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COLUMN LEACH STUDY 1:HEAVY METAL DISSOLUTION CHARACTERISTICS FROM SELECTED COPPER MINE TAILINGS

by
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ABSTRACT

Mill tailings collected from seven copper mine mill sites in the western United States were examined by researchers from the Bureau of Mines for metal dissolution properties using a column leaching procedure involving a formulated "western rain" leachant. Studies investigated effects of height of waste column, wet/dry cycle, and maximum leachability of waste tailings. Further studies on selected samples indicated that treatment of acid-producing tailings with chemical stabilizers such as phosphates and carbonates did not greatly affect mobilization of heavy metals leached from these samples. Increased metal mobilization from unsaturated columns was often associated with decreased leachate pH and increased sulfate production, but was not observed in all samples examined. Results from these and other studies suggest that the driving force for metal dissolution and/or acid formation in unsaturated mine tailings is the oxidation of metal sulfides by atmospheric oxygen. The maintenance of tailings at or near saturation or the exclusion of atmospheric oxygen appear to produce leachates of nearly constant to slowly decreasing metal concentrations with each subsequent leaching.

INTRODUCTION

The rapid release of acid and metals from mining wastes by natural leaching processes presents a great potential threat for the contamination of groundwater and is perhaps the most serious impact mining can have on the environment. Although there are many methods designed to predict the amount of acid mine drainage (Ferguson 1985; Ferguson and Erickson 1987) none are completely successful. Characteristics of the waste, leachate percolation rates and pathways, and availability of atmospheric oxygen may greatly affect metal dissolution and acid formation. When mine wastes are disposed of on the surface, conditions are especially favorable to accelerated oxidation of pyrite and subsequent production of acid (Bainbridge et al. 1980).

In previous studies (Doepker 1988, 1989) selected mine tailings were examined to determine the parameters that affect the dissolution and transport of metal ions in mine tailings. It was found that metal dissolution and/or acid formation increased in unsaturated tailings, presumably as a result of atmospheric oxidation of sulfide minerals (Nordstrom 1982; Nordstrom et al. 1979). It was further demonstrated that leachate metal concentrations were independent of residence time if the columns were maintained at or near saturation. However, these studies all involved basic tailings, that is, tailings that produced basic leachates.

The purpose of the present study is to extend investigations to those tailings that produce acid leachate and to relate leachate concentrations to parameters such as type of metal mined, mineralogy, element composition, etc. This report describes results of approximately 2 years of tests on tailings collected from western copper mines.

MATERIALS AND METHODS

The copper mine tailings were obtained from seven different sites. Characteristics of each of these tailings samples are described below.

Gold-Copper Mine Tailings, Washington

A composite sample of tailings as formulated from samples taken at three locations within a main tailings containment area was used in this study. Iron phases dominate the oxide fraction of the tailings and include magnetite (Fe_3O_4), hematite (Fe_2O_3), and goethite ($FeO(OH)$). The major gangue constituent is quartz (Si02). The sulfide fraction consists of pyrite (FeS_2), chalcopyrite ($CuFeS_2$), and rare chalcocite (Cu_2S). Pyrite is abundant and generally occurs as liberated grains, but it is also locked with quartz gangue. Grain size for the pyrite averages 10-20 microns. Chalcopyrite is significantly finer grained (5-10 microns) than the pyrite, and is virtually always locked with gangue quartz. The abbreviated results of the "maximum leachability assay" (a nondestructive, mixed HCl-HN03 assay) (Kuryk et al. 1985) for these and all tailings studied in this investigation are given in Table 1.

Copper Mine A Tailings, Montana

One large sample (approximately 100 lb) of tailings was used in all studies discussed in this report. Abundant free pyrite is the most distinguishing feature of these tailings. Magnetite is present in relatively significant amounts, as is ilmenite ($FeTiO_3$). Chalcopyrite occurs in minor amounts, usually locked with gangue particles. Gangue is predominantly quartz and orthoclase (potassium feldspar, $KAlSi_3O_8$). Several rare but interesting minerals were also identified, including several grains of an iron-zinc silicate, pyromorphite [$(PbCl)Pb_4(PO_4)$], and finally, a lead-copper-antimony phase identified as either bournonite ($2PbS.Cu2S.Sb_2S_3$) or lead-bearing tetrahedrite (3Cu2S.Sb2S).

Table 1. Assay of maximum leachable concentrations.

Sample	Depth, in	Elements, pct										
		Al	Ca	Cu	Fe	K	Mg	Mn	Na	Pb	S	Zn
Gold-copper mine[1]		0.35	0.06	.0.11	1.01	.0.06	.0.18	0.00	0.01	0.00	1.00	.07
Copper mine A[2]		.54	.45	..07	1.19	..32	..45	.01	.02	.01	1..48	.04
Copper mine B	0-6	.84	.83	.04	1.05	.74	1.14	.01	.08	0	.79	0
	6-12	.63	.99	.03	1.04	.51	.86	.01	.05	0	.98	0
Coppermine C[2]		..01	..02	.14	.45	.04	. 01	.01	.02	.05	.32	.17
Copper mine D	0-6	.09	.11	.16	.11	.08	.07	.01	.01	0	.26	0
	6-12	.09	.09	.07	.1	.07	.07	.01	.01	0	.25	0
Copper mine E:												
Hole 1	0-6	.25	.17	.04	1.1	.32	. 23	.02	.03	.02	.97	.01
	6-12	.20	.13	.03	.84	.26	.19	.01	.02	.02	.73	.01
Hole 2	0-6	.34	.24	.13	1.17	.39	. 29	.03	.06	.02	1.05	.01
	6-12	.37	.24	10	1.21	.38	.28	.02	.03	.02	.97	.01
Copper mine F:												
Hole 1	0-6	.42	1. 06	0	.95	.29	.45	.02	.03	0	.86	.01
	6-12	.40	.97	.01	.85	.28	.43	.02	.02	0	.64	0
Hole 2	0-6	.53	1.05	.01	1.09	.37	.56	.02	.03	0	.69	.01
	6-12	.46	.94	.01	.99	.33	.49	.02	.02	0	.79	0

[1] Composite sample, no depth recorded.
[2] No depth recorded.

