

IMMOBILIZATION OF U-Th-Ra IN MINE WASTES BY PHOSPHATE MINERALIZATION

F.H. MURRAY, J.R. BROWN*, W.S. FYFE AND B.I. KRONBERG

Department of Geology, University of Western Ontario, London, Ontario N6A 5B7

ABSTRACT

The geochemistry of natural phosphates of the apatite group indicates that these minerals have a high capacity for retention of uranium and its daughter products. ESCA spectroscopy shows that U and Ba (cf. Ra) are strongly absorbed on apatite. Large, reactive surfaces of apatite have been created by partial replacement of calcite and gypsum by phosphate solutions at the 300 ppm level. The same replacement has been achieved in impermeable calcite-rich, glacial tills. When typical waste effluents from a uranium mine are treated with such active phosphatic materials, radium-leach values are reduced to levels below 0.1 pCi/L, values in the range of ocean waters and high-quality fresh water.

Keywords: uranium, mine tailings, radium immobilization, phosphate mineralization, apatite.

SOMMAIRE

La géochimie des phosphates naturels du groupe de l'apatite démontre que ces minéraux possèdent une forte capacité de rétention pour l'uranium et ses produits de désintégration. La spectroscopie ESCA montre que U et Ba (cf. Ra) sont fortement absorbés sur l'apatite. De grandes surfaces réactives d'apatite ont été créées par le remplacement partiel de la calcite et du gypse par des solutions de phosphate à niveau de concentration de 300 ppm. Le même remplacement a pu être réalisé dans des tills glaciaires imperméables, riches en calcite. Lorsque des effluents typiques des rebus de mines d'uranium sont traités par ce matériau phosphaté actif, les valeurs en Ra des lessivages tombent en-dessous de 0.1 pCi/L, devenant ainsi comparables à celles d'eaux océaniques et d'eaux douces de haute qualité.

(Traduit par la Rédaction)

Mots-clés: uranium, rebus de mines, immobilisation du radium, minéralisation en phosphate, apatite.

INTRODUCTION

In 1981, Canada produced 8,400 tonnes of uranium, with over 60% coming from Ontario. Rio Algom Limited, situated at Elliot Lake, is the major Ontario producer, and its operation is the central focus for reviewing the problem of tailings disposal.

Uranium was discovered in the Elliot Lake area in 1950, and by 1961 Rio Algom had up to nine mines operating. The deposit is of Proterozoic age, lying at the base of the Huronian Supergroup (2.2-2.5 Ga) (Robertson 1969). The major uranium minerals, uraninite, brannerite and monazite, are held in a matrix of fine-grained quartz, sericite and feldspar, the so-called quartz-pebble conglomerate beds (Stanton 1972). The average chemical composition of Elliot Lake ore is shown in Table 1 (Skeaff 1979). The occurrence of 6% pyrite has long-range consequences on the stability of the waste, as the pyrite may be oxidized rapidly to sulfuric acid by bacterial catalysis.

The ore grade runs from 0.8 to 1.25 kg U₃O₈ per tonne. Consequently, each tonne of ore mined results in the disposal of about 999 kg of solid wastes along with approximately 100 kg of milling reagents (Murray & Moffett 1977). The major reagents used in the milling and the resulting composition of the tailings are shown in Tables 2 and 3 (Raicevic 1979, Moffett 1979). The solid tailings contain 85% of the radioactivity in the parent ore since only uranium is removed, at approximately only 90% efficiency. Radium-226 is the isotope of major environmental concern (Moffett 1979) because of the combination of its low maximum permissible concentration (MPC_w) of 3 picocuries per litre (pCi/L), as set by the Ontario Ministry of the Environment, and its high content in the ore.

Since the late 1960s, addition of lime and limestone at the mill exit has produced alkaline tailings (pH 10.5-11) (Vivyrka 1975). Radium is coprecipitated with barium sulfate by the addition of barium chloride to the decant water. Retention times of over forty hours in settling ponds are required to insure settling of the radium - barium sulfate sludge. A typical composition of the final discharge is listed in Table 4 (Moffett 1977), indicating that radium concentrations of less than 3 pCi/L can be obtained by this method.

Unfortunately, the interactions of pyrite, oxygen and bacteria may regenerate acidic conditions, exhausting the alkaline buffering capacity of the tailings (see Lush *et al.* 1978). Under acidic conditions sulfate, uranium, thorium and radium are mobilized. Because of the increased rate of pyrite oxidation in the older unlimed tailings, the leaching processes take place in a much shorter time-frame than in the

*Present address: Energy, Mines & Resources, CANMET/ERL, 555 Booth Street, Ottawa, Ontario K1A 0G1

recently neutralized wastes. This situation has led to efforts to find more suitable long-term techniques of waste stabilization so that leach rates of radium-226 will be closer to background levels. This study focuses on immobilization of radium by phosphate mineralization.

