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**ACID GENERATION AND METAL MOBILITY OF SOME METAL- MINING
RELATED WASTES IN COLORADO**

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ABSTRACT

Four metal-mining related wastes, two from near Silverton, Colorado, and two from near Leadville, Colorado were studied in the laboratory to evaluate mineralogy, chemistry, and their reactions to multiple deionized water leachates in solid:leachate ratios ranging from 1:20 to 1:8,000. These wastes were weathered for more than 50 years, but still contain pyrite and minor Cu, Zn, and Pb.

Mineralogical studies did not determine the acid-generating phase, but in two sets of three serial leaches, significant acid-generation was measured, showing that initial solid:leachate ratios of 1:20 or 1:4,000 do not completely remove acid-generating phases in 24 h. Leaching studies used a passive method in which deionized water was poured onto the samples and the mixture was stirred once for five seconds after one hour, but at rest otherwise for 24 h in glass beakers.

Three large volume serial leaches of 1:4,000, 1:8,000, 1:8,000 produced 44-63 times more acid than three small-volume 1:20, 1:200, 1:100 leaches conducted under identical laboratory conditions. In terms of dissolved metals that are potentially toxic to aquatic-life; Cu was two to six times higher in the large-volume leachates (than in the small-volume leachates), Zn was more than two times higher in the large-volume leachates (than in the small-volume leachates), and Pb was two to seventeen times higher in the large-volume leachates (than in the small-volume leachates). Hydrolysis of Fe and the associated precipitation of amorphous orange Fe-oxide appears to be a source of acid generation in both the small-volume and large-volume leachates. We suspect that unidentified Fe sulfates were mainly responsible for generated acidity in leachates.

The study of large-volume leachate exposures of surficial metal-mine wastes to deionized water of pH about 5 was intended to simulate spring/summer snowmelt runoff; if this approach is appropriate, it shows that large amounts of acid generation and associated toxic-metal mobility may be relevant factors in water-quality degradation in terms of Class 1 Aquatic Life standards.

INTRODUCTION

This study was done for the mine waste characterization project that is focussed on the chemical, mineralogical, physical, biological, and geophysical aspects of abandoned mine land (AML) wastes in the Rocky Mountain region. The effort here is directed toward the mineralogical and chemical characteristics of surficial wastes from four waste piles and the reactions of these waste samples with deionized water in the laboratory. The wastes we studied contain significant pyrite, and minor amounts of zinc and lead (originally in sphalerite and galena); and all of them have been exposed to natural weathering for more than 5 decades.

Surficial waste sampling was done in such a way as to minimize sampling error to 17 percent or less by sampling the < 2 mm fraction in 30 equally-spaced cells on the surface of each waste pile and them compositing these into one homogeneous sample prior to further study.

The four samples studied here include the samples from waste piles at the May Day and Yukon mines along Cement Creek near Silverton, Colorado and the Venir and Sunday No.2 mines near Leadville, Colorado. The two waste piles near Silverton occur at elevations of about 9,880 feet above mean sea level; the two waste piles near Leadville

occur at elevations between 11,600 and 12,000 feet above mean sea level. Both areas receive between 40-50 inches of precipitation per year, and most of it is as snowfall.

MINERALOGICAL, CHEMICAL, AND LEACHING STUDIES OF FOUR METAL MINING RELATED WASTES MINERALOGY

Splits of the < 2mm fraction, aggregating several kg each from the May Day and Yukon mines (both from near Silverton, CO) and from the Venir and Sunday No. 2 mines, (both from near Leadville, CO) were studied in the laboratory. The mineralogy of each of these was studied by X-ray diffraction, non-destructive X-ray fluorescence analysis, microscopic methods, preparation of heavy-mineral concentrates, and separation of size fractions by dry sieving and by decantation of acetone slurries. X-ray diffraction (XRD) studies used Ni-filtered Cu K α radiation in diffractometer mode. Minerals found by these methods are given for each of the four wastes in Table 1. Minerals listed for the <0.150 mm fraction, obtained by dry sieving, represent the major minerals in each sample. On a short-term basis (24-48 h.) most of these are relatively insoluble and none of them have a large acid-neutralizing or large acid-generating potential.

Also in Table 1 are minerals in the heavy-mineral concentrate of three other size fractions. These concentrates were obtained by mechanical panning on a Wilfley table (English and others, 1987) using deionized water (pH = 4.9-5.2) in a solid:liquid ratio of 1:600 in order to minimize acid generation from the solids (maintain a pH above 4.0). These concentrates reveal that pyrite is present in all sized fractions. Anglesite crystals in the size range of about 0.010-0.020 mm were identified in the two smallest size fractions of the May Day and Venir wastes (table 1) by scanning electron microscopy (SEM) using an energy-dispersive X-ray fluorescence detector in semi-quantitative analysis mode. XRD analysis confirmed anglesite which is a product of oxidation of galena. Cerrusite was identified in the Sunday No. 2 heavy-mineral concentrates as small (<0.020 mm) crystals, and as crusts or coatings on galena.

The acetone decantation solid concentrates (table 1) were obtained using about 20 g of dry-sized (< 2 mm) solids in 500 ml of acetone, shaking the mixture in a circular motion before immediate decantation of the slurries for which the solids were retained on filter paper. The air-dried acetone decantations were studied by XRD and non-destructive XRF analysis. The minerals identified by XRD analysis are given at the bottom of Table 1; the XRF analyses for Fe, Cu, Zn, and Pb are given in Table 2 for these acetone decant solids.

