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THE EFFECTS OF BARIUM CHLORIDE TREATMENT OF URANIUM ORE ON ^{222}Rn EMANATION AND ^{226}Ra LEACHABILITY FROM MILL TAILINGS

by

Shawki A. Ibrahim[1], Shawna L. Church[2]
and F. Ward Whicker[3]

ABSTRACT

The purpose of this laboratory study was to investigate the effectiveness of barium chloride treatment of uranium ore on ^{222}Rn emanation from mill tailings, ^{226}Ra level in wastewater, and the leachability of radium from tailings. It has been shown that barium sulfate is an excellent carrier for radium and that barium sulfate crystals have high retention capacity for radon gas produced by radium trapped within the lattice.

Ground uranium ore from a mine in Wyoming was mixed with water to form a 1:1 ratio before barium and potassium chlorides were added at concentrations of 0, 10, 25, 50, and 100 mg per liter of slurry. The ore was then subjected to a simulated mill process using sulfuric acid leaching. The liquid representing tailings pond water was separated and analyzed for ^{226}Ra and the solid fraction, representing mill tailings, was tested for radon emanation and the leachability of radium by deionized water.

This study suggests that barium treatment of uranium ore prior to sulfuric acid leaching could be effective in reducing radon emanation from tailings and also in reducing the ^{226}Ra concentration of wastewater. Leachability of radium from treated tailings was markedly reduced.

INTRODUCTION

Removal of uranium from ore creates large quantities of waste tailings that contain most of the total radioactivity that was originally present in the ore. The mining and milling process necessitates the disposal of these wastes. The 140 million tons of tailings now in existence contain about 85,000 curies of each daughter product of uranium decay. This includes ^{226}Ra and ^{230}Th, both of which are bone

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1. Shawki A. Ibrahim, Assistant Professor of Radiology and Radiation Biology, Colorado State University, Fort Collins, Colorado.

2. Shawna L. Church, Associate Engineer, Yankee Atomic Electric Co., Farmingham, Massachusetts.

3. F. Ward Whicker, Professor of Radiology and Radiation Biology, Colorado State University, Fort Collins, Colorado.

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seeking alpha emitters. Most existing tailings are not well isolated from the environment and large amounts of ^{222}Rn gas and other radionuclides are escaping to the environment. ^{222}Rn and its daughters account for almost all of the human population dose from the nuclear fuel cycle (Carter 1978).

To comply with the "Uranium Mill Tailings Radiation Control Act of 1978," the Department of Energy has implemented a remedial action program at certain inactive uranium mill tailings sites. The goal of this program is to contain ^{222}Rn and water leachable radionuclides in tailings. In keeping with this goal, a technology development program has been pursued to evaluate concepts such as earthen covers, asphalt emulsion sealants, biobarriers, actinide separation (by leaching), and thermal stabilization. In this study, the conversion of ^{226}Ra to a chemically and ecologically stable form was investigated. Specific objectives of this study included: assessment of the efficiency of barium chloride treatment of uranium ore to coprecipitate ^{226}Ra into an insoluble form; determination of the effect of this treatment on radon emanation from tailings; investigation of the stability of ^{226}Ra using accelerated leaching procedures.

Barium sulfate has been shown to be an excellent carrier, particularly for radium and thorium when incorporated into the crystal lattice; however, uranium is not carried unless it is reduced under extreme chemical conditions (Sill 1969). In such form, these elements are distributed homogeneously throughout the mixed crystal lattice and are virtually nonleachable. Experiments have also shown that radon loss from barium sulfate is negligible (Ames et al. 1949).

MATERIALS AND METHODS

A five kilogram quantity of ground ore was collected from a uranium mill in Wyoming. The ore was oven-dried at 70°C for 12 hours and ground to ≤ 42 mesh (350 microns). The homogeneity of the radium content was verified using gamma spectrometry. Aliquots of ore were mixed with deionized water to form a 1:1 solid to liquid ratio and soluble potassium and/or barium chlorides were added at concentrations of 0, 10, 25, 50, and 100 mg/L of slurry. The mixtures were subjected to a simulated mill process using sulfuric acid leaching. The treatment process used in this investigation closely parallels that of the actual milling process (Fig. 1). Time in the leach circuit, amounts of chemicals, heating, and mixing were duplicated from a standard mill operation. Referring to Fig. 1, the quantities of reagents added were, as a percentage of the mass of ore, 5% sulfuric acid, 0.15% sodium chlorate, 0.5% sodium chloride, and 0.065% ammonia.

