exception of medical exposure of patients). For emergency exposure situations and existing exposure situations, the Commission proposes the term 'reference level' to describe this level of dose. The difference in terminology between planned and other exposure situations (emergency and existing) has been retained by the Commission to express the fact that, in planned situations, the restriction on individual doses can be applied at the planning stage, and the doses can be forecast so as to ensure that the constraint will not be exceeded. With the other situations a wider range of exposures may exist, and the optimisation process may apply to initial levels of individual doses above the reference level."

As far as NORM activities are in most cases existing exposure situations, the first step of the optimisation process is to set an appropriate reference level. The reference level represents, in emergency or existing controllable exposure situations, the level of dose or risk above which is judged to be inappropriate to plan to allow exposures to occur, and for which therefore protective actions should be planned and optimised. In case of NORM activities considered or managed as planned exposure situation, the dose restriction will be a dose constraint.

According to *Publication 103*, the chosen value for a reference level or a dose constraint will depend upon the prevailing circumstances of the exposure situation under consideration (ICRP, 2007; paragraph 234). In order to provide guidance for selecting appropriate values, the Commission defined a dose scale (ICRP, 2007; Table 5) reflecting the fact that, within a continuum of risk (linear non-threshold assumption), the risk that everyone is ready to accept depends on the exposure context. This scale is divided into three bands reflecting the more or less important need for action which is depending on the characteristics of the exposure situation: controllability of the source; individual or societal benefit from the situation; requirements with regard to information, training and dosimetric or medical surveillance. Numerically speaking, the three bands are: <1 mSv, 1-20 mSv and 20-100 mSv (in acute or annual doses). They should be seen as indicators.

The Commission recommends, for the sake of consistency, the value in the order of of 10 mSv per year as the upper value for a reference level in existing exposure situations, which is the middle of the band 1-20 mSv. This level fits with most NORM exposures. However, many NORM activities can easily been controlled so that the relevant reference level can be more ambitious and chosen in the band < 1 mSv. Doses constraint for the public, in case of a situation managed as a planned exposure situation, should be chosen in that band < 1 mSv.

4.2.2. Optimisation process

According to paragraph 22 of *Publication 101* (ICRP, 2006), "to provide the best protection under the prevailing circumstances (in normal, emergency or existing controllable situations), the process of optimisation below a dose restriction must be implemented through an ongoing, cyclical process (called the optimisation process) that involves evaluation of the exposure situation to identify the need for action (framing of the process); identification of the possible protective options to keep the exposure as low as reasonably achievable; selection of the best option under the prevailing circumstances; implementation of the selected option through an effective optimisation programme; and regular review of the exposure situation to evaluate if the prevailing circumstances call for the implementation of corrective protective actions."

The Commission considers now that for the sake of clarification, when dealing with existing exposure situations, the distinction should be made between prevention aimed at maintaining exposure as low as reasonably achievable under the prevailing circumstances and mitigation aimed at reducing exposure as low as reasonably achievable (see Fig. 1). The optimisation process is implemented through relevant protection strategies.

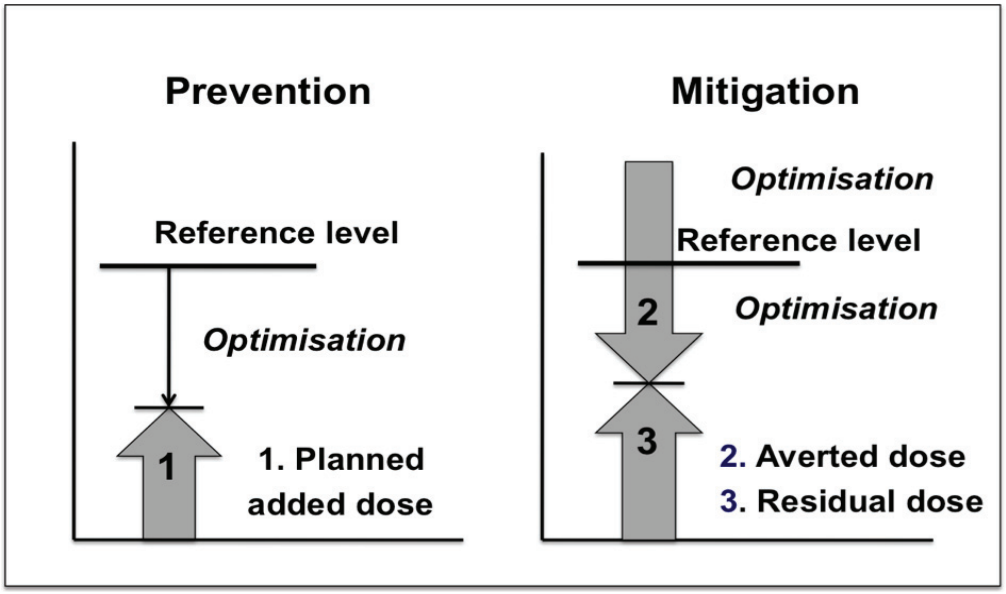

Fig. 1: The implementation of the optimisation principle in existing exposure situations

4.2.3. Graded approach

The large spectrum of situations in NORM activities shows clearly the need for a graded approach in defining and implementing appropriate and adapted strategies. Such a graded approach should be based on both ambition and realism. Any NORM strategy should also aim to effectiveness.

The degree of enforcement of the actions that are warranted is very much related to the ambition of the radiological protection strategy and the degree of responsibility for the situation. In situations comprising legal responsibilities (e.g. employer/employee, seller/buyer, public building with high occupancy…), mandatory provisions may be required. Such requirements should be commensurate with the degree and the type of responsibility. The consequence of a failure in the compliance with the reference level when required is also dependent upon the situation.

There are also existing exposure situations for which it will be obvious that action to reduce exposures is not warranted. It is the case in several NORM activities. The decision as to what components of existing exposure are not amenable to control requires a judgement by the regulatory authority that will depend on the controllability of the source or exposure, and also on the prevailing economic, societal, and cultural circumstances (see ICRP, 2007, paragraph 284).

According to Publication 103 (ICRP, 2007, paragraph 52), there are two distinct concepts that delineate the extent of radiological protection control, namely (i) the exclusion of certain exposure situations from radiological protection legislation, usually on the basis that they are not amenable to control with regulatory instruments (cannot be regulated), and (ii) the exemption from some or all radiological protection regulatory requirements for situations where such controls are regarded as unwarranted, often on the basis that the effort to control is judged to be excessive compared to the associated risk (need not be regulated).

In the draft publication related to radon exposure, a specific graded approach is recommended for workplaces. Where workers' exposures to radon are not considered as occupational exposures, i.e. when workers exposures to radon cannot reasonably be regarded as being the responsibility of the operating management, the first step is to reduce concentration of radon-222 as low as reasonably achievable below the same reference level as set for dwellings (even though the corresponding level in dose is below 10 mSv per year because the conditions of exposure in workplace are different than those in dwellings). If difficulties are met in the first step, a more realistic approach is recommended as the second step. It means optimising exposure on the basis of a dose reference level of 10 mSv per year taking into account the actual parameters of the exposure situation. Then, if despite all reasonable efforts to reduce radon exposure, the exposure remains durably above the dose reference level of 10 mSv per year, and/or where workers' exposure to radon can reasonably be regarded as being the responsibility of the operating management (e.g. some underground workplaces, spas…), the workers should be considered as occupationally exposed. In such cases, the Commission recommends applying the optimisation principle and the relevant requirements for occupational exposure.

In the future publication related to NORM activities, the Commission would recommend a similar, although adapted, graded approach in which the workers should be considered as occupationally exposed either when, despite all reasonable effort, the exposure cannot be maintained below the appropriate reference level (quantitative criterion) or when the work activity is in a positive list established at national level (qualitative criterion).

4.3. Application of dose limits

According to *Publication 103* (ICRP, 2007; paragraph 203), the principle of application of dose limits is the third fundamental principle of the ICRP system. It is individual-related and applies in planned exposure situations. It means that the total dose to any individual from regulated sources in planned exposure situations other than medical exposure of patients should not exceed the appropriate limits recommended by the Commission. In the following paragraph (paragraph 204), it is explained that regulatory dose limits are determined by the regulatory authority, taking account of international recommendations, and apply to workers and to members of the public in planned exposure situations.

Dose limits apply only in planned exposure situations. For the sake of consistency, dose limit should apply in NORM exposure situations considered or managed as planned exposure situations.

5. Implementation

The future ICRP publication will provide recommendations on the implementation of the Commission's recommendations in some types of NORM activities.

6. Conclusions

The ICRP is developing a common approach for the application of its general recommendations in various types of existing exposure situations. The key elements of this approach are the following:

- Similar characteristics of the situations:
  - ubiquity of the radiation;
  - source not easy to control;
  - large distribution of individual exposure;
  - exposure of workers may be adventitious;
  - lack of awareness of the concerned parties,
  - including responsible persons;
  - exposure dependant on the individual behaviour (self-help protective actions);
  - long term perspective;
- Development of a radiological protection culture;
- Implementation of a simple, realist and ambitious protection strategy;
- Strategy based mainly on the principle of optimisation of the protection;
- Periodic assessment and review;
- Upper value of the reference level of the order of 10 mSv per year;
- Prevention and mitigation;
- Involvement of relevant stakeholders;
- Graded approach, in particular for workers;
- Use of the concepts of exemption and exclusion as relevant;
- Incentive and mandatory provisions combined;
- Application of self-help protective actions;
- Application of the dose limits up to the national authorities.

The future publication related to NORM activities will be based on this approach.

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Application of clearance levels to metal scraps contaminated with NORM

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Abstract

Throughout the last twelve years more than one hundred pieces of metal scrap contaminated with natural radioactive materials (NORM) have been detected in Spanish scrap yards and melting installations (about 60% of the total detected pieces). This scrap is mainly originated in the decommissioning of ore processing industries and in oil and gas extraction and production facilities. The detection of these materials is a consequence of the global programme established in Spain to control the presence of radioactivity in metal scraps. According with their activity content the materials can either be melted in the facility or removed as a radioactive waste by ENRESA. The clearance level, for this kind of materials, established in Spain is based on the EU document Radiation Protection 89 ("Recommended radiological protection criteria for the recycling of metals from de dismantling of nuclear installations").

Other clearance levels could be applied, as the values established on IAEA Safety Guide RS-G 1.7 ("Application of the Concepts of Exclusion, Exemption and Clearance") or on the EU document Radiation Protection 122 Part II ("Application of the concepts of exemption and clearance to natural radiation sources") and also specific values calculated for the applicable scenarios.

In this paper the applicability of these values is analyzed and also a study of the radiological consequences provoked by melting of these materials prepared by ENRESA is presented. The study focuses on the characteristics of Spanish facilities and the overall process, from the scrap yard to the melting facility, including the production and use of consumer products.

The global conclusion of this study is that there is no risk altogether to workers or general public when common quantities of materials contaminated with natural radioelement are detected in facilities; therefore this material can be melted unrestrictedly.

Introduction

Throughout the last twelve years more than one hundred pieces of metal scrap contaminated with natural radioactive materials (NORM) have been detected in Spanish scrap yards and melting installations (about 60% of the total detected pieces). This kind of scrap is mainly originated in the decommissioning of ore processing industries (not uranium and thorium), in oil and gas production facilities, in phosphate (fertiliser production) and phosporic industries and in other industries.

In oil and gas production industries during the extraction, purifying and production of crude oil and natural gas, several by-products are generated (slags and deposits) and also contaminated equipments are produced. Part of these by-products are disposed at sea or on land, and scraps are mostly recycled. In the other industries also contaminated equipments can appear.

The detection of these materials is a part of a global programme called "Spanish Protocol for Collaboration on the Radiation Monitoring of Metal Materials" (the "Protocol" thereafter). The object of this Protocol is

to set radiological control systems of metal materials and final products in order to detect the existence of radioactive materials. This programme was widely implemented in Spain after the accidental melting of a high activity Cs-137 source in a melting facility in 1998.

The Protocol was signed in November 1999 by all the parties concerned: the corresponding Ministries, the Nuclear Safety Council (CSN), the Spanish National Company for Radioactive Waste Management (ENRESA), the Trade Unions and the Industrial Companies that recover, handle, store and recycle metal scrap. The Companies included in this programme installed monitoring systems to detect the presence of any kind of radioactivity in scrap before entering the plants. They also have additional fixed and/or portable equipment to segregate and control the detected radioactive materials and to control the melting products, the slags and the off-gas dust.

The Protocol is complemented by a Transfer Authorisation general permit published by the Ministry of Industry and Energy (February 2000) that contains the radioactivity content levels proposed by the CSN to classify the detected radioactive materials as radioactive waste. These values are based on the recommendations of the European Commission for recycling of metals resulting from dismantling of nuclear installations ("Radiation Protection nº 89").

From 1998 ENRESA has carried out 409 interventions and 282 collections and transportation from 25 melting facilities and 39 scrap yards. The material involved was 295 radioactive sources, 36% of which were industrial and medical sources and 78% low activity radium sources. More than 3300 pieces formed by sources, consumer goods (lightning rods, luminous dials), depleted uranium (shieldings and counterweights) and contaminated materials, have been detected. About 57 % of these pieces were contaminated with NORM (Fig. 1).

Figure 1. Pieces contaminated with Norm

Characteristics of the materials contaminated with Norm

The general characteristic of the materials detected are that they are contaminated with natural radioelements Ra-226 and Th-232, deposited inside pipes and other components like pumps, valves or sheet, or they are residual materials resulting from cleaning-up of facilities. Also other material containing natural radionuclides, as concrete, slag or refractory are detected. Table 1 includes the distribution of the materials detected.

Table 1. Type of materials with Norm

Type of material	Number	%
Tubing	358	32.9
Miscellaneous parts	536	49.3
Sheet	109	10
Sleeve filters	1	0.1
Valves	15	1.4
Compacted parts	6	0.6
Safety deposits box or similar	9	0.8
Slag	9	0.8
Refractory material	24	2.2
Drums	15	1.4
Others	4	0.4
Wastes	1	0.1
Earths	1	0.1

The dimensions of these pieces vary considerably and depend on whether the scrap has been previously cut for whatever reason. In general, the tubing varies in length from a few centimetres to one or two metres, with a thickness of between 0.2 and 0.5 cm, a diameter of between 5 and 30 cm and a weight of tens of kilograms. The sheet usually between 10 and 30 cm in length and 10 and 50 cm in width, also weighting tens of kilograms.

Figure 2. Typical pieces contaminated with Norm (sheet, pipe, vlave)

From the radiological point of view, most pieces present a dose rate of 0.3 to 1 or 2 microSv/h, although in certain cases the dose rate may reach 20 or 30 microSv/h. In any case, given the way in which this material is handled, with magnets and slings, the dose received by the workers is not significant. Furthermore, the total amounts detected per year are not large, as a result of which the exposure time is also minimal.

The materials that these pieces contain present a highly variable activity concentration, as may be seen in table 2. On certain occasions, values in excess 100 Bq/g have been measured. In general the activities of Ra-226 are higher than those of Th-232.

Table 2. Activity concentration in pieces with Norm

Range (Bq/g)	Ra-226 (%)	Ac-228 (%)
< 0.1	1.7	8.7
0.1 - 1	6.9	21.7
1 – 10	20.0	0.0
10 – 100	31.4	47.8
100 – 1000	36.0	17.4
1000 – 5000	2.9	4.3
> 5000	1.1	0.0

Measurements are carried out via the gamma emitters of the Radium and Thorium series, with the activity of Ra-226, Pb-214 and Bi-214 being determined in the case of Radium, and Ac-228, Pb-212 and Tl-208, in the case of thorium. In general, certain equilibrium may be observed in the radium chain, with factors of between 0.9 and 1 in 66% of the samples studied, both between Ra-226 and Pb-214 and between Ra-226 and Bi-214. In the case of thorium, equilibrium may be observed between Ac-228 and Pb-212 in 27% of the cases studied, although in 55% of cases a higher concentration of Pb-212 may be observed; the factor for Ac-228 and Tl-208 is between 0.3 and 0.4 in 55% of the samples studied.

In general the activity concentration in the pieces is below the reference level, established in the "general permit" issued by the Ministry of Industry (1Bq/g for Ra-226 and Th-232 including their progeny in secular equilibrium), so they can be incorporated into the smelting process. If the value is higher, ENRESA removes the material as a radioactive waste; otherwise, a report is issued indicating that the material may be incorporated into the process, based on the criteria established by the CSN. Experience shows that pieces presenting a dose rate of around 2 microSv/h or lower may normally be incorporated into the process.

The pieces detected, with activities higher than the reference levels, are managed as radioactive wastes and sent to the ENRESA facility in Córdoba (Cabril Disposal Facility) for final disposal. In many cases it is necessary to undertake additional conditioning in order to their placement in suitable containers for transport and disposal. In these cases, the pieces are cut until their dimensions are compatible with the container. Likewise, in order to reduce the volume of the radioactive wastes removed, and when it is possible, the piece is cut, normally "in situ" and the soil material containing the natural radioactive material removed. Following this, a check is made to ensure the absence of radioactive material on the metal part of the piece which may then be incorporated into the process, while the soil material is retired as radioactive waste.

Figure 2. Cutting of a pipe to remove the Norm material

1. Reference levels

1.1 Safety Guide RS-G-1.7

This IAEA document, published in 2004, aims to clarify application of the concepts of exclusion, exemption and clearance. Exclusion applies to any exposure to natural radiation whose magnitude or likelihood is essentially unamenable to control through the requirements of the Standards is deemed to be excluded from the Standards. Examples of excluded exposure given in the Basic Safety Standards are: exposure from K-40 in the body, from cosmic radiation at the surface of the earth and from unmodified concentrations of radionuclides in most raw materials. But the reference to unmodified concentrations points to the fact that the processing of some raw materials, which may have typical concentrations of radionuclides of natural origin, may generate products or wastes that have higher concentrations of radionuclides or give rise to exposures that should not be excluded from regulatory control.

Furthermore, this guide aims to establish the generic quantitative values applicable to each of the concepts. The values established in this guide apply to all commodities in bulk amounts, other than foodstuffs and drinking water. These values apply to exclusion, but it is also noted that the regulatory authorities may use them to determine whether a particular material could be cleared.

The values of activity concentration for radionuclides of natural origin set out in this guide have been selected on the basis of consideration of the upper end of the worldwide distribution of activity concentrations in soil provided by UNSCEAR]. Doses to individuals as a consequence of these activity concentrations would be unlikely to exceed about 1 mSv in a year, excluding the contribution from the emanation of radon, which is dealt with separately.

The values of activity concentration for radionuclides of natural origin, derived using the exclusion concept, are given in Table 3 and applied to the natural decay chains in secular equilibrium; that is, those decay chains headed by U-238, U-235 or Th-232, with the value given to be applied to the parent of the decay chain. The values can also be used individually for each decay product in the chains or for the head of subsets of the chains, such as the subset with Ra-226 as its parent.

Table 3. Values of activity concentration for radionuclides of natural origin

Radionuclide	Bq/g
K-40	10
All other radionuclides	1

It is also noted that values up to 10 times these amounts could be considered exempt if so decided by the national regulatory authority.

Although conceptually, the concept of clearance does not apply to scrap metal from unregulated facilities, there is nothing to prevent the derived values being applied, as they satisfy the dose limits established for the exclusion of practices that generate them, including where the dose criteria on which the derived values are based are more restrictive (10 microSv/year versus 1mSv/year). In addition, the quantities taken into account in the calculations to obtain the levels derived from scrap metal levels are much lower, at around 1 ton.

1.2 Safety Series 111-P-1.1

This document refers to the application of exemption to recycling and reuse of materials from nuclear facilities. It specifically analyses the recycling of metallic materials.

A value of 10 microSv/year is used as a dose criterion and it is considered that 100 tons of contaminated steel are processed.

It should be noted that although the calculation methodology applied is suitable for the recycling of scrap metal contaminated with natural radionuclides, the document only includes results for artificial radionuclides characteristic of nuclear power plants. The only natural isotope included is U-238 with a derived exemption value of 1 Bq/g.

1.3 Radiation Protection 89

As noted above, the reference values used in Spain for scrap metal are included in the European Union Radiation Protection 89 document. This document establishes the values for recycling metallic materials generated during the decommissioning of nuclear power plants. The amount of material considered is 4000 tons per year in an arc furnace, as used in Spain, and 2000 tons in an induction furnace. The specific scenarios considered are developed in another document (Radiation Protection 117), and are those listed below:

Transportation from the nuclear plant to the foundry.
Exposure of foundry workers and members of the public in the vicinity.
Exposure of workers in the production of resulting products.
Exposure of users of the products manufactured.
Final disposal of the manufactured products.

The values derived for NORM radionuclides are detailed in the table 4.

Table 4. Nuclide specific clearance levels for metal scrap recycling

Radionuclide	Bq/g
Ra-226	1
Th-232	1

The established scenarios are clearly adapted to the management of scrap metal for recycling, although the amounts assumed to be processed at the foundry are greater than those that have been detected in Spain.

Furthermore, as part of the calculations of these scenarios, the dose criterion used for clearance to be viable, has been 10 microSv per year. It should be noted here that for natural radionuclides the internationally accepted standard dose criteria is 300 microSv per year, and therefore the concentration limit values may be higher (up to 30 Bq/g).

1.4 Radiation Protection 122

The European Union document, Radiation Protection 122, Part II, refers to the practical application of the concepts of exemption and clearance to natural radiation sources. This document sets out the different scenarios that can be used to obtain values derived from activity in naturally occurring radioactive

materials that can be handled without being subject to regulatory control (exempt). However, it should be noted that according to Annex II of the document, only scenarios related to the handling, processing, use and disposal of waste generated at these installations are analysed, because scenarios relating to the workers at them have already been extensively studied. The radiological evaluations carried out cover the following:

- Workers and the general public who have contact with natural materials other than the specific work scenarios.
- Development of exemption/clearance levels based on exposure pathways relevant to natural materials.
- Dose criterion for workers and members of the public in general equal to 300 microSv/year.
- Scenarios based on common practices for recycling and disposal options for industrial Norm residues.
- Distinction between the following material types: waste rock, ash, sand, slag, sludge from the oil/gas industry.
- The scenarios do not include effluent discharges to the atmosphere or to water, or situations that apply to work on or restoration of mine sites.

This document establishes values for the unconditional clearance of products, materials and sub-products containing radioactive materials, both artificial and natural. However, in the case of natural, it only applies to those materials that are not exploited for their radioactive properties.

This document is divided in two major parts. In the first part a short overview of the literature is given concerning the radionuclide contents in various NORM. The second part contains an overview of the scenarios and parameters used for the radiological assessment. Based on this data, radionuclide specific exemption/clearance levels for bulk quantities of residual material from the non-nuclear industry are calculated. For this purpose specific scenarios are developed, which describe the following exposure situations:

- Transport of material: workers;
- Storage of material: workers;
- Disposal in a landfill or on a heap: landfill operators and people dwelling near the landfill or heap;
- Recycling as additive in building material: workers and members of the general public living in the house;
- Recycling as filling material in road construction: workers and members of the general public staying on public places.

The values derived for clearance of NORM radionuclides are detailed in the table 5.

Table 5. General clearance levels (Bq/g)

Radiouclides	All materials	Wet sludges from oil and gas industry
U 238sec incl. U 235 sec	0.5	5
U nat	5	100
Th 230	10	100
Ra 226+	0.5	5
Pb 210+	5	100
Po 210	5	100

Radiouclides	All materials	Wet sludges from oil and gas industry
U 235sec	1	10
U 235+	5	50
Pa 231	5	50
Ac 227+	1	10
Th 232sec	5	100
Ra 228+	1	10
Th 228+	0.5	5
K –40	5	100

The scenarios established clearly do not include the management of any scrap metal generated during maintenance or dismantling of the industries considered, for recycling by the foundry industry. Also the quantities considered in this study are much higher than those used in the RP 89 study as it considers what are called bulk amounts.

2. ENRESA study

ENRESA carried out a study of the radiological consequences of melting of detected scrap contaminated with NORM. The study analysed the overall process from the scrap yard to the melting facility, including manufacturing of consumer products and their use. The study also included the usage and disposal of the generated by-products (slag and dust).

The general characteristics of the materials considered in the study were materials contaminated with Norm (Ra-226 and Th-232), deposited inside pipes and other components like pumps, valves or sheets, and residual materials resulting from cleaning-up of facilities. The specific characteristics were of the materials detected in metal recycling industries.

In the study, specific parameters of Spanish installations were considered. That is why the annual capacity of melting facilities was fixed between 200.000 and 600.000 tons per year. In the scrap yard, between 20.000 and 100.000 tons handled per year. The trucks that transported the scrap from the scrap-yard to melting facilities were loaded with a maximum of 18 tons. The annual capacities of the disposal installations were 50.000 tons per year for industrial wastes and 150.000 tons per year for innocuous waste. The study was based on the assumption that 1, 3 or 100 tons of contaminated material was melted in an arc furnace.

The scenarios and formulae used were based on the European Commission document "Radiation Protection nº 117". Radium and thorium were considered together with their progeny in secular equilibrium, so all the isotopes of natural chains were included on the calculations.

The individual doses for all scenarios and quantities were calculated. The highest doses were related to transportation from scrap yard to melting facility and to working on a ship.

The corresponding maximum concentration for doses below the exemption criteria (10 uSv/y) for each scenario and quantity was also calculated. The radium activity concentration in the materials that can be transported and processed is between 10 and 100 Bq/g, when 100 tons or 1 ton are handled respectively. For thorium, the results depended on the kind of installation. At the scrap yard between 1 and 100 tons of contaminated materials between 100 and 1 Bq/g can be handled. At the melting facility can be processed materials with a concentration between 10 and 1000 Bq/g in quantities between 100 and 1 ton.

3. Conclusions

- Most of the metallic pieces detected at the entry of the recycling metal industry facilities contain natural radioactive materials (Norm).
- Many of these pieces have a very low value of concentration activity and may be incorporated into the smelting process following a rigorous procedure to support the decisions.
- For this kind of materials can be applied the values established for metallic scarp, but they are not calculated for this materials.
- The exception/clearance levels established for Norm materials are not applicable specifically to this kind of materials.
- It is possible establish specific values for scraps contaminated with Norm.

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Waterworks residues from the radiological point of view

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Abstract

Revising the basic safety standards for the protection against dangers from exposure to ionizing radiation, the European Community is establishing a new framework for radiation protection. Especially the regulations concerning natural radioactivity are more detailed and restrictive than before. Within this proposal, a list of relevant industrial practices involving naturally occurring radioactive material (NORM) is introduced. Groundwater filtration facilities are specified on this list and therefore, residues from this process have to be investigated.

The German Federal Office for Radiation Protection (BfS) performed an internal study dealing with the exposure to radiation originating from residues of waterworks. Based on a Bavarian study about the content of radionuclides in residues from water treatment facilities an estimation on the radiological relevance of waterworks residues on a national scale was made. One major focus was to investigate which kind of water treatment technology would result in residues with an enriched content of radionuclides from the ^{238}U or ^{232}Th decay series. The accumulation of NORM in water treatment facilities depends on several factors, like activity concentration of the raw water, treatment specific mass transfer coefficient and the efficiency of eliminating radionuclides during the water treatment procedure. As a result, residues from the elimination of iron, manganese and/or arsenic are of highest radiological concern.

Based on the recommendations of the German Technical and Scientific Association for Gas and Water (DVGW) concerning the re-use of waterworks residues, a dose assessment of the most common recycling pathways as well as the disposal scenario of residues was performed. In summary, only manganese-dioxide coated filter gravel from the elimination of iron, manganese and/or arsenic might be of radiological significance.

1. Introduction

Generally, rocks are containing different amounts of natural radionuclides of the ^{238}U and ^{232}Th decay series. When groundwater comes in contact with rocks, traces of radionuclides are dissolved. The activity concentration of radionuclides in the aquifer is depending on several factors: the source (specifically the radionuclide concentration of the rocks), the chemical properties of the element in question, complexing agents, and physico-chemical properties like the pH or the redox potential. Under the prevailing geochemical conditions, the predominant radionuclides found in groundwater include ^{238}U, ^{226}Ra, ^{226}Ra, ^{210}Pb and ^{210}Po (BfS 2009). In comparison, thorium (here ^{232}Th, ^{230}Th and ^{228}Th) is rather immobile in a wide range of pH and redox conditions, and thus it is scarcely found in groundwater layers.

In many cases groundwater is treated to remove impurities to meet the legal requirements of the German Drinking Water Ordinance (TrinkwV 2001). The aim of the most common treatment technologies is to achieve certain hygienic or chemical standards, but not the elimination of radionuclides. The radionuclides may be removed from water by chance and accumulate in different kinds of waterworks residues.

While introducing the protection of man and the environment against naturally occurring radiation sources during work activities as a part of the German Radiation Protection Ordinance (RPO) in 2001,

the surveillance limit was derived from the internationally accepted limit of the effective dose of 1 mSv per year for members of the general public (StrlSchV 2001). The recycling or disposal of residues requiring surveillance is regulated within this ordinance according to this dose limit. For this purpose, a list of industrial residues which should be taken into account was established (positive list). Residues of water treatment facilities are not included in this list. Nevertheless, since that time, there has been a lively discussion whether or not these residues are of radiological concern and consequently should be added to the positive list in future amendments of the RPO. In the light of the revision of the European basic safety standards for protection against the dangers arising from exposure to ionising radiation, the question of radiological relevance of waterworks residues even gains in importance (BSS 2011). In Annex V of this proposal a list of relevant industrial practices concerning NORM is introduced. Residues from groundwater filtration facilities are specified in this list.

Therefore, the German Federal Office for Radiation Protection (BfS) performed an internal study dealing with exposure to radiation originating from residues from waterworks. Based on a Bavarian study about the specific activity of radionuclides in waterworks sludges (LfU 2006, LfU 2008), an estimation on the radiological relevance of waterworks residues on a national scale was made. The aim of our study was to identify water treatment technologies leading to residues with an enhanced content of radionuclides from the ^{238}U or ^{232}Th decay series. According to the RPO, materials are categorised as "enriched" if the sum of the radionuclide with the greatest specific activity of the radionuclides from the ^{238}U and ^{232}Th decay series exceeds 1 Bq/g. For this purpose, a stepwise procedure was performed: (i) identification of treatment technologies which lead to enriched concentration of natural radionuclides in the residue, (ii) determination of a trigger activity concentration in the groundwater, and (iii) estimation of the annual amount of residues with enriched concentration of radionuclides. Finally, a dose assessment for the most common recycling pathways and the disposal scenario was performed.

2. Methods

2.1. Identifying treatment technologies with residues of enriched concentrations of radionuclides

The specific activity of residues from waterworks treatment technologies depends on the raw water activity concentration (C_W), the volume of water per mass of the residue (MTC) and the degree of eliminated radionuclides from the water (EE), which can be calculated from equation 1.

$$C_R = C_W * MTC * E \qquad (1)$$

In Germany, multiple water treatment technologies are in use, but only four of those are widely spread: (i) oxidisation to eliminate iron, manganese and/or arsenic, (ii) flocculation by adding coagulating agents, (iii) water decarbonisation and (iv) pH adjustment (deacidification). This categorisation is not strict, and there are combinations of different treatment technologies like oxidisation, deacidification or activated carbon filtration in the same waterworks LfU (2006). In case of oxidisation, flocculation and sometimes deacidification, small particles arise which are filtered by means of gravel or sand filter systems. In time, the filters clog due to the particles. To keep them properly working, they have to be back-flushed with water and air witch results in continuously arising sludges as residues. The filter gravel can also be considered as residue, but it lasts over decades in waterworks. A categorisation of the most common waterworks residues in iron sludges (from oxidisation), flocculation sludges and limy residues (from decarbonisation and deacidification) can be found in Wichmann et al. (2002).

2.1.1 Efficiency of elimination

Even though the aim of water treatment technologies mentioned in section 2.1 is not the reduction of radionuclides from groundwater, they are partly removed during the treatment procedure as well. Taking data from literature, the mean efficiency of elimination for radium is 36% (oxidisation), 42% (flocculation) and 87% (decarbonisation), respectively (Haberer & Raff 1999, Haberer 1999, HGN 2003). The removal of uranium is of similar efficiency, but like in the case of radium, strongly depends on the pH.

2.1.2 Mass transfer coefficient (MTC)

Each water treatment technology produces different amounts of residues per volume of water. The mass transfer coefficient (MTC) gives an idea of the water volume which is necessary to produce one kilogram of residue. From Wichmann et al. 2002, the MTC for iron sludges 100,000 l/kg), flocculation sludges (50,000 l/kg) and limy residues (5,000 l/kg) can be estimated. In other words, limy residues and flocculation respectively show twenty times and two times higher masses of residues per volume of water compared to iron sludges.

2.1.3 Concentration of raw water

The results of the BfS drinking water survey (BfS 2009) show that the activity concentration for the radionuclides of the ^{238}U and ^{232}Th decay series in groundwater is about one order of magnitude higher than in surface waters. This ratio is in agreement with other publications (BMU 2003, US-EPA 2008). As a consequence, assuming the same treatment technology for ground and surface water, an enrichment of radionuclides in residues should appear more frequent in groundwater filtration facilities than in surface water treatment facilities.

2.1.4 Relative specific activities of residues from water treatment technologies

Bearing in mind the information of the EE, MTC and the raw water activity concentration, it is not obvious, which kind of treatment technology would produce residues of highest radiological concern. Therefore, a new parameter called relative specific activity was introduced. This parameter should give an idea, which residue theoretically shows the highest specific activity in the residues. Standardising the EE, MTC and activity concentration to each minimum value, the residue with the expected highest concentration can be determined using equation 1. Table 2 shows the relative specific activities for residues stemming from different water treatment technologies. In summary, iron sludges from groundwater treatment facilities should show the highest specific activities.

Table 2: Standardised parameters necessary to calculate relative specific activities of residues from water treatment technologies – A: surface water, and B: groundwater

		stand. activity concentration (C_n)	stand. *MTCn*	stand. *EEn*	**rel. specific activity (C_n x MTC_n x EE_n)**
A	limy residues	1	1	2.4	**2.4**
	flocculation sludges		10	1.2	**12**
	iron sludges		20	1	**20**
B	limy residues	10	1	2.4	**24**
	flocculation sludges		10	1.2	**120**
	iron sludges		20	1	**200**

2.2 Specific activity in waterworks residues of oxidisation processes

The Bavarian Environment Agency published several surveys dealing with radionuclides in waterworks residues (LfU 2002, 2006, 2008). In total, they analysed more than 500 residues from different water treatment processes. With regard to residues from oxidisation processes the content of radionuclides was determined for approximately 260 iron sludges. In sludges ^{226}Ra and ^{228}Ra show the highest activity of radionuclides for the ^{238}U and ^{232}Th decay series, respectively (see table 3). The minimum, maximum and the median value for both radium isotopes are listed in table 3.

Table 3: Minimum, maximum and median value of the specific activity for ^{226}Ra and ^{228}Ra from Bavarian surveys.

		^{226}Ra [Bq/g]			^{228}Ra [Bq/g]		
	N	min	median	max	min	median	max
elimination of iron (2006)	19	0.079	1.06	11.6	0.049	0.47	6.4
elimination of arsenic, iron or manganese (combined, 2006)	133	0.029	1.04	32.5	0.012	0.68	22.7
iron sludges (2008)	109	0.018	0.64	45.58	0.004	13.5	0.421

As this kind of residue only arises over long periods of time, information about the content of radionuclides in filter gravel is rare. Judging from the limited available data (N<30), the specific activity for ^{226}Ra is in the range of 0.3 Bq/g to 40 Bq/g and for ^{228}Ra of 0.2 Bq/g to 13 Bq/g, respectively. At first glance, the activity of filter gravel is comparable to those of iron sludges. But there are some hints in literature that the activity of filter gravel can be higher than the corresponding iron sludges (Wisutec 2005). Taking the data from Wisser & Walsdorf (2006), the filter gravel show 4 to 6 times higher activity values for ^{226}Ra and ^{228}Ra. The statement of an enrichment of radionuclides in filter gravel in comparison to iron sludges is based on very limited data, so it is not appropriate to derive a general conclusion.

2.3 Amounts of NORM arising from waterworks

2.3.1 Iron sludges

With regard to a dose assessment, it is not appropriate to take the whole amount of iron sludges into account. Instead, the fraction of sludges with enriched content of radionuclides has to be identified. Applying the criterion of the RPO to iron sludges, residues are categorised as enriched, if the sum of the activities for ^{226}Ra and ^{228}Ra exceeds the value of 1 Bq/g. Therefore, knowledge of the proportion of ^{226}Ra to ^{228}Ra is essential. Looking at the data of iron sludges from Bavaria (s. section 2.2), the ratio of ^{226}Ra to ^{228}Ra with an activity of up to 2 Bq/g is about 1.5. As a consequence, sludges with a specific activity for ^{226}Ra of more than 0.6 Bq/g can be considered as residues with an enriched amount of natural radionuclides.

Assuming a constant EE and MTC (see sections 2.1.1 and 2.1.2), a back calculation from the specific activity in sludges to a groundwater activity concentration is possible (rearrangement of equation 1). Taking a value for iron sludges of 0.6 Bq/g, a trigger value of 16.7 mBq/l for the groundwater activity concentration was determined. If that value is exceeded, an oxidisation during the water treatment procedure would result in iron sludges with enriched specific activity. Looking at the dataset of the comprehensive BfS survey on raw and groundwater activity concentrations, 25% of the samples exceed the trigger value for ^{226}Ra of 16.7 mBq/l. Assuming that each waterworks treats the same volume of water, 25 % (6,500 t) of the total amount of iron sludges (26,000 t, Wichmann et al. 2002) should show enriched contents of radionuclides.

2.3.1 Filter gravel

As mentioned above, knowledge about specific activities and the amount of filter gravel is *incomplete*. As a consequence, an estimate of the amount of filter gravel with enriched specific activities or activity in this residue is *uncertain as well*. Under the following assumptions:

- 75% of the 5,000 waterworks in Germany are groundwater filtration facilities, and 75% of them have an oxidisation treatment available.
- Each waterworks exchanges 500 t of filter gravel every 30 years.
- The specific activity in filter gravel is five times higher than in iron sludges

an estimate on the total amount of filter gravel of 45,000 t per year, of which 30,000 t should show an enriched specific activity was achieved.

3. Dose assessment

The dose assessment of this study does not follow a generic approach, but estimates the resulting dose for workers *and* members of the public on the basis of realistic assumptions. According to the recommendation of the German Technical and Scientific Association for Gas and Water, iron sludges can be re-used in building materials, in sewage treatment plants, landscaping/re-cultivation, road construction and metallurgy (DVGW 2000). The re-use of iron slugdes in the farming industry is mentioned as well, but due to waste legislation aspects this recycling pathway is unlikely. In the opinion of Pilz (2008), 40% of iron sludges are brought to sewage treatment plants, 20 % to disposal sites and another 40 % are recycled. Based on the DVGW recommendations and the evaluation of Pilz we performed a dose assessment for the following cases:

- disposal scenario
- re-use in building materials
- re-use in road construction or landscaping/re-cultivation
- discharge into sewage treatment plants.

The re-use in metallurgy has not been considered, due to dilution effects of the small amounts (a few thousands of tons) of residues compared to the enormous iron production (approximately 30 million tons).

3.1 General assumptions

There is only little information available about the fate of filter gravel. Therefore, we used the same options for the re-use of filter gravel as those for iron sludges. Throughout Germany, data of the specific activity were not available, neither for iron sludges nor for filter gravel. In order to be able to make a dose assessment, we estimated a theoretical specific activity of iron sludges according to equation 1. The value for the groundwater activity concentration is the ninetieth percentile of those data taken from the BfS drinking water survey, which exceed the trigger value 16.7 mBq/l for ^{226}Ra. The values for EE and MTC are given in the section 2.1.1 and 2.1.2, respectively. This procedure results in a specific activity of iron sludges of 4.0 Bq/g for ^{226}Ra and 2.4 Bq/g for ^{228}Ra, respectively. For filter gravel, the calculation was done with a trigger value of 3.4 mBq/l, which is in line with the conservative assumption of an enrichment factor of 5. For filter gravel, this results in an estimated specific activity of 8.8 Bq/g for ^{226}Ra and 5.3 Bq/g for ^{228}Ra, respectively. For the dose assessment, we assumed equilibrium of daughter nuclides, but the parents remains disregarded.

In each re-use option listed in section 3 as well as in the disposal option, large amounts of materials are handled. Assuming the companies involved get water work residues from several filtration facilities, then, as a consequence, working personal of recycling/disposal sites deals with a larger amount of waterworks residues than a single worker in a filtration facility. Nevertheless, a dose assessment for workers in groundwater filtration facilities was performed as well. The general procedure of dose assessment for each exposure scenario follows the recommendations of the BfS "Calculation guide mining" (BfS 2011).

3.2 Disposal scenario

3.2.1 Specific assumptions

In line with the RPO, a base seal for the disposal scenario was not considered. If *members of the public* live close to a landfill, they can be exposed by ingestion of contaminated water and irrigated food, gamma radiation and inhalation of radon. In Germany, about 1,500 landfills are in use. Conservatively, it was assumed that filter gravel and iron sludges are disposed at merely 75 disposal sites (5% of the total number of sites. Assuming that each of the 75 landfills is in use for twenty years, having a size of one hectare and disposing equally filter gravel and iron sludges, this would result in a theoretical thickness of the contaminated layer of 0.1 m in case of iron sludges and 0.5 m in case of filter gravel at the end of the deposition phase. Assuming that each of the 75 landfills is in use for twenty years, having a size of one hectare and disposing equally filter gravel and iron sludges, this would result in a theoretical thickness of the contaminated layer of 0.1 m in case of iron sludges and 0.5 m in case of filter gravel at the end of the deposition phase. Since the amount of iron sludges and filter gravel is limited, thicker layers are unlikely. The inhalation of dust and the deposition of dust on vegetables are not taken into account.

Since *workers* from different industries are dealing with waterworks residues, a dose assessment was performed for workers in waterworks, for truck drivers (transportation) and for workers at disposal sites. They can be exposed to external radiation, direct ingestion of contaminated material, inhalation of radon (except truck drivers) and the inhalation of contaminated dust (only in case of filter gravel). The transport of iron sludges from waterworks to disposal sites is supposed to happen twice a year. This results in a conservative exposure time of 20 h for the worker in water works. Since the same truck driver can pick up iron sludges from different waterworks we assume a exposure time of 25 h for the truck driver as well as for the worker on a disposal site as well. Due to larger amounts of filter gravel exposure times for the different workers were set to 80 h (waterwork) and 100 h (transportation, disposal).

3.2.1 Dose assessement

For the disposal scenario, the dose assessment for members of the general public results in the highest effective dose for the *age group "<1 a"*. With the aforementioned assumptions, the dose arising from the disposal of iron sludges and filter gravel for this age group is 22 µSv/a and 260 µSv/a, respectively. About 60% of this dose arises from the consumption of drinking water, 20% from external exposure to gamma radiation and 15 % from ingestion of food irrigated with contaminated water.

For the dose assessment, the water content of iron sludges (60%) and the shielding effects of the driver's cabin are taken into account. The results of the dose assessment are listed in table 3. In comparison with iron sludges, the disposal of filter gravel leads to higher doses for all workers involved. Due to the contribution of radon inhalation, the effective dose of 2,230 µSv/a is highest for workers in waterworks.

Table 3: Effective dose of workers involved in the disposal scenario [µSv/a]

	filter gravel			iron sludges		
exposure from	waterworks	transportation	disposal	waterworks	transportation	disposal
external radiation	408	78	510	25	5	32
inhalation of dust	94	118	118	0	0	0
inhalation of radon	1,715	0	136	54	0	1
ingestion of material	13	16	16	0	1	1
sum	**2,230**	**212**	**780**	**79**	**6**	**34**

3.3 Re-use in road construction or landscaping/re-cultivation

3.3.1 Specific Assumptions

In this scenario, waterworks residues are mixed with other residues (e.g. sewage slugdes) to build artificial layers. Workers can be exposed either during material mixing or placement of the material on site. Due to the limited amounts of waterworks residues, we assume a layer of 0.50 m thickness (portion of waterworks residues 20%) within an area of 1,000 m². The exposure situation for *workers* is supposed to be similar to those for workers from the disposal scenario. Thus, a separate dose assessment is not essential.

Members of the public can live close to roads or a reshaped landscape. They can be exposed by the ingestion of contaminated water, external exposure to gamma radiation and inhalation of radon.

3.3.2 Dose assessment

For the landscaping or road construction scenario, the dose assessment results in the highest effective dose for the age group "<1 a". With the aforementioned assumptions, the dose arising from the re-use of iron sludges and filter gravel for this age group is 290 µSv/a and 1,200 µSv/a, respectively. About 95% of this dose stems from external exposure to gamma radiation.

3.4 Discharge into sewage systems

The discharge of iron sludges into sewage systems is considered as re-use, because iron (hydr)oxides are able to suppress the formation of hydrogen sulphide. The 10,000 German sewage treatment plants produced 2.26 million tons (dry matter) of sludge in 2004. We conservatively assume that 40% of the iron sludges are brought to only 2% of the sewage treatment plants (200 facilities). The German commission on radiological protection stated in their recommendation that radionuclides should be equally distributed between sludge and cleared water (SSK 1998). This assumption results, on the one hand, in a specific activity in sewage sludges of 0.125 Bq/g for ^{226}Ra and of 0.075 Bq/g for ^{228}Ra and, on the other hand, in an activity concentration in clear water of 27 mBq/l for ^{226}Ra and 16 mBql/l for ^{228}Ra. The specific activity in sewage sludges and in clear water are in the range of background values for both radium nuclides. Concerning a dose assessment, the *worker* may be exposed in the same manner as workers at disposal sites. Members of the public can only be exposed due to sewage sludges and clear water. Thus, being of the same magnitude as the natural background levels, a dose assessment for members of the public is not necessary.

3.5 Re-use in building material

In principle, residues from waterworks can be utilised as secondary raw material in building material industries (brick producing and cement industries). Due to the demand of meeting quality standards in

the final product over a long period of time, the re-use of waterworks residues in the building material industry is problematic. Ensuring quality standards of the final product, producers tend to utilise raw materials, which have a composition that remains constant over a long period of time. Since the composition of residues from waterworks (even iron sludges themselves) can be quite different from each other, their addition as raw material in the building material industry is restricted to small amounts. For example, iron sludges are used as a colorant for bricks.

3.5.1 Dose assessment

The exposure situation of *workers* handling waterworks residues is expected to be similar to the situation of workers at disposal sites. Hence a separate dose assessment is not necessary.

According to Radiation Protection 112, the exposure from final building materials for members of the genereal public is less than one millisievert per year, if the requirements of the conservative index formula given in equation 2 are fulfilled (EC 1999). Data from a BfS survey on typical building materials in Germany showed only very few cases exceeding the index criteria at all. Due to the fact that the use of iron sludges as an additive is technologically restricted to small amounts, the exceeding of the dose criteria in such building materials is expected only in very exceptional cases.

$$I = \frac{C_{Ra}}{0.3Bqg^{-1}} + \frac{C_{Th}}{0.2Bqg^{-1}} + \frac{C_K}{3Bqg^{-1}} \leq 1 \qquad (2)$$

4. Conclusion

The different treatment processes in waterworks treatment plants were analysed systematically. As a result, iron sludges and filter gravel from oxidisation are of the highest radiological concern. Therefore, the dose assessment was focussed on these residues.

According to the recommendations of the DVGW for the re-use of iron sludges, the dose assessment was performed for all relevant recycling pathways. Taking into account realistic assumptions, the effective dose is below the legal dose reference value of 1 mSv/a for all workers involved as well as members of the general public, and also for each recycling option or the disposal of iron sludges. Hence, a restriction of the re-use or disposal for *iron sludges* is not necessary.

No recommendations of the DVGW are available for the re-use of filter gravel. As these residues are similar to the iron sludges, we assumed the same recycling pathways. The effective dose for members of the public within the disposal scenario leads to an effective dose below 1 mSv/a, according to our assumptions, but the effective dose of 2.2 mSv/a for workers in water filtration plants exceeds this reference value. Considering a small ventilation rate for the dose assessment, the highest contribution to the total dose arises from radon inhalation. Degassing of radon is limited to non-closed treatment procedures (e.g. bed filter), but especially in small water treatment facilities closed rapid filter systems are favoured to remove iron or manganese. With the use of a ventilation system for working rooms in which filter gravel is handled, the exposure arising from the inhalation of radon can easily be minimised. In any case, water treatment facilities are already mentioned in the list of working environments with increased radon levels (appendix XI of RPO).

The assumption of the disposal scenario includes some conservatism. Taking advantage of a base seal, as German waste legislation demands, the exposure arising from the ingestion of contaminated water

should be reduced. Due to the missing parent nuclide and the short half lives of ^{228}Ra and its daughters, the contribution of the ^{232}Th-series to the effective dose will be lower. Strictly taking into account health and safety instruction, the dose arising from ingestion of contaminated materiel can be neglected.

According to our dose assessment, the effective dose for members of the public with 1.2 mSv/a (age group "<1 a") exceeds the dose reference value of 1 mSv/a. The effective dose mainly arises from the exposure to external radiation (95%). Actually, it is not known whether or not filter gravel would be re-used to a major extent for road construction and landscaping. Even if they would be recycled this way, the utilization of filter gravel in road covering layers is unrealistic due to their consistency. Within our dose assessment, the shielding effect of a covering layer made of inert material is not taken into account.

Besides the re-use options for filter gravel and iron sludges mentioned in this study, there are other recycling pathways of minor importance like the desulphurisation of gas. For such rather exotic recycling options, a separate dose assessment does not seem to be necessary. For the sake of completeness, there are other NORM residues in waterworks (e.g. adsorbing resins, activated coal, scales in plant components.), but they show smaller tonnages in residues

With respect to the values for clearance and exemption for NORM of 1 Bq/g proposed in the EU-BSS, our dose assessment for residues of waterworks is in line with the dose constraint of 0.3 mSv/a for members of the general public and 1 mSv/a for workers, respectively.

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Po-210 and Pb-210 in the Netherlands: releases to air from industrial plants compared to environmental monitoring

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Abstract

The only industrial plant in Europe producing elemental phosphorus by means of a thermal process is located in the Netherlands, where it is responsible for the largest release of Po-210 and Pb-210 to air from industrial sources. The determination of the environmental load is difficult, because the deposition rate and the excess activity concentration in air caused by the plant emissions are, close to the plant, smaller or comparable to the natural background level.
Measurements at our institute, located at a distance of over 100 km from the phosphorus plant, show a natural Pb-210 background level of 399 microBq/m^3 in air and a deposition rate varying from 60 to 180 Bq/m^2/y. This is compared to the excess activity concentration in air and deposition rate due to this plant, as is estimated by making use of an air dispersion model, at the nearest residential area, which is located at approximately 4 km distance from the plant.

In addition to effective dose estimates arising from inhalation of the modelled air concentration, a (conservative) committed ingestion dose is determined by modelling the uptake of the radionuclides Pb-210, Bi-210 and Po-210 from contaminated farmland. The ingestion model assumes a food basket thought to be fairly representative for the nutritional habits of the population of the Netherlands. Ingrowth of Po-210 from the deposited Pb-210 is also modelled. The largest contribution to the collective effective dose is from ingestion. The committed dose per inhabitant is of the order of 1 microSv/y.

1. Introduction

In the Netherlands, the policy addressing Naturally Occurring Radioactive Materials was developed starting from 1983, when an environmental survey revealed elevated radionuclide concentrations above the background level. The source was identified as an industrial plant producing elemental phosphorus, by means of a thermal process, where the dust from the furnaces is filtered and largely recycled through the sintering process (Erkens 1997). Since 1987 this industrial plant reports its emission data of radioactive substances, see Figure 1 (top), to the mandated Ministry, which since the end of 2010 is the Ministry of Economic Affairs, Agriculture and Innovation.

The fluctuations with time are caused by changes in throughput, industrial process, and differences in the composition of the ores. Igneous rocks, of volcanic origin, contain less natural radionuclides and heavy metals (Cd, Pb, Zn) than sedimentary rocks, but they are not widespread, and are difficult to obtain. The composition of the more common sedimentary rocks varies greatly around the globe. Falck and Wymer 2006 report U-238 activity concentration of 70 Bq/kg for Kola igneous ore, and > 600 Bq/kg for most sedimentary rock. Until the year 2000 the thermal phosphorus plant was using a mix of igneous ore and Florida sedimentary ore, which can have an exceptionally low activity concentration of < 100 Bq/kg U-238, but after 2000 the Florida ore was no longer available (due to the mines becoming exhausted), and after 2002 the delivery of igneous ore also stopped. The consequence was an increased emission to air of NORM and heavy metals.

Because of the high temperatures of the industrial processes, the radioactive particles deposit on aerosols of sizes less than 1 micron (Mora 2011).

