

The Department of NORM in the Processing of a Phosphate Ore Containing Rare Earths

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Abstract. The Nolans Bore deposit, located in central Northern Territory, Australia, contains naturally occurring radioactivity. The department of NORM radionuclides in any chemical treatment process is determined by the minerals hosting uranium and thorium and by the processing conditions. The Nolans Bore ore contains apatite, which usually hosts most of the uranium decay chain activity, and “monazite-type” family minerals, which usually host most of the thorium decay chain activity. The management of ^{238}U and ^{232}Th decay chain radioactivity is required in the processing of phosphate ores that contain NORM, for the recovery of rare earths and phosphate. From a regulatory perspective, management is required to protect the workforce and the public by minimising their exposure to radioactivity, and to protect the environment by appropriate management of processing wastes. Several processing options to separate phosphate and rare earth elements were assessed in preliminary studies and the distribution of the uranium and thorium and other radionuclides were tracked. Some separation of uranium and thorium from the valuable components was achieved.

1. Introduction

Rare earths are often found in association with phosphate rocks. The concentration of the rare earths in these deposits tends to be low, and therefore their recovery has been reported as a by-product of wet phosphoric acid production or as a by-product of fertiliser production via the nitrophosphoric acid route. There is considerable literature available on the presence of radioactivity in phosphate ores [1, 2] and the association of NORM radioactivity with rare earths [3–5]. In particular, uranium is often associated with apatite deposits, with the uranium content typically ranging from 5 to 300 ppm U. In the past, uranium has been recovered as a by-product of wet phosphoric acid production, using solvent extraction technology. Under some circumstances, the radioactivity concentration in process wastes has been a major determinant of the viability of a project.

The Nolans Bore deposit, located in the Northern Territory in Australia, contains considerably higher concentrations of rare earths when compared to most phosphate rock deposits. However, the radioactivity content of the ore, including uranium, is also relatively high. The nature of the mineralogy requires that a process be developed specifically tailored to take into account the ore mineralogy. The objective of the current study was to examine the distribution of various radionuclides at an early stage of process development, in order to ensure appropriate management of the contained radioactivity in accordance with best practice.

2. Radioactivity in the ore

The Nolans Bore ore contains 250 to 500 ppm U and 5000 to 9000 ppm Th, depending on the location of the ore in the deposit. These concentrations correspond to 3.1 – 6.2 Bq/g ^{238}U and 20.4 – 36.7 Bq/g ^{232}Th , respectively. These concentrations of radioactivity in the ore have required that a radiation management plan is in place during exploration drilling, and will require that a proposed mine, plant and waste disposal facilities have a radiation management plan in place before commencement. The ore is classified radioactive for transport purposes.

The major potential pathways to radiation exposure include external gamma rays and dust inhalation. As is frequently observed with NORM, the NORM host minerals report preferentially to the finest particle size fractions when milled. This has particular implications in regard to exposure from dust inhalation and the need for dust suppression during drilling, ore handling and comminution. For one Nolans Bore ore sample containing on average 4.2 Bq/g U and 21.6 Bq/g Th, the finest, < 45 μm fraction from milling contained 5.1 Bq/g and 24 Bq/g of the two radionuclides, respectively. Finer, respirable particle sizes may contain still more enhanced concentrations of radioactivity and, as a proactive measure, exploration personnel are currently monitored for exposure to dust.

The U and Th are, to a large extent, hosted by different minerals. The two main economic minerals in the Nolans bore ore are:

fluorapatite	$\text{Ca}_5(\text{PO}_4)_3(\text{F},\text{OH})$
cheralite	$(\text{LREE},\text{Ca},\text{Th})\text{PO}_4\cdot\text{H}_2\text{O}$

Because of the complex mineralogy and fine mineral grain size, as shown in Fig. 1, the potential for mineral processing to a concentrate before chemical processing was considered unlikely to be successful, but examination of mineral processing options is the subject of a current study.

