THE INTERRELATION OF FACTORS INFLUENCING THE DISSOLUTION OF METALS
IN COLUMNS OF MINE TAILINGS[1]

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Abstract.--The dissolution of metal species from silver mine mill tailings containing quartz (70%) and manganiferous siderite was investigated using a column leach procedure. The effects of leachant ionic strength, pH, and buffering ability were examined. The results indicated increased metal transport with increased ionic strength and decreased pH. In another test series, matched sets of columns were compared to determine the effect of leachate residence time on metal concentration. In these tests, leachate metal ion concentrations more than doubled in columns that were allowed to evaporate (wet/dry cycle) about 30% of their pore leachate volume. The pH of the leachate eluted from the dry cycle (unsaturated column) decreased while the conductance increased. Increases of five times were observed for lead and manganese, while increases of two orders of magnitude were seen for zinc and cadmium. The wet/dry cycle effect was enhanced during subsequent cycles, but appeared not to be influenced by the addition of sodium lauryl sulfate, sodium benzoate, or phenol, which are known to inhibit microorganism involvement. Increased sensitivity to further oxidation of those columns that underwent the dry cycle became apparent through increased deviation of the ion yields from duplicate columns. The interrelation of the above factors with the composition of the tailings present adds complexity to determining dissolution mechanisms.

INTRODUCTION

It is generally accepted that rain percolating through mine wastes can dissolve and transport metals through the wastes and into the surrounding area. Depending on the toxicity of the metals in question and their relative concentrations, such a situation could lead to contamination of surface and ground waters, rendering them toxic to plants, fish, and animals. The question is, therefore, how can it be determined whether an individual site contains hazardous material?

The methods presently used to predict acid mine drainage (Ferguson 1987), although not completely successful, do offer one factor that may well influence the concentrations of leached metal species, and that is acidity. Studies by Calspan (Brainbridge 1980) and A. D.

Table 1.--Assay of silver mine tailings, pct.

Si	Fe	Al	C	Mn	Pb	Ca	Mg	S	Zn	K	Cu	As
35.4	6.6	2.4	1.8	0.65	0.43	0.25	0.25	0.16	0.11	0.08	0.04	0.02

Little, Inc. (Kuryk 1985), have produced additional information and protocols for column leach studies that may permit controlled laboratory experiments to intersect, divide, and isolate those kinetic and thermodynamic processes that influence the environmental mobilization of metal species through and out of mine mill tailings.

The laboratory program for this project involved a series of tests on mill tailings from a silver mine. We examined the effects of leachant ionic strength, leachant acidity, the presence of acetate ions, and the influence of a "wet and dry cycle" on the dissolution of metals. Analyses were performed on the leachates for aluminum (Al), calcium (Ca), cadmium (Cd), copper (Cu), iron (Fe), lead (Pb), manganese (Mn), magnesium (Mg), nickel (Ni), potassium (K), sodium (Na), and zinc (Zn). Ionic conductivity and pH were also determined for each leachate. The purpose of the study was to isolate certain parameters and to determine their kinetic effects on the overall transport of metal species within the tailings sample.

MATERIALS AND METHODS

Waste

The silver mine tailings used in this investigation contained partially liberated quartz (70%) and manganiferous siderite ($FeCO_3$-Mn) as principal gangue minerals. The quartz and chert ranged from 10 to 15 micrometers and the siderite from 10 to 100 micrometers. The principal metallic minerals were pyrite (FeS_2), galena (PbS), sphalerite (ZnS), minor chalcopyrite ($CuFeS_2$), minor tetrahedrite [$(Cu,Fe,Zn,Ag)_{12}Sb_4S_{13}$], and minor muscovite [$KAl_3Si_3O_{10}(OH)_2$]. Particles of these minerals ranged from 1 to 20 micrometers in diameter. A trace of digenite (Cu_2S) and possibly arsenopyrite (FeAsS) were detected by X-ray diffraction. The pyrite was generally not attached to other minerals and had shiny unaltered surfaces even though the tailings were weathered. A few pyrite grains had inclusions of galena and chalcopyrite. About one-half of the galena was completely included within siderite or, rarely, quartz. Most of the remaining galena was attached to siderite grains but had exposed surfaces; only a minor portion of the galena was free. Sphalerite occurred as large unattached grains or smaller grains attached to siderite. Chalcopyrite and tetrahedrite most commonly occurred

together as small inclusions in siderite or galena. A partial listing of the results of the destructive assay of the tailings is given in table 1.

The tailings samples used for all experiments were oven dried at 160° F in half-filled 55-gal drums. The material was crushed to its original size range, mixed well, and stored in large plastic drums.

Chemicals

All chemicals in this study were commercially available, analytical-grade reagents (A.R. grade) used without further purification. The deionized water was produced in the laboratory through distillation (Barnstead glass still) then deionized with a Barnstead NANOpure II Demineralizer[3] (18.8 megohm-cm). Leachant solutions were prepared by standard analytical techniques using only A.R. grade chemicals and prepared deionized water. They were then stored in carboys (Nalgene) until used.

Column Test Equipment and Methods

Leach columns were constructed from 2- or 4-ft lengths of 3-in-inside-diameter (ID) PVC pipe equipped with cemented couplings and bushings in which perforated Nalgene plates had been installed. A 9-cm G6 (Fisher Scientific) borosilicate glass fiber filter was placed on the perforated plate before installation of the bushing. Twenty of the 2-ft columns were mounted in a rack and arranged in groups of four, permitting a test sequence for five parameters. Combinations of other 2- and 4-ft columns were used for various specific experiments. A series of 10 similarly constructed 1-1/2-in-ID PVC columns were used to examine the effects of sample depth and column surface-to-volume ratios. These columns were arranged in series of two, again for a five-parameter study. Leachants were introduced to the columns drop by drop from a 1-liter polypropylene storage bottle through tygon tubing fitted with a screw clamp. Volumes of leachant used depended on an experimentally determined pore volume. Estimates of pore volume were made by weighing out 100 g of tailings, saturating the sample with deionized water, and placing it in a Buchner funnel. The

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[3]Reference to specific products or manufacturers does not imply endorsement by the Bureau of Mines.

