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Radiological implications of NORM in the production of rare-earth compounds

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Abstract. The composite rare earth chloride produced from monazite contain low levels of natural radionuclides and is being used as the input material for the production of individual rare earth compounds which have wide applications. Gross alpha, beta and ^{228}Ra activity concentrations in composite rare earth chloride and individual rare earth compounds such as oxides of Ce, Nd, Pr, Sm, Gd etc are presented. The significant radionuclide of environmental concern is identified as ^{228}Ra and the activity level varied between 0.1 and 7.8 Bq.g^{-1} in different compounds. Sporadic ^{228}Ra levels up to 16 Bq.g^{-1} was observed in Lanthanum oxide. The external gamma exposure rates and airborne activity due to thorium and thoron progeny in the process locations are studied. The activity levels in liquid effluent and potential exposure scenarios are indicated.

1. INTRODUCTION

Radiation protection and management of wastes generated by industries that process minerals and raw materials containing naturally occurring radioactive materials (NORM) are of concern in the context of long term environmental implications of waste disposal. Chemical compounds of rare-earth (RE) elements (La to Lu) have wide applications in daily life. They are commercially exploited from minerals such as monazite, bastnasite, xenotime, allanite etc. Most of these natural ores and minerals contain low or significant levels of thorium and uranium series nuclides. The thorium content varies from 0.1% to 10% and uranium content varies from very low percentage to 0.8% depending on the mineral and region of occurrence [1]. Monazite (Ce,La,Th)PO_4, a phosphate mineral containing nearly 9% thorium as ThO_2 is the starting material for the production of rare earth compounds in India. Caustic digestion followed by selective extraction in HCl is the method used to separate composite rare-earths chloride.

Limited studies on the radiation protection aspects in rare-earths industry are reported [2, 3]. A variety of diversified RE compounds that have wide applications in daily life and advanced scientific research are produced from the composite RE chloride by different chemical processes such as precipitation, solvent extraction and ion-exchange methods. The present studies are carried out in a rare-earths producing plant typically convert composite RE chloride to different compounds such as RE fluoride, oxide, carbonate and other individual rare earths compounds with emphasis on radiological aspects.

2. MATERIALS AND METHODS

Different types of rare earths compounds were collected from the production plant and analysed for gross alpha, gross beta and ^{228}Ra activity concentrations. The gross alpha and beta activity concentration in the samples were estimated by standard counting methods using a ZnS(Ag) alpha counter (Nucleonix Model.AP165) and a Geiger Muller counter (Nucleonix Model: RC605A). ^{228}Ra activity in the samples were estimated by counting in a well-type $2'' \times 2''$ NaI(Tl) gamma spectrometer. (ECIL, Model SC604C). The combined ^{228}Ac peaks of 911 keV and 960 keV was used for the estimation of ^{228}Ra activity assuming transient equilibrium between the isotopes in the samples. The set-up was calibrated

Table 1. Activity concentration in rare earth compounds.

Rare earth (RE) compounds	Gross alpha $Bq.g^{-1} \pm SD$	Gross beta $Bq.g^{-1} \pm SD$	^{228}Ra $Bq.g^{-1} \pm SD$
Composite RE chloride*	1.3 ± 0.6	1.5 ± 0.7	0.45 ± 0.20
RE fluoride	4.3 ± 0.8	3.4 ± 0.9	1.23 ± 0.27
RE carbonate	7.0 ± 1.0	6.4 ± 0.9	3.80 ± 0.45
RE oxide	4.7 ± 0.8	4.2 ± 0.8	1.90 ± 0.35
Cerium oxide – A grade	14.5 ± 1.2	18.3 ± 1.3	5.20 ± 0.70
Cerium oxide – B grade	7.7 ± 1.0	10.3 ± 1.1	2.30 ± 0.37
Cerium hydrate	3.7 ± 0.8	3.5 ± 0.9	1.40 ± 0.27
Cerium nitrate	<0.5	<0.5	<0.15
Neodymium oxide	3.1 ± 0.7	1.2 ± 0.7	0.20 ± 0.12
Lanthanum oxide	18.1 ± 1.4	22.4 ± 1.4	7.80 ± 0.80
Praseodymium oxide(99%)	<0.5	1.5 ± 0.8	0.54 ± 0.20
Samarium oxide(99%)	1.3 ± 0.6	5.2 ± 0.8	0.83 ± 0.27
Gadolinium oxide(99%)	<0.5	1.7 ± 0.8	0.48 ± 0.20

*Mean value of 15 samples. All other values are mean values of 3 samples each.

using a standard monazite ore of known ^{228}Ra content in an identical geometry. The typical counting time was 10000 s and the minimum detectable activity was $0.15\,Bq.g^{-1}$ at 1σ confidence level. The external gamma exposure rates at different locations were measured using a Scintillometer. Air samples were collected using vacuum pumps having a flow rate of 50 lpm. The samples were collected on glass fibre filter papers having a collection surface of 2.5 cm dia representing breathing zones. A programmed alpha counting method [3] was used to estimate potential alpha energy concentration (PAEC) due to thoron progeny and long-lived alpha activity. The committed annual effective dose from the inhaled intake of thorium activity was estimated. In the case of thoron progeny, the inhalation dose was estimated by using the dose conversion factor 1.67 mSv per Working Level Month (WLM) as given by Basis Safety Standards [4]. In order to assess the radiological impact due to waste streams, samples of liquid effluent were collected from the plant analysed for gross alpha, gross beta and ^{228}Ra activities by the standard analytical procedures [5].

3. RESULTS AND CONCLUSIONS

Table 1 shows the gross alpha and beta activities and concentration of ^{228}Ra in different types of chemical compounds of rare earth produced. Wide variations in the activity levels were observed depending upon the process conditions and chemical nature of the compounds.

