*Mine Water and The Environment, Vol 10, Annual Issue, 1991, pp 73- 92*
( Formerly International Journal of Mine Water)

# COLUMN LEACH STUDY II: HEAVY METAL DISSOLUTION CHARACTERISTICS FROM SELECTED LEAD-ZINC MINE TAILINGS

by

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## ABSTRACT

Metal dissolution from tailings from six lead-zinc mine and milling sites in the western United States was examined by researchers from the Bureau of Mines using a column leaching procedure involving a formulated "western rain" leachant. This 2-year laboratory study included the effects of column waste depth, dry cycles with and without oxygen, and pore water evaporation. The results indicated that leachate metal concentrations gradually decreased with each leaching, but that the degree of enhanced metal mobilization from unsaturated tailings varied widely from waste to waste. Further studies on selected samples from this group of tailings demonstrated that the driving force behind enhanced metal dissolution is the oxidation of sulphide minerals by atmospheric oxygen during the evaporation of pore water from the columns of tailings. Leachates from water-saturated columns of these tailings gave pH values from 6.5 to 8.5; acid production and dissolved metal concentrations were enhanced by alternating wet and dry cycles. All studies to date indicate that maintaining tailings at or near saturation and/or excluding atmospheric oxygen produce leachates of nearly constant to slowly decreasing metal concentrations with each subsequent leaching.

## INTRODUCTION

Over the past hundred years, the mining industry has generated vast quantities of solid wastes as by-products of total mining operations. Crushing, grinding, and other physical and chemical beneficiation processes create waste products (tailings) that may undergo rapid weathering when they are disposed of on the surface. This crushed waste rock was taken from environments that may be reducing or, at best, nonoxidizing and placed into an oxygen containing atmosphere where conditions are especially favourable for the accelerated oxidation of sulfphide minerals such as pyrite. Acid production and metal release may be the result of this oxidation (Bainbridge et al., 1980).

Table 1. Assay of maximum leachable concentrations, mg/g

| | Depth in | | | Element, mg/g | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Al | Ba | Ca | Cd | Co | Cu | Fe | K | Mg | Mn | Na | Ni | Pb | S | Zn |
| Lead-zinc mine A: | | | | | | | | | | | | | | | | |
| Hole 1 | 0-6 | 0.124 | 0.002 | 50.9 | 0.002 | 0.040 | 0.075 | 9.31 | 0.126 | 33.1 | 1.74 | 0.230 | 0.024 | 0.514 | 2.93 | 0.052 |
| | 6-12 | .089 | .002 | 49.6 | .002 | .043 | .083 | 8.18 | .093 | 32.7 | 1.59 | .147 | .026 | .42 | 2.7 | .041 |
| Hole 2 | 0-6 | .24 | .003 | 74 | .019 | .037 | .068 | 17.8 | .186 | 47.7 | 2.27 | .186 | .019 | .681 | 4.5 | .948 |
| | 6-12 | .193 | .004 | 72.5 | .012 | .04 | .051 | 17.6 | .189 | 46.5 | 2.38 | .184 | .015 | .362 | 5.23 | .647 |
| Lead-zinc mine B | | .189 | .002 | 182 | .008 | .036 | .227 | 23.9 | .218 | 81.2 | 1.41 | .311 | .057 | 1.56 | 19.8 | .962 |
| Silver-lead-zinc mine C | | .306 | .008 | .844 | .089 | <.001 | .169 | 93 | .008 | 2.7 | >4.6 | .033 | .002 | 1.59 | 3.53 | 3.46 |
| Lead-silver mine D | | .455 | <.001 | 2.7 | <.001 | .003 | .791 | 2.36 | .362 | .372 | .362 | .156 | .003 | .086 | .452 | .017 |
| Zinc mine E | | .186 | .011 | 60.8 | .004 | <.001 | .029 | 3.04 | .136 | 37.8 | .086 | .071 | 0 | .364 | 2.83 | 1.78 |
| Lead-zinc mine F | | .113 | <.001 | 152 | .029 | <.001 | .439 | 15.1 | .173 | 63.7 | 1.14 | .224 | .379 | 16 | 14.2 | 2.77 |
| Lead-zinc mine F, sample 2 | | .127 | .001 | 161 | .054 | .029 | .316 | 25.8 | .09 | 79.5 | 1.37 | .257 | .595 | 22.9 | 26.5 | 3.68 |

In a previous study (Doepker, 1988), silver mine tailings were examined to determine the parameters that affect the dissolution and transport of metal ions. In another study (Doepker, 1989) a lead-zinc mine tailings was tested to examine enhanced metal release from unsaturated tailings, and a group of copper mine tailings were examined (Doepker and O'Connor, 1990) to determine their sensitivity toward oxidation. Presumably the enhanced metal release observed from these tailings resulted from the interaction of atmospheric oxygen with the sulphide minerals present in the unsaturated tailings (Nordstrom et al., 1979; Nordstrom, 1982).

The purpose of the present investigation is to examine a group of lead-zinc mine tailings and to relate column leachate concentrations to parameters such as type of metal mined, mineralogy, mineral composition, column length, pore water evaporation, and the effect of drying. This paper describes results of approximately 2 years of tests on tailings collected from Western lead-zinc mines.

## MATERIALS AND METHODS

### Waste

### Procedure:

Samples were studied to determine any mineralogical variations caused by near-surface exposure. Polished sections were prepared from the samples. The sections were examined initially on a reflected light microscope (RLM) to establish descriptive mineralogy and then on a scanning electron microscope (SEM) with energy dispersing x-ray micro-analysis (El)X). The abbreviated results of a modified maximum leachability assay (a non-destructive, mixed HCl-HN03 assay) (Kuryk et al., 1985) for all tailings studied in this investigation are given in Table 1.

### Lead-zinc mine A tailings, Missouri:

Samples from two locations were taken from depths of 0 to 150 mm and 150 to 300mm below the surface. All four samples were air dried. Grain size varied slightly between the two locations, possibly because of the samples' respective distances from the source area (finer grained tailings would be found farther from the pipe bringing tailings to the pond). Samples from borehole 2 exhibited slightly larger grain sizes than samples from borehole 1. The general mineralogy was the same for all four samples. Gangue consisted predominantly of dolomite ($CaMg(C0_3)_2$). Quartz ($SiO_2$) was present in lower concentrations. Sulphide minerals included pyrite ($FeS_2$), marcasite ($FeS_2$), chalcopyrite ($CuFeS_2$), sphalerite ($ZnS$), and galena ($PbS$), all in trace amounts, although pyrite and marcasite accounted for over 75 pct of the sulphides. Total sulfphide content also appeared to be greater in samples from hole 2. On the basis of the observations on grain size and sulphide content, it appeared that hole 2 was located closer to the source pipe in the tailings pond, where the larger and heavier particles (the sulphides) settled out first. The lighter gangue particles (dolomite and quartz) were carried farther (hole l) from the source. There, most of the sulphides are found as extremely fine-grained inclusions in the gangue, resulting in less exposed surface area for alteration. Therefore, greater amounts of acid runoff would be expected near the source pipe.

The presence of pyrite and marcasite is of interest because the marcasite is less stable. Both minerals will alter to form limonite ($2Fe_20_3$ $3H_20$) with excess sulphuric acid. Samples from both locations contained nearly equal concentrations of marcasite relative to pyrite in the lower layer 150mm to 300mm below the surface), but pyrite was more abundant than marcasite in the upper layer (O to 150 mm below the surface). Limonite and goethite ($Fe_20_3$-$H_20$) were present in sections from both layers, but appeared more abundant in the upper layer. Goethite occurred exclusively as alteration rims on pyrite grains. The upper layer appears to have undergone a greater degree of oxidation and alteration, which is to be expected.

Lead-zinc mine B tailings, Missouri: One large (approximately 80 Kg) sample was furnished directly to the laboratory by the mine operator. These tailings have been studied extensively over the past several years and were used again in this study. A chemical description appears in Table 1.

The general mineralogy of the mine B samples was very similar to that of the mine A samples. Dolomite was the predominant gangue constituent with lower concentrations of quartz. Total sulfphide content was higher than in mine A samples, and pyrite and marcasite were the most abundant phases. Sphalerite, chalcopyrite, and galena were also more abundant in mine B samples than in the mine A samples, which could be caused by the initial source (ore) being of a higher grade or the result of poor control during benefication.

Grain size for dolomite ranged from under 10 to over 200 micrometers in diameter, and varied among the sulphide phases. Pyrite and marcasite are not concentrated during the milling process and generally occur as larger grains (1 to 200 micrometers) than do the other sulphides. Successive circuits in the mill concentrate galena, sphalerite, and chalcopyrite, resulting in a corresponding decrease in grain size for each phase in the tailings. Most of the sphalerite and chacopyrite grains (1 to 25 micrometers) were still locked with dolomite gangue. However, several extremely large (+200 micrometer), liberated grains of galena were present in the tailings. Several large compound sulfphide grains, consisting of galena, sphalerite, chacopyrite, and pyrite, were present as well.

Silver-lead-zinc mine C tailings, Montana: A single, 6.69 Kg grab sample of silver-lead-zinc mine C tailings was obtained, air dried, analyzed (Table 1), and stored in a sealed polyethylene bag.

Quartz was the predominant gangue mineral, often containing inclusions of apatite [$Ca_5(PO_4)_3(F,OH,Cl)$]. Numerous other silicates (amphiboles, micas) were present as minor constituents of the gangue. Pyrite was the most abundant sulfphide, but occurred in trace amounts. Chalcopyrite was rare. No lead or zinc sulphides, carbonates, or any silver phases were identified in the samples. This suggests either an extremely fine grain size for these phases or insufficient blending of the sample prior to preparation. Iron oxides were present and included goethite, magnetite ($Fe_3O_4$), and/or hematite ($Fe_2O_3$). Goethite occurred as an alteration product of the iron sulphides and oxides. Most of the non-silicates occurred as locked particles with the silicate gangue. Grain size for the iron sulphides and oxides ranged from 1 to 100 micrometers.