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sample was covered, allowed to drip-dry overnight, and then reweighed. The difference in weight represented the weight of water stored in the pores of the sample. The columns to be used in a test series were then filled with the appropriate weight of tailings and enough leachant to saturate the column plus an additional 150 cm³. The difference between the leachant and leachate volumes gave a corrected pore volume. In all experiments, the leachant introduced was equal to or a specific fraction of the pore volume.

Slurry Test Methods

Where slurry procedures were used, a weighed sample of the tailings was placed into a 500 cm³ polypropylene rectangular bottle (Nalgene). Leachant was introduced in predetermined solid-to-liquid ratios. The bottles were placed on a variable-speed, reciprocating shaker for 4 to 16 hours. The samples were then filtered through no. 42 Whatman filter paper. The pH and conductivity of the leachate was determined, after which the leachate was acidified to 0.01$\underline{M}$ nitric acid for analysis by atomic absorption techniques or to about 2% nitric acid for analysis with ICP.

Equipment

Most of the metal analyses reported in this investigation were carried out with the aid of an IL 551 atomic absorption spectrometer. With the acquisition of a Perkin-Elmer Plasma II, ICP became the method of choice for metal analyses.

DISCUSSION OF RESULTS

Ionic Strength Effect

Tables 2-A and 2-B report leachate concentrations for leachants of various ionic strengths and pH's. The experimental method utilized 3-in columns; 2 kg of tailings samples (10.5-11 in, depth) per each column; four replicates; five different leachants of 0.001$\underline{M}$, 0.01$\underline{M}$, and 0.10$\underline{M}$ KNO$_3$; deionized water; and a sample of Western synthetic rain (Bainbridge 1980). The pore volume for this series was determined to be 500 cm³. Leachant pH was adjusted to approximately 5.5 (table 2-A) or 2.0 (table 2-B) with nitric acid.

It should be noted that all species demonstrated a rapid decrease in concentration from that shown in the initial saturation experiment (test 84) when from two to three pore volumes of leachant were added. After this initial decrease, leachate concentrations reached a near-constant value for all species. In nearly all cases, the concentration of metal contaminants was greatest for the 0.10$\underline{M}$ KNO$_3$ leachant. In general, the magnitude of this increased concentration was found to be due to changes in

solubility as a result of changes in activity coefficients. Unfortunately, the increased leachate pH of nearly 0.4 was above similar expectations. Furthermore, it was expected that this increased leachate pH would decrease metal dissolution, resulting in a combined effect of little to no apparent change in ion concentration.

With the adjustment of the leachant pH to a value of 2.0 using nitric acid, metal dissolution increased while the solution maintained the previous ionic strength effect and the leachate pH decreased to a value between 4.1 and 4.5. This sample of silver mill tailings appeared to have a strong buffer region between a pH of 4.5 to 3.5. The pH of a 20:1 liquid:solid slurry formed with deionized water and the silver mill tailings when varying amounts of sulfuric acid were added reproduced this buffer region (fig. 1). Table 2-B shows that leachate concentrations for most metal species (tests 012 through 016) declined after the initial influence of the acidic leachant, and that repeated "washing" with deionized water returned the system to the pre-acid leaching condition. Nickel concentrations in the leachates were found to be below detection limits (0.06 ppm) until the pH 2 leachant was used. A value of 1.06 ppm was observed for nickel concentrations of 0.10$\underline{M}$ KNO$_3$, 0.86 ppm for 0.01$\underline{M}$ KNO$_3$, and 0.82 for 0.001$\underline{M}$ KNO$_3$ (test 013). Initial cadmium leachate concentrations (test 84) were 0.39, 0.29, and 0.27 ppm for 0.10$\underline{M}$, 0.01$\underline{M}$, and 0.001$\underline{M}$ KNO$_3$, respectively. These values decreased to below detection limits (0.01) for all leachant systems except the 0.10$\underline{M}$ KNO$_3$ leachant (at 0.021) after the addition of two pore volumes of leachant (test 90). Cadmium concentrations remained below detection limits for all leachings until the acid leachant effect was observed, whereupon concentrations of 0.04 to 0.02 ppm were noted.
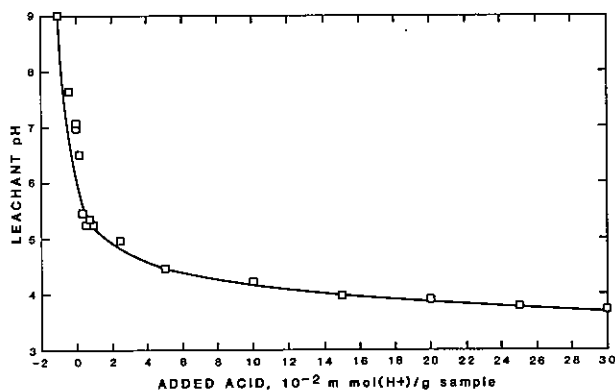

Figure 1.--Leachate pH as a function of added acid.

To further test the ionic strength effect, newly prepared columns containing 1.5 kg of the silver mill tailings were first leached with deionized water and then subjected to one of five leachants (0.10M̲ KCl, 0.033M̲ K₂SO₄, 0.10M̲ KNO₃, 0.033M̲ Na₂SO₄, or 0.10M̲ LiNO₃) of iden-tical ionic strengths. The results of the tests are summarized in table 3 and show that, in general, the ionic strength effect previously observed was independent of the salt used to control the ionic strength.

