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E. R. Landa · J. R. Gray

## US Geological Survey research on the environmental fate of uranium mining and milling wastes

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**Abstract** Studies by the US Geological Survey (USGS) of uranium mill tailings (UMT) have focused on characterizing the forms in which radionuclides are retained and identifying factors influencing the release of radionuclides to air and water. Selective extraction studies and studies of radionuclide sorption by and leaching from components of UMT showed alkaline earth sulfate and hydrous ferric oxides to be important hosts of radium-226 ( $^{226}\text{Ra}$ ) in UMT. Extrapolating from studies of barite dissolution in anoxic lake sediments, the leaching of  $^{226}\text{Ra}$  from UMT by sulfate-reducing bacteria was investigated; a marked increase in  $^{226}\text{Ra}$  release to aqueous solution as compared to sterile controls was demonstrated. A similar action of iron(III)-reducing bacteria was later shown. Ion exchangers such as clay minerals can also promote the dissolution of host-phase minerals and thereby influence the fate of radionuclides such as  $^{226}\text{Ra}$ . Radon release studies examined particle size and ore composition as variables. Aggregation of UMT particles was shown to mask the higher emanating fraction of finer particles. Studies of various ores and ore components showed that UMT cannot be assumed to have the same radon-release characteristics as their precursor ores, nor can  $^{226}\text{Ra}$  retained by various substrates be assumed to emanate the same fraction of radon. Over the last decade, USGS research directed at offsite mobility of radionuclides from uranium mining and milling processes has focused on six areas: the Midnite Mine in Washington; Ralston Creek and Reservoir, Colorado; sites near Canon City, Colorado; the Monument Valley District of Arizona and Utah; the Cameron District of Arizona; and the Puerco River basin of Arizona and New Mexico.

**Key words** Uranium mining · Milling wastes · Radionuclides

### Historical background

The US Geological Survey (USGS) has conducted research dealing with radioactive waste disposal since the early days of the American civilian and defense nuclear programs. Major programs have existed for identifying environments suitable for the disposal of high-level waste (HLW), and for developing geohydrologic criteria to be used in the siting, design, and operation of low-level waste-disposal sites. A program area relatively untouched by the USGS through the late 1970s was uranium mill tailings (UMT). UMT are the crushed residues of ore remaining after the extraction of uranium by either sulfuric acid or sodium carbonate. As the ore grade is typically low, and most of the uranium daughter products remain with the tailings, these materials constitute a high-volume, low-specific activity radioactive waste. The present inventory of UMT in the United States is more than 230 million tons (US Department of Energy 1993, 1994).

Studies by nuclear engineers around 1976 showed the relative ingestion hazard (an index of radiotoxicity) from HLW from nuclear fuel reprocessing to initially be about 10,000 times greater than that from UMT. However, due to the relatively short half-lives of the fission products present in these wastes, the hazard index for the HLW falls below that of UMT after about 600 years. Using these findings as part of its data base, an American Physical Society study group on nuclear fuel cycles and waste management (Hebel and others 1978) concluded:

The relative magnitudes of the actinide activity in mill tailings, TRU [transuranic] wastes and HLW or spent fuel, per unit of energy generated, suggest that all three waste streams may present problems of comparable magnitude for the very long term (i.e., greater than a thousand years). Careful evaluation of the relative hazards to present and future generations associated with current and proposed treatments of all waste streams is needed to provide a necessary perspective to decisions concerning waste management. (p. S109)

Though the [tailings] pile can be constructed and managed for minimal erosion over a conventional engineering time span, it certainly must be considered as no more secure than any other surface feature over a period of several tens of thousands of years. (p. S79)

Accessibility of uranium mill tailings, as handled in the past, appears undesirable from the point of view of local and regional exposure. Accordingly, procedures and criteria for handling mill tailings need to be reexamined. (p. S9)

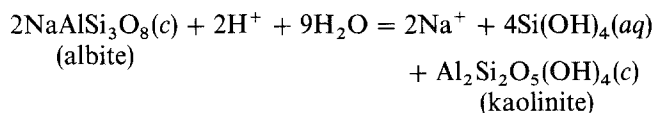
The concerns expressed here with respect to the long-term hazards associated with UMT were central to a 1978 decision by the research managers of the Water Resources Division of USGS to establish a project to study geochemical controls on the migration of radionuclides from UMT. Cooperative studies with the US Bureau of Indian Affairs and US Bureau of Land Management (Sumioka 1991), US Environmental Protection Agency (Hearne and Litke 1987), Navajo Nation (Longworth 1994), and Office of Navajo and Hopi Indian Relocation, US Bureau of Indian Affairs, Arizona Department of Environmental Quality, Arizona Department of Water Resources, Navajo Nation, and New Mexico Environmental Division (Gray and Webb 1991; Gray and Fisk 1992; Van Metre and Gray 1992), in addition to research by Yang and Edwards (1984) have addressed the environmental effects of uranium mining and milling over the last decade. A spinoff of fundamental research on microbial transformations of iron and other metals was the development of techniques for the bioremediation of uranium-contaminated waters (Lovley and Phillips 1992) and soils (Phillips and others 1994) at uranium mining and milling sites, and other nuclear fuel cycle sites.

### Uranium milling research

Due to its high radiotoxicity and affinity for accumulating in bones,  $^{226}\text{Ra}$  (half-life = 1625 years) is generally the uranium daughter product of most concern in hazard assessments of water supplies and food chains associated with UMT. To understand the fate and transport of  $^{226}\text{Ra}$

in a geologic timeframe, one must also consider the geochemical behavior of its long-lived parent,  $^{230}\text{Th}$  (half-life = 80,000 years). An early review of the literature (Landa 1980) revealed numerous leaching studies focusing on  $^{226}\text{Ra}$ , but no clear picture of either the host phases of  $^{226}\text{Ra}$  in UMT or how milling changes the hosts of uranium daughter product radionuclides and other contaminants in UMT as compared to the original uranium ore. To address this gap, the ore entering the acid leaching circuit of an operating mill in the western United States and the UMT being discharged to the waste pond were sampled and put through a five-stage, sequential leaching scheme (Table 1) to identify radionuclides possibly hosted in the following fractions: (1) water soluble, (2) ion exchangeable, (3) carbonate and readily acid soluble forms, (4) iron and manganese hydrous oxides, and (5) alkaline earth sulfate (e.g.,  $\text{BaSO}_4$ ,  $\text{SrSO}_4$ ) and/or organic matter. The water-soluble plus exchangeable inventory of  $^{226}\text{Ra}$  in the tailings (18%) was about four times that in the ore. Iron and manganese oxides, and alkaline earth sulfate/organic matter were shown to be important hosts of  $^{226}\text{Ra}$  in both the ore and tailings (Landa 1982). For both the ore and tailings, only extraction 5, using alkaline DTPA, showed greater than 5% removals of  $^{230}\text{Th}$ .

The resistate character of  $^{230}\text{Th}$  is of interest, as laboratory and in-mill sampling of tailings liquids and solids from the sulfuric acid milling of sandstone ores have shown  $^{230}\text{Th}$  extraction into the acid to be as high as 90% (Landa 1980; Landa and Bush 1990; Nirdosh and Muthuswami 1988). Yet the  $^{230}\text{Th}$  concentrations of samples taken at tailings piles are typically far less depleted in  $^{230}\text{Th}$  (assuming initial secular equilibrium in the ore and using the  $^{226}\text{Ra}$  concentration as a conservative tracer of the initial uranium series inventory) than a 90% extraction would produce (Sill 1977; Ibrahim and others 1982a,b). It would appear that upon "aging" in the tailings pond, the solubilized  $^{230}\text{Th}$  becomes reassociated with the tailings solids. A likely mechanism is the slow consumption of  $\text{H}^+$  ions by reaction with aluminosilicate minerals (Hem 1985, p. 13):



**Table 1** Extraction of  $^{226}\text{Ra}$ ,  $^{230}\text{Th}$ , and U from ore and tailings sampled at an operating acid-leach uranium mill<sup>a</sup>

Sequence step	Extractant	Percentage of originally present radionuclide inventory extracted					
		$^{226}\text{Ra}$		$^{230}\text{Th}$		U	
		Ore	Tailings	Ore	Tailings	Ore	Tailings
1	distilled water	0.7	4.5	0.02	3.1	0.3	22
2	0.1 M NaCl	4.1	13	0.05	0.02	0.3	0.4
3	1 M acetic acid	1.3	4.3	1.1	1.1	50	28
4	hydroxylamine HCl	39	26	4.1	3.9	17	14
5	alkaline DTPA	8.4	14	23	20	1.4	<0.6

<sup>a</sup> Values shown are means of three replicate samples (Landa, 1982)

Nirdosh and Muthuswami (1988) note precipitation of  $^{230}\text{Th}$  in sulfuric acid–uranium ore leachate to begin as the pH is raised above 1.4. Sorption by tailings solids or coprecipitation by insoluble sulfates or iron–manganese hydrous oxides precipitating from mill pond acid are other possible mechanisms returning the thorium to the solid phase.

