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THE INTERRELATION OF FACTORS INFLUENCING THE DISSOLUTION METALS IN COLUMNS OF MINE TAILINGS

by
Richard D. Doepker

Spokane Research Center
Bureau of Mines
U.S. Department of the Interior
Spokane, Washington, USA

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 (Bainbridge, 1980) and A. D. 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.

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	0.03	0.04	0.02

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, analyticalgrade 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[1] (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 600mm or 1200 mm lengths of 75 mm insidediameter (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 600 mm and 1200 mm columns were used for various specific experiments. A series of 10 similarly constructed 37 mm -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 l-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 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 0.01M 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

Table 2 reports leachate concentrations for leachants of various ionic strengths and pH's. The experimental method utilized 75 mm columns; 2 kg of tailings samples (266.7 - 279 mm, depth) per each column; four replicates; five different leachants of 0.001M, 0.01M, and 0.10M KNO_3; deionized water; and a sample of Western synthetic rain (Bainbridge, 1980). The pore volume for this series was determined to be 500 cm^3. Leachant pH was adjusted to approximately

5.5 or 2.0 (Table 2) 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 O.lOM 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 (Figure 1). Table 2 shows that leachate concentrations for most metal species 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 O.lOM KNO_3, 0.86 ppm for O.OlM KNO_3, and 0.82 for O.OOlM KNO_3. Initial cadmium leachate concentrations were 0.39, 0.29, and 0.27 ppm for O.lOM, O.OlM, and O.OOlM KNO_3, respectively. These values decreased to below detection limits (0.01) for all leachant systems except the O.lOM KNO_3 leachant after the addition of two pore volumes of leachant. 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.

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 (O.lOM KCl, 0.033M K_2SO_4, O.lOM KNO_3, 0.033M Na_2SO_4, or O.lOM $LiNO_3$) of identical 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.

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). In order to examine this effect further, the columns used in the "salt" study (Table 3) were divided into pairs, two of which were

Table 2. Ionic strength effect on silver mine tailings
(Note: Columns 3 in ID, 10-1/2 to 11 in high, filled with 2 kg tailinlgs)

Leachant	Residence time,	Leachate	Conductance,	Element, mg/L				
pH	hr[1]	pH	mmho	Ca	Fe	Mg	Pb	Zn
			DISTILLED WATER, CONDUCTANCE = 0.0036 mmho					
	Leachant col. 250 ml:							
	Start	6.90	3.68	590	0.08	145	3.38	21.3
	72	7.07	2.51	627	.05	12.7	2.26	7.35
	96	7.23	2.22	598	.05	2.72	1.50	3.48
	48	7.41	1.952	95.9	<.01	2.86	.49	.64
	48	7.36	.197	29.7	.15	2.44	.34	.22
	48	7.34	.162	22.6	<.01	2.28	.31	.16
5.4	96	7.44	.178	25.3	<.01	2.90	.24	.16
	96	7.61	.150	22.4	<.01	2.23	.18	.14
	Leachant vol. 500 ml:							
	48	7.44	.126	17.0	<.01	1.99	.16	.11
	288	7.47	.166	22.6	<.01	3.21	.24	.19
	48	7.52	.125	16.9	<.01	1.97	.17	.15
	288	7.66	.139	19.5	<.01	2.50	.17	.27
	48	7.79	.123	16.6	<.01	2.13	.13	.21
	168	7.65	.421	55.0	<.01	6.06	.27	.89
2.0[2]	168	4.65	2.11	137	219	44.3	13.2	15.0
	216	4.17	2.18	72.5	336	22.4	3.59	19.2
	336	4.35	ND	70.2	337	24.8	2.67	32.7
	120	4.77	1.97	36.4	321	22.3	.41	31.4.
	216	6.56	.125	10.2	16.6	2..52	.20	3.3
5.4[3]	168	7.27	.105	13.7	9.14	1.71	<.05	1..3
	168	7.53	.113	14.2	4.43	1.66	<.05	.90
	456	7.66	.165	24.7	.14	2.33	<.05	.90
			0.001 M. KNO_3 CONDUCTANCE = 0.156 mmho					
	Leachant vol. 250 ml:							
	Start	6.98	3.70	630	0.07	150	3.34	20.3
	72	7.10	2.56	668	.04	11.8	2.42	9.51
	96	7.23	2.31	606	.05	3.27	1.64	3.59
	48	7.43	.648	97.5	<.01	2.44	.49	.64
	48	7.35	.302	28.9	.92	2.55	.39	.25
5.46	48	7.48	.289	23.6	.12	2.45	.34	.20
	96	7.56	.311	26.3	<.01	2.85	.27	.20
	96	7.69	.288	22.7	<.01	2.09	.24	.16
	Leachant vol. 500 ml:							
	48	7.55	.265	16.4	.11	2.02	.13	.11
	288	7.44	.312	22.3	<.01	2.80	.26	.28
	48	7.56	.257	18.2	<.01	1.90	.17	.19
	288	7.72	.274	21.6	<.01	2.38	.25	.33
	48	7.80	.261	17.7	<.01	2.07	.12	.21
	168	7.71	.471	47.5	<.01	5.05	.40	.62
2.0[2]	168	4.56	2.21	137	181	38.1	8.63	16.8
	216	4.13	2.27	74.0	321	21.7	4.16	18.7
	336	4.40	ND	55.2	314	24.8	2.37	30.7
	120	4.81	2.00	34.4	330	19.6	.21	31.4
	216	6.91	.147	9.74	12.9	2.26	<.05	2.9
5.4[3]	168	7.48	.116	12.8	5.39	1.63	<.05	1.1
	168	7.65	.119	14.4	3.93	1.60	<.05	.90
	456	7.69	.169	24.6	.18	2.48	<.05	.90

