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Interaction of Uranium Mill Tailings Leachate with Soils and Clay Liners

Laboratory Analysis / Progress Report

Prepared by G.W. Gee, A.C. Campbell, D.R. Sherwood,
R.G. Strickert, S.J. Phillips

Battelle-Pacific Northwest Laboratory

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SUMMARY

Laboratory tests were conducted to evaluate leachate from uranium mill tailings and its interaction with materials taken from the Morton Ranch Uranium Mill site in central Wyoming. Laboratory tests included:

1. Physical and chemical characterization of geologic materials from the Morton Ranch. The materials characterized were typical of those found in the area of the proposed tailings pits.
2. Physical and chemical characterization of acid leach tailings and tailings solution from the nearby Exxon Highland Mill.
3. Leaching tests with selected tailings materials and leach solutions.
4. Adsorption studies measuring the sorption characteristics of heavy metals and radionuclides on the Morton Ranch geologic materials under low and neutral pH conditions.
5. Clay liner stability tests. These tests were designed to evaluate the mechanisms of clay liner alteration under acid attack and to assess any long term changes in permeability of the clay liner materials.

Constitutents of the tested tailings solution that are possible contaminants to ground water include arsenic, cadmium, chromium, copper, iron, manganese, selenium, zinc, sulfate, and several of the uranium daughter products including Ra-226, Th-230, Pb-210, and Po-210.

Leaching studies indicated that excessive leaching was required before the tailings pH rose significantly. Leaching with alkaline ground water (pH 8) required 30, 42 and 50 pore volumes to increase the effluent pH above 4 for sands, tailings, and slimes, respectively. The results indicate that these materials will remain a potential source of soluble contaminants for long periods of time.

When tailings solution was neutralized either by addition of NaOH or by contact with the Morton Ranch clay liner or overburden material, significant decreases in potential contamination were obtained for all nonradioactive elements. Upon neutralization, most of the potential contaminants listed above dropped to or below the maximum permissible concentration (MPC). All soluble

radioactive constituents dropped significantly below MPC values. Upon contact of the tailings solution with the geologic materials tested, the radionuclides showed moderate to strong sorption even at low pH.

Tests on clay liner material from the Morton Ranch indicated the following:

1. Environmental Protection Agency liner criteria are met by the Morton Ranch clay liner - indicating that the test material should be a suitable barrier to contaminant migration.
2. The clay is not dispersive, hence piping-type erosion will not occur.
3. Mineralogy of the clay material changes only slightly even after extended contact with the tailings solution. For the pH and dissolved solids concentration of the tailings solution, acid dissolution of crystalline clay minerals appears to be countered by precipitation reactions and secondary mineral formation.
4. Permeability of clay liner material always decreased with time. The decreases in permeability were most likely due to pore plugging by secondary clay minerals and precipitates.
5. Packing of the clay liner affected permeability more than any other single factor. Packing of clay to optimum density should assure that minimum permeability is obtained in clay-lined pits or ponds.

ACKNOWLEDGMENTS

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CONTENTS

FIGURES

TABLES

INTRODUCTION

Pit disposal of uranium mill tailings has been proposed for the Morton Ranch uranium mill in central Wyoming (USNRC 1979a). The placement of tailings near the ground water has raised concerns about potential contamination of ground water by leachate from the acid tailings. This study evaluates leachate-soil interactions that will take place at the Morton Ranch for certain disposal alternatives. Laboratory tests were conducted to evaluate the following:

1) physical and chemical characteristics of geologic materials from the Morton Ranch,
2) physical and chemical characteristics of acid leach tailings and tailings solution,
3) leaching tests with selected tailings materials and leach solutions to evaluate the leachability of contaminants with time under specific disposal alternatives,
4) adsorption studies measuring the sorption characteristics of heavy metals and radionuclides on the geologic materials at Morton Ranch,
5) clay liner stability tests to evaluate effects of acid leachate on clay mineralogy and clay permeability.

1.0 CHARACTERIZATION OF MATERIALS

CHARACTERIZATION OF MORTON RANCH GEOLOGIC MATERIAL

The Morton Ranch Uranium Mine and Mill Site is located in central Wyoming in Converse County (Figure 1.1). The geology of the area is discussed in detail in the UNC Environmental Report (UNC 1976). Briefly, the site lies in the southernmost part of the Powder River Basin. This basin is a large structural depression bounded on all sides by areas of uplift (See Figure 1.2). The area to the east rises to the Black Hills and the area to the west rises into the eastern slopes of the Big Horn and Wind River ranges of the Rocky Mountains. Since pre-Cambrian times, the history of the Powder River Basin has consisted largely of periods of subsidence and sedimentation. Accumulation of sedimentary rocks has occurred to depths of 4570 m (15,000 ft). The underlying sediments of the basin are primarily carbonates, sands and shales deposited in a marine environment. The uppermost sediments are fresh water fluvial (river transported) deposits of the Fort Union and Wasatch Formations. The Wasatch Formation is the uppermost bedrock unit exposed throughout the mill site area. In this area, all but the bottom +100 m (+330 ft) has been stripped away by stream erosion. The Wasatch Formation is comprised of fluvial sediments of interbedded silty claystones and sandy siltstones that contain thick lenses of coarse, arkosic (granular) sandstone. A few thin limestone and coal seams (less than 1 m thick) occur locally within the formation. The Fort Union Formation underlies the Wasatch formation and typically consists of poorly consolidated continental deposits about 100 m thick. At the mill site area, the formation consists of fluvial, interbedded silty claystones, sandy siltstones, relatively clean sandstones and granular sands. The sandstones of the upper Fort Union Formation are the host rocks for the uranium deposits.

It is the Wasatch Formation materials and surface alluvium that will be mined and mixed to comprise the overburden and the clay liner materials used in the pit and pond disposal sites at the Morton Ranch Mill. The clay liner material will be selected primarily for its silt and clay content. The

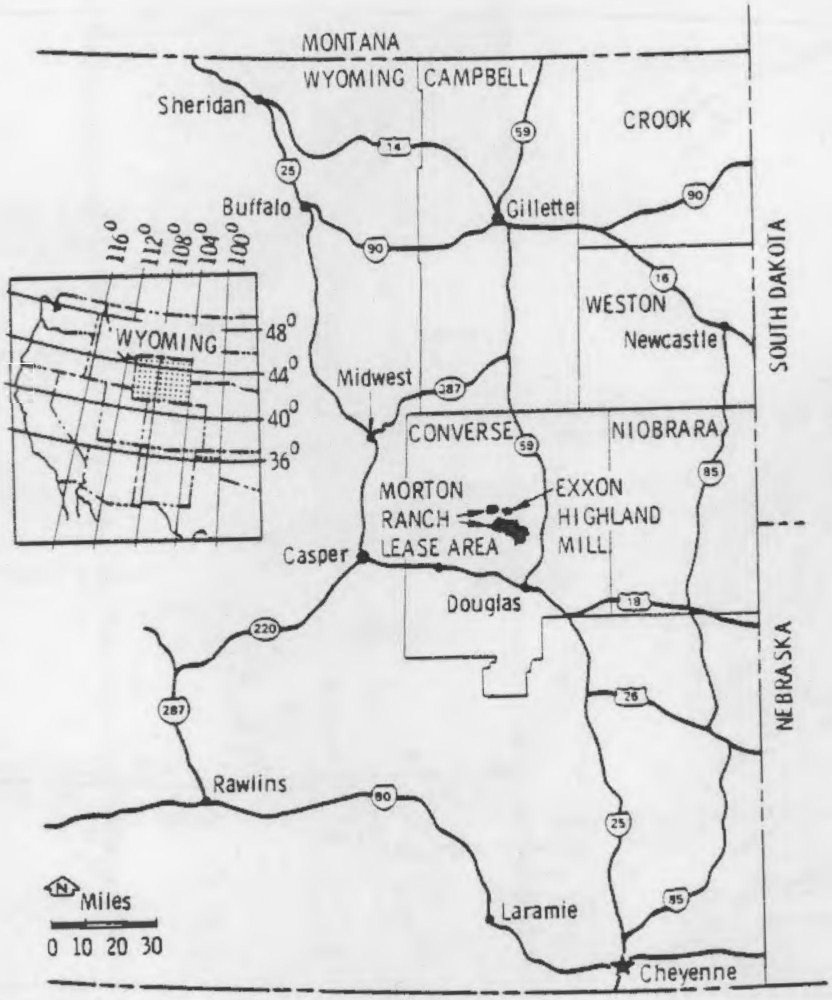
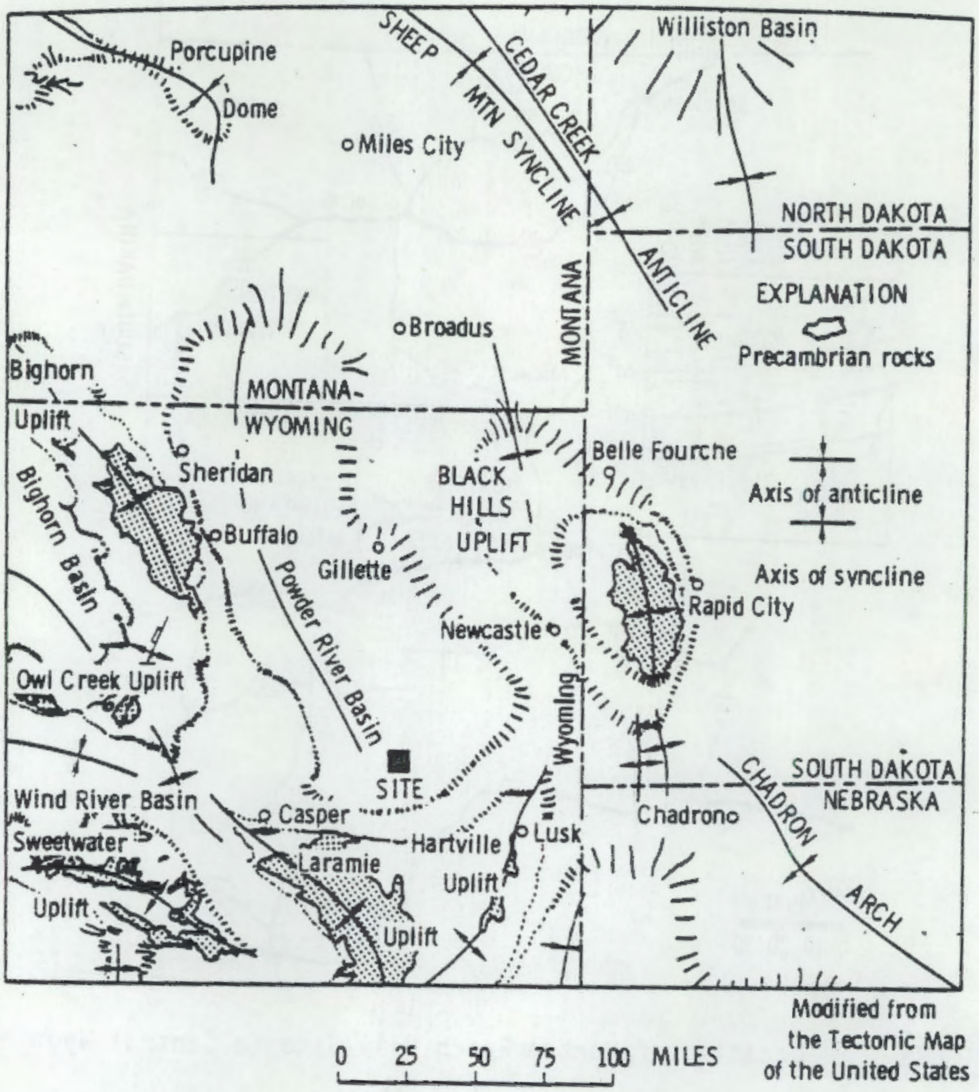


FIGURE 1.1 Location of Morton Ranch Mill Site in Central Wyoming

claystones and siltstones of the Wasatch Formation are the likely choices for the liner material. The overburden used as backfill material at the pits and for fill at the evaporation pond will be a mixture of clay, silts and sands from both the Wasatch Formation and the overlying alluvium. The exact mixture will be site specific and will depend on the proportions of sandstones, shales and claystones present in a particular excavation and the resulting mix of these materials in the excavation and stockpiling process. There is no way at present to determine, a priori, what the mixture, even at a particular pit, will be since mixing and stockpiling procedures tend to produce a random mix of materials.



Modified from the Tectonic Map of the United States

FIGURE 1.2. Generalized Map of the Powder River Basin in Relation to Structural Features (after USNRC 1979a)

In attempting to analyze the physical, chemical and hydrologic character of materials at the Morton Ranch site and proposed disposal area, we had to use personal judgment to select materials that are typical or characteristic of the site. Cross-section data with attendent geologic strata identified were supplied by United Nuclear Corporation personnel. In addition, representative samples of clay liner, overburden, and sandstone materials were taken from the

1704 pit area at the Morton Ranch. In consultation with Morton Ranch personnel, it was felt that these materials reflected the typical characterisics of the geologic materials that would be found at the tailings disposal sites. The mill tailings material was obtained from the Exxon Highland Mill. It was shipped to Battelle Pacific Northwest Laboratory as a 1:2 slurry of tailings and tailings solution.

Morton Ranch clay liner material, overburden, and sandstone were characterized using standard procedures (Black 1965). All the materials were taken from exposed side walls of the partially-mined 1704 pit at the Morton Ranch site. The clay liner material analyzed was a composite of sandstone, siltstone, mudstone, and shale. Results of physical and chemical analysis are given in Table 1.1. Figure 1.3 shows the particle size analysis for the geologic materials tested.

TABLE 1.1. Characterization of Morton Ranch Clay Liner, Overburden, and Sandstone

Parameter	Clay Liner	Overburden	Sandstone
pH of Saturation Paste (Distilled Water)	8.2	8.3	7.5
Particle Density (g/cm^3)	2.72	2.68	2.67
$CaCO_3$ Equivalent (%)	0.04	0.02	0.009
Organic Matter Content (%)	1.44	0.18	ND
Cation Exchange Capacity (meg/100g)	31.6	10.3	9.47
EC of Saturation Paste (mmhos/cm)	0.70	0.34	ND
SAR (meq/l)	0.58	0.76	ND
Particle Size Distribution			
Sand (50 - 2000 μm)	12.0	75.5	86.3
Silt (2 - 50 μm)	54.0	15.0	7.2
Clay (<2 μm)	34.0	9.5	6.5
Surface Area (m^2/g)	230	78	11

ND = Not determined

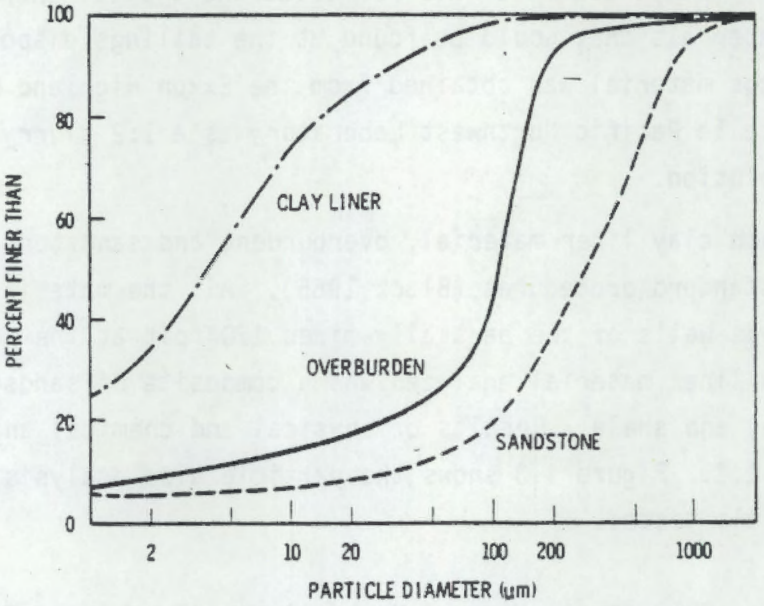


FIGURE 1.3. Particle Size Summation Percentage Curve for Morton Ranch Test Materials

CHARACTERIZATION OF TAILINGS AND TAILINGS SOLUTION

A tailings slurry sample from Exxon's Highland Mill was analyzed for its physical, chemical, and radiological properties. The acid leach processing of ore at the Highland Mill is similar to that proposed for Morton Ranch, so the tailings should be characteristic of the type that will be produced at the Morton Ranch Mill. A sample of Exxon's mill process water was also analyzed.

The slurry was separated into its tailings and solution portions for analysis. A portion of the slurry was further divided into its sand (>74 μm to 2000 μm) and slime (<74 μm) fractions. Physical and chemical properties of the tailings are listed in Table 1.2. The separated tailings had a pH of 2.3, and is classified as a sandy loam based on particle-size distribution. The dispersant, sodium-hexametaphosphate, was used to resuspend fines that acted as sands in the particle-size distribution tests. Flocculant, added in the mill process, apparently increased the ratio of sand to slime in the tests in which dispersant was not used (Table 1.2).

TABLE 1.2. Characterization of Highland Mill (Acid Leach) Tailings

Parameter	Value
Water Content (g/g)	
Mill Tailings Slurry	1.994
Saturation Paste (distilled water)	
Tailings	0.410
Sands (>74 μm)	0.321
Slimes (<74 μm)	0.928
pH of Saturation Paste (distilled water)	
Tailings	2.55
Sands (>74 μm)	2.69
Slimes (<74 μm)	2.38
Particle Size Distribution (wt%)	
Sands (50-2000 μm)	67.5 ± 2.9
Silt (2-50 μm)	17.6 ± 1.7
Clay (<2 μm)	15.0 ± 1.8
Sands (>74 μm)(a)	66.4 ± 2.6
Slime	33.6 ± 2.6
Sands (>74 μm)(b)	75.3 ± 4.8
Slime	24.7 ± 4.8
Particle Density (g/cm^3)	
Tailings	2.912 ± 0.033
Sands (>74 μm)	2.812 ± 0.078
Slimes	2.998 ± 0.049
Mineralogy of Clay Fraction	Quartz with moderate amounts of smectites
$CaCO_3$ (wt%)	0
Organic Matter Content (wt%)	0.27
Cation Exchange Capacity (meq/100 g)	12.8 ± 0.8

(a) With dispersant
(b) Without dispersant

Characterization of the tailings solution and mill process water is shown in Table 1.3. Use of inductively-coupled argon plasma spectroscopy (ICP) and ion chromatography provided multi-elemental analysis (see also Appendix A). The values reported are similar or lower than those reported for typical mills as given in Table E-3.1 of NRC's Draft Generic Environmental Impact Statement (GEIS) (USNRC 1979b). Maximum permissible concentrations (MPC), established by the U.S. Public Health Service, and modified by the U.S. Environmental Protection Agency are also listed in Table 1.4 for comparison.

The reported arsenic (As) value appears high. The results for some elements in ICP analysis suffer from matrix interferences, which is apparently the case for As (see Appendix B).

