

Naturally Occurring Radioactive Materials (NORM) in the Extraction and Processing of Rare Earths

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

1. Introduction

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

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

2. Rare earth minerals and NORM

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

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

TABLE 1. TYPICAL COMPOSITION OF SOME RARE EARTH MINERALS

	Composition (%)			
	TREO ^a	U ₃ O ₈	ThO ₂	P ₂ O ₅
Monazite, Australia	61.33	0.34	6.55	26.28
Monazite, India	59.68 (60)	0.37 (0.35)	9.58 (8.0)	26.23 (27)
Monazite, Malaysia	59.65	0.24	5.90	25.70
Monazite, Thailand	60.20	0.44	5.76	26.52
Monazite, Korea	60.20	0.45	5.76	26.52
Monazite, DPRK	42.65	0.18	4.57	18.44
Bastnaesite	58–74	—	0.11–0.20	0.64–0.94
Xenotime, Malaysia	54.00	0.81	0.83	26.20
Gadolinite	32–46	—	up to 2	—

^a Total rare earth oxides.

3. Radiological properties of the thorium and uranium decay chains

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

3.1. Concept of secular equilibrium

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

3.2. Radiological hazards of thorium

The hazards from thorium can be from both external and internal sources. External hazards are due to high energy beta and gamma rays, while internal hazards are mainly due to alpha emitting radionuclides

deposited inside the body. The internal hazard is mainly by way of inhalation of thorium bearing dust and short-lived decay products of thoron gas (^{220}Rn). Inhaled thorium bearing dust is deposited in different regions of the respiratory tract depending on the particle size. The probability of deposition in different regions of the respiratory tract depends on the Activity Median Aerodynamic Diameter (AMAD) [4]. A fraction of deposited activity becomes solubilized and/or transported to various body tissues through body fluids.

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

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

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

4. Mining, mineral separation and concentration of rare earth ores

4.1. Monazite

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

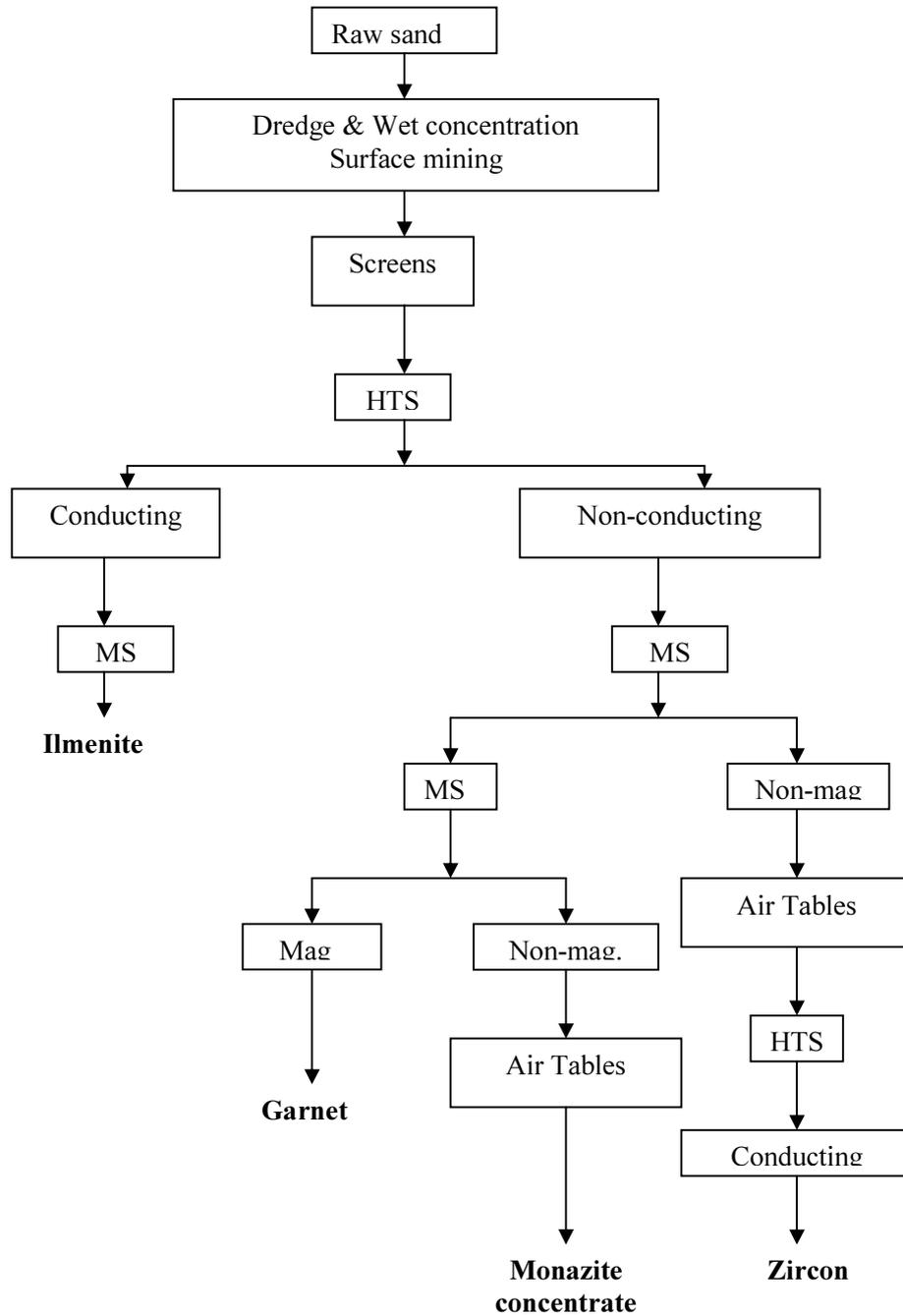
TABLE 2. TYPICAL RADIOACTIVITY CONTENT OF BEACH SANDS AND MONAZITE (INDIA)