Table 2 (Continued)

0.01 M. KNO_3 CONDUCTANCE = 1.343 mmho								
	Leachant vol. 250 ml:							
	Start	6.94	4.53	680	0.08	148	3.60	22.9
	72	7.12	3.74	774	.04	13.7	2.55	9.56
	96	7.23	3.43	623	.05	6.62	1.67	4.89
	448	7.26	1.72	91.3	<.01	4.32	.63	1.31
	48	7.29	1.46	33.5	.13	3.49	.51	.68
	48	7.50	1.48	26.5	.30	2.88	.42	.44
5.43	96	7.60	1.48	28.7	<.01	3.36	.33	.29
	96	7.75	1.46	24.2	<.01	2.37	.29	.23
	Leachant vol. 500 ml:							
	48	7.71	1.45	17.9	.80	2.39	.17	.17
	288	7.72	1.50	23.9	<.01	3.07	.25	.24
	48	7.76	1.45	21.5	<.01	2.44	.14	.20
	288	7.86	1.48	22.8	.06	2.64	.24	.33
	48	7.99	1.47	19.2	<.01	2.40	.11	.25
	168	7.84	1.79	33.5	<.01	3.80	.23	.42
2.0^2	168	4.71	3.38	118	195	47.9	10.4	22.4
	216	4.21	3.40	68.1	325	22.4	6.50	20.3
	336	4.39	ND	71.0	290	26.4	2.77	39.9
	120	4.92	2.98	36.8	307	18.8	1.36	34.8
	216	7.39	.282	11.2	6.69	2.13	<.05	2.0
5.43^3	168	7.70	.150	13.6	3.83	1.74	<.05	1.1
	168	7.75	.139	15.4	2.31	1.77	<.05	.90
	456	7.72	.183	25.9	.19	2.57	<.05	.80
0.01 M. KNO_3 CONDUCTANCE = 11.54 mmho								
	Leachant vol. 250 ml:							
	Start	6.92	13.2	982	0.11	144	6.88	33.1
	72	7.15	13.2	958	..08	16.8	4.07	15.4
	96	7.21	11.7	406	.08	13.13	1.90	8.33
	48	7.31	10.7	48.4	<.01	5.01	2.90	2.58
	48	7.51	11.0	39.5	.05	3.85	.67	1.0
	48	7.96	11.5	32.8	<.01	3.30	.52	.51
5.61	96		11.7	34.2	.04	4.20	.41	.29
	96	8.06	11.6	31.5	<.01	3.15	.26	.24
	Leachant vol. 500 ml:8.03							
	48	8.02	11.6	20.2	<.01	2.88	.20	.19
	288	7.94	11.7	31.1	<.01	4.75	.28	.28
	48	7.99	11.8	21.0	<.01	2.68	.17	.24
	288	8.00	11.8	28.4	.04	2.80	.21	.44
	48	8.21	11.9	20.4	<.01	2.61	.16	.29
	168	8.06	12.3	28.2	.14	3.52	.18	.33
2.0^2	168	4.79	13.5	103	173	46.5	8.65	28.8
	216	4.25	13.5	76.0	323	23.8	1.65	26.0
	336	4.43	ND	64.6	324	26.7	.33	45.6
	120	5.04	11.9	39.7	310	19.0	.17	38.8
	216	7.92	.714	4.06	.88	.77	<.05	.50
5.4^3	168	7.90	.234	10.5	1.29	.95	<.05	.70
	168	7.85	.162	14.2	1.42	1.17	.17	.80
	456	7.82	.262	32.6	<.01	3.06	<.05	.80
SYNTHETIC RAIN <.01. CONDUCTANCE = 0.0144 mmho								
	Leachant vol. 250 ml:							
	Start	6.96	3.59	643	0.08	138	4.21	19.9
	72	7.12	2.59	678	.07	11.5	2.67	7.55
	96	7.25	2.16	574	.04	2.65	1.87	3.60
	48	7.38	.434	76.4	.04	2.10	.48	.52
	48	7.38	.186	27.4	.04	2.22	.32	.21
	48	7.54	.156	21.4	<.01	1.94	.27	.17
	96	7.60	.174	24.3	<.01	2.34	.27	.15
4.5	96	7.67	.146	20.1	<.01	1.70	.25	.13

