



## **Health and safety issues in REE mining and processing**

### **An internal EURARE guidance report**

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# Table of contents

<b>1</b>	<b>INTRODUCTION.....</b>	<b>2</b>
<b>2</b>	<b>EXPERIENCE AND BENCHMARKS .....</b>	<b>6</b>
2.1	INTRODUCTION .....	6
2.2	ENVIRONMENTAL AND HEALTH ISSUES IN REE MINING AND PROCESSING IN DIFFERENT COUNTRIES .....	6
2.2.1	<i>Brazil</i> .....	6
2.2.2	<i>China</i> .....	7
2.2.3	<i>India</i> .....	9
2.2.4	<i>Malaysia</i> .....	9
2.2.5	<i>United States</i> .....	9
2.3	POTENTIAL HEALTH RISKS OF REES .....	11
2.3.1	<i>REEs</i> .....	11
2.3.2	<i>Environmental Risk Assessment</i> .....	11
2.3.3	<i>Environmental exposure</i> .....	13
2.3.4	<i>Toxicity and carcinogenicity of REEs</i> .....	14
2.3.5	<i>Ecotoxicological and environmental effects of REEs</i> .....	17
2.3.6	<i>Some epidemiological findings of REEs</i> .....	19
2.3.7	<i>Occupational health issues with REE</i> .....	20
2.3.8	<i>Actinides</i> .....	21
2.3.9	<i>Safety precautions</i> .....	22
<b>3</b>	<b>RADIATION PROTECTION – REGULATIONS AND RECOMMENDATIONS .....</b>	<b>23</b>
3.1	INTRODUCTION .....	23
3.2	BASIC RADIATION PROTECTION CONSIDERATIONS .....	23
3.2.1	<i>Radiation protection standards</i> .....	23
3.2.2	<i>The concepts of exclusion, exemption and clearance</i> .....	24
3.2.3	<i>General exemption and clearance values in the Basic Safety Standards (BSS, 2013)</i> .....	24
3.2.4	<i>Activity concentrations in the EURARE ores</i> .....	26
3.2.5	<i>Regulatory control of workplaces</i> .....	27
3.2.6	<i>Record keeping</i> .....	27
3.3	RADIOACTIVE WASTE MANAGEMENT .....	28
3.3.1	<i>International radioactive waste classification scheme</i> .....	28
3.3.2	<i>Disposal of low activity NORM waste</i> .....	30
<b>4</b>	<b>RADIATION PROTECTION ADVICE .....</b>	<b>32</b>
4.1	GENERAL .....	32
4.2	HOW TO CALCULATE EXPOSURE .....	32
<b>5</b>	<b>REFERENCES.....</b>	<b>34</b>
	<b>APPENDIX 1. THE DECAY CHAINS OF <sup>238</sup>U, <sup>232</sup>Th AND <sup>235</sup>U .....</b>	<b>39</b>

# 1 Introduction

The EURARE project aims at developing a sustainable exploitation scheme for Europe’s Rare Earth Element (REE) ore deposits. This involves developing methods in all parts of the production chain, i.e. exploration, mining, ore beneficiation, extraction of REEs from ore concentrates, isolation of the individual REEs and the production of REE metals and alloys.

The current report is intended for internal guidance within the EURARE project on health and safety issues in the mining and processing of REE ores. According to the description of work, the report should act both as a project baseline and as a guide to ensure the health and safety of all people involved in the current project. Due to the radionuclide content of some of the EURARE ores, consisting of natural uranium and/or thorium and their decay chains, the report addresses radiation protection issues. The report structure is as follows:

- Experience of health and safety issues in REE mining and processing in other parts of the world.
- Radiation protection standards and recommendations of relevance to the handling of REE ore, concentrates and waste streams
- Advice on radiation protection issues to the organisations involved in the EURARE project

In a later phase of the project, EU legislation and legislation from countries outside Europe will be analysed. A preliminary analysis of the relevance of European legal acts to EURARE is summarised in Table 1-1.

*Table 1-1 European legislation, directives and guidance documents and an assessment of their relevance to EURARE. The general name used for each piece of legislation is given in brackets.*

<b>Legislation</b>	<b>Title</b>	<b>Relevance</b>
<b>Related to radioactivity</b>		
EC directive 2013/59/EURATOM <b>(BSS, 2013)</b>	laying down basic safety standards for protection against the dangers arising from exposure to ionizing radiation	All materials used and created in the different stages of processing that have sufficient radioactivity to be considered radioactive.  Updates BSS 1996 (96/29/Euratom)
EC directive 2013/51/EURATOM	laying down requirements for the protection of the health of the general public with regard to radioactive substances in water intended for human consumption	Provides reference concentrations for radionuclides in drinking water based on a 0.1 mSv a <sup>-1</sup> critical group dose limit. If more than one radionuclide is present, the sum of the concentration of each radionuclide divided by the relevant reference concentration should be less than or equal to 1.
Commission regulation (Euratom) No 3227/76 and amendments 220/90 and 2130/93	Concerning the application of the provisions on Euratom safeguards	Control of nuclear materials (i.e. U, Th and Pu) to safeguard their use in civil applications

<b>Legislation</b>	<b>Title</b>	<b>Relevance</b>
<b>Related to chemicals and hazardous components</b>		
EC directive 2012/18/EU <b>(Seveso III)</b>	amending and repealing Council Directive 96/82/EC on the control of major-accident hazards involving dangerous substances (Seveso)	“disused mines.... as well as operational tailings disposal facilities, including tailing ponds or dams, containing dangerous substances shall be included within the scope of this Directive”
EC regulation 1907/2006 of the European Parliament and Council <b>(REACH)</b>	concerning the registration, evaluation, authorisation and restriction of chemicals	All chemicals but not the ore or ore concentrates
<b>EC Regulation</b> No 1272/2008 of the European Parliament and of the Council <b>(Classification, Labelling and Packaging Regulation)</b>	on classification, labeling and packaging of substances and mixtures, amending and repealing Directives 67/548/EEC and 1999/45/EC, and amending Regulation (EC) No 1907/2006 (REACH)	Includes mineral ores and ore concentrates as well as the products
<b>Related to waste management and emissions</b>		
EC Directive 2006/21/EC of the European Parliament and Council <b>(Mining Waste Directive)</b>	on the management of waste from extractive industries and amending Directive 2004/35/EC (Environmental Liability Directive)	waste resulting from the prospecting, extraction, treatment and storage of mineral resources and the working of quarries
EC decision 2009/360/EC	completing the technical requirements for waste characterisation laid down by Directive 2006/21/EC (Mining waste directive)	waste characterisation
Directive 2010/75/EU <b>(Industrial Emissions Directive)</b>	on industrial emissions (integrated pollution prevention and control) (Recast)	“Processing of non-ferrous metals (2.5). Production of non-ferrous crude metals from ore, concentrates or secondary raw materials by metallurgical, chemical or electrolytic processes“  Radioactive substances are covered by the BSS and so are exempt
Directive 2008/98/EC <b>(Waste Framework Directive)</b>	on waste and repealing certain Directives	Wastes not covered by the Mining Waste Directive. Waste waters are also out of scope, as they are covered by the Industrial Emissions Directive.
Directive 1999/31/EC <b>(Landfill Directive)</b>	on the landfill of waste	
<b>Environmental and health protection regulations</b>		
Directive 2000/60/EC <b>(Water Framework Directive)</b>	establishing a framework for Community action in the field of water policy	Important for the aqueous emissions and tailings management; addresses impacts off-site

<b>Legislation</b>	<b>Title</b>	<b>Relevance</b>
Directive 2006/118/EC <b>(Groundwater Directive)</b>	on the protection of groundwater against pollution and deterioration	Important for aqueous emissions and tailings management
Directive 92/43/EEC <b>(Habitats Directive)</b> and Directive 2009/147/EC <b>(Birds Directive)</b>	on the conservation of natural habitats and of wild fauna and flora, and on the conservation of wild birds	Identify Natura 2000 sites (i.e. protected sites); "Mining projects in and around Natura 2000 sites are not automatically ruled out, but they must be appropriately assessed if likely to have a significant effect on a protected site. If such effects are expected, mining projects must either be avoided or amended"
<b>Emissions Trading Directive</b>	amending Directive 2003/87/EC so as to improve and extend the greenhouse gas emission allowance trading scheme of the Community	
Directive 2011/92/EU <b>(Environmental Impact Assessment Directive)</b>	on the assessment of the effects of certain public and private projects on the environment (codification)	"-pit mines and quarries with a surface area exceeding 25 hectares"
Directive of the European Parliament and of the Council 2004/35/EC <b>(Environmental Liability Directive)</b>	on environmental liability with regard to the prevention and remedying of environmental damage	Polluter pays principle, prevention and remediation of environmental damage
Council Directive 98/83/EC <b>(Quality of Drinking Water Directive)</b>	on the quality of water intended for human consumption	Indicator parameters are listed for selected substances
<b>Work place regulations</b>		
Council Directive 89/391/EEC <b>(Health and Safety at Work Directive)</b> and later amendments	on the introduction of measures to encourage improvements in the safety and health of workers at work	
Council directive 92/104/EEC	on the minimum requirements for improving the safety and health protection of workers in surface and underground mineral-extracting industries	Specifically for mining
Council Directive 92/91/EEC	concerning the minimum requirements for improving the safety and health protection of workers in the mineral- extracting industries through drilling	Specifically for drilling in the extracting industries
Directive 2002/49/EC <b>(Environmental Noise Directive)</b>	relating to the assessment and management of environmental noise	

<b>Legislation</b>	<b>Title</b>	<b>Relevance</b>
Directive 2006/42/EC <b>(Machinery Directive)</b>	on machinery	

## 2 Experience and benchmarks

### 2.1 Introduction

The rare earth elements (REE) are a group of metals comprised of yttrium (Y), the fourteen lanthanide elements, i.e. lanthanum (La), cerium (Ce), praseodymium (Pr), neodymium (Nd), promethium (Pm), samarium (Sm), europium (Eu), gadolinium (Gd), terbium (Tb), dysprosium (Dy), holmium (Ho), erbium (Er), thulium (Tm), ytterbium (Yb), and lutetium (Lu), and sometimes scandium (Sc). Rare earths are used in a wide range of technologies and are currently listed as critical raw materials (European Commission, 2014). However, as described on a country-by-country basis below, REE mining and production have led to some significant environmental and health impacts.

### 2.2 Environmental and health issues in REE mining and processing in different countries

#### 2.2.1 Brazil

Chemical processing of monazite sand for production of rare earth elements was performed in USAM Santo Amaro mill (USAM) which operated since the 1950's. The mill was located in a densely populated residential district of São Paulo City. The growth of urban areas around the site led to the decision to decommission the facility.

Monazite processing has generated a great amount of radioactive residues, being stored in buried concrete tanks and drums, in temporary storage buildings and in sealed trenches. In the past, there were no regulation concerning radiation protection and radioactive residue storage. Radioactive residues were used as landfills and the residues of chemical processes contaminated floors and buildings. The decommissioning process has generated tons of waste that has been added to previously produced wastes (da Costa Lauria and Rochedo 2005).

Monazite processing produced two radioactive residues: cake II and mesothorium cake. Thorium concentrate cake (cake II) was a by-product with an average content of 20 % thorium hydroxide and 1 % uranium hydroxides, and a specific activity around 1800 Bq g<sup>-1</sup>. Mesothorium cake (Ba(Ra)SO<sub>4</sub>) was a waste with a specific activity around 4400 Bq g<sup>-1</sup> (Briquet et al. 2004). Cake II residue was stored in drums and bins at three sites: São Paulo city (590 t) and Botuxin city (3 500 t) in São Paulo State, and Caldas city (11 630 t) in Minas Gerais State (L.F. da Silva, pers. comm. 2013).

In Botuxin city, the 3500 t of cake II was stored in seven rectangular pools, 3.5 m deep with concrete walls 15 cm thick, from 1975 to 1981. Each pool was 1 m above the soil surface and 2.5 m underground. At that time the Brazilian Nuclear Energy Commission (CNEN) did not have regulations for this kind of activity. Neither the radiological environmental impact nor geological studies were considered in the choice of the storage place (Briquet et al. 2004). The pools were built in a farm region encircling a basin, streams of other declivities, wells and springs that supply the local inhabitants, in the São Paulo State. A river flows across the property into the public water supply of a city, 12 km from the site. Activity concentrations of <sup>228</sup>Ra up to 70 000 Bq kg<sup>-1</sup> were identified in the soil, contaminated by radionuclides of the <sup>232</sup>Th series. Site remediation issues include soil and groundwater contamination, the lack of a suitable disposal site for the material, and the need for specific regulations and guidance (Briquet et al. 2004).

The monitoring programme performed by The Institute for Radiation Protection and Dosimetry (IRD/CNEN) showed values up to 4.0 Bq L<sup>-1</sup> for <sup>226</sup>Ra, with average values of 0.1

Bq L<sup>-1</sup> in a site well. The same programme has pointed out some soil contaminated areas with activity concentrations of up to 70 000 Bq kg<sup>-1</sup> for <sup>228</sup>Ra, 890 Bq kg<sup>-1</sup> for <sup>226</sup>Ra and 13 000 Bq kg<sup>-1</sup> for <sup>238</sup>U (Briquet et al. 2004).

