LEACHING STUDIES OF SCHWERTMANNITE-RICH PRECIPITATES FROM THE ANIMAS RIVER HEADWATERS, COLORADO AND BOULDER RIVER HEADWATERS, MONTANA

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ABSTRACT

X-ray diffraction (XRD) analysis and reflectance spectroscopy show that orange-colored precipitates that have accumulated in pH 3.5 to 4.0 headwaters of the Animas River in Colorado and the Boulder River in Montana may consist chiefly of schwertmannite [$Fe_{16}O_{16}(OH)_{9.6}(SO_4)_{3.2} \cdot 10H2O$]. This mineral is present in streams of coal-mining areas in Ohio but has not been previously reported to occur in the western U.S. These precipitates, which may be accompanied by other solid phases including silicates, goethite, and XRD undetectable amorphous material, were often called "ochre- or orange-colored colloids" by other investigators who noted they may contain significant concentrations of Cu, Cd, Pb, Zn, and As. The toxicity of these metals to aquatic organisms was recognized in prior studies as were the potentially harmful effects of colloidal Fe-hydroxides accumulating on the gills of salmonids (trout).

Passive serial leaching tests in the laboratory showed that as little as one gram of schwertmannite-rich precipitate generated enough acid to lower the pH of two liters of deionized water from 5 to 3.5 in an initial leach of 24 hours. Acid generation continued for eight successive leaches and was accompanied by the release of metals and sulfate into solution. Comparable results were obtained when the same amount of precipitate was serially leached with 3- and 4-liter quantities of water. The results indicate that 43 to 48 percent of schwertmannite was removed from the precipitates by total water volumes of 18, 27, and 36 liters in the three sets of leaches. Field test along 3.5 km of Cement Creek in the Animas River basin in October of 1998, a time of low flow, indicate the schwertmannite-rich precipitates accumulated at a rate equivalent to 370 kg day^{-1} of Fe. The results of this study infer that acid formation during subsequent leaching of the accumulated precipitates during spring and summer snow-melt runoff may pose another problem to the aqueous environment.

INTRODUCTION AND BACKGROUND

Prior to this study we found no published reports of schwertmannite in the Rocky Mountain region of the western U.S. However, J. M. Bigham (Pers. Comm., 1999) identified schwertmannite in samples from St. Kevin Gulch, near Leadville, Colorado. Runnells and Rampe (1989), Ranville and others (1989), Kimball and others (1995), and Church and others (1997) described "ochre-colored colloids" in suspension and as "precipitates" coating rocks in both the Arkansas River and Animas River headwaters of Colorado but the phase was not identified. These investigators have referred to the orange precipitates as "hydrous iron-oxide colloids", although some may be schwertmannite because the pH of some of the drainages is favorable for schwertmannite precipitation. High magnification (>50,000 X) transmission electron microscopy is necessary to identify the morphology of schwertmannite crystals (Bigham and others, 1990, 1994). Schwertmannite also has a unique spectral reflectance signature. In the original description of schwertmannite, the empirical formula was given as $Fe_{16}O_{16}(OH)_{9.6}(SO_4)_{3.2}.10H_2O$ (Bigham and others, 1994). In later reports, Bigham, Schwertmann, and Pfab (1996a) used $Fe_8O_8(OH)_6SO_4$ and Bigham and others (1996b) used $Fe_8O_8(OH)_{5.5}(SO_4)_{1.25}$. The results of this study support a formula with an 8:1.25 molar ratio of Fe:SO_4.

A major reason for our interest in schwertmannite-rich material is that metals such as Cd, Cu, Pb, Zn, and As may be sorbed to this phase and may be released during desporption in concentrations that are toxic to aquatic organisms (Lee, 1975; Jenne, 1977; Morel and Gschwend, 1987; Stumm and Morgan, 1996). A second reason for the present report is our recognition that schwertmannite-rich material causes a significant drop in pH by reaction with deionized water because of dissolution of schwertmannite. This acid generation will enhance solubility of toxic metals temporarily sequestered in both the suspended and precipitated Fe-rich solids in the stream bed. Significant acid generation from natural schwertmannite-rich material in a stream bed has not been previously reported. However, Bigham and others (1996b) measured significant acid generation in long-term exposure of synthetic schwertmannite to distilled water (initial pH = 3.9) that appeared to equilibrate in about 1,000 days, and traces of goethite were detected as a decomposition product after 65 days. In that experiment, there was a nonstoichiometric release of Fe and SO_4, and the molar ratio of $H^+:SO_4^{-2}$ was 2:1. The following was given by Bigham and others (1996b, p. 2114) for the hydrolysis of schwertmannite:

$$Fe_8O_8(OH)_{5.5}(SO_4)_{1.25(s)} + 2.5\ H_2O_{(l)} \Rightarrow 8\ FeOOH_{(s)} + 2.5\ H^+_{(aq)} + 1.25\ SO_4^{2-}{}_{(aq)}.$$

They concluded that "a complete description of aqueous solubility relationships for schwertmannite would presumably require a combination of solubility calculations and surface complexation modeling" (Bigham and others, 1996b).

The selection of the stream reaches and sampled sites studied (fig. 1) was based on prior investigations which showed that very high concentrations of iron and associated potentially toxic metals occur in both Cement Creek and Mineral Creek in the Animas River headwaters, and that colloidal Fe may be a dominant contributor to water quality degradation downstream (Owen, 1997; Church and others, 1997). Selection of the two sampled sites in the Boulder River headwaters was partly based on the fact that Nimick and Cleasby (1998) measured elevated toxic metals in both Uncle Sam Gulch and Jack Creek (which is downstream from the large Bullion mine waste piles and associated acidic drainage water from an adit).

