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Patrick A. Longmire and Douglas G. Brookins
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GEOCHEMICAL STUDIES OF DISCHARGE WATER FROM A URANIUM ACID-LEACH PROCESS

P. A. LONGMIRE

New Mexico Environmental Improvement Division
Box 968
Santa Fe, New Mexico 87503

and

D. G. BROOKINS

Department of Geology
University of New Mexico
Albuquerque, New Mexico 87131

INTRODUCTION

Sohio Western Mining L-Bar tailings site occupies approximately 65 ha (160 acres) of Quaternary alluvial deposits resting unconformably on the Cretaceous Mancos Shale in the Laguna-Paguete uranium district, Cibola County, New Mexico. The site is located 4.8 km (3 mi) east of the village of Seboyeta, approximately 64 km (40 mi) northwest of Albuquerque. The Mount Taylor volcanic complex borders the site to the north and west. The mill tailings result from a sulfuric-acid leach processing of uranium ore and have been accumulating since 1976. The tailings are piled to a height of approximately 5 m and are contained to the west by a tailings dam, including a compacted starter dam, and to the northeast by a saddle dam constructed from local soils and clay materials. The tailings are characterized by low pH, high concentrations of soluble salts, a high moisture content, and interstitial fluids of high ionic strength. Chemically, toxic and radioactive elements occur in anomalous concentrations with nonuniform distribution.

The interstitial fluids of the tailings are potential sources of mobile, toxic, and radioactive species, and contain a pH less than one. This fluid has come in contact with the locally unconfined first Tres Hermanos aquifer, a fine- to medium-grained, well-sorted orthoquartzite-subarkose (Moench and Schlee, 1967), which acts as a recharge boundary near the base of the tailings. Ground water in the aquifer is dominantly a sodium, calcium, sulfate-bicarbonate rich, alkaline pH water. Interstitial calcite occurs as a precipitate, constituting up to 3 percent by volume, in response to major element chemistry of the ground water. Contact of highly acidic tailings fluids and the moderately alkaline ground water in the first Tres Hermanos aquifer produces an interface boundary resulting in neutralization and precipitation of various toxic and radiological species.

The objective of this paper is to summarize some results of the investigation of contaminant behavior and mobility within the localized hydrologic environment near the L-Bar tailings pile. The investigation has resulted from an extensive review of Sohio's ground-water discharge plan by NMEID (New Mexico Environmental Improvement Division) staff.

METHODS OF STUDY

The investigation is based upon ground-water samples obtained from monitoring wells installed and maintained by Sohio, from tailings decant liquor, and from solid-tailings samples. Ground-water samples and tailings decant liquor are analyzed for pH, specific conductance, cations (Al, As, Ba, Ca, Cd, K, Mg, Mo, Na, NH₄, Pb, Ra, Se, Si, U, V, and Zn), and anions (Cl, NO₂, NO₃, and SO₄). All analyses were performed according to standard procedures at the State Scientific Laboratory in Albuquerque. Data interpretation is based on numerical analyses, geochemical modeling (including pH, Eh, solubility, and precipitation relationships), and thermodynamic considerations through

the use of Eh, pH, solubility, and activity diagrams. Both theoretical and empirical approaches have been drawn upon to evaluate the chemical interactions between tailings seepage, ground water, and the porous medium, the first Tres Hermanos sandstone.

CHARACTERIZATION OF PRE-EXISTING HYDROGEOLOGIC CONDITIONS

In order to accurately assess the effects uranium tailings may have on local geologic and hydrologic environment, it is important to establish the pre-existing conditions and to determine how the localized environment has responded to such changes. Since 1971, Sohio has collected monitoring data in the vicinity of the tailings pile consisting of ground-water chemistry, soil-moisture measurements, soil temperature, and ground-water measurements (Sohio Hydro-Engineering, 1981).

