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Removal of Hazardous Radionuclides from Uranium Ore and/or Mill Tailings: Progress Report for the Period October 1, 1978, to September 30, 1979

F. M. Scheitlin
W. D. Bond

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REMOVAL OF HAZARDOUS RADIONUCLIDES FROM URANIUM ORE AND/OR MILL TAILINGS: PROGRESS REPORT FOR THE PERIOD OCTOBER 1, 1978, TO SEPTEMBER 30, 1979

F. M. Scheitlin
W. D. Bond

Date Published: January 1980

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SUMMARY

Studies made during this report period emphasized the leaching of uranium ore and mill tailings to remove radium. A few scouting tests were performed to obtain data on the recovery of radium, thorium, and uranium from leach liquors and on the recycle of leaching agents. Nitric acid, hydrochloric acid, ethylenediaminetetraacetic acid (EDTA), and diethylenetriaminepentaacetic acid (DTPA) were evaluated as leachants using one sample of a western U.S. ore and two samples of tailings obtained from different uranium mills that employ the sulfuric acid leach process.

Leached solids with radium contents approaching 10 pCi/g (98% radium removal) were obtained after six stages of batch, crosscurrent leaching with 3 M HNO_3 at 33% concentration of solids and a temperature of 60°C. Hydrochloric acid, EDTA, and DTPA have not yet been tested through six stages of crosscurrent leaching. However, on the basis of two-stage tests on mill tailings, 0.5 M EDTA solutions at pH values of 8.2 to 11.6 were found to be more effective, while hydrochloric acid in two- or three-stage tests was less effective, than nitric acid. Solutions of 0.3 M EDTA (pH, 4.0) and 0.05 M DTPA (pH, 4 to 10) were ineffective.

Essentially no important differences were observed in the leaching behavior of ore and of mill tailings derived from the same ore. The residue remaining after six stages of nitric acid leaching was relatively intractable to radium leaching with water or additional nitric acid leaching. Initial tests indicated that the recycle of nitric acid is chemically feasible by evaporating the leach liquors to recover unused acid and then thermally decomposing the metal salts to recover consumed acid. Radium recoveries of $99^{+}\%$ by carrying on barium sulfate were shown to be chemically feasible in a series of experiments with leach liquors, but processing applications would probably require methods for barium recycle and barium-radium separation. Recovery of ^{230}Th and uranium from nitrate leach liquors by tri-n-butyl phosphate extraction appears promising in initial tests.

1. INTRODUCTION

Present methods for processing uranium ore produce mill tailings which represent a potential radiological hazard for thousands of years and thus would require long-term surveillance.[1] The radiological hazard stems from the presence of the uranium decay chain members ^{230}Th, ^{226}Ra, and ^{210}Pb, whose decay half-lives are 80,000, 1620, and 19.4 years respectively (Fig. 1).

Even though impoundment, below-grade burial, and maintaining a good cover on a long-term basis have been proposed as control measures,[1] tailings management methods of these types require perpetual surveillance. Eventual water invasion or loss of physical integrity could cause problems relative to water pollution or radioactive radon gas emission.

One solution to the above-mentioned problems would be to find a process (or a combination of processes) suitable for removing the ^{226}Ra and the ^{230}Th parent of ^{226}Ra and concentrating them by factors which would allow the concentrates to be stored in a manner similar to that

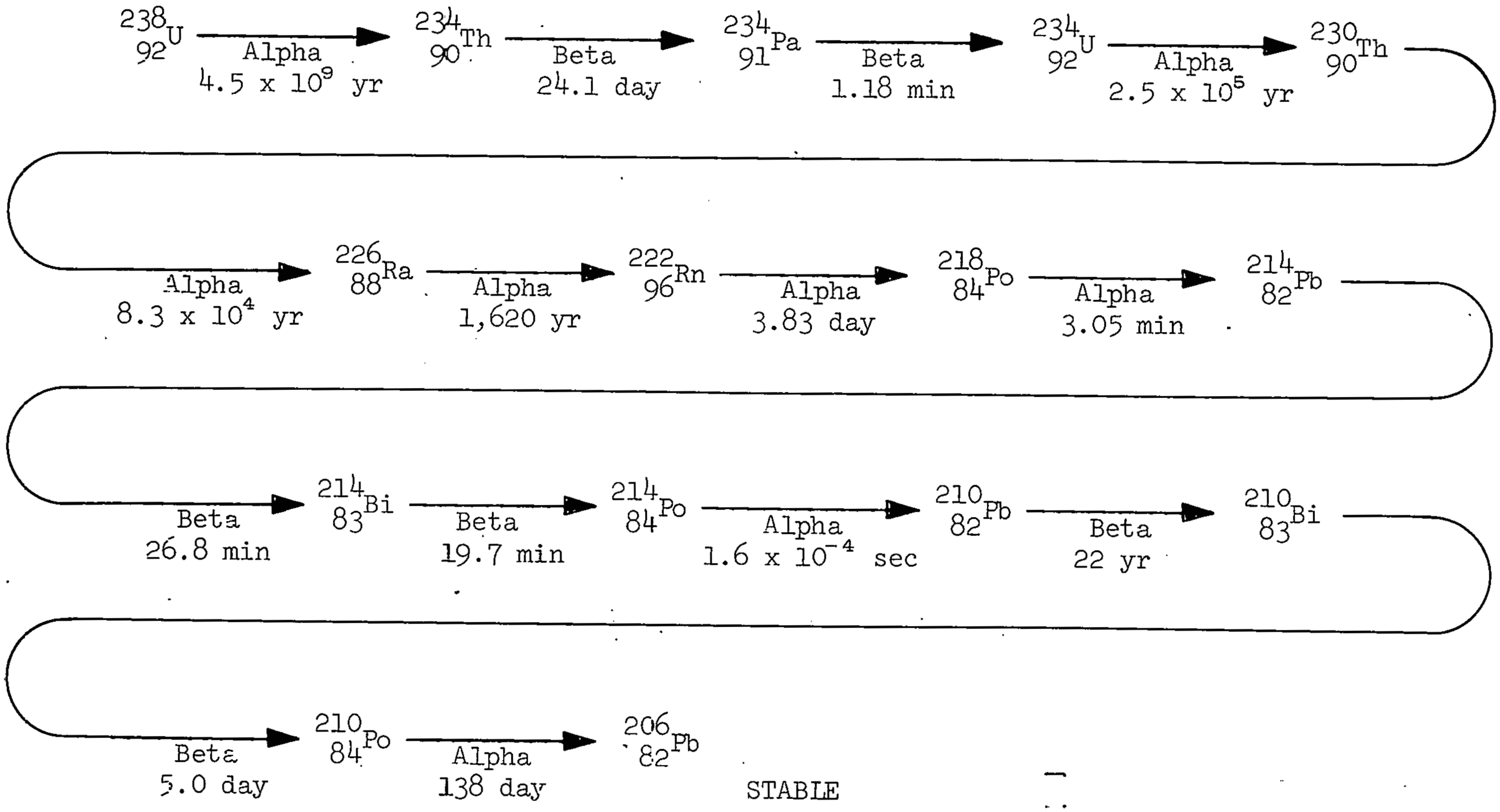

Fig. 1. Uranium-238 decay chain - minor branches not shown.

used for reactor fuel wastes. The heat loads of such concentrates would be much lower than those of reactor fuel wastes. For example, if a concentration factor of 1 million could be obtained, the $\sim$140 million metric tons (MT) of tailings estimated to be in surface piles at 21 operating mills and 22 abandoned sites in January 1979[2] would produce a concentrate of 140 MT of solids with ^{226}Ra and ^{230}Th contents of $\sim$1 mCi/g each.

The most immediate concern posed by these tailings involves ^{226}Ra itself or its daughter ^{222}Rn, which is an alpha-particle-emitting gas with a 3.8-day half-life. The "maximum permissible concentrations" of ^{226}Ra and ^{230}Th in drinking water are 3.3 and 667 pCi/liter respectively. The "suggested" limit for ^{226}Ra in soil and building materials is 20 pCi/g.[3] These limits have been somewhat controversial and are still being debated; nevertheless, the limits of 3.0 pCi/liter in water and 20 pCi/g in solids may be considered as goals for the present.

Most uranium ores (0.2% U_3O_8) and tailings have ^{226}Ra concentrations of $\sim$800 pCi/g;[1,4] therefore, a reduction factor of at least 800/20 = 40 (97.5% removal) is required for the solids to be below the 20-pCi/g level. Tailings have essentially the same radium content as the original ore since both of the major ore processing methods - sulfuric acid and sodium carbonate methods - result in radium reporting to the tailings solids or ponds.[5] Nitric acid leaching of ore and/or tailings has been shown to have promising potential and thus was continued as the main thrust of our work this year.[4] A few scouting tests using other leachants were also performed. Only a few scoping tests were made to obtain data on recovery of radionuclides from the leach liquor and on recycle of the nitric acid.

2. EXPERIMENTAL MATERIALS, APPARATUS, AND PROCEDURES

Many of the procedures used in this work are adaptations of methods that have been described previously.[4] However, descriptions of the materials and methods used are included here.

2.1 Materials

The samples of uranium ore and mill tailings used in the majority of this work were sandstone types from the western part of the United States, and were designated as No. 4 ore and tailings by Ryon and Seeley.[4] A significant amount of work has also been done with refractory tailings No. 1, which was reported by Ryon and Seeley[4] to be the least amenable to nitric acid leaching. Both of the mill tailings samples, Nos. 1 and 4, were obtained from uranium mills that use the sulfuric acid leach process. No work was done using tailings from mills that employ the carbonate leach process. The analyses for the ore and tailings samples, as reported by Ryon and Seeley,[4] are given in Table 1. The samples were obtained as follows: Approximately 100 lb of dry material was blended and divided by quartering and riffling; then 100 g of the resulting product was ground to <100 mesh (149 μm) and blended to provide 1- to 2-g portions for analysis.

Results of sieve tests on the riffled ore and tailings, along with the radium content of each fraction, are given in Table 2. The materials were initially ground to completely pass through the 1180-μm (U.S. mesh 16) screen; then a 25-g sample was added to the top screen, and the assembled screen nest was placed on a Ro-Tap sieve-shaker for 20 min. The trend shown in Table 2 is unmistakable - the finer material is richer in radium,

Table 1. Analyses of uranium ore and mill tailings

Component	No. 1	No. 4	
	Tailings	Ore	Tailings
	Analysis, in pCi/g		
^{226}Ra	910	768	716
^{230}Th	322	991	133
^{210}Po	395	206	176
	Analysis, in wt %		
U	0.015	0.23	0.0065
Ba	0.15	0.091	0.10
Ca	2.5	1.2	0.73
Mg	0.40	0.32	0.20
Na	0.70	1.4	1.7
Fe	1.4	1.3	0.87
Al	3.9	5.7	5.2
SO_4^{2-}	4.89	0.38	0.99
Total	2.6	0.93	1.1

Table 2. Particle size distribution of No. 4 uranium ore and tailings

Screen fraction (μm)	Tailings wt %	Tailings ^{226}Ra (pCi/g)	Ore wt %	Ore ^{226}Ra (pCi/g)
500-1180[a]	53.6	653	38.7	317
300-500	18.8	424	26.4	658
150-300	15.3	613	22.3	855
105-150	5.0	885	4.5	1125
88-105	1.9	b	2.2	1320
44-88	4.0	1555	4.5	1514
<44	1.4	2799	1.3	2657

[a] No material was found on 1180-μm screen.

[b] Not determined.

which agrees with the data of Seeley[6] and of Sears et al.[1]

Ryon and Seeley[4] had found No. 1 tailings to be very refractory, presumably due to their high sulfate (4.89%) and organic carbon (0.23%) contents. Thus, many of the later scouting tests were conducted with this material since it would provide the most stringent requirements for a leaching reagent.

2.2 Apparatus and Analytical Instrumentation

2.2.1 Leaching apparatus

Two different sets of apparatus were used in the leaching experiments, depending on whether the scale of the work was with 100 to 200 g or 5 g of solids. The 100- to 200-g leaching apparatus, shown in Fig. 2, consists of 1-liter stainless steel beakers that are immersed in a thermostated water bath. Stirring is provided by an overhead-mounted stirrer whose shaft passes through a Teflon sleeve in the water-cooled lid. Cooling of the lid was found to be necessary in order to prevent excessive loss of volume by vaporization, especially for the longer (48-hr) leaching runs.