CURRENT STUDY

Schwertmannite-rich material has been identified in acidic drainage water in Colorado and Montana by XRD, spectral reflectance analysis, and leaching experiments. Table 1 gives the locations of samples, pH of water, other minerals detected in the coatings, date collected, and pH of 1:4,000 (solid:water) leachates plus the concentrations of some trace metals. The Colorado samples are from sites 2,926 m (9,600 ft.) to 3,170 m (10,400 ft.) above mean sea level; those from Montana are from sites 2,134 m (7,000 ft.) to 2,243 m (7,360 ft.) above mean sea level. National Atmospheric Deposition data for the two nearest monitoring sites for the Colorado study area and the Montana study area are given in Appendix I. All of these samples are from stream beds except A98D17 which is from a mine adit drainage. The stream samples occur in two similar environments; one is downstream from the mixing of higher pH stream water which is met by lower pH Fe-bog water, as in Cement Creek (fig. 1), and the other is where higher pH stream water mixing with lower pH mine waste water runoff, or mine adit drainage water, for the two Montana occurrences. Except for the 30-day samples, all were collected from rocks or boulders by scraping off the orange precipitate with a wooden "tongue depressor" and placing the sample in a sealed plastic container which was refrigerated until air drying in the laboratory. The 30 day precipitates were collected on three or four 1.5 X 4.0 X 30 cm wooden stakes at each of three sites along Cement Creek. The stakes were submerged (horizontally) downstream from Fe bogs with low pH water that emerge near stream level near Prospect Gulch. The precipitates were allowed to air dry in the laboratory before removal from the stakes. The thickness of the coatings ranged from about 2-7mm. Comparable thicknesses of schwertmannite were observed on the boulders. All samples were sieved (stainless steel) to remove pine needles, other leaves, and plant stems before weighing. Based upon the masses of schwertmannite on the measured areas of the wooden stakes placed at three sites (A98D16, A98D12, and A98D14, fig 1.) for 30 days, we can estimate that Fe precipitation was about 370 kg d^{-1} in the 3.5 km stream reach studied. The pH of waters from which schwertmannite-rich material was collected ranged from 3.08 to 4.25 (table 1), which is within the pH range of 2.8 to 4.5 that Bigham and others (1996b) have shown is most favorable for schwertmannite-dominant precipitates.

At three sites sampled, schwertmannite-rich material collected in August, 1997 had no XRD-detectable goethite; for material collected in early September, 1998 from the same sites, all contained goethite, in addition to schwertmannite.

The amounts of Cu, Zn, As, and Pb sorbed in the schwertmannite-rich material from Cement Creek varies significantly, even for samples collected from the same three sample sites (table 1).

Table 1. Locations of schwertmannite-rich orange deposits in Colorado and Montana with pH of stream water, other minerals, date collected, and concentrations of Cu, Zn, As, and Pb in schwertmannite-rich material. [XRD = X-ray diffraction, n.d. = not determined, * = mean of three measurements, ## = Arsenic greater that 1 weight percent]

Number	Long.	Lat.	Other minerals present (XRD)	pH of water	coll. date	pH of 1:4,000 leachate	Trace elements			
							Cu	Zn	As	Pb
							parts per million			
Animas River headwaters, Colorado										
Cement Creek drainage										
A97D12	107°40’34”	37°50’55”	none	n.d.	8/28/97	3.91	n.d.	n.d.	n.d.	n.d.
A98D12			goethite	4.22	9/01/98	3.65	40	<40	<50	470
A98D12-30 days			goethite	n.d.	10/03/98	4.14	45	140	<50	450
A97D14	107°40”34”	37°50’08”	none	n.d.	8/28/97	3.87	n.d.	n.d.	n.d.	n.d.
A98D14			goethite	4.25	9/02/98	3.66	100	140	<50	550
A98D14-30 days			goethite	n.d.	10/03/98	4.16	45	180	<50	440
A97D15	107°40’30”	37°51’50”	none	n.d.	8/28/97	3.98	190	70	<50	350
A97D16	107°40’30”	37°52’06”	none	n.d.	8/28/97	3.66*	65	100	<50	330
A98D16			goethite	3.98	9/02/98	3.42	80	<40	<50	250
A98D16-30 days			goethite	n.d.	10/03/98	4.00	45	130	<50	350
A98D17	107°40’12”	37°52’44”	goethite	3.36	9/01/98	3.54	65	65	<50	140
Mineral Creek										
A97D13	107°43’23”	37°52’35”	none	n.d.	8/28/97	3.98	620	460	6,000	820
Boulder River headwaters, Montana										
Bullion mine drainage, Basin Creek drainage										
D98B37	112°17’42”	46°21’26”	sericite & quartz	3.58	9/22/98	3.95	n.d.	n.d.	##	n.d.
Near Crystal mine adit, Uncle Sam Gulch, Cataract Creek drainage										
D98B38	112°15’35”	46°20’52”	none	3.08	9/22/98	3.85	n.d.	n.d.	##	n.d.