Recently, ground-water samples from the alluvial and first Tres Hermanos aquifers, tailings decant fluids, and tailings salts have been collected and analyzed for total and dissolved major- and trace-element chemistry. These results are tabulated in Table 1. Even though the reported analyses are recent, the chemistry of monitoring-well 9 (Table 1), located approximately 610 m northwest of the tailings pile, can be considered to still represent ground water in the first Tres Hermanos sandstone unaffected by tailings seepage. Chemically conservative parameters, such as SO₄, NO₃, and Cl, are mobile in ground water because of their nonreactive nature and moderately low background concentrations for this particular aquifer. The water chemistry of monitoring-wells 2A and 3A (Table 1), located approximately 213 m northwest of the tailings pile, contains higher concentrations of these and other parameters, indicating that the seepage from the tailings pile has already affected ground water in the vicinity of these wells. These parameters are appropriate to monitor tailings seepage because H₂SO₄, NaClO₃, and (NH₄)₂SO₄ are used in the ore-extraction process and are concentrated in tailings fluid. Most of the wells are located hydrologically down gradient from the tailings pile and are affected by tailings seepage to a varying degree.

The major cations in the first Tres Hermanos aquifer are Ca²⁺ and Na⁺, and the major anions are SO₄²⁻ and HCO₃⁻ for pre-operational conditions (Table 1). The activity-activity diagram for part of the Al₂O₃-Na₂O-SiO₂-H₂O system at 25°C (Helgeson and others, 1969) shown in Figure 1 indicates that the ground-water composition is regulated by apparent equilibration with Na-montmorillonite and possibly kaolinite, in addition to the carbonate equilibria previously mentioned. Kaolinitization of K-rich feldspars in the first Tres Hermanos sandstone has been described by Moench and Schlee (1967). Ion exchange between ground water, Na-montmorillonite, and kaolinite contributes an additional

Table 1. Comparison of mill tailings decant with ground water in the first Tres Hermanos aquifer. Concentrations are expressed as mg/l. Monitoring wells 1a, 2a, 3a, 3b, 4a, 6, 7, 8, 9, and 10 are located in the tailings reservoir. Monitoring well 17 is located immediately northeast of the tailings reservoir.

Parameter (Total)	Tailings Decant	Parameter (Dissolved)	1A	2A	3A	3B
Mg ²⁺	1275	Mg ²⁺	17.6	739	2884	1708
HCO ₃ ⁻	0	HCO ₃ ⁻	631	1035	440	784
Ca ²⁺	352.0	Ca ²⁺	45.8	578	417.0	390.0
Cl ⁻	370.9	Cl ⁻	277.0	1843.8	1344.7	973.6
K ⁺		K ⁺	6.6	40.2	2.0	2.0
Na ⁺	926.9	Na ⁺	1318	3349	11638	6992
SO ₄ ²⁻	36,865	SO ₄ ²⁻	1913	6237	34770	21007
		SiO ₂	31.9	30.9	28.6	32.3
NO ₃ ⁻ + NO ₂ ⁻	2.22	NO ₃ ⁻ +NO ₂ ⁻	44.39	628.09	5.38	6.88
NH ₃	199.0	NH ₃	0.00	0.20	5.6	3.18
*As	1.11	pH	7.33	6.62	7.82	7.68
Ba ²⁺	0.30	Field	5000	14000	33000	26500
		Conductance (umhos)				
Cd ²⁺	0.02	Temperature (°C)	17.5	21.5	23	21.5
*Pb	2.15	TDS	4048	16115	54255	34480
Mo	0.31	As	0.047	0.800	0.515	0.007
*Se	4.18	Ba ²⁺	<0.100	<0.100	0.150	<0.100
*U	4.23	Cd ²⁺	<0.001	<0.001	0.001	<0.001
V	48.33	Pb	<0.005	<0.005	<0.005	<0.005
Zn ²⁺	5.24	Mo*	<0.010	<0.010	0.014	0.010
Al ³⁺	1110	Se*	0.041	0.580	0.866	0.590
TDS	39,760	U*	<0.010	<0.028	0.047	0.130
pH (SU)	0.98	V*	0.011	<0.010	0.025	0.015
Conductance umhos	71,523					
Gross Alpha (pCi/l)	31000±2000	Zn ²⁺	0.080	0.170	0.050	<0.050
Ra ²²⁶ (pCi/l)	25±8					

* multivalent specie
su standard unit
TDS total dissolved solids
pCi/l picocurie per liter

