

U. S. DEPARTMENT OF THE INTERIOR

U. S. GEOLOGICAL SURVEY

**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**

George A. Desborough¹ and David L. Fey¹

Open-File Report 97-478

This report is preliminary and has not been reviewed for conformity with U.S. Geological Survey editorial standards or with the North American Stratigraphic Code. Any use of trade, product, or firm names is for descriptive purposes only and does not imply endorsement by the U.S. Government.

¹Denver, Colorado

CONTENTS

	Page
Abstract.....	1
Introduction.....	1
General methods of study.....	2
Characteristics of mine wastes and their leachates.....	2
Major and minor minerals.....	2
Concentrations of selected elements in bulk wastes.....	6
Characteristics of waste leachates.....	7
Ranking of potential water quality degradation for mining-related wastes.....	9
Characteristics of fresh rocks and their acid-neutralizing capacities.....	11
Minerals originating from surficial sulfide oxidation in mining-related wastes.....	15
Summary.....	16
References cited.....	17

ILLUSTRATIONS

Figure 1. Location of mining-related waste piles in the Basin and Cataract Creek drainages, northern Jefferson County, Montana.....	18
Figure 2. Relations of the concentration of certain dissolved toxic metals in leachates to the pH of the leachate.....	19
Figure 3. Relations of dissolved Pb to the final pH of the waste leachates.....	20

TABLES

Table 1. Major and minor minerals in mine-related wastes in Basin and Cataract Creek drainages, northern Jefferson County, Montana.....	4
Table 2. High-density minerals in mine-related wastes in Basin and Cataract Creek drainages, northern Jefferson County, Montana.....	5
Table 3. Concentrations of certain metals in mine-related wastes in Basin and Cataract Creek drainages, northern Jefferson County, Montana.....	6
Table 4. Final pH of leachates and concentrations of certain metals in leachates from mine-related wastes in Basin and Cataract Creek drainages, northern Jefferson County, Montana.....	8

Table 5. Ranking of potential water-quality degradation of mining-related wastes in Basin and Cataract Creek drainages, northern Jefferson County, Montana.....10

Table 6. Concentrations of certain elements in fresh rocks of Basin and Cataract Creek drainages, northern Jefferson County, Montana.....11

Table 7. High-density minerals in fresh rocks in Basin and Cataract Creek drainages, northern Jefferson County, Montana.....12

Table 8. Acid-neutralizing potential of fresh crystalline rocks in the Basin and Cataract Creek drainages, northern Jefferson County, Montana.....13

Table 9. Acid-neutralizing potential of fresh crystalline rocks in the Basin and Cataract Creek drainages, northern Jefferson County, Montana.....15

ABSTRACT

Investigations of the physical and chemical characteristics of metal-mining-related wastes and fresh rocks in the Basin and Cataract Creek drainages of northern Jefferson County, Montana were done to evaluate potential water quality degradation. Basin and Cataract Creeks are part of the Boulder River watershed. Field and laboratory studies were conducted to determine what methodologies might be used effectively to measure the acid-generating capacities and associated dissolution of toxic metals in the mining-related wastes that might pollute drainage water. In addition, the acid-buffering capacities of the fresh rocks that are areally dominant, but host the Fe, Cu, Zn, Pb, and As sulfide veins that were explored and mined, were tested for their acid neutralizing capacities.

A method of ranking the potential acid generation and associated toxic-metal dissolution from mining wastes is given so that the immediate drainage water pollution caused by snowmelt and stormwater runoff from these wastes can be assessed. It is clear that the mineralogical characteristics of both the wastes and the fresh rocks is a dominant factor in the chemical composition of waters that evolve from the contact of precipitation as rain or snow with mining wastes and adjacent fresh rocks before the drainage water joins stream reaches that might be habitat that is chemically suitable for salmonoids (trout).

The recognition of small amounts of calcite in the fresh rocks of the Boulder batholith is probably one of the most important results of this study. However, this fact is consistent with the recent water quality studies which show that only one or two sites in the Basin and Cataract Creek drainages have water with pH of less than about 6.0. This is in spite of the fact that the present study of leaching the mine wastes shows that they may generate acidity as low as $\text{pH} = 2.75$. Preliminary study of the fresh batholith rocks in terms of their acid-neutralizing potential shows that they contain an average of about 3 weight percent of calcite, or about 60 pounds of calcite per ton of rock. Laboratory tests show that the calcite-bearing Boulder batholith rock in a rock:water ratio of 1:20 will raise acidic pH of 3.0 to above 6.5 in 24 hours. No significant amounts of acid-generating minerals such as pyrite were found in the fresh rock.

INTRODUCTION

Metal-mining related wastes in the Rocky Mountain region have been implicated in detrimental affects on water quality with regard to acid generation and toxic-metal solubility during snowmelt and stormwater runoff. This degradation of water quality is defined chiefly by the "Class 1 Aquatic Life Standards" that give the limits for certain concentrations of dissolved metals according to a defined water alkalinity (Montana Department of Health and Environmental Sciences, 1994).

