Radiological implications due to thorium in titanium mineral separation and chemical processing

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

1. Introduction

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

2. Methodology

Ilmenite and rutile samples from mineral separation plants at Chavara in Kerala were obtained and counted in a gamma spectrometer (4″x3″ NaI(Tl) detector coupled to a 4K MCA, HPD, BARC Model) after equilibrium ingrowths of the progeny of radon and thoron. The external gamma exposure rates at different locations (1 m above the ground) where workers are normally deployed were measured using a Geiger Muller Survey meter and a Scintillometer (Electronics Corporation of India Ltd, Models MR121D and SM141D). Over a period of two years, 85 air samples were collected on a monthly basis from process plants with reference to ilmenite and rutile streams. The samples were collected on GFA filter papers representing breathing zones and were analysed for thorium and thoron progeny by a programmed alpha counting method described elsewhere [3]. A few air samples were also collected from titanium dioxide (TiO_2) pigment plants where TiO_2 is manufactured from ilmenite by the chloride process. The likely occupational inhalation exposures were estimated using ICRP dose conversion factors. In order to assess the radiological impact due to waste tailings, samples of liquid effluent and solid tailings were collected and activity concentrations were analysed by gross alpha counting (using an ECIL Model SP-647 ZnS(Ag) counter having a counting efficiency of 25% and a detection surface diameter of 4.5 cm), gross beta (using an ECIL GM counter having an efficiency of 15%) and gamma spectrometric methods.

3. Results and discussion

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

TABLE 1. NORM ACTIVITY CONCENTRATIONS IN ILMENITE AND DERIVED PRODUCTS

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

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

TABLE 2. EXTERNAL GAMMA DOSE RATES IN TITANIUM MINERALS PROCESSING

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

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

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

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

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

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

4. Conclusion

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

Acknowledgement

The authors are grateful to Mr. H.S. Kushwaha, Director, HS&E Group, Bhabha Atomic Research Centre, Mumbai for guidance and support.

TABLE 4. ANALYSIS OF TAILINGS AND EFFLUENT IN MINERAL SEPARATION PLANTS

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

TABLE 5. ANALYSIS OF SOLID TAILINGS IN THE CHEMICAL PROCESSING OF TITANIUM MINERAL

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

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