While the in-mill “heads” and “tails” sampling described above did not demonstrate great differences in host phases of radionuclides as a result of acid milling, other investigators had shown redistribution between particle size fractions to occur with  $^{226}\text{Ra}$  in both acid and alkaline leaching circuits; radium became enriched in the finer particles of the tailings when compared with the original distribution in the uranium ore. While dissolution followed by sorption (coprecipitation and/or adsorption) preferentially on fine-grained substrates seemed likely, the identification of sorbing phases was not made in the studies. As gangue (matrix) materials in the ore represent potential sorbents, these were investigated (Landa and Bush 1990) under simulated acid milling conditions. Uranium-bearing sandstone ore was milled on a laboratory scale with 0.75 N sulfuric acid (pH 0.45). At regular intervals, filtrate from this suspension was placed in contact with mixtures of quartz sand and various potential sorbents, which occur as gangue in uranium ores; the potential sorbents included clay minerals, iron and aluminum oxides, feldspar, fluorspar, barite, jarosite, coal, and volcanic glass. After equilibration, the quartz sand–sorbent mixtures, referred to here as synthetic substrates (SS), were separated from the filtrate and radioassayed by gamma-spectrometry to determine the quantities of  $^{238}\text{U}$ ,  $^{230}\text{Th}$ ,  $^{226}\text{Ra}$ , and  $^{210}\text{Pb}$  sorbed (Table 2). Sorption of

$^{238}\text{U}$  was low in all cases, with maximal sorptions of 1–2% by the bentonite- and coal-bearing samples.  $^{230}\text{Th}$  sorption also was generally less than 1%; maximal sorption here was observed in the fluorspar-bearing sample. While gypsum formed during the reaction of the  $\text{CaF}_2$  with the  $\text{H}_2\text{SO}_4$ , and the  $^{230}\text{Th}$  sorption observed was thought to be the result of coprecipitation with gypsum, subsequent experiments (Landa and others 1994) showed gypsum to have only limited ability to coprecipitate thorium. Removals from solution seen here may be associated with the formation of an insoluble thorium fluoride compound at the surface (Ryabchikov and Gol’braikh 1969, p. 44).  $^{226}\text{Ra}$  and  $^{210}\text{Pb}$  generally showed higher sorption than the other nuclides—more than 60% of the  $^{226}\text{Ra}$  solubilized from the ore was sorbed on the barite-bearing sample. The mechanism(s) for this sorption by a wide variety of substrates is not yet understood. The leaching of  $^{226}\text{Ra}$  from these SS was later examined (Landa 1991). The sequence of extractants and targeted radium species are shown in Table 3. The  $^{226}\text{Ra}$  contents of the SS at the start, and the fractional removals with each extraction are shown in Table 4. Radium retained by the kaolinite and quartz materials (Ottawa sand only and fine silica) appears to be the most easily desorbed, with about 60–70% extracted by the dilute  $\text{H}_2\text{SO}_4$  and the two sequential deionized water washes. In contrast, the coal-, fluorspar-, barite-, and bentonite-bearing SS released less than 6% of their radium inventory with these three leaches. As noted above, significant quantities of gypsum formed during the sorption phase in the fluorspar SS. The lack of radium

**Table 2** Sorption of radionuclides and radon emanation coefficients of synthetic substrates (*i.e.*, Ottawa sand and constituent listed below) exposed to uranium milling liquor<sup>a</sup>

Constituent	Sorption (%)				Radon emanation coefficient (%)
	$^{238}\text{U}$	$^{230}\text{Th}$	$^{226}\text{Ra}$	$^{210}\text{Pb}$	
Ottawa sand only	ND	ND	5.2	1.1	6
Fine silica	0.2	0.5	28	4.8	10
Potassium feldspar	0.05	0.3	26	5.0	11
Sodium feldspar	0.07	ND	58	16	15
Pyrophyllite	0.6	0.4	23	4.6	15
Kaolinite	0.4	ND	22	4.0	4
Bentonite	2.1	2.2	51	18	14
Bauxite	0.1	4.5	36	13	10
Hematite	0.3	0.2	21	3.4	12
Magnetite	0.2	ND	48	11	10
Barite	0.04	0.03	64	20	8
Jarosite	0.4	0.3	49	27	11
Fluorspar	0.2	13	52	21	13
Volcanic ash	0.5	ND	50	14	17
Coal	1.4	0.2	53	29	31

<sup>a</sup> The percent sorption value represents the ratio of that retained by the synthetic substrate to that extracted from the ore. ND = not detected (Landa and Bush 1990)

**Table 3** Sequence of solutions used for leaching tests (Landa 1991)

Sequence number	Solution	Remarks
I	0.005 M $\text{H}_2\text{SO}_4$	To simulate the effect of dilute $\text{H}_2\text{SO}_4$ as might be encountered at the end of the washing circuit of an acid-leach uranium mill.
II, III	Deionized water	Two extractions in sequence to simulate the effect of further dilution of the sulfuric acid as might be encountered with exposure of tailings to dilute natural waters following disposal.
IV	1.0 M $\text{NH}_4\text{Cl}$	The exchangeable and other “easily-extractable” forms of $^{226}\text{Ra}$ as noted by Steger and Legeyt (1987).
V	1.0 M HCl	While the action in step IV is displacement of the trace quantities of $^{226}\text{Ra}$ from the surface by ion competition for the same adsorption sites, the solution here does that plus provides acidity to enhance the dissolution of the sorbent surface. Single extractions of this type have often been used to characterize soils and aquatic sediments for biologically available metals.

**Table 4**  $^{226}\text{Ra}$  concentration of synthetic substrates (SS) after exposure to acid uranium milling liquor, and subsequential extraction reported as a percentage of initial radium concentration (Landa 1991)

SS (identified by varying constituent)	$^{226}\text{Ra}$ concentration (pCi/g)	I 0.005 M $\text{H}_2\text{SO}_4$ (%)	II $\text{H}_2\text{O}$ -(1) (%)	III $\text{H}_2\text{O}$ -(2) (%)	IV 1.0 M $\text{NH}_4\text{Cl}$ (%)	V 1.0 M HCl (%)	Total extraction by summation (%)
Ottawa sand only	2.0	31	29	10	26	2.0	98
Fine silica	10.1	8.5	30	33	26	1.6	99
Potassium feldspar	9.1	4.3	16.5	21	54	4.5	100
Sodium Feldspar	20.4	1.2	4.2	14	87	6.8	113
Pyrophyllite	7.2	1.0	8.3	8.2	50	11	79
Kaolinite	6.6	18	34	7.6	48	5.6	113
Bentonite	16.5	0.7	1.6	3.3	97	3.1	106
Bauxite	13.1	3.7	9.8	20	66	5.4	105
Hematite	6.5	10	18	22	55	0.9	106
Magnetite	15.9	1.1	3.5	8.6	94	4.1	111
Barite	22.0	0.08	0.03	0.03	0.03	0.09	0.26
Jarosite	16.5	0.1	1.1	8.2	83	0.2	95
Fluorspar	18.8	0.8	0.6	0.7	31	48	81
Volcanic ash	17.3	0.5	2.8	6.9	94	3.7	108
Coal	18.1	0.6	0.9	1.9	88	15	106

\* (1) and (2) denotes the first and second sequential water extracts

leaching by either the dilute  $\text{H}_2\text{SO}_4$ <sup>1</sup> or deionized water here suggests that it is retained in a form other than gypsum. Alternatively, the radium may occur initially as a gypsum coprecipitate and upon dissolution of the gypsum, the radium may be sorbed by another phase.