### 2.2.2 China

China's high REE production, combined with limited environmental regulations, has resulted in significant environmental damage to the areas surrounding mining and processing operations. Operations range from large government-owned activities and processing facilities to small illegal endeavors. Often, smaller operations have little or no environmental controls, and larger operations have only recently begun adopting such measures (U.S. Environmental Protection Agency 2012).

China produced over 130 000 tons of rare earth elements in 2008 alone. Extrapolation of the waste generation estimates over total production yields large amounts of waste. With little environmental regulation, stories of environmental pollution and human sickness remain frequent in areas near Chinese rare earth element production facilities (Paul and Campbell 2011).

After 40 years of operation, the Bayan Obo mine has an 11 km<sup>2</sup> tailings impoundment that has radioactively contaminated the soil, groundwater and vegetation of the surrounding area. According to the Chinese Society of Rare Earths, every ton of rare earth produced generates approximately 8.5 kg of fluorine and 13 kg of dust. The use of concentrated sulfuric acid during high-temperature calcinations produces 9 600 to 12 000 m<sup>3</sup> of waste gas containing dust concentrate, hydrofluoric acid, and sulfur dioxide, and approximately 75 m<sup>3</sup> of acidic wastewater, as well as 1 ton of radioactive waste residue. Additionally, the REE separation and refining process known as saponification had been used extensively in China until recently, generating harmful wastewater (U.S. Environmental Protection Agency 2012).

In Bayan Obo, a large amount of waste rock, comprising topsoil, host rock and low grade mineralized rock, is generated during mining and is deposited in piles at the mine site. Sprinklers are deployed to control the generation of dust. A small portion of the low grade mineralized rock is used for road construction and for the embankment of new tailings pond and plans are in place for more to be used in the future. The topsoil and host rock may be returned to the excavation as backfill when the mining operation is complete. Tailings from the beneficiation process are pumped to a tailings pond for storage. In order to reduce airborne dust, water spraying is applied to wet the surface of the tailings, the tailings pond is covered with waste water from ore processing and trees are planted in the surrounding area (IAEA 2011).

The production of iron and steel generates blast furnace slag and ferrous slag in Bayan Obo. The slag is conveyed to a slag dump for storage and about half of it is used to recover iron and to make building materials. Liquid effluents are pumped to the tailings pond. The production of construction materials from blast furnace slag involves mixing it with low activity material such as flyash in a ratio such that the activity concentration is sufficiently reduced to meet the radiological requirements for construction materials. A formula from a manufacturer for making bricks is: 60-70 % steel slag, 10-15 % blast furnace slag, about 10 % flyash and 12-17 % cement (IAEA 2011).

The incremental annual effective dose for individuals living in houses constructed from bricks containing slag residues from gamma radiation attributable to the use of such bricks was found to be about 0.2 mSv. Indoor thoron (Rn-220) progeny concentrations were reported to

be three times normal levels, with an incremental annual effective dose of 0.02 mSv (IAEA 2011).

The Bayan Obo mine employs nearly 7000 workers, of which about 3000 are exposed to thorium containing airborne dust. Elevated thoron concentrations in air are also found. Exposure to gamma radiation is significant only in the mining areas. The general level of external gamma exposure is moderate in all working areas of the mine (IAEA 2011).

The dustiest working area is the crushing area in Bayan Obo. The higher airborne dust concentrations measured in the crushing area are clearly reflected in higher thorium lung burdens. General workers in areas of elevated gamma dose rates are estimated to receive a dose of 0.24 mSv a<sup>-1</sup>, assuming an annual exposure period of about 2000 h. Workers involved in mining, including trucking of the ore, are estimated to receive a dose of about 1 mSv a<sup>-1</sup> or more, while for workers at disposal sites the estimated dose is 0.7 mSv a<sup>-1</sup> (IAEA 2011).

In Bayan Obo, the mean committed effective doses received by workers from the inhalation of thorium containing dust for the dustiest area (the crushing area) is 0.58 mSv a<sup>-1</sup> and from the dose distribution it can be seen that very few workers are likely to receive a dose of more than 1 mSv, irrespective of the type of dusty area in which they work. The committed effective doses received by workers from the inhalation of thoron and radon progeny can be estimated by applying the dose coefficients to the potential alpha energy exposures. For the area with the highest thoron and radon progeny concentrations (the crushing area), the mean committed effective dose, assuming an annual exposure period of 2000 h, is 1.68 mSv a<sup>-1</sup> for thoron progeny and about 0.56 mSv a<sup>-1</sup> for radon progeny (IAEA 2011).

During the period 1983-1991, average airborne dust concentrations in the workplaces were reduced by a factor of 20 (from 1144 to 48 mg m<sup>-3</sup>) as a result of improvements to the ventilation and dust control equipment in Bayan Obo. Other measures to reduce dose included instruction in the use of personal protective equipment and the introduction of job rotation for workers. As a result of these dose reduction measures, the average thorium lung burdens of dust exposed workers decreased by a factor of three (IAEA 2011).

Soil in areas downwind of the mine, including the Bayan Obo city area, was found to be contaminated with dust that had blown in from the mining facility. The activity concentration of <sup>232</sup>Th in the upper 10 cm layer of soil was 0.08–0.12 Bq g<sup>-1</sup>. The additional dose received by the public as a result of these elevated levels was reported to be 0.044 mSv a<sup>-1</sup>. Thoron progeny concentrations in the city were also elevated (IAEA 2011).

The ore and several of the mineral concentrates obtained from it have <sup>232</sup>Th activity concentrations greater than 1 Bq g<sup>-1</sup>. Consequently, the mining and beneficiation operations at Bayan Obo would need to be considered for regulatory control as a practice. Annual effective doses received by workers from gamma radiation and dust inhalation are each generally less than 1 mSv. However, the dose from inhalation of thoron and radon progeny combined could be as high as about 2 mSv. Annual effective doses received by the public are expected to be a very small fraction of 1 mSv (IAEA 2011).

In view of the possibility of some workers receiving doses moderately above 1 mSv per year, the appropriate regulatory option might be to require authorization in the form of registration in order to ensure the ongoing monitoring of exposure and that basic measures are taken to keep doses as low as reasonably achievable (IAEA 2011).

### 2.2.3 India

In India, rare-earth compounds are produced from the beach sand mineral monazite. Caustic digestion of the mineral followed by selective acid extraction is the method used to separate composite rare-earth fraction. The composite rare-earth chloride contains low levels of natural radionuclides and is the starting material for individual rare-earth compounds which have wide applications (Haridasan et al. 2008).

RE compounds manufactured from monazite generally contain low levels of natural radionuclides. The different types of RE compounds analysed show gross alpha and beta activities ranging from <math><0.5</math> to 18.1 and <math><0.5</math> to 22.4 Bq g<sup>-1</sup>, respectively. The <sup>228</sup>Ra activity in all the samples was below the exempt activity concentration of 10 Bq g<sup>-1</sup> stipulated by IAEA for regulatory purpose. Large-scale handling and processing of these chemicals result in occupational radiation exposures. The external gamma exposure, inhalation of thoron progeny and long-lived alpha activity are identified as the major routes of exposure. The average annual occupational dose is estimated to be 1.9 mSv in the plant where the studies are carried out (Haridasan et al. 2008).

### 2.2.4 Malaysia

Malaysia's last rare earth refinery in northern Perak state was closed in 1992 following protests and claims that it was the source of radionuclides that were identified as the cause of birth defects and leukaemia among nearby residents. The refinery is one of Asia's largest radioactive waste cleanup sites (U.S. Environmental Protection Agency 2012).

Lynas Corporation Ltd owns Mount Weld deposit and concentration plant in Western Australia and rare earths processing plant (LAMP) near Kuantan in Pahang, Malaysia. Open pit mining is used at Mount Weld and the ore is then crushed, ground, stockpiled and concentrated by flotation in the concentration plant to produce a rare earths concentrate for export to LAMP. Construction of the LAMP in Malaysia was completed in 2012 and first rare earths concentrate arrived from Western Australia in November 2012. Lynas commenced commercial production and shipments of rare earths products from the LAMP in June 2013.

### 2.2.5 United States

#### *Mountain Pass*

The Mountain Pass deposit in California was discovered by a uranium prospector in 1949 and the Molybdenum Corporation of America bought the mining claims. The Mountain Pass mine and refinery began operation in 1952. Production expanded greatly in the 1960s, to supply demand for europium used in color television screens. The deposit was mined in a larger scale between 1965 and 1995. During this time the mine supplied most of the world wide rare earth metals consumption.

The Molybdenum Corporation of America changed its name to Molycorp in 1974. The corporation was acquired by Union Oil in 1977, which in turn became part of Chevron Corporation in 2005. The mine closed in 2002, in response to both environmental restrictions and lower prices for REEs. The mine remained inactive post 2002, though processing of previously mined ore continued at the site.

In 2008, Chevron sold the mine to privately held Molycorp Minerals LLC, a company formed to revive Mountain Pass. In December 2010, Molycorp announced that it secured all the environmental permits. Active mining at Mountain Pass recommenced in December of 2010, for the first time since 2002.

In the past, few environmental controls existed. The site contains an open-pit mine, overburden stockpiles, a crusher and mill/flotation plant, a separation plant, a mineral recovery plant tailings storage area, on-site evaporation ponds, and off-site evaporation ponds, as well as laboratory facilities to support research and development activities, offices, warehouses and support buildings (Paul and Campbell 2011).

Groundwater and soil contamination is known to exist around the facility in Mountain Pass. Contaminants include barium, gross alpha, gross beta, nitrate, sodium lignin sulfonate, strontium, total dissolved solids, total lanthanides, total petroleum hydrocarbons (kerosene/diesel), total radium, total thorium, and total uranium. Claims have been brought under environmental laws, regulations, and permits for toxic torts, natural resource damages and other liabilities, as well as for the investigation and remediation of soil, surface water, groundwater and other environmental media (Paul and Campbell 2011).

The primary source of environmental contamination at the Molycorp Mountain Pass site was process wastewaters and tailings impoundments. Prior to 1980, the facility utilized onsite percolation-type surface impoundments to dispose of wastewater, while conventional dam impoundments were utilized to dispose of tailings. These past operations have impacted groundwater at the site. The greatest impact has been an increase in total dissolved solids (TDS), primarily as a result of neutralizing HCl in the wastewater with sodium hydroxide (NaOH). Groundwater TDS concentrations impacted by unlined impoundments have been reported by the current operator in the range of 10,000 mg L<sup>-1</sup>. Background concentrations of TDS have been documented by the current operator from 360 to 800 mg L<sup>-1</sup> TDS, with low but detectable concentrations of barium, boron, strontium, and radiological constituents (U.S. Environmental Protection Agency 2012).

Additional constituents such as metals, nutrients, and radiological constituents in the wastewater and tailings have potentially had a negative impact on groundwater quality in Mountain Pass. In 1980 and 1987, two additional off-site evaporation ponds were constructed to dispose of wastewater. During the time of operation of these units, multiple instances of mechanical failure of the pipeline connecting the Mountain Pass site to the evaporation ponds resulted in surface soil contamination. Specifically, two wastewater spills were documented at the site. The first spill, as reported by U.S. Environmental Protection Agency (EPA), occurred in 1989 and involved the surface discharge of 3 375 gallons of tailings and process wastewater from a failed pipeline. The second spill occurred in 1990 and involved the surface discharge of 45 000 gallons of process wastewater from a failed pipeline. Both spills were contained onsite and deemed insignificant due to the low risk to human health and the environment (U.S. Environmental Protection Agency 2012).

Contaminated groundwater is actively being remediated in Mountain Pass. Groundwater interceptor wells and the mine pit have resulted in a cone of depression that is allowing capture and treatment of the contaminated plumes. Additionally, the pipeline involved in the wastewater spills is currently being removed by the former mine owner (U.S. Environmental Protection Agency 2012).

The new facility in Mountain Pass utilizes multiple technologies and management strategies to minimize environmental impacts. The primary improvement involves the management of water and tailings. Dewatered tailings result in a “paste” that is pumped to an onsite location and layered into a stable containment mound. The process will result in the elimination of 120 acres of evaporation ponds. Reverse osmosis (RO) will be used to treat and reuse 90 % of the wastewater, while the RO reject will be further treated to produce value-added products that can be reused in the process or sold. However, as with any reuse technology, the result is

often a concentrated wastewater stream that will require disposal. Pollutants such as heavy metals concentrated in the RO reject are destined for precipitation and removal via nanofiltration. The brine from this process will be dried in on-site evaporation ponds prior to final disposal (U.S. Environmental Protection Agency 2012).

### ***South Maybe Canyon***

REE-containing mineral deposits were mined in South Maybe Canyon Mine Site, in the Blackfoot River Sub Basin, in southeast Idaho. An Administrative Order of Consent for South Maybe Canyon Mine Site was entered into by the U.S. Forest Service and Nu-West Mining, Inc., in 1998. The primary reason for the order was the release of hazardous substances, including selenium, from the site into groundwater and surface waters above Idaho state water quality standards. It should be noted that rare earth metals were not identified as hazardous substances that had been released from the site. The South Maybe Canyon Mine was developed for the production of phosphate, and REEs were recovered as a by-product. This mine has been identified as a possible source of REEs for future development (U.S. Environmental Protection Agency 2012).