PHOSPHATE MINERALIZATION

To improve the control of radium leach-rates, it is necessary to find mineral phases that have maximum stability during weathering. Soviet work (Gavshim *et al.* 1973) has shown that apatite phases are highly enriched in uranium and thorium and strongly retain the daughter products of radioactive decay. In Brazil, apatite-rich carbonatites are used as a source of phosphate. Intense leaching results in the

TABLE 4. TYPICAL COMPOSITION OF FINAL DISCHARGE WATER INTO WATERCOURSE*

| | Acid leach mill ($\mu\text{g mL}^{-1}$ except pH and Ra) |
|--------------------------------------|--|
| pH | 7.0 |
| Suspended solids | 5 |
| total dissolved solids | 2250 |
| SO_4^{2-} | 1350 |
| NO_3^- | 275 |
| NH_4^+ | 18 |
| Ca^{2+} | 580 |
| Na^+ | 10 |
| Cl^- | 10 |
| Fe | 0.5 |
| Cu | 0.05 |
| Pb | 0.05 |
| Zn | 0.01 |
| Ni | 0.03 |
| Co | 0.03 |
| Ra (after BaCl_2 treatment) | 1-5 pCi/L** |

*from Moffett (1977)

**Ra 800 pCi/L before BaCl_2 treatment

TABLE 1. TYPICAL COMPOSITION OF URANIUM ORE FROM ELLIOT LAKE*

| Element | wt. % | Element | wt. % |
|---------|-------|------------------------|-----------|
| Si | 39.3 | U | 0.107 |
| Al | 3.55 | Th | 0.044 |
| Fe | 3.07 | (R.E. + Y) | 0.19 |
| S | 3.10 | P_2O_5 | ~.05 |
| K | 1.45 | TiO_2 | ~.50 |
| Na | 0.05 | Pb | ~.04 |
| Ca | 0.09 | | |
| Mg | 0.07 | Ra-226 | 355 pCi/g |
| C | 0.05 | | |
| Ba | 0.06 | | |

*From Skeaff (1979)

TABLE 2. MAJOR REAGENTS USED IN MILLING PROCESS*

| Reagent | Reagent Usage (kg/tonne ore milled) |
|-------------------------|--|
| H_2SO_4 | 38 |
| CaO | 13 |
| CaCO_3 | 21 |
| HNO_3 | 2.7 |
| NH_3 | 0.41 |

* from Moffett (1979)

TABLE 3. CHEMICAL COMPOSITION OF TAILINGS*

| Old Tailings | | wt. % |
|------------------------|-------------|-----------|
| Total S | | 2.37 |
| Sulfate S | | 1.52 |
| Sulfide S | | 0.85 |
| Total Fe | | 2.15 |
| U_3O_8 | | 0.003 |
| Th | | 0.007 |
| Rare Earths | | 0.05 |
| Ti | | 0.15 |
| Cu | | 0.01 |
| P | | 0.02 |
| Au | 0.17g/tonne | |
| Ra-226 | 290 pCi/g | |
| New Tailings | | wt. % |
| S | | 2.5-3.5 |
| U | | 0.0065 |
| Th | | 0.025 |
| Ra-226 | | 225 pCi/g |

*from Raicevic (1979)

breakdown of the carbonatite matrix, and fine-grained apatite is concentrated and mined from the laterite debris. In the large Ceará uranium deposits of Brazil, even under intense weathering, secondary apatite concentrates uranium and thorium (Forman *et al.* 1981). Such observations suggest that the apatite species would be more stable than sulfate species in the tailings environment. The experiments outlined here were designed to verify this concept and test its efficiency in radium immobilization.

EXPERIMENTAL VERIFICATION

Initial experiments showed that powdered calcite and gypsum were replaced by apatite in days or months by treatment with 0.1 molar phosphate solution at room temperature (Brown *et al.* 1981). The relevant chemical reaction for calcite replacement by apatite is as follows:

$$5\text{CaCO}_3 + 3\text{K}_3\text{PO}_4 + \text{H}_2\text{O} \rightarrow \text{Ca}_5(\text{PO}_4)_3(\text{OH}) + 4\text{K}_2\text{CO}_3(\text{soln}) + \text{KHCO}_3(\text{soln})$$

Whereas apatite growth on BaSO_4 was not observed, there was 50% replacement of calcite and 10% replacement of gypsum in less than one month.