While the 1 M  $\text{NH}_4\text{Cl}$  extractant could potentially increase the solubility of sparingly soluble salts such as  $\text{BaSO}_4$  and  $\text{PbSO}_4$ , which are known to be good sinks for radium (Steger and Legeyt 1987), the presence of residual sulfate from the sorption stage and from the first extractant in the sequence here will tend to suppress dissolution (Benes and others 1981). Thus, the large releases of radium seen at this step can probably be attributed solely to ion exchange reactions. Conversely, the lack of radium leaching seen with the barite SS suggests that the sorbed radium here is nonexchangeable.

The HCl-extractable fraction was generally less than 10%; however, for the fluorspar-bearing SS, it amounted to almost 50%. Work at the US Atomic Energy Commission's Winchester Laboratory in the late 1950's (National Lead Company 1960) showed that radium could be efficiently removed from an acidic (pH 1.8) uranium mill effluent by addition of NaF to precipitate  $\text{CaF}_2$ . Thus the  $\text{CaF}_2$  structure appears capable of including Ra, presumably by substitution into the Ca lattice position. The solubility of  $\text{CaF}_2$  is only slightly greater in 1 M  $\text{NH}_4\text{Cl}$  than in water (Linke 1958, pp. 601, 603); hence the large release of Ra seen in Table 3 with  $\text{NH}_4\text{Cl}$  is thought to be due to ion-exchange displacement. However, the solubility of  $\text{CaF}_2$  increases by almost two orders of magnitude going from water to 1.0 M HCl (Linke 1958, pp. 601, 602). Hence, the HCl leach used here, which released almost 50% of the  $^{226}\text{Ra}$  in the SS, is thought to cause this action by dissolution of  $\text{Ca}(\text{Ra})\text{F}_2$ .

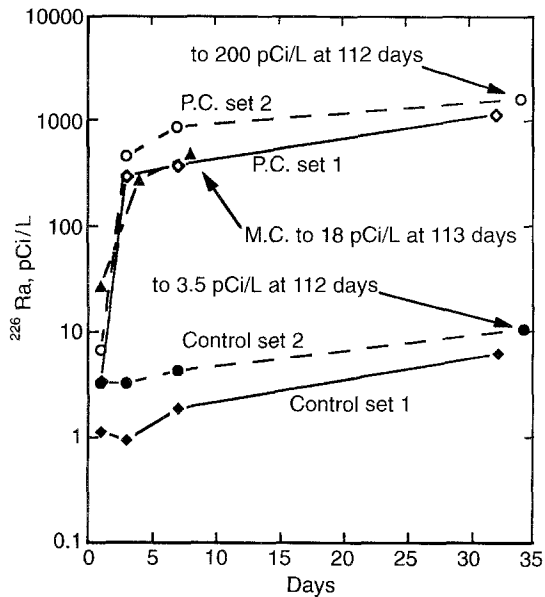
<sup>1</sup> The solubility of gypsum in 0.005 M  $\text{H}_2\text{SO}_4$  is about the same as in water—about 2.1 g/L at 25°C (Linke 1958, p. 663).

As compared with the other SS tested, the most anomalous behavior was exhibited by the barite SS. While the five-step extraction provided nearly complete recovery of  $^{226}\text{Ra}$  for most of the SS, for the barite SS, the recovery was less than 0.5%. The desorption pattern of the quartz sand that makes up 94% by weight of the barite SS was completely masked in the mixture. This effect may be due to competition by barite for radium sorption during the earlier exposure to the acid milling liquor. It may also result from resorption by barite of any radium desorbed from the quartz during the five-stage leaching described here. While  $\text{BaSO}_4$  solubility is significantly greater in 1.0 M HCl as compared to water (Benes and others 1981), the presence of soluble sulfates will suppress the reaction. This is the probable reason for the lack of radium release seen here with the barite SS. Indeed, Benes and others (1981) used 1.0 M HCl spiked with 60 ppm sulfate to selectively dissolve "acid-soluble" forms of radium and barium (e.g., that carried on ferric hydroxide), while preserving radium held as  $\text{Ba}(\text{Ra})\text{SO}_4$ . Seeley (1976) reported essentially no leaching of  $^{226}\text{Ra}$  by 0.01–1.0 M HCl from synthetic tailings in which radium was coprecipitated with  $\text{BaSO}_4$  onto quartz sand.

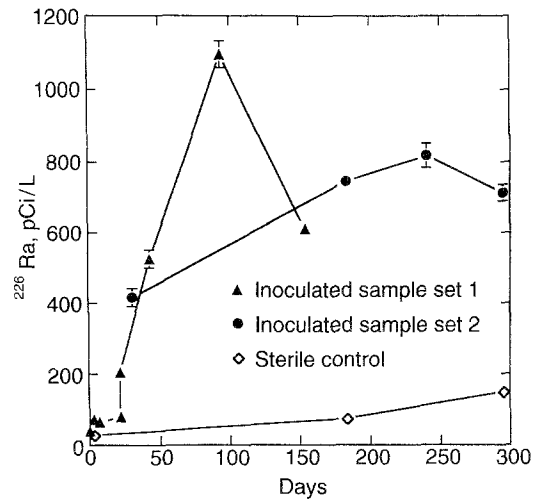
In the present study, the radium is sorbed onto preformed barite crystals rather than being coprecipitated from solution. However, it is likely that during the sorption period, the radium initially retained by the exchange of ions between the solution and those composing the surface of the crystal is slowly incorporated into the crystal lattice during recrystallization of the barite. Such a recrystallization process would be enhanced by the elevated temperature at which the sorption took place. The final product would thus resemble a  $\text{Ba}(\text{Ra})\text{SO}_4$  coprecipitate, except that the radium would occur only in the outer rind of the barite particles. A microautoradiographic study of uranium mill tailings from Monticello, Utah, by Stieff (1985), showed particles that were tentatively

identified on the basis of birefringence and high relief as barites, which were loci for elevated concentrations of  $^{226}\text{Ra}$ . The resistance to NaCl and HCl leaching shown here for radium sorbed on barite may help to explain a part of the unextractable, refractory fraction observed during investigations (Ryon and others 1977; Levins and others 1978) of the use of electrolytes and acids in remedial action and novel milling schemes aimed at reducing the radium contents of tailings to levels below regulatory concern.

The important role of alkaline earth sulfates in the retention of  $^{226}\text{Ra}$  and other radionuclides in acid-milled uranium tailings is supported by other recent investigations. Morrison and Cahn (1991) examined acid-leached tailings from several mills that used Colorado Plateau sandstone ores and found most of the alpha activity was associated with barium-strontium sulfate grains. Alpha-track maps of polished thin sections showed both grains with uniform track densities, as might happen with coprecipitation, and grains with only alpha-tracked rims, indicative of sorption/mineral replacement. From a purely analytical chemistry point of view, the insolubility of  $\text{BaSO}_4$  ( $K_{\text{sp}} = 1.08 \times 10^{-10}$  at  $25^\circ\text{C}$ ) might lead one to believe radium coprecipitated with  $\text{BaSO}_4$  to be very immobile. However, Landa and others (1986) showed that  $^{226}\text{Ra}$  leaching from UMT was greatly enhanced in the presence of sulfate-reducing bacteria (SRB) bacteria (Fig. 1). These bacteria were isolated in low numbers from tailings samples but were isolated in relatively high numbers in organic matter-rich cover soils used in tailings reclamation



