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Nitric Acid Leaching of Radium and Other Significant Radionuclides from Uranium Ores and Tailings

A. D. Ryon
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NITRIC ACID LEACHING OF RADIUM AND OTHER SIGNIFICANT RADIONUCLIDES FROM URANIUM ORES AND TAILINGS

A. D. Ryon, F. J. Hurst, and F. G. Seeley

ABSTRACT

Nitric acid leaching of representative uranium ores and mill tailings from the western U.S. mining districts removes up to 98% of the ^{226}Ra and ^{230}Th, yielding a residue containing 17 to 60 pCi of radium per gram. At best, this is an order of magnitude greater than that in surrounding soils, but about the same level as a standard proposed for building materials in the United Kingdom. Data are also presented on the water penetration and leaching of tailings, the solubility of $BaSO_4$, and radon emanation coefficients of ores, tailings, and nitric acid-leached residues.

Aug 1977

1. INTRODUCTION

Uranium is usually extracted from ore by leaching with either sulfuric acid or sodium carbonate. These reagents yield greater than 90% recovery of uranium without dissolving significant quantities of radium or other daughters in the decay chain of uranium, which consists of 14 radionuclides. Disposal of the leached uranium ore residues (tailings) which contain these radionuclides presents a problem. At present, millions of tons of tailings exist at 22 abandoned sites where uranium mills were operated during the period 1948-1970. Fifteen mills are currently in operation with a total daily capacity of 28,000 tons of ore. The major radiation hazards of tailings are from ^{226}Ra that may be in water supplies to the food chain (MPC is 5.5 pCi/liter)[1] and from its daughter, ^{222}Rn, whose daughters in air present a health hazard to the lungs. Other radionuclides of importance are ^{230}Th (which is the parent of ^{226}Ra), ^{210}Pb, and ^{210}Po. The latter two are relatively short-lived and would soon decay if their long-lived parent ^{226}Ra were removed.

An engineering analysis of methods for treating milling wastes, including tailings from a uranium mill, was made in 1973 at ORNL.[2] The

study evaluated several different methods of treatment of tailings to determine the cost vs benefit as measured by the reduced radiation dose to man and environment. One of the advanced and more speculative methods considered was the use of nitric acid to leach out most of the radionuclides of interest, such as radium, thorium, lead, and polonium, in addition to the uranium. The process was based on encouraging data obtained in a few scouting tests.[3] Subsequently, a few more tests were made using hydrochloric acid.[4]

The major purpose of the present study was to measure the effectiveness of nitric acid for leaching radium, thorium, lead, polonium, and uranium from representative samples of uranium ores and tailings from the major mining districts of the United States. Secondary objectives were: (1) to determine the radon emanation from ores, tailings, and nitric acid residues; (2) to elucidate the possible chemical state of radium in ores; (3) to simulate the conditions of an arid climate in order to study the possibility of leaching radium from tailings by rainwater.

2. SUMMARY AND RECOMMENDATIONS

Samples of representative uranium ore and mill tailings from New Mexico, the Colorado Plateau, and Wyoming were collected and prepared for analysis and leaching tests. The results of leaching tests with nitric acid show that up to 98% of the radium is leached in two stages with hot 3 M HNO_3. The fraction of thorium leached was generally greater than that of radium, while the fractions of polonium and lead were less. The concentration of radium remaining in the residue after leaching ranged from 17 to 60 pCi/g for different ore and tailings samples. Virtually no difference was observed between ore and tailings from either sulfuric acid or carbonate leach mill processes. The lowest value is about an order of magnitude above that in the soils in the western U.S. mining districts. It is about the same as the level proposed as a standard for building materials in the United Kingdom. The sand fraction (+140 mesh) of the residues after nitric acid leaching ranged from 33 to 88 wt % and contained 40 to 70% of the radium at approximately one-half of the concentration of that in the slime

fraction. A few scouting tests have shown that the residual radium is not dissolved with additional leaching with acid, complexing agents, or roasting, which indicates that the radium is probably in the form of some refractory mineral and not present as sulfate or carbonate. The solubility of $BaSO_4$ in nitric acid was measured to aid in interpretation of the leaching data. Radium was leached from sulfate tailings by distilled water to produce solutions containing radium at concentrations greater than an order of magnitude above the MPC for drinking water. Results of tests in which the penetration of water into tailings was simulated for an arid climate showed that penetration may be limited by the evaporation that occurs between infrequent rain or snow. The radon emanation coefficients of samples of ore, tailings, and nitric acid-leached residues were measured. Although these coefficients varied from 8 to 45%, no consistent trend was observed. The rate of radon emanation from nitric acid residues was only 2 to 10% of that for mill tailings. This was a result of the lower radium content rather than any significant change in radon emanation coefficient.

It is recommended that leaching studies be extended in an effort to identify the form in which the more refractory radium exists in the tailings, that is, whether it is concentrated in some minerals as indicated by the hot sand grains or merely adsorbed on the large surface areas of the sand and clay minerals. Methods for recovering the uranium, thorium, radium, polonium, and lead from the leach liquor need to be tested to develop the nitric acid process flowsheet. Solvent extraction with a solvent such as tributyl phosphate could probably be used for uranium and thorium; however, the other radionuclides would probably have to be recovered by other methods such as precipitation. The water penetration and leaching studies should be extended to determine the ion exchange properties (with respect to radium in particular) of typical soils on which tailings may be deposited either for new mills or for relocation of the abandoned tailings that constitute a problem in their present location.

3. DESCRIPTION OF ORE AND TAILINGS SAMPLES

Representative samples of uranium ore and mill tailings were supplied by five operating mills in New Mexico, Utah, and Wyoming; tailings were also obtained from an abandoned site in Salt Lake City, Utah. Three of the operating mills use sulfuric acid leaching, and two of them use sodium carbonate leaching. Samples of ore and corresponding tailings which were representative of the materials and processes in use during the sample period (March-May 1976) were obtained for the tests. The ore samples were taken from the feed to the leach circuit; consequently, the particle size was less than 4 mesh, and most of the material was less than 20 mesh. Approximately 100 lb of dry sample material was blended and divided by quartering and riffling to obtain multiple fractions for the leaching tests.

Analytical results for the ore and tailings samples are shown in Table 1. To ensure representative samples, 100 g of each sample was ground to less than 100 mesh and blended to provide 1- to 2-g portions for analysis. The constituents that may relate to the dissolution of radium are barium, calcium, and sulfate. The barium concentrations ranged from 0.06 to 0.15%, the highest being found in No. 1 tailings. Very little difference was noted between pairs of ore and tailings samples. The concentrations of calcium ranged from 0.5 to 6.1%, with the higher values being associated with those ores processed by sodium carbonate leaching. The concentrations of sulfate ranged from 0.2 to 4.9%, the highest being present in No. 1 tailings; the tailings from the acid leach processes were higher than those from carbonate leaches. One ore contained a significantly higher total sulfur content, probably as pyrite, which may be oxidized to sulfate by nitric acid. The uranium concentrations of the ores ranged from 0.10 to 0.32%, and the ^{226}Ra and ^{230}Th concentrations generally show that they are in secular equilibrium with the uranium. The ^{230}Th concentration in the tailings from mills using the sulfuric acid process was significantly lower as the result of leaching by the sulfuric acid; as expected, essentially no thorium leaching occurred in the alkaline leach.