### ***Pea Ridge***

In 2010, the EPA imposed administrative penalties against Upland Wings, Inc. for Clean Water Act violations at the former Pea Ridge Mining Operation in Washington County, Missouri. Violations were associated with the discharge of metals and other constituents (oil and grease, copper, chromium, cadmium, iron, lead, and total suspended solids) in concentrations that exceeded permitted levels. Earth-moving equipment was also used to dredge iron ore tailings from settling ponds and to dispose of the materials in a nearby creek without a permit that affected nearby wetlands (U.S. Environmental Protection Agency 2012).

Thorium waste will be produced along with rare earths mined from the proposed operations at Pea Ridge. The owners of the mine have proposed to construct a rare earth refinery and regional thorium stockpile along the Mississippi River near St. Louis. Thorium storage facility might help address environmental liability concerns in the production of rare earths. Thorium would be stockpiled in anticipation of using it for nuclear power production (U.S. Environmental Protection Agency 2012).

## **2.3 Potential health risks of REEs**

### **2.3.1 REEs**

The REEs are traditionally sub classified into "Heavy Rare Earths" (HREEs) and "Light Rare Earths" (LREEs). La, Ce, Pr, Nd, Pm and Sm fall into subclass LREE. Y, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu fall into subclass HREE. Yttrium is also included with the REE group, because it has similar chemical and physical properties than the lanthanides. Scandium is found in most REE deposits and is sometimes classified as a rare earth element. Although yttrium is the lightest REE, it is usually included with the HREE group, because it has similar chemical and physical properties than the HREEs. Usually REEs occur at trace levels in the upper continental crust total content ranging from <1 to 70 ppm (Table 2-1). REEs are used in agriculture as fertilizer to improve crop growth and production and therefore increasing the concentrations of REEs in soil (Yasumi et al. 2012). Toxicological characteristics of Y and Sc appear to be similar to those of REEs (Hirano and Suzuki 1996).

### **2.3.2 Environmental Risk Assessment**

The geological environments of metal mines are usually similar to the geological settings of REE deposits (EPA 2012). Mining processes and beneficiations of REEs are also similar to

the other hard rock mines and therefore the risk characterization of the metal mines is likely relevant to that of mining REEs (EPA 2012). All activities in mining processes could create risk to human health or environment. Environmental Risk Assessment (ERA) examines processes, emissions, the spread of contaminants and exposures to humans and biota. ERA is a systematic procedure for predicting potential risks to human health or the environment. A complete ERA process includes both ecological and human health risk assessments and the preceding assessment of hazards and the related exposure concentrations. The MINERA project (Improving environmental risk assessments for metal mines) was carried out in collaboration between the Geological Survey of Finland (GTK), the National Institute for Health and Welfare (THL) and the University of Eastern Finland (UEF) during 2010–2013. The Minera-project developed the general model for environmental risk assessment for metal mine site. The Minera-model consists of both, ecological and health risk assessments that are preceded by an examination of the mining processes, emissions, the transport of contaminants and the resulting concentrations in the surrounding media (Kauppila et al. 2013, Figure 2-1).

*Table 2-1 REEs, atomic numbers, and abundances in the upper crust (adapted from Castor and Hedrick 2007).*

<b>Element</b>	<b>Symbol</b>	<b>Atomic number</b>	<b>Upper crust abundance ppm*</b>
<b>Yttrium</b>	Y	39	22
<b>Scandium</b>	Sc	21	16-30**
<b>Lanthanum</b>	La	57	30
<b>Cerium</b>	Ce	58	64
<b>Praseodymium</b>	Pr	59	7.1
<b>Neodymium</b>	Nd	60	26
<b>Promethium</b>	Pm	61	na
<b>Samarium</b>	Sm	62	4.5
<b>Europium</b>	Eu	63	0.88
<b>Gadolinium</b>	Gd	64	3.8
<b>Terbium</b>	Tb	65	0.64
<b>Dysprosium</b>	Dy	66	3.5
<b>Holmium</b>	Ho	67	0.80
<b>Erbium</b>	Er	68	2.3
<b>Thulium</b>	Tm	69	0.33
<b>Ytterbium</b>	Yb	70	2.2
<b>Lutetium</b>	Lu	71	0.32

\* Original data Taylor and McClellan 1985, \*\* Kabata-Pendias-Mukherjee 2007.

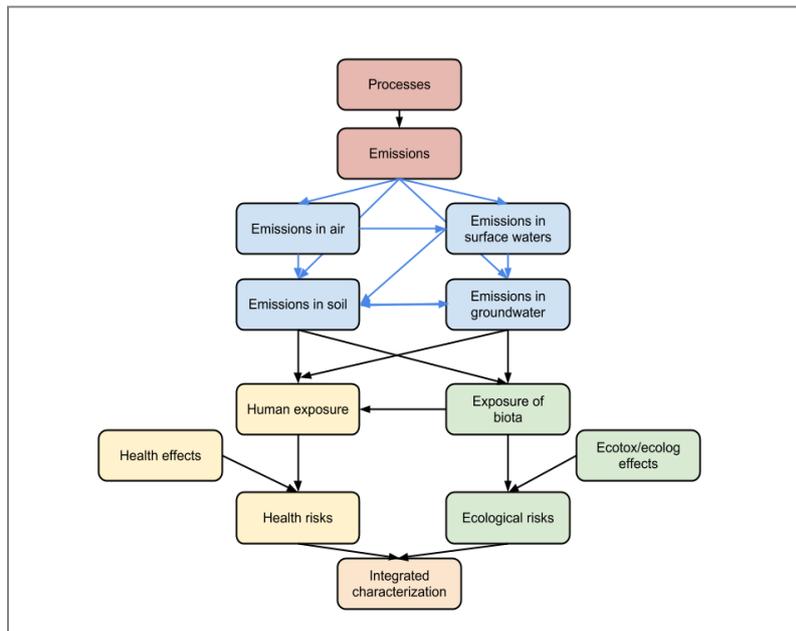


Figure 2-1 General conceptual model for risk assessment by Minera (after Kauppila et al. 2013).

A Conceptual Site Model (CSM) describes the sources of emissions, the mechanisms of the emission releases, the pathways and the potential risks for human health and ecological exposure to emissions in the environment (EPA 2012). Ten receptor types have been identified around the mine site during the life time of the mine: Construction worker, outdoor worker, indoor worker, off-site tribal practitioner, recreational user, agricultural worker, trespasser, off-site resident, on-site resident and ecological receptors (EPA 2012). The potential emission sources and activities in REE mining areas summarized by US EPA are given in Table 2-2.

### 2.3.3 Environmental exposure

Exposure is defined as a contact with a substance by swallowing, breathing, or touching the skin or eyes. Exposure may be short-term (acute exposure), of intermediate duration, or long-term (chronic exposure) (ATSDR 2009). An exposure pathway is the way in which a person may come in contact with a material such as soil, water, or air. A route of exposure describes how the material enters the body (eating, drinking, breathing, or touching). A receptor population is people who potentially or actually are exposed (ATSDR 200, EPA 2013).

Table 2-2 Potential emissions point and pollutants associated with mining, processing, and recycling of REEs ( EPA 2012).

Activity	Emission Source (s)	Primary Pollutants of Concern
Mining (aboveground and underground methods)	Overburden Waste Rock Sub-ore Stockpile ▪ Ore Stockpile	Radiologicals Metals Mine Influenced Waters/Acid Mine Drainage/Alkaline or neutral mine drainage Dust and Associated Pollutants
Processing	▪ Grinding / Crushing	▪ Dust
	▪ Tailings ▪ Tailings Impoundment ▪ Liquid Waste from Processing	▪ Radiologicals ▪ Metals ▪ Turbidity ▪ Organics ▪ Dust and Associated Pollutants
Recycling	▪ Collection	▪ Transportation Pollutants
	▪ Dismantling and Separation ▪ Scrap Waste ▪ Landfill	▪ Dust and Associated Pollutants ▪ VOCs ▪ Metals ▪ Organics
	▪ Processing	▪ Dust and Associated Pollutants ▪ VOCs ▪ Dioxins ▪ Metals ▪ Organics

### 2.3.4 Toxicity and carcinogenicity of REEs

Toxicological data for REEs are summarised below. There are relatively few data available.

#### Scandium

Elemental scandium is considered non-toxic, and little animal testing of scandium compounds has been done. The half lethal dose (LD50) levels for scandium (III) chloride for rats have been determined as 4 mg kg<sup>-1</sup> for intraperitoneal, and 755 mg kg<sup>-1</sup> for oral administration (Rim et al. 2013). The average human daily Sc intake is less than 0.1 microgram and therefore only trace amounts generally reach the food chain. Scandium does not have any biological role (Lenntech 2013). Sc could be a hazard in the working environment because damps and gases could be inhaled with air.

#### Yttrium

Water soluble compounds of yttrium are considered mildly toxic, while its insoluble compounds are non-toxic. In experiments on animals, yttrium and its compounds caused lung and liver damage. In rats, inhalation of yttrium citrate caused pulmonary edema and dyspnea, while inhalation of yttrium chloride caused liver edema, pleural effusions, and pulmonary hyperemia. Exposure to yttrium compounds in humans may cause lung disease (Rim et al. 2013). Inhaling yttrium gases in working environment could be a health hazard. Long-term exposure to inhaled yttrium can cause lung embolisms. Yttrium can also cause cancer with humans, as it enlarges the chances of lung cancer when it is inhaled (Lenntech 2013).

### Lanthanum

In animals, the injection of lanthanum solutions produces hyperglycaemia, low blood pressure, degeneration of the spleen and hepatic alterations. Lanthanum oxide (1312-81-8) LD50 in rat oral is  $> 8,500 \text{ mg kg}^{-1}$ , mouse intraperitoneal (i.p.)  $530 \text{ mg kg}^{-1}$  (Rim et al. 2013).

### Cerium

Cerium is a strong reducing agent, and ignites spontaneously in air at  $65^{\circ}\text{C}$  to  $80^{\circ}\text{C}$ . Fumes from cerium fires are toxic. Animals injected with large doses of cerium have died due to cardiovascular collapse. Cerium (IV) oxide is a powerful oxidizing agent at high temperatures, and will react with combustible organic materials. Ceric oxide (1306-38-3) LD50 in rats is: Oral  $5,000 \text{ mg kg}^{-1}$ , dermal  $1,000\text{-}2,000 \text{ mg kg}^{-1}$ , and inhalation of dust  $5.05 \text{ mg L}^{-1}$  (Rim et al. 2013). Cerium can be a threat to the liver when it accumulates in the human body. Cerium has no known biological role, but it has been noted that cerium salts stimulate metabolism (Lenntech 2013)

### Praseodymium

Praseodymium is of low to moderate toxicity (Pałasz and Czekaj 2000). Soluble praseodymium salts are mildly toxic by ingestion, but insoluble salts are non-toxic. They are skin and eye irritants. Praseodymium is mostly dangerous in the working environment, due to the fact that dusts and gases can be inhaled with air. This can cause lung embolisms, especially during long-term exposure. Praseodymium can be a threat to the liver when it accumulates in the human body (Lenntech 2013).

### Neodymium

Neodymium compounds are of low to moderate toxicity; however its toxicity has not been thoroughly investigated. Neodymium dust and salts are very irritating to the eyes and mucous membranes, and moderately irritating to the skin. Neodymium oxide (1313-97-9) LD50 in rat oral  $> 5,000 \text{ mg kg}^{-1}$ , mouse i.p.  $86 \text{ mg kg}^{-1}$ , and  $\text{Nd}_2\text{O}_3$  was investigated as a mutagen (Rim et al. 2013). According to Palmer et al. (1987), the LC50 for neodymium oxide was  $101 \mu\text{M}$ , displaying significant cytotoxicity. Ingested neodymium salts are regarded as only slightly toxic if they are soluble and non-toxic if they are insoluble (Lenntech 2013).

### Promethium

Bone tissue may be affected by interaction with promethium. No dangers, aside from the radioactivity, have been shown (Rim et al. 2013).

### Samarium

The total amount of samarium in adults is about  $50 \mu\text{g}$ , mostly in liver and kidneys, and with about  $8 \mu\text{g L}^{-1}$  being dissolved in the blood. Insoluble salts of samarium are nontoxic, and the soluble ones are only slightly toxic. When ingested, only about 0.05 % of samarium salts is absorbed into the bloodstream, and the remainder is excreted. From the blood, about 45 % goes to the liver, and 45 % is deposited on the surface of the bones, where it remains for about 10 years; the balance of 10 % is excreted (Rim et al. 2013).

### Europium

There are no clear indications that europium is particularly toxic compared to other heavy metals. Europium chloride nitrate and oxide have been tested for toxicity: europium chloride shows an acute i.p. LD50 toxicity of  $550 \text{ mg kg}^{-1}$ , and the acute oral LD50 toxicity is  $5,000 \text{ mg kg}^{-1}$ . Europium nitrate shows a slightly higher i.p. LD50 toxicity of  $320 \text{ mg kg}^{-1}$ , while the

oral toxicity is above 5,000 mg kg<sup>-1</sup> (Rim et al. 2013). The general population may get exposed to europium by ingestion (drinking water and nutrition) and inhalation. Eu is not easily absorbed and is generally deposited in the liver and on the surface of the bones (both 40 %) and in the kidney (6 %). Radioactive Eu cause a health hazard because the beta particles and gamma-rays increase the cancer risk in the liver and bones (Fedele et al. 2008).