Silver-lead mine D tailings, Montana: Tailings from silver-lead mine D have been collected for many projects. A simple grab sample from 3.65m3 of stock material was used in this study.

Quartz and orthoclase ($KAlSi_3O_8$) were the predominant constituents of the gangue, with quartz the most abundant of the two. Many quartz grains contained very fine-grained inclusions (1 to 20 micrometers) of native silver. Galena was present in trace amounts, and grain sizes ranged from 5 to 50 micrometers. Zircon ($ZrSiO_4$) occurred as free grains and as inclusions in the other gangue materials.

Zinc mine E tailings, Washington: A single grab sample taken from 300 to 600 mm below the surface was obtained at this mining and milling site. Quartz, calcite ($CaCo_3$), and wollastonite ($CaSiO_3$) were the major components of the gangue. Dolomite and diopside [$CaMg(SiO_3)_2$] occurred in lower concentrations. Other silicates (pyroxenes) were present, but not in significant amounts.

The mineralogy of the gangue indicates that the host rock for the mine E ore has undergone contact metamorphism, resulting in the silicification of the carbonates. Sulphide mineralogy included pyrite, sphalerite, and chalcopyrite, which occurred as fine-grained inclusions in the gangue and as free grains. Grain sizes varied from 5 to 50 micrometers. Examination on the SEM-EDX confirmed the presence of iron-bearing sphalerite (marmatite) containing up to 20 pct iron.

Lead-zinc mine F tailings, Missouri: One grab sample of approximately 6.69 Kg was collected originally. A second sample was later requested, and was collected and delivered by the mine operators. The chemical analyses of these two samples (samples 1 and 2) are reported in Table 1.

The mineralogy of mine F samples was very similar to samples from mines A and B. Dolomite was again the major component of the gangue and grains ranged in size from 50 to 300 micrometers. Quartz was a minor constituent. Many of the dolomite grains contained fine-grained inclusions (5 to 10 micrometers) of sulfphide minerals. As confirmed by bulk chemistry, total sulfphide content was higher in mine F tailings than in any of the other mines in this study. Sulphide mineralogy included pyrite, marcasite, galena, sphalerite, and chalcopyrite. Bravolite ($FeNiS_2$) was present as rare inclusions in dolomite. Many compound sulfphide grains up to 100 micrometers in diameter suggest that insufficient grinding in the mill resulted in losses of valuable sulphides to the tailings and, consequently, contributed to the base metal content of the tailings.

## Chemicals

All chemicals in this study were commercially available, analyticalgrade reagents (A.R. grade) used without further purification. The de-ionized water was produced in the laboratory through distillation (Barnstead glass still) and then de-ionized with a Barnstead NANOpure II De-mineralizer (18.3 Mohm-cm).[3] Leachant solutions were prepared by standard analytical techniques using only A.R. grade chemicals and prepared de-ionized water. The leachants were stored in carboys. Simulated western rain was prepared as described by Bainbridge et al. (1980).

## Column Test Equipment and Methods

Leach columns were constructed from 600 or 1200 mm lengths of 75 mm inside-diameter (ID) polyvinyl chloride (PVC) pipe equipped with cemented couplings and bushings in which perforated Nalgene plates had been installed. A 90 mm G6 (Fisher Scientific) borosilicate glass fibre filter was placed on the perforated plate before installation of the bushing. In one study, nine 2-ft columns and nine 4-ft columns were matched in nine sets. A single air dried tailings sample was distributed between one 600mm (1.75 kg) and one 1200 mm (7.0 kg) column. One and one-half litres of de-ionized water was added drop by drop to the 1200 mm column of dry tailings while 500 mL was added drop by drop to the 600 mm column. The leachate was collected, and pH, conductivity and volume were determined. The difference between the volume of leaching solution added (leachant) and the volume of leaching solution recovered (leachate) represents the retained leachate pore volume of the column.

A series of 12 similarly constructed 37 mm ID PVC columns were used to examine the effects of atmosphere on metal dissolution from two different tailings. Two sets of six columns each were filled with 600 g of each waste. Three columns of each waste were placed in a chamber where a nitrogen atmosphere was maintained. The remaining three columns of each waste were exposed to normal laboratory atmosphere and used for comparison.

In another exploratory study, sixteen 350 mm lengths of 75 mm ID acrylic tubing were used to construct columns in the same manner as used for the PVC columns. One kilogram of lead-zinc mine B tailings was added to each column. After a series of leachings with de-ionized water, eight of these columns were placed into a Precision Scientific, Model 625, forced-air oven maintained at 85° F and a low setting (2) on the air flow. Columns stored in the oven were removed two at a time each week for 4 weeks, leached with de-ionized water and compared to the laboratory columns maintained at saturation or opened to laboratory air.

### Analytical Methods and Equipment

Kuryk's method of maximum leachability assay (Kuryk et al., 1985) was modified in this study by replacing the digestion cycles with shaking. One gram of waste (tailings) was placed into a 500 mL rectangular polyethylene bottle and 5 mL of concentrated nitric acid, 2 mL of concentrated hydrochloric acid, and 25 mL of de-ionized water were added. The bottle was then capped and placed into a mechanical laboratory oscillating shaker for 4 hours. The sample was then gravity filtered through Whatman No 42 filter paper, and washed with acidified (nitric acid) water. The filtrate and all washings were combined and diluted to 100 mL in a volumetric flask. This total filtrate was then analyzed with an inductively coupled plasma spectrometer. The metal analyses were carried out with the aid of a Perkin-Elmer Plasma II ICP Spectrometer (ICP). Anion analysis was conducted with a Dionex 4000i ion chromatograph (IC) equipped with an A54A separation column. Analyses of all acidified (1 to 2 pct $HN0_3$) leachates by ICP included total sulfur when the ICP became available, sulphate analyses were also determined, but from leachate samples before acidification. Total sulfur and/or sulphate concentrations are reported in all the data tables.

## DISCUSSION AND RESULTS

In an on-going study, tailings from six lead-zinc mines have been leached 23 times over the past 2 years. The procedure involved leaching the columns with synthetic rain approximately once a month, punctuated by two dry cycles of 2 months each. The basic experimental set-up included two columns for each sample, a 1200 mm column containing 7.0 kg of waste and a 600 mm column with 1.75 kg. The columns were filled with dry tailings of the appropriate weight and leached with de-ionized water to determine leachant pore volume. The pore volume of the longer column was determined to be nearly four times the shorter. With each subsequent leaching, 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.

### Lead-zinc mine A tailings, Missouri:

The four samples obtained from lead-zinc mine A were used in eight columns, four containing 7.5 kg (40-in column depth) of a tailings sample and another four containing 1.75 kg (250 mm column depth). Table 1 shows that the chemical composition of samples collected from both depths (O to 150 mm deep and 150 to 300 mm ) at the same location were identical within expected experiment uncertainties whereas samples from two different locations differed in several elements, in particular, iron, manganese, sulfur and zinc. It was also found that leachate metal concentrations were nearly identical for tailings samples from the same location but from different depths (Table 2). In general, leachate metal concentrations obtained from longer columns were considerably higher than the concentrations obtained from shorter columns for any one leaching; however, on a pore volume-to-pore volume comparison the concentrations were similar.

Table 2. Leachate concentrations from lead-zinc mine A tailings
(1.75 kg sample; 10 in column depth; 400 $cm^3$ synthetic rain leachant)