Table 1. Analyses of samples of ores and tailings

Component	No. 1	No. 2		No. 3		No. 4		No. 5		No. 6	
	Tailings	Ore	Tailings	Ore	Tailings	Ore	Tailings	Ore	Tailings	Ore	Tailings
					Analysis, in pCi/g						
^{226}Ra	910	575	668	760	609	768	716	267	237	1070	667
^{230}Th	322	635	88	1020	414	991	133	346	324	1120	604
^{210}Po	395	187	238	219	248	206	176	106	100	275	194
					Analysis, in wt %						
U	0.015	0.21	0.0056	0.28	0.016	0.23	0.0065	0.10	0.0083	0.32	0.029
Ba	0.15	0.061	0.073	0.067	0.073	0.091	0.10	0.072	0.10	0.10	0.10
Ca	2.5	1.8	1.8	0.70	0.52	1.2	0.73	1.8	2.5	5.5	6.1
Mg	0.40	0.21	0.12	0.13	0.12	0.32	0.20	0.15	0.16	1.0	1.1
Na	0.70	1.3	0.85	2.0	1.9	1.4	1.7	1.1	2.3	0.77	1.4
Fe	1.4	0.96	0.50	2.3	2.3	1.3	0.87	0.92	1.0	1.7	1.6
Al	3.9	3.3	3.3	6.2	6.2	5.7	5.2	3.6	3.4	3.2	2.5
R_2O_3	11.8	9.7	8.1	17.1	17.8	14.8	13.0	9.3	10.1	13.9	13.2
CO_3	0.27	2.0	0.18	0.55	0.017	0.70	0.31	1.2	2.1	3.4	2.4
Organic C	0.23	0.074	0.088	0.11	0.19	0.049	0.050	0.061	0.067	0.20	0.19
PO_4	0.17	0.064	0.025	0.12	0.079	0.074	0.030	0.066	0.066	0.18	0.17
SO_4	4.89	0.34	3.73	0.39	1.19	0.38	0.99	0.22	0.62	0.27	0.70
Total S	2.6	0.45	2.1	2.6	3.3	0.93	1.1	0.81	0.87	0.38	0.30

4. NITRIC ACID LEACHING TESTS

4.1 Procedure

Nitric acid leaching tests were performed on 100-g samples of each ore and tailings as received. Most of these tests were made at 33% solids, using the following procedure: The single-stage leaching tests consisted of stirring a 100-g sample with 200 ml of HNO_3 (1 M or 3 M for 5 hr at 70°C), filtering, washing with 80 ml of 0.1 M HNO_3, repulping with 200 ml of 0.1 M HNO_3, stirring overnight (∿16 hr), filtering, and washing with 80 ml of 0.1 M HNO_3. The filter cake was air-dried, weighed, and sealed in an 8-cm-diam x 3.5-cm-high plastic Petri dish for radium determination via gamma counting. The filtrate was analyzed for free acid, barium, and sulfate. Two-stage leaching tests were made by contacting the residue after the first repulp wash with 200 ml of fresh HNO_3 (1 M or 3 M for 5 hr at 70°C), followed by filtering, repulp washing, filtering, and washing.

The concentration of ^{226}Ra in the solid feeds and nitric acid residues was measured by counting the gamma activity (295, 352, and 609 keV) of ^{214}Pb and ^{214}Bi granddaughters in equilibrium with the ^{226}Ra. Each sample was stored for at least 2 weeks in a plastic Petri dish which was sealed by applying three layers of polyethylene tape to the slip joint of the dish. The counting was done with a high-resolution Ge(Li) detector coupled to a 4096-channel analyzer. The counter was calibrated by standard uranium ore samples (uranium analyses certified) that were stored and counted in the same manner as the test samples. Other constituents in the nitric acid residues were determined after grinding (in a porcelain mortar) the residue from 100 g of starting material to -100 mesh to ensure that 1- to 2-g samples would be representative.

4.2 Radium-226 Leaching

The results of the leaching tests are summarized in Table 2. These data show that most of the radium can be leached with nitric acid, although some samples require more vigorous treatment than others. A single-stage

Table 2. Summary of results obtained by leaching radium with nitric acid

Leach conditions					^{226}Ra concentration in solids (pCi/g)										
No. of stages	Percent solids	HNO_3 (M)	Temp. (°C)	Time per stage (hr)	No. 1	No. 2		No. 3		No. 4		No. 5		No. 6	
					Tailings	Ore	Tailings	Ore	Tailings	Ore	Tailings	Ore	Tailings	Ore	Tailings
		Feed			910	575	668	760	609	768	716	267	237	1070	667
1	33	1	25	18	850[a]	88	589	238	574	798	689	48	311	920	684
1	33	3	70	5	712[a]	38	60	200	298	115	168	90	85	849	526
1	14	3	70	15		37		61		19		42		53	
2	33	3	70	5	51	38	39	62	51	17	17	45	29	42	24
3	17	3	70	5	34	36		54		15		36		17	

[a]Leached at 25% solids with 3.2 M HNO_3.

leach with 1 M or 3 M HNO_3 at 33% solids is effective for only two ores, Nos. 2 and 5. An additional stage of leaching at 33% solids with 3 M HNO_3 proved effective for all samples. A single-stage leach made with a more dilute slurry (14% solids) was as effective as two stages at 33% solids for all of the ore samples (tailings were not tested). Three stages at 17% solids showed a slight further improvement, the maximum change being an additional 3% of the initial radium leached (No. 6). The radium concentration in the residue after three-stage leaching ranged from 15 to 54 pCi/g, which corresponds to a range of 88 to 99% removal by leaching. Greater than 94% of the radium was leached from each ore except the No. 5 sample, which originally contained only about one-third as much radium as the other samples. The results from the two-stage leaching tests show nearly equal leaching from sulfuric acid tailings and ore sample pairs (No. 2-4); however, leaching was more effective from alkaline tailings than the corresponding ores (Nos. 5 and 6).

The results of "standard" leaching tests made with 3 M HNO_3 at 33% solids for 5 hr at 70°C are summarized in Table 3, where the fractions of radium leached are shown for one-, two-, and three-stage operations. In addition, the fractions of barium, calcium, and total sulfur leached are tabulated. The most striking result is that very little barium (<5%) was leached in one stage, while up to 94% of the radium was leached; and with the exception of the No. 6 samples, less than 30% of the barium was leached in two stages. This is strong evidence that most of the radium was not associated with the barium except possibly in the case of No. 6 ore and tailings and, to some extent, No. 1 tailings where both radium and barium leachings increased sharply in the second stage. The leaching of calcium was much more complete than that for barium, ranging from 67 to 99% in two stages; there was no apparent correlation with radium. The leaching of total sulfur, which includes any sulfides that would be oxidized to sulfate by the hot nitric acid, was virtually complete in a single stage. Such effective removal of sulfate in the first stage probably caused the increased leaching of barium in the second stage. However, the concentration of barium in the leach filtrates was, in general, significantly lower than the solubility of $BaSO_4$ in nitric acid of the

Table 3. Comparison of leaching results for radium with those for barium, calcium, and sulfur ($3\ \underline{M}\ HNO_3$ at 33% solids for 5 hr at 70°C)

	No. 1	No. 2		No. 3		No. 4		No. 5		No. 6	
	Tailings	Ore	Tailings	Ore	Tailings	Ore	Tailings	Ore	Tailings	Ore	Tailings
				^{226}Ra, % leached							
One stage	31[a]	94	92	76	52	86	78	69	68	36	36
Two stages	95[a]	94	95	93	92	98	98	85	90	97	97
Three stages[b]	97	95	-	94	-	98	-	88	-	99	-
				Barium, % leached							
One stage	1[a]	4	1	1	1	1	1	1	1	4	2
Two stages	30[a]	5	3	-	8	3	3	10	18	67	85
				Calcium, % leached							
Two stages	92[a]	96	95	81	73	77	67	94	91	99	99
				Total sulfur, % leached							
One stage	92[a]	93	99	93	93	94	94	92	94	86	92
Two stages	97[a]	94	100	94	94	95	96	94	97	91	96
				SO_4 concentration, g/liter							
First-stage filtrate	13[a]	4.1	16	21	24	6.4	7.1	5.8	6.1	3.0	2.3
Second-stage filtrate	0.60[a]	0.04	0.11	0.13	0.28	0.07	0.12	0.10	0.17	0.15	0.10
				Ba concentration, mg/liter							
First-stage filtrate	2.9[a]	9.3	2.3	1.4	0.82	2.7	3.0	3.0	4.3	16	7.4
Second-stage filtrate	109[a]	2.9	5.5	-	15	6.9	6.5	29	53	230	320
				$BaSO_4$ solubility[c] in HNO_3, mg(Ba)/liter							
First-stage filtrate	53[a]	38	50	31	31	38	53	31	31	5.2	3.8
Second-stage filtrate	65[a]	52	52	53	53	53	50	53	53	53	53

[a]Leached at 25% solids with $3.2\ \underline{M}\ HNO_3$.

[b]Leached at 17% solids.