Table 1. Minerals found in wastes of the May Day, Venir, Yukon, and Sunday No. 2.
[Minerals are listed in decreasing order of abundance]

Bulk <0.150 mm Samples

May Day: quartz, muscovite, jarosite, plagioclase, K-feldspar

Venir: quartz, muscovite, kaolinite, jarosite, K-feldspar

Yukon: quartz, plagioclase, muscovite, jarosite, pyrite

Sunday No. 2: quartz, jarosite, muscovite, kaolinite

Sized Fractions of Heavy-Mineral Concentrates		
<u>0.50-2.0 mm</u>	<u>0.090-0.50 mm</u>	<u><0.090 mm</u>
	May Day	
pyrite, galena coated with anglesite	pyrite, ferberite, sphalerite, <0.050 mm anglesite	pyrite, ferberite, <0.050 mm anglesite, barite
	Venir	
pyrite, <0.050 mm anglesite, ferberite	pyrite, <0.050 mm anglesite and barite, ferberite, native Au	pyrite, anglesite, barite, ferberite, native Au
	Yukon	
pyrite, ferberite	pyrite, ferberite	pyrite, ferberite
	Sunday No.2	
galena coated with cerrusite, pyrite, sphalerite, <0.050 mm cerrusite	<0.050 mm cerrusite, pyrite, galena	<0.050 mm cerrusite, barite, pyrite

Acetone Decantation Solids from <0.090 mm Fraction

May Day: quartz, jarosite, muscovite, chlorite (clinochlore), kaolinite, anglesite

Venir: quartz, muscovite, kaolinite, jarosite, chlorite (clinochlore), anglesite

Yukon: quartz, muscovite, jarosite, gypsum, kaolinite, anglesite, pyrite

Sunday No. 2: quartz, jarosite, muscovite, kaolinite, gypsum, anglesite (?)

Comparisons of the Fe, Cu, Zn, and Pb concentrations in the untreated <0.090 mm fractions and the acetone decant of the <0.090 mm fractions are interesting. Both Fe and Pb are enriched significantly in the acetone decant fractions, compared to the untreated <0.090 mm fractions (table 2). Jarosite is significantly enriched in the acetone decant fractions, compared to the untreated fraction. These observations indicate that an Fe-rich phase and a Pb-rich phase are present as extremely small particles that stayed in suspension in the decanted fraction. The increased concentrations of jarosite in the decanted fractions are not sufficient to account for the increased concentrations of Fe for the May Day and the Sunday No. 2 samples. The increased amounts of jarosite, as well as the concentration of chlorite in the May Day and Venir decants might be sufficient to account for the increased Fe in these fractions. The enrichment of pyrite in the acetone decant of the Yukon material may account for the increased iron content. There is no XRD detectable Fe mineral in the Sunday No. 2 decant that is present in concentrations sufficient to account for the iron enrichment. The increased amounts of Pb in the decants of the May Day, Venir, and Yukon are due to the concentrations of fine-grained anglesite. For the Sunday No. 2, the decant probably concentrated the fine-grained cerrusite identified in heavy-mineral concentrates. Because of X-ray peak interferences of kaolinite with cerrusite, the presence of cerrusite in this decant could not be confirmed.

PASSIVE LEACHING STUDIES WITH SMALLER LEACHATE VOLUMES

About 100-200 g from each < 2mm fraction of these was sized to obtain a <0.090 mm fraction of 30-60 g. Each of these was split with a microsplitter to obtain two approximately 12-15 g fractions. One of these was used as a reference sample for XRD and non-destructive chemical analysis. The other, aggregating 10 g was exposed to leachates sequentially using deionized water of pH = 5.0 in waste:water ratios of 1:20, 1:200, and 1:100 for 24 hour periods each, in side-by-side tests. During each exposure the pH of the leachate was measured shortly after initial exposure and at the end (24 h) of the exposure of waste to leachate. At the end of each test, the leachate was sampled for cation analyses; 60 ml leachate samples were filtered (0.45 micrometer), and the leachates for cation analysis were acidified with nitric acid. After sampling the leachate, the liquid was decanted prior to the following leach test. Samples were not allowed to dry between sequential leaches. The initial total concentrations of Fe, Cu, Zn, and Pb are given in Table 2 prior to any leach test. Table 3 gives the concentrations of 12 elements dissolved in the three separate leachates based on ICP/MS analysis. In each case, the concentrations of Cu, Zn, and Pb in the leachates were 5 mg L⁻¹ or less. The sums of the 12 dissolved cations in each leachate, converted to mg g⁻¹ are also given in Table 3, as are the final pH of the three leachate solutions. Using the sums of the cations, the relative percentages of the sums in each leachate are given. Eighty nine to 97 percent of the 12 dissolved cations (table 3) were released in the first (1:20) leach of the Venir, Yukon, and Sunday No.2 wastes; the May Day waste released only 61 percent during the first leach. Figures 1, 2, 3, and 4 show the amounts of dissolved Ca, Fe, Cu, Zn, Cd, and Pb in each of the three serial leaches for the May Day, Venir, Yukon, and Sunday No. 2, respectively. For the most part, the largest amounts of each dissolved cation was in the

first leach, partly because the pH of the first leachate was significantly lower than subsequent leaches. The exception to this is Fe for the May Day leach (fig. 1).

The concentrations of Ca in the first leaches of the Yukon and Sunday No. 2 (table 3 and figs. 3 and 4) are due to the dissolution of gypsum, found in the acetone decantation solids (table 1).

The untreated <0.090 mm fraction splits show the highest Pb concentration to be in the Sunday No. 2 waste (table 2), and the most abundant Pb mineral in the <0.090 mm heavy-mineral concentrate of this waste is the Pb-carbonate, cerrusite (table 1) which is present as <0.050 mm crystals. One might expect that the fine crystals of cerrusite would contribute significant Pb to the first (1:20) leachate, of pH = 2.67, as compared to the two other <0.090 mm wastes samples (May Day and Venir) which have anglesite as the major mineral in the <0.090 mm fraction (table 1). However, the dissolved Pb from the first (1:20) leachates of the May Day (pH = 3.14) and the Venir (pH = 2.58) significantly exceeded those of the Sunday No. 2. (table 3).