	Activity concentration (Bq/g)		Radiation field, infinite spread ($\mu\text{Gy/h}^1$)
	^{232}Th	^{238}U	
Raw sand	0.32–6.44 (78.5–1570ppm Th)	0.04–0.74 (2.9–58.8 ppm U)	0.5–5.0
Monazite	322 (78 543 ppm Th)	37 (2942 ppm U)	180–250

Note: Th chain activity (equilibrium) = $10 \times ^{232}\text{Th}$ activity
 U chain activity (equilibrium) = $14 \times ^{238}\text{U}$ activity.

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

Lanka, Malaysia, Vietnam, Taiwan, Brazil, Australia, South Africa, Egypt, Burundi, DRC, Madagascar and USA [1].



HTS - High Tension Separator
MS - Magnetic Separator

Fig. 1. Simplified process flow sheet for monazite separation

4.2. Bastnaesite

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

4.3. Complex ores – China

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

5. Rare earth extraction processes

5.1. Processing of monazite.

India, Brazil and Malaysia are the major producers of rare earth concentrates from monazite. Production of rare earths from black monazite by Pacific Ocean Rare Earths in Taiwan has also been reported. Malaysian tin ore, ‘amang’, contains other minerals along with monazite and xenotime. Malaysian Rare Earth Corporation (xenotime) and Asian Rare Earth Sdn started working in 1982 for production of RECl₃. China is known to be producing rare earths from monazite of Hunan province from 1977 [2].

5.1.1. Sulphuric acid decomposition of monazite [7]

Several variations of the sulphuric acid digestion of the mineral concentrate were in vogue during the early years of processing of monazite. Essentially the process consisted of digestion of the ground (ball milled) mineral using fuming H₂SO₄ at 200–220^oC in a cast iron or silicon iron or glass lined reactor. The mineral is decomposed exothermically forming a pasty mixture of sulphates and acid sulphates suspended in phosphoric acid and excess sulphuric acid. This is further treated with cold water to form a stable solution of sulphates of RE, Th and U. The residue contains unreacted monazite, silica and other impurity minerals. Neutralization causes precipitation of thorium phosphate and leaves most of the rare earths and uranium in the solution. Various processes had been developed for the production of individual rare earths and concentrates. However, extensive purification of the rare earths fraction was required for removing the thorium, a significant portion of which precipitate with the rare earth double sulphate. This process has been now replaced with alkali digestion

5.1.2. Alkali digestion of monazite and selective acid extraction of rare earths

Chemical processing of monazite, an orthophosphate of Th and the rare earth elements, is done by alkali digestion and selective extraction with hydrochloric acid. Fig 2 gives a simplified process flow sheet of the process [8, 9].