Copper Mine B Tailings, Utah

Two grab samples at the surface (0 to 150 mm and 150 to 300 mm deep) of these tailings were taken. The chemical compositions of these two samples are very similar (Table 1). Mineralogical analyses show that these tailings contain more orthoclase than quartz. The sulfide fraction consists essentially of pyrite and chalcopyrite. As with copper mine A tailings, much of the pyrite is liberated, while the chalcopyrite is almost always locked with the quartz or feldspar gangue.

Copper Mine C Tailings, Montana

A single, 6.69 Kg grab sample of copper mine C tailings was obtained, air-dried, and stored in a plastic bag. These tailings were used in two test protocols. Of interest is that the chemical composition of mine C tailings (Table 1) differs from mine A tailings, even though the origins of both are in the same mining district. The gangue in mine C tailings is predominantly quartz, the majority of the grains are whole, and there are no major intergrowths. Iron oxide (magnetite) and hematite are relatively abundant. Pyrite is present, but is not as abundant as in copper mine A tailings. Sphalerite (ZnS) occurs as both liberated and locked grains (1020 microns). Although sphalerite can not be considered a major constituent in the sample, its abundance is significantly higher in these tailings than in any of the others discussed in this report. Many of the quartz grains are rimmed with a combination of iron and potassium silicate (K_2SiO_3), probably feldspar with iron sulphide inclusions. The iron sulfide (most likely pyrite) has been oxidized, forming a coating on the rim of the original grain. Barite ($BaSO_4$) occurs in minor amounts, but its presence confirms the presence of sulphates in the tailings. Galena (PbS) and wolframite [$(Fe,Mn)WO_4$] were identified as well.

Copper Mine D Tailings, Arizona

Samples of these tailings were collected at O to 150 mm and 150 mm to 300 mm below the surface, analyzed, and used in a standardized test protocol. These Arizona tailings are similar to tailings from copper mines A and B in composition of the gangue, predominantly quartz and potassium feldspar. However, several other mineral phases distinguish these tailings from the others. Most of the copper in the tailings occurs in the form of chalcocite locked with quartz and feldspar grains, although chalcopyrite occurs in lesser quantities. Several iron minerals are present in the tailings, including pyrite, magnetite, hematite, and ilmenite.

Copper Mine E Tailings, Arizona

Four samples were taken from this mine-mill site at two locations in a large tailings impoundment. Samples were taken at O to 150 mm and 150 mm to 300 mm below the surface and subjected to a test protocol. These tailings contain the same phases as previously described for the other three Arizona samples. Quartz and orthoclase gangue predominate, and relatively abundant titanium-bearing iron oxides (magnetite, hematite) and titanium oxides (ilmenite, rutile [TiO_2]) are present.

Perhaps the major distinction of these tailings is the relatively abundant chalcopyrite, which occurs both as inclusions in the gangue and as liberated grains. The copper analyses for the three Arizona tailings support the determination made in the characterization study. Copper content is significantly higher in copper mine D and E tailings as compared to mine F tailings (Table 1). However, the major copper phase differs between the mine D and E tailings: chalcocite (20% sulfur) at mine D and chalcopyrite (35% sulfur with 30% iron) at mine E.

Copper Mine F Tailings, Arizona

The last set of tailings were collected at O to 6 and 6 to 12 in below the surface from two locations within a single tailings impoundment. It should be noted that all three Arizona operations are in the same geological region. Quartz and orthoclase gangue predominates. Pyrite and chalcopyrite are the major sulfides present, but no chalcocite was found in these tailings. Several oxide phases were found, including titanium-bearing magnetite and hematite, ilmenite, and rutile. Several zircon grains were identified, as well as apatite $L(CaF)Ca_4(PO_4)_3]$. Barite and anhydrite ($CaSO_4$) occur in compound grains, some including celestite ($SrSO_4$).

The tailings samples used for all experiments were air dried in the laboratory, crushed manually to break up agglomerated particles formed during drying, blended, and stored in closed plastic containers.

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)[3] and then deionized with a Barnstead NANOpure II Demineralizer (18.3 Mohm/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 until used. Simulated western rain was prepared as described by Bainbridge et al. (1980).

COLUMN TEST EQUIPMENT AND METHODS

Leach columns were constructed from 600 mm- or 1200 mm lengths of 75 mm inside-diameter (11)) polyvinyl chloride (PVC) pipe equipped with cemented couplings and bushings in which perforated Nalgene plates had been installed. A 9-cm G6 borosilicate glass fiber filter was placed on the perforated plate before installation of the bushing.

In one study, fifteen 600 mm columns and fifteen 1200 mm columns were matched into 15 sets. A single tailings sample was distributed between one 600 mm (1.75 kg) and one 1200 mm (7.0 kg) column. In another series (residence-time effect), a single tailings sample was used in thirty-two 600 mm columns, each containing 1.5 kg of tailings. A series of 12 similarly constructed 37 mm ID PVC columns were used to examine the effect of atmosphere on metal dissolution from two different tailings, with six columns being filled with 650 g of each waste. Leachants were introduced to the columns drop by drop from a l-L polypropylene storage bottle through Tygon tubing fitted with a screw clamp. Volumes of leachant depended on an experimentally determined tailings "pore" volume. Estimates of the pore volume were made by filling the columns with the appropriate weight of dry tailings and enough leachant to saturate the column plus an additional 100 cm^3 or so. The difference between the leachant and leachate volumes led to the defined pore volume.