In the small-scale scouting tests, mixing was accomplished via a shaker apparatus* which was contained in a controlled-temperature water bath measuring 25 in. long x 14 in. wide x 16.5 in. deep. A motor-operated shaker and holder permitted up to eight samples to be leached simultaneously. Samples were contained in glass culture tubes (16 mm diam by 150 mm long) equipped with a plastic screw cap and polyethylene cone gaskets. In each test with this apparatus, 5 g of solids was contacted

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*Model "Magni-Whirl" from Blue M Electric Co., Blue Island, Ill.

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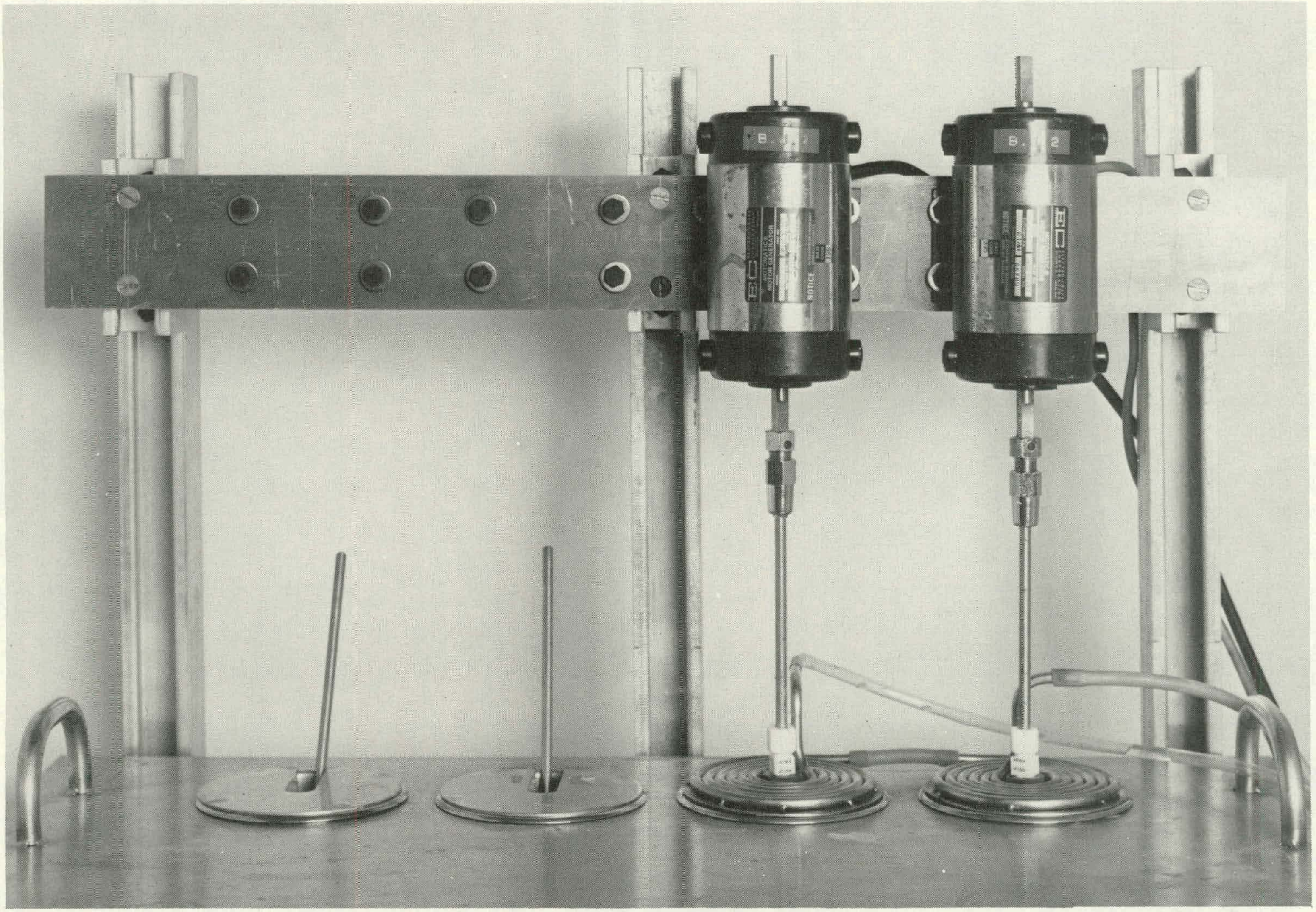

Fig. 2. Leaching apparatus used with 100- to 200-g samples of ore or tailings.

with 10 ml of the leachant being evaluated.

2.2.2 ^{226}Ra counting instruments

Two gamma counting instruments are used for ^{226}Ra analysis. In each, the 609-keV gamma ray from the ^{214}Bi decay product of ^{226}Ra is used for making analytical calculations (see Sect. 2.4.1).

Large (100-g) solid samples are counted in the apparatus shown in Fig. 3, using the procedure detailed in Sect. 2.4.1. This instrument is a 3-in.-diam NaI, well-type gamma counter that has been modified to accept a 3- by 1.5-in. closed plastic dish (see Fig. 4). The detector signal is sent to a TN-1218 amplifier and a Tracor-Northern multichannel pulse-height analyzer (Model TN-1706) provided with a TN-1314 display unit.

The other gamma-counting system (Searle Analytic, Inc., automatic gamma counting system Model 1185) can be set to a particular gamma-energy window and has the capability of automatically counting up to 300 samples for a chosen counting time. The detector is also a 3-in.-diam, well-type NaI crystal. Small samples (1 to 5 g of solids) are counted in the 16-mm-diam by 125-(or 150-)mm-long culture tube sample bottles. This system (Fig. 5) is used for the counting of sealed samples of $^{226}RaSO_4$ carried on $BaSO_4$ (see Fig. 4 and Sect. 2.4.1) and of the residues from the small-scale (5-g) leach tests (Sect. 2.3.3).

2.3 Leaching Procedures

Three types of leaching tests were carried out during this report period: (1) 100- to 200-g quantities of solids (ore or tailings) were leached with acids for various times; (2) 100 g of acid-leached residues or tailings were leached with water; and (3) scouting tests were made using 5 g of solids.

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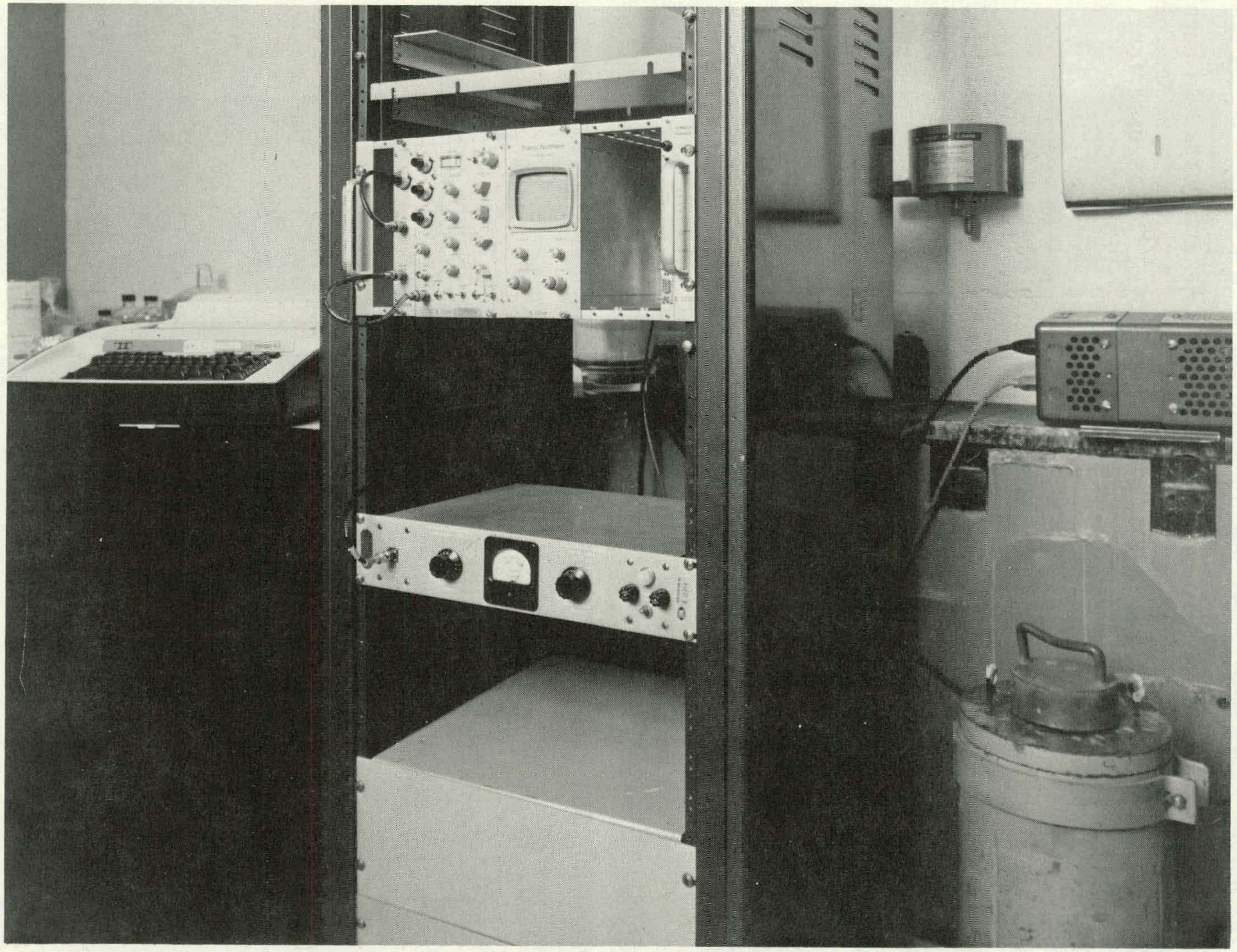

Fig. 3. NaI gamma-ray counter and electronics (Tracor-Northern)

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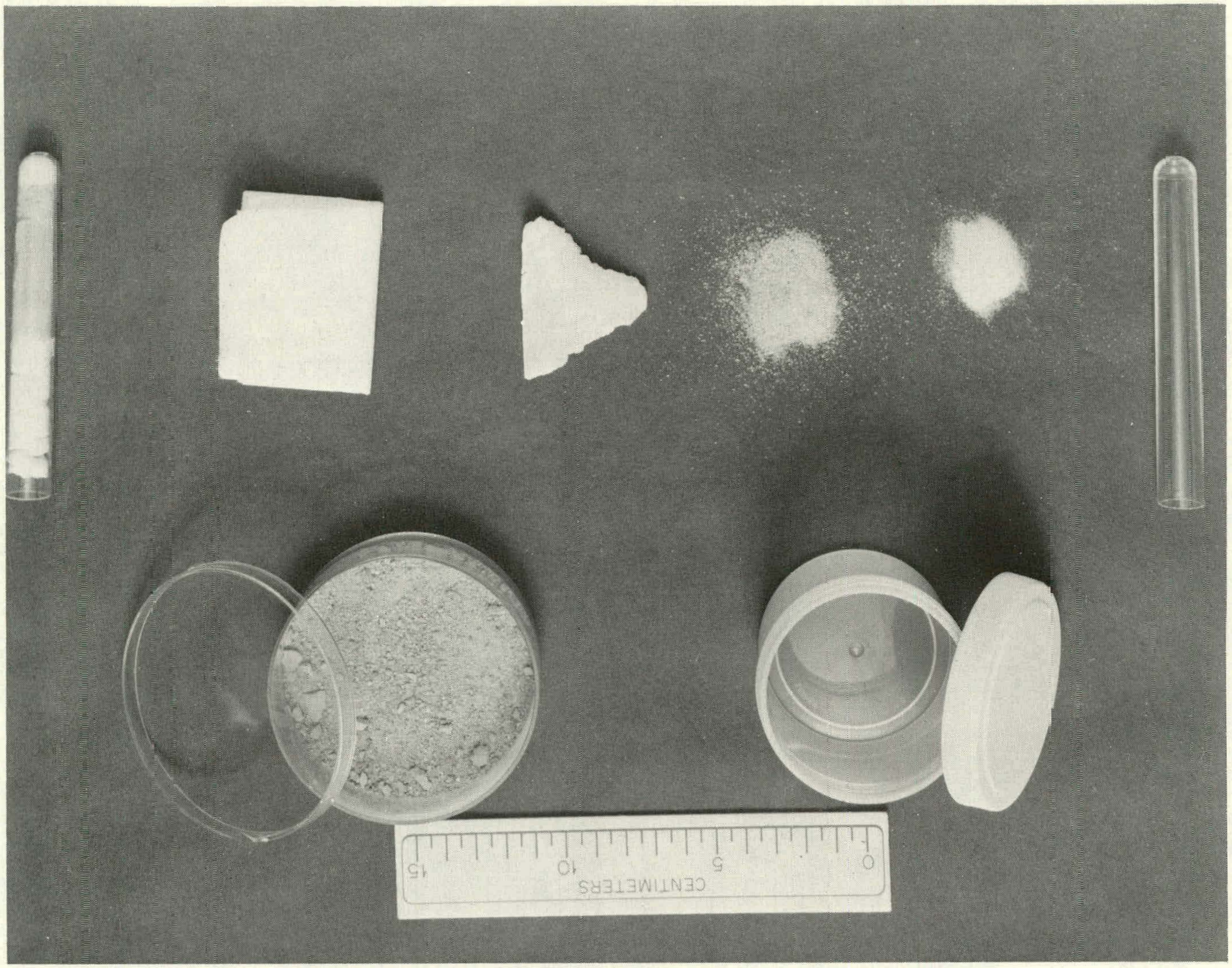

Fig. 4. Sample containers used for ^{214}Bi gamma counting.