Veins enriched in iron, copper, lead, zinc, and arsenic sulfides, as well as gold, and silver were explored and mined in the Basin and Cataract Creek drainages of the Boulder River headwaters over more than 70 years starting more than a century ago. During near-surface weathering, including biota activity, these sulfides were oxidized to soluble acid-generating sulfates containing Fe, Cu, Zn, Pb, and As. Most of the mining-related wastes on the surface are due to exploration, but some are mill tailings that are wastes left from the mechanical/chemical concentration of ore minerals.

The present study is an examination of the metal-mining related waste piles (exploration waste or tailings) that might contribute acid or dissolved metals to Basin and Cataract Creek drainage water

during snowmelt or stormwater runoff. Most of the metal-mining related wastes in the Basin and Cataract Creek drainages were identified and studied by the Montana Bureau of Mines and Geology (Metesh and others, 1994; Metesh and others, 1995; Marvin and others, 1996). Their extensive studies did physical and chemical investigations of numerous sites with mining-related wastes. They also observed degradation of biota activity such as vegetation kills as well as potential physical hazards.

Our study included surface sampling of mining wastes in order to assess potential water-quality degradation. To do this we sampled each of several waste piles, and each sample consisted of 30 or more composited subsamples collected from the surface of each waste pile. The composited subsamples were collected from the surface to a depth of about 50-70 mm; each subsample consists of about four to six 50-80 gram scoops of material taken from each of the 30 or more sample areas across all of the surface of each waste pile. The locations of these waste piles are shown on Figure 1. In addition, fresh or unaltered rocks were also collected to assess their chemistry, mineralogy, and potential acid-buffering capacity. Unaltered or fresh rocks are those that have been unaffected by surficial weathering and unaffected by sulfide mineralization, but are hosts to sulfide mineralized veins that were explored and mined in the area.

GENERAL METHODS OF STUDY

Waste samples ranged from 5-12 kg and were dried in the laboratory (40⁰C) before mechanical sizing to obtain a < 2 mm fraction which was split into two fractions using a Jones sample splitter. One fraction (split) was further split into a 200-250 g sample that was used for: 1.) bulk chemical analysis for selected elements, 2.) X-ray diffraction analysis to determine mineralogy, 3.) heavy mineral concentrates to identify high-density minerals, and 4.) static leaching tests using deionized water to determine acid-generating potential and the amounts of dissolved toxic metals in the leachates. Large samples (5-10 kg) of fresh rocks from the study area were returned to the laboratory and trimmed to remove surficial oxidation effects before crushing and sizing; fine fractions (< 0.090 mm) of fresh rock were exposed to acidic leachates to determine acid-neutralizing capacities. Samples of weathered hydrothermally altered samples were collected from a few localities to determine what sulfates, arsenates, and primary sulfides were present.

CHARACTERISTICS OF MINE WASTES AND THEIR LEACHATES

Major and Minor Minerals

Minerals were determined using X-ray diffraction diffractometer (Cu-radiation) techniques on 50 grams of the < 2 mm 250 g split pulverized in a Spex mill. Major and minor minerals for each sample are listed in Table 1. This method may not detect minerals present in small amounts of one to five percent. In addition, amorphous, or poorly crystallized minerals may also go undetected. Heavy-mineral concentrates were obtained by mechanical panning of a 30 gram scoop from each < 2 mm 250 gram fraction in order to identify high-density minerals present in the waste samples. These minerals were identified by X-ray diffraction, X-ray fluorescence, and optical microscopy and are listed in Table 2.

Both anglesite and jarosite are present in about 80 percent of the waste pile samples (table 1).

While anglesite is chemically simple (PbSO_4) jarosite is not. Studies of gossan-derived members of the alunite-jarosite family of minerals by Scott (1987) show that although the general formula is $\text{AB}_3(\text{XO}_4)_2(\text{OH})_6$, the large cation A may be Na, K, Ag, NH_4 , H_3O , Ca, Pb, Ba, Sr, or Ce, whereas the B sites may be occupied by Al^{3+} , Fe^{3+} , Cu^{2+} , or Zn^{2+} . The anion (XO_4) may be SO_4 , PO_4 , AsO_4 , CO_3 , SbO_4 , CrO_4 , or SiO_4 . In the present study, the X-ray diffraction pattern is that of the jarosite family, not alunite, and the major anion is SO_4 , with some AsO_4 substitution where arsenic is abundant. Although Alpers and others (1994, p 252) list the jarosite family as "less soluble sulfates" our laboratory studies of a natural pure natrojarosite [$\text{NaFe}_3^{+3}(\text{SO}_4)_2(\text{OH})_6$] show that one gram of <0.90 mm material in 40 ml of deionized water (pH = 6.0) reduces the pH to 3.5 in 15 minutes. Thus the fine-grained jarosites are highly soluble and generate significant acidity. The leachate data in Table 4 show that large amounts of iron were dissolved from samples B017, B018, and B012, and in addition these three leachates contained 119-315 mg/L of SO_4 ; thus we infer that jarosites were dissolved from these samples. Sample B012, that produced the lowest leachate pH (2.75), contained more Cu, Zn, Ca, and Na than any other. It is significant that the primary zinc mineral, sphalerite, was not present in the heavy mineral concentrates (table 2). Thus Zn probably occurs in a sulfate, perhaps jarosite. It is noteworthy that white botryoidal crusts of precipitate at the lower end of the largest waste pile at the Bullion mine was identified by X-ray diffraction as goslarite [$\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$] and is spatially associated (despoited on) with anglesite and jarosite.