After the third leach, each of the remaining solids was air dried and pulverized in tungsten carbide (WC) lined mills with WC balls for 5 minutes. These pulverized solids were then exposed to deionized water (pH = 5.0) in a ratio of 1:100 for 24 hours. The pH of these leachates is listed at the bottom of Table 3. Except for that of the Sunday No. 2 residue, the pH of the leachates is lower than the final pH of third 1:100 leach. This is believed to indicate that a water-soluble, acid-generating mineral or minerals were liberated or exposed by the reduction in grain size (pulverizing).

Table 2. Concentrations of selected elements in untreated, dry sized (<0.090 mm) and an acetone decanted solids fraction from <0.090 mm splits from four waste dumps. X-ray diffraction (XRD) intensities for jarosite are given for each fraction. Final pH of the 1:200 leachate (24 h) for each fraction are also shown.

	Fe wt. %	Cu ---parts per million---	Zn	Pb	pH of leachate	XRD jarosite peak intensity
MAYDAY						
Untreated	6.1	270	1500	6500	3.85	20
Acetone decant solids	9.0	460	770	12000	3.79	27
VENIR						
Untreated	5.6	220	200	2200	3.25	11
Acetone decant solids	6.6	310	250	3600	3.20	22
YUKON						
Untreated	9.3	560	1000	3000	3.48	12
Acetone decant solids	10.7	300	470	4300	3.36	32
SUNDAY No. 2						
Untreated	5.5	340	540	7900	3.34	21
Acetone decant solids	10.0	590	800	14600	3.28	31

Table 3. Concentrations of 12 elements dissolved in each of three serial leachates of 10-gram samples of the <0.090 mm fraction from four waste piles determined by ICP/MS and ICP/AES (of 0.45 micron filtered leachates).

leach ratio	Na	Mg	Al	Si	K	Ca	Mn	Fe	Cu	Zn	Cd	Pb	Σ	% of total
-----milligrams L ⁻¹ -----														
MAYDAY														
1:20	1.3	1.0	0.6	1.8	0.7	4.4	0.2	0.84	0.13	1.2	0.007	2.7	0.29	61
1:200	0.12	0.03	0.2	0.1	<0.001	0.07	0.005	0.11	0.004	0.03	0.0002	0.06	0.132	31
1:100	0.03	0.02	0.01	0.1	<0.001	<0.05	0.004	0.12	0.003	0.02	0.0001	0.05	0.036	8
VENIR														
1:20	1.1	8.7	16.1	1.3	0.2	14.7	1.2	44.2	5.1	1.0	0.017	0.83	1.89	97
1:200	<0.02	0.02	<0.002	<0.002	<0.001	<0.05	0.002	0.12	0.01	0.003	0.00005	0.05	0.041	2
1:100	<0.02	0.01	<0.002	<0.002	<0.001	<0.05	0.001	0.08	0.006	0.003	0.00004	0.03	0.013	1
YUKON														
1:20	1.1	6.2	12.8	1.5	0.1	106.0	2.3	23.1	0.8	1.6	0.01	0.04	3.111	91
1:200	<0.02	0.04	0.1	0.14	<0.001	0.42	0.12	0.24	0.007	0.02	0.00009	0.05	0.206	7
1:100	<0.02	0.02	0.1	0.1	<0.001	0.3	0.007	0.12	0.005	0.007	0.00003	0.03	0.069	2
SUNDAY No. 2														
1:20	1.2	0.9	8.0	1.0	0.2	17.3	1.1	15.8	0.38	5.2	0.036	0.50	1.032	89
1:200	<0.02	0.01	0.02	0.4	<0.001	<0.05	0.002	0.05	0.002	0.02	0.0001	0.05	0.111	10
1:100	<0.02	0.004	<0.002	0.1	<0.001	<0.05	0.002	0.02	0.001	0.01	0.0001	0.01	0.015	1

Leachate pH values after each of three leaches
[ratios are solid:liquid]

	MAYDAY	VENIR	YUKON	SUNDAY No.2
First 1:20	3.14	2.58	2.80	2.67
Second 1:200	3.93	3.82	3.73	3.81
Third 1:100	4.07	4.12	3.91	3.98

Leachate pH after the four samples, already leached three times, were pulverized for 5 minutes in a tungsten carbide ball mill using tungsten carbide balls and then leached with the pH 5.00 deionized water for 24 hours

1:100	3.82	3.89	3.81	4.03
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PASSIVE LEACHING WITH LARGER LEACHATE VOLUMES

These experiments were done to simulate metal mobility and acid generation during spring freezing-thawing and associated snowmelt runoff. Diurnal thawing and runoff will result in exposure of relatively thin (a few to several cm) surficial layers to very large natural leachate volumes.

Splits from the <0.090 mm solid fractions were used to obtain 0.5 g samples from each of the four untreated waste samples that were used in the prior leaching experiments. These 0.5 g samples were exposed to deionized water, side-by-side in solid:liquid ratios of 1:4,000, 1:8000, and 1:8,000 in three serial 24 h periods each. Leachate samples (0.45 µm filtered) of 60 ml each were obtained for cation analysis (HNO₃ acidified) and sulfate analysis, respectively, from each of the 12 leachates. Analytical data for the ICP/MS analyses and the sulfate analyses as well as the final pH of each leachate are given in Table 4.

After the end of the second 24 h leach of the Venir waste, an orange precipitate was visible on the upper surface of the leached waste. This is believed to be an amorphous Fe-oxide, or Fe-oxyhydroxide precipitated from the leachate. No detectable Fe was present in any of the leachates with a pH higher than 4.48, even though significant acid was generated in all of the leachates (table 4). The Fe detection limit is < 0.2 µg L⁻¹.