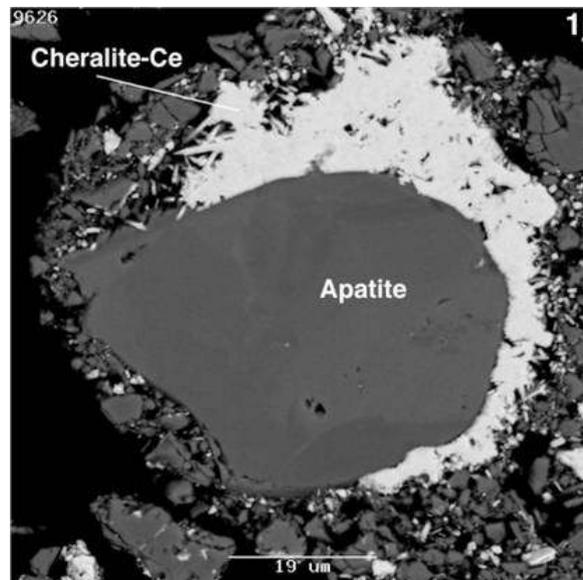


FIG. 1 Rare earth host mineral association

Apatite is more readily dissolved in acid than the more refractory cheralite. Most apatite ores are low in Th (5-40 ppm). The uranium content of Nolans Bore ore is high in comparison with other “apatite” ores. The majority of the Th is present in the chemically more refractory phosphate “monazite-type” minerals, together with the major fraction of the rare earths. This is an important issue for the separation of a higher grade RE intermediate and the production of phosphate and rare earths containing low concentrations of radioactive impurities. The Th/REE ratio in Nolans Bore ore is high and the thorium concentrations are comparable to those in other monazites [6].

3. The deportment of radioactivity during processing

Process development was primarily driven by the need to achieve effective separation of phosphate and rare earths. Because of the high concentrations of radioactivity and their occupational health and product quality implications, the behaviour of radioactivity was monitored during the early stages of a process options study. The analysis of solids was carried out using neutron activation analysis (NAA) for thorium, gamma spectrometry for ^{232}Th and ^{238}U decay chain progeny and XRF for uranium. Solutions were analysed using gamma spectrometry and ICP MS.

At the early stages of development, a broad framework for processing Nolans Bore ore was defined. This was based on an acid pre-leach process to remove the apatite, followed by conventional rare earth processing to recover the rare earth values from the pre-leach residue. Conventional rare earth technology considered included a sulphuric acid roast followed by water leaching or caustic conversion followed by acid leaching.

Both nitric acid and hydrochloric acid were considered for the pre-leach. Sulphuric acid leaching is inappropriate in this case, due to gypsum formation, resulting from the presence of high concentrations of calcium. It has been reported that, under the more aggressive sulphuric acid digestion conditions typical of wet phosphoric acid processing, the rare earths report with the solid gypsum.

The conceptual process flowsheets considered in this study are shown in Figs 2 and 3. Process conditions in the nitric acid pre-leach were optimised to maximise calcium and phosphate dissolution and minimise rare earth dissolution. Treatment of the pre-leach liquor follows the conventional nitrophosphate route for NPK fertiliser production, incorporating a rare earth recovery step. The second option involves a hydrochloric acid pre-leach step, followed by phosphoric acid recovery by solvent extraction [7].