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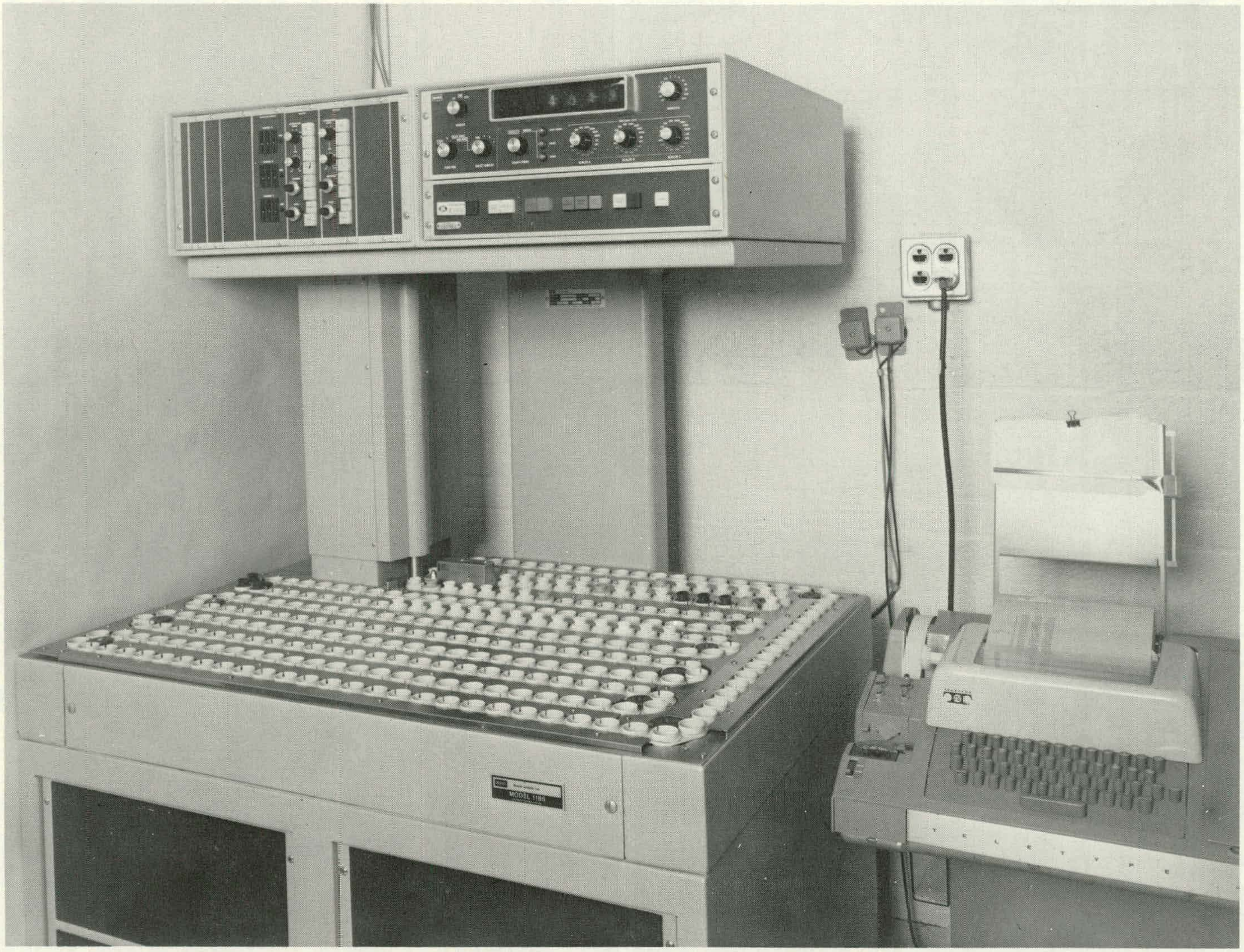

Fig. 5. Searle Analytic, Inc., Model 1185 automatic gamma counting system.

2.3.1 Acid leach tests with 200-g quantities of solids

The procedure used in the acid leaching tests consisted of five steps, which can be described as follows:

1. Two 100.0-g samples of ore (or tailings) were counted separately on the Tracor-Northern instrument to arrive at an average ^{226}Ra analysis, in picocuries per gram.
2. These two samples plus 400.0 ml of acid of the desired strength were added to a 1.0-liter stainless steel leach beaker; the latter was then placed the water bath apparatus (Fig. 2).
3. The slurry was stirred at 500 rpm for the specified time at the desired temperature level.
4. The leached slurry was filtered using a Whatman No. 42 filter paper. The filtered solids were water-washed from the paper into a beaker and refiltered, dried at 100°C in an oven, weighed, and counted.
5. This procedure was used for "33% solids" (i.e., 200 g of solids per 400 ml of acid). In cases where other ratios were used, the volume of acid to the weight of solids was appropriately adjusted. In our definition, the density of the liquid is always arbitrarily taken as 1.0. For example, the above conditions are calculated as follows: $\% \text{ solids} = \frac{200}{200 + 400} \times 100 = 33.$

2.3.2 Water leach test procedure

The procedure used in the water leaching test consisted of four steps, which can be described as follows:

1. A 100-g sample of dry solids was put into a 4-liter beaker, and 3000 ml of distilled water was added.
2. The slurry was stirred for the specified time at a rate which gave good suspension of the solids.
3. At the end of the test period, the slurry was centrifuged and the liquid decanted through a Whatman No. 42 filter paper.
4. A 2000-ml volume of the filtrate was used as a sample for determining radium content, as described in Sect. 2.4.1.

2.3.3 Scouting tests using 5-g quantities of solids

Scouting tests with small quantities of solids were initiated to permit determination of conditions that would warrant further study on a larger scale. All solids used in these tests were passed through a U.S. 16 standard sieve (1190-μm opening) to break up agglomerates prior to leaching.

Duplicate 5.0-g portions of ore or tailings were weighed into a 16-mm-diam by 150-mm-long Pyrex culture tube with threaded top, and an initial gamma count for radium content was obtained by using the Searle automatic counter system. After a 10-ml volume of the appropriate leach solution to be used had been added to the solids, the threaded cap with polyethylene gasket was screwed on tightly. The tubes were then placed in the shaker bath (eight can be accommodated simultaneously) and shaken for a specified time at a selected temperature. At the end of the leaching period the sample tubes were removed and then centrifuged; the supernatant was used for liquid sample analyses. The residue was washed with water in the tube by adding 10.0 ml of water, shaking to mix the solids, and recentrifuging. After the wash water had been drawn off and discarded, a "final count" of the solids was made. This method was especially convenient because the solids did not have to be transferred after leaching and washing. The culture tube could be inserted in the NaI crystal well of the Searle counter directly.

2.4 Analytical Procedures

A knowledge of the amounts of various constituents is obviously essential to the interpretation of the results of these experiments. Methods that were capable of giving reasonably accurate results for a large number of samples in a reasonable time were desired.

2.4.1 Analysis of ^{226}Ra by means of 609-keV gamma counting

Evaluation of the results of trial processing methods for radium removal from uranium ore tailings obviously requires a method of analysis that is reliable, preferably simple, reasonably accurate, and rapid. Ryon and Seeley[4] and Yagnik[7] had concluded that most of these requirements were met by $BaSO_4$ carrying of $RaSO_4$ and subsequent counting of the 609-keV gamma emission from the ^{214}Bi daughter of ^{226}Ra. The radon emanation method,[8] which relies on complete evolution of the ^{222}Rn daughter, alpha counting of the gas, and direct alpha counting of the ^{226}Ra after electrodeposition, has many undesired aspects and possible pitfalls, especially when a large number of samples are involved. There remained, however, some uncertainty as to whether nitric acid would cause undue interference in the radium carrying on $BaSO_4$.[8] Section 3.3.2 addresses this problem in greater detail. Considerable effort was required to set up and develop a reliable procedure for analyzing the ^{226}Ra contents of nitric acid solutions.

The ^{214}Bi activity must be determined under conditions where it can be used to calculate the ^{226}Ra activity or concentration. The most desirable situation for this measurement is when secular equilibrium exists for the uranium decay chain (see Fig. 1), where the activities of ^{226}Ra and ^{214}Bi are equal. In the event that the equilibrium between radium and its daughters is disturbed, the sample must be sealed to prevent escape of ^{222}Rn and an interval of about 30 days must be allowed for reestablishment of equilibrium. However, an estimate of the ^{226}Ra to within ∿1 to 2% of its true value can be made after 4 days if two points are measured on the ^{214}Bi activity growth curve at two different times, t, where $t_1 > 4$ hr and $t_2 > 4$ days $+ t_1$. We found this method to be especially useful for liquid samples; details are further described later in this section.

The NaI gamma-ray spectrum of ^{226}Ra is presented in Fig. 6, and an actual photograph of one of our samples on the cathode-ray tube display unit of our multichannel analyzer is shown in Fig. 7. The well-resolved 609-keV gamma-ray peak from ^{214}Bi may be seen at the right in each figure. The relative intensities of the gamma rays from ^{226}Ra are given in Table 3, which shows that the 609-keV gamma ray is the most abundant and is present to the extent of 43% of the disintegrations of ^{226}Ra at equilibrium.

Solids analysis for ^{226}Ra. As previously stated, complete retention of the ^{222}Rn daughter is necessary since this guarantees that the subsequent daughters are at equilibrium (in 1 hr or so at the most). Both our experience and data reported by Ryon and Seeley[4] indicate that original uranium ore or tailings or leached ore or tailings do not lose a signifi-

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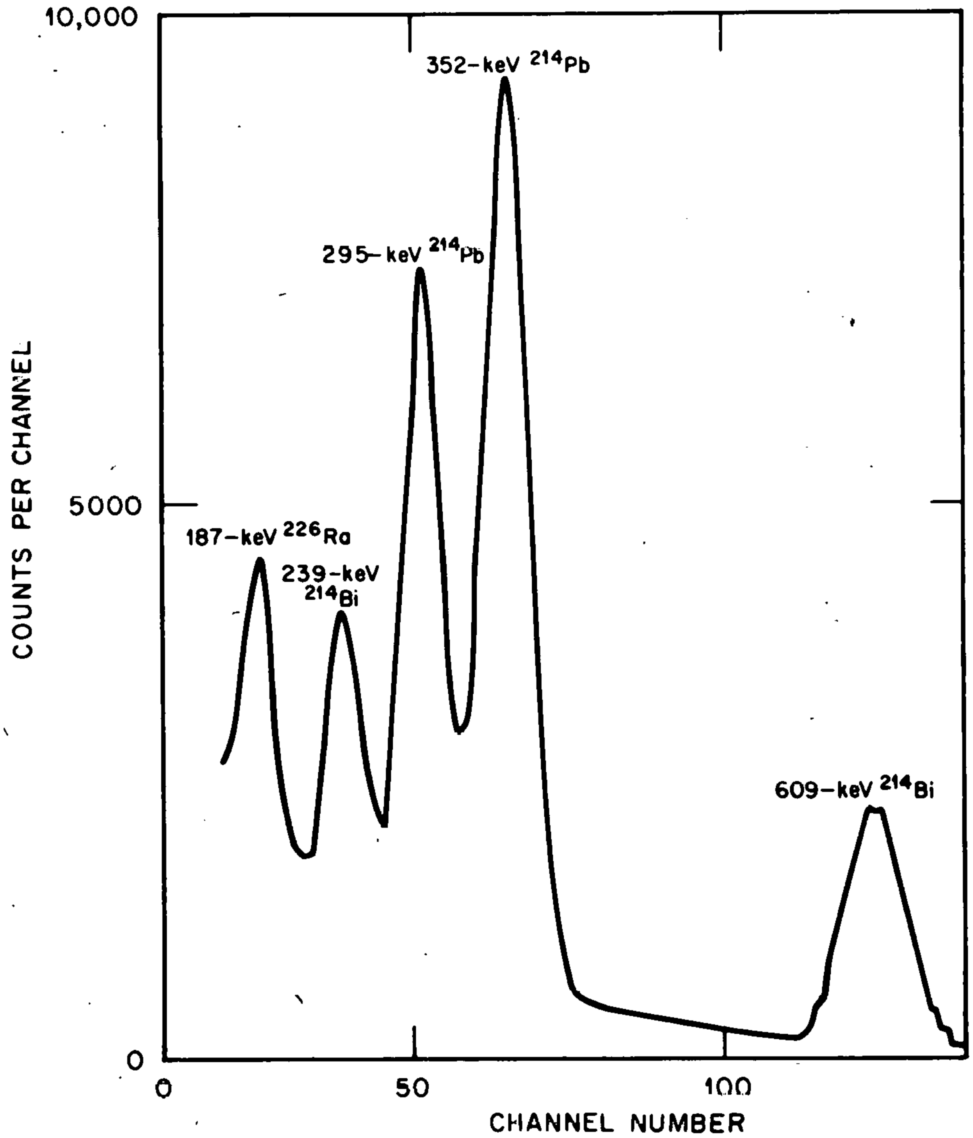

Fig. 6. NaI gamma-ray spectra of ^{226}Ra decay series.