Based on the relative abundance of anglesite (tables 1 and 2) and the concentrations of Pb in the leachates (table 4) it appears that the anglesite in these samples is soluble only when the leachate pH is lower than about 3.5. This is clearly illustrated in Figure 3 which is a plot of dissolved Pb versus pH of the waste leachates.

The presence of dolomite in the upper waste pile (MT007, table 1) at the Boulder Chief mine and the calcite in the waste of the Waldy mine (MT011, table 1) cause these waste leachates to be buffered above a pH of 6.5. These two leachates have two to four times more dissolved Ca (12 and 22 mg/L) than any others.

Table 1. Major and minor minerals in mine-related wastes in Basin and Cataract Creek drainages, northern Jefferson County, Montana. Minerals determined by X-ray diffraction. [tr. = trace, >> = much greater than, > = greater than]

Long.	Lat.	
Sample No.	-size(tons)	Minerals, listed in decreasing order of abundance

Basin Creek drainage

46.3561 D97B017-6,000 D97B018-7,000 D97B019-12,000 D97B002-500	112.2944	Bullion mine, waste dumps quartz, >> muscovite, jarosite, anglesite quartz, >> jarosite, anglesite, tr. muscovite quartz, >> anglesite, jarosite, tr. muscovite quartz, >> muscovite, jarosite, anglesite
D97B001-1,200 D97B003-3,600		Bullion mine, tailings quartz, >> muscovite, jarosite, > anglesite quartz, >> muscovite, jarosite, anglesite
46.3980 D97B004-5,000 D97B005-10,000	112.2944	Buckeye/Enterprise mines, waste dumps quartz, orthoclase, plagioclase, jarosite, kaolinite quartz, >> muscovite, jarosite, orthoclase, anglesite, tr. kaolinite
D97B006-16,000		Buckeye/Enterprise mines, tailings quartz, >> muscovite, anglesite
46.2955 D97B012-300	112.2952	Daily West mine, waste dump quartz, >> pyrite, jarosite, anglesite, tr. kaolinite

Cataract Creek drainage

46.3305 D97MT007-3,500 D97MT008-3,500	112.2094	Boulder Chief mine, waste dumps quartz, orthoclase, plagioclase, kaolinite, muscovite, dolomite (?) quartz, >> kaolinite, muscovite, jarosite, > anglesite
46.3228 D97MT009-4,000 duplicate	112.2364	Cracker mine, waste dump quartz, >> jarosite, muscovite, kaolinite, anglesite quartz, >> anglesite, jarosite, kaolinite
46.3500 D97B014-20,000 D97B015-10,000 D97B016-4,000	112.2606	Crystal mine, waste dump quartz, >> plagioclase, orthoclase, jarosite, tr. muscovite quartz, >> plagioclase, orthoclase, jarosite, tr. muscovite quartz, >> orthoclase, plagioclase, anglesite, tr. muscovite
46.3128 D97MT013-1,000	112.2400	Morning/Mare mines, waste dump quartz, >> orthoclase, anglesite, jarosite, tr. muscovite
46.3361 D97MT010-5,000	112.2444	Sirius mine, waste dump quartz, >> orthoclase, muscovite, anglesite, jarosite
46.3039 D97MT011-700	112.2175	Waldy mine, waste dump quartz, >> orthoclase, plagioclase, muscovite, kaolinite, calcite

Table 2. High-density minerals in mine-related wastes in Basin and Cataract Creek drainages, northern Jefferson County, Montana.

Long.	Lat.	
Sample No.		High-density minerals in heavy-mineral concentrates
Basin Creek drainage		
46.3561	112.2944	Bullion mine, waste dumps
D97B017		pyrite, anglesite, ilmenite
D97B018		pyrite, anglesite
D97B019		anglesite, zircon, pyrite
D97B002		zircon, amphibole, pyrite, chalcopyrite, native gold
Bullion mine, tailings		
D97B001		zircon, amphibole, native gold
D97B003		zircon, amphibole, magnetite, pyrite
46.3980	112.2944	Buckeye/Enterprise mines, waste dumps
D97B004		magnetite, brown Fe-oxide (?)
D97B005		pyrite, anglesite, zircon
Buckeye/Enterprise mines, tailings		
D97B006		anglesite, pyrite, native gold
46.2955	112.2952	Daily West mine, waste dump
D97B012		pyrite, anglesite
Cataract Creek drainage		
46.3305	112.2094	Boulder Chief mine, waste dumps
D97MT007		pyrite, apatite, zircon, barite
D97MT008		pyrite, anglesite
46.3228	112.2364	Cracker mine, waste dump
D97MT009		pyrite, anglesite, zircon, native gold
46.3500	112.2606	Crystal mine, waste dumps
D97B014		zircon, ilmenite, magnetite
D97B015		zircon, ilmenite, magnetite
D97B016		zircon, ilmenite, magnetite
46.3128	112.2400	Morning/Mare mines, waste dump
D97MT013		zircon, pyrite, trace anglesite
46.3361	112.2444	Sirius mine, waste dump
D97MT010		pyrite, magnetite, anglesite, zircon, galena cubes coated with anglesite
46.3039	112.2175	Waldy mine, waste dump
D97MT011		pyrite