ANALYTICAL EQUIPMENT

The metal analyses reported in this investigation were carried out with the aid of a Perkin-Elmer Plasma II ICP spectrometer. Anion analysis was conducted with a Dionex 4000i ion chromatograph equipped with an AS4A separation column.

DISCUSSION AND RESULTS

In a previous study (Doepker 1988), there was evidence from column leach experiments that leachate metal concentrations depended on leachate residence time (i.e., the total time a pore volume of leachate remained in contact with column waste material). For any experimental protocol that utilizes 1 pore volume per leaching, the residence time is simply the time between leachings. Later work (Doepker 1989), showed that this residence-time effect occurred in unsaturated tailings while saturated tailings exhibited no increase in metal concentrations with increased residence time. These studies involved tailings that produced near-neutral to slightly basic leachates. Table 2 shows a part of a similar study using acidic copper mine A tailings. Leachate metal concentrations from saturated columns remained constant over a 54-day period while unsaturated tailings produced the enhanced metal dissolution characteristics of oxygen-sensitive sulfides containing waste.

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

Table 2. Residence time effect on column leachate concentrations, wet/dry cycle, copper mine A tailings.

Residence time days	pH	SO^4 mg/L	Element, mg/L Al	Ca	Cu	Fe	K	Mq	Mn	Na	Pb	S^2	Zn
Sat	3.05	1,830	13.7	604	25.9	12.9	0.6	41.6	2.1	0.83	0.1	647	6.45
Unsat	3.08	1,850	13.9	607	26.9	4.17	.5	48.8	2.28	.93	.1	695	7.18
14													
Sat	3.26	1,850	11.0	566	30.4	11.5	1.2	46	3.75	.97	.02	720	7.86
Unsat	2.89	2,000	24.5	612	52.9	3.88	1.5	52.3	3.22	1.06	.04	690	9.8
21													
Sat	3.43	1,890	12.4	592	35.2	16.1	1.1	49.3	2.47	1.10	0	656	8.4
Unsat	3.25	2,060	22	511	49.2	7.38	1.4	54.9	2.85	1.49	.11	692	9.21
28													
Sat	3.28	1,840	13.7	566	36.4	6.39	.7	40.8	2.3	1.32	.12	653	6.98
Unsat	2.62	2,400	54.5	579	77.4	14.3	2.7	58.2	3.24	2.01	.1	859	11.5
Sat	2.93	1,880	16.8	567	29.7	11.5	.4	43.8	2.60	1.48	.1	670	8.62
Unsat	2.47	2,470	78.9	576	92.6	17.4	2.2	65.2	4.24	2.23	.12	910	12.5
43													
Sat	3.03	1,890	17.9	578	30.5	13.6	.5	40.8	1.97	1.53	.07	664	9.17
Unsat	2.54	2,640	74.1	545	78.7	15.1	2.2	59.2	3.61	2.12	.05	839	11.4
49													
Sat	3.07	1,900	16.4	619	32	20.9	.4	41.5	2.13	1.45	.13	576	9.61
Unsat	2.49	2,800	106	606	114	20.2	1.6	83	4.8	2.57	.11	958	16.7
56													
Sat	2.90	1,900	17.9	630	31.5	26.5	.4	41.9	2.58	1.36	.14	655	11.3
Unsat	2.68	2,640	83.8	620	118	15.5	1.4	82.7	2.92	2.69	.12	980	14.1

[1] Analysis with ion chromatograph.

[2] Analysis with Plasma II ICP spectrometer.

The role of atmospheric oxygen was further examined with two different Montana copper mine tailings, mine A and C. Three columns of each tailings were placed into a chamber in which a nitrogen atmosphere was maintained while the leachant was allowed to be saturated with oxygen. Three other columns of each tailings were exposed to the normal laboratory atmosphere and used as a comparison. It should be mentioned that although the chamber atmosphere was maintained at or below 2% oxygen, leachate metal concentrations between the chamber and the laboratory atmosphere were identical within experimental variability. It can also be shown that a 28-day dry cycle produced very little enhanced metal dissolution in either the chamber or the laboratory atmosphere. Two explanations can be considered. First, sufficient oxygen to maintain a slow degradation of the tailings was present in the undegassed leachants or, second, microorganisms still active at these low oxygen pressures were responsible for the dissolution. If one considers the limited amount of enhanced metal dissolution from the unsaturated tailings observed in this test series, it is conceivable that the leachate metal concentrations were simply solubility-controlled dissolution from sulfate-rich tailings.

Six 75mm OD, 711mm -long PVC columns were "pushed" into the tailings in a main tailings impoundment of the gold-copper mine. Two locations were examined, using three columns each. The columns were then removed from the tailings and the top 75- 100 mm of tailings within the columns were discarded to facilitate the addition of leachants. These six columns were subsequently leached with synthetic rain and later with 0.01 M Na2tlP04, pH = 9.30 (table not included).

The results indicate that, although the two sites produced different leachate metal concentrations, both showed the same overall behaviour with each subsequent leaching, as well as very little dry cycle effects. It should be added that the addition of phosphate to these samples over 7 pore volumes (seven leachings) had very little effect on the metal dissolution or on a 29-day dry cycle. An exception to this statement was an eight- to tenfold increase in leachate sulfate after the columns appeared to become saturated with phosphate. It appears that phosphate simply replaced sulfate as the principal anion. Other studies conducted with gold-copper mine tailings, and copper mine tailings A and C showed similar results with the addition of phosphate leachant.