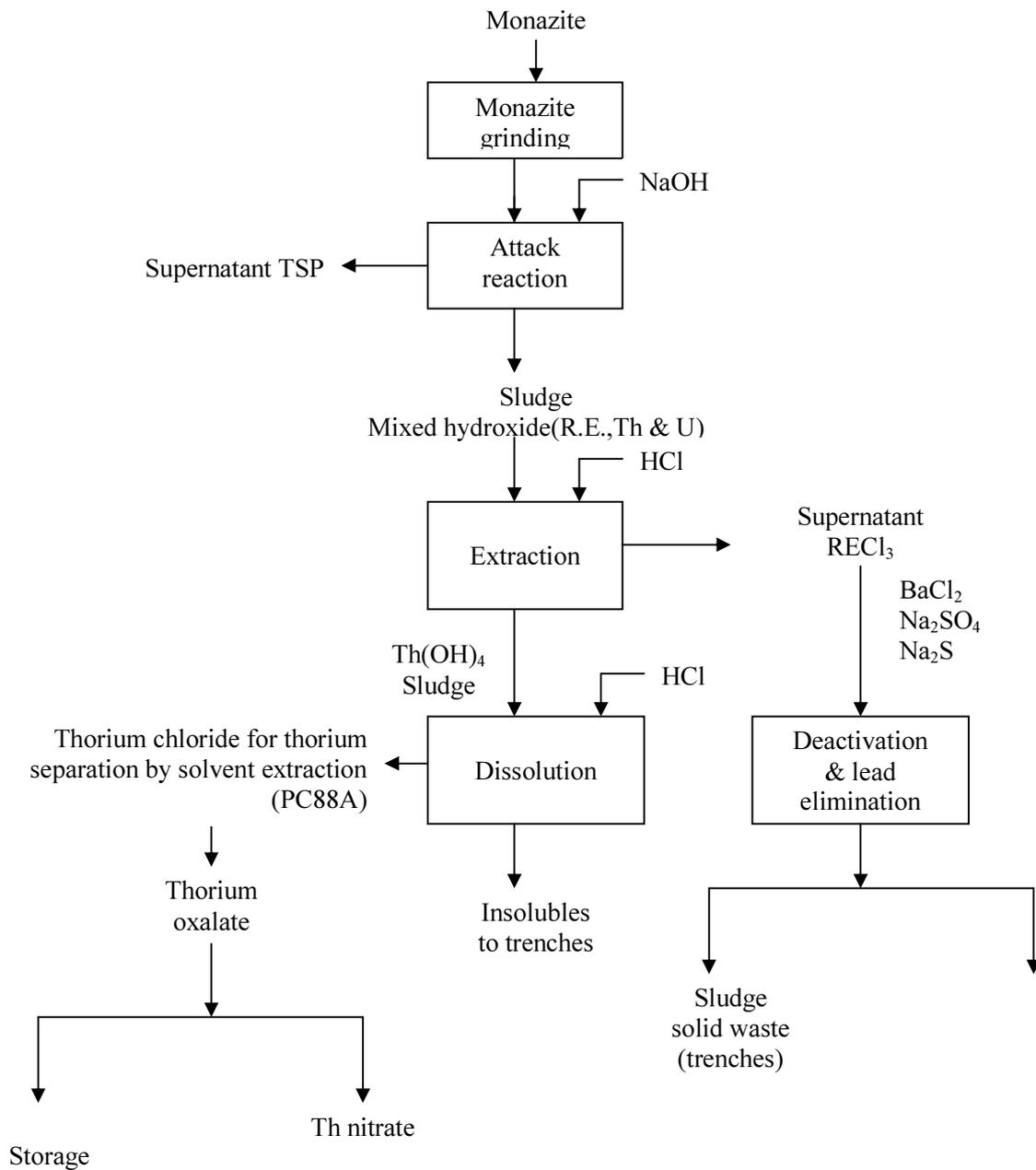
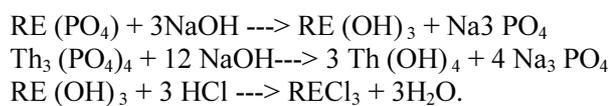