The three uranium minerals identified at Morton Ranch are coffinite, zippeite, and liebigite. These occur primarily as coatings on the individual grains of the host rock sandstone. The chemical makeup of the minerals, given by Kimberly (1978) is as follows:

Coffinite	$U(SiO_4)_{1-x}(OH)_{4x}$
Zippeite	$(UO_2)_2(SO_4)(OH)_2 \quad 2H_2O$
Liebigite	$Ca_2U(CO_3)_4 \quad 10\ H_2O$ -or- $Ca_2UO_2(CO_3)_3 \quad 10\ H_2O$

High concentrations of heavy metals are not found in association with these uranium minerals. Electron microprobe results reported in Kimberly (1978) show that Si is the only element besides hydrogen and oxygen that accompanies the uranium in coffinite. Only S is present in zippeite; and only Ca is present in liebigite. Selenium and arsenic, therefore, should be at concentrations lower than are found in most other uranium ore types.

Based on the radiological information given in Table 1.4, ^{238}U is the only isotope in the tailings solution with a concentration less than NRC's maximum permissible concentration for soluble radioactive materials that can

TABLE 1.3. Characterization of Tailings Solution and Mill Process Water, mg/l Unless Otherwise Noted

Parameter	Highland Mill Tailings Solution	Highland Mill Process Water	USPHS-USEPA Maximum Permissible Concentration
By inductively-coupled argon plasma spectroscopy:			
Al	577	<0.1	(No limit)
As	3.5	<0.01	0.05
Ca	484	53.0	200
Cd	<0.1	<0.01	0.01
Cr	2.7	<0.05	0.05
Cu	2.3	<0.01	1
Fe	2,215	<0.1	0.3
Li	<0.9	<0.05	(No limit)
Mg	649	11.0	(No limit)
Mn	63.5	0.01	0.05
Mo	<5.0	0.5	1.0
Na	330	91	200
Ni	2.6	<0.01	0.2
P	30	<0.1	(No limit)
Pb	<1.0	<0.1	0.05
Se	<1.0 (0.6)(a)	<0.1	0.01
Si	233.5	3.5	(No limit)
Sr	11	0.9	(No limit)
Th	<1	<0.1	See Table 1.4
U	100 (39.7)(b)	0.5	See Table 1.4
Zn	7.8	0.05	5
By Ion Chromatography:			
Cl	97.1	35.5	250
NO_3	16.5	3.6	10
SO_4	12,850	181.4	250
EC (mmhos/cm)	18.2	0.82	
Hardness (as mg $CaCO_3$/1)	10,231	73.5	
pH (Units)	1.8	8.2	6-9

(a) Gaseous hydride method
(b) Radiochemical analysis

TABLE 1.4. Radionuclide Concentrations in the Highland Mill Tailings and Tailings Solution

Radionuclide	Tailings[a] (pCi/g)	Tailings Solution[b] (pCi/l)	Maximum Permissible Concentration[e] Unrestricted Area[c] (pCi/l)	Maximum Permissible Concentration[e] Restricted Area[d] (pCi/l)
^{238}U	8.6	13,216	40,000	1,000,000
^{226}Ra	368.5	2,252	30	400
^{230}Th	39.6	227,286	2,000	50,000
^{210}Pb	275.7	9,701	100	4,000
^{210}Po	Not Determined	28,222	700	20,000

(a) Value corrected to exclude the contribution due to salt.
(b) Value based on 22.7 g salt/l of solution.
(c) Unrestricted area is defined as any area to which access is not controlled by the licensee for purposes of protection of individuals from exposure to radiation and radioactive materials, and any area used for residential quarters.
(d) Restricted area is defined as any area to which access is controlled by the licensee for purposes of protection of individuals from exposure to radiation and radioactive materials.
(e) Code of Federal Regulations. Title 10, Part 20, Appendix B.

be released in effluents. ^{226}Ra, ^{230}Th, ^{210}Pb, and ^{210}Po concentrations in the tailings solution are greater than those allowed by NRC. Sulfate salts of radium and lead are insoluble in dilute sulfuric acid, whereas uranium and thorium sulfate salts are moderately soluble. The concentration of polonium in the tailings, although not determined, is expected to equal that of ^{210}Pb.

2.0 LEACHING STUDIES

Leaching studies were designed to simulate the following alternatives for tailings disposal:

1) leaching of dewatered tailings placed below the ground-water table with ground water
2) leaching of slimes with ground water
3) leaching of sands with ground water
4) leaching of tailings slurry with diluted tailings solutions
5) leaching of ore grade material with ground water.

Mill process water as received from Exxon was used as the ground water. The diluted tailings solution was a 1:4 ratio of filtered tailings solution and distilled water. Samples were leached in a once-through flow system using a mechanical vacuum extractor (Concept Engineering, Inc., Lincoln, Nebraska) at an average rate of 39.8 cm/day with an average residence time of 1.6 hrs per pore volume of effluent. The experimental parameters are listed in Table 2.1. Effluent pH was monitored and is plotted with its respective pore volume in Figure 2.1. A leach cycle was completed after every 55 ml of solution added.

Effluent pH values were initially similar for segregated (slime versus sand) and nonsegregated tailings. Continued leaching by ground water (Highland Mill process water) resulted in slowly increasing pH values for the tailings, slimes, and sands, with pH values increasing most rapidly for the sand samples. There was very little change in effluent pH for the tailings slurry leached with diluted tailings solution. Soils with higher proportions of organic matter and clay tend to resist changes in pH because of greater surface areas and higher cation exchange capacities, which can sequester the hydrogen ion. The effluent pH values reflect these differences in buffering capacity of various components of the tailings. Data from the leaching studies indicate that the equivalent of 42.5 pore volumes of ground water at pH 8.1, would be required to neutralize the tailings to a pH of 4.

TABLE 2.1. Experimental Parameters for Leaching Studies

Parameter	Tailings	Slimes	Sands	Ore	Tailings Slurry
Leaching Solution	-----Mill Process Water-------				Dilute Tailings Solution
Influent pH	-------------8.10-------------				2.50
Average Pore Volume of Samples, ml	15.82	16.30	14.80	11.33	15.23
Leaching Rate, cm/day	------------------39.80------------------				
Particle Density, g/cm^3	2.91	3.00	2.81	2.68	2.91
Average Bulk Density, g/cm^3	1.52	1.23	1.54	1.40	1.38

Analysis of the leachate effluents indicates some removal and/or adsorption of ions from the soil/solution system. The ICP results are given in Table 2.2. Effluent concentrations greater than those of the leaching solution reflect leaching of the ions from the tailings material. Generally, the effluent from the first leach cycle contained higher concentrations of cations and anions than the effluent from later cycles. In the cases in which the ion concentration increased after leaching, exchange or desorption from the media occurred (e.g., calcium and chloride from the slimes, and silica from the sand). Magnesium concentrations were reduced below influent levels due to exchange or precipitation.

The leaching tests suggest that acidified tailings that are subjected to prolonged leaching will continue to remain acidic for long periods of time. Reduction of contaminant concentrations will be obtained by dilution, but potential for contaminant transport remains high as long as the tailings remain acidic. Direct contact of tailings with ground water would not be desirable. Leaching of tailings by percolation of surface water would need to be minimized to assure that acid leachate would not eventually reach ground water.

TABLE 2.2. Chemical Analysis of Leachate Solutions

Parameter	Dewatered Tailings		Slimes		Sands		Ore		Mill Process Water	Tailings Slurry		Diluted Tailings Solution
Pore Volume	2.59	20.1	2.5	19.5	2.8	21.6	0-13	13-28		3.8	21	
Leach Cycle	1	6	1	6	1	6	1-3	4-6		1	6	
pH	2.3	3.6	2.4	3.4	2.4	3.7	7.7	8.0	8.1	2.3	2.5	2.5
	mg/l											
Al	299	4	1050	15	316	<1	<1	<1	<0.1	319	154	157
As	6	0.5	20	<0.1	5.9	<0.1	<0.1	<0.1	<0.01	5.6	3.1	2.2
Ca	581	435	559	665	435	14	76	50	53	529	336	123
Cd	0.4	<0.1	0.8	<0.1	0.3	<0.1	<0.01	<0.1	<0.01	0.3	0.2	0.2
Cr	1.7	<0.1	34.2	0.2	2.1	<0.1	0.13	<0.1	<0.05	1.6	0.9	0.7
Cu	1.0	<0.1	2.7	0.1	0.9	0.2	<0.01	<0.1	<0.1	1.2	0.7	0.6
Fe	636	3	1490	13	802	<1	<0.1	<0.1	<0.1	668	499	402
Mg	364	<0.5	1250	1.2	340	0.8	22.5	15	11	431	188	190
Mn	31	<0.1	112	<0.1	31	<0.1	0.03	0.04	<0.01	37.4	18.1	15.2
Na	188	95	444	97	209	101	86	95	91	172	94	75
Ni	1.5	<0.1	24.3	<0.1	1.3	<0.1	<0.01	0.1	<0.01	2.2	0.7	0.6
Se	<1	<1	<1	<1	<1	<1	<2.0	<1	<0.1	<1	<1	<0.5
Si	28.4	22	55	29	16	20	4.5	4.2	3.5	81	66	58.4
Sr	4.4	1.6	5.2	2.7	4.5	<0.1	1.1	0.6	0.9	4.9	3	2.6
Th	1.5	<1	7	<1	1.8	<1	2.2	<1	<0.1	2.7	1.4	1.7
Zn	6.4	0.9	17.1	0.7	5.3	1.0	0.2	0.4	<0.05	6.7	2.8	1.8
SO_4	6667	1171	16,000	1858	6154	200	240	179	181	7083	4177	3889
Cl	126	31	21	32	125	32	29	27	36	300	76.5	75

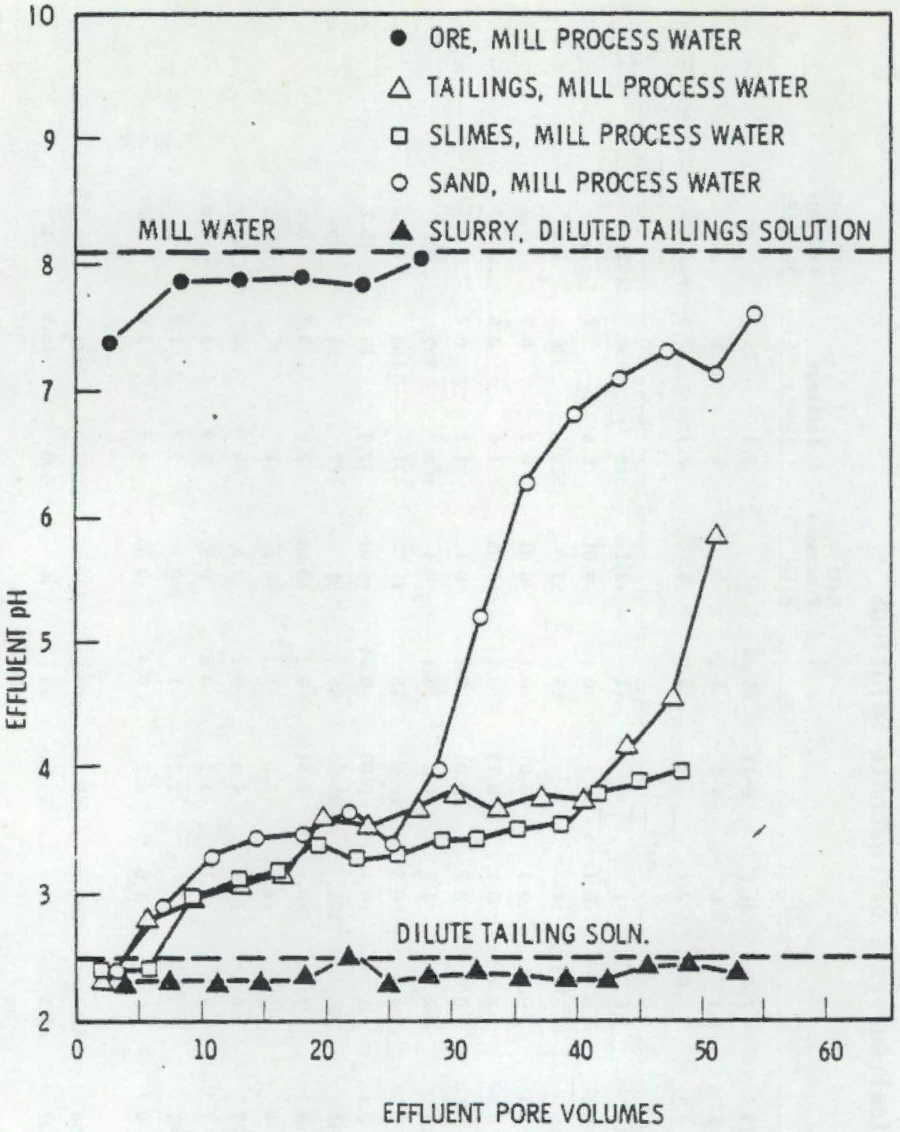


FIGURE 2.1. Changes in Effluent pH Due to Leaching

3.0 ATTENUATION STUDIES

ATTENUATION OF CONTAMINANTS

Attenuation studies were designed to determine the ability of the Morton Ranch sediment samples to retard the movement of hazardous materials into the surrounding soil and water systems from disposed tailings. Movement is retarded by adsorption on the soil media, or by precipitation within the system. An element's affinity for movement through media can be estimated by measurement of its distribution coefficient (Kd). Kd is defined as the ratio of the amount of solute (heavy metal or radionuclide, etc.) sorbed on the solid surfaces of the test material to the amount of solute remaining in solution. Low Kd values indicate movement while high Kds reflect retardation. For transport calculations, Kd values equated to zero indicate transport at the same rate as water.

Various factors affect Kd values. Mineralogy and surface area of the solid sample are very influential. Parts of the solid may be highly selective in sorbing specific constituents and result in abnormally high Kd values. The presence of calcite or dolomite affects solution pH and composition, which influence Kd values. Surface area is a function of the solid's mineralogy, particle size distribution, and method of crushing. As surface area of a solid increases, Kd values oftentimes also increase. The composition of the contacting solution is also important. Sorption of multivalent elements is dependent on the oxidation state of the consituent, which is affected by solution-solid pH-Eh values. The concentration of salts within the solution and entrained salts also affect sorption. Sorption coefficients measured using high salt solutions are often low due to the additional ions competing for the sorption sites. The method and rigor of shaking samples determines whether the solid is broken into small particles. These "fines" can bias Kd values both high and low. Surface area increases with the production of fines, causing higher Kd values, while fines not removed from the solution prior to counting can contribute to lower Kd values. Solution:soil ratio affects Kd values in its relationship to the amount of fines. The effect of fines is not as evident in samples with high solution:soil ratios as it is in samples with lower solution:soil ratios (Barrow and Shaw 1979). Other factors affecting Kd values are temperature and pressure, which influence the solubility of some elements.

It was proposed that leachate from the previous studies be used in the attenuation studies. The studies to date were performed with undiluted tailings solution to represent the worst condition that could be encountered, that in which solution is not separated from the tailings and is allowed to sit without treatment. Neutralization of the tailings solution was also performed to see its effects on attenuation by the Morton Ranch materials.

Attenuation studies on the Morton Ranch materials were performed using batch distribution coefficient (Kd) tests. In these tests, a known volume of tailings solution contacted a known amount of clay liner material, overburden, or sandstone. After ten days the solution was separated by centrifugation and analyzed. Kd values were then calculated from the ratio of the tracer (constituent) concentration in the sample to the concentration remaining in solution. The concentration in the sample is the difference between the starting solution concentration and that remaining in solution at the end of the contact period.

TESTS RESULTS

After being contacted with untreated tailings solution, the clay liner, overburden, and sandstone did not remove significant amounts of the nonradioactive elements from solution. The high salt concentration and acidity of the tailings solution accounts for the low sorption. In contrast, the radionuclides ^{238}U, ^{226}Ra, ^{230}Th, and ^{210}Pb were sorbed by each of the Morton Ranch materials in varying degrees (Table 3.1). More ^{210}Pb was removed from solution than the other nuclides, with the clay liner removing the most.

Kds for the neutralized solution samples showed greater sorption by the clay liner than the Kds from the untreated solution (Tables 3.2 and 3.3). Higher values were calculated but there were wide differences between samples, as evidenced by the high coefficients of variation. Sorption was greater for radium and thorium, and lower for uranium and lead than for the untreated solution. This apparent decrease in sorption is a function of the lower

TABLE 3.1. Batch Kd Values (ml/g) Using Untreated and Neutralized Uranium Mill Tailings Solution for 10-Day Contact Periods (ml/g) with Morton Ranch Materials. Mean Values of Duplicate Samples.

	Clay Liner	Overburden	Sandstone
	pH		
Element	2.4	2.2	2.2
U-238	1.3	1.0	1.7
Th-230	1.2	1.1	1.9
Ra-226	13	10	18
Pb-210	1848	13	68

concentrations due to neutralization. The untreated and neutralized solution compositions used in the tests, given in Table 3.2, are markedly different. Neutralization using NaOH caused the precipitation of most of the constituents, especially Al, Fe, Mn, Si, and the radionuclides. Comparison of the neutralized blank values with MPC levels given in Tables 1.3 and 1.4 show concentrations were reduced below MPC for Cu, Zn, U, Th, and Pb. Other concentrations were reduced up to three orders of magnitude.

The determined Kd values in Table 3.1 reflect both sorption and precipitation reactions, with the main attenuation process being precipitation or scavanging of trace metals by formation of unsoluble hydrous oxides (see Section 4).

The effect of neutralization was significant removal of elements. By reducing concentrations, the process of attenuation was enhanced. When Kds were calculated using the blank values from the untreated solutions and the neutralized clay liner values, Kd values increased considerably. These effective values due to neutralization are reported in Table 3.3. By reducing the concentrations of hazardous materials, leachate from disposed tailings poses a smaller threat to the surroundings.

TABLE 3.2. Data Used in Calculating Batch Kd Values

Parameter	Untreated Tailings Solution		Neutralized Tailings Solution	
	Blank	Clay Liner	Blank	Clay Liner
Sample pH	2.1	2.4	4.9	7.7
ICP Analysis, (mg/l)				
Al	663(26)(a)	687(21)	0 ---	0 ---
As	6.2(1.9)	7.4(1.7)	1.2(23)	3.4(4.8)
Ca	586(59)	616(62)	446(13)	443(13)
Cd	3.4(1.3)	3.2(0.5)	0.4(0.5)	0.3(0.4)
Cr	3.0(0.2)	3.1(0.2)	0.1(0.2)	0.2(0.2)
Cu	3.0(0.7)	3.1(0.5)	0.2(0.2)	0.4(0.4)
Fe	2,075(104)	2,046(102)	0.3(0.3)	1.0(0.6)
Mg	717(36)	770(31)	610(12.2)	603(12)
Mn	68(3.0)	68(2.7)	18(0.7)	13(0.6)
Na	308(22)	315(16)	5,118(204)	5,050(151)
Ni	26(19)	3.5(1.0)	1.4(1.7)	0.4(0.1)
Si	264(34)	299(33)	3.1(3.5)	9.3(1.5)
Sr	12(0.4)	14(0.6)	9(0.4)	10(0.3)
Th	9(1.8)	9(2.0)	0.4(0.5)	0.4(0.6)
Zn	9(1.3)	11(1.0)	0.8(0.6)	0.7(0.6)
Radiochemical Analysis, (pCi/l)				
U-238	9,685(194)	247(52)	26(0.8)	29(9.9)
Ra-226	13,198(264)	12,632(126)	44(7.9)	17(9.5)
Th-230	227,252(2272)	218,233(2182)	595(77)	85 ---
Pb-210	2,252(676)	1,583(317)	28(20)	28(20)

(a) Number in parentheses is standard deviation

TABLE 3.3. Effective Kd Values Due to Neutralization

Element	Morton Ranch Clay Liner, pH 2.2	7.7
Al	0	19,860
As	0	25
Cd	0	310
Cr	0	420
Cu	0	195
Fe	0.4	62,220
Mn	0	127
Ni	0	165
Si	0	822
Sr	0	6
Zn	0	356
U-238	1.3	23,292
Th-230	1.2	80,189
Ra-226	13	2,383
Pb-210	1848	10,005

4.0 CLAY LINER TESTS

INTRODUCTION

The Nuclear Regulatory Commission (USNRC 1979b) has considered a number of options for tailings management at the Morton Ranch mill site. Most of these options include a clay liner for seepage control. The clay liner is to be constructed from on-site materials. These materials must have the proper characteristics and be placed in such a way that their presence as a liner either eliminates seepage of toxic materials into the ground water system or reduces it to the "maximum extent reasonably achievable". The Environmental Protection Agency (USEPA 1978) has proposed a number of criteria for "soil" liner materials for hazardous waste containment. These criteria include certain textural, particle-size, pH, and permeability specifications (Table 4.1). A maximum permeability of 1×10^{-7} cm/s is required for liner material with the additional specification that the permeability is not adversely affected by the anticipated waste.