Table 4. Concentrations of selected elements dissolved in each of three serial leachates for 0.5 g of <0.090 mm fractions from four waste piles determined by ICP/MS on acidified 0.45 µm-filtered samples. [Na <20, and K <30 micrograms per liter, leach ratios refer to solids:leachate]

leach ratio	Mg	Al	Si	Ca	Mn	Fe	Cu	Zn	Cd	Pb	SO ₄	final pH
-----micrograms per liter-----												
MAYDAY												
1:4000	2.4	<0.2	67	<50	0.5	<0.2	2.0	4.4	0.02	14.0	600	4.48
1:8000	0.8	<0.2	46	<50	0.1	<0.2	0.3	1.0	<0.01	2.4	100	4.80
1:8000	0.6	<0.2	47	<50	0.1	<0.2	0.2	0.9	<0.01	0.5	100	4.90
VENIR												
1:4000	38.5	37.4	43	<50	4.3	120.0	22.0	5.8	0.04	53.0	2800	4.05
1:8000	1.7	<0.2	36	<50	0.2	<0.2	1.2	<0.5	<0.01	4.7	300	4.60
1:8000	0.6	<0.2	<20	<50	0.1	<0.2	0.3	0.5	0.01	2.1	200	4.66
YUKON												
1:4000	22.3	21.1	52	268	7.7	23.0	3.1	8.1	0.04	2.8	2600	4.19
1:8000	1.8	<0.2	41	<50	0.5	<0.2	0.6	0.9	<0.01	0.9	400	4.55
1:8000	0.8	<0.2	87	<50	0.2	<0.2	0.2	0.8	<0.01	0.8	300	4.66
SUNDAY No. 2												
1:4000	4.6	9.0	24	71	5.0	14.0	2.1	28.0	0.14	31.0	1800	4.12
1:8000	1.0	<0.2	61	<50	0.3	<0.2	0.2	1.7	<0.10	3.8	300	4.67
1:8000	0.8	<0.2	34	<50	0.2	<0.2	0.1	2.1	<0.10	2.0	200	4.82

Table 5 summarizes the comparison of some parameters of the smaller volume leachates versus those of the larger volume leachates. For Fe the smaller volume leachates left the most dissolved Fe, except for the Venir leachate; the much higher pH values of the large volume leachates caused initially dissolved Fe to be precipitated as amorphous Fe-oxyhydroxide. For Cu, Zn, and Pb, the larger volume leachates produced twice as much, or more dissolved metals. In terms of acid generation, the large volume leachates produced 45-63 times more H⁺ than the smaller volume leachates. One can infer from these comparisons that the greatest detrimental impact on drainage waters from waste piles (natural leaching) probably occurs during spring runoff from snowmelt in environments of thick snowfall accumulations such as Silverton (Animas River headwaters) and Leadville (Arkansas River headwaters) Colorado, and the Boulder River headwaters in northern Jefferson County, Montana.

The data presented in Table 5 also demonstrate that the potential for metal mobility (solubility) and acid generation, on a short term (leaching) basis (e.g. 24-72 h) for old (40-100 yr) metal-mining related wastes is best determined using large leachate volumes (1:4000) rather than small leachate volumes. This applies for climatic conditions where snowfall accumulations are more than about 100-200 cm y⁻¹ and spring/summer thawing melts virtually all of the snow.

Table 5. Sum of selected metals dissolved in two sets of three passive 24 hour serial leachates of the four mine-related waste dumps. One set has a relatively low ratio of liquid to solid, the second has a relatively high ratio of liquid to solid. Relative amounts of acid generation are also given in terms of H⁺. The sum of dissolved metals is expressed in micrograms per gram of solid.

Ratios of solid to liquid in three serial leaches	Fe	Cu	Zn	Pb	pH of serial leachates	Moles of H ⁺ g ⁻¹ X 10 ⁻⁴
	-----micrograms gram ⁻¹ -----					
MAYDAY						
1:20; 1:200; 1:100	51	4	32	71	3.14, 3.93, 4.07	0.049
1:4000; 1:8000; 1:8000	<8	24	66	158	4.48, 4.80, 4.90	2.2
VENIR						
1:20; 1:200; 1:100	916	105	21	30	2.58, 3.82, 4.12	0.104
1:4000; 1:8000; 1:8000	960	200	54	533	4.05, 4.60, 4.66	6.2
YUKON						
1:20; 1:200, 1:100	522	18	37	14	2.80, 3.73, 3.91	0.093
1:4000; 1:8000; 1:8000	184	38	92	50	4.19, 4.55, 4.66	5.9
SUNDAY NO. 2						
1:20; 1:200; 1:100	328	8	110	21	2.67, 3.81, 3.98	0.095
1:4000; 1:8000; 1:8000	112	22	268	341	4.12, 4.67, 4.82	4.5

ACID-GENERATING CAPACITIES OF SOME Fe-DOMINANT SECONDARY SULFATES

Fe-rich hydrated sulfates originating from the oxidation of pyrite-rich metal-mining related wastes, or natural oxidation of pyrite-rich deposits may generate highly acidic conditions in many environments (Alpers and others, 1994). Four simple leaching experiments were done using natural copiapite [$\text{Fe}^{+2}\text{Fe}^{+3}(\text{SO}_4)_6(\text{OH})_2 \cdot 20\text{H}_2\text{O}$] and natural coquimbite [$\text{Fe}_2^{+3}(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$] from the Vulcan mine near Gunnison, Colorado, and ferricopiapite [$\text{Fe}^{+3}_5(\text{SO}_4)_6\text{O}(\text{OH}) \cdot 20\text{H}_2\text{O}$] obtained by evaporation of 2 L of laboratory leachate of the Sunday No. 2 waste, and a synthetic preparation of rhomboclase [$\text{H}^{+1}\text{Fe}^{+3}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$]. Each was identified by XRD. In order to simulate what may happen when a metal-mining related waste aggregating 100 grams, but only containing 0.2 g, or 0.2 weight percent of one of these four minerals, 0.2 grams of each of them was exposed to 2 L of deionized water of pH = 5.0. The results are given in Table 6 which shows that after 24 hours, large amounts of acid are generated, even though the ratio of hydrated Fe-sulfates to leachates is 1:10,000. Such small amounts of hydrated Fe-sulfates, in the range of 0.2 to even 0.5 weight percent in bulk (<2.0 mm) samples, will probably not be detected by conventional XRD analysis. The values given in Table 6 are those that were measured before precipitation of any visible Fe-oxyhydroxides.