**Fig. 1** Uranium mill tailings and sulfate-reducing bacteria (SRB) leaching experiment. Change in soluble  $^{226}\text{Ra}$  concentration as a function of time. P.C. refers to samples inoculated with pure cultures of *Desulfovibrio desulfuricans*. M.C. refers to samples inoculated with mixed cultures of SRB and other bacteria that had been enriched from freshly collected UMT. Set 1 and Set 2 refer to series of samples inoculated on different dates and incubated along with a series of sterile control samples. From Landa and others (1986)



**Fig. 2** Soluble  $^{226}\text{Ra}$  in uranium mill tailings and media inoculated with *Shewanella putrefaciens* and in sterile uninoculated controls. Times shown are days since beginning growth on  $\text{H}_2$ . Set 1 and set 2 represent independent runs using different batches of *S. putrefaciens* inoculum. Two-sigma error bars based on counting statistics are shown here. From Landa and others (1991)

and revegetation (Miller and others 1987). Radium release to solution did not appear to be an indirect influence of chelates excreted by the bacteria, but rather was probably due to the dissolution of barite and similar phases in the tailings. A similar effect was later demonstrated with iron(III)-reducing bacteria, which do not reduce sulfate (Landa and others 1991). The action of these microorganisms in dissolving ferric hydrous oxide phases in UMT results in the release of  $^{226}\text{Ra}$  to solution (Fig. 2). These findings suggest that engineering measures or natural forces that place UMT in anaerobic environments may enhance the release and transport of  $^{226}\text{Ra}$ . Eberl and Landa (1985) showed clay minerals also enhance the dissolution of  $\text{BaSO}_4$ ,  $\text{SrSO}_4$ , and the release of  $^{226}\text{Ra}$  from UMT, presumably by acting as sinks for cations ( $\text{Ba}^{2+}$ ,  $\text{Sr}^{2+}$ ,  $\text{Ra}^{2+}$ ).

The release of gaseous  $^{222}\text{Rn}$  to the atmosphere from UMT is a critical pathway for human exposure to radiation from these waste materials. The radon emanation coefficient (REC) is the fraction of the radon produced by decay of the parent  $^{226}\text{Ra}$  that escapes the mineral lattice and enters the pore spaces; thus, it will influence the radon flux into the atmosphere from UMT disposal sites. Therefore, a knowledge of the geochemical and geotechnical properties that influence the REC is valuable in designing features of UMT repositories, such as the thickness and permeability of radon-barrier cover materials. Specific variables addressed in studies to date include particle size (Landa 1987a), uranium mineralogy and milling processes (Landa 1987b), and ore matrix mineralogy (Landa and Bush 1990).

Alkaline-circuit and mixed (acid- and alkaline-circuit) U mill tailings sampled at an inactive mill site near Monticello, Utah, and tailings from an active, acid-leach U mill were separated into particle-size fractions ranging from

+ 10 mesh to - 325 mesh by dry and wet separation techniques. Dry tailings show a high degree of aggregation that tends to mask the relation of properties, such as Ra content and REC, to particle size. In contrast, wet-separated coarse-tailings fractions (+ 325 mesh) had emanation coefficients that were from 25 to 45% lower than those of their fine-fraction counterparts. The reason for the observed particle size/REC relationship is probably more than just a surface area effect. In some sedimentary rock samples, the REC has been shown to be proportional to the square root of the particle diameter. However, as demonstrated in several investigations with soils and rocks, a direct correlation between  $^{222}\text{Rn}$  (or  $^{220}\text{Rn}$ ) emanating power and particle size (over a large range of particle sizes) can be expected only where the Ra isotope precursors are uniformly distributed in the soil or rock. Such a distribution is not the norm in soils and rocks, and certainly not in UMT, where redistribution of  $^{226}\text{Ra}$  during both acid-circuit milling (Whitman and Beverly 1958; Skeaff 1981) and alkaline-circuit milling (Lakshmanan and Ashbrook 1978), and inherited patterns from ore, tend to concentrate  $^{226}\text{Ra}$  in the fine fraction of the UMT. These findings question the assumptions that the higher REC of the fines is purely a function of their smaller particle dimensions and that the higher emanation coefficients generally observed for alkaline-circuit, as compared to acid-circuit, UMT is due only to their finer grinding. Other factors, perhaps related to the chemical/mineralogical form of

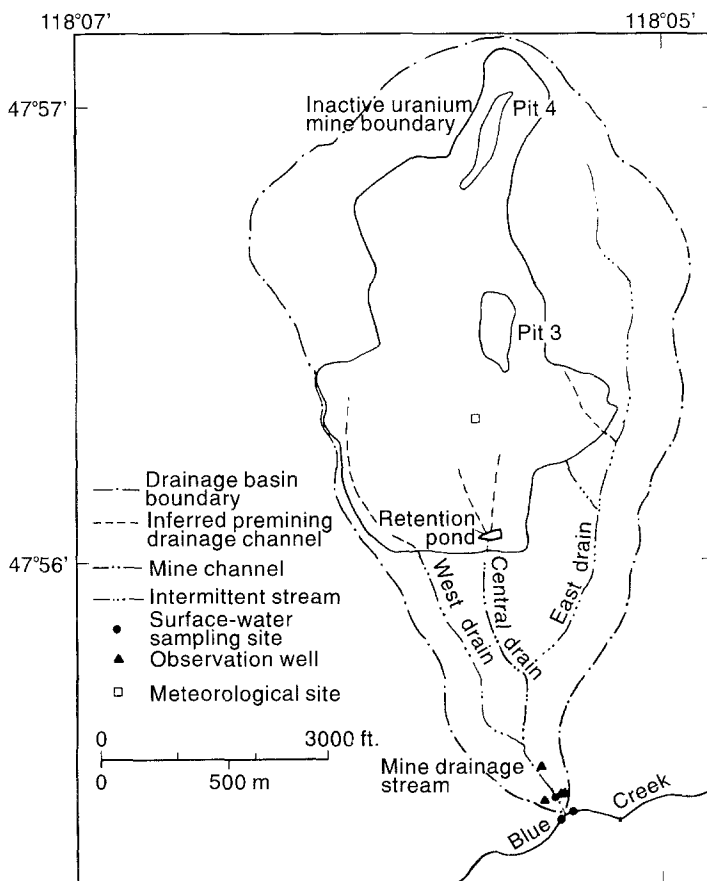
$^{226}\text{Ra}$  in the fine UMT (and in alkaline-circuit UMT), also may enhance their emanating power.

Uranium mill tailings cannot be assumed to have the same radon-release characteristics as their precursor ores (Landa 1987b), nor can  $^{226}\text{Ra}$  retained by various substrates be assumed to emanate the same fraction of radon. For example, in the simulated-milling, synthetic-substrate experiments described earlier (Table 2), subbituminous coal-bearing SS were shown to have an REC around 30%, compared to 4–17% for the other SS tested. While the literature indicates that radium coprecipitated with  $\text{BaSO}_4$  emanates almost no radon, the  $^{226}\text{Ra}$  sorbed on quartz sand with preformed barite crystals had an REC of 8% (Landa and Bush 1990).

### Case Studies: Uranium mining and milling research

Over the last decade, USGS research directed at offsite mobility of radionuclides from uranium mining and milling processes has focused on six areas: The Midnite Mine in Washington; Ralston Creek and Reservoir, Colorado; near Canon City, Colorado; the Monument Valley District of Arizona and Utah; the Cameron District of Arizona; and the Puerco River basin of Arizona and New Mexico.

**Fig. 3** Location of pits, retention pond, and surface-drainage features at Midnite Mine, Washington. From Sumioka (1991)



## Midnite Mine, Stevens County, Washington

As part of USGS research on abandoned mine sites, Sumioka (1991) studied the Midnite Mine,<sup>2</sup> an open-pit uranium mine in eastern Washington operated from 1956 to 1982. The disturbed area, about 130 ha, is restricted to a single 336-ha drainage basin. Three small streams flow into a single channel near the southern end of the basin (Fig. 3), which discharges to Blue Creek about 5.6 river km from Franklin D. Roosevelt (FDR) Lake.