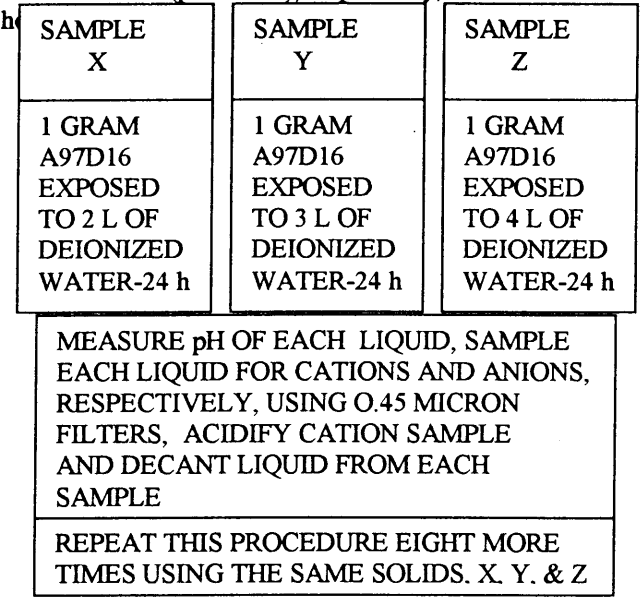
Table 2 shows the concentrations of several elements and sulfate in water and pH at four sites sampled in Cement Creek. The pH of water at site A98D18 is elevated due to upstream liming treatment of drainage water by Sunnyside Gold Corporation to remove metals by precipitation. Figure 2 shows the relations of the concentrations of these elements with respect to the Fe bog between sites 18 and 16. Data in Table 2 show that Al and Fe concentrations are four or five times higher at site A98D16 which is about 1.3 km downstream from the Fe bog (Fig. 2). Zn is only enhanced about 20 percent but Pb is increased by about 3.5 times and Cu is increased about 2.4 times.

Table 2. Concentrations of cations and sulfate in water samples, and pH of water at four sites along Cement Creek collected at the time the A98D-series schwertmannite-rich samples were obtained. [Water samples were 0.45 µm filtered and acidified at the time of collection. Cation analysis by ICP/MS ACTLABS, 15485 W. 44th Ave. Golden CO 80403. Sulfate analysis by Huffman Laboratories, Inc. 4630 Indiana St. Golden, CO 80403]

Sample	Na	Mg	Al	K	Ca	Mn	Fe	Cu	Zn	Cd	Pb	SO_4	pH
	micrograms L^{-1}											mg L^{-1}	
A98D18	2020	4500	840	640	149000	1280	2330	8.8	400	2	3.4	380	5.51
A98D16	2060	5040	4110	1100	142500	1320	9360	21	500	2	12	450	3.98
A98D12	2150	4730	3410	970	137300	1390	3480	26	470	2	13	420	4.22
A98D14	2190	4760	3400	1670	135500	1400	2490	29	480	2	13	430	4.25

DEIONIZED WATER LEACHATES OF A SCHWERTMANNITE-RICH SAMPLE FROM CEMENT CREEK NEAR SILVERTON, COLORADO

Three one-gram splits from air-dried A97D16 solids (table 1) were each exposed to 2, 3, and 4 L of deionized water (pH = 5.00), respectively, in nine serial leaches, at rest, side-by-side, for 24 h each as sh



Appendix II lists the concentrations of ten cations, sulfate, final pH, and exposure time for all 27 leachates. Dissolved Fe was detected in only four of the 27 leachates and amounted to a total of 43-62 µg g^{-1} of the samples or 0.004 to 0.006 weight percent of the original samples. Detection limits for Fe were 0.2 µg L^{-1}. Between 0.5-10.3 mg L^{-1} of sulfate was found in all 27 leachates. Concentrations of H^+ and sulfate in solution show a linear relationship ($R^2 = 0.98$) for the leachates (figure 3, Appendix III). The sums of the mmol ratios of $H^+:SO_4^{-2}$ for each of the three sets of serial leaches are 3.70:1, 3.92:1, and 4.09:1, averaging 3.90:1 which is more than twice the ratio obtained by Bigham and others (1996b). They found a ratio of 1.81:1 after 1739 days. The reason for this difference in these ratios is probably due to the fact that the leaching done here was a very short term compared with that of Bigham and others (1996b) and equilibrium was not reached in these short term leaches. In addition, adsorption of sulfate onto the precipitated solid Fe phases cannot be quantified. The sum of all dissolved cations in all of the nine serial leachates is less than one mg. The sum of H^+ for each of the nine serial leaches of the three samples ranges from 1.938-2.248 millimoles g^{-1} of solid.

The chemical compositions of the untreated and leached samples are given in Table 3.

The chemical data for the three untreated samples show Fe and S are the major elements and that molar Fe:S is 6.3-6.5 which is essentially identical to the ratio (6.4) given by Bigham and others (1996b) for schwertmannite. The concentrations of sorbed Cu, Zn, and Pb are noteworthy in terms of their potential toxicity to aquatic life, if released to the water. For the sample splits leached nine times, S has been reduced in concentration and Fe has been enhanced. This can mostly be attributed to the loss of sulfate in the dissolution of schwertmannite and the retention of Fe as precipitates of XRD-amorphous ferric oxides. XRD analysis shows that schwertmannite is a major phase in the three splits leached nine times (table 2), even though almost half of the schwertmannite was removed (dissolved), based on the dissolved sulfate in each of the leachates. The leached schwertmannite-rich samples have Fe:S in the range of 9.9-10.8 (table 3) but these values may be too high, if sulfate was adsorbed on resulting amorphous Fe oxides or remaining schwertmannite as was observed by Rose and Ghazi (1997). Small losses in Na, Al, and Ca observed for the leached samples are not considered significant.