| Time between leachings, weeks | pH | mmho | $SO_4$, mg/L | Ba | Element, mq/L | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | B | Ca | Co | Cu | Fe | K | Mg | Mn | Na | Ni | Pb | S | Zn |
| HOLE 2, 6-12 in sampling depth | | | | | | | | | | | | | | | | | |
| Start | 8.33 | 0.226 | n.d. | 0.088 | n.d. | 29.1 | 0.04 | 0.01 | 0.00 | n.d. | 12.3 | 0.00 | n.d. | n.d. | n.d. | 7.0 | 0.01 |
| 3 | 8.24 | .475 | n.d. | .109 | n.d. | 50.5 | .22 | .43 | .07 | n.d. | 24.8 | 1.7 | n.d. | n.d. | n.d. | 39.3 | .34 |
| 3 | 8.4 | .368 | n.d. | .215 | n.d. | 45.4 | .55 | 0 | 0 | n.d. | n.d. | .09 | n.d. | n.d. | n.d. | 17.4 | .09 |
| 4 | 8.28 | .487 | n.d. | .125 | n.d. | 68.9 | .64 | .01 | .38 | n.d. | 31.7 | 0 | n.d. | n.d. | n.d. | 63.2 | 0 |
| 3 | 8.28 | .428 | n.d. | .109 | n.d. | 64.2 | .51 | 0 | 0 | n.d. | 22.8 | .01 | n.d. | n.d. | n.d. | 43.8 | .07 |
| 4 | 8.26 | .488 | n.d. | .081 | n.d. | 56.1 | .42 | .02 | .03 | n.d. | 23.2 | .02 | n.d. | n.d. | n.d. | 46.2 | .06 |
| 4 | 8.02 | .487 | n.d. | .083 | n.d. | 52.2 | .42 | 0 | .01 | n.d. | 21.4 | 0 | n.d. | n.d. | n.d. | 39.5 | .04 |
| 4 | 8.05 | .572 | n.d. | n.d. | .38 | 81.6 | .6 | .03 | .09 | 1.1 | 31.7 | .02 | 3.73 | 0.25 | .06 | 62.3 | .08 |
| 8[1] | 7.72 | .836 | n.d. | .08 | .47 | 124 | .5 | .03 | .03 | 1 | 48.1 | 0 | 6.95 | .19 | 0 | 123 | .03 |
| 4 | 7.67 | .745 | n.d. | 0 | .32 | 103 | .37 | 0 | 0 | .6 | 31.3 | 0 | 4.31 | .14 | .05 | 69.9 | .03 |
| 4 | 7.85 | .686 | n.d. | .057 | .46 | 105 | .49 | 0 | 0 | 1 | 37.8 | 0 | 6.28 | .2 | 0 | 91.7 | .06 |
| 4 | 7.87 | .634 | n.d. | .128 | .38 | 81.1 | .63 | 0 | .42 | .4 | 33.7 | 0 | 3.45 | .31 | .07 | 71.6 | .07 |
| 4 | 8.06 | .652 | n.d. | .029 | .35 | 62 | 1.01 | .02 | .41 | .1 | 29.1 | 0 | 2.95 | .45 | .03 | 76.5 | .1 |
| 4 | 7.85 | .622 | n.d. | .065 | .36 | 61.2 | .79 | .06 | 1.1 | 0 | 27.6 | 0 | 3.97 | .37 | 0 | 66.1 | .11 |
| 4 | 7.86 | .926 | n.d. | .063 | .42 | 50.9 | .55 | .12 | .7 | .4 | 20.4 | .03 | 3.48 | .25 | 0 | 60.9 | .07 |
| 4 | 7.94 | .557 | 178 | .063 | .38 | 60.7 | .54 | 0 | .12 | .5 | 25.8 | .02 | 3.59 | .23 | 0 | 54 | .03 |
| 4 | 7.94 | .576 | 184 | .062 | .42 | 69.1 | 1.13 | 0 | .03 | 0 | 27.4 | .04 | 3.84 | .23 | 0 | 60.7 | 0 |
| 8[1] | 7.7 | .73 | 272 | .059 | .51 | 95 | .99 | 0 | .02 | .4 | 39.5 | 0 | 6.18 | .36 | 0 | 103 | .18 |
| 4 | 7.87 | .632 | n.d. | .04 | .38 | 64.7 | .92 | 0 | 0 | 0 | 24.6 | 0 | 2.3 | .26 | 0 | 62.5 | .1 |
| 4 | 8.01 | .536 | 80.6 | .037 | .42 | 63.1 | .81 | 0 | .02 | 0 | 23.3 | 0 | 3.16 | .25 | 0 | 61.4 | .14 |
| 2 | 7.95 | .413 | 104 | .035 | .34 | 47.6 | .54 | 0 | .01 | 1.5 | 17.1 | .02 | 3.33 | .14 | 0 | 32.2 | .04 |
| 2 | 7.72 | .394 | n.d. | .053 | .34 | 40.5 | .82 | 0 | .02 | 0 | 14 | .01 | 2.52 | .13 | .03 | 27.8 | 0 |
| 3 | 8.03 | .407 | 95.1 | .058 | .35 | 43.5 | .3 | .06 | .34 | 0 | 17.3 | .01 | 2.8 | .12 | .14 | 29.9 | .08 |

n.d. No data.

[1] Dry cycle, opened to atmosphere.

Table 2. continued

| Time between leachings, weeks | pH | mmho | $SO_4$, mg/L | Element, mg/L | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | Ba | B | Ca | Co | Cu | Fe | K | Mg | Mn | Na | Ni | Pb | S | Zn |
| HOLE 2, 6-12 in sampling depth | | | | | | | | | | | | | | | | | |
| Start | 7.82 | 2.83 | n.d. | 0.022 | n.d. | 476.0 | 0.03 | 0.00 | 0.00 | n.d. | 30.3 | 0.19 | n.d. | n.d. | 0.00 | 598.0 | 0.55 |
| 3 | 7.99 | 2.89 | n.d. | .038 | n.d. | 508 | .07 | .01 | 0 | n.d. | 131 | .05 | n.d. | n.d. | n.d. | 585 | .64 |
| 3 | 8.04 | 2.61 | n.d. | .032 | n.d. | 574 | .07 | 0 | 0 | n.d. | 74.1 | 0 | n.d. | n.d. | n.d. | 559 | .56 |
| 4 | 8.11 | 2.51 | n.d. | .029 | n.d. | 477 | .1 | O | C | n.d. | 17.3 | .05 | n.d. | n.d. | n.d. | 689 | 1.07 |
| 3 | 8.1 | 2.37 | n.d. | .033 | n.d. | 614 | .1 | O | O | n.d. | 18.9 | .04 | n.d. | n.d. | n.d. | 505 | .72 |
| 4 | 7.99 | 2.36 | n.d. | .084 | n.d. | 595 | .C9 | .01 | .03 | n.d. | 16.8 | .1 | n.d. | n.d. | n.d. | 479 | .66 |
| 4 | 7.87 | 2.34 | n.d. | .064 | n.d. | 489 | .09 | .Cl | .01 | n.d. | 14.7 | .04 | n.d. | n.c. | n.d. | 494 | .44 |
| 4 | 7.78 | 2.35 | n.d. | n.d. | n.d. | 692 | .17 | .06 | .13 | 2.2 | 21.9 | .17 | 2.14 | 0.11 | .08 | 631 | .52 |
| $8^1$ | 7.74 | 2.6 | n.d. | .032 | 0.49 | 722 | .11 | O | .03 | 2.74 | 78.7 | .12 | 8.04 | .04 | 0 | 558 | .87 |
| 4 | 7.54 | 2.41 | n.d. | O | .37 | 646 | .09 | 0 | .01 | 2.2 | 28.2 | .08 | 3.59 | .04 | .08 | 467 | .99 |
| 4 | 7.82 | 1.84 | n.d. | .032 | .52 | 381 | .08 | .18 | .12 | 1.8 | 20.8 | .06 | 4.08 | .04 | 0 | 469 | .89 |
| 4 | 7.82 | 1.021 | n.d. | .267 | .39 | 201 | .02 | 0 | .42 | .94 | 17.4 | 0 | 3.44 | .01 | 0 | 136 | .25 |
| 4 | 8.08 | .474 | n.d. | .044 | .34 | 46.3 | .02 | 0 | .4 | .59 | 16.7 | 0 | 2.52 | .02 | .06 | 42.2 | .11 |
| 4 | 7.94 | .373 | n.d. | .094 | .37 | 32.3 | 0 | .01 | 1.06 | .32 | 19.3 | 0 | 3.57 | 0 | .03 | 24.5 | .09 |
| 4 | 7.82 | .363 | n.d. | .107 | .43 | 36.7 | 0 | .05 | .66 | .94 | 22.1 | .01 | 4.06 | .01 | .03 | 28.4 | .09 |
| 4 | 8.05 | .345 | 67.9 | .089 | .32 | 33.9 | 0 | 0 | .12 | 1 | 20.6 | 0 | 1.88 | 0 | 0 | 22.2 | .06 |
| 4 | 8.14 | .366 | 71.8 | .083 | .29 | 30.2 | .01 | 0 | .1 | .2 | 18.3 | .02 | 1.77 | 0 | 0 | 22.5 | 0 |
| $8^1$ | 7.84 | .58 | 186 | .083 | .04 | 59.3 | .01 | O | .03 | 1.5 | 38.6 | 0 | 3.48 | .01 | 0 | 70 | .28 |
| 4 | 7.86 | .449 | n.d. | .076 | .23 | 38.4 | 0 | 0 | 0 | 0 | 23 | 0 | 1.53 | 0 | 0 | 33.7 | .13 |
| 4 | 8.1 | .397 | 157 | .067 | .27 | 39.7 | .01 | O | .01 | .5 | 21.6 | 0 | 2.02 | .03 | 0 | 35.1 | .17 |
| 2 | 7.88 | .332 | 57.8 | .075 | .19 | 35.1 | .01 | O | 0 | 2.1 | 18.9 | .01 | 2.01 | 0 | 0 | 17.9 | .09 |
| 2 | 7.89 | .325 | n.d. | .116 | .14 | 29.8 | .02 | 0 | .04 | 0 | 14.3 | .02 | 1.02 | .01 | 0 | 15.1 | O |
| 3 | 7.61 | .291 | 39.7 | .137 | .16 | 27.3 | .01 | .05 | .28 | .1 | 14.1 | .01 | 1.8 | .02 | .17 | 11 | .13 |

n.d. No data.
[1] Dry cycle, opened to atmosphere.

As a general rule, leachate metal concentrations obtained from columns of air-dried metal-mine tailings peak within one to four leachate pore volumes and then decrease with each subsequent leaching. Although ICP sulphur (Table l) from hole 2 was only twice that from hole 1, leachate sulphur (Table 2) showed a tenfold difference at the start. During the first open or drying cycle, sulphur showed an increase (approximately 60 mg/L) for the sample from hole 1 but none from hole 2, whereas in the second drying cycle sulphur increased from 25 to 40 mg/L in samples from both holes. Leachate sulphur analyses of these samples can be equated to approximately one-third the sulphate yield. During the first dry cycle nearly 50 pct of the leachate pore water evaporated while the second dry cycle yielded only a 20 pct loss. This relatively small degree of sulphate production and the absence of major enhanced metal releases after a drying cycle suggest that these tailings are not subject to major atmospheric oxidation of unsaturated tailings.

### Lead-zinc mine B tailings, Missouri:

A single sample of lead-zinc mine B tailings was subjected to the same column test protocol previously discussed. Table 3 reports the results of this test series for both the 1200 mm deep column and the 254 mm deep column. These results demonstrated that a four-fold increase in tailings column depth did not greatly increase the leachate metal concentrations when near-saturation was maintained in the columns. On the other hand, if unsaturated conditions occur and the tailings are subject to oxidation, the shorter column may produce large increased leachate metal concentrations and a much smaller increase may be observed from the longer column. Sulphate (Table 3, 1.75-kg sample) increased from 82.5 mg/L (3 times sulphur) to 5730 mg/L (3 times sulphur) with 50 pct evaporation of pore water, while the longer column produced changes of approximately 450 mg/L associated with a 15-pct loss in pore water. Leachate pH changes from 7.85 to 7.79 and 8.18 to 3.98 for the long and short columns, respectively, demonstrated the greater buffering ability of a long waste column. Ca, Co, Cu, Mg, Mn, Pb, S(504), and Zn all showed enhanced metal dissolution during the first dry cycle. Enhanced metal and sulphate dissolutions from the second dry cycle were greatly reduced. This may have been caused by less pore-water evaporation (20 pct and 17 pct from the long and short columns, respectively), by the depletion of some more reactive sulphides, or the coating of sulphides by re-precipitated gypsum.