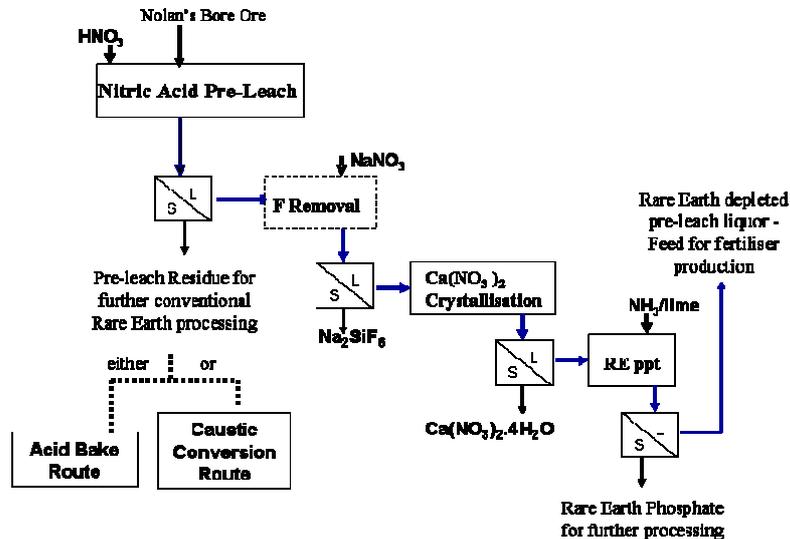


FIG. 2. Conceptual treatment of Nolans Bore ore using nitric acid

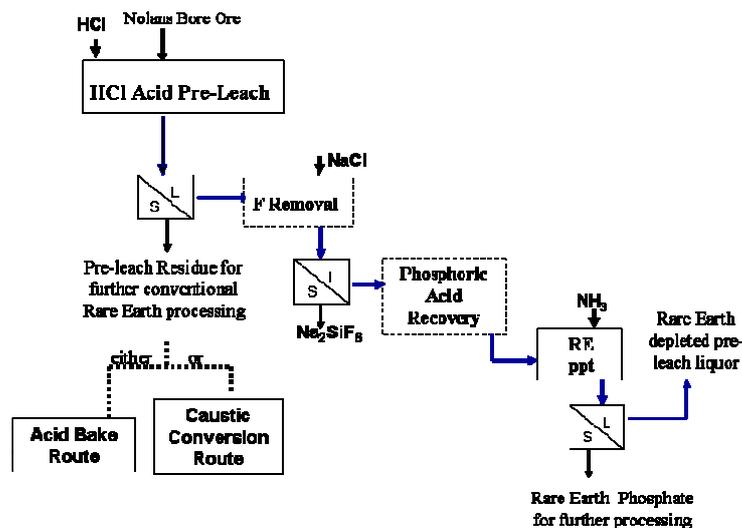


FIG. 3. Conceptual treatment of Nolans Bore ore using hydrochloric acid

The concentrations of radionuclides in these processes are given in Tables 1 and 2. The concentration of radioactivity in process solid phases increased through the process flowsheet, as the relative mass of solids flow in the process stream decreased. Preliminary results, not reported here, indicated that, with further processing to recover the rare earths, the total radioactivity concentrations in downstream process solids will be still higher. Based on the relative mass flows, the distribution of long lived radionuclides was determined and is also presented in Tables 1 and 2.

For convenience, the indicated total activity concentrations were estimated based on the assumption that shorter half life radionuclides will grow back into equilibrium with their longer half life parents (U, Th, Ra and Pb radionuclides) within a few weeks. This assumption is valid for radioactivity in waste and product streams, but not when considering occupational health and safety (OHS) effects from dynamic processes in an operating plant.

TABLE 1. RADIOACTIVITY CONCENTRATIONS AND DISTRIBUTIONS IN NITRIC ACID PRE-LEACH PROCESS STREAMS

	Chemical assays (ppm)		Radionuclide assays (Bq/g)								Total estimated activity (Bq/g)
			²³² Th decay chain			²³⁸ U decay chain				²³⁵ U	
	Th	U	²³² Th	²²⁸ Ra	²²⁴ Ra	²³⁸ U	²³⁴ Th	²²⁶ Ra	²¹⁰ Pb		
Nitric acid pre-leach: ore	5300	490	22	22	22	6.1	5.9	5.0	5.0	0.4	291
HNO ₃ pre-leach residue	9900	830	40	29	37	10	11	8.5	8.8	0.7	499
Calcium nitrate	250	20	1.0	0.3	0.3	0.25	0.07	0.03	0.2	DL	6
RE precipitate from HNO ₃ pre-leach	38 000	200	155	64	140	2.5	DL	9.4	44	1.7	1491
<i>Relative percentage distributions of radionuclides (%)</i>											
Estimated dissolution in pre-leach relative to the ore			46	62	50	51	49	51	49	52	51
Radioactivity in calcium nitrate solid relative to the ore			4.1	1.3	1.0			0.5	3.5		1.7
Radioactivity in rare earth precipitate relative to the ore			43	18	39	2.4		11	53		31

TABLE 2. RADIOACTIVITY CONCENTRATIONS AND DISTRIBUTIONS IN HYDROCHLORIC ACID PRE-LEACH PROCESS STREAMS

	Chemical assays (ppm or mg/L)		Radionuclide assays (Bq/g or Bq/L)							²³⁵ U	Total estimated activity (Bq/g or Bq/L)
			²³² Th decay chain			²³⁸ U decay chain					
	Th	U	²³² Th	²²⁸ Ra	²²⁴ Ra	²³⁸ U	²³⁴ Th	²²⁶ Ra	²¹⁰ Pb		
Hydrochloric acid pre-leach: ore	5300	490	22	22	22	6.1	5.9	5.0	5.0	0.4	291
HCl pre-leach residue	12 800	930	52	39	46	12	13	9	10	0.4	605
HCl pre-leach liquor	400	80	1628	838	2096	988	838	170	1035	67	26860
RE precipitate from HCl pre-leach liquor	26 500	200	108	38	114	2.5	8.4	7.4	DL	1.8	1046
<i>Relative percentage distributions of radionuclides (%)</i>											
Estimated dissolution in pre-leach relative to the ore			22	42	32	39	31	42	38	66	33
Radioactivity in rare earth precipitate relative to the ore			19	7	20	2	5	6		16	14

The results indicate that a nitric acid pre-leach extracted approximately 50% of the radionuclides from both the ^{238}U and ^{232}Th decay chains. A hydrochloric acid pre-leach extracted a significantly lower portion of the activity, approximately 30%, contained in the ore. With HCl, there was a greater variability in the extraction of various radionuclides. The 30% extraction corresponds approximately to the indicated weight percent of apatite in the ore. The more aggressive nitric acid leach appears to attack some of the more refractory minerals (including some RE minerals) to a greater extent. It is likely that a radium separation process will be required for the treatment of recycled pre-leach process solutions.