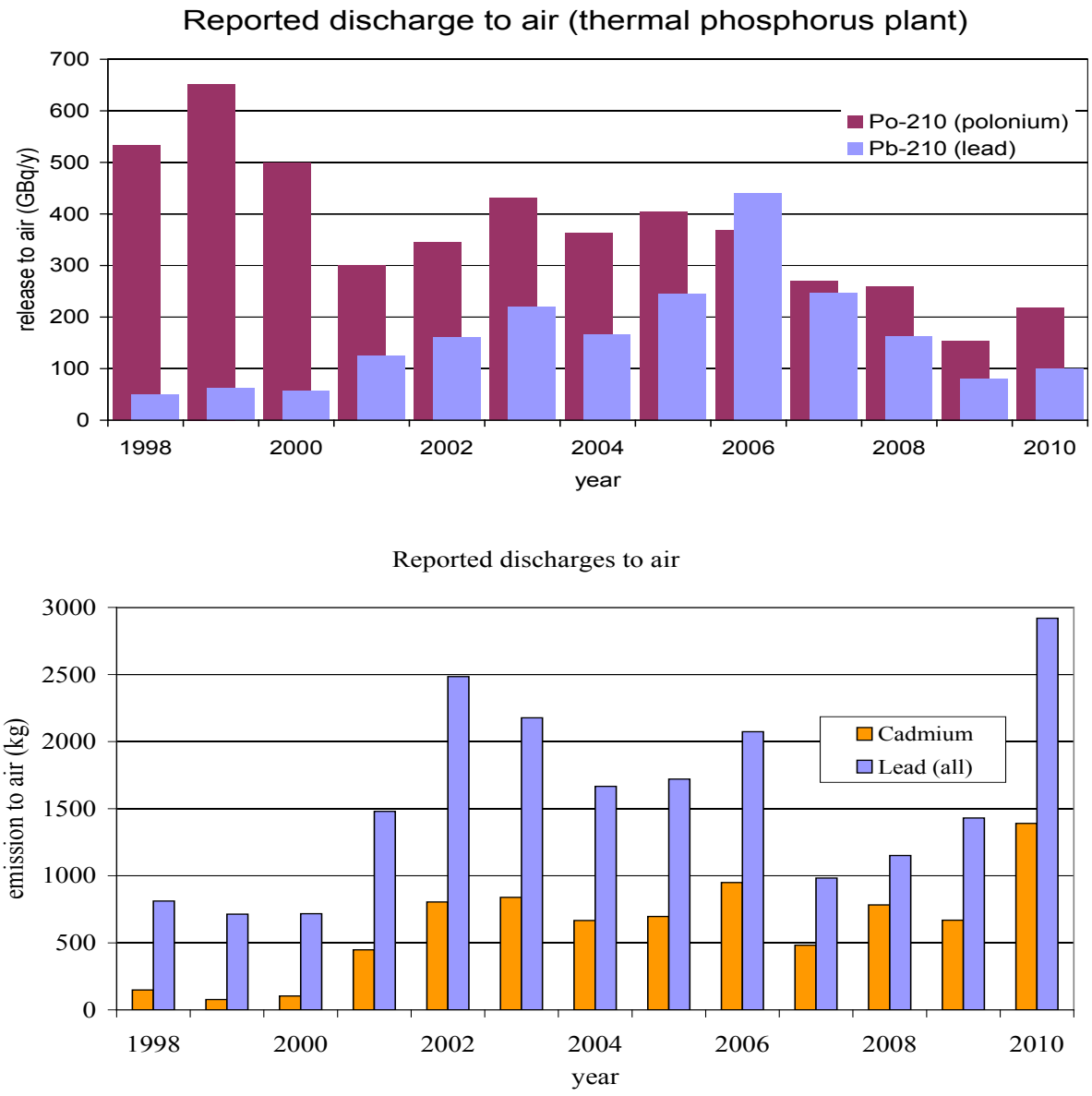

Figure 1. Annual discharges to air of Po-210 and Pb-210 reported by the thermal phosphorus plant in the Netherlands over the years 1998-2010. The emission (Thermphos data 2011) of all lead and cadmium isotopes (chemically determined) is also shown. Comparing the two figures shows that the activity of Pb-210 is not simply proportional to the total weight of lead emitted to air: the ratio varies between 34 to 250 MBq/kg. For comparison: the activity concentration of Pb-210 measured in the precipitator dust and the calcinated dust is 1 MBq/kg (Erkens, 1997).

Additional discharges to air of Po-210 and Pb-210 in the Netherlands arise from a primary steel production plant with blast-furnaces. This plant also reports emission activities to air since 1983. Its emissions are much smaller than the emissions from the thermal phosphorus plant. This is reflected by the limits at the site boundary set in their operating permits: 10 microSv/y for the primary steel plant and 40 microSv/y for the thermal phosphorus plant.

2. Environmental monitoring

The Dutch government has the obligation to measure radioactivity in air, water and soil under the terms of the Euratom Treaty of 1957. The sampling is done on the RIVM premises in Bilthoven, located at over 100 km from the thermal phosphorus plant. Air dust samples are collected weekly with a High Volume Sampler, with a sample volume of 50000 m^3. For a detailed description of the sampling, sample treatment and the analytical method, see Overwater 1998, van Tuinen 1986 and Tax et al. 1994.
Figures 2 and 3 (Groot and Knetsch 2011) show that the average natural background level of Pb-210 in air is 399 microBq/m^3 and the yearly deposition rate varies between 60 and 180 Bq/m^2/y. The yearly deposition rate of Po-210 is of the order of 10 to 35 Bq/m^2/y (Figure 4).

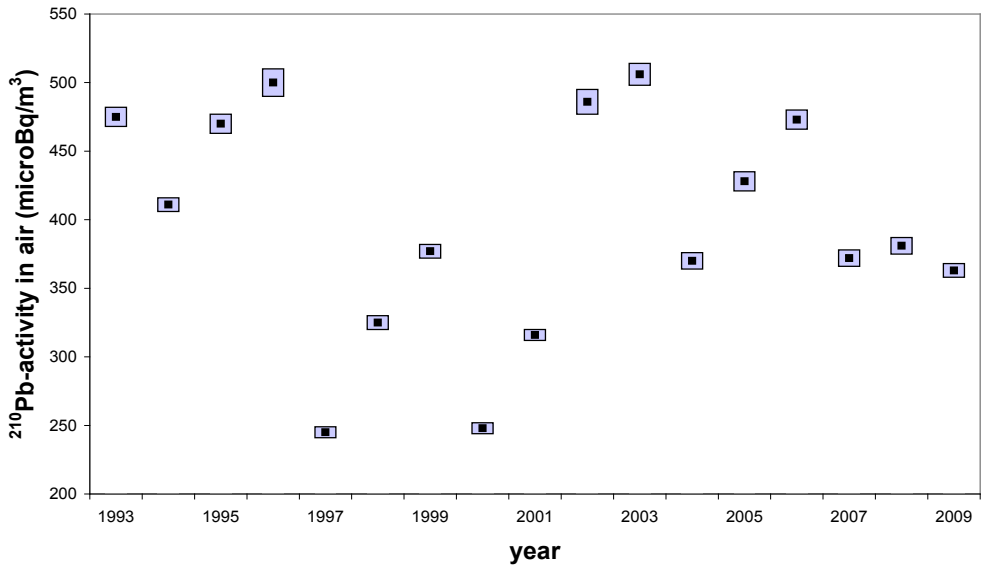

Figure 2. Yearly Pb-210 activity in air in Bilthoven, NL. Yearly averages (black dot) are given with a 68% confidence range (coloured bar).

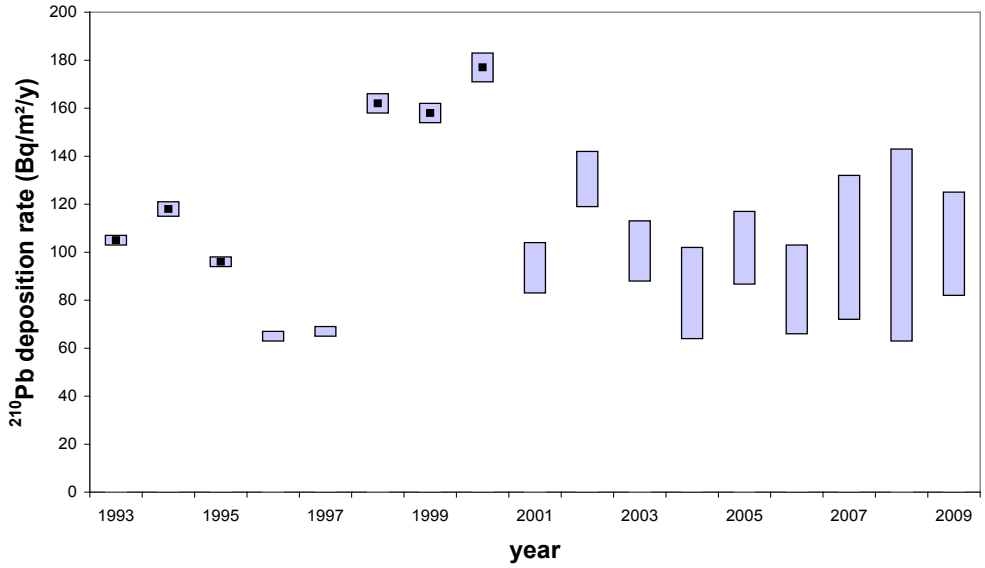

Figure 3. Yearly Pb-210 activity deposited in Bilthoven, NL. Yearly averages (black dot) are given with a 68% confidence range (coloured bar). If at least one weekly measurement is at or below the detection limit, only the 68% confidence range is given.

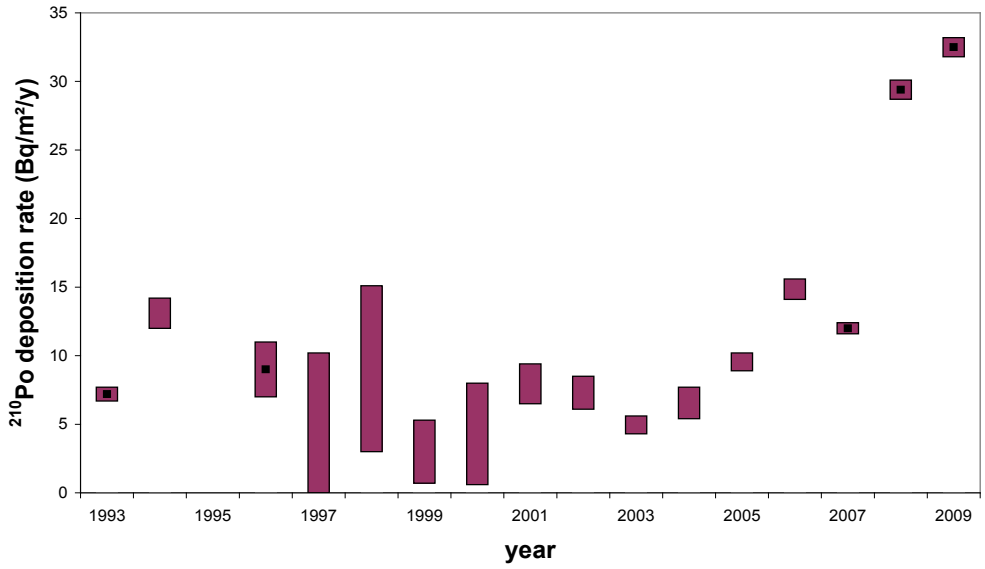

Figure 4. Yearly Po-210 activity deposited in Bilthoven, NL. Yearly averages (black dot) are given with a 68% confidence range (coloured bar). If at least one weekly measurement is at or below the detection limit, only the 68% confidence range is given.

3. Air dispersion modelling

The emissions from the plant are modelled with the air dispersion model OPS (van Jaarsveld 2004). OPS is used within the Dutch national air quality collaboration programs GCN and GDN of the Dutch Ministry of Infrastructure and the Environment and the Ministry of Economic Affairs, Agriculture and Innovation: the OPS air quality maps produced within that project have legal status (Velders et al. 2011). The version 4.3.12 of July 2011, where some parameters such as the roughness surface length along the trajectory have been improved, is used here. The height of the emission stack is 55 m with 1.5 MW heat content.

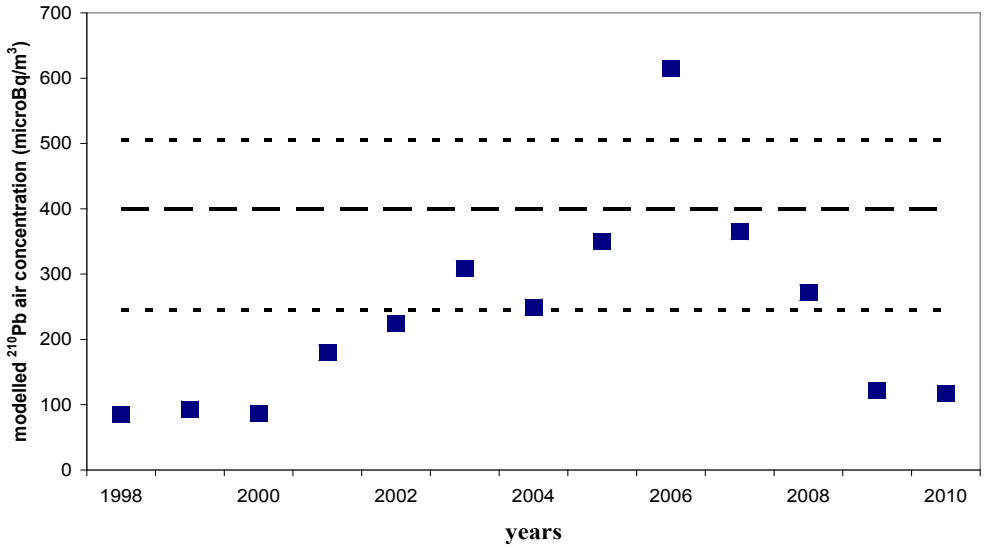

Figure 5. Excess air concentration modelled with the OPS air dispersion model at the Nieuwdorp village, 4 km distance from the plant and in the predominant wind direction. Units are microBq/m^3. The dashed line gives the average over 1998 and 2007 measured at 100 km distance in Bilthoven, the dotted lines the extreme values (from Figure 2).

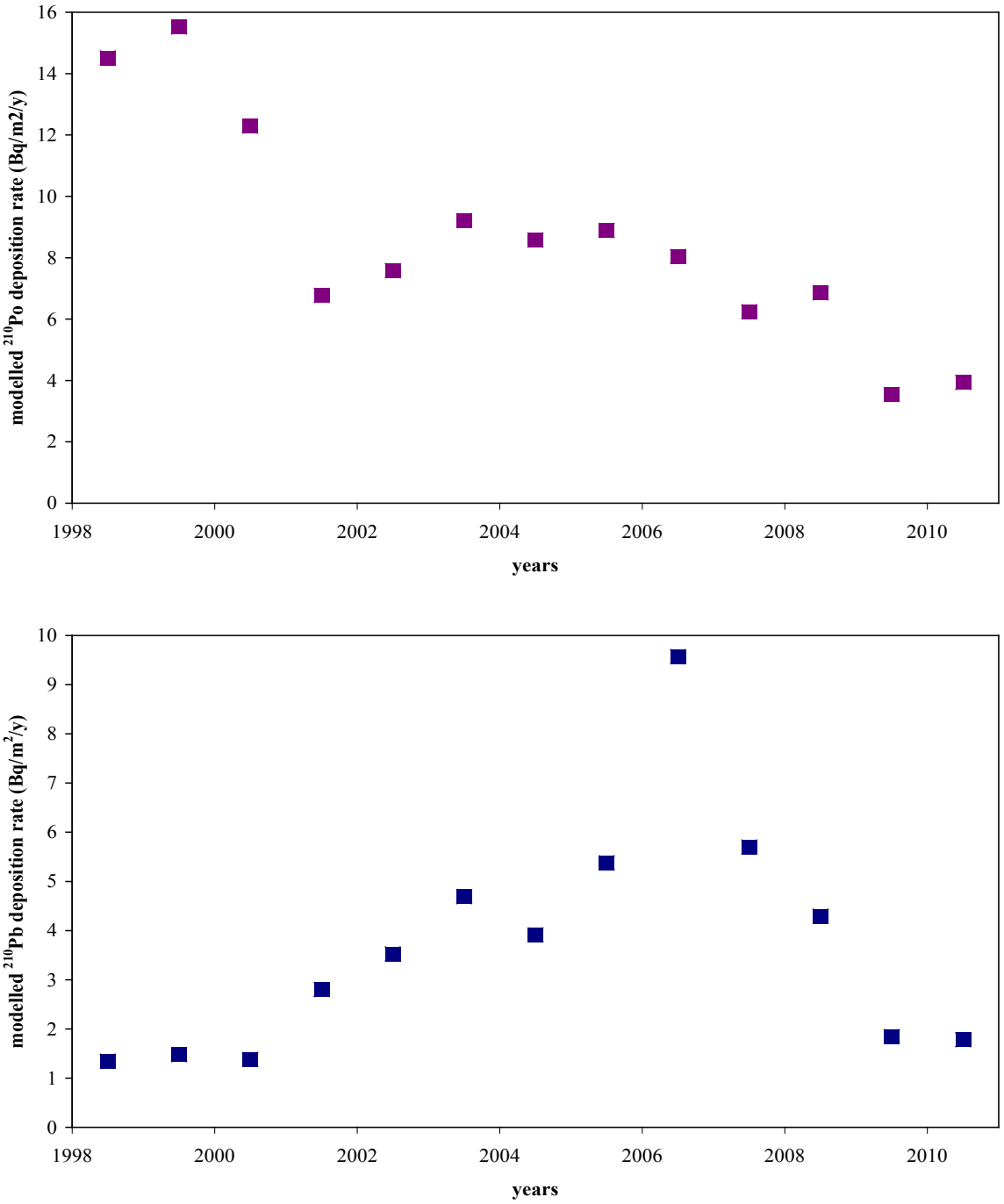

Figure 6. Modelled deposition rates calculated with the OPS air dispersion model at the Nieuwdorp village, 4 km distance from the plant and in the predominant wind direction. Units are Bq/m^2/y. The largest emissions to air of Pb-210 took place in 2006.

The comparison of Figure 6 with Figures 3 and 4 shows that, while the Po-210 deposition rate calculated at 4 km distance from the plant is of the same order of the background level, the Pb-210 deposition rate is an order of magnitude lower. This is a consequence of the submicron size of the particles: the higher the particle sizes, the higher is the deposition rate predicted by the model.

Assuming an emission of 500 GBq/y from the thermal phosphorus plant, the OPS air dispersion model predicts a deposition rate of 1.2 Bq/m^2/y averaged over a square area of approximately 10^5 km^2 covering all of the Netherlands, which is negligible when compared to the natural background, which varies between 100 and 170 Bq/m^2/y. It follows that we cannot subscribe the conclusion of Beks 1998, where the emission

from industrial sources is deemed significant for the measured deposition rates in the Netherlands. In the past the industrial emissions to air were indeed larger than at present (they were estimated at 1700 GBq/y in Beks 1998): however in that paper the flux is calculated making the assumption that all the emission is deposited on a square surface covering the Netherlands. For high temperature processes, which are responsible for most of the emission, the submicron particles will travel much further, beyond the Dutch national borders (Tanzi 2008).

4. Estimates of effective dose

For the estimate of the effective dose, the screening approach of IAEA, 2001 is followed. For external radiation and the ingestion of contaminated farmland produce the following assumptions are made for the dose associated to each calendar year: the industry starts its emission 25 years before the reported calendar year, at an emission rate equal to the rate reported in that calendar year.

The ingrowth of the Pb-210 daughters Bi-210 and Po-210 is also modelled (with the KREM2 model, Tanzi 2010). The yearly ingestion of 19 kg of fruit is also taken into account in the estimate of the ingestion dose, in addition to the 51 kg of tuberous plants, 71 kg of cereals, 10 kg of meat (cow, sheep), 147 litres of milk and 42 kg of vegetables. With the exception of 3.5 kg of leafy vegetables, which are assumed to be consumed locally, the activity concentration in food is averaged over all of the Netherlands. Table 1 shows the dose estimates: for each year these estimates are scaled with the reported activity emitted to air (top of Figure 1). Figure 7 shows a map of the estimated committed dose for the year 2010.

Table 1. Ingestion dose calculated with average meteorology 1998-2007, averaged activity concentration in food and fodder over all of the Netherlands.

	potatoes	cereals	fruit	vegetables	milk	meat	total
Yearly consumption (kg)	51	71	19	42	147	10	340
500 GBq/y Po-210 Effective dose (microSv/y)	0.3	0.2	0.6	0.6	<0.1	<0.1	1.7
500 GBq/y Pb-210 Effective dose (microSv/y)	0.7	0.3	0.6	0.7	<0.1	<0.1	2.3

For comparison, the same KREM model can be applied to determine the effective dose due only to the measured environmental concentrations. Assuming for simplicity (the measuring location of the environmental monitoring is inland while the thermal phosphorus plant is located on an estuary) the environmental monitoring values of 500 microBq/m^3 for air concentration and 100 Bq/m^2/y for the deposition rate, the effective dose at equilibrium, reached after 10 times the half-life of 22.2 years of Pb-210, is 163 microSv/y from Pb-210 (in equilibrium with Bi-210), of which 23 microSv/y are due to inhalation. The measured deposition rate of 10 Bq/m^2/y of Po-210 contributes an additional 7 microSv/y.

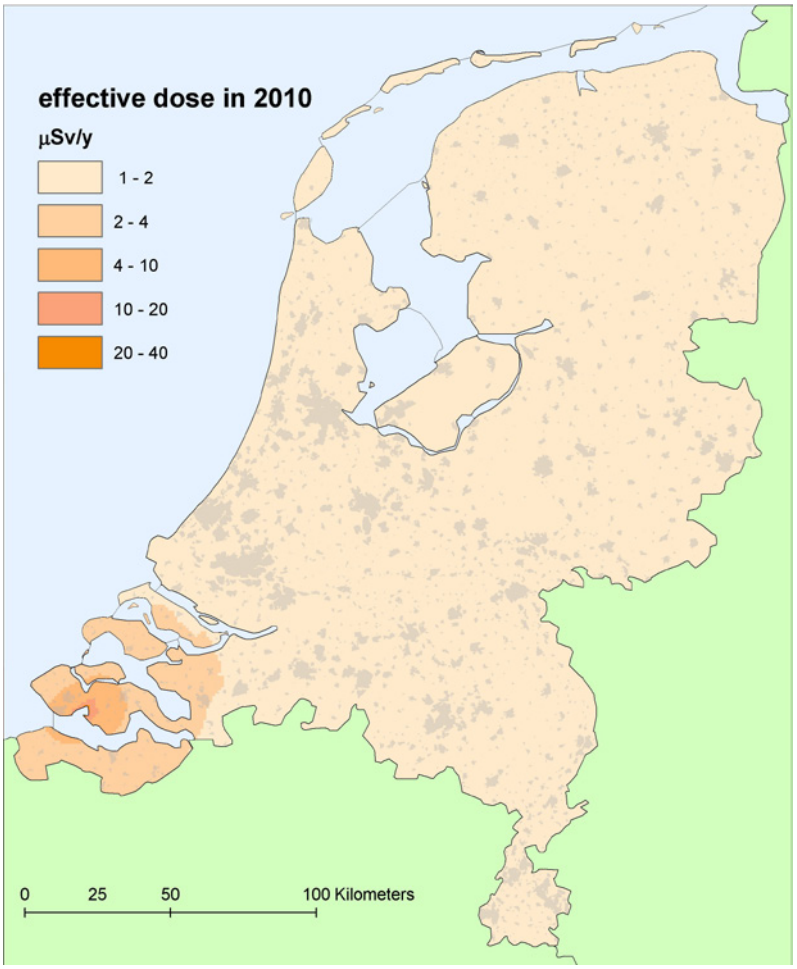

Figure 7. Effective dose estimated with the KREM2 model. Housing is indicated by the grey areas. The dose falls under 20 microSv/y at a few hundred meters distance from the emission point. This estimated dose may be compared with the 170 microSv/y which are estimated by the same model from the measurements of the natural background of Pb-210 and Po-210 in the middle of the country.

From figure 7 the collective dose can be calculated making use of the known population density distribution. However, in order to stress the variations in emission throughput, a climatology (i.e., average weather data) is used for a long series of data (Figure 8). Compared to previous estimates (Tanzi 2010), the addition of ingestion of fruit causes an approximate 30% increase in the dose, while an additional increase can be attributed to changes in the air dispersion model with respect to the previous version.

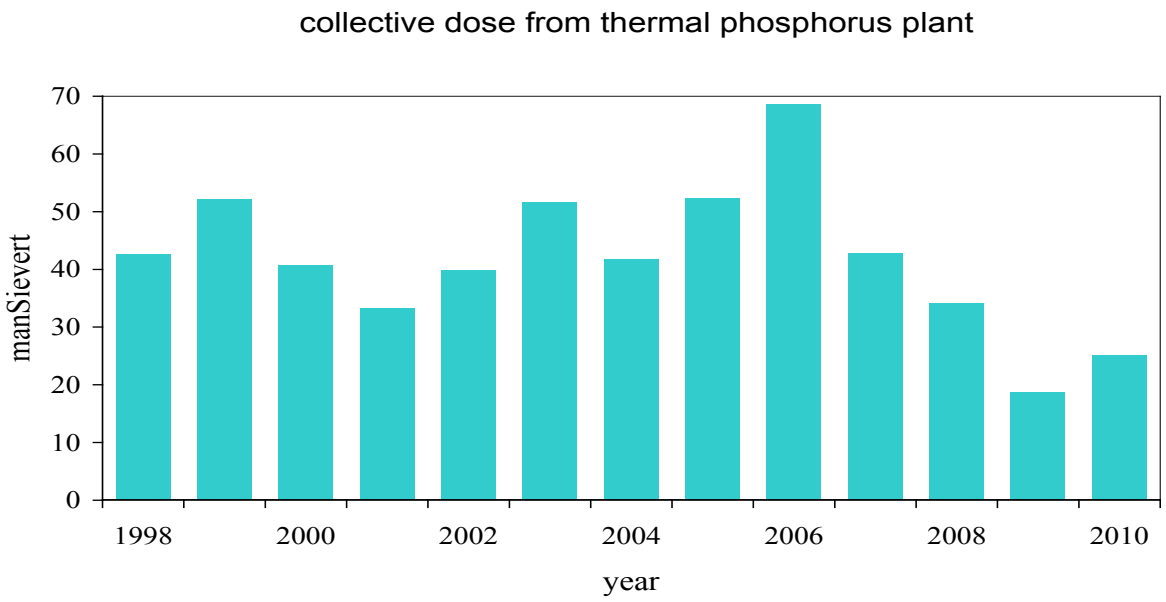

Figure 8. Collective effective dose from the thermal phosphorus plant, estimated with the KREM2 model, with the 1998-2007 climatology.

4. Conclusions

Air dispersion modelling of the only thermal phosphorus plant in Europe shows that the contribution of the NORM emissions to the environment in the vicinity of the plant is comparable to the natural background level, of 399 microBq/m^3 of Pb-210 in air and a deposition rate varying between 60 and 180 Bq/m^2/y, which are determined by weekly measurements at the RIVM institute, at a distance of 100 km from the plant.

In addition to dose estimates based on the modelled air concentration, a (conservative) committed ingestion dose is determined by modelling the uptake of the radionuclides Pb-210, Bi-210 and Po-210 from contaminated farmland. A food basket is assumed to be fairly representative for the nutritional habits of the population of the Netherlands. The ingestion of 19 kg of fruit is also taken into account. Ingrowth of Po-210 from the deposited Pb-210 is also modelled. The largest contribution to the collective effective dose is from ingestion, which is in the order of 1 microSv/a committed dose per inhabitant in 2010. This can be compared to the estimate of 170 microSv/y due exclusively to the environmental background.

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Preliminary screening assessment of the potential impact of the phosphate industry on wildlife.

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Abstract

The activities of the phosphate industry may lead to enhanced levels of naturally occurring radioactivity in terrestrial and freshwater ecosystems. We here perform a preliminary environmental risk assessment (ERA) of the activities of the phosphate industry (phosphate ore mining, phosphate fertilizer factories, phosphate export platforms). We evaluated the environmental impact of 5 phosphate fertilizer plants (located in Belgium, Spain, Syria, Egypt, Brazil) and one phosphate-mine and phosphate-export platforms in the harbour (both located in Syria) These sites were selected because of the enhanced concentrations of naturally occurring radionuclides in the surrounding environments. The ERICA non-human biota assessment tool was used to predict radiation dose rates to the reference organisms and associated risks. Reference organisms were those assigned as default by the ERICA Tool. Potential impact is expressed as a risk quotient (RQ) based on a radiation screening value of 10 μGy h^{-1}. If RQ<1, the environment is unlikely at risk. For all the cases assessed, RQ exceeded 1 for at least one of the reference organisms. ^{226}Ra or ^{210}Po were generally the highest contributors to the dose. At the Huelva estuary (Spain) and the terrestrial environment around the P-mine in Palmyra (Syria) the ecosystems are predicted most at risk.

Keywords: Environmental impact assessment, wildlife, radioactivity, releases, phosphate industry

1. Introduction

The need for investigating potential risks induced by contaminants on non-human biota and ecosystems is now internationally recognized (ICRP, 2003, 2007; IAEA, 1992; UNSCEAR, 1996). Recommendations and guidelines on international level and a comprehensive system to protect the environment from ionizing radiation are under development. As a consequence, a number of approaches/tools to estimate dose rates to wildlife have been developed and some of them are being used in a regulatory context (Copplestone et al., 2001; US-DOE, 2002). Initially, risk assessment focused exclusively on human health protection but the demand for ecological risk assessment (ERA) has now been extended to include wildlife. As a consequence, ecological or environmental risk assessment (ERA) as a science has undergone considerable development in the last decades with guidelines being developed (Environment Canada, 1997; EC, 2003). ERA is an increasingly important component in any decision-making process that aims to provide transparent management decisions on environmental practices and associated problems.
Phosphate rocks contain relatively high concentrations of naturally occurring radioactive materials from the uranium and thorium decay series (^{238}U and ^{232}Th). The mean uranium content in the ore from Moroccan origin is 125 mg kg^{-1} (1500-1700 Bq kg^{-1} ^{238}U; 1500-1700 Bq kg^{-1} ^{226}Ra; 10-200 Bq kg^{-1} ^{232}Th; Martin *et al.*, 1996). Phosphate ores are particularly insoluble and the primary step in the production process is the leaching of phosphate from the rock with strong acids. In 90% of the cases, ore is treated with sulphuric acid to produce phosphoric acid and gypsum. Uranium and thorium become enriched in the fertiliser to about 150% of their original concentrations and radium reduced to 10% of the original concentration. About 80% of the ^{226}Ra, 30% of the ^{232}Th and 14% of the ^{238}U is left in the phosphogypsum waste. The production of 1 tonne of phosphate requires the extraction of 3 tonnes of ore resulting in the generation of 4 to 5 tonnes of phosphogypsum with a mean ^{226}Ra content of 800-1250 Bq kg^{-1}. Historically,

the local dump sites, containing TBq of radium, are often unprotected from rainfall and are hydraulically connected to surface waters and to the shallow aquifers. The ^{226}Ra present is fairly insoluble but, given the high concentration of calcium present in the waste, it can be solubilised.
If hydrochloric acid is used to extract phosphate from the ore, ffertilizers and chemicals free from radioactivity is produced and most ^{226}Ra present in the phosphate ore is released in the liquid effluent. The ^{238}U released from the ore will be precipitated by lime addition and build up with CaF_2 sludge on the dump site. Adding a $BaSO_4$ precipitation step will effectively decontaminate the liquid effluents but results in an accumulation of ^{226}Ra in the dump site and may create local environmental problems due to ^{222}Rn emissions (Baetslé, 1991).
Mining, milling, transporting of phosphate ores, manufacturing of phosphate fertilizers and using phosphate fertilizers containing uranium are ways in which workers, public and environment are exposed to enhanced natural radioactivity (IAEA, 2004). Most of these natural radionuclides are found in the solid waste of the phosphate fertilizer industry such as phosphogypsum, and to a lesser extent in discharged effluents and dust. Many studies in the world have been carried out to assess the risk to man and the environment (e.g. Othman and Al-Masri, 2007; Carvalho et al., 1997; Martinez et al., 1994).
Radon emanation and particulate air emissions from the mine areas, phosphogypsum piles, from phosphate ore storage and loading activities in harbours, leaching of radionuclides from phosphogypsum into groundwater and effluent discharges to rivers and marine environments have resulted in contamination of the surrounding environment. As a result, enhanced concentrations were recorded in surrounding soil and plants, sediment, water and aquatic organisms, marine biota, groundwater (e.g. Carvalho et al., 1997; McCartney et al., 2000; IAEA, 2004; Villa et al., 2009)
A preliminary assessment of the potential impact on wildlife by the P-industry was carried out for following 5 case studies: (1) Belgium: P-fertilizer plant at Tessenderlo-Chemie; (2) Syria: P-mining (Palmyra), P-fertilizer plant (Homs) and P-export platforms (Tartuous port); (3) Spain: P-fertilizer plant (Huelva estuary); (4) Egypt: P-fertilizer industry (Nile River); (5) Brazil: P-fertilizer plant (State of Gioás, Bugre and Mogi Rivers).

2. Approach

ERA is a multistage process, starting with hazard identification, followed by exposure, effects and risk assessment. The first stage of any ERA is the problem formulation, which deals amongst others with the characterisation of the contaminant source term and the identification of potential ecological targets and the associated exposure pathways. The ERICA non-human biota assessment tool (Beresford et al. 2007) was used to calculate dose rates to selected biota based on this information.

2.1. Derivation of environmental concentrations

Information on environmental contamination levels (soil, sediment and water concentrations) were collected from literature data. For soils and sediments in the vicinity of P-mines or P-export platforms in harbours, secular equilibrium for the ^{238}U chain was assumed and for broken chains, equilibrium with the most appropriate member of the decay chain was assumed. For missing data, it is assumed that ^{234}Th, ^{234}U and ^{230}Th are in equilibrium with ^{238}U and that ^{210}Po is in equilibrium with ^{210}Pb and ^{226}Ra. However, assuming 20 % loss due to ^{222}Rn emanation, the ^{210}Po and ^{210}Pb concentrations in soil and sediment will be 80 % of the concentration of ^{226}Ra. Generally no information was available for ^{232}Th chain radionuclides. If data were presented, ^{232}Th chain radionuclides were at least a factor 10 lower in concentration than ^{238}U chain radionuclides and were therefore not considered in the assessment, except for the Brazil scenario, where reported concentrations for ^{238}U and ^{232}Th were comparable. Since the Dose Conversion Coefficients (DCC) of a parent nuclide in the ERICA tool includes all daughters with half-life up to 10 d, only daughter nuclides with half-life > 10 d were considered.
For releases from phosphogypsum piles (H_2SO_4 wet process), no equilibrium with the parent nuclide was

assumed for ^{226}Ra since U is mainly retained in the fertilizers. For releases from the phosphate-fertilizer plant of Tessenderlo-Chemie (TC) in Belgium (HCl wet process) to the aquatic environment, 30-40 % of the radium in the ore is retained in the CaF_2 sludge together with virtually all U and Th. The contamination of the surface water was mainly due the radium released with the soluble $CaCl_2$ waste streams in which no U or Th was present. Therefore, no equilibrium with the parent was supposed for ^{226}Ra released to the rivers.
If concentrations in water were not provided, they were calculated with the default solid-liquid coefficients (K_d) provided by the ERICA tool. Also the concentration ratios (CR) for the selected radionuclides and the default reference organisms used in the assessment were those provided default by the ERICA tool (Beresford et al., 2007).
Only the ^{238}U series and ^{232}Th series (if data available) were considered in the dose evaluation. The ^{235}U-series was not considered.

2.2. Selection of reference organisms, assessment of dose rate and associated risk

The ERICA tool (Beresford et al., 2007) was used to assess radiation dose rates to the reference organisms and associated risks. Reference organisms were those assigned as default by the Tool. Potential impact is expressed as a risk quotient (RQ) based on a radiation screening value of 10 μGy h^{-1} (Garnier-Laplace and Gilbin, 2006; Andersson et al., 2008). This derived screening value screens out sites where contamination is of no concern for fauna and flora. Hence, if RQ≤1, the environment is unlikely at risk and requires no further action. If RQ>1, the assessment should continue in a higher tier, using site-specific information. All assessments performed in present screening level assessment are Tier 2 assessments. If RQ>1, this implies that more thorough assessment at Tier 3 is required.

3. The case studies

3.1. Belgium – Phosphate-fertilizer production with HCl wet process at Tessenderlo Chemie

Tessenderlo Chemie treats Moroccan ore at Tessenderlo and Ham, Belgium. The hydrochloric acid leaching process is applied which results in the production of predominantly CaF_2 containing waste. $CaCl_2$ is formed as an effluent and until 1995, 70% of the ^{226}Ra in the raw phosphate was released with the liquid effluent leading to an accumulation of radium in the bed sediment. By introducing a $BaSO_4$ precipitation step, radium solubility was decreased and nowadays most radium is disposed on the CaF_2 dump (Baetslé, 1991). For the ERA, we use data that are presented in Tables 1 (Vanmarcke and Paridaens, 1999) and Table 2 (FANC 2001, 2003). The values for ^{226}Ra are those recorded in literature; ^{210}Po and ^{210}Pb concentrations in soil and or sediment are assumed to be at 80 % of the ^{226}Ra concentration.

Table 1: Concentrations (Bq kg^{-1}) on right river border of Grote Laak

	^{226}Ra	^{210}Pb*	^{210}Po*
Mean concentrations	811	649	649
Mean concentration for soil sampled at highest dose rate locations	5822	4658	4658

** ^{210}Po and ^{210}Pb concentrations in soil are calculated taking 80 % of the concentration for ^{226}Ra*

Table 2: ^{226}Ra concentrations in river water (Bq L^{-1}) and sediment (Bq kg^{-1}) of Grote Laak and Winterbeek (FANC, 2001, 2003) (Average and maxima for period 1998 - 2001)

		1998		1999		2000		2001	
		Water	Sediment	Water	Sediment	Water	Sediment	Water	Sediment
Grote Laak	average	0.14	818	0.18	528	0.21	475	0.13	327
	maxima	0.37	1200	0.43	902	0.34	629	0.38	461
Winterbeek	average					0.33	676	0.17	523
	maxima					0.63	852	0.34	629

3.2. Syria: Phosphate-mining (Palmyra), Phosphate-fertilizer plant (Homs), Phosphate-export platforms (Tartuous port)

The environmental impact assessment for the phosphate-industry in Syria is carried out using the environmental concentrations presented by Othman and Al-Masri (2007). In Syria, the main phosphate mines are situated near Palmyra. For more than 20 years, most of the mined phosphate ore (around 2.8 million tonnes per year) has been exported in large quantities via one of the main Syrian ports (Tartous) situated on the eastern part of the Mediterranean Sea. Since the early 1980s, about 300,000 tonnes of phosphate ore are locally processed and transferred from the mines by train to the phosphate fertilizer factory in Homs. Ores are treated with sulphuric acid and the phosphogypsum sludges are currently placed in a large plastic lined depot near the factory. The depot was built in 1995 and since then disposition of phosphogypsum outside this pit is prohibited in order to avoid additional environmental pollution. Phosphogypsum is transferred from the factory and pumped into the pit through pipes by mixing with water. The water is pumped back to the factory for re-use after filtration.

Table 3: Concentrations of natural radionuclides in soil samples (Bq kg^{-1}) collected in the vicinity of the mine (all data from Othman and Al-Masri, 2007)

	^{238}U*	^{234}Th	^{234}U	^{230}Th	^{226}Ra	^{210}Po	^{210}Pb
Mine area Village, main gate Table 2 line 6	1168	750	*750*	*750*	820	1557	1184
P-fertilizer plant East of factory Table 5 line 6	38	*38*	*38*	*38*	56	60.6	39.7
Soils collected near load platform Tartuous city, 2 km S. East	159	*159*	*159*	*159*	144	238	224

** U measured in mg kg^{-1} was assumed to be ^{238}U; data presented in italic are derived according to the equilibrium principle*

Naturally occurring radionuclide concentrations were monitored in the surrounding environment of mines, phosphate fertilizers factory and phosphate export platform. Air particulates, soil, water, biota and plant samples were collected and analyzed.

For the ERA, the data presented in Table 3 were used. As can be deduced from the reported monitoring data, secular equilibrium did not occurring. The high ^{210}Po and ^{210}Pb concentrations may be due to high radon concentrations in the area and hence high ^{210}Po and ^{210}Pb fluxes. Therefore, radon gas, which is generated from the mine area, the gypsum piles and the phosphate piles stored near the platform in large quantities before exporting, can be considered the main hazard of these sites. The impact of radon gas on wildlife is not assessed in this study as it is not default available in the ERICA tool. Current developments (Vives i Batlle et al., 2011-2012) will make these assessments possible in the future.

3.3. Spain: phosphate-fertilizer plant (Huelva estuary)

The Huelva Estuary in Huelva, Spain, has historically been affected by waste releases, enriched in radionuclides from the U-decay series discharged by local factories devoted to the production of phosphoric acid and phosphate fertilizers (Villa et al., 2009). The Odiel and Tinto River, a system of channels and several watershed areas affected by tidal flooding are the main elements of this estuary. Since 1998, releases of phosphogypsum to the Huelva Estuary were prohibited and input of natural radionuclides into the rivers was drastically reduced. In Table 4 the environmental concentrations used in this ERA are shown. These data are based on data provided by Villa et al. (2007) in their Tables 1 and 2 for Odiel-4 (O4).

Table 4: Concentrations of ^{226}Ra, ^{210}Po and ^{210}Pb in water (Bq l^{-1}) and sediment (Bq kg^{-1}) for the Huelva estuary at Odiel-4 (Villa et al., 2007) recorded in 1990 and 1999.

	Water			Sediment		
	^{226}Ra	^{210}Pb	^{210}Po	^{226}Ra	^{210}Pb	^{210}Po
1990	86	29	*29*	432	624	*624*
1999	12	2.3	*2.3*	318	615	*615*

Data presented in italic are derived according to the equilibrium principle

3.4. Egypt: phosphate-fertilizer industry (Nile)

Mourad et al. (2009) conducted an environmental survey in the vicinity of a phosphate fertilizers production plant discharging to the Nile (Egypt). They investigated the environmental pollution caused by the wastewater from this (further undefined) phosphate fertilizer plant by, amongst others, monitoring the concentrations of these natural radionuclides in environmental samples (water, sediment and plant). Samples were collected in the area around the outlet of the wastewater discharge pipes of a superphosphate fertilizer company located in the Nile Delta region, Egypt. Sediment samples were taken at 20-30 cm depth. The dominant plant species *Phragmites australis* (a graminae) was collected close to the Nile river shore. The environmental concentrations used for the ERA are presented in Table 5. For sediments, the ^{226}Ra daughter nuclides were considered to be 80 % of the concentration of ^{226}Ra and for ^{232}Th the whole decay chain was considered in equilibrium.

Table 5: Concentrations of ^{226}Ra and ^{232}Th in sediments (Bq kg^{-1}), water (Bq l^{-1}) and plants (Bq kg^{-1}) in vicinity of outlet of phosphate-fertilizer industry discharging to the Nile.

Sample	Position	^{226}Ra	^{232}Th
Sediment	Upstream	17.1	10.9
	Downstream	24.8	16.1
Water	Upstream	0.6	
	Downstream	0.3	
Plants	Upstream	11.8	6.9
	Downstream	17.0	22.5

3.5. Brazil: phosphate-fertilizer plant (State of Gioás, Bugre and Mogi Rivers)

Santos and co-workers (2006) investigated the environmental impact of disposed phosphogypsum from the P-fertilizer complex located in the State of Goiás, Central Brazil. The Bugre River (BR), tributary of the Mogi River (MR), is located close to the gypsum pile. The aquatic environment near the disposal area was assessed by measuring natural radionuclide concentrations in river water and sediments in vicinity of gypsum dump. Data for the ERA were extracted from Santos et al. (2006, Table 3). For the Mogi River, the average of 9 sampling locations was taken (Table 6). Since the screening dose rate derived by ERICA only

relates to the dose increment, we also considered background radiation levels, measured 5 km away from the gypsum piles on a location opposite to the predominant wind direction. These soil concentrations were used as background values to compare the sediment concentrations with.

Table 6: Concentrations of ^{232}Th and daughters and ^{238}U and daughters in sediments (Bq kg^{-1}) of the Bugre and Mogi River impacted by the Phosphate industry and background (BG – deep core soil profile) in the State of Goiás, Brazil.

	^{232}Th	^{228}Ra	^{228}Th	^{238}U	^{234}Th	^{234}U	^{230}Th	^{226}Ra	^{210}Pb	^{210}Po
Bugre River	198	86	*86*	118	*118*	*118*	*118*	43	56	*56*
Mogi River (mean of 9 locations)	93	73	*73*	72	*72*	*72*	*72*	43	60	*60*
Background (BG)	61	71	*71*	54	*54*	*54*	*54*	45	57	*57*
Bugre River minus BG	137	15	*15*	64	*64*	*64*	*64*	-2	-1	*-1*
Mogi River minus BG	32	2	*2*	18	*18*	*18*	*18*	-2	3	*3*

Data presented in italic are derived according to the equilibrium principle

4. Results and discussion

4.1. Belgium – phosphate-fertilizer production with the HCl wet process at Tessenderlo Chemie

In Table 7, RQs are presented for the terrestrial wildlife exposed to concentrations monitored on the river banks of the Grote Laak. RQs were derived for average concentrations observed and averages of hot spots. The latter is an extremely conservative assumption, certainly for migratory fauna.

Table 7: Risk Quotients (RQ) to terrestrial wildlife residing at river banks of the Grote Laak and exposed to average soil concentrations or average hot spot soil concentrations

Organism	**Average soil concentration**	**Average soil concentration of hot spot areas**
Amphibian	0.4	*3.1*
Bird	0.5	*3.3*
Bird egg	0.4	*3.1*
Detritivorous invertebrate	*1.1*	*7.8*
Flying insects	*1.0*	*7.4*
Gastropod	0.6	*4.0*
Grasses & Herbs	0.7	*5.1*
Lichen & bryophytes	*15.1*	*108.2*
Mammal (Deer)	0.3	*2.3*
Mammal (Rat)	0.4	*2.6*
Reptile	0.4	*3.1*
Shrub	0.5	*3.5*
Soil Invertebrate (worm)	*1.1*	*7.7*
Tree	0.1	0.8

Italics refer the values higher the RQ of 1 for a screening value of 10 µGy h^{-1}

Table 7 reveals that the average soil concentrations are unlikely to impact the terrestrial fauna and flora living on the river bank of the Grote Laak. For detritivorous insects and soil invertebrates, RQs are slightly above one but effects data provided within the ERICA tool show no effects at the associated dose rates. Dose rates to lichens and bryophites are predicted to be 150 µGy h^{-1} for the average soil concentration and exceed the screening dose rate by a factor of 15. There are no effects data available in the ERICA database for these or higher dose rates. ^{226}Ra is the highest contributor to the dose, except for lichens and

bryophites. The high dose rate for the latter species are due to the very high concentration ratio of ^{210}Po (CR=6 kg kg^{-1}), reflecting the high mobility of ^{210}Po. For all scenarios analysed, dose rates were almost entirely due to internal exposure.

The situation is very different for the aquatic environment of the Grote Laak. High RQs are obtained for the 4 years monitored even for the average concentrations reported (and hence *in extenso* for the maxima recorded). For 7 groups of reference organisms, the predicted dose rate exceeds the screening dose rate of 10 μGy h^{-1}.

Table 8: Risk Quotients (RQ) obtained for the freshwater ecosystem of the Grote Laak and Winterbeek exposed to average or maximal sediment and water concentrations.

	Grote Laak								Winterbeek			
	Average				Maximum				Average		Maximum	
Organism	**1998**	**1999**	**2000**	**2001**	**1998**	**1999**	**2000**	**2001**	**2000**	**2001**	**2000**	**2001**
Amphibian	0.23	0.30	0.35	0.22	0.62	0.72	0.57	0.64	0.56	0.29	*1.06*	0.57
Benthic fish	0.28	0.34	0.39	0.24	0.70	0.79	0.62	0.69	0.61	0.32	*1.14*	0.62
Bird	0.24	0.32	0.37	0.23	0.65	0.75	0.59	0.66	0.58	0.30	*1.10*	0.60
Bivalve mollusc	*15.71*	*20.97*	*23.85*	*15.07*	*42.83*	*49.57*	*38.62*	*43.63*	*37.98*	*19.79*	*72.38*	*39.19*
Crustacean	*6.30*	*8.27*	*9.48*	*5.95*	*16.94*	*19.61*	*15.35*	*17.27*	*15.03*	*7.81*	*28.64*	*15.50*
Gastropod	*9.38*	*12.50*	*14.22*	*8.98*	*25.54*	*29.54*	*23.02*	*26.00*	*22.64*	*11.79*	*43.13*	*23.36*
Insect larvae	*6.36*	*8.31*	*9.52*	*5.98*	*17.03*	*19.68*	*15.40*	*17.30*	*15.08*	*7.85*	*28.70*	*15.55*
Mammal	0.24	0.32	0.37	0.23	0.65	0.75	0.59	0.66	0.58	0.30	1.10	0.60
Pelagic fish	0.24	0.32	0.37	0.23	0.65	0.75	0.59	0.66	0.58	0.30	1.10	0.60
Phytoplankton	*11.25*	*15.03*	*17.10*	*10.81*	*30.70*	*35.55*	*27.71*	*31.31*	*27.24*	*14.18*	*51.92*	*28.11*
Vascular plant	*4.87*	6.31	*7.29*	*4.55*	*12.96*	*15.00*	*11.80*	*13.22*	*11.51*	*5.96*	*21.93*	*11.86*
Zooplankton	*11.26*	*15.05*	*17.12*	*10.82*	*30.74*	*35.59*	*27.74*	*31.34*	*27.27*	*14.20*	*51.99*	*28.15*

Italics refer the values higher the RQ of 1 for a screening value of 10 μGy h^{-1}; Underlined values refer to RQ>1 if organism group specific screening values were considered.

At the dose rates predicted for bivalve molluscs and gastropods, some effects were observed: for example for oyster a two-fold increase in frequency of abnormal larvae was reported at a dose rate of 125 μGy h^{-1}. For insect larvae, no effects were observed up to a dose rate of 200 μGy h^{-1}. For all the other organisms for which RQ>1, either no effects were observed for the dose rates obtained or no effects data are provided by ERICA.

Under the PROTECT project, organism group specific screening values were derived (Andersson et al., 2008). For plants, a screening value of 70 μGy h^{-1} was derived, for invertebrates a screening value of 200 μGy h^{-1}. Even if these higher screening values would be applied, RQs would be higher than one (values underlined in Table 8). ^{210}Po followed by ^{226}Ra were the highest dose contributors. As for terrestrial ecosystems, internal exposure was dominant. Since screening assessments are generally conservative, it is very conservative to perform the assessments with maximum concentrations recorded. As expected, RQs are much higher for the maximum concentrations. The same reference organisms are affected.

For the aquatic ecosystem of the Winterbeek, similar conclusions can be drawn. Environmental concentrations are on average two-fold higher, and so are RQs. The same reference organisms are predicted to be affected as for the Grote Laak.

Since the RQs are higher than 1 for both river systems impacted by the releases from the phosphate-fertilizer plant of Tessenderlo, it is advisable to assess the potential impact on the environment further in Tier 3.

4.2. Syria: phosphate-mining (Palmyra), phosphate-fertilizer plant (Homs), phosphate-export platforms (Tartuous port)

From the RQs presented in Table 9, it is clear that the terrestrial environment surrounding the phosphate-mining area is potentially more at risk than those in the vicinity of a phosphate-fertilizer plant or the export platforms of Tartuous port. RQs are not exceeding 1 in the surroundings of the P-fertilizer plant. At the P-export platforms, only for lichens and bryophytes, RQs higher than 1 were obtained and the predicted dose rates are almost entirely due to ^{210}Po. At the predicted dose rate of 50 μGy h^{-1}, no effect on lichens was observed.
For the phosphate-mine scenario, RQ is just above 1 for detritivorous invertebrates, flying insects, grasses and herbs and trees. At these dose rates, no effects on these organisms were observed in literature. For lichens and bryophytes, the predicted dose rate was ~250 μGy h^{-1}. There are no effects data available in the ERICA database for this dose rate.
For all three scenarios, the most dose contributing radionuclide is generally ^{226}Ra, explaining around 90 % of the total dose rate. For grasses and shrubs ^{226}Ra and ^{210}Po equally contributed to the total dose rate (each ~42 %), for trees ^{210}Po exposure explained 70 % of the total dose rate and for lichens and bryophytes 90%.