Table 2 (Continued)

	Leachant vol. 500 ml:							
	48	7.48	.123	14.2	<.01	1.82	.19	.11
	288	7.50	.164	22.6	.04	3.04	.25	.23
	48	7.60	.122	16.6	<.01	1.88	.19	.15
	288	7.66	.138	19.8	<.01	2.43	.19	.26
	48	7.78	.121	16.7	<.01	1.98	.15	.20
	168	7.64	.433	56.3	.05	7.54	.21	.79
2.0[2]	168	4.72	2.10	118	203	58.5	10.9	17.7
	216	4.15	2.22	65.9	354	22.3	1.58	18.5
	336	4.30	ND	56.3	354	23.6	2.43	35.8
	120	4.87	1.96	31.7	318	19.3	.20	30.9
5.4[3]	216	6.73	.129	7.93	13.0	2.05	.11	2.8
	168	7.58	.108	11.7	7.17	1.62	<.05	1.4
	168	7.71	.113	13.8	3.79	1.50	<.05	.90
	456	7.65	.162	23.7	.24	2.35	<.05	.80

[1]Hours between addition of leachant.
[2]Addition of distilled water of pH 2.0.
[3]Addition of distilled water of pH 5.4.

ND No data.

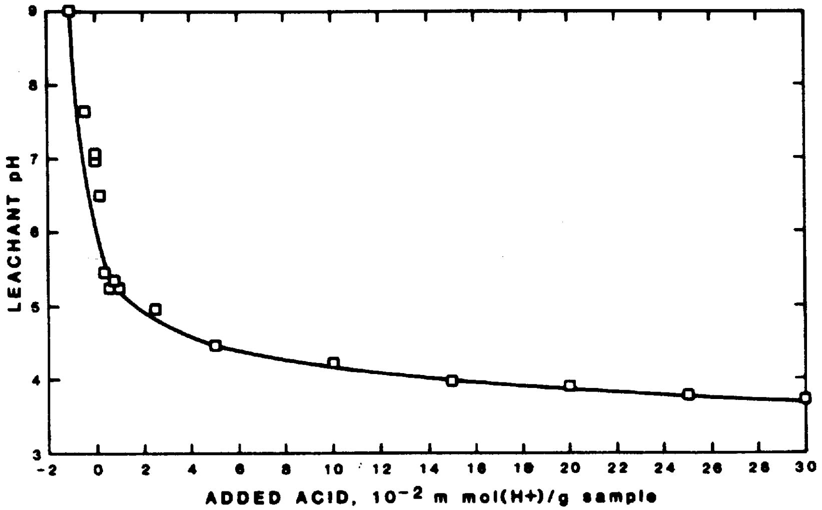

Figure 1. Leachate pH as a function of added acid.