[c]Solubility of $BaSO_4$ at nitric acid concentration existing at end of leaching operation (see Fig. 1).

concentration existing at the conclusion of the leach. Notable exceptions were the second-stage filtrates from No. 6 ore and tailings and No. 1 tailings, where the barium concentration was as much as six times the solubility of $BaSO_4$, indicating that the barium was probably present as some other compound in these samples. Since the No. 6 ore and tailings contain significant carbonate, it is possible that the barium exists in the ore as a carbonate. In some of the special leach tests of No. 1 tailings, such as those made with 3 M HNO_3 at 3% solids, only 70% of barium was leached even though the solubility data would predict that all of the barium should have dissolved if it were present as $BaSO_4$.

4.2.1 Sand-slime fractions

The distribution of mass and radium between sand and slime fractions of No. 1 tailings and Nos. 2-6 ore samples after a two-stage leach with 3 M HNO_3 is shown in Table 4. The solids were separated by wet screening on 140 mesh U.S. standard sieve. Each fraction was air-dried and weighed, and the radium content was determined by gamma counting of daughters. The sand fraction (+140 mesh) ranged from 33 to 88 wt %; it was greater than 50 wt % in every case except No. 6 ore. The concentration of radium in the slime fraction averaged about twice that in the sands. The fraction of total radium that was in the sand fraction ranged from 40 to 71%, averaging 55%. This nearly equal distribution of radium in the sand and slime fractions of nitric acid residues is markedly different from sulfuric acid tailings, where the slime fraction contains most of the radium, probably associated with a calcium sulfate precipitate.

Relatively "hot" sand grains were isolated from fractionated, +100 mesh nitric acid-leached residues of several different ores, indicating that the residual radium is not uniformly distributed. Single grains were estimated to contain more than 50×10^6 pCi of radium per gram. Unfortunately, time did not permit identification of the mineral assemblage of these grains. This information, of course, could be extremely important in determining the potential hazard, if any, of the residual radium and in assessing the prospects for its removal.

Table 4. Solids size fractions and ^{226}Ra concentration in residue after double 3 M HNO_3 leach at 33% solids for 5 hr at 70°C

Source	Weight percent sand (+140 mesh)	^{226}Ra concentration (pCi/g)			Fraction of total Ra in sand (%)
		Sand (+140 mesh)	Slime (-140 mesh)	Slime/Sand	
No. 1 tailings	53	42	59	1.4	45
No. 2 ore	82	31	58	1.9	71
No. 3 ore	66	39	92	2.4	45
No. 4 ore	74	13	31	2.4	57
No. 5 ore	88	35	109	3.3	70
No. 6 ore	33	53	39	0.7	40
Average	66 ± 20	36 ± 13	66 ± 33	2.0 ± 0.9	55 ± 13
Average (except No. 6)	73 ± 14	32 ± 11	72 ± 33	2.3 ± 0.7	57 ± 13

4.2.2 Nitric acid consumption

The amount of nitric acid consumed during the leaches was calculated from the difference in the initial concentration and the amount of free acid remaining in the leach solution. The free nitric acid in the leach solution is shown in Table 5; the calculated acid consumption is given in Table 6. The nitric acid consumption ranged from a low of 30 lb for the 1 M HNO_3 leach of sulfate tailings to a high of 620 lb per ton of alkaline tailings. As would be expected, the ores that are normally processed by a sodium carbonate leach, such as Nos. 5 and 6, consumed more acid than those leached by sulfuric acid. In general, the tailings from sulfuric acid-processed ore consumed less nitric acid than the corresponding ores. Normally these ores consume 100 to 200 lb of sulfuric acid per ton.

4.2.3 Leaching of other radionuclides

In addition to radium, the radionuclides of interest are ^{230}Th, ^{210}Po, ^{210}Pb, and uranium. Thorium-230 is very important because it is the precursor of ^{226}Ra and has a long half-life (80,000 years). Consequently, it must be leached and stored in a manner similar to that used for radium. Both ^{210}Po and ^{210}Pb have relatively short half-lives and decay soon after the radium is removed. They are of interest only if they are leached, because under such circumstances they would have to be removed from the solution before its discharge to the environment. Leaching of uranium is, of course, an important part of the efficiency of the milling process.

The data in Table 7 show the various radionuclides obtained by two stages of leaching with 3 M HNO_3 at 33% solids at 70°C for 5 hr. The leaching of ^{230}Th was generally more effective than that for ^{226}Ra. The concentration of ^{230}Th in the residues ranged from 7 to 32 pCi/g, corresponding to 99 to 92% leaching.

The concentration of ^{210}Po in the residues ranged from 16 to 140 pCi/g, corresponding to 90 to 49% leaching. The concentration of ^{210}Pb in the residues ranged from 51 to 120 pCi/g, corresponding to 83 to 25% leaching. The concentration of uranium in the residues ranged from 3.5 to 15 ppm for all samples except for No. 1 tailings, which analyzed 25 ppm.

Table 5. Concentration (molarity) of nitric acid at end of leach

Description of leach	Source 1 Tailings	2 Ore	2 Tailings	3 Ore	3 Tailings	4 Ore	4 Tailings	5 Ore	5 Tailings	6 Ore	6 Tailings
First stage, 1 M HNO_3, 25°C, 18 hr	0.8	0.3	0.9	0.7	0.4	0.6	0.8	0.4	0.2	0.0	0.0
First stage, 3 M HNO_3, 70°C, 5 hr	2.9[a]	2.3	2.7	2.0	2.0	2.3	2.9	2.1	2.1	0.7	0.6
Second stage, 3 M HNO_3, 70°C, 5 hr	3.2[a]	2.8	2.8	2.9	2.9	2.9	2.7	3.3	2.9	2.9	2.9

[a]Initial HNO_3 concentration was 3.2 M.

Table 6. Consumption of nitric acid

Description of leach	Pounds HNO_3 (100%) per ton of solids 1 Tailings	2 Ore	2 Tailings	3 Ore	3 Tailings	4 Ore	4 Tailings	5 Ore	5 Tailings	6 Ore	6 Tailings
First stage, 1 M HNO_3	75	170	30	90	150	110	60	150	210	260	260
First stage, 3 M HNO_3	140	190	80	260	260	180	20	220	230	580	600
Second stage, 3 M HNO_3	0	40	20	40	20	20	20	0	30	20	20

Table 7. Analyses of residues after two-stage leach with 3 M HNO_3 at 33% solids for 5 hr at 70°C

	1	2		3		4		5		6	
	Tailings	Ore	Tailings	Ore	Tailings	Ore	Tailings	Ore	Tailings	Ore	Tailings
Activity, pCi/g											
^{226}Ra	51	38	39	62	51	17	17	45	29	42	24
^{230}Th	22	8.3	7.3	20	20	20	13	18	17	32	22
^{210}Po	76	34	48	72	25	35	22	16	16	140	52
^{210}Pb	69	71	68	86	94	55	51	79	74	120	120
^{238}U[a]	8.1	2.2	3.0	3.2	3.8	2.2	2.1	1.6	1.2	4.9	4.0
Content, ppm											
U	25	6.7	9.1	9.7	7.5	6.6	6.3	4.7	3.5	15	12
Ba	940	610	680	670	880	1100	1100	840	880	710	530
Ca	2100	770	820	1300	1400	2700	2400	1100	2200	600	550
SO_4	1800	240	41	2800	220	290	150	<70	<70	870	<70
Total S	690	270	<50	1600	1900	480	420	490	250	330	110
Percent leached											
^{226}Ra	95	94	95	93	92	98	98	85	90	97	97
^{230}Th	93	99	99	96	96	98	92	96	95	97	97
^{210}Po	81	82	80	67	90	86	87	85	84	49	73
^{210}Pb[b]	83	62	71	61	62	73	71	25	26	56	38
U	84	99.7	84	99.7	93	99.7	90	99.6	96	99.5	96

[a]Calculated from total uranium concentration (0.33 μCi per gram of uranium).

[b]Based on the assumption that the ^{210}Pb and ^{210}Po concentrations in the feed are equal.

The leaching of uranium was greater than 99.5% for the ore samples. Generally, there was no significant difference in the leaching of radionuclides from ores or from alkaline or acid tailings.