Table 6. Minimum measured acid-generating capacity of four soluble hydrated Fe sulfates determined by exposing 0.2 g of each of them to 2 L of deionized water (pH= 5.0 \pm 0.3) for 24 h. [After about 24 h, precipitation of amorphous Fe-oxyhydroxides may occur and this will further reduce the pH of the leachates. e.g. for ferricopiapite the pH of the leachate was 3.30 at 24 h. After 48 h significant precipitation of highly visible orange colloidal or amorphous Fe-oxyhydroxides, the pH of the leachate was 3.10]

Mineral	Acid generation potential H^+ in millimoles g^{-1}
rhomboclase	0.114
coquimbite	0.069
copiapite	0.060
ferricopiapite	0.056

SIGNIFICANCE OF JAROSITE-MEMBER MINERALS OF THE ALUNITE GROUP IN ACID-GENERATING METAL-MINING RELATED WASTES

From our studies of the minerals present in more than 100 separate waste piles, it is apparent that the jarosite members of the alunite group (Fleischer, 1993, p. 187) seem to be most frequently associated with the wastes that generate the most acidity, and thereby the most mobile (dissolved) heavy metals ($Z > \text{Fe}$). These sulfates of the jarosite members include: argentojarosite, beaverite, hydronium jarosite, jarosite, natrojarosite, osarizawaite, and plumbojarosite. They have the general formula of $\text{AB}_3(\text{SO}_4)_2(\text{OH})_6$, where A = Ag, K, Na, H, Pb; and B = Al, Cu, Fe^{+3} , but many substitutions of other ions may occur (Scott, 1987). The jarosite members of the alunite group have Fe^{+3} in the B

site, rather than Al, which occupies the B site in alunite. The term jarosite, as used here, refers to any of the minerals of the jarosite family listed above which have the strongest XRD reflection (hkl = 113) at $29.0 \pm 0.2^\circ 2\theta$ using Cu X-radiation.

Jarosite is the dominant sulfate detected by XRD analysis of splits of 111 metal-mining related waste pile samples from the Animas River headwaters near Silverton, Colorado collected in 1997. Desborough and Fey (1997) reported jarosite, found by XRD analysis, to be the dominant sulfate in 15 of 19 metal-mining related waste piles in the headwaters of the Boulder River near Basin, Montana. Table 7 shows the relations of XRD detected jarosite in waste samples, and the final pH of 1:20 (waste:leachate) leachates of some mine wastes in Colorado and Montana. The significant differences in the mean pH of leachates of those samples with XRD detectable jarosite versus those without XRD detectable jarosite seems to indicate some association of the presence of jarosite with wastes that produce more acidic leachates.

Table 7. Relations of X-ray diffraction detected jarosite in metal-mining related wastes and the final pH of their leachates after exposure of 100 grams of waste to 2 L of deionized water for 24 hours.

111 Animas River headwater wastes near Silverton, Colorado	
70 samples with XRD detectable jarosite	41 samples without XRD detectable jarosite
Mean pH = 3.51	Mean pH = 4.72
pH range = 2.65-6.65	pH range = 2.83-7.77
19 Boulder River headwater wastes near Basin, Montana	
15 samples with XRD detectable jarosite	4 samples without XRD detectable jarosite
Mean pH = 3.69	Mean pH = 5.12
pH range = 2.75-5.93	pH range = 3.25-6.78

It is important to recognize that the association of jarosite minerals with acid-generating capacities of these wastes does not prove that these minerals are responsible for acid generation. Other more soluble iron sulfates, possibly present in these wastes, but not detectable by XRD studies, may be responsible for significant amounts of the acid generated in leachates. However, the jarosite-group minerals probably have different solubilities, and mineral grain size will also affect their solubilities. Bigham and others (1994, 1996) show that in low temperature oxidizing (weathering) conditions jarosite-group minerals form chiefly at a pH in the range of 2.0-3.6 in Fe-rich and sulfate-rich waters. Therefore the identification of jarosite in metal-mining related wastes is

important in identifying those wastes that may have significant adverse water-quality degradation. The presence of jarosites in metal-mining related wastes can only be verified by XRD or detailed electron microscopy because these jarosites are extremely fine grained, shown by Bigham and others (1990, fig. 1f and 1996, fig. 3c) to be less than 0.05 micrometers.

Presently, it is not clear whether or not jarosites in mine wastes that we have studied might contribute acidity or soluble metals to our water leachates. Baron and Palmer (1996) show that jarosite [$\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6$] is essentially insoluble. We conclude that the jarosite-group minerals present in our wastes are probably much less soluble than the hydrated Fe-rich sulfates that we infer are present in these wastes.

SUMMARY

We have been unable to identify the principal acid-generating mineral(s) or amorphous phase(s) present in the metal-mining related wastes studied here. We presume this is due to the fact that soluble Fe and/or Al sulfates generating acid are present in such low concentrations that our XRD methods did not detect these phases.

A single laboratory leach (24 h.) of weathered mine waste using deionized water, regardless of the ratio of solid waste: leachate in the range of 1:20 to 1:4000, probably will not reveal the total short-term acid-generating capacity and metal mobility that might be of concern for degradation of water quality for aquatic life.

Mineralogical and waste leaching studies of about 140 metal-mining related waste piles show that those wastes with XRD-detectable jarosite generally produce leachates with a lower pH than those wastes without XRD-detectable jarosite. This does not indicate jarosite contributes to acid generation, because it is virtually insoluble in deionized water.