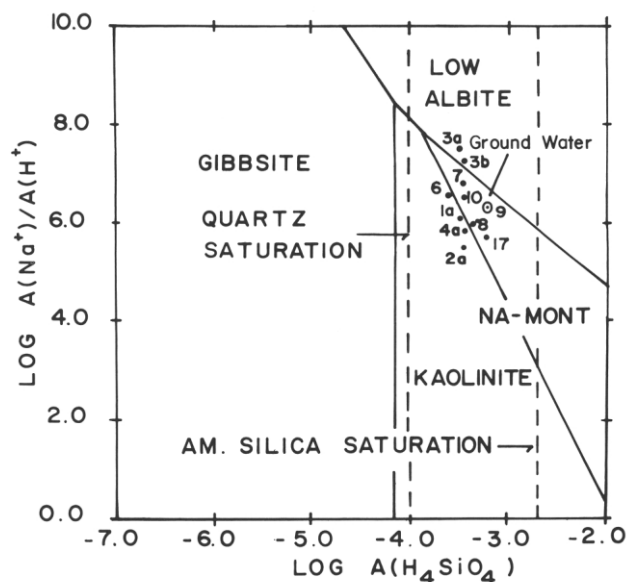


Figure 1. Plot of $\log a_{Na^+}/a_{H^+}$ versus $\log a_{H_4SiO_4}$ and ground-water data (○) from the first Tres Hermanos sandstone and alluvium. Water quality data for wells 1a, 2a, 3a, 3b, 4a, 6, and 7 may not be in equilibrium due to seepage effects. Well 9 probably represents pre-seepage conditions.

mechanism for equilibration of the aqueous phases, including tailings seepage, with these types of clays.

Ground-water flow in the first Tres Hermanos aquifer, prior to construction and use of the tailings pile, was probably to the northwest where recharge occurs along outcrop areas. The aquifer is moderately fractured where exposed and is characterized by prominent north-trending vertical joints. Secondary bedding joints are also common in recharge areas. These structural features may serve as conduits through which tailings seepage may flow. The tailings pile has had a considerable effect on the local ground-water flow patterns for the first Tres Hermanos sandstone due to recharge effects. Because of indirect recharge by vertical infiltration through the alluvium, recharge from the tailings pile to the aquifer allows flow directions to emanate away from the tailings pile toward the west, north, and northeast. Further down gradient, regional flow to the north-northwest should be dominant, given uniform hydrologic conditions.

DISCUSSION

Sohio Hydro-Engineering (1981) has shown the chemical characteristics of ground water in the vicinity of the tailings pile by use of an extensive monitoring system. The chemical quality of the tailings in the pile is significantly different than the seepage that is detected in the down-gradient monitoring wells (Table 1). These changes in water chemistry are reflective of the natural processes which may operate in the subsurface including: (1) dilution, (2) buffering of pH, (3) chemical precipitation by reaction with components of the solid porous medium, (4) hydrolysis and precipitation of insoluble hydroxides, (5) precipitation resulting from oxidation and reduction, (6) radioactive decay, and (7) sorption. Other factors leading to the alternation of contaminants in the subsurface, such as volatilization resulting in loss as a gas and biological degradation or assimilation, may not be operative under the present set of circumstances. Redox potential and pH are considered the two most important variables.