4.2.4 Special leaching of No. 1 tailings

Because of the special interest in treating the No. 1 tailings and their more refractory nature, additional leaching tests were made with these samples. The results are shown in Table 8. The high sulfate content (4.9% SO_4) of these tailings suggested that the poor (31%) leaching of radium in a single-stage leach at 33% solids may have been caused by the coprecipitation of radium with barium or calcium sulfate. Therefore, a single-stage leach could be effective if a lower-density slurry were used to facilitate dissolution of the slightly soluble sulfates. This is confirmed by the data in Table 8, which show that the fraction of radium leached increased with decreased solids content until at 6% solids the residual radium was virtually the same as after a two-stage leach at 33% solids. Results for three-stage leaching at 17% solids show that 1.1 M HNO_3 is essentially as effective as 3.2 M HNO_3. Grinding the tailings to -140 U.S. mesh increased single-stage leaching, producing a residual radium concentration of 31 pCi/g as compared with 49 pCi/g for single-stage leaching of the sample as received. The tailings were pretreated by roasting at 800°C to determine whether the refractory radium was bound in clay in the same manner as aluminum, which is known to be converted to a more soluble form by roasting. The radium concentration in the residue after the roasting and leaching treatment was only slightly lower, 39 pCi/g vs 49 pCi/g, suggesting that the quantity of radium associated with aluminum in the clay fraction was small. Roasting with NaCl, KF, or Na_2CO_3 prior to nitric acid leaching did not improve radium recovery. Leaching with EDTA solutions yielded variable results, depending on the pretreatment. The lowest residual radium concentration obtained from any test was 29 pCi/g, which was obtained by leaching with 3 M HNO_3 at 3% solids followed by leaching with 0.5 M EDTA at 22% solids.

Second-stage leaching of the residue from the 3 M HNO_3 leach at 10% solids with reagents such as 6 M H_3PO_4, 0.5 M $Ba(NO_3)_2$, and HF was not as

Table 8. Summary of leaching tests on No. 1 tailings

Number of stages	Percent solids	HNO_3 (M)	Temp. (°C)	Time (hr)	Ra in residue (pCi/g)	Pretreatment
1	25	1.0	25	18	852	None
1	25	3.2	25	18	942	
1	25	3.2	70	5	712	
1	33	7.5	80	5	260	
1	17	3.2	80	5	582	
1	10	3.0	70	5	296	
1	9	3.2	80	5	135	
1	6	3.2	80	5	52	
1	3	3.2	70	5	49	
2	33	3.0	70	5	51	
2	25	3.2	70	5	44	
3	17	1.1	80	5	36	
3	17	3.2	85	3	34	
1	10	0.1 + 1 M $Ca(NO_3)_2$	70	3	740	
1	5	0.1 + 1 M $Ca(NO_3)_2$	70	3	560	
1	1	0.1 + 1 M $Ca(NO_3)_2$	70	3	156	
1	3	3.2	70	5	31	After grind to -140 U.S. mesh
1	3	3.2	85	5	39	After roast at 800°C for 3 hr
1	3	3.2	85	5	39	After roast at 800°C for 3 hr with 10% NaCl
1	3	3.2	85	5	81	After roast at 800°C for 3 hr with 10% KF
1	3	3.2	85	5	75	After roast at 800°C for 3 hr with 10% Na_2CO_3-K_2CO_3
1	25	0.5 (Na_4EDTA)	80	5	272	After roast at 800°C for 3 hr with 20% Na_2CO_3
1	22	0.5 (Na_4EDTA)	80	5	29	After 3 M HNO_3 leach at 3% solids at 85°C for 5 hr (residue contained 39 pCi Ra/g)
1	23	0.5 (Na_4EDTA)	80	5	49	After 3 M HNO_3 leach at 10% solids at 70°C for 5 hr (residue contained 296 pCi Ra/g)
1	10	3.0	25	168	36	
1	33	7.5	110	24	31	
1	33	6 (H_3PO_4)	70	5	198	
1	33	0.5 ($Ba(NO_3)_2$)	25	168	250	
1	33	(Dist. H_2O)	25	168	184	
1	33	(HF)[a]	25	<1	417	

[a]Approximately 50% of solid dissolved.

satisfactory as with 3 M HNO_3. In conclusion, the results of the special leach tests on No. 1 tailings indicate the presence of a "refractory" fraction of radium that is bound up in a different way from the bulk of the easily leached radium and does not seem to be associated with sulfate or clay. The slightly improved results obtained by three-stage leaching with 3 M HNO_3 vs two-stage leaching with all of the ore samples indicate that the residual radium is probably bound differently from the bulk of the radium. The fact that the uranium is leached to a level about one order of magnitude lower than observed for radium is evidence supporting the assumption that the residual radium is not associated with some primary uranium mineral contained within the sand grains (Table 7).

4.2.5 Discussion of leaching data

It is difficult to evaluate the leaching data with regard to their application to the control of radium in uranium milling. Ideally, it would be desirable to remove radium to the extent that its concentration in the residue would be the same as or lower than that naturally occurring in the soil. The radium concentration in soil surrounding the uranium milling sites is generally of the order of 1 to 3 pCi/g (4 pCi/g in soil in Washington County, Maryland).[5] This is an order of magnitude lower than that obtained by the best nitric acid leach (15 pCi/g). The next reasonable goal appears to be one that is being considered in the United Kingdom, 25 pCi/g for soil and building materials.[4] The best results of the multistage nitric acid leach meet this goal. A further consideration making this level of radium activity acceptable is that most of the uranium ore deposits are in sparsely populated areas; hence the population dose is relatively small. The hazard associated with radium seeping into groundwater from disposal of nitric acid-leached residues should be very much lower than from conventional tailings because the radium remaining after such strong leaching conditions is virtually insoluble in water. The hazard from the radon emanating from the nitric acid residue should be reduced directly as the radium content of the residue; thus it would be only 2 to 7% of that for sulfuric acid-leached tailings. In all cases, except those in which the residue is under or incorporated in a building, the dose from radon and its daughters would be negligible.

The limited results of leaching ^{230}Th show that its concentration in the residue after a two-stage leach is generally less than that of ^{226}Ra. This is important because ^{230}Th is the precursor of ^{226}Ra and has a long half-life. Most of the ^{210}Po (half-life = 138 days) and ^{210}Pb (half-life = 21 years) are leached; therefore, a nitric acid process would have to provide for their recovery and temporary storage to permit decay. The small amounts left in the leach residue would probably not cause serious consequences because of their insolubility and short half-lives. The excellent results obtained by leaching uranium (>99.5%) from the ore samples could provide some economic compensation for the higher reagent cost of nitric acid as compared with the conventional use of sulfuric acid or sodium carbonate, which generally yields about 92% uranium leaching.

5. SOLUBILITY OF BARIUM SULFATE IN NITRIC ACID

Literature references[6,7] to the solubility of $BaSO_4$ in various concentrations of nitric acid show considerable disparity. For this reason, $BaSO_4$ solubility measurements were made by precipitating $BaSO_4$ from solutions with HNO_3 concentrations ranging from 0.0 to 10 N. Each solution was traced with ^{133}Ba ($\sim 10^6$ counts min^{-1} ml^{-1}) and allowed to equilibrate for 24 hr before precipitation. After addition of the dilute H_2SO_4, the samples were shaken for 24 hr on a Burrell shaker and then allowed to settle for 24 hr before being sampled. The solutions were sampled a second time after being allowed to settle for an additional 4 days. A third sample was made after an additional 52 days of settling.

Generally, the concentration of barium in the supernatant decreased with time, with a relatively small change being observed between samples taken at 5 days and those taken at 52 days. The latter data, which are assumed to be representative of samples at equilibrium, are shown in Fig. 1. The data fit well on an exponential curve showing that the solubility of $BaSO_4$ increases about 1000-fold over the acid concentration range of 0.02 to 10 N. The lowest point was measured with no addition of nitric acid, the H^+ being supplied by the sulfuric acid used to precipitate the