maintained at near-saturation conditions while the other was allowed to dry partially. The averages of the two saturated and unsaturated 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 O.O1$\underline{M}$ KNO_3 and O.O1$\underline{M}$ KNO_2 leachants were used

Table 3. Salt effect on silver mine tailings (VIII)

(Note: Three-inch ID columns, 1.5 kg tailings, 350 cm^3 leachant)

Leachant	Residence time,	Leachate	Conductance,	Element, mg/L				
pH	hr[1]	pH	mmho	Ca	Fe	Mg	Pb	Zn
		0.1 M. KCl, CONDUCTANCE = 12.58 mmho						
5 49	168	7.24	2.16	149	0.14	12.2	0.64	1.55
	168	7.30	12.27	54.5	.17	5.77	.76	1.52
	168	7.61	12.92	35.8	.09	3.02	.37	.61
	168	7.73	13.17	27.8	.06	3.00	.28	.44
	366	7.87	13.26	33.1	.08	4.41	.30	.84
	192	7.93	12.76	26.2	.05	3.28	.20	.76
	72	7.96	13.13	17.0	.10	2.57	2.45	.58
	168	7.97	13.04	28.3	.16	3.29	.34	.55
		0.33 M. K_2SO_4, CONDUCTANCE = 7.53 mmho						
5 59	168	7.28	1.18	98.8	0.22	11.3	0.63	1.07
	168	7.43	7.35	64.4	.08	6.19	.69	1.12
	168	7.82	7.84	35.7	~.04	2.64	.34	.58
	168	7.95	8.39	26.9	.05	2.80	.23	.42
	366	8.15	8.09	35.9	.04	4.28	.29	.69
	192	8.08	7.76	28.5	.05	3.77	.24	.64
	72	8.15	7.91	20.8	.14	2.78	1.27	.45
	168	8.10	8.00	34.7	.11	3.58	1.30	.42
		0.1 M. KNO_3, CONDUCTANCE = 11.80 mmho						
5 39	168	7.27	2.23	123	0.37	12.3	0.61	1.57
	168	7.39	11.57	60.2	.06	5.63	.43	1.20
	168	7.72	12.22	33.6	.05	2.96	.43	.41
	168	7.86	12.46	25.3	.04	2.86	.34	.37
	366	7.99	12.63	27.5	.05	3.91	.24	.52
	192	7.96	12.05	25.5	<.04	3.28	.14	.44
	72	8.01	12.19	17.7	.27	2.72	10.7	.32
	168	8.02	12.34	31.1	.09	3.21	.48	.42
		0.33 M. Na_2S0_4, CONDUCTANCE = 6.20 mmho						
5 63	168	7.57	1.24	80.4	0.08	7.64	0.42	0.76
	168	7.46	6.25	65.5	.18	6.13	.44	.77
	168	7.79	6.55	30.6	.17	2.49	.20	.63
	168	7.91	7.13	27.1	<.04	2.37	.29	.52
	366	8.06	6.81	33.1	.07	3.33	.25	.75
	192	8.07	6.49	31.8	<.04	3.38	.26	.42
	72	ND	ND	26.1	.16	3.14	.23	.33
	168	8.14	6.57	25.3	.14	3.50	1.08	.59
		0.1 M. $LiN0_3$, CONDUCTANCE = 8.95 mmho						
5.58	168	7.47	1.79	74.4	0.11	7.44	0.39	1.12
	168	7.55	8.85	59.2	.25	5.67	.34	.92
	168	7.74	9.09	32.2	.15	2.46	.33	.51
	168	7.85	9.40	24.5	.08	2.60	.26	.41
	366	7.95	9.33	28.8	.07	3.09	.26	.45
	192	7.95	8.87	29.8	.08	2.88	.19	.40
	72	ND	ND	26.4	.14	3.15	3.68	.27
	168	7.98	8.95	29.5	.22	5.16	ND	.40

[1] Hours between addition of leachant.