Table 3. Chemical compositions of three untreated A97D16 schwertmannite-rich samples and three splits - X, Y, and Z-each leached nine times for 24 h. ICP/AES analysis except for total sulfur analyzed by Huffman Laboratories, Inc. 4630 Indiana Street, Golden, Co 80403. [n.d. = not determined ;Ag, Be, Cd, Co, Cr, Eu, La, Li, Mo, Ni, Y, and Yb are < 5 parts per million; As, Au, Bi, Ce, Ga, Ho, Nb, Nd, Sn, and Th are <20 parts per million.]

	Untreated Samples			Splits Leached Nine Times		
Element	A97D16R	A97D16B	A97D16N	A97D16X	A97D16Y	A97D16Z
	weight percent					
Na	0.06	0.1	0.08	0.03	0.03	0.03
Mg	0.1	0.2	0.07	0.26	0.2	0.2
Al	1.2	1.6	0.8	0.96	0.78	0.79
P	0.1	0.1	0.08	0.09	0.09	0.08
S	3.98	3.68	4.11	2.71	2.58	2.54
K	0.32	0.52	0.2	0.26	0.2	0.2
Ca	0.09	0.1	0.06	<0.01	<0.01	<0.01
Ti	0.07	0.09	0.04	0.05	0.05	0.05
Fe	44	42	46	47	48	48
Organic Carbon	1.1	0.9	n.d.	n.d.	n.d.	n.d.
	parts per million					
Ba	830	850	800	840	870	880
Cu	72	64	65	100	58	56
Mn	140	220	71	68	46	44
Pb	350	330	300	270	280	280
Sr	28	50	10	20	5	6
V	75	80	54	59	56	56
Zn	94	150	54	96	53	44
Molar Fe:S	6.3	6.5	6.4	9.9	10.6	10.8

Table 4 shows the total amounts of Fe, Cu, Zn, Pb, and sulfate in all of the nine leachates for each split from sample A97D16. Although dissolved Fe was detected in only the first of the nine leachates of each split (with one exception), Cu, Zn, and Pb were present in all 27 leachates (Appendix II). These data demonstrate the leachability or mobility of Cu, Zn, and Pb by initial pH 5 water, even after multiple exposures to large volumes of water. The amounts of Pb in each of the first leachates of each sample ranged from 5.1-10.8 $\mu g\ L^{-1}$ which exceeds the Class 1 Aquatic Life standard (which is 4 $\mu g\ L^{-1}$ for alkalinity values of 0-100 $mg\ L^{-1}$). Trace metal release is clearly important to the ultimate fate of sorbed toxic metals associated with schwertmannite-rich and amorphous ferric oxide precipitates which may release sorbed metals when exposed to unsaturated rainfall or snowmelt runoff, or if pH of water is raised by remediation.

Table 4. Sum of total mass of dissolved Fe, Cu, Zn, Pb, and sulfate in nine serial leachates of one gram of schwertmannite-rich material. [ICP/MS analysis of cations by ACTLABS, 15485 W. 44th Ave., Goldlen, CO 80403 and sulfate analysis by Huffmann Laboratories, Inc. 4630 Indiana Street, Golden, CO 80403.]

Sample	Fe	Cu	Zn	Pb	SO_4	Leachate
	--------------micrograms--------------				milligrams	volume, L
A97D16X	62.4	11.5	25.7	44.5	50.8	18
A97D16Y	48	13.3	45.7	43.6	51.0	27
A97D16Z	43	13.2	46.9	40.1	56.4	36

The serial leaching experiments were done to simulate the influence of relatively pure water of pH 5.0 (representative of rainfall or snowmelt runoff), on schwertmannite-rich and ferric oxide precipitates. It is important to note that these precipitates accumulate significantly at low-flow conditions of late August through October in the Animas and Boulder River headwaters. It is significant that these precipitates generate large amounts of acid in 24 h when exposed to large volumes of unsaturated water of pH of about 5.

Nimmo and others (1998, p. 917), in a study of the New World mining district (upstream from Yellowstone National Park), observed that anoxia was principally responsible for daphnid and fathead minnow mortality in 24 h for stream waters that precipitated Fe-rich phases. Dissolved oxygen concentrations were reduced by half in two h due to high chemical oxygen demand of the Fe-oxide precipitates. The study of Nimmo and others (1998) also implicated Cu as the principal element that is detrimental to trout viability and they state that "It is hypothesized that the availability of copper and metals is closely linked to fine sedimentary clays or colloids and to floodplain storage of tailings, which are mobilized, transported and deposited downstream by high flows occurring principally in the spring." They also observed that copper at sites upstream of the park boundary ranged from 7 to 11 $\mu g\ L^{-1}$ in the spring of 1995 and from 3 to 9 $\mu g\ L^{-1}$ in the fall of 1995.

Table 3 of this report shows that leaching of schwertmannite-rich samples from Cement Creek of one gram each, which were exposed to 18,000, 27,000, and 36,000 ml of deionized water released 11.5-13.3 μg of Cu in nine serial leaches. Appendix II shows that the individual leaches produced Cu concentrations well below the Class 1 Aquatic Life Standards. We do not know if this might simulate spring runoff conditions, but it must be considered in light of the studies of Nimmo and others (1998).