ORNL PHOTO 2481-79

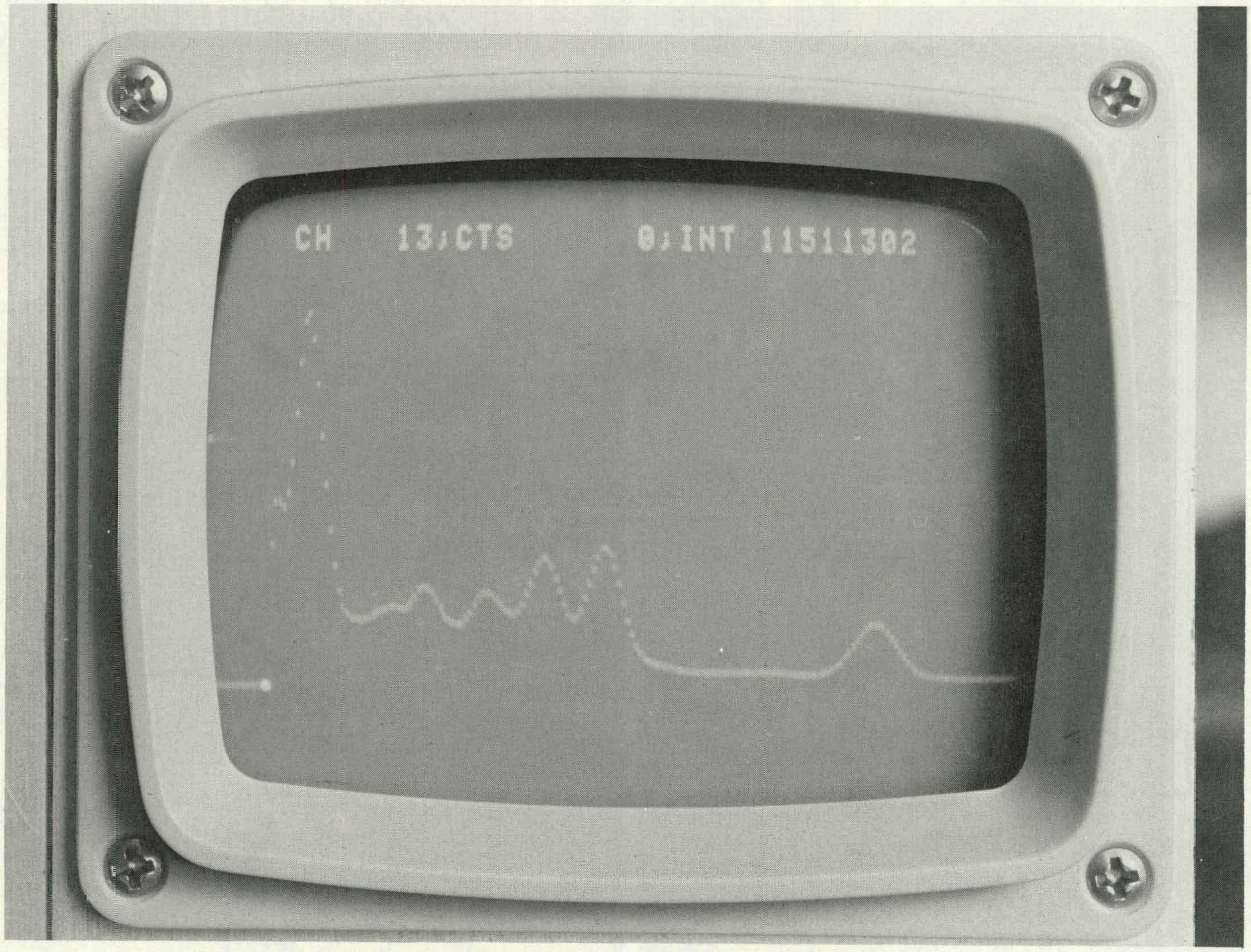

Fig. 7. Display of gamma-ray spectra of ^{226}Ra and its daughters on cathode ray tube as obtained from Tracor-Northern counter.

Table 3. Gamma-ray energies and relative intensities of ^{226}Ra daughters

Radionuclide	Energy (keV)	Relative intensity
^{214}Pb	295	18
^{214}Pb	352	35
^{214}Bi	609	43
^{214}Bi	1120	14
^{214}Bi	1765	17

cant amount of ^{222}Rn when temperatures of less than ∿150°C are involved. Hence, these types of solids can be counted immediately. On the other hand, $RaSO_4$ carried on $BaSO_4$ from solution must be sealed to trap ^{222}Rn because the radium is separated from its daughters during the precipitation. The sealed sample container for counting ∿100-g solid samples is shown in Fig. 3.

The gamma counters were calibrated by using uranium standard samples Nos. 102, 103, and 104 containing 0.1, 0.05, and 0.01% uranium, respectively, obtained from the New Brunswick Laboratory (NBL). These samples contained pitchblende ore dispersed in SiO_2 in radioactive equilibrium and hence could be attested to contain 333, 166.5, and 33.3 pCi of ^{226}Ra per gram respectively. Samples previously analyzed by Ryon and Seeley[4] and a standard ^{226}Ra solution from the original stock of the late S. C. Lind (kindly provided by F. Seeley) were also used for comparison purposes. Reasonably good agreement was obtained. The calibration factor for the Tracor-Northern "100-g" geometry was determined to be 14.6 (i.e., the factor to convert counts per minute, cpm, to picocuries was 14.6). The efficiency of detection of the 609-keV gamma of ^{214}Bi was 7.2%. Background for the same channel window setting was quite stable at 12.56 cpm (σ = 0.66 cpm).

The Searle apparatus was set to count the 609-keV gamma-ray energy and calibrated for both a 1.0-g and a 5.0-g geometry. The corresponding calibration factors obtained were 3.6 and 3.9. Background at the same setting was very stable at 18.86 cpm (σ = 0.34 cpm), a rate which is equivalent to 68 pCi using the 3.6 factor. The efficiencies of counting the 609-keV gamma for 1-g and for 5-g samples were 29 and 27% respectively.

The higher counting efficiencies are to be expected since small-volume counting "in the well" of the NaI crystal, as is done in this instrument, would be expected to be more efficient (27 to 29%) than counting on top of the crystal, as in the case of the Tracor-Northern setup (7.2% efficiency). The calibrations discussed above served for both solid and liquid sample analyses since the liquid samples involved carrying the radium on $BaSO_4$ and counting the solid $BaSO_4$ at several times after sealing.

The sample counting time for the Tracor-Northern assembly was 10,000 or 20,000 sec. for 100-g samples in the range of ~500 to 700 pCi/g, and a 60,000 sec counting time was used to determine background. Based on 8 separate determinations over a 6-month period, the average values of background and its standard deviation were 12.56 and 0.66 cpm, respectively.

Sample counting time for the Searle instrument is 100 min. Three blanks (background) and three standards are counted, along with each group of samples. The results for the background averaged 18.86 cpm with a standard deviation of 0.34 cpm, based on 17 groups of 5 samples each measured over a period of 5 months.

Analysis of ^{226}Ra in liquids. The method used to analyze liquids for radium involved the precipitation of $BaSO_4$ to carry the $RaSO_4$. The precipitate was then isolated, sealed under paraffin to retain the gaseous ^{222}Rn daughter, and counted in the Searle instrument. Since many of the liquids contained nitric acid, which has been reported to interfere in radium carrying,[8] a special study was necessary to ensure good analytical results. The use of $BaSO_4$ in recovery processes for radium is also discussed in Sect. 3. The steps in the procedure are as follows:

1. Take an appropriate aliquot of sample such that its final acidity after dilution to a final volume of 200

ml is 0.3 M or less and pipette it into a 250-ml beaker.

2. Add 20.0 ml of 0.1 M H_2SO_4, bring the volume up to ∿180 ml, and heat to boiling.
3. Add 20.0 ml of 0.1 M $Ba(NO_3)_2$ solution from a burette while stirring (add in 1 to 2-ml portions over a ∿10-min period).
4. Continue heating for approximately 10 min; let cool and stand overnight.
5. Decant off most of the liquid; remove the solids adhering to the sides and the bottom of the beaker with a rubber policeman, and quantitatively transfer the $BaSO_4$ to the counting tube. Centrifuge, decant, and discard the supernatant liquid, being careful not to unduly disturb the centrifuge cake. Add ∿1/2 in. of sea sand, pour ∿2 in. of melted paraffin on top to seal in the ^{222}Rn, and record the sealing time.
6. Wait at least 4 hr after sealing, and then count using the Searle instrument. Recount after an additional 4-day wait and compute an estimate of the equilibrium value of ^{214}Bi (Fig. 8). Confirm the estimate with an additional count after 30 days to obtain the true equilibrium value of ^{214}Bi, which equals the ^{226}Ra disintegration rate.

Figure 8 gives the equations for estimating the ^{226}Ra. Calculations are conveniently made using a programmable calculator. The data required are the count rates at ∿4 hr, the rate at least 4 days after that, and the

COUNTING THE 609-keV GAMMA OF Bi-214 DAUGHTER AT TWO TIMES AFTER SEALING FOR RADON-222 RETENTION

CRITERIA

1. TIME T_1 MUST BE GREATER THAN 4 hours (0.17 days)
2. ΔT MUST BE GREATER THAN 4 days (i.e. $T_2 > 4.17$ days)

THEN: $$C_3 = \frac{C_2 - C_1 e^{-0.1812\ \Delta T}}{(1 - e^{-0.1812\ \Delta T})}$$

WHERE

C_3 = EQUILIBRIUM COUNT RATE OF Bi-214 = RADIUM-226
C_2 = COUNT RATE OF Bi-214 AT TIME T_2
C_1 = COUNT RATE OF Bi-214 AT TIME T_1
$\Delta T = T_1 - T_1$

DERIVATION BY R. E. LEUZE

Fig. 8. Method for estimating ^{226}Ra in samples not at secular equilibrium.

corresponding times after sealing. These equations were derived by R. E. Leuze, of ORNL, who used the Bateman equations[9] for describing the quantities of chain members at any time and making simplifying assumptions. The estimates have given very good agreement with actual values at secular equilibrium (i.e., when counts are made at ∿30 days after sealing).

Analysis of water leach samples for ^{226}Ra. The analysis of water leach samples required a slightly different procedure from that used for ore leach samples because of the lower ^{226}Ra concentrations. The filtered 2000-ml samples (Sect. 2.3.2) were made acidic by adding 40 ml of concentrated HCl. Subsequently, 100 ml of a 0.0145 M $BaCl_2$ solution (2 mg Ba/ml) and 40 ml of concentrated H_2SO_4 were added; then the solution was heated to boiling and allowed to stand overnight. The $BaSO_4$ was separated, placed into a counting tube, and counted in the Searle instrument. This procedure for analysis of radium in water is a modification of a standard method[10] of radium determination. The standard method was modified to permit the use of direct gamma counting in place of radon emanation and alpha scintillation counting.

2.4.2 Nitric acid and nitrates

Nitric acid solutions (0.5 to 8.0 M) were analyzed by titrating suitable aliquots with sodium hydroxide using a pH meter for end-point detection. Since many of these solutions contained appreciable quantities of iron and other elements, the end point was taken as pH 2.0. The error introduced by this procedure was small (of the order of 1 to 3%), depending on the initial acid concentration and the dilution that occurred during titration.