### Silver-lead-zinc mine C tailings, Montana:

The initial leachate sulphate concentration (approximately 3 times the sulphur, Table 4) of 4,230 mg/L reached a maximum of 6,840 mg/L after approximately 1.4 pore volumes of leachate had been collected. The initial volume of leachate represented only 40 pct of a pore volume while the second leaching was 1 pore volume (the short column) or one-quarter pore volume (1200 mm columns). The rapid fall-off of sulphate with subsequent leachings suggests that these tailings were subject to oxidation which should be further reflected by an increased sulphate concentration during a drying cycle. As seen in Table 4, an 8-week drying cycle (60 pct evaporation of pore water) resulted in an enhanced sulphate dissolution of 741 mg/L. The effect on metal dissolution was minimal although leachate pH dropped from 7.11 to 6.58. This relatively small dry-cycle effect coupled with the initial rapid drop of sulphate concentrations suggests that considerable weathering occurred before the tailings were subjected to the column leach protocol. The results for the 4-ft column are not included in Table 4, but they showed similar effects in that sulphate concentrations fell rapidly from a maximum of over 15,000 mg/L to a value of 1,000 mg/L after leachings of 4 to 5 pore volumes.

### Lead-silver mine D tailings, Montana:

Tailings from lead-silver mine D contain far less sulphide (Table 1) than do the other tailings reported upon in this study. Although the effects of oxidation on the tailings under unsaturated conditions are shown in Table 5, the enhanced metal and sulphate concentrations are small. For example, the first dry cycle (50 pct pore water evaporation) increased sulphate dissolution by 185 mg/L while the second 8-week dry cycle (25 pct pore water evaporation) showed a small 27 mg/L increase in sulphate.

### Zinc mine E tailings, Washington:

The sulphur ICP assay given in Table 1 suggests that the dry cycle reactivity of zinc mine E tailings might be similar to those of lead-zinc mine A, hole 1, tailings. The maximum sulphate concentration of 1,425 mg/L coupled with the rapid decrease in leachate sulphate during the next two leachings (Table 6) suggest that zinc mine E tailing have a moderate oxidative reactivity or have simply undergone extensive weathering. A net change of 483 mg/L in sulphate leachate concentration as a result of a 70 pct loss in pore water during the first dry cycle indicated a degree of activity similar to lead-zinc mine A tailings along with considerable weathering. Metal concentrations in these tailings are small and are only observed at or near their ICP detection limits.

### Lead-zinc mine F tailings, Missouri:

Lead-zinc mines A, B, and F all came from the same Missouri mining district. As do lead-zinc mine B tailings, mine F tailings contain nearly 2 pct sulfur (Table 1) and showed considerable metal- and sulphate-enhanced dissolution during dry cycles. Leachate sulphate concentrations of 1,770 mg/L (Table 7) dropped off to 900 mg/L after leaching with 4 to 5 pore volumes, suggesting considerable oxidative reactivity. This is evident in an increased sulphate concentration of nearly 18,000 mg/L after the first dry cycle of 8 weeks. The smaller amount (1,200 mg/L) of sulphate following the second dry cycle may be an indication of reduced reactivity or the fact that 90 pct of the pore water was lost during the first evaporation as compared to 30-pct evaporation during the second dry cycle. Lead-zinc mine F tailings contained considerable amounts of lead, zinc manganese and other metals (Table 1); these metal were reflected in the metal concentrations observed in the column leachates. Increases in leachate concentrations as a direct result of the dry cycle (for example lead increased from 0.5 to 4.7 mg/L, manganese from 1 to 16 mg/L and zinc from 8 to 25 mg/L) point to potential concern over the stability of such tailings in the environment. Even though lead-zinc mine B and F tailings are nearly 80 pct dolomite, acidic leachates are possible (Tables 3 and 7) after a dry cycle.

## Effect of Oxygen on Dissolution

In order to further investigate the role of oxygen in the enhanced dissolution of metal and sulphate during drying of the tailings, six 37 mm ID columns of lead-zinc mine B and F were isolated in a chamber containing open beakers of water to maintain the relative humidity at approximately 70 to 80 pct. Nitrogen was then introduced into the chamber. An identical set of columns was set up in the laboratory as controls. During this test series, the relative humidity of the laboratory remained between 35 to 40 pct. All columns were leached with 1 pore volume of de-ionized water and the leachates were analyzed with the ICP and IC. After four leachings, dry nitrogen was introduced into the chamber and the water beakers were removed. A 21-day drying cycle was carried out while the laboratory columns were open to laboratory air. The test procedure was again followed with wet-nitrogen for three leachings followed by a dry-nitrogen cycle for 31 days, and by a 28-day dry cycle using dry air. The results of this test protocol are given in Table 8.

The results clearly demonstrated that if evaporation of pore water occurs without oxygen, enhanced metal release or sulphate formation is minimized. In the

Table 3. Leachate concentrations from lead-zinc mine B tailings
(350 $cm^3$ synthetic rain leachant)

| Time between leachings, weeks | pH | mmho | $SO_4$, mg/L | Element, mg/L B | Ca | Cd | Co | Cu | Fe | K | Mg | Mn | Na | Ni | Pb | S | Zn |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1.75 kg WASTE (10-in column depth) | | | | | | | | | | | | | | | | | |
| Start | 7.6 | 3.81 | n.d. | 0.05 | >150.0 | 0.00 | 0.21 | 0.04 | 0.02 | 106.0 | 205.0 | 0.30 | n.d. | 0.27 | 0.22 | 1170.0 | 2.08 |
| 3 | 8.03 | 2.96 | n.d. | n.d. | >150 | 0 | .18 | .01 | .01 | 28.5 | 145 | .13 | n.d. | .29 | .01 | 948 | .31 |
| 3 | 8.07 | 4.86 | n.d. | .2 | 563 | 0 | .29 | .03 | 0 | 22 | >300 | .03 | 93.9 | .58 | .02 | 926 | .26 |
| 4 | 8.28 | 5.62 | n.d. | .09 | 563 | 0 | .38 | .6 | .04 | 66 | 11.1 | .33 | 16 | .71 | 0 | 1630 | 1.31 |
| 3 | 7.92 | 3.66 | n.d. | .14 | 560 | 0 | .35 | .02 | .01 | 103 | 284 | .2 | 7.84 | .64 | 0 | 1260 | 1.25 |
| 4 | 7.86 | 2.79 | n.d. | .11 | 544 | .01 | .28 | .05 | .1 | 38.1 | 93 | .19 | 2.56 | .4 | .06 | 549 | 2.2 |
| 4 | 7.81 | 2.56 | n.d. | .07 | 496 | 0 | .15 | 0 | 0 | 19 | 51.4 | 0 | .41 | .31 | 0 | 442 | .55 |
| 4 | 7.85 | 2.61 | n.d. | .11 | 623 | .01 | .22 | .03 | .05 | 20.8 | 44.6 | .13 | 1.48 | .45 | 0 | 470 | .69 |
| 8[1] | 7.79 | 2.57 | n.d. | .14 | 759 | 0 | .61 | .02 | 0 | 17.3 | 64.1 | .92 | 2.06 | .93 | .05 | 614 | 1.36 |
| 4 | 7.68 | 2.43 | n.d. | .09 | 613 | 0 | .27 | 0 | .15 | 10.2 | 27.6 | .1 | .93 | .5 | 0 | 557 | .31 |
| 4 | 7.76 | 2.35 | n.d. | .14 | 699 | 0 | .53 | .08 | .13 | 7.9 | 28 | .14 | 2.45 | 1.04 | 0 | 755 | .93 |
| 4 | 7.66 | 2.35 | n.d. | .13 | 628 | 0 | .28 | .02 | .5 | 3.9 | 12.5 | .05 | 1.65 | .55 | .03 | 479 | .25 |
| 4 | 7.62 | 1.399 | n.d. | .08 | 351 | 0 | .11 | 0 | .34 | 3.4 | 10 | .01 | 1.88 | .21 | .01 | 265 | .06 |
| 4 | 7.67 | .381 | n.d. | .16 | 36.7 | 0 | .01 | .05 | .93 | 4.1 | 10.4 | 0 | 2.24 | .02 | .04 | 35.4 | .2 |
| 4 | 7.76 | .378 | n.d. | .08 | 44.5 | .01 | 0 | 0 | .07 | 6.2 | 16 | .03 | 1.71 | .04 | 0 | 25.7 | .01 |
| 4 | 7.97 | .365 | 74.4 | .09 | 42.6 | 0 | .02 | 0 | 0 | 5.1 | 16.9 | .01 | 1.18 | .05 | 0 | 25.6 | 0 |
| 4 | 7.92 | .384 | 78.5 | .1 | 48.6 | 0 | .06 | 0 | .03 | 4.4 | 16.9 | .07 | 1.4 | .08 | 0 | 26.9 | 0 |
| 8[1] | 7.76 | .749281 | | .09 | 91.5 | 0 | .16 | 0 | .03 | 3.9 | 31.9 | .05 | 1.2 | .25 | .1 | 92.5 | .45 |
| 4 | 7.8 | .41 | n.d. | .09 | 55.4 | 0 | .05 | 0 | .02 | 4.9 | 20.9 | .04 | 1.11 | .09 | 0 | 31.9 | 0 |
| 4 | 7.91 | .394 | 90.8 | .09 | 49.9 | 0 | .1 | 0 | 0 | 4.9 | 17.3 | .02 | 1.73 | .06 | 0 | 30.9 | .2 |
| 2 | 7.75 | .416 | 91.7 | .09 | 38 | 0 | .06 | 0 | .02 | 3.3 | 13.5 | .04 | 1 | .07 | 0 | 23.5 | .04 |
| 2 | 7.85 | .373 | n.d. | .1 | 41.3 | 0 | .03 | 0 | .08 | 2.8 | 15.8 | .02 | 1.42 | .07 | .11 | 20.4 | 0 |
| 3 | 7.97 | .347 | 62.3 | .06 | 40.9 | 0 | .03 | .11 | .32 | 3.4 | 17.8 | .02 | 1.62 | .04 | .14 | 20 | .25 |

n.d. No data.