TABLE 4.1. EPA Soil Liner Criteria (USEPA, 1978)

1. Soil classification must be CL, CH, SC or OH under the Unified Soil Classification System
2. Allow greater than 30 percent passage through a No. 200 sieve
3. Have a liquid limit equal to or greater than 30 units
4. Have plasticity greater than or equal to 15 units
5. Have a pH of 7 or higher
6. Have a permeability not adversely affected by anticipated waste.

The concern that the tailings solution could interact with the clay liner and in time cause liner failure (i.e., result in an increase in permeability) has prompted an investigation into possible mechanisms of clay liner failure at the Morton Ranch site.

Clay dispersion, clay dissolution, volume change, and change in clay wettability have all been identified as mechanisms that can act to cause failure of a clay liner. A detailed review of these mechanisms is given by Brown and Anderson (1980). For pit disposal of tailings, where the liner is permanently buried and the tailings solution is inorganic, the only mechanisms that could act to cause failure are clay dispersion and clay dissolution. Laboratory tests were designed to evaluate clay dispersion, clay dissolution, and time dependence of clay permeability for the Morton Ranch clay liner materials.

MATERIALS AND METHODS

Clay liner material taken from the 1704 pit at Morton Ranch (Figure 2.13 in USNRC, 1979a, Figure 4.1) was used in all tests. Physical and chemical characteristics for this material are described in Table 1.1. For comparison purposes, Wyoming bentonite and saline seal (sodium-treated Wyoming) were obtained from a commercial vendor (American Colloid Co., Skokie, Illinois) and were tested along with the Morton Ranch clay liner material for mineralogical changes occurring after contact with tailings solution. Details of specific methods are discussed in the following section on mineralogy. ASTM (1978) methods were used to evaluate clay texture, fineness, liquid limit and plasticity. Clay dispersion criteria followed methods of Sherard et al. (1976). X-ray analysis, scanning electron microscopy, and X-ray fluorescence were all used to evaluate the physical and mineralogical changes in the clay liner material subjected to contact with tailings solution. Permeability tests were run on the clay liner and overburden using both the tailings solution and a synthetic solution containing equivalent macro-ion constituents but no radionuclides. Flow through the clay liner was enhanced by using a pressurized permeameter designed to accommodate acid leach solutions. Details of packing procedures and cell volumes are given in the section on permeability.

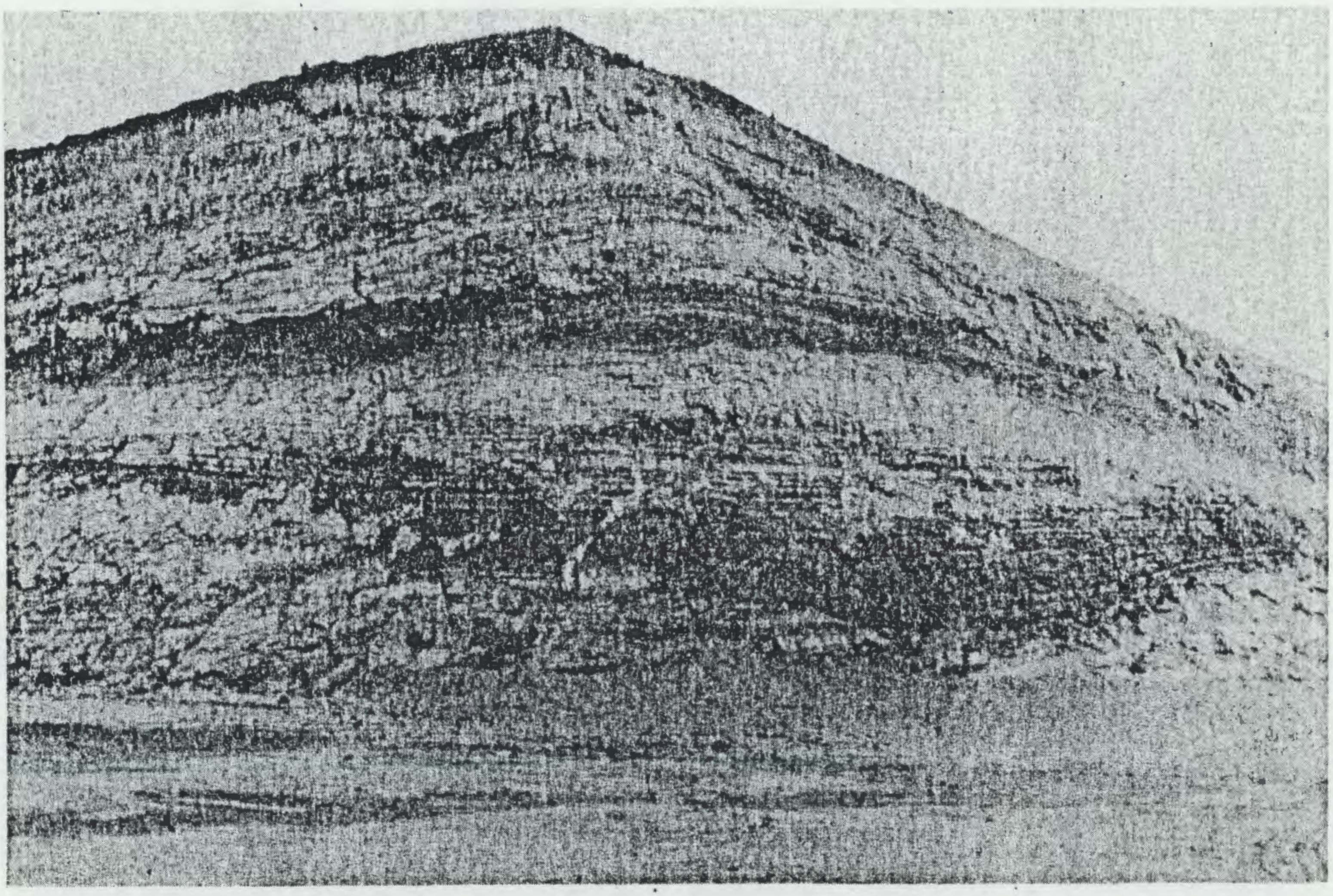


FIGURE 4.1. 1704 Pit at Morton Ranch. Clay liner material taken from shale and siltstone material similar to that seen exposed on pit wall.

RESULTS AND DISCUSSION

Liner Criteria

Table 4.2 shows the results of the measurements made to test the Morton Ranch clay liner against EPA criteria. The data indicate that all measureable parameters for the Morton Ranch clay liner meet the EPA liner criteria. Extended leaching of the liner with tailings solution had no apparent adverse effect on the clay liner permeability. The permeability results are discussed in detail in a later section.

TABLE 4.2. EPA Criteria and Morton Ranch Clay Liner Characteristics

Characteristic	EPA	Morton Ranch Liner
1. Soil Classification (Unified Soil Classification System)	CL, CH, SC or OH	CL (clayey silt)
2. Fineness	$\geq 30\%$ thru 73 μm screen (200 mesh)	95%
3. Liquid Limit	> 30	43
4. Plasticity	≥ 15	21
5. pH	≥ 7	8
6. Permeability (cm/s)	10^{-7}	$< 5 \times 10^{-8}$

Dispersion Test Results

Results of the initial tests for clay dispersion by the crumb test gave the clay liner a dispersion rating of 1 to 1.5. This rating indicates that the clay is nondispersive. Gee et al. (1978) have previously observed that in this dispersion range, crumb tests correlate well with the pinhole test (Sherard et al. 1976), hence, the more detailed pinhole test was not run.

Testing of the soil solution using criteria established by Sherard et al. (1976) indicated that the tailings solution would not contribute to the dispersion. Solution chemistry data for tailings solution, diluted tailings solution and leachate from tailings using mill process water are plotted in Figure 4.2. All data indicate that the solution would have a non-dispersive

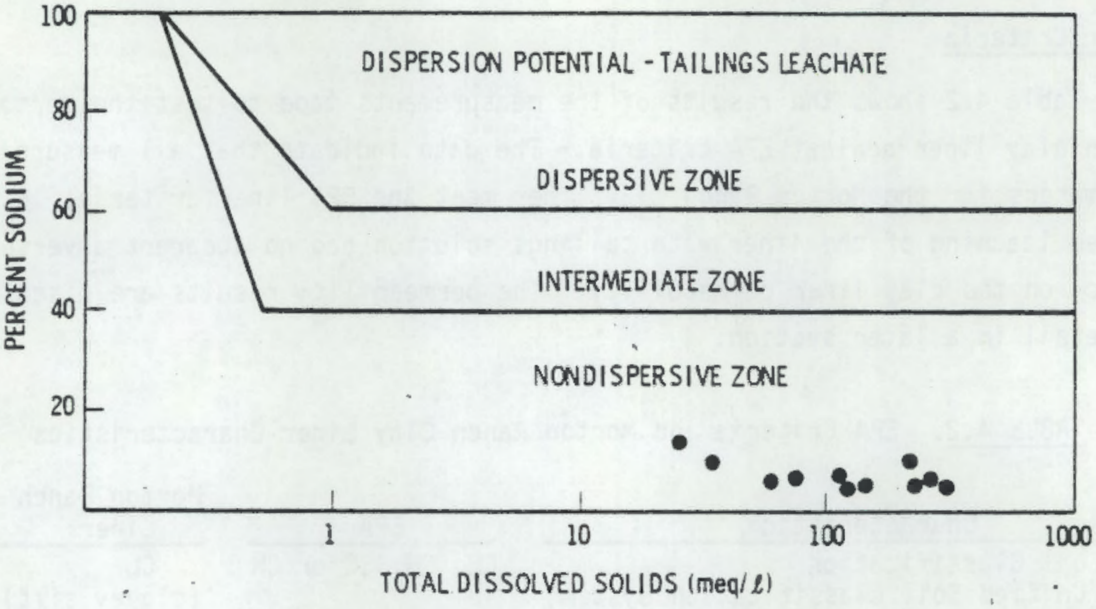


FIGURE 4.2. Solution Composition of Tailings Solution and Leachate from Tailings Related to Dispersion Potential Criteria Established by Sherard et al. 1976

influence on the clay material. The percent sodium in the soil solutions is less than 15 in all cases. Gee et al. (1978) have previously observed that when the percent sodium is less than 20, no dispersion of the sample is observed using a pinhole test. Since neither the clay material nor the tailings solution has any dispersive tendencies, we conclude that clay dispersion cannot be a mechanism for failure of the clay liner even after extended time.

Minerological Tests

Results from total elemental analyses by X-ray fluorescence are presented in Table 4.3. There was no significant decrease in silicon or aluminum, as might be expected if mineral dissolution were occurring. There was a consistent increase in Fe_2O_3 and FeO content, which suggests that secondary ion minerals may have been forming during the 90-day test period. The most significant change in composition was the Na_2O reduction after treatment for the bentonite and saline seal. The relative change in sodium for the saline seal suggests that some of the effectiveness of the sodium saturation of this liner

TABLE 4.3. Total Elemental Analysis of Morton Ranch Clay Liner, Bentonite, and Saline-Seal Liner Before and After Treatment with Tailings Solution

Sample	SiO_2	Al_2O_3	TiO	Fe_2O_3	FeO	MnO	CaO	MgO	K_2O	Na_2O	P_2O_5
					% of Total						
Untreated											
Clay Liner	73.0	16.4	0.8	2.0	2.3	0.02	1.0	1.3	2.5	0.7	0.07
Bentonite	66.9	22.1	0.2	1.9	2.2	0.02	1.2	2.2	0.6	2.6	0.2
Saline Seal	67.6	19.9	0.2	2.0	2.3	0.05	1.6	1.5	1.0	3.3	0.4
Treated(a)											
Clay Liner	72.3	15.6	0.8	2.9	3.3	0.02	0.8	1.2	2.6	0.5	0.1
Bentonite	66.4	22.6	0.2	2.6	3.0	0.03	1.0	2.3	0.6	1.1	1.2
Saline Seal	67.4	19.8	0.8	2.7	3.1	0.04	1.4	1.8	1.0	1.6	0.4

(a) 5:1 (tailings solution:solid) sample shaken for 90 days at room temperature

TABLE 4.4. Identified Clay Minerals and Relative Abundance Determined by X-Ray Diffraction Analysis on Liner Samples Material Treated as Specified in Table 4.3

Sample	Smectites	Kaolins	Chlorites	Inter-grade	Quartz	Feldspars	Micas
Morton Ranch Clay Liner							
untreated	++	+	++	++	++++	+	+
treated	++	-	++	++	++++	+	+
Bentonite							
untreated	++++	-	+	+	+	+	+++
treated	++++	-	+	++	+	+	++
Saline Seal							
untreated	++++	-	+	+	++	++	+++
treated	++++	-	+	++	++	++	++

Relative Abundance

++++ = High
+++ = Moderate
++ = Low
+ = Trace
- = Absent

material might be lost due presumably to exchange with hydrogen and other competing ions. It appears that if minor amounts of dissolution are occurring, mineralization or precipitation reactions are also occurring at the same time, which tend to maintain similar total elemental compositions. We conclude from these observations that mineral dissolution is not a significant factor in clay liner permeability changes for the Morton Ranch clay liner material, and we speculate that mineral formation or precipitation may be a possible factor in actually causing permeability decreases.

X-ray Diffraction

X-ray diffraction analyses of the materials analyzed before and after contact with mill-tailings solution showed only minor changes in the mineralogy of a few sample mineral constituents. Table 4.4 summarizes the minerals present in each of the studied samples. Their relative abundance before and after contact with uranium mill tailings is also shown semiquantitatively. The predominant change in mineralogy occurs within the smectite, intergrade and hydrous mica whereby contact appears to reduce the amount of each mineral. Figures 4.3, 4.4 and 4.5 show generalized X-ray diffraction patterns of the composite clay liner, bentonite and saline seal, respectively, before and after contact. Each of these diffraction patterns shows some degradation of the smectite and intergrade, as distinguished by a broadening of the basal spacing of the peaks and by a reduction in peak intensity. Peak intensity reduction typically is diagnostic of a reduction of mineral crystallinity. Chlorite, feldspars and quartz minerals were not found to significantly change in relative abundance or crystallinity when subjected to contact with uranium mill tailings solution.

In general, within the limits of experimental error and the semiquantitative nature of X-ray diffraction data, only small mineralogical changes of layer lattice clay minerals were observed. These mineralogical changes are probably a direct result of some dissolution of minerals by the sulfuric acid present in the mill tailings solution, ion exchange of solution constituents, and precipitation reactions whereby the clay minerals are partially destroyed or transformed into other clay minerals.

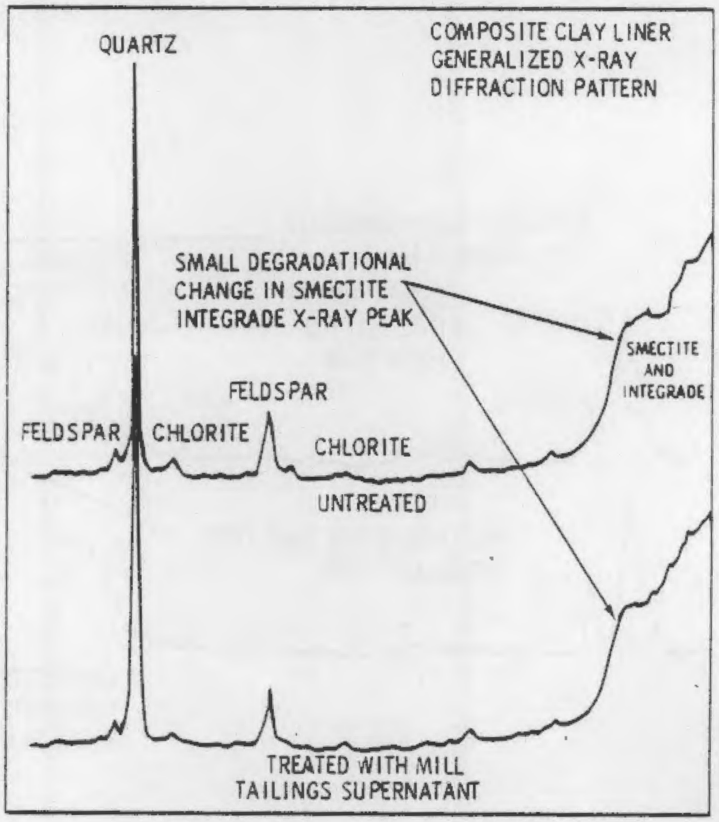


FIGURE 4.3. X-ray Diffraction of the <10 μm Fraction of Morton Ranch Clay Liner Material

Scanning Electron Microscopy

Scanning electron microscopy (SEM) was used to determine if there was any change of mineral surface morphology of bentonite, saline seal, and the Morton Ranch clay liner materials when contacted with the tailings solution. Scanning electron photomicrographs were taken at magnifications of 5,000 to 10,000 for each of the treated and untreated samples. Photomicrographs of the composite clay liner, bentonite, and the saline seal are shown in Figures 4.6ab, 4.7ab and 4.8ab, respectively.