Table 9: Risk Quotients (RQ) obtained for terrestrial ecosystems in the vicinity of the phosphate-mine at Palmyra, the phosphate-fertilizer plant at Homs, the phosphate-export platforms (Tartuous port)

	Phosphate-mine	Fertilizer plant	Phosphate-export platform
Amphibian	0.45	0.03	0.08
Bird	0.47	0.03	0.08
Bird egg	0.44	0.03	0.08
Detritivorous invertebrate	*1.18*	0.08	0.21
Flying insects	*1.11*	0.07	0.20
Gastropod	0.63	0.04	0.11
Grasses & Herbs	*1.09*	0.05	0.20
Lichen & bryophytes	*26.18*	0.97	*4.91*
Mammal (Deer)	0.33	0.02	0.06
Mammal (Rat)	0.38	0.03	0.07
Reptile	0.44	0.03	0.08
Shrub	0.74	0.04	0.13
Soil Invertebrate (worm)	*1.15*	0.08	0.20
Tree	0.21	0.01	0.04

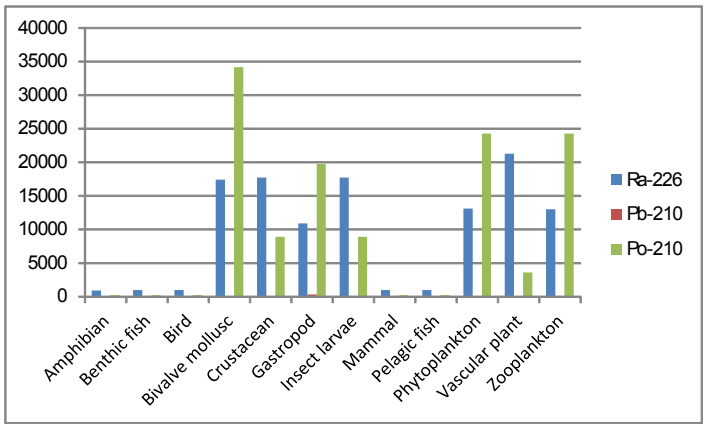
Italics refer the values higher the RQ of 1 for a screening value of 10 μGy h^{-1}

4.3. Spain: phosphate-fertilizer plant (Huelva estuary)

Predicted dose rates and associated RQ (Table 10) for the Huelva estuary are extremely high. For the lower species, effects at these doses are either non-existent or not major. Dose rates similar to those predicted for the vertebrates were shown to result in effects. ^{226}Ra and ^{210}Po generally contribute equally to the dose. During the period 1990 -1999, water concentrations decreased, but sediment concentrations decreased barely. Since dose rate is determined by the internal dose rate, which depends solely on the concentration ratio and the concentration in water, it is almost entirely the water concentration that drives the assessment.

Table 10: Risk Quotients (RQ) obtained for the freshwater ecosystem of the Huelva estuary exposed to contaminated sediment based on results from the 1990 and 1999 monitoring programme. The right figure gives the contribution of the radionuclides present to the total dose (values for 1999).

	1990	1999
Amphibian	*115*	*15*
Benthic fish	*120*	*15*
Bird	*120*	*15*
Bivalve mollusc	*5158*	*514*
Crustacean	*2668*	*318*
Gastropod	*3104*	*312*
Insect larvae	*2668*	*318*
Mammal	*120*	*15*
Pelagic fish	*120*	*15*
Phytoplankton	*3739*	*375*
Vascular plant	*2488*	*326*
Zooplankton	*3736*	*375*



Italics refer the values higher the RQ of 1 for a screening value of 10 μGy h^{-1}

4.4. Egypt: phosphate-fertilizer industry (Nile)

For the downstream sampling location, high RQs (27-70) are obtained for 6 reference organisms (molluscs, crustacean, gastropod, insect larvae, phytoplankton and zooplankton) as shown in Table 11. The associated dose rates are dose rates for which effects are recorded in the ERICA tool. For all 5 vertebrates, RQ is virtually 1. For the upstream location, RQs were lower, but still 6 reference organisms had RQs ranging from 15 to 38. Since the screening value proposed by ERICA (10 μGy h^{-1}) is considered as an additional dose rate (above background dose rate), we calculated RQ based on concentration differences between downstream and upstream locations resulting in very low RQ. So the additional risk due to the radioactive releases from the phosphate-fertilizer industry to the river is negligible.

Table 11: Risk Quotients (RQ) obtained for the aquatic ecosystem of the Nile for locations upstream and downstream the discharge points

	Downstream	Upstream	Downstream-upstream
Amphibian	*1.03*	0.57	0
Benthic fish	*1.07*	0.59	0.0007
Bird	*1.07*	0.59	0
Bivalve mollusc	*70.30*	37.85	0.0008
Crustacean	*27.60*	14.53	0.0010
Gastropod	*41.86*	22.54	0.0008
Insect larvae	*27.60*	14.54	0.0021
Mammal	*1.07*	0.59	0
Pelagic fish	*1.07*	0.59	0
Phytoplankton	*50.90*	28.63	0
Vascular plant	0.34	0.75	0.4125
Zooplankton	*50.74*	27.91	0

Italics refer the values higher the RQ of 1 for a screening value of 10 μGy h^{-1}

Brazil: phosphate-fertilizer plant (State of Gioás, Bugre and Mogi Rivers)

For the Bugre sampling location, relatively high to very high RQs (1.52 to 35.67) are obtained for 6 reference organisms (molluscs, crustacean, gastropod, insect larvae, phytoplankton and zooplankton)

as shown in Table 12. At the associated dose rates either no effects were recorded in the ERICA tool or no data were available, except for insect larvae for which moderate effects were observed (e.g. moderate increase in cytogenetic damage of somatic cells of the insect larvae *Dero obtusa*).

Table 12: Risk Quotients (RQ) at Bugre and Mogi Rivers and for background conditions and for incremental radiation dose at Bugre and Mogi Rivers

	Bugre River	Mogi River	Background	Bugre River minus BG	Mogi River Minus BG
Amphibian	0.37	0.23	0.17	0.20	0.06
Benthic fish	0.38	0.23	0.18	0.20	0.06
Bird	0.37	0.23	0.17	0.20	0.06
Bivalve mollusc	*2.28*	*1.41*	*1.08*	*1.20*	0.34
Crustacean	*6.21*	*3.81*	*2.88*	*3.33*	0.94
Gastropod	*2.26*	*1.39*	*1.06*	*1.20*	0.34
Insect larvae	*6.22*	*3.83*	*2.89*	*3.33*	0.94
Mammal	0.37	0.23	0.17	0.20	0.06
Pelagic fish	0.37	0.23	0.17	0.20	0.06
Phytoplankton	*1.52*	0.94	0.72	0.80	0.22
Vascular plant	*35.67*	*21.80*	*16.37*	*19.30*	*5.43*
Zooplankton	0.63	0.40	0.31	0.32	0.09

Italics refer the values higher the RQ of 1 for a screening value of 10 μGy h^{-1}

For the Mogi river, with lower measured environmental concentrations, RQ was higher than 1 for the same reference organisms as for the Bugre River except for phytoplankton. But also for the background conditions, RQs were higher than one for the same 5 reference organisms. Considering incremental dose rate for Bugre River, RQs were still higher than 1 for 5 Reference Organisms whereas for Mogi River only for vascular plant RQ was still substantially above 1.

5. Conclusions

These few examples of sites where the environment is contaminated by releases from the phosphate industry show that (past) activities may lead to environmental contamination where the ecosystem is at risk (Huelva estuary) or where at least a more profound investigation is required to unequivocally show that wildlife is at risk or not. This may require more in depth site monitoring for environmental concentrations, radionuclide concentrations in biota, effects studies on species concerned in lab and/or in field. When performing field tests, also the non-radioactive contaminants should be evaluated (e.g. heavy metals associated with the phosphate-ore) since effects exerted by conventional contaminants may be more important than effects resulting from exposure to radionuclides.

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Mineral waters and TENORM

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Abstract

Some mineral waters have high activity concentration of natural radionuclides like ^{226}Ra, ^{228}Ra, ^{228}Th and ^{40}K. To reduce activity zeolit filters are used. Natural radionuclides accumulate in zeolite filter and activity in filters can overestimate regulated values. Mesurements of specific activities of natural radionuclides in zeolite filters showed that 100000 m^3 of filtrated mineral water can contaminate filters over regulated value. For this reason filters are periodically cleaned by fresh water and overheated on 80 °C.

1. Introduction

Mineral waters can contain higher activity of natural radionuclides like ^{226}Ra, ^{228}Ra and ^{40}K. Some works in Slovenia exporting mineral waters in Europe and USA. Because of different legislation in different countries regarding specific activities of natural radionuclides in mineral waters thay have to use zeolite filters for extracting some radionuclides from mineral waters. Regarding our legislation (Off. Gaz. of the RS, 67/2002, 115/2003, 48/2004, 49/2004, and 49/2006) works have to take care about specific activities of natural radionuclides in zeolite filters. To avoid problems with enchanced specific activities of natural radionuclides special filtration system was used (Fig. 1).

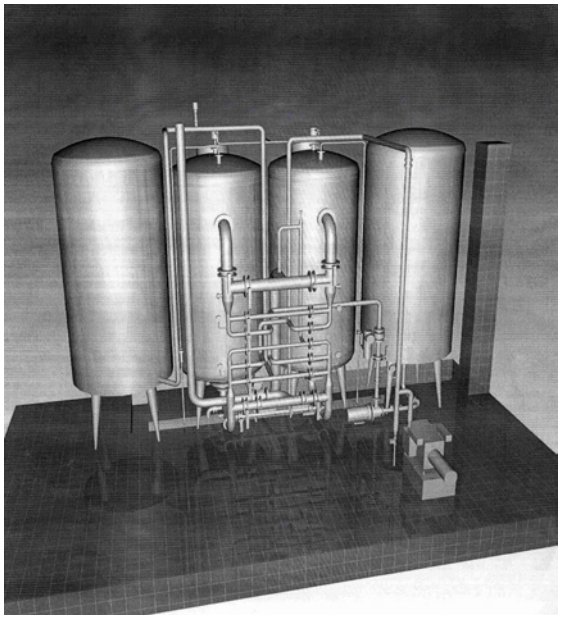

Figure 1. Filtration system for mineral water

Filtration system is a metallic container about 5 m high and it has diameter of 1.8 m. Mineral water comes in through the pipe on the top and get out through the pipe on the bottom of the container. Three layers of sand with different granulation lie on the bottom of the container. Obout 2 m dick layer of zeolit filter is placed on the sand. Filtering system has to be cleaned by 20 m^3 each day. Once a year or after filtering of 50000 m^3 mineral water filtering system is overheated on 80 °C. Because of accumulation of natural radionuclides in zoolit filters specific activities of natural radionuclides can overestimate regulated values.

The main purpose of the project was to define the volume of mineral water flowing through filtering system at which zeolite filter must be overheated not to overestimate exemption levels for natural radionuclides.

2. Sampling and measurements

With special probe three samples of zeolite filter on three different depths were taken. Samples were prepared and gamma lines of natural radionuclides were measured on high purity germanium detector. Samples were taken three times, first at the beginning of filtering, second after about 5000 m^3 filtered mineral water and the last sampling was done after the overheating of filtration system.
Average values of specific activities of natural radionuclides for three samples in different sampling periods were taken into account. Results of the measurements of specific activities of natural radionuclides ^{226}Ra, ^{228}Ra and ^{228}Th are presented in Table 1. On the table also exemption levels for natural radionuclides are presented.

Table 1. Specific activities of natural radionuclides on zeolite filter

	Specific activity (Bq / kg)									Exemption levels
Radionuclide	1. sampling			2. sampling			3. sampling			(Bq/kg)
^{226}Ra	1003,8	±	23,0	1327,0	±	21,3	1067,8	±	39,6	10000
^{228}Ra	1525,2	±	37,1	2083,0	±	35,9	1638,8	±	51,9	10000
^{228}Th	155,9	±	6,8	295,7	±	7,8	159,5	±	17,7	10000
* Decree on activities involving radiation										

Results of measurements show higher specific activities of natural radionuclides on the filter after the second sampling than after the first sampling. It is also evident that after the filter overheating (third sampling) specific activities are reduced almost to the initial value.
From data of measurements and volume of mineral water flowing through the filter in the period between first two measurements the slope of accumulation of natural radionuclides on the zeolite filter was calculated (Fig. 2).
On the Figure 2 accumulation of natural radionuclides ^{226}Ra, ^{228}Ra and ^{228}Th on the filter versus volume of mineral water filtered is presented. The bigest problem represents ^{228}Ra, which can reach exemption level when 100000 m^3 of mineral water is filtered, ^{226}Ra and ^{228}Th reach it after filtration of 160000 m^3 and 360000 m^3 mineral water, respectivelly.

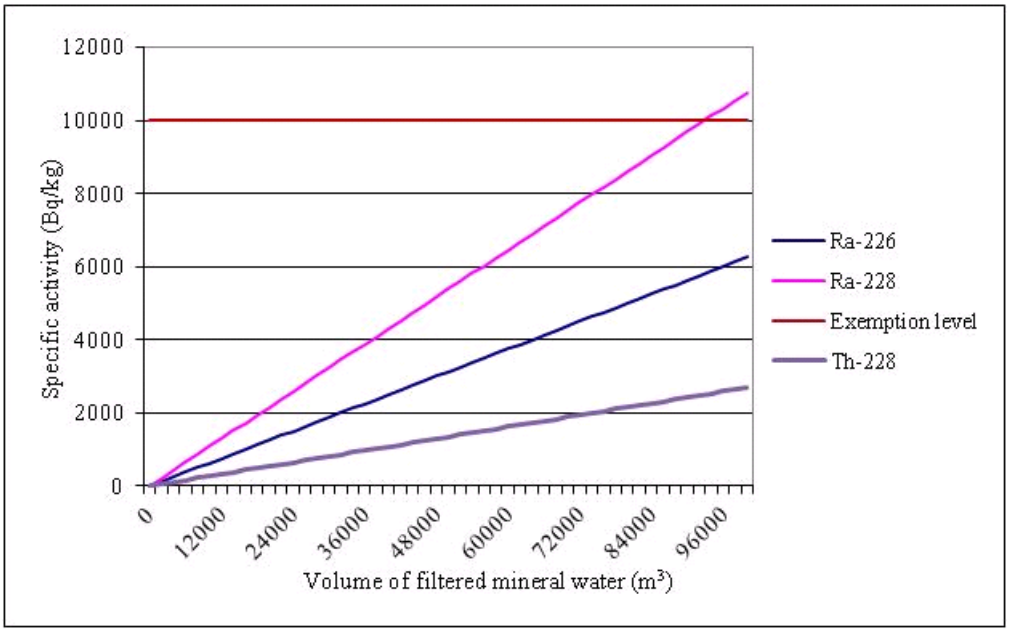

Figure 1. Specific activity of natural radionuclides accumulated on the filter

3. Conclusions

Exempion level for ^{228}Ra can be reached when 100000 m^3 of mineral water is filtered. Filtering system is overheated on 80 °C after filtering of each 50000 m^3 of mineral water. There is no problem with enchanced natural radioactivity and TENORM.

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Building material with enhanced or elevated levels of natural radioactivity: analyses of the use of index criteria for limiting their use

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Abstract

In the last 10 years the authors have set up a wide database of natural radionuclide activity concentrations in building materials used in the European Union. This database was presented and discussed in international literature, and also analysed by means of the activity concentration index I, as defined in the EC guideline *Radiation Protection 112*. Various indexes have been developed in the last decades in several countries and some of them also account for the contribution of radon to the annual effective dose. In this paper the authors review some of these indexes and apply them to the database. The results are compared.

1. Introduction

A wide database of activity concentration measurements of natural radionuclides (^{226}Ra, ^{232}Th and ^{40}K) in building material has been set up in the last years, through a large review of scientific literature and personal communications from some experts. Since in some publications only the average values are reported, in order to make data comparable the authors decided to use only the arithmetic means (source data set) for each material reported in each paper. For this reason, the variability of activity concentration is underestimated (Trevisi et al., 2012).

The database refers to about 10,000 samples of both bulk material (bricks, concrete, cement, natural-gypsum and phospho-gypsum, sedimentary and igneous bulk stones) and superficial material (igneous and metamorphic stones) used in most Member States of the European Union (MS). The number of non-stony bulk materials (bricks, concrete, cements and gypsum: about 6900 samples) for each MS is quite different -in some cases very low- and activity concentrations vary widely (Trevisi et al., 2012).

By means of this database the authors calculated the *activity concentration index I* (I_{RP112}), as defined in the EC guideline *Radiation Protection 112* (European Commission, 1999), for some of these non-stony bulk materials (Trevisi et al., 2010). This is an important starting point for a discussion at the European level on the consequences of future legislative requirements, since this index was adopted in the *Proposal for a COUNCIL DIRECTIVE laying down basic safety standards for protection against the dangers arising from exposure to ionising radiation* (ECBSS), as a screening tool to harmonise the control, and allow the free movement, of building products within the EU (European Commission, 2011).

Aim of this paper was to analyse some indexes found in the literature, apply them to the database, and then compare the results in terms of the materials that may possibly be excluded from the market.

2. Review of some activity concentration indexes for screening building material

Numerous methods have been published in the literature to screen building materials from the radiological protection point of view. Several of them estimate effective dose indoors from gamma radiation, and some of them also account for the contribution from radon exhaled by such materials. This is the case with Austrian index, which has long been in force as national regulation. Some of these methods were reviewed and are summarised in the following.

2.1. The general approach to an index I

An index was created as a screening tool to limit gamma exposure from building materials; it consists of the sum of the contributions of the natural radionuclides to the gamma dose. In order that the material complies with the screening, 1 is the highest value this index is generally set to (see equation 1).

$$I = \frac{C_{Ra-226}}{A_{Ra-226}} + \frac{C_{Th-232}}{A_{Th-232}} + \frac{C_{K-40}}{A_{K-40}} \leq 1 \quad (1)$$

where
C_x = measured activity concentration (Bq kg^{-1})
A_x = fixed parametric values (Bq kg^{-1}).

The A_x parametric values are calculated after assuming a dose criterion to be complied with and a background to be subtracted. These values also depend on the geometric and structural characteristics of the indoor environment and the dose coefficients per unit activity concentration used, i.e. the chosen room model. For this reason the A_x used may also vary widely from country to country. This approach and its evolution in the RP112 guide (European Commission, 1999), as explained in the next paragraph, were the basis for the I_{RP112} screening tool adopted in the new ECBSS (European Commission, 2011).

2.2. The index I_{RP112}

The guideline Radiation Protection 112 (European Commission, 1999) chose the values 300 Bq kg^{-1}, 200 Bq kg^{-1} and 3000 Bq kg^{-1} for $A_{Ra-226,}$ A_{Th-232} and A_{K-40}, respectively, for bulk building material, therefore the I_{RP112} index is defined in the following way

$$I = \frac{C_{Ra-226}}{300\,\text{Bq kg}^{-1}} + \frac{C_{Th-232}}{200\,\text{Bq kg}^{-1}} + \frac{C_{K-40}}{3000\,\text{Bq kg}^{-1}} \quad (2)$$

The A_x values were obtained assuming a dose criterion of 1 mSv y^{-1} -as the excess to the average background originating from the Earth's crust- an occupancy factor of 7000 h y^{-1} and a dose coefficient 0.7 Sv Gy^{-1}. The background dose rate, corresponding to an average value outdoors in Europe, was assumed to be 50 nGy h^{-1}.

RP112 also considers a second dose criterion of 0.3 as an exemption level and provides the relevant A_x values: 121 Bq kg^{-1}, 101 Bq kg^{-1}and 1390 Bq kg^{-1} for radium, thorium and potassium, respectively. However, it concluded that "...the same activity concentration index can be used if its limit value is set at 0.5 instead of 1".

Lastly, the guideline also considers how to screen material to be used superficially, but this is not discussed in this paper.

2.3. The index I in Austria

In 2009 Austrian legislation established an index I, that accounts for exposure from both gamma radiation and radon exhalation from building material (Önorm S 5200, 2009):

$$I = (1 + 0{,}07\varepsilon\rho d)\frac{C_{Ra-226}}{880\,Bqkg^{-1}} + \frac{C_{Th-232}}{530\,Bqkg^{-1}} + \frac{C_{K-40}}{8800\,Bqkg^{-1}} \leq 1 \quad (3)$$

where ε is the radon emanation power, ρ the wall density and d the wall thickness. Where specific information is not available, ε can be set at 10%, d at 0.3 m and ρ at 2000 kg m^{-3}. These parameters affect only the contribution of the radon term, and the estimation of the excess gamma dose remains independent of the density of the material and geometry of the room. The dose criterion used to calculate the A_x is 1 mSv y^{-1}, and the assumed outdoor background dose is 1.2 mSv y^{-1} (Maringer, 2009).

2.4. The *Ra equivalent* (Ra_{eq})

In 1985 Beretka and Mathew (Beretka and Mathew, 1985) had proposed a criterion to limit radioactivity in building material based on the definition of the *radium equivalent activity* (Ra_{eq}), which is still used by some authors, see e.g. (El Taher, 2009).
Ra_{eq} is defined (see equation 4) as the weighed sum of ^{226}Ra, ^{232}Th and ^{40}K activity concentrations, and accounts for the external gamma radiation hazards associated with them.

$$Ra_{eq} = C_{Ra} + 1.43\,C_{Th} + 0.077\,C_K \quad (4)$$

where C_{Ra}, C_{Th} and C_K are the activity concentration of ^{226}Ra, ^{232}Th and ^{40}K in Bq kg^{-1}.
This definition was based on the authors' assessment that 10 pCi g^{-1} (now 370 Bq kg^{-1}) of ^{226}Ra, 7 of ^{232}Th and 130 of ^{40}K yield the same gamma dose rate, estimated in 150 mrad y^{-1} (now 1.5 mGy y^{-1}, corresponding for this energy spectrum to about 1 mSv y^{-1}). In order to limit the gamma dose from materials to this value, Ra_{eq} should be lower than or equal to 10 pCi g^{-1} (now 370 Bq kg^{-1}).

3. Application of the indexes to the building material database

The database contains data for 24 out of the 27 MS, as the authors could not find data for Estonia, Latvia and Malta (Trevisi et al., 2012). Some literature data were incomplete and the activity concentrations of ^{226}Ra, ^{232}Th and ^{40}K were not available for all the samples. In these cases no index could be calculated and this is the reason why the number of samples to which the indexes were applied is lower than the total number of data for each category of material.

The results of the application of index I_{RP112} to the database are summarised below (Trevisi et al., 2010). For each country Figures 1 and 2 show I_{RP112} values calculated on the minimum, maximum and mean values of activity concentrations of bricks and concrete, respectively. The number of samples is specified in parenthesis for every country with complete data sets (23 out of 24 MS).

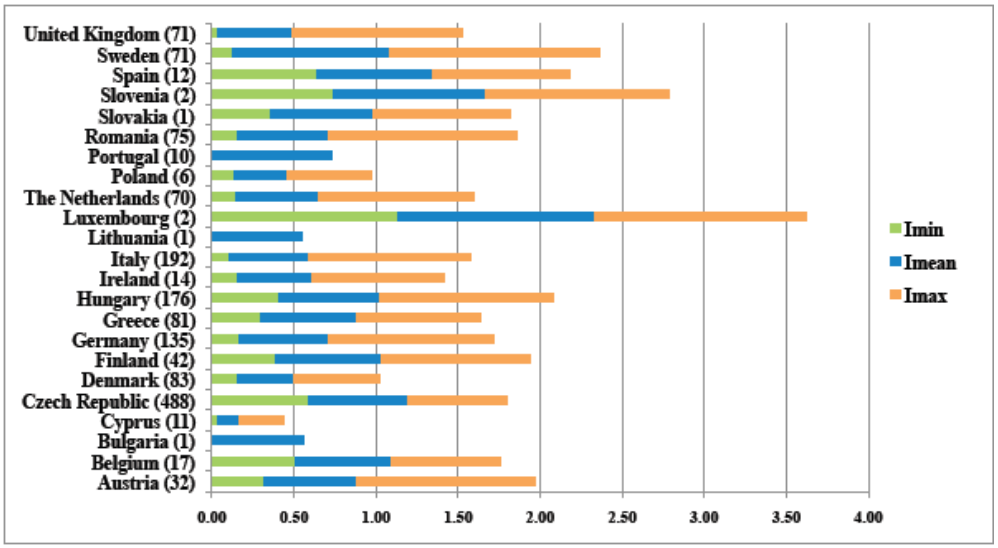

Fig. 1. Index I_{RP112} in bricks (on 1593 samples out of a total of 1676)

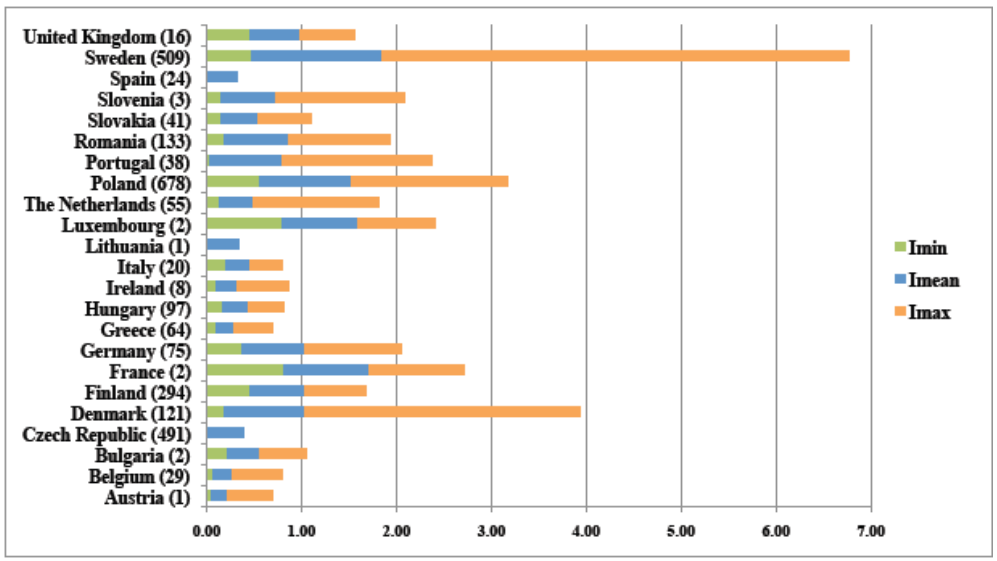

Fig. 2. Index I_{RP112} in concrete (2704 samples out of a total of 2727)

The percentage of materials exceeding the two dose criteria of I_{RP112} –0.3 and 1 mSv y^{-1}- was also evaluated and reported in Table 1. 91% of bricks and 62% of concrete samples exceeded the dose criterion of 0.3 mSv y^{-1}, whereas only 5% of samples exceeded 1 mSv y^{-1} (Trevisi et al., 2012).

Table 1. Percentage of EU brick and concrete samples exceeding 0.3 and 1 mSv y^{-1}

Bulk Material	N of samples with complete data sets	Dose criterion (mSv y^{-1})	
		0.3	1
Brick	1593	91%	5%
Concrete	2704	62%	5%

The Ra_{eq} and the Austrian index were applied to the building material database, even if these indexes start from different hypotheses, which are summarised in Tab. 2 for the sake of comparison.

Table 2. Dose criteria and background hypotheses of the indexes applied to the database

Hypotheses	Screening tool			
	I_{RP112}		Ra_{eq}	Austrian index
Dose criterion (mSv y^{-1})	≤0.3	≤1	≤ 1	≤ 1
Outdoor background* (mSv y^{-1})	0.25	0.25		1.2

*Outdoor gamma background dose - calculated with the indoor occupancy factor - subtracted from the indoor dose in the index calculation

Table 3 reports the percentages of materials which do not comply with the indexes.

Table 3. Percentages of samples exceeding the limits of the listed indexes

Building material	Screening tool			
	I_{RP112}		Ra_{eq}	Austrian index
	0.3 mSv y^{-1}	1 mSv y^{-1}		
Bricks	91%	5%	0%	0%
Concrete	62%	5%	4%	3%

In all cases –except for I_{RP112} with the dose criterion of 0.3 mSv/y- the percentage of concrete samples exceeding the limit value of the screening method is equal to or higher than the percentage of bricks. This may be due to ^{226}Ra concentration, which is quite high (> 300 Bq kg^{-1}) in the concrete of some countries.

4. Conclusions and future prospects

The application of these indexes to the building material database yielded similar results as for which materials should be excluded from the market, when the same dose criterion is chosen. However, there are other indexes with much different hypotheses (e.g. the Israeli standard) and other methods available as decision-making support, which do not make use of indexes but of more elaborate models.

Having recently developed a more accurate *room model* (Nuccetelli et al., 2011), the authors intend to continue investigating the use of other indexes and room models.

An analysis will also be devoted to the potential impact that the Euratom Basic Safety Standards draft, with its harmonisation aim, will have when implemented in countries that have already enforced regulations regarding building material.

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Recycling of Metallic Residues with NORM Contamination by Melting

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Abstract

Radionuclides are existing everywhere in the ground soil, the socalled primordial nuclides have developed during the genesis of the earth. These nuclides decay to a series of daughter nuclides. During decay, energy in form of ionising radiation is released to which we are exposed day by day from the ground. In medicine, ionising radiation and radioactive substances are applied in various administrations, from x-ray to radiation therapy. Flying in an airplane at a height of about 10 km we are exposed to a cosmic radiation which is approximately 100 times higher than that on average sea level.

Moreover, natural radioactivity appears in many branches of industry dealing with raw materials. In various processes of production and manufacturing these naturally occurring radionuclides are inevitably being accumulated. In oil and gas production, for example, nuclides are accumulating in scales and sludges which are extracted from the ground together with oil or gas. Other affected branches of industry for example are paper and phosphate industry where also raw materials are used in production processes. Another representative is the so-called tungsten processing industry. In order to improve the thermal stability and ignition properties of electrodes in gas discharge lamps and welding rods these electrodes are doped with naturally radioactive thorium.

In the past 14 years Siempelkamp has specialised in the recycling of naturally radioactively contaminated metallic residues from various industries in a melting plant being licensed according to BImSchG (federal immission control act). Annual dose rate of the plant's employees is below 1 mSv/y. In compliance with the European Basic Safety Standards and the radiation protection ordinance, no legal licensing procedure or regulatory control of radiation protection is required for treating the scrap in the plant. During the treatment process in the GERTA plant, natural radioactivity is separated from the metals and transferred to slag and filter dust. Only about 5 % of the input material has to be disposed off as secondary waste. The remaining 95 % can be returned to the steel cycle (90% steel) or reused as road construction material on landfill sites (5% slags).

In this paper, the layout of the GERTA plant, experiences from 14 past years of operation as well as measures for assuring radiation protection in the plant shall be presented.

1. Introduction

Since 1998 Siempelkamp Nukleartechnik GmbH is operating at their main premises at Krefeld a melting plant for recycling of naturally radioactively as well as chemically and toxically contaminated steel scrap from various industrial areas. For naturally radioactive contamination mainly oil and gas industry, fertilizer industry, paper industry and tungsten industry can be mentioned. Materials which are chemically and toxically contaminated with mercury originate predominantly from chlorine electrolysis resulting from the amalgam procedure as well as from oil and gas industry. Cross contaminations with other hazardous materials like asbestos, PCB, PCDD/F cannot be completely excluded in any industrial branch and under consideration of particular limitations can also be melted and recycled in the GERTA plant which was especially designed for these contaminations.

Limit values for acceptance in GERTA are summarized in table 1.

GERTA plant was developed on the basis of the melting plant CARLA for slightly radioactively contaminated metal scrap from nuclear power plants and research institutes which was already successfully established in the market. Main difference between both plants is based on licensing regulations. Whereas CARLA plant is subject to a licence considering the German Radiation Protection Ordinance (StrlSchV), GERTA plant is licensed according to BImSchG (federal emission control act). Annual capacity of the GERTA plant is amounting to 2,000 Mg per calendar year. Since start of the plant in 1998 approximately 20,000 Mg of contaminated metal scrap could be successfully melted and reused.

Table 1. Acceptance criteria GERTA

Contamination	Acceptance limit
NORM	individual check
Mercury	< 1 weight %
Asbestos	< 0.1 weight %
Σ PCB	< 50 mg/kg
PCDD/F	< 10,000 ng/kg
Organics	< 5 weight %
Metal	> 95 weight %

Concerning the processing of NORM contaminated scrap the annual dose exposure to workers does not exceed 1 mSv in the GERTA plant and therefore no licensing nor radiation surveillance or protection is required according to German Radiation Protection Ordinance (RPO 2008). But nevertheless workers dose exposures is controlled by the own radiation protection team.

2. Layout

GERTA plant is operating according to a discontinuous process in five steps (Fig. 1):

1. Acceptance of material
2. Cutting
3. Melting
4. Flue gas treatment
5. Disposal of secondary waste

In this context, discontinuous means that cutting and melting is not performed parallel but is alternating in a scheduled scope of approx. 2 weeks.

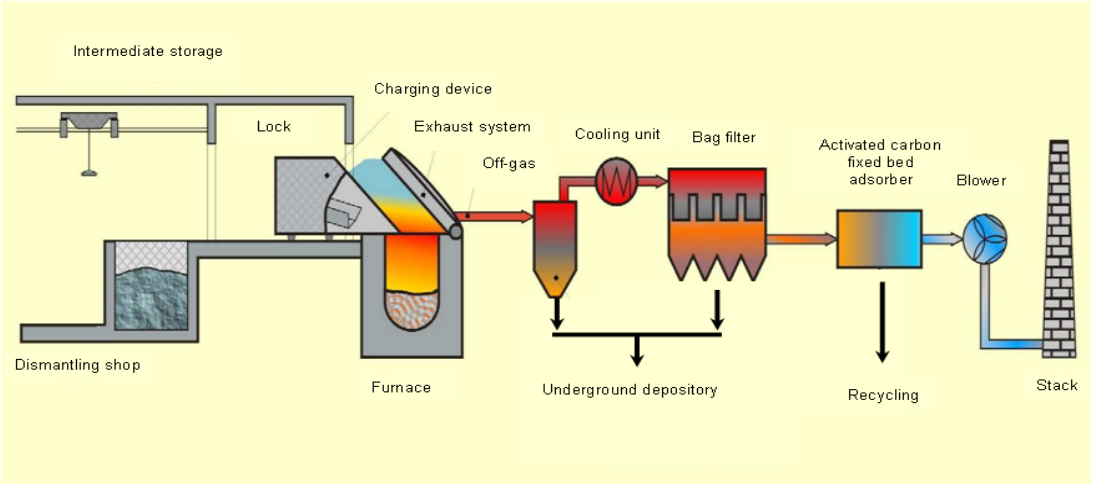

Figure 1. Layout of GERTA Melting plant

2.1. Acceptance of Material

All incoming material is subject to an income control. This control comprises visual checks of the scrap and the verification that all limit values for acceptance are met, random checks of chemical contaminations as well as pre-checks of the radiological inventory by means of a gate detector. In suspicious cases an extended control is performed by means of taking samples for gammaspectrometrical analysis in the in-house accredited radiological laboratory.

Acceptance criteria of GERTA are based on principle limitations for foundry scrap, safety related limitations as well as individual specific limit values for the different contaminations (Tab. 1). Limitations for the radiological load of the scrap are based on limit values for the disposal of secondary waste. Backgrounds for this will be discussed later-on.

2.2. Cutting

In the cutting section of the GERTA plant components of a weight up to approx. 25 Mg can be handled. The outer dimensions are limited to a maximum of 15 m length and a diameter of 3.5 m. All parts will be cut to dimensions of approx. 0.3 x 0.3 x 0.3 m^3. This is necessary in order to assure an automatic charging of the melting furnace. Components are cut by means of thermal cutting tools like gas and plasma torch and a guillotine scrap shear with a cutting force of 650 Mg. These tools facilitate cutting of even thick walled scrap. After cutting the resulting scrap pieces will be separated according to material kind and will be stored in three different scrap bunkers. The capacity of this interim storage for cut scrap is sufficient for a consecutive melting campaign of two weeks duration.

2.3. Melting

Melting of the scrap pieces is effected in an 8 Mg mains frequency induction furnace at a melt temperature of approx. 1,350° - 1,580° C, depending on the applied kind of material. The furnace is automatically charged with the pre-cut scrap from the bunkers via a charging jumbo which is guided through a lock to the final position above the furnace. At its final position the jumbo is connected directly with the filter system by means of the furnace hood. Thus, the flue gas can be captured immediately upon charging. The actual process of charging scrap to the furnace is affected by vibration conveyance.

During the melting process the contaminations are separated from the metal and are transferred to the various waste streams. During this process different behaviours of the individual hazardous materials and radionuclides can be observed. Elementary mercury is completely evaporating and will be captured by the extraction unit. Adherences, like asbestos, PCBs and organic materials will burn up or will become innoxiously in the high melt temperatures. Naturally occurring radioactive materials behave differently during the melting process depending upon the radionuclide.

After melting, oxides of radium, uranium and thorium isotopes can mainly be found in the slag. Volatile isotopes like lead (Pb-210) and polonium (Po-210) are filtered in the bag filters of the flue gas cleaning system and remain in the filter dust (Kreh et al 2004), (Quade and Kluth 2010), (Ferriere et al 2010). A survey of the distribution coefficients of the individual nuclides is given in tab. 2.

After deslagging the melt is cast in permanent moulds with a capacity of approx. 1 Mg. These ingots can be returned to the conventional steel cycle.

Table 2. Nuclide distribution after melting (Ferriere et al 2010)

Nuclide	Melt	Slag	Dust
U-238, U-235	1 %	98 %	1 %
Th-232, Th-234	< 1 %	> 98 %	1 %
Ra-226, Ra-228	-	98 %	2 %
Pb-210	-	7 %	93 %
Po-210	-	2 %	98 %

2.4. Exhaust Air Cleaning

For the complete exhaust air conditioning of the GERTA plant, two filter systems with 15,000 m^3/h and 13,500 m^3/h suction outputs are available. Suction is producing a continuous low pressure in the plant. Thus, it is prevented that contaminated flue gas or dust is emitted from the plant to the environment. Inside the plant, contaminated ambient air is withdrawn at various suction points. Well-directed air injection is assuring a continuous air exchange. Cleaning of the exhaust air is performed in a three-step process. At first rough particles are separated from the exhaust air by a cyclone filter. This cyclone filter is also serving as protective layer against sparks and hot particles into the bag filter. In a subsequent air cooler the hot exhaust air of the furnace is cooled down to approx. 60°-70° C before it reaches the bag filter. Before entering the bag filter the flue gas stream is recharged with lime. This lime absorbs part of the gaseous mercury and enlarges the grain size of the dust being carried by the exhaust air. Thus in the bag filters the exhaust air is cleaned more efficiently. Dust is continuously removed from the bag filters by an automatic cleaning function. Loose dust is transferred to a dust mixer via a screw conveyor. It is then mixed with lime and water and packed into drums. There, the dust is slowly hardening. Subsequently, the share of the remaining mercury as well as the recreated cyclic chlorite hydrocarbons is filtered from the exhaust air stream by an activated carbon absorber.
Due to such elaborate exhaust air conditioning in the GERTA plant by means of cyclone, bag filter and activated carbon filter, the maximum content of mercury in the exhaust air is below 50 $\mu g/m^3$. This corresponds to the maximum admissible limit value (Quade et al 2002). The residual content of dust in the exhaust air is below 20 mg/m^3. Measurements of naturally occurring radioactive particles in the exhaust air at the chimney during treatment of NORM scrap show values far below the admissible limit values.

2.5. Waste Disposal / Product Recycling

The German Radiation Protection Ordinance postulates the monitoring of NORM-contaminated residues if the dose exposure to the public may exceed 1 mSv/y (RPO 2008). To check this limit value, exposure calculations for the slag from NORM melting campaigns were carried out by a radiological expert team and all possible paths of exposure for the slag processing, were taken into consideration (Thierfeld and Wörlen 2002). The calculation based on the assumption of 100 Mg slag production from NORM-contaminated scrap melting of 1,000 Mg per year. Tab. 3 shows the results of the calculation as specific activity values for the slag to be sent for recycling. A common practice is recycling of slags from induction furnace process to road construction material, but for the 100 Mg of NORM slag the recycling was licensed under the conditions that (Thierfeld and Wörlen 2002):

-
- NORM slags are mixed on site in a quota of 1:4 with slags free of NORM.
- processing is contracted with a recycling company of an annual throughput of approx. 100,000 Mg/a
- Recycling to construction material for landfill sites like temporary roads etc.

Since starting operation of GERTA melting plant, 100 % of the slag could be recycled by this path. Based on that fact the acceptance limits for scrap can be calculated related to the mass and specific activity of each batch of incoming material.

Table 3. Nuclide specific activity limits for slag to be sent for recycling (Thierfeld and Wörlen 2002)

Nuclide	Specific activity [Bq/g]	Max. annual activity [10^9 Bq]
U-238sec	21	8.4
Th-232sec	15	6.0
Ra-226+	25	10
Pb-210++	40	16

The slag is free of any toxic impurities but contains a certain amount of the radio-isotopes.

Only 1-2 wt.-% of the input-material is dust retained in the bag filter and in the cyclone. Both kinds of dust are mixed with quick lime and are then filled into storage drums. Underground storage in rock salt mines up to a depth of 200 metres offers a disposal solution for hazardous waste in Germany, which has long been regarded as safe for the environment. The radiation exposure to the mine workers and to the public has to be less than 1 mSv/y, which Siempelkamp also proved by an expert opinion (Urban 2000). Additionally, the filter dust must not be radioactive in the sense of the former ADR regulation for transport that means the total activity of Pb-210/Po-210 must be below 70 Bq/g (Urban 2000).

Products of the GERTA facility are metal ingots of about one ton each. The ingots are almost free from any radioactivity. Further on the metal is free of any chemical contamination. So far 100 % of the produced ingots, amounting to almost 18,000 Mg could be reused in the steel cycle.

3. Experiences from the recent years

Since 1998, approx. 20,000 Mg of contaminated metals could be successfully molten in the GERTA plant with subsequent recycling. About 92 % were returned to the metal cycle. 5 % of the molten quantities were recycled as slag in ongoing construction measures on landfills. Only 3 % had to be finally disposed of as filter dust. Effectively, this corresponds to a recycling rate of 97 %.

The share of NORM contaminated metals amounts to approx. 31 % of the total quantity. The predominant part (68 %) is represented by the chemical contamination with mercury. In the past years, however, an increasing trend into the direction of NORM contamination can be recorded. Main cause for this is probably the increasing upgrading of the scrap and metal industry with measurement devices for the determination of radioactive parts in scrap and product metal. Fig. 2 shows the mass distribution of the molten scrap to the different industrial branches.

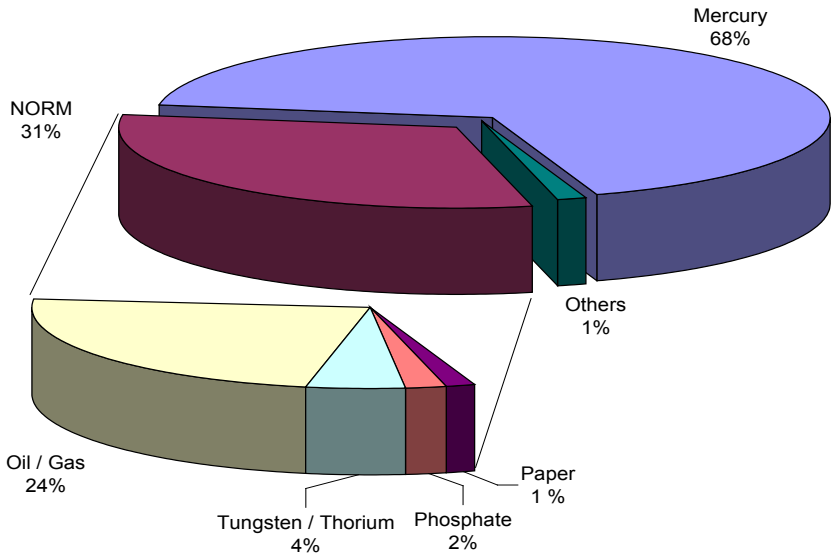

Figure 2. Mass distribution of scrap from served industries (Quade and Kluth 2010)

A detailed break down proves to be rather difficult, because many findings of the srap industry are of unclear origin.

In oil and gas industry, mercury and/or dissolved NORM particles are extracted from the reservoir together with deposit water but also with the product stream. In case of NORM, these particles deposit at the inner tube surface in form of oxides and sulphides and form solid incrustations. Mercury condenses at falling temperatures in tubings and components and diffuses into the metallic surfaces, from where it can only be dissolved away with great difficulties (Quade et al 2002), (Quade and Kluth 2010).

Phosphorous fertilizers are produced from „raw phosphates“ by means of various exploration methods which are excavated from sedimentary (fossil) or magmatic deposits. Raw phosphates from sedimentary deposits are characterized by the high content of uranium which precipitates at the plants during processing (Beddow et al 2004), (Quade and Kluth 2010).

In paper industry, various filler materials and additives are applied which are also extracted from fossil deposits. Precipitations of radioactive particles in paper industry can mainly be found in large mixing tanks, where these filler materials are added (Quade and Kluth 2010).

Unlike in the industrial branches already cited, in tungsten industry 2-4 % of thorium oxide is specifically added to the tungsten alloys in order to achieve physically desired features like inflammability of welding electrodes and heat stability of lamp electrodes (Kreh at al 2004). For this reason, tungsten industry is a special case in comparison to the other industries.

Table 4. Summary of lessons learned from past projects of different industries

	Oil / Gas	Tungsten/Thorium	Phosphate	Paper
Amount	~ 4,800 Mg	~ 800 Mg	~ 400 Mg	~ 200 Mg
Contamination	NORM Mercury	NORM	NORM	NORM
NORM decay chain	Ra-226++	Th-232sec	U-238sec U-235+ Th-232sec	Ra-226++
Specific activity of adherences	Up to 250 Bq/g Ø 10 Bq/g	Up to 65 Bq/g Ø 12 Bq/g	Up to 130 Bq/g Ø 60 Bq/g	Up to 250 Bq/g Ø 3,5 Bq/g

Our experiences regarding radiological contamination of the scrap from the mentioned industrial branches is illustrated in table 4.

4. Radiation protection measures for works with NORM

According to present legislations in Germany no measures for assuring radiation protection are needed as long dose rates during work activities with NORM results in less than 1 mSv/y. Up to 6 mSv/y general protection for work activities has to be applied, which includes measurement of airborne activities and external doses. When the dose limit of 6 mSv/y can be exceeded, investigations to survey the workers have to be notified to authorities. A reporting of the kind of work, the numbers persons exposed > 6 mSv/y as well as description of dose reduction measures will be requested (RPO 2008).

In order to protect the population against naturally occurring radioactive materials an effective dose limit value of 1 mSv/y must be observed for individual persons of the population when conditioning or disposing of residues which require supervision (RPO 2008).

As already mentioned above, GERTA melting plant has the objective of treating chemically toxically as well as NORM contaminated steel scrap in the scope of the 1 mSv/y criterion. For this reason, the 1 mSv/y criterion is decisive for the whole process of recycling including processing of generated secondary waste by Siempelkamp.

Basis of the concept for radiation protection to observe the 1 mSv/y criterion in the GERTA plant is an internal observation of the dose exposure of employees associated with expert opinions as to the dose observation of employees and population by recycling of slag and dumping of filter dust. The results of the expert opinion for recycling of GERTA secondary waste have already been described under point 2.5. The determined relevant limit values indirectly form the GERTA conditions for acceptance of NORM contaminated scrap.

4.1. Internal study of dose exposure of GERTA employees

The aim of the performed study was to verify the compliance of the 1 mSv/y criterion in the GERTA plant during processing of NORM waste. To this end, the local dose was determined with help of thermoluminescense dosimeters (TLD) and electronic dosimeters (EPD) as well as the personal dose equivalent using electronic dosimeters (EPD). Data were recorded for three measurement campaigns involving dismantling and melting of NORM materials (Kreh and Dewji 2007).

Based on 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 exposure per worker was calculated (Tab. 5). Work place measurements gave the highest calculated annual dose.

From this point of view, the TLDs give a sufficient conservative value with a max. dose of approx. 0.3 mSv/y for the working areas in GERTA. Under the assumption of practical positioning, according to the working conditions, for instance a measuring point in an average working distance to the contaminated material, TLD measurements are easy to carry out and give a good conservative estimation for the real working situation in GERTA (Kreh and Dewji 2007).

Table 5. Results of dose measurement in GERTA

Method	Cutting [mSv/y]	Melting [mSv/y]	calculated annual Dose [mSv/y]
personal EPD	0.04	0.10	0.14
workplace EPD	0.03	0.26	0.29
TLD	0.07	0.21	0.28

Figure 3 shows the recorded dose for 13 employees during the monitoring period, after deduction of the background radiation. The mean dose of exposure is indicated by the red line. The mean dose exposure during the measuring period is about 35 µSv. Extrapolated over a period of one calendar year from processing of similar material, this means a dose rate of 250 µSv (Quade et al 2004).

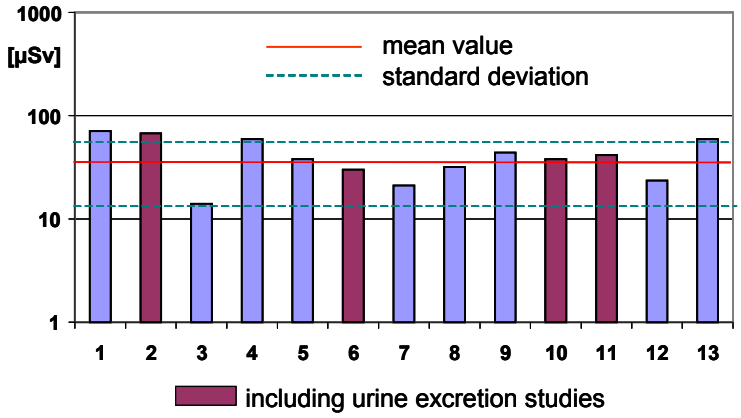

Figure 3. Personal dose of staff from direct radiation (background corrected) (Quade et al 2004)

The most significant dose risk to employees during the processing of NORM is incorporation. In particular, the inhalation of Th-232 and some of its daughters can cause organ damaging doses. As part of the study was for this reason the determination of the influence of incorporation to the workers dose. For this purpose, the activity values in the indoor air were measured and from this values the resulting radiation exposure to employees due to incorporation were calculated. In Addition excretion analytics for four members were performed which were in contact with contaminated material (Kreh et al 2004), (Quade et al 2004). All tests carried out showed activity values below the detection limit. Figure 3 shows that these employees were not exposed to above average dose (Kreh at al 2004).

Nevertheless the result gained up to show that the NORM processing activities in the GERTA plant result in exposure doses to the workers of about 0.5 mSv/y and thus well below 1 mSv/y.

Because of the present mercury in the GERTA plant special filter masks of type Hg-P3 must be worn when working in the plant. This filter masks provide an additional protection against the incorporation of NORM particles.

5. Summary

With the GERTA melting plant, Siempelkamp Nukleartechnik is offering a unique service throughout the world to decontaminate NORM contaminated scrap in a melting process and to return the recovered metal to the economic cycle. Even cross contaminations with other materials being harmful to the environment do not form any obstacle due to the legally licensed layout of the plant. The applied process has delivered an optimal performance in the past. Besides the actual melting process, the scope of service comprises the disposal of secondary waste as well as analytics. The 1 mSv/y criterion is observed during the whole process including cutting, melting and waste disposal. The long-term experience in handling radioactive materials enables us to treat NORM scrap professionally and safely. Periodic medical examinations of our employees and radiological work place supervision assure a high level of work and environmental protection. Thus we offer an all-inclusive package to the customer.

In times of scarce raw materials, recycling is gaining more and more importance. In future, it cannot be afforded any more to dump waste materials, because valuable secondary raw materials can be extracted from them.

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The use of portable equipment for the Activity Concentration Index determination of building materials: Methodology and first results

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Abstract

The Euro BSS requires that in the near future the activity concentration index (ACI) for building material for application in dwellings or buildings such as offices or workshops is assessed. Therefore it is expected that a large number of building material analyses will have to be performed.
NuTeC's goal is to develop an easy to operate and low-cost alternative to the standard laboratory analyses with high purity germanium spectrometry and 21 days equilibrium delay.
A LaBr(Ce) scintillation probe is used to obtain the spectral data. The data acquisition runs for 12 hours; e.g. overnight.
The efficiency of the complete measurement setup, including the detector characteristics, is calculated via commercially available software. The activity concentrations of ^{226}Ra; ^{232}Th and ^{40}K are determined with Genie 2000.
The obtained ^{226}Ra activity concentration can be accepted without correcting for natural occurring uranium to provide a "safe overestimation" of the ACI. Otherwise, it can be corrected for the uranium concentration. A third option is to calculate the ^{226}Ra activity concentration via its daughters ^{214}Pb and ^{214}Bi.
This paper presents the new method's first results and compares it to standard laboratory high-resolution analysis procedure.

1. Introduction

On average, one stays for 80% of the time indoors. Therefore, it is relevant to assess the radiation dose that a person receives from the building materials. Most building materials contain certain amounts of the naturally occurring radionuclides (NORM) ^{226}Ra, ^{232}Th and ^{40}K. Building materials of natural origin reflect the geology of their origin (Haquin).

Besides this, the trend to re-use industrial by products in building material may enhance the building material activity concentration.

Therefore, it is relevant to study NORM in building materials. Moreover, NORM in building materials will be legally regulated in the near future (Euratom 2010).

The Basic Safety Standards (BSS) is a European Directive concerning (among others) the protection of the public and the workers against the dangers of ionizing radiation. It is expected that the EU member states will ratify the Directive by 2015.
The new BSS, mentions natural radioactivity in building materials in title IX 'Protection of the members of the public', article 101: "Building Materials".

Article 101 states that

> "The competent authority shall make arrangements for the classification of identified types of building materials, as laid down in Annex 15, on the basis of their intended use and *activity concentration index* I."

The article also states that the radiological information shall be published before marketing the material.

If the allowed activity concentration index I is exceeded, the competent authority shall decide on appropriate measures ranging from registration and general application of relevant building codes, to specific restrictions on the envisaged use of such materials.