Overburden and waste eventually accumulated in and covered the upper reaches of the stream draining the central part of the mine; however, flow continued from the channel at the toe of the southernmost (most down-gradient) waste pile. In 1978, a yellow–white precipitate appeared in the watercourse extending from the toe of this waste pile for a distance of at least 0.8 km downstream. A chemical analysis of the precipitate indicated it was a mixture of “aluminous salts and gypsum” that contained between 3 and 6% uranium oxide (U<sub>3</sub>O<sub>8</sub>).

To prevent mineralized water from entering Blue Creek and, subsequently, FDR Lake, the mine operator constructed a clay-lined retention pond behind an earthen dam immediately downstream from the southernmost waste pile. Although the dam retarded flow from the waste pile, water continued to seep from the toe of the dam during the study period (1984–1985). In November 1980, the total dissolved solids concentration of this seep was about 6000 mg/l with a discharge of about 0.3 l/s.

Dissolved-solids concentrations in surface water increases in mineralization with distance downstream through the mine. However, this relation is not straightforward due to pumpage between pits by the mine operator to minimize the potential for pit overflow. The pH range for pit 4 was 6.7–7.6. Pit 3, downstream from pit 4 and upgradient from the retention pond, had a pH range of 4.5–4.7, while pH values measured in the retention pond ranged from 3.5 to 3.8.

Dissolved manganese and dissolved nickel were the only trace metals detected in water from pit 4 in concentrations in exceedence of US Environmental Protection Agency (EPA) limits (50 µg/l and 13.4 µg/l, for drinking water, respectively) (US Environmental Protection Agency, 1991). Dissolved manganese concentrations in pit 4 exceeded EPA limits by more than an order of magnitude; by 2–3 orders of magnitude in pit 3; and by 4 orders of magnitude in the retention pond. Dissolved nickel concentrations in pit 4 were about triple the EPA limit. These concentrations in pit 3 were nearly 2 orders of magnitude larger than EPA’s limit, and two of the three concentrations determined for the retention pond exceeded the EPA limit by almost 3 orders of magnitude.

Activities of dissolved <sup>226</sup>Ra in six of nine samples collected from pit 4 exceeded EPA’s maximum contaminant

level (MCL) of 5 pCi/l<sup>3</sup>; the largest <sup>226</sup>Ra value was 8.3 pCi/l. Radium-226 activities in pit 3 and the retention pond exceeded the largest value from pit 4 by factors of about 2.5 and 6, respectively. Total dissolved uranium concentrations in pit 4, which ranged from 1700 to 10000 µg/l, exceeded EPA’s proposed MCL for U in drinking water of 20 µg/l by 2–3 orders of magnitude. Total dissolved uranium concentrations in pit 3 were usually within a factor of 2 of those in pit 4. Those in the retention pond, however, were 2–3 orders of magnitude larger than those in pit 4.

Because pit 4 is upgradient of most of the disturbed areas with highly leachable sulfide minerals, its opportunity to receive highly mineralized water is considerably less than for pit 3 and the retention pond. Lower pH values and generally higher concentrations of radionuclides and other trace metals in pit 3 were attributed to inflow of runoff that had been in contact with waste piles and exposed sulfide-bearing rocks and, to a lesser degree, pumpage from the retention pond. Lowest pH values and highest concentrations of radionuclides and other trace metals measured in the retention pond are likely a result of inflow of groundwater that has been in contact with acid-producing sulfide minerals. Uranium concentrations in most samples from the pits and retention pond exceeded the maximum limit for uranium-mine effluent of 4000 µg/l. Radium-226 activities in all samples exceeded EPA criteria for drinking water.

It may be possible to use microbial reduction of uranium to treat mine drainage water for uranium removal. The soluble oxidized form of uranium, U<sup>6+</sup>, is reduced by anaerobic bacteria to insoluble U<sup>4+</sup>, which precipitates as uraninite (Lovley and others 1991; Gorby and Lovley 1992). The process was not inhibited by low pH (pH 4.0), or relatively high concentrations of copper (4.5 µM), zinc (85 µM), or other trace metals in a uranium mine drainage water. Copper (either Cu<sup>+</sup> or Cu<sup>2+</sup> at 100 µM (6350 µg/l) inhibited U<sup>6+</sup> reduction (Lovley and Phillips 1992). By combining an initial bicarbonate extraction with microbial reduction/precipitation, it may be possible to decontaminate soils containing uranium in a variety of forms including ore, mill tailings, and munitions alloys (Phillips and others 1994).

## Schwartzwalder uranium mine, Ralston Creek, and Ralston Reservoir, Colorado

Yang and Edwards (1984) and Essed (1981) investigated radionuclide transport mechanisms from the Schwartzwalder uranium mine through Ralston Creek to Ralston Reservoir (Fig. 4), which supplies water to Denver’s western suburbs. Inflow to Ralston Reservoir is dominated by water diverted from Colorado’s western slope through the Moffat tunnel.

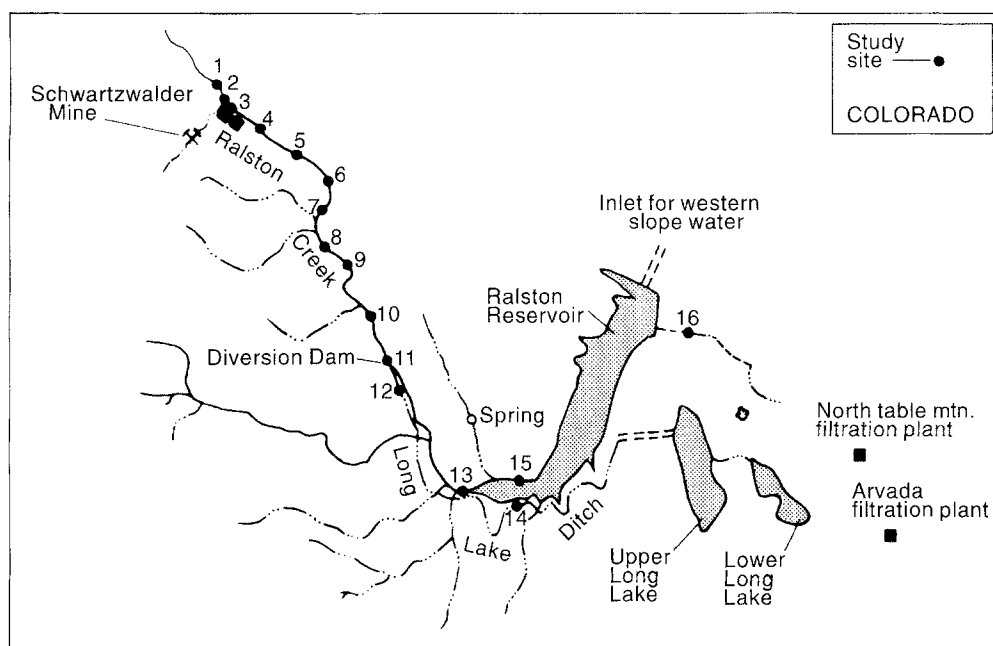
Beginning in 1972, water pumped from the mine—

<sup>2</sup> The use of industry or firm names in this paper is for location purposes only and does not impute responsibility for any present or potential effect on the natural resources.

<sup>3</sup> The proposed <sup>226</sup>Ra MCL is 20 pCi/l.



**Fig. 4** Map of Ralston Creek and Reservoir, near Golden, Colorado. From Yang and Edwards (1984)



mostly naturally occurring groundwater—and recycled water from a sorting plant were treated to reduce radium concentrations before release to the creek. Treatment consisted of addition of barium chloride to coprecipitate Ra as  $\text{Ba}(\text{Ra})\text{SO}_4$ , followed by sequential settling in four constructed ponds.

The dissolved component in a sample of wastewater outfall to Ralston Creek contained  $1700 \mu\text{g/l}$  of uranium and  $0.58\text{--}1.03 \text{ pCi/l}$  of  $^{226}\text{Ra}$ . The range in dissolved  $^{226}\text{Ra}$  values is uniformly less than the EPA's drinking water MCL of  $5 \text{ pCi/l}$ , whereas the dissolved uranium value exceeds EPA's proposed MCL by about 2 orders of magnitude. In Ralston Creek, downstream from the wastewater outfall, dissolved uranium values of  $600\text{--}1200 \mu\text{g/l}$  persisted for about 3 km, then decreased to less than  $200 \mu\text{g/l}$  at Ralston Reservoir inlet, about 6 km downstream from the outfall. Dissolved  $^{226}\text{Ra}$  values ranged from 1 to 2 pCi/l in the 3-km reach downstream from the outfall, then decreased to less than 1 pCi/l at the reservoir inlet.