Photomicrographs 4.6b, 4.7b and 4.8b, which show the surface morphology of the <10μm fraction of treated materials, show only a little evidence of structural degradation. Figures 4.6a, 4.7a, and 4.8a show the surface morphology of the same materials not subjected to treatment. The untreated materials generally appear somewhat more crystalline, in that the clay mineral

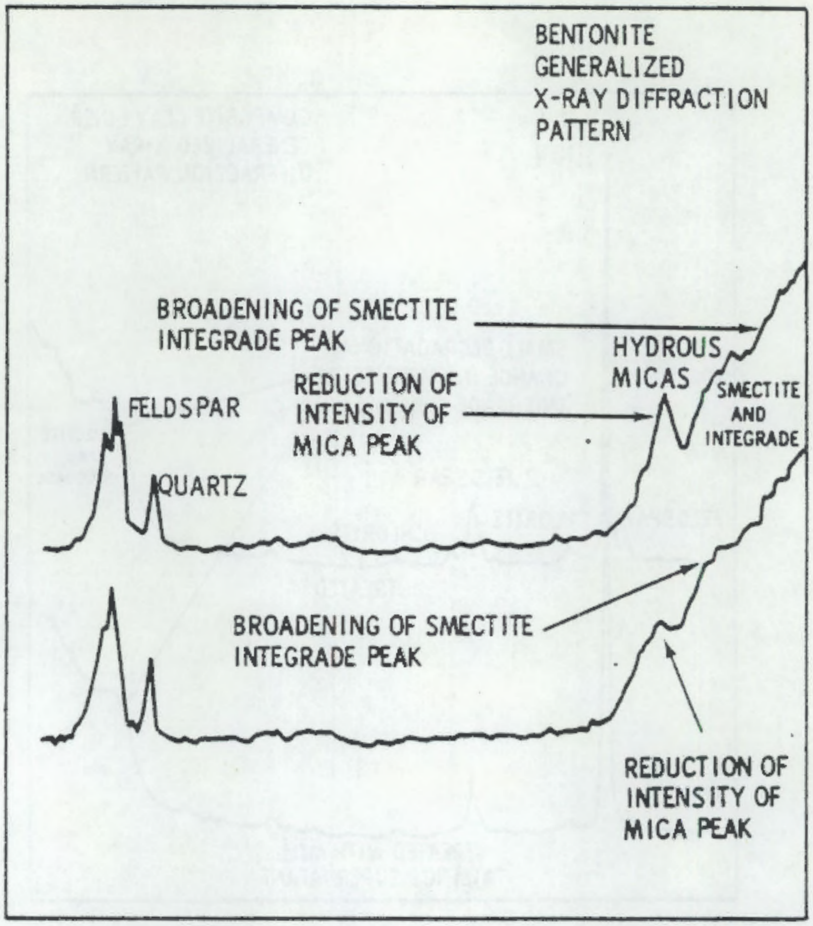


FIGURE 4.4. X-ray Diffraction of the <10 μm Fraction of the Bentonite Clay Liner Material

particles have better edge contrast in the photomicrographs. The untreated particles also show a somewhat definitive texture, whereas the treated particles tend to show a texture diagnostic of a reduced crystallinity. This also could be a result of secondary mineral formation on the clay surfaces due to precipitation reactions.

The SEM photomicrographs tend to indicate that acid within the uranium mill tailings may have slightly degraded the crystal structure of the <10 μm fraction of the liner materials studied. However, no drastic changes were observed for the 90-day test period, suggesting that if structural breakdown is occurring, it is doing so at a very slow rate. Additional SEM analyses will be run for samples that have been treated for over 180 days to determine if extended contact time results in further degradation.

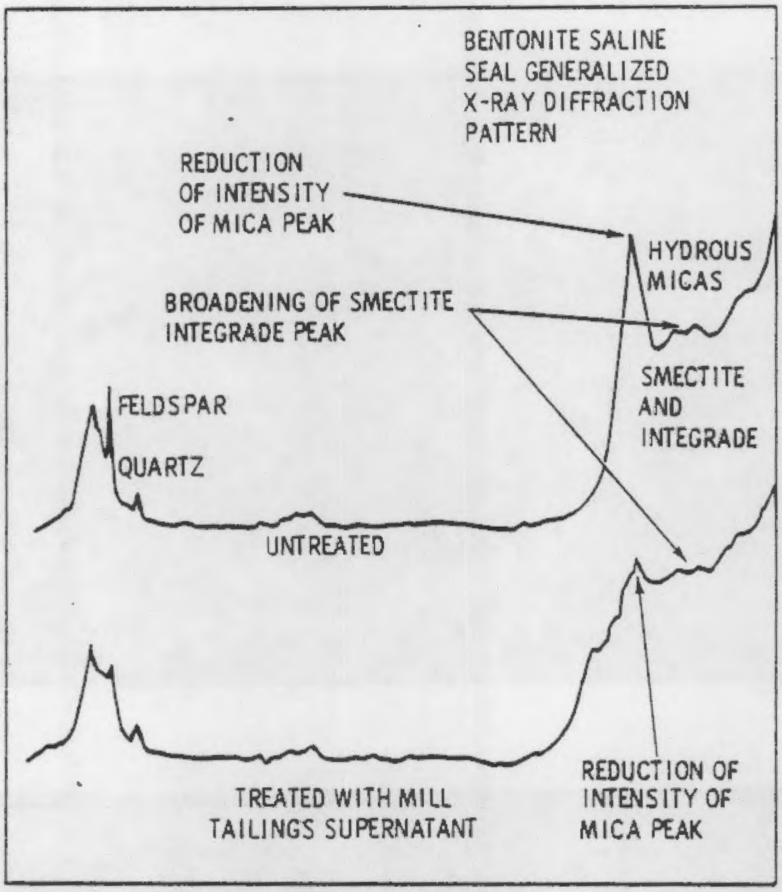


FIGURE 4.5. X-ray Diffraction of the <10 μm Fraction of the Saline Seal Clay Liner Material

Extrapolation of the results of these mineralogical tests to clay liner stability can only be indirect. The mineralogy tests indicate that no drastic or substantial changes are occurring due to contact of the clay liner materials with the acid tailings solution. The treatment optimized the contact of solution-to-solid surfaces (5:1 ratio), hence, if dissolution were a serious problem, it should have been observed in the treated samples. We conclude, therefore, that clay distribution, even if occurring, should not contribute to Morton Ranch clay liner failure since reaction rates for tailings solution at pH 2 appear to be very slow.

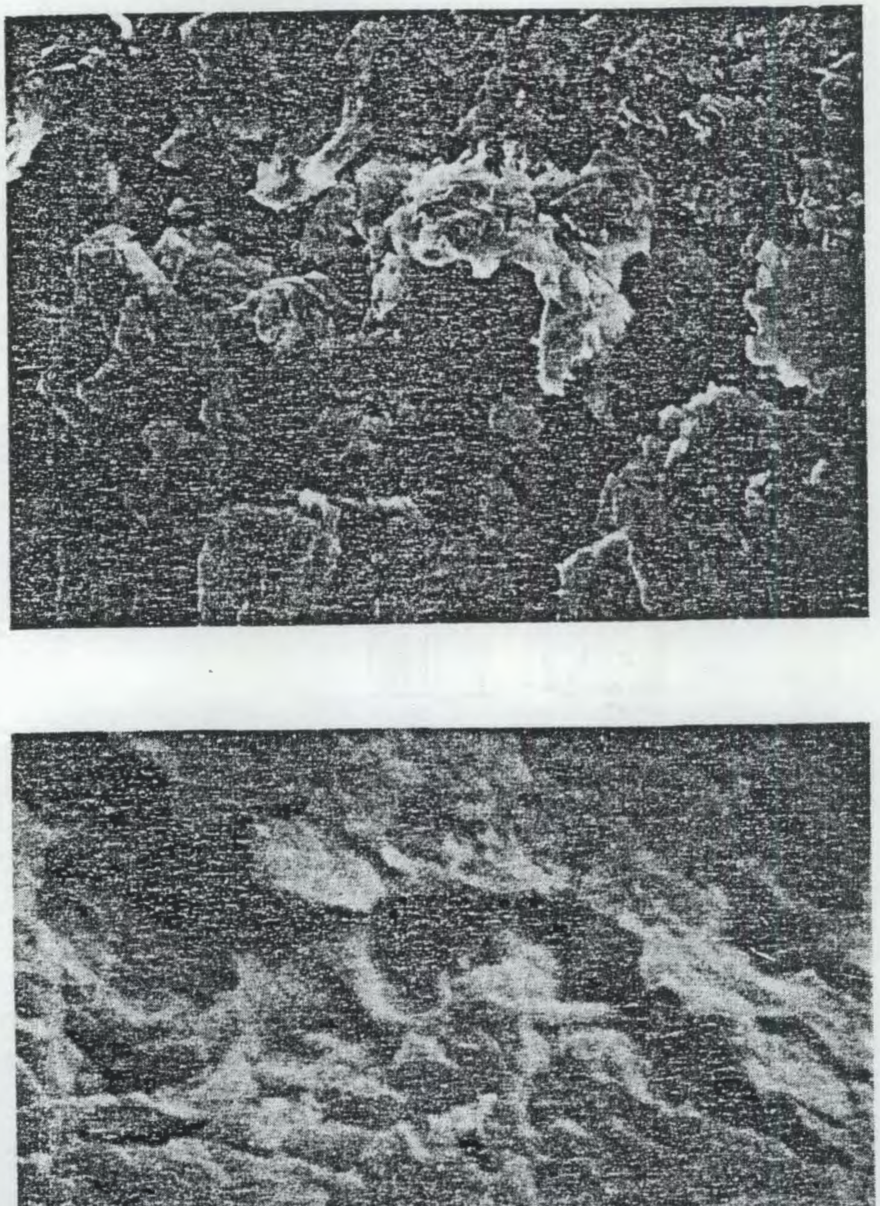


FIGURE 4.6a (upper) and b (lower).
SEM Photomicrograph of Composite Clay Liner
(magnification of 4a = 5,000; b = 10,000)

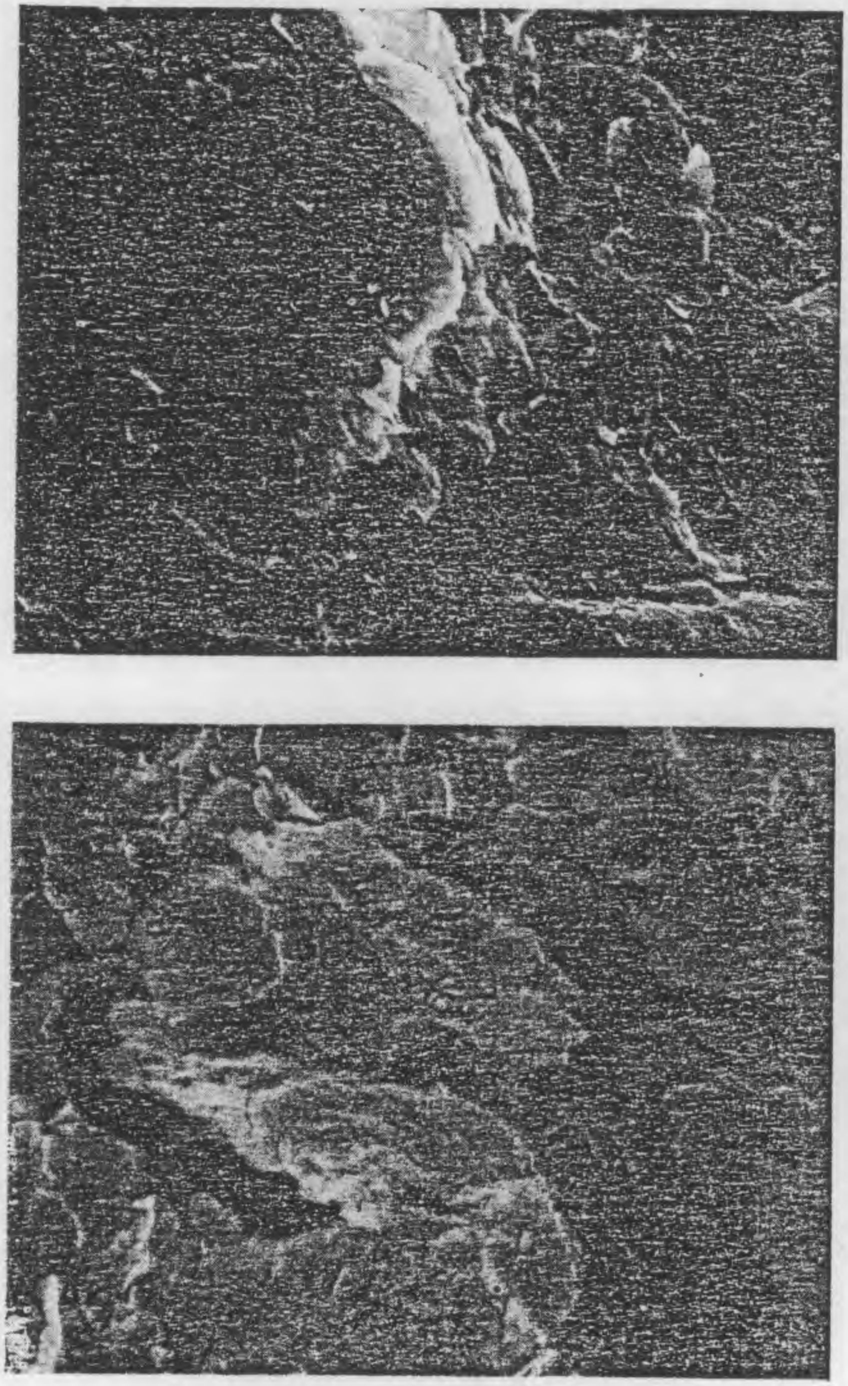


FIGURE 4.7a (upper) and b (lower).
SEM Photomicrograph of Bentonite
(magnification of 4a = 10,000; b = 10,000)

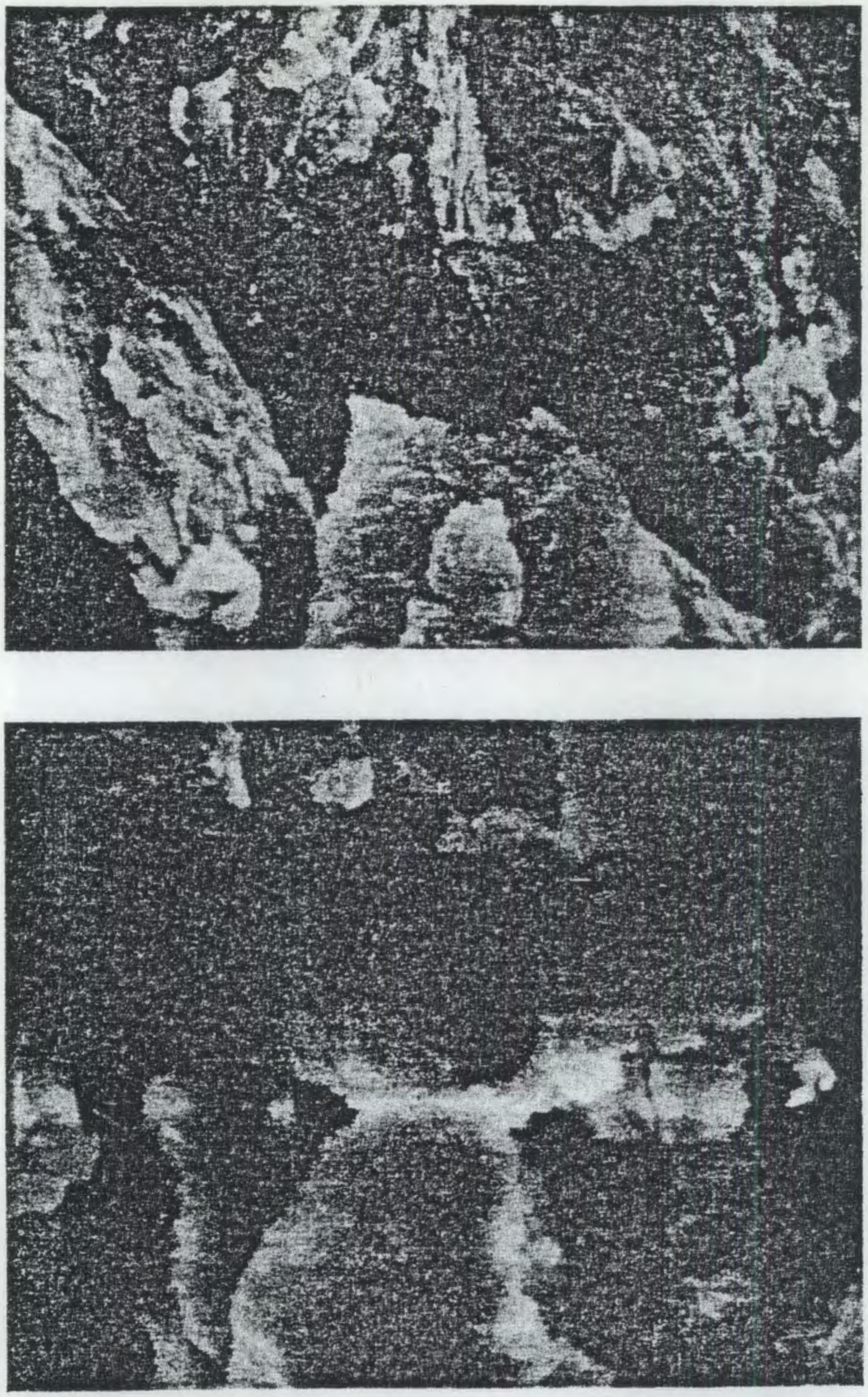


FIGURE 4.8a (upper) and b (lower).
SEM Photomicrograph of Bentonite Saline Seal
(magnification of 4a = 10,000; b = 10,000)

Permeability Tests

Morton Ranch clay liner and overburden materials were used in the tests. These materials were compacted into cylindrical cells with an approximate volume of 90 cm^3. The method used for compaction was a variation of the sliding-weight tamper method (ASTM 1978). The data for each cell are given in Table 4.5.

TABLE 4.5. Physical Data for Test Materials

Material	Cell No.	Cell Diameter (cm)	Length (cm)	Volume (cm^3)	Initial Moisture (wt%)	Sample Weight (g)	Bulk Density (g/cm)	% of Maximum Compact(a)	Pore Volume(b) (cm^3)
Clay Liner	1	5.03	4.50	89.6	9.6	159.7	1.78	97	31.6
Clay Liner	2	5.00	4.60	90.3	9.0	157.8	1.75	95	32.8
Clay Liner	3	5.00	4.67	91.7	10.5	155.6	1.70	92	35.1
Clay Liner	4	4.98	4.50	87.85	10.5	157.7	1.80	98	31.4
Clay Liner	5	4.98	4.50	87.8	10.5	154.2	1.76	95	32.7
Clay Liner	6	4.98	4.50	87.8	10.5	156.4	1.78	97	31.9
Overburden	7	4.98	4.60	90.1	12.5	171.4	1.90	95	26.1
Overburden	8	4,95	4.60	88.5	12.5	169.6	1.92	96	24.9
Overburden	9	5.05	4.55	91.5	12.5	174.0	1.90	95	26.2

(a) Maximum compaction was determined for both materials by a standard procter test. Maximum compaction for the clay liner material was 1.84 g/cm^3, and the overburden material was 2.00 g/cm^3.

(b) Pore Volume = Volmume of void space in total sample volume (cm^3).

Each cell was packed to about 95% of maximum compaction. All of the cells, with the exception of Cell 1, were saturated with ground water. Cell 1 was contacted initially with a synthetic tailings solution. Constant head permeability tests were then run on all cells. Cells 1, 2, and 3 were contacted with synthetic solution and the remaining six cells were contacted with tailings solution. The synthetic solution contains the major constituents of the tailing solution, but is free of radioactivity (see Table 4.6).

The method used for determining permeability was the ASTM Method for determining constant head permeability, with some minor modificiations (ASTM

TABLE 4.6. Macroconstituents of Tailings Solution

	Tailings Solution (mg/l)	Synthetic Solution (mg/l)
pH	2.0 units	2.0 units
Al^{3+}	578	580
Ca^{2+}	484	480
Fe^{2+}	2,200	2,200
Mg^{2+}	650	650
$Na+$	330	330
Si	233	0
Cl^-	97	100
NO_3^-	16	15
$SO_4{}^{2-}$	12,850	13,000

1978). The flow through the cells was from bottom to the top to ensure saturated flow conditions. Figure 4.9 shows a block diagram of the saturated flow apparatus used for all of the samples. Figure 4.10 shows three permeameter cells connected to the pressure system and to outflow collection cylinders.