In an on-going study, tailings from seven copper mines have been leached over the past 2 years with synthetic rain and subjected to two dry cycles of 2 months each. Tailings have shown a very systematic decrease in metal dissolution with time, but some have demonstrated enhanced activity during unsaturation (dry cycle). Space precludes the inclusion of all of these data, but a number of observations will be made here. The basic set-up included two columns for each sample, each containing 7.0 kg or 1.75 kg of waste. Approximately 1 pore volume of leachant was added to the shorter column while the same volume (equivalent to 1/4-pore volume) was added to the longer columns. Leachings of these columns were carried out approximately once a month with synthetic rain.

Gold-Copper Mine Tailings

Table 3. Leachate concentrations from gold-copper mine tailings
(1.75 kg waste; 10 in column depth; 375 cm^3 synthetic rain leachant)

Time between leachings weeks	pH	mmho	SO_4 mg/L	Element, mg/L Al	Ca	Cu	Fe	Mg	Mn	Zn
Start	3.36	7.45	6,900	>800	498	1,150	46.7	102	0.22	487
3	2.93	12.13	14,800	>800	449	1,150	247	267	11.3	>400
3	2.96	5.52	5,500	466	467	569	52.2	96.2	3.64	314
4	2.93	2.88	NA	154	128	NA	NA	33.6	5.5	~400
3	2.95	1.88	924	41.6	232	33.8	32.2	10.4	1.05	30.2
4	3.07	1.38	531	22.9	81.6	24.4	10.5	8.98	.93	20.4
4	2.73	1.48	495	36.6	44.6	22.8	17.6	7.91	.39	23.5
4	2.61	1.68	705	69	60.4	49.6	22.6	15.8	.95	32.2
8[1]	2.34	8.8	8,640	1,410	138	828	205	120	6.94	438
4	2.53	3.29	2,190	264	47.7	151	141	60	3.11	114
4	2.51	2.65	1,690	193	52.9	69.2	165	45.4	2.61	79.4
4	2.63	2.3	1,200	129	41.3	36	102	38.3	1.17	41.7
4	2.63	1.66	736	73.1	36.4	21.1	66.6	31.3	1.44	26.8
4	2.66	1.25	465	34.1	21.9	10.5	27.2	20.1	1.17	15.4
4	2.69	1.08	444	31.7	29.5	9.14	37.3	19.2	1.07	13.1
4	2.69	1.07	356	24.3	25.1	6.65	30.8	17.5	.84	11
4[1]	2.82	1.01	350	21.2	28.1	6.12	26.9	18.3	1.01	10
8	2.65	4.61	5,290	631	111	109	99.6	95.5	3.44	84.7
4	2.53	2.23	1,040	98.9	25.7	26.2	145	37.1	1.28	29.4
4	2.62	1.84	915	51.9	15.3	11.9	32.9	27.3	.99	20.4
2	2.55	1.45	619	42.1	18.6	10.2	69.7	37.7	1.19	20.5
2	2.72	1.17	368	20.1	14.8	6.54	30.7	20.5	.62	9.93
3	2.8	1.02	301	13.8	13.6	4.33	30.9	16.9	.49	6.62

NA No analysis.

[1] Dry cycle, columns opened to atmosphere.

The initial leachate metal concentrations from both long and short columns were similar although the sample depths were 40 and 10 in. Concentrations plotted on a per-pore volume base for the two columns were the same within experimental variance. Table 3 presents an abbreviated set of element analyses of leachates from the shorter of these columns. This sample shows considerable metal enhancement when the columns were allowed to partially dry (Table 3).

Copper Mine A Tailings

As reported above, the leachate metal concentrations from both the long and short columns were initially the same and remained so on a per-pore volume basis. Therefore, Table 4 reports selective data for the short column only. High sulfate and high metal concentrations were observed to diminish slowly with each pore leaching, but little enhanced metal dissolution occurred from unsaturated conditions.

Table 4. Leachate concentrations from copper mine A tailings
(1.75 kg waste; 9.5 in column depth; 400 cm ^{3} synthetic rain leachant)

Time between leachings weeks	pH	mmho	SO_4 mg/L	Element, mq/L						
				Al	Ca	Cu	Fe	Mg	Mn	Zn
Start	3.31	NA	7,140	NA	446	NA	>400	1,510	>160	490
3	3.18	7.3	6,890	113	455	341	569	479	61.2	113
3	3.07	4.72	4,360	46.5	490	166	13	351	20.5	54.5
4	3.04	4.31	3,900	39.3	541	134	5.87	325	20.6	55
3	2.94	3.66	2,690	26.4	486	80.1	4.51	194	9.93	27.4
4	3.02	3.45	1,400	10.5	301	30.3	2.22	83	2.99	12.4
4	2.7	3.37	1,910	18.6	446	31.6	5.36	114	3.19	19.1
4	2.77	3.41	2,320	21.4	642	44.5	8.61	130	5.64	28.1
8[1]	2.38	4.46	2,710	148	517	203	29.2	127	6.21	41.4
4	2.52	3.45	1,940	55.5	660	79.8	16.7	66.6	3.02	31.9
4	2.65	3.01	1,860	51.4	703	67.8	16.8	60.4	3.2	43.9
4	2.72	2.99	2,010	35.9	639	41.6	9.19	23.1	1.42	19.8
4	2.7	2.96	1,840	29.5	685	29.8	9.45	13.8	.88	11.7
4	2.61	2.91	2,020	23.7	574	20.8	7.41	8.93	.62	11
4	2.68	2.74	2,650	33.1	772	27.7	8.13	9.77	.82	12.4
4	2.71	2.72	2,120	23.3	564	20.2	5.63	9.05	.59	11.8
4	2.87	2.72	1,680	21.7	700	18.5	3.11	3.35	.52	9.19
8[1]	2.54	3.56	2,270	57.8	568	34.7	17.6	18.6	1.42	21
4	2.61	2.91	1,460	36.4	523	25.3	8.47	11.3	.92	16.4
4	2.66	2.44	1,420	26.9	404	24.5	7.13	8.77	.87	13.8
2	2.67	2.33	1,310	25.4	429	29.6	7.99	13.2	1.19	18.5
2	2.78	2.03	1,060	13	320	18.8	4.83	7.59	.69	11.3
3	2.8	2.15	1,120	15.7	378	23.7	4.44	13.7	.8	15

NA No analysis.