Concentrations of Selected Elements in Bulk Wastes

The concentrations of certain elements of interest in the < 2 mm fraction are given in Table 3. Values given are the mean of three analyses of 3-gram portions of each 50 gram pulverized (Spex mill) sample using energy-dispersive X-ray fluorescence methods. X-ray element excitation used ¹⁰⁹Cd and ²⁴¹Am radioisotope sources and the correction program of Yager and Quick (1992)

Table 3. Concentrations of certain metals in mine-related wastes in Basin and Cataract Creek drainages, northern Jefferson County, Montana.

[Energy dispersive X-ray fluorescence analysis using Yager and Quick (1992) program. Cd detection limit is 1 part per million, 0 = <1 ppm]

Long. Lat. Sample No.	Fe wt. %	Cu	Zn	As	Cd	Pb
	-----parts per million-----					
Basin Creek drainage						
46.3561 112.2944	Bullion mine, waste dumps					
D97B017	3.9	210	260	10,000	0	4,300
D97B018	3.7	360	600	5,500	0	4,100
D97B019	5.0	560	1,200	5,000	1	10,000
D97B002	5.5	50	290	3,600	0	1,000
	Bullion mine, tailings					
D97B001	1.5	160	170	3,600	0	3,700
D97B003	1.4	180	120	3,700	0	3,700
46.3980 112.2944	Buckeye/Enterprise mines, waste dumps					
D97B004	7.6	75	160	8,800	0	1,200
D97B005	4.1	150	220	15,000	0	5,900
	Buckeye/Enterprise mines, tailings					
D97B006	2.2	160	680	16,000	0	21,000
46.2955 112.2952	Daily West mine, waste dump					
D97B012	7.0	930	7,000	50	4	20,000
Cataract Creek drainage						
46.3305 112.2094	Boulder Chief mine, waste dumps					
D97MT007	2.0	75	650	65	0	660
D97MT008	2.4	130	1,100	50	1	3,200
46.3228 112.2364	Cracker mine, waste dump					
D97MT009	2.8	90	1,200	50	1	8,400
46.3500 112.2606	Crystal mine, waste dumps					
D97B014	3.3	300	1,000	2,700	1	3,200
D97B015	4.9	250	510	2,400	0	920
D97B016	2.6	320	810	3,500	0	4,300
46.3128 112.2400	Morning/Mare mines, waste dump					
D97MT013	2.9	240	290	240	1	1,100
46.3361 112.2444	Sirius mine, waste dump					
D97MT010	3.2	210	470	9,600	0	6,600
46.3039 112.2175	Waldy mine, waste dump					
D97MT011	3.4	60	780	200	0	1,900

Characteristics of Waste Leachates

Samples of < 2 mm waste used for leach tests weighed 100 grams and were split from the 250 gram split, and no mechanical size reduction was done. These 100 g samples were exposed to 2.0 liters (L) of deionized water (pH = 6.0 ±0.3) in 4 L glass beakers. The leachate was poured onto each < 2 mm sample and left at rest for 24 hours (h) during which each leachate pH was measured intermittently, and at the end of each test. Leachate tests were done on five or six samples side-by-side simultaneously. At the end of each leach, a 60 ml sample of leachate was collected (filtered 0.45 um) for inductive coupled plasma-atomic emission spectroscopy analysis. Leached wastes were collected on filters, dried at 40°C and weighed to determine weight loss. Some of the lower pH leachates were retained for later tests of buffering capacities of fresh batholith rocks. Table 4 gives the final pH of the leachates and the concentrations of certain elements in the filtered leachates. Figure 2 shows the leachate pH and the corresponding sum of dissolved Cu+Zn+As+Cd+Pb.

Table 4. Final pH of leachates and concentrations of certain metals in leachates from mine-related wastes in Basin and Cataract Creek drainages, northern Jefferson County, Montana.

[Analysis by inductive coupled plasma-atomic emission spectroscopy. Detection limits for each element are given in parentheses. Entries of 0 indicate value is < detection limit.]