TABLE 2-A   IONIC STRENGTH EFFECT
Ag-MINE TAILINGS   3-inch (i.d.) column; 2.00 kg in each; height ~10.5-11 inches.
AVERAGE (4 columns)

#	84	86	88	90	92	94	96	98	100	104	110	114
Resident time(hr)	start	72	96	48	48	48	96	96	48	288	48	288
Leachant volume	250	250	250	250	250	250	250	250	500	500	500	500
----------LEACHANT----------												
pH												
DW, pH = 5.40	6.90	7.07	7.23	7.41	7.36	7.34	7.44	7.61	7.44	7.47	7.52	7.66
0.001M,KNO3,pH=5.46	6.98	7.10	7.23	7.43	7.35	7.48	7.56	7.69	7.55	7.44	7.56	7.72
0.01M,KNO3,pH=5.43	6.94	7.12	7.23	7.26	7.29	7.50	7.60	7.75	7.71	7.72	7.76	7.86
0.10M,KNO3,pH=5.61	6.92	7.15	7.21	7.31	7.51	7.96	8.06	8.03	8.02	7.94	7.99	8.00
RAIN,(SYN),pH=4.50	6.96	7.12	7.25	7.38	7.38	7.54	7.60	7.67	7.48	7.50	7.60	7.66
Calcium (Ca), mg/L												
DW	590	627	598	95.9	29.7	22.6	25.3	22.4	17.0	22.6	16.9	19.5
0.001M,KNO3	630	668	606	97.5	28.9	23.6	26.3	22.7	16.4	22.3	18.2	21.6
0.01M,KNO3	680	774	623	91.3	33.5	26.5	28.7	24.2	17.9	23.9	21.5	22.8
0.10M,KNO3	982	958	406	48.4	39.5	32.8	34.2	31.5	20.2	31.1	21.0	28.4
RAIN,(SYN)	643	678	574	76.4	27.4	21.4	24.3	20.1	14.2	22.6	16.6	19.8
Conductance, mmho.												
DW, 0.0036 mmho	3.68	2.51	2.22	1.952	0.197	0.162	0.178	0.150	0.126	0.166	0.125	0.139
0.001M,KNO3, 0.156	3.70	2.56	2.31	0.648	0.302	0.289	0.311	0.288	0.265	0.312	0.257	0.274
0.01M,KNO3, 1.343	4.53	3.74	3.43	1.72	1.46	1.48	1.48	1.46	1.45	1.50	1.45	1.48
0.10M,KNO3, 11.54	13.2	13.2	11.7	10.7	11.0	11.5	11.7	11.6	11.6	11.7	11.8	11.8
RAIN,(SYN), 0.0144	3.59	2.59	2.16	0.434	0.186	0.156	0.174	0.146	0.123	0.164	0.122	0.138
Iron (Fe), mg/L												
DW	0.08	0.05	0.05	*	0.15	*	*	*	*	*	*	*
0.001M,KNO3	0.07	0.04	0.05	*	0.92	0.12	*	*	0.11	*	*	*
0.01M,KNO3	0.08	0.04	0.05	*	0.13	0.30	*	*	0.80	*	*	0.06
0.10M,KNO3	0.11	0.08	0.08	*	0.05	*	0.04	*	*	*	*	0.04
RAIN,(SYN)	0.08	0.07	0.04	0.04	0.04	*	*	*	*	0.04	*	*
-----* below dl, dl=0.04----------												
Magnesium (Mg), mg/L												
DW	145	12.7	2.72	2.86	2.44	2.28	2.90	2.23	1.99	3.21	1.97	2.50
0.001M,KNO3	150	11.8	3.27	2.44	2.55	2.45	2.85	2.09	2.02	2.80	1.90	2.38
0.01M,KNO3	148	13.7	6.62	4.32	3.49	2.88	3.36	2.37	2.39	3.07	2.44	2.64
0.10M,KNO3	144	16.8	13.13	5.01	3.85	3.30	4.20	3.15	2.88	4.75	2.68	2.80
RAIN,(SYN)	138	11.5	2.65	2.10	2.22	1.94	2.34	1.70	1.82	3.04	1.88	2.43
Lead (Pb), mg/L												
DW	3.38	2.26	1.50	0.49	0.34	0.31	0.24	0.18	0.16	0.24	0.17	0.17
0.001M,KNO3	3.34	2.42	1.64	0.49	0.39	0.34	0.27	0.24	0.13	0.26	0.17	0.25
0.01M,KNO3	3.60	2.55	1.67	0.63	0.51	0.42	0.33	0.29	0.17	0.25	0.14	0.24
0.10M,KNO3	6.88	4.07	1.90	2.90	0.67	0.52	0.41	0.26	0.20	0.28	0.17	0.21
RAIN,(SYN)	4.21	2.67	1.87	0.48	0.32	0.27	0.27	0.25	0.19	0.25	0.19	0.19
-----* below dl, dl=0.10----------												
Zinc (Zn), mg/L												
DW	21.3	7.35	3.48	0.638	0.218	0.164	0.160	0.138	0.109	0.185	0.150	0.267
0.001M,KNO3	20.3	9.51	3.59	0.536	0.254	0.201	0.197	0.157	0.114	0.284	0.193	0.325
0.01M,KNO3	22.9	9.56	4.89	1.31	0.679	0.440	0.294	0.226	0.174	0.242	0.195	0.328
0.10M,KNO3	33.1	15.4	8.33	2.58	1.00	0.506	0.292	0.240	0.193	0.277	0.235	0.440
RAIN,(SYN)	19.9	7.55	3.60	0.519	0.210	0.168	0.151	0.133	0.114	0.231	0.152	0.259

DW - deionized water

TABLE 2-B IONIC STRENGTH EFFECT
Ag-MINE TAILINGS   3-inch (i.d.) column; 2.00 kg in each; height ⁻10.5-11 inches.
AVERAGE (4 columns)

	008		010	012	013	014		016	018	019	021	022
Resident time(h	48		168	168	216	336		120	216	168	168	456
Leachant volume	500		500	500	500	500		500	500	500	500	500