[1] Dry cycle, columns open to atmosphere.

Table 5. Leachate concentrations from copper mine B tailings
(1.75 kg waste; 9.5 in column depth; 450 cm³ synthetic rain leachant)

Time between leachings weeks	pH	mmho	SO_4 mg/L	Element, mq/L						
				Al	B	Cu	K	Mg	Mo	Na
SAMPLING DEPTH, 0-6 IN										
Start	7.05	>20	852	0.09	0.27	158	55	68.6	2.52	2,190
3	7.83	6.42	1,830	.04	.21	545	129	110	2.89	490
3	7.85	3.26	1,983	<.01	.33	419	78	82.2	2.07	104
4	8.15	1.545	675	<.01	.28	282	45	19.3	NA	43.6
3	8.7	.415	93.6	.03	.31	68.9	23.4	3.89	1.38	38.5
4	8.26	.391	63.6	<.01	.27	28.9	15.3	2.45	NA	20.9
4	7.87	.393	78	<.01	.32	40.7	18	2.48	.54	12.9
4	8.1	.54	145	.02	.4	78	24.7	5.53	.63	8.64
8[1]	7.48	1.59	912	.04	.64	409	58.3	26.7	2.83	14.6
4	7.86	.961	336	.03	.36	173	41.3	12.2	1.21	11.7
4	7.95	.721	293	.07	.44	89.6	21.5	10.4	3.55	4.48
4	7.84	.627	175	.3	.65	99.1	27.5	8.83	6.38	5.48
4	7.99	.641	176	.21	.43	97.2	29.4	8.53	8.34	6.46
4	7.85	.638	220	.29	.54	106	28.7	10.4	11.7	7.1
4	7.88	.644	169	.93	.58	89.7	22.8	8.22	9.94	5.53
4	8.02	.616	175	<.01	.42	86.4	23.2	10.6	11.3	5.07
4	8.14	.684	219	<.01	.41	106	25.6	6.92	7.51	6.24
8[1]	7.63	.952	376	.1	.53	133	23.3	10.9	7.45	5.58
4	7.78	.802	305	<.01	.68	157	27.8	9.65	5.37	7.1
4	8.04	.827	333	.07	.55	148	27.4	9.46	4.02	7.4
2	7.85	.677	214	<.01	.4	89.6	18	6.6	2.06	4.13
2	7.92	.694	173	.06	.38	101	19.4	5.32	1.34	4.47
3	7.91	.662	192	.24	.68	100	19	8.07	1.55	4.53
SAMPLING DEPTHL 6-12 in										
Start	7.72	5.21	2,910	0.24	0.51	502	88.8	150	2.13	650
3	8.19	2.15	816	8.19	.14	183	31.8	32.7	1.31	179
3	8.24	.483	94.5	<.01	.42	46.9	24.6	8.64	1.32	24
4	8.64	.603	185	<.01	.46	94.5	41.4	18.1	NA	18.6
3	8.7	.547	128	.01	.31	94.8	33.9	13.2	.53	9.01
4	8.4	.651	203	<.01	.37	86.2	31.8	15.4	NA	5.82
4	8.1	.691	178	.01	.39	87.5	31.2	15.6	.29	3.57
41	8.01	.735	222	<.01	.56	109	38.9	20.5	.34	4.88
8[1]	7.15	1.71	864	.01	.95	135	52.6	51.8	.69	9.45
4	7.9	.867	309	.01	.51	131	34	19.1	.57	10.8
4	8.01	.715	299	.04	.58	84.2	21.9	18.9	1.81	4.96
4	7.9	.677	191	.26	.69	96	25.8	16.7	3.47	5.32
4	8.06	.667	198	.18	.49	98.7	29.8	15.7	5.03	6.21
4	7.85	.67	209	.12	.57	98.3	28.4	16.7	6.16	5.69
4	7.93	.648	119	.79	.53	83	22.6	8.92	3.96	5.09
4	8.04	.64	182	<.01	.45	98.6	23.7	15	5.54	4.34
4	8.04	.68	204	<.01	.51	97.8	22.9	12.3	5.2	4.75
8[1]	7.86	1.02	411	.05	.68	138	23.4	18.7	5.39	5.05
4	7.8	.953	385	<.01	.68	171	28.3	19.9	3.87	5.57
4	8.05	.877	202	.03	.57	136	22.5	15.5	2.57	4.88
2	7.96	.816	283	<.01	.44	103	17.7	13.2	1.58	3.37
2	7.98	.642	148	.05	.46	92.6	19.2	9.17	1.25	3.85
3	7.89	.537	129	.21	.68	76.4	15.2	9.15	.92	3.49

NA No analysis.

[1] Dry cycle, columns opened to atmosphere.

Copper Mine B Tailings

Table 5 reports the results of the short-column studies of samples taken at two depths within the same tailings impoundment. Although there appears to be some variation of metal and sulfate concentrations in the column leachates, the overall characteristics of metal dissolution remain the same for both sample depths. Sulphate production is somewhat affected by unsaturation as well as a drop in leachate pH. It should be emphasized that these effects are nearly lost when columns depths of 39 in are used.