In order to determine the building material activity concentration index I, one has to measure the radionuclides ^{226}Ra; ^{232}Th and ^{40}K specific activity. These different formulae exist for the calculation of the activity concentration index; e.g. (Steger, Kunsch et al. 1992) but the most widespread formula is the one used in the BSS:

$$I = C_{Ra-226} / 300 Bq \cdot kg^{-1} + C_{Th-232} / 200 Bq \cdot kg^{-1} + C_{K-40} / 3000 Bq \cdot kg^{-1} \qquad (1)$$

With: C = specific activity of the respective nuclide in secular equilibrium [Bq/kg]

The index is related to the extraneous gamma radiation dose, resulting from the use of the respective materials. It is applicable for the material as a whole and not for its constituents. The extra gamma radiation dose may not exceed the level of 1 mSv/a. The constants in the formula are derived for a described room and a material with a certain density (EC 1999). If the actual room or material circumstances differ from the circumstances on which formula (1) is based, it may not be completely accurate. This causes, among relevant parties, some discussion concerning the applicability of one formula for all different building materials.

If the index has been determined, and the intended use for the building material is known, the material can be classified according to table 1. For categorizing a building material, the intended use can be "bulk material" or "superficial material". The latter category is allowed to have a higher index I than the former category, since superficial materials are only used in relatively limited amounts.

Table 1: Building material classification according to BSS

	Category (corresponding default dose)	
Use	A (≤ 1 mSv)	B (> 1 mSv)
(1) materials used in bulk amounts	A1 I≤1	B1 I>1
(2) superficial and other materials with restricted use.	A2 I≤6	B2 I>6

If the building material is classified A1 or A2, no restrictions or extra requirements are set. However, if a building material is classified B1 or B2, the relevant authority is to take a decision concerning possible restricted use or extra requirements

The requirement to determine the activity concentration index implies that in the near future, numerous gamma spectrometric analyses have to be performed on building materials.

In the B-NORM project, NuTeC strives for the development of an easy to operate; *in-situ* measurement method (Bronson 2008), that facilitates companies with gamma spectrometric measuring tools. This method is intended to be a valuable *in situ* screening tool that may be combined with "conventional" high resolution gamma spectrometry in a laboratory.

2. Materials and Methods

Building materials

The current paper is focused on building materials that are available on the Belgian market. All types of building materials that are applied in the construction of dwellings are eligible. Special attention is given to tiles and stones.

B-NORM method

NuTeC applies its *B-NORM* method. In the *B-NORM method*, a Canberra Inspector 1000 (In1k) equipped with an intelligent stabilized 1.5" $LaBr_3$(Ce) probe to obtain the spectral data. The $LaBr_3$(Ce) probe is an ambient temperature operated scintillation probe with improved properties compared to NaI(Tl) probes: it has a 2.9% resolution at 662 keV (7% for NaI(Tl)) 160% relative light output and fast decay time of 16 ns.

The In1k can be set-up in any room with a reasonable low and stable background. In a first stage, a background spectrum is acquired. Then, the sample is positioned and the spectrum is acquired. The spectrum acquisition is a "one-touch and allow to run" operation that can be performed by untrained personnel.

The sample geometry consists of well-positioned whole building materials, e.g. a stack of tiles, a stack of packs of tiles, a pallet of bricks or a stack of concrete testing cubes from the firm's own material testing lab. An example of an actual measurement setup is shown in fig. 1. We carefully determine the geometry dimensions, mass, shape, material composition and detector configuration and position. This information is loaded into Canberra *In Situ Object Counting Software* (ISOCS) to determine the counting efficiency of the measurement setup.

Spectrum analysis is performed with Genie2000. The analysis includes (besides net peak area calculation) a peaked background correction, efficiency correction, selection of applicable peaks from the nuclides of interest and an interference correction.

When the specific activities of the nuclides are determined, the ACI is calculated. The nuclide ^{226}Ra can be assessed in three different ways. First option is to directly determine ^{226}Ra by measuring its 186.2 keV line and *not* correcting for natural ^{235}U. This is an overestimation of the actual ^{226}Ra specific activity. Second option is to measure the 186.2 keV line and applying a correction of 57.1% for natural ^{235}U (185.9 keV). This correction is only correct if the assumption that the natural equilibrium has not been disturbed is true. The third option is to determine the ^{214}Pb and ^{214}Bi daughters of ^{226}Ra. This option will be accurate only if the secular equilibrium is not disturbed. Since building materials are usually dense materials, and the material thickness is also large since we are not milling the materials, we assume the secular equilibrium condition to be met.

"Standard"analysis method and quality control

The current accepted "standard" method for gammaspectrometric analysis is in a laboratory with a lead-shielded high purity germanium detector. The geometry is a precisely defined, usually relatively small sample holder. Before analyzing the sample, the sample holder is usually tightly closed for 21 days in order to obtain secular equilibrium. This method is an accepted and high quality method. However, it is a relatively slow and complicated analysis method, and it can only be performed in an equipped laboratory.

In order to assess the results of the *B-NORM* method, the same samples are analyzed with the standard method(NEN 2011) in an accredited laboratory. The sample preparation for the laboratory analysis was performed by an accredited construction material laboratory. This is a work in progress.

Figure 1. B-NORM method: counting a sample

3. Results and discussion

Determining an optimal sample size

The *B-NORM* method is very flexible concerning sample size; in fact, we can use as much sample as there is building material available on the measurement site. It is interesting to determine a relation between sample weight and detection efficiency: this relation will provide the necessary insight to use a relevant sample weight. To obtain data, we use the software to model a concrete cube, with the detector face-centered on the cube. We calculate the detection efficiency for various sample weights between 2.14 and 300 kg and various photon energies: 200; 800 and 1500 keV.
The results are shown in fig. 2.

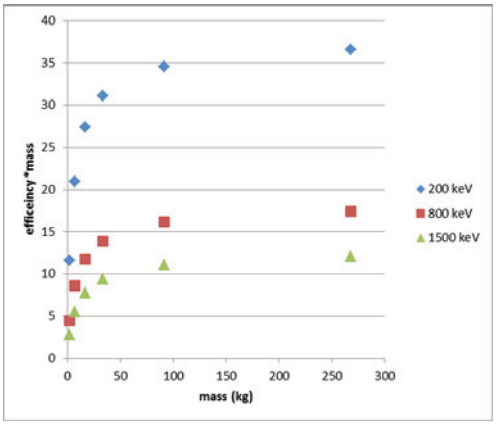

Figure 2. Detection efficiency versus sample weight (concrete cube)

Figure 2 shows that once a sample weight of 25 – 50 kg is obtained, the efficiency gain from adding more sample strongly decreases. If the sample weight already is high, one extra kilo will make only a little difference. The efficiency gain per extra sample weight becomes less in larger samples, even taken this into account. This is caused by the facts that (1) the "extra" weight is positioned further away from the detector. Therefore, gammas have to travel a longer distance and their detection efficiency is thus lower. (2) In a larger sample, gammas have to travel a longer distance through dense material, reducing their detection efficiency. Taking practical work into account, a sample size of 25-50 kg is a suitable balance between sample weight and efficiency.

Determining an optimal sample geometry

The *B-NORM* method is flexible concerning the geometry shape. Virtually any sample shape can be modeled and counted. In practice, one will usually *stack* bricks, tiles, concrete blocks, etc. to obtain suitable sample geometry. Taking practical considerations into account, the resulting stack will be rectangular or cubical. Two cases are modeled in the software. Case 1: Stack the samples like a cube. This results in shorter average distance to the detector, but gammas need to travel via a long path through dense material. Case 2: Stack the samples like a flat rectangular plane. This results in larger distance to the detector, but gammas do not need to travel via a long path through dense material. In Fig. 3 the two cases are calculated for actual concrete bricks; for gamma energies of 200, 800 and 1500 keV. In this case, the flat plane has a thickness of 10 cm. Formula (2) is calculated and the results are shown in Fig.3

$$relative\ efficiency = \frac{efficiency \cdot mass(cube)}{efficiency \cdot mass(plane)} \qquad (2)$$

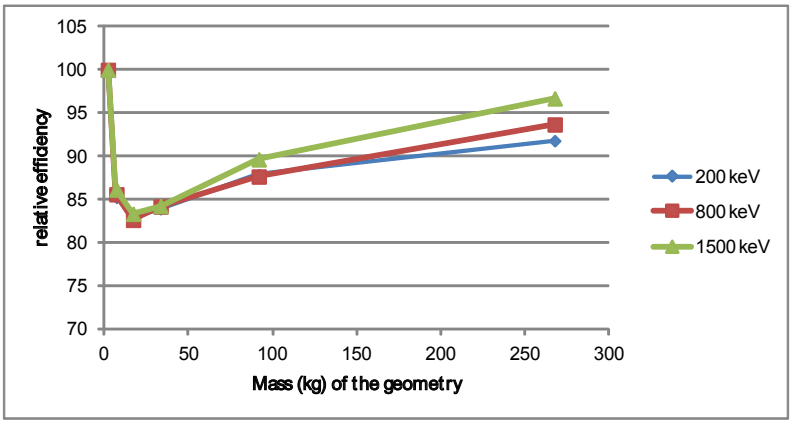

Figure 3. Ratio of detection efficiency of cube versus plane.

Fig. 3 shows that a flat plane geometry results in better counting efficiency than cubic geometry. The difference is about 15% for a 25-50 kg sample. The energy of the gammas is only slightly relevant, especially at lower sample mass. Therefore, we will strive for a relatively flat geometry to count the samples.

First results

Although the *B-NORM* project is a work in progress, numerous building materials have already been analyzed. These materials include bricks, cement, concrete, gypsum, thermal insulation bricks, tiles, and stone.

Table 1 presents an overview of materials analyzed by the *B-NORM* method. In the categories "tiles" and "stone" several materials with ACI>1 have been encountered. Since the intended use for these materials

is "surface material", the materials are allowed to have ACI up to 6. We did not yet observe B category materials with the *B-NORM* method. The number of materials analyzed will be continually increased.

Table 1: Activity index I in building materials: number of samples (n); lowest measured index (I_{min}) and highest measured index (I_{max})

Building material	*n*	I_{min}	I_{max}
Façade bricks	5	0.56	0.79
Thermal insulating bricks	3	0.51	0.70
Cement	8	0.23	0.65
Concrete	4	0.30	0.50
Tiles	66	0.42	1.42
Stone	24	0.21	3.68

Quality control

The *B-NORM* method is currently under development. Therefore we perform reference analyses in an accredited lab; according to the standard procedure. So far, 24 samples have been analyzed in the laboratory. The data analysis in progress, however, some important conclusions can already be adopted. If we compare ACI data based on ^{226}Ra via daughters, and accept the laboratory measurement as 100%, than the *B-NORM* method measures between 76% and 108% of the laboratory measurement and shows a good linearity. The laboratory measurement ACI explains on average 89% of the observed *B-NORM* ACI between ACI 0.54 and 1.51. If a wider ACI range is accepted (ACI 0.3-3.5), the laboratory measurement ACI explains the *B-NORM* ACI for >98%. These preliminary findings indicate that the *B-NORM* method can be successfully applied to perform a fairly good estimation of the building material ACI, by performing an in-situ measurement. In the near future, the quality control results will be thoroughly analyzed and increased in number; and the *B-NORM* method may be further optimized.

4. Conclusion and future perspectives

The *B-NORM* method for *in-situ* building material ACI analysis has been applied on several building materials on the Belgian market. No building materials that should be categorized as "B" materials have been encountered this far. The *B-NORM* method under development is assessed and quality control indicates that the *B-NORM* method can provide a fairly good estimation of the building material ACI.

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Valorization of waste coming from titanium dioxide and phosphate fertilizer NORM industries in sulfur polymer concrete

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Abstract

The aim of this work is the valorization of two hazardous wastes, phosphogypsum (PG) and non-dissolved ilmenite mud (MD), as additive in sulfur polymer cements (SPC). Physico-chemical and radiological characterization was previously performed in these wastes and in the obtained sulfur polymer concretes. An optimized mixture of the materials was designed containing a sulfur/waste ratio ranging from 10 to 30 wt%, and resulting in highest compressive strength (55 to 62 MPa to SPC-PG and 36 to 64 MPa to SPC-MD). The activity concentration index (*I*) in the PG-SPC is lower than the reference value given by the most international regulations, and therefore these cements can be used without radiological restrictions in the manufacture of building materials. However the values of *(I)* in the MD-SPC are higher than in PG cements, so these they could be used with radiological restrictions.

1. Introduction

It is well known that all industrial processes involving minerals as raw materials often generate inorganic wastes. In this sense, the recycling, or valorization, of these generated waste is a research field of high interest because of the appropriate treatment of industrial waste could even lead to the generation of co-products of economic value and broad application [Campos et al, 2004; Shen et al, 2009; López-Delgado et al, 2009]. Obviously, the environmental and health impacts of these co-products must comply with existing regulations. One potential use highly developed for certain industrial wastes is their incorporation in materials used in civil engineering fields [Puertas et al, 2008; Chandara et al, 2009].

This paper is focused on the valorisation of two hazardous waste; phosphogypsum (PG) and un-dissolved ilmenite mud (MD), which come from the phosphate fertilizer and titanium dioxide industries, respectively, in order to be they used as additive of sulfur polymer cement (SPC). Is important to note that these factories are considered as NORM industries, because of the raw materials used (ilmenite used in the titanium dioxide production and phosphate rock (PR) for fertilisers), present high concentrations in natural radionuclides from U- and Th-series [Bolívar et al, 2009; Gázquez et al, 2011]. Phosphogypsum, $CaSO_4 \cdot 2H_2O$, is a by-product coming from the processing of fluoroapatite resulting in H_3PO_4 production. In the process, fluoroapatite is dissolved using sulfuric acid. Phosphoric acid, phosphogypsum, and hydrofluoric acid are obtained as products.

PR contain high concentrations of natural radionuclides from ^{238}U decay-series, in secular equilibrium, which are about 50 times higher than the ones in typical soils. During the industrial process a fractionation of radioelements contained in PR is produced. In the factory of Huelva, ^{226}Ra remains in PG (practically 100%), ^{210}Pb - ^{210}Po (about 90%), and ^{230}Th (70%) [Bolívar et al, 2009]. Nowadays a number of researches are focused on the uses of PG in different applications, being some of these the manufacture of cements [Kacimi et al, 2006: Kuryatnyk et al, 2008]. But only the 15 % of the worldwide PG production is recycled.

The remaining 85 % of the PG is deposited without any treatment in regulated stacks.

Un-dissolved mud (MD), is a waste coming from the titanium dioxide pigment industry. The studied factory produces pigments by applying the sulphate process and uses two raw materials as feedstock: ilmenite ($FeTiO_3$), and titaniferous slag. The undissolved mud are generated in the digestion step where a blend of ilmenite and slag is mixed with highly concentrated sulphuric acid (80%-95%) [Gázquez et al, 2009]. Ilmenite is a heavy mineral containing 43–65 % titanium dioxide [Chernet, 1999], while titaniferous slag (70–80 % TiO_2), is a co-product of ilmenite smelting [Pistorius and Coetzee, 2003]. Also, recent studies [Gázquez et al, 2011] has been obtained that the mud contains a total concentration of radionuclides greater than 1 Bq g^{-1} (mainly ^{226}Ra and ^{228}Ra), which is a considerable fraction of the radioactivity originally present in the ilmenite. Until now, this mud has been disposed of in a controlled disposal area.

In this paper we have carried out a new application of these wastes in civil engineering as additive of sulfur polymer cement (SPC). The advantages of sulfur concrete over Portland cement concrete are [Mohamed and Gamal, 2009; Abdel-Jawad and Al-Qudah, 1994]: quick hardening and reaching the required characteristics in only 24 h; high strength and fatigue resistance; very low water permeability; exceptional resistance to acid and salt agents, which allows its use in extremely aggressive environments. Attempts were made by various investigators to improve sulfur cement concrete products by using chemical additives for sulfur modification [Beaudoin and Feldmant, 1984; Lin et al, 1995; Vroom, 1977]. A plasticized concentrate or modified sulfur, called STXTM is first formulated from the polyolefin and elemental sulfur and then added to additional elemental sulfur and aggregates. This kind of elemental sulfur is denominated sulfur polymer concrete (SPC).

Different international recommendations [Radiation Protection, 112] have been propose as reference values for the natural radionuclide concentrations in building materials. In this sense, the external risk index (I), also called activity concentration index, Eq. (1), has been proposed to ensure that external gamma dose rate inside a room from building materials does not exceed 1 mSv per year.

$$I = C(^{226}Ra)/300 + C\,(^{228}Ra)/200 + C\,(^{40}K)/3000 \quad (1)$$

where $C(^{226}Ra)$, $C(^{228}Ra)$ and $C(^{40}K)$ are the activity concentrations for ^{226}Ra, ^{228}Ra and ^{40}K, respectively, in the building material considered, expressed in Bq kg^{-1}.

Other countries considered the equivalent radium concentration parameter, Ra(eq), which is shown in Eq. (2):

$$Ra(eq) = C(^{226}Ra) + 1.43C(^{228}Ra) + 0.077C(^{40}K), \quad (2)$$

where $C(^{226}Ra)$, $C(^{228}Ra)$ and $C(^{40}K)$ are the activity concentrations for ^{226}Ra, ^{228}Ra and ^{40}K in Bq kg^{-1} respectively, being 370 Bq kg^{-1} the reference value for Ra(eq) for building materials.

Taking into account the previous considerations, we have stated two main objectives. The first one has been to study the degree of stabilization/solidification of both phosphogypsum (PG) and mud (MD) inside the matrix cement, and after to evaluate if the building materials manufactured with these cements are safe in relation to their radioactivity levels. In addition, the second objective has been to characterize the mechanical properties of the sulfur polymer cements manufactured, and to evaluate their potential environmental radiological impacts.

2. Experimental

2.1 Materials

The raw materials used for this study were a granular elemental sulfur (99.4 wt.%, size < 60 μm, type Rubber Sul 10) supplied by Repsol IPF (Madrid, Spain), gravel (<6.3 mm) and a siliceous sand (<4 mm) were used as commercial mineral aggregated materials. A modified sulfur containing polymer (STX™ supplied by Starcrete™ Technologies Inc. Québec, Canada) was used as thermoplastic material. STX™ polymer improves fine sulfur crystal formation and grain size control, which supplies higher mechanical properties. Finally, the samples of waste used in this study were phosphogypsum (PG) supplied by Fertiberia factory (2009) and un-dissolved ilmenite mud (MD) supplied by Tioxide factory (2011). Both samples were dried at 50 ◦ C for 48 h.

2.2 Sample preparation

The mixture of typical SPC's was listed in Table 1. The ratio of gravel/sand and sulfur/modified sulfur (STX™) were maintained constant at 0.5 and 10 respectively for all samples.

Table 1. Composition of different sulfur polymer cement samples with phosphogypsum (PG) (SPC-PG) and with mud (SPC-MD) (expressed as wt %)

Samples	Elemental Sulfur (S)	Gravel	Sand	PG	MD	Modified sulfur (STX™)	Ratio Elem. Sulf./ wast.
SPC-21*	21.00	23.10	46.14	0.00	0.00	2.10	0.70
SPC-PG-17-10	17.00	23.77	47.53	10.00	0.00	1.70	1.70
SPC-PG-19-20	19.00	19.70	39.40	20.00	0.00	1.90	0.95
SPC-PG-21-30	21.00	15.63	31.27	30.00	0.00	2.10	0.70
SPC-MD-17-10	17.00	23.77	47.53	0.00	10.00	1.70	1.70
SPC-MD-21-20	21.00	18.97	37.93	0.00	20.00	2.10	1.05
SPC-MD-21-30	21.00	15.63	31.27	0.00	30.00	2.10	0.70

*10% calcium carbonate

Ratio Gravel/Sand= 0.50; ratio Sulfur/STX™= 10.00

It should be noted that the percentage of modified sulfur plays an important role in the workability and mechanical strength of SPC [McBee and Sullivan, 1979]. PG and MD wastes have been added to the mixtures at dosages between 10 and 30 wt % (see Table 1). A total of 7 SPC cement samples were prepared: one reference sample (SPC) and three sulfur polymer cements samples containing phosphogypsum (SPC-PG) and three mud (SPC-MD). Each of the samples were denominated as SPC-X-Y-Z where "X" is the king of waste incorporated in the SPC (phosphogypsum or mud), "Y" is the wt % of elemental sulfur, and "Z" is the percentage wt.% of the waste in the mixtures.

The aggregates (gravel/sand and waste (PG and MD)) were heated in an oven up to 130–135 °C for 4 h. The specific amount of sulfur, gravel, sand and mud were heated in a preheated mixing bowl where the temperature was controlled at 135–140 °C for 10 min. The heated mixture was properly mixed until a homogeneous viscous mixture was obtained. Then the modified sulfur was added with continuous mixing. Finally the mixture is stirred at 140–145 °C for 4–5 min to ensure the total fusion of the thicker particles. A steel mold with dimension 40 mm × 40 mm × 160 mm was used. The molds were preheated to approximately 120 °C before adding the sulfur polymer cement, the material was compacted using

a vibration of 3000 rpm for 30 s on a vibrating table. The storage of the molds was done at a room temperature. The specimens were de-molded at an age of 24 h after placement in steel molds.

The SPC sample reference (called SPC-21) was manufactured similarly to the waste SPC samples, but in this case calcium carbonate (99.5% purity, Panreac) was added as filler (10% of the mixture) in substitution of waste.

2.3 Samples Characterization

The major elements were measured for X-ray fluorescence (XRF) with a Bruker S4 Pioneer. The mechanical properties of the SPCs samples were measured according to the standard UNE 196-1:2005. Compressive strength (Cs) was measured in the 7 SPC samples cured at ambient temperature for 1 day of age. In addition, the normalized tests for Ordinary Portland Cement (OPC) have been also carried out. All the results were obtained as an average value of six measurements performed using a universal press Ibertest model Autotest 200-10-W.

Gamma emitting radionuclides determinations were carried out by using a gamma spectrometry system XtRa with carbon window to detect the low gamma energies, while Po, Th and U-isotopes activity concentrations were determined by alpha-particle spectrometry with semiconductor detectors [Oliveira and Carvahlo, 2006].

The leaching experiments of SPC samples were tested in buffers of different pH, by submerging them in demineralised water for 24 h. Then they were dried, weighed, and again submerged for 21 days in 250 mL of buffer solutions at different pH (2-10) (Panreac) (n = 3 for each pH). After this time the samples were air-dried and weighed to make sure their weight had not changed by more than ± 2 g compared to their starting weights. The samples were then again submerged in their respective buffers for another 21 days. The variation in weight and the coefficient of absorption with respect to the pH (A_C) determined as follows:

$$A_c\ (\%) = \frac{P_{3i} - P_{1i}}{P_{1i}} \cdot 100\ A_c\ (\%) = \frac{P_{3i} - P_{1i}}{P_{1i}} \cdot 100 \qquad (3)$$

where P_{3i} is the weight after 42 days of immersion, and P_{1i} the initial weight of each sample after immersion in water for 24 h. After the 42-day experimental period the solutions were filtered and their radionuclide concentrations determined. The percentage of each leached radionuclide was determined by the leaching coefficient (L_c) according to Eq. (4).

$$L_c\,(\%) = \frac{A_L\,(Bq \cdot l^{-1})}{A_s (Bq \cdot g^{-1})} \cdot \frac{V_t\,(l)}{P_{1i}\,(g)} \cdot 100\ L_c\,(\%) = \frac{A_L\,(Bq \cdot l^{-1})}{A_s (Bq \cdot g^{-1})} \cdot \frac{V_t\,(l)}{P_{1i}\,(g)} \cdot 100 \qquad (4)$$

where A_L is the concentration of the corresponding radionuclide in the leachate (expressed in $Bq \cdot l^{-1}$), V_t is the total volume of the solution after 42 d (0.250 L in all cases), A_s is the concentration of the corresponding radionuclide in the concrete (expressed as $Bq \cdot g^{-1}$), and P_{1i} the weight of the concrete sample after 42 days of immersion in the corresponding buffer (g).

3. Results and discussion

3.1. Characterization of raw materials

Table 2 shows the chemical composition for the major elements in the PG, MD and the gravel and sand used.

Table 2. Concentration (%) of major elements

Component	LOI	SiO_2	Al_2O_3	CaO	Fe_2O_3	MgO	TiO_2	SO_3	P_2O_5	K_2O	Na_2O
PG	2.4	2.43	0.4	40.3	0.23	0.04	0.04	52.41	0.95	0.03	0.13
MUD	11.19	11.88	1.44	0.73	12.49	0.94	52.92	7.79	0.02	0.16	0.16
Gravel	7.86	29.12	1.27	57.83	0.8	0.63	0.13	0.27	-----	0.25	-----
Sand	8.9	79.89	10.75	0.42	0.74	0.26	0.11	-----	-----	5.3	1.78

The main components in PG are CaO (40%) and S (expressed as SO_3 with 54 %), as expected and their percentage it is close to 90% of total, which is confirmed by XRD where the main component is gypsum, $CaSO_4.2H_2O$. Also we found P_2O_5 in a 0.96%, which remains in PG later the washing in the industrial process and non-negligible percentages of SiO_2 [Rentería-Villalobos et al, 2010]. In the mud samples it is important to point out the high concentration of titanium oxides (53 %) and appreciable amounts of iron and silicon oxides, 12.5 % and 11.88 % respectively, similar to the observed for other author [Gázquez et al, 2011]. The concentration of S is approximately 7.8 %, which is unsurprising if we consider that the mineral digestion where the mud is generated.

3.2. Characterization of mud SPC cements
The compressive (Cs) and flexural strength (Fs) in the SPCs cements is shown in Table 3. Each result in this table is the average of three tests performed on three different samples formed from the same paste. The same table also shows the comparative results for the SPC 21 taken as reference.

Table 3. Values of compressive strength (Cs) and flexural strength (Fs) in the SPC samples, for one day of age and ratio Sulfur/wastes

	Fs (Mpa)	Cs (MPa)	Ratios Sulfur/ wastes
SPC 21	7.07 ± 0.66	57.70 ± 1.98	0.70
SPC-PG 17-10	9.36±0.24	55.41±1.37	1.70
SPC-PG 19-20	11.20±0.14	62.11±0.86	0.95
SPC-PG 21-30	10.72±0.60	56.76±5.20	0.70
SPCMD 17-10	9.83 ± 1.82	58.45 ± 3.82	1.70
SPC-MD 21-20	13.25 ± 0.77	64.38 ± 1.62	1.05
SPC-MD 21-30	9.40 ± 0.52	36.77 ± 2.58	0.70

The compressive strength of the SPCs has values between 55 and 62 MPa for PG, and 36 to 64 MPa for MD cements. Other authors have reported similar compressive strength, as for example López et al. (2009) gave 54 and 58 MPa for metacinnabar SPCs. Mohamed and Gamal (2007) obtained compressive strength of 54 MPa for SPC with fly ash. Lin [Lin et al, 1995] showed that the SPC obtained from lead-

contaminated wastes have a compressive strength of 48.5 MPa. Sandrolini [44Sandrolini et al, 2006] reported that the compressive strength of SPC with a recycle aggregate coming from a ceramic industry is between 65-73 MPa. Moreover, these results can be compared with the most used cement in the world, the Ordinary Portland Cement (OPC). For example, a typical OPC is characterized by the follows characteristics: mixture of clinker (97%), natural gypsum (3%) and compressive strength category 52.5 N/mm^2 (final strength higher than 52.5 MPa for 28 days according to UNE-EN 196-1). In relation with the OPC tests, the results obtained were the follow: flexural strength of 10.1 ± 1.2 MPa for 28 days of age, and compressive strength of 61.3 ± 1.0 MPa for 28 days. In this sense, is very important to note that these values are similar or slightly lower than the values obtained for the SPC-PG 21-30, SPC-MD 17-10 and SPC-MD 21-20 samples in one day, Table 3.

3.3 Radiological characterization of samples

Taking into account that the wastes come from NORM industry, they need a radioactive characterization of different SPC samples obtained (Table 4). The activity concentration of ^{238}U and ^{226}Ra in the pure PG used in this work are around 100 and 600 Bq/kg respectively (Table 4), being in agreement with typical values given in the literature for other PGs with sedimentary origin, which are significantly higher than the average world-wide values from soils (25 Bq/kg of ^{238}U and ^{232}Th daughter [UNSCEAR, 1993]). Radionuclide with the highest activity concentration in the PG-SPCs are ^{226}Ra (and its daughters of small half live) and ^{40}K. As it is expected, activity concentration of ^{226}Ra shows a linear dependence ($y = 5.49 \cdot x + 8.95$; R^2=0.9988) with the percentage (x) of PG added. However, ^{40}K concentration decreases linearly ($y = -5.82 \cdot x + 529$; R^2= 0.9041), fact that is due the potassium content in PG is practically negligible (< 18 Bq/kg of ^{40}K, or < 0.06% in natural potassium).

Table 4. Natural radionuclide concentrations (Bq kg^{-1}) in cement polymeric samples (SPCs) and waste sample (gypsum and mud). Radium equivalent activity and the activity concentration index "I" calculated for the SPCs and wastes samples

Code	PG	SPC-PG 17-10	SPC-PG 19-20	SPC-PG 21-30	MD	SPC-MD 17-10	SPC-MD 21-20	SPC-MD 21-30
% Waste	100	10	20	30	100	10	20	30
^{210}Pb	624±37	70±5	143±9	219±13	247 ± 11	28 ± 4	40 ± 4	76 ± 7
^{238}U(^{234}Th)	97±6	21±2	12±2	38±3	184 ± 12	25 ± 4	61 ± 5	84 ± 7
^{232}Th (^{212}Pb)	8.2±1.0	9.4±0.7	8.6±0.6	8.1±0.5	250 ± 15	54 ± 3	115 ± 7	182 ± 11
^{226}Ra (^{214}Pb)	589±34	63±4	115±7	179±11	521 ± 30	51 ± 3	123 ± 7	194 ± 11
^{228}Ra (^{228}Ac)	8±1	8.6±0.8	8.8±0.8	6.9±0.7	1919 ± 112	212 ± 13	426 ± 26	674 ± 39
^{40}K	< 18	528±32	394±24	347±21	334 ± 21	512 ± 31	493 ± 32	413 ± 24
Index "I"	3.9	0.43	0.56	0.75	11.4	1.4	2.7	4.2
Ra (eq)	621.4	117	253	158	3291	394	770	1189

On the contrary, in MD sample the radionuclide with the highest activity concentration is ^{228}Ra (around 2000 Bq kg^{-1}), which is in agreement with typical values given in the literature [Gázquez et al, 2011]. The activity concentration of ^{228}Ra also shows a linear dependence ($y=18.7 \cdot x+ 59.6$; R^2 = 0.9976) with the percentage (x) of MD added in the MD-SPC samples. A similar behavior we see for the ^{210}Pb, 234Th and ^{232}Th. In relation to the ^{40}K, we can see that the activity concentration decreases when increase the mud content in the sample.

Activity concentration index (*I*) in the SPC-PG samples is below the EU reference value for bulk building materials (see table 5), as well as the Ra (eq) for all SPC-PG samples are also below the threshold of 370 Bq kg^{-1} considered in USA. However in the samples SPC-MD, the index *I* is higher than EU reference value for materials used in bulk amounts, and being the values of Ra (eq) also higher of 370 Bq kg^{-1}.

Table 5. Activity concentration index *"I"*.

Dose criterion	0.3 mSv y^{-1}	1 mSv y^{-1}
Materials used in bulk amounts, e.g. concrete	I ≤ 0.5	I ≤ 1
Superficial and other materials with restricted use: tiles, boards etc.	I ≤ 2	I ≤ 6

Table 6 shows the leaching experiments results recorded according to Eq. 3. The SPC 21 shows absorption coefficients, Ac, smaller than the SPC-PG 21-30 with a mean values 1.07 and 1.48 %, respectively, but sample SPC-MD 21-20 presents smaller absorption coefficients than SPC 21 for all the pH measured.

In relation with the leaching test, we can affirm that any of the following radionuclides was detected in the leachates: ^{226}Ra, ^{234}Th, ^{232}Th, ^{40}K nor ^{210}Pb, being their concentrations below 1 Bq·L^{-1}), and thus providing leaching coefficients of < 0.1%. Only U-isotopes and ^{210}Po were detected by alpha-particle spectrometry. The mean concentrations of ^{238}U leachate in the SPC-21 was between 0.078 and 0.143 Bq·L^{-1} for the acidic media, and 0.011 Bq·L^{-1} for pH=8, similar to the values recorded for inland water bodies (0.005–0.5 Bq L^{-1}) [Mas et al, 2006]. The mean leaching coefficient, Lc Eq. (4), for ^{238}U was 0.26% for the SPC 21, being higher in acidic media (0.34%) than basic media (0.03 %). The SPC 21-30 leachate had a mean ^{238}U concentration of around 1 Bq L^{-1} in acidic media higher than SPC 21, falling to 0.07 Bq L^{-1} for basic media (close to the upper limits allowed for groundwater affected by mining residues [1 Bq·L^{-1}] [Bolivar et al, 2010]. This, plus the results outlined in Table 6, shows that the contamination of water by uranium isotopes by SPC-PG 21-30 would be negligible.

Table 6. Water absorption coefficients, ^{238}U and ^{210}Po concentrations, and leaching coefficients with respect to pH

Sample	pH	Ac (wt%)	^{238}U (Bq L^{-1})	^{210}Po (Bq L^{-1})	^{210}Po Lc (%)	^{238}U Lc (%)
Reference SPC-21	2	1.63	0.08±0.003	<0.01	<0.01	0.27
	4	1.01	0.143±0.012	0.039±0.019	0.19	0.48
	6	1.25	0.078±0.005	0.017±0.011	0.09	0.26
	8	0.95	0.0106±0.0003	<0.01	<0.01	0.03
	10	0.75	<0.01	<0.01	<0.01	<0.01
SPC- PG 21-30	2	1.50	1.09±0.05	0.97±0.07	0.18	1.17
	4	1.86	0.73±0.05	0.15±0.03	0.03	0.78
	6	1.99	1.14±0.04	0.067±0.017	0.01	1.22
	8	1.46	0.09 0.03	<0.01	<0.01	0.09
	10	0.87	0.05±0.01	<0.01	<0.01	0.05
SPC-MD 21-20	2	0.37	0.463±0.025	0.871±0.020	0.86	0.26
	4	0.36	0.363±0.078	0.891±0.027	0.88	0.30
	6	0.34	0.340±0.020	0.862±0.020	0.84	0.20
	8	0.38	0.111±0.008	0.906±0.023	0.90	0.18
	10	0.46	0.009±0.004	0.807±0.026	0.77	0.05

At 0.001-0.1 Bq L^{-1}, the range of concentrations recorded for ^{210}Po was 1-2 orders of magnitude lower than for ^{238}U. Table 6 shows that, for the reference sample, the activity is between 0.039 and 0.017 Bq L^{-1} for acid media, below the mean 0.01 Bq L^{-1} recorded for basic media. For SPC-PG 21-30 it was somewhat

higher (at around levels for inland water bodies) in acidic media, but lower (0.01 Bq L^{-1}) in basic media. The leaching coefficient in the acidic media was 0.14% for SPC 21, and 0.07% for SPC-PG 21-30. The concentration of ^{238}U was about twice that of ^{210}Po in the leaching, in agreement with the fact that Po tends to become more strongly fixed to particulate material than U.

The SPC-MD 21-20 leaching has an activity concentration of ^{238}U around 0.38 Bq L^{-1} in acidic media (pH=2 – pH=6), falling to 0.1 Bq L^{-1} for pH=8, and 0.009Bq l^{-1} for pH=10. Therefore we can affirm that the contamination of water by uranium isotopes due to the MUD-SPC cements would be negligible. The concentration ^{210}Po for all pHs in the SPC-MD 21-20 sample is very similar, around 0.8 Bq L^{-1}, being in general the leaching coefficient for ^{210}Po higher than the ^{238}U one; in a factor of 3 or even factor 15 for pH10.

4. Conclusions

The results confirm the stabilisation/solidification of PG and MD with a low radionuclide activity using sulfur polymer cement in radioactivity safe conditions. The following major conclusions may also be drawn from the study:

a) The S/S process has permitted to obtain a solidified material with an optimal mixture ratio of sulfur/phosphogypsum = 1:0.9 and sulfur/mud = 1:1, and a waste dosage = 10-30 wt% resulting in highest strength (55 to 62 MPa to SPC-PG and 36 to 64 MPa to SPC-MD).

b) The activity concentration index (*I*) in the study PG-SPCs are agree with the EU references and PG-SPCs can be used without radiological restriction in the manufacture of building materials. However the values of (*I*) in the SPC-MD are higher international regulations, so these cements can be used with radiological restrictions.

c) Finally, the leaching tests for SPC-PG 21-30 and SPC-MD 21-20 showed that leaching coefficients in acidic media are always higher than in alkaline solution, as it is expected, and for all studied cases they are under the international recommendations, thus the potential pollution of waters affected by these cements can be considered negligible.

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The IAEA Environmental Modelling for Radiation Safety programme (EMRAS II) – working group on "Reference approaches to modelling for management and remediation at NORM and legacy sites"

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Abstract

Working group II of the IAEA programme EMRAS II focuses on the issue of "NORM and legacy sites". An overview of the objectives and achievements of the working group – composed of both modellers and regulators - is given. The group performed a review of several NORM and legacy sites from 16 countries and developed a General Assessment Methodology. Two sites were selected for a modelling exercise: the Gela phosphogypsum stack in Italy and the former uranium mining and milling site of Bellezane near Limoges, France.

1. Introduction

The general aim of the *Environmental Modelling for Radiation Safety* (EMRAS II) programme of the International Atomic Energy Agency (IAEA) is "*to improve capabilities in the field of environmental radiation dose assessment by means of acquisition of improved data for model testing, comparison, reaching consensus on modelling philosophies, approaches and parameter values, development of improved methods and exchange of information*". This programme is the follow up of previous IAEA-sponsored programmes in the field of radioecological modelling, which included VAMP (Validation of Model Predictions, 1988-1996), BIOMASS (BIOsphere Modelling and ASSessment, 1996-2001) and EMRAS I which ran from 2003 to 2007. The BIOMASS Remediation Assessment Working group already focused on the application of different models to a site contaminated with radium [IAEA, 2004]. In EMRAS I, a working group on modelling of NORM releases and of the remediation benefits for sites contaminated by extractive industries was set up and collected information about NORM industries, available data and existing models [IAEA, 2007]. In EMRAS II, working group II focused on the development of reference approaches for NORM and legacy sites for the assessment of environmental impacts and risks.

A large number of NORM and nuclear legacy sites exist around the world and there is concern about how to make sound decisions on the future management and remediation of these sites. "Legacy sites" here is taken to mean sites which have been operated in the past and need, or are expected to need, some form of remediation so as to properly protect human health and the environment. The sites may be contaminated by man made radionuclides or by NORM. Some of these sites may still be operational or under some form of control, rather than totally abandoned. A common feature of the sites is that they were formerly operated without adequate controls – according to today's standards –, leading to radioactive contamination of larger areas. The sites may be in need of clean-up operations and fall within the definition in ICRP 103 of "existing exposure situations" [ICRP, 2007].

Working group II was composed of both modellers and regulators. Cross-interactions and dialogues between modellers and regulators are of importance: the regulators will often define what is the assessment purpose and what are the end-points of the modelling process and will have to take regulatory decisions on basis of assessment carried out by modellers. The development of reference approaches necessitate that both modellers and regulators are aware of their mutual needs and constraints.

The EMRAS II programme has ended in 2011. The final report from the EMRAS II Working Group 2 will contain a description of various specific NORM and legacy sites, a description of available modelling tools, the General Assessment Methodology developed by the group and the application of this methodology to various real sites. It will also contain the results of a modelling exercise for the two test-cases which had been selected: the phosphogypsum stack of Gela in Italy and the uranium tailings repository of Bellezane in France.

2. NORM and legacy sites around the world

Participants of the working group presented several NORM and legacy sites covering 16 countries from almost all continents. This illustrates the ubiquity of the issue and shows clearly the importance of exchange of information and experience between various countries.
These sites will be described in details in the final report of the working group. They may be classified in three main categories:

- nuclear legacy sites, e.g. former test-sites of atomic bombs;
- NORM sites, e.g. phosphogypsum stacks;
- Uranium milling and mining sites;

Table 1 gives an overview of all sites presented. While – by definition – a legacy site is a non-operational site, regardless of the type of radionuclide (artificial or natural), several NORM sites are still in operation – which means that the modelling process may not only aim at *remediation* of existing contamination but also at *prevention* of possible radioactive legacies. Moreover, for NORM industries in operation, the radiological assessment does not only focus on the possible impact of the site on the public and the environment but also on the operational radiation protection of the workers in the industry.

For most of the sites, data may be structured as follows:

1. Description of the source term: volume of contaminated materials, area of site, relevant nuclides and ranges of activity concentration, etc.
2. Description of the site: hydrogeology, climate, soil type, transfer factors,...
3. Monitoring data: dose-rate on site, nuclides concentration in ground- and surface water and/or in percolate, radon exhalation measurements, activity concentration in plants and animals, etc.
4. For sites which are already in the remediation stage, description of the remediation measures.

It constitutes an embryo of what could be a catalogue of NORM and legacy sites around the world. Using a similar structure in the description of these sites facilitate the identification of common characteristics and differences between the various sites, so that – hopefully – general lessons about radiological risk-assessments could be more easily drawn (like the identification of the most sensitive parameters in the risk-assessment process).

Table 1: overview of the sites

Country	Category	Name of site
Argentina	*U mining and milling*	Los Gigantes
Australia	*Legacy*	Maralinga nuclear test site
Belgium	*Legacy*	Olen (radium production)
	NORM	Tessenderlo (phosphate processing)
	NORM	Other Belgian NORM sites (phosphogypsum stacks, ferro-niobium processing)
Brazil	*U mining and milling*	Poços de Caldas Uranium mine and milling
	NORM	Botuxim site (storage residues from monazite processing)
Bulgaria	*U mining and milling*	"Iskra" site (Katina)
		Uranium Milling plant "Zvezda"
China	*NORM*	Baotou sites (rare earth extraction and steel industry)
Estonia	*Legacy*	Paldiski (former nuclear submarine training facility)
	U mining and milling / legacy	Sillamäe (Uranium mine tailings + former nuclear material production facility)
France	*U mining and milling*	Uranium mining sites of Limousin region
Greece	*NORM*	Megalopolis - Coal Fired Power Plant
	NORM	Kavala phosphogypsum stack
Italy	*NORM*	Gela phosphogypsum stack
Norway	*NORM*	Soeve site (Niobium mining and processing)
Poland	*NORM*	Several sites in the Upper Silesia coal basin
Slovenia	*U mining and milling*	Žirovski vrh wastes piles
Spain	*NORM*	Compostilla - Coal Fired Power Plant
Ukraine	*U mining and milling*	Pridneprovsky plant (Dniprodzerzhinsk)
USA	*U mining and milling*	Abandoned Uranium Mine Sites on Navajo Nation

3. General assessment methodology

The working group agreed on a general assessment methodology to perform the radiological impact assessment of NORM and legacy sites. This methodology is consistent with the recommendations of IAEA documents (see e.g. [IAEA WS-G-3.1, 2007]) on the subject and with methodologies developed by several national states. It is a graded approach in which the essential steps are the following:
- identification of the problem;
- preliminary site investigation and characterization;
- screening assessment using conservative assumptions and exposure scenarios;
- more realistic assessment;
- detailed assessment;
- remedial action;

The final report gives illustrations of the application of this methodology for some specific sites: the monazite processing site of Botuxim (Brazil), the niobium mining and processing site of Soeve (Norway),

the former atomic weapons test site of Maralinga (Australia), the phosphate residues dumpsite of Tessenderlo and the former radium production site of Olen (both in Belgium).

4. Modelling exercises

4.1 The phosphogypsum stack at Gela (Italy)

i) Site description

A description of the site may be found in the EMRAS I report [IAEA, 2007]. The modelling exercise focussed on the phosphogypsum (PG) stack located a few hundred metres off the coast. This stack is about 55 ha wide; the mean height of phosphogypsum residues is 14.5 m. The stack is positioned in an area where a bed of clay is present. In 2002, a 60 cm thick bentonite wall was constructed at a distance of about 5 m from the heap of residues. This wall penetrates 3 m into the clay bed. A drainage trench between the wall and the heap was constructed, with a series of wells to collect rainfall percolate. In addition, an experimental station for chemical treatment of percolate was installed, in order to separate the dry component - to be deposited back in the landfill - from purified water. Figure 1 gives a schematic view of the design of the site.

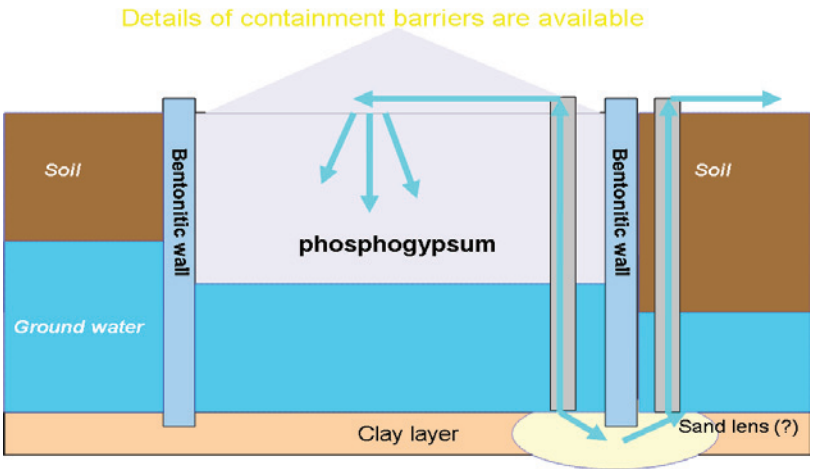

Figure 1: Schematic view of the Gela PG stack

Groundwater flows towards the sea but the groundwater level is very dependent on rainfall; for long periods during the year piezometers and well are dry.

ii) Modelling

The modelling exercise focused on two main tasks:

1. Try to simulate the situation without the retaining wall – this means matching the predicted radionuclide concentrations in well water against the measured values. This allows the model to be calibrated.
2. Try to simulate the situation with the retaining wall – this means finding a way to simulate the very low transfer rate of leachate to the environment.

Calculations were performed with RESRAD-OFFSITE [Yu et al, 2007] as well as DOSDIM [IAEA, 2004], [IAEA, 2007].

Table 2 gives an example of measured activity concentration in well-water (where percolate is collected):

Table 2: nuclide concentration in well-water (all results in Bq/l)

Sampling date	U-238	U-234	Ra-226	Pb-210	Po-210
30/01/2007	14.083 (±1.547)	15.428 (±1.693)	0.312 (±0.047)	12.91 (±2.11)	6.427 (±0.705)

The first task requested an optimisation of the hydraulic conductivity of the aquifer: in RESRAD-OFFSITE this parameter was increased from 500 m/yr to 1500 m/yr, in order to obtain estimates comparable with the Ra-226 concentrations measured in the well-water after 30 years of rainfall infiltration.

For the second task, as RESRAD-OFFSITE does not provide for modelling of a vertical barrier, the confinement due to the vertical barrier was simulated by inserting a horizontal clay barrier between the PG stack and the aquifer. Fig. 2 shows the modelling results for Ra-226 concentration in well-water with and without this fictitious clay barrier and for different values of the hydraulic conductivity of the contaminated zone and of the aquifer. The hydraulic conductivity of the contaminated zone has no influence on the results, so that the blue and red curves are merged on the graph.

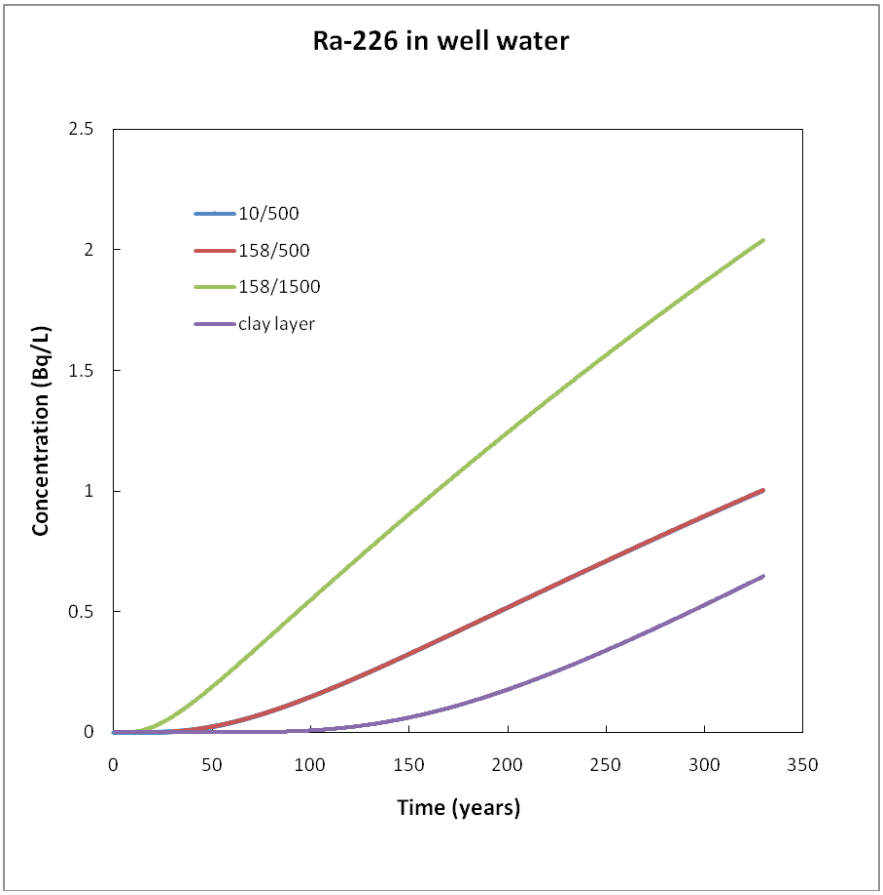

Figure 2: Ra-226 concentration in well-water. The label indicates the hydraulic conductivity of contaminated zone (left) and aquifer (right).

The figure clearly shows the predicted impact of the clay barrier (purple curve). It delays the break-through of radionuclides into the groundwater by approximately 100 years, compared with a predicted delay time of 10-15 years without the clay barrier in place. The calculations also suggest that the presence of the clay barrier should reduce the Ra-226 concentrations in ground water by a factor of at least 4 compared with the situation without the barrier.

4.2 The uranium tailings repository of Bellezane (France)

i) Site description

Uranium mining activities have taken place on the site of Bellezane (Limousin region, France) between 1975 and 1992. These extraction activities consisted both in underground mining works and in open pit mining. The open pit mines ("pit 68" and "pit 105") were filled with uranium tailings between 1988 and 1992. Finally they were covered with waste rocks and a vegetal cover. They are separated by a dike. The remediation of the site was completed in 1996. Water collected from the site, like run-off water or water running through the former mining galleries, is handled at a water treatment facility.

The total mass of tailings may be estimated to 1,512,000 tons. The average nuclide concentration is around 32 Bq/g for Ra-226 and 1.6 Bq/g for U-238. The nuclide concentration in the waste rock covers (total volume ~ 295,000 m^3) amounts to 0.5 Bq/g U-238 in secular equilibrium.

An extensive environmental surveillance program has been implemented and covers the following compartments: groundwater, surface water, air, fish, sediments, milk, soil, vegetables and animals (the latter represent, so far, too few data to be usable).

ii) Modelling

Two exposure scenarios have been defined:
- a current situation scenario which corresponds to the configuration of the site nowadays. The representative person is considered to be an adult who lives and works in the nearest village (~ 1 km away from the site). A part of his diet is made of locally grown products (meat of cows pasturing on fields close to the tailings repository, and vegetables grown on fields close to the repository). In summer, the locally cultivated vegetables are irrigated with ground water taken from a well located on the field.
- an intrusion scenario: A family lives in a house on site. They work at home and have a garden where they grow some vegetables. These vegetables are irrigated in summer with water from a well pumping directly from the groundwater. Every exposure pathways are considered.

Two models were used to perform the calculations: SATURN [SATURN, 2011] and RESRAD-OFFSITE.
For the current situation scenario, both modelling results have shown that the human dose impact is trivial during the calculational time frame of 1000 years; this is due to the very long travel time (more than 40,000 years) of the radionuclides to surface water and groundwater.

For the intrusion scenario, both models give significant dose estimates but a meaningful comparison between the RESRAD-OFFSITE and the SATURN results is difficult to establish due to different modelling assumptions and approaches, for instance in the modelling of the source term and of the exposure pathways: while in the RESRAD-OFFSITE calculations, the pits 68 and 105 containing the tailings of the Bellezane repository had been replaced by an average single source term, SATURN calculated contributions of both pits separately. SATURN focused on a few specific exposure pathways – neglecting for example the drinking water pathway - while RESRAD-OFFSITE included all of them.

The RESRAD-OFFSITE calculations took into account the contribution of the nuclide content of the waste rock cover and showed that, in a timeframe of 1000 years, both tailings and waste rock contribute to the dose. Up to 450 years, the main contribution to the dose comes from the radon emanating from the waste rock layer, containing radium-226 levels comparable with those in e.g. phosphogypsum. The tailings will affect the water-dependent pathways, which dominate on longer time-scale.
In spite of the different modelling assumptions, the quantitative results in the intrusion scenario for the dose from ingestion of plants turned out to be very similar in both models. At t= 100 yr, this dose

amounts to 1.18 mSv/yr in the RESRAD-OFFSITE calculations while the SATURN calculations give 1.33 mSv/yr for pit 68 and 0.65 mSv/yr for pit 105.