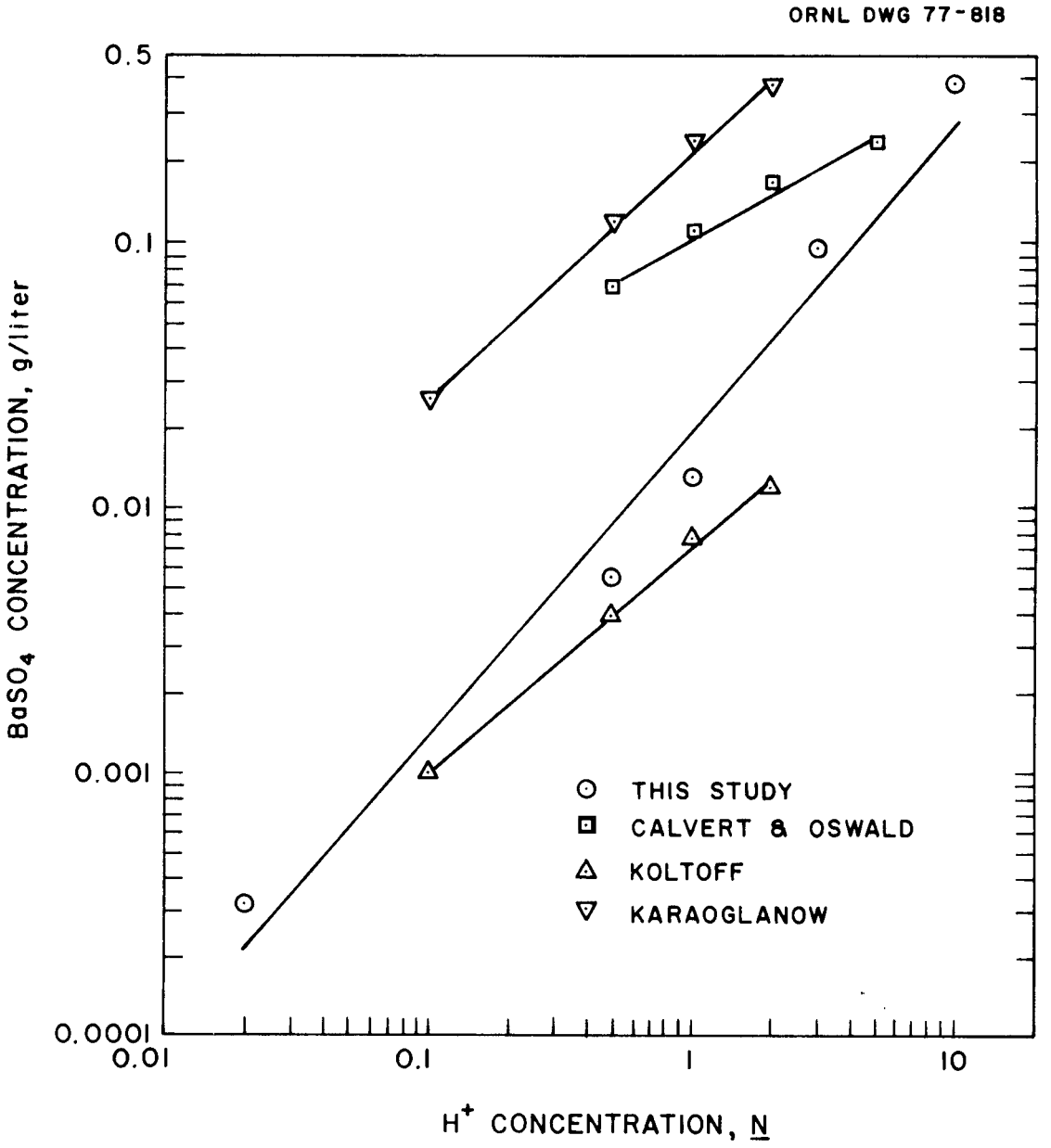

Fig. 1. Solubility of $BaSO_4$ in nitric acid.

barium. Three other curves from data in the literature are shown; only one (Koltoff) of these agrees with our data, while the other two show solubilities about an order of magnitude higher.

6. LEACHING OF RADIUM FROM NO. 1 TAILINGS WITH DISTILLED WATER

The leachability of radium from No. 1 tailings by water was simulated by successive exposure of a sample of the tailings to fresh portions of distilled water. A 100-g sample of No. 1 tailings was stirred with 3-liter portions of water at about 25°C for periods varying from 15 to 90 hr. The solids were separated by filtration, and the radium content of the filtrate was measured by gamma counting a barium-carried sulfate precipitate. (The efficiency of radium precipitation was greater than 99% as determined with a standard radium solution.)

The results of ten successive leaches are shown in Fig. 2. With the exception of the first leachate, in which the radium concentration was about three times higher than in other leachates, the radium concentration increased with contact time until at 90 hr it was approximately twice that at 20 hr, indicating slow attainment of solution equilibrium. The radium concentration did not change over the series as shown by comparing leachates (e.g., the third and the ninth) at the same contact time; this indicates possible leaching of the same radium compound or complex. The lowest concentration was 65 pCi of radium per liter, which is about an order of magnitude greater than the MPC for drinking water (5.5 pCi/liter). The total amount of radium leached with a total of 300 ml of water per gram of tailings was less than 5%, and the concentration in the leachate showed no tendency to decrease with successive leaches. Therefore, long-term leaching of the tailings by unlimited volumes of water would constitute a continued source of radium contamination of the effluent water at levels significantly above MPC.

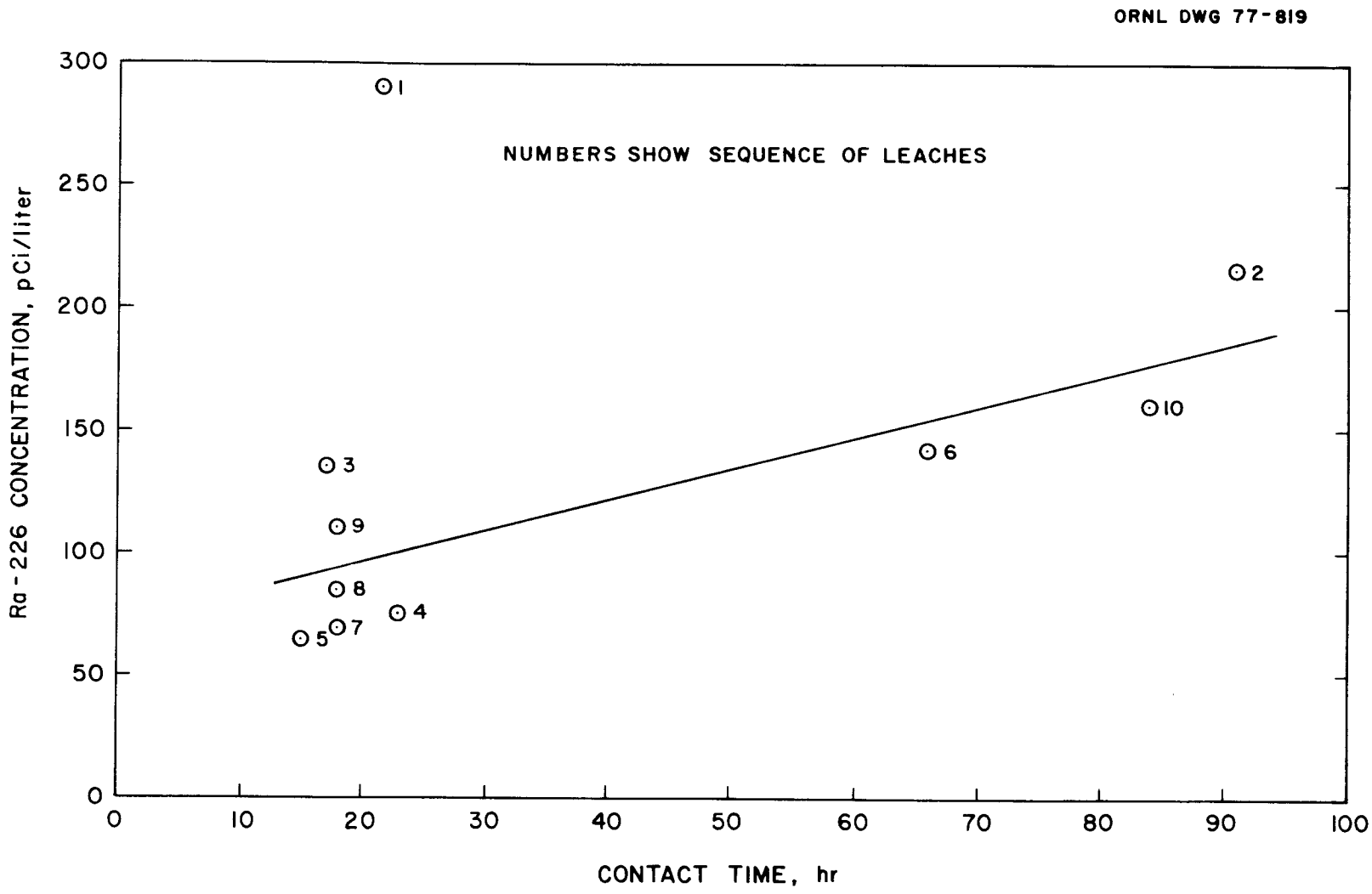

Fig. 2. Leach of No. 1 tailings by successive contacts of distilled water at 30 ml/g.