Long.	Lat.	Leachate	Fe	Cu	Zn	As	Cd	Pb	Sum	Cu+Zn
Sample No.-size		pH	(10)	(5)	(5)	(20)	(5)	(5)	+As+Cd+Pb	
		tons	-----micrograms per liter-----							
Basin Creek drainage										
46.3561	112.2944		Bullion mine, waste dumps							
D97B017-6,000		2.94	9,600	760	490	100	15	2,700		4,063
D97B018-7,000		3.08	6,400	1,400	3,800	0	43	770		6,018
D97B019-12,000		3.74	150	175	3,100	34	35	220		3,564
D97B002-500		3.62	220	0	42	0	0	0		42
			Bullion mine, tailings							
D97B001-1,200		3.92	70	7	39	100	7	0		153
D97B003-3,600		3.90	160	0	17	200	0	9		226
46.3980	112.2944		Buckeye/Enterprise mines, waste dumps							
D97B004-5,000		3.75	60	5	15	80	0	0		100
D97B005-10,000		3.33	200	0	10	100	0	2,400		2,510
			Buckeye/Enterprise mines, tailings							
D97B006-16,000		3.25	660	65	140	450	6	12,700		13,361
46.2955	112.2952		Daily West mine, waste dump							
D97B012-300		2.75	34,000	1,700	30,000	0	235	4,300		36,251
Cataract Creek drainage										
46.3305	112.2094		Boulder Chief mine, waste dumps							
D97MT007-3,500		6.78	0	0	20	21	0	0		41
D97MT008-3,500		3.23	660	370	5,800	0	63	340		6,573
46.3228	112.2364		Cracker mine, waste dump							
D97MT009-4,000		3.46	58	16	630	21	7	7,100		7,774
duplicate		3.42	100	42	1,200	0	14	4,200		5,456
46.3500	112.2606		Crystal mine, waste dumps							
D97B014-20,000		5.93	0	12	734	0	0	0		746
D97B015-10,000		4.76	0	47	210	15	0	0		272
D97B016-4,000		3.84	0	204	1,400	0	28	190		1,822
46.3128	112.2400		Morning/Mare mines, waste dump							
D97MT013-1,000		3.65	0	9	96	0	0	0		104
46.3361	112.2444		Sirius mine, waste dump							
D97MT010-5,000		3.33	165	35	820	47	8	1,100		2,010
46.3039	112.2175		Waldy mine, waste dump							
D97MT011-700		6.60	0	0	27	0	0	0		27

**RANKING OF POTENTIAL WATER QUALITY DEGRADATION
FOR MINING-RELATED WASTES**

A method is devised to rank the combined acid-generating potential, toxic metal solubility, and mass (or size) of each waste pile with regard to potential water-quality degradation during snowmelt or stormwater runoff. These ranking methods were used only for preliminary relative comparisons of waste piles in the study area and may not, or will not, apply to other areas with metal mining related wastes. The three factors we used are insufficient for an adequate evaluation because they do not include proximity to drainage of interest, erodability (slope), or location within, or remoteness from the drainage of interest. However, we propose a method of ranking for the three factors that are given here. The numbers used here are relative, for semiquantitative ranking. No prior guidelines have been given for such ranking.

The following procedure was used for three categories as follows:

ACID-GENERATING POTENTIAL OF LEACHATE

pH =	>6.0	4.5-6.0	3.5-4.5	<3.5
Ranking number:	0	1	2	3

DISSOLVED TOXIC METALS IN LEACHATE (Sum of Cu+Zn+As+Cd+Pb, ug/L)

Sum, ug/L:	<500	500-1,000	1,000-5,000	>5,000
Ranking number:	0	1	2	3

MASS OR TONNAGE

tons:	<500	500-2,500	>2,500
Ranking number:	1	2	3

For each waste pile, sum each of the above ranking numbers for a maximum of 9 and a minimum of 1.

Using the above ranking method and the required data listed in Table 4, a ranking value is given for each waste pile in Table 5, along with the sample number and an abbreviated description of the relative location of each waste pile at each site.

Table 5. Ranking of potential water-quality degradation of mining-related wastes in Basin and Cataract Creek drainages, northern Jefferson County, Montana, based on acid- generating potential, dissolved toxic metals, and tonnage.

[Values of 9 indicate the greatest potential water-quality degradation, and values of 1 indicate the least potential water-quality degradation]

Long. Sample No.	Lat.	Potential water-quality degradation ranking
Basin Creek drainage		
46.3561 D97B017	112.2944	Bullion mine, waste dumps Uppermost dump, upper adit 8
D97B018		Middle dump, middle adit 9
D97B019		Lower dump, lower adit 7
D97B002		Lowest small dump, lowest adit 4
Bullion mine, tailings		
D97B001		Upper tailings 4
D97B003		Lowest tailings 5
46.3980 D97B004	112.2944	Buckeye/Enterprise mines, waste dumps Brown waste on east side 5
D97B005		Light-gray waste on west side 8
Buckeye/Enterprise mines, tailings		
D97B006		Light-gray tailings near creek 9
46.2955 D97B012	112.2952	Daily West mine, waste dump Yellow waste at creek bed 7
Cataract Creek drainage		
46.3305 D97MT007	112.2094	Boulder Chief mine, waste dumps Waste above mine adit from open cut 3
D97MT008		Waste below mine adit 9
46.3228 D97MT009	112.2364	Cracker mine, waste dump Waste from adit 9
46.3500 D97B014	112.2606	Crystal mine, waste dumps Waste along east open cut 6
D97B015		Waste along west open cut 5
D97B016		Waste at ore bins near creek 6
46.3128 D97B013	112.2400	Morning/Mare mines, waste dump Waste piles from adit 4
46.3361 D97MT010	112.2444	Sirius mine, waste dump Waste dump at adit 8
46.3039 D97B011	112.2175	Waldy mine, waste dump Waste dump at adit 2