AMORPHOUS ORANGE PRECIPITATES
FORMED IN LESS ACIDIC WATER

Two samples of Fe-rich (> 30 wt. %) X-ray diffraction-amorphous orange precipitates obtained from the Cement Creek drainage (Animas River headwaters) in the fall of 1998 had high concentrations of sorbed Cu, Zn, and Pb. Table 5 and Figure 1 shows the locations, water pH, and concentrations of Cu, Zn, and Pb in these air-dried precipitates. Although the water cannot be considered harmful with respect to acidity, the high concentrations of Cu, Zn, and Pb in the precipitates are a potential threat to downstream aquatic life if they are desorbed during spring runoff.

Table 5. Locations, water pH, collection date, and concentrations of Cu, Zn, and Pb in two amorphous Fe-rich orange precipitates in the Cement Creek drainage near Silverton, Colorado of the Animas River headwaters.

Sample	Long.	Lat.	pH of water	Coll. date	Trace Elements			
					Cu	Zn	As	Pb
					parts per million			
A98D18 Just above Fe bog in Cement Creek	107° 39’ 44’	37° 53’ 15’	5.51	9/02/98	500	540	<50	930
A98D5 Anglo Saxon mine adit drain	107° 40’ 35’	37° 51’ 34’	6.45	9/02/98	220	3,300	<50	300

In order to evaluate the potential mobility of some of the elements in the two Fe-rich precipitates listed in Table 5, they were exposed to a pH of 3.66 leachate of schwertmannite A97D16 (obtained by exposure of 1 g of A97D16 to 4 L deionized water for 24 h), here called the primary leachate. Two ratios of solid:primary leachate were used, one was 1:1,000 and the other was 1:4,000; they were leached without agitation. Analysis of the primary leachate and the concentrations of selected elements in subsequent leachates of the two Fe-rich orange precipitate samples are shown in Table 6. These results can be inferred to indicate that when the XRD-amorphous Fe-rich precipitates are flushed into the schwertmannite-rich environments of Cement Creek during spring runoff, significant amounts of metals such as Al, Cu, Cd and Zn may be desorbed from them. We do not claim that these experiments simulate natural conditions, in the absence of field tests. However, these results indicate potential toxic metal mobility for Fe-rich precipitates when they are exposed to acid-generating schwertmannite-rich solids in Cement Creek during spring-summer runoff.

Table 6. Concentrations of selected elements in the primary schwertmannite leachate and the subsequent leachates of two Fe-rich orange precipitates. [0.45 μm filtered and acidified; ICP/MS analysis by ACTLABS, 15485 W. 44th Ave., Golden, CO 80403

Sample (solid:liquid leach ratio)	Al	Mn	Fe	Cu	Zn	Cd	Pb
	----------------------micrograms L^{-1}						--------------------------------
Primary leachate from schwertmannite	41	12	49	2.6	8.9	0.08	13.7
A98D5							
(1:1000)	137	184	5	6.6	646	0.68	>0.1
(1:4000)	176	83	22	14.9	279	0.62	0.9
A98D18							
(1:1000)	1000	75	68	73	192	0.65	1.5
(1:4000)	600	29	72	65	63	0.30	7.2

SUMMARY

Schwertmannite-rich precipitates are reservoirs for acid-generating potential and toxic-metal release to aquatic environments when exposed to unsaturated water of pH 5 or higher.

Precipitation of schwertmannite, formation of amorphous colloidal Fe oxide, goethite, or ferrihydrite, result in chemical depletion of dissolved oxygen that might inhibit life sustainability in aquatic environments.

Schwertmannite-rich and amorphous colloidal Fe oxides formed at low-flow stream conditions may be mobilized at high-flow stream conditions and pollute initially unsaturated snow-melt runoff by generating acidic conditions and cause mobility of sorbed toxic metals such as Cu, Zn, and Pb in downstream environments.