FIG. 2. Simplified process flow sheet for monazite processing

Monazite is finely ground in a ball mill and mixed with caustic soda in reaction vessels known as 'attack tanks'. The reacted mass, which contains the trisodium phosphate and hydroxides of thorium, uranium and rare earths along with unreacted monazite, is leached with water when trisodium phosphate gets dissolved leaving behind the hydroxides. This is subsequently leached with dilute hydrochloric acid when the rare earth fraction goes into solution leaving behind the insoluble hydroxides. The reactions can be represented as follows:



The trisodium phosphate (TSP) byproduct is converted into crystals, packed and sold. Thorium hydroxide is stored as such or the crude thorium hydroxide from the extraction stage is dissolved in concentrated HCl. The unattacked sand is separated by filtration and thorium is converted to thorium oxalate and stored. During the above process the radium (^{228}Ra) and lead present in monazite appear in the rare earth composite chloride (RECl_3) fraction. These are removed from the product by a process known as 'deactivation' with 'lead elimination'. Radium present in rare earth is carried down by barium sulphate by precipitating barium chloride with sodium sulphate. Lead is eliminated by sodium sulphide. The solid radioactive waste obtained from the deactivation with lead elimination termed as "mixed cake" is suitably contained and disposed of as active waste. The deactivated and lead free composite rare earths chloride is evaporated and made into flakes and marketed. For the separation of individual rare earths, a solvent extraction process is employed.

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

5.1.3. Processing of bastnaesite and other ores

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

At present mixed bastnaesite-monazite concentrate is industrially treated using a high temperature sulphuric acid process at about 800°C , followed by solvent extraction. This process leads to a large amount of HF containing waste gas and a slag-to-concentrate weight ratio of up to 0.66, annually yielding tens of thousands of tons of slag containing 0.2 weight percent of thorium. This has to be stored as active waste. The recent development of a Stepwise Carbo-chlorination–Chemical Vapour Transport (SC-CVT) process for rare earth extraction from bastnaesite and mixed bastnaesite-monazite concentrate of Chinese origin is reported in Ref. [12]. This process is claimed to be more environment friendly and energy saving.

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

6. Occupational exposures

Radiological safety in the different stages of the rare earth industry (monazite based) is assured by ensuring compliance with the relevant IAEA standards as well as national regulations [13–15].

6.1. Mineral separation plants

Typical radiation fields observed at various stages of the operations are provided in Table.3. It is seen that background radiation fields in the plants range from 1 to $100 \mu\text{Gy}\cdot\text{h}^{-1}$. The mineral separation plants are situated at the natural high background areas and radiation fields in the range of 1 to $3 \mu\text{Gy}\cdot\text{h}^{-1}$ are typically the background in the area. Mineral processing especially dry milling gives rise to dust which contains radioactive particles due to finer grains of monazite which get airborne in the process. Since the activity involved is long-lived (Th-nat), this give rise to committed Dose (CD). The air activity levels due to Th encountered in these plants are of the order of less than 1/20 of the corresponding Derived Air

Concentration [16, 17]. Internal dose attributable to thoron and thoron daughters is not significant in the mineral separation plants due to very low emanation of thoron from the mineral [6].

TABLE 3. TYPICAL RADIATION FIELDS ASSOCIATED WITH MINERAL SEPARATION

Location	Radiation field, $\mu\text{Gy h}^{-1}$
Mining areas	1.0 – 4.0
Raw Sand	1.0 – 4.0
Concentration plant	1.0 – 1.5
Sand concentrate (dump yard)	4.0 – 15.0
Sand concentrate storages	5.0 – 20.0
Screens	2.0
Primary *HTS	4.0
Monazite HTS	6.0
Magnetic separators	2.0 – 4.0
Monazite air tables	8.0 – 20.0
Monazite wet circuit	5.0 – 30.0
Monazite bags	200
Zircon	2.0 – 4.0
Ilmenite, rutile, garnet	2.0
Gen. background	1-3

* HTS: High Tension Separators

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

6.2. Chemical processing of monazite [18, 19]

Radioactive equilibrium of Th chain is broken at the acid extraction stage. Thereafter the build-up and decay of activity at different stages follow separate routes. The activity inventory at various stages is marked by disequilibria and each stage has to be accounted for its activity by taking the material balance, fractionation and build-up/decay. Typical radiation fields observed at different stages of monazite processing are given in Table.4. The fields in the normally occupied areas range from 0.5 to 8 $\mu\text{Gy h}^{-1}$. Radiation fields up to 1500 $\mu\text{Gy h}^{-1}$ are observed on some of the deactivation tanks due to the build up of ^{228}Ra activity on the rubber lining of these tanks. Occupancy in such areas is controlled by standard radiation protection practices.