At the end of the treatment process, the liquid fraction representing the tailngs water was decanted from the solids, filtered through a 0.45 um membrane filter and analyzed for soluble ^{226}Ra using the standard emanation technique. The solid fraction, representing the tailings, was dried at 70°C for 12 hours and two gram aliquots were transferred with 25 ml of deionized water to radon bubblers. An "initial deemanation" (20 minutes of compressed air bubbling through the slurry) was performed to drive off any radon and to establish

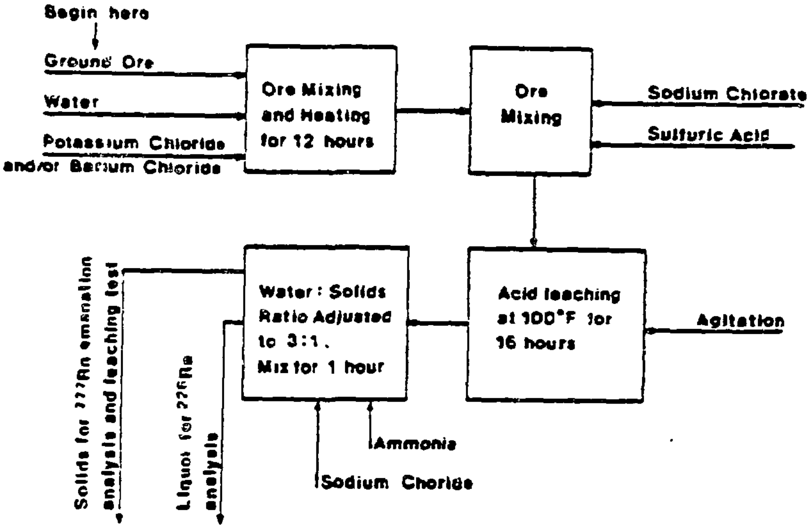

FIGURE 1. Schematic of barium and potassium treatment of uranium ore.

the zero time for calculation of radon ingrowth. Samples were stored for a known period of time to allow sufficient regrowth of radon. For measurement, the "available radon" was transferred to an evaluated scintillation cell by passing air through the bubblers. The time of commencement of bubbling was taken as the end of the ingrowth period for radon. Alpha particles produced by the radon daughters in the scintillation cell were detected by a photomultiplier tube in a light tight box, amplified, and counted. Calibration of the counting system was achieved by an NBS standard of ^{226}Ra in the same manner. Other solid aliquots were leached in deionized water with gentle agitation for 24 hours. Twenty-five ml of the leach solutions were filtered and analyzed for ^{226}Ra content using the standard emanation procedure.

RESULTS AND DISCUSSION

1. ^{226}Ra Level in Wastewater from Treated Ore

Radium removal from acidic leach solutions by coprecipitation with barium and potassium sulfate was studied by introducing barium and potassium chlorides to uranium ore prior to the sulfuric acid leaching process. Previous work has shown that if potassium is present and the barium is added before the sulfate concentration is increased, precipitation of radium is generally more efficient and the interference of other elements is much less than when potassium is absent or the barium is added after radium has been dissolved in sulfuric acid (Sill 1969). Results of barium chloride treatment of ore on the ^{226}Ra concentration in leach solutions is illustrated in Figure 2. ^{226}Ra concentrations decreased as the amount of Ba^{++} added increased to 50 mg/L of slurry. There was no significant difference between ^{226}Ra levels in controls and samples treated with 10 mg/L Ba^{++}. The optimum precipitant dose without altering the solution pH or the actual milling process was determined to be from 25 to 50 mg/L of Ba^{++}. An increase in the pH value has been shown to improve the removal of radium (Averill et al. 1982; Kharbanda et al. 1982) but this was not attempted in our study. It is our opinion that the acidic nature of the tailings systems is a strong deterrent against biological intrusion and subsequent contaminant transport. Thus, maintaining them in their present chemical form might prove environmentally advantageous.