Nitrates were analyzed by taking suitable aliquots, diluting if necessary, and analyzing the solution using a specific ion electrode for nitrate (ORION Model 93-07) together with the ORION Research Ion-Analyzer, Model 901. Proper care must be taken to avoid interfering ions for which data are provided with the electrode.

2.4.3 Uranium and other elemental constituents of ore and tailings leach solutions

Analyses of the ore samples and the mill tailings leach solutions were provided by the ORNL Analytical Chemistry Division; the methods used for the various constituents are summarized in Table 4.

3. RESULTS AND DISCUSSION

The removal of hazardous nuclides from uranium ore or mill tailings requires that the nuclides be solubilized. Many agents, including nitric[4] and hydrochloric[2] acids, sodium chloride,[11] sodium nitrate,[11] and complexing agents such as ethylenediaminetetraacetic acid (EDTA) and diethylenetriaminepentaacetic acid (DTPA),[6,7] have been tested for this purpose. Since nitric acid had shown promising results,[4] it was emphasized in our initial work. A few tests were also performed using HCl, EDTA, and DTPA as leachants. A few scoping studies were carried out to obtain data on the recovery of radionuclides from leach liquors and on the recycle of nitric acid.

3.1 Effectiveness of Nitric Acid as a Leachant for Radium

3.1.1 Dissolution of ^{226}Ra from uranium ore

Table 5 and Fig. 9 show results obtained for uranium ore leached

Table 4. Methods used for analyzing ore and mill tailings leach solutions

Constituent	Method
U	Spectrophotometric or fluorimetric
Ba	Flame photometer
Ca	Flame photometer
Fe	Atomic absorption
Al	Atomic absorption
SO_4	$BaSO_4$ or colorimetric

Table 5: Batch, crosscurrent leaching of No. 4 uranium ore with 3 M HNO_3 at 60°C

Conditions: 33% solids concentration and 4-hr contact time per stage except where indicated

Run No.	Stage No.	Initial wt of solids (g)	Initial ^{226}Ra conc. (pCi/g)	^{226}Ra conc. in residue (pCi/g)	Cumulative % ^{226}Ra leached
1	1	400	670	a	a
	2	a	a	30.3	95.5
	3	347	30.3	a	a
	4	a	a	12.5	98.1
	5	325	12.5	a	a
	6	a	a	9.25	98.6
2	1	200	650	222	65.8
	2	183	222	32.3	95.0
	3[d]	175	32.3	12.9	98.0
3[b]	1	100	1419	a	a
	2	a	a	224	84.2
	3	83.5	224	52	96.3
4[c]	1	125	615	63	89.8
5	1[d]	200	650	113	82.6

[a] Not determined.

[b] Leaching of a slime fraction separated from the ore.

[c] 20% solids concentration.

[d] In-stage leaching time was 48 hr. The concentration of dissolved radium as a function of time was also determined in Run 5 and is shown in Table 6.

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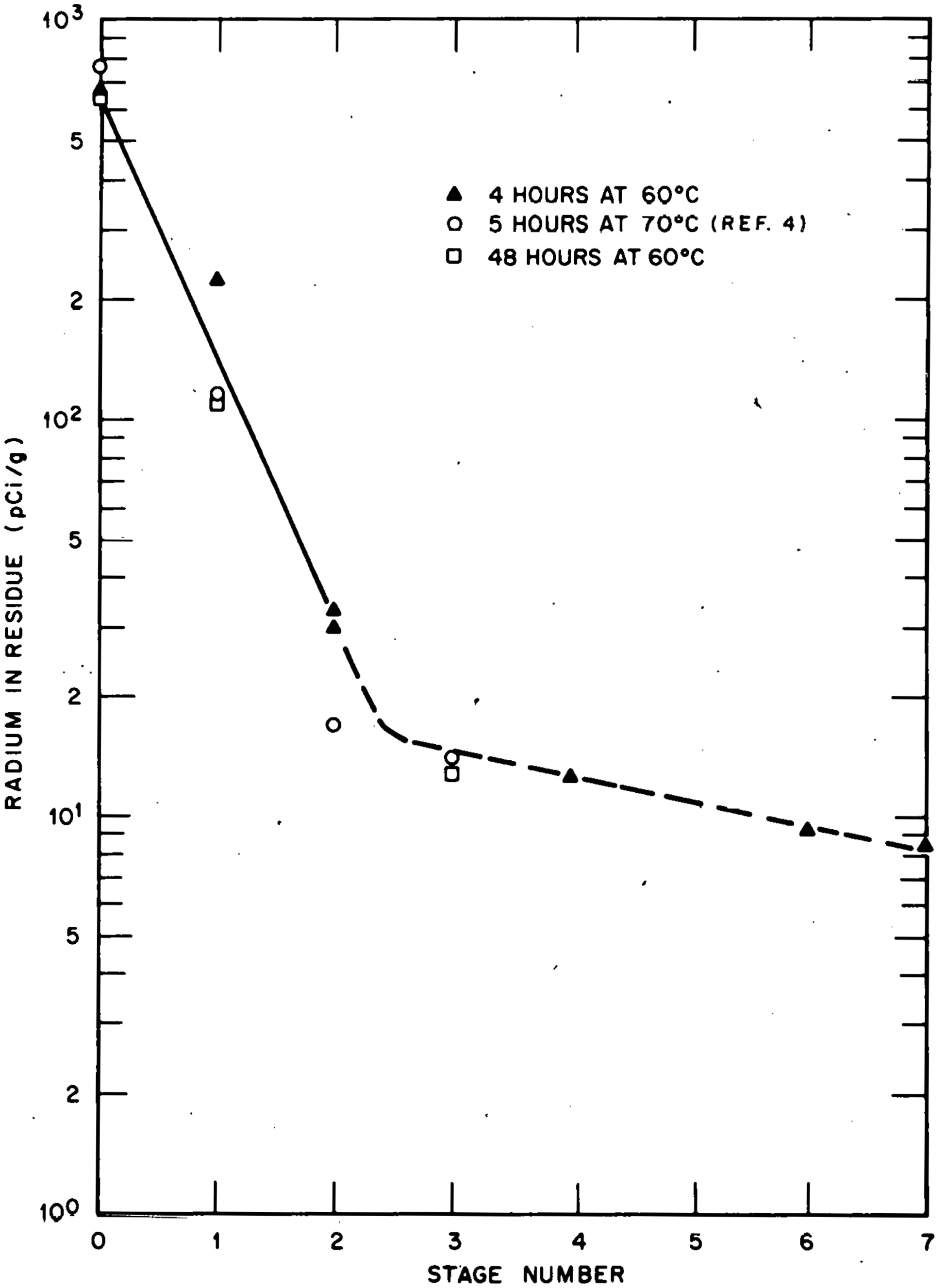

Fig. 9. Uranium ore leached with 3 M HNO_3 at 30% solids.

with 3 M HNO_3 for 4 hr and 33% solids concentration (i.e., 200 g of solids in 400 ml of acid). Nitric acid at this strength is an effective agent for leaching radium, as shown by Ryon and Seeley.[4] Their data obtained at 70°C using 100 to 200 g of solids in each stage are included in Fig. 9 for comparison purposes. Subsequent scouting-type tests were performed using 5-g amounts (Fig. 10), and no significant differences were noted. The small differences that are observed are probably the result of variability in the composition of the original samples. Difficulty was encountered in obtaining representative samples from master blends when 5-g amounts were used; however, the use of 100- to 200-g amounts presented no problems.

The leaching of radium from ore becomes more difficult as leaching proceeds (see Figs. 9 and 10). A much more refractory residue remains after the first three leaches (at 33% solids), and very little further leaching of radium occurs after about the 10-pCi/g level is reached. This fact may have important consequences with respect to the environmental behavior of nitric acid-leached ore residue. As shown in Table 5 and Fig. 9, two stages of 3 M nitric acid leaching remove ∿96% of the initial radium; however, the efficiency of leaching diminishes rapidly thereafter. This behavior is further corroborated by the scouting test data shown in Fig. 10, where the radium removal becomes negligible at ∿2% (∿15 pCi/g) residual radium.

Results of initial studies of the effect of time on the leaching of uranium ore in a single-stage test indicated that an essentially constant concentration of dissolved radium was attained after ∿1 hr (Table 6). This suggests that the radium was being dissolved from sparingly soluble

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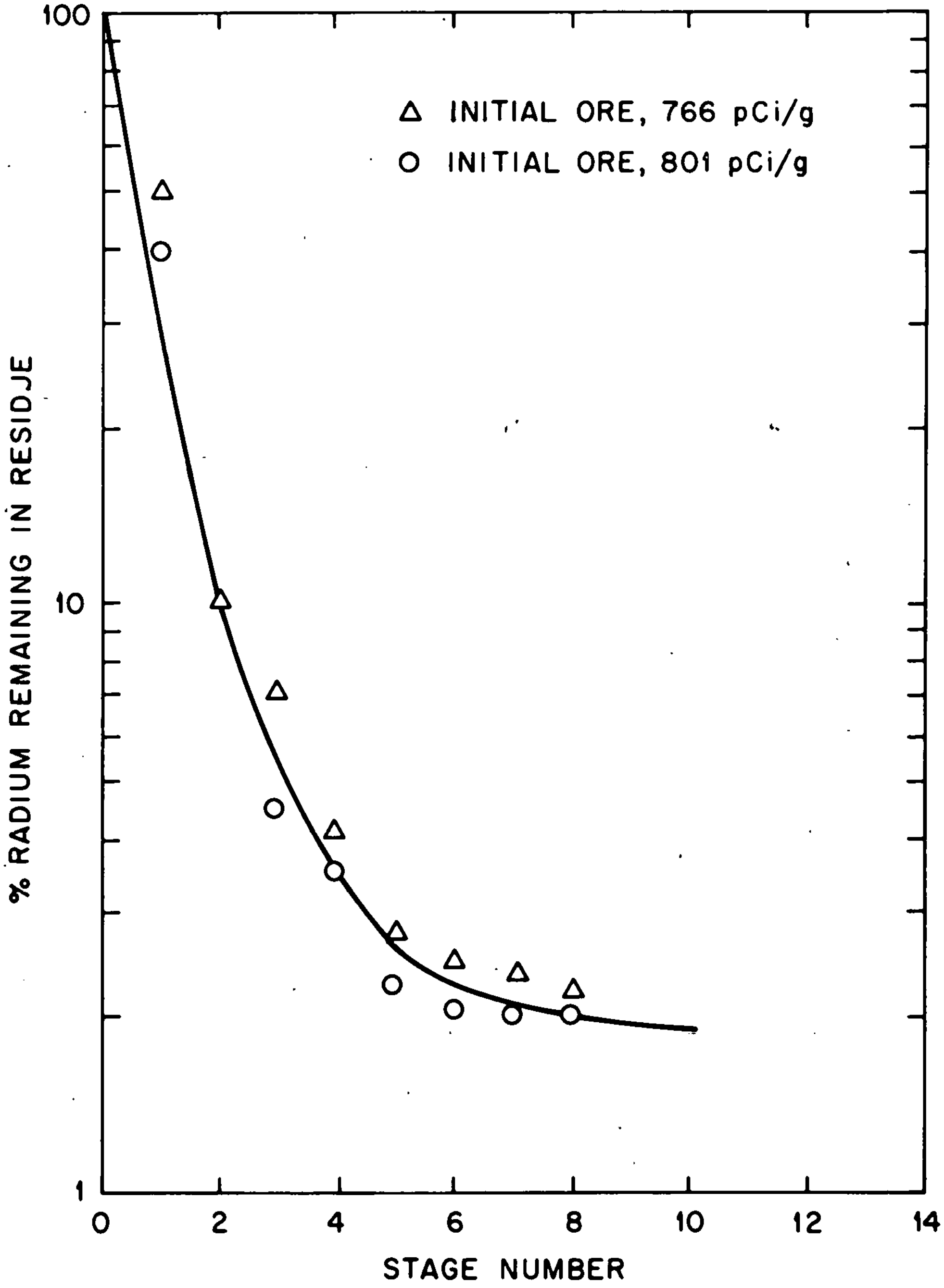

Fig. 10. Scouting tests of batch, crosscurrent leaching of No. 4 uranium ore with 3 M HNO_3 at 60°C (5 g of ore shaken with 10 ml of acid).