TABLE 4. TYPICAL RADIATION FIELDS ASSOCIATED WITH MONAZITE PROCESSING

Location	Radiation field, $\mu\text{Gy h}^{-1}$
<i>Caustic Soda Digestion plant:</i>	
Gen Background	0.5 – 2.0
Ball milling	1.0 – 5.0
Ball mill	15 - 20
Monazite bag, 50 kg	200
Digestion area	2.0 – 5.0
Digestion tanks	10 - 15
<i>Rare Earths Extraction plant:</i>	
Gen Background	1.0 – 8.0
Mixed hydroxide filters	15 - 20
Re Extraction area	2.0 - 5.0
Extraction tanks	20 - 25
Thorium Conc. filtration	10 - 35
Th. Conc. filter	30 - 35
Deactivation area	15 - 40
Deactivation tanks	300 – 1000
RE Chloride Evaporation area	1.0 – 2.0
RE Chloride drums	1.0 – 2.0
Diversified RE Products Plant	<0.5 – 1.5
Heavy Rare Earths Plant	<0.5
Nd-Pr concentrate plant	<0.5
Product handling area/store	<0.5 – 2.0
<i>Active wastes:</i>	
Mixed cake (solid waste)	400- 600
Thorium concentrates (wet)	60 – 70
Thorium oxalate	200
Aged thorium concentrates	500 - 600
Insoluble waste (Unreacted monazite)	30 - 100
Effluent Plant cake	2.0

Apart from external exposure, chemical processing involve significant internal exposure mainly due to inhalation of airborne long lived activity due to thorium and short lived activity due to thoron and daughter products. High emanation of thoron is observed from surfaces contaminated by spillages and from thorium concentrate. The thoron daughter concentrations in the plants generally are in the range of 25 to 200 mWL (Derived Air Concentration, DAC= 1000mWL). However, these levels could be as high as 1 to 3 WL in contaminated areas and bulk storages (restricted entry/ no entry /entry with respiratory protection) which are under constant surveillance. Inhalation of thorium bearing dust is possible in case of releases from ball milling, drying etc. By engineered and operational controls, the air activity levels of less than 1/20th of DAC are achieved in these plants. Typically external and internal exposures contribute equally to the total exposure in monazite processing plant [6]. In the case of a plant processing 3000 to 4000 tons of monazite annually, the individual annual exposures for the past 25 years were in the range 3.0 - 9.0 mSv. The representative exposures for rare earth production are in the range 0.30 – 1.00 person mSv (mean = 0.64, SD = \pm 0.19) per ton of rare earth concentrate produced by chemical processing of monazite. The wide range in these exposures was due to the plant conditions prevalent from time to time, modifications, control measures etc. Table 5 gives the occupational exposure history in the Indian rare earths industry for the past few years [18, 19].

TABLE 5. RADIATION EXPOSURES IN BEACH MINERAL PROCESSING INDUSTRY (1995-2003) [6, 18, 19].

	Minerals Plant I Low monazite	Minerals Plant II Higher monazite	Rare Earths Plant	Exposure Limit
Average per-capita Yearly dose Range (mSv)	1.50 – 2.50	4.20 – 7.00	3.00 - 9.00	20 mSv/year
Collective dose Annual (PersonSv) -range	0.13 - 0.70	1.3 0- 2.60	2.30 - 3.90	-----

6.3. Radioactivity concentrations in rare earth concentrates and compounds

The ^{228}Ra concentrations in the rare earths chloride concentrate before deactivation vary from 200 to 300 Bq g^{-1} . The Deactivated lead free rare earths chloride concentrate contains ^{228}Ra in the range 0.5 to 1.5 Bq g^{-1} . The Cerium hydrate and Nd-Pr carbonate contain ^{228}Ra of the same order, 4–5 Bq g^{-1} . The Sm-Gd concentrate has very low content of ^{228}Ra , approx. 0.2 Bq g^{-1} . These are below the exempt levels specified in BSS115 [16].