The permeability (K) is calculated by multiplying the flow rate in ml/day by a cell constant. The cell constant is the length of the cell (L) divided by the cross-sectional area times the hydraulic head.

$$\text{Cell Constant} = \frac{L(cm)}{A(cm)^2\ H(cm)} \times \frac{1}{sec/day}\ \frac{1}{86400}$$

The permeability was computed by multiplying measured daily flow volumes by the cell constant.

$$K(cm/s) = \frac{Q(cm)^3}{T(days)} \times \frac{L(cm)}{A(cm)^2\ H(cm)86400\ s/day} = \text{Flow Rate} \times \text{Cell Constant}$$

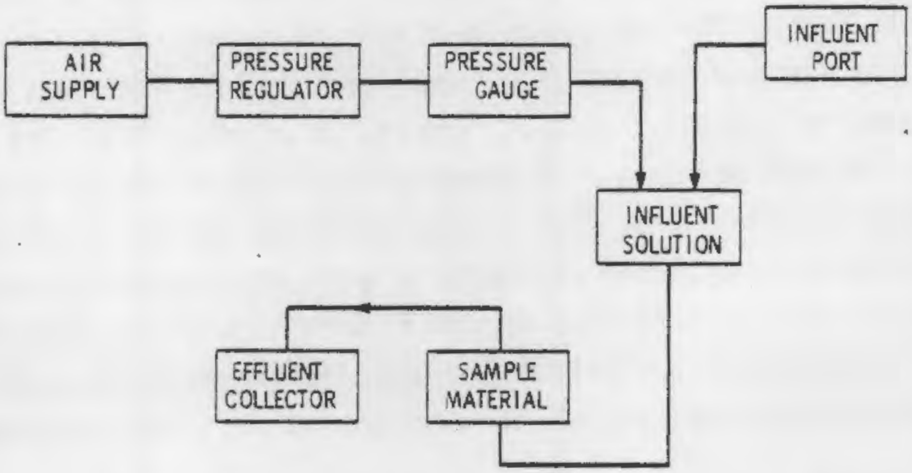


FIGURE 4.9. Pressurized Flow System for Determining Constant Head Permeability

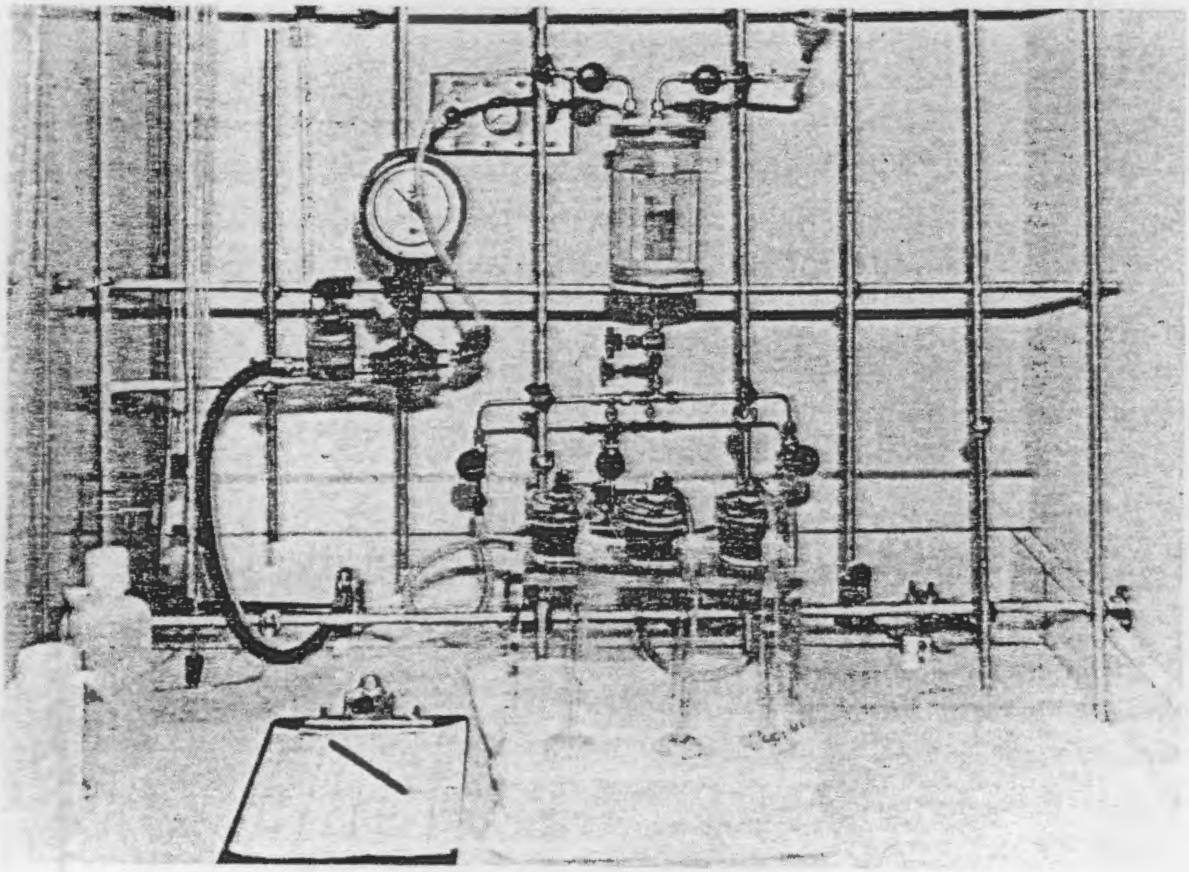


FIGURE 4.10. Pressurized Permeameter Setup for Measuring Permeability of Clay Liner Materials

The cells packed with the clay liner material were pressurized to accelerate the flow through the test materials. This technique was tried initially on the synthetic solution-clay liner samples. This enabled us to simulate long-term effects in a shorter time period. For cell 1, the pressure was increased at three different points over time to determine if there was any effect on the measured permeability (see Figure 4.11). There was no measurable influence of hydraulic head differences on permeability. The hydrualic head has since been maintained at approximately 1460 cm for all clay samples. To determine the effect that flow through fractures has on the permeability, material in cell 2 was packed initially in a slightly undersized cell and then transferred to cell 2. After 50 days of flow through cell 2, the surface of the clay liner material was recompacted with the tamper to see what the change in permeability would be, and if recompaction had any effect on chemical migration.

Results of Permeability Tests

The permeabilities of the Morton Ranch clay liner material varied from 5 x 10^{-8} cm/s to 1.5 x 10^{-10} cm/s. The apparent reason for such a wide range of permeabilities can be attributed to packing differences of the clay material. The average permeability for all the clay sample cells is 7.5 x 10^{-9} cm/s. The change in permeability has been very small for the samples with initial permeabilities of less than 1 x 10^{-8} cm/s. The scatter in the data for cell 4 is due to the inability to accurately measure a flow rate of 0.1 ml/day or less.

On all but two of the clay liner samples, we noted an initial rapid decrease in permeability. For cell 2 (which was recompacted in place after 50 days of solution contact), the permeability dropped by an order of magnitude after recompaction (Figure 4.11). For the clay liner material after the initial 50 days, all tests have shown either near steady flow or slow decreases in flow rates with time. Some samples have been under solution contact for 8 months, and outflows from the most permeable columns have exceeded 10 pore volumes. The data suggest that physical manipulation (compaction) has a rather dramatic effect on permeability, and that physical mechanisms which

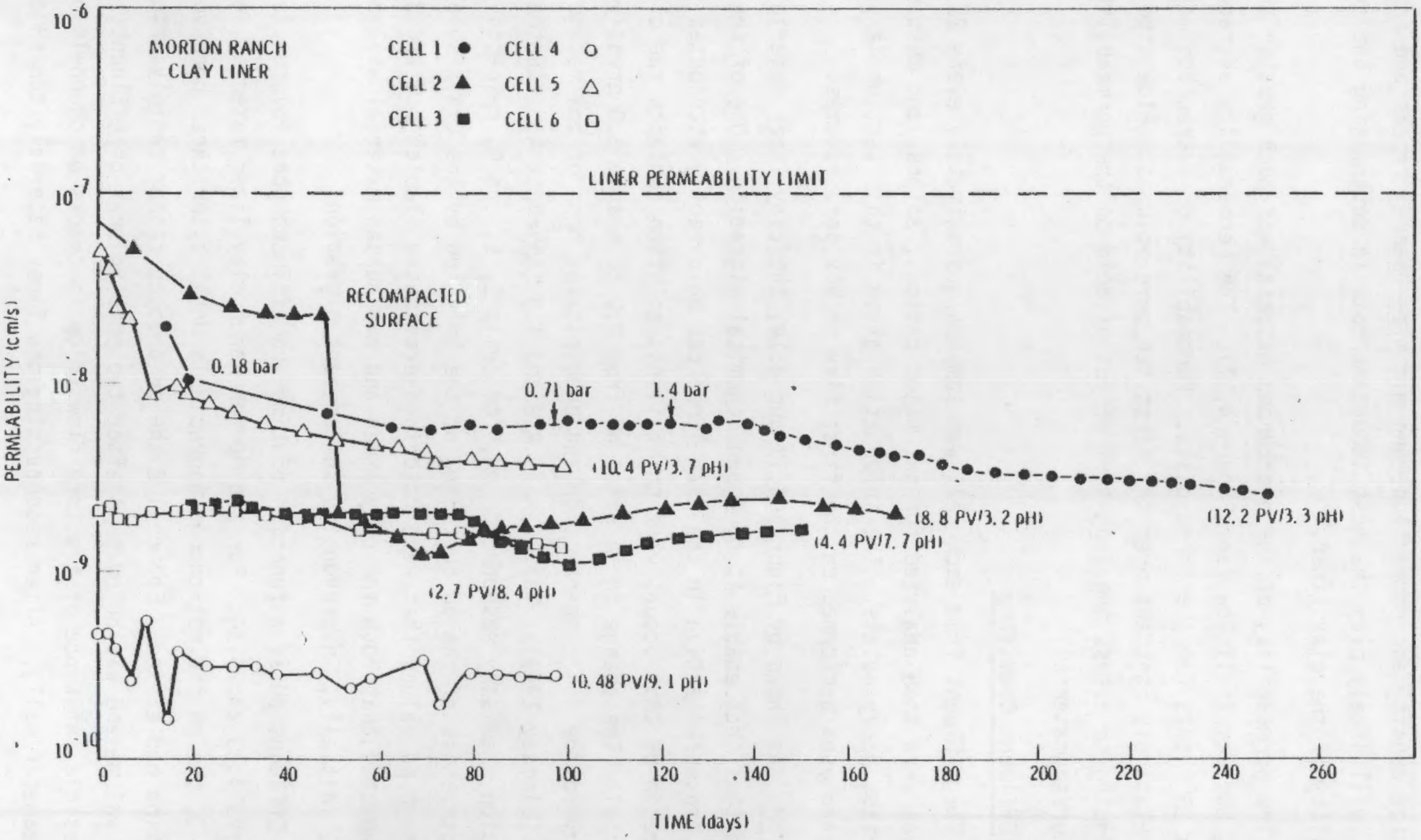


FIGURE 4.11. Permeability of Morton Ranch Clay Liner Material as a Function of Time (Effluent pore volumes and pH are indicated for the last data point for each cell.)

optimize density and compaction, and minimize channel cracks and fracture flow, will likely play the most important role in determining the overall permeability of the clay liner.

The permeability of the overburden material was much greater than the clay, but was still low (see Figure 4.12). The permeability averaged 3.7×10^{-7} cm/s for the three cells. Permeability of overburden material was relatively constant over the first ten pore volumes. Flow studies are continuing to assess the long-term effect of acid on the permeability of the overburden material.

Effluent Chemistry

The effluent from each cell was sampled approximately every 20 ml. These samples were then analyzed for pH, major cations, anions, and most of the important heavy metals. The information given in this section is primarily from analyses performed on the first five to six pore volumes.

pH. As shown by Figures 4.13 and 4.14, the clay liner material does have properties that enable it to impede chemical migration. One of the attenuation processes active in the clay liner can be directly attributed to the change in pH that occurs when the tailings solution contacts the clay liner material. The change in solution pH from 2.0 to nearly 8.0 greatly increases the hydroxide ion concentration and precipitates most of the metals as hydroxides (Lindsay 1979). Tables A.7, A.8 and A.9 (Appendix A) illustrate the solution chemistry response to pH, for cells 1, 5, and 8, respectively. The effectiveness of the pH buffering of the solution by the clay is reflected in the high Kd values that were described previously (Tables 3.2 and 3.3) and it is expected that both the clay liner and overburden material will be effective, initially, in preventing contaminant migration.

Effluent pH as a function of time and effluent pore volumes is shown in Figures 4.13 and 4.14. For the Morton Ranch clay liner material, except for cell 2, the pH did not change appreciably until after three pore volumes of solution had eluted. For cell 2 the pH dropped rather rapidly after the first pore volume and was below pH 4 after two pore volumes of effluent, suggesting a possible influence of fracture flow (flow in cracks or channels or along the permeameter wall). After recompacting the liner material, the pH decreased

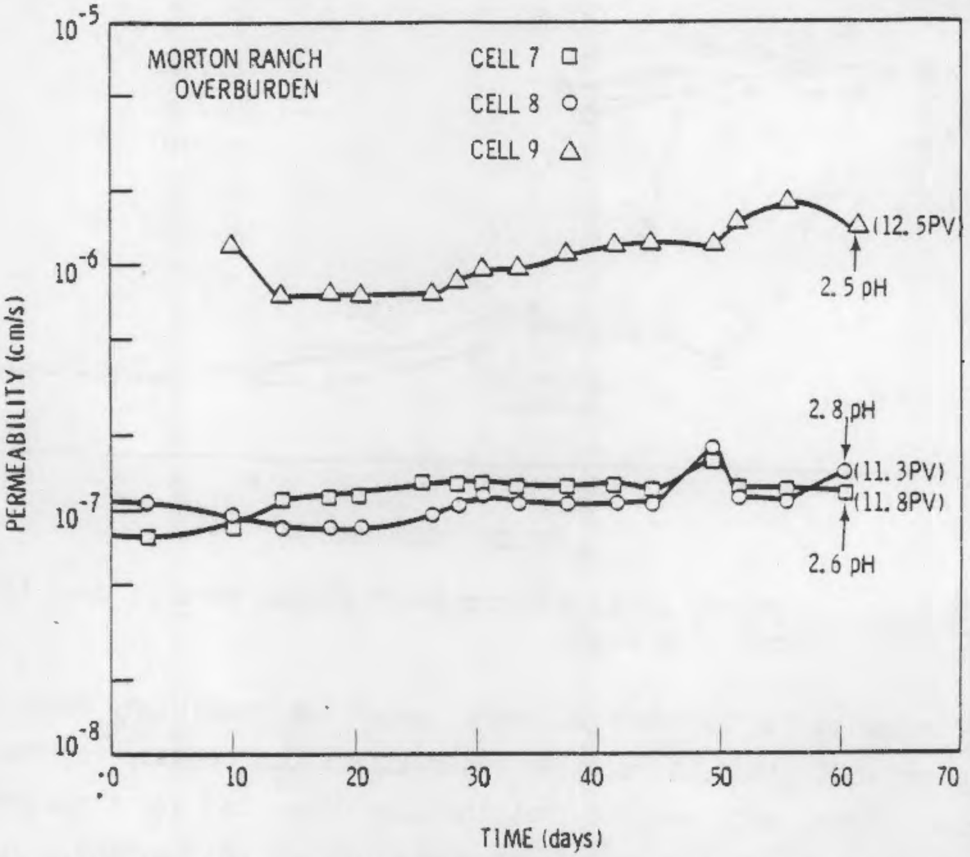


FIGURE 4.12. Permeability of Morton Ranch Overburden as a Function of Time (Effluent pore volumes and pH are indicated for the last data point for each cell.)

slowly and in a manner similar to the other clay liner materials. None of the clay liner samples dropped in pH below three during the testing period. The data suggest that if the clay liner is adequately compacted and no fracture flow occurs, the pH will remain above 4 for rather long periods of time.

For a compacted clay liner 1 m thick, with a permeability of 10^{-8} cm/s, the maximum flow through the liner would be less than 2 pore volumes in 20 years, if we assume a constant pressure head gradient of 10. This size of head gradient might exist in an evaporation pond that was constantly filled to a depth of at least 9 m (30 ft), but would be conservatively high (by a factor of 5 to 10) for any pit tailings disposal alternatives (Nelson et al. 1980). From Figures 4.11 and 4.13, the clay liner material can be shown to have adequate buffer capacity and sufficiently low permeability to neutralize all

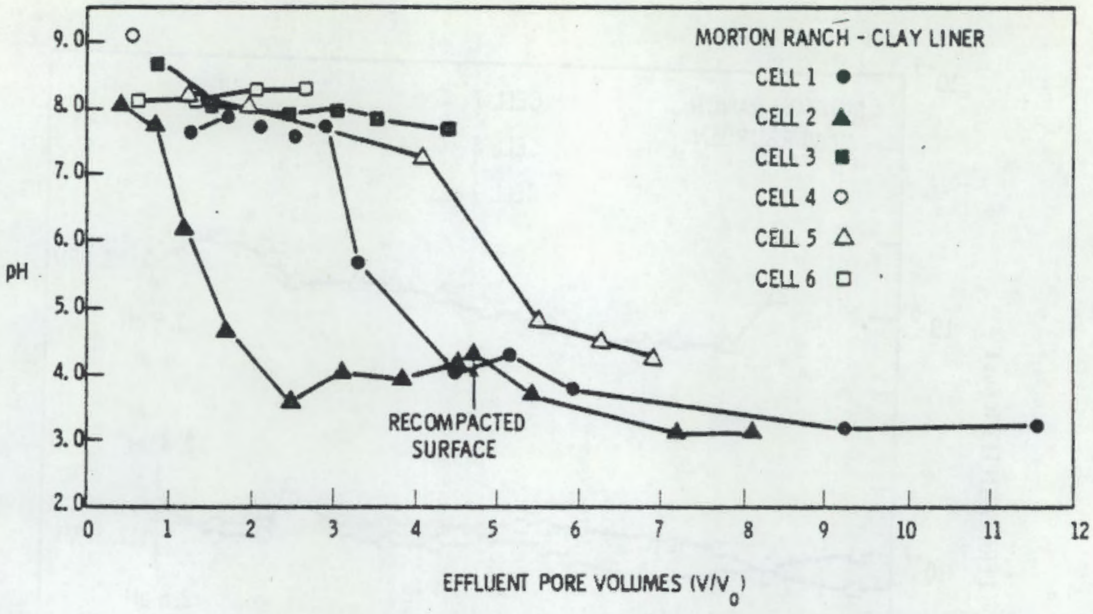


FIGURE 4.13. Effluent pH as a Function of Eluted Pore Volumes for Morton Ranch Clay Liner

effluent solution for at least 20 years, under the conditions described above. From Figures 4.12 and 4.14, similar observations can be made for the compacted overburden. These data suggest that the clay liner and overburden materials will provide a barrier to contaminant migration not only by their low permeability but also by their buffer capacity (see also Nelson et al. 1980). Long-term effects of low pH on chemical transport through liner and overburden materials are not well documented and should be the subject of additional research. The following data illustrate the initial effects of acid leaching of clay liner materials.