[1] Dry cycle, opened to atmosphere.

first dry cycle reported, a 17 pct evaporation of pore water resulted in no apparent increase

Table 3. Continued.

| Time between leachings, weeks | pH | mmho | $SO_4$, mg/L | Elements, mg/L B | Ca | Cd | Co | Cu | Fe | K | Mg | Mn | Na | Ni | Pb | S | Zn |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1.75 kg WASTE (10-in column depth) | | | | | | | | | | | | | | | | | |
| Start | 5.03 | n.d. | n.d. | 0.07 | >150.0 | 0.01 | 0.17 | 0.08 | 0.68 | 39.4 | 128.0 | 0.46 | n.d. | 0.18 | 0.47 | 710.0 | 2.37 |
| 3 | 7.96 | 2.93 | n.d. | n.d. | >150 | .02 | .31 | .02 | 0 | 15.6 | 153 | .49 | n.d. | .36 | .23 | 904 | 4.29 |
| 3 | 8.03 | 2.54 | n.d. | .28 | 642 | 0 | .22 | .05 | .02 | 10.8 | 39.7 | .05 | 2.78 | .29 | .08 | 741 | 1.38 |
| 4 | 8.15 | 1.99 | n.d. | .1 | 106 | 0 | .18 | .14 | 0 | 17.7 | 116 | .1 | 14.9 | .4 | .03 | 1000 | 1.79 |
| 3 | 8.11 | .414 | n.d. | .24 | 68 | 0 | .02 | 0 | 0 | 3.75 | 14.5 | 0 | .394 | .06 | 0 | 46.8 | 0 |
| 4 | 8.17 | .45 | n.d. | .27 | 64.2 | 0 | .05 | .07 | .11 | 3.23 | 19.5 | .06 | 1.81 | .08 | .06 | 38.5 | .39 |
| 4 | 8.09 | .391 | n.d. | .3 | 41.6 | 0 | .02 | 0 | .01 | 2.52 | 16.2 | 0 | .324 | .03 | 0 | 27.6 | .04 |
| 4 | 8.18 | .409 | n.d. | .33 | 44.8 | 0 | .03 | .02 | .08 | 3.26 | 18.3 | .02 | 1.26 | .03 | 0 | 27.5 | .07 |
| 8[1] | 3.96 | 6.45 | n.d. | .85 | 636 | .04 | 4.11 | 1.89 | .91 | 16.2 | 821 | 3.1 | 8.91 | 4.85 | .72 | 1910 | 16.5 |
| 4 | 7.56 | 2.69 | n.d. | .83 | 629 | 0 | .49 | 0 | .16 | 6.96 | 108.4 | .35 | 2.47 | .35 | .01 | 713 | 2.26 |
| 4 | 7.67 | 2.36 | n.d. | 1.04 | 756 | .01 | .65 | .08 | .14 | 5.39 | 60.5 | .46 | 3.86 | .63 | .22 | 956 | 5.93 |
| 4 | 7.63 | 1.323 | n.d. | .59 | 311 | 0 | .13 | 0 | .55 | 1.99 | 7.36 | .04 | 2.8 | .12 | .02 | 228 | .62 |
| 4 | 8.02 | .386 | n.d. | .56 | 59.4 | 0 | .02 | 0 | .34 | 1.37 | 8.77 | 0 | 2.89 | 0 | 0 | 26 | .06 |
| 4 | 7.79 | .358 | n.d. | .64 | 50.9 | 0 | .02 | .03 | 1 | 1.13 | 12.8 | 0 | 3.16 | .01 | .03 | 31.8 | .21 |
| 4 | 7.79 | .34 | n.d. | .37 | 42.9 | 0 | .01 | O | .05 | 1.79 | 10.8 | .02 | 2.33 | 0 | 0 | 18.6 | .02 |
| 4 | 7.98 | .332 | 60.1 | .43 | 46.5 | 0 | .02 | 0 | 0 | 1.8 | 12.7 | .01 | 1.29 | .02 | 0 | 20.7 | .02 |
| 4 | 7.99 | .356 | 67.1 | .49 | 53.3 | 0 | .07 | 0 | .19 | 1 | 14.7 | .1 | 2.35 | .01 | .1 | 22.2 | 0 |
| 8[1] | 7.79 | 1.6 | 910 | .63 | 199 | O | .29 | 0 | .04 | 3 | 93.9 | .12 | 3.24 | .31 | .1 | 277 | .71 |
| 4 | 7.9 | .453 | n.d. | .58 | 59.5 | O | .06 | 0 | .05 | 1.2 | 24.4 | .04 | 2.63 | .03 | 0 | 38.6 | 0 |
| 4 | 7.98 | .371 | 72.5 | .48 | 43.4 | 0 | .07 | 0 | 0 | 2.2 | 16.2 | .01 | 2.39 | .01 | 0 | 24.7 | .1 |
| 2 | 7.82 | .328 | 49.3 | .32 | 30.1 | 0 | .03 | 0 | .01 | .6 | 10.8 | .03 | 1.18 | .01 | O | 11 | O |
| 2 | 7.87 | .311 | n.d. | .3 | 33.6 | 0 | .03 | 0 | .06 | .1 | 11.8 | .01 | 1.98 | .03 | .1 | 11.5 | O |
| 3 | 7.96 | .288 | 43.2 | .33 | 35.5 | 0 | .03 | .09 | .42 | 1.1 | 14.1 | .01 | 2.51 | 0 | .24 | 11.8 | .19 |

n.d. No data.

[1] Dry cycle, opened to atmosphere.

**Table 4. Leachate concentrations from silver-lead-zinc mine C tailings (350 cm$^3$ synthetic rain leachant)**

| Time between leachings, weeks | pH | mmho | $SO_4$, mg/L | Elements, mg/L | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | Ag | B | Ca | Cd | Co | Cu | Fe | K | Mg | Mn | Ni | Pb | S | Zn |
| 1.75 kg WASTE (10-in column depth) | | | | | | | | | | | | | | | | | |
| Start | 6.22 | 5.04 | n.d. | 0.03 | n.d. | 434 | 0.31 | 0.61 | 0.11 | 0.85 | 11.4 | 421 | >210 | 0.14 | 0.09 | 1410 | 31.5 |
| 3 | 4.2 | 8.64 | n.d. | .19 | n.d. | 182 | .35 | 1.13 | .01 | 21.5 | 7.9 | n.d. | >210 | .24 | .19 | 2280 | 50.7 |
| 3 | 4.26 | 5.04 | n.d. | .08 | n.d. | 105 | .23 | .64 | 0 | 35.5 | 7.2 | >255 | >20 | .13 | .13 | 1710 | 43 |
| 4, | 4.77 | 1.492 | n.d. | .02 | n.d. | 32.2 | .08 | .35 | .06 | 7.77 | 3 | 70.8 | 209 | .08 | .01 | 253 | 15.9 |
| 3 | 5.88 | 1.008 | n.d. | .04 | n.d. | 15.4 | .07 | .27 | .06 | 7.23 | 1.8 | 54.2 | 138 | .06 | ,01 | 182 | 17.1 |
| 4 | 6.8 | .887 | n.d. | 0 | n.d. | 13.8 | .04 | .11 | .09 | 4 | 1.2 | 45.8 | 108 | .03 | .01 | 137 | 11 |
| 4 | 6.8 | .845 | n.d. | .01 | n.d. | 12.4 | .04 | .11 | 0 | 2.44 | .2 | 43.8 | 69.8 | .02 | 0 | 111 | 11.2 |
| 4 | 7.11 | .964 | n.d. | .03 | 0.13 | 22.8 | .06 | .18 | .06 | 1.3 | 2 | 77.9 | 144 | .03 | .01 | 155 | 14.9 |
| 8[1] | 6.58 | 2.33 | n.d. | .02 | .229 | 33.3 | .07 | .12 | .1 | .18 | 2.1 | 268 | 104 | .01 | .16 | 402 | 6.43 |
| 4 | 6.2 | 1.86 | n.d. | .05 | .122 | 46.6 | .07 | .21 | .11 | .21 | 2.2 | 211 | 168 | .04 | .03 | 378 | 15 |
| 4 | 6.3 | 1.37 | n.d. | .06 | .133 | 34.7 | .06 | .39 | .05 | 3.47 | 1.6 | 129 | 255 | .1 | .01 | 325 | 12.2 |
| 4 | 6.92 | 1.186 | n.d. | .05 | .096 | 29 | .09 | .32 | .06 | .93 | 1.5 | 71.5 | 256 | .08 | .08 | 220 | 31.6 |
| 4 | 6.93 | 1.04 | n.d. | .04 | .1 | 27.3 | .08 | .28 | .01 | 1.29 | 1.4 | 51.7 | 145 | .06 | .01 | 173 | 36 |
| 4 | 7.03 | .972 | n.d. | n.d. | .093 | 17.2 | .08 | .24 | 0 | 1.54 | .7 | 43.1 | 133 | .04 | 0 | 167 | 36.3 |
| 4 | 7.01 | .928 | n.d. | .03 | .105 | 24.4 | .08 | .26 | 0 | .93 | 1.6 | 51.7 | 135 | .04 | 0 | 178 | 43.4 |
| 4 | 7 | .943 | 475 | .03 | .097 | 20.1 | .07 | .23 | 0 | .72 | 1 | 53.6 | 130 | .05 | 0 | 159 | 43 |
| 4 | 6.82 | .964 | 501 | .04 | .12 | 20.7 | .06 | .56 | 0 | .8 | .4 | 59.5 | 132 | .06 | .1 | 167 | 46.4 |
| 8[1] | 6.82 | 1.424 | 815 | .05 | .11 | 26 | .07 | .34 | .07 | .26 | 1.5 | 118 | 145 | .04 | 0 | 246 | 34.3 |
| 4 | 6.5 | 1.16 | n.d. | .06 | n.d. | 20.4 | .07 | .23 | 0 | .11 | .3 | 80.2 | 129 | .04 | 0 | 183 | 37.1 |
| 4 | 6.64 | .98 | 508 | .09 | n.d. | 14.9 | .06 | .18 | 0 | .06 | .8 | 53.1 | 101 | .03 | 0 | 164 | 30.2 |
| 2 | 6.39 | .82 | 403 | .07 | .11 | 15 | .07 | .23 | 0 | .26 | .1 | 46.4 | 105 | .01 | .13 | 129 | 52.2 |
| 2 | 6.53 | .689 | n.d. | .06 | .08 | 9.9 | .05 | .17 | .01 | .1 | .2 | 25.9 | 78.1 | .02 | 0 | 97.9 | 29.5 |
| 3 | 6.83 | .611 | 255 | .02 | .09 | 11.8 | .05 | .13 | .03 | .58 | .5 | 23.8 | 77.2 | .02 | .07 | 87 | 38.6 |