7. Waste management and environmental impact

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

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

7.1. Generation, treatment and disposal of radioactive waste

7.1.1. Mining and mineral separation

Solid waste

Surface mining of beach washings and inland placers as well as dredge mining generate large volumes of overburden which include topsoil, clay, silica sand, slime, peat, organic waste (vegetation, trees, roots etc.), screen-overs and shells. The volume of waste generated depends on the heavy mineral concentration in the mined raw sand and the recovery achieved in the processes. Typically 600 to 700 kg of tailings are generated per ton of raw sand mined and is used as backfill. The mineral free tailings from the pre-

concentration stages, mainly containing silica, are used for refilling the dredged area. The tailings sand generated in the dry mill typically vary from 70 kg to 100 kg per ton of concentrated feed sand processed in the mill. The mill tailings, which contain unrecovered monazite and other minerals, are recycled along with fresh feed to the dry mill. The dry and wet solid tailings are transported by mechanized means such as pumping, conveyors, and covered trucks and dump trucks/bins to the disposal site. The water used for wet concentration of minerals also carries solid tailings. The crude monazite concentrate also requires appropriate management. For long-term storage, the monazite rich fraction of the processed mineral sand/monazite bearing waste is segregated appropriately transported and stored in earthen trenches. The crude monazite concentrate slurried in water is directly pumped into the trench and periodically topped with about 1 m of mineral free sand to reduce the radiation fields to natural levels encountered in the area (NHBRA levels). These trenches are in controlled areas located away from normally occupied areas well demarcated with boundary fencing/wall and identifiable with prominent caution boards. Table 6 gives typical radioactivity levels associated with solid waste from mining and mineral separation. The mined and refilled areas are replanted and rehabilitated. There is a continuous reforestation programme for restoring the ecological balance to the maximum extent possible [23].

TABLE 6. TYPICAL RADIOACTIVITY IN SOLID WASTE (MINING AND MINERAL SEPARATION)

Solid waste	gross alpha (Bq g ⁻¹)	gross beta (Bq g ⁻¹)	radiation field (μGy h ⁻¹)
Mining tails	0.3 - 0.5	1.6- 4.6	0.3 - 0.5
Preconcentration tails	0.3 - 0.8	1.7- 3.8	0.3 - 0.4
Mill tails	50- 80	250 – 350	30 – 50

Liquid effluents

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

TABLE 7. TYPICAL RADIOACTIVITY IN WATER (MINING AND MINERAL SEPARATION)

	Mining	Pre-concentration	Mill
Gross alpha (Bq.l ⁻¹)	0.04	0.01	0.05
Gross beta (Bq.l ⁻¹)	0.04	0.03	0.09

The gaseous releases are mainly the exhausts from the driers which may contain SPM, SO₂ etc. the release of radioactivity through the exhaust air during the mineral separation is negligible

7.1.2. Chemical processing of monazite

Solid waste:

Chemical processing of monazite results in the following solid wastes:

- (a) Unreacted monazite (insoluble)

In addition to unreacted monazite from the monazite caustic soda reaction, this waste also contains traces of RE, Th, Ra and U and is acidic in nature. The insoluble waste separates in the process for the recovery and conversion of thorium hydroxide to thorium oxalate using solvent extraction

process. Otherwise usually this waste goes along with the thorium hydroxide cake. Approximately 80 - 100 kg of insoluble waste is produced per ton of monazite processed.

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

The significant radionuclide in the waste is ^{228}Ra and its specific activity range from 400 - 1000 Bq g^{-1} . The radiation field on contact with the insoluble waste is around 30- 100 $\mu\text{Gy h}^{-1}$ and the radiation field over the sealed trenches ranges from 2 - 4 $\mu\text{Gy h}^{-1}$ [6].