CHARACTERISTICS OF FRESH ROCKS AND THEIR ACID NEUTRALIZING CAPACITIES

Six samples of fresh batholith rocks and one sample of overlying fresh Elkhorn volcanics were sampled. Deep weathering (oxidation) and the presence of extensive glacial cover in the area resulted in limited access to fresh rocks without drilling. However, some samples were obtained from roadcuts, and from rockfalls at small cliffs.

After sawing to remove weathering-oxidation effects from blocks as large as 10 kg, portions of these samples (500-1,000 g) were crushed in a jaw crusher. The <170 mesh (<0.090 mm) fraction was isolated for tests of acid neutralizing potential. A high-density mineral concentration was made from 20 grams of the < 0.090 mm fraction, and a 50 gram sample of the >170 < 5 mesh (>0.090 <4.0 mm) fraction was pulverized for bulk chemical analysis and X-ray diffraction analysis to determine bulk mineralogy, and acid neutralizing potential.

Concentrations of certain elements in the fresh rocks are listed in Table 6 for the seven samples studied.

Table 6. Concentrations of selected elements in six fresh Boulder batholith samples and one Elkhorn volcanic sample of the Basin and Cataract Creek drainages, northern Jefferson County, Montana.

[Energy dispersive X-ray fluorescence analysis using Yager and Quick (1992) program.]

Sample No. Lat. Long.	K	Ca	Fe	Cu	Zn	As	Pb
	-weight percent-			----parts per million-----			
F97B007B1 46.3086 112.3025	3.0	3.1	2.3	50	80	<15	45
F97B007B2 46.3086 112.3025	3.9	2.3	2.2	<30	65	<15	<40
F97B007B3 46.3086 112.3025	3.9	1.9	1.9	45	60	<15	<40
F97B010 46.3305 112.3283	3.5	2.6	3.3	40	65	<15	<40
F97MT011 46.2703 112.2189	3.5	2.7	3.0	35	50	<15	<40
F97MT012* 46.3305 112.2094	3.5	2.3	2.0	<30	60	<15	<40
F97B013 46.3500 112.2606	4.3	1.9	1.6	<30	<40	<15	<40

* Elkhorn volcanic rock sample

Table 7 lists the high-density minerals identified in heavy mineral concentrates from fresh rocks obtained by mechanical panning of 1 gram of the <0.090 mm fraction.

Table 7. High-density minerals in fresh rocks in Basin and Cataract Creek drainages, northern Jefferson County, Montana.

Sample No.	High-density minerals in heavy mineral concentrates
F97B007B1	magnetite, >> zircon (two pyrite grains)
F97B007B2	magnetite, zircon
F97B007B3	magnetite, >> zircon (two pyrite grains)
F97B010	magnetite, hornblende, zircon (three pyrite grains)
F97MT011	magnetite, zircon, green hornblende, biotite (two pyrite grains)
F97MT012	magnetite (three pyrite grains)
F97B013	magnetite, >> zircon (one pyrite grain)

The acid-neutralizing potential of the fresh rocks was tested using acidic ($\text{pH} = 2.96 \pm 0.02$) leachates (table 4) that were filtered to remove particulate material. For the first test, one gram of the <0.090 mm fraction of fresh rock was exposed to 20 ml of the acidic leachate for 24 hours at rest, except that each of the seven was stirred once for 3 seconds after one hour of exposure. Results of these tests are given in Table 8. A second test was done using 1 gram of each of the pulverized samples (90% <0.050 mm) in 20 ml of the acidic leachate for 24 hours at rest, except for stirring each once for 3 seconds after one hour of exposure. After this test the samples were retained on filters and dried to determine weight losses. These dried samples were reweighed, and exposed to fresh leachate for a second time for 24 hours, retained on filters, dried, and weighed to determine weight loss, if any. The values of the initial and final pH for each solution are given in Table 8, along with the associated weight losses for the second set of tests.

Table 8. Acid-neutralizing potential of fresh crystalline rocks in the Basin and Cataract Creek drainages, northern Jefferson County, Montana. Sized fractions of ground fresh rock were exposed to filtered acidic waste leachates for 24 hours.