Sensitivity analysis was performed with both models (e.g. on some K_d values) while a probabilistic approach was also used in the SATURN modelling for the dose due to consumption of plants. This probabilistic simulation accounts for uncertainties in K_d, transfer factors and some other parameters. It was assumed that uncertainty ranges of K_d and transfer factors are log-normally distributed. Due to lack of time, such a probabilistic simulation was not performed with RESRAD-OFFSITE.

Sensitivity and probabilistic analysis are important tools in identifying the most relevant parameters in the impact assessment.

The model-model intercomparison showed up to be rather a "modeller-modeller" comparison – showing how two independent groups of modellers could make different assumptions about a same complex reality.

Conclusions

The EMRAS II working group on "NORM and legacy sites" collected a significant amount of specific data for about 20 sites around the world. These data sets are not only important for modellers who wish to test their model for real situations but they may also be useful for experts in other field of environmental studies (e.g. measurements on nuclides concentration in animals and plants).

A general assessment methodology was developed and tested on a few case studies. Modelling exercises were carried out for the PG stack of Gela (Italy) and the uranium tailings repository of Bellezane (France). These exercises showed the importance of developing a well-defined detailed conceptual model of the site including the different exposure pathways. Modelling a NORM or legacy site is a complex task due to the difficulty in collecting site-specific data on all parameters, which may affect the results. Sensitivity and probabilistic analysis are key-elements of the modelling and decision-making process.

Due to lack of time, the modelling exercises, and in particular the comparison between different models, could not be completed. IAEA launched a follow up programme to EMRAS II called MODARIA (*Modelling and Data for Radiological Assessment*). Further work on the modelling of NORM and legacy sites could be carried out in this new programme. Points of attention could be, among other things:

- development of the capability to carry out probabilistic calculations and development of rigorous methods of estimating uncertainties in model predictions and estimates;
- modelling of the effectiveness of different remediation actions for real sites;
- cross-over between working groups, e.g. submit real site data to other working groups for possible integration in their own modelling objectives.

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Radioactivity in residues and effluents from Estonian waterworks treatment plants

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Abstract

Considerable levels of radium were detected in a certain fraction of the Estonian drinking water supply network. Some of these waterworks are supplied with treatment systems for the removal of iron and manganese from drinking water. Three of these waterworks and another one equipped with a radium removal pilot plant were examined, and a specific study was conducted in order to assess public exposure from effluents and residues produced in the plants. ^{226}Ra and ^{228}Ra activity concentrations were analysed in both liquid (backwash water) and solid (sand filter and sediment) materials to evaluate, from the radiological point of view, their environmental acceptability on the basis of international technical documents that propose reference levels for radium in effluents and residues. First results indicate that releases of backwash water generally fall within reference levels, whereas solid residues exceed them. A preliminary analysis was also done of possible consequences of the transposition of the European *Basic Safety Standards* Draft into Estonian law.

1. Introduction

In 2009 the European Union sponsored the Twinning Project between Estonia and Italy *Estimation of concentrations of radionuclides in Estonian ground waters and related health risks*, within the framework of the Estonian Transition Facility Programme.
It is well known that in some regions of the Republic of Estonia, the amount of natural radioactivity in groundwater is not negligible (Mokrik et al. 2009). This gave rise to a remarkable number of non-compliances in local aqueducts when EC Directive 98/83 (European Council 1998) was transposed into national law, which conservatively established the parametric value of 0.1 mSv/year as a limit for the Total Indicative Dose (TID) in drinking water. In Northern Estonia, this dose value is often exceeded mainly as a result of relatively high concentrations of ^{226}Ra and ^{228}Ra. The project aimed at 1) revising existing data on radioactivity in water resources; 2) evaluating population dose and establishing criteria for a risk assessment; 3) giving suggestions for a monitoring upgrade, both in terms of analytical techniques and sampling plans; 4) suggesting strategies to set up local-scale and sustainable remedial actions. The outcomes of this project are fully exposed in the Final Technical Report (European Commission 2010a), and points 1-3 were further discussed (Forte et al. 2010).
The highest radium concentrations are known to be found in the oldest and deepest Estonian aquifer (Raidla et al. 2009), called Cambrian-Vendian (Cm-V). This aquifer becomes shallower in Northern Estonia, close to the coastal area, where it is widely used as a drinking water reservoir. Being the most populated area as well, the radioprotection concern involves a high percentage of Estonian population.
Many analytical data on waterworks, especially in Northern Estonia, were available, albeit rather inhomogeneous. Upon a first examination, they showed that 92% of the Water Supply Zones (WSZs) served by the Cm-V aquifer - *vs.* 21% of WSZs served by other aquifers - exceeded the 0.1 mSv/year value. The WSZs fed by the Cm-V aquifer are 140 out of 912 in the whole country, and they serve roughly 250,000

people, 22% of Estonian population. Of particular concern is the younger population: as for infants (< 1 year of age), the 0.1 mSv/year TID was exceeded in the water of all the aquifers analysed. Specifically, 97% data of Cm-V water resulted in doses higher than 1 mSv/year in, up to 12 mSv/year (Forte et al. 2010).
The adoption of effective countermeasures for radium removal from drinking water is hampered both by the lack of cheap, selective processes, and the fragmentation of the water distribution network: in Estonia 75% of the water supply zones serve less than 1,000 people each. Notwithstading, many treatment plants, especially in the coastal area, are working at removing excess iron and manganese from drinking water. But when their effectiveness in removing radium was investigated, it appeared quite poor (decontamination factors for both ^{226}Ra and ^{228}Ra were slightly above 10%). In any case, the problem of enriched wastes from these treatment stations was addressed.

2. Effluents and residues from existing treatment plants

Four Estonian aqueducts with waters rich in ^{226}Ra and ^{228}Ra were surveyed in the year 2009. These waterworks have treatment systems, and data were collected for a preliminary evaluation of the potential impact on the environment of the effluents and residues formed during the treatment processes. All the collected information on the examined waterworks is reported in Table 1: annual backwash discharge rate, treatment type and fate, ^{226}Ra and ^{228}Ra activity concentration, and annual activity discharge rate.
Radium activity concentrations in water and residues were assessed by several laboratories, among them the Estonian Radiation Protection Centre, the Tartu University and the STUK (Finland).
The ground water network of *Tallinn waterworks* consists of 85 wells afferent to 56 pumping stations, of which 19 are supplied with treatment systems. Water is filtered through sand and gravel to remove Fe, Mn and NH_4; an aeration stage precedes the filtering. Filters are periodically cleaned by backwash water, which is then channelled to sewage. All backwash waters are conveyed to a single sewer (that of Tallinn city) that serves about 400,000 inhabitants. Sludge from Tallinn sewer is used as filling material in landscape construction projects, whereas purified water is released into the sea. Table 1 reports detailed data about waters from four treatment stations (Jugapuu, Raba, Toome-Õitse, Tiskre). Radium data were not available for the other stations in Tallinn. Total radium discharge rate from all Tallinn treatment stations was then estimated on the basis of total water discharge rate and average radium values (Table 1).
Filtering material is very rarely replaced (once in several years). In 2009 the Merivälja (Tallinn) pumping station filter was removed, and its radioactivity content was measured. Results are given in Table 2. It is worth noting that also ^{228}Th and its decay products occur in filter material, presumably due to ^{228}Th growth from the ^{228}Ra on the filter.
In *Keila waterworks*, groundwater from 4 wells is mixed before being collected in treatment tanks, where Fe and Mn removal techniques - similar to those of Tallinn - are applied. Waters are conveyed to sewage; the resulting sludge is not used in agriculture. Two samples of filter material (sand) were analysed to assess ^{226}Ra, ^{228}Ra and ^{228}Th (for the reason reported above). Results are shown in Table 2.
In *Rakvere waterworks*, 5 groundwater wells deliver water to a treatment plant of the same kind as the previous ones. Backwash water is cleared to sewer; the sludge is used as farmland fertilizer and purified waters are released into a small river. Activity concentrations (in particular of ^{226}Ra, ^{228}Ra and ^{228}Th) on filter material (sand) and backwashing sediment are shown in Table 2.

Table 1. Information on effluents from waterworks treatment plants

Waterworks	Treatment Station	Treatment type	Backwash water					
			(m^3/y)	^{226}Ra (Bq/m^3)	^{228}Ra (Bq/m^3)	Fate	^{226}Ra (Bq/y)	^{228}Ra (Bq/y)
Tallinn	Jugapuu	Stations with sand/gravel filters for Fe, Mn, and NH_4 removal (pre-aerated)	1708	3100	8700	Sewer	5.29E+06	1.49E+07
	Raba		507	8730	14710		4.43E+06	7.46E+06
	Toome - Õitse		1018	9350	13650		9.52E+06	1.39E+07
	Tiskre		581	5320	6040		3.09E+06	3.51E+06
	All other Stations		17428	n.a.°	n.a.°			
	TOTAL		21242	6625*	10775*		1.41E+08	2.29E+08
Keila	All 4 wells	Sand filters for Fe and Mn removal (preaerated)	1400	1380	1580	Sewer	1.93E+06	2.21E+06
Rakvere	All 5 wells	Sand filters for Fe removal (aerated)	36500	1774	1796	Sewer	6.48E+07	6.56E+07
Viimsi	Well No. 412	column I + column II (in parallel) for Ra purification	9.0	1805	2050	Sewer	1.62E+04	1.85E+04

* Average concentration value. ° not available

Table 2. Information on residues from waterworks treatment plants

Waterworks	Treatment station	Material	^{226}Ra (Bq/kg)	^{228}Ra (Bq/kg)	^{228}Th (Bq/kg)	^{40}K (Bq/kg)
Tallinn	Merivälja	Sand	8603	8681	5798	n.a.°
Keila	All 4 wells	Sand filter 1	5524	5754	3817	40
		Sand filter 2	5202	5618	3139	35
Rakvere	All 5 wells	Sand filter	3788	3047	1768	n.a.°
		Backwash water sediment	20103	15034	7176	1054

° not available

In *Viimsi waterworks*, water is drawn from 35 wells that are independent of one another. A pilot treatment device, devoted to radium purification, operates at well n. 412 (Katlamaja road). It is made of two parallel filtration columns, followed by an additional common cleaning stage. ^{226}Ra and ^{228}Ra content of waters used to wash the two columns are presented in Table 1, together with relevant information on flow and fate. Backwash water is conveyed to the same sewer used by the Tallinn waterworks.

3. Reference documents for clearance levels and effluent discharge screening levels

In water treatment, residues and effluents are formed which contain ^{226}Ra, ^{228}Ra (and ^{228}Th in solid materials). It is thus important to check the adequacy, from the radiological point of view, of the disposal procedure of solid materials and backwash water.

In the investigated cases, backwash water is conveyed straightaway to sewage, without purification in sedimentation basins, thus apparently no sludge is formed in the filter cleaning procedure (filtering material is replaced from time to time). Nevertheless, one sample of backwash water sediment was collected in Rakvere waterworks (see Table 2). It cannot be excluded that other waterworks in Estonia, not involved in this study, use sedimentation processes after filter cleaning.
Waterworks treatment processes may be regarded as work activities involving NORM: actually the EC Basic Safety Standards draft (European Commission 2011) includes them in the positive list of NORM activities. Estonian national legislation (Estonia Radiation Act 2004) does not define reference values for NORM wastes or discharges; therefore to evaluate the adequacy of processes, reference should be made to available international or national technical guides. These documents address solid and air/liquid waste production and discharge from NORM industries, and assess their radiological impact, considering various exposure pathways and scenarios, i.e., workplaces and environmental compartments (rivers, coastal sea, agricultural land, etc.).

3.1. Solid residues

In the analysed waterworks, solid residues are mainly sand filters, since backwash waters are sent directly to sewage, with the exception of Rakvere plant, which produces backwash water sediments. The document Radiation Protection 122 (RP 122) - part II "Practical use of the concepts of clearance and exemption - Application of the concepts of exemption and clearance to natural radiation sources" (European Commission 2002) is a useful and convenient European Commission publication by which to classify waterworks solid residues. It derives General Clearance Levels (GCLs) for natural radionuclides in residues and waste from work activities involving NORM (see Table 3).

Table 3. General Clearance Levels from RP 122 part II

	$^{226}Ra^{*}$ (Bq/kg)	$^{228}Ra^{*}$ (Bq/kg)	$^{228}Th^{*}$ (Bq/kg)
All materials	500	1000	500

* In secular equilibrium with short half-life decay products

These clearance levels can be used to test the radiological compliance of residues, i.e. residues with activity concentrations lower than the clearance levels can be reused, recycled, delivered for disposal with no constraint as for their radiological aspects. GCLs were determined to comply with the exemption-clearance dose criterion of 0.3 mSv/y for the individual effective dose.
The EC BSS draft (European Commission 2011) sets exemption or clearance values of 1000 Bq/kg for naturally occurring radionuclides of the ^{238}U and ^{232}Th series in solid materials in secular equilibrium with their progeny, and 10000 Bq/kg for ^{40}K. It specifies that 1) the clearance of solid materials should be intended for re-use, recycling, conventional disposal or incineration; 2) the values may not be used to exempt the incorporation into building materials of residues from industries processing naturally occurring radioactive material; 3) higher values may be defined for specific materials or specific pathways at certain conditions. These exemption and clearance values were adopted "for the sake of aligning to the international Basic Safety Standards" (European Commission 2010b) as laid down in an IAEA document (IAEA, 2004), and set by the interim edition of the IAEA BSS (IAEA 2011), rather than using those in RP 122. This choice was heatedly debated by the *Group of experts referred to in Article 31 of the Euratom Treaty*: "... Nevertheless, several experts consider that the Community guidance has a better scientific basis, in particular the exemption values for naturally occurring radionuclides, and they are concerned with the increase of some of the values" (European Commission 2010b).

3.2. Effluents

In order to assess the radiological impact of effluent discharges from the analysed Estonian waterworks three documents were consulted: 1) the IAEA Safety Report "Generic models for use in assessing the impact of discharges of radioactive substances to the environment" (IAEA 2001); 2) the publication RP 135 - Radiation Protection 135 "Effluent and dose control from European Union NORM industries: assessment of current situation and proposal for a harmonised Community approach" (European Commission 2003); 3) the National Radiological Protection Board document "Generalised Derived Constraints for Radioisotopes of Polonium, Lead, Radium and Uranium", NRPB 13 n.2 (NRPB 2002). Not all these documents have the same weight: IAEA and EC documents suggest reference values at the international level, whereas NRPB document only sets national standards.
All the documents give discharge screening levels based on conservative scenarios. RP 135 and NRPB calculated screening levels starting from a dose criterion of 0.3 mSv/y (individual effective dose), whereas IAEA suggests screening levels in terms of individual annual dose for unit discharge of main radionuclides. The EC BSS draft (European Commission 2011) also considers 0.3 mSv/y the dose for public exposure to NORM work activities corresponding to a general clearance criterion, explicitly referring to the impact from gaseous and liquid discharges as well.
IAEA and NRPB assessed reference levels for liquid discharge into small rivers and sewers. However, IAEA chose workers exposure in the sewing plant as the critical scenario for discharge into sewer, whereas NRPB, the use of sludge on farmland. Lastly, screening levels of RP 135 concern release into rivers of various sizes and into coastal sea.

4 Comparison of radioactivity in effluents and residues with international reference levels

4.1. Solid residues

^{226}Ra, ^{228}Ra and ^{228}Th activity concentrations of solid residues of filtration systems were compared with General Clearance Levels of RP 122 part 2 (European Commission 2002), shown in Table 3, to check whether conditions for unrestricted clearance of residues (whatever their fate) do apply. The comparison (Table 4) was carried out through the *sum index*, i.e. the sum of ratios of single nuclide activity to the relevant screening level. For compliance, the sum index should be less than 1.
The activity concentrations of all materials were higher than GCLs. GCLs were selected as the worst (most conservative) conditions (material type, reference scenario and population group) recorded in the modelled exposure situations. Actually, the adopted scenario, i.e. people living in a house whose building materials contain the radioactive residues, does not appear realistic for the case we are discussing, i.e., solid residues from drinking water treatment plants. In any case, even if a different, more realistic scenario were selected (e.g. exposure of workers that use contaminated material for road construction or people living in houses close to a disposal site of contaminated residues), compliance would not be achieved.
No solid material complies with the reference levels, not even when compared with the clearance levels of the EC BSS draft (1000 Bq/kg individually applied to ^{226}Ra, ^{228}Ra and ^{228}Th, with or without short half-life progeny in secular equilibrium) (European Commission 2011).

Table 4. Comparison between activity concentrations of solid residues from existing treatment plants and GCLs of RP 122

Waterworks	Treatment station	Material type	Sum index*
Tallinn	Merivalja	Sand	37
Keila	All 4 wells	Sand filter (sample 1)	24
		Sand filter (sample 2)	22
Rakvere	All 5 wells	Sand filter	14
		BackWash water sediment	70

**The sum index is the sum of ratios of single nuclide activity to the respective GCLs; for compliance it should be less than 1.*

4.2. Effluents

Table 5 reports the screening levels suggested in the cited international documents and used for comparing the activity discharged with backwash water.
For Tallinn, discharge rates (based on the average radium concentration of available data) regard all 19 pumping stations. As backwash waters from Tallinn and Viimsi treatment plants flow into the same sewer (Tallinn city), their contributions were added for the comparison.
The choice of discharge screening levels needs some comment. Waters from filter cleaning of Tallinn and Keila plants have an impact on the sewer, but the sludge that forms in the process is not used in agriculture. This is the reason why in this case the IAEA values (IAEA 2001) for sewer were adopted, coherently with the actual conditions, screening levels being computed on the basis of the 0.3 mSv/y dose criterion.
The Rakvere backwash waters also flow to the sewage system, but the resulting sludge is used in farmland treatment: therefore, the more restrictive NRPB General Derived Constraint in sewer (NRPB 2002) was used. NRPB considers the agricultural scenario to be the most critical one in case of discharge into the sewer. Unfortunately, the test could only be carried out for ^{226}Ra, because the ^{228}Ra GDC is not available in the NRPB document (NRPB 2002)

Table 5. Discharge screening levels used to assess compliance of backwash water from existing treatment plants

Compartment	Critical pathway	^{226}Ra (Bq/y)	^{228}Ra (Bq/y)	Reference
Sewer	Sewer workers	$1.9 \cdot 10^{8}$	$1.4 \cdot 10^{8}$	IAEA 19
Sewer	Sewer workers	$3.8 \cdot 10^{9}$	$2.7 \cdot 10^{9}$	IAEA 19 (Tallinn)*
Sewer	Sludge for agriculture	$1 \cdot 10^{7}$	n.a.	NRPB 13 n.2
Coastal sea	Ingestion (fish)	$2.2 \cdot 10^{13}$	$1.2 \cdot 10^{13}$	RP 135
Small river	Ingestion (fish)	$7.5 \cdot 10^{10}$	$4.2 \cdot 10^{10}$	RP 135

**Screening levels scaled to account for the number of inhabitants served by the Tallinn sewer.*

For Tallinn, discharge screening levels were scaled to account for the number of inhabitants served by the Tallinn sewer, which is higher than the number modelled in the IAEA document, i.e. 400,000 vs. 20,000. This corresponds to a larger amount of produced sludge and a proportional dilution of the radioactivity in it.
In Tallinn, purified waters from the sewer are known to be released into the sea. Therefore, the alternative conservative assumption was assumed: that sewer sludge contains no radium from backwash water, that radium is wholly discharged into the sea. The comparison was then carried out with RP 135 screening levels for coastal sea (European Commission 2003).

The same holds for Rakvere, where the purified waters of the sewer are finally released into a small river: the alternative conservative assumption was assumed, that no radium content of backwash water is associated with sludge, that all is discharged into the river. The comparison was again carried out with RP 135 screening levels for discharge into a river (European Commission 2003).

Table 6. Comparison between discharge rates and screening levels for backwashing waters of existing treatment plants

Waterworks	Compartment	Sum index*	Reference
Tallinn and Viimsi	Sewer	1.22E-01	IAEA 19
Tallinn and Viimsi	Coastal sea	2,55E-05	RP 135
Keila	Sewer	2.60E-02	IAEA 19
Rakvere	Sewer	6.48	NRPB 13 n. 2
Rakvere	River (small)	2.42E-03	RP 135

**The sum index is the sum of ratios of single nuclide activity to the respective screening level; for compliance it should be less than 1. In the case of the NRPB document, the sum index is only the ratio for ^{226}Ra.*

Table 6 shows the comparison between discharged activity - in terms of the sum index - and screening levels.
It can be noticed that backwash waters of the waterworks in Tallinn and Viimsi -although based, at the moment, on few analytical data-, Keila and Rakvere (river compartment) comply with the sum index. For Rakvere, the ratio of ^{226}Ra activity discharged to its screening level is higher than 1 in backwashing water in the sewer compartment. This is due to the use of the sewer sludge on farmland (NRPB 2002), which entails more restrictive discharge screening levels. Moreover, as already specified, for this waterworks the sewer compartment compliance test was only carried out for ^{226}Ra, because ^{228}Ra GDC is not available in the NRPB document (NRPB 2002).

5. Conclusions

Some conclusions may be drawn from the application of international and national reference levels to solid residues and liquid effluents of these Estonian waterworks treatment stations.
As regards solid residues (sand filters and backwash water sediments), ^{226}Ra, ^{228}Ra and ^{228}Th activity concentrations are higher than both the general clearance levels suggested by RP122 part II (European Commission 2002) and the exemption and clearance levels set by the EU BSS draft (European Commission 2011). However, compliance could be demonstrated case by case with dose calculations in specific scenarios, taking into account the actual use and radiological impact of the residues.
As regards liquid effluents, all but those from the Rakvere treatment plant (sewer compartment) comply with IAEA and EC suggested discharge screening levels. As for the Rakvere sewer compartment, its liquid effluents should not be discharged: this is all too evident by just comparing ^{226}Ra activity concentration in backwash water with its respective reference level. This result arises from the fact that Rakvere sewer sludge is used on farmland, and that NRPB assumptions for calculating screening levels are highly conservative. Therefore, a more robust assessment would require a more realistic scenario and that all radionuclides in the backwash water be accounted for.
In any case, this preliminary analysis indicates that special care must be taken when managing solid residues from drinking water treatment stations and more detailed surveys and systematic analyses of radiation protection aspects should be made as soon as the new EC BSS will be transposed in the Estonian legislation.

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Surveying programme of the NORM situation of the Hungarian waterworks

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Abstract

In Hungary, the drinking water can be derived from surface water bodies, groundwater, karstic water and water from deep aquifer, and about 4000 pieces of wells and 120 waterworks can be found in the country. The content of radioactive elements depends on the NORM content of the given pathways (layers) through which the water has infiltrated, so the occurring radionuclides and their activity in the water can change from well to well. Close to the whole part of the raw waters obtained from different sources (wells) is to be purified and treated. The raw water treatment includes several filtration processes applying different filters (charcoal, gravel bed) and finally more or less sludge and used filter material arise.
In Hungary, the waterworks are not yet involved in the NORM regulation, therefore a preliminary survey study has been launched. Firstly, 25 waterworks represented from different parts of the country were chosen for the survey programme and then raw water, used filter material and sludge samples were taken. The activity of samples was measured by using gamma-ray spectrometry and the radionuclides of ^{226}Ra and ^{228}Ra in the raw waters were separately analyzed, too.
The results of the measurements show that the activity concentration of some sludge and used filter material samples are less than the activity concentration of NORM of the average soil in Hungary, but the activity concentration of the other sludge and used filter material samples are higher by a factor 10 to 15 to the average soil, and few sludge samples contain elevated radium activity concentration that are higher than 1 Bq/g.

1. Introduction

According to the proposal for the new EU Basic Safety Standards, the natural radioactivity (NORM) is to be more emphasized on the regulation of radiation protection. To create a better regulation, the accurate knowledge of the domestic NORM situation is necessary. In Hungary, a lot of surveying of NORM/TENORM were performed (Juhász 2005), but to date, surveying programme has not been carried out for the NORM situation of the waterworks. The Decree 47/2003 designates the activities concerning the occurrence of TENORM in Hungary:

- coal mining, coal fired power plants
- bauxite mining, alumina industry
- metal ore mining, metallurgy
- exploitation of oil, gas
- fertilizer industry, usage of phosphate ore
- usage of geothermal energy
- usage of zircon sand, ceramics factory
- rare earth ore mining, milling
- uranium mining and milling

The waterworks were out of these designated activities, probably, because there was not enough information about the NORM situation of the Hungarian waterworks that time. Nevertheless, a surveying programme has been launched in order to set up a suitable database of the NORM situation for waterworks before the regulation should be modified.

2. Basis of the survey program for waterworks

In Hungary, the drinking water can be derived from surface water bodies, groundwater, karstic water and water from deep aquifer. The groundwater is less supplied for drinking by waterworks, because pollution can often take place in this, so the water supplying from groundwater is below 5 % of the total drinking water consumption. The karstic water for drinking water is rated in about 10 % of the total supplied water. The rate of surface (near surface) water supplied for drinking is about 25 % of the total water consumption, and this water mainly arises from the bank parts of the rivers after natural filtering. In Hungary, more than 60% of the drinking waters are supplied from the deep aquifer through drilled wells. The typical depth of these wells is in the range of 50 m to 250 m.
Firstly, the waterworks supplying water from drilled wells were focused on, and secondly few waterworks using surface water were involved in the survey. The examination of karstic water and groundwater is to be planned in the next step.
In Hungary about 4000 pieces of wells and 120 waterworks have been established. In general, the waterworks are operated by private firms, and the operators have a little kick against any radioactive examination, but finally, firms from the planned representative areas could be found for the cooperation with the surveying programme.
Otherwise, this surveying programme was supported by the Hungarian Atomic Energy Authority, too.

3. Water treatment

The water by the aid of the complex hydrogeology transport processes reaches the different source points (surface water bodies, aquifer), and owing to these transport processes the content of solved elements in the water is very altering at each source well. In Hungary, close to the whole part of the raw waters obtained from different sources (wells) is to be purified and treated. This treatment is firstly performed to remove the pollutants, like manganese, iron, and arsenic. The treatment includes several filtration processes applying different filters (charcoal, gravel bed) and finally more or less sludge and used filter material arise (Fig. 1). Otherwise, the filtration process for the pollutants takes out also the great parts of radioactive elements containing the raw water, therefore the sludge and used filter materials comprise different radionuclides, too. So these residues of waterworks can be regarded as a NORM.
In Hungary, different amount of water is treated and supplied by the different waterworks, so the amount of the residues is very diverse. The range of the volume of the residues can be from 1 m^3 to 100 m^3 in a year. The operators of the waterworks emplace firstly the residues in a landfill, but many operators reuse these residues, if it is possible concerning chemical pollutants, such as gravel bed for filling.

Figure 1. The gravel bed filter system

4. Sampling

The content of radioactive elements depends on the NORM content of the given pathways (layers) through which the water has infiltrated, so the occurring radionuclides and their activity in the water can change from well to well.

Figure 2. The sampling places for the waterworks in Hungary

At the first step, 25 waterworks represented from different parts of the country (not including the karstic area) were chosen for the surveying programme, then raw water, used filter materials and sludge samples were taken. The Figure 2 shows the sampling places, and the collection and drying pools for sludge at one of the waterworks can be shown on the Figure 3.

Figure 1. The collection and drying pools for sludge

5. Measurements

After the preparation of samples, the activity concentration of samples was measured by using gamma-ray spectrometry. The occurring radionuclides and their activity concentration of the representative samples can be found in the Table 1. The results of the measurements show that the activity concentration of some sludge and used filter material samples are higher by a factor 10 to 15 to the average soil and few sludge samples contain elevated radium activity concentration that are higher than 1 Bq/g, which is realized in the Figure 4.

Table 1. The activity concentration of the representative samples in Bq/kg

Place (sample)	^{232}Th-series		^{238}U-series		
	^{228}Ac	^{208}Tl (^{224}Ra)	^{226}Ra	^{214}Bi	^{214}Pb
Pápa - Kemenesszentpéter (sludge)	2725±46	1710±31	1336±51	380±10	374±7
Mezőkövesd (sludge)	189±4	95,8±2,8	430±16	113±3	117±3
Mezőkövesd (charcoal)	100±3	80,4±2,9	46,2±6,2	90,6±2,3	92,3±1,9
Szolnok (sludge 1)	32,5±1,3	31,2±1,4	25,4±2,9	28,8±1	29,8±0,7
Szolnok (sludge 2)	49,3±1,8	51,3±2,6	68±14	74,9±2,6	62,8±3,1
Bonyhád - Kakasd (sludge)	1328±22	1224±35	562±49	543±17	560±12
Kiskunhalas (sludge)	654±11	286±9	282±20	270±6	259±5
Győr - Csorna (filter)	17,6±0,4	9,2±0,4	11,8±1,1	14,5±0,3	14,4±0,3
Sátoraljaújhely - Ricse (sludge)	204±4	205±5	158±8	112±3	116±2
Sopron - Csápordjánosfa (sludge)	587±12	147±8	2594±408	490±11	509±23
Sárvár (sludge)	121±3	113±3	88,1±4,6	75,2±1,7	78,4±1,4
Siklós – Ivándárda (sludge)	267±9	87,8±5,7	116±6	104±3	109±3

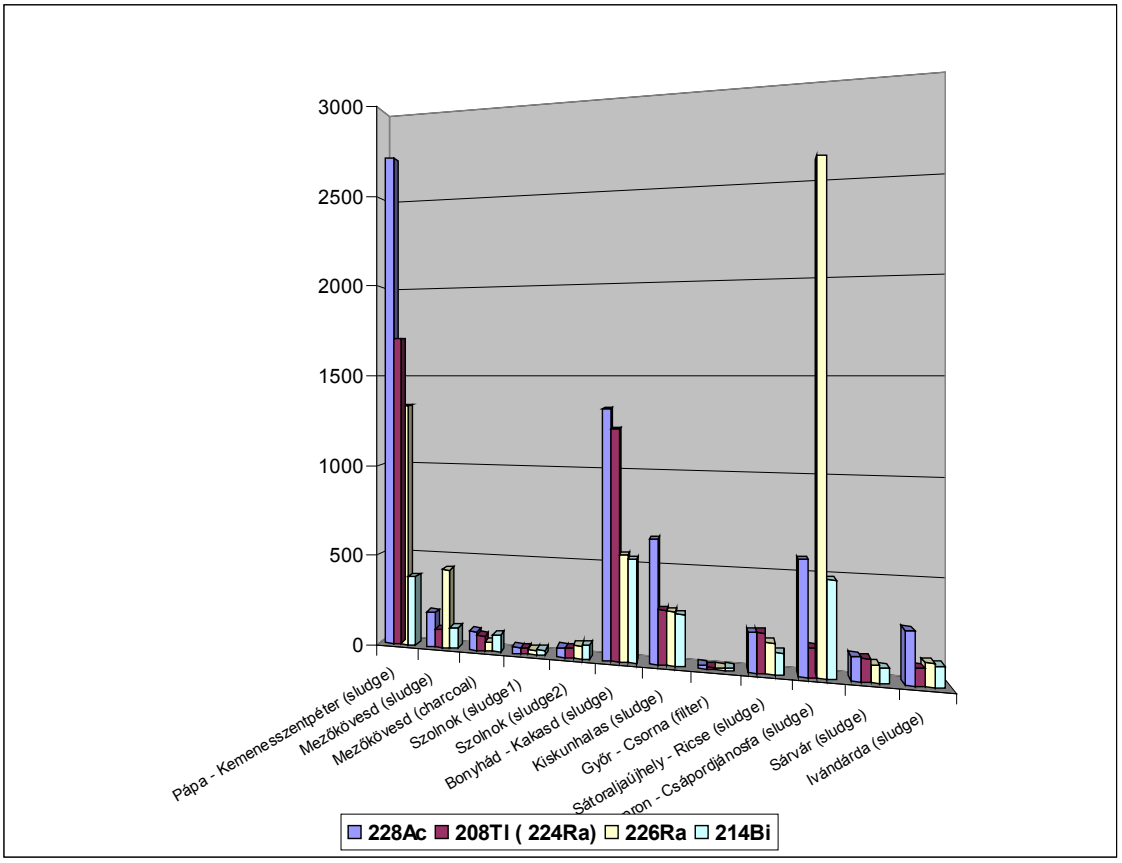

Figure 4. The activity concentration of the representative samples in Bq/kg

The radionuclides of ^{226}Ra and ^{228}Ra in the raw waters were separately analyzed, too. The results are put in the Table 2 and the radium activity concentration of few samples is close to the 1 Bq/l, which shows the Figure 5.

Table 1. The radium activity concentration of the representative raw waters in Bq/l

Place	^{228}Ra	^{226}Ra
Pápa-Csorna	0,003	0,011
Sárvár	0,002	0,006
Kiskunhalas	0,025	0,01
Kecskemét	0,12	0,218
Ivándárda	0,45	0,247
Mezőkövesd	0,16	0,325
Szeghalom	0,07	0,122
Mohács	0,06	0,092
Szigetvár	0,22	0,347
Kakasd	0,59	0,364

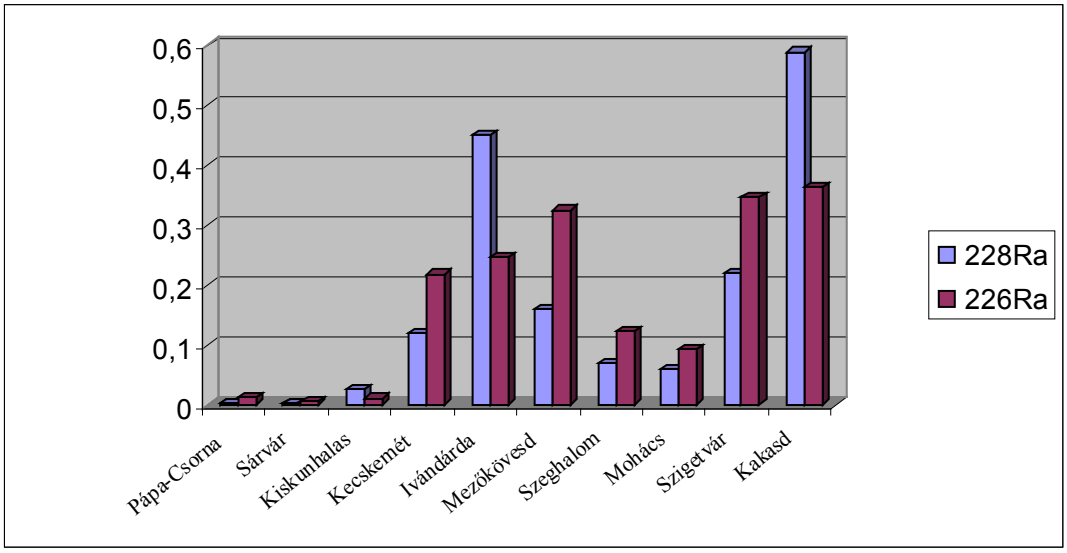

Figure 5. The radium activity concentration of the representative raw waters in Bq/l

6. Conclusions

Before the modification of the Decree 47/2003, a complementary investigation is to be carried out for the waterworks of karstic water and for the other waterworks, where the drinking waters are derived from the surface water bodies and groundwater. It is concluded that to date, very high elevated activity concentration of the NORM arising from the waterworks have not been measured and the amount of the residues is not too much. It is also remarked that lately in Hungary, the consumption of the mineral waters is more and more increasing, and these waters are also derived from the deep aquifers, so an extension of the survey of the NORM is considered in the future to this way.

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The pattern of radiation exposure at former uranium production sites and measures for exposure minimization

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Abstract

The pattern of radiation exposure at former uranium mining and milling sites is very site-specific, both for members of the local public as well as for workers engaged with remedial activities. In this regard, the situation at uranium production sites is very similar to that at sites where large volumes of NORM are handled. Remediation of the sites is mainly dedicated to reduce environmental risks, including to minimizing radiation exposures. In-situ remediation by re-shaping and coverage of large piles and tailings bodies, controlled mine flooding, water treatment, radon mitigation and the safe disposal of radioactive residues are the main remedial measures. The success of remediation needs to be demonstrated by source as well as environmental monitoring This will be exemplified by in the paper by two case studies: a) by the development of the radiation exposure at former uranium mining and milling sites in Saxony and Thuringia, Germany (WISMUT sites), and b) by the development of the radiological situation at the tailings management facility site in Sillamäe, Estonia.

1. Introduction

Determination of the radiation exposure at former uranium mining and milling sites requires a detailed exposure analysis whereby the site specific conditions for the radiological impact of the radioactive legacies have to be taken into account. The contribution of different exposure pathways to the effective dose depends on the type and volumes of legacies left behind by uranium ore mining and milling, the local meteorological, hydrological, hydro/geo-chemical as well as morphological conditions for propagation of radio-nuclides in the environment and the relevant exposure scenarios, which are in turn site specific. The principal exposure pathways for the local public as well as for workers engaged with remedial activities are summarized in Table 1. In Fig. 1 relevant exposure pathways for members of the public living next to an uncovered radioactive waste rock pile are illustrated.

In order to arrive at recognised values for the effective dose, exposure analyses have to be carried out on the base of a scientifically based and well accepted guideline. Therefore, in Germany in 1999 the Federal Ministry for Environment, Nature Conservation and Nuclear Safety published Calculation Bases for the Determination of Radiation Exposure due to Mining-caused Environmental Radioactivity (CBM – Calculation Bases Mining), with a view of harmonising and providing transparency in the establishment of radiation exposure (German Federal Ministry 1999). Their scope includes all age groups in line with EC Directive 96/29/EURATOM (European Commission 1996). The effective dose to the reference person is calculated at the most unfavourable point or site of exposure. Basically, this implies a conservative assessment approach. However, taking site-specific conditions (whenever possible, use of measured nuclide concentrations versus modelling results, consideration of local consumption habits, elimination of low-realistic exposure pathways, consideration of site-specific background levels) into account will allow to calculate sufficiently realistic values for doses to the population at mining locations.

Table 1. Relevant exposure scenarios at uranium production legacy sites

Exposure pathway	Local public	Workers
External radiation	X	X
Inhalation of long-lived alpha/beta emitters	X	X
Inhalation of radon and its short-lived daughter nuclides	X	X
Direct ingestion of contaminated material	X	
Ingestion of contaminated food via the chains: → drinking water consumtion → water → fish → fish consumtion → water → plant → plant consumtion → water → livestock → meat consumtion → water → plant → livestock → meat consumtion → soil → plant → livestock → meat consumtion → water → plant → livestock → milk/milk product consumption → soil → plant → livestock → milk/milk product consumption → water/plant/meat/milk/milk product → mother → mother milk consumption	X	-

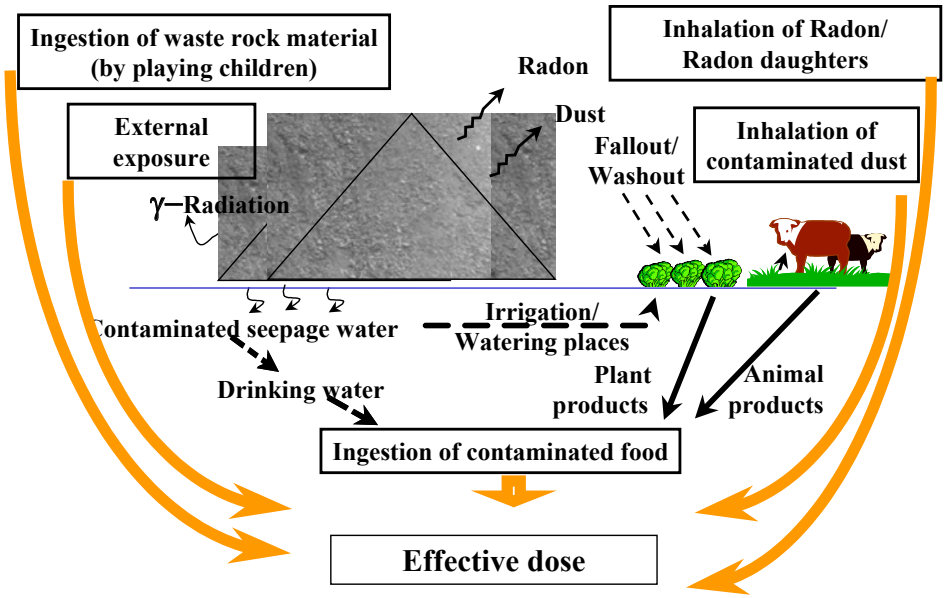

Figure 1. Exposure pathways for members of the local public living next to an uncover-red radioactive waste rock pile

In cases the nuclides are not in radioactive equilibrium (nuclide in water, in food, in residues which underwent chemical processes or natural leaching), the exposure analysis has to take into account the complete radionuclide vector, Dose relevant nuclides thereby are U-238, U-234, Th-230, Ra-226, Po-210, Pb-210, U-235, Pa-227 and Ac-227, respectively.

2. Typical pattern of radiation exposure

The following three examples illustrate typical exposure scenarios in the vicinity of uranium mining legacies.

Example A: Radiological exposure in the vicinity of an unremediated mine dump (typical radiological values encountered at waste rock piles at WISMUT sites)

The findings of an exposure pathway analysis established for a kid in the age group of 2 – 7 years and an adult reference person living permanently in the immediate neighbourhood of a large uncovered mine dump and using seepage water to irrigate their garden are represented in Fig. 2. The analysis was based on the following mining-induced radiological data (i.e. without background radiation):

- Mean specific activity of U-238 in waste rock material = 1 Bq/g, in radioactive equilibrium with daughter nuclides;
- Rn-222 concentration on top of and alongside the mine dump: 150 Bq/m³;
- Ambient dose rate on top of and alongside the mine dump: 530 nSv/h;
- Concentration of long-lived alpha emitters on top of and alongside the dump: 1 mBq/m³;
- Seepage water concentrations: 1 mg/l U_{nat} ; 0,5 Bq/l Ra-226 and Th-230; 0,1 Bq/l Po-210 and Pb-210; 0,01 Bq/l Pa-231 and Ac-227.

Relevant exposure pathways in the case under consideration include:

- Exposure by ingestion of locally grown garden products, (Food (25 % locally prodiced));
- External exposure by soil gamma radiation (Ext);
- Exposure by inhalation radon and its short-lived decay products (Rn/DPr);
- Exposure by inhalation of dust-borne long-lived alpha emitters (LLA);
- Exposure by direct ingestion of waste rock material (Dir-Ing).

In accordance with (German Federal Ministry 1999), an annual dwelling period of 7.000 hours near the mine dump and a total annual sojourn on the dump surface of 250 hours (child) and 100 hours (adult), respectively, were assumed.

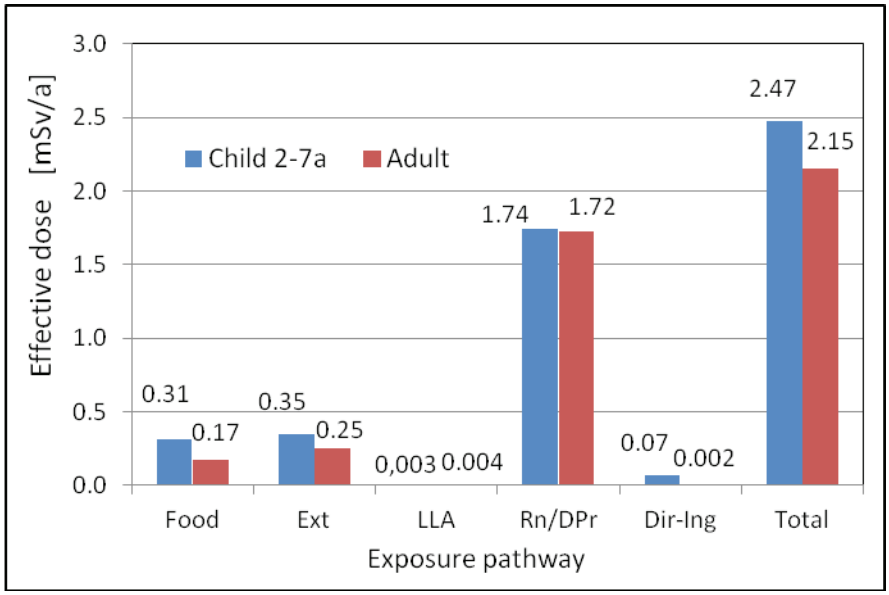

Figure 2. Typical exposure situation at unremediated uranium mine dumps

Example A illustrates the predominance of the exposure pathway "Inhalation of radon and its short-lived decay products". Such predominance is found in mine dump surroundings in most instances as long as the water pathway, and in particular the use of contaminated water for drinking or for preparing baby food, does not become relevant (cf. Example B).

Example B: Exposure by the use of water from watercourses contaminated by seepage leaking from an unremediated tailings management facility, WISMUT site Seelingstädt

This example considers the use of a watercourse for the irrigation of field and garden crops, livestock watering (each contributing 25 % locally produced food to annual consumption rate) and for drinking (100 %), plus fish consumption. The nuclide vector, which has to be determined completely, has a dominating influence on the calculation result. The vector considered in this case was identified at a small creek running between two large tailings management facilities at WISMUT. Typically, the nuclide vector of surface water at such sites is dominated by uranium nuclides (see Table 2).

Table 2 Nuclide vector for a watercourse in the surroundings of a not yet remediated tailings management facility (C_i – activity concentration of nuclide i in the water)

Nuclide	U-238	U-234	Th-230	Ra-226	Pb-210	Po-210	U-235	Pa-231	Ac-227
C_i [Bq/l]	5,2	6,1	0,17	0,02	0,025	0,025	0,24	0,015	0,015

Fig. 3 shows the results of the exposure pathway analysis for the age group [< 1a] and for adults. They detail dose contributions by the exposure pathways drinking water (DW), fish consumption (Fi), mothers' milk/baby food consumption (MM_BF), consumption of field and garden crops other than cereal products (FGP) and the consumption of dairy and meat products (DMP). Such a scenario typically identifies an effective dose in excess of 1 mSv/a solely for the baby, wherein radiation exposure levels are dominated by the use of water for drinking purposes and the preparation of baby food (Schmidt and Lindner 2006).

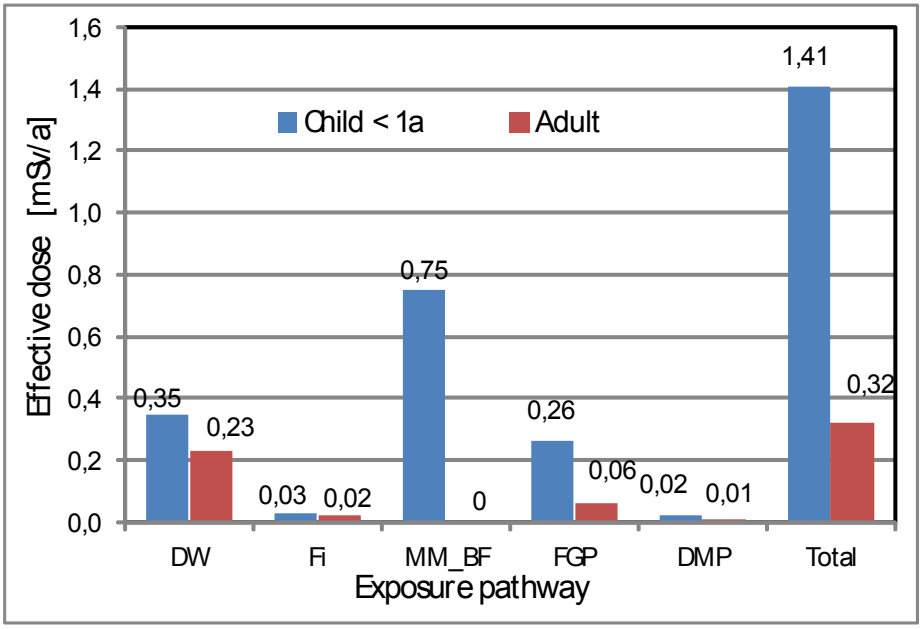

Figure 3. Typical exposure pattern via the water pathway at an unremediated tailings management facility

Example C: Doses for workers engaged with rehabilitation activities

The experience gathered at WISMUT sites in East Germany demonstrate, that the exposure of workers dealing with remediation of waste rock piles, with the demolition of above ground facilities and with site reclamation, is rather low. This is due to the relative low specific activities of the materials handled (not higher than 1 Bq/g for the key nuclide Ra-226). Annual occupational doses for these workers are in the order of 1 – 2 mSv/a. On tailings, the radioactive residues of the uranium ore processing showing specific activities of up to 10 Bq/g Ra-226, higher doses are possible. Typical effective doses for workers

dealing with the stabilisation and coverage of tailings range up to 4 mSv/a (note: these workers do not permanently stay on tailings areas). The highest doses however are observed for workers who prepare in the underground the flooding of mines. In cases of non-optimized mine ventilation those workers may be subject of annual occupational doses of up to 10 mSv.

3. Case studies

3.1 The Wismut Rehabilitation Project

From 1946 to 1990 the Soviet-German WISMUT company produced 231.000 tons of uranium. Due to the mining of low grade ore, about 800 Million tonnes of waste rock material, radioactive sludge's and overburden material were deposited at the sites. The mining and milling activities resulted in seriously affected and devastated areas of about 10.000 km² in Saxony and Thuringia, in East Germany. In 1990 after the German re-unification the uranium production was ceased and the German government was faced with one of its largest ecological and economic challenges because WISMUT turned at once from the production to the decommissioning phase without any preparation or preplanning. Since 1991 the national corporation Wismut GmbH has been charged with decommissioning of the mines, mills and other facilities and with the rehabilitation of the sites. The government earmarked a total of € 6,4 billion (recently adjusted to € 6,8 billion, appr. US$ 9 billion) to rehabilitate the uranium mining and milling legacy at the affected sites. Major environmental impacts due to the legacies as well as rehabilitation measures aimed at their mitigation are listed in Table 3.

Table 3. Residues, environmental impacts, and key rehabilitation measures under the WISMUT Project

Remaining objects / residues	Environmental impacts/ exposure pathways	Rehabilitation options
5 Underground mines	Groundwater contamination due to mine flooding	Controlled flooding including surface treatment of mine water
	Settlements, mine damages	Stabilisation of near-surface mine workings (backfilling)
48 Mine dumps	Radon exhalation; external radiation; incorporation of contaminants; contamination of water bodies	Mine dump relocation (underground, offsite); rehabilitation in situ involving regrading, covering and vegetating
1 Worked-out open pit mine, overburden dumps	Landscape devastation, groundwater impacts	Relocation of overburden dumps into worked-out open pit mine, covering and vegetating
Continuation Table 3		
4 Tailings Management Facilities	Radon exhalation; external radiation; incorporation of contaminants; groundwater impacts	Dry in situ rehabilitation (removal of supernatant water; sludge stabilisation using deep drains; covering; treatment of supernatant, pore and seepage waters)
Contaminated structures	Use restriction	Demolition, decontamination, salvage, safe storage of contaminated materials
Contaminated plant areas	Groundwater impacts; use restriction	Area remediation (excavation/safe storage of contaminated materials, in situ soil restoration)
Remediation related low level waste (e. g. WT residues)	Radon exhalation; external radiation;	Immobilisation; storage underground, in tailings pond beach areas or engineered facilities

Rehabilitation of uranium mining legacies at the WISMUT sites has been going on for two decades now. Mine flooding is well advanced though it must not be overlooked that the final flooding stages pose the greatest challenge in terms of technical effort and of minimising radiological, conventional toxic and geotechnical environmental impacts. All sizeable waste rock piles were either covered (Schlema site) or relocated into the worked-out Lichtenberg open pit mine (Ronneburg site). Rehabilitation of the large tailings management facilities (Seelingstädt and Crossen sites) is 60 % complete. Physical work at these sites will have to continue till 2020, making tailings pond rehabilitation the longest running remedial measure.

Remediation accomplishments achieved are reflected in the positive development of radiological parameters. In March 2009, WISMUT has drawn up an interim balance on the achievement of radiological protection targets at the various sites under remediation. This stocktaking came to the following conclusions:

- Due to the progress in covering waste rock piles and tailings management facilities, in area cleanup as well as in catchment and treatment of contaminated seepage waters, the exposure pathways of dust inhalation, direct access to contaminated material and water usage are no longer of relevance for radiation protection.
- Except for a few locally elevated radon concentrations at the Schlema site, there is general compliance with the guidance value of 1mSv/a.

The positive development embarked on is best demonstrated by the following three examples. As a first example, Fig. 4 illustrates the trends in controlled water-born discharge of uranium and Ra-226 as the principal radiological components in the water. Effluents are mainly mine waters from the Ronneburg, Schlema, Pöhle, Gittersee and Königstein mine sites (flooding of mines with concurrent treatment of flood water). The significant decrease in concentrations in discharged waters reflects a stronger drop in contaminant and activity releases, respectively, in comparison to decreasing water discharge volumes. These results were achieved since high-performance water treatment (WT) plants went on line at all WISMUT sites.