Copper Mine C Tailings

These tailings were found to be the most diverse of the all the samples in the variety of distinct mineral phases present. The results from the short column (Table 6) show thaL tailings produce high metal dissolution and that are extremely sensitive to a dry cycle. It should be pointed out that a second sample reported to come from the same source as mine C tailings was used in the chamber study reported upon earlier in this paper. No such dramatic dry-cycle effect was observed.

Table 6. Leachate concentrations from copper mine C tailings
(1.75 kg waste; 8.5 in column depth; 250 cm^3 synthetic rain leachant)

Time between				SO_4	Element, mg/L						
leachings weeks	pH	mmho	mg/L	Al	As	Ca	Cd	Cu	Fe	Mn	Zn
Start	2.98	1.95	6,750	326	4.66	>160	49.6	>3,200	2,140	>170	>400
3	2.76	10.04	7,710	52.5	13.4	117	.02	>3,200	506	47.8	>400
3	2.74	4.47	4,590	14.9	8.1	40.1	2.25	1,270	218	15.8	>400
4	2.26	3.81	2,060	13.8	.1	45.2	.51	140	126	9.96	250
3	2.48	2.71	1,610	5.91	4.3	7.37	.39	190	373	7.83	176
4	2.36	3.6	1,800	8.99	NA	13.3	.08	197	344	3.99	80.3
4	2.15	3.44	1,450	12.3	6	11.2	.77	128	361	1.52	53.7
4	2.13	3.6	2,200	30.5	11.9	23.2	1.29	148	615	3.36	72.6
8[1]	1.53	19.32	11,800	199	305	25.5	54.5	1,400	3,560	5.44	497
4	1.82	11.02	6,870	79.5	165	17.7	8.16	667	2,080	5.02	379
4	1.79	7.07	3,840	33.5	39.4	8.25	2.1	279	1,269	3.01	257
4	2.21	4.13	2,310	13.8	24	1.9	.73	118	719	1.21	126
4	2.23	2.7	1,350	7.2	6.4	4.5	.36	70.8	420	1.37	100
4	2.19	2.37	929	4.6	3	1.86	.25	32.5	247	1.07	71.5
4	2.3	2.19	925	4.93	3.1	4.19	.24	25.9	278	1.16	79.8
4	2.3	2.18	804	3.72	2.2	1.94	.27	21.7	206	.91	83.9
4	2.43	2.01	780	4.4	2.4	.667	.3	26	189	.82	106
8[1]	2.02	10.26	6,980	63.5	44.8	6.68	1.92	292	1,100	2.31	476
4	2.15	2.35	999	6.56	1.7	<.01	.38	43.6	231	.47	116
4	2.51	1.9	830	2.62	1.4	<.01	.24	27.9	156	.4	75.8
2	2.33	1.62	494	1.3	1.6	<.01	.13	12.6	87.3	.28	42
2	2.62	1.311	266	.75	0	<.01	.09	8.65	43.8	.17	29.2
3	2.65	1.26	258	1.02	2	.13	.1	8.04	44.6	.2	27.7

NA No analysis.
[1] Dry cycle, columns opened to atmosphere.

Copper Mine D Tailings

Although these tailings are mineralogically similar to copper mine A and B tailings, the metal concentrations from dissolution seem to mirror the low leachate

Table 7. Leachate concentrations from copper mine D tailings
(1.75 kg waste; 9 in column depth; 0-6 in sampling depth; 325 cm^3synthetic rain leachant)

Time between				SO_4	Element, mg/L						
leachings weeks	pH	mmho	mg/L	B	Ca	Cu	K	Mg	Mn	Mo	Na
Start	8.25	0.377	157	0.02	79.1	0.33	41.9	5.5	0.03	0.75	2.1
3	8.18	.987	348	.13	138	.22	52	10	.08	1.15	3.5
3	8.28	.443	99.3	.11	55	.12	32.8	4.11	.01	.87	2.56
4	8.19	.381	57.6	.12	44.1	.1	27.2	3.15	<.01	NA	2.37
3	8.11	.324	54	.21	45.4	.13	24.4	6.03	.03	.56	2.4
4	8.08	.334	68.7	.16	48.7	0	23.9	3.48	<.01	NA	2.1
4	7.84	.32	61.5	.24	41.5	.12	18.1	2.96	.02	.64	2.17
4	8.05	.35	59.7	.26	48.8	.15	16.8	3.09	.01	.99	2.72
8[1]	7.8	.531	178	.3	82.3	.08	20.1	5.28	.03	6.9	4.2
4	7.74	.37	143	.53	63.7	.24	13.8	4.34	<.01	8.56	4.71
4	7.8	.436	158	.55	96.5	.29	18.5	7.02	.01	15.9	7.51
4	7.49	.436	104	.46	67.2	.24	11.6	3.96	<.01	10.4	5.43
4	7.89	.412	92.2	.19	138	.35	41.4	11.5	.1	20.2	3.77
4	7.63	.395	100	.48	55	.52	8.1	3.68	<.01	11.5	6.04
4	7.85	.411	107	.7	63.6	.44	7	4.14	.04	13.7	7.52
4	7.79	.413	106	.48	61.6	.39	6	3.38	.02	15.2	5.87
4	7.61	.443	120	.55	77.5	.54	6.3	1.35	.02	19.2	7.01
8[1]	7.13	.637	240	.65	127	.35	7.3	4.21	.03	34	7.29
4	7.24	.476	150	.56	78.1	.35	4.5	1.59	.04	20.4	7.26
4	7.24	.41	135	.44	60.9	.25	3.4	.63	.02	18.3	5.27
2	7.23	.303	69.3	.46	45.3	.27	3.3	.2	.04	12.9	4.05
2	7.15	.282	63.9	.39	35.1	.17	1.9	<.01	.03	9.55	3.67
3	7.44	.268	64.8	.3	40	.52	1.7	2.01	.03	10.3	4.04

NA No analysis.