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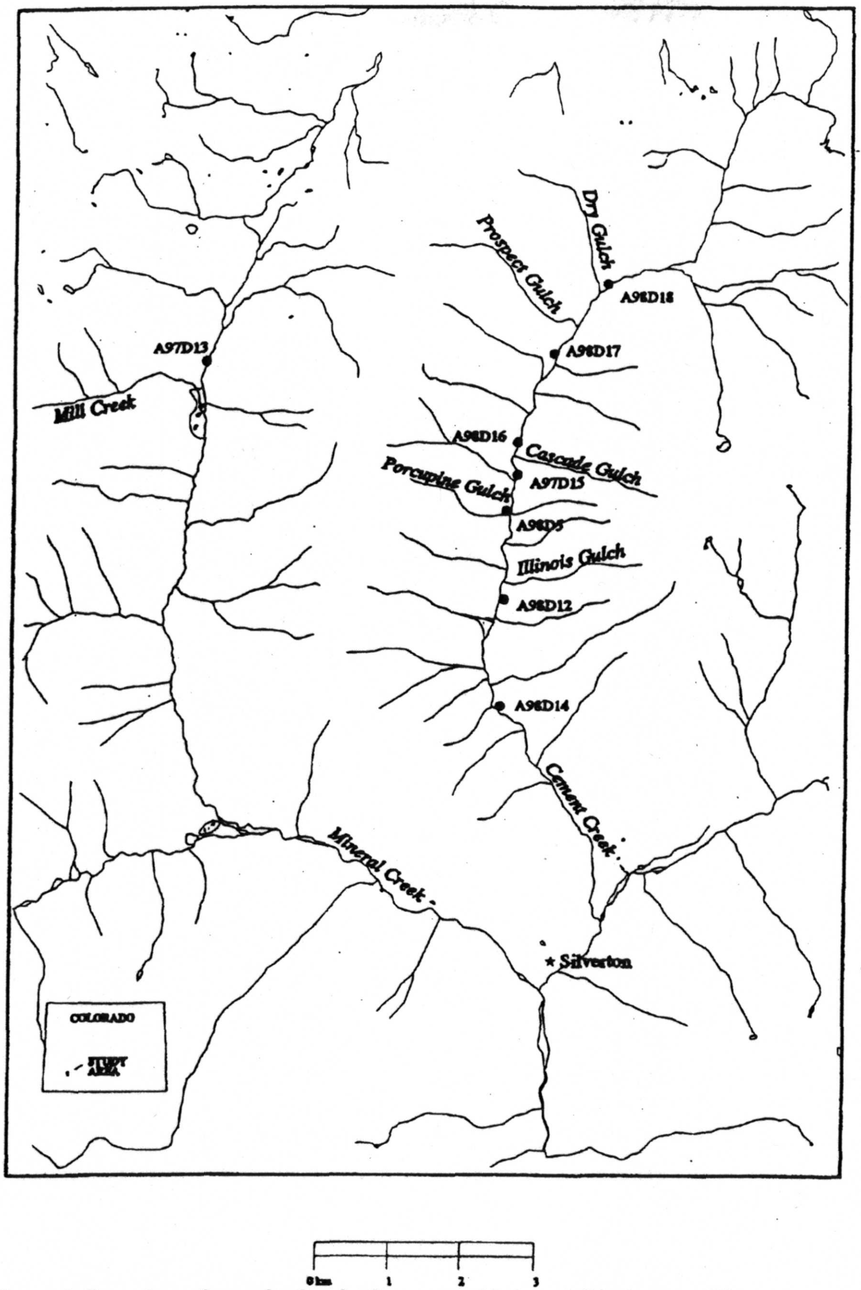

Figure 1. Location of sample sites in Cement and Mineral Creeks near Silverton, Colorado. The Fe bog extends from A98D17 , upstream to the junction of Prospect Gulch with Cement Creek.