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REFERENCES CITED

- Alpers, C.N., Blowes, D.W., Nordstrom, D.K., and Jambor, J.L., 1994, Secondary minerals and acid mine-water chemistry: *in* Short course handbook on environmental geochemistry of sulfide mine-wastes, Mineralogical Association of Canada, Waterloo, Ontario, May, 1994, pp. 247-270.
- Baron, D., and Palmer, C.D., 1996, Solubility of jarosite at 4-35°C; *Geochimica et Cosmochimica Acta*, v. 60, pp.185-195.
- Bigham, J.M., Schwertmann, U., Carlson, L., and Murad, E., 1990, A poorly crystallized oxyhydroxysulfate of iron formed by bacterial oxidation of Fe(II) in acid mine waters: *Geochimica et Cosmochimica Acta*, v. 54, pp. 2743-2758.
- Bigham, J.M., Carlson, L., and Murad, E., 1994, Schwertmannite, a new iron oxyhydroxy-sulphate from Pyhasalmi, Finland, and other localities: *Mineralogical Magazine*, v. 58, pp. 641-648.
- Bigham, J.M., Schwertmann, U., and Pfao, G., 1996, Influence of pH on mineral speciation in a bioreactor simulating acid mine drainage: *Applied Geochemistry*, v. 11, pp. 845-849.

- Desborough, G.A., and Fey, DL., 1997, Preliminary characterization of acid-generating potential and toxic metal solubility of some abandoned metal-mining related wastes in the Boulder River headwaters, northern Jefferson County, Montana: U.S. Geological Survey Open-File Report 97-478, 21 p.
- English, B.L., Desborough, G.A., and Raymond, W.H., 1987, A mechanical panning technique for separation of fine-grained gold and other heavy minerals: U. S. Geological Survey Open-File Report 87-364, 9 p.
- Fleischer, M., 1983, Glossary of mineral species: the Mineralogical Record, Inc., Tucson, Arizona, 202 p.
- Scott, K.M., 1987, Solid solution in, and classification of, gossan-derived members of the alunite-jarosite family, northwest Queensland, Australia: *American Mineralogist*, v. 72, pp.178-187.

Cations dissolved in each of three leaches of Mayday <0.090 mm fraction

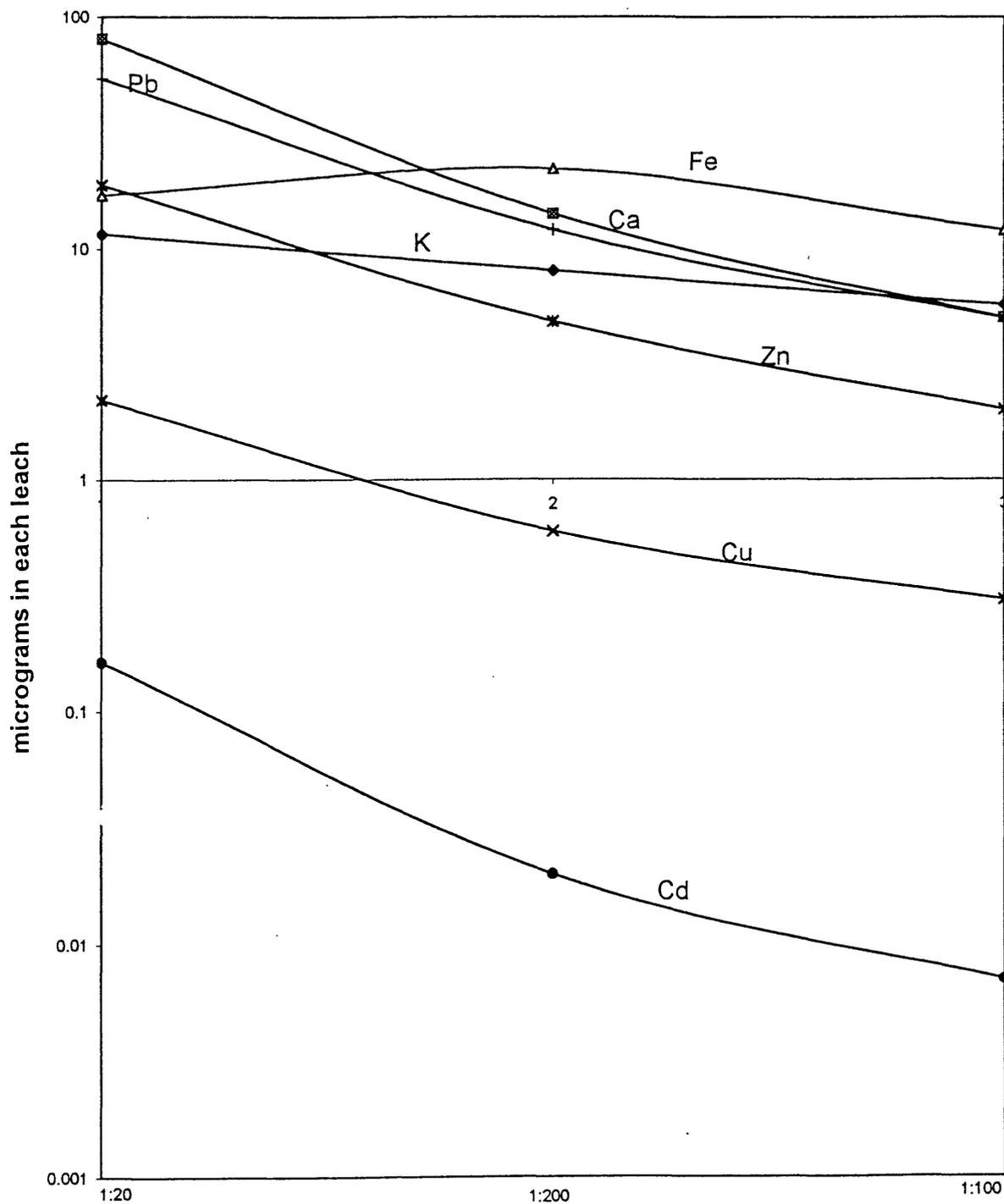


Figure 1. Cations dissolved in each of three leaches of Mayday <0.090 mm fraction.