------LEACHANT----------		--LEACHANT--					--LEACHANT--					
pH		pH = 2.00										
DW	7.79	DW	7.65	4.65	4.17	4.35	OW	4.77	6.56	7.27	7.53	7.66
0.001M,KNO3	7.80	0.001M,KNO3	7.71	4.56	4.13	4.40	DW	4.81	6.91	7.48	7.65	7.69
0.01M,KNO3	7.99	0.01M,KNO3	7.84	4.71	4.21	4.39	DW	4.92	7.39	7.70	7.75	7.72
0.10M,KNO3	8.21	0.10M,KNO3	8.06	4.79	4.25	4.43	DW	5.04	7.92	7.90	7.85	7.82
RAIN,(SYN)	7.78	RAIN,(SYN)	7.64	4.72	4.15	4.30	DW	4.87	6.73	7.58	7.71	7.65
--------------------LEACHANT--							--LEACHANT--					
Ca, mg/L		pH = 2.00										
OW	16.6	OW	55.0	137	72.5	70.2	DW	36.4	10.2	13.7	14.2	24.7
0.001M,KNO3	17.7	0.001M,KNO3	47.5	137	74.0	55.2	DW	34.4	9.74	12.8	14.4	24.6
0.01M,KNO3	19.2	0.01M,KNO3	33.5	118	68.1	71.0	DW	36.8	11.2	13.6	15.4	25.9
0.10M,KNO3	20.4	0.10M,KNO3	28.2	103	76.0	64.6	DW	39.7	4.06	10.5	14.2	32.6
RAIN,(SYN)	16.7	RAIN,(SYN)	56.3	118	65.9	56.3	OW	31.7	7.93	11.7	13.8	23.7
--------------------LEACHANT--							--LEACHANT--					
Conductance,mmho		pH = 2.00										
DW	0.123	OW	0.421	2.11	2.18	nd	OW	1.97	0.125	0.105	0.113	0.165
0.001M,KNO3	0.261	0.001M,KNO3	0.471	2.21	2.27	nd	DW	2.00	0.147	0.116	0.119	0.169
0.01M,KNO3	1.47	0.01M,KNO3	1.79	3.38	3.40	nd	DW	2.98	0.282	0.150	0.139	0.183
0.10M,KNO3	11.9	0.10M,KNO3	12.3	13.5	13.5	nd	OW	11.9	0.714	0.234	0.162	0.262
RAIN,(SYN)	0.121	RAIN,(SYN)	0.433	2.10	2.22	nd	DW	1.96	0.129	0.108	0.113	0.162
--------------------LEACHANT--							--LEACHANT--					
Fe, mg/L		pH = 2.00										
DW	*	DW	*	219	336	337	OW	321	16.6	9.14	4.43	0.14
0.001M,KNO3	*	0.001M,KNO3	*	181	321	314	DW	330	12.9	5.39	3.93	0.18
0.01M,KNO3	*	0.01M,KNO3	*	195	325	290	DW	307	6.69	3.83	2.31	0.19
0.10M,KNO3	*	0.10M,KNO3	0.14	173	323	324	DW	310	0.88	1.29	1.42	*
RAIN,(SYN)	*	RAIN,(SYN)	0.05	203	354	354	DW	318	13.0	7.17	3.79	0.24
* below dl, dl=0.04		--LEACHANT--					--LEACHANT--					
Mg, mg/L		pH = 2.00										
DW	2.13	DW	6.06	44.3	22.4	24.8	DW	22.3	2.52	1.71	1.66	2.33
0.001M,KNO3	2.07	0.001M,KNO3	5.05	38.1	21.7	24.8	DW	19.6	2.26	1.63	1.60	2.48
0.01M,KNO3	2.40	0.01M,KNO3	3.80	47.9	22.4	26.4	DW	18.8	2.13	1.74	1.77	2.57
0.10M,KNO3	2.61	0.10M,KNO3	3.52	46.5	23.8	26.7	DW	19.0	0.77	0.95	1.17	3.06
RAIN,(SYN)	1.98	RAIN,(SYN)	7.54	58.5	22.3	23.6	OW	19.3	2.05	1.62	1.50	2.35
--------------------LEACHANT--							--LEACHANT--					
Pb, mg/L		pH = 2.00										
DW	0.13	OW	0.27	13.2	3.59	2.67	DW	0.41	0.20	*	*	*
0.001M,KNO3	0.12	0.001M,KNO3	0.40	8.63	4.16	2.37	DW	0.21	*	*	*	*
0.01M,KNO3	0.11	0.01M,KNO3	0.23	10.4	6.50	2.77	DW	1.36	*	*	*	*
0.10M,KNO3	0.16	0.10M,KNO3	0.18	8.65	1.65	0.33	DW	0.17	*	*	0.17	*
RAIN,(SYN)	0.15	RAIN,(SYN)	0.21	10.9	1.58	2.43	DW	0.20	0.11	*	*	*
* below dl, dl=.010		--LEACHANT--					--LEACHANT--					
Zn, mg/L		pH = 2.00										
DW	0.211	DW	0.886	15.0	19.2	32.7	OW	31.4	3.3	1.3	0.9	0.9
0.001M,KNO3	0.209	0.001M,KNO3	0.615	16.8	18.7	30.7	DW	31.4	2.9	1.1	0.9	0.9
0.01M,KNO3	0.249	0.01M,KNO3	0.416	22.4	20.3	39.9	DW	34.8	2.0	1.1	0.9	0.8
0.10M,KNO3	0.290	0.10M,KNO3	0.334	28.8	26.0	45.6	DW	38.8	0.5	0.7	0.8	0.8
RAIN,(SYN)	0.199	RAIN,(SYN)	0.787	17.7	18.5	35.8	DW	30.9	2.8	1.4	0.9	0.8

DW - deionized water

Residence Time, Wet/Dry Cycle Effect

Tables 2 and 3 indicate that the leachate ion concentrations appeared to be influenced by the residence time, that is, the time while the leachate remained in the column. A close inspection of these tables reveals that the concentrations of most species increased with increasing residence time, with the possible exception of lead (table 3) (test 055 compared to 063). In order to examine this effect further, the columns used in the "salt" study (table 3) were

TABLE 3   SALT EFFECT
Ag-MINE TAILINGS VIII 3-inch (i.d.) column; 1.50 kg in each; leachant volume, 350cc.
AVERAGE (4 columns)

#	032	035		037	042	045	049	055	059	063	068
Resident time(hr)	start	144		168	168	168	168	366	192	72	168
---------LEACHANT----------------			LEACHANT								

pH

	DW	6.47	6.49	0.10M,KCl,pH=5.49	7.24	7.30	7.61	7.73	7.87	7.93	7.96	7.97
	DW	6.53	6.25	0.033M,K2SO4,pH=5.59	7.28	7.43	7.82	7.95	8.15	8.08	8.15	8.10
	DW	6.28	6.96	0.10M,KNO3,pH=5.39	7.27	7.39	7.72	7.86	7.99	7.96	8.01	8.02
	DW	6.57	7.00	0.033M,Na2SO4,pH=5.63	7.57	7.46	7.79	7.91	8.06	8.07	n.d.	8.14
	DW	6.33	7.13	0.10M,LiNO3,pH=5.58	7.47	7.55	7.74	7.85	7.95	7.95	n.d.	7.98