n.d. No data.

[1] Dry cycle, opened to atmosphere.

Table 5. Leachate concentrations from lead-silver mine D tailings
(350 cm$^3$ synthetic rain leachant)

| Time between leachings, weeks | pH | mmho | $SO_4$, mg/L | Element, mg/L | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | Ba | B | Ca | Cu | Fe | K | Mg | Mn | Na | Ni | Pb | S | Zn |
| 1.75 kg WASTE (10-in column depth) | | | | | | | | | | | | | | | | |
| Start | 8.41 | 0.416 | n.d. | 0.088 | n.d. | 17.8 | 0.08 | 0.10 | 43.9 | 4.40 | 0.33 | n.d. | 0.00 | 0.02 | 23.8 | 0.01 |
| 3 | 8.36 | .65 | n.d. | .056 | n.d. | 45.9 | .09 | 0 | 58.6 | 14 | .94 | n.d. | 0 | 0 | 68.5 | .02 |
| 3 | 8.38 | .376 | n.d. | .047 | n.d. | 16.3 | 0 | 0 | 26.6 | 5.63 | .18 | n.d. | 0 | .03 | 29 | 0 |
| 4 | 8.13 | .248 | n.d. | .058 | n.d. | 11.3 | .02 | 0 | 15.8 | 3.21 | .19 | n.d. | 0 | 0 | 18.4 | 0 |
| 3 | 8.16 | .221 | r,.d. | .116 | n.d. | 14.4 | 0 | 0 | 17 | 3.94 | .32 | n.d. | 0 | .01 | 9.19 | 0 |
| 4 | 8.14 | .217 | r.d. | .133 | n.d. | 25.4 | 0 | .08 | 16.7 | 5.2 | .47 | n.d. | .01 | .03 | 10.3 | .06 |
| 4 | 7.87 | .261 | n.d. | .098 | n.d. | 24.2 | 0 | 0 | 11.6 | 3.48 | .24 | n.d. | 0 | 0 | 10.1 | .03 |
| 4 | 8.3 | .323 | n.d. | .08 | 0.33 | 33.2 | .06 | .02 | 14.1 | 5.77 | .7 | 5.98 | 0 | 0 | 14.6 | .02 |
| 8[1] | 7.88 | .691 | n.d. | .055 | 1.26 | 88.2 | .15 | .28 | 19.1 | 14.5 | 1.39 | 12.3 | .01 | .18 | 76.2 | .2 |
| 4 | 8.11 | .416 | n.d. | .05 | .48 | 57.2 | .09 | .01 | 20 | 8.54 | .93 | 12.7 | .02 | 0 | 37.8 | .06 |
| 4 | 7.93 | 404 | n.d. | .064 | .68 | 78.2 | .12 | .07 | 17.8 | 16.5 | 1.78 | 7.68 | .02 | 0 | 58.9 | .15 |
| 4 | 7.78 | .395 | n.d. | 1.61 | .67 | 50.4 | .08 | .27 | 14.8 | 8.91 | 1.12 | 6.91 | .02 | .02 | 28.3 | .08 |
| 4 | 8.19 | .384 | n.d. | 1.86 | .42 | 53.2 | .07 | .22 | 16 | 7.96 | 1.27 | 7.54 | .01 | 0 | 27.4 | .04 |
| 4 | 7.83 | .372 | n.d. | 0 | .52 | 46.7 | .02 | .84 | 13.5 | 7.45 | 1.43 | 6.44 | 0 | 0 | 31.1 | .02 |
| 4 | 7.74 | .346 | n.d. | .03 | .37 | 51.5 | .01 | .07 | 12.5 | 6.53 | 1.16 | 6.35 | 0 | .04 | 25.9 | 0 |
| 4 | 7.98 | .31 | 57.7 | .767 | .64 | 51.2 | .14 | 0 | 11.7 | 5.82 | 1.29 | 6.37 | 0 | 0 | 24.1 | .01 |
| 4 | 8.09 | .333 | 62.1 | .06 | .56 | 39.8 | 0 | 0 | 7.3 | 1.83 | .96 | 4.7 | 0 | 0 | 22.1 | 0 |
| 8[1] | 7.71 | .358 | 95.7 | 0 | .79 | 42.7 | 0 | .01 | 7.3 | 2.7 | .73 | 5.68 | 0 | .1 | 31.6 | 0 |
| 4 | 7.86 | .325 | n.d. | .066 | .71 | 49.3 | 0 | .03 | 8.9 | 2.11 | .74 | 9.12 | .02 | 0 | 23.1 | 0 |
| 4 | 7.9 | .296 | 52.8 | .077 | .67 | 39 | 0 | 0 | 8.2 | .646 | .65 | 7.14 | .01 | .06 | 18.3 | 0 |
| 2 | 7.84 | .274 | 41.1 | .091 | .67 | 35.5 | .08 | .03 | 6.9 | 1.82 | .68 | 6.12 | .01 | .19 | 7.6 | .25 |
| 2 | 7.77 | .269 | n.d. | .107 | .42 | 32.4 | .04 | .06 | 6 | .29 | .67 | 4.98 | .02 | 0 | 10.9 | .01 |
| 3 | 7.81 | .237 | 38.8 | .144 | .47 | 39.4 | .14 | .59 | 6.6 | 2.77 | .64 | 5.84 | 0 | .12 | 10.6 | .14 |

n.d. No data.

[1] Dry cycle, opened to atmosphere.

Table 6. Leachate concentrations from lead-zinc mine E tailings
($325 \text{ cm}^3$ synthetic rain leachant)

| Time between leachings, | | | $SO_4$, | Element, mg/L | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| weeks | pH | mmho | mg/L | Ba | B | Ca | Fe | K | Mg | Mn | Na | Ni | S | Zn |
| 1.75 kg WASTE (10-in column depth) | | | | | | | | | | | | | | |
| Start | 7.34 | 2.60 | n.d. | n.d. | 0.09 | 149 | 0.01 | 5.4 | 20.2 | 0.04 | n.d. | 0.01 | 258 | 0.70 |
| 3 | 7.75 | 2.18 | n.d. | n.d. | n.d. | >140 | 0 | 6.6 | 72.8 | .03 | n.d. | 0 | 475 | .46 |
| 3 | 8.28 | .514 | n.d. | n.d. | .13 | 65.5 | 0 | 2.5 | 19.9 | O | n.d. | 0 | 122 | 0 |
| 4 | 8.48 | .303 | n.d. | n.d. | .11 | 33.9 | 0 | 2.7 | 8.23 | 0 | n.d. | 0 | 22.5 | 0 |
| 3 | 8.14 | .273 | n.d. | n.d. | .17 | 39.7 | 0 | 2.5 | 10.6 | 0 | n.d. | 0 | 20.7 | .04 |
| 4 | 8.12 | .34 | n.d. | n.d. | .07 | 35.3 | .06 | 1.8 | 11.5 | O | n.d. | .01 | 23.5 | .04 |
| 4 | 7.85 | .275 | n.d. | 0.089 | .21 | 27.7 | 0 | 1.3 | 9.58 | 0 | n.d. | 0 | 17.4 | .04 |
| 4 | 7.85 | .317 | n.d. | .094 | .26 | 37.6 | .04 | 1.8 | 12.5 | 0 | 1.28 | 0 | 22.4 | .04 |
| 8[1] | 7.44 | 1 | n.d. | .059 | .69 | >134 | 0 | 5.5 | 57.3 | .01 | 5.91 | .01 | 183 | .16 |
| 4 | 7.68 | 7.8 | n.d. | O | .29 | 61.8 | 0 | 3.1 | 20.2 | 0 | 3.21 | 0 | 61.1 | .06 |
| 4 | 7.8 | .397 | n.d. | .044 | .3 | 24.7 | .21 | 1.2 | 12.9 | .02 | 1.41 | .02 | 35.8 | .07 |
| 4 | 7.54 | .368 | n.d. | .96 | .31 | 41.8 | .44 | 2.5 | 17 | 0 | 3.13 | 0 | 29.8 | .05 |
| 4 | 7.86 | .363 | n.d. | .07 | .34 | 44.7 | .34 | 2.9 | 17.1 | 0 | 2.97 | 0 | 31.1 | .03 |
| 4 | 7.82 | .355 | n.d. | O | .27 | 14.6 | .99 | .7 | 5.57 | 0 | 1.31 | 0 | 20.3 | 0 |
| 4 | 7.78 | .345 | n.d. | .107 | .36 | 53.2 | .73 | 3.9 | 22.5 | 0 | 4.35 | 0 | 29.1 | .06 |
| 4 | 7.83 | .336 | 77.2 | .931 | .37 | 48.6 | .15 | 2.8 | 20.8 | .21 | 2.86 | 0 | 32 | .03 |
| 4 | 7.94 | .352 | 78.4 | .076 | .32 | 42.7 | .02 | 2.5 | 13.8 | .01 | 2.08 | .01 | 26.4 | 0 |
| 8[1] | 7.75 | .448 | 136 | 0 | .37 | 52.5 | .02 | 2.7 | 16.1 | .01 | 2.52 | 0 | 43.1 | .01 |
| 4 | 7.71 | .377 | n.d. | .071 | .41 | 52 | 0 | 2.2 | 16.4 | .01 | 3.35 | 0 | 34.7 | 0 |
| 4 | 7.81 | .357 | 93.1 | .024 | .34 | 44.4 | 0 | 3 | 13.7 | 0 | 2.86 | 0 | 30.8 | .04 |
| 2 | 7.82 | .314 | 62 | .056 | .26 | 31.1 | .03 | 1.2 | 9.09 | .02 | 1.58 | .01 | 15.1 | O |
| 2 | 7.77 | .321 | n.d. | .092 | .24 | 34.2 | .01 | .7 | 9.86 | 0 | 1.54 | 0 | 18.5 | 0 |
| 3 | 7.96 | .34 | 77 | .095 | .2 | 37 | .38 | 1.6 | 12.6 | 0 | 1.76 | 0 | 22.4 | .03 |