Table 6. Concentration of dissolved radium as a function of time during the single-stage leaching of No. 4 uranium ore in 3 M HNO_3 at 33% solids concentration and 60°C

Conditions: 200 g of ore stirred with 400 ml of 3 M HNO_3

Leach time (hr)	^{226}Ra conc. (pCi/ml)	% ^{226}Ra leached[a]
0.5	227	54.5
1.0	232	58.9
1.5	227	63.3
2.0	213	67.4
2.5	223	71.7
3.0	224	76.0
3.5	219	80.2
4.0	218	84.4
48.0	217	84.4

[a] The percent of ^{226}Ra leached increases with time, although the concentration is approximately constant because 25-ml samples were taken for ^{226}Ra analysis from the 400-ml aqueous volume and replaced with 25 ml of fresh 3 M HNO_3 after each time period indicated.

compounds (e.g., a mixture of Ba, Ca, and Ra sulfates), and that dissolution continued until the solution became saturated. The conditions under which the experiment was carried out, however, left some doubt as to the validity of the indicated dissolution mechanism. Replacement of the leach liquor samples that were withdrawn for ^{226}Ra analysis with fresh 3 M HNO_3 was necessary in order to maintain a constant volume of liquid throughout the experiment. This procedure made it necessary to dilute the concentrations of all the solution species (except HNO_3) by a factor of 1.07. It was possible, although not very likely, that dissolution rates were just of the right magnitude to return the radium concentration to its original value in the 1-hr time intervals between 1 and 4 hr. Therefore, additional experiments were performed in which only the solids were removed and no additions of fresh acid were required. The radium concentration of the solids showed no further decrease after about 1 hr of leaching time (Table 7). Thus, it appears that saturation of the solution with sparingly soluble salts is limiting with regard to the removal of radium in the first two stages of leaching unless the concentration of solids is decreased sufficiently. After most of the $CaSO_4$ and $BaSO_4$ have been removed in the first two stages of leaching (see Sect. 3.1.2), the opportunity for radium saturation at our leaching conditions is no longer present.

3.1.2 Dissolution of ^{226}Ra from tailings

Initial studies showed that 3 M HNO_3 at 60°C was effective for leaching No. 4 tailings, whereas 0.5 M HNO_3 was not (Table 8). Further studies were therefore conducted on Nos. 1 and 4 mill tailings to better establish the effects of HNO_3 concentration and temperature on radium leaching (Tables 9 and 10). Increasing the acid concentration or increasing the

Table 7. Concentration of radium in residual solids as a function of time during the single-stage leaching of No. 4 uranium ore in 3 M HNO_3 at 33% solids concentration and 60°C

Conditions: 5 g of ore shaken with 10 ml of solids

Run No.	Time (hr)	^{226}Ra in solids (pCi/g) Initial[a] ore	Residue	Cumulative % of ^{226}Ra leached
1	0.25	835	322	61
	0.50	800	434	43
	0.75	772	400	48
	1.0	721	367	49
	2.0	754	382	49
	3.0	736	362	51
2	0.25	876	541	38
	0.50	854	480	44
	1.0	798	450	44
	2.0	801	433	46
	4.0	808	485	40

[a] Variability in ^{226}Ra content of initial ore is thought to be due to inability to obtain a representative sample when taking 5-g amounts of the original ore. A separate sample of ore was used for each time interval tested for Runs 1 and 2.

Table 8. Batch, crosscurrent leaching of No. 4 uranium mill tailings at 33% solids concentration in nitric acid at 60°C

Conditions: 200 g of solids and 400 ml of HNO_3 and a 4-hr leaching time employed per stage except where indicated

Run No.	Stage No.	HNO_3 ($\underline{M}$)	^{226}Ra content in solids (pCi/g)		Cumulative % Ra leached	Leach liquor analyses[a] (mg/liter)						
			Initial	Final		U	Ba	Ca	SO_4^{2-}	Fe	Al	Na
1	1	3.0	738	349	52.7	90	6	1340	11,460	2540	455	39
	2	3.0	349	27.5	96.3	14	15	91	166	307	238	8
	3	3.0	27.5	15.9	97.8	--	--	--	--	--	--	--
	4[b]	3.0	15.9	12.3	98.3	--	--	--	--	--	--	--
2	1	3.0	654	209	68.0	90	7	1350	11,200	2560	452	38
	2	3.0	209	22.4	96.6	14	7	117	233	254	210	9
	3	3.0	22.4	16.7	97.4	--	--	--	--	--	--	--
	4[b]	3.0	16.7	12.2	98.1	--	--	--	--	--	--	--
3	1	0.5	578	454	21.5	23	<0.2	1450	9,450	1900	327	41
	2	0.5	454	334	42.2	2.4	3.5	127	990	770	457	43
4	1	0.5	548	449	18.1	22	<0.2	1400	9,530	1920	325	51
	2	0.5	449	228	58.4	2.9	4.6	123	840	660	434	41
5[c]	1	0.5	586	312	46.8	8.9	1.6	465	3,730	900	231	22
6[c]	1	0.5	602	348	42.2	6.5	1.4	460	3,680	900	235	22

[a] Symbol -- denotes not determined.

[b] A 48-hr leach time in stage 4.

[c] 14.3% solids (i.e., 110 g per 660 ml of acid).

Table 9. Effects of nitric acid and temperature on the leaching of radium from uranium mill tailings in single-stage leach tests

Conditions: 5 g of tailings shaken with 10 ml of acid for 4 hr

Type of sulfate tailings	Temperature (°C)	HNO_3 ($\underline{M}$)	^{226}Ra in solids (pCi/g) Initial tailings[d]	^{226}Ra in solids (pCi/g) Residue	Cumulative % Ra leached
No. 4	60	8.3	796	186	77
		8.3	846	316	63
		3.6	850	505	41
		3.6	887	543	39
		3.6	754	391	48
		3.6	996	577	42
		2.3	855	558	35
		2.3	708	449	37
		1.8	761	529	30
		1.8	698	468	33
No. 4	80	3.6	798	228	71
		3.6	695	110	84
		2.3	708	335	53
		2.3	753	375	50
		1.8	745	471	37
		1.8	824	544	34
No. 1	60	8.0	773	416	46
		8.0	824	435	47
		3.0	804	545	32
		3.0	801	553	31
		2.0	823	650	21
		2.0	804	628	22
	80	3.0	798	437	45
		3.0	805	438	46

[a] Variability in ^{226}Ra content of the initial tailings of each type is thought to be due to inability to obtain a representative sample when taking 5-g amounts of master samples. A separate sample of tailings of each type indicated was used in each test.

Table 10. Batch, crosscurrent leaching of No. 1 uranium mill tailings at 33% solids concentration in 3 M HNO_3 at 80°C

Conditions: 5 g of solids and 10 ml of 3 M HNO_3 in each stage

Run No.	Stage No.	^{226}Ra content in solids (pCi/g) Initial tailings	Residue	Cumulative % Ra leached
1	1	798	437	45
	2	437	223	72
	3	223	106	87
2	1	805	438	46
	2	438	197	76
	3	197	112	86

temperature increased radium removal from the solids. The increase of radium leachability with increasing acid concentration in single-stage tests is expected from the solubility of $BaSO_4$ in nitric acid, as reported by Ryon and Seeley.[4] Formation of the bisulfate ion (HSO_4^-) and ionic strength effects increase the solubility of sparingly soluble sulfates as the nitric acid concentration is increased. Increasing the temperature from 60 to 80°C increases the radium removal by a factor of ∿2. However, further studies are needed to determine the effects of nitric acid concentration and temperature after the sulfates have been dissolved.

The radium is more difficult to leach from No. 1 tailings than from No. 4 tailings, which is in agreement with Ryon and Seeley.[4] Only ∿86% is leached after three stages of contact with 3 M HNO_3 at 80°C with No. 1 tailings (Table 10), whereas ∿98% is leached from No. 4 tailings (Table 8) at the lower temperature of 60°C. Studies of the effect of leaching time on radium removal (Tables 11 and 12) showed that essentially no additional radium was leached after ∿1 hr, as was previously observed in ore leach tests. Thus, the dissolution of radium appears to be controlled by the degree of saturation of the solution with sparingly soluble carrier salts for radium, such as $CaSO_4$ and $BaSO_4$, during the first two leaching stages where these compounds are still present. The concentrations of soluble barium, calcium, and sulfate were essentially constant after ∿0.5 hr when No. 4 ore or Nos. 1 and 4 tailings were leached. Figure 11 shows the data for No. 1 mill tailings. Results for the No. 4 ore and tailings were closely similar, except that the saturation values for barium, calcium, and sulfate were different.

In three-stage leach tests, the results for No. 4 tailings differed

Table 11. Concentration of dissolved radium as a function of time during the single-stage leaching of No. 4 uranium mill tailings at 33% solids concentration in 3 M HNO_3 at 60°C

Conditions: 200 g of ore stirred with 400 ml of 3 M HNO_3

Leach time (hr)	^{226}Ra conc. (pCi/ml)	% ^{226}Ra leached[a]
0.25	94	32
0.50	105	40
1.0	155	62
1.5	150	63
2.0	140	61
2.5	150	62
3.0	140	65
3.5	140	66
4.0	145	67
48.0	140	68

[a] The percent of ^{226}Ra leached increases with time after 1 hr, although the concentration is approximately constant because 25-ml samples were taken from the 400-ml aqueous volume for ^{226}Ra analysis and replaced with 25 ml of fresh 3 M HNO_3 after each time period indicated.

Table 12. Effect of time on the percentage of radium leached from uranium mill tailings in a single-stage leach with 3 M HNO_3 at 33% solids concentration and 60°C

Conditions: 5 g of tailings shaken with 10 ml of acid

Type of tailings	Leaching time (hr)	^{226}Ra in solids (pCi/g)		% Ra leached
		Initial tailings[a]	Residue	
No. 4	0.25	765	473	38
	0.50	809	475	41
	0.75	794	460	42
	1.0	863	563	35
	2.0	838	492	41
	4.0	822	404	51
No. 1	0.25	812	526	35
	0.50	828	569	31
	0.75	801	518	35
	1.0	814	537	34
	2.0	850	535	37
	4.0	814	518	36

[a] Variability in ^{226}Ra content of the initial tailings of each type is thought to be due to inability to obtain a representative sample when taking 5-g amounts of master samples. A separate sample of the tailings type indicated was used for each time interval tested.

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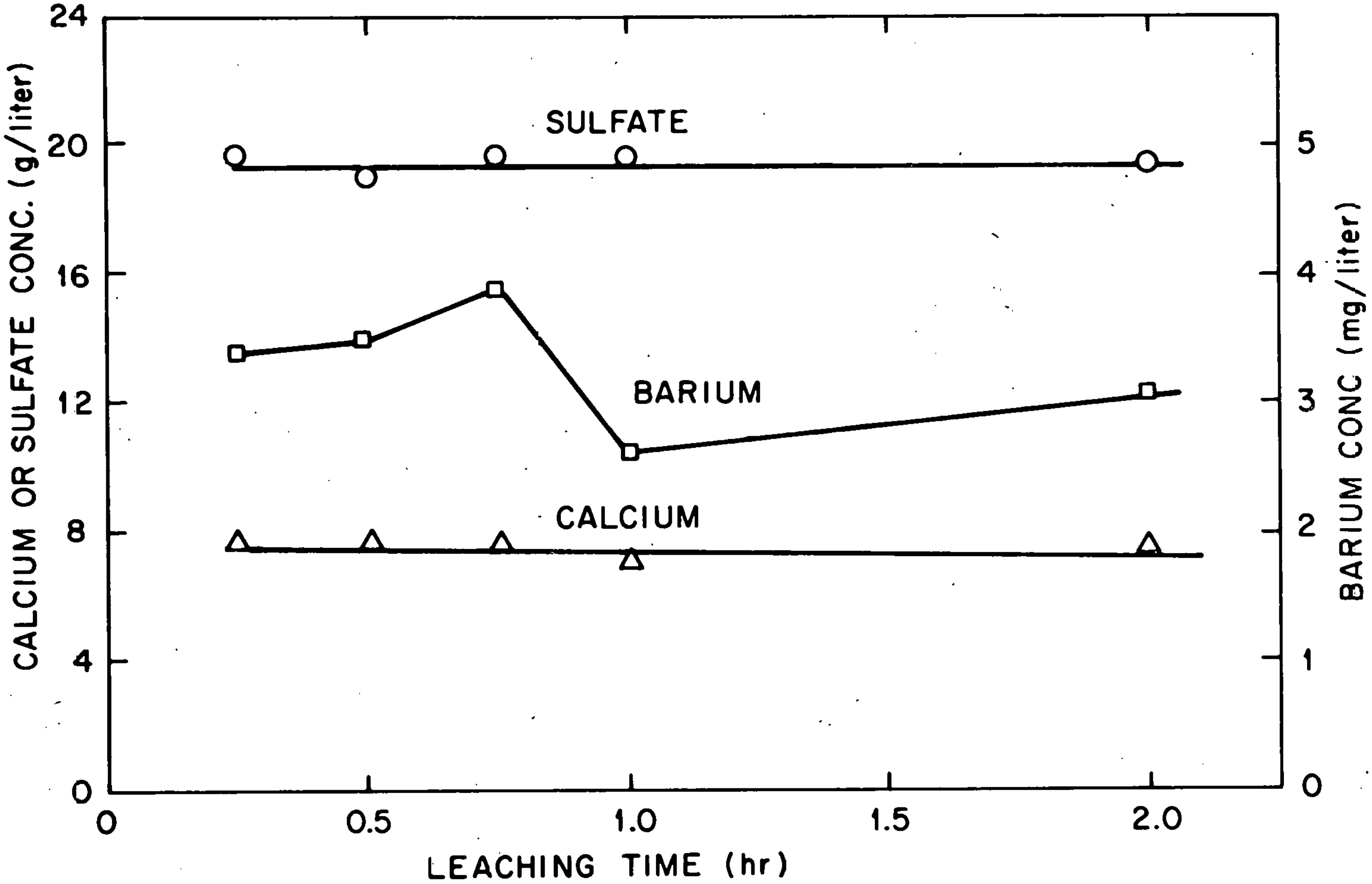

Fig. 11. Concentrations of calcium, barium, and sulfate as a function of time during the single-stage leaching of No. 1 uranium mill tailings at 33% solids concentration in 3 M HNO_3 at 60°C.

from those for ore only slightly in the first stage (compare Runs 1 and 2 in Table 8 with Runs 1 and 2 in Table 5). This difference in stage 1 is probably due to the higher concentration of sulfate in tailings (Table 1). The bulk of the sulfate is leached out in the first stage, and the two materials behave about the same in subsequent leaching stages.