--- n.d. not determined ---

CALCIUM (Ca), mg/L

	DW	655	277	0.10M, KCl	149	54.5	35.8	27.8	33.1	26.2	17.0	28.3
	DW	672	239	0.033M, K2SO4	98.8	64.4	35.7	26.9	35.9	28.5	20.8	34.7
	DW	656	239	0.10M, KNO3	123	60.2	33.6	25.3	27.5	25.5	17.7	31.1
	DW	635	231	0.033M, Na2SO4	80.4	65.5	30.6	27.1	33.1	31.8	26.1	25.3
	DW	687	178	0.10M, LiNO3	74.4	59.2	32.2	24.5	28.8	29.8	26.4	29.5

CONDUCTANCE, mmho

	DW	2.72	1.04	0.10M,KCl,12.58mmho	2.16	12.27	12.92	13.17	13.26	12.76	13.13	13.04
	DW	2.73	0.99	0.033M,K2SO4,7.53mmho	1.18	7.35	7.84	8.39	8.09	7.76	7.91	8.00
	DW	2.74	1.04	0.10M,KNO3,11.80mmho	2.23	11.57	12.22	12.46	12.63	12.05	12.19	12.34
	DW	2.69	0.98	0.033M,Na2SO4,6.20mmho	1.24	6.25	6.55	7.13	6.81	6.49	n.d.	6.57
	DW	2.70	0.82	0.10M,LiNO3,8.95mmho	1.79	8.85	9.09	9.40	9.33	8.87	n.d.	8.95

--- n.d. not determined ---

IRON (Fe), mg/L

	DW	0.13	0.09	0.10M, KCl	0.14	0.17	0.09	0.06	0.08	0.05	0.10	0.16
	DW	0.12	0.07	0.033M, K2SO4	0.22	0.08	<.04	0.05	0.04	0.05	0.14	0.11
	DW	0.24	0.11	0.10M, KNO3	0.37	0.06	0.05	0.04	0.05	<.04	0.27	0.09
	DW	0.08	0.19	0.033M, Na2SO4	0.08	0.18	0.17	<.04	0.07	<.04	0.16	0.14
	DW	0.12	0.08	0.10M, LiNO3	0.11	0.25	0.15	0.08	0.07	0.08	0.14	0.22

MAGNESIUM (Mg), mg/L

	DW	43.3	5.07	0.10M, KCl	12.2	5.77	3.02	3.00	4.41	3.28	2.57	3.29
	DW	41.0	4.98	0.033m, K2SO4	11.3	6.19	2.64	2.80	4.28	3.77	2.78	3.58
	DW	43.7	4.81	0.10M, KNO3	12.3	5.63	2.96	2.86	3.91	3.28	2.72	3.21
	DW	41.6	5.01	0.033M, Na2SO4	7.64	6.13	2.49	2.37	3.33	3.38	3.14	3.50
	DW	40.3	4.26	0.10M, LiNO3	7.44	5.67	2.46	2.60	3.09	2.88	3.15	5.16

LEAO (Pb), mg/L

	DW	2.86	1.14	0.10M, KCl	0.64	0.76	0.37	0.28	0.30	0.20	2.45	0.34
	DW	3.12	0.66	0.033M, K2SO4	0.63	0.69	0.34	0.23	0.29	0.24	1.27	1.30
	DW	2.93	0.78	0.10M, KNO3	0.61	0.43	0.43	0.34	0.24	0.14	10.7	0.48
	DW	2.94	1.20	0.033M, Na2SO4	0.42	0.44	0.20	0.29	0.25	0.26	0.23	1.08
	DW	3.38	0.82	0.10M, LiNO3	0.39	0.34	0.33	0.26	0.26	0.19	3.68	n.d.

--- n.d. not determined ---

ZINC (Zn), mg/L

	DW	12.8	2.50	0.10M, KCl	1.55	1.52	0.61	0.44	0.84	0.76	0.58	0.55
	DW	13.4	1.75	0.033M, K2SO4	1.07	1.12	0.58	0.42	0.69	0.64	0.45	0.42
	DW	13.3	1.89	0.10M, KNO3	1.57	1.20	0.41	0.37	0.52	0.44	0.32	0.42
	DW	13.8	2.57	0.033M, Na2SO4	0.76	0.77	0.63	0.52	0.75	0.42	0.33	0.59
	DW	13.4	2.29	0.10M, LiNO3	1.12	0.92	0.51	0.41	0.45	0.40	0.27	0.40

DW - deionized water

divided into pairs, two of which were maintained at near-saturation conditions while the other was allowed to dry partially. The averages of the two saturated (even-numbered) and unsaturated (odd-numbered) columns before and after the wet/dry cycle are presented in table 4. It becomes apparent that those columns allowed to evaporate approximately 30% to 40% of their pore liquid produced an environment that resulted in increased metal dissolution and decreased leachate pH. After stabilization (addition of three pore volumes of "salt" leachant), the process was repeated. The results were similar. Presumably, this

was because of atmospheric oxidation of the sulfide minerals present in the unsaturated zone and the subsequent formation of acid (Nordstrom et al. 1979, Nordstrom 1982). In order to examine a possible relation between microorganism activity and oxidation, sodium lauryl sulfate, sodium benzoate, or phenol (Watzlaf 1986) were added to three sets of columns, while 0.01$\underline{M}$ KNO$_3$ and 0.01$\underline{M}$ KNO$_2$ leachants were used on the remaining two sets. Although the presence or absence of microorganisms was not experimentally established, it was assumed that the treatment should have eliminated them from contributing to the next wet/dry cycle experiment. It may be noted that this test (test 104) produced effects

TABLE 4-A.   SAT./UNSAT. EFFECT
Ag-MINE TAILINGS   3-inch (i.d.) column; 1.50 kg in each; leachant volume, 350 cc
AVERAGE (2 columns)