Cations dissolved in each of three leaches of Venir <0.090 mm fraction

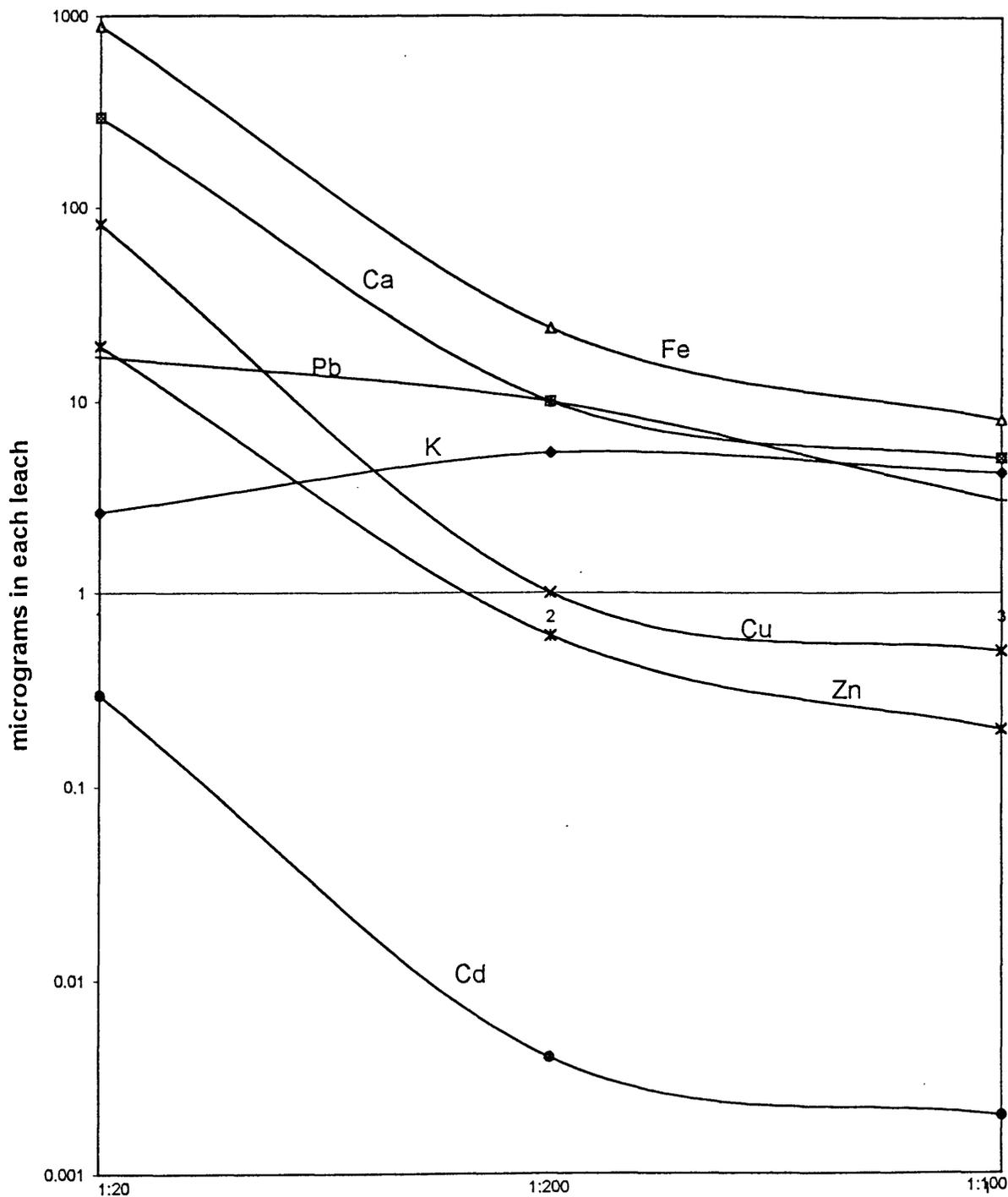


Figure 2. Cations dissolved in each of three leaches of Venir <0.090 mm fractions.