Sulfate. Chemical reactions occurred in the clay liner to markedly reduce the sulfate concentration of the column effluent substantially below the concentration of the influent. Figure 4.15 shows sulfate breakthrough curves for Morton Ranch clay liner material (cells 1 and 2) and illustrates the response of the sulfate concentration with increasing effluent pore volumes. Additional data on sulfate response are presented in Appendix A (Tables A.7, A.8 and A.9). These data indicate that sulfate is reacting with the clay liner material and that for well compacted samples, the effluent is

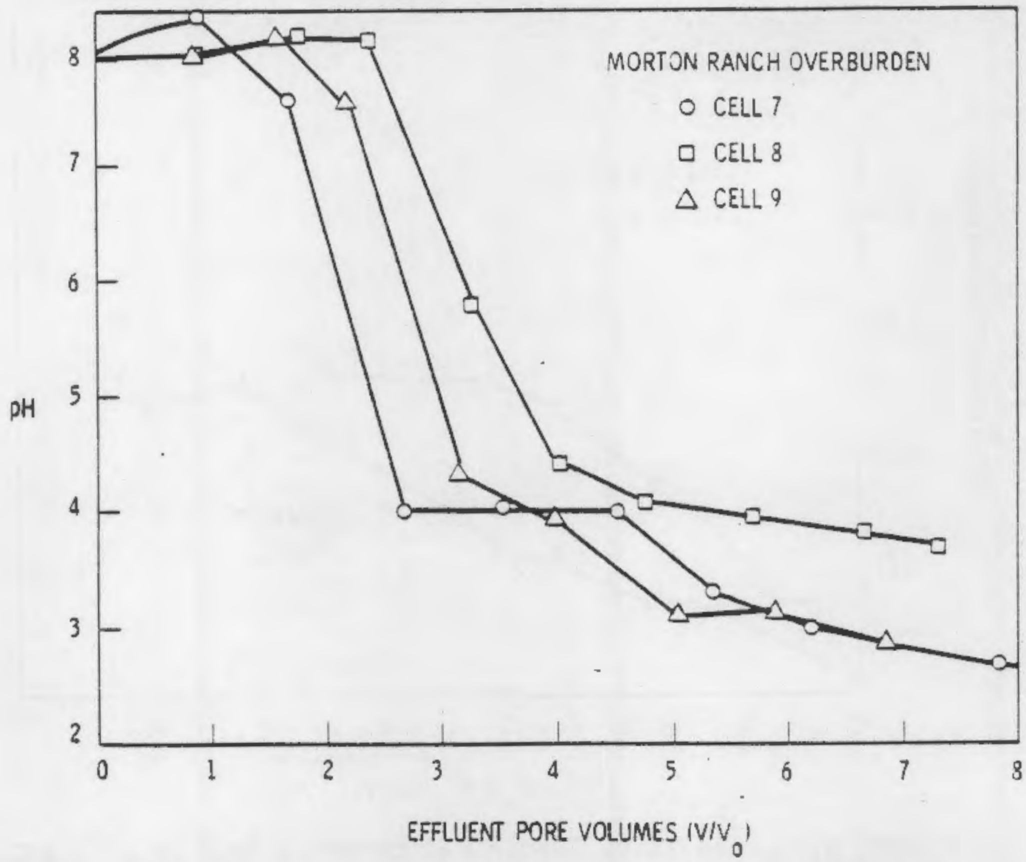


FIGURE 4.14. Effluent pH as a Function of Pore Volumes Eluted from Morton Ranch Overburden

substantially less concentrated than the influent, particularly for the first 3 or 4 pore volumes. The previous section's analysis of seepage rates through a 1-m thick clay liner for a 20-year period suggests that the sulfate concentration potentially reaching the ground water would never be more than about 2600 mg/l for a tailings solution whose initial concentration is 13,000 mg/l. These results suggest that the model analysis of contaminant transport by Nelson et al. 1980 is highly conservative since they considered the sulfate to be water coincident, i.e., with no chemical reactions taking place. The exact nature of the chemical reaction between the clay and the sulfate has not been thoroughly investigated, but the next sections on aluminum and iron suggest possible ways that sulfate is interacting with the clay liner material.

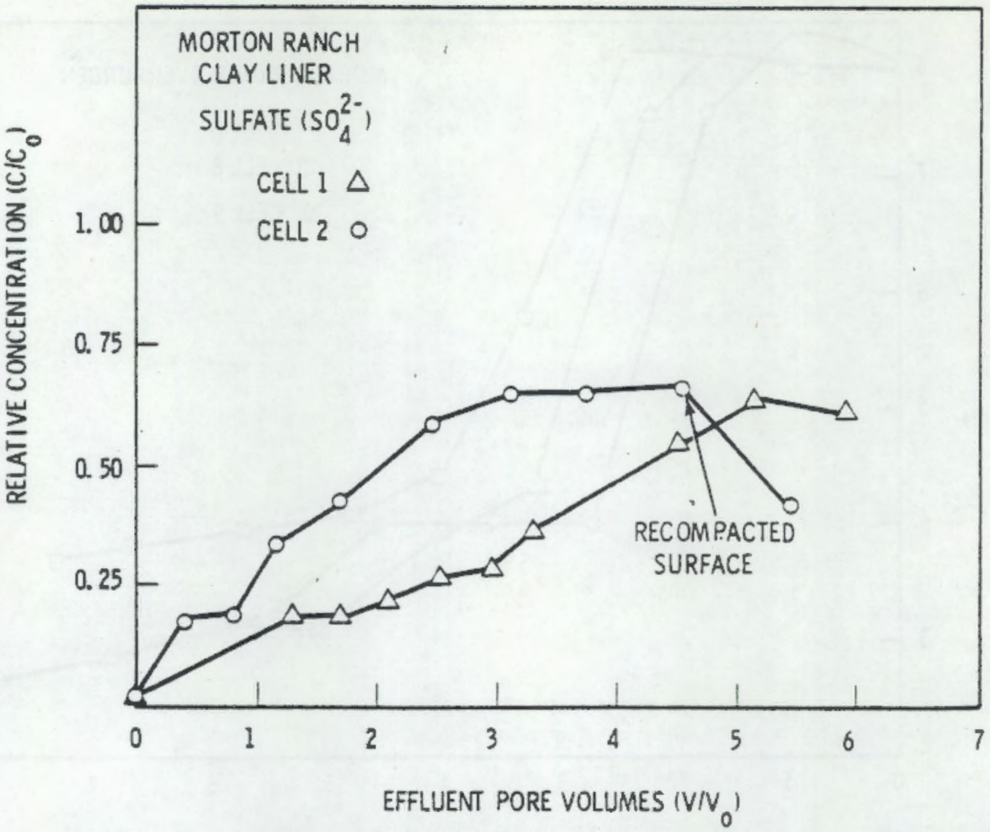


FIGURE 4.15. Relative Concentration of Sulfate in Effluent from Morton Ranch Clay Liner as a Function of Effluent Pore Volumes

Aluminum. Figure 4.16 shows the aluminum and iron concentrations in the effluent from Morton Ranch clay liner samples after prolonged leaching with tailings solution. The solubility of the iron and aluminum (and hence, the effluent concentration of these species) is controlled by the chemical and mineral equilibrium that exists within the solution when it comes in contact with the clay liner material. In the case of aluminum, numerous equilbria govern its solubility. Several aluminum oxides, hydroxides, and complex aluminosilicates exist in soils. In the test flow system, the aluminum concentration is dependent on amorphous forms of all these aluminum compounds. From the species that are present in the effluent solution, it would appear that as the acid front begins to move through the clay material, silicon is dissolved from

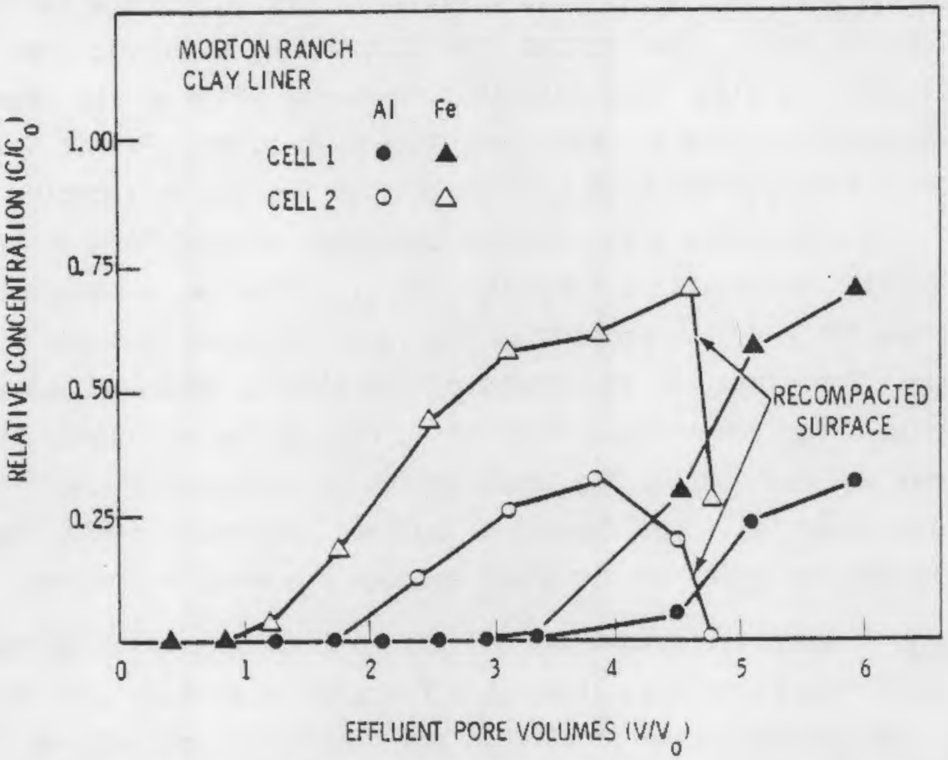


FIGURE 4.16. Relative Concentration of Al and Fe in Effluent from Morton Ranch Clay Liner as a Function of Effluent Pore Volumes

the clay and combined with the silicon already present in the tailings solution, and aluminosilicates begin to precipitate. The important point to consider is the fact that the major portion of the aluminum, silicon, and other elements which form amorphous mineral precipitates are supplied by the tailings solution. This decreases the weathering power of the tailing solution, because it must first redissolve the less stable amorphous solids before attacking the more stable crystalline forms of the soil (Lindsay 1979). Weathering of the crystalline forms will still take place in that portion of the clay material that is approaching the influent pH (2 to 3). As dissolution of primary clay minerals continues, a group of more stable secondary forms begins precipitating. Secondary mineral formation has been documented by several authors (Breeman 1976, Rhodes and Lindsey 1978, Bolt and Bruggenwert 1978). Conditions required for this process to occur have been found in nature and are characterized by high sulfate concentration, soluble aluminum or iron, and a pH of below 4. At pH's below 4, an amorphous mineral form of alunite — $KAl_3(SO_4)_2(OH)_6$ — which is less soluble than gibbsite — $Al(OH)_3$ — is the primary solid phase.

Iron. The iron in the tailings solution is present in the ferrous (Fe^{2+}) oxidation state. The ferrous iron is oxidized to ferric iron (Fe^{3+}) after contacting the clay liner material. This was noted by the change in color of the solution from a light green to a rust color. Ferric hydroxide precipitate — $Fe(OH)_3$/amorphous — forms at high pHs and only begins to redissolve as the pH approaches 4.0. Another amorphous mineral form of iron that will precipitate is jarosite — $KFe_3(SO_4)_2(OH)_6$. Jarosite, a member of the alunite group, has chemical properties that are analogous to those of alunite for aluminum. The formation of members of the alunite group is common in acid sulfate soils. From the concentration of sulfate in the effluent, it is apparent that at least 50% of the total amount of sulfate has been removed by the clay liner material. The removal of sulfate continues even at low pHs, which reinforces the case for amorphous secondary mineral formation.

Silicon. Figure 4.17 shows the silicon (Si) concentration in the effluent from the Morton Ranch Clay liner as a function of pore volumes of effluent. The initial low concentration of silicon and subsequent increase with decreasing pH suggests that some solubility of the Si occurs as pH decreases, in keeping with concepts of mineral solubility (Lindsay 1979) for solutions of low concentration in contact with silicate minerals. However, Table A.8 indicates that when the solution has a high initial concentration of Si, as does the tailings solution, that the subsequent concentration of Si is well below the initial concentration (by a factor of 9 to 10) even after extensive leaching (8 pore volumes), which suggests that Si is being precipitated or that it is reacting chemically with the clay minerals.

The scope of this section has been to determine to what extent the tailings solution has dissolved the clay liner material and whether the clay liner is a good barrier to chemical migration. Several conditions that are important to determining when the clay liner material has been chemically breached, can be summarized as follows.

1) Significant pH changes. The primary dependence of effluent chemical composition is on pH. Heavy metal and radionuclide effluent concentrations do not change until the buffering capacity is overcome and the pH of the effluent drops.

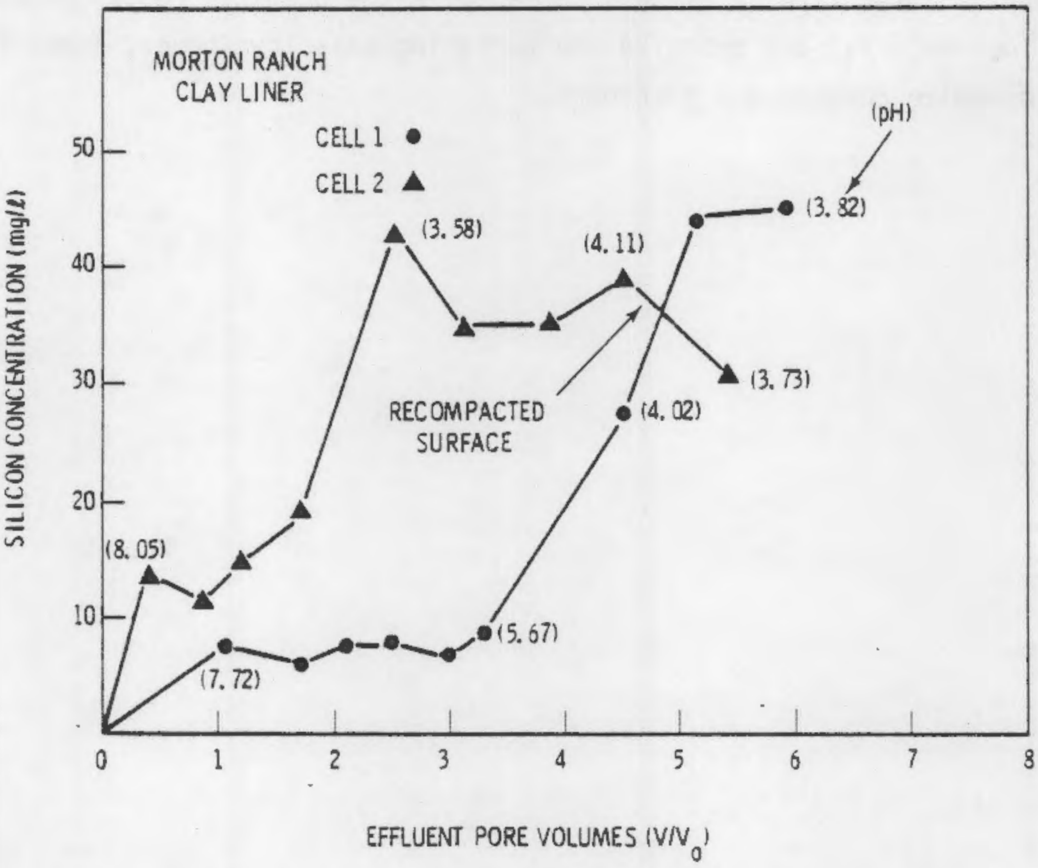


FIGURE 4.17. Relative Concentration of Sulfate in Effluent from Morton Ranch Clay Liner as a Function of Effluent Pore Volumes

2) Increased sulfate concentrations. Sulfate concentrations of effluent increase somewhat more rapidly than pH but are always less than influent values.

3) Increased iron and aluminum concentrations. In low-permeability media, the iron and aluminum breakthrough is severely retarded, because these species will precipitate as hydroxides and as amorphous members of the alunite mineral group. The dependence of these reactions on flow can be illustrated by the dramatic drop in iron and aluminum concentrations after recompation of cell 2 (see Figure 4. 16). These precipitates tend to decrease permeability.

In summary, we can say that the permeability has not yet been adversely affected by the tailings solution. In addition, with a decrease in permeability, the clay liner material will have an increased ability to impede chemical transport. Lower flow rates tend to maximize the chemical reactions with the clay liner material and optimize the buffering capacity; hence, lower flow rates minimize contaminant transport.

RECOMMENDATIONS

Based on the laboratory test results, several general recommendations can be made regarding mill tailings management at Morton Ranch.

1. No disposal of untreated tailings that would allow ground water to come into direct contact with the tailings should be permitted. Acid leachate of low pH (below 3) contains heavy metals and radionuclides in concentrations exceeding MPC values.

2. Neutralization of the tailings will provide optimum control for long-term protection against ground water contamination by leachate. However, for drained tailings in clay lined pits, leachate losses should be minimal because compacted clay liner permeabilities are very low.

3. Chemical analysis for heavy metals in tailings solution and seepage water from tailings pits or ponds should be run against standards that correct for matrix interference by sulfate and total dissolved solids. ICP analysis is not recommended for uranium or thorium. Radiochemical data from properly calibrated intrinsic germanium diodes should provide the most direct way to analyze for uranium and the most important uranium daughter products found in mill tailings and mill tailings solution.

4. On-site clay and siltstone materials to be used for clay liners should be tested to assure that EPA liner requirements are met, particularly regarding texture and clay percentages. In addition, 90% or greater compaction is recommended to assure that minimum permeability is achieved.

REFERENCES

ASTM. 1978. Annual Book of ASTM Standards Part 19. American Society for Testing and Materials, Philadelphia.

A.P.H.A. 1975. Standard Methods for the Examination of Water and Waste Waters. 14th Edition, APHA. Washington, D.C.

Barrow, N. J., and T. C. Shaw. 1979. "Effects of Solution:Soil Ratio and Vigour of Shaking on the Rate of Phosphate Adsorption by Soil." J. Soil Sci. 30:67-76.

Black, C. A. 1965. Methods of Soil Analysis. Part 1. Physical and Minerological Properties Including Statistics of Measurement and Sampling. American Society of Agronomy Monograph 9.

Bolt, G. H. and M. G. M. Brugenwert. 1978. Soil Chemistry. A. Basic Elements, p. 166. Elsevier Scientific Publishing Company, Amsterdam, The Netherlands.

Breeman, N. van. 1976. "Genesis and Solution Chemistry of Acid Sulfate Soils in Thailand." Agric. Res. Rep. (Versl. landbouwk Onderz.) 848. Wegeningen, The Netherlands.