(b) PbS-Ba (Ra) SO_4 mixed cake

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

The specific activity (^{228}Ra) was of the order of 10^4 Bq g^{-1} (dry) in early years where as it is reduced to a level of about 2000-5000 Bq g^{-1} (dry) in recent years due to process changes entailing repeated deactivation. The radiation field on contact with the cake is around 400 - 600 $\mu\text{Gy h}^{-1}$. Presently the cake is directly pumped to FRP lined RCC trenches which results in reduced radiation exposure to workers. These trenches are sealed when full and the radiation field over the sealed trenches is of the order of 3 - 5 $\mu\text{Gy h}^{-1}$ [6].

(c) Solid waste from effluent treatment. (ETP Cake)

Phosphate sludge results from the neutralization and calcium phosphate precipitation of acidic and alkaline effluents generated during the processing of monazite. The ETP cake mainly contains phosphate and carries low levels of radioactivity (mainly ^{228}Ra , specific activity = 25 - 100 Bq g^{-1}). The quantity of this waste generated amounts to approximately 100 kg per ton of monazite processed. This waste is disposed in controlled area in earthen trenches. The earthen trenches are provided with 0.5 to 1 meter soil topping. The disposal site is well demarcated, fenced and identified with suitable caution boards. Radiation field on contact with the cake is less than 2 $\mu\text{Gy h}^{-1}$. Radiation field above the soil-topped area is comparable to the natural background prevailing in the area [6]

(d) Thorium concentrate

Thorium hydroxide cake produced during the extraction of Rare Earths from monazite contains the uranium fraction as well as the un-reacted monazite. Radiation fields on contact with this wet cake range from 60 to 70 $\mu\text{Gy h}^{-1}$. Aged thorium concentrate gives radiation field of 500 - 700 $\mu\text{Gy h}^{-1}$. The radiation fields on contact with thorium oxalate filled bags vary from 200 to 220 $\mu\text{Gy h}^{-1}$. The quantity generated amounts to nearly 250 kg per ton of monazite processed. This sludge is disposed of in engineered RCC silos. These are engineered structures with adequate shielding which ensures that there is no enhancement of the external radiation background in the public premises. The thoron/thoron daughters produced decay inside the silo itself, as these are closed structures. Table 8 gives the radioactivity levels usually observed in solid wastes produced during the chemical processing of monazite.

TABLE 8. TYPICAL RADIOACTIVITY IN SOLID WASTE; CHEMICAL PROCESSING OF MONAZITE

Solid waste	gross alpha (Bq g ⁻¹)	gross beta (Bq g ⁻¹)	²²⁸ Ra (Bq g ⁻¹)	radiation field (μGy h ⁻¹)
Monazite insoluble	800 - 2500	800 - 3000	400 - 1000	30 - 100
Mixed cake	2000 - 4000	3000 - 7000	2000 - 5000	400 - 600
ETP cake	75 - 100	300 - 600	25 - 100	2 - 3
Thorium oxalate	8000	---	--	200 - 220

(e) Contaminated scrap

Surface contaminated scraps (metallic, non-metallic, flammable etc) are generated during routine maintenance/ modifications etc.

Liquid Effluents

Acidic and alkaline effluents from the processing plants and water and chemicals used for decontamination constitute the liquid effluents in monazite processing. Nearly 15 m³ of effluents are generated per ton of monazite processed. The characteristics of the liquid effluents are given in Table 9. Acidic effluents and alkaline effluents after adequate settling are treated at effluent treatment plant (ETP) to remove the activity content. The two streams are mixed in a flash mixer followed by calcium phosphate precipitation by the addition of calcium chloride. The major pollutants in the effluents are phosphate, fluoride and radionuclides (mainly ²²⁸Ra). The radionuclides are co-precipitated along with calcium phosphate which also removes most of the phosphate and fluoride ions in the effluent. After adding suitable flocculating agent the slurry is let into a clarifloculator and allowed to settle. The supernatant is collected in a post treatment tank for monitoring and discharge to river. The sludge is filtered in a rotary drum filter and collected in HDPE laminated bags and disposed off. The discharges were within the prescribed discharge limits for liquid effluents for the plant of M/s Indian Rare Earths Ltd. [24, 25]