### Gadolinium

As a free ion, gadolinium is highly toxic, but magnetic resonance imaging contrast agents are chelated compounds, and are considered safe enough to be used in most persons. The toxicity depends on the strength of the chelating agent. Anaphylactoid reactions are rare, occurring in approximately 0.03-0.1 % (Rim et al. 2013). Gadolinium salts are suspected to be tumorigens (Lennetch 2013).

### Terbium

As with the other lanthanides, terbium compounds are of low to moderate toxicity, although their toxicity has not been investigated in detail (Rim et al. 2013).

### Dysprosium

Soluble dysprosium salts, such as dysprosium chloride and dysprosium nitrate, are mildly toxic when ingested. The insoluble salts, however, are non-toxic. Based on the toxicity of dysprosium chloride to mice, it is estimated that the ingestion of 500 g or more could be fatal to a human (Rim et al. 2013).

### Holmium

Holmium, as with other REEs, appears to have a low degree of acute toxicity (Rim et al. 2013).

### Erbium

Erbium compounds are of low to moderate toxicity, although their toxicity has not been investigated in detail (Rim et al. 2013).

### Thulium

Soluble thulium salts are regarded as slightly toxic if taken in large amounts, but the insoluble salts are non-toxic. Thulium is not taken up by plant roots to any extent, and thus does not get into the human food chain (Rim et al. 2013).

### Ytterbium

All compounds of ytterbium should be treated as highly toxic, because it is known to cause irritation to the skin and eye, and some might be teratogenic (Rim et al. 2013).

### Lutetium

Lutetium is regarded as having a low degree of toxicity: for example, lutetium fluoride inhalation is dangerous and the compound irritates skin. Lutetium oxide powder is toxic as well if inhaled or ingested. Soluble lutetium salts are mildly toxic, but insoluble ones are not (Rim et al. 2013).

Concentration of some REEs in human tissues and fluids are provided in **Table 2-3**.

Agents Classified by the International Agency for Research on Cancer IARC Monographs, Volumes 1–107 (updated in April 2013) does not contain the classification of carcinogenicity of REEs.

**Table 2-3 Concentrations of rare earths in human tissue and fluids, for tissues in ng g<sup>-1</sup> or for fluids in mg L<sup>-1</sup> (Redling 2006).**

	Liver <sup>a</sup>	Ovary <sup>a</sup>	Skin <sup>a</sup>	Urine <sup>a</sup> 24 h (μg)	Lymph-nodes <sup>b</sup>	Cerebrospinal-fluid <sup>b</sup>
La	0.08	0.002	0.072	0.28 - 0.71	61.4 ± 8.8	0.1 ± 0.06
Ce	0.08	0.006	-	36	158.3 ± 58	1.6 ± 0.08
Nd	-	-	-	-	51 ± 10.4	0.1 ± 0.06
Sm	-	-	0.07	-	9.8 ± 3.5	0.1 ± 0.06
Eu	-	-	-	-	61.4 ± 8.8	0.1 ± 0.06
Gd	-	-	-	-	-	-
Tb	-	-	-	1.6 ± 8.8	0.034 ± 0.03	-
Yb	-	-	-	-	5.7 ± 2.4	0.015 ± 0.05

<sup>a</sup>Iyengar et al., 1978), <sup>b</sup> Sabbionia et al., 1992

### 2.3.5 Ecotoxicological and environmental effects of REEs

Elevated concentrations of REEs may cause toxic reactions and negative effect on plants (Tyler 2004). However, there is much supporting evidence that small amounts of REEs may have beneficial effects to biomass production and growth of vascular plants. Lanthanum and cerium have been used as fertilizers in plant production in China over 20 years (Xiong 1995, Zhang et al. 2001). In study on rice, La<sup>3+</sup> promoted yields at 0.05-1.5 mg L<sup>-1</sup> in nutrient solution, 0.05-0.75 mg L<sup>-1</sup> increased root dry weight, and 0.05-6 mg L<sup>-1</sup> increased the number of grains produced ( Xie et al. 2002, Tyler 2004). Diatloff et al. (1999) reported that foliar and soil application of La and Ce at rates recommended in Chinese agriculture did not show any positive effect to shoot mass production in maize and mung bean. Higher rates caused foliar damage and reduced shoot dry weight, both if sprayed with La or Ce solutions or with a commercial REE fertiliser. In solution culture, La or Ce concentrations as low as 0.03 mg L<sup>-1</sup> were toxic to mungbean. Maize was less sensitive, reductions being measured at >0.7 mg L<sup>-1</sup> of La or Ce (Diatloff et al., 1999, Tyler 2004). Anthropogenic REEs are usually more soluble, reactive and bioavailable forms when entering the environment (Zhang and Shan 2001).

Barry and Meehan (2000) measured the acute and chronic toxicity of La to *Daphnia carinata*. Lanthanum in soft tap water was most toxic to *Daphnia* with a 48-h EC50 of 43 μg L<sup>-1</sup> compared with a value of 1180 μg L<sup>-1</sup> in hard water. The calculated 48-h EC50 for La in the diluted sea water was 49 μg L<sup>-1</sup>. 100% mortality was found at concentrations above 80 μg L<sup>-1</sup> of La by day six of the experiment using soft water, but no effect on survival growth or reproduction at lower concentrations. In the hard water, La caused significant mortality to *Daphnia* at concentrations above 39 μg L<sup>-1</sup> (Barry and Meehan 2004).

Zhang et al. (2010) used *Caenorhabditis elegans* (*C. elegans*) as a test organism and life-cycle endpoints to evaluate the aquatic toxicity of lanthanum. La<sup>3+</sup> had significant adverse effects on the growth and reproduction of worms above a concentration of 10 μM (Zhang et al. 2010). Scandium could cause damage to the cell membranes of water animals. This may have a negative influence on reproduction and on the nervous system functions (Lennetch 2013).

Zhang et al. (2012) investigated the biotransformation of CeO<sub>2</sub> nanoparticles (NPs) in plant systems. Biotransformation is a critical factor that may modify the toxicity, behavior and fate of engineered nanoparticles in the environment. In the process of biotransformation, either enhanced toxicity or detoxification is possible (Abramowicz 1990). Transmission electron microscopy (TEM) images showed needle-like clusters on the epidermis and in the

intracellular spaces of cucumber roots after a treatment with 2000 mg L<sup>-1</sup> CeO<sub>2</sub> NPs for 21 days (Zhang et al. 2012). By using soft X-ray scanning transmission microscopy (STXM) technique, the needle-like clusters were verified to be CePO<sub>4</sub>. Near edge X-ray absorption fine structure (XANES) spectra showed that Ce is present in the roots as CeO<sub>2</sub> and CePO<sub>4</sub> while in the shoots as CeO<sub>2</sub> and cerium carboxylates. Simulated studies indicate that reducing substances (e.g. ascorbic acids) played a key role in the transformation process and organic acids (e.g. citric acids) can promote particle dissolution. The authors speculated that CeO<sub>2</sub> NPs were firstly absorbed on the root surfaces and partially dissolved with the assistance of the organic acids and reducing substances excreted by the roots. The released Ce(III) ions were precipitated on the root surfaces and in intercellular spaces with phosphate, or form complexes with carboxyl compounds during translocation to the shoots (Zhang et al. 2012).

The bioconcentration factor (BCF) for Ce in soil cultivated soybean pods was low (Table 2-4) (Hernandez-Viezcas et al. 2013). However, the results of linear combination fitting (LCF) analysis suggested that most of the Ce stored in the soybean pods was in the form of CeO<sub>2</sub> NPs. The results of a peak fitting (PF) data analysis also suggested that a small percentage of the Ce in the pod could be changing its oxidation state from Ce(IV) to Ce(III). The results of these analyses proved that CeO<sub>2</sub> nanoparticles (NPs) in soil can be taken up by food crops. The authors concluded that CeO<sub>2</sub> NPs can reach the food chain and the next soybean plant generation (Hernandez-Viezcas et al. 2013).

*Table 2-4 Bioconcentration Factors BCF (Metal in Tissue/Metal in Soil). After Hernandez-Viezcas et al. (2013)*

soil metal concentration	root	nodule	stem	pod	leaf
<b>Control: 30.91 mg Ce/kg<sup>a</sup></b>	0.0095	0.0038	0.0013	0.0024	6 x 10 <sup>-6</sup>
<b>1000 mg of CeO<sub>2</sub>/kg</b>	0.21	0.011	0.0001	0.00004	3 x 10 <sup>-7</sup>

<sup>a</sup> Ce naturally present in soil; therefore, the bioconcentration factors of the control were considered. Calculated from values reported in Priester et al. 2012.

The predicted no-effect concentration (PNEC) is the concentration below which exposure to a substance is not expected to cause adverse effects. PNEC values for lanthanum oxide and cerium was only available. The following PNEC values are derived from European Chemical Agency ECHA.

#### Lanthanum oxide

PNEC aqua (freshwater) 10 mg L<sup>-1</sup>

PNEC aqua (marine water) 1 mg L<sup>-1</sup>

PNEC sediment (freshwater) 15.5 mg kg<sup>-1</sup> sediment dw

PNEC sediment (marine water) 15.5 mg kg<sup>-1</sup> sediment dw

PNEC soil 18.9 mg kg<sup>-1</sup> soil dw

PNEC oral 156 mg kg<sup>-1</sup> food

#### Cerium

PNEC aqua (freshwater) 0.6 mg L<sup>-1</sup>

PNEC aqua (marine water) 60.9 µg L<sup>-1</sup>

### 2.3.6 Some epidemiological findings of REEs

The effects of environmental exposure to REEs on health among children aged 7-10 years were studied in Xunwu county, Jiangxi in China (Fan et al. 2004). In the rare earth ore area, the concentration of blood REEs was significantly ( $P < 0.01$ ) higher,  $2.10 \pm 0.88 \text{ ng g}^{-1}$ , compared to concentration of blood in the control area,  $1.26 \pm 1.35 \text{ ng g}^{-1}$ . The score of Intelligence Quotient (IQ) was significantly lower in the exposure group than in the control group. The percentage of high IQ decreased while the percentage of low IQ increased. The distance from home to the REE area influenced the score of children's IQ. The authors concluded that the children in REE ore area may have higher REEs body burden, and get exposed to REEs could have adverse health effects (Fan et al. 2004).

In another Chinese study (Zhu et al. 2005) blood samples were analysed from 156 farmers aged between 20 and 45 years living in high-REE-background areas. 45 farmers were from a heavy REE (HREE) mining area, 62 were from a light REE (LREE) mining area, and 49 were from a control area. Test results showed that serum total protein and globulin from both HREE and LREE areas, as well as albumin from the LREE area, were significantly lower ( $p < 0.05-0.01$ ) compared to the results from the control area, whereas albumin from the HREE area showed no significant variance ( $p > 0.05$ ). The chi-square test showed that serum-glutamic pyruvic transaminase (SGPT) in both areas were not significant ( $p > 0.05$ ), whereas the IgM in the HREE area was significantly elevated. The authors concluded that long-term ingestion of REE affected activities of some digestive enzymes, causing malabsorption and indigestion, and might further lead to a low-protein effect for the villagers (Zhu et al. 2005).

Wu et al. (2003) studied the correlation on radioactive contamination of lanthanon to leukemia in mining areas of rare-earth elements. The main risk factors found in this study were frequently drinking water from river (OR = 5.543), distance from residence to rare-earth mine area and years for living in the area (OR = 3.308) and an exposure to organophosphorus pesticide (OR = 3.014). The association of leukemia and environmental pollution with rare-earth elements around the residential areas and organophosphorus pesticide exposure was reported (Wu et al. 2003).

The association between cerium status and risk of first acute myocardial infarction (AMI) was examined in a case-control study in 10 centres from Europe and Israel (Gómez-Aracena et al. 2006). Cerium concentration in toenails was assessed in 684 cases and 724 controls aged 70 years or younger. Mean concentrations of cerium were  $186 \mu\text{g kg}^{-1}$  in cases and  $173 \mu\text{g kg}^{-1}$  in controls. Cases had significantly higher Ce levels than controls after adjustment for age and centre and further increased after adjustment for cardiovascular risk factors. The authors suggested that toenail cerium levels may be associated with an increased risk of AMI (Gómez-Aracena et al. 2006).

In French study, the retention of cerium-containing particles in the lungs of people previously exposed to mineral particles was evaluated (Pairon et al. 1994). The absolute concentration of cerium-containing particles in the bronchoalveolar lavage (BAL) fluid and lung tissue samples showed high retention of these particles in 1.2% (from BAL fluid) and 1.5% (from lung tissue) of subjects.

The concentration of REEs in hair can be used as a bio-marker to reflect human exposure to REEs (Peng et al. 2003, EPA 2012). For example, the concentration of REE in the hair of young children and their mothers decreased with the distance of their home to a REE mining area in Jiangxi Province, China (Peng et al. 2003).

The aim of Italian study was to develop an analytical method to determine rare earth elements for the control of the geographic origin of tomatoes. The content of REE in tomato plant samples was collected from an agricultural area in Piacenza, Italy. They found the following sequence: roots > leaves > stems > berries. The LREE content was significantly higher than that of HREE for each plant district, in particular for berries (Spalla et al. 2009). REE concentrations in tomatoes are provided Table 2-5.