7. PENETRATION OF WATER INTO NO. 1 TAILINGS

A laboratory test simulating the arid climate that prevails at most uranium mills was made to measure the penetration of water from rain or snow into the tailings. The fate of precipitation falling on the surface of a tailings pile is to evaporate and/or penetrate into the pile. The purpose of the test was to determine how much penetration occurred in competition with evaporation. Water was poured on the surface of a column of tailings, and dry air was blown on the surface; then further additions of water were alternated with drying. The record of water addition and penetration for 145 days is shown in Fig. 3.

A 4-in.-diam x 36-in.-high column was filled with a 60% solids slurry of No. 1 tailings in water. After standing about 2 weeks, dry air was blown across the top to promote evaporation. Large vertical cracks formed as drying proceeded and progressed downward over the entire length of the column. Although the tailings were still wet and plastic, attempts to close the cracks so that water could be added to the surface were not successful; therefore, the study of this column was abandoned and a new column was set up with dry tailings to avoid this problem.

A 1.5-in.-diam x 36-in.-high glass column was filled with dry No. 1 tailings and gently tamped. The height of tailings was 32-3/8 in. and the weight was 1364 g, which gave a bulk density of 1.45 g/ml. Distilled water was added dropwise (30 ml over a period of 15 min) to simulate 1 in. of rain. This was repeated until a total of 120 ml of water had been added over a 2-day period. The wet line indicating penetration was easily observed; at the end of 2 days, the penetration was 12 in. below the top of the tailings. The porosity calculated from these data is 35%, in excellent agreement with published data which indicates that the water was filling voids in the tailings. A stream of dry air was blown across the surface of the tailings for 1 day; then 30 ml of water was added and the air flow resumed. The weight loss, during three such cycles of water addition followed by drying, was equivalent to 0.4 in./day, which is in the evaporation rate range for an arid climate. The data (Fig. 3) show

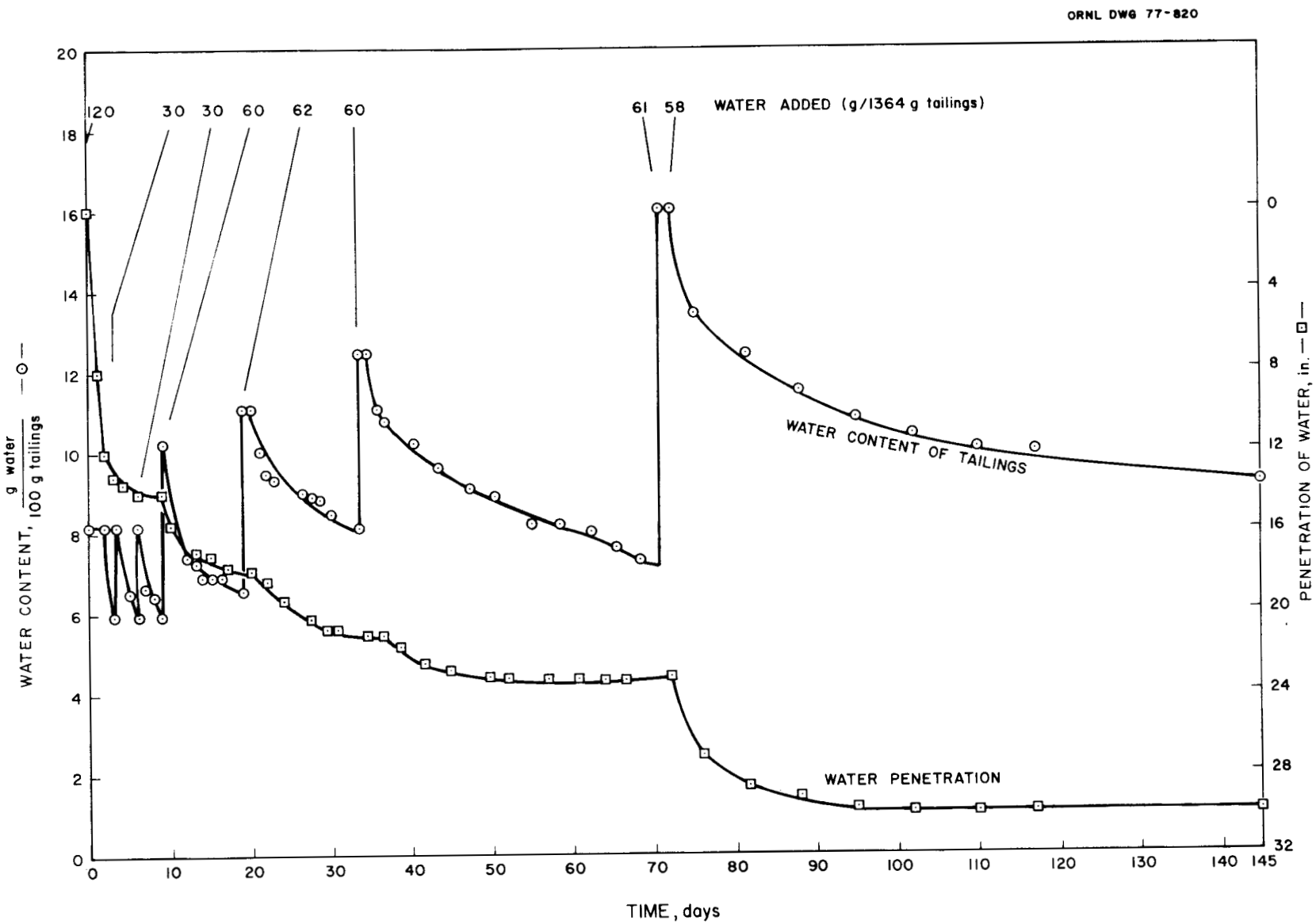

Fig. 3. Penetration of water into a column of tailings simulating conditions in an arid climate.

that each 30-ml increment of water, which is equivalent to 1 in. of rain, was evaporated; the penetration into the tailings leveled off at 14 in.

A series of three 60-ml additions of water (each equivalent to 2 in. of rain) followed by air flow showed that the penetration increased each time and about 65% of the water was lost by evaporation. The penetration after the third 60-ml addition was only 2 in. more than after the second addition, indicating that the penetration would level off even after a 2-in. rain. The average moisture content at the end of each evaporation period was only 7%.

The last addition of water amounted to a total of 119 ml, simulating 4 in. of rain; actually it would more closely simulate melting snow or a very prolonged rain because of the time required (2 days) for the water to soak into the tailings. This indicates that most of the water from a flash flood would run off. Again, the penetration leveled off, the final line being 30 in. below the top. Of the total of 481 ml of water added, 74% was evaporated.

8. STUDIES OF RADON EMANATION

The percentage of radon produced by decay of radium that escapes from the sand grains and becomes available for diffusion from the tailings dump must be known in order to completely assess the hazards of uranium mill tailings. This ratio of radon escape to radon production has been defined by others as the emanation coefficient.[8] The two mechanisms that have the greatest effect on the release or emanation of radon atoms from the production site are the recoil energy from alpha decay and diffusion through cleavage planes or other crystal defects.[8] The diffusion rate is dependent on the crystalline properties of the minerals involved as well as on the grain size. For example, the emanation coefficient can vary from less than 1% from zircons, which have very tight crystal lattices, to as much as 70% from carnotites, which have an open lattice. With respect to grain size, tests have shown that emanation rates are greatest in the size range of 50 to 150 mesh.[9]

8.1 Emanation from Ore Feeds, Sulfuric Acid Tailings, and Nitric Acid Residues

Emanation coefficients measured for the five ore feed samples (2-6) ranged from 9 to 35%, averaging 24% (Table 9). A range of this magnitude may be expected in view of the variations in particle size and mineralization of the various ore feeds. For example, mesh sizes ranged from -20 to -28 mesh for the acid mill feeds to -200 mesh for the alkaline mill feeds, while mineralization ranged from highly emanating carnotite in the oxidized zones to lower emanating uraninite in the deeper reducing zones, along with mixtures of both as well as with other uranium-containing minerals such as tyuyamunite, coffinite, etc. These minerals are found as coatings on individual sand grains and as interstitial fillings in the sandstone.