A series of experiments was conducted in which solutions of U, Th and Ba with initial concentrations of 1 ppm were added to fine-grained Florida collophanitic apatite for a period of two weeks. Barringer Research Limited analyzed the solutions and reported final concentrations of 1 ppb U, Th below detection (1 ppb), and Ba (*cf.* Ra) reduced to 5 ppb (Brown *et al.* 1981).

Surface trapping was studied using Electron Spectroscopy for Chemical Analysis (ESCA) (Bancroft *et al.* 1979). U and Ba (*cf.* Ra) solutions were equilibrated with polished single-crystal apatite plates. After multiple washings, the surface layer of the crystals was analyzed (thickness 1-5 nm). Strong adsorption coverage of U was observed from 1 ppm solutions in a period of 70 hours. On the basis of these preliminary studies, experiments with

phosphate additions were conducted on actual mine tailings supplied by Rio Algom Limited.

Results from the tailings study are summarized in Table 5. Two types of effluents were used: (A) dried tailings from an active waste-pile and (B) fresh wet effluents taken directly from the mill discharge in slurry form. In one study, tailings were treated with powdered calcium carbonate and potassium phosphate solutions in the concentration range 1–0.01 molar. In another study, Port Hope glacial tills were pretreated with phosphate solutions and mixed with the tailings and then further treated with 0.1 M phosphate solution. The purpose of adding the till is to reduce the permeability of the tailings after phosphate fixation. In laboratory studies using loosely packed till, permeabilities of 10^{-4} darcy were easily obtained. The tills have a large component of calcite, and the pretreatment with phosphate was intended to induce apatite growth before addition to the tailings. In related permeability experiments, addition of thin (1–2 cm) layers of bentonite further reduced the permeability, which would correspond to an effective permeability of less than 10^{-8} darcy when confined by few metres of overburden.

In the tailings study, unless otherwise specified, 125 g of tailings were treated with 2.5 L of solution for times ranging from 11 to 227 days before samples were removed for radium analysis by Beak Consultants of Mississauga. Samples were either 100 mL or 1000 mL in volume. The radium detection limit

for 100 mL samples was 1 pCi/L and for 1000 mL samples, 0.1 pCi/L. Each solution was carefully filtered through micropore filters in the range 1.2–0.5 μm , 0.45 μm being the most commonly used.

The data in Table 5 show that extremely low radium values can be obtained. The observed values for one-litre samples at or below the detection limit of 0.1 pCi/L are in the range of average ocean-water values (0.08 pCi/L) and high-quality fresh water (0.14 pCi/L) (Haury & Schikarski 1977). Many of the leached samples were superior to the tap water locally available (4 pCi/L). From the data, it is also apparent that dilute phosphate treatment (0.01 M, 300 ppm) was comparable to or better than treatment with more concentrated phosphate (1 M, 30,000 ppm).

Surface ESCA studies were performed on the products of samples that had been treated with phosphate for more than 200 days using facilities at the CANMET laboratories of the Department of Energy, Mines and Resources in Ottawa. ESCA studies of the calcite-rich regions of the powdered products (sample area observed was approximately 0.5 cm^2) showed high concentrations of fixed phosphate phases. The major-element concentrations that could be detected included Ca, P, C, O, K, Si, Fe and, in one case, minor uranium. Quantitative studies of the ESCA scans gave Ca/P ratios close to that expected for apatite formation [1.70 measured, compared with 1.67 predicted from the ideal formula $\text{Ca}_5(\text{PO}_4)_3\text{OH}$]. Table 6 shows a typical chemical composition of the calcite-rich region scanned using ESCA.