As a second example, Fig. 5 illustrates the impact which regrading and covering of waste rock pile no. 66/207 at the Schlema site had on radon concentration at the toe of the dump. Regrading of the waste rock pile resulted in flattening the slopes and an improved circulation of air in the area around the dump where residential areas are located. Thus, an initial improvement of the local radon situation was achieved (cf. comparison of summer data 2002 versus 2001). But it was not before the dump slopes were covered with a 1 m thick layer of inert material exhibiting adequate radon proofing properties that the convective fluxes within the waste rock pile were eliminated in summer 2003. Since then, radon exhalation rates have been kept permanently at a low level and ensuing radon concentrations remain low. Regular measurements have exhibited long-term radon concentrations of below 80 Bq/m^3 resulting in mine-related effective doses to residents close to the dump toe of less than 1 mSv/a (Schmidt and Regner 2004).

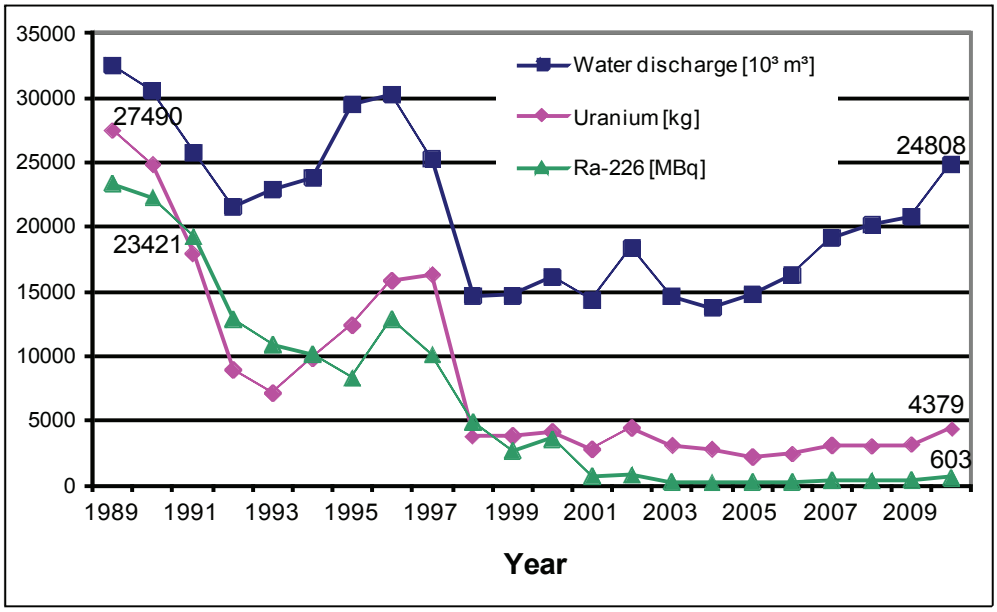

Figure 4. Evolution of controlled discharges with water (sum of discharges from all WISMUT sites)

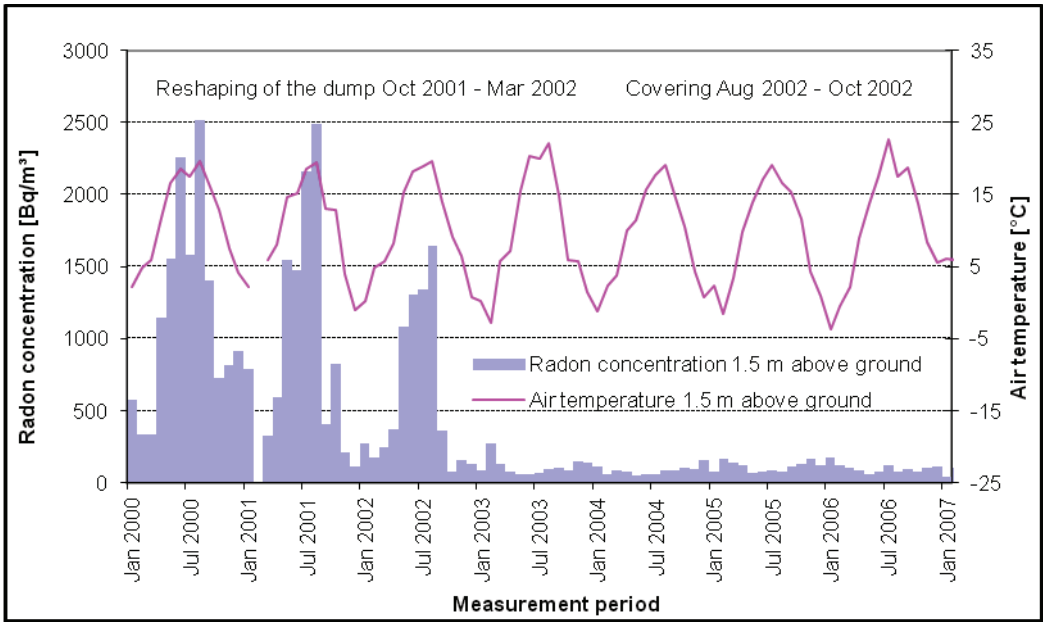

Figure 5. Evolution of pre- and post-rehabilitation radon concentrations at the mine dump 66/207, Wismut site Alberoda

As the third example, Table 4 reflects the changes in the nuclide vector towards lower radioactivity for the watercourse in the surroundings of the tailings management facility as a result of remediation progress (cf. Table 2, in chapter 2, Example B – typical exposure situations,)

Table 4 Pre- and post rehabilitation nuclide vector for a watercourse in the surroundings of a tailings management facility (C_i - activity concentration of nuclide i in water)

Nuclide	U-238	U-234	Th-230	Ra-226	Pb-210	Po-210	U-235	Pa-231	Ac-227
C_i [Bq/l] - pre	5,2	6,1	0,17	0,02	0,025	0,025	0,24	0,015	0,015
C_i [Bq/l] - post	0,83	0,85	0,001	0,02	0,002	0,006	0,04	0,008	0,001

3.2 Remediation of the Sillamäe Tailings Pond

The Sillamäe radioactive tailings pond facilitate was rehabilitated from 2002 to 2008 on the base of a concept which was developed by WISMUT and C&E, in collaboration with the Estonian company Ecosil Ltd. (Wismut and C&E 2001).

Starting in 1948, the hydro-metallurcic ore processing plant SILMET in Sillamäe, Ida-Viru county in the North Eastern part of Estonia, has been processing local uranium ores, but also uranium ores from East-European countries. Since 1987 ores for gained rare earth elemenets has been processed. From 1959 till 2003, mill tailings from the SILMET plant were deposited in the Sillamäe tailings pond. The pond contains 9 Mio tons of processing residues, including 4 Mio tons of radioactive uranium mill tailings. Fig. 6 shows the tailings pond in 1999, i. e. before remediation. Location of the 50 ha large pond is directly on the shoreline of the Gulf of Finland, in a distance of 800 m to the nearest residential areas of town Sillamäe.

Figure 6. Sillamäe tailings pond, unremediated in 1999 (source: Wismut and C&E 2001)

Before remediation, there were three types of environmental hazards connected with the Sillamäe tailings pond:

a) The marginal stability of the dam presented an acute problem. Geotechnical stabilisation measures and protection of the dam from further sea erosion were identified as the most urgent rehabilitation measures.
b) The continuous release of radioactive and other toxic substances (Amonium compounds, heavy metalls) via seepage from the tailings into the sea revealed as a steady source of hazard.
c) Elevated gamma radiation on and near the pond, development of dust-born long-lived alpha emitters towards the SILMET plant and town Sillamäe as well as radon exhalation were sources for exposure of members of the public and of workers at the SILMET plant.

An exposutre analysis was carry out based by WISMUT experts using the German Calculation Bases Mining. Site specific data were provided by the Estonian experts of the local Sillamäe branch of Ecosil Ltd.. The results of the analysis are summerized in Table 5.

Table 5. Eeffective annual doses for reference person before remediation of the Sillamäe tailings pond (WISMUT and C&E 2000)

Reference Person	Effective Dose [mSv/a]		Critical exposure pathways
	Children (2-7 a)	Adults	
P1 - Person with residence in dwellings near the pond	0,6 mSv/a	0,6 mSv/a	Inhalation of radon
P2 - Person walking/playing over/on the pond area	1,6 mSv/a *	0,7 mSv/a	External gamma radiation * plus direct ingestion
P3 - Worker engaged with remediation	-	12 mSv/a **	External gamma radiation (** Occupational exposure)

The effective doses estimated for the local public (cf. Reference Persons P1 and P2, respec-tively) are in the order of the reference level of 1 mSv/a which is internationally applied as a benchmark to decide on the justification for remedial measures at uranium mining legacy sites. In the present case it is necessary to recognise, that with a realistic view the release of radionuclides with seepage into the Baltic Sea does not cause significant exposure of the public. With other words, the identification of the optimized remediation option for the Sillamäe tailings pond has not been driven by radiological constraints. Rather, the protection of the aquatic environment (Baltic Sea water and sediments) and the need to minimize - in compliance with international treaties and agreements - the discharges of chemo-toxic substances into the Sea, were the primary facts that have been driving remediation.

As a result of a comprehensive optimization procedure the combination of two remedial measures was identified as best-suitable remedial option:

a) Establishment of a multi-layer cover involving a 0,3 m thick sealing layer of low water permeability (< 10^{-9} m/s), with the target to minimize the water infiltration rate below 5 %,
b) Construction of a surface water drainage system plus a drainage trench in the hinterland of the pond, both with the target to further minimize the entrance of water into the facility.

Implementation of both remedial measures has been carried out between 2002 and 2008. Figure 7 illustrates the situation in 2008 after termination of the pond remediation.

Figure 7. Sillamäe tailings pond in coverage, with the new-bult Sillamäe harpour (source: Ecosil Ltd. 2011, presented at WISSYM2011, Chemnitz, Germany, May 2011)

The present radiological situation can be summarised as follows: With the altogether > 3 m thick cover, gamma radiation is at natural background level. Access to the contaminated material is impeded. Development and propagation of radioactive dust is no longer possible. The radon exhalation rate on the cover is reduced to low levels in the order of 0,2 Bq/(m^2s). This facts are proven by the post-remedial environmental monitoring conducted by Ecosil Ltd.. A significant exposure of the local public does no longer exist.

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Radiological impact of rutile covered welding electrodes

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Abstract

Shielded metal arc welding is the most commonly used welding process. Where, the welding is made using covered welding electrodes. Sometimes the covering contains Naturally Occurring Radioactive Materials (NORM), so people who are in contact with these electrodes are exposed to radiation. In Spain the most consumed electrodes are those covered with rutile mixed with other materials. Rutile is mainly titanium dioxide and contains some detectable natural radionuclides, so it can be considered a NORM material. This paper mainly focuses on the radiological impact of the rutile covered electrodes.

To know the radiological impact of them throughout their life, attention must be paid to the storage of raw materials used to make them, the manufacturing process (and the waste generated throughout it), the storage and the use.

To do this, in an electrodes factory, areas of highest radiation and positions of workers have been identified and after that, considering a worst possible scenario, effective annual dose to workers has been calculated by means of MCNP. The value obtained is always lower than the limit on the effective dose for public, 1 mSv y^{-1}.

Prior this, the method used has been validated by a pressurized ionization chamber measuring the ambient equivalent dose rate at different factory positions and comparing these values with the given ones by some personal dosimeters at the same positions and the theoretical ones calculated by MCNP. These sets of values match quite well taking into account the uncertainties related to the whole process.

In this paper the validation of the procedure used and the external effective dose values obtained, are presented.

1. Introduction

The International Atomic Energy Agency (IAEA) published, in 1996, the International Basic Safety Standards (BSS) [1] for the control of exposure to artificial and natural radiation sources. In recent years, the IAEA has been working to increase the BSS guidance and information on natural sources, and therefore on work activities involving NORM.

Provisions on NORM were introduced in the Council Directive 96/29/EURATOM [2]. In that, the Title VII leaves Member States to decide which work activities are to be subject to national control.

In Spain, the Title VII of the *Real Decreto 783/2001* on Health Protection against Ionizing Radiation [3] enacts the Directive 96/29/EURATOM in similar terms. The *Consejo de Seguridad Nuclear* (CSN) and other public organisations are carrying out an Action Plan for the development of the Title VII, conducting research programmes to identify the potential impact of NORM industries on workers and public and also ensure their safety from ionizing radiation.

Among this programmes, and supported by the CSN, the authors studied some years ago the radioactivity of thoriated electrodes and its radiological impact on manufacturing workers and welders [4].

In a new research project, also supported by the CSN, the most conventional non thoriated electrodes have been studied. To do this, the covering of the most sold electrodes used in shielded metal arc welding processing in Spain [5] were measured by gamma spectrometry, looking for radionuclides. The most used electrodes in Spain have rutile covering, which is also the most radioactive; therefore this is the main focus of the study.

In this project the process from electrode manufacture to welding has been analysed, because workers can be exposed to natural radiation during manufacture and storage and also during welding.

In the first stage of this electrodes manufacture process, rutile and other raw materials are mixed. Then, this mixture is used to make cylinders, which are pressed around a rod, and covered electrodes automatically come off the presses. After that, they are firstly pre-dried at room temperature and then in furnaces (continuous or static). Finally, they are packed to be stored. So, loss of radioactive material is not expected during this process.

On the other hand, during the welding process the covering of the electrode blends and some radioactive materials goes into the atmosphere. There, they can be inhaled or deposited and also they can result in atmospheric background.

The objectives of this research project are to analyse the covered welding electrode's radioactive content and to determine the radiological impact on workers during the manufacture (and waste generation), storage and welding of electrodes. For this, a Spanish factory where this type of electrodes are manufactured, stored and also used has been studied, performing theoretical simulations using MCNP (according to a worst possible scenario) and some measurements. In this paper, preliminary data on method validation and the external effective dose in the manufacturing process are presented.

2. Materials and methods

To study the external effective dose received by workers in the manufacturing process during a working year, a procedure has been developed at a given time and considering a worst possible case scenario. This procedure has been focused on numerical simulations carried out by MCNP. To do this, it has been necessary to measure the radioactive content of the rutile covered electrodes and also the adaptation and validation of the MCNP simulation program.

The materials used and the methods followed are listed below.

2.1. Materials

2.1.1. Covered electrodes

Welding consumables can be classified into electrodes or wires for metal arc welding and flux for submerged arc welding. Electrodes can be covered or uncovered and wires can be solids or flux cored. Covered electrodes for shielded metal arc welding consist of a core rod (about 70% by weight) coated with a covering (about 30% by weight).

The core rod must be compatible with the metal being welded, and therefore its composition must be very similar to it. Its length is usually between 200 and 450 mm and its diameter between 1.5 and 6 mm.

There are different types of coverings, depending on their chemical composition, leading to the covered electrodes classified as follows: oxidizing (iron oxides), acidic (silica and silica derivatives), basic (calcium or magnesium carbonates with fluorspar), neutral (unstable iron and manganese oxides), rutile and cellulosic.

After measuring different types of electrode coverings by gamma ray spectrometry, the most radioactive was the coverture made mainly with rutile. Electrodes covered by rutile are also the most consumed, that is why they have been chosen in this work.

2.1.2. Gamma spectrometry

In order to calculate the external effective dose for workers it is necessary to quantify the gamma photons emitted by radionuclides present in the electrode's covering. For this purpose, a gamma spectrometer was used, equipped with a High-Purity Germanium detector (HPGe) and the programme Gamma Vision, version 6.01.

The spectrometer was calibrated in energies and efficiencies using a calibration source made with the same geometry and density as samples (± 10%) and spiked with known quantities of radionuclides which emit photon energies between 46.54 and 1836.06 keV. So, the absorption and geometry factors and uncertainties are disregarded in Equations 1 and 2.

Following the gamma spectrometry the activity (1), the associated uncertainty (2) and the detection limit (LID) (3) of the radionuclides present in each sample have been calculated [6].

The radionuclide activity (in Bq) is given by

$$A_i = \frac{N_{Ei}}{t \cdot \varepsilon_E \cdot \gamma_{Ei}} A_i = \frac{N_{Ei}}{t \cdot \varepsilon_E \cdot \gamma_{Ei}} \quad (1)$$

Where:

A_i = activity of radionuclide i , in Bq.
N_{Ei} = net peak area for peak at energy E of radionuclide i, in counts.
t = live time (measuring real time, corrected for dead time) in seconds.
$\varepsilon_E \varepsilon_E$ = detector efficiency at energy E.
$\gamma_{Ei} \gamma_{Ei}$ = gammas/disintegration for energy E of radionuclide i.

In cases where a radionuclide presents two or more peaks, its activity is calculated by a weighted average activity. The obtained activity is corrected to sampling date and decay correction during acquisition is considered. [6].

To obtain N_{Ei} other nuclide's gamma radiation and spectrometer background contributions are subtracted from peak counts in the sample. The spectrometer background is calculated measuring a nonradioactive sample, similar to radioactive ones, during a similar time.

The activity uncertainty is determined by addition in quadrature the individual uncertainties from parameters in Equation 1.

$$u_{A_i} = \sqrt{(u_{N_{Ei}}^2 + u_{\varepsilon_E}^2)} u_{A_i} = \sqrt{(u_{N_{Ei}}^2 + u_{\varepsilon_E}^2)} \quad (2)$$

Where:

$u_j u_j$ = standard uncertainty associated with the parameter *j*. *j* being each one of the parameters which appears in Equation (1). Uncertainties of the counting time and of $\gamma_{Ei}\gamma_{Ei}$ are considered as negligible.

The detection limit, following the Nureg 4.16 method [6] is given by:

$$LID = \frac{(2.71 + 4.66\ \sqrt{B})}{t} LID = \frac{(2.71 + 4.66\ \sqrt{B})}{t} \quad (3)$$

Where:

B = spectrometer background for the peak zone, in counts.

2.1.3. Ionization chamber

To validate the use of MCNP to simulate these situations, a FHT 6020 ionization chamber was used. Its measurement accuracy was verified in respect of ^{137}Cs and its measuring and energy range are 100 nSv h^{-1} – 1 Sv h^{-1} and 30 keV – 7 MeV (± 30%), respectively [7].

The ionization chamber measured "in situ" the ambient dose. It was located at four different positions at the factory. Every 10 minutes, dose rate values were obtained, and when they reached stability, the position of the ionization chamber was changed.

2.1.4. MCNP

Los Alamos National Laboratory's MCNP is an international code based on the Monte Carlo method for analysing the transport of neutral particles, i.e. neutron and gamma rays [8]. In this case, only the transport of gamma rays (including Compton gammas and disregarding electrons) is studied. The version used to develop was MCNP.

In the MCNP input file, the user must define the problem's geometry, materials, source, photon energy and emission probability, detector type and its position, number of paths to the detector a standard particle (photon) runs and variance reduction technique, if it is required.

The geometry is outlined as regions defined by surfaces or macrobodies (rectangular parallelepiped, right circular cylinder and truncated cone), of which's union or intersection form cells. Cells contain materials, whose density and composition must be specified, as well as photon interaction data.

The source and type of radiation particles are defined by the SDEF command. The normalized photon emission probability for each energy value must be introduced, and it is obtained by:

$$P_{Ei} = \frac{A_i \cdot \gamma_{Ei}}{\phi} P_{Ei} = \frac{A_i \cdot \gamma_{Ei}}{\phi} \quad \text{where} \quad \phi = \sum_{E,i} (A_i \cdot \gamma_{Ei}) \phi = \sum_{E,i} (A_i \cdot \gamma_{Ei}) \quad (4)$$

Being:

$P_{Ei}P_{Ei}$ = normalized gamma emission probability for energy *E* of nuclide *i*.

$\phi\ \phi$ = flux or number of photons emitted by the source per unit of time, in s^{-1}.

Thus, it is possible to unify the photons of radionuclides belonging to different radioactive series and with different activities.

The simulation result is the number of photons per cm^2 reaching the detector per each photon emitted by the source. In order to obtain the results in pSv per emitted photon (R) the conversion coefficients of ICRP 74, that transforms photon^1 cm^{-2} to pGy and then to pSv, can be added to the input file. To do this, rotational geometry has been chosen [9]. In the same way, conversion coefficients of ICRP 74 are used to calculate the ambient dose and validate the method.

The conversion coefficients are referred to photon energy from 0.01 to 10 MeV. Photons with energy less than 0.04 MeV, did not contribute to the total dose and increased the relative error. Therefore, energy cut-off variance reduction technique at 0.04 MeV was used, so gammas with energies between 0.04 and 10 MeV were only considered in Equation 4.

For the detector type definition, a photon point detector was chosen and located in cells. This type of selection is considered generally reliable when the accompanied estimated relative error is less than 0.05.

For a well-behaved detector, the relative error is proportional to $1/\sqrt{N}$,$\sqrt{N}$, where N is the number of paths to the detector a standard photon can run. For a poorly behaved detector, the relative error may increase as N increases. MCNP relative error calculation refers only to the precision of the result, and precision is understood as uncertainty [10].

2.2. Methods

A Spanish company which produces about 1,000,000 covered electrodes per day, 80% being rutile covered allowed visiting its facilities to carry out this study.

To determine the activity to which workers may be exposed, rutile, rutile mixture and covered electrodes samples were taken to determine if during the manufacturing process radioactive material were lost. After removing covering from the rod, the sample was adjusted to a standard source's density using a ball mill and it was collected in a 110 mL petri dish. Rutile and rutile mixture samples were collected in 110 mL petri dishes, too. After that, samples were measured by gamma spectrometry and activity was estimated for each radionuclide present (see 2.1.2.).

Having determined the real distribution of rutile and rutile covered electrodes in plant, 4 positions were selected to measure the ambient dose rate with the ionization chamber: next to rutile bags, in the electrodes pre-drying area, in the store and near raw materials store.

Simulations by MCNP were carried out to calculate the ambient dose rate at the same positions in which the ionization chamber was located and some personal dosimeters were installed. Data were compared and the method developed using MCNP could be validated (see 2.1.3. and 2.1.4.).

Finally, considering all emission sources that workers are exposed and their working places (positions) during the manufacturing process, the effective dose that each worker receives during a working year, and according to a worst possible scenario, was estimated using the following formula:

$$E = R \cdot \phi \cdot KE = R \cdot \phi \cdot K \quad (5)$$

Where:

E = effective dose, in μSv y^{-1}.

K is a numerical factor that takes into account the working time in a year and the transformation from pSv to μSv.

The uncertainty of annual effective dose (E) is calculated by [11]:

$$u_E = \sqrt{\left(u_R^2 + u_\phi^2\right)} u_E = \sqrt{\left(u_R^2 + u_\phi^2\right)} \quad \text{where} \quad u_\phi^2 = \frac{\Sigma_{E,i}\left(\left(u_{A_i}^2 + u_{\gamma_{Ei}}^2\right)\cdot\left(A_i\cdot\gamma_{Ei}\right)^2\right)}{\left(\Sigma_{E,i}\left(A_i\cdot\gamma_{Ei}\right)\right)^2}$$

$$u_\phi^2 = \frac{\Sigma_{E,i}\left(\left(u_{A_i}^2 + u_{\gamma_{Ei}}^2\right)\cdot\left(A_i\cdot\gamma_{Ei}\right)^2\right)}{\left(\Sigma_{E,i}\left(A_i\cdot\gamma_{Ei}\right)\right)^2} \qquad (6)$$

Where:

$u_E u_E$ = relative uncertainty of the annual effective dose, E .

$u_R^2 u_R^2$ = relative uncertainty of the MCNP result, R .

$u_\phi^2 u_\phi^2$ = relative uncertainty of the flux emitted by the source, $\phi\phi$.

3. Results

3.1. Specific activity content in rutile electrodes

The results of the activity concentration obtained for pure rutile, rutile mixture samples and rutile covering of electrodes are presented in Table 1.

At it can see in that Table, results obtained for rutile mixture samples and rutile covering of electrodes are similar, that means that there is no loss of radioactive material in the electrodes production process. The three radioactive natural series and the ^{40}K are present in both types of samples.

Comparison between electrode covering and pure rutile shows that nuclides from radioactive natural series come from rutile itself, although ^{40}K comes from the raw material used in the mixture of rutile in order to produce the covering.

Table 1. Specific activity content (Bq kg^{-1}) in rutile, rutile mixture and rutile covering.

Natural Series/ Isotope	Rutile		Rutile mixture		Rutile covering	
	Sp. Activity Bq kg^{-1}	Uncertainty Bq kg^{-1}	Sp. Activity Bq kg^{-1}	Uncertainty Bq kg^{-1}	Sp. Activity Bq kg^{-1}	Uncertainty Bq kg^{-1}
^{232}Th	1.051E+02	1.753E+00	4.304E+01	1.081E+00	5.347E+01	1.266E+00
^{235}U	2.162E+01	1.261E+00	7.328E+00	0.999E+00	1.024E+01	0.948E+00
^{238}U	3.035E+02	0.716E+01	1.331E+02	0.500E+01	1.352E+02	3.808E+00
^{40}K			7.914E+02	1.065E+01	8.924E+02	1.046E+01

3.2. Validation of MCNP data

At four defined positions in the facility, the high volume ionization chamber has been used to obtain ambient dose rate, and at the same positions, some personal dosimeters have been installed. Obtained sets of values have been compared and results matched quite well. Following these experimental measurements, theoretical simulations have been performed at the same positions using MCNP in order to validate its results with the experimental ones. Considering the approaches made and the uncertainties of both methods, theoretical results are compatible with the experimental ones.

3.3. Effective dose obtained using MCNP

The manufacturing of rutile covered welding electrodes is carried out in 7 stages: rutile and raw materials mixture, mixture kneading, cylinders production, electrodes production, electrodes pre-drying, drying and packing (Fig. 1). At the factory some working places where workers could be exposed were identified along the production process. In Fig. 2 these places (workers) are signalled by W_i, being i from 1 to 11. Every production stage, or radiation source area, is represented in Fig. 2, and the effective dose that these source areas provoke in each worker, considering a worst possible scenario, has been estimated.

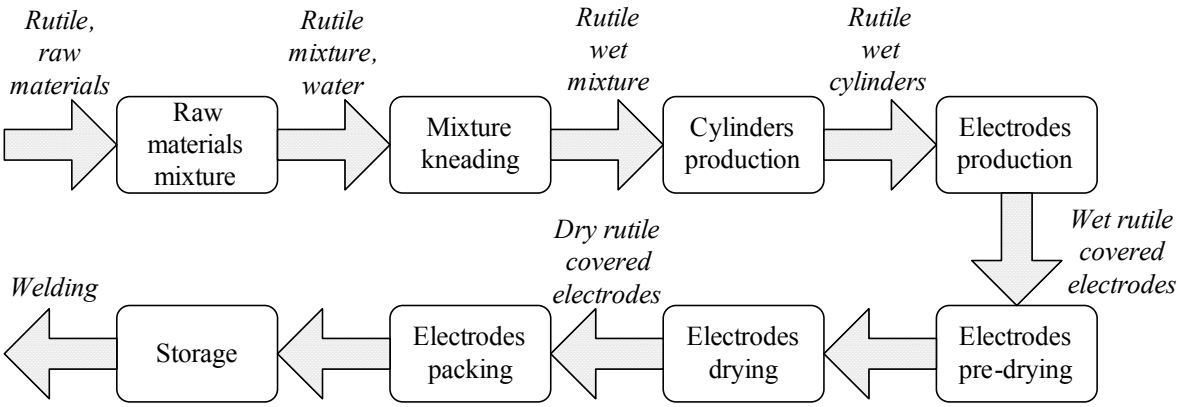

Figure 1. Process of rutile covered electrodes manufacturing.

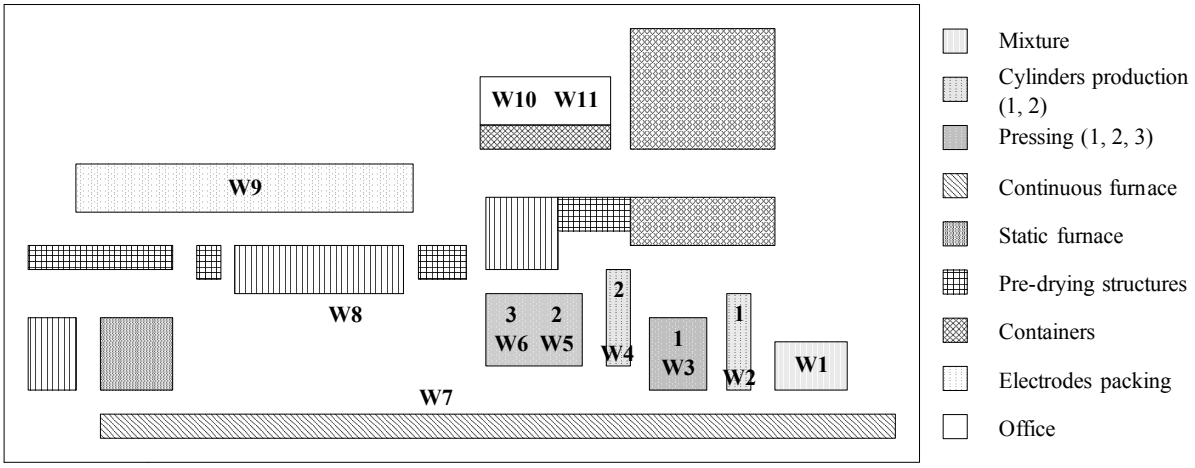

Figure 2. Covered electrodes production area diagram and workers positions.

The mixture area, where there is a rutile silo, some mixture hoppers and the produced dust, affects to worker W1 and to worker W2, who works closely making cylinders with the mixture.

Both worker W2 and worker W4 produce mixture cylinders, but in different areas. Worker W12 moves mixture hoppers from mixture area to cylinders production area, therefore only receives radiation moving hoppers and spends 44.4 h y^{-1} doing it. W2 produces manually about 10% of cylinders, which is why he is only exposed to radiation about 98 h/year. Instead, W4 manually makes all cylinders.

Workers W3, W5 and W6 introduce cylinders and wire into presses to produce covered electrodes. There is a press for each worker, but in different areas.

There are two furnaces to dry the electrodes produced: one static and other continuous. Anyway, before drying at any furnace, the electrodes must be pre-dry.

Electrodes that are going to the continuous furnace are pre-dried in structures with 25 separated trays and about 200 electrodes per tray on a treadmill 135 m in length (Furnace area), so that affect nearby workers W1, W2, W3, W4, W5, W6 and W7, especially W7.
In contrast, electrodes that are going to the static furnace are pre-dried near the production area in a similar structure which contains 40 separated trays and about 400 electrodes per tray. These structures affect all workers considered, but especially worker W8, who manages them.
Once the electrodes are dried, they are put into containers which contain about 18,000 electrodes each, waiting to be packed. The containers affect all workers.

Finally, the electrodes are packaged by worker W9 and carried to final product store.

Near the production area there is a small office where workers W10 and W11 spend 50% and 80% of the day respectively. This office is affected by pre-dry structures and containers.

It was considered that each worker spends all possible working time in the same place, not moving, and a worst possible scenario is always chosen (no protection, rutile silo is always full, continuous furnace is full of electrodes, there is always maximum pre-dry structures and container number, etc.).

In these conditions, the annual effective dose received by workers is presented in Table 2 for each one of the source areas and in total

Table 2. Effective dose received by workers during a working year (μSv y^{-1}) in manufacture process.

			Annual effective dose (μSv y^{-1}) from each source area											
		Working h y^{-1}	Mixture	Cylinders 1	Cylinders 2	Press 1	Press 2	Press 3	Furnace	Pre-drying	Containers	Packing	Hoppers	TOTAL DOSE
Annual effective dose (μSv y^{-1}) by worker	W1	1705	367.1						16.6	0.3	10.0			394.0
	W2	53	8.0	1.4					1.5	0.0	0.2			11.2
	W3	1705				0.3			24.3	0.6	7.3			32.5
	W4	533			13.7				4.4	0.3	1.7			20.1
	W5	1705					0.3		8.0	1.9	3.5			13.7
	W6	1705						0.3	8.1	2.2	2.4			13.0
	W7	1705							48.3	1.3	1.9			51.5
	W8	1705								73.7	1.1			74.8
	W9	1705								6.5	0.3	3.2		10.0
	W10	852								1.3	3.1			4.4
	W11	1364								2.6	5.6			8.2
	W12	44.4											0.7	0.7

As it can see in this Table 2, none of the workers receive an annual effective dose exceeding the dose limit for public (1 mSv y^{-1}). It can also be said that except for the dose received by worker W1 (0.4 mSv y^{-1}) the remaining external effective dose is insignificant and therefore no relevant radiological impact exists.

4. Conclusions

The covered electrodes which contain the highest amounts of NORM materials are the rutile ones. In them, rutile contributes with radionuclides from the three natural decay series, which are in equilibrium. Some amount of ^{40}K also appears, but comes from different materials that are mixed with rutile to make the electrode.

The developed method using MCNP Monte-Carlo based programme has been validated comparing ambient dose results with experimental ones obtained by a high volume ionization chamber and some personal dosimeters.

After analysing a representative and real electrodes factory and even considering a worst case scenario, no worker receives an annual effective external dose in the manufacturing process exceeding dose limit for public, 1 mSv y^{-1}. The highest dose, 0.4 mSv y^{-1}, is received by the worker who conducts his work in the mixture area. But the remaining dose is insignificant and therefore no relevant radiological impact exists.

5. Acknowledgments

We would like to thank the *Consejo de Seguridad Nuclear* (CSN) for giving us the opportunity to research this topic within the project "*Estudio del riesgo radiológico en la soldadura por arco*".

Also, we appreciate the contribution of the Spanish covered electrodes manufacturing company, for its complete collaboration.

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Building materials as a dominant radon source in modern buildings

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Abstract

Usually it is supposed that the soil is the dominant source of radon in buildings. The radon entry from building materials is typically considered as insignificant. Nevertheless under some conditions the diffusion radon entry in the building can dominate and the resulting radon levels also can be significant. Measurements of indoor radon concentration in Yekaterinburg city, Russia were conducted. It was shown that the average radon concentration in modern monolithic and brick multi-storey buildings is significantly higher compared to buildings constructed before 1990. High radon concentrations (70 - 230 Bq/m3) were observed on both the lower and the upper floors of the modern buildings. It was shown that the building materials can be dominant radon source in modern buildings. According to the results of survey the conditions under which radon concentration exceed 200 Bq/m3 are quite probable in the buildings with diffusion radon entry mechanism. Radon concentration levels in the modern buildings, built with materials passed through inspection, are close to action level in accordance with radiation safety standards. The reason of this effect may be connected with new construction technologies using fine finders (sand, slag and ash) as a filler of load-bearing structures and wall materials.

Key Words: radon; radon entry mechanism; air change rate; Effective Leakage Area

1. Introduction

It is well known that radon is the second most important factor after smoking, which leads to the lung cancer (Zeeb and Shannoun, 2009). The latest epidemiological data on indoor radon exposure (Darby et al., 2005; Krewski et al., 2005) reveals connection between lung cancer incident and radon exposure in dwellings.

Usually it is supposed that the soil is the dominant source of radon in buildings. The radon entry from building materials is typically considered as insignificant. Nevertheless under some conditions the diffusion radon entry in the building can dominate and the resulting radon levels also can be significant. From 1993 to 2000 the radon survey in Sverdlovsk region (Russia) was conducted by the Institute of Industrial Ecology (Yarmoshenko et al., 1999; Zhukovsky et al., 1999). But the detailed radon survey in Yekaterinburg city (capital of Sverdlovsk region) was conducted only from 2007 to 2009. Measurements were performed in 404 apartments in Yekaterinburg residential buildings. About half of the measurements were carried out in buildings constructed between 1950 and 1989, and quarter of the buildings was built in the last two decades. In general, the sample of dwellings formed for radon survey of Yekaterinburg is representative by the size and structure. The special attention was paid to a relatively high levels of radon in apartments on the upper floors of buildings, built from 1990 to the present time (91 apartments). These buildings were constructed according to the standards for new buildings where radon concentration should not exceed 200 Bq/m^3. It was shown that the average radon concentration in modern monolithic and brick multi-storey buildings is significantly higher compared to buildings constructed before 1990. High radon concentrations (70 - 230 Bq/m3) were observed on both the lower and the upper floors of the modern buildings. Therefore building materials were supposed to be dominant radon source in modern

buildings. To prove this assumption a series of continuous radon concentration measurements was conducted and experimental technique for radon entry rate assessment in the building was developed.

2. Modeling approach for radon entry

Basically there are two ways of radon entry in buildings: diffusion due to the gradient of radon concentration in the environment and advection caused by the pressure difference between building envelope and outdoor atmosphere. Sherman's concept (Sherman, 1998a, 1998b, 1998c, 1998d) of Effective Leakage Area (ELA) and Radon Leakage Area (RLA) can be applied to describe the processes of radon entry in buildings.
When compiling the equation describing the accumulation of radon in dwellings, the following main processes were considered (Sherman, 1998b):

- the diffusion entry from the soil and materials of building constructions S_D,
- advective entry due to stack effect,
- infiltration of air with radon concentration (A_R^{atm}) and ventilation rate Q associated with this mechanisms.

The general equation describing the process of radon entry in dwellings and concurrent air exchange is very cumbersome. It includes a fairly large number of parameters which are unknown for a specific building. However, we can introduce a number of generalizing coefficients permanent for each individual building. This allows us to write the general equation for the dependence of steady state values of radon concentration as:

$$A_r = \frac{A_\infty RLA\left[X_S \frac{\Delta T}{T_1}\right]^{n_r} + S_D}{ELA\left[\left[Y_S \frac{\Delta T}{T_1}\right]^{n} + Y_W\right]} + A_R^{atm} \qquad (1)$$

For a specific building the ventilation rate due to wind effect is constant and proportional to some value which depends on the distribution of entry and escape areas in the building. In turn, air change rate due to stack effect is proportional to Y_S and dependent on the temperature difference between indoor and outdoor air. Radon entry rate due to stack effect is also defined by the temperature difference and is proportional to some quantity characterizing the position of the neutral plane (the level where the stack effect caused by the pressure difference between indoor and outdoor air is zero). Detailed descriptions of radon entry mechanisms and air exchange, as well as equations for the quantities X_S, Y_S, Y_W can be found in (Sherman, 1998b, 1998c, 1998d).
In case the advection mechanism of radon entry in the room is dominant and the first term in the numerator of equation (1) is much larger than S_D, the change of temperature difference ΔT will influence both radon entry rate and air change rate. Recall that the exponent n»2/3, and the exponent n_r in the numerator is taken equal to unity for most of the buildings, except buildings with underground space and dirt floor. Numerator of equation (1) increases faster than the denominator in case of ΔT increasing, therefore radon concentration in the building for a winter season should be higher than for a summer. When the diffusion mechanism of radon entry is dominant the numerator does not have pronounced temperature dependence. At the same time the seasonal increase of ΔT in the winter leads to a significant increase of denominator in equation (1), i.e. to the increase of the air change rate in the building primarily

due to stack effect. In this case radon concentration in the building for the winter season will be lower than for the summer.

Variation of radon concentration depending on temperature difference between indoor and outdoor air for different relations between the advective and diffusion mechanisms of radon entry is shown on the Fig. 1.

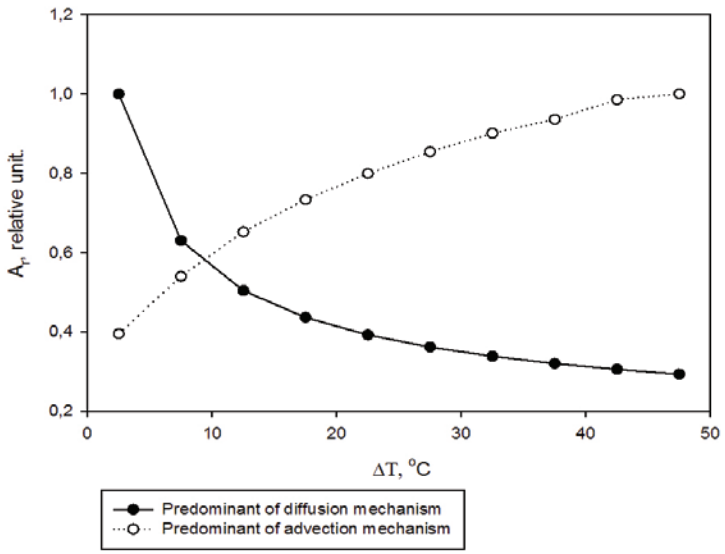

Fig. 1. Dependence of radon concentration on temperature difference for different mechanisms of radon entry

3. Measurement technique and equipment

There are a number of methods and tools for measuring radon concentration in the atmosphere of dwellings. For the purposes of mass radon surveys the most suitable methods for integrating measurements are solid-state track detectors. This technique is recommended by WHO for national and regional radon surveys.

For the purposes of continuous measurements radon-monitor AlphaGUARD was selected. It allows carrying out continuous measurements of radon concentration, atmospheric pressure and room temperature. The measurement interval was set to 60 minutes. Additionally, for number of dwellings AlphaGUARD Multisensor Unit was used, which allowed to measure the temperature and pressure difference between the envelope of the building and the outdoor atmosphere.

The task to determine the following characteristics was set:

1. Air change rate;
2. Radon entry rate per unit of air volume in the room;
3. Effective Leakage Area.

The method consists of the continuous measurement of radon concentration, temperature and pressure difference between indoor and outdoor atmosphere.

Typically, rooms are used under two conditions: active mode (with human activity in the room) and a steady state (when people leave the room at the end of the day or go to bed). In the steady state condition natural ventilation in the room is usually less than in the active mode. In the steady state the accumulation of radon is a process of attaining of the equilibrium between radon entry and its removing by ventilation. The whole curve of radon accumulation during exposure, not only average value of radon concentration was proposed to use. A series of measurements of radon concentration is described by nonlinear mathematical regression, characterized by the accumulation of radon in a room in steady-state condition of room use (Zhukovsky et al., 1999):

$$A(t) = A_{\max}(1 - e^{-\lambda \cdot t}) + A_0 \cdot e^{-\lambda \cdot t} + A_R^{atm} \quad (2)$$

where A_0 is radon concentration in the initial time except A_R^{atm}, A_R^{atm} =10 Bq/m^3 – radon concentration in outdoor air, A_{max} is the maximum radon concentration, which can be achieved in a room under the given conditions, λ is air ventilation rate, h^{-1}.
Equation (2) can be considered as a base for modeling the radon entry and accumulation in the atmosphere of the dwellings. Using the values of A_{max} and λ estimated from the equation (2) we can determine radon entry rate:

$$\dot{A} = A_{\max} \cdot \lambda \quad (3)$$

where $\dot{A}$ – radon entry rate, Bq×m^{-3}×h^{-1}.

4. Results and discussion

A series of continuous measurements in four modern buildings with high radon concentrations were conducted in Yekaterinburg, Russia during May 2008 – December 2011. A typical form of radon concentration time series for one of the representative room is shown in Fig. 2. To determine the intervals of radon accumulation in the general experimental data special software was developed. After the identification of the radon accumulation time series, a statistical analysis of accumulating curve was performed. Separate series of measurements was described by equations of nonlinear mathematical regression (2) and used for calculating the numerical values of the random errors and the asymptotic values of A_0, A_{max} and λ.

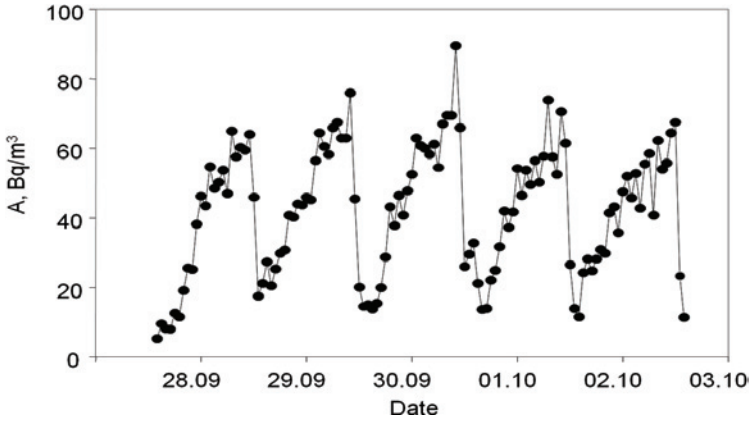

Fig. 2. Typical radon concentration time series

For sufficiently long term measurements, including warm and cold seasons, one can obtain the dependence of ventilation rate on the difference between indoor and outdoor temperature. For each room dozens of daily radon accumulation curves were analyzed. The obtained data were grouped according to temperature ranges and presented in Fig. 3. For all rooms under steady-state conditions the rise of ventilation rate under increasing temperature difference was observed. The observed dependence of the ventilation rate on the temperature difference agrees well with the theoretical curve (Sherman, 1998b).

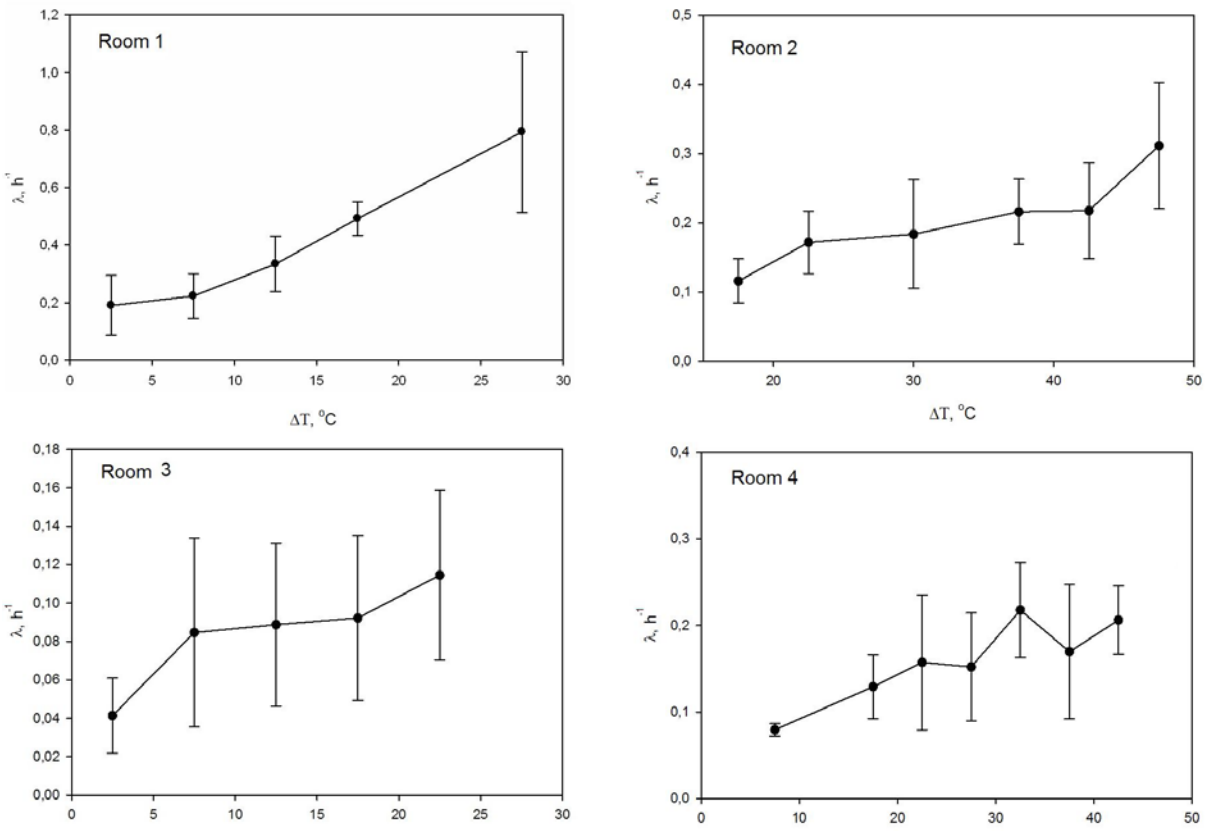

Fig. 3. Dependence of ventilation rate on the temperature difference

The dependence of radon entry rate on temperature difference ΔT between indoor and outdoor atmosphere allows to estimate the dominant radon entry mechanism – diffusion or advective mechanism. Fig. 4 shows such dependence for all the surveyed rooms. Three of them 1-3 are apartments on the upper floors in monolithic multi-storey buildings. As can be seen from Fig.4 radon entry rate for rooms 1-3 remains almost unchanged at increasing temperature difference. Therefore the diffusion mechanism of radon entry in the buildings is predominant. Room 4 is an apartment on the ground-floor. There is a significant growth of radon entry rate, which indicates the predominance of the advective mechanism.
Situation in the room number 2 (apartment on 17th floor in 25 storey building) is of significant interest due to maximum values of the radon entry rate and diffusion mechanism of radon entry. Therefore the building materials are dominant radon source in this building. Average value of radon concentration in the warm and cold periods for this dwelling is about 200 Bq/m3. Obtained values are close to action level in accordance with radiation safety standards in spite of building materials having passed through inspection. The reason of this effect may be connected with new construction technologies using fine finders (sand, slag and ash) as a filler of load-bearing structures and wall materials.

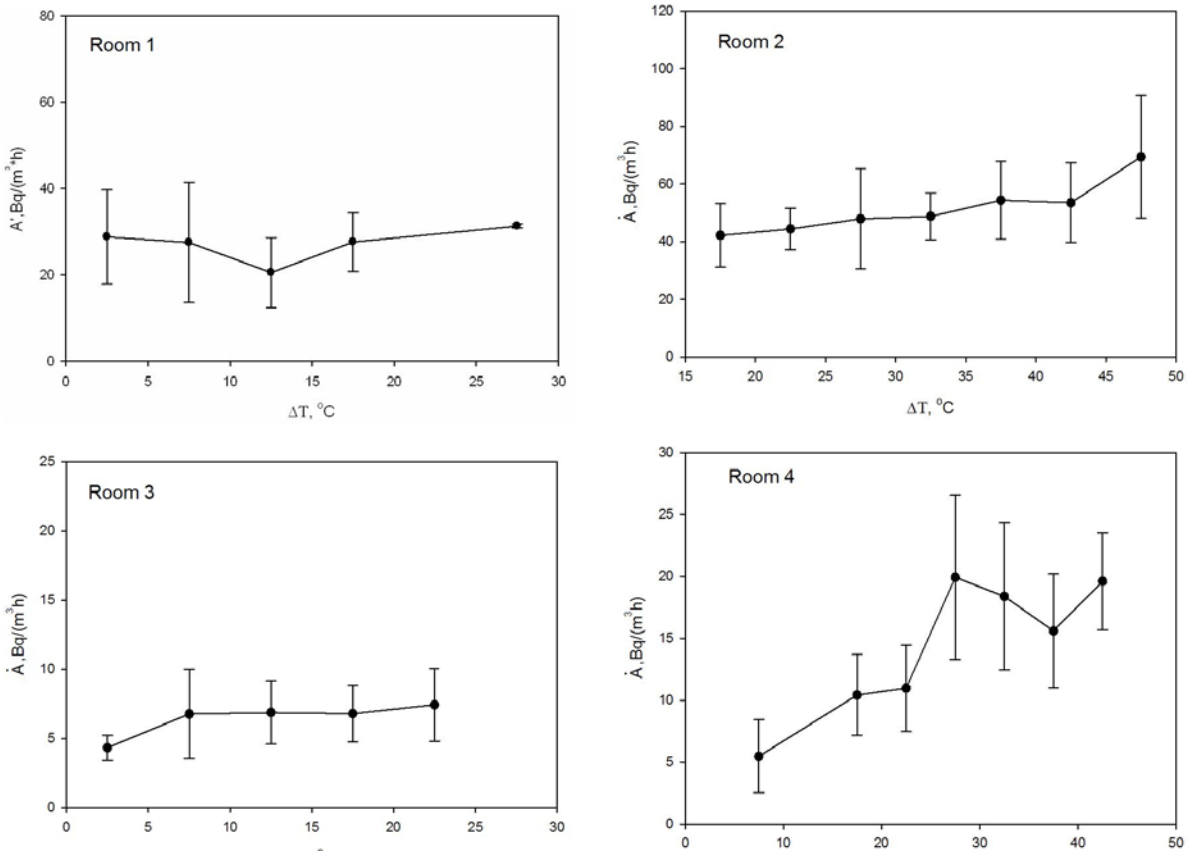

Fig 4. Dependence of radon entry rate on temperature difference ΔT between indoor and outdoor atmosphere

Also significant amount of additional information on air exchange processes can be obtained by conducting measurements of the pressure difference between the indoor and outdoor atmosphere. Such measurements were conducted in the room 1. Dependence of the pressure difference between the building envelope and the outdoor atmosphere on the temperature difference is shown in Fig. 5.

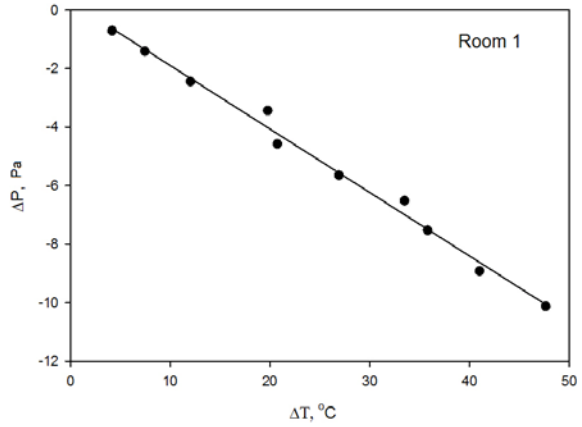

Fig. 5. Dependence of the pressure difference on the temperature difference

Using the estimates of the minimum ventilation rate for corresponding pressure difference it is possible to estimate dependence of the effective leakage area on the temperature difference between the building envelope and the outdoor atmosphere (Fig. 6).