#	059	068	AVG.	073	075	080	083	088	LEACHANT	095	104	108
Resident time(hr)	192	168		504	168	168	504	168		336	576	120
				SAT/UNSAT			SAT/UNSAT		LEACHANT LEACHANT		SAT/UNSAT	
AVG. pH LEACHANT	KCl								OW(ALL) SLS			LEACHANT DW(ALL)
2&4 (0.10M)	7.92	7.98	SAT.	7.91	8.00	8.07	8.03	8.05	550mg/L	7.88	7.89	7.74
1&3 pH=5.49	7.94	7.97	UNSAT.	7.25	7.81	7.96	7.31	7.72	pH=5.40	7.78	7.32	7.70
K2SO4									NaBz			
6&8 (0.033M)	8.09	8.11	SAT.	8.09	8.15	8.17	8.12	8.21	578mg/L	8.00	8.10	7.91
5&7 pH=5.59	8.06	8.09	UNSAT.	7.80	8.01	8.07	7.55	7.96	pH=6.13	7.92	7.18	7.74
KNO3									KNO3			
10&12 (0.10M)	7.90	8.03	SAT.	8.09	7.89	8.07	7.98	8.02	0.01M	7.82	7.97	8.01
9&11 pH=5.39	8.02	8.01	UNSAT.	7.51	7.85	8.00	6.92	7.82	pH=5.40	7.71	5.00	6.99
Na2SO4									PHENOL			
14&16 (0.033M)	8.11	8.15	SAT.	8.06	8.13	8.18	8.16	8.30	578mg/L	7.82	8.00	7.97
13&15 pH=5.63	8.04	8.13	UNSAT.	6.95	7.87	8.19	7.38	8.03	pH=5.10	8.02	7.97	8.04
LiNO3									NaNO2			
18&20 (0.10M)	7.94	8.00	SAT.	7.98	7.89	8.07	7.93	8.06	0.01M	7.95	7.96	7.97
17&19 pH=5.58	7.95	7.97	UNSAT.	7.55	7.82	7.98	7.18	7.94	pH=6.06	7.74	5.66	7.20
CALCIUM (Ca), mg/L												
2&4 KCl	27.80	29.30	SAT.	20.30	26.95	21.15	23.80	18.10	SLS	1.31	1.53	0.89
1&3 (0.10M)	24.70	27.40	UNSAT.	53.75	28.30	21.85	112.25	27.20	550mg/L	6.55	47.9	10.9
6&8 K2SO4	28.50	38.00	SAT.	23.05	31.35	24.00	29.20	18.45	NaBz	2.53	4.18	4.98
5&7 (0.033M)	29.60	31.50	UNSAT.	47.60	27.90	23.05	68.30	18.20	578mg/L	2.75	59.5	12.9
10&12 KNO3	25.90	35.90	SAT.	17.95	22.60	16.35	24.30	14.90	KNO3	13.0	17.2	10.5
9&11 (0.10M)	25.20	26.30	UNSAT.	50.30	23.80	18.40	81.75	15.15	0.01M	18.8	101	18.6
14&16 Na2SO4	33.30	24.70	SAT.	21.30	32.05	22.45	26.55	23.80	PHENOL	12.0	14.6	13.6
13&15 (0.033M)	30.30	26.00	UNSAT.	96.75	37.85	31.85	232	52.70	578mg/L	17.1	81.3	30.7
18&20 LiNO3	29.30	31.60	SAT.	21.30	37.60	24.60	31.20	22.95	KNO2	11.8	15.7	12.3
17&19 (0.10M)	30.30	27.40	UNSAT.	56.10	21.40	27.50	90.75	18.00	0.01M	20.7	82.9	15.4
MAGNESIUM (Mg), mg/L												
2&4 KCl	3.43	3.30	SAT.	3.16	3.84	2.71	1.30	2.26	SLS	0.15	0.27	0.11
1&3 (0.10M)	3.14	3.27	UNSAT.	10.2	4.02	4.12	11.9	2.90	550mg/L	0.75	7.02	1.63
6&8 K2SO4	3.70	3.84	SAT.	3.21	4.30	3.29	2.08	2.54	NaBz	0.25	0.50	0.42
5&7 (0.033M)	3.85	3.32	UNSAT.	8.62	3.74	3.94	8.15	2.36	578mg/L	0.28	7.33	1.77
10&12 KNO3	3.33	3.28	SAT.	3.64	3.38	2.69	1.45	2.08	KNO3	0.92	1.70	1.27
9&11 (0.10M)	3.23	3.15	UNSAT.	8.82	3.59	3.30	8.48	1.87	0.01M	1.82	14.9	3.01
14&16 Na2SO4	3.29	3.53	SAT.	2.60	4.59	3.33	1.33	6.26	PHENOL	1.15	1.34	1.14
13&15 (0.033M)	3.46	3.47	UNSAT.	14.5	5.07	4.57	26.4	4.06	578mg/L	3.12	10.7	3.92
18&20 LiNO3	2.99	5.90	SAT.	2.43	4.33	3.30	1.38	2.68	NaNO2	1.24	1.71	1.61
17&19 (0.10MO)	2.72	4.43	UNSAT.	7.98	3.63	4.91	7.85	2.15	0.01M	2.03	11.9	2.36

DW - deionized water

TABLE 4-B   SAT./UNSAT. EFFECT.
Ag-MINE TAILINGS, 3-inch (i.d.) column; 1.50 kg in each; leachant volume, 350cc.
AVERAGE (2,columns)

#	059	068		073	075	080	083	088		095	104	108
Resident time(hr)	192	168		504	168	168	504	168		336	576	120
			SAT/UNSAT				SAT/UNSAT				SAT/UNSAT	
AVG. LEACHANT			AVG.					LEACHANT DW(ALL)	LEACHANT SLS			LEACHANT DW(ALL)
CONDUCTANCE KCl									NaBz			
2&4 (0.10M)	12.76	13.04	SAT.	10.79	13.02	13.42	12.72	11.68	550mg/L	0.429	0.393	0.275
1&3 12.58mmh	12.75	13.01	UNSAT.	15.54	13.53	13.66	16.55	10.85	0.165mmho	0.521	0.835	0.330
K2SO4									NaBz			
6&8 (0.033M)	7.78	8.03	SAT.	6.60	8.07	8.59	8.89	6.94	578mg/L	0.567	0.519	0.432
5&7 7.53mmho	7.74	7.98	UNSAT.	8.92	8.60	8.89	10.60	6.94	0.363mmho	0.590	1.105	0.510
KNO3									KNO3			
10&12 (0.10M)	12.14	12.56	SAT.	9.76	11.89	10.60	12.23	10.94	0.01M	1.635	1.715	1.411
9&11 11.88mmh	11.97	12.12	UNSAT.	14.25	12.97	13.31	15.61	10.40	1.507mmho	1.720	2.850	1.434
Na2SO4									PHENOL			
14&16 (0.033M)	6.45	6.56	SAT.	5.52	6.74	7.11	6.72	5.87	578mg/L	0.106	0.135	0.112
13&15 6.20mmho	6.54	6.58	UNSAT.	7.67	6.96	6.67	9.46	5.85	0.059mmho	0.222	0.546	0.243
LiNO3									NaNO2			
18&20 (0.10M)	8.88	8.97	SAT.	7.81	9.04	0.00	8.92	8.07	0.01M	1.420	1.476	1.261
17&19 8.95mmho	8.86	8.94	UNSAT.	10.93	9.41	9.78	11.69	7.38	1.301mmho	1.465	2.335	1.209