Table 4. Effects of saturated and unsaturated (wet/dry cycles) conditions on silver mine tailings
(Note: Three-inch ID columns, 1.5 kg tailings, 350 cm^3 leachant)

Condition/ treatment	Residence time,		Conductance,	Element, mg/L			
pH	hr[1]	pH	mmho	Ca	Mg	Pb	Zn
0.1 M. KC1, CONDUCTANCE = 12.58 mmho, pH = 5.49							
Saturated	192	7.92	12.76	27.8	3.43	0.22	0.95
	192	7.94	12.75	24.7	3.14	.18	.56
	168	7.98	13.04	29.3	3.30	.28	.75
	168	7.97	13.01	27.4	3.27	.39	.35
Wet/dry cycle:							
Saturated	504	7.91	10.79	20.3	3.16	.11	.56
Unsaturated	504	7.25	15.54	53.8	10.2	10.66	5.32
Saturated	168	8.00	13.02	27.0	3.84	.22	.53
	168	7.81	13.53	28.3	4.02	.69	.96
	168	8.07	13.42	21.2	2.71	.12	.42
	168	7.96	13.66	21.8	4.12	.21	.83
Wet/dry cycle:							
Saturated	504	8.03	12.72	23.8	1.30	.32	.63
Unsaturated	504	7.31	16.55	112	11.9	1.71	12.3
Saturated:							
Dis. H_2O flush.	168	8.05	11.68	18.1	2.26	.14	.34
	168	7.72	10.85	27.2	2.90	.43	2.60
SLS leachant[2]	336	7.88	.429	1.31	.15	<.1	.08
	336	7.78	.521	6.55	.75	.14	.31
Wet/dry cycle:							
Saturated	576	7.89	.393	1.53	.27	<.1	.39
Unsaturated	576	7.32	.835	47.9	7.02	.51	3.60
Saturated:							
Dis. H_20 flush.	120	7.74	.275	.89	.11	<.1 .	.25
	120	7.70	.330	10.9	1.63	.17	.86
0.033 MM. K_2SO_4, CONDUCTANCE = 7.53 mmho, pH = 5.59							
Saturated	192	8.09	7.78	28.5	3.70	0.24	0.54
	192	8.06	7.74	29.6	3.85	.24	.75
	168	8.11	8.03	38.0	3.84	1.31	.40
	168	8.09	7.98	31.5	3.32	1.30	.43
Wet/dry cycle:							
Saturated	504	8.09	6.60	23.0	3.21	.13	.28
Unsaturated	504	7.80	8.92	47.6	8.62	.48	1.43
Saturated	168	8.15	8.07	31.4	4.30	.25	.27
	168	8.01	8.60	27.9	3.74	.43	.84
	168	8.17	8.59	24.0	3.29	.13	.22
	168	8.07	8.89	23.0	3.94	.19	.66
Wet/dry cycle:							
Saturated	504	8.12	8.89	29.2	2.08	.16	.31
Unsaturated	504	7.55	10.60	68.3	8.15	1.39	4.86
Saturated:							
Dis. H_2O flush.	168	8.21	6.94	18.4	2.54	.12	.15
	168	7.96	6.94	18.2	2.36	.42	1.01
NaBz leachant[3].	336	8.00	.567	2.53	.25	.09	.05
	336	7.92	.590	2.75	.28	.16	.18
Wet/dry cycle:							
Saturated	576	8.10	.519	4.18	.50	<.1	.10
Unsaturated	576	7.18	1.105	59.5	7.33	.55	5.35
Saturated:							
Dis. H_2O flush.	120	7.91	.432	4.98	.42	<.1	.08
	120	7.74	.510	12.9	1.77	.37	1.95

Table 4. (Continued)