*Table 2-5 REE concentration range and mean value ( $\mu\text{g kg}^{-1}$  dw) in tomato, berries, leaves, stems and roots. (Spalla et al. 2009).*

REE	Berries ( $\mu\text{g kg}^{-1}$ )			Leaves ( $\mu\text{g kg}^{-1}$ )			Stems ( $\mu\text{g kg}^{-1}$ )			Roots ( $\mu\text{g kg}^{-1}$ )			Roots/berries
	Min	Max	Mean	Min	Max	Mean	Min	Max	Mean	Min	Max	Mean	ratio mean
<sup>139</sup> La	2.97	15.69	7.49	131	792	322	28.3	167	95.3	207	467	341	45.5
<sup>140</sup> Ce	3.78	11.44	7.97	205	757	469	39.4	317	161	463	717	613	76.9
<sup>141</sup> Pr	1.06	3.25	2.00	27.1	92.3	52.2	10.1	61.1	34.8	116	153	133	66.5
<sup>144</sup> Nd	2.47	7.11	4.61	141	481	280	28.9	177	103	483	644	562	122
<sup>151</sup> Eu	0.20	0.61	0.40	4.47	13.3	9.12	1.41	8.88	5.37	20.6	39.4	27.0	67.5
<sup>152</sup> Sm	0.71	2.58	1.58	20.6	62.7	42.2	6.77	47.2	27.8	130	203	152	96.2
<sup>159</sup> Tb	0.14	0.49	0.31	2.83	8.66	5.91	0.86	5.71	3.50	14.2	25.9	18.1	58.4
<sup>160</sup> Gd	0.46	1.67	1.02	17.7	66.8	41.4	6.45	41.8	25.7	120	205	150	147
<sup>164</sup> Dy	0.58	2.20	1.40	11.8	44.1	28.7	4.33	30.3	18.5	88.9	150	112	80
<sup>165</sup> Ho	0.11	0.40	0.24	2.56	9.08	5.84	0.80	5.49	3.39	15.3	25.3	19.2	80
<sup>166</sup> Er	0.27	0.97	0.61	6.07	22.0	14.4	2.13	14.6	8.91	47.1	70.4	56.7	93
<sup>169</sup> Tm	0.04	0.08	0.06	0.91	3.27	2.11	0.25	1.95	1.15	5.31	7.37	6.19	103
<sup>172</sup> Yb	0.22	0.63	0.43	5.03	16.1	11.2	1.77	12.2	7.20	38.7	50.4	43.9	102
<sup>175</sup> Lu	0.02	0.07	0.04	0.98	2.61	1.82	0.26	1.68	1.00	4.95	6.20	5.59	140

### 2.3.7 Occupational health issues with REE

Occupational health and safety risks in the rare earth industry may relate to the mining, transportation, processing or waste disposal stage, and may include physical, chemical and radiological risks. The specific occupational health and safety issues associated with the REEs themselves, as identified by Rim et al. (2013), are given in Table 2-6. Further toxicity, epidemiology and ecotoxicity findings are found in e.g. EPA (2012).

Table 2-6 Occupational health and safety issues with rare earths (Rim et al. 2013).

Z	Symbol	Name	CAS No.	Occupational health and safety issues*
21	Sc	Scandium	7440-20-2	It is mostly dangerous in the working environment, due to the fact that fumes and gasses can be inhaled with air.
39	Y	Yttrium	7440-65-5	Workers exposed to yttrium compounds can cause shortness of breath, coughing, chest pain, and cyanosis. NIOSH recommends a time-weighted average limit of 1 mg/m <sup>3</sup> , and an IDLH of 500 mg/m <sup>3</sup> . Yttrium dust is flammable.
57	La	Lanthanum	7439-91-0	The application in carbon arc light led to the exposure of people to RE oxides and fluorides, sometimes leading to pneumoconiosis [38].
58	Ce	Cerium	7440-45-1	Workers exposed to cerium have experienced itching, sensitivity to heat, and skin lesions. OEL (Russia) of ceric oxide (1306-38-3) is 5 mg/m <sup>3</sup> [14,15].
59	Pr	Praseodymium	7440-10-0	Praseodymium compounds are controversial subjects with their biological roles [29].
60	Nd	Neodymium	7440-00-8	Breathing the dust can cause lung embolisms, and accumulated exposure damages the liver. Neodymium also acts as an anticoagulant, especially when given intravenously. Neodymium magnets have been tested for medical uses, such as magnetic braces and bone repair, but biocompatibility issues have prevented widespread application. If not handled carefully, they come together very quickly and forcefully, causing injuries. For example, there is at least one documented case of a person losing a fingertip, when two magnets he was using snapped together from 50 cm away [28].
61	Pm	Promethium	7440-12-2	The element, like other lanthanides, has no biological role. In general, gloves, footwear covers, safety glasses, and an outer layer or easily removed protective clothing should be used. Sealed promethium-147 is not dangerous. However, if the packaging is damaged, then promethium becomes dangerous to the environment and humans.
62	Sm	Samarium	7440-19-9	Samarium metal compounds are controversial subjects regarding their biological roles in human body.
63	Eu	Europium	7440-53-1	Dust of its metal compounds present fire and explosion hazard [2].
64	Gd	Gadolinium	7440-54-2	Gadolinium has little information on its native biological roles, but its compounds are used as research tools in biomedicine. Gd <sup>3+</sup> compounds are components of magnetic resonance imaging contrast agents [40].
65	Tb	Terbium	7440-27-9	Terbium compounds are controversial subjects regarding their biological roles [13,34].
66	Dy	Dysprosium	7429-91-6	Like many powders, dysprosium powder may present an explosion hazard when mixed with air and when an ignition source is present. Thin foils of the substance can also be ignited by sparks or by static electricity. Dysprosium fires cannot be put out by water. It can react with water to produce flammable hydrogen gas [80].
67	Ho	Holmium	7440-60-0	Holmium compounds are controversial subjects regarding their biological roles in humans, but may be able to stimulate metabolism [79].
68	Er	Erbium	7440-52-0	Metallic erbium in dust form presents a fire and explosion hazard [2].
69	Tm	Thulium	7440-30-4	Thulium compounds are controversial subjects with their biological roles, although it has been noted that it stimulates metabolism.
70	Yb	Ytterbium	7440-64-4	Although ytterbium is fairly stable chemically, it should be stored in air-tight containers and in an inert atmosphere, to protect the metal from air and moisture. Metallic ytterbium dust poses a fire and explosion hazard [13].
71	Lu	Lutetium	7439-94-3	Lutetium nitrate may be dangerous as it may explode and burn once heated. Lutetium has no known biological role, but it is found even in the highest known organism, the humans, concentrating in bones, and to a lesser extent in the liver and kidneys [13].

\*Mostly referred from ChemIDplus Advanced (<http://chem.sis.nlm.nih.gov/chemidplus/>) and material safety data sheets information in KOSHANET (<http://www.kosha.or.kr/bridge?menuId=69>).

### 2.3.8 Actinides

Uranium, thorium, protactinium and actinium are naturally occurring actinides. The most abundant actinides in the Earth's crust are uranium and thorium. Protactinium and actinium are included in the uranium and thorium decay chains.

The solubility, transport properties, bioavailability and toxicity of actinides are dependent on the oxidation state, molecular-level structure and phase in which the element or molecule

occurs (Maher et al. 2013). Uranium is chemically toxic to the kidneys when taken internally in larger amounts, but the effects from environmentally-relevant concentrations are less clear. Ingestion of water from drilled wells is a source of high uranium exposure in some populations. Uranium exposure is associated with greater diastolic and systolic blood pressures, and cumulative uranium intake is associated with increased glucose excretion in urine. Continuous uranium intake from drinking water, even at relatively high exposures, is not found to have cytotoxic effects on kidneys in humans (Kurttio et al. 2006).

### **2.3.9 Safety precautions**

Special attention should be paid to the sufficient ventilation of dusty working areas, the appropriate hygiene on the part of the workers, and the proper use of personal protective equipment (such as breathing respirators); this reduces exposures and reduces the risk from lung related diseases, such as pneumoconiosis (Sabbioni et al. 1982, Vocaturo et al. 1983). In general, REE should be kept in air-tight containers and in an inert atmosphere so as to be protected from air and moisture. These elements should also be kept away from sources of sparks and static electricity. Gloves, footwear, covers, safety glasses, and an outer layer or easily removed protective clothing should be used.

Overall, further research is required to evaluate the hazards or risks for personnel working with REE, including the concentrations of REEs in the body at which health problems occur. Environmental and occupational toxicology testing of REEs requires the development of agreed testing protocols and guidelines, to allow for the comparison and interpretation of data from the studies.

## 3 Radiation protection – regulations and recommendations

### 3.1 Introduction

This chapter is intended to give an overview of regulatory requirements and recommendations that can be applied to radiation protection in the REE production chain. The following topics are covered in the following sections:

- Basic radiation protection considerations including definitions of basic terms and dose limits for various exposure situations
- The concepts of exemption and clearance applied to NORM
- Regulatory control of workplaces
- Classification of radioactive waste based on activity and longevity of the radionuclides

### 3.2 Basic radiation protection considerations

#### 3.2.1 Radiation protection standards

Requirements for the protection of health against exposure to ionizing radiation (radiation) and for the safety of radiation sources are set out in Basic Safety Standards (BSS). New Basic Safety Standards have recently been set by the EC in Council Directive 13/59/ EURATOM (BSS 2013) as well as by the IAEA (2014). Basic Safety Standards are based on information on the detrimental effects attributed to radiation exposure provided by the United Nations Scientific Committee on the Effects of Atomic Radiation (UNSCEAR) and the principles of radiation protection and safety developed by the International Commission on Radiological Protection, ICRP.

The Basic Safety Standards apply to the start-up and the continuation of practices that involve radiation exposure, and to existing situations in which exposure or the probability of exposure can be reduced by remedial actions. BSS (2013) has integrated NORM into its overall requirements, meaning that industries processing NORM will be managed within the same regulatory framework as other practices. Therefore the definition of the term "practice" is now "a human activity that can increase the exposure of individuals to radiation from a radiation source and is managed as a planned exposure situation". Previously, practices were only relevant to artificial radionuclides, or naturally occurring radionuclides processed because of their radioactive, fissile or fertile properties. Activities involving incidental exposure to NORM were then termed "work activities". Member States are required to ensure the "identification of classes or types of practice involving naturally-occurring radioactive material and leading to exposure of workers or members of the public which cannot be disregarded from a radiation protection point of view".

The Basic Safety Standards from the EU and IAEA address the protection of exposed workers and members of the public. An exposed worker is any person who works (either as an employee or self-employed) within a regulated activity and has recognised rights and duties in relation to occupational radiation protection. Basic Safety Standards therefore include dose limits to individual members of the public and workers. The effective dose limit for members of the public is  $1 \text{ mSv a}^{-1}$ . In special circumstances, a higher effective dose may be authorised in a single year, provided that the average over five consecutive years does not exceed  $1 \text{ mSv a}^{-1}$ . There is also a limit on equivalent dose for the lens of the eye of  $15 \text{ mSv a}^{-1}$  and for the skin of  $50 \text{ mSv a}^{-1}$  regardless of the area exposed.

Dose limits for exposed workers are 100 mSv in a five-year period and a maximum effective dose of 50 mSv in any single year. The limit for workers on equivalent dose for the lens of the eye is 150 mSv a<sup>-1</sup> and the limit for equivalent dose for the skin is 500 mSv a<sup>-1</sup>.

The dose limit for members of the public concerns all radiation sources to which an individual is exposed, and is set at 1 mSv a<sup>-1</sup> (BSS 2013). Therefore, a fraction of this dose limit is often allowed when considering the radiological impact of a single practice.

### 3.2.2 The concepts of exclusion, exemption and clearance

Exclusion, exemption and clearance are concepts which enable low-risk materials to stay outside or be removed from the regulatory system.

**Exclusion** applies when exposure to naturally occurring radiation sources cannot be controlled, such as exposure from materials in their natural state. These materials are excluded from the scope of BSS (2013) and do not require regulation.

Industries that process NORM extracted from the Earth's crust are identified in BSS (2013) as a source of exposure that can be controlled, and so these activities cannot be excluded. Additionally, NORM industries are identified in Annex VI of BSS (2013), i.e. those that are not eligible for exclusion, and include "extraction of rare earths from monazite" and "mining of ores other than uranium ore". In the UK, "Extraction, production and use of REE and REE alloys" are specifically in scope of the radioactive substances regulations (Environment Agency 2013).

**Exemption** is used to avoid unnecessary regulation by removing the reporting requirement from a practice when radiological risks are considered to be low. Materials that are exempt do not enter the regulatory system. This is therefore the process by which the mining and processing of REE ores with low levels of radioactivity will be released from the regulatory system.

**Clearance** is used to release material with low levels of radionuclide contamination from a regulated practice. The concept of clearance is very close to that of exemption, but they relate to different stages of regulatory control.

Two kinds of clearance levels can be derived to release materials from regulation; general clearance levels, when the destination of a material is not defined, and specific clearance levels for specific reuse of the material or a specific disposal option. Since recycling, reuse or disposal of materials can occur following general clearance, the levels for general clearance are equal to or more restrictive than levels for specific clearance. Specific clearance levels are set by the national competent authority on the basis of a case-by-case evaluation. In EURARE, clearance is important for low activity waste streams arising from the processing of regulated materials, both in terms of management and cost.

### 3.2.3 General exemption and clearance values in the Basic Safety Standards (BSS, 2013)

The BSS (2013) provides activity concentration values that can be used by default for the exemption and clearance of solid materials. It also defines the requirements for the exemption or clearance of materials with higher activity concentrations.