n.d. No data.

[1] Dry cycle, opened to atmosphere.

Table 7. Leachate concentrations from lead-zinc mine F tailings
(250 cm$^3$ synthetic rain leachant)

| Time between leachings, weeks | pH | mmho | SO$_4$, mg/L | Elements, mg/L B | Ca | Cd | Co | Cu | Fe | K | Mg | Mn | Na | Ni | Pb | S | Zn |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1.75 kg WASTE (10-in column depth) | | | | | | | | | | | | | | | | | |
| Start | 4.75 | 2.65 | n.d. | 0.07 | 407 | n.d. | 0.30 | 0.00 | 0.01 | 4.9 | 11.2 | n.d. | n.d. | 0.33 | 1.27 | 589 | 0.76 |
| 3 | 7.43 | 4.97 | n.d. | .24 | 603 | n.d. | 1.6 | .04 | .01 | 18 | 266 | n.d. | n.d. | 1.39 | 1 | 678 | 1.23 |
| 3 | 8.05 | 4.5 | n.d. | .19 | 530 | n.d. | 1.36 | 0 | 0 | 25.9 | n.d. | n.d. | n.d. | 2.87 | .35 | 984 | 3.11 |
| 4 | 7.98 | 2.8 | n.d. | .12 | 523 | n.d. | 1.86 | .04 | 0 | 7.5 | 163 | n.d. | n.d. | 2.75 | .47 | 961 | 5.06 |
| 3 | 8.24 | 1.46 | n.d. | .1 | 224 | n.d. | 1.37 | .17 | .02 | 3.4 | 105 | n.d. | n.d. | 3.12 | .41 | 309 | 3.06 |
| 4 | 8.02 | 1.38 | n.d. | .08 | 206 | n.d. | 1.2 | .28 | .06 | 3.2 | 81.5 | n.d. | n.d. | 2.18 | .17 | 232 | 1.75 |
| 4 | 7.82 | 1.61 | n.d. | .1 | 240 | n.d. | 1.57 | .3 | .11 | 3.2 | 95.3 | n.d. | n.d. | 2.66 | .23 | 312 | 3.01 |
| 4 | 7.7 | 1.76 | n.d. | .14 | 216 | 0.03 | 3.16 | .5 | .17 | 1.6 | 167 | 1.16 | 0.45 | 5.28 | .52 | 455 | 7.83 |
| 8[1] | 4.06 | 13.33 | n.d. | .14 | 548 | .17 | 5.26 | 1.61 | .54 | 7.7 | 801 | 15.8 | 7.95 | 2.74 | 4.67 | 6370 | 24.6 |
| 4, | 4.52 | 5.35 | n.d. | .05 | 567 | .05 | 1.94 | .56 | .63 | 6.4 | 367 | 3.44 | 1.84 | 1.08 | .89 | 1055 | 6.18 |
| 4 | 7.45 | 4.29 | n.d. | .13 | 616 | .04 | 4.25 | .5 | .09 | 3.9 | 575 | 3.86 | 2.55 | 3.84 | .56 | 1207 | 9.59 |
| 4 | 7.57 | 3.69 | n.d. | .07 | 536 | .02 | 3.66 | .61 | .46 | 2.3 | 322 | 2.74 | 2.8 | 5.72 | .28 | 831 | 13.1 |
| 4 | 7.8 | 3.24 | n.d. | .14 | 405 | .01 | 4.84 | .18 | .45 | 1.6 | 186 | 2.55 | 2.08 | 7.05 | .22 | 829 | 16.3 |
| 4 | 7.73 | 3.07 | n.d. | .1 | 521 | .02 | 4.65 | 1.04 | 1.24 | 1.2 | 151 | 2.72 | 1.88 | 6.94 | .29 | 790 | 11.5 |
| 4 | 7.65 | 2.89 | n.d. | .06 | 378 | .01 | 3.98 | .17 | .71 | 1.3 | 114 | 1.93 | 1.69 | 5.67 | .17 | 609 | 10.7 |
| 4 | 7.73 | 2.91 | 1860 | .07 | 320 | .05 | 3.34 | .2 | .15 | 2 | 144 | 3.23 | 2.74 | 13.9 | .15 | 891 | 23.1 |
| 4 | 7.76 | 3.01 | n.d. | .06 | 393 | .09 | 3.19 | 1.01 | .11 | 1.8 | 230 | 4.1 | 1.48 | 3.5 | .8 | 791 | 19 |
| 8[1] | 7.19 | 4.35 | 3450 | .1 | 740 | .11 | 23.7 | .62 | .2 | 2.5 | 662 | 8.48 | 2.88 | 16.7 | .5 | 1198 | 45.5 |
| 4 | 7.07 | 2.67 | 3560 | .06 | 526 | .07 | 12 | .59 | .29 | .4 | 180 | 3.87 | 3.13 | 9.9 | .9 | 620 | 39.5 |
| 4 | 7.48 | 2.66 | 1490 | .05 | 515 | .05 | 6.11 | <.01 | .09 | .7 | 81 | 2.39 | 1.54 | 5.85 | 0 | 596 | 8.94 |
| 2 | 7.31 | 2.52 | 1620 | .07 | 566 | .04 | 7 | <.01 | .06 | 2.3 | 71 | 2.37 | 2.05 | 7.22 | .06 | 546 | 4.86 |
| 2 | 7.54 | 2.7 | n.d. | .04 | 656 | .01 | 8.62 | <.01 | .02 | <.1 | 36.8 | 1.44 | 1.06 | 4.3 | .04 | 513 | 4.37 |
| 3 | 7.62 | 2.64 | 1530 | .09 | 647 | .02 | 2.75 | .21 | .5 | <.1 | 35.7 | 1.07 | 1.72 | 4.48 | .28 | 503 | 3.15 |

n.d. No data.

[1] Dry Cycle, opened to atmosphere.

Table 8. Effects of oxygen on leachate concentrations, lead-zinc mines B and F tailings