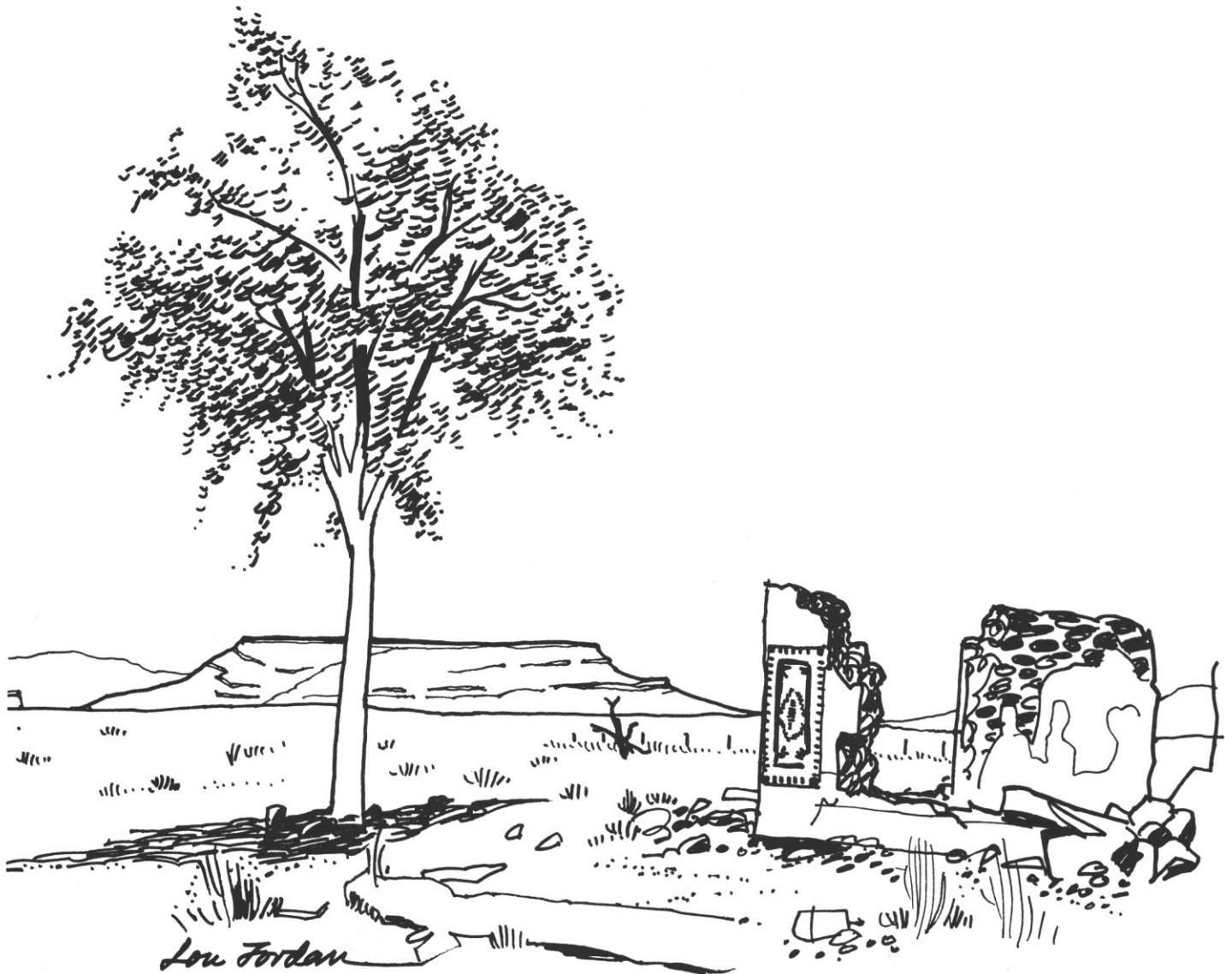
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The dissociation of H_2SO_4 and dissolution of the various salts and metal hydroxides maintain a low pH in the tailings fluid (Table 1). Measured pH values ranged between 0.96 to 1.35. Dissolution of iron hydroxide, $Fe(OH)_3$, results from the very acidic solution, and Fe^{3+} is reduced to Fe^{2+} as the tailings solution encounters ground water. Representative, "in situ," Eh measurements have yet to be determined. The chemistry of the tailings fluid is probably controlled by sulfate-salt reactions and redox reactions of iron.

Buffering of pH is a critical factor in controlling the mobility of tailings seepage at the L-Bar facility. Further, buffering of pH is one of the main mechanisms for attenuation of both major and minor elements such as Mg, Ca, Na, K, Al, U, Cd, and others. The pH of ground-water samples taken from the first Tres Hermanos and alluvial aquifers range from 6.62 to 7.95, indicating that the acidic-tailings pH front has not yet significantly affected ground water. The natural buffering capacity, as a function of the various types of silicate and carbonate minerals present in the first Tres Hermanos sandstone and alluvium, greatly enhances stability of the various chemical species associated with seepage.

Thermodynamic calculations were used to evaluate the mobility of aqueous species as a function of pH, redox potential, and concentration. The mobility of various species including Fe, Mn, Mo, Se, As, U, Pb, Th, and V can be further understood by a critical evaluation of the literature (Longmire and others, 1981; Markos, 1981). In a low-pH environment, U, Th, Cr, Cu, Fe, and Mn exist as charged aqueous species and tend to be mobile; whereas, other species such as Mo, Se, and Pb are immobile (Longmire and others, 1981). Aluminosilicates such as kaolinite and montmorillonite are unstable in acid-tailings environment (Markos, 1981), thus contributing cations as well as active solid surfaces for sorption and reaction sites.