	0.1 M. KNO_3. CONDUCTANCE = 11.88 mmho. pH = 5.39						
Saturated	192	7.90	12.14	25.9	3.33	0.14	0.50
	192	8.02	11.97	25.2	3.23	.14	.39
	168	8.03	12.56	35.9	3.28	.53	.44
	168	8.01	12.12	26.3	3.15	.43	.40
Wet/dry cycle:							
Saturated	504	8.09	9.76	18.0	3.64	<.1	.31
Unsaturated	504	7.51	14.25	50.3	8.82	.35	1.86
Saturated	168	7.89	11.89	22.6	3.38	.15	.40
	168	7.85	12.97	23.8	3.59	.32	.78
	168	8.07	10.60	16.4	2.69	<.1	.31
	168	8.00	13.31	18.4	3.30	<.1	.60
Wet/dry cycle:							
Saturated	504	7.98	12.23	24.3	1.45	.11	.45
Unsaturated	504	6.92	15.61	81.8	8.48	1.38	7.20
Saturated:							
Dis. H_20 flush.	168	8.02	10.94	14.9	2.08	2.37	.27
	168	7.82	10.40	15.2	1.87	.23	1.13
$KN0_3$ leachant [4]	336	7.82	1.635	13.0	.92	.07	.28
	336	7.71	1.720	18.8	1.82	.11	.51
Wet/dry cycle:							
Saturated	576	7.97	1.715	17.2	1.70	<.1	.41
Unsaturated	576	5.00	2.850	101	14.9	5.46	15.4
Saturated:							
Dis. H_20 flush.	120	8.01	1.411	10.5	1.27	.10	.19
	120	6.99	1.434	18.6	3.01	1.88	5.97
	0.33 M. Na_2SO_4 CONDUCTANCE = 6.20 mmho. pH = 5.63						
Saturated	192	8.11	6.45	33.3	3.29	0.24	0.44
	192	8.04	6.54	30.3	3.46	.27	.39
	168	8.15	6.56	24.7	3.53	.86	.33
	168	8.13	6.58	26.0	3.47	1.30	.85
Wet/dry cycle:							
Saturated	504	8.06	5.52	21.3	2.60	.17	.22
Unsaturated	504	6.65	7.67	96.8	14.5	3.01	24.1
Saturated	168	8.13	6.74	32.0	4.59	.24	.23
	168	7.87	6.96	37.8	5.07	.64	2.07
	168	8.18	7.11	22.4	3.33	.12	.16
	168	8.19	6.67	31.8	4.57	.18	.82
Wet/dry cycle:							
Saturated	504	8.16	6.72	26.6	1.33	.19	.25
Unsaturated	504	7.38	9.46	232	26.4	2.05	42.3
Saturated:							
Dis. H_2O flush.	168	8.30	5.87	23.8	6.26	.24	3.65
	168	8.03	5.85	52.7	4.06	.24	1.33
Phenol leach.[5].	336	7.82	.106	12.0	1.15	.14	.11
	336	8.02	.222	17.1	3.12	.10	.61
Wet/dry cycle:							
Saturated	576	8.00	.135	14.6	1.34	.10	.12
Unsaturated	576	7.97	.546	81.3	10.7	.10	.59
Saturated:							
Dis. H_2O flush.	120	7.97	.112	13.6	1.14	.11	.06
	120	8.04	.243	30.7	3.92	.14	.50
	0.1 $LiNO_3$ CONDUCTANCE = 8.95 mmho. pH = 5.58						
Saturated	192	7.94	8.88	29.3	2.99	0.20	0.39
	192	7.95	8.86	30.3	2.72	.19	.42
	168	8.00	8.97	31.6	5.90	ND	.37
	168	7.97	8.94	27.4	4.43	ND	.44
Wet/dry cycle:							
Saturated	504	7.98	7.81	21.3	2.43	.20	.39
Unsaturated	504	7.55	10.93	56.1	7.98	5.14	1.73
Saturated	168	7.98	9.04	37.6	4.33	.29	.57
	168	7.82	9.41	21.4	3.63	.45	.79
	168	8.07	0	24.6	3.30	<.1	.30
	168	7.98	9.78	27.5	4.91	.20	.70

Table 4. (Continued)

Wet/dry cycle:							
Saturated	504	7.93	8.92	31.2	1.38	.14	.63
Unsaturated	504	7.18	11.69	90.8	7.85	2.20	11.8
Saturated:							
Dis. H_2O flush.	168	8.06	8.07	23.0	2.68	<.1	.36
	168	7.94	7.38	18.0	2.15	.60	1.62
$NaNO_2$ leach.[6]	336	7.95	1.420	11.8	1.24	.25	.18
	336	7.74	1.465	20.7	2.03	.25	.98
Wet/dry cycle:							
Saturated	576	7.96	1.476	15.7	1.71	.10	.20
Unsaturated	576	5.66	2.335	82.9	11.9	7.51	17.1
Saturated:							
Dis. H_2O flush.	120	7.97	1.261	12.3	1.61	.11	.24
	120	7.20	1.209	15.4	2.36	1.95	3.79

[1] Hours between additions of leachant.