Suspended sediment ( $>0.45 \mu\text{m}$ ) in the wastewater contained  $2400 \mu\text{g/g}$  of uranium and  $1300 \text{ pCi/g}$  of  $^{226}\text{Ra}$ . Adjusted for the suspended-sediment concentration of  $6 \text{ mg/l}$  in the sample, suspended concentrations of uranium and  $^{226}\text{Ra}$  in wastewater totaled  $14 \mu\text{g/l}$  and  $7.8 \text{ pCi/l}$ , respectively. Based on a mean wastewater outflow rate of  $27 \text{ l/s}$ , Yang and Edwards (1984) calculated daily dissolved plus suspended releases of about  $3.9 \text{ kg}$  of uranium and  $19,000 \text{ pCi}$  of  $^{226}\text{Ra}$  to Ralston Creek. Maximum suspended concentrations of uranium and  $^{226}\text{Ra}$  in Ralston Creek immediately downstream from the wastewater outfall were  $1000 \mu\text{g/g}$  of uranium and  $600 \text{ pCi/g}$  of  $^{226}\text{Ra}$ , respectively.

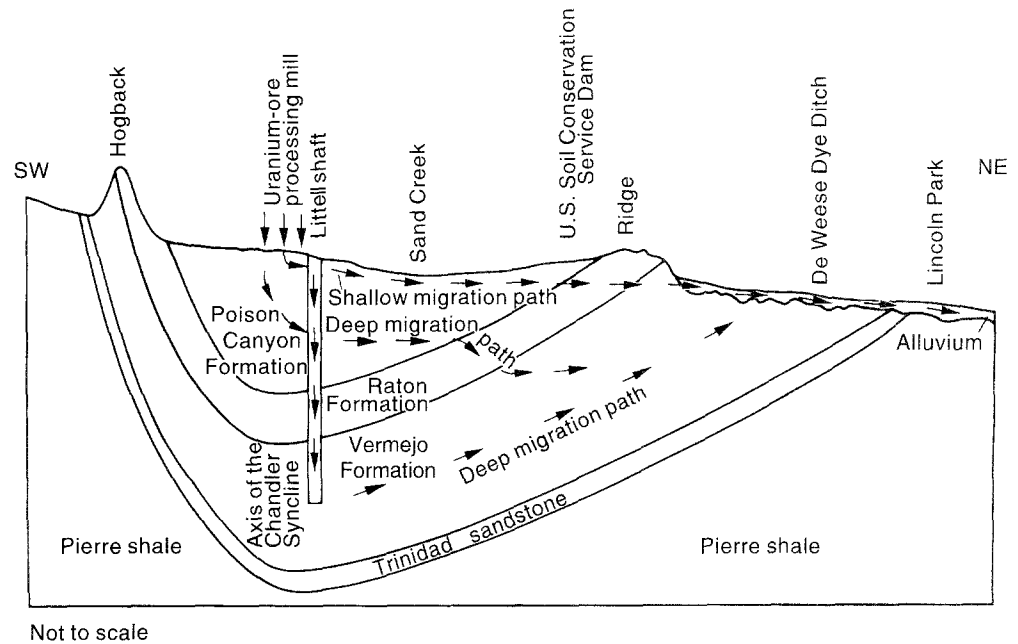
Concentrations of uranium and  $^{226}\text{Ra}$  in bed sediments tended to increase as particle size decreased. Maximum uranium and  $^{226}\text{Ra}$  concentrations were measured in bed

sediments about 1 km downstream from the wastewater outfall, then generally decreased to near-minimum values in the study reach about 4 km downstream from the wastewater outfall. Yang and Edwards (1984) proposed that uranium-ore particles discharged by the mine before wastewater was treated are present in the sediment. Larger concentrations of uranium and  $^{226}\text{Ra}$  in bed sediments in the reach within 2.4 km downstream of the wastewater outfall were attributed to deposition of ore particles and preferential sorption of dissolved uranium on sediments nearer to the wastewater outfall. Using  $\text{HCl}$ ,  $\text{Na}_2\text{EDTA}$ ,  $\text{BaCl}_2$ , and  $\text{KCl}$  to leach uranium and  $^{226}\text{Ra}$  from selected bed-sediment size fractions, they concluded that most of uranium and  $^{226}\text{Ra}$  was not retained on the sediment-particle surfaces by cation exchange. Rather, these radionuclides are associated with minerals of uranium ores, with  $\text{Ba}(\text{Ra})\text{SO}_4$  from the wastewater treatment, or are partly trapped inside the colloidal hydroxides of iron and manganese coated on the sediment.

#### Uranium ore processing mill, Canon City, Colorado

Hearne and Litke (1987) studied groundwater flow and quality in the vicinity of a uranium mill near Canon City, Colorado, that began operation in 1958. Uranium ore was not mined in the Canon City area, but was transported to the mill from other regions. Coal mining from 1860 to the mid-1950 in the Upper Cretaceous Vermejo Formation (a predominately fine- to medium-grained sandstone) left features that may have formed preferential pathways for radionuclide migration (Fig. 5). Water obtained by Canon City from the Arkansas River, about 5 km northeast from the mill, was used for process water. Both acid leaching and sodium carbonate leaching were used at the uranium-ore processing mill to extract uranium from ores. Raffi-

**Fig. 5** Generalized geologic section normal to the Chandler syncline showing potential groundwater migration paths from the uranium-ore processing mill to Lincoln Park, Colorado. From Hearne and Litke (1987)



nate, characterized by large concentrations of molybdenum, selenium, and uranium, were discharged into unlined tailings ponds in the Sand Creek basin. After 1979, tailings and raffinate were discharged into a large lined pond. The old unlined ponds were dredged, and the spoil placed in the lined pond. Water in aquifers that underlie Lincoln Park, a suburban community between the mill and the Arkansas River that lies partly within the Sand Creek basin, contains large concentrations of chemical constituents commonly associated with raffinate.

The mill straddles the axis of the Chandler syncline near and upgradient from the Littell coal-mining shaft (Fig. 5). The Upper Cretaceous Pierre Shale, about 1200 m thick, underlies the syncline and is assumed to be an efficient hydrologic barrier. Three subsurface pathways for transport of chemical constituents from the mill area downgradient toward the Arkansas River were hypothesized. These include shallow movement of water through the alluvium, which is interrupted by a ridge formed by the Raton Formation (a medium- to coarse-grained sandstone with thin carbonaceous layers in the upper part) northeast of the US Soil Conservation Service (SCS) dam; movement from the land surface to the coal-mined Vermejo formation, which is the shallow bedrock in the Lincoln Park area, via the Littell shaft; and by surface infiltration to the Vermejo Formation via the Poison Canyon (consisting of interbedded claystone, siltstone, sandstone, and conglomerate) and Raton Formations. Surface-water transport by Sand Creek runoff and airborne transport also might also serve to distribute mill wastes.

Modifications to the hydrologic system include a SCS flood-control dam on Sand Creek at the ridge formed by the outcrop of the Raton Formation. No streamflow in Sand Creek between the mill area and Lincoln Park has been reported from 1970, when the dam was constructed, through 1986. The Littell shaft was filled and plugged in

1978. Leakage from the De Weese Dye irrigation ditch mixes with alluvial groundwater, as does water from applied irrigation percolating into the alluvium.