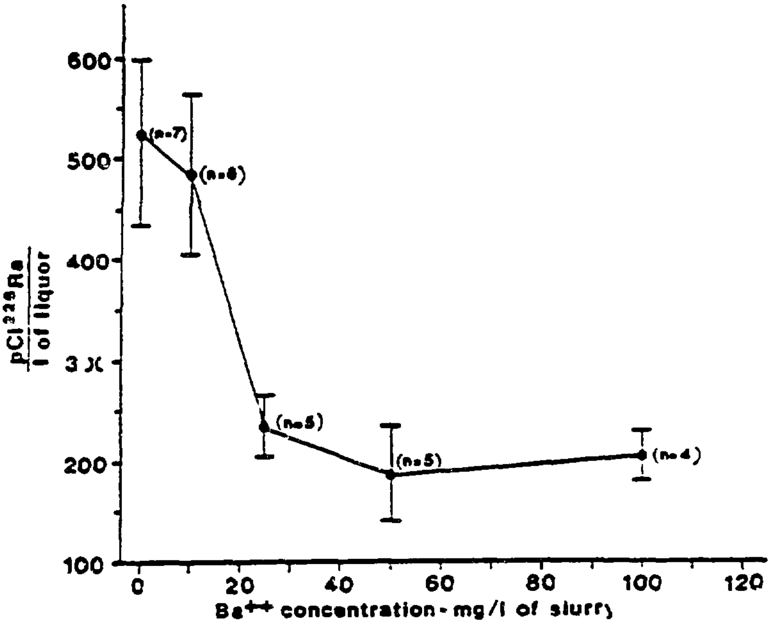

FIGURE 2. Concentrations of ^{226}Ra in liquor as a function of the amount of Ba^{++} added per liter of slurry (error bars represent ± 1 standard error).

When uranium ore was treated with barium and potassium chlorides at concentrations of 0, 10, 25, 50, and 100 mg/L as Ba^{++} and K^{+}, the same trend was observed with a similar degree of ^{226}Ra removal. However, no significant difference between the Ba^{++} only treatment and the combined Ba^{++} + K^{+} treatment on ^{226}Ra levels was detected.

^{238}U was also measured in the leach solutions to determine the effect of the treatment on uranium recovery. The 63 KeV of ^{234}Th was counted using a coaxial GeLi detector after reaching equilibrium with its parent, ^{238}U. No significant difference was observed for ^{238}U concentrations in leach solutions between treated and untreated ore. This was fully expected since previous work has shown that uranium is not coprecipitated with barium sulfate unless it is reduced to the quadrivalent state by strong reducing agents. It is also interesting to note that in the conventional acid leach extraction process, the strong oxidant sodium chlorate is added to maintain the uranium in an oxidized state, making its coprecipitation with barium sulfate virtually impossible.

2. Leachability of ^{226}Ra from Tailings

The radium retention capacity of barium-treated ore was tested with an accelerated leaching experiment. Figure 3 shows that the release of ^{226}Ra from solids decreased as a function of the amount of Ba^{++} used to treat the uranium ore. ^{226}Ra leachability was reduced by about 85% in solids treated with 50 mg/L Ba^{++} as compared with untreated solids. All but the group treated with 10 mg/L of Ba^{++} showed significant ^{226}Ra retention differences from the control. The optimum precipitant dose appears to be about 50 mg/L Ba^{++}.

Thus, the use of barium stabilizes radium activity in solids and minimizes its release to the overlying waters. Other accelerated leaching tests with acids or EDTA may be attempted at a later date in order to ascertain the long term stability of treated solids.

3. ^{222}Rn Emanation from Treated Solids

The most straightforward method to determine the radon emanation coefficient is to measure sample activity before it is sealed in a radon-tight container and after equilibrium has been reached between ^{222}Rn and its daughter, ^{214}Bi. The 1.76 MeV photon of ^{214}Bi can be detected with gamma spectrometry. Preliminary experiments for this investigation have shown that the emanation fraction of unprocessed uranium ore averaged about 15 ± 4% using the above method. Athough this technique may be adequate for routine measurements, it was not sufficiently sensitive due to its higher detection limit. A more sensitive method of assaying radon emanation was developed based on measuring available ^{222}Rn. "Available ^{222}Rn" can be defined as that ^{222}Rn which is not trapped in the mixed crystals of $BaSO_4$. Therefore, it could be transferred to a scintillation cell and detected via the standard radon emanation technique used for ^{226}Ra measurements. The "available ^{222}Rn" corresponds closely with the radon emanation coefficient. The detection limit of the developed method is 0.1 pCi per sample, compared to approximately 100 pCi per sample for a 100 minute count using the gamma counting procedure.