3.2 Release of Radium and Nitrate from HNO_3-Leached Residues into Water

As was previously discussed in Sect. 1, the effect of water (simulating weathering, etc.) on ore tailings is very important and constitutes one of the reasons for these investigations. The comparison of the water leaching of a residue from nitric acid leaching with water leaching of a sample of mill tailings generated by a sulfuric acid process is shown in Table 13. The large amount of nitrate washed out in Run W-1 was caused by an inadequate wash of the starting ore residue; subsequent washes show that adequate washing is possible. The radium results are the most interesting since they show that nitric acid-leached ore whose radium content has been decreased to <10 pCi/g will not further leach radium appreciably. In contrast, results on the water leaching of radium from sulfate tailings show that the radium is present in a readily leachable form. In future studies, water leach tests will be carried out on residues obtained from leaching sulfate tailings with nitric acid. At this point, it would appear that the nitric acid leaching could have advantages over sulfuric acid leaching since it produces tailings less subject to radium leaching by water. However, several disadvantages such as higher costs, etc., would have to be assessed.

Table 13. Batch, crosscurrent leaching of nitric acid-leached ore residues and of uranium mill tailings with water at 25°C

Conditions: 100 g of solids and 3 liters of H_2O per stage (i.e., 3% solids concentration)

	HNO3 residue[a]			Leach liquor analyses		
Run No.	Stage No.	Leaching time (hr)	Ra in initial solids (pCi/g)	Ra (pCi/liter)	pH	NO_3^- (ppm)
			Nitric acid-leached ore residues			
W-1	1	18	9.25	23.8	c	160
	2	24	8.5	<1.0	c	c
	3	120	8.5	3.0	5.3	<2
W-2	1	24	8.5	<1.0	3.9	2
	2	120	8.5	3.0	4.0	<2
			Uranium mill tailings[b]			
TW-1	1	16	654	590	4.6	c
	2	24	c	229	6.0	c
	3	120	c	1619	4.5	c

[a] From sample of No. 4 uranium ore.

[b] From sample of No. 4 tailings, which was obtained from a mill using the sulfuric acid leach process.

[c] Not determined.

3.3 Recovery of Radionuclides and Nitric Acid Values from Leach Liquors

Since ^{230}Th and ^{226}Ra are the most critical uranium decay chain members from the standpoint of a long-range hazard potential, an acceptable method for their removal from leach liquors may be desired. Three possible methods for removing ^{226}Ra are being studied: (1) solvent extraction, (2) ion exchange, and (3) carrying on $BaSO_4$. The last method was also needed to ensure proper analytical procedures for radium analysis from nitrate solutions. Only a few scoping tests have been performed on these methods to date.

3.3.1 Solvent extraction with tri-*n*-butyl phosphate (TBP)

Tri-*n*-butyl phosphate (TBP) is known to extract both uranium and thorium, but not radium,[12] from nitric acid. However, there were some questions in the cases where sulfates were involved and such small weights of materials ($\sim$51 mg of ^{230}Th per MT of 0.1% uranium ore) were being extracted. Table 14 shows the results of a batch, crosscurrent extraction test for the extraction of thorium and uranium from a nitrate leach liquor into a 30 vol % TBP--*n*-dodecane organic phase.

The results indicate a good yield when uranium and thorium are extracted by 30% TBP in about four to five stages with a reasonable organic/aqueous ratio (e.g., 2/1). Evaporating the leach solution to obtain a more concentrated solution could be used to further enhance the extraction. However, such an evaporation process may not be desirable until the radium has been removed from the aqueous phase. Although methods for separating the uranium and thorium from the TBP extract have not yet been investigated, the thorium can probably be stripped away from uranium into 6 *M* HCl.

Table 14. Batch, crosscurrent extraction of uranium and ^{230}Th from a nitrate leach liquor with 30% TBP

Leach liquor[a] composition: 2.5 M HNO_3, 1430 mg U/liter, and 572 pCi ^{230}Th/ml

Solvent composition: 30% TBP--70% n-dodecane

Stage No.	Phase ratio, O/A	Uranium (mg/liter)		D_A^O	Thorium (pCi/ml)		D_A^O
		Organic	Aqueous		Organic	Aqueous	
1	1.0	1360	50	27	158	198	0.80
2	1.0	40	2	20	72	117	0.62
3	1.0	1.9	0.09	21	30	79	0.38
4	5.0	0.025	<0.02	-	8.1	13.1	-
		<0.02	<0.02	-	1.6	3.4	-

[a] Obtained from a 3 M HNO_3 leach of No. 4 uranium ore.

Thorium does not form a chloride complex, as is the case with uranium in 6 M HCl; thus, this stripping step is known to work well in uranium-thorium separation processes that utilize amine extractants.[12,13] Similar extraction experiments with tailings leach solution will be performed in which possible sulfate interference will need particular attention.

3.3.2 Carrying of radium on $BaSO_4$ precipitates

Radium has been concentrated by carrying on $BaSO_4$ since the discovery of the element.[14] This early processing method included concentration of radium by carrying on $BaSO_4$, conversion to carbonate, and dissolution in hydrochloric acid. Our interests in these experiments have usually involved nitrate solutions and/or nitric acid. Sill and Williams[8] have reported that nitrate ion interferes in radium carrying by $BaSO_4$ but does not give details or conditions.

A series of experiments was performed using the procedure previously described in Sect. 2.3.1, except that the barium concentration was varied from 0.5 to 10.0 mM and the nitric acid concentration was varied from 0.1 to 2.5 M. The results are shown in Table 15 and Fig. 12. It is apparent that a barium concentration of 10 mM is needed when the nitric acid concentration is 0.1 to 1.0 M. The yield of radium carried decreases rapidly at higher acid concentrations or barium concentrations that are <10 mM. Further information will be needed to determine whether these results are applicable to processing leach solutions; however, they were directly usable for our analytical needs. Processing applications will probably require that methods be developed for recycling the barium; hence radium-barium separation methods would also be required.

Table 15. Effects of barium and nitric acid concentrations on the carrying of radium on $BaSO_4$

Conditions: Total sulfate conc. = 10 m$\underline{M}$

Barium concentration, m$\underline{M}$	0.5	1.0	2.5	5.0	10.0
Radium precipitated, %					
0.1 $\underline{M}$ HNO_3	70.0	69.0	92.5	98.7	∿100
0.3 $\underline{M}$ HNO_3	62.7	76.6	89.1	98.3	∿100
1.0 $\underline{M}$ HNO_3	70.6	75.0	83.9	93.0	∿100
2.5 $\underline{M}$ HNO_3	--	1.0	48.3	85.3	98

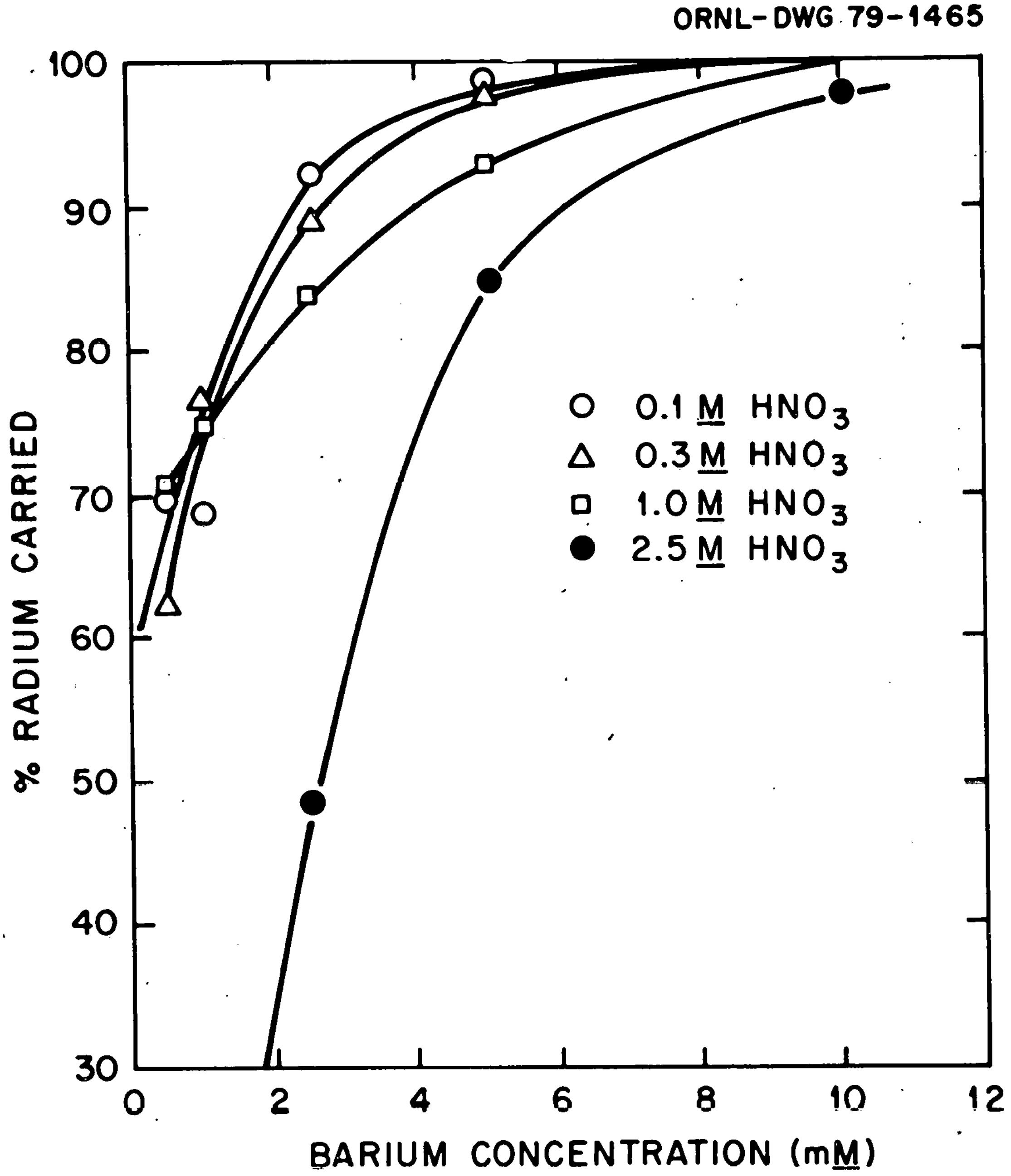

Fig. 12. Carrying of radium on $BaSO_4$ as a function of barium concentration in 0.1 to 1.0 M HNO_3 solutions.