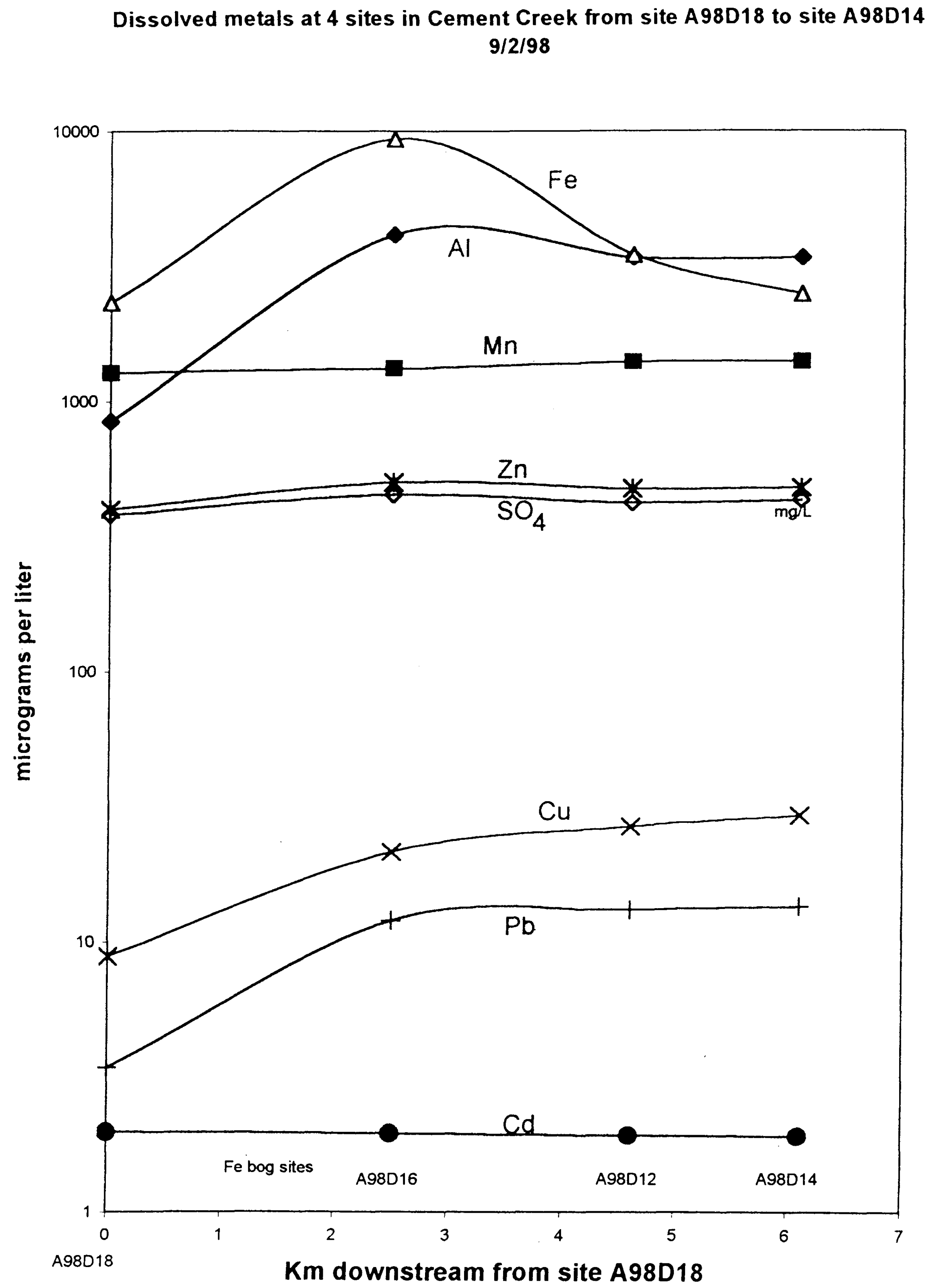

Figure 2. Concentrations of some metals and sulfate in water at four sites along Cement Creek.

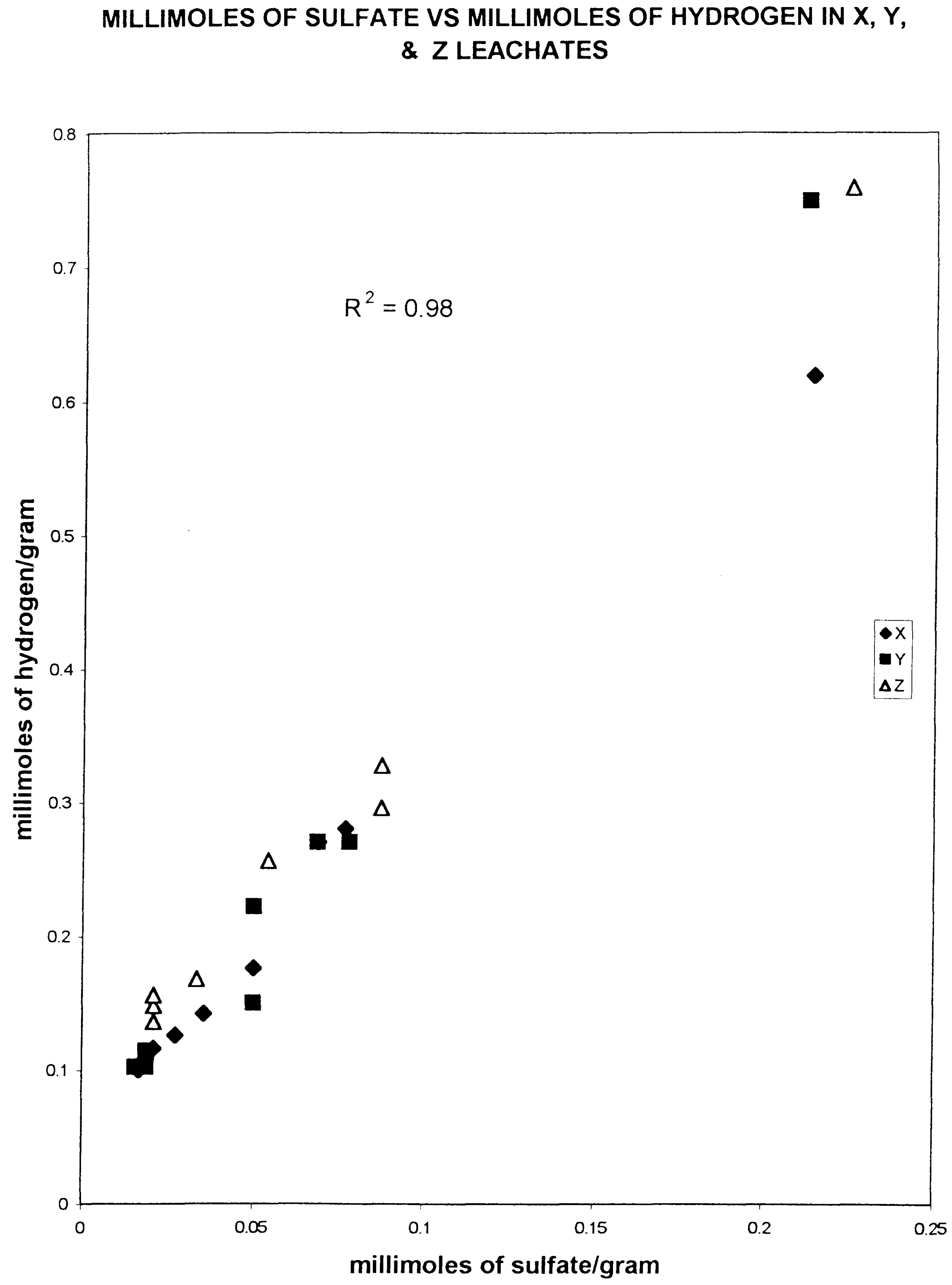

Figure 3. Relations of dissolved sulfate and H^+ in leachates of three schwertmannite-rich samples from site A98D16 along Cement Creek.