Emanation coefficients from the four sulfuric acid-leached tailings (samples 1-4) were significantly lower and varied over a narrower range, 9 to 17% (averaging 12%), than those obtained from the ore samples. This is not surprising since most of the dissolved radium is thought to precipitate as radium sulfate along with the more preponderous amounts of calcium sulfate (gypsum) and is found in the fine slime fraction. On the other hand, emanation coefficients from the alkaline-leached tailings (samples 5 and 6) were higher than those obtained with the corresponding ores. This could be due to the exposure of more surface area as a result of the finer grind used for alkaline leach or the scouring action of the leach since very little radium is thought to be dissolved by the alkaline solutions.

Even after essentially all of the leachable radium had been removed from the ore feed and tailings samples by treatment with nitric acid as described in Sect. 4.0, the residues continued to emanate radon (Table 9). Although the emanation coefficients varied over a rather wide range, from 8 to 43%, the rate of radon emanation is rather small (0.02 to 0.12 pCi per hour per gram of residue) and represents a substantial reduction ($\geq$84%) from that emanating from the ore or tailings.

Table 9. Summary of radon emanation data

Component	No. 1	No. 2		No. 3		No. 4		No. 5		No. 6	
	Tailings	Ore	Tailings	Ore	Tailings	Ore	Tailings	Ore	Tailings	Ore	Tailings
Ore and tailings samples as received											
^{226}Ra[a]	910	575	668	760	609	768	716	267	237	1070	667
E,[b] %	10	28	17	26	12	20	9	35	45	9	14
^{222}Rn,[c]	0.70	1.22	0.86	1.49	0.55	1.16	0.49	0.71	0.81	0.73	0.70
Nitric acid residues (see Table 2 for leach conditions)											
^{226}Ra[a]	44	38	39	62	51	17	17	45	29	42	24
E,[b] %	22	8	8	15	14	43	30	17	21	38	37
^{222}Rn,[c]	0.07	0.02	0.02	0.07	0.05	0.06	0.04	0.06	0.05	0.12	0.07
RRE,[d] %	10	2	2	5	9	5	8	8	6	16	10

[a]Picocuries per gram of ore.

[b]Radon emanation coefficient.

[c]Radon emanation rate = pCi Ra/g x E% x 0.01 x λ_{Rn} hr^{-1} = pCi Rn g^{-1} hr^{-1}.

[d]Relative radon emanation = [^{222}Rn (HNO_3 residue)/^{222}Rn (ore or tailings)] x 100.

8.1.1 Emanation from sand and slime fractions

In every case (Table 10), the radon emanation coefficient for the slime fraction (17 to 57%, average, 37%) was greater than that for the sands (5 to 36%, average 15%). However, because of the wide spread in the ratio of sands to slimes, the fraction of the total radon emanating from the nitric acid-leached residues from the sands varied from 50% for sample 2 to only 15% from sample 3 (Fig. 4). It seems unlikely that any advantage can be realized by keeping the slimes separate from the sands.

8.1.2 Effect of roasting on radon emanation

When samples of nitric acid-leached residues were roasted at 800°C, emanation coefficients were reduced to about one-third of the original values (Table 11). The emanation coefficient for a sulfate-leached tailings sample as received (sample 1) was also reduced significantly, from 10% to 3%, by roasting at 900°C. It is well known that annealing at high temperatures can restore the order of the atoms in the crystal lattices of many minerals which have been damaged or displaced by radiation from alpha particles and recoiling nuclei.[8] It is thought that this disruption of the crystal lattice allows diffusion of the radon through and out of the dense ore particles.[8]

8.2 Emanation Coefficients from Miscellaneous Materials

Emanation coefficients for two NBS uranium standards, containing 33 and 182 pCi $^{226}Ra/g$, were found to be 10%. The radium in these standards was present in pitchblende (uraninite) mixed with quartz sand (-325 mesh). Another NBS standard, containing 1800 pCi of radium per gram, in which the uraninite was blended with dunite also emanated 10%. This indicates that the emanation is dependent on the radium-containing mineral and is affected only slightly, if at all, by the diluent.

A finely ground sample of phosphate rock (apatite) feed to a wet-process acid plant containing 0.015% uranium and 55 pCi of radium per gram had an emanation coefficient of only 5% before processing, while a sample of waste gypsum obtained from the phosphate plant after processing

Table 10. Radon emanation from sand and slime fractions of nitric acid residues[a]

	No. 1 Tailings		No. 2 Ore		No. 3 Ore		No. 4 Ore		No. 5 Ore		No. 6 Ore	
	Sand	Slime	Sand	Slime	Sand	Slime	Sand	Slime	Sand	Slime	Sand	Slime
Wt, %	53	47	82	18	66	34	74	26	88	12	33	67
^{226}Ra, pCi/g	42	59	31	58	39	92	13	31	35	109	53	39
E, %	14	43	7	17	5	24	19	57	10	34	36	48
Total ^{226}Ra, %	45	55	71	29	45	55	54	46	70	30	40	60
Total ^{222}Rn, %	21	79	50	50	15	85	30	70	47	53	33	67

[a]See Table 4 for information on sand-slime separations.

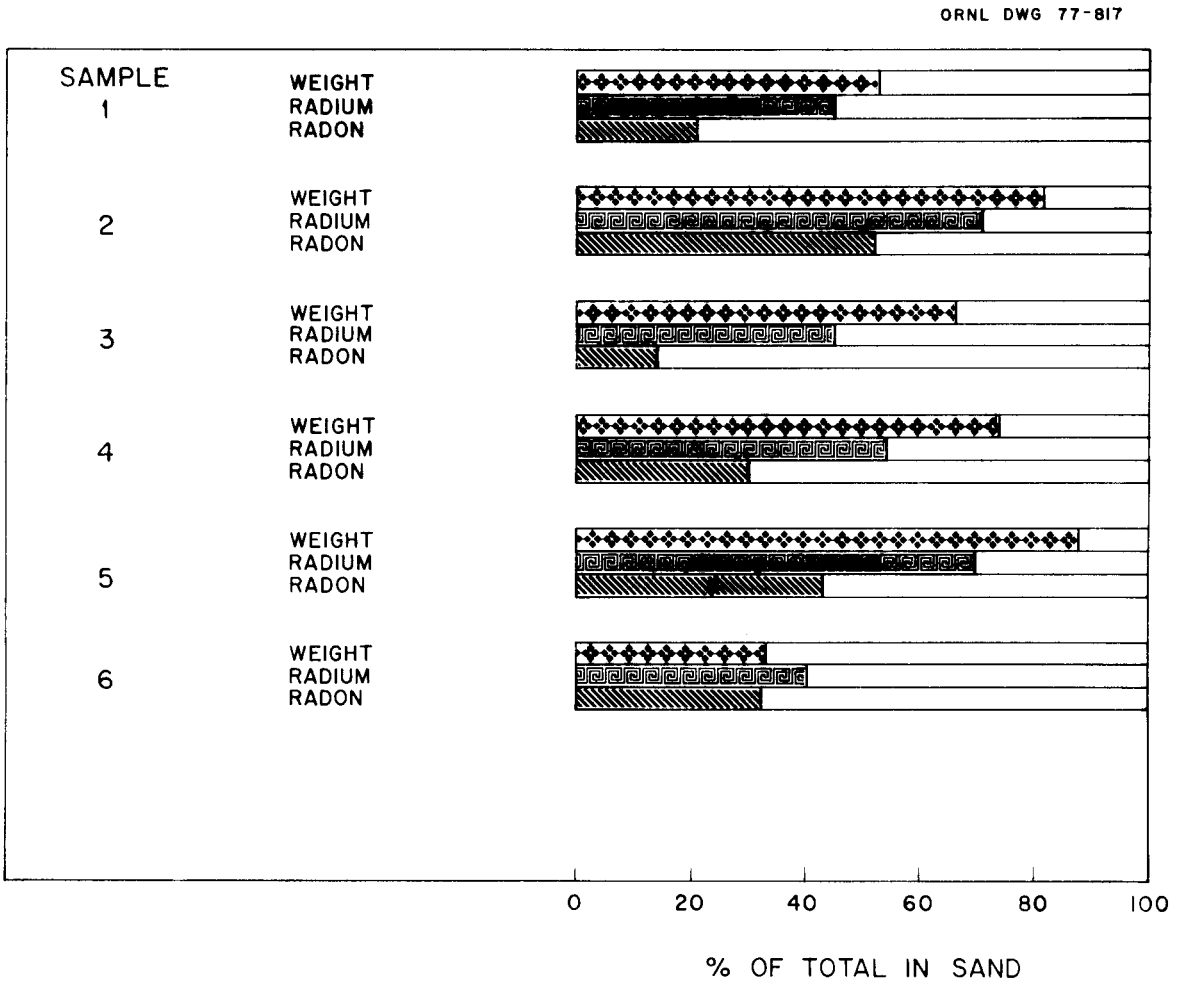

Fig. 4. Percentage of weight, radium, and radon emanation attributed to the sand fraction in residues after HNO_3 leach of ores.