**General exemption and clearance:** Default exemption values are specified for relevant radionuclides in solid materials in three separate tables in Annex VII of BSS (2013):

- Table A Part 1 specifies the maximum activity concentration of each artificial radionuclide when it is either the only radioactive component in a solid material or is in equilibrium with its short-lived progeny. A material containing a mixture of artificial radionuclides would be exempt if it fulfils Equation 1.

$$\sum_{i=1}^n \frac{C_i}{C_{Li}} \leq 1.0 \quad \text{[Equation 1]}$$

Where  $c_i$  is the total activity of radionuclide  $i$  in the material per unit mass ( $\text{Bq kg}^{-1}$ )  
 $c_{Li}$  is the exemption limit of the radionuclide  $i$   
 $n$  is the number of radionuclides in the mixture

- Table A Part 2 specifies the maximum activity concentration of naturally occurring radionuclides in secular equilibrium with their progeny (natural radionuclides from the  $^{238}\text{U}$  and  $^{232}\text{Th}$  decay series (see Appendix 1), and  $^{40}\text{K}$ ). Higher values may be applied to sections of the decay chain that are not in equilibrium with their parent. The values given may NOT be used to exempt the “incorporation into building materials of residues from industries that process NORM”. This is due to the risk of increasing the radiological doses received by the future inhabitants.
- Table B specifies total activity and activity concentration values for artificial and natural radionuclides in moderate amounts of any type of material. These values allow the exemption of higher activity concentrations than in Table A if a maximum overall activity is not exceeded, and apply to less than one tonne of material. However, it is stated that, in general, these values only apply to naturally occurring radionuclides when they are used in consumer products. Member states should specify the specific practices that these values apply to.

As a result of the similar roles of exemption and clearance in terms of radiation protection, the default exemption values in Table A Part 1 and Table A Part 2 of BSS (2013) also apply as the general clearance values. These exemption and clearance values were derived by the IAEA (2004, 2005), and for radionuclides of natural origin this was through “consideration of the worldwide distribution of concentrations of radionuclides of natural origin”. The aim here was to exempt nearly all soils but not ores, mineral sand, industrial residues and wastes that have a significant activity concentration. The values selected were  $10 \text{ kBq kg}^{-1}$  for  $^{40}\text{K}$  and  $1 \text{ kBq kg}^{-1}$  for all other radionuclides of natural origin. In the BSS (2013), “all other radionuclides of natural origin” was narrowed down to natural radionuclides from the  $^{238}\text{U}$  and  $^{232}\text{Th}$  decay series.

The approach in IAEA (2005) for deriving NORM exemption and clearance values differed significantly from previous approaches based on dose limits, for example in Radiation Protection 122 Part II (2001). The values for artificial radionuclides were, however, derived using scenario analysis and a dose limit to the public of  $10 \mu\text{Sv a}^{-1}$  (IAEA, 2005). The adoption of the IAEA (2004, 2005) values makes the values derived in the Commission’s publications Radiation Protection 122 Part I (2000) and II (2001) redundant.

**Specific exemption and clearance levels:** Competent national authorities can apply higher exemption or clearance levels to a particular practice if they are satisfied that the following three criteria are fulfilled:

- (i) the radiological risks to individuals caused by the practice are sufficiently low, as to be of no regulatory concern; and
- (ii) the type of practice has been determined to be justified; and
- (iii) the practice is inherently safe.

Exemption may apply to the notification stage, i.e. informing the competent authority of the intention to carry out a practice, or the authorisation stage, i.e. registration or licensing. The definition of a sufficiently low radiological risk in (i), when applied to the the notification stage, is that workers should not be classified as exposed workers (see Section 3.2.5), and the following criteria are met for members of the public in all feasible circumstances:

- For artificial radionuclides

The effective dose expected to be incurred by a member of the public due to the exempted practice is of the order of 10  $\mu\text{Sv}$  or less in a year.

- For naturally-occurring radionuclides:

The dose increment, allowing for the prevailing background radiation from natural radiation sources, liable to be incurred by an individual due to the exempted practice is of the order of 1 mSv or less in a year. The assessment of doses to members of the public shall take into account not only pathways of exposure through airborne or liquid effluent, but also pathways resulting from the disposal or recycling of solid residues. Member States may specify dose criteria lower than 1 mSv per year for specific types of practices or specific pathways of exposure.

Less restrictive dose criteria may be applied to the exemption of practices from authorization.

There is a marked difference in the dose-criteria applied to clearance/exemption values for natural and artificial radionuclides. This is because, for natural radionuclides, the trivial risk criteria (10  $\mu\text{Sv}$ ) applied to artificial radionuclides would be a small fraction of the natural background dose, and is below natural background variability. Exemption/clearance values for naturally occurring radionuclides are therefore derived using higher dose constraints. Although the dose increment (i.e. increment to the local background) defined in the BSS (2013) is 1 mSv  $\text{a}^{-1}$ , 0.3 mSv  $\text{a}^{-1}$  may be adopted by member states to allow for exposure from more than one source and to be consistent with the dose constraints used for other purposes, e.g. the exemption values proposed for building materials (RP 113) and the control of effluents (recommended by ICRP). In addition, a 1 mSv  $\text{a}^{-1}$  dose constraint is at the lower marker point for the control of exposed workers, see Section 3.2.5.

### 3.2.4 Activity concentrations in the EURARE ores

Approximate concentrations of  $^{238}\text{U}$  and  $^{232}\text{Th}$  in the ores used in the EURARE project are given in Table 3-1. The processing of the Kvanefjeld and Rødberg ores requires regulation. Moreover, since the radionuclides follow the REE during beneficiation, their concentration in the ore concentrate will be higher than in the ore.

The concentration of radionuclides in the beneficiation and processing wastes and products should be investigated for all ores and concentrates, even Norra Kärr, to understand the flow of radionuclides in the processes developed in EURARE and the possibility of producing non-exempt wastes. In some cases, it may be possible to use a mass balance to demonstrate that the radionuclides in the starting material cannot concentrate sufficiently in the wastes to require regulation. In others, more detailed characterization of radionuclide behavior may be

required. Taking due care of radionuclide concentration pathways will also help ensure that the best available techniques (BAT) are properly defined and the wastes are managed appropriately and do not need remediation in the future.

*Table 3-1 Approximate concentrations of <sup>238</sup>U and <sup>232</sup>Th in the EURARE ore materials*

	Th-232 (ppm)	Th-232 (kBq kg <sup>-1</sup> )	U-238 (ppm)	U-238 (kBq kg <sup>-1</sup> )
Rødberg ore (max Th)	1000	4.07	10	0.12
Rødberg ore (average Th)	500	2.04	10	0.12
Fen limestone	150	0.61	10	0.12
Norra Kärr	7	0.03	14	0.17
Kvanefjeld	600	2.50	232	2.89

### 3.2.5 Regulatory control of workplaces

Reference activity concentrations of naturally occurring radioactive materials have been derived to assist the regulatory control of NORM work activities in workplaces (Radiation Protection 95 and Radiation Protection 107). Scenarios were designed for normal exposure during a number of processes within several of the key EU NORM industries. The activity concentrations required to deliver a dose of 1, 6 and 20 mSv a<sup>-1</sup> via those scenarios were then calculated. These dose levels align with the control of practices in the Basic Safety Standards, and the four band system employed is shown in Table 3-2. The applicability of the scenarios used to EURARE needs consideration and it may be appropriate to carry out specific scenario analysis.

The BSS (2013) also states that radon concentrations in places of work should be below the national reference level, thus radon and exposure reduction measures should be taken if the national reference level is exceeded. However, if exposure of workers is liable to exceed an effective dose of 6 mSv per year, the work should be managed as a planned exposure situation, i.e. require regulation. A dose of 6 mSv a<sup>-1</sup> corresponds to a radon concentration of 1000 Bq m<sup>-3</sup>.

*Table 3-2 Classification system for work activities*

Band	Regulation requirement	Effective dose (mSv a <sup>-1</sup> )	
		Normal scenario	Unlikely scenario
Band 1	No regulation necessary	<1	<6
Band 2	Lower level of regulation	1-6	6-20
Band 3	Higher level of regulation	6-20	20-50
Band 4	Process not permitted	>20	>50

### 3.2.6 Record keeping

Even if a material and all processing wastes are identified as exempt, all partners handling that material should keep documentation as evidence. This is so it can be shown to the regulatory authority, if they were to choose to investigate the situation.

All materials and activities falling under the regulations will require the maintenance of records that are readily available for inspection. Guidance on this will be available from the relevant authority and radiation protection advisors. It is likely to involve documenting safety protocols for the handling of materials as well as the date each material was brought onto the premises, their activity concentrations, the location of materials and wastes, and the date and method of disposal.

When working with regulated materials, a dose assessment should be carried out to assess whether the workplace also falls under regulatory control, i.e. whether the workers should be classified as exposed workers. Although a similar approach may be taken to that in Section 4.2, activities in an industrial environment are likely to be more prescribed and controlled than in a research laboratory, and so more realistic exposures can be calculated and/or measured. Previous scenario analyses can also aid this process (Section 3.4.2). External dose rates can be also measured for inclusion in calculations, and external doses to workers can be monitored through the use of a dose badge if appropriate.

### 3.3 Radioactive waste management

#### 3.3.1 International radioactive waste classification scheme

The IAEA has published a scheme for classification of radioactive waste in a safety guide (IAEA 2009). The safety guide defines the following waste categories based on the radioactivity of the waste and the longevity of this radioactivity:

- Exempt waste (EW): Waste that meets the criteria for clearance, exemption or exclusion from regulatory control for radiation protection purposes.
- Very short-lived waste (VSLW): Waste containing only radionuclides of very short half-life with concentrations above clearance levels. Such waste can be stored until the activity has fallen beneath the levels for clearance.
- Very low-level waste (VLLW): Waste containing an activity concentration in the region of and slightly above clearance levels. Substantial amounts of such waste may arise, e.g. from the mining or processing of ores and minerals, or the decommissioning of nuclear facilities. The management of this waste requires radiation protection provisions, but these are very limited in comparison to those required for more radioactive waste in the classes described below.
- Low level waste (LLW): Waste containing such an amount of radioactive material that it requires containment and isolation for limited periods of time, up to a few hundred years. This type of waste is suitable for near surface disposal.
- Intermediate-level waste (ILW): Waste containing long-lived radionuclides in quantities that need a higher degree of containment and isolation from the biosphere than provided by near surface disposal. Disposal in a facility at a depth between a few tens and a few hundreds of meters is indicated, in a facility providing a long period of isolation from the accessible environment.
- High-level waste (HLW): Waste containing large concentrations of both short and long-lived radionuclides, requiring a high degree of containment and isolation from the biosphere, usually provided by the integrity and stability of deep geological disposal including engineered barriers.

Figure 3-1 shows the different waste categories, and also indicates the likely classification of NORM-wastes. The NORM waste area in the diagram indicates that the radionuclides in NORM have long half-lives and that the activity concentrations of the waste material

normally falls in the VLLW or LLW range but that some of the NORM-waste can reach ILW-levels.

IAEA has published a report describing the method for the calculation of radioactivity limits for low- and intermediate level waste in near surface disposal facilities, which provides illustrative values that can be used for reference purposes, for example at the preliminary planning stage of a disposal facility (IAEA 2003). The concentrations are given for different near-surface facility constructions, including trench disposal in different geospheres and climates.

The radiation protection criteria that the calculations are based on are the following dose increments:

- 20 mSv a<sup>-1</sup> for workers (note that here it is assumed that the waste disposal facility worker is in a controlled activity, which is not the case in ordinary landfill sites).
- 1 mSv a<sup>-1</sup> for members of the public (0.3 mSv a<sup>-1</sup> from a single source).

The public exposure dose limits applied to nuclear waste disposal in nation states are often **more stringent** than these.

The calculations were performed for surface waste disposal facilities during the operational period and post-closure during the period of administrative control (100-300 years) and after the administrative control period (up to 100 000 years). The scenarios considered for the operational period included gas release from the waste facility, accidents, damage to a waste shipment), flooding, release of leachate, release of dusts, and fire.

The scenarios considered for the post-closure period include functional barriers, partly functional barriers and non-functional barriers, e.g. as a result of barrier degradation. Scenarios included release of leachate, construction in the waste facility (e.g. road-building), and exposure for the residents of houses built on top of the facility. The calculated activity limits for trench-disposal in clay in temperate climates are summarised in Table 3-3.