LEAD (Pb), mg/L	059	068		073	075	080	083	088		095	104	108
2&4 KCl	0.22	0.28	SAT.	0.11	0.22	0.12	0.32	0.14	SLS	<.1	<.1	<.1
1&3 (0.10M)	0.18	0.39	UNSAT.	10.66	0.69	0.21	1.71	0.43	550mg/L	0.14	0.51	0.17
6&8 K2SO4	0.24	1.31	SAT.	0.13	0.25	0.13	0.16	D.12	NaBz	D.09	<.1	<.1
5&7 (0.033M)	0.24	1.30	UNSAT.	0.48	0.43	0.19	1.39	0.42	578mg/L	0.16	0.55	0.37
10&12 KNO3	0.14	0.53	SAT.	<.1	0.15	<.1	0.11	2.37	KNO3	0.07	<.1	0.10
9&11 (0.10M)	0.14	0.43	UNSAT.	0.35	0.32	<.1	1.38	0.23	0.01M	0.11	5.46	1.88
14&16 Na2SO4	0.24	0.86	SAT.	0.17	0.24	0.12	0.19	0.24	PHENOL	0.14	0.10	0.11
13&15 (0.033M)	0.27	1.30	UNSAT.	3.01	0.64	0.18	2.05	0.24	578mg/L	0.10	0.10	0.14
18&20 LiNO3	0.20	n.d.	SAT.	0.20	0.29	<.1	0.14	<.1	KNO2	0.25	0.10	0.11
17&19 (0.10M)	0.19	n.d.	UNSAT.	5.14	0.45	0.20	2.20	0.60	0.01M	0.25	7.51	1.95

ZINC (Zn), mg/L	059	068		073	075	080	083	088		095	104	108
2&4 KCl	0.95	0.75	SAT.	0.56	0.53	0.42	0.63	0.34	SLS	0.08	0.39	0.25
1&3 (0.10M)	0.56	0.35	UNSAT.	5.32	0.96	0.83	12.3	2.60	550mg/L	0.31	3.60	0.86
6&8 K2SO4	0.54	0.40	SAT.	0.28	0.27	0.22	0.31	0.15	NaBz	0.05	0.10	0.08
5&7 (0.033M)	0.75	0.43	UNSAT.	1.43	0.84	0.66	4.86	1.01	578mg/L	0.18	5.35	1.95
10&12 KNO3	0.50	0.44	SAT.	0.31	0.40	0.31	0.45	0.27	KNO3	0.28	0.41	0.19
9&11 (0.10M)	0.39	0.40	UNSAT.	1.86	0.78	0.60	7.20	1.13	0.01M	0.51	15.4	5.97
14&16 Na2SO4	0.44	0.33	SAT.	0.22	0.23	0.16	0.25	3.65	PHENOL	0.11	0.12	0.06
13&15 (0.10M)	0.39	0.85	UNSAT.	24.1	2.07	0.82	42.3	1.33	578mg/L	0.61	0.59	0.50
18&20 LiNO3	0.39	0.37	SAT.	0.39	0.57	0.30	0.63	0.36	KNO2	0.18	0.20	0.24
17&19 (0.10M)	0.42	0.44	UNSAT.	1.73	0.79	0.70	11.8	1.62	0.01M	0.98	17.1	3.79

OW - deionized water

very similar to those observed prior to treatment, which would indicate that the effects of microorganisms were minimal and that atmospheric oxidation was primarily responsible for increased leachate contamination. It should be pointed out, however, that somewhat greater pH decreases were observed for the untreated samples than had been previously seen.

Both nickel and cadmium were below detection limits (nickel = 0.06, cadmium = 0.01) prior to the first wet/dry cycle. Concentrations of nickel ranged from 0.55 (with a Na_2SO_4 leachant) to 0.12 ppm (with $LiNO_3$) for unsaturated columns while ranges below detection (using Na_2SO_4) to 0.08 ppm (using KCl) were observed for those columns that remained

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saturated. Similar results were also seen for cadmium, except values ranged from 0.26 (Na_2SO_4) to 0.024 ppm (KNO_3) for unsaturated columns. All saturated columns recorded concentrations below detection.

Acetate Ion Effect

At the present time, acetic acid buffers are used to control the pH of a specific leachate. The EP toxicity and the TCLP (U.S. EPA 1985) slurry tests are two examples where acetic acid is used. There have also been suggestions involving the mixing of mine tailings with other organic matter as a prelude to growing a vegetation cover. Since acetate ions are known to complex with certain metal species (for example, lead), a series of tests were conducted to examine the effects of acetate ions on the dissolution of metal from the silver mill tailings. The results of the initial series tests are given in table 5. Here, five sets of four columns each were leached with leachants of 0.10M NaOAc, pH = 6.03; 0.01M NaOAc, pH = 6.02; 0.001M NaOAc, pH = 6.04; 0.10M KNO_3, pH = 5.79-control; and 0.10M NaOAc, pH = 6.97 to establish the influence of acetate ions.

All species reported in table 5 demonstrate increasing metal concentrations with increasing acetate concentrations. Furthermore, the metal ion concentrations of 0.10M acetate, pH = 6.03, were greater than those of 0.10M KNO_3, pH = 5.79. This would indicate that acetate complex formation does increase the dissolution of metals within this sample of tailings. However, one major difficulty remains, i.e., the presence of potassium nitrate elevates the leachate pH above that of the acetate leachate even though the leachant pH is lower for the potassium nitrate solution. It should also be noted that the metal ion concentrations obtained for the acetate buffer at pH = 6.97 are somewhat greater than those of the potassium nitrate control even though the resulting leachate pH is greater for the acetate buffer. These results would seem to indicate that the presence of acetate ions will increase the dissolution of metals from mine wastes.