Brown, K. W. and D. Anderson. 1980. "Effect of Organic Chemicals on Clay Liner Permeability." In Proceedings of the Sixth Annual Research Symposium on Disposal of Hazardous Waste, Chicago, Illinois.

Davis, S. N. and R. J. DeWiest. 1966. Hydrogeology. John Wiley and Sons. New York. 463 p.

Erdtmann, G. and W. Soyka. 1975. "The Gamma-ray of Radionuclides, Ordered by Atomic and Mass Number." J. Radioanalytical Chem. 27:137-286.

Gee, G. W., A. Bauer, and R. S. Decker. 1978. "Physical Analyses of Overburden Materials and Mined Land Soils." Amer. Soc. of Agron. 38:665-686, In F. W. Schaller and P. Sutton (eds.) Reclamation of Drastically Disturbed Lands. Madison, Wisconsin.

Kimberley, M. M. 1978. Uranium Deposits, Their Minerology and Origin. Short course by the Minerological Association of Canada, Volume 3.

Lindsay, Willard L. 1979. Chemical Equilibria in Soils. p. 35,129, John Wiley and Sons. New York, New York.

Nelson, R. W., A. E. Reisenauer and G. W. Gee. 1980. Model Assessment of Alternatives for Reducing Seepage of Contaminants from Buried Uranium Mill Tailings at the Morton Ranch Site in Central Wyoming. PNL-3378, Pacific Northwest Laboratory, Richland, Washington.**

Quinby-Hunt, M. S. 1978. "A Survey of Instruments Used for Monitoring Metals in Water." Amer. Lab. 10(13):17-37.

Rhodes, E. R. and W. L. Lindsay. 1978. "Solubility of Aluminum in Some Soils of the Humid Tropics." J. Soil Sci. 29:324-330.

Reisenauer, A. E. 1973. Calculation of Soil Hydraulic Conductivity from Soil Water Retention Relationships. BNWL-1710, Pacific Northwest Laboratory. Richland, Washington. **

Sherard, J. L., L. P. Dunningan, and R. S. Decker. 1976. "Identification and Nature of Dispersive Soils." Am. Soc. Civil Engr. J. Geo-tech. Eng. Div. 101 (GT4).

U.S. Environmental Protection Agency. 1978. Hazardous Waste. Proposed Guidelines and Regulations and Proposal on Identification and Listing. Federal Register, 43(243):58946-59026.

U.S. Environmental Protection Agency. 1979. "Selenium, Method 270.3, Gaseous Hydride." In Methods for Chemical Analysis of Water and Wastewater. EPA-600/4-79-020. U.S. EPA, Cincinnati, Ohio. **

U.S. Nuclear Regulatory Commission. 1979a. Final Environmental Statement: Morton Ranch Wyoming Uranium Mill, United Nuclear Corporation. NUREG 0532. Washington, D.C. *

U.S. Nuclear Regulatory Commission. 1979b. Draft Generic Environmental Impact Statement on Uranium Milling. NUREG 0511, Washington, D.C. ***

Ward, A. F., H. R. Sobel and R. L. Crawford. 1976. "The Preservation of Accuracy in the Determination of Trace Elements in Complex Matrices Using Inductively Coupled Argon Plasma Optical Emission Spectroscopy." Paper presented at the 3rd Annual FACSS Meeting, November, 1976. Philadelphia.

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APPENDIX A

ICP ANALYSIS OF THE URANIUM MILL TAILINGS SOLUTIONS

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Knowledge of the chemical make-up of the tailings solution was necessary for understanding its interactions with pit liner materials. An increasingly common technique for multielement analysis was used for our study: inductively coupled argon plasma emission spectroscopy (ICP). For a wide range of samples analyzed by ICP, there are virtually no chemical interferences. The extremely high temperatures achieved with the plasma completely break down compounds and discourage the formation of new ones. Also, most element concentrations are linear for a range of greater than 100,000 units. This permits analysis of samples with extremes in element concentrations. Detection limits are also very low for many elements. The concentration that gives a signal equal to twice the standard deviation of the background is defined as the detection limit. Table A.1 lists the range of detection limits for water that have been reported from different sources.

TABLE A.1. Detection Limits for Water Reported by Several Manufacturers of Inductively Coupled Argon Plasma Emission Spectrometers (in μg/l)(a)

Element	Detection Limit	Element	Detection Limit
Ag	4-15	Mo	5-22
Al	7-15	Na	1-75
As	20-330	Ni	6-19
Ba	0.2-5	P	30
Ca	0.9-4	Pb	20-50
Cd	1-5	Se	20-93
Co	2-5	Si	10
Cr	2-6	Sn	6-70
Cu	1-2	Th	75-1000
Fe	0.5-3	U	75
Mg	0.5-50	Zn	2-10
Mn	0.2-0.5	Zr	2-5

(a) Taken from Quinby-Hunt (1978)

MATERIALS AND METHODS

The samples were analyzed using a Jarrell-Ash Plasma AtomComp Direct-Reading Spectrometer with its inductively coupled argon plasma source. The atomized sample is carried on a stream of argon gas into the argon plasma. Elements are thermally excited and they emit light which is collimated and directed onto a grating surface. The diffracted light is converted to electrical energy proportional to the light's intensity by photomultiplier tubes. A computer then converts the signals to concentration units and outputs the information.

Standards

The high excitation temperatures of ICP reduce the need for careful sample standard matrix matching. Standards, prepared from Spex certified standards, were periodically analyzed to monitor machine calibration. These standards were originally formulated for use in analyzing geothermal samples, which typically are acidic and have a wide complement of heavy metals. The chemical composition of the standards used and their ICP detection limits are listed in Table A.2. Table A.3 contains ICP computer printout data for two of the standards. Values, in mg/l, are reported for more elements than were actually added for the standard. Detection limits were established based on these spectral interferences.

For samples with concentrations greater than the standards, dilution was required before analysis. Distilled, deionized water was used to make the five-, ten-, or one hundred-fold dilutions. Whenever a sample was diluted to bring it within the range of the standards, the detection limits had to be adjusted accordingly; i.e., a ten-fold dilution statistically corresponded with a ten-fold increase in detection limit. This explains the different detection limits reported for an element for two different solutions.

TABLE A.2. Standard Composition and Detection Limit for ICP Analysis (mg/l)

Parameter	Concentration in Standards	Detection Limit
Ag	10	0.04
Al	10	0.1
As	10	0.1
Ca	50	0.1
Cd	10	0.01
Cr	10	0.01
Cu	10	0.1
Fe	10	0.1
Li	10	0.05
Mg	10	0.05
Mn	10	0.01
Mo	10	0.1
Na	500	5.0
Ni	10	0.08
P	10	0.5
Pb	10	0.1
Se	10	0.1
Si	100	0.1
Sr	10	0.01
Th	10	0.1
U	10	0.05
Zn	10	0.05
Zr	10	0.05

TABLE A.3. ICP Data for Two Standards Showing Matrix Interferences

```
0/   STD 3
EHGCGHAC

BURN # 1   GEOT         8:27    30JAN80
  1676
 9.999   .0080  10.11   .2408  10.17    23.2  9.790   .1426     503   .2136
 .3163   10.17
 .0173   .1339  .0061 <     0  .0040   .0124  .0022   10.07   10.23 <     0
 9.599 <     0  10.14   .6517  10.01   .4384 <     0   .0725   9.924


BURN # 2   GEOT         8:28    30JAN80

AVERAGE    GEOT         8:28    30JAN80
   IS
  1677
   AL       B      BA      CA      FE       K      LI      MG      NA       P
 9.990   .0078  10.11   .2398  10.16    26.3  9.758   .1365     504   .2877
   SI      SR
 .3199   10.17
   AG      AS      CD      CO      CR      CU      MN      MO      NI      PB
 .0284   .1189  .0037 <     0  .0056   .0121  .0022   10.08   10.19 <     0
   SB      SE      SN      TH      TI      TL       U      ZN      ZR
 9.569 <     0  10.04   .6596  10.00   .4819 <     0   .0583   9.932

*0/   STD 4
EHGCGHAC

BURN # 1   GEOT         8:54    30JAN80
  1679
<    0   9.897  .0000   .4824  .0149    7.78  .0021   .2045    1278   9.871
 101.7   .0149
 .0070   10.48 <     0 <     0  9.593   .0021  .0012   .0765   .0195   .0084
 .0195   8.269 <     0 <     0  .0080 <     0  .0030 <     0   .0231


BURN # 2   GEOT         8:55    30JAN80

AVERAGE    GEOT         8:55    30JAN80
   IS
  1679
   AL       B      BA      CA      FE       K      LI      MG      NA       P
<    0   9.941  .0001   .4390  .0125    10.4  .0026   .2157    1280   10.07
   SI      SR
 102.0   .0140
   AG      AS      CD      CO      CR      CU      MN      MO      NI      PB
 .0089   10.47  .0011 <     0  9.617   .0019  .0002   .0734   .0033   .0000
   SB      SE      SN      TH      TI      TL       U      ZN      ZR
 .0088   8.234 <     0  .0047   .0087 <     0  .0328 <     0   .0224
```

RESULTS

Matrix Interferences

Sample matrix problems are not totally eliminated in ICP analyses. Solution viscosity and dissolved solids content are the most prevalent matrix problems. Ward, Sobel and Crawford (1976) reported interferences from sulfuric acid and dissolved solids. A 1M sulfuric acid solution showed significant suppression of element concentrations over unacidified standards. Hydrochloric, perchloric and nitric acid exhibited only small influences at the 1M level. This information is reproduced in Table A.4.

Uranium mill tailings solution from the sulfuric acid leach process should experience matrix interferences. The Highland Mill tailings solution had a 0.13M sulfuric acid concentration. It was assumed that the reported ICP results were suppressed because of the sulfuric acid, but the extent was not determined for all elements. The recommended procedure for future analysis of uranium mill tailings solutions is preparation of elemental standards more closely matching sample acidity for all reported elements.

TABLE A.4. Effect of 1M Acids on Analytical Signals of Elements at the 250 μg/l Level

Element	HCl	$HClO_4$	HNO_3	H_2SO_4
Al	+5%	0	-11%	-30%
Ca	(a)	(a)	-14%	-42%
Cd	+2%	-4%	-10%	-29%
Co	+2%	-4%	-7%	-26%
Cu	+1%	-5%	-7%	-30%
Mg	+2%	-5%	-7%	-23%
Na	-11%	(a)	+3%	-45%
Ni	0	-5%	-8%	-30%
Zn	+5%	-3%	-10%	-30%

(a) No measurement due to acid impurities

The other major matrix problem, dissolved solids content, causes unwanted radiation that enhances elemental values. All unwanted radiation reaching the detector is treated as background. Corrections were made wherever possible or the detection limits were raised to account for the excess. Ward, Sobel and Crawford (1976) reported the effects of 1000 mg/l concentrations of Al, Ca, Fe and Mg on Al, As, Cd, Co, Cr, Cu, Fe, Mn, Pb and background. Iron produced the highest interferences of the four cations tested. Table A.5 shows the results.

These interferences were observed from the analysis of six synthetic uranium mill tailings solution samples. The synthetic solution was formulated to contain the major elements of the tailings solution except for the radionuclides. Positive signals for elements not added to the synthetic solution appeared in the uncorrected data. The composition of the synthetic solution and the analytical results are listed in Table A.6. One or more of the tabulated values for As, Cd, Co, Cr, Cu, Mn, Pb, Si, Sr, Th and Zn were observed greater than the corresponding detection limit. The average of the

TABLE A.5. Matrix Interference from 1000 mg/l Concentrations of Al, Ca, Fe and Mg with Other Elements (expressed in µg/l)

Element	Wavelength	Al	Ca	Fe	Mg
Al	308	(a)	40	400	180
As	197	4350	0	1350	300
Cd	227	40	0	320	40
Co	239	12	5	10000	20
Cr	268	7	12	150	30
Cu	325	30	15	125	65
Fe	260	70	45	(a)	160
Mn	258	20	4	90	20
Pb	220	1900	0	810	150
BKg	252	120	65	11300	280

(a) Major element

TABLE A.6. Analysis of UMT Synthetic Solution, in mg/l

Element	Amount Added to Solution	Amount Found in Solution
Al	577	571 (8)[a]
As	3.5	6.6 (31)
Ca	484	530 (7)
Cd	-	1.6 (74)
Cr	-	0.2 (113)
Cu	-	2.3 (193)
Fe	2215	2226 (30)
Mg	650	656 (5)
Mn	-	2.2 (8)
Na	308	348 (6)
Ni	-	0.4 (58)
Se	-	none reported
Si	-	1.8 (101)
Sr	-	0.3 (29)
Th	-	0.7 (57)
Zn	-	0.7 (80)

(a) Coefficient of variation

values did fall below the detection limits for all except Cd, Cu and Mn. There were no apparent interferences for Ag, Mo, Ni, Se, Sn, U and Zr. In general, the detection limits derived from the geothermal standards did account for the matrix interferences from dissolved solids at high concentrations.

Problem Elements

Arsenic

The reported arsenic value of 3.5 mg/l is very questionable. As a check, synthetic tailings solution without As added was submitted for ICP analysis. It was reported to have 6.8 mg/l As, which was similar to that reported for five samples with 3.5 mg/l. To date, the spectral interferences have not been identified for arsenic.

Selenium

It is suspected that the presence of sulfuric acid suppresses the Se signal. No selenium had been detected in the uranium mill tailings or synthetic solutions below a pH of 4.0. The gaseous hydride method (EPA 1979) gave a value of 0.6 mg/l for the mill tailings solution. Values greater than 1 mg/l were reported in neutralized samples from the attenuation studies. Since the neutralized solution had been separated from the tailings, neutralization could not have released selenium from the tailings. The actual concentration of selenium in mill tailings solution could not be determined accurately from ICP analysis.

Uranium

ICP is reported as a good method for detecting uranium, however, sulfuric acid suppression is again suspected. Samples supposedly containing uranium were analyzed but no uranium was detected. This observation was brought to the attention of the analyst, who then determined the U concentration to be 100 mg/l. Based on radiochemical results, the level of uranium in the solution was calculated to be approximately 40 mg/l, which more closely reflects the concentration expected to remain from the mill processing. Here again, the actual concentration of uranium in mill tailings solution could not be accurately determined by ICP analysis.

Permeability Cell Data

Results from the ICP analysis for a series of leachate samples from cells P1, P5, and P8 are shown in Tables A.7, A.8, and A.9, respectively. Also presented are anion data from ion chromatography analysis run on the same samples. These tables reflect the type of the chemical analysis performed on the leachate samples. Where the analysis was below detection limits for a particular element, it is so indicated. Adequate analysis was obtained for the macroions Ca, Mg, Na and a number of the metal ions, particularly, Al, Fe, and Mn.

CONCLUSIONS

Within the limits specified, ICP is a good multi-element analysis method for uranium mill tailings solutions. There are some matrix interferences due to the complex nature and acidity of the solutions. Detection limits are higher than those for solutions with less complex matrices. Future use of standards acidified with sulfuric acid should reduce the uncertainty associated with some of the elements in uranium mill tailings solutions.

TABLE A.7. ICP Analysis: Permeability Cell P1 - Clay Liner and Synthetic Tailings Solution

	Leachate Samples (mg/l)									
Pore Volume:	1.26	1.68	2.12	2.54	2.95	3.30	4.47	5.15	5.89	Detection Limit(1)
pH:	7.72	7.90	7.75	7.68	7.80	5.67	4.02	4.30	3.82	
Element										
Al	DL(1)	DL	DL	DL	DL	DL	28.3	140	186	0.1
As	DL	DL	DL	DL	DL	DL	0.6	4.4	3.6	0.1
Ca	618	508	633	680	644	675	595	570	541	0.1
Cd	DL	DL	DL	DL	DL	0.02	0.4	0.9	0.7	0.01
Cr	DL	DL	DL	DL	DL	DL	0.2	0.5	0.02	0.01
Cu	0.02	DL	DL	DL	0.4	0.06	DL	0.2	0.2	0.01
Fe	DL	DL	DL	DL	DL	31.5	645	1312	1582	0.1
Li	DL	DL	DL	0.2	0.2	0.3	0.3	0.4	0.5	0.05
Mg	340	362	382	478	650	744	981	1091	1063	0.05
Mn	0.2	0.7	1.4	2.6	4.2	5.2	7.0	8.0	7.9	0.01
Mo	DL	DL	DL	DL	DL	DL	DL	DL	DL	0.1
Na	220	231	238	256	304	330	350	420	399	5.0
Ni	DL	DL	DL	0.44	1.2	1.9	3.8	5.3	4.9	0.08
P	DL	DL	DL	DL	DL	1.2	9.5	12.0	12.9	0.5
Pb	DL	DL	DL	DL	DL	DL	0.9	2.0	DL	0.1
Se	DL	DL	DL	DL	DL	DL	1.5	3.3	DL	0.1
Si	7.2	5.8	7.2	7.8	6.8	8.3	27.8	44	45	0.1
Sr	10.0	7.3	11.5	14.0	19.0	21.3	21.0	19.8	18.7	0.01
Th	DL	DL	DL	DL	DL	DL	2.0	2.4	0.4	0.1
U	DL	DL	DL	DL	DL	DL	23.1	44	DL	0.05
Zn	0.50	0.56	DL	0.46	3.0	2.1	7.1	9.1	7.2	0.05
By Ion Chromatography										
Cl	121	98	97	83	88	94	100	123	97	0.05
SO_4	2445	2340	2690	3444	3833	4714	7147	8304	7984	0.1

---

(1) DL = Less Than Detection Limit

TABLE A.8. ICP Analysis: Permeability Cell P5 - Clay Liner and Tailings Solution

	Leachate Samples (mg/l)					
Pore Volume:	1.35	3.46	5.54	6.24	7.91	
pH:	8.20	8.00	4.80	4.20	3.80	Detection(1) Limit
Element						
Al	DL(1)	DL	DL	45.2	161	0.1
As	DL	DL	DL	0.7	0.8	0.1
Ca	592	551	739	461	421	0.1
Cd	DL	DL	0.2	0.4	0.8	0.01
Cr	DL	DL	0.08	0.1	0.1	0.01
Cu	DL	DL	0.08	0.1	0.2	0.01
Fe	DL	DL	127	538	950	0.1
Li	DL	0.4	1.2	1.0	1.1	0.05
Mg	192	490	1340	1466	1671	0.05
Mn	DL	2.4	41.2	64.4	89.6	0.01
Mo	DL	DL	DL	DL	DL	0.1
Na	152	272	408	296	285	5.0
Ni	0.2	0.4	3.6	0.7	9.6	0.08
P	DL	DL	2.0	2.8	2.8	0.5
Pb	DL	DL	DL	DL	0.4	0.1
Se	DL	DL	DL	DL	DL	0.1
Si	3.2	7.2	15.2	23.2	28.8	0.1
Sr	9.6	13.6	26.4	22.4	22.0	0.01
Th	DL	DL	0.8	2.0	3.2	0.1
U	0.4	0.56	DL	DL	DL	0.05
Zn	0.5	0.64	8.4	14.4	19.6	0.05
By Ion Chromatography						
Cl	132	292	402	303	306	0.05
SO_4	2220	3704	7864	9492	12192	0.1