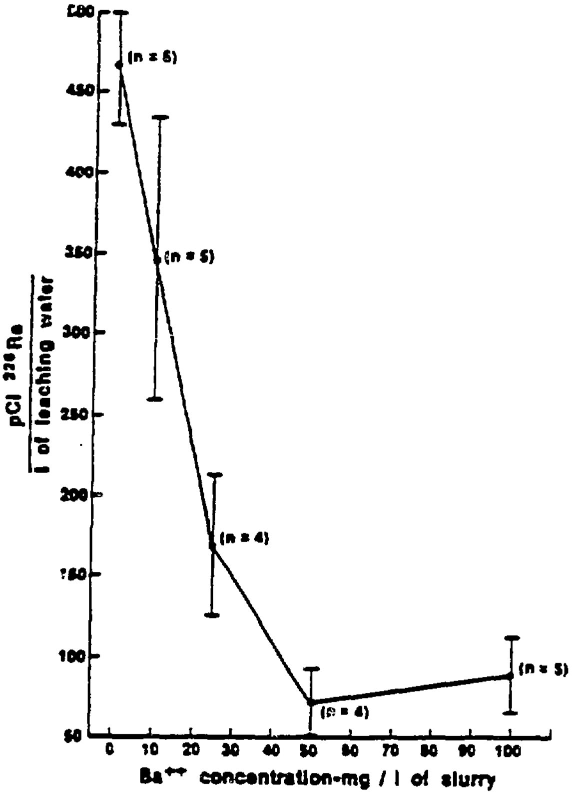

FIGURE 3. Concentrations of ^{226}Ra in leaching water as a function of Ba^{++} added per liter of slurry (error bars represent ± 1 standard error).

Results in Figure 4 illustrate the fraction of "available ^{222}Rn" as a function of Ba^{++} and K^+ concentration used in the treatment. Radon released from solids decreased as the amount of Ba^{++} and K^+ increased. A 45% radon emanation reduction from controls was obtained with solids treated with 0.5 mg/g ore. When treatment groups of 0.50, 0.75, and 1.0 mg Ba^{++} and K^+ per gram of ore were compared with the untreated control group using a pooled variance t-test, the difference between means was significant in every case at $P < 0.10$. However, this comparison did not yield significant differences with samples treated with Ba^{++} only. Although the exact mechanism for the potassium ion's participation in the coprecipitation of radium on barium sulfate is not clear, double potassium barium sulfate has been suggested as the actual compound formed in this reaction (Sill 1969).

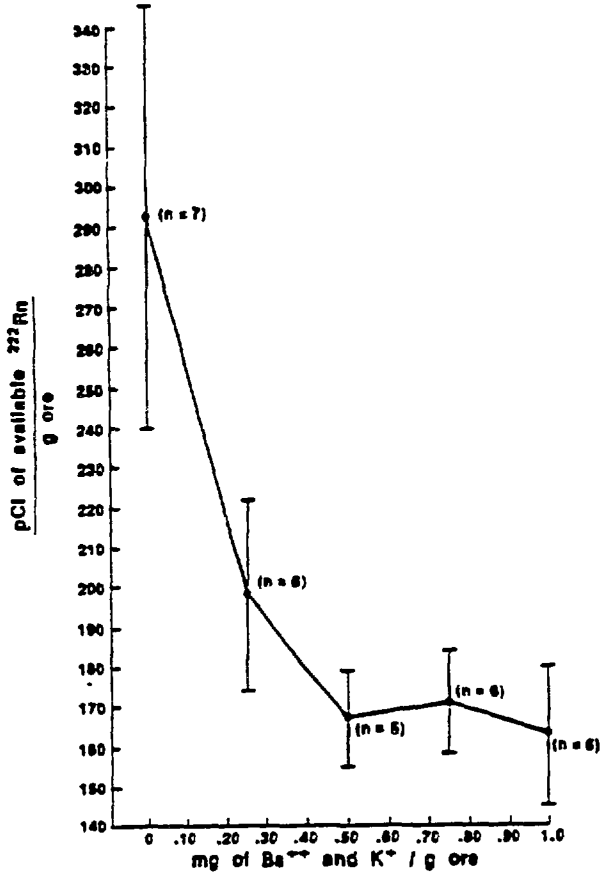

FIGURE 4. Available ^{222}Rn as a function of Ba^{++} and K^{+} added per gram of ore (error bars represent ± 1 standard error).

CONCLUSIONS

A chemical treatment process developed in this investigation consists of ^{226}Ra coprecipitation on barium and potassium sulfates. The process could be employed during the actual ore grinding phase in the mill without any other modifications to the uranium milling operation. The treatment could be performed without altering the acidic nature of mill tailings. The process demonstrated, on a bench-scale, significant reduction in radon emanation and ^{226}Ra leachability from tailings. ^{226}Ra concentration in tailings water was markedly reduced also. On the basis of the same coprecipitation principles, this treatment process should also be effective with other radionuclides from the uranium chain, such as ^{230}Th, ^{210}Pb, and ^{210}Po, and should be investigated. The treatment is economically feasible and could reduce the amount of earthen cover needed to reduce radon emanation to levels recommended by NRC and EPA. We suggest that research be directed toward upgrading the performance of this treatment and conduct additional testing on a larger scale.

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