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

Effluent	pH	gross alpha (Bq l ⁻¹)	gross beta (Bq l ⁻¹)	²²⁸ Ra (Bq l ⁻¹)	F ppm	PO ₄ ppm
Acidic effluent	1.6 - 2.0	100 - 300	400 - 600	150 - 200	70	--
Alkaline effluent	12 - 13	600 - 900	900 - 1000	300 - 400	--	3000

Gaseous Effluents

During the various chemical processing stages, gaseous and particulate emissions take place. The radionuclides of concern in the emission are thoron daughters (²¹²Pb, ²¹²Bi) and Th (²³²Th, ²²⁸Th). The major source of thoron daughter is thorium storage silos, however, since the silos are sealed structures most of the thoron gas and daughter get decay inside itself. Release of airborne activity take place mainly from processing plants and the effluents are discharged through stacks. The stack heights are decided on

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

The releases are much below the authorized discharge limits [25] Gaseous effluents such as HCl, Cl₂ and H₂S are also released during normal operations. NaOH scrubbers in the ventilation system effectively control the releases, which conform to the limits set by national authorities. The environmental impact of airborne releases from mining and mineral separation and chemical processing of monazite is insignificant [6].

7.1.3. Decommissioning waste [26]

Solid waste

The solid wastes resulting from decommissioning of mining and mineral separation plants are inactive. Considerable quantity of solid waste like radioactive sludge accumulated in tanks, surface contaminated equipment, tanks, filters, motors, pumps pipelines etc, electrical fittings, contaminated structural materials, wall cement plaster, floor/wall chipping are generated during the decontamination of chemical processing plants. Classification of these wastes into various categories is done based on the radionuclide content/contamination levels and the wastes are disposed as per approved waste disposal practices

Surface contaminated equipment like large tanks are decontaminated and the contamination free material are disposed of as inactive scrap. Other contaminated equipment like filters, electrical fittings, pipelines etc are decontaminated by washing and reused or disposed off. Contaminated structural parts and floor/wall cement plaster chipping should be disposed off in RCC trenches/ earthen trenches depending on the radionuclides, activity content and radiation fields.

Liquid waste

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

Gaseous wastes

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

7.2. Environmental impact

7.2.1. Mining and mineral separation

Radiation field, air activity, ground water, soil etc are regularly monitored at the environment around the mineral separation plants and chemical processing plants. The mined areas refilled with minerals free sand show external radiation fields in the range of 0.3 to 0.5 $\mu\text{Gy}\cdot\text{h}^{-1}$; an order of magnitude lower than the respective original levels. The emanation of thoron from monazite mineral is only approx.0.1% and the operations do not give rise to enhanced levels of thoron or thoron daughters in the vicinity of the MSPs. Environmental air monitoring show that the long-lived alpha activity and thoron daughter concentrations in air near the MSPs are within the range of natural variations observed at the high background areas. The mining and mineral separation activities results in a net reduction of the notional individual exposures by factors ranging from 2 to 5 [6, 23].

7.2.2. Chemical processing of monazite (rare earths extraction)

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

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

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

8. Conclusion

The mining of beach sands, mineral separation and chemical processing of monazite for the recovery of rare earths involve occupational radiation hazards of varying magnitudes. The average per capita occupational exposures range from 1.0 to 9 mSv per year. Internal exposure contributes to nearly half of the exposure which is unique to this industry. Mechanization of the operations, process modifications, administrative controls and constant surveillance has over the years helped to reduce the exposures and to maintain them at levels ALARA. Production of rare earths from monazite involves occupational exposure, typically 0.64 ± 0.19 person mSv per ton of rare earths concentrate. Rare earths extraction from sources other than monazite, especially bastnaesite involve radiological safety problems of much lower magnitude.

Wastes from the mining and milling of radioactive ores are potential sources of radiological impact, both for those working in the industry and for members of the public who may be exposed if wastes are dispersed in the environment. These wastes are characterized by large volumes and low activity concentration of materials containing NORM with very long radioactive half-lives. Engineering and administrative controls ensure that exposures to public resulting from the releases from mining, mineral separation and monazite processing are not significant. However, there is also a need to consider exposures, for example due to human intrusion into the waste at some future time. Mine and mill tailings will continue to present a potential hazard to human health even after closure, and therefore additional measures may be needed to provide for the protection of future generation.

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