Table 11. Effect of roasting on radon emanation coefficient

Conditions: ore samples roasted 2 hr

Ore sample	^{226}Ra content (pCi/g)	Roast temperature (°C)	Radon emanation coefficient (%)
No. 1 tailings: as received	910	0	10
		900	3
No. 1 tailings: HNO_3-leached residue	44	0	22
		800	6
		900	8
No. 2 tailings: HNO_3-leached residue	39	0	8
		800	3
		900	2
		1000	2

contained 15 ppm of uranium plus 20 pCi of radium per gram and had an emanation coefficient of 60%. The lowest emanation coefficient (0.04%) was obtained with a sample of zircon that contained 107 pCi of radium per gram.

8.3 Effect of De-emanation and Aging on Radium Analyses

Since ^{226}Ra analyses were made by gamma-ray spectrometry of gamma rays that originate from the post-radon daughters, there was some concern over (1) the possible loss of radon through the plastic sample containers used in the radium measurements and (2) the time required to approach sufficiently close to equilibrium to obtain accurate measurements. Neither of these problems proved to be very serious. For example, as shown in Table 12, equilibrium radium analyses were essentially the same whether the samples were sealed in plastic or metal containers. Also, radium analyses obtained within 2 to 3 hr after de-emanation were not significantly lower than those obtained for the samples at equilibrium. This may be accounted for by the low emanation coefficients for these samples (8 to 20%) and by the rapid ingrowth of radon daughters, much of which occurs in the first few hours after de-emanation. This rapid ingrowth also accounts for the lower values of the "indicated" emanation coefficient, which were only 50 to 65% of the measured values.

8.4 Unsupported Radon

A minor but interesting problem encountered in analyzing the low-level nitric acid-leached residues (and the one that dictated the waiting period between leaching and radium analysis) was the decay of unsupported radon. To study this problem, a 100-g sample of ore was leached for 1 hr at 70°C with 200 ml of 3 N HNO_3, filtered, and washed; the cake remaining after air-drying was then submitted to a time-decay study. These measurements showed that the activity of the sample decreased with a half-life of 3.82 days and indicates that trapped, unsupported radon was decaying from the sample. This suggests that the radium parent of

Table 12. Effect of de-emanation on approach to equilibrium[a]

Before de-emanation	^{226}Ra concentration[b] (pCi/g) After de-emanation (days) <0.1	3	9	14	21	E (%) Measured[c]	Indicated[d]
897	872 ± 16	895 ± 4	921 ± 6	908 ± 8	915 ± 6	10	5
589	535 ± 17	597 ± 15	594 ± 15	601 ± 8	603 ± 17	20	13
38	35 ± 1	35 ± 1	36 ± 2	38 ± 2	36 ± 1	8	5

[a]Procedure: Samples were sealed in metal containers and aged for 30 days to ensure equilibrium conditions before analyzing for ^{226}Ra using the gamma method. The samples were then de-emanated by evacuating the radon, resealed, and counted periodically to measure the approach to equilibrium.

[b]Based on measurement of 295-, 352-, and 609-keV gamma peaks.

[c]Lucas cell measurements of radon directly.

[d]$$\frac{\text{Ra concentration at equilibrium} - \text{Ra concentration immediately after de-emanation}}{\text{Ra concentration immediately after de-emanation}} \times 100.$$

this radon had been selectively leached from the ore. The radon had evidently migrated through microscopic fractions or pores into an impervious portion of the sand grains or resistate minerals.

8.5 Procedure for Radon Measurements

A procedure was developed which was based on results of previous investigators.[9,10] Usually a 100-g sample of ore or tailings was placed in a de-emanation vessel, which was subsequently sealed. The vessel was then alternately evacuated (using an aspirator) and opened to the atmosphere three times. Following this de-emanation procedure, the sealed vessel was stored at atmospheric pressure for a specified period of time, usually 16 to 60 hr, to allow the radon to grow in. Tests showed that the time allowed for ingrowth of radon did not affect the accuracy of the measurements. At the end of this time period, the vessel was connected to a Lucas-type scintillation chamber (which had been evacuated to less than 10 μ) for 2 min to allow the accumulated radon to equilibrate between the two vessels. After a 4-hr waiting period to permit the short-lived ^{220}Rn and ^{219}Rn to decay and to allow ^{222}Rn and its daughters to attain transient equilibrium, the chamber was counted for 5 min in a radon analyzer.

Two types of de-emanation vessels were used. The first was a special 1-in.-deep x 3-in.-diam stainless steel dish made for lunar samples. A piece of 1/8-in. stainless steel tubing, a semineedle valve, and a 12/5 stainless steel outer ball joint for connecting to the Lucas cell were sealed to the dish. After a sample had been placed in the dish, the top was silver-soldered to the bottom to completely seal the system. Although this arrangement worked very satisfactorily, the operation was time-consuming because it required the solder joint to be made and broken for each test. The second vessel was made with a 250-ml Erlenmeyer flask, a glass stopcock, and a ball joint. Comparative tests gave the same results and indicated that no radon was lost through the ground-glass joints or adsorbed by the stopcock grease. The total volume of the metal

system was 115 ml as compared with 288 ml for the glass system. The excellent agreement between the measurements made with the two vessels increased our confidence in the values.

The following equation was used to calculate the emanation coefficient, E:

$$E, \% = \frac{\alpha}{\Sigma\alpha \times E_f \times G_f} \times V_{CF} \times 100,$$

where

α = measured alpha counts per minute (cpm) calculated at time 0;

$\Sigma\alpha$ = total alpha cpm assuming 100% emanation

= (pCi Ra/g) x (sample weight, g) x (3 α particles/dis) x (3.7×10^{-2} dis/sec-pCi) x (60 sec/min);

E_f = 0.81, the counting efficiency of the total system;

G_f = growth factor = $1 - e^{-\lambda t}$, where t = time after de-emanation and λ is the decay constant for radon;

V_{CF} = volume correlation factor

$$= \frac{[V_{SC} - (\frac{1 - P}{\rho})W] + V_C}{V_C};$$

V_{SC} = volume of the empty de-emanation vessel, ml;

V_C = volume of the counting chamber or Lucas cell, 95 ml;

P = porosity of the sample, 0.36;

ρ = density of the sample, 1.40 g/ml;

W = sample weight, g.

The 81% efficiency (E_f) correction of the total emanation system, including sample collection and counting statistics, that we used was obtained as follows: Very small volumes (0.05 to 0.10 ml) of two different standard radium solutions were transferred to the 250-ml Erlenmeyer flasks used in this study. A drop of wetting agent was then added in an attempt to spread the solution in a monomolecular layer over the bottom of the flask. The contents of the flask were de-emanated and processed in the manner described previously for determining radon emanation

coefficients from the ore and tailings samples. The efficiency was then calculated, assuming that 100% of the radon escaped from the dried sample layer. Using this technique, we arrived at an E_f of 81% ± 3% (Table 13). This value compares favorably with the estimated, or approximate, value of 85% obtained from the measuring equipment vendor and gives us added confidence in our measurements. However, we feel that a well-documented powdered standard, with a certified radium analysis and radon emanation coefficient, is needed for this purpose.

Table 13. Efficiency calibration of the radon emanation system

Standard ^{226}Ra solution			
Number	^{226}Ra concentration (pCi/ml)	Volume (ml)	E_f
1	6000	0.05	0.80
		0.05	0.85
		0.10	0.80
		0.10	0.83
2	2000	0.10	0.79
		0.10	0.76
	Average		0.81
	Standard deviation		0.03
	Standard error		0.013

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