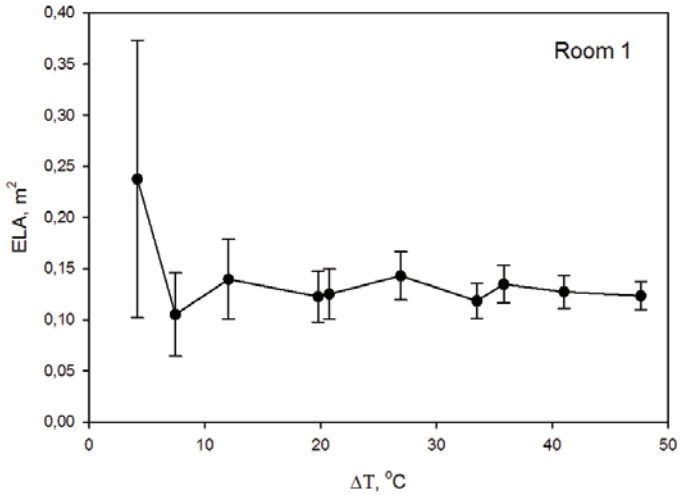

Fig. 6. Dependence of the effective leakage area on the temperature difference between the building envelope and the outdoor atmosphere

5. Conclusions

- The experimental technique of radon entry rate and air change rate assessment was developed and experimentally verified. It was shown that dependence of radon entry rate on temperature difference ΔT between indoor and outdoor atmosphere allows to estimate the dominant radon entry mechanism.
- It was demonstrated that radon entry rate for apartments in modern monolithic multi-storey buildings on upper floors can be almost unchangeable at increasing temperature difference. It was shown that the building materials can be dominant radon source in modern buildings.
- According to the results of survey the conditions under which radon concentration exceed 200 Bq/m3 are quite probable in the buildings with diffusion radon entry mechanism. Radon concentration levels in the modern buildings, built with materials passed through inspection, are close to action level in accordance with radiation safety standards.
- An improved understanding about the radon entry will lead to more effective ways to reduce or to prevent the entrance of radon into buildings.

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NORM Related Production of Rare Earth Metals in Estonia

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Abstract

Since 1970's rare earth, Nb and Ta metals and their compounds are produced in the plant, located at Sillamäe, Estonia. In imported mineral ores, which are used as commercial feedstock materials, NORM concentrations (both ^{238}U and ^{232}Th decay chain radionuclides) vary greatly, however they are usually high enough to cause exposure to workers and even sometimes concerns to the public. During processing operations radionuclides become mobilized, migrate to dusts, scales and process residues, leading to the enrichment in these materials. This means that the materials used and NORM waste produced as the by-product of processing, require proper management taking account the safety concerns. At workplaces doses to workers from external exposure, from radon/thoron and dusts in the air are or might be significantly higher than the dose limit for a member of the public. For this reason, these production activities are regulated as a radiation practice.

The paper gives an overview of performed studies and assessments on the impact of NORM, including material and waste streams, radiation exposures during pre-processing, chemical processing, generation of NORM waste, waste management and disposal, their environmental impact, etc. A comprehensive discussion on the establishment of the Estonian regulatory framework for NORM and the arising practical problems is also presented.

1. Introduction

In last decades multiple studies have identified the radiological concerns requiring regulatory control in specific NORM industries. EU has introduced the regulation of 'work activities' within its Directive 96/29/EURATOM (EC, 1996) and issued the recommendations for the implementation (EC, 1997). Production of niobium and tantalum, as well as of rare earths, belongs to work activities involving both potentially significant exposure of workers at the work-place (EC, 1999) and potential significance with regard to public exposure as a result of wastes and discharges (EC, 2003). The minerals in niobium (Nb) ores, various concentrates, oxides, etc., raw materials contain enhanced levels of NORM, mostly of ^{238}U, ^{232}Th and their decay products. Tantalum (Ta) occurs usually in combination with niobium and rare earths.

A major production facility of Nb, Ta and rare earths, Molycorp Silmet AS, is located at Sillamäe, North East Estonia. The large industrial complex produces the above materials (Nb, Ta metals and light rare earth metals as well as their compounds) from various imported ores and by-products.

The present paper discusses the establishment of the Estonian regulatory framework for NORM, the brief history of the facility at Sillamäe, performed studies and assessments on the impact of NORM at the Silmet facility, problems related to the generation of NORM waste, waste management and disposal, their environmental impact.

2. Radiation Act and related legislation

Estonia is a member state of the European Union since 1st May 2004. Thus, the regulations of the Union are in force in Estonia. When necessary, the Estonian regulations have been modified to take into account the EU regulations. The Radiation Act as the principal legal instrument of the radiation protection infrastructure was brought into force in 1997, while a new upgraded version was enforced in 2004 (Radiation Act, 2004). The Act bases on the concepts, principles, terms, and limits laid down in the International Basic Safety Standards (IAEA, 1995) and Directive 96/29/EURATOM (EC, 1996). The basic internationally approved principles, e.g., justification of practices, optimization of protection and safety, limitation of individual doses, adoption of justified and optimized interventions, the primary responsibility of the licensee, and authorization of practices, are explicitly formulated as provisions of the Act. The EU criteria for the exemption of practices from the requirements of the Act are adopted.

The Act sets requirements for identification and regulation of the work activities relevant to NORM. The general radiation safety principles apply also to the management of radioactive waste, including NORM waste, as well as those arising from decommissioning of a nuclear facility. According to the definitions given in the article 3 of the Radiation Act, radioactive waste is any material or object which contains or is contaminated by radionuclides, the activity or activity concentration of which exceeds the established clearance levels and for which no future use is foreseen.

The licensee in radiation practice is required to take any measures to render harmless radioactive wastes arising from its operation. The Regulation of the Minister of Environment No 10 (2005) issued under the Radiation Act specifies the requirements for radioactive waste management. Radioactive waste will be categorized by activity or specific activity, by half-life, by type of radiation and by heat generation as a result of radioactive decay. In conditioning and storing of radioactive waste their producer has to take into account, beside their type, also physical, chemical and biological properties of radioactive waste. Radioactive waste categorization includes NORM waste, which are defined as radioactive waste arising from processing of natural radionuclides, the activity concentration of which is higher than the exemption levels.

Article 59 of the Radiation Act sets that the dispersion, clearance and management of NORM waste, including the way of their storage, interim storage and disposal shall be determined by the license conditions. The Government Regulation No 163 (2004) enforces exemption levels for radionuclide activity and activity concentration in accordance with the terms and levels equal to those stipulated in the BSS (IAEA, 1995) and the EU Directive (EC,1999, 2003). Exemption levels are considered as basic criteria for decisions on licensing radiation practices. No license is needed for operations with activities or activity concentrations of radionuclides below the exemption levels. Examples of the exemption levels relevant to the raw material and waste containing NORM are given in Table 1.

Table 1. Exemption levels for NORM radionuclides

Radionuclide	Activity (Bq)	Activity concentration (kBq/kg)
^{210}Pb, ^{226}Ra, ^{235}U, ^{238}U	10^4	10
^{228}Th, ^{230}Th	10^4	1
^{232}Th nat, ^{238}Unat	10^3	1

For multiple radionuclides or mixtures in the materials, the sum of their activity or specific activity ratios to the corresponding exemption levels should be less than 1.

Environmental impact assessment procedure is required for radioactive waste management facilities, as they are considered in the legislation as activities with a significant environmental impact (EIA, 2005).

In 2009 in the course of reorganization, the Estonian Radiation Protection Centre, the former authority since 1996, was merged as a department with the Environmental Board. It is empowered to authorize practices by licensing, to assess practices and sources, to maintain the dose and source registers, to monitor and to assess radiation levels, to implement international conventions and agreements, to notify about the radiation accidents, etc. The other body, the Environmental Inspectorate, is provided to carry out regular inspections of the licensed radiation practices.

3. History of the Silmet facility

The large industrial complex at Sillamäe, about 190 km East from Tallinn, was launched as a top secret facility in 1948 for mining and milling of local alum shale (*dictyonema argillite*) containing ~ 0.03 % of U. Before Estonia regained independence, the facility under different names, including the Sillamäe Metallurgy Plant, was managed by the former USSR Ministry of Medium-Scale Engineering and it produced uranium for military and civil use. Later the mines were closed and much richer uranium ore of up to 1 % of U was imported from the Eastern European countries. Waste arising from uranium production was stored in a depository located near the Sillamäe plant, 20 - 50 m from the waterline of the Baltic Sea. After processing as a total of about 4 million tons of uranium ore, the uranium production was closed in 1977.

In the beginning of the 1970s the facility was modified for production of niobium, tantalum and rare earth metals, using loparite as a NORM-containing raw mineral from the Kola Peninsula. Later (till now) rare earths were produced from rare earth chloride mix. Composition of raw materials varies depending on the deposit, as niobium/tantalum are usually combined with iron, tin, titanium, manganese, radioactive elements (uranium, thorium) and their decay products. The composition and amount of technological waste from the processing depends on the share of each raw material type in its total amount. As the waste contained small amounts of thorium and uranium as well as their decay products, which were not recovered, the arising NORM waste were dumped together with other waste to the pond on top of uranium tailings depository near the plant. Since 1990 the main activity of the plant has been the continuation of the production of Nb and Ta metals and light rare earth metals as well as their compounds from various imported ores, e.g., columbite and chloride melts. In 1992 the facility becomes the state joint-stock company RAS Silmet, later AS Silmet and now Molycorp Silmet AS, which continues the production of Nb, Ta and rare earths.

With the establishment of the radiation protection infrastructure in Estonia, the NORM related working activities at the Silmet facility were considered of radiological concern, which required regulation as a licensed radiation practice. The performed studies, showed that at workplaces doses to workers from external exposure, from radon/thoron and dusts in the air were or might be higher than the established dose limits for a member of the public (see, e.g., Mustonen, R., et al., 2000). In addition, an analysis showed that the use of the former uranium tailings depository for dumping of the NORM waste might cause some radiological concerns to the members of the public (Realo, 2000).

4. Need for new NORM-waste management system

Until 2004 all radioactive waste from the rare earth and the rare metal production was dumped in the tailings pond. The first environmental impact assessment for the tailing pond was done in 1994 (Ehdwall et al, 1994, Nordlinder. S, et al. 1995). Mostly because of the impacts caused by releases and discharges of chemical pollutants from the depository and from the pond on its top, an international PHARE remediation project was initiated and the use of depository was terminated. The remediation project was

successfully finished in 2008. As a result, the need arouse to work out a new waste management option for the produced NORM waste. For creation of the new waste management system according to the Radiation Act and waste laws, international agreements and other legal acts, a number of assessments and studies there have been carried out.

It became clear that future radioactive waste arising would be caused exclusively by the production process of the Silmet facility (CASSIOPEE, 2002). The volume and activity of radioactive waste to store or respectively to dispose of would depend on from the following:

- content of NORM radionuclides in the raw materials,
- amount of processed raw materials,
- waste management system.

In the period 2001-2003 the developed radioactive waste management system included radioactive waste separation at an early stage of the technological process. The volume of future radioactive waste arising was estimated to be maximum 2000 t/y before vitrification. The specific α-activity of about 7000 Bq/g was estimated for non-vitrified radioactive waste. It was considered that all radioactive waste should be treated and conditioned together and after packaging in the special containers, it would be stored in an interim storage facility of a modular type. After 50-100 years of the interim storage period the waste could be used as feedstock for further processing or disposed of in a final repository (Behre Dolbear & Company, 2002). In case of the final disposal, the waste vitrification option was considered. The vitrified radioactive waste would be dumped into the existing oil-shale ash storage of the local power plant located at the Western side of the former tailings pond dam. This solution represented practically a final near-surface disposal of vitrified long-lived radioactive waste.

5. Environmental impact assessment for NORM waste management

The EIA process for all waste management systems of the facility (including also other forms of waste produced at the plant) was initiated in 2001 (E-Konsult, 2003). As the EIA report provided limited information about the proposed management system for the NORM waste and about the proposed guarantees or assessments for financing of the management options, a special EIA process of the NORM waste management was started in 2003 (E-Konsult, 2004). To meet the public concerns, the EIA program was amended and points covering the possibilities for the future waste management were included. This EIA process was finished in June 2004 and the proposed NORM waste management system was approved.

As the starting point of the EIA process it was taken into account that annually up to 2000 t of NORM waste with activity concentrations of 3000-4000 Bq/g were produced. The estimated amounts and activities of waste are given in Table 2. It was planned that this waste in the drums should be stored temporarily outdoors before the interim storage facility would be finished. In the same time it was expected that after 50 year storage period there would be enough material collected to be of interest to the reprocessing companies, e.g., in Russia or elsewhere.

Table 2. Estimate of NORM-waste in 2003

Production line	Average amount of waste per 1 t of processed raw material (kg)	Average activity concentrations of waste (Bq/g)	Estimated annual amounts of waste (t)
Rare earth metals	300-350	4300	1400
Rare metals	170-200	2300	600

Three different storage packages were investigated:

1. concrete containers with the dimensions of 1.63x1.63x1.35 m, which could contain up to 2.1 tons of the solidified NORM-waste. Putting these containers in 4 layers, would allocate up to 3.15 t of waste on 1 m^2 of the storage,
2. containers used in sea transportation, where the waste would be put in the plastic bags,
3. metal drums with the plastic inside cover of the volume of 0.43 m^3 for or 0.38 t of waste.

As the waste contains ^{235}U and ^{232}Th with their decay products, including radon, after several assessments and practical experiments the preference was givent to the last option. Radon was estimated as the major factor in causing doses for the radiation workers. The studies resulted in the conclusion that the best solution was the use of double package, which should avoid the leakage of radon for at least 10 y.

The first stage of the EIA process resulted in rather high dose estimates to the radiation workers, e.g., with annual doses over 20 mSv at some operations. A significant overestimation of doses, as it appeared later, was mostly due to the fact that at the start only few real data were available and that many default values and extremely conservative assumptions were used in the assessments. After data corrections and considering realistic protective measures, more realistic dose assessments were performed. As a result of these additional improvements the estimated average annual doses to the radiation workers remained under 4 mSv. The maximum annual doses of about 15 mSv/y, requiring limited working hours in that area were identified for the workers at the packaging facility.

In the safety assessment a number of accident scenarios were also considered:

1. falling and breaking of the drum containing the solid NORM waste in the packaging area or during the transportation;
2. falling and breaking of the drum containing the solid NORM waste in the interim storage;
3. fire in the storage of raw material or in the interim storage of NORM waste;
4. release of the material in the production process.

Based on the assessments and changes on the market, the Silmet plant started to import raw materials with significantly lower NORM radionuclide concentrations, which had resulted in the decrease of produced annually waste volumes by more than 10 times. E.g., they managed to find raw material for the rare earth metal production, which contained NORM below the exemption levels. Nevertheless, the production of Nb and Ta still uses radioactive raw material and the NORM waste generation continues.

6. Radiation practice license

Based on the radiation practice licence No 08/004, the Silmet plant is allowed to generate annually no more than 48 t of radioactive NORM containing waste with the activity concentration lower than 300 kBq/kg. At the facility, the generation of NORM waste is not constant in time and it depends to a great extent on the specific production line and the ore used. There is more than 31 t of NORM waste with the average ^{238}U and ^{232}Th activity concentrations of 98.8 kBq/kg and 36 kBq/kg, respectively, in the temporary storage. The composition and amount of the processing waste depends on the fraction of each raw material type in the total amount and on their Th, U and their progeny composition.

Under the Radiation Act, the producer of radioactive waste should transfer the arising waste to the radioactive waste management operator in at least 5 years. Unfortunately, there is no radioactive waste management operator for NORM waste in Estonia. At the moment, the NORM waste produced by the Silmet plant is temporarily stored and the company is continuing the search for possible management

solutions in the future. Unfortunately, so far without any success, as the amount of produced NORM waste is too small for further processing, while their activity concentrations significantly vary. One of the most realistic proposed management options might be the clearance of NORM waste under specified conditions.

7. Possible clearance option

The Silmet facility has a functioning power plant, which uses local oil-shale for producing of energy. The estimated annual production of oil-shale ash is around 100 000 t. The Estonian Environmental Board has allowed the use of oil-shale ash in the construction of the Sillamäe harbour, which is built close to the remediated waste depository. In the Environmental Impact Assessment of the Sillamäe Harbour it is estimated that the harbour building needs about 8.45 million m^3 of filling material, including about 2-3 million m^3 of oil-shale ash. Taking account the activity concentrations of NORM in oil-shale ash in Table 3 (Realo et al, 1996) and similarity of physical properties of oil-shale ash and the NORM waste produced in Sillamäe, a clearance option for possible management of the latter has been proposed. The clearance option bases on the assumption that the NORM waste and oil-shale mix (110000 tons of oil-shale ash together with 48 tons of NORM-waste) could be used (instead of oil-shale ash only) in the construction of the harbour.

Table 3. Activity concentrations of radionuclides in the Estonian oil-shale ash

Radionuclide	Activity concentrations (Bq/kg)
^{226}Ra	48 ... 78
^{238}U	48 ... 64
^{235}U	2.2 ... 3.0
^{232}Th	23 ... 30
^{40}K	530 ... 1100

The clearance levels of 1 kBq/kg for both ^{235}U and ^{232}Th based on the Radiation Act. The legislation also states that clearance of radioactive waste is possible if:

- the caused annual dose to the public is lower than 0.01 mSv;
- the caused collective annual dose is lower than 1 manSv;
- in the case of the NORM-containing material and waste, the public to the public is lower than 0,3 mSv/y.

The assessment of the annual public and collective doses caused by using the oil-shale and NORM waste mix in the construction of the Sillamäe harbour was performed (Lust, 2009). For the assessment of clearance options of NORM waste an assumption that future radioactive waste arising is caused exclusively by the production of the AS Silmet plant was taken into account. The doses were assessed for both workers and the public considering the following scenarios:

1) transportation of NORM waste;
2) inhalation in the process of NORM waste management;
3) ingestion in the process of NORM waste management;
4) fire in the waste management facilities;
5) doses to the harbour workers;
6) dose to the farmer, who lives and farms on the harbour area.

The main results of the assessment are the following. For the workers the highest doses arise via inhalation pathway. The highest doses for the public are characteristic of the farmer, who lives and produces in the area filled using the above mix. However, even in the case of the farmer the clearance requirement of NORM, i.e., annual doses lower than 0.3 mSv, is fulfilled with the probability of 95%. Taking into account that the harbour is been built next to the remediated radioactive waste tailings depository, it is hard to believe that farming is a very realistic scenario.

8. Conclusions

The outcome of active discussions and dialog between the operator and the regulator was the development of the waste management system for NORM waste, which, however, currently covers only the short range activities. Based on the performed assessments it was proved that in case using the NORM waste and oil-shale ash mix in the construction of the Sillamäe harbour, the clearance requirements would be fulfilled. Additionally, it can be easily proved that of the proposed management option is the optimal solution considering the type, radionuclide composition and amount of the radioactive waste. The final solution for the NORM-waste management is still under discussion.

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Radioactive impact on estuarine sediments affected by Acid Mine Drainage (AMD) and effluents from NORM phosphate fertilizer industries

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Abstract

In this paper is studied the estuary of Huelva formed by the Tinto and Odiel rivers, which are seriously affected by acid mine drainage (AMD) due to the long-term mining activities done in Iberian Pyrite Belt, and, as a consequence, their waters present an very low pH (< 3), and for that they contain very high heavy metals concentrations. Additionally, a large industrial complex is located in the surroundings of this estuary, which includes five phosphate rock processing plants that produce a waste called phosphogypsum (PG) containing high U-series radionuclides concentrations.

This estuary is governed by two mixing processes: 1) salt-induced mixture process, typical of the majority of estuaries, and 2) pH-induced mixture process, consisting in an acid neutralization as result of the mixture of acidy fluvial water coming from the drainage basins when reach the estuary. These mixture processes affect to the behavior of both heavy metals and natural radionuclides that reach the estuarine waters. The analysis of the radionuclides concentrations have allowed us to demonstrate that the behavior of these elements are very affected by these mixing processes, and to affirm that U-, Ra- and Th-isotopes levels in the current sediments are very dependent of the hydrochemical properties of the waters (mainly pH and chlorinity). This study has global significance for other polluted environmental systems that are impacted by AMD and PG.

1. Introduction

Estuaries are zones of complex interaction between fluvial and marine processes, where there are large mass exchanges, and big changes in the salinity, nutrients, sedimentary conditions and living organisms. The use of radioactive tracers is a valuable tool to analyze the transfer mechanisms between the different involved system phases (Zöllmer and Irion 1993).

The estuary formed by the Tinto and Odiel rivers presents a great interest due to it is very conditioned by two hydrochemical facts. The first one comes from fact that both rivers are seriously affected by acid mine drainage (AMD) from long-term mining activities developed in the Iberian Pyrite Belt, which produce in these rivers the transport of high amounts of heavy metals and radionuclides due to their extremely low pH (2.5-3.5) (Grande et al 2003). Secondly, in their mouths there is a large industrial complex which includes several phosphate rock processing plants that produce annually about 2.5 million tons of a by-product, called phosphogypsum (PG), containing enhanced U-series radionuclides levels (about 200 Bq kg^{-1} of ^{238}U, 650 Bq kg^{-1} of ^{226}Ra, and 450 Bq kg^{-1} of ^{230}Th). Until 1998, about 20 % of the generated PG was discharged directly into the estuarine waters, while the remaining 80 % was pumped in suspension with sea water (20 % PG plus 80 % seawater) to be disposed in large piles located on the Tinto river salt-marshes (Bolivar et al 2002). Since 31st December 2010, all P_2O_5 production plants were closed and for that the phosphogypsum production was stopped. Currently there is an environment al plan under study

to restore the PG piles, and it is estimated to take 10 years to complete this plan.These facts explain that estuary of Huelva is one of the most polluted estuarine systems in the world.

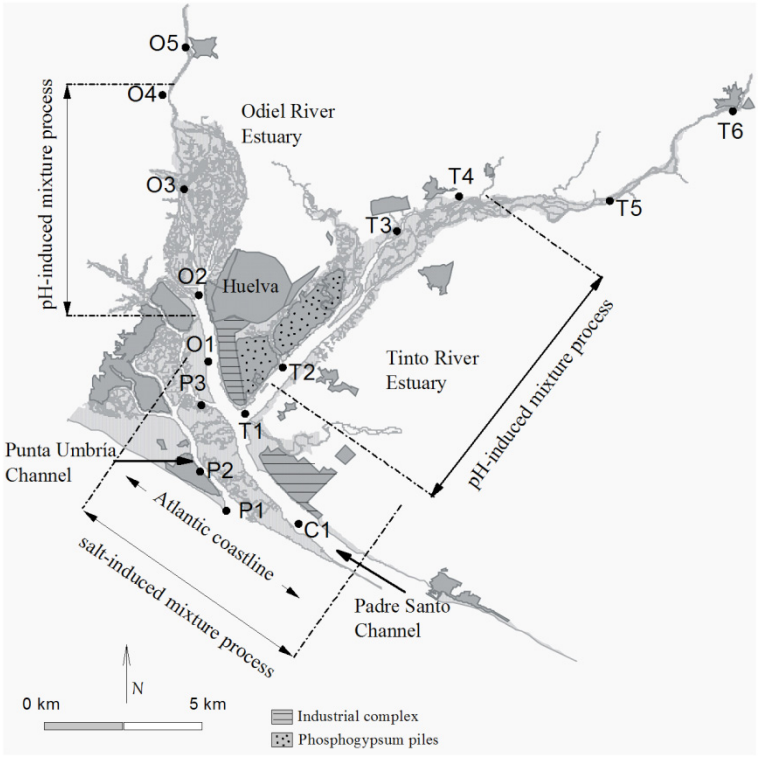

Figure 1. Map of the estuary of the Tinto and Odiel rivers with sampling points

It has been demonstrated that hydrochemical characteristics of the water in this estuary suffer two mixture processes, the salt-induced mixture process, and the pH- induced mixed. A strong tidal influence controls the salt-induced process, and it has been extensively studied by measuring the changes in the salinity of the mixing water. Specifically the process follows the mixture between seawater (pH over 8 and chlorinity above 21 g L^{-1}) and estuarine water (with pH around 6.0 - 7.0 and chlorinity average over 10 - 15 g L^{-1}). This is located in Padre Santo and Punta Umbría Channels, but can reach the upper sectors of the estuary during high tides (Fig. 1). The pH-induced mixture process is the neutralization resulting from the mixing of estuarine water (pH = 6.0 - 7.0) with the fluvial water (pH < 3), containing very high concentrations of dissolved materials, including metals and radionuclides. This neutralization process by dilution of water is restricted to estuarine areas of both rivers, and produces a positive gradient in the pH with a strong directionality outwards from the system (Carro et al 2006).

Taking in consideration previous facts, main aim of this work has been to report the behavior of different natural radionuclides in the surface sediments from an estuarine system very affected by both salt-induced and pH-induced water mixing processes.

2. Materials and methods

2.1. Sampling

Fifteen sampling stations were selected to study this system along Tinto River estuary (sampling points with code “T”), Odiel River Estuary (code “O”), where is clearly produced both the pH-induced and salt-induced mixing processes. Moreover, sampling points in Padre Santo Channel (code C1) connecting Punta Umbría Channel (code P) with the Odiel Channel have been selected since they are estuary sectors with

mainly marine influence, and for that in principle very low influenced by the AMD of the mining rivers and the PG piles (Fig.1). In selected sampling stations surface sediments were collected using sediment traps during each season (4 times a year). Samples were collected at the end of May 2007 (spring), December 2007 (autumn), March 2008 (winter) and September 2009 (summer). In addition to the sediment samples, superficial water samples were collected and the pH and conductivity were measured in situ.

2.2 Radionuclide determinations

Alpha-emitting radionuclides of U-isotopes were determined by alpha-particle spectrometry using ion-implanted silicon detectors in geometry with 25 % absolute efficiency. To the isolating of the radioelements (U, Th and Po), a sequential well-established radiochemical method based on extraction chromatography (UTEVA resins) was applied (Oliveira and Carvalho 2006).

^{226}Ra and ^{228}Ra were determined by gamma-ray spectrometry using a coaxial ultra pure germanium detector (HPGe ORTEC) with ~20 % relative efficiency and FWHM of 1.10 keV at 122 keV and 1.90 keV at 1333 keV. The photopeaks used in the radionuclides determination were: ^{226}Ra (352 keV - ^{214}Pb), ^{228}Ra (911 keV - ^{228}Ac). The efficiency calibration used in the gamma measurements is described in detail in our earlier papers (Pérez-Moreno et al., 2002).

3. Results and discussion

3.1 Physical-chemical parameters

In Figure 2 the pH and conductivity in water samples of Odiel-Tinto rivers estuary, Padre Santo and Punta Umbría channels are shown. In relation to the bulk densities of sediments for each season varied with a wide range, from 0.36 to 1.49 g cm^{-3}. For each season, the densities are similar for both Odiel and Tinto estuaries, with the highest values in summer and lowest in autumn.

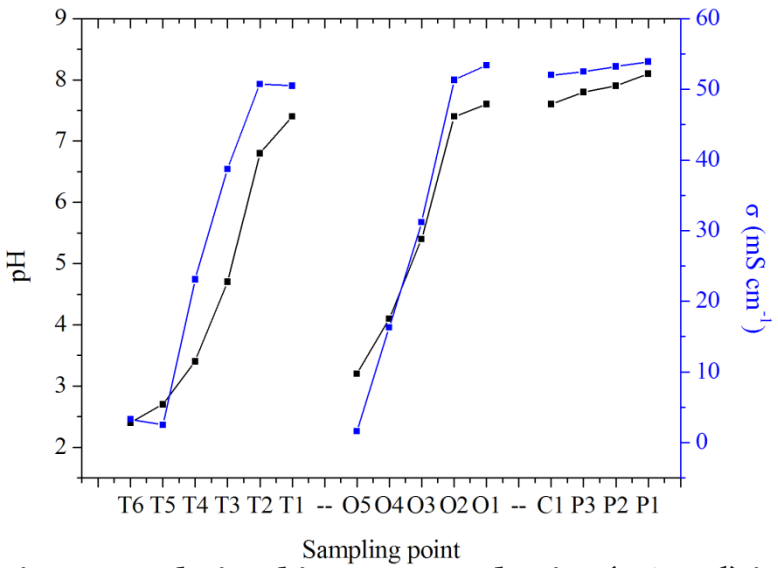

Figure 2. Relationship pH vs. conductivy (mS cm^{-1}) in water samples.

A progressive increase in pH towards the mouth of both rivers is observed in the estuary due to pH-induced and salt-induced mixture processes. The pH values ranged from 1.9 (Tinto River, T6-summer) up to 8.1 (sample C1-spring), showing high and similar gradients in the estuary for both rivers (pH varied between acid values lower than 3 and neutral conditions, higher than 7). On the contrary, the pH in both

Padre Santo and Punta Umbría channels showed few variations, oscillating between 7.0 and 8.1, fact coming from the proportion of seawater is very high.

As it is expected, the lowest pH is observed during autumn when the fluvial inputs are greater being more intensive the AMD, observing that location 3 (T3 and O3) reaches pH around 3-4, whereas during summer (lowest or null flows), the pH of the estuary is more uniform, with values higher than 5.4 in most of the stations (Fig. 2). This fact can be justify by the low fluvial contribution in summer allowed fast neutralizations of the acid water in the upper sector of the mixing zone.
On the other hand, as it is expected in figure 2 is observed that conductivity presents an similar pattern that pH, which is ratified by the good linear regression fit obtained between both parameters, σ (mS cm^{-1}) = - (18±4) + (8.3± 0.7)·pH, and observing that conductivity and pH increase towards the mouth of both rivers reaching typical values of seawater in the sample situated out of estuary (sample P1). One of the main features of the rivers that end in this estuary is their high dissolved sulphate concentrations due to the severe acid drainage mine they are receiving (Carro et al., 2006). This peculiarity is consistent with the high conductivity values measured in the fluvial zone of both estuaries (O5, T6 and T5), with values between 1-5 mS cm^{-1}, which is one order of magnitude higher than the typical surface waters (< 0.1 mS cm^{-1}) (Carro et al., 2006) (Fig. 2). As we move towards the Padre Santo and Punta Umbria channels, an increase in the marine component of the water occurs reaching values around 50 mS cm^{-1} (samples P1) which are typical of seawaters.

3.2 Uranium-isotopes

The annual average ^{238}U activity concentration at every sampling point is shown in figure 3. The ^{238}U and ^{234}U activity concentrations spatially vary over a wide range, from 6.6 to 2580 Bq kg^{-1} throughout the study period. Some differences can be seen between both the Odiel and Tinto channels. So, Tinto River estuary supports a greater burden of uranium, because it carries a higher concentration of uranium that will precipitate when both the river water and leached PG stacks water mixes with the estuarine water. In both estuaries the lowest values of activity concentrations of uranium are found in summer, when the rivers and PG piles have the smallest discharges. However, the highest values in both Tinto and Odiel estuaries are found in winter (followed by autumn), which correspond with the seasons of highest rainfall. This effect is more significant in the Tinto Channel. Due to the AMD received for both rivers, the activity concentrations for both ^{238}U and ^{232}Th nuclides in their surface waters generally range in the interval 0.1 - 1 Bq L^{-1}, which are 1 - 3 or 3 - 5 orders of magnitude, respectively, higher than worldwide typical rivers (Ketterer et al., 2011).

The highest activity concentrations are found in the Tinto Channel due to additional contribution of acid waters coming from PG piles due to the rain, which contain very high concentrations of U-series radionuclides as ^{238}U (50-200 Bq L^{-1}), ^{226}Ra (0.5-2.0 Bq L^{-1}), ^{210}Pb-^{210}Po (1-20 Bq L^{-1}), or ^{230}Th (1-5 Bq L^{-1}) (unpublished data). Rainwater that fall on the surface of the un-restored PG stack (more than 400 ha) dissolves a fraction of pollutant contained in PG, and so they are released into the estuary with high acidity (pH < 2), and contain high levels of radionuclides (especially U to be the most soluble at this low pH, although its concentration in PG is lower than other radionuclides, and other pollutants.By considering an average rainfall of 550 L m^{-2} and that 50% of this amount reaches the estuary, it can be estimated that annually about 0.3 million tons of these acid polluted waters are released into the Tinto Channel containing radionuclides concentrations of about 10^2 Bq L^{-1} for ^{238}U and 10^0 - 10^1 Bq L^{-1} for the rest of radionuclides from U-series (^{226}Ra, ^{230}Th, ^{210}Pb) (Bolívar et al., 2009). The effect of this PG-laden water releases are shown in the peak of ^{238}U concentration in the sediments found in points located near the PG stacks (points T2 and T3).

With regard to the sampling sites in the fluvial zone (O5, T6 and T5; Fig. 3), the values of uranium concentration in sediments are typical of unperturbed rivers (UNSCEAR, 1988), with about two orders of magnitude lower U than the estuarine sediments affected by the pH-induced processes. In these locations both rivers have highly acidic waters with a high loading of radionuclides, but they will not precipitate until these waters are mixed with the estuarine waters and pH increases to > 4.

Towards the sampling stations O4 and T4 the pH-induced process begins and the pH increases from 1.9 (fluvial zone) to 4.4 (O4 or T4), and finding similar changes found for all seasons. Higher values of uranium in these sampling points, T4 (421 Bq kg^{-1} for ^{238}U) and O4 (115 Bq kg^{-1} for ^{238}U) were found compared to unperturbed sediments of the fluvial zone (Fig. 3). UO_2^{2+} uranyl ion the is the most soluble specie in the Tinto and Odiel rivers (pH ~ 2-3), but an abrupt change of pH in this zone will produce the co-precipitation of uranium as metallic hydroxides, or sulphate salts, which will scavenge a very significant fraction of the dissolved metals (including the U one) carried out by the acid water of the rivers.

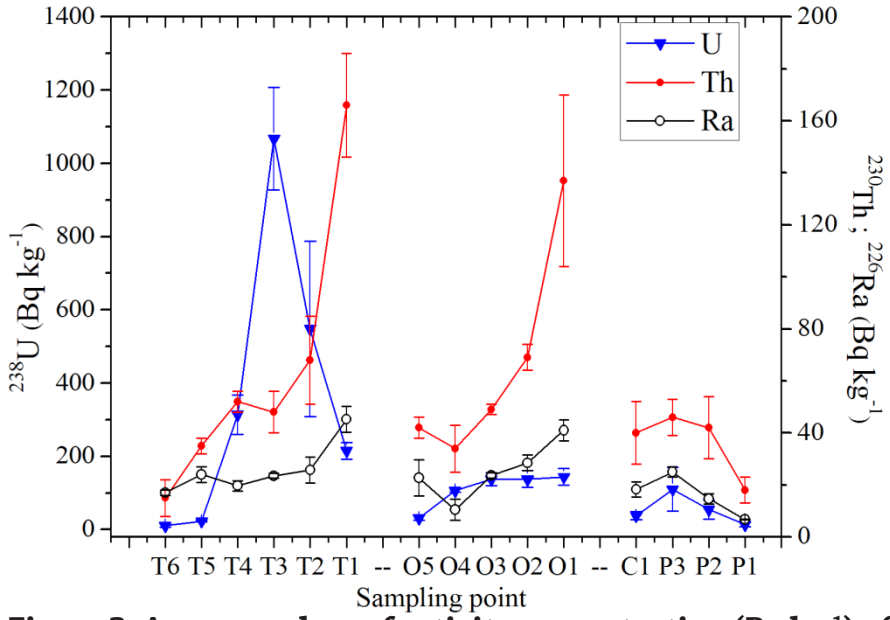

Figure 3. Average values of activity concentration (Bq kg^{-1}) of ^{238}U, ^{230}Th and ^{226}Ra in the sampling points.

In the sampling stations O3 and O2; T3 and T2 the pH-induced process continues. In this zone an abrupt change of pH (from 4.5 to 7) occurs in all seasons. Such a marked change in pH is expected to result in significant precipitation of U and, therefore, in a significant enhancement of its concentration in the sediments. The ^{238}U concentration was found to be the highest in T3 among all the sampling sites in the Tinto River, with an average concentration of 1342 Bq kg^{-1}, but for its equivalent point (O3) in Odiel River, the average concentration is much smaller (150 Bq kg^{-1}) (Fig. 3). This could be due to; a) the differences in the dissolved U concentrations in these waters (Tinto U concentration is twice than the Odiel one), and/or b) presence of acidic water releases from PG piles. Moreover while we move to offshore and the pH values are going up, the removal of uranium may also take place associated with adsorption of U^{6+} onto organic matter and Fe/Mn compounds (McKee et al., 1987), or phosphate complexes which compete with carbonate to complex U in the range 4-7.5 and the partial reduction of uranium VI to IV, a more insoluble form (Toole et al., 1987).

In locations T1 and O1, sited at the end of both estuaries (Tinto and Odiel, respectively), the values of pH, for the four samplings campaigns, range from 7.1 to 7.8 (average 7.4), and ^{238}U activity concentrations (215 Bq kg^{-1} ^{238}U for T1, and 144 Bq kg^{-1} ^{238}U for O1) are similar at both points. The salt-induced coagulation and precipitation is expected to be minimal at this zone. The exchange of sediment from this zone to the shelf is likely a significant mechanism of sediment transport to the shelf regions. In addition, ^{238}U

concentrations in the Punta Umbria Channel, which has a very low water exchange with the Odiel Channel, the radionuclide activity concentrations found were similar than in unperturbed sediments (Bolivar et al., 1995). Opposite of, the samples from P3 (El Burro Channel) were found to have slightly higher U concentration (171 Bq kg^{-1} of ^{238}U), which is expected because this channel exchanges water between the Odiel Channel (polluted) and the Punta Umbria Channel (un-polluted) (Fig. 3).

The impact of the new waste management policy resulting in no PG releases into Odiel Channel can be evaluated by the temporal analysis of the radionuclide concentrations evolution in sediments. Firstly, in the Tinto estuary the average ^{238}U activity concentration for the whole estuary in the sediments was constant in the years 1999 (policy changed in 1998), 2001 (Absi, 2004) and 2008, with ^{238}U concentrations of 219 ± 97 Bq kg^{-1}, 252 ± 112 Bq kg^{-1} and 380 ± 123 Bq kg^{-1}, respectively, while in the Odiel estuary these average concentrations decreased continuously from 343 ± 96 Bq kg^{-1} (1999 year) till 113 ± 11 Bq kg^{-1} (2008 year). The value found in 2000 is very similar to the average activity concentration found in our study, indicating that the sources of U in the Odiel estuary have been significantly reduced, but in the Tinto estuary the U sources have remained constant over time, and the new policy waste management has not resulted in a significant decrease in U concentration due to the release of radionuclides from 450 ha of un-restored PG piles.

3.3 Thorium-isotopes

In for the case of thorium isotopes, we observed that their concentrations throughout the study area are similar to uncontaminated estuarine sediments, except at certain points where ^{230}Th concentrations increase significantly (Fig. 3).

The ^{232}Th concentrations are relatively uniform along the study area and similar to the typical values obtained in unperturbed sediments (30 - 60 Bq kg^{-1}) (Martín et al., 1978). This is because of relatively less amount of leaching of ^{232}Th and PG does not contain high concentrations of ^{232}Th. On the contrary, ^{230}Th presents higher levels (from 5.9 to 232 Bq kg^{-1}), increasing from the fluvial zone towards the end of the estuary, and reaching the maximum values for all seasons at point 1 for both rivers (zone of salt induced processes, with averages of 175 Bq kg^{-1} for T1 and 153 Bq kg^{-1} in O1), which is the estuarine area where there are high and uniform values of pH (around 7.0). This is due to scavenging of Th by suspended particulate matter when the pH is ~7.

3.4 Radium-isotopes

In figure 3 and 4 is observed that the distribution pattern of both ^{226}Ra and ^{228}Ra is very similar throughout study area. The activity concentration of ^{226}Ra increases from the fluvial zone up to the end of the estuary, with a maximum at T1 and O1 in all seasons (average of 45 Bq kg^{-1} in T1 and 41 Bq kg^{-1} in O1), locations that represent only salt-induced processes (pH = 6.5 - 7). This ^{226}Ra behavior is similar to the ^{238}U and ^{230}Th ones discussed earlier, but ^{228}Ra does not present a clear pattern along both Tinto and Odiel channels, showing similar concentrations than unperturbed sediments (30 - 60 Bq kg^{-1}), the amount of radionuclides derived from the ^{232}Th-series both in AMD and PG piles are not significant. This very low impact found for Ra-isotopes comes from two facts; firstly, the very low solubility of Ra in aqueous solutions containing high concentrations of sulphates (as it is our case), and secondly, it is very established that radium tends to remain in dissolution for the majority of estuaries (Somayajulu and Goldberg, 1966; Martín et al., 1978).

Several studies in global estuarine systems have documented that radium is non-conservative in estuaries, with the release of Ra when Ra-laden suspended particulate matter in rivers are delivered into the river mouth and thus, higher dissolved ^{226}Ra concentrations were found. For example, studies in several

natural estuaries like Hudson estuary (Li et al., 1977), or Amazon estuary (Key et al., 1985) showed similar results. In figure 3 the average of ^{226}Ra concentration in sediments increases with pH towards the mouth of the estuary. This fact could be due to one or more of these two reasons: i) sediments with higher concentrations of ^{226}Ra are trapped near the confluence of both channels, as was seen for ^{238}U and other ^{238}U-series members; and ii) release of ^{226}Ra from suspended particulate matter which subsequently undergo pH-induced coagulation and eventual precipitation to the sediments (Aguado, 2003).

Reduction in the ^{226}Ra in sediments along the estuary since 1998 has been documented, primarily due to the elimination of the direct phosphogypsum releases into the estuarine system. The activity concentration of ^{226}Ra significantly decreased in the sediments from both Odiel and Tinto channels, falling from an average of around 700 Bq kg^{-1} in both channels before 1998 up to ~ 70 Bq kg^{-1} in 2005 (Villa et al., 2009), and finally reaching 28 ± 3 Bq kg^{-1} in 2008 year (our study). Therefore, the enhanced ^{226}Ra levels in the points 1 are likely due to resuspension of older polluted sediments. From the distribution of Ra in sediments, two observations can be made: first, the effect of the new waste management policy from 2008 year can be discerned in the current concentration of ^{226}Ra attaining typical values of background levels in sediments (20 - 50 Bq kg^{-1}, UNSCEAR, 1988). Second, it is noticeable from the concentrations found along the sampling points (Fig. 3), there is a fairly homogenization of the little remaining pollution in the sediments that still exist in the estuary.

3.5 Activity ratios

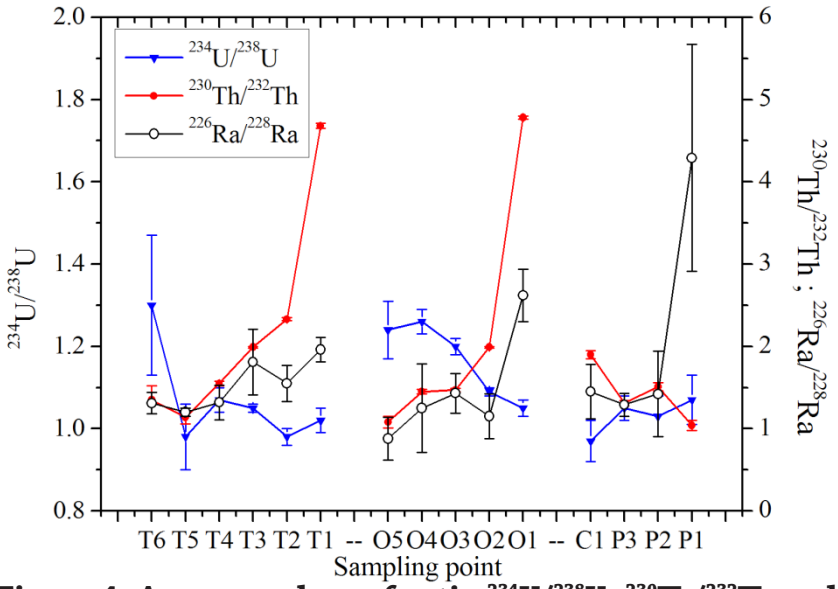

Figure 4. Average values of ratio ^{234}U/^{238}U, ^{230}Th/^{232}Th and ^{226}Ra/^{228}Ra in the sampling points.

Some of the discussions presented earlier can be validated by using activity ratios as ^{234}U/^{238}U, ^{230}Th/^{232}Th, ^{226}Ra/^{228}Ra ratios (Fig. 4). The ^{234}U/^{238}U activity ratios in our samples ranged from 0.89 to 1.58 in the Tinto River estuary and 1.01 to 1.39 in the Odiel River estuary. This result is in agreement with the activity ratios reported for different worldwide rivers (Scott, 1982). Overall, the ^{234}U/^{238}U activity ratios are slightly higher in Odiel River estuary compared to that in Tinto. Higher values are found in the fluvial zone and the values in the estuary are influenced by the U precipitation and the values in seawater (seawater AR is 1.14). Precise measurements with ICP-MS will aid in tracing the pathways and transport of U in the river/estuarine system.

The ^{230}Th/^{232}Th activity ratio varied between 0.6 and 5.0, with the highest values in Odiel River estuary in Spring. Although the amount of ^{232}Th derived from PG piles and the AMD discharge are likely negligible,

high variations appear to be due to variations in ^{230}Th derived from both PG and AMD. The average activity ratios of ^{230}Th/^{232}Th increase uniformly up to point 1 where it reaches a value of around 5, a value significantly higher than the one found in uncontaminated estuarine sediments from Huelva (Bolivar et al., 1995) and worldwide (Somayajulu and Goldberg, 1966). The surface sediment contamination of ^{230}Th samples from points 1, can proceed from two routes; either by direct transport from PG and AMD, or by resuspension of contaminated sediments, or by the adsorption of dissolved ^{230}Th on to suspended particulate matter before the implementation of policy (Bolívar et al., 2002). If we consider that the main pathway of contamination is through direct deposition of particulate phosphogypsum, resulting in high ^{238}U and its daughter products a high fraction of the sediments must be contaminated by this by-product. Since we are finding high concentrations in selected areas, the resuspended material could be a source of contamination in this estuary. The contamination by radionuclides from U-series of the sediments is also supported from the observed values of ^{226}Ra/^{228}Ra in figure 4, where a slow increase of this ratio can be seen in samples T1 and O1, demonstrating that radium is not removed from sediments.

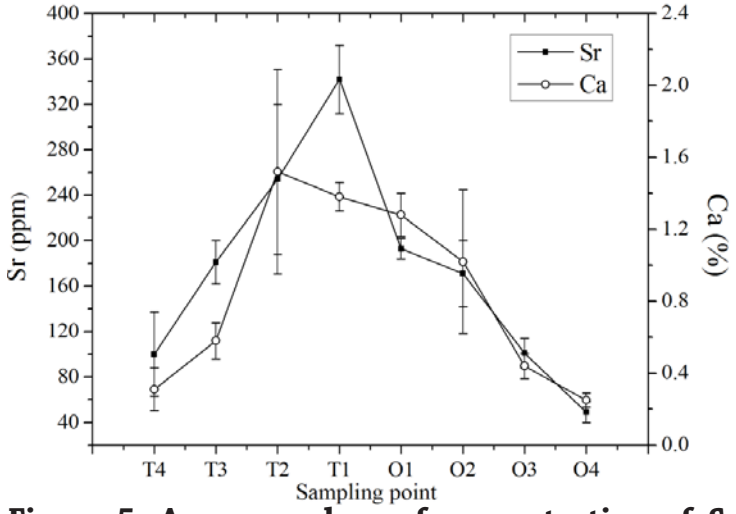

Figure 5. Average values of concentration of Sr (ppm) and Ca (%) in the sediments samples in the sense of the waterflow from T3 to O4.

To finish this extended abstract, to comment that in Figure 5 are observed significant peaks for both Sr and Ca in the points T2 and T1 (the points closest to the PG stacks), which could come from the PG piles leaching released generated by the rainy waters, and not from inputs from the acid rivers. To ratify this hypothesis, it is known (data unpublished) that average concentration of Sr and Ba in PG are very high and around 4×10^4 and 9×10^4 ppm, respectively, producing in its leaching waters that go into Tinto River estuary high levels of these elements (2×10^1 and 5×10^2 ppm, respectively), and being them very much higher that the found ones in the another source of pollution, the Tinto River waters (0.280 and 76.6 ppm for Sr and Ca, respectively). Taking into account the previous data, and the similar chemical behavior of these three elements (Ra, Sr, Ca), the same pattern found suggests that they share with the same source for their origin.

4. Conclusions

The hydrogeochemical characteristics of the water in both Tinto and Odiel rivers estuaries where analyzed, founding that acid fluvial water and marine water are mixed allows us to define the intervention of two geochemical processes: a typical process of salt-induced mixture bound to a neutralization process of acid water.

The temporal and spatial variations of indicators as pH and chlorinity regulate the behavior of U-, Th- and Ra-isotopes. This fact is produced by the adsorption (or co-precipitation) of the dissolved uranium onto the particulate matter in zones where is produced pH values between 4.0 - 5.0. In fact, the highest values of ^{238}U concentration are reached in these zones (values up 2520 Bq kg $^{-1}$), which are about fifty times higher than ones un-perturbed sediments. The maximum concentrations for ^{230}Th and ^{226}Ra are produced for higher values of pH (about 6.0 - 7.0) and the concentrations are much lower than those of uranium. So a non-conservative behavior of uranium has been verified in this estuary, and consequently the estuary of Huelva acts as a sink for U and other natural radionuclides. This effect is less important for Th- and Ra-isotopes.

And, as final remark, the enhanced levels from U-series in recent sediments from the estuary of Huelva, and very specially for U-isotopes, are mainly three sources: (1) leaching of phosphogypsum stacks located nearby, (2) the flows incoming from the Odiel and Tinto rivers that contain very high levels coming from the acid mine drainage existing along the Iberian Pyrite Belt, and (3), the waters from the Atlantic ocean entering into the estuary containing a significant concentration of U-isotopes (40 mBq L^{-1}) which could precipitate during the mixing pH processes.

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The influence of airthightness on the indoor radon concentration in dwellings

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Abstract

Natural Occurring Radioactive Materials (NORM) are often used in building materials. Some of these radioactive elements decay to radon, which can be released by the building materials. Exposure to high radon concentrations is harmful to human health. Since one spend a lot of time indoor, the radon exposure is a non negligible topic in health safety and protection.
In this study we investigate the influence of airtightness and building materials to the indoor radon concentration and their possible relation.
The radon concentration in the air is measured during 3 days in the Winter of 2012.
Several radon measurements are performed in consecutive construction stages of new dwellings. Our study considers a case study of a set of several side by side located residential units under construction, all with well specified building materials. In this way differences due to geological background were excluded. The differences in the ventilation regime in the studied dwellings were determined by airtightness measurements. As a matter of fact, the relation between these parameters could be determined.

Introduction

In the last decade, there is a lot of interest in passive and low energy housing. One of the important parameters for a low-energy dwelling is isolation. The airthightness is the isolation of the air inside the dwelling. This airthightness is of huge importance regarding the construction of low-energy dwellings.

The earth crust consists out of naturally occurring radioactive materials (NORM). Many elementary materials of the building materials originate from the earth crust and NORM containing additives could be added to building materials. As a matter of fact, many building materials contain NORM. Some of these elements may decay to Radon. Radon is harmful for human health and is known to be one of the reasons for lung cancer.[Bern] Due to physical properties of this element, it is a gas, Radon can escape out of the building materials and enter the dwelling. In this way the indoor Radon concentration can rise. As a matter of fact, a good ventilation is necessary to prevent too high indoor radon concentration. Since the natural ventilation rate is limited in new and low-energy dwellings, this can possibly cause radon problems. For this reason, we studied the radon concentration in a series of dwellings in combination with their airhightness.

Methodology

The indoor radon concentration was measured during 3 days using a Sun Nuclear 1029 continuous radon monitor or a Sarad Radon Scout. The former with an integration time of 2 hours, the latter with an integration time of 1 hour. The monitor was placed in the middle of a room at the ground floor. The dwellings were uninhabited during the whole time of the experiment. The measurements were performed in the winter of 2012. Simultaneously 3 months measurements were performed with α-track-etch detectors, the results and analysis of these measurements are expected in the near future.

The airthightness of the dwellings was characterized by the V50, v50 and n50 values. V50 is the air leak flow rate at a pressure difference of 50 Pa. This pressure difference is obtained by a Blower Door airtightness system. The air leak flow rate is obtained as an average of the rate in case of underpressure and overpressure. For both situations, 10 different pressure setting were used and at each particular pressure 100 measurement points were taken to obtain an accurate V50 value. The n50 and v50 values which are more common used to characterize the airthightness of a dwelling take into account the protected volume of the building and the outer surface respectively. The regulations of the NBN EN 13829:2001 norm were used to determine these values.

Results

In this study we discuss the investigation of the indoor radon concentrations in a series of side by side located residential units. In this way, the radon differences due to the geological differences were excluded. The dwellings were located in Neeroeteren (Ophovestraat) in Belgium, in this area the soil consists of (wet) sand. [AGIV] Furthermore, previous radon measurements in this area have demonstrated that the average indoor radon concentrations exceed the value of 400 Bq /m^3 in less than 1% of the dwellings. As a matter of fact, the measured radon concentrations in this survey are expected very low.