Calcite is a common mineral in the alluvium and first Tres Hermanos sandstone. Gypsum ($CaSO_4 \cdot 2H_2O$) has been observed in soils exposed in the vicinity of the L-Bar facility, typically constituting 2-3 volume percent. The solubility of calcite increases in acidic solutions under low temperatures. Consequently, if seepage from acidic uranium tailings occurs into subtailings soil, calcite should undergo dissolution. Since the tailings are enriched in SO_4^{2-} , the calcite dissolves, and the Ca^{2+} reprecipitates as gypsum. This phenomena is represented by the following equation:



Calcite is expected to coexist with gypsum below the base of the tailings, in light of the above considerations. In order for gypsum to precipitate, H_2SO_4 must be present as seepage in the subsoil. The soil, at present, is well-buffered and has neutralized the acidic-tailings seepage, as is suggested by the near-neutral pH values observed from ground-water monitoring data. The long-term effect of tailings seepage on the first Tres Hermanos sandstone and alluvium, in terms of buffering capacity, are not completely understood and require further attention.

Predicting the potential magnitude of ground-water contamination associated with uranium tailings is a complex technological undertaking. The simultaneous presence of numerous interactive physical, chemical, and biological mechanisms makes it difficult to obtain an accurate description of the hydrogeological setting prior to contamination by uranium tailings. Consequently, numerous investigators have resorted to the use of predictive, geochemical, and hydrological modeling for evaluating the performance of a certain waste-disposal site. Such analysis may be considered to be a simplified representation of a real system, and proper care must be used during such an analysis in order to consider what conservative but reasonable parameters representing the real system.

Thermodynamic calculations depicting supersaturation of various minerals in contact with tailings solution and ground water were performed with the PHREEQE computer program (Parkhurst and others, 1980). PHREEQE is a Fortran IV computer program designed to model geochemical reactions including such variables as pH, redox potential,

and mass transfer as a reaction progresses. Since quartz and kaolinite are present in the first Tres Hermanos sandstone (Moench and Schlee, 1967), this computer program was utilized for a case study where tailings fluid (Table 1) was equilibrated with both minerals under ground-water conditions at the site. Supersaturation of gypsum and barite results, leading to the precipitation of these two minerals under conditions described above. Quartz occurs in equilibrium with the tailings solution. Gypsum, barite, chalcedony, and quartz are predicted to precipitate due to supersaturation in the tailings pile. Precipitation of gypsum, barite, chalcedony, and quartz will result when the tailings solution comes in contact with kaolinite. Gibbsite remains undersaturated and dissolves; it should occur in the subsurface under existing conditions. In all cases an increase in pH results, contributing to partial neutralization of tailings seepage.

Mixing three parts tailings fluid to one part ground water, a composition identical to chemical composition of monitored-well number 9 (representing background conditions), results in the precipitation of gypsum, barite, chalcedony, quartz, gibbsite, and kaolinite. Additionally, ground water alone is supersaturated in these minerals so they are expected to precipitate under pre-seepage conditions. Neutralization of seepage accompanies such chemical reactions. Verification of modeling will be carried out by coring of subsoils and subsequent laboratory analyses.

CONCLUSIONS

The results of this preliminary study support the following conclusions:

1. There is very limited movement of radionuclides and metal hydroxide species from the tailings pile affecting ground water in the first Tres Hermanos sandstone and alluvium, due to buffering of pH and favorable redox conditions.
2. Chemically conservative-nonreactive species including Cl^- , NO_3^- , and SO_4^{2-} are very mobile in ground water and exhibit breakthrough of seepage from the tailings pile.
3. Local ground water and seepage emanates from the tailings pile to the west, north, and northeast with a range of hydrologic conductivity of 0.03 to 0.15 m/day (0.1 to 0.5 ft/day) (Sohio Hydro-Engineering, 1981). Acidic-seepage front is migrating at a much slower rate due to the extensive buffering capacity operating in the subsurface. Interstitial calcite, kaolinite, and Na-montmorillonite constitute the buffering system.
4. The rate of seepage from the tailings pile is estimated to range from 19 to 53 liters/day (5 to 14 gpd) according to a water-balance study conducted by Sohio. Sohio has developed an extensive monitoring program and has committed to expand its pumpback and monitoring systems in order to capture seepage emanating from the tailings impoundment.

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