_Sample No. Lat. Long.	First test		Second tests						
	1 g <0.090 mm in 20 ml, 24 h		1 g 90% <0.050 m in 20 ml, 24 h			remainder from first test reexposed to fresh in 1:20, 24 h			
	initial pH	final pH	-----first exposure-----		wt. loss percent	-----second exposure-----		Total wt. loss percent	
			initial pH	final pH		initial pH	final pH		
_F97B007B1 46.3086 112.3025	2.98	5.38	2.96	6.82	2.3	2.94	4.60	2.6	
F97B007B2 46.3086 112.3025	2.98	4.50	2.96	5.80	3.5	2.94	4.41	3.5	
F97B007B3 46.3086 112.3025	2.98	7.03	2.96	7.30	3.2	2.94	5.63	4.5	
F97B010 46.3305 112.3283	2.98	7.20	2.96	7.25	0.6	2.94	5.27	1.7	
F97MT011 46.2703 112.2189	2.98	7.36	2.96	7.41	2.8	2.94	5.29	2.9	
F97MT012 46.3305 112.2094	2.98	5.10	2.96	7.04	3.2	2.94	4.87	3.2	
F97B013 46.3500 112.2606	2.98	4.54	2.96	5.35	1.9	2.94	4.17	1.9	

The mineralogy, texture, chemistry, and field relations of the crystalline quartz monzonite rocks of the Boulder batholith were studied extensively by Ruppel (1963) who examined about 250 petrographic sections and did modal analysis on 28 of them. He reported intermediate plagioclase, potassium feldspar, quartz, hornblende, and biotite in these rocks and alteration minerals are sericite replacing plagioclase and epidote and chlorite replacing mafic minerals. No mention was made of carbonate minerals in these rocks, although his chemical data (Ruppel, 1963, table 3) based on CO₂ analyses for seven quartz monzonites shows an average of 0.6 weight percent calcite, if all of the CO₂ is in calcite; they range from less than 0.1 to 1.8 weight percent calcite, if all of the CO₂ is in calcite. The accuracy of these CO₂ analyses are uncertain because they were done prior to 1960.

The high density mineral concentrates (table 7) of the present study show that minor magnetite, zircon, hornblende, and biotite may be present. These concentrates were made chiefly to see if sulfides, especially pyrite, were present in significant amounts. The pyrite present in fresh rocks amounts to less than one part per million. The fresh rocks are not significant acid generators.

After the acid-neutralizing potential data for the fresh crystalline rocks were examined (table 8), it was suspected that an acid soluble carbonate was present because of the relatively rapid increases in pH of the acidic leachates. Sawed slabs of the fresh rock samples were placed on a binocular microscope stage and exposed to the "alizerin red S" stain test for calcite (Dickson, 1965). Except for sample F97B007B2, all rock slabs showed red staining that indicates the presence of calcite that is widely dispersed throughout each sample. Some of the calcite is associated with clusters of mafic minerals, some is along hairline cracks, and some rarely occurs as discrete grains as large as 0.5 X 1.0 mm. Calcite was not detected in X-ray diffractometer scans of the powdered fresh rocks. One reason for this is that a diffraction peak of orthoclase is very close to the strongest diffraction maxima of calcite. Even in the absence of orthoclase, it is doubtful that 5 weight percent of calcite would be detected by the instrument we used. Based on the weight losses after exposure to the acidic leachates it appears that calcite amounts might range from about 1.5 to 4.5 weight percent (table 8). However, because the acidic waste leachate has high sulfate concentrations (120-315 mg/L), the increased pH caused by calcite dissolution from the fresh rocks may result in gypsum precipitation; thus weight loss measurements for these tests may underestimate the amount of calcite dissolved by the acidic solution if gypsum was precipitated. In order to pursue the weight loss factor in terms of acid-soluble minerals in the fresh rocks, two-gram samples of the pulverized fresh rocks were exposed to 80 ml of pH = 2.75 aqueous solution made with HCl. The pH of 2.75 was used because this was the lowest pH of the waste leachates (table 4). Results of these tests are given in Table 9. Samples MT011, MT012, and B013 were done twice because of a weight loss of eight percent in the first test for the basal Elkhorn volcanic rock sample (MT012, table 9). This large weight loss is much greater than the weight loss measured after exposure to the acidic sulfate solution (table 8). X-ray diffraction analysis of the HCl solution leached and unleached sample show that a mineral with a 7 Å diffraction peak was removed from sample MT012 by the pH = 2.75 HCl solution. This mineral is probably an Fe-bearing chlorite that was destroyed by the acidic (pH = 2.75) solution. However, in terms of waste repositories, the wastes considered are acidic SO₄-rich, rather than acidic chloride-rich, so these mineral-degrading effects are not relevant.

The acid-neutralizing data for the six Boulder batholith samples given in Tables 8 and 9 show weight losses of about 2.9 and 3.0 weight percent using the two different types of acidic solution. We therefore infer that for these samples there is an average of about 3 weight percent calcite.

Table 9. Acid-neutralizing potential of fresh crystalline rocks in the Basin and Cataract Creek drainages, northern Jefferson County, Montana. Sized fractions of ground fresh rock were exposed to pH = 2.75 aqueous HCl solutions using 2 grams of fresh rock in 80 ml of acidic solution for four hours.