[1] Dry cycle, columns opened to atmosphere.

sulphate and the sample's total sulphur as opposed to general mineralogy. The overall behaviour of the metal dissolution follows the general rules of the other samples except that dissolution enhancement from unsaturated tailings is very small. Table 7 reports a portion of the collected data from this tailings sample.

Copper Mine E Tailings

The major difference among the Arizona tailings may be seen in the mineral form of the copper present in the tailings. These tailings (Table 8) produce extremely high amounts of sulfate along with high amounts of copper-containing leachates, while relatively abundant chalcopyrite appears in the tailings. These tailings did not produce the expected enhanced dissolution associated with unsaturation, but this may be due Lo the fact that these tailings contain a considerable amount of fines, which prevents a great deal of evaporation, and produce columns that require many weeks to elute 1 pore volume of leachate. Table 8 reflects the differences and similarities in composition often observed in sampling two locations within the same tailings impoundment.

Copper Mine F Tailings

Pyrite and chalcopyrite are present and yet the copper concentration (short columns) in leachates remain equal to or below 0.1 mg/L; iron is below 1.0 mg/l.. High sulfate production (Table 9) was observed in both the long and short columns and yet metal dissolution appears low. Leachate pH remains high for both copper mine D and F tailings, while high metal concentrations were observed for the low pH leachate of copper mine E tailings.

Table 8. Leachate concentrations from copper mine E tailings
(1.75 kg waste; 9 in column depth; 0-6 in sampling depth; 400 cm3 synthetic rain leachant)

Time between leachings, weeks	pH	mmho	SO4, mg/L	Element, mg/L											
				Al	B	Ca	Cd	Co	Cu	Fe	Mg	Mn	Na	Ni	Zn
HOLE 1															
Start	3.02	>20	25,900	1,400	0.2	179	0.43	77.8	1,290	77.7	312	~800	798	NA	123
3	3.09	8.46	5,850	302	.29	403	.05	13	248	7.57	410	193	168	NA	18.2
10	3.18	4.13	3,090	84.1	.36	480	.38	2.92	70.2	5.09	213	49.2	86.6	NA	6.15
8	2.95	3.33	2,710	66.8	.4	536	.01	1.23	47.1	3.81	92.1	15.3	48.6	0.57	4.01
12[1]	2.84	1.58	2,140	88.6	.38	658	<.01	.82	24.6	2.93	51	10.8	46	.69	1.98
8	2.51	1.51	2,230	73.9	.29	584	.01	.41	27.5	3.67	24	3.43	22.1	.29	1.99
8	2.92	2.93	1,690	67.9	.27	631	.01	.27	17.5	2.54	15.8	2.02	18.7	.15	.82
4	2.98	2.8	1,840	33.9	.19	351	<.01	.02	7.77	5	6.85	.94	7.2	.04	.88
4	2.93	2.65	2,120	48.2	.23	790	<.01	.04	7.02	5.81	6.7	.87	15	.08	.06
4	2.92	2.72	1,910	39.9	.17	654	<.01	<.02	4.41	3.46	4.11	.57	12.7	.03	.58
4	3.22	2.56	1,840	27	.16	643	.01	~.02	1.36	.58	0	.08	10.2	.01	<.01
8[1]	3.36	2.34	1,330	16.6	.14	558	<.01	.04	2.15	1.77	.39	.4	10.9	.02	.79
HOLE 2															
Start	2.77	<20	21,100	84.6	.38	134	1.1	54.5	2,450	4.8	242	~780	2,500	NA	326
3	2.82	7.09	5,430	33.3	2.27	432	.16	14.2	784	1.27	307	83.3	654	NA	234
10	4.1	4.11	2,740	12.6	.99	268	.91	2.64	186	.94	124	47.8	25.3	NA	18.3
8	3.81	3.44	2,890	16	1.28	518	.04	2.35	250	.39	93.2	53.3	11.6	2.69	18.7
12[1]	3.2	8.98	2,650	59.6	1.24	558	.03	2.43	354	14	78	34.1	9.6	2.24	17.6
8	3.02	3.41	2,910	39.7	.85	343	.03	1.68	247	3.46	56	22	2.98	1.71	23.8
8	3.03	2.89	1,900	42.7	1.09	641	<.01	.8	130	.7	33.4	7.69	7.92	.88	4.9
4	3.25	2.72	1,960	30.8	.88	438	<.01	.43	90.1	1.98	21.6	5.85	4.96	.52	3.44
4	3.25	2.58	2,120	36.7	1.2	702	.01	.7	100	.85	32.8	7.18	6.99	.89	4.17
4	3.37	2.49	2,080	8.04	.36	624	.01	.22	40	.78	6.99	2	1.7	.24	1.57
4	3.51	2.44	1,530	6.76	.29	544	.01	.32	31.1	0	1.79	.95	1.85	.12	1.02
8[1]	3.14	2.78	1,960	25.8	.34	611	<.01	.57	81.4	1.35	9.61	1.79	2.86	.28	2.5

NA No analysis.

[1] Dry cycle, columns open to atmosphere.