For both process options, a fraction of the rare earths in the ore was leached during the pre-leaching step, but can be recovered from the pre-leach solution by precipitation. These rare earth precipitates contained significant radioactivity concentrations, 1000-1500 Bq/g total activity, as shown in Tables 1 and 2. Varying fractions of the decay chain radionuclides co-precipitate with the RE from the pre-leach solutions.

The separation of voluminous crystalline calcium nitrate from the nitric acid pre-leach solution did not result in significant radioactivity separation (<2% of the activity in the ore), and the nitrate product would not be considered to be radioactive from a regulatory perspective. Remaining traces of contained radioactivity are likely to be further removed by improved product washing/liquor separation conditions.

The rare earths present in the cheralite need to be converted to a soluble form for subsequent rare earth extraction. The preleached solids can be treated using various processes, such as caustic conversion or sulphation roasting, before the treated solids are leached to extract the rare earths. These processes for treating the pre-leach residue must enhance rare earth extraction, and at the same time enable some separation of impurities, including radionuclides. This is the subject of current studies.

Uranium extraction during pre-leach was higher using nitric acid (51%) compared with hydrochloric acid (39%). There is some experience [1,2,8] with the recovery of uranium from these types of acidic phosphate solutions and this is a subject of the current study. Very little uranium is separated during rare earth precipitation from the pre-leach solutions (approximately 2% of the uranium in the ore).

Although the present work gives a picture of the department/distribution of radioactivity for various process options, relatively small quantities of radionuclides can also accumulate in small masses of process streams in the form of scales and/or dusts, which can become significant OHS and waste disposal issues. Similarly, small quantities of radionuclides can contaminate process equipment, which then requires particular measures to be taken in regard to plant maintenance and the final disposal of equipment.

The leach residues from downstream rare earth processing (sulphation roasting and leach or caustic conversion and leach) are the main process wastes and may be combined with process solution purification and waste water treatment residues for waste management. Careful attention to the analysis of these residues will reveal whether or not all the radionuclides have been accounted for in the overall process.

In regards to waste management and product quality, the department of radioactivity is determined primarily by the behaviour of the parent radionuclides and the decay chain progeny, which have comparatively long half lives.

4. Summary

The use of a new approach/process has required the monitoring of radionuclides to ensure that OHS issues can be appropriately managed and that product quality specifications are met. Pre-leaching the Nolans Bore ore has achieved an effective separation of phosphorous from the ore, and upgraded the rare earth content of leached ore solids. Significant radioactivity (30-50%) also leaches during this process, however, processes are available to separate impurity radionuclides and to recover uranium. The distribution of radioactivity in various process options for further rare processing, such as acid roasting and caustic conversion, is currently being investigated.

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REFERENCES

- [1] BUNUS, F.T., Phosphoric acid by wet process; radioactive components in phosphoric acid and their removal, *Environ. Sci. Pollut. Control Ser.*, **10**, Pollution Control in Fertilizer Production (1994), 237–252.
- [2] INTERNATIONAL ATOMIC ENERGY AGENCY, The Recovery of Uranium from Phosphoric Acid, IAEA-TECDOC-533, IAEA, Vienna (1989).
- [3] HART, K.P., LEVINS, D.M., Management of wastes from the processing of rare earth minerals, Chemeca 88 Conference, Sydney (1988).
- [4] HART, K.P., BROWN, S.A., LEVINS, D.M., The behaviour of radionuclides in the processing of rare earth minerals, Rare Earths '93, ANSTO Lucas Heights, (1993), October
- [5] INTERNATIONAL ATOMIC ENERGY AGENCY, Extent of Environmental Contamination by Naturally Occurring Radioactive Material (NORM), Technical Reports Series No. 419, Appendix III, IAEA, Vienna (2003).
- [6] INTERNATIONAL ATOMIC ENERGY AGENCY, Thorium Fuel Cycle — Potential Benefits and Challenges, IAEA-TECDOC-1450, IAEA, Vienna (2005).
- [7] HABASHI, F., AWADALLA, F.T., YAO, W., The hydrochloric acid route for phosphate rock, *J. Chem. Tech. Biotechnol.* **38** (1987) 115-126.
- [8] HABASHI, F., AWADALLA, F.T., ZAILAF, M., The recovery of uranium and lanthanides from phosphate rock, *J. Chem. Tech. Biotechnol.* **36** (1986) 259-267.