At the moment of the experiment, the investigated houses were in a different building stage. This implies a different airthightness. As a matter of fact, the correlation between airthightness and the indoor radon concentrations could be very well investigated. During the test period, i.e. Winter 2012, no further construction works were carried out. Even more, during the short time measurements, no one entered the building, the ventilation systems were switched of and windows and doors were kept closed. In this way, the influences of these important parameters were excluded.

The series of dwellings is numbered 1 (North) to 6 (South). The construction of house number one was by far the most advanced. Here, the stucco works were performed as well as the screed -the thin, top layer of material (traditionally sand and cement), poured in situ on top of the structural concrete , on top of which other finishing materials can be applied- works. In the dwellings number 2 and 3 no screed works were performed yet, but the stucco was finished. In dwellings 4, 5 and 6 nor the stucco, nor the screed works were started. These different building stages gives rise to different airthightness values as can be seen in Table 1.

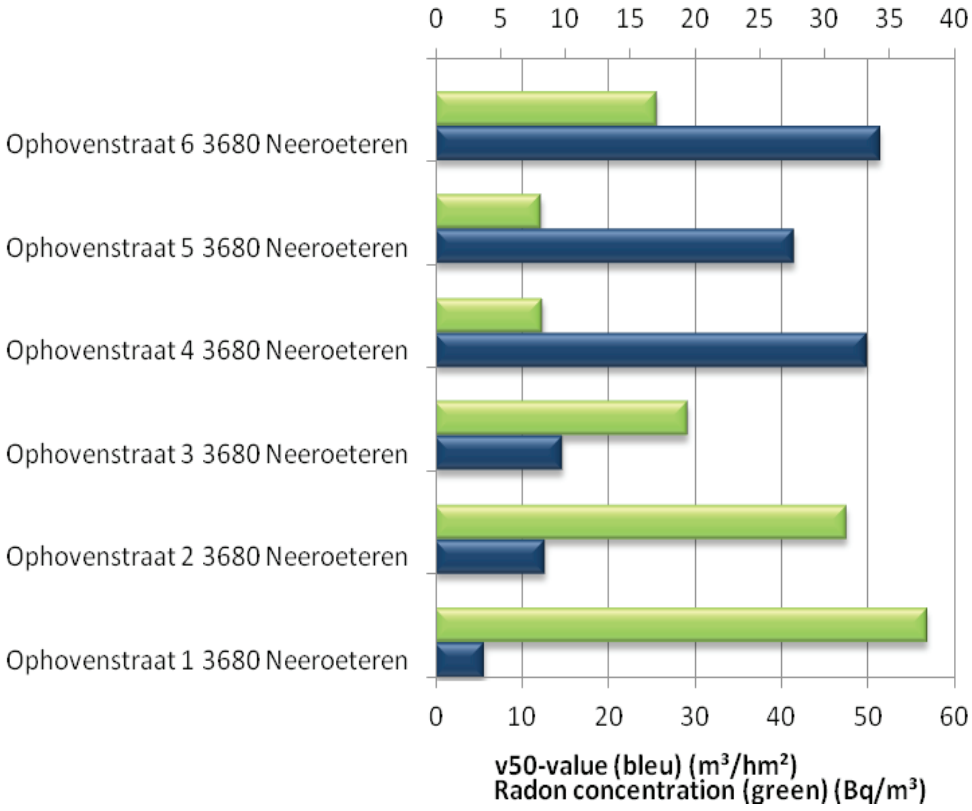
Table 1. The construction stage of the buildings, the N50 (m^3/h) and v50 (m^3/h.m^2) values and the indoor radon concentrations (Bq/m^3).

Dwelling	1	2	3	4	5	6
Performed work	screed + stucco	stucco	stucco			
N50	3.28	8.79	9.40	31.86	27.93	29.68
v50[a]	3.69	8.34	9.68	32.50	26.46	33.89
Radon concentration	57	48	29	13	12	26

[a] *The v50 was obtained regarding the* NBN EN 13829:2001 norm.

The data of the v50 and the radon concentration are also graphical presented in Figure 1. From this Figure it is clear that there is a relationship between the airthightness, quantified by the v50 value, and the radon concentration. Taken into this conclusion it is important to take care of a good indoor ventilation in passive and low energy housing.

Figure 1. The v50 values and the indoor radon concentration in a series of dwellings.



Conclusions

The indoor radon concentration is clearly higher in buildings with a better airthightness. For this reason, it is important to take care of a good and working ventilation system in low-energy and passive dwellings. In this way the radon risk can be limited.

Future perspectives

Regarding the more accurate results that can be obtained by a 3 month measurement, these measurements have also been carried out. However, the data are not analyzed at this moment. Furthermore, since all the building materials used are well-known, the activity concentration index of these materials will be determined in the near future which can provide possible other relationships.

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Naturally occurring radioactivity in residues of drinking water treatment

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Abstract

In 2004 - 2008 about 500 samples of sludge of drinking water treatment plants in Bavaria were analyzed. About 5 % showed specific activities for radionuclides, such as Ra-226 and Ra-228, above 1 Bq/g. To find out how much of these radionuclides accumulate on the filter gravel in the filter tanks throughout the years this study was extended in 2011 to analyze filter gravel. The criteria for the first set of samples (all together 26 samples) was that the respective sludge had specific activities above 10 Bq/g (either for one radionuclide or the sum of the highest activities of the U-238 and the Th-232 decay chains). The rest of the samples (11) were picked out randomly from all over Bavaria.
The specific activities of the approximately 40 analyzed samples range from below detection limit to approximately 13 Bq/g for diverse radionuclides such as Ac-228, Ra-228, Pb-214, Ra-224, and Pb-212. The maximal concentration of Ra-226 was 42 Bq/g. In 84 % of all the analyzed samples the activities of the radionuclides are below 10 Bq/g. About 50 % show activities below 1 Bq/g. The accumulation factors between sludge and filter gravel, which were determined, range from 0.1 to 5.3.
Gravel showing increased activity usually originates from treatment plants for deferrisation as well as for demanganisation.
Dose estimations for workers doing daily duties at the sites as well as for the determined disposal routes of filter gravel will be presented. Further more the data is brought in context with the geologic background. Most of the samples which show increased specific activities originate from two hydro geological regions of Bavaria: the Franconian Keuper and the Swabian-Franconian Jura.

1. Introduction

703 of the approximately 2,500 water suppliers (WS) in Bavaria have to purify the drinking water. The different types of treatment include deferrisation, demanganisation, deacidification, dearsenisation and removal of aluminum or uranium. This is done by various methods such as filtration through gravel or activated carbon, ion exchange, ultra filtration or reverse osmosis. Ra-226, which is enriched in the sludge as well as in the filter gravel, is usually the dominant radionuclide. The possible correlations with geological region, type of treatment and the water chemistry of the raw water were investigated.
In addition to the continuously accruing sludge, used filter gravel occurs as a discontinuous residue. These filters have operating times of several years to decades. Radionuclides, which have accumulated on the filter gravel, originate from the groundwater, used for making drinking water. The groundwater dissolved the radionuclides from the parent rock material. In the precipitation of elements the physico-chemical conditions, such as oxygen content (oxidizing / reducing conditions) or the pH value, often play an important role. Many elements, including radionuclides, are precipitated with other substances. There is no radioactive equilibrium within the natural decay chains in water. This is caused by the different mobility of the individual radionuclides in the open system of air, water and soil.
The analyzed residues are from filters for deferrisation, demanganisation and in some cases also for deacidification. Increased radionuclide concentrations were measured mainly in sludge of the first two kinds. Especially Ra-226 and Ra-228 precipitate with ferric oxides. Radium is a decay product of uranium and thorium and occurs primarily in basement rocks as well as in granite. Traces of Ra-226, however, are

present in every rock type.
The so-called hydro-geological regions of Bavaria are primarily defined by the top aquifer. Often it is not the top aquifer that is used but subjacent aquifers. These may also belong to another geological region, which continues below the unit at the surface. Within the geological unit of the Jura, for example, the ferruginous sandstones of the Dogger and Lias are located underneath the limestone of the Malm. In all regions it is not unusual that more than one aquifer contributes to a single well [1].

2. Regulation for NORM in Bavaria - the German Radiation Protection Ordinance

Part 3, §§ 97-102 of the German Radiation Protection Ordinance (StrlSchV) [2] regulates the protection of the public from NORM in Germany. Annex XII, part A StrlSchV contains a list of residues for which the natural radioactivity has to be taken into account ("residues requiring monitoring") and monitoring limits have been laid down (StrlSchV appendix III part B and C). Residues from drinking water treatment are currently not in the above-mentioned list and are therefore not per se subject to the provisions of the StrlSchV. However, the handling or the disposal of these materials can lead to significant increased exposure for workers or the public. If this exposure is not to be disregarded from a radiation protection point of view, the competent authority takes appropriate action according to § 102 StrlSchV.

In Bavaria, the competent authority for the enforcement of the StrlSchV is the Bavarian Environment Agency (LfU). The LfU considers a radiation exposure of more than 1 millisievert per year (1 mSv/a) as “significantly increased” following § 97 StrlSchV. Otherwise residues from drinking water treatment are no radioactive substances within the meaning of § 2 subparagraph 1 of the Atomic Energy Law. In this case NORM material has to be disposed of in accordance to the Recycling and Waste Management Act [3].

Exposure estimations for workers handling NORM waste (including the staff during loading of the waste, the truck driver and the excavator driver at the landfill) are reasonable once the activity concentration of the disposed NORM waste exceeds 1 Bq/g. Which way of recycling or disposal of the material applies is determined analogous to residues requiring monitoring.
It must be proved that the dose for the public in the surrounding field of the landfill shall not be increased substantially, by the deposition of the NORM waste. For this purpose, similar to [4] exposure estimations are made for different exposure pathways (food, ground water, breast milk) and for different age groups to determine if § 102 StrlSchV applies. To keep the time and effort as low as possible, secondary values and criteria for specific activities in the waste have been defined in [5]. Complying with these values and criteria results in a dose less than 1 mSv/a in case the landfill meets certain criteria (for example a landfill for municipal waste).

The current draft of the European Basic Safety Standards Directive (EU BSS [6]) of the European Commission contains a list of NORM industries (annex V), for which regulations apply. This list includes residues from groundwater treatment. It will very likely result in an extension of the list of residues requiring monitoring (StrlSchV, annex XII, part A).

2. Activity concentrations in residues of drinking water treatment in Bavaria

Based on the existing data on residues from drinking water treatment (approximately 500 samples) [1], [7], a survey was done on filter gravel in 2011. A total of 38 samples of filter gravel from 29 drinking water treatment plants were analyzed by gamma spectrometry. A summary of the results is shown in Table 1. Since the wet samples had to be dried before being analyzed, the activity concentrations correspond to the dry mass of the filter material.

Table 1: Activity concentrations in sludge ([1], [7]) and filter gravel of drinking water treatment

Radionuclide	Specific activity concentration [Bq/g]					
	Sludge (N=483)			Filter gravel (N = 38)		
	Median	Minimum	Maximum	Median	Minimum	Maximum
U-238	0.041	0.0008	5.4	0.1	0.0022	2
Th-234	0.044	0.0014	4.4	0.03	0.0025	1.1
Pa-234m	0.19	0.014	5.6	0.1	0.007	1.1
Ra-226	0.49	0.0055	58	1.4	0.004	42
Pb-214	0.08	0.0016	24	0.28	0.001	9.6
Bi-214	0.069	0.0015	21	0.25	0.001	8.8
Pb-210	0.22	0.0026	18	0.08	0.0047	2
Ra-228 / Ac-228	0.29	0.0009	23	1	0.00038	13
Th-228	0.16	0.0006	16	0.82	0.001	11
Ra-224	0.22	0.0049	16	0.82	0.001	11
Pb-212	0.13	0.0006	14	0.82	0.00043	11
Bi-212	0.17	0.0004	13	0.82	0.0008	9.9
U-235	0.0019	0.00004	0.25	0.01	0.0001	0.08

The filter gravel was used for deferrisation, demanganisation, deacidification (or a combination of them) of drinking water. For the process of deferrisation and demanganisation, which frequently occur combined, first of all the raw water is oxidized in the so-called offset oxidizer. During this process, the divalent, soluble Fe^{3+} and Mn^{4+} ions (both poorly soluble) are oxidized and precipitated. Sessile microorganisms, which adhere to the filter gravel, are used as catalysts, especially for demanganisation. Co-precipitates of radionuclides occur. In the next step the water runs through the filter tanks filled with gravel. There the suspended iron- and manganese-(hydr-)oxides adhere to the gravel. These filter tanks are back-washed at regular intervals to prevent constipation. Ferric oxides are washed off from the filter gravel during the backwashing process and accumulate predominantly in the sludge. The precipitated manganese oxide (pyrolusite) is adhered to the filter gravel together with the microorganisms mentioned above. Ra-226 and Ra-228 do not wash off completely. Adsorption on pyrolusite occurs. Depending on the lifetime of the filter gravel higher activities may accumulate on the filter gravel than in the predominantly ferrous sludge.

The maximum activity concentration measured in sludge was 58 Bq/g (Ra-226). However, only in 5 % of the total amount of sludge in Bavaria the sum of the maximum activity concentrations of both natural decay series (U-238 and Th-232) in sludge exceeds an activity concentration of 0.2 Bq/g. The median lies at 0.006 Bq/g ([1], [7]). This value is representative for the whole of Bavaria due to the high number of samples and the geographic distribution of the sampled water treatment plants. Remarkable is furthermore that the maximum values often are more than twice as high as the maximum values in the filter gravel. In sludge from deacidification plants, which are found mainly in the Northeast Bavarian Crystalline Basement, the dominant radionuclide is often Pb-210 with specific activities of up to 18 Bq/g. The elevated activity concentrations of Pb-210 in sludge collected in this region are due to increased values of radon [1]. Filter gravel from this region has not yet been taken into account.

The highest activity concentration measured in filter gravel was 42 Bq/g (Ra-226). The median of the observed activity concentrations of Ra-226 is 1.4 Bq/g. Among the radionuclides of the Th-232 decay series, increased activities (higher than 1 Bq/g) were detected for Ra-224, Pb-212 and Bi-212 for almost 30 % of the analyzed filter gravel. Due to the pre-selection of filter gravel samples from drinking water treatment plants that already have significantly increased activity concentrations in the sludge the values are not representative for the whole of Bavaria.

Most of the activity concentrations higher than 1 Bq/g occur in drinking water treatment plants located in the Franconian Keuper sandstone and Swabian and Franconian Jura. The highest activity concentrations were found in the geologic unit of the Keuper sandstones (a region around Nuremberg), which show elevated levels of uranium and radium.

2. Accumulation of activity concentrations in sludge and filter gravel

The question was if or rather how much the increased activity concentrations in the used sludge lead to increased activity concentrations in the filter gravel. The accumulation factors (AF) of radionuclides from the sludge (RS) to the respective filter gravel (FK) is determined by the measured activity concentrations (C) using the following equation:

$$AF_i = \frac{C(FK)_i}{C(RS)_i} \qquad \text{(Gl. 1)}$$

- AF > 1: The activity concentration in the filter gravel is higher than the one in the accompanying sludge.
- AF = 1: The activity concentration in the filter gravel equals the one in the sludge.
- AF < 1: The activity concentration in the filter gravel is lower than the one in the sludge.

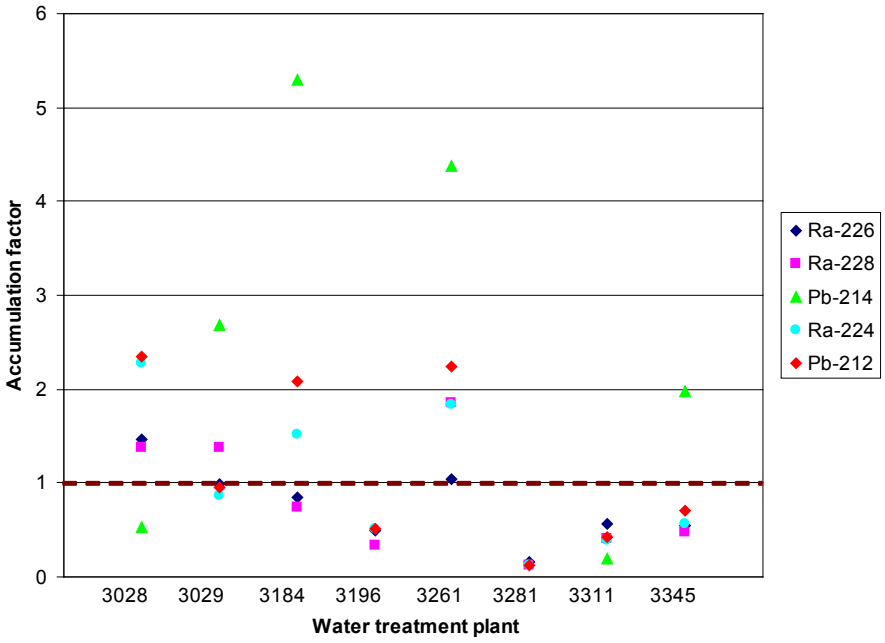

Fig. 1: Accumulation factors of filter gravel and sludge of a selection of WS (N = 8)

The ratio of the activity concentrations of the sludge and the filter gravel primarily depends on the lifetime of the filter gravel and the type of water treatment. For deferrisation only less Ra-226 and Ra-228 absorbs to the filter gravel than for demanganisation or a combination of both. The accumulation factors were determined for eight water treatment plants (Fig. 1). For those plants data of the activity concentrations of raw water, purified water, sludge and filter gravel exist. The type of water treatment carried out in all those treatment plants is a combination of deferrisation and demanganisation.

In [8] the results of a similar investigation are presented. There the activity concentrations of Ra-226 and Ra-228 of the filter material were 4 - 6 times higher than the ones measured in the according sludge.

However, our results show accumulation factors mainly between 0,12 and 3 (Fig. 1). For all radionuclides shown both accumulation factors above and below 1 occur. In six out of eight cases the activity concentration of Ra-226 and Ra-228 is higher in the sludge than in the filter gravel.

In the future the question will be addressed to what extent the accumulation of radionuclides on filter gravel is influenced by the following parameters:

- the method of collection of the raw water
- the quality of the raw water
- the performed treatment (deferrisation, demanganisation, deacidification)
- the lifetime of the filter gravel
- the kind of unused filter gravel
- other factors that might influence the accumulation of radionuclides

4. Dose Assessment

For the evaluation of the radiological relevance of the filter gravel dose assessment for the staff of the investigated WS was carried out. The estimated dose results from stays next to the filters and handling of filter gravel.Since the filter gravel usually is in a wet condition during handling, a dose caused by inhalation or ingestion can be neglected. The relevant exposure pathway is the external radiation.

The ambient dose rate was measured at different workplaces in eight water treatment plants where filter gravel had shown increased activity concentrations. The annual dose was estimated for workers based on the reported period of stay and the measured dose rate in a distance of 50 cm from the filter tanks. The results are shown in Table 2. The existing background radiation is already subtracted from the measured values of the dose rate. In only two cases the doses exceeded 0.1 mSv/a. These cases are presented as examples:

The first case is about weekly stays in close proximity to the filter tanks, which are required in the course of the back-washing of the filters. To be conservative 3 hours per week for activating the back-washing process were estimated. The relevant dose rate reaches 1.16 mSv/h. This results in an effective supplemental dose of 0.17 mSv/a caused by the filter gravel.

The second case is about the regular cleaning inside of a special kind of filter tanks, which are usually covered by a slip-on aluminum cover that can be opened. The exposure rate was measured directly on the surface of the filter gravel. The observed additional dose rate reached 3.16 mSv/h, and in a distance of 50 cm it still was 2.06 mSv/h. Due to the limited period of stay inside the filter tanks (a total of 144 h/a for cleaning purposes: 6 h/filter, 6 filters, the cleaning is done once a quarter), the exposure adds up to 0.3 mSv/a, which is still lower than 1 mSv/a.

Both examples clearly show that the radionuclides accumulated on the filter gravel can increase the dose rate around the material significantly. This should certainly be considered when removing or disposing the material.

Table 2: Dose assessment for various drinking water treatment plants

	Dose rate, 50 cm distance [mSv/h]	Exp. time [h/a]	Absorbed dose rate [mSv/a]
Stay directly at the filter during back-washing	1.16	150	0.17
Stay directly at the filter during the weekly back-wash	0.76	50	0.038
Stay in the immediate vicinity of a filter	1.40	25	0.035
Stay in the immediate vicinity of a filter	1.05	25	0.026
Stay during the back-wash of the filter	0.28	37.5	0.011
Interior cleaning of an open filter	2.06	144	0.30
Stay during mechanical activation of the weekly back-wash of the filter	0.20	50	0.01
Stay in the immediate vicinity of the upper central portion of the filter	0.48	25	0.012

5. Waste management of residues from drinking water treatment

The quantities of accumulated sludge per WS are usually low. The median value of all WS investigated is 1.6 m^3/a. The main amount of the sludge is disposed of in municipal wastewater treatment plants (25.6 %), by disposal companies (20.3 %) or at landfills class DK I or DK II (23.3 %). Dose estimations for different exposure scenarios during the disposal (including the staff of WS, the truck driver and the landfill worker) have shown that in any case a dose of 1 mSv/a is not exceeded. The use of sludge in agriculture is not recommended. Otherwise a gamma spectrometric analysis of the material as well as possibly a dose calculation will be required [1].
Our results claim that further consideration of the disposal routes of filter gravel from drinking water treatment is justified. The interval of the disposal of the filter material in Bavaria averages out 27 years. Only in a fraction of WS the filter gravel has been replaced at least once since the construction of the plant. The disposal of small quantities on a regular basis is only practiced by few WS. The average amount of filter gravel in a filter tank is 40 tons, which will be disposed together once the filter has to be renewed.

Our aim is that all WS, which use filter gravel showing increased activity concentrations, will contact the LfU once a disposal is planned. Together a reasonable way of disposal from a radiological point of view can be found without disregarding economical aspects. Due to the very different lifetimes of the filter systems, which can achieve multiple decades, a reliable estimation of the annual amount of the filter material for disposal is not possible.

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Occurrence of ^{238}U, ^{234}U, ^{230}Th and ^{232}Th in sediments and biota from the Ebro River Reservoir in Flix (southern of Catalonia)

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INTRODUCTION

Industrial waste containing radioactive isotopes was released into the Ebro River basin due to the activity of a dicalcium phosphate (DCP) plant located in Flix (Southern Catalonia), for a period of more than two decades [1,2]. In a previous study of our group, high values for gross alpha and gross beta activities were obtained in different sediment samples collected in that industrial area [3]. Taking into account these results, it was considered important to perform a more detailed radiological characterization of the area of influence of that industrial plant, by measuring the activities of different isotopes of uranium, thorium and radium in these sediments and in biota samples from the same area of influence. Previously to that measurement, the samples had to be digested. For that purpose, two different digestion processes were compared, one based on the use of a conventional mineralization process with aqua regia and the second based on microwave digestion. After that step, the isotopes were precipitated and then, radiochemical separation was carried out using the specific resins (Uteva®). Alpha spectrometry was used for the measurement of the activities of both isotopes. The method used in this study was validated using samples from intercomparison exercises.
The main aim of the present study was to evaluate the activities of a group of natural radioisotopes such as ^{238}U, ^{234}U, ^{230}Th and ^{232}Th in different sediment and biota samples located in the influenced area of the DCP factory.

EXPERIMENTAL PART

Sampling and Methods

The studied area, centered in the Ebro River, is comprised between Riba-Roja reservoir and Ebro Delta estuarine located in the southern part of Catalonia, with a length of approximately 109 Km. In particular, to perform this study, we focused in a non influenced area (Riba-Roja), the area influenced by the DCP factory in Flix, and downstream in the Delta estuarine (Figure 1).

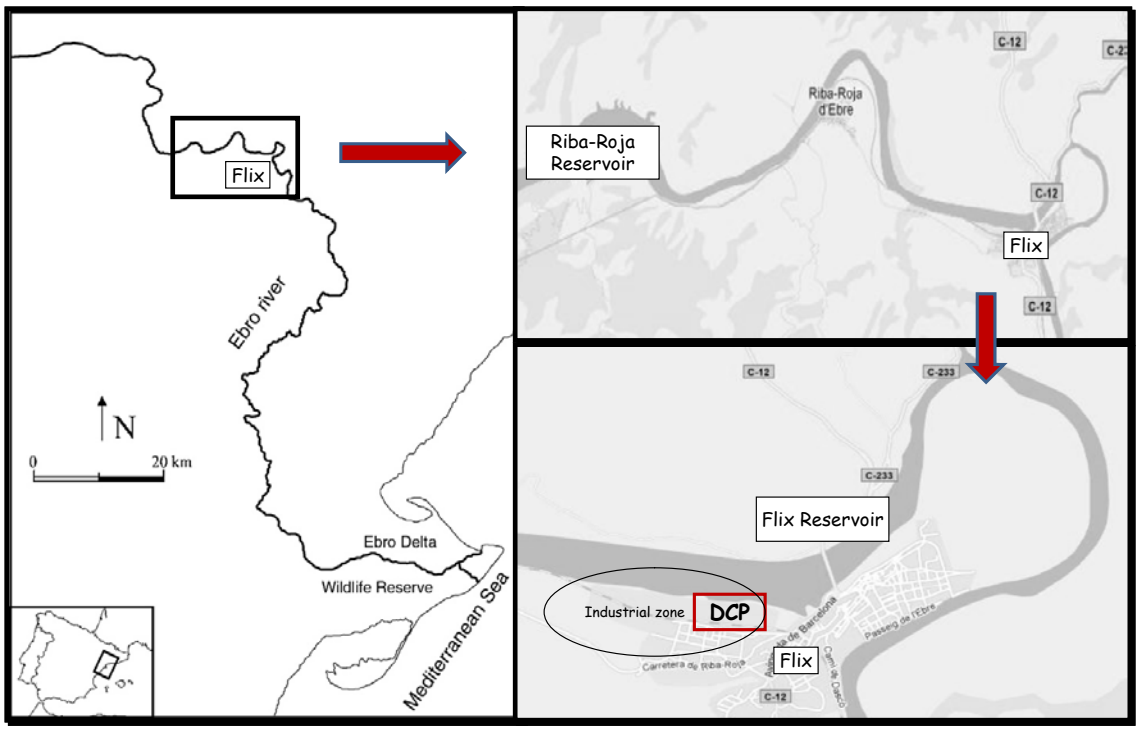

Figura 1. The studied area

In order to choose the best digestion method (microwave digestion or aqua regia digestion) for sediments and biota samples, a phosphogypsum sediment sample from an intercomparison exercise was analyzed. After the digestion of the sample, the selective extraction of uranium and thorium was carried out using a specific resin, the Uteva® resin. The eluate from the separation was electrodeposited onto a stainless steel planchet and finally, the measurements were performed using alpha spectrometry.
Once the method was developed and validated, different biota and sediments samples were analyzed. The sediment ssamples were collected in different points located in the influenced zone of the DCP factory in Flix. Moreover, one sampling point was located before the DCP factory as this was considered a blank sample. On the other hand, three kinds of biota samples were collected: algae, blue and zebra mussels and catfish. The biota samples were collected in three different points. The first point was in Riba-Roja (before the DCP factory), the second point was located next to the DCP factory and the last one was located in the Delta estuarine (after the DCP factory).

RESULTS AND DISCUSSION

The digestion method was evaluated using the phopshogypsum sample from an intercomparison exercise. In Table 1, the results obtained for the different methods used are shown. In this table, different digestion methods and different agents to precipitate the uranium and thorium for the extraction method are compared. Also, the recoveries of the process for ^{234}U and ^{230}Th tracers, the obtained activities in Bq/Kg, the intercomparison sample reference activity, the Z-score values and the precision and trueness (in %) are reported.

Table 1. Summary of the results obtained for the different digestion methods tested

Sample Amount	Dig. Method	Precip. agent	Recovery (%)	Activity (Bq/Kg)	Ref. Activity	Z score	Precision (%)	Trueness (%)
				^{234}U				
2.5	Aqua regia	$Fe(OH)_3$	75	55 ± 12		0.1	28	2
2.5	Aqua regia	$Ca_3(PO_4)_2$	95	54 ± 14	56 ± 10	0.2	31	5
0.5	MW	$Ca_3(PO_4)_2$	98	59 ± 13		0.3	28	11
				^{230}Th				
2.5	Aqua regia	$Fe(OH)_3$	27	357 ± 81		0.4	30	12
2.5	Aqua regia	$Ca_3(PO_4)_2$	61	311 ± 71	332 ± 66	0.3	30	11
0.5	MW	$Ca_3(PO_4)_2$	82	354 ± 82		0.3	31	10

As we can see in the Table 1, the best recoveries were obtained with the method which involves the precipitation of uranium and thorium using $Ca_3(PO_4)_2$. Even that in all the tested conditions, UTEVA columns were used, in the first aqua regia procedure, the recovery was lower for uranium and thorium and in this case, the losses could be attributed to iron co-precipitation. For uranium, it was not observed a significant difference between the results obtained for the different digestion methods used. However, for thorium, the highest recoveries were obtained when microwave digestion was used. For this reason the microwave digestion was selected to digest all the sediments and biota samples.

The sediments samples were collected in different sampling points and samples at different depths were taken. In Table 2 the results obtained for one of the sampling points located in front of the DCP factory at different depths are summarized. It is important to highlight that the higher activity values for ^{230}Th, ^{234}U and ^{238}U in all sampling points were obtained at the superficial levels. In contrast, for deeper samples the quantified activity values were found to be very similar to the natural radionuclide content in soil.

In Table 2, the activities of uranium and thorium isotopes in the algae, mussels and catfish samples in the sampling point in front of the DCP factory are summarized. For the algae samples no differences were observed in the activity concentration values for thorium between the samples collected in the influenced and the non-influenced area of the phosphate industry, while for uranium, an increase in the activity was observed in the sampling point in front of the DCP factory.

In the case of zhe zebra mussel, the behavior was different. For the samples collected close to Flix we obtained the highest concentration of thorium in comparison with the rest of the biota samples collected. However, for uranium this situation was not observed, and the species that showed the maximum concentration of uranium correspond to the green algae.

Catfish samples were also analysed. In particular, samples for this specie were taken in three different zones (before, in front of and after the DCP factory). The results showed that the catfish collected in front of the DCP factory presents two or three times higher activities of uranium an thorium isotopes than the collected before the DCP factory. In the sample collected after the DCP factory the results presents a slightly decrease in the activities concentration of uranium and thorium isotopes in comparison to the sample collected in front of the DCP factory.

Table 2 Activity concentrations in Bq/Kg in sediments and biota sample in front of the DCP factory

Sample	Depth	^{234}U	^{238}U	^{230}Th	^{232}Th
Sediments	1	2599 ± 1021	2476 ± 983	3520 ± 1168	48 ± 25
	2	2713 ± 1218	2636 ± 1091	3624 ± 1112	39 ± 20
	3	1040 ± 331	956 ± 306	1668 ± 469	37 ± 17
	4	234 ± 93	207 ± 83	339 ± 125	30 ± 15
	5	33 ± 17	30 ± 15	34 ± 16	29 ± 14
	6	41 ± 21	35 ± 18	38 ± 18	25 ± 13
Green algae	-	113 ± 2	102 ± 6	15 ± 2	4.5 ± 0.5
Zebra Mussel	-	80 ± 1	71 ± 5	41 ± 2	13 ± 1
Catfish	-	6.3 ± 0.4	5.3 ± 0.4	7 ± 1	0.5 ± 0.01

CONCLUSIONS

In this research, the occurrence of uranium and thorium isotopes has been studied in an area influenced by a DCP factory. The presence of isotopes of both elements in sediments at different depths have been demonstrated, the maximum concentration was found in the sample point collected in front of the DCP factory in the first three meters of depth. In the biota samples, in all species we observed a slightly increased in the sampling point in front of the DCP factory. In all samples the activity concentration of uranium was higher than the activity concentration of thorium. Among all the biota samples analyzed, the highest activity for ^{234}U, ^{238}U, ^{230}Th was observed in algae samples. For ^{232}Th the maximum concentration was found in the zebra mussel. The results obtained in this study demonstrate the influence in the environment of the industrial activity developed in this area.

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^{210}Po and ^{210}Pb in NORM mineral processing industries

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Introduction

There are a variety of industries, which use NORM minerals, where thermal processes are applied. Among them, melting processes to produce or refine metals, roasting or calcining processes to extract minerals or produce stabilized products or ceramics and, simply, combustion processes of minerals in the form of fossil fuels such as coal for power generation, are the most common. In all these thermal processes, the heating of the feedstock provokes the volatilization of radionuclides with low boiling point, particularly ^{210}Pb and ^{210}Po, increasing the exposure of plant workers due to the possible inhalation of furnaces fumes enriched in these nuclides. These volatile radionuclides, a) can additionally be partially released to the nearby environment through the atmosphere, generating an environmental and public impact that, in each specific case, needs to be evaluated, or b) can be also condensed in scrubbers and filters generating an inhalation risk for the workers in charge of maintenance operations in these areas.

The occupational and public radiological impact associated to the volatilization of ^{210}Pb and ^{210}Po in industries applying thermal processes to minerals will be very much dependent on the content in these radionuclides of the raw material treated, the characteristics of the process applied, and the countermeasures taken to avoid its dispersion to the nearby environment. In this contribution, a review of the most important NORM thermal processes will be exposed, taking into account the occupational and public radiological impacts, associated to the volatilization of ^{210}Pb and ^{210}Po.

NORM Industries Processing Minerals

Background

All minerals and raw materials contain radionuclides of natural terrestrial origin. The activity concentrations of these natural radionuclides in normal rocks and soils are variable but generally low. However some minerals, that are exploited commercially, contain uranium and thorium series radionuclides at a significantly elevated activity concentration. These radionuclides, during its industrial physical or chemical processing may become unevenly distributed between the various materials arising from the industrial process. Even, in some cases, although the treated mineral presents low uranium and/or thorium concentrations, the special feature of their industrial processing can lead to the special accumulation of some radionuclides in a particular generated material or in a specific place of the industrial process. The industries where these minerals are treated are called NORM (naturally occurring radionuclide material) industries and need special radiological consideration because they may lead to a significantly increase in exposure to natural sources

From the radiological point of view, a considerable body of knowledge and experience has been gained during the last twenty years concerning NORM industrial operations. Even, nowadays, there is a quite established list of industrial sectors involving in the processing of minerals where occupational and environmental radiological evaluations are imperative, and when necessary, radiological regulatory control are established (IAEA, 2007).

The processes applied to the minerals in the NORM industries for obtaining the commercial products are quite variable, depending very much of the characteristics of the raw material and of the final product to be obtained. But, the great majority of NORM industrial activities are based in one of the two following general processes:

a) Chemical treatment of the mineral or raw material with strong acids (wet chemical processes), and b) Thermal processes.

This distinction is extremely important concerning the behavior and radiological impact of the ^{210}Pb and ^{210}Po (radionuclides belonging to the uranium series) associated initially to the raw material, because both radionuclides are well known for its low boiling point (elevated volatility at high temperature). In NORM industrial activities involving thermal processes the occupational and public exposures due to ^{210}Pb and ^{210}Po needs to be assessed, being even necessary in some cases the establishment of regulatory controls. On the other hand the role on ^{210}Pb and ^{210}Po, from the radiological point of view, is more limited in NOM industries where their activities are based in wet chemical processes, as it will be shown in the following sections

Industrial NORM activities based in the application of wet chemical processes

In a set of well-defined NORM industries, the applied processes are mostly based in the dissolution of the raw materials with strong acids, and the posterior chemical or physical isolation of the elements or compounds of interest without the use of high temperatures. In these cases, the behavior of the ^{210}Pb and ^{210}Po nuclides, originally present in the raw material, is dominated by the chemical reactions induced in the process, being accumulated both nuclides in one or various of the products generated. In the commented chemical processes, the volatilization of ^{210}Pb and ^{210}Po is quite reduced, being quite limited their possible occupational and/or public radiological impact due to inhalation.

One typical NORM activity that can be included in the group under consideration in this section is the devoted to the production of phosphoric acid by treating the raw material (phosphate rock) by the wet method with sulphuric acid. In this case, the reaction that summarizes the production process is the following:

Phosphate rock + Sulfuric acid ---------- Phosphoric acid + Phosphogypsum

In the process, and together with the commercial product (phosphoric acid) it is formed a co-product called phosphogypsum (calcium sulphate dyhidrate) that although it has some value in agriculture or in the cement industry, generally is disposed forming big stacks in nearby areas of the phosphoric acid factories. This phosphogypsum accumulates most of the ^{210}Po and ^{210}Pb originally present in the raw material (Bolivar et al., 1996), as it can be deduced from the data shown in Table 1. In this table, the activity concentrations for both nuclides in the raw material and products generated in a phosphoric acid factory located at the South-west of Spain are shown. Taking into account that for each kg of phosphate rock treated, 1,5 kg of phosphogypsum is generated, it is easy to deduce that around 90% of the ^{210}Pb and ^{210}Po originally present in the raw material finish in the mentioned co-product. In the chemical process, sulphates of lead and polonium are formed, which are quite insoluble compounds.

Table 1.- Activity concentrations (Bq/kg) of ^{210}Pb and ^{210}Po in raw materials and products generated in a phosphoric acid plant

Sample	^{210}Pb (Bq/kg)	^{210}Po (Bq/kg)
Phosphate Rock 1	1540 ± 70	1640 ± 50
Phosphate Rock 2	1660 ± 70	1710 ± 60
Phosphoric Acid 1	100 ± 7	26 ± 1
Phosphoric Acid 2	55 ± 4	12 ± 1
Phosphogypsum 1	760 ± 40	760 ± 35
Phosphogypsum 2	740 ± 50	950 ± 50

The disposal of the majority of the ^{210}Pb and ^{210}Po with the phosphogypsum in the big stacks, their low solubility preventing its migration to neighboring aquifers and the low resuspension of the phosphogypsum, made their radiological impact quite limited.

Other typical NORM activity that can be included in the group analyzed in this section is the dedicated to the manufacture of dioxide titanium pigments via the sulphate process. In these industries a titanium rich mineral like the illmenite (with activity concentrations of 100-1500 Bq/kg of ^{238}U series radionuclides) is treated with strong sulphuric acid for the dissolution of the mineral. The titanium, dissolved in this first step together with other metals (mostly Fe) and compounds, is then isolated by hydrolysis and precipitation, and the pigment formed. The ^{210}Pb and ^{210}Po, originally present in the raw material in secular equilibrium with their progenitor (^{238}U), is in a big proportion accumulated in the unattacked residue generated in the first step of digestion of the raw material. As in the previous analyzed case, the treatment of the raw material with sulphuric acid conduits to the generation of lead and polonium sulphates that due to their low solubility finish associated to the unatacked residue,

This residue can contain activity concentrations of ^{210}Pb and ^{210}Po six to eight times higher than in the treated raw material, and is separated from the process immediately after the finalization of the digestion process. This residue, in wet form is generally disposed in authorized areas, with a quite low radiological impact due to their ^{210}Pb and ^{210}Po content. More details about the ^{210}Pb and ^{210}Po behavior in this type of industry can be found in García-Tenorio and Bolivar, 2011.

We will finish this section talking about the paradigmatic case of the gas industry, because can be considered the only NORM industry where being thermal processes not applied, the role of ^{210}Pb and ^{210}Po in increasing the exposure of workers cannot be considered minor (strictly, and attending to the title of the wok presented the inclusion of this industrial activity in this paper can be questioned because not mineral processing is performed).

During the extraction of natural gas, lead deposits sometimes are formed. These deposits may form a serious threat to operations because they tend to block production equipments or injection pumps and tubing (Godoy et al., 2005). In some cases, ^{210}Pb is present in these compounds at levels greater than regulatory concern, which necessitates additional safety measures during operations and maintenance.

In addition, the water which is present in the gas formations can contain radium isotopes dissolved from the reservoir rock, together with the decay progeny (^{222}Rn and daughters). For that reason, the gas after isolation from these waters can contain ^{222}Rn (noble gas) that in the storage tanks and conductions can decay through very short half-lives nuclides to ^{210}Pb. This ^{210}Pb tends to be deposited, and consequently can be found in high concentrations as thin layers in the internal surfaces of tanks and deposits where the extracted gas is stored. These thin layers can have a non-negligible occupational radiological importance

during maintenance operations, because being ^{210}Pb a beta emitter is only a concern when these internal surfaces become exposed (Bland and Chiu, 1996).

Industrial NORM activities based in thermal processes

The role of the ^{210}Pb and ^{210}Po, from the radiological point of view, needs to be considered carefully in most of the NORM industrial activities based in the application of thermal processes. In the thermal processes, the heating of the raw material provokes the volatilization of radionuclides with low boiling point as ^{210}Pb and ^{210}Po, increasing the exposure of plant workers due to the possible inhalation of furnaces fumes enriched in these nuclides, and even of the public if these radionuclides are partially released to the atmosphere

The number of NORM industrial activities based in the application of thermal processes is far from being limited. It includes for example all the industrial activities associated to the extraction of different metals (iron, tin, cupper, etc) from raw materials which are based in the application of melting processes. In these cases the ^{238}U series radionuclide content in the feedstock are quite variable, and consequently will be quite variable the ^{210}Pb and ^{210}Po content in the fly ash (sintering dust) and furnace coal ash (blast furnace dust) produced by as a result of the smelting process, where both radionuclides are accumulated.

However, as it is stated in IAEA, 2007, particularly the following NORM industrial activities, based in the application of thermal processes, need to be assessed from the radiological point of view associated to the behavior of ^{210}Pb and ^{210}Po, and even can require regulation based in worker dose.

a) Iron and steel production

Elected in this paper as representative of the industries devoted to extraction and isolation of metals, we can start indicating that the production of primary iron from iron ores consists of two main steps: the first one where sinters and/or pellets are generated from iron ore, and the second one where the primary iron is produced in blast furnaces from the previously generated sinters and pellets. In both steps, processes at elevated temperatures are applied provoking the volatilization of ^{210}Po and ^{210}Pb.

The iron sinters are produced from mixtures of ore, cokes and recycled dust, with the activity concentrations for most of the radionuclides from the decay chains of ^{238}U and ^{232}Th in the feed mix in the order of 15Bq/kg (^{210}Po and ^{210}Pb concentrations can be somewhat higher because of the recycling of enriched dust). The sinters are fired with gas and temperature reaches 1400ºC, provoking the volatilization of ^{210}Po and ^{210}Pb and their posterior condensation on dust particles also carried out by the off gas. Dust from sintering is enriched in ^{210}Po relative to ^{210}Pb (boiling points of 960ºC and 1740 ºC, respectively) and strongly depleted in all other natural radionuclides present in the raw material. The off-gas is “cleaned” with electrostatic precipitators or high-pressure water scrubbers, although the small particles particularly enriched in ^{210}Po, and in a less extent in ^{210}Pb, can escape, being emitted to the surrounding environment. The magnitude of the dust emissions to the atmosphere will depend on the efficiency of the off-gas cleaning systems.

The iron pellets are generated by applying a process similar to the described in the previous paragraphs, with the application of elevated temperatures, In both cases atmospheric emissions enriched in ^{210}Po and ^{210}Pb are produced, originating a public radiological impact which magnitude should be evaluated. In addition, significant amounts of dust particles are present and recycled along the sintering and/or pelletizing processes enriched particularly in ^{210}Po, increasing the exposure of plant workers due to the possible inhalation of furnaces fumes enriched in these nuclides. Inhalation is clearly the most important route for occupational exposure increments in the iron sintering and pelletizing plants.

Primary iron is produced from sinters and/or pellets and cokes in blast furnaces, being generated in addition blast furnace gas carrying dust. Because of the high temperature, ^{210}Pb and ^{210}Po, still present in the feed materials are volatilized and condensed preferentially in the dust particles carried by the gas. ^{210}Pb concentrations in this dust are higher than those of ^{210}Po because the latter radionuclide had, on a large extent, being removed in the sintering or pellet process due to its significantly lower boiling point.

Together with the primary iron, it is formed in the process a solid residue (slag) which can contains 100 to 150 Bq/kg of the radionuclides of the ^{238}U and ^{232}Th, with the exception of ^{210}Po and ^{210}Pb strongly depleted, and that, consequently does not generate any special concern in relation with potential increments in the worker exposures inside the iron plant, More concern is the possible exposure increments due to inhalation of dust enriched in ^{210}Pb and ^{210}Po, specially during maintenance operations. The finer fraction of the dust collected in filters from scrubbing the blast furnace gas can contain up to 15-25 Bq/g of ^{210}Pb and a few Bq/g of ^{210}Po, and special countermeasures should be taken in order to avoid the possible inhalation of the fine material by the workers.

b) Niobium Processing

The niobium is an element used on a large scale in all kinds of electronic equipment, in nuclear reactors and in the aerospatiale industry, which is extracted from ores that contains enhanced levels of the decay chains of ^{238}U and ^{232}Th. The niobium ore is processed by melting, dissolution with strong acids, reduction to metallic niobium at 800ºC and isolation for the removal of impurities. Due to the thermic process applied, this industrial activity may involve discharges into the air of ^{210}Pb and ^{210}Po, volatile elements, and accumulation of both radionuclides in the dust collected in precipitators and filters used for cleaning off the gases released to the atmosphere.

The precipitator dust in the process of niobium extraction can contain from 100 to 500 Bq/g of ^{210}Pb and ^{210}Po (IAEA, 2007). Consequently, occupational exposure to dust in the production process may be a need to be controlled.

c) Production of elemental phosphorous

A typical elemental phosphorous production process starts with a granulation step where a binder (clay) is added as a slurry on a rotating dish, together with ground phosphate rock (the phosphate rock can contain around 1-2 Bq/g of ^{238}U and daughters in secular equilibrium if it has a sedimentary origin). Afterwards, the pellets which are obtained in this way are dried and sintered at 800 °C. The rock pellets are then mixed with coke (reducing agent) and fed into a furnace. The furnace is heated to 1500 °C by passing a large current through carbon electrodes in the furnace.

At the commented elevated temperature, phosphate is reduced to P. This leaves the furnace as a gas, together with the by-product CO and some dust. This dust is removed in an electrostatic precipitator and recycled into the process. The P is then condensed. The resulting CO gas stream is used as fuel for the sintering plant and other on-site processes.

During the sintering process, ^{210}Po, volatilizes and escapes from the feedstock material. It passes through the scrubbers that wash the sinter gases and is emitted into the atmosphere. Most of the ^{210}Pb, which is less volatile than ^{210}Po, remains in the sintered feedstock.

In the furnace, the radionuclides above ^{222}Rn in the ^{238}U decay chain remain in the melt and become part of the slag. Of the radionuclides escaping from the melt, the relatively long-lived ^{210}Pb (half-life 22 years) builds up in the precipitator dust during the recycling process to an activity concentration of about 1000

Bq/g, representing a thousand-fold enrichment of this radionuclide (Erkens, 1999), while due to the loss of ^{210}Po during the sintering of the pellets, the activity concentration of ^{210}Po in the precipitator dust is initially only about 60 Bq/g, considerably lower than the activity concentration of ^{210}Pb. The progeny of ^{210}Pb (^{210}Bi and ^{210}Po) have half-lives of 5 and 138 days, respectively, and after about 4 half-life periods these progeny are present again in the precipitator dust at nearly the same activity concentration as that of the parent nuclide ^{210}Pb.

The annual discharge of ^{210}Po is in fact even higher than the annual input with the ore because of the recycling of electrostatic precipitator dust that is highly enriched in ^{210}Pb. As a consequence, this recycling ^{210}Pb has a relatively long residence time in the production facilities and gives rise to "additional" ^{210}Po which is then discharged largely in the sintering process. This ^{210}Po is additional in the sense that is more that would be expected from a simple calculation of the ^{210}Po content of the phosphate used to produce the batch of phosphorous (European Commission, 2003)

The main source of exposure of phosphorus plant workers is the precipitator dust recycled in the process, due to its high ^{210}Pb and ^{210}Po activity concentrations. Doses reaching 1 mSv/y can be received by the workers associated to the inhalation of precipitator dust (IAEA, 2007).

Finally, to put in context the magnitude of the Po-210 and Pb-210 atmospheric emissions of these elemental phosphorous production plants, we can indicate that the emission from an elemental phosphorus plant is responsible for the highest emission to air of Po-210 and Pb-210 in the Netherlands (Tanzi, 2008). The plant operates under a permit, with the statutory assumption of an operational life of 25 years for the calculation of the dose. The collective dose due to the emissions from the plant is estimated combining the effective dose with the spatial distribution of the population in the Netherlands. For emission of ^{210}Po it is estimated in the order of 23 manSv. For Belgium the estimate is 7 manSv.

d) Manufacture of zirconia

The mineral zircon is heavy mineral sand with a wide range of industrial applications that contains elevated activity concentrations of the ^{238}U and ^{232}Th series. It is particularly the material used as feedstock for the manufacture of zirconia (zirconium dioxide), compound with commercial applications as refractories, ceramic pigments and abrasives.

The zirconia generally is manufactured through the fusion of zircon mineral. Zircon sand (mixed with coke) is melted in an electric arc furnace at a temperature near 3000°C. At the mentioned temperature the zircon dissociates into ZrO_2 and SiO_2 and the coke react with the SiO_2 to produce SiO and CO_2. On contact with air, the SiO forms SiO_2 fume which is removed from the furnace by a fume collection system, passed through scrubbers and collected as a very fine dust. The ZrO_2 (zirconia) remaining in the furnace is afterwards conditions for commercial use.

The fusion process liberates all the radionuclides originally present in the zircon, which ends either in the zirconia product or in the silica dust. Concerning ^{210}Po and ^{210}Pb, low concentrations have been measured in zirconia products as expected because both radionuclides volatilizes in the furnace being incorporated to the silica fume and attached to the formed silica dust particles in the gas collection systems. This dust can contain up to 600 Bq/g of ^{210}Pb and ^{210}Po, conducting to a potential worker dose of 0.25 to 3.0 mSv/y via inhalation. The exposure of workers to silica fume needs then to be controlled.

e) Combustion of coal

Although the great majority of the coal used to produce heat and electricity contains moderate amounts of U and Th, their combustion results in the generation of fly ash that accumulates the ^{210}Pb and ^{210}Po due to their volatility.

The concentrations of radionuclides in the ashes generated in coal combustion processes tend to be significantly higher than in the coal, being reported in the case of ^{210}Pb, concentrations as higher as 100 Bq/g. A good management policy should be applied for the disposal or reuse (for example in the cement industry) of the fly ash in order to minimize the occupational doses received by the workers.

A small amount of the ash can be discharged via the stack along with volatilized radionuclides such as ^{210}Po and ^{210}Pb. However, fly-ash emissions from the stack of coal-fired stations depend on the efficiency of the flue gas cleaning by electrostatic precipitators and scrubbers and so the amount of fly ash emitted to the atmosphere will vary between plants. As is quoted in UNSCEAR (2000) the annual emissions in GBq by a "typical" 600 MW coal fired power station was 0.4 for ^{210}Pb and 0.8 for ^{210}Pb, although for modern plants the aerial discharge of NORM nuclides is clearly lower because they have efficient filter systems to prevent the aerial discharge of fly ash.

In addition, enhanced amounts of ^{210}Pb/^{210}Po can be found in the internal walls of the furnaces and pipes involved in the combustion processes, where they are attached, associated to particulates transported by the flue gases generated in the combustion, in the form of deposits or scales (Hipkin et al, 1998; Robles et al., 2008). Special consideration to these deposits should be taken, particularly during maintenance operations along the production process, in order to minimize the exposures received by the workers involved in these operations.

f) Cement production

The production of cement involves the heating, calcining and sintering of blended and ground raw materials, typically limestone and clay or shale and other materials to form clinker. This clinker burning takes place at 1450°C in kilns. The formed clinker is then ground and mixed with small amounts of gypsum to give Portland cement, although, in addition, blended cements are produced from cement clinker with fly-ash. Large cements plants can produce of the order of 4000t of cement per day.

Because of the very high temperature of the raw materials in the kilns, volatilization of ^{210}Po and ^{210}Pb is the main potential source of aerial discharges. Data included in UNSCEAR 2000 indicates that the estimated Annual aerial discharges for a 'typical' cement plant with a 2000 kt/y output of different types of cement are the following: 0.2 GBq/y for ^{210}Pb and 78 GBq/y for ^{210}Po. These estimations are based on the assumption that 50% of the polonium escapes from the thermal process.

The production of bricks and roofing tiles deserve similar comments and conclusions as the obtained ones by the cement industry The firing temperature of the ovens used to treat the clay for production of bricks and tiles produces the volatilization between 40 and 100% of the ^{210}Po, which is released to the atmosphere in a proportion which depends on the extent of the off-gas cooling and cleaning installed mainly to abate dust and HF emissions.

An upper estimate of the aerial discharge of ^{210}Po from a brick factory can be based on the following assumption: typical production 30 kt/y, average concentrations in clay 35 Bq/kg, volatilization 100%, trapping in off-gas 0%. The maximum annual emission for such a plant is 1 GBq of ^{210}Po.

Conclusions

In this paper it has been highlighted the important role of ^{210}Pb and ^{210}Po in increasing the exposure of workers in NORM industries where thermal processes are applied. In other type of NORM industrial activities the mentioned role is clearly minor with the possible exception of the gas industry.

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