[2] 550 mg/L of sodium lauryl sulfate at a conductance of 0.165 and a pH of 5.40.

[3] 3578 mg/L ol NaB~ at a conductance of 0.363 mmho and a pH of 6.13.

[4] 0.01 M of KN03 at a conductance of 1.507 mmho and a pH of 5.40.

[5] 578 mg/L of phenol at a conductance of 0.059 mmho and a pH of 5.10.

[6] 60.01 M of NaN02 at a conductance of 1.301 mmho and a pH of 6.06.

ND No data.

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 the wet/dry cycle following the SLS treatment produced effects 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_2S0_4 leachant) to 0.12 ppm (with $LiN0_3$) for unsaturated columns while ranges below detection (using Na_2S0_4) to 0.08 ppm (using KCl) were observed for those columns that remained saturated. Similar results were also seen for cadmium, except values ranged from 0.26 (Na_2S0_4) to 0.024 ppm ($KN0_3$) 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 O.1OM NaOAc, pH = 6.03; O.O1M NaOAc, pH = 6.02; O.OO1M NaOAc, pH = 6.04; O.1OM $KN0_3$, pH = 5.79-control; and O.1OM 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 O.1OM acetate, pH = 6.03, were greater than those of O.1OM $KN0_3$, pH = 5.79.

Table 5. Acetate ion effect on silver mine tailings
(Note: Three-inch ID columns, 1.5 kg tailings, 350 cm3 leachant)

Leachant	Residence	Leachate		Element, mg/L				
pH	time, hr[1]	pH	Ca	Mg	Mn	Ni	Pb	Zn
0.1 M. KNO_3								
	144	7.86	46.2	7.52	11.3	0.12	0.28	3.74
5.79	192	7.72	34.7	3.49	8.89	.08	.23	2.25
	168	7.95	21.2	2.27	2.92	.01	.07	.92
	168	8.05	20.4	2.23	2.22	.03	.36	.91
Dis, water[2]	168	8.18	15 6	1 70	1 55	.01	<.03	.46
	168	8.37	1.05	<.05	.04	<.005	<.03	.02
0.1 M. OAc-[2]								
	144	7.11	60.3	10.2	18.3	0.17	2.94	3.91
6.03	192	7.55	83.4	6.80	26.8	.20	6.94	4.08
	168	7.61	65.4	6.40	14.8	.20	3.40	5.60
	168	7.53	69.6	7.15	13.0	.25	5.09	10.42
Dis. water[2]	168	7.63	54.6	5.80	9.43	.22	1.17	6.80
	168	8.20	4.6	.43	.69	.01	.11	.52
0.01 M. OAc-								
	144	7.82	16.2	1.79	2.92	0.03	0.18	0.95
	192	7.78	21.3	1.97	2.71	.02	.19	.77
6.02	168	7.94	11.8	1.27	1.62	<.005	.08	.52
	168	7.77	12.6	1.201	1.68	.01	.19	.55
Dis. water[3]	168	8.05	10.3	1.05	1.31	.01	.06	.37
	168	8.09	2.5	.15	.36	<.005	.03	.12
0.001 M. OAc-								
	144	7.92	19.5	2.70	2.09	0.04	0.11	0.40
6.04	192	7.91	14.8	1.80	1.53	.02	.08	.26
	168	7.94	13.1	1.72	1.20	.01	.04	.24
	168	7.41	13.2	1.63	1.25	.02	.45	.26
Dis, water[2]	168	7.90	12.0	1.50	1 06	.01	<.03	.20
	168	7.87	11.9	1.45	1.28	.02	.03	.23
0.1 M. OAc-								
	144	7.63	60.3	13.2	7.40	0.06	1.59	2.99
6.97	192	7.91	30.3	3.58	4.77	.02	1.44	1.36
	168	8.20	15.2	1.77	2.17	<.005	.58	.76
	168	8.30	14.0	1.53	2.55	.02	.57	.86
Dis. water[2]	168	8.38	12.8	1.53	2.62	.01	.40	.72
	168	8.52	.7	<.05	.04	<.005	<.03	.03

[1] Hours between addition of leachant.
[2] Acetate ion (CH_3COO -).
[3] Addition of distilled water.

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 O.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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