| Residence | Chamber | | | | | | | | Laboratory | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| time, | pH | $SO_4$, | Element, mg/L | | | | | | pH | $SO_4$, | Element, mg/L | | | | | |
| days | | mg/L | Ca | Co | Mn | Ni | Pb | Zn | | mg/L | Ca | Co | Mn | Ni | Pb | Zn |
| LEAD—ZINC MINE B TAILINGS | | | | | | | | | | | | | | | | |
| 1 | 7.54 | n.d. | 466 | 0.54 | 0.50 | 0.68 | 0.41 | 1.44 | 7.16 | n.d. | 467 | 0.84 | 0.83 | 1.01 | 0.37 | 2.10 |
| 4 | 7.87 | 2420 | 574 | .3 | .38 | .38 | .42 | 1.81 | 7.82 | 1860 | 563 | .25 | .26 | .34 | .32 | .97 |
| 7 | 8.10 | 1480 | 810 | .19 | .19 | .24 | .25 | .88 | 8.06 | 1460 | 788 | .21 | .2 | .32 | .19 | .89 |
| 14 | 8.08 | 657 | 252 | .23 | .24 | .31 | .25 | 1.38 | 8.02 | 784 | 294 | .44 | .35 | .55 | .19 | 1.83 |
| 24[1] | 8.48 | 128 | 35.2 | .01 | 0 | 0 | .02 | .03 | 7.72 | 2300 | 542 | 1.12 | .66 | 1.99 | .74 | 5.49 |
| 15 | 8.48 | 46.8 | 31.3 | .02 | 0 | .01 | .02 | .06 | 7.99 | 704 | 151 | .24 | .08 | .41 | .03 | .96 |
| 3 | 8.61 | 15.2 | 32.8 | C | .04 | 0 | .16 | .17 | 8.26 | 156 | 75.4 | .07 | .07 | .13 | .18 | .48 |
| 7 | 8.45 | 17.7 | 25.3 | .01 | .01 | .01 | .03 | .02 | 8.38 | 87.2 | 64.1 | .05 | .03 | .09 | .05 | .22 |
| 31[1] | 8.05 | 62 | 45 | .05 | .06 | .04 | .02 | .15 | 7.77 | 3260 | 889 | 4.12 | 1.9 | 7.24 | .68 | 23.3 |
| 28[2] | 7.68 | 3160 | 1016 | 2.48 | 1.31 | 4.59 | 1.07 | 13.9 | 7.62 | 2760 | 872 | 5.45 | 1.56 | 9.06 | .56 | 25.5 |
| 7[3] | 7.93 | 1733 | 673 | 1 | .57 | 1.84 | .24 | 7.36 | 7.96 | 1410 | 664 | 1.64 | .75 | 3.16 | .41 | 13.6 |
| LEAD—ZINC MINE F TAILINGS (sample 2) | | | | | | | | | | | | | | | | |
| 1 | 5.30 | n.d. | 416 | 4.40 | 5.40 | 4.40 | 3.77 | 24.3 | 6.68 | n.d. | 444 | 4.00 | 5.00 | 4.00 | 3.07 | 24.8 |
| 4 | 7.39 | 4020 | 600 | 2.65 | 2.68 | 1.25 | .72 | 3.26 | 7.38 | 4500 | 540 | 3.57 | 3.45 | 1.48 | .62 | 4.26 |
| 7 | 7.92 | 1640 | 668 | .76 | .85 | .55 | .42 | 1.05 | 7.67 | 1680 | 768 | 1.37 | 1.38 | .75 | .31 | 2.15 |
| 14 | 7.88 | 1670 | 541 | 1.79 | 1.38 | 1.54 | .51 | 2.46 | 7.68 | 1700 | 489 | 2.23 | 1.99 | 1.67 | .71 | 3.93 |
| 24[1] | 7.42 | 1500 | 494 | 1.11 | .76 | 1.16 | .28 | 1.56 | 6.38 | 2200 | 433 | .96 | 1.84 | .31 | .29 | 1.55 |
| 15 | 7.99 | 1530 | 314 | 1.03 | .54 | 2.01 | .17 | 3.1 | 7.75 | 2140 | 316 | .62 | .79 | .43 | .15 | .96 |
| 3 | 8.05 | 1390 | 445 | 1.12 | .51 | 2.05 | .27 | 2.51 | 7.65 | 1600 | 395 | .88 | 1.33 | .69 | .3 | 1.44 |
| 7 | 7.92 | 1000 | 701 | 1.66 | .64 | 2.62 | .21 | 3.82 | 7.97 | 1260 | 782 | 1.4 | 1.27 | .8 | .36 | 1.99 |
| 31[1] | 7.56 | 1380 | 611 | 1.19 | 1.14 | 1.57 | .22 | 2.13 | 6.29 | 3430 | 755 | 2.24 | 3.33 | .88 | .44 | 4.73 |
| 28[2] | 4.5 | 3570 | 957 | 1.88 | 2.79 | 1.02 | .88 | 3.1 | 5.96 | 3570 | 784 | 4 | 5.79 | 2.35 | .91 | 10.2 |
| 7[3] | 6.88 | 2023 | 678 | 1.61 | 1.32 | 1.38 | .39 | 2.18 | 7.31 | 2290 | 749 | 3.41 | 3.4 | 3.08 | .81 | 10.4 |

n.d. No data.

[1] Dry nitrogen introduced into chamber; laboratory columns open to air.

[2] Dry air introduced into chamber; laboratory columns open to air.

[3] Wet air introduced into chamber; laboratory columns covered.

in leachate sulphate or metal concentrations when oxygen was excluded, while sulphate formation increased by 1,520 mg/L (2,300-780) for lead-zinc mine B (17 pct loss in pore water during the dry cycle) and 500 mg/L with lead-zinc mine F (15 pct loss in pore water during the dry cycle) for tailings exposed to laboratory air. The second dry cycle again showed only a small increase in sulphate (within experimental uncertainty) when nitrogen was the atmosphere surrounding the columns, yet dramatic increases in sulphate when air was the surrounding atmosphere. The second dry cycle was accompanied by a 20 to 25 pct evaporation of pore water. Table 8 shows that if dry air replaces nitrogen in the chamber protocol, sulphate production occurs along with enhanced metal dissolution. This latter dry cycle resulted in a 30 to 35 pct loss in pore water. The volume of leachate collected from each experiment was within 5 pct of the pore volume.

In a previous study (Doepker, 1989) it was reported that enhanced metal and sulphate release from columns of lead-zinc mine B tailings did not occur within a residence time of 28 days if the environment was maintained at 100 pct relative humidity. This indicated that major oxidation occurred from columns of tailings only if atmospheric oxygen was present and the tailings were at least partially dried.

Table 9. Effects of drying time on leachate concentrations, lead-zinc mine L tailings

| Residence time, days | Column conditions | Percent loss pore water | pH | $SO_4$, mg/L | Element, mg/L Ca | Mg | Mn | Ni | Zn |
|---|---|---|---|---|---|---|---|---|---|
| 7[1] | Sat | 2.5 | 7.81 | 1540 | 797 | 38.5 | 0.31 | 0.22 | 1.38 |
|  | Lab. air | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. |
|  | Forced air | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. |
| 7[1] | Sat | 2.5 | 7.48 | 1400 | 740 | 18.1 | .22 | .16 | 1.15 |
|  | Lab. air | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. |
|  | Forced air | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. |
| 7 | Sat | 2 | 7.3 | 1130 | 644 | 24.3 | .15 | .14 | 1.03 |
|  | Lab. air | 25 | 2.99 | 990 | 642 | 70.6 | .39 | .49 | 2.18 |
|  | Forced air | 77 | 2.23 | 3700 | 611 | 494 | 1.1 | .71 | 4.48 |
| 14 | Sat | 2.5 | 6.75 | 1270 | 906 | 32.3 | .17 | .06 | 1.08 |
|  | Lab. air | 54 | 2.12 | 2910 | 1010 | 274 | 1.3 | 3.37 | 16.3 |
|  | Forced air | 88 | 3.55 | 4040 | 592 | 626 | 1.15 | .56 | 5.18 |
| 21 | Sat | 2.5 | 6.85 | 916 | 696 | 23.2 | .13 | .11 | .79 |
|  | Lab. air | 66 | 2.04 | 3470 | 1060 | 742 | 2.19 | 4.09 | 18.1 |
|  | Forced air | 90 | 3.54 | 3910 | 697 | 793 | .8 | .18 | 1.59 |
| 28 | Sat | 1.5 | 7.07 | 1001 | 632 | 25 | .12 | .14 | .99 |
|  | Lab. air | 71 | 2.31 | 3880 | 1210 | 648 | 1.8 | 3.03 | 12.4 |
|  | Forced air | 85 | 5.11 | 4030 | 544 | 618 | .75 | .22 | 1.81 |

n.d. No data.

[1] Stabilization period, all columns remained saturated in laborotory.

## Effect of Evaporation Rate

A series of 75 mm ID columns containing lead-zinc mine B tailings were leached with distilled water until stabilized, that is, all columns produced similar leachate metal concentrations. Half was placed into a forced-air oven (temperature at 85° F) while the remaining half was held in the laboratory. Half of this latter group was maintained at saturation while the other half was open to laboratory air. At 7, 14, 21, and 28 days, columns of each of the three groups were leached with 1 pore volume of de-ionized water. A summary of the results of this experiment is found in Table 9.

Leachate sulphate was nearly constant for columns maintained at saturation for 7, 14, 21, and 28 days. The concentration of sulphate obtained from the forced air-dried columns reached a value of 3,700 mg/L in 7 days, while a similar concentration of 3,880 mg/L was leached from columns open to laboratory air for total of 28 days. Pore water evaporation from the 7 days of forced air and 28 days of laboratory exposure was 85 and 71 pct, respectively. It appears that sulphate formation was more related to the rate of pore water evaporation than to leachate residence time. This indicates that rate of sulphide oxidation by oxygen must be tightly controlled by the distribution of water and oxygen on the sulphide surface. Leachate pH of both the laboratory-dried sample and forced air-dried sample dropped below 3 within 7 days. Although the pH of columns exposed to laboratory air continued to fall, surprisingly, the lowest pH observed for the forced air-dried columns was 2.2 after 7 days. Columns maintained under similar conditions for 28 days produced a leachate pH of 5.1. A simple calculation of ion balance using principal cations Ca and Mg and the only reported anion SO4 reveals that excess cations are seen in the laboratory-dried columns while a cation-to-anion balance is obtained from the forced air-dried columns. Although the IC anion analysis method detects halogens, nitrate, nitrite, phosphate and sulphate, only sulphate was found. Carbonate/bicarbonate cannot be determined through the method used, but should be important in a carbonate system such as lead-mine B tailings. Thus it becomes apparent that the rise of leachate pH observed in the forced air-dried columns may be accounted for by the formation of carbonic acid (acid dissolution of dolomite) and its subsequent thermal decomposition to water and carbon dioxide. This loss of carbon dioxide, coupled with the decreased rate of oxidation (acid formation) due to either evaporation of that pore water needed to produce acid, or to coating of reactive sulphides, leads to formation of leachates with a higher pH.

## SUMMARY AND CONCLUSIONS

Although this research is limited to a few lead-zinc mine tailings, results presented are in complete agreement with other studies from the Bureau of Mines laboratories. Column leach experiments are able to demonstrate potential problem tailings. As noted, basic tailings with large acid-buffering capacities may still produce acid leachates as a result of the oxidation of sulphides--in particular, pyrite--within the tailings. Enhanced metal release as a result of the oxidation of unsaturated tailings may follow even when leachate pH remains near normal. In general, high sulphate yields initially observed in column leaching procedures flag potential oxidizable tailings, but may be a result of past activity as opposed to present activity. Due to enhanced solubility of metal-sulphate complexes, leachates containing large amounts of sulphate may also exhibit high metal loading. A reduced oxygen atmosphere may be the only method to stabilize metal dissolution from tailings at an acceptable level. The flushing of oxidation products from unsaturated tailings by rainfall or snowmelt may produce acid seeps and/or heavy-metal loading, but even this may depend on the neutralization rate (in the unsaturated zone), water content, and residence time.

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