The composite rare earth chloride showed mean gross alpha activity of $1.3 \pm 0.6\,Bq.g^{-1}$ and beta activity of $1.5 \pm 0.7\,Bq.g^{-1}$. As ^{228}Ra is expected to be the major contaminant in rare earth compounds extracted from monazite, analyses were carried out to assess ^{228}Ra activity in all the samples. The mean ^{228}Ra in rare earth chloride was found to be $0.45 \pm 0.2\,Bq.g^{-1}$. The gross alpha and beta activities in other commercial grade rare earth samples such as oxides, carbonates, fluorides etc were in the range 2.2 to $18.1\,Bq.g^{-1}$ and 2.4 to $22\,Bq.g^{-1}$ respectively. ^{228}Ra in these samples varied between 0.87 and $7.8\,Bq.g^{-1}$. Higher activity was observed in lanthanum and cerium oxides. In lanthanum oxide, ^{228}Ra activity upto 16 Bq.g-1 was observed. High purity rare earth compounds showed still lower activity levels as expected. The ^{228}Ra activity levels were below the exemption limit as per the safety standards where a limit of $10\,Bq.g^{-1}$ is specified for regulation [4].

3.1 External gamma dose

The external gamma exposure rates measured at different locations in the rare earth process pant are shown in Table 2. The radiation fields were generally below $1\,\mu Gy.h^{-1}$. Accumulated sludge/scales in

Table 2. External gamma exposure rates in rare earth compounds processing.

Location	Gamma exposure rate (μ Gy.h^{-1})	
	Range	Mean
RE chloride storage tanks	0.6–1.2	1.0
RE chloride storage tank – sludge/scales	10–40	15 (Max.100)
Cerium hydrate tanks	0.3–0.7	0.4
RE carbonate tanks	0.7–1.0	0.8
Mixer settlers – solvent extraction	0.6–0.9	0.8
REF process tanks	1.0–2.0	2.0
Calciner/Product drier	0.5–1.0	0.7
Mixer settlers – cerium purification	0.2–0.4	0.3
Filter presses	0.4–0.6	0.5
General background	0.3–0.8	0.5

the RE chloride solution storage tank showed gamma exposure rate upto 100 μ Gy.h^{-1}. The average general background in the worker occupied areas was 0.5 μ Gy.h^{-1} and the natural background outside the plant premises was measured as 0.15 μ Gy.h^{-1}. Hence the likely incremental external dose for the occupancy period of 2000 h in a year is estimated to be 0.7 mSv and can be considered as the potential dose in the case of large scale processing of rare earth chloride to produce high purity RE compounds. As many of these compounds are used only in small quantities for various applications, the likely external dose received by a worker exposed to gamma from small quantities of the compounds is estimated to be in the range 0.03 to 1.3 mSv per year using the conversion factors given by IAEA safety report series No.49 [6] for 2000 hours of occupation. In real situations the actual occupancy will be much lower and hence the likely external doses also will be much lower than estimated.

3.2 Inhalation dose due to thoron progeny and long-lived alpha activity

The potential alpha energy concentration (PAEC) due to thoron progeny and airborne long-lived alpha activity due to ^{232}Th in rare earth process plant are provided in Table 3. Measurements were carried out during the period 2003 to 2007.

The annual average PAECs were in the range 15–42 mWL whereas individual samples showed PAEC ranging from 2 to 162 mWL. The average for the five years data is worked out to be 30 mWL. The derived air concentration limit for the occupational settings applicable to the plant is 1000 mWL and the current levels are only 3% of the limit. Hence the annual inhalation dose to occupational workers due the intake of thoron progeny PAEC is estimated as 0.6 mSv, assuming 2000 h of work occupancy. Airborne ^{232}Th activity at various locations in the plant ranged between 0.001 and 0.023 Bq m^{-3}. The mean activity during the period was 0.005 ± 0.002 Bq m^{-3}. Assuming a breathing rate of 1.2 m^3 h^{-1} for 2000 working hours in a year, the likely inhalation dose is worked out as 0.62 mSv. Including the external dose component of 0.7 mSv, the likely total annual dose to occupational worker is estimated to be 1.92 mSv.

Table 3. Airborne activity in the RE Process plant.

Year	Thoron progeny, PAEC (mWL)		^{232}Th(Bq.m^{-3})	
	Range	Mean $\pm$ SD	Range	Mean $\pm$ SD
2003	5–90	15 ± 5	0.001–0.012	0.008 ± 0.003
2004	7–155	30 ± 7	0.002–0.014	0.006 ± 0.002
2005	5–148	42 ± 10	0.001–0.023	0.007 ± 0.003
2006	3–162	35 ± 8	0.001–0.018	0.005 ± 0.002
2007	2–139	41 ± 10	0.001–0.011	0.003 ± 0.001

Table 4. Activity in liquid effluent before treatment.

Activity	Range Bq.l^{-1}	Mean $\pm$ SD, Bq.l^{-1}
Gross alpha	40–160	107 ± 62
Gross beta	50–350	142 ± 69
^{228}Ra	5–46	24 ± 10

3.3 Effluents/wastes

Table 4 gives the radioactivity analysis of the liquid effluent generated in the plant before treatment for final disposal into aquatic environs. The gross alpha, beta and ^{228}Ra activities in the effluent showed mean values 107 ± 62, 142 ± 69 and 24 ± 10 Bq.l^{-1} respectively. These are treated to contain the activity levels specified by the regulators before discharge into the environment. The gaseous releases from the plant normally contain only low levels of thoron progeny. Measurements indicated no significant environmental concentration of thoron progeny attributable to the plant operation. As ^{228}Ra is observed to be the potential environmental contaminant further work on the ingestion dose contribution to the public through the waste disposal is required.

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