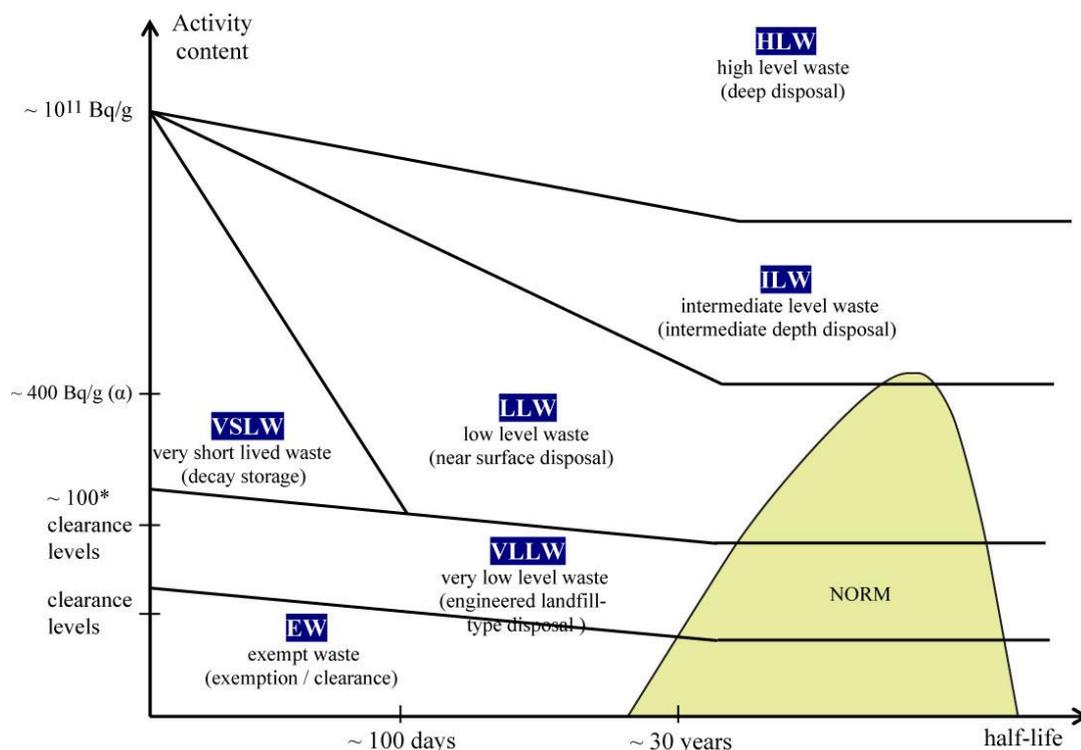


Figure 3-1 The classification of radioactive waste, showing NORM-wastes as an example of the classification scheme.

Table 3-3 Activity limits for the disposal of radioactive waste in a trench-facility in a clay-geosphere.

	Operational scenario		Post closure road construction and residence		Post-closure, leaching scenario
	Activity conc (kBq kg <sup>-1</sup> )	Limiting scenario	Activity conc (kBq kg <sup>-1</sup> )	Limiting scenario	Total activity (Bq)
U-238*	2,000	Worker, fire release	100	on-site residence, soil contact	8•10 <sup>14</sup>
U-234	2,000	Worker, fire release	300	on-site residence, soil contact	4•10 <sup>19</sup>
Ra-226*	100	Public, liquid release	0.8	on-site residence, soil contact	1•10 <sup>20</sup>
Pb-210*	20	Public, fire release	not calculated	on-site residence, soil contact	not calculated

\* No values calculated for Th-234 and Th-230

### 3.3.2 Disposal of low activity NORM waste

The regulations regarding NORM waste disposal may vary between EU member states. The scheme applied in the UK is shown in Figure 3-2, and is based on scenario analysis with a dose limit of 0.3 mSv a<sup>-1</sup>.

The IAEA also recommends a 0.3 mSv a<sup>-1</sup> dose limit for the disposal of mine tailings, including from U and Th mining (IAEA 2002).

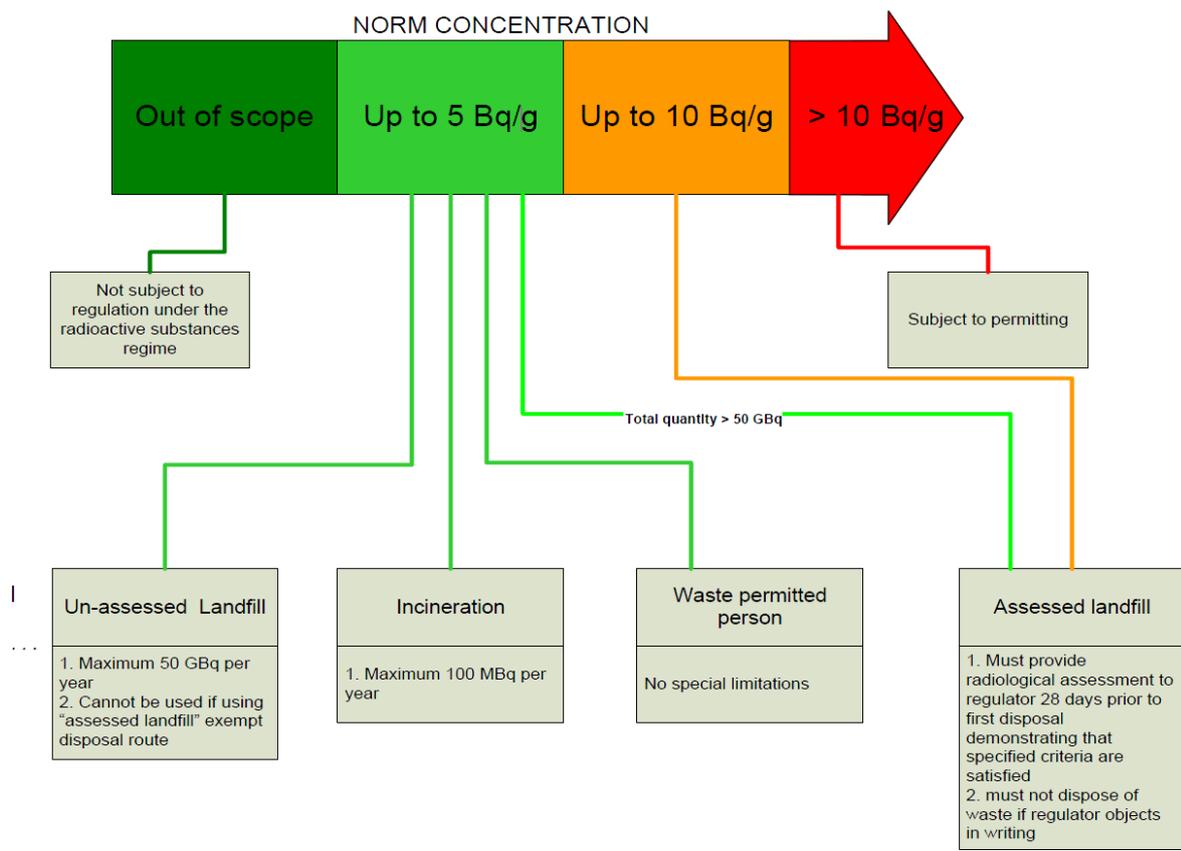


Figure 3-2 UK restrictions for NORM waste disposal. Note that “NORM concentration” is essentially the highest activity concentration in the  $^{238}\text{U}$  decay chain plus that in the  $^{232}\text{Th}$  decay chain.

## 4 Radiation protection advice

### 4.1 General

This chapter provides advice for laboratory work. It does not replace the need to contact your local radiation protection advisor or supervisor before working with a non-exempt material. It is important to ensure you follow local regulations before receiving materials or starting work.

Simple (and fairly obvious) steps to minimizing exposure to radioactivity are through good laboratory practice, as follows:

- a) Always wear a laboratory coat, gloves and safety goggles when working in a laboratory
- b) Do not eat, drink, chew or smoke in the laboratory
- c) Handle dry materials in a fume hood and wear a protective facemask
- d) Work cleanly and avoid the distribution of materials by working in a large tray
- e) Minimise the time spent near radioactive materials
- f) Maximise the distance between you and the source
- g) Use shielding for high activity sources
- h) Place wastes in two sealed plastic bags before disposal

Doses arising from exposure to characterised materials can be assessed (see below), but it should be noted that any laboratory work may produce products or waste streams that are enriched in one or more radionuclides. Since these materials may be hazardous, the above guidelines should be followed at all times.

### 4.2 How to calculate exposure

In any dose assessment, it is sensible to use a conservative, simple scenario in the first instance. If it is possible to demonstrate safety even when very conservative parameters are used, then the work is clearly safe.

The most active ore in the project comes from Kvanefjeld, and the ore concentrate has a  $^{238}\text{U}$  activity concentration of  $53.5 \text{ Bq g}^{-1}$ . This is used in calculations below to illustrate how doses to laboratory workers can be calculated and the most important exposure routes identified.

#### *External exposure*

External exposure depends on the:

- activity, physical dimensions and material of the source as these all affect the radiation intensity leaving the source
- time spent near the source
- distance between the person and the source
- shielding (only practical for high activity sources)

Dose rates can be calculated using programs such as Microshield, to take these factors into account. As an example, if there were  $19 \text{ kg}$  of the  $53 \text{ Bq g}^{-1}$  ore concentrate in a cubic form, the dose rate  $1 \text{ cm}$  from the surface has been calculated to be approximately  $0.01 \text{ mSv hr}^{-1}$  ( $10 \mu\text{Sv h}^{-1}$ ). This probably doesn't relate very directly to any laboratory exposure situation, so if you have a calibrated dose meter, the dose rates from your material(s) should be measured at appropriate distances. Alternatively, Kemakta can carry out representative calculations relating to your laboratory practice using Microshield.

### ***Internal exposure***

Internal exposure can be assessed using dose coefficients ( $\text{Sv Bq}^{-1}$ ) for inhalation and ingestion (e.g. Radiation Protection 122 part II, 2001). For  $^{238}\text{U}$  in equilibrium with its decay chain, these are  $5.7 \times 10^{-5}$  and  $2.57 \times 10^{-6} \text{ Sv Bq}^{-1}$  (for adult members of the public), respectively (Radiation Protection 122 part II, Tables 23 and 25). In a laboratory, the dose should ideally be below  $1 \text{ mSv a}^{-1}$ , corresponding to a maximum intake of 17.5 Bq by inhalation or 390 Bq by ingestion per year. In terms of amount of material, one would have to inhale 0.33 g or ingest 7.3 g of the Kvanefjeld ore concentrate per year to reach this dose.

To generate dose values, one can use information on the laboratory processes and some assumptions. For example, a person may only work with the Kvanefjeld concentrate in a dry, dust generating form for a maximum of 50 hours a year. If this work is documented to be carried out in a fume hood or wearing a mask, it can be assumed that the maximum dust from the material in the air they breathe is 1/10 of the maximum permissible level for a workplace ( $5 \text{ mg m}^{-3}$ ), i.e.  $0.5 \text{ mg m}^{-3}$ . Using a breathing rate of  $1.2 \text{ m}^3 \text{ h}^{-1}$ , the person would inhale 0.03 g of ore concentrate per year, or receive an inhalation dose of  $0.09 \text{ mSv a}^{-1}$ .

Radiation Protection 122 (part I; 2000) estimates a maximum ingestion of 20 g per working year ( $\sim 0.1 \text{ g day}^{-1}$ ) for a dusty workplace. In a laboratory, the dust level should be controlled and the dust material will not arise solely from the ore concentrate. However, if these factors are ignored and the worker is again assumed to work with the material in a dry, dust generating form for 50 hours a year (of a  $\sim 2000$  hour working year), ingestion of the ore concentrate would be  $0.5 \text{ g a}^{-1}$  and the dose would be  $0.07 \text{ mSv a}^{-1}$ .

Both inhalation and ingestion doses are dependent on the concentration of the radionuclides in the material. If the radionuclides became concentrated in a waste stream, the doses could be higher. This also highlights the need to follow the laboratory guidelines given above throughout the processing of the ore concentrate. Also, if a particular material arising from the ore concentrate was to be dried and ground into a powder, for example, it would be useful to assess the associated risk directly.

### ***Total exposure***

The values from the three exposure routes should be summed to show that the intended handling of the material is safe, e.g.:

External dose ?

Inhalation dose  $0.09 \text{ mSv a}^{-1}$  (0.03 g inhaled)

Ingestion dose  $0.07 \text{ mSv a}^{-1}$  (0.5 g ingestion)

Total internal dose =  $0.16 \text{ mSv a}^{-1}$

Although this involves a rather random selection of data, it provides an example of how laboratory procedures can be assessed quite easily and demonstrated to be safe.

## 5 References

Abramowicz, D. A. (1990) Aerobic and Anaerobic Biodegradation of PCBs: a Review. *Crit. Rev. Biotechnol.* 10, 241-251.

ATSDR Glossary. <http://www.atsdr.cdc.gov/glossary.html>. Last updated January 2009. [Accessed June 2013].

Barry MJ and Meehan BJ. 2000. The acute and chronic toxicity of lanthanum to *Daphnia carinata*. *Chemosphere* 41(10):1669-74.

Briquet, C., Cipriani, M., Ferreira, A.C (2004), "Soil contamination in a rural site used for rare earth industry by-product disposal", Naturally Occurring Radioactive Materials (NORM IV), IAEA TECDOC-1472, IAEA, Vienna, 2004.

British Geological Survey – Rare Earth Elements (2011). (<http://www.mineralsuk.com>)

BSS (2013): Council Directive 96/29/EURATOM of 13 May, 1996, laying down basic safety standards for protection against the dangers arising from exposure to ionizing radiation.

Castor, S.B., and Hedrick, J.B. (2006) Rare earth elements, in Kogel, J.E., Trivedi, N.C., Barker, J.M., and Krukowski, S.T., eds., *Industrial minerals & rocks—Commodities, markets, and uses* (7th ed.): Littleton, Colo., Society for Mining, Metallurgy, and Exploration, Inc. (SME), p. 769–792.

ChemIDplus Advanced. <http://chem.sis.nlm.nih.gov/chemidplus/> . [Accessed June 2013]

Chen Z. (2010). Outline on the development and policies of China rare earth industry: Chinese Society of Rare Earths. <http://wenku.baidu.com/view/d1dc1918227916888486d702.html> [Accessed June 2013]

Da Costa Lauria, D., Rochedo, E.R.R. (2005). The legacy of monazite processing in Brazil, *Radiat. Prot. Dosim.* 114, 546-550.