Sample No. Lat. Long.	Initial pH	pH at 3 hours	pH at 4 hours	Weight loss percent, 4 hours
F97B007B1 46.3086 112.3025	2.75	5.44	5.54	2.2
F97B007B2 46.3086 112.3025	2.75	4.73	4.83	2.2
F97B007B3 46.3086 112.3025	2.75	6.28	6.40	5.2
F97B010 46.3305 112.3283	2.75	5.95	6.02	3.2
F97MT011 46.2703 112.2189	2.75	6.02*	6.10*	3.8*
F97MT012 46.3305 112.2094	2.75	5.18*	5.26*	8.2*
F97B013 46.3500 112.2606	2.75	4.30*	4.34*	1.8*

* indicates mean of two separate determinations

MINERALS ORIGINATING FROM SURFICIAL SULFIDE OXIDATION IN MINING-RELATED WASTES

Secondary minerals derived chiefly from aqueous oxidation of primary hydrothermal sulfides are those minerals that contribute significant acid and associated dissolved toxic metals that degrade water quality in the absence of acid buffering minerals. Although amorphous phases or minerals not detected by X-ray diffraction analysis of bulk samples may be involved in acid generation from these wastes, we believe that the most important acid-generating minerals in the Basin and Cataract Creek drainages are sulfates of the jarosite family.

Although anglesite [PbSO₄] may be somewhat soluble in acidic solutions below a pH of about 3.5, anglesite in the absence of an acid-generating mineral seems to be relatively insoluble. Likewise, goslarite [ZnSO₄·7H₂O] alone may generate only slightly acidic conditions (pH = 5.4), based on our laboratory tests, but it is highly soluble (>5 g/100ml) and abundant Zn will be dissolved. Thus neither anglesite nor goslarite alone produce significant acidity when exposed to near-neutral pH water. In this

context, Li and St-Arnaud (1997) observed that "the presence of gypsum in oxidized waste rock inhibits the dissolution of anglesite until the gypsum is dissolved".

Waste adjacent to a prospect pit on the north side of Jack Creek one mile (1.7 km) north of the Bullion mine contains significant amounts of very fine-grained white scorodite $[\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}]$ associated with arsenian pyrite. Based on laboratory tests this scorodite is highly soluble and generates significant amounts of acid; one gram in 20 ml of deionized water produced a pH of 3.3 in four minutes and in 1 hour the pH was down to 3.15. This will produce significant As pollution because of the high solubility. This mineral was also found in small amounts associated with a jarosite at the mine waste pile in the north part of the town of Basin.

SUMMARY

This preliminary study examined simple empirical methods of evaluating and ranking some metal-mine related wastes in the Basin and Cataract Creek drainages in terms of acid generation and toxic metal solubility. Major acid-generating minerals appear to be chiefly those of the jarosite family. Study of a few fresh Boulder batholith rocks indicate some significant acid-neutralizing capacity due to the presence of about 3 weight percent calcite.

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, eds. J.L. Jambor and D.W. Blowes, Mineralogical Association of Canada, p.247-270.
- Becraft, G.E., Pinckney, D.M., and Rosenblum, Sam, 1963, Geology and mineral deposits of the Jefferson City quadrangle, Jefferson and Lewis and Clark Counties, Montana: U. S. Geological Survey Professional Paper 428, 101 p.
- Dickson, J.A.D., 1965, A modified staining technique for carbonates in thin section: *Nature*, v. 205, p. 587.
- Li, M.G., and St-Arnaud, Luc, 1997, Hydrogeochemistry of secondary mineral dissolution: column leaching experiment using oxidized waste rock: in Proceedings of the Fourth International Conference on Acid Rock Drainage, Vancouver, B.C. Canada, May 31-June 6, 1997, p.465-477
- Marvin, R., Metesh, J., Hargrave, P., Lonn, J., Watson, J., Bowler, T., and Madison, J., 1996, Bureau of Land Management abandoned- inactive mines program, Abandoned-inactive Mines of Montana: Montana Bureau of Mines and Geology Open-File Report,196 p.
- Metesh, J., Lonn, J., Duaiame, T., and Wintergerst, R., 1994, Abandoned-inactive mines program DeerLodge National Forest, Volume I-Basin Creek drainage: Montana Bureau of Mines and Geology Open-File Report 321, 131 p.
- Metesh, J., Lonn, J., Duaiame, T., Marvin, R., and Wintergerst, R., 1995, Abandoned-inactive mines program Deerlodge National Forest, volume II-Cataract Creek drainage: Montana Bureau of Mines and Geology Open-File Report 321, 163 p.
- Montana Department of Health and Environmental Sciences, 1994, Montana Numeric Water Quality Standards, Circular WQB-7, 39 p.
- Ruppel, E.T., 1963, Geology of the Basin Quadrangle Jefferson, Lewis and Clark, and Powell Counties, Montana: U.S. Geological Survey Bulletin 1151, 121 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.
- Yager, D.B., and Quick, J.E., 1992, SuperXap Manual: U.S. Geological Survey Open-File Report 93-12, 45 p.