DL(1) = Less Than Detection Limit

TABLE A.9. ICP Analysis: Permeability Cell P8 - Overburden and Tailings Solution

	Leachate Samples (mg/l)								
Pore Volume:	Ground water	0.84	1.75	2.59	3.24	4.03	8.77	10.55	
pH:	8.12	7.95	8.10	8.10	5.80	4.40	3.70	3.00	Detection Limit (1)
Element									
Al	DL	DL	DL	5.3	DL	89	939	1021	0.1
As	DL	DL	DL	0.8	DL	1.2	6.6	8.4	0.1
Ca	91.3	276	1421	815	721	492	432	450	0.1
Cd	DL	DL	DL	DL	0.04	0.2	0.2	0.2	0.01
Cr	DL	0.01	DL	0.1	DL	0.12	1.0	1.6	0.01
Cu	0.04	0.04	0.1	0.02	0.04	0.2	1.2	2.4	0.01
Fe	DL	DL	DL	0.1	1.2	146	90	112	0.1
Li	DL	DL	0.3	0.7	0.6	1.0	1.3	1.2	0.05
Mg	47.6	83.6	446	737	1037	1384	1082	960	0.05
Mn	DL	0.04	0.3	7.6	32.8	62.7	75.6	74	0.01
Mo	DL	DL	DL	0.2	DL	DL	DL	DL	0.1
Na	41.9	82.4	210	296	298	302	289	280	5.0
Ni	DL	0.08	DL	0.5	1.2	3.2	4.4	3.6	0.08
P	DL	DL	DL	10.2	2.0	1.2	0.8	1.6	0.5
Pb	DL	0.16	DL	0.4	DL	DL	DL	DL	0.1
Se	0.71	DL	DL	1.7	DL	DL	DL	DL	0.1
Si	11.3	6.4	12.3	17.0	15.2	39	104	158	0.1
Sr	1.4	3.7	17.2	15.7	18.0	18.8	10.4	8.4	0.01
Th	0.13	0.24	DL	1.6	DL	2.8	9.2	10.0	0.1
U	1.6	2.1	6.8	4.4	DL	DL	DL	DL	0.05
Zn	DL	0.68	0.4	0.5	3.0	8.8	12.8	12.8	0.05
By Ion Chromatography									
Cl	41.0	52	216	347	326	296	303	306	0.05
SO_4	222	783	3793	4518	5752	8492	13700	13972	0.1

DL(1) = Less than Detection Limit

APPENDIX B

METHOD FOR DETERMINATION OF GAMMA EMITTING RADIONUCLIDES IN URANIUM MILL TAILINGS AND TAILINGS SOLUTION

APPENDIX B

METHOD FOR DETERMINATION OF GAMMA EMITTING RADIONUCLIDES IN URANIUM MILL TAILINGS AND TAILINGS SOLUTION

Uranium ore contains ^{238}U, ^{235}U, and 23 radioactive decay products. The time and effort involved in chemical separation of these nuclides make it impractical to use wet chemical techniques for their determination. As an alternative to chemical extraction, high resolution gamma spectroscopy is used. This method yields information on the majority of isotopes in both the ^{238}U and ^{235}U decay series. Accurate measurements by this method depend on reproducible sample geometry, detector efficiency calibration, and the choice of good analytical peaks. This appendix provides an explanation of the parameters involved in spectroscopic analysis done for this project.

SAMPLE PREPARATION

A fundamental principle for any good analytical technique is reproducible sample preparation. All solid samples were pressed into thin discs. These discs were made to the same standard dimensions. Soil samples were ground and mixed with a cellulose binder material at a fixed ratio. The mixed sample was then placed in a mold and pressed with 3.45 x 10^8 N/m^2 (50,000 lbs/in^2) pressure. Effluent solution samples were analyzed in the same fixed geometry disc form. A specific volume of solution was evaporated to dryness, and the remaining solids were quantitatively transferred. A total weight of solids was taken, and the amount of sample needed to achieve the proper ratio was mixed with the binding material and pressed. The weight of solids used, divided by the weight of solids from the total volume evaporated, multiplied by the volume of effluent evaporated, gives the equivalent volume of solution

$$\frac{\text{Solids Used (g)}}{\text{Solids in Total Volume (g)}} \times \text{Total Volume (ml)} = \text{Volume Used (ml)}$$

that was used in the disc. If the solids from the evaporated solution are less than that required to achieve the desired sample-to-binder ratio, a low activity sand is added to achieve the proper weight ratio. This procedure places both solid and liquid samples in a consistent geometry and allows for a single detector calibration on only one size and shape sample. To optimize detector performance, the sample is pressed to a thickness of less than 0.6 cm (0.25 in.), thereby minimizing sample self-attenuation. The samples are also sized to a diameter equal to that of the active diameter detectors of the beryllium window. By placing all of the sample in a direct line of sight to the diode, detector efficiency is maximized. Once all of these physical parameters have been fixed, counting can begin.

CALIBRATION

In calibrating an intrinsic germanium diode, three major steps must be taken. The first step is to obtain a standard material that has multiple peaks and similar activity over the range of energies to be used for sample analysis. This material should be an interlaboratory comparison standard of verifiable quality. The second step is to put the standard material in the same geometry as described for the samples. The third step in accurate detector calibration is to determine a photopeak, or full energy, efficiency curve for the analytical energy range. The detector photopeak efficiency is the fraction of gamma rays of a particular energy emitted from a source that appears in the corresponding photopeak of the pulse-height spectrum. The efficiency curve is determined by counting standards with known gamma ray activities in the same geometry that will be used for the experimental samples. Rate-dependent factors, such as dead-time and peak summing, should be considered and if necessary, corrections must be made for these effects. Insofar as the standard and experimental discs are of low activity, such rate-dependent factors are not expected to be significant.

The reciprocal of the product of the efficiency, $\epsilon\gamma$, and the absolute abundance, $\alpha\gamma$, for a gamma ray of energy, $E\gamma$ gives a scaler called the "d/c" (disintegration/net peak count). This scaler will convert the net photopeak counts to the absolute disintegration rate provided that no interference occurs at that energy level from gamma rays of other radioisotopes. The absolute abundance for a particular gamma ray is defined as the probability of emission per decay. Absolute abundance values are available from the literature and have been compiled by several authors.

PEAK SELECTION

Once the calibration of the detector has been completed, a list of all possible gamma energies with an abundance high enough to be analyzed is tabulated. Some energies will be used as analytical peaks, others to determine the overlap of peaks, and some will be unimportant because of the low activity of a certain nuclide in the sample. The relative peak heights of the various nuclides may change from sample to sample.

The two compilations used for comparison were the Table of Isotopes (TOI) (Lederer and Shirley, 1978) and "The Gamma-Ray Lines of Radionuclides, Ordered by Atomic and Mass Number," from the Journal of Radioanalytical Chemistry (JRC) (Ertmann and Soyka 1975). These two compilations were compared empirically by developing efficiency curves for a detector using each set of absolute abundance values and the known d/c. The curve developed with the TOI values had smaller deviations from the calibration points than did the JRC values. As a result of this empirical comparison, the TOI values were used for all calculations.

A good illustration of this is to compare the spectra of uranium ore and uranium mill effluent solutions. The uranium ore sample is in its natural equilibrium state, and its gamma spectrum consists of peaks from daughter radionuclides that are in equilibrium with the parent uranium isotopes. The mill effluent solution has been recycled several times. Uranium isotopes and their decay products are not in equilibrium in such a solution. Relative quantities of the nuclides in this sample are now dependent on each element's solubility as well as the decay constants. Some of these radionuclides are concentrated in the effluent solution, and their gamma peaks, which were not resolvable from background in the ore samples, are now significant.

To determine whether or not a peak is of analytical quality, several situations need to be addressed:

1) Can the peak be resolved from other peaks in its energy region?
2) If the peaks in one energy region cannot be resolved, can the contribution of each nuclide be quantified by calculating the contributions of one or more nuclides from another known peak?
3) If the gamma peaks from one particular nuclide are so close that they cannot be resolved, may the peaks still be used for analysis by summing the absolute abundances for each gamma photon?

The best method for continually checking the results for different nuclide concentrations is to use multiple peak analysis for as many nuclides as is possible within each sample. This process involves the comparison of the activity value of a single nuclide calculated for as many of its gamma energies as possible. Inconsistent results could go undetected if these cross-checking methods are not employed.

EXAMPLE ANALYSIS

To illustrate the applications of this method, here is the step by step procedure used for the analysis of ^{227}Ac in tailings solution. The reason for choosing ^{227}Ac is that its concentration can be confirmed by the many gamma energies of its short-lived daughters. The verifications of ^{227}Ac also incorporate many of the useful points in this method.

^{227}Ac emits no detectable gamma rays of significance, but it has a half-life that is long (22 years) when compared to its daughters. The effluent solution tested had been separated from the tailings solids for several months to insure that the nuclides in the ^{235}U decay chain, which occur after ^{227}Ac, were in equilibrium with the ^{227}Ac parent. This allows the use of any photo peaks emitted from the five gamma-emitting daughters to be used for analysis or confirmation.

The first step is to tabulate a list of all of the photo-peak energies that could possibly be used for calculation of ^{227}Ac activity. Table B.1 contains a list of the isotopes, absolute abundances, counting efficiencies,

TABLE B.1. Analysis Information for ^{227}Ac Measurement

ISOTOPE	Peak Energy (kev)	Efficiency	Absolute Abundance	Channel of Peak
^{227}Th	49.9, 50.1	0.14	0.0766	250
^{227}Th	236.0	0.025	0.112	1180
^{227}Th	256.0	0.21	0.0627	1280
^{223}Ra	269.6	0.19	0.140	1348
^{219}Rn	271.0	0.10	0.10	1355
^{223}Ra	324.0	0.0135	0.0412	1620
^{223}Ra	338.6	0.0125	0.0296	1693
^{211}Bi	351.1	0.0120	0.127	1755

TABLE B.2. Radionuclide Concentrations from Energy Spectrum Analysis

Isotope	Net Counts	Net Counts/min	d/c	d/m	d/m/l (a)
^{227}Th	8,043	20.52	93	1,908	9,976
^{227}Th	2,023	5.16	357	1,842	9,630
^{227}Th	1,041	2.66	759	2,019	10,554
^{223}Ra	1,996	5.09	276	1,913	10,004
^{219}Rn	1,531	3.91	526	2,057	10,751
^{223}Ra	331	0.844	1,798	1,517	7,933(b)
^{223}Ra	235	0.5995	2,703	1,620	8,468(b)
^{211}Bi	1,182	3.02	656	1,981	10,356

(a) d/m/l - disintegrations per minute per liter
(b) These peaks were not used for confirmation because of the low count rate.

channels near peak maximum, and gamma photon peak energies for the analysis of ^{227}Ac. The counting efficiency of the detector is taken from the efficiency curve at each respective energy (Figure B.1). For each peak of interest, a calculation of net counts must be made. In Figure B.2 this has been done for the 49.9 and 50.1 kev doublet peak of ^{227}Th. The net counts are calculated by subtracting background counts from gross counts at each channel in the

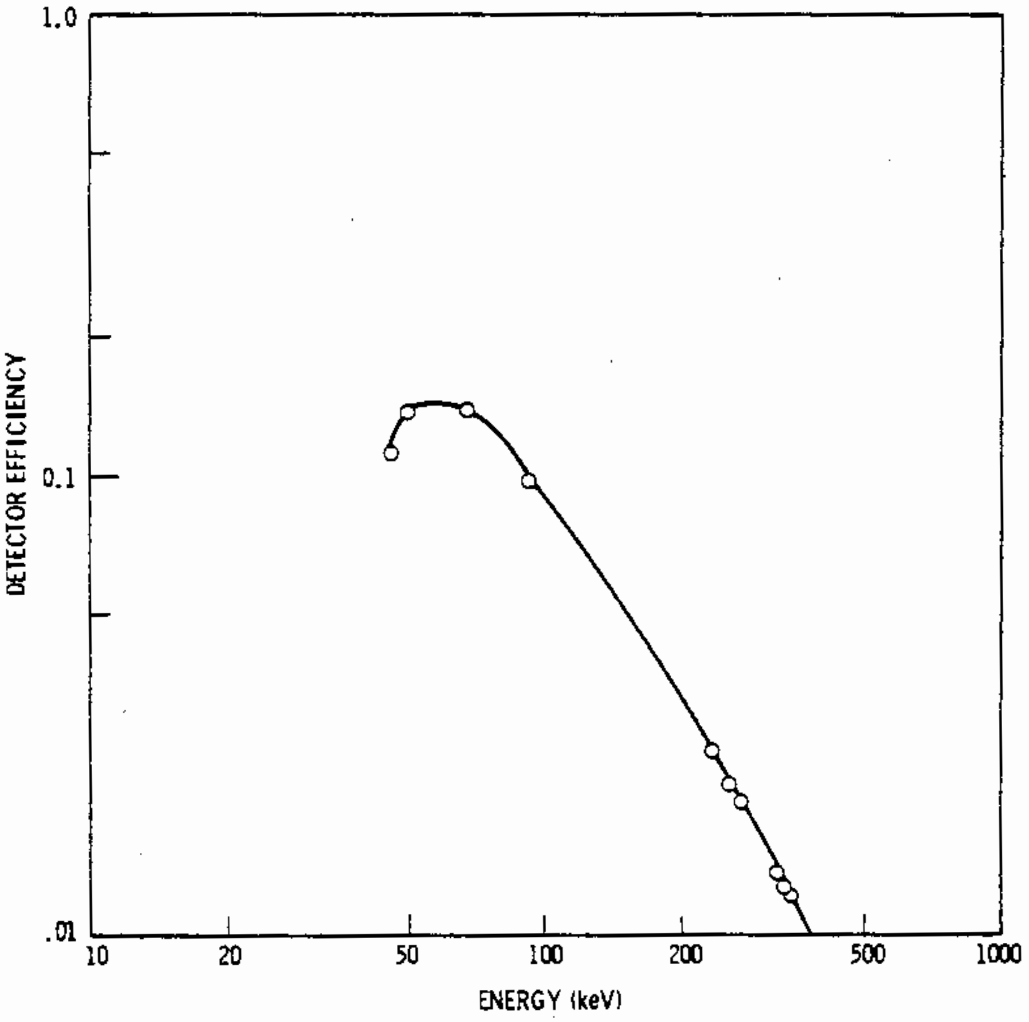
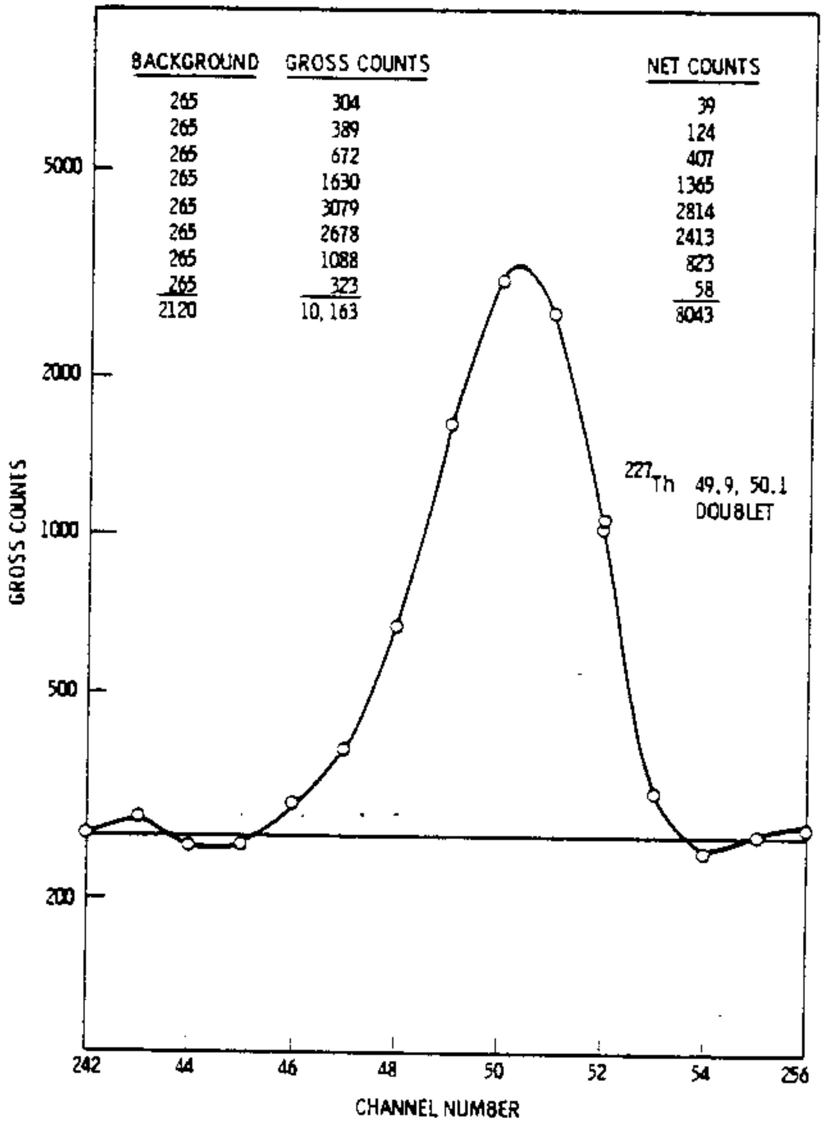


FIGURE B.1. Detector Efficiency Curve for Intrinsic Germanium Diode

peak. The net count is then divided by the counting time in minutes. The result of this division is the net count rate for a particular gamma photo peak. The net count rate is multiplied by the 'd/c' for that photo peak.

Calculation for ^{227}Th @ 49.9, 50.1 kev Doublet:

Gross Counts	10,163	8,043 net cts ÷ 392 min = 20.52 net cts/min
Background	2,120	20.52 net cts/min x 93 disintegration/net cts
Net Counts	8,043	= 1,908 disintegration/min



BACKGROUND	GROSS COUNTS	NET COUNTS
265	304	39
265	389	124
265	672	407
265	1630	1365
265	3079	2814
265	2678	2413
265	1088	823
265	323	58
2120	10,163	8043

FIGURE B.2. Energy Spectrum for ^{227}Th Double Peak for Intrinsic Germanium Diode (^{227}Th doublet occurs at 49.9 and 50.1 Kev.)

The disintegration rate that has been calculated is for a weight of salts for an equivalent volume. This disintegration rate (d/m) is then divided by the equivalent volume to give disintegration rate in disintegrations/min/liter: 1,908 d/m in 1,913 l counted = 9,974 d/m/l ^{227}Th.

These same calculations were done for all of the other peaks listed in Table B.1. Table B.2 shows the activity of the various ^{227}Ac daughters at all other tabulated energies. This method was used for all gamma spectroscopy measurements taken for this project.

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Laboratory tests were conducted to evaluate leachate from uranium mill tailings & its interaction with materials taken from the Morton Ranch Uranium Mill site in central Wyoming. Laboratory tests included:

1. Physical and chemical characterization of geologic materials from the Morton Ranch. The materials characterized were typical of those found in the area of the proposed tailings pits.
2. Physical and chemical characterization of acid leach tailings and tailings solution from the nearby Exxon Highland Mill.
3. Leaching tests with selected tailings materials and leach solutions.
4. Adsorption studies measuring the sorption characteristics of heavy metals and radionuclides on the Morton Ranch geologic materials under low and eeutral pH conditions.
5. Clay liner stability tests. These tests were designed to evaluate the mechanisms of clay liner alteration under acid attack and assess any long term changes in permeability of the clay liner materials.

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