Diatloff E, Asher CJ, Smith FW. (1999). Foliar application of rare earth elements to maize and mungbean. *Australian Journal of Experimental Agriculture* 39:189–194.

ECHA. European Chemicals agency. <http://echa.europa.eu/web/guest/information-on-chemicals/registered-substances> [Accessed June 2013]

Environment Agency (2013). Exemption Guidance: Guidance for NORM industrial activities on how to comply with the radioactive substances exemption regime.

EPA (2012). Rare Earth Elements: A Review of Production, Processing, Recycling, and Associated Environmental Issues EPA/600/R-12/572. <http://nepis.epa.gov/Adobe/PDF/P100EUBC.pdf> [Accessed May 2013].

European Commission (2014). [http://ec.europa.eu/enterprise/policies/raw-materials/critical/index\\_en.htm](http://ec.europa.eu/enterprise/policies/raw-materials/critical/index_en.htm) [Accessed September 2014].

Fan G, Yuan Z, Zheng H, Liu Z. (2004). Study on the effects of exposure to rare earth elements and health-responses in children aged 7-10 years. *Journal of hygiene research* 33(1):23-8. [Article in Chinese].

Fedele L, Plant J.A, De Vivo B & Lima A. (2008). The rare earth element distribution over Europe: geogenic and anthropogenic sources. *Geochemistry: Exploration, Environment, Analysis*, Vol. 8 2008, pp. 3–18

- Gómez-Aracena, J., R. A. Riemersma, et al. (2006). Toenail cerium levels and risk of a first acute myocardial infarction: The EURAMIC and heavy metals study. *Chemosphere* 64(1): 112-120.
- Haridasan P.P, Pillai P.M.B, Tripathi R.M and Puranik V.D. (2008). Occupational radiation EXPOSURE due to norm in a rare-earth compounds production facility. *Radiation Protection Dosimetry* Vol. 131, No. 2, pp. 217–221.
- Hernandez-Viezcas JA, Castillo-Michel H, Andrews JC, Cotte M, Rico C, Peralta-Videa JR, Ge Y, Priester JH, Holden PA, Gardea-Torresdey JL. (2013). In situ synchrotron X-ray fluorescence mapping and speciation of CeO<sub>2</sub> and ZnO nanoparticles in soil cultivated soybean (*Glycine max*). *ACS Nano*. 26;7(2):1415-23.
- Hirano S. & Suzuki K.T. (1996). Exposure, metabolism, and toxicity of rare earths and related compounds. *Environmental Health Perspectives* 104.(Supp. 1), 85–95.
- IAEA (2002): Management of radioactive waste from the mining and milling of ores. IAEA Safety Guide WS-G-1.2. International Atomic Energy Agency, Vienna.
- IAEA (2003): Derivation of activity limits for the disposal of radioactive waste in near surface disposal facilities. IAEA-TECDOC-1380. International Atomic Energy Agency, Vienna.
- IAEA (2004): Application of the concepts of exclusion, exemption and clearance. Safety guide. Safety Standards Series no. RS-G-1.7. International Atomic Energy Agency, Vienna.
- IAEA (2005): Derivation of activity concentration values for exclusion, exemption and clearance. Safety Reports Series No.44. International Atomic Energy Agency, Vienna.
- IAEA (2009): Classification of radioactive waste. General Safety Guide No GSG-1. International Atomic Energy Agency, Vienna.
- IAEA (2011) International Atomic Energy Agency: Radiation protection and NORM residue management in the production of rare earths from thorium containing minerals. — Vienna : International Atomic Energy Agency, 2011.
- IAEA (2014). Radiation Protection and Safety of Radiation Sources: International Basic Safety Standards. IAEA No. GSR Part 3. IAEA, Vienna.
- IARC. (2012) Monographs on the Evaluation of the Risks to Humans. Agents classified the IARC Monographs, Volumes 1–107. Updated 10 .4.2013 .  
<http://monographs.iarc.fr/ENG/Classification/ClassificationsAlphaOrder.pdf> [Accessed June 2013].
- Iyengar G. V , Kollmer W. E, and Bowen H. J. M. (1978). The elemental composition of human tissues and body fluids, volume 1. Weinheim, New York : Verlag Chemie.
- Kabata-Pendias A. and Mukherjee A.B. (2007). Trace Elements from Soil to Human. Springer. New York. 550 p.
- Kauppila, T. (ed.), Komulainen, H. (ed.), Makkonen, S. (ed.) & Tuomisto, J. (ed.). (2013) Metallikaivosalueiden ympäristöriskinarviointiosaamisen kehittäminen: MINERA-hankkeen loppuraportti. Summary: Improving Environmental Risk Assessments for Metal Mines: Final Report of the MINERA Project. Geological Survey of Finland, Report of Investigation 199, 223 p.
- KOSHANET. <http://english.kosha.or.kr/english/main.do>. [Accessed June 2013].

Kurttio, P., Harmoinen, A., Saha, H., Salonen, L., Karpas, Z. Komulainen, H., Auvinen, A. 2006. Kidney Toxicity of Ingested Uranium From Drinking Water. American Journal of Kidney Diseases. Volume 47, Issue 6, Pages 972-982, June 2006.

Lenntech. <http://www.lenntech.com/periodic/elements/sc.htm> [Accessed June 2013].

L. F. Da Silva ( Pers. comm. 2013). Luiz Felipe da Silva, IAEA/OECD Uranium Group.

Maher K, Bargar JR, Brown GE Jr.(2013). Environmental speciation of actinides. Inorg Chem. 1;52(7):3510-32. doi: 10.1021/ic301686d.

Pairon J.C, Roos F, Iwatsubo Y, Janson X, Billon-Galland MA, Bignon J, Brochard P. (1994). Lung retention of cerium in humans. *Occupational and Environmental Medicine* 51:195-199.

Pałasz A, Czekaj P. (2000). Toxicological and cytophysiological aspects of lanthanides action. *Acta Biochim Pol* 2000;47:1107-14.

Palmer RJ, Butenhoff JL, Stevens JB. (1987) Cytotoxicity of the rare earth metals cerium, lanthanum, and neodymium in vitro: comparisons with cadmium in a pulmonary macrophage primary culture system. *Environ Res* 1987;43:142-56.

Paul, J. and Campbell, G. (2011) Investigating Rare Earth Element Mine Development in EPA Region 8 and Potential Environmental Impacts. U.S. Environmental Protection Agency. EPA Document-908R11003, 2011.

Peng RL, Pan XC, Xie Q. (2003). Relationship of the hair content of rare earth elements in young children aged 0 to 3 years to that in their mothers living in a rare earth mining area of Jiangxi. *Zhonghua Yu Fang Yi Xue Za Zhi*. 37(1):20-2. [Article in Chinese, abstract in English]

Priester, J. H.; Ge, Y.; Mielke, R.; Horst, A. M.; Cole Moritz, S.; Espinosa, K.; Gelb, J.; Walker, S. L.; Nisbet, R. M.; An, Y. J.; et al. (2012). Soybean Susceptibility to Manufactured Nanomaterials with Evidence for Food Quality and Soil Fertility Interruption. *Proc. Natl. Acad. Sci. U.S.A.* [www.pnas.org/cgi/doi/10.1073/pnas.1205431109](http://www.pnas.org/cgi/doi/10.1073/pnas.1205431109).

Radiation Protection 95: Reference levels for workplaces processing materials with enhanced levels of naturally occurring radionuclides. European Commission, Directorate-General Environment.

Radiation Protection 107: Establishment of reference levels for regulatory control of workplaces where materials are processed which contain enhanced levels of naturally occurring radionuclides. European Commission, Directorate-General Environment.

Radiation Protection 113: Recommended radiological protection criteria for the clearance of buildings and building rubble from the dismantling of nuclear installations. Recommendations of the group of experts set up under the terms of Article 31 of the Euratom Treaty. European Commission, Directorate-General Environment.

Radiation Protection 122 (2000): Practical use of the concepts of clearance and exemption: Part I - Guidance on General Clearance Levels for Practices. European Commission, Directorate-General Environment.

Radiation Protection 122 (2001): Practical use of the concepts of clearance and exemption: Part II - Application of the concepts of exemption and clearance to natural radiation sources. European Commission, Directorate-General Environment.

Redling K. (2006) Rare earth elements in agriculture with emphasis on animal husbandry. Academic dissertation. Tierärztlichen Fakultät der Ludwig-Maximilians-Universität München.

Rim KT, Koo KH and Park JS. (2013) Toxicological Evaluations of Rare Earths and Their Health Impacts to Workers: A Literature Review. *Saf Health Work* 2013;4:12-26.

Sabbionia E, Minoiab C, Pietraa R, Fortanera S, Gallorinic M, and Saltellia A. (1992) Trace element reference values in tissues from inhabitants of the European Community. II. Examples of strategy adopted and trace element analysis of blood, lymph nodes and cerebrospinal fluid of Italian subjects. *The Science of the Total Environment*, 120(1-2):39 – 61.

Spalla S, Baffi C, Barbante C, Turetta C, Cozzi G, Beone GM, Bettinelli M. 2009. Determination of rare earth elements in tomato plants by inductively coupled plasma mass spectrometry techniques. *Rapid Commun Mass Spectrom*. 23(20):3285-92

Tyler, Germund (2004) . Rare earth elements in soil and plant systems – A review. *Plant and Soil* 267: 191–206,

U.S. Environmental Protection Agency (2012) Rare Earth Elements; EPA 600/R-12/572 | December 2012 | [www.epa.gov/ord](http://www.epa.gov/ord): Rare Earth Elements: A Review of Production, Processing, Recycling, and Associated Environmental Issues.

US Geological Survey.

[http://www.google.com/imgres?imgurl=http%3A%2F%2Fgulfsci.usgs.gov%2Ftampabay%2Fdata%2F2\\_biogeochemical\\_cycles%2Fimages%2Fdecaychain.gif&imgrefurl=http%3A%2F%2Fgulfsci.usgs.gov%2Ftampabay%2Fdata%2F2\\_biogeochemical\\_cycles%2Fradionuclides.html&docid=fQgbp83ox\\_ZtsM&tbnid=NeMzVp85r1430M%3A&w=840&h=600&ei=-twbVIn7N6TmyQOG94LQDQ&ved=0CAIQxiAwAA&iact=c](http://www.google.com/imgres?imgurl=http%3A%2F%2Fgulfsci.usgs.gov%2Ftampabay%2Fdata%2F2_biogeochemical_cycles%2Fimages%2Fdecaychain.gif&imgrefurl=http%3A%2F%2Fgulfsci.usgs.gov%2Ftampabay%2Fdata%2F2_biogeochemical_cycles%2Fradionuclides.html&docid=fQgbp83ox_ZtsM&tbnid=NeMzVp85r1430M%3A&w=840&h=600&ei=-twbVIn7N6TmyQOG94LQDQ&ved=0CAIQxiAwAA&iact=c). [Accessed June 2013].

Vocaturro G., Colombo F., Zanoni M., Rodi F., Sabbioni E., Pietra, R., (1983). Human exposure to heavy metals. Rare earth pneumoconiosis in occupational workers. *Chest*, 83, 780-783.

Wu L, Zhou YP, Zhong HJ. (2003) A case-control study on the risk factors of leukemia in mining areas of rare-earth in South Jiangx. *Zhonghua Liu Xing Bing Xue Za Zhi*. 2003 Oct;24(10):879-82. Article in Chinese, abstract in English.

Xie Z B, Zhu J G, Chu H Y, Zhang Y L, Zeng Q, Ma H L and Cao Z H (2002). Effect of lanthanum on rice production, nutrient uptake, and distribution. *J. Plant Nutr*. 25, 2315–2331.

Xiong B. K. (1995) Application of Rare Earths in Chinese Agriculture and their perspectives of Development. In *Proceeding of the Rare Earths in Agriculture Seminar*, 20. September 1995, pages 5 – 9, Canberra, ACT Australia, 1995.

Zhang S. and Shan X.-Q. (2001) Speciation of rare earth elements in soil and accumulation by wheat with rare earth fertilizer application. *Environmental Pollution*, 112:395 – 405, 2001.

Zhang F. S., Yamasaki S., and Kimura K. (2001) Rare earth element content in various waste ashes and the potential risk to Japanese soils. *Environment International*, 27(5):393 – 398, 2001.

Zhang H, He X, Bai W, i Guo X, Zhang Z, Chaia Z and Zhaoa Y. (2010) Ecotoxicological assessment of lanthanum with *Caenorhabditis elegans* in liquid medium. *Metallomics* 2, pp.806-810.

Zhang P, Ma Y, Zhang Z, He X, Zhang J, Guo Z, Tai R, Zhao Y, Chai Z. (2012) Biotransformation of ceria nanoparticles in cucumber plants. *ACS Nano*. 2012 27;6(11):9943-50.

Zhu W, Xu S, Shao P, Zhang H, Wu D, Yang W, Feng J, Feng L. (2005) Investigation on Liver Function Among Population in High Background of Rare Earth Area in South China. *Biological Trace Element Research*. Vol. 104.

## Appendix 1. The decay chains of $^{238}\text{U}$ , $^{232}\text{Th}$ and $^{235}\text{U}$ (US Geological Survey)