Cations dissolved in each of three leachates of Yukon <0.090 mm fraction

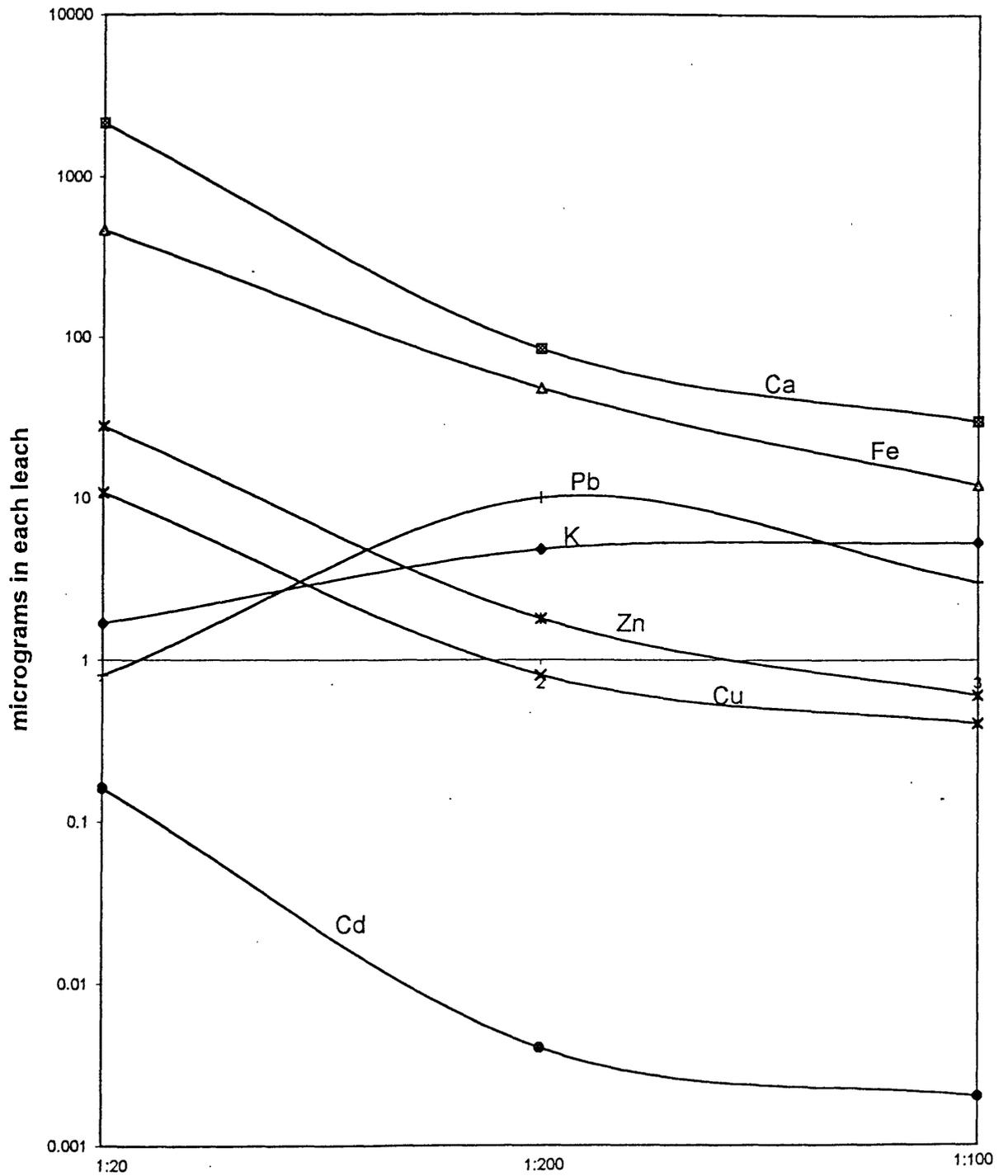


Figure 3. Cations dissolved in each of three leachates of Yukon <0.090 mm fractions.

Cations dissolved in each of three leachates of Sunday No. 2, <0.090 mm fraction

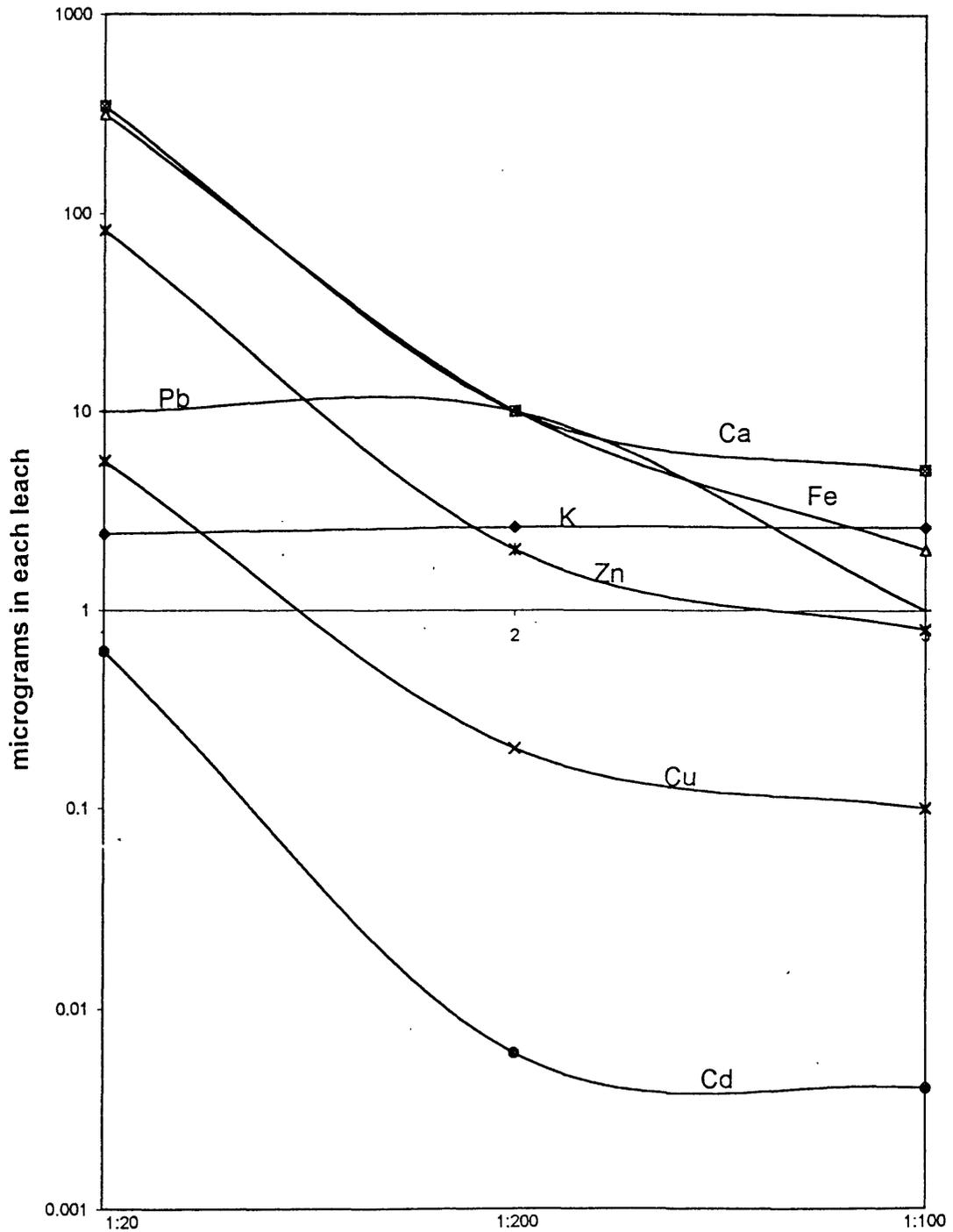


Figure 4. Cations dissolved in each of three leachates of Sunday no. 2, <0.090 mm fractions.