3.3.3 Cation exchange of nitric acid leach solution

Ion exchange is another option in the processing of leach solutions to separate and/or to concentrate radium. A single cation exchange run has been made to test for radium removal from a 0.5 $\underline{M}$ HNO_3 tailings leach solution. Dowex 50-X8 cation resin, 100-200 mesh, in the hydrogen form (75 ml) was placed in a 20-mm-diam by 25-cm-long glass column. The total feed volume was 200 ml and was loaded at a flow rate of ∿0.5 ml cm^{-2} min^{-1}. The feed and effluent compositions are shown in Table 16. It is apparent that cation exchange will remove radium and uranium from 0.5 $\underline{M}$ HNO_3; however, it also removes calcium, iron, and aluminum, which are present in much higher concentrations than radium and therefore compete for cation exchange sites more strongly. Conditions required for further processing steps will be studied to determine whether cation exchange can be used advantageously for the separation of radium and uranium from iron, aluminum, and calcium.

Arnold and Crouse[15] have studied radium removal from uranium mill effluents[16,17] with various inorganic ion exchangers, including barytes (a mineral form of barium sulfate), but obtained poor results with acidic solutions.

3.3.4 Recovery of nitric acid values via evaporation and ignition

If nitric acid were to be used in very large amounts, it would have to be recycled for economic as well as environmental reasons. The bulk of the nitric acid value can be reclaimed by simple evaporation, but an ignition method is necessary to decompose the nitrate salts. A simple bench-top test was done to see whether evaporation and subsequent ignition of the metal salt residues might be applicable. The procedure was to

Table 16. Compositions of feed and effluent solutions for the treatment of a nitrate leach liquor by cation exchange

Conditions: 200 ml of feed solution and 75 ml of resin; flow rate, ∿0.5 ml cm^{-2} min^{-1}

Constituent (mg/liter)[b]	Feed[a]	Effluent
Ra, pCi/liter	5300	50
U	23	0.2
Ca	1450	0.5
Ba	<0.2	<0.1
Fe	1900	<0.01
Al	327	<0.01
Na	41	11
SO_4^{2-}	9450	8760
HNO_3, M	0.50	0.50

[a] Feed was a nitric acid leach liquor obtained from leaching No. 4 uranium mill tailings with 0.5 M HNO_3.

[b] Unless specified otherwise.

slowly drip a 3 M HNO_3 ore leach solution from a burette into a Pyrex beaker heated to 300°C (by a heating mantle) until enough solids had been collected for analysis. Chemical analysis showed that the nitrate content of these solids was 16.7%.

In the subsequent thermogravimetric analysis, these solids were reheated to 600°C in air. As shown in Fig. 13, ∿20% weight loss occurred on heating to 600°C and the nitrate content decreased from 16.7% to 0.5%. The weight loss observed on thermogravimetric analysis is greater than that due to the decrease in nitrate content (20% vs 16%). The difference is probably due to the loss of sorbed H_2O since no particular care was taken with regard to atmospheric protection in the handling and storage of the initial nitrate-bearing solids. The nitrogen oxide gases resulting from the ignition step could be converted to nitric acid by absorption methods. Counce[18,19] has studied the absorption of nitrogen oxide vapors to recover nitric acid.

3.4 Effectiveness of Hydrochloric Acid and Chelating Agents as Leachants

Some small-scale scouting experiments were carried out using solutions of HCl, EDTA, and DTPA (Tables 17-20). Initial tests showed that 2 to 6 M HCl or 0.5 M EDTA solutions of pH 8.2 and 11.6 were effective leachants for removing radium from No. 1 uranium tailings at 80°C and 33% concentration of solids. However, 2 to 6 M HCl was not quite as effective as 3 M HNO_3 (see Table 10), while 0.5 M EDTA solutions in the pH range 8.2 to 11.6 were more effective on the basis of two-stage leach tests. Further tests are needed to better evaluate these leaching solutions with regard to their utility at various concentrations of initial reagent,

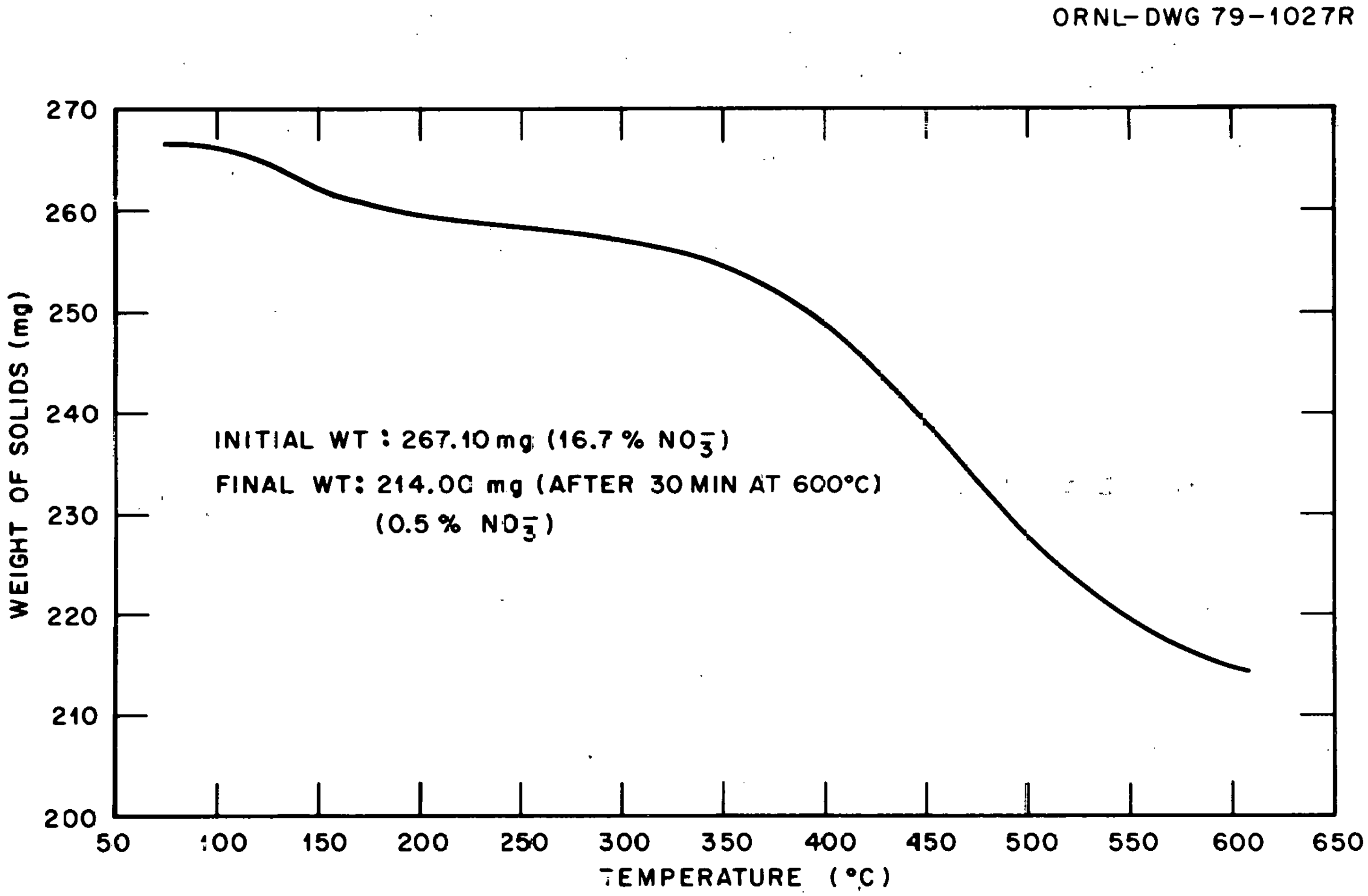

Fig. 13. Weight loss of nitrate-bearing salts obtained from nitric acid leach liquors as a function of ignition temperature.

Table 17. Effect of hydrochloric acid concentration on the batch, crosscurrent leaching of radium from No. 1 uranium mill tailings at 33% solids concentration and 80°C

Conditions: 5 g of solids shaken with 10 ml of leach solution in each stage for 4 hr

HCl conc. (M)	Run No.	Stage No.	^{226}Ra in solids (pCi/g) Initial solids	Residue	Cumulative % Ra leached
2.0	1	1	807	527	35
		2	527	459	43
		3	459	258	68
	1A	1	812	528	35
		2	528	441	46
		3	441	271	67
3.0	2	1	778	490	37
		2	490	329	58
		3	329	277	64
	2A	1	800	528	34
		2	528	356	55
		3	356	274	66
6.0	3	1	819	524	36
		2	524	436	47
		3	436	346	58
	3A	1	804	473	41
		2	473	396	49
		3	396	329	59

Table 18. Effect of pH on the crosscurrent leaching of radium from No. 1 uranium mill tailings with 0.5 M EDTA at 33% solids concentration and 80°C

Conditions: 5 g of solids shaken with 10 ml of leach solution in each stage for 4 hr

pH of leach solution[a]	Run No.	Stage No.	^{226}Ra in solids (pCi/g) Initial solids	Residue	Cumulative % Ra leached
11.6	1	1	802	179	78
		2	179	94	88
	1A	1	829	169	80
		2	169	98	88
8.2	2	1	822	465	43
		2	465	131	84
	2A	1	824	468	43
		2	468	125	85
6.4	3[b]	1	814	649	20
		2	649	471	42
	3A	1	854	693	19
		2	693	437	38

[a] The pH was adjusted to correspond to solutions of sodium salts having the following mole ratios of sodium to aminopolycarboxylic acid:

pH	Na/EDTA
6.4	2
8.2	3
11.6	4

[b] EDTA was used in 0.33 M concentrations because the reagent was not soluble at 0.5 M concentrations at pH = 6.4.

Table 19. Effect of pH on the crosscurrent leaching of radium from No. 1 uranium mill tailings with 0.05 M DTPA at 33% solids concentration and 80°C

Conditions: 5 g of solids shaken with 10 ml of leach solution in each stage for 4 hr

pH[a]	Run No.	Stage No.	^{226}Ra in solids (pCi/g) Initial solids	Residue	Cumulative % Ra leached
4.0	1	1	805	678	16
		2	678	668	17
	1A	1	811	678	16
		2	678	644	21
6.4	2	1	810	685	15
		2	685	665	18
	2A	1	836	685	18
		2	685	674	19
9.5	3	1	824	696	16
		2	696	672	18
	3A	1	830	701	16
		2	701	681	18

[a] The pH was adjusted to correspond to solutions of sodium salts having the following ratios of sodium to aminopolycarboxylic acid:

pH	Na/DTPA ratio
4.0	2
6.4	3
9.5	4

Table 20. Comparison of several leachants for their effectiveness of ^{226}Ra removal from No. 1 uranium mill tailings at 33% solids concentration and 80°C

Leaching agent	% ^{226}Ra leached		
	Stage 1	Stage 2	Stage 3
3 $\underline{M}$ HNO_3	46	74	87
3 $\underline{M}$ HCl	36	57	65
6 $\underline{M}$ HCl	39	48	59
0.5 $\underline{M}$ EDTA, pH = 11.6	79	88	a
0.5 $\underline{M}$ EDTA, pH = 8.2	43	85	a
0.05 $\underline{M}$ DTPA, pH = 4-9.5	16	18	a

[a] Not determined.

the ratios of leaching solution to solids used in leaching, and the optimum number of leaching stages. Also, tailings samples from different sources need to be tested. At the conditions and the particular tailings sample employed to date, radium leaching is nearly independent of HCl concentration over the range 2 to 6 M. Little difference was observed between the effectiveness of 2 and 3 M HCl; however, when the concentration was increased to 6 M HCl, it was decreased by about 5 to 10% (Table 17).

4. TENTATIVE CONCLUSIONS AND FUTURE PLANS

A reliable procedure has been developed for the analysis of ^{226}Ra in nitric acid leach solutions of uranium ore and tailings.

Nitric acid is an effective leachant of radium from uranium ore or tailings, and the residue produced by nitric acid leaching is refractory with respect to further radium leaching by water. No important differences were observed in the leaching behavior of ore and mill tailings derived from the same ore. Initial results show that thorium and uranium can be extracted from leach solutions by TBP and that radium can be carried on $BaSO_4$ with good yield from nitrate solutions under the proper conditions or can be loaded onto cation exchange resin.

Future work should include studies of the leaching of thorium and uranium using nitric or hydrochloric acids and their subsequent recovery by solvent extraction and ion exchange methods.

Scouting tests with complexing agents such as EDTA and DTPA at different pH conditions and with HCl and HNO_3 will be expanded to include a larger variety of ore and mill tailings samples. Recycle of nitric acid and other promising agents will be investigated in greater detail. Eventually, we expect to develop a technically feasible flowsheet, based on established technology, to isolate and concentrate ^{230}Th and ^{226}Ra from the huge bulk of mill tailings. The flowsheet for removing the long-lived radionuclides must also be compatible with the main-line process that is used to recover uranium from the original ore.

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