SUMMARY AND CONCLUSIONS

Although limited to the tailings from a single mine, the results of this study indicate an ionic strength effect on the dissolution of contaminants from mine tailings. This effect may be partially explained through the standard secondary salt effect (effect on species activity coefficients) through ion exchange between the leachant and the tailings. Thus, treatments of tailings with materials that produce high ionic strength leachate may well enhance the dissolution of specific components in the

wastes. It would also appear that the chemical nature of the inorganic ion within the range of an ionic strength of 0.1M has very little effect on the concentration of metal species leached from the tailings.

It appears that this sample, which is a low-pyrite, high-siderite sample, will undergo destructive oxidation resulting in decreased leachate pH and increased metal dissolution. This oxidation originates in the unsaturated zone and does not appear to involve microorganisms.

The presence of acetate ions has a pronounced effect on the dissolution of metals from mine waste samples. Increased solubility of magnesium, manganese, and lead would be expected through the formation of acetate complexes. The dissolution of other species, such as zinc, nickel, and cadmium, also appears to be increased in the presence of acetate ions. Care must be exercised regarding actions that could lead to acetate production in the proximity of mine tailings.

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TABLE 5.   ACETATE ION EFFECT
Ag-MINE TAILINGS 3-inch (i.d.) column; 1.50 kg in each; leachant volume, 350cc.

AVERAGE (4 columns)	#	110	115	117	119		3-01	3-05
	Resident time(hr)	144	192	168	168	LEACHANT	168	168
pH	LEACHANT							
PRIOR	0.10M,KNO3,pH=5.79	7.86	7.72	7.95	8.05	DW	8.18	8.37
LEACHANT	0.10M,OAc,pH=6.03	7.11	7.55	7.61	7.53	DW	7.63	8.20
(DW)	0.01M,OAc,pH=6.02	7.82	7.78	7.94	7.77	DW	8.05	8.09
	0.001M,OAc,pH=6.04	7.92	7.91	7.94	7.41	DW	7.90	7.87
	0.10M,OAc,pH=6.97	7.63	7.91	8.20	8.30	DW	8.38	8.52
CALCIUM (Ca)								
mg/L PRIOR	0.10M,KNO3,pH=5.79	46.2	34.7	21.2	20.4	DW	15.6	1.05
LEACHANT	0.10M,OAc,pH=6.03	60.3	83.4	65.4	69.6	DW	54.60	4.60
(DW)	0.01M,OAc,pH=6.02	16.2	21.3	11.8	12.6	DW	10.3	2.50
	0.001M,OAc,pH=6.04	19.5	14.8	13.1	13.2	DW	12.0	11.9
	0.10M,OAc,pH=6.97	60.3	30.3	15.2	14.0	DW	12.8	0.70
MAGNESIUM (Mg)								
mg/L PRIOR	0.10M,KNO3,pH=5.79	7.52	3.49	2.27	2.23	DW	1.70	<0.05
LEACHANT	0.10M,OAc,pH=6.03	10.2	6.80	6.40	7.15	DW	5.80	0.43
(DW)	0.01M,OAc,pH=6.02	1.79	1.97	1.27	1.20	DW	1.05	0.15
	0.001M,OAc,pH=6.04	2.70	1.80	1.72	1.63	DW	1.50	1.45
	0.10M,OAc,pH=6.97	13.2	3.58	1.77	1.53	DW	1.53	<0.05
MANGANESE (Mn)								
mg/L PRIOR	0.10M,KNO3,pH=5.79	11.3	8.89	2.92	2.22	DW	1.55	0.04
LEACHANT	0.10M,OAc,pH=6.03	18.3	26.8	14.8	13.0	DW	9.43	0.69
(DW)	0.01M,OAc,pH=6.02	2.92	2.71	1.62	1.68	DW	1.31	0.36
	0.001M,OAc,pH=6.04	2.09	1.53	1.20	1.25	DW	1.06	1.28
	0.10M,OAc,pH=6.97	7.40	4.77	2.17	2.55	DW	2.62	0.04
NICKEL (Ni)								
mg/L PRIOR	0.10M,KNO3,pH=5.79	0.12	0.08	0.01	0.03	DW	0.01	<.005
LEACHANT	0.10M,OAc,pH=6.03	0.17	0.20	0.20	0.25	DW	0.22	0.01
(DW)	0.01M,OAc,pH=6.02	0.03	0.02	<.005	0.01	DW	0.01	<.005
	0.001M,OAc,pH=6.04	0.04	0.02	0.01	0.02	DW	0.01	0.02
	0.10M,OAc,pH=6.97	0.06	0.02	<.005	0.02	DW	0.01	<.005
LEAD (Pb)								
mg/L PRIOR	0.10M,KNO3,pH=5.79	0.28	0.23	0.07	0.36	DW	<.03	<.03
LEACHANT	0.10M,OAc,pH=6.03	2.94	6.94	3.40	5.09	DW	1.17	0.11
(DW)	0.01M,OAc,pH=6.02	0.18	0.19	0.08	0.19	DW	0.06	0.03
	0.001M,OAc,pH=6.04	0.11	0.08	0.04	0.45	DW	<.03	0.03
	0.10M,OAc,pH=6.97	1.59	1.44	0.58	0.57	DW	0.40	<.03
ZINC (Zn)								
mg/L PRIOR	0.10M,KNO3,pH=5.79	3.74	2.25	0.92	0.91	DW	0.46	0.02
LEACHANT	0.10M,OAc,pH=6.03	3.91	4.08	5.60	10.42	DW	6.80	0.52
(DW)	0.01M,OAc,pH=6.02	0.95	0.77	0.52	0.55	DW	0.37	0.12
	0.001M,OAc,pH=6.04	0.40	0.26	0.24	0.26	DW	0.20	0.23
	0.10M,OAc,pH=6.97	2.99	1.36	0.76	0.86	DW	0.72	0.03

DW - deionized water