Water in the shallow aquifer in the Sand Creek basin south of the SCS dam flows from the vicinity of the old tailings ponds in a northeasterly direction toward the SCS dam. Water from wells that lie within this shallow flow route have been affected by raffinate, based on relatively large dissolved concentrations of sulfate (2300–4500 mg/l), molybdenum (9800–27800  $\mu\text{g/l}$ ), selenium (estimates of 81–130  $\mu\text{g/l}$ ), and uranium (5500–5700  $\mu\text{g/l}$ ). Specific conductance values measured in this shallow aquifer ranged from 3910 to 7700  $\mu\text{S/cm}$ . Samples affected by raffinate all have tritium concentrations indicative of post-1952 (post-bomb) water, an expected finding as the source of the water was the Arkansas River. Isotopes of hydrogen and oxygen in raffinate-affected groundwater were heavier than the local meteoric water. This is indicative of evaporation, which likely occurred as raffinate water passed through the tailings ponds.

None of the wells in the Vermejo Formation yielded sample water that contained large concentrations of raffinate components. Low tritium values in all samples indicated that the sample water was of pre-1952 origin, whereas raffinate-affected water principally consists of post-1952 water. The major-ion composition of water does not indicate substantial flow from the Vermejo Formation to the alluvial aquifer in Lincoln Park. Geochemical data indicate that raffinate mixes with water from the Poison Canyon Formation, which then mixes with alluvial water—results that support the presence of a shallow migration route for raffinate-affected water.

Hearne and Litke (1987) concluded that the hypothesized deep migration pathways are probably less important than the shallow migration pathway for migration of raffinate-affected water. In the shallow aquifer system in

Lincoln Park, raffinate-affected water seems to be diluted through mixing with native groundwater. However, the route of raffinate movement from the mill area to Lincoln Park cannot be defined due to the absence of saturation in the shallow alluvium between the SCS dam and the De Weese Dye ditch, and lack of raffinate-affected water found in this area's deep wells.

#### Uranium mines in Monument Valley and Cameron districts, Arizona and Utah

During 1991–1992, Longworth (1994) characterized the chemistry of surface water in pits and groundwater beneath pits and in drill holes left from uranium-mining operations on the Navajo Indian Reservation of northern Arizona and southern Utah. In the Monument Valley District, about  $4 \times 10^6$  kg of  $U_3O_8$  was extracted from 73 pits during 1948–1969 from the Shinarump member of the Triassic Chinle formation. The Cameron District produced about  $0.55 \times 10^6$  kg of  $U_3O_8$  from 98 pits from 1950 to 1963, most of which was mined from 67 deposits in the lower Petrified Forest member of the Chinle formation. In their present state, many of the abandoned mines are potential safety and health hazards and may enhance mobility of radionuclides by erosion, leaching, or increased hydraulic pressure (Don Payne, The Navajo Nation, written communication 1986). The Navajo Nation Abandoned Mine Lands Reclamation Department is considering reclaiming pits by backfilling with mine-spoil material. There is concern that reclamation efforts may result in contamination of water supplies with uranium, radium, and other trace metals if the shallow groundwater associated with many of the mines is hydrologically interconnected to wells and springs used by local inhabitants.

Significant differences in water chemistry were determined between the two mining districts and between sites within each district. In the Monument Valley District, filtered samples of groundwater from two shallow drive-point wells at the Moonlight Mine contained the largest concentrations or activities of a series of constituents found in groundwater or surface water during the study. Activities of  $^{238}U$  were 11,000 and 14,000 pCi/l;  $^{226}Ra$ , 44 and 110 pCi/l; gross-alpha (expressed as natural uranium), 18,000 and 19,000 pCi/l; and  $^{222}Rn$ , 53,000 and 250,000 pCi/l. In contrast, water from a well located 3 km west of the mined area had a  $^{238}U$  activity of 0.50 pCi/l, and activities of  $^{226}Ra$  of 0.16 pCi/l, gross-alpha (expressed as natural uranium) of 3 pCi/l, and  $^{222}Rn$  of 590 pCi/l. The disparity in the constituent concentrations between water associated with shallow pit groundwater and those in well water not directly associated with pits indicate that shallow groundwater associated with the pits was heavily influenced by uranium mineralization.

Analyses of water from four mines in the Cameron District showed marked variations in dissolved constituent concentrations and radionuclide activities. The largest radionuclide activities in the Cameron District were mea-

sured in Jack Daniels Mine pit water and shallow groundwater from a drill hole. Respective activities for  $^{238}U$  were 150 and 180 pCi/l. Gross-alpha activities (expressed as natural uranium) were 480 and 680 pCi/l, and  $^{226}Ra$  activities were 0.10 and 0.52 pCi/l, respectively.

Water from wells and springs in the Cameron District in some instances exceeded State of Arizona water-quality standards. For example, analyses of selected constituents in a water sample from the Arizona Inspection Station well, about 1 km south of the Jack Daniels Mine, had a  $^{238}U$  activity of 20 pCi/l. Gross-alpha activity expressed as natural uranium for the sample was 60 pCi/l, or double Arizona's maximum allowable limit of 30 pCi/l gross-alpha plus gross-beta radiation. Radionuclide activities determined in most well-water samples not directly associated with mine pits may be indicative of background levels of these constituents in this uranium-rich region.

Chemical data from leachate analyses indicate significant radionuclide dissolution from spoil material in laboratory batch tests using natural water. Radionuclide activities in the leachate samples generally correlate with field gamma measurements made when the samples were collected. Uranium activities in the five leachates from Monument Valley District experiments ranged from 20 to 7700 pCi/l and had a median value of 2500 pCi/l, compared to the native water uranium concentration of about 1.4 pCi/l. Radium-226 activities ranged from 1 to 34 pCi/l, and had a median value of 6.5 pCi/l. The range of values is 1–2 orders of magnitude larger than the  $^{226}Ra$  activity of 0.16 pCi/l in the native water used to leach these spoil samples.

The maximum value of uranium activities in eight samples of leachate from the Cameron District experiments, ranging from 38 to 3800 pCi/l, was about half that from the Monument Valley District tests. The median uranium value of 2300 pCi/l for these tests was 8% less than that for those from the Monument Valley District. The maximum uranium value is nearly 2 orders of magnitude larger than the 45 pCi/l of uranium in the native water used in the leaching experiments for spoil samples from the Cameron District. The minimum value indicates that about 16% of the dissolved uranium in native water sorbed to spoil material; however, measurement errors inherent in the tests can probably account for the approximately 7 pCi/l of uranium "lost" in this test. Radium-226 activities, ranging from 0.95 to 21 pCi/l, with a median value of 6.2 pCi/l, is likewise similar to those results from the Monument Valley District.

Size analyses of spoil-material samples indicated large differences in the size distribution of the sediments. For example, gravel and large-size sediments composed the bulk of sediments at the Moonlight, Radium Hill, and Jack Daniels mines, whereas sand is predominant at the Jeepster No. 1 mine. Larger-size material in spoil piles from reclamation may increase water velocities due to larger pore openings and entrain additional oxygen that would tend to increase mobilization of uranium. pH values, ranging from 7.0 to 9.5, and alkalinity values, ranging from 63 to 837 mg/l as calcium carbonate, generally

render uranium soluble and hence more mobile in the sub-surface under oxidizing conditions.