Appendix I. National Atmospheric Deposition Program (NADP) data for monitoring sites near the Colorado study area and the Montana study area for 1997. [from http://nadp.sws. uiuc. edu/97 maps. Html]

	NADP monitoring site for Cement and Mineral Creek Colorado study area is within 25 km of the CO96 (Molas Pass station)	NADP monitoring site for the two Montana sites is less than 20 km from the MT07 (Clancy station)
	1997	**1997**
annual precipitation:	79 cm	41 cm
mean pH:	4.9	5.1
mean SO_4 (mg/L):	0.5	0.4
mean Σ[Na+K+Mg+Ca] (mg/L):	0.21	0.196

Appendix II. Major and minor cations and sulfate is nine leachates of A97D16X, A97D16Y, and A97D16Z. [cations determined by ACTLABS, 11485 West I-70 Frontage Road North, Wheat Ridge, CO 80033; sulfate determined by Huffman Laboratories, Inc., 4730 Indiana Street, Golden, CO 80403]. Na is < 20 $\mu g\ L^{-1}$, K is <10 $\mu g\ L^{-1}$, Sr and Ba are < 3.0 μgL^{-1}, cations analyzed but which are not reported here were <0.6 μgL^{-1} for all 27 leachates.

Exposure	Mg	Al	Si	Ca	Mn	Fe	Cu	Zn	Cd	Pb	SO_4	final	Exposure
	- ---------micorgrams L^{-1}---------										mgL^{-1}	pH	time, hr.
Sample A97D16X-solid:liquid = 1:2000													
1	11.0	21.3	197	141	6.5	27.6	3.0	4.1	0.03	10.8	10.3	3.57	24
2	0.9	4.0	191	<50	0.4	<0.2	0.4	2.0	<0.01	3.4	3.3	3.89	24
3	<0.5	3.5	199	<50	0.2	<0.2	1.2	1.2	0.30	2.8	3.7	3.88	48
4	<0.5	1.5	164	<50	0.2	<0.2	0.3	1.3	0.02	1.8	2.4	4.00	24
5	0.5	<0.1	130	<50	0.1	<0.2	0.2	1.4	<0.01	1.0	1.7	4.12	24
6	2.0	<0.1	165	<50	0.1	3.6	0.3	1.1	<0.01	0.7	1.3	4.20	24
7	<0.5	<0.1	158	<50	0.05	<0.2	<0.1	0.8	<0.01	0.7	1.0	4.24	24
8	<0.5	<0.1	162	<50	0.07	<0.2	0.1	<0.5	<0.01	0.6	0.9	4.25	24
9	<0.5	<0.1	122	<50	0.12	<0.2	0.2	0.9	<0.01	0.5	0.8	4.28	24
Sample A97D16Y-solid:liquid = 1:3000													
1	7.0	13.6	174	90	4.2	16.0	2.0	2.4	0.01	7.6	6.8	3.66	24
2	1.0	1.6	128	<50	0.2	<0.2	0.3	<0.5	<0.01	1.7	2.2	4.00	24
3	<0.5	1.7	173	<50	0.1	<0.2	0.5	1.1	0.10	1.6	2.5	4.00	48
4	0.5	1.1	166	<50	0.1	<0.2	0.4	2.6	0.01	1.3	1.6	4.10	24
5	<0.5	1.1	170	<50	0.1	<0.2	0.2	1.6	0.05	0.6	1.6	4.27	24
6	<0.5	<0.1	151	<50	0.1	<0.2	0.1	4.6	<0.01	0.5	0.6	4.40	24
7	<0.5	<0.1	148	<50	0.06	<0.2	0.2	0.9	<0.01	0.4	0.6	4.42	24
8	<0.5	<0.1	176	<50	<0.05	<0.2	0.4	0.7	<0.01	0.4	0.6	4.38	24
9	<0.5	<0.1	195	<50	0.07	<0.2	0.3	1.3	<0.01	0.4	0.5	4.42	24
Sample A97D16Z-solid:liquid = 1:4000													
1	5.8	10.0	200	72	3.4	10.7	1.5	2.5	0.02	5.1	5.4	3.75	24
2	0.5	<0.1	170	<50	0.1	<0.2	0.2	0.9	0.01	1.3	2.1	4.09	24
3	<0.5	1.0	201	<50	0.1	<0.2	0.2	1.6	0.01	1.4	2.1	4.04	48
4	<0.5	<0.1	198	<50	<0.5	<0.2	0.2	1.5	0.02	0.8	1.3	4.19	24
5	<0.5	<0.1	167	<50	0.6	<0.2	0.4	1.1	<0.01	0.4	0.8	4.34	24
6	<0.5	<0.1	235	<50	0.6	<0.2	0.1	1.5	<0.01	0.3	0.5	4.48	24
7	<0.5	<0.1	196	<50	<0.5	<0.2	0.3	0.6	<0.01	0.3	0.5	4.48	24
8	<0.5	<0.1	203	<50	<0.5	<0.2	0.1	1.0	<0.01	0.3	0.5	4.46	24
9	<0.5	<0.1	212	<50	<0.5	<0.2	0.2	0.9	<0.01	<0.1	0.9	5.16	24

Appendix III. Concentrations of sulfate and hydrogen ion in leachates of X, Y, and Z on a per gram basis.

millimoles SO4/g	millimoles H+/g
X LEACHATES	
0.214	0.62
0.069	0.27
0.077	0.28
0.05	0.176
0.0354	0.142
0.0271	0.126
0.0208	0.116
0.0188	0.108
0.0167	0.1
Y LEACHATES	
0.2125	0.75
0.0687	0.27
0.0781	0.27
0.05	0.222
0.05	0.15
0.0188	0.108
0.0188	0.102
0.0188	0.114
0.0156	0.102
Z LEACHATES	
0.225	0.76
0.0875	0.296
0.0875	0.328
0.0542	0.256
0.0333	0.168
0.0208	0.148
0.0208	0.136
0.0208	0.156