TABLE 5. RADIUM ACTIVITY IN TREATED SAMPLES OF TAILINGS FROM URANIUM MINES

| Sample No. | Tailing Type | Till (g) | [PO_4^{3-}] (M) | Time (days) | Filter Size (μm) | CaCO_3 (g) | Ra (pCi/L) |
|-------------------|--------------|----------|----------------------------|-------------|-------------------------------|---------------------|------------|
| A-1 | B | - | 0.01 | 11 | 0.45 | 25 | <1 |
| A-3 | B | - | 1.0 | 11 | 0.45 | 25 | 15 |
| A-3 | B | - | 0 | 11 | 0.45 | 25 | 11 |
| A-4 | A | - | 0.01 | 11 | 0.45 | 25 | 3 |
| A-4 | A | - | 0.01 | 11 | 0.45 | 25 | 3 |
| A-6 | A | - | 1.0 | 11 | 0.45 | 25 | 57 |
| A-12 ¹ | B | - | - | - | 0.05 | - | 170 |
| A-12 ¹ | B | - | - | - | 0.05 | - | 170 |
| A-13 ¹ | B | - | - | - | 1.2 | - | 240 |
| A-14 ² | A | - | - | 48 | 0.45 | - | 200 |
| A-14 ² | A | - | - | 48 | 0.45 | - | 200 |
| A-16 ² | A | - | - | 41 | 0.45 | - | 260 |
| A-16 ² | B | - | - | 11 | 0.45 | - | <1 |
| A-17 | A(85g) | 213 | 0.1 | 11 | 0.45 | - | <1 |
| A-19 | B(85g) | 213 | 0.1 | 11 | 0.45 | - | <1 |
| A-20 ³ | A | - | - | - | - | - | 140* |
| A-20 ³ | A | - | - | - | - | - | 130* |
| A-20 ³ | A | - | - | - | - | - | 130* |
| A-21 ⁴ | A | - | - | - | 0.45 | - | 1 |
| B-2 | A(85g) | 213 | 0.1 | 84 | 0.45 | - | 0.2 |
| B-2 | A(85g) | 213 | 0.1 | 84 | 0.45 | - | 0.3 |
| B-3 | B | - | 1.0 | 69 | 0.45 | 25 | 7.8 |
| B-4 | B | - | 0.01 | 87 | 0.45 | 25 | 14 |
| B-5 | B(85g) | 213 | 0.1 | 84 | 0.45 | - | 0.1 |
| B-5 | B(85g) | 213 | 0.1 | 84 | 0.45 | - | 0.1 |
| B-6 | A | - | 1.0 | 69 | 0.45 | 25 | 17 |
| B-7 | B | - | 0.01 | 87 | 0.45 | 25 | 1.6 |
| B-7 | B | - | 0.01 | 87 | 0.45 | 25 | 1.2 |
| B-12 ⁵ | B | - | 1.0 | 87 | 0.45 | 525 | 2.4 |
| B-13 ⁶ | A | - | 1.0 | 87 | 0.45 | 525 | 13 |
| B-14 ² | A | - | - | 124 | 0.45 | - | 24 |
| B-14 ² | A | - | - | 124 | 0.45 | - | 21 |
| B-16 ² | B | - | - | 117 | 0.45 | - | 91 |
| B-16 ² | B | - | - | 117 | 0.45 | - | 98 |
| B-21 ⁵ | - | - | - | - | 0.45 | - | 4.0 |
| C-1 | A | - | 0.01 | 227 | 0.45 | 25 | <0.1 |
| C-2 | B | - | 0.01 | 227 | 0.45 | 25 | 0.1 |
| C-3 | A | - | 0.1 | 227 | 0.45 | 25 | 0.1 |
| C-4 | B | - | 0.1 | 227 | 0.45 | 25 | 0.1 |
| C-9 | A(85g) | 213 | 0.1 | 224 | 0.45 | - | 0.3 |
| C-10 | B(85g) | 213 | 0.1 | 224 | 0.45 | - | 0.3 |

B-2, B-3, B-5, B-6, B-7 and all C series were 1 L samples; all others were 0.1 L.
¹ filtrate from wet tailings. (B) type. ² tailings in deionized water. ³ dry tailings. (A) type. ⁴ acidified deionized water. ⁵ acidified tap water. ⁶ 25 g of CaCO_3 for first 69 days; 500 g more CaCO_3 added for last 18 days. * expressed in pCi/g.

CONCLUSION

It has been shown that matrices with apatite or phosphate-treated calcite (with subsequent formation of apatite) can effectively fix uranium and radium. Radium levels in leachates are reduced to those comparable to high-quality fresh waters. It remains for those involved in actual mine-operations to assess the possibilities of using such a system, which may have better long-term stability than the barium sulfate system currently in use.

TABLE 6. SURFACE COMPOSITION OF CARBONATE MATERIAL BASED ON ESCA

| ELEMENT | ATOMIC % | WT. % |
|--|----------|-------|
| O | 53.7 | 40.2 |
| C | 17.0 | 9.5 |
| P | 8.2 | 12.6 |
| Ca | 15.7 | 29.4 |
| Fe | 0.9 | 2.4 |
| Si | 2.2 | 2.9 |
| K | 1.3 | 2.4 |
| Ca/P = 1.70 (experimental, corrected for CaCO_3) | | |
| Ca/P = 1.67 (theoretical, from $\text{Ca}_5(\text{PO}_4)_3\text{OH}$) | | |

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