Little Colorado River basin downstream from Grants Mineral Belt, Arizona and New Mexico

Releases from uranium mining and milling operations in the Grants Mineral Belt of New Mexico resulted in increased levels of radioactivity in the Puerco River and parts of its near-channel aquifer, within the Little Colorado River basin of Arizona and New Mexico (Fig. 6). Major uranium deposits in the Westwater Canyon Member of the Jurassic Morrison formation in the Grants Mineral Belt, New Mexico, were mined from shafts averaging 500 m deep that extended below the water table. Water seeping into as many as three mine shafts was pumped in 1960–1961 and 1967–1986 to prevent shaft flooding. Effluent was released to Pipeline Arroyo, a small tributary of

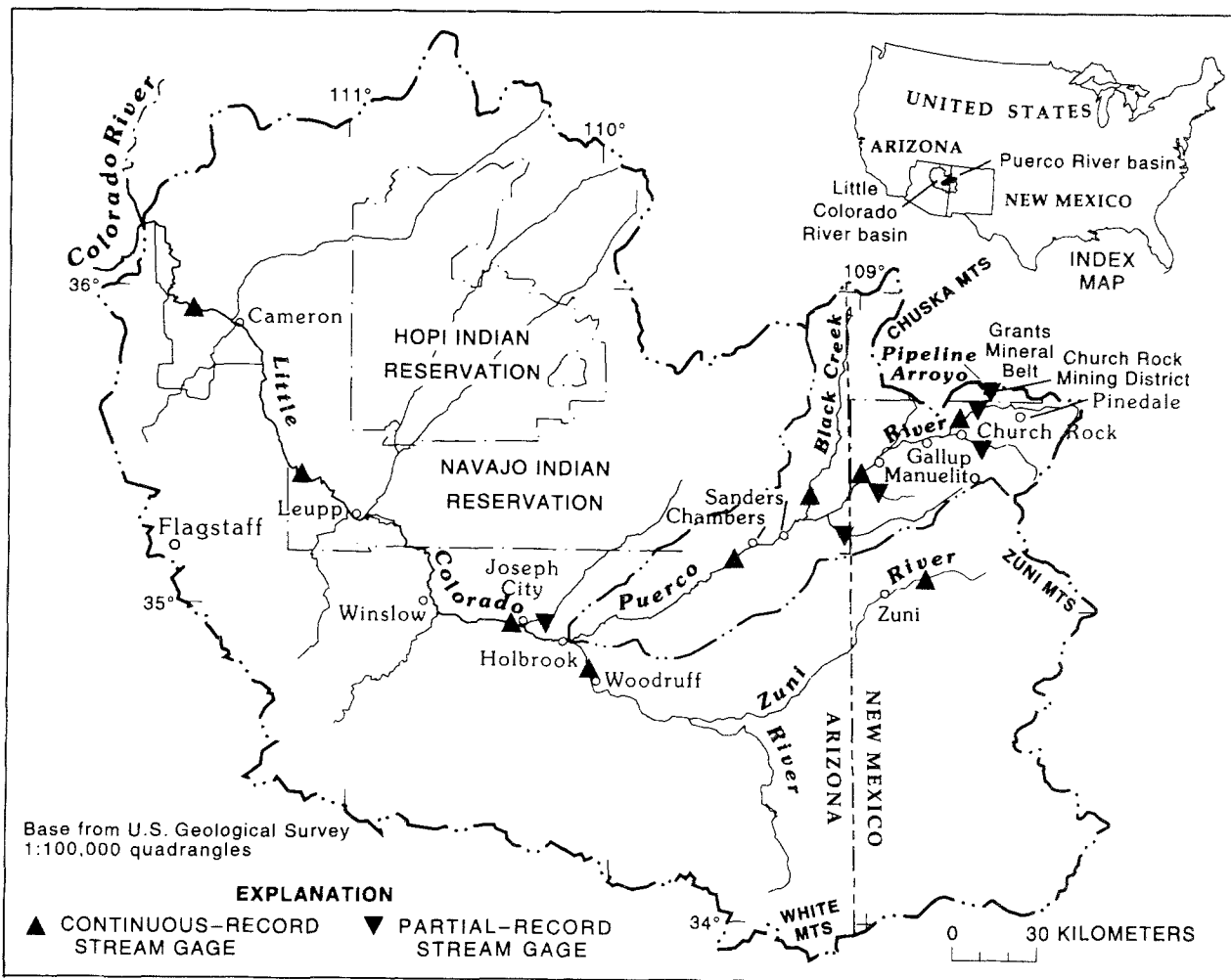
the naturally ephemeral Puerco River. In the absence of runoff, the effluent evaporated or infiltrated the streambed.

Before the mid-1970s, untreated mine effluent was released directly into Pipeline Arroyo. Beginning in the mid-1970s, effluent was treated in ponds using barium chloride to coprecipitate radium and a flocculent to reduce suspended solids concentrations. From 1975 to 1982, a separate ion exchange treatment reduced average dissolved-uranium concentrations by about 85%.

On 16 July 1979, a tailings pond dike failed at the United Nuclear Corporation uranium mill near Pipeline Arroyo, resulting in the largest single release of uranium tailings liquid in US history. An estimated 360,000 m<sup>3</sup> of uranium mine tailings liquid and 1,000,000 kg of tailings were discharged to the Puerco River via Pipeline Arroyo. The pH of the tailings liquid was about 1.6, and the total gross-alpha activity was estimated to be 130,000 pCi/l.

A reconnaissance-level study by the USGS on the water chemistry of the Puerco River alluvial aquifer in 1986 (Webb and others 1987) and a review of historical ground- and surface-water chemistry (Gray and Webb 1991; Wirt and others 1991) indicated that water from five of 14 shallow wells contained gross-alpha (minus uranium and radon) activities equal to or larger than the EPA's MCL for drinking water of 15 pCi/l. Samples of Puerco River

Fig. 6 Map of Little Colorado River and Puerco River Basins, Arizona and New Mexico. From Gray and Fisk (1992).



streamflow collected in Arizona from 1979 to 1985 typically contained total gross-alpha plus gross-beta activities of 1–3 orders of magnitude larger than Arizona's maximum allowable limit of 30 pCi/l of gross-alpha plus gross-beta activity in surface water.

From 1988 to 1991, surface-water chemistry and suspended-sediment concentrations were monitored at 15 sites (Gray and Fisk 1992). Thirty-one monitor wells were installed at six sites in the Puerco River alluvium from near Manuelito, New Mexico, to near Chambers, Arizona.

Van Metre and Gray (1992) estimated that a total of about 560,000 kg of uranium and about 310 Ci of gross-alpha activity were released by shaft dewatering and the tailings pond spill. Of these totals, a cumulative 22 years of mine dewatering accounted for more than 99% of the uranium and 85% of the gross-alpha activity. Radium-226 and  $^{230}\text{Th}$  accounted for most of the activity in the tailings pond spill. Mass balance estimates indicate that most uranium released did not remain in solution, but was sorbed onto sediments.

In 1989, a zone of above-background concentrations of dissolved uranium in Puerco River alluvial groundwater was discernible as far as 70 km downstream from the mines (Wirt 1993). Analyses of groundwater samples collected in 1990–1991 from near the streambed at several sites had smaller concentrations of dissolved uranium than those measured in 1989, suggesting that water quality was improving. Except for selected locations near the streambed, all groundwater samples collected from the alluvial aquifer downstream from Gallup, New Mexico, met the EPA's secondary MCL for uranium, MCL for  $^{226}\text{Ra}$ , and State of Arizona MCL for gross-alpha plus gross-beta radiation.

Wirt (1993) used variations in the ratio of  $^{234}\text{U}$  to  $^{238}\text{U}$  to identify sources of uranium in shallow groundwater beneath the Puerco River. Groundwater in the basin unaffected by mining has  $^{234}\text{U}/^{238}\text{U}$  values ranging from 1.5 to 2.7. Ratios exceeding unity (secular equilibrium) result from alpha recoil of solid-phase  $^{238}\text{U}$  over geologic time causing the  $^{234}\text{U}$  daughter to be placed in favorable leaching sites. As ore bodies were dewatered, increased availability of oxygen caused uranium to dissolve rapidly without preference to  $^{234}\text{U}$  over  $^{238}\text{U}$ . The mean  $^{234}\text{U}/^{238}\text{U}$  ratio of 1.1 calculated for Puerco River alluvial groundwater indicates that the above-background concentrations of uranium measured five years after mining operations ceased were principally attributable to mine-dewatering releases.

Samples of unfiltered runoff from 1988 to 1991 at all streamflow-gaging stations typically had radium and gross-alpha plus gross-beta activities and concentrations of arsenic, beryllium, cadmium, chromium, calcium, lead, and nickel in excess of applicable water-quality standards. Suspended-sediment concentrations, which often exceeded 10% by weight, typically carried more than 99% of these analyzed constituents. The dissolved fraction of runoff monitored at the streamflow gages typically met drinking water-quality standards. Similarities found in the chemistry of suspended sediments at three sites on tributaries

unaffected by mining and those downstream from the uranium mines led to the conclusion that, in the absence of mining releases, constituent concentrations in runoff reflect those for natural conditions in this mineral-rich region.

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