Table 9. Leachate concentrations from copper mine F tailings
(0-6 in, hole 1 sampling depth; 350 cm^3 synthetic rain leachant)

Time between leachings weeks	pH	mmho	SO_4 mg/L	Element, mg/L						
				B	Ca	K	Mg	Mn	Mo	Na
				1.75 KG WASTE: 8.5 IN COLUMN DEPTH						
Start	8.28	5.56	2,740	0.39	417	80.6	16.6	0.27	1.55	892
3	8.02	3.89	1,840	.55	487	93.6	24.7	.37	1.92	258
3	8.01	3.76	2,340	.54	534	87.5	23	.25	.82	390
3	8.04	2.9	2,110	.58	653	87	25.5	.29	.24	96.8
3	7.93	2.65	1,800	.5	724	93.3	39	.62	.35	96.5
4	7.98	2.53	1,410	.4	483	46.2	17.8	.26	.09	12.7
4	7.76	2.51	1,580	.52	467	40.7	16.2	.31	.09	10.6
4	7.88	3.72	1,420	.66	533	36.4	19	.38	.12	4.04
8[1]	7.73	2.61	1,760	.81	667	49.4	18.4	.45	.42	19.6
4	7.8	2.52	2,100	1.35	633	40.9	21.5	.43	1.33	20.1
4	7.77	2.45	2,820	1.36	686	28.2	23.1	.35	1.05	8.71
4	7.71	2.43	1,560	1.13	713	29.6	12.6	.39	.27	11.1
4	7.95	2.39	2,140	1.18	516	21.1	10.1	.55	.29	8.92
4	7.77	2.42	1,440	.77	458	17.3	5.3	.41	.19	10.6
4	7.89	2.38	1,140	1.06	361	11.9	3.48	.29	.14	8.81
4	7.94	2.42	1,450	1.08	531	12.8	6.19	.68	.26	6.78
4	7.75	2.46	1,330	.92	564	12.3	<.005	.24	.16	9.59
8[1]	7.65	2.46	1,360	.92	702	11.4	1.04	.34	.37	12.4
4	7.8	2.34	1,300	.88	642	9.2	<.005	.37	.57	10.9
4	7.85	2.25	1,400	1.02	612	7.9	<.005	.23	.57	10.6
2	7.68	1.81	970	.95	441	5.5	<.005	.15	.52	8.8
2	7.7	1.44	767	.79	341	4.1	<.005	.06	.36	10.8
3	7.76	1.06	492	.55	238	3.7	.53	.04	.29	9.63
				7 KG WASTE: 34 IN COLUMN DEPTH						
Start	8.27	7.03	3,630	0.54	448	88.1	5.4	0.24	5	1,340
3	8.19	6.3	342	.7	367	94.5	20.5	.22	2.39	1,070
3	8.06	5.14	2,970	.33	481	98.4	23.2	.18	.99	809
4	7.98	4.97	1,860	.33	738	128	35.3	.31	.81	492
3	7.91	4.11	1,640	.48	742	89.8	37.7	.55	.81	116
4	8	3.11	1,800	.19	531	84.7	32.6	.43	.81	108
4	7.84	3.35	2,100	.23	504	83.5	30.9	.6	.18	244
4	7.88	3.72	1,650	.24	488	70.7	27.6	.49	.17	108
8[1]	7.8	3.44	1,960	.36	535	93.2	29.8	.46	.31	283
4	7.74	2.99	2,530	.43	533	80.2	34.7	.4	.48	126
4	7.66	2.77	3,090	.59	658	92.5	58.5	.61	.7	77.8
4	7.67	2.73	1,540	.36	632	85	31.8	.06	.36	56.7
4	7.86	2.67	1,740	.43	501	76.3	35.3	.2	.38	37.1
4	7.65	2.71	1,560	.43	474	63.1	28.1	.15	.37	27.7
4	7.82	2.69	1,530	.77	512	77	28.2	.19	.59	29.3
4	7.86	2.72	1,630	.74	570	74.4	45.1	.28	.88	24.8
4	7.67	2.77	1,820	.62	626	79.2	29.9	.21	.98	29.1
8[1]	7.59	2.75	1,820	.61	622	86.4	32.4	.17	2.91	29.4
4	7.7	2.58	1,550	.71	651	91.2	29.7	.23	3.19	23.8
4	7.75	2.57	1,540	.66	533	66	25.4	.22	3.21	21.2
2	7.71	2.64	1,560	.75	631	66.4	23	.41	3.44	19.4
2	7.74	2.79	1,640	.71	621	70	19.9	.45	3.04	19.7
3	7.8	2.74	1,530	.62	624	57.2	20.1	.45	3.14	16.5

[1] Dry cycle, columns opened to atmosphere.

SUMMARY AND CONCLUSIONS

Although this study was limited to seven copper mine tailings, the results reported here and in other on-going studies seem to indicate certain common behaviours. High sulfate production is more commonly associated with high metal concentrations and is indicative of tailings that are susceptible to atmospheric oxidation. If tailings produce acidic leachates, dry cycles often produce relatively small changes (less than one order of magnitude) in metal concentrations, while tailings that normally produce basic leachates may demonstrate enhanced metal dissolution of one to two orders of magnitude. Leachate concentrations from packed columns of 6 to 12 in produce observable wet/dry cycle effects while longer columns reveal little observable metal enhancement from unsaturated conditions. The high leachate sulfate, and high metal concentrations initially observed in air-dried tailings, followed by rapidly falling concentrations with subsequent leachings, appear to reflect oxidative reactivity and/or highly oxidized tailings samples. Acid tailings (tailings that produce acid leachates) appear to be sulfate driven, that is, sulfate is present in the sample from mobile metal sulfate complexes. It is suspected that the use of biocides and other treatment methods may have little effect on metal dissolution until this "excess" sulfate is eluted.

It must be pointed out that column test protocols appear to have the ability to distinguish potentially reactive tailings from benign tailings, but do not necessarily reflect what may occur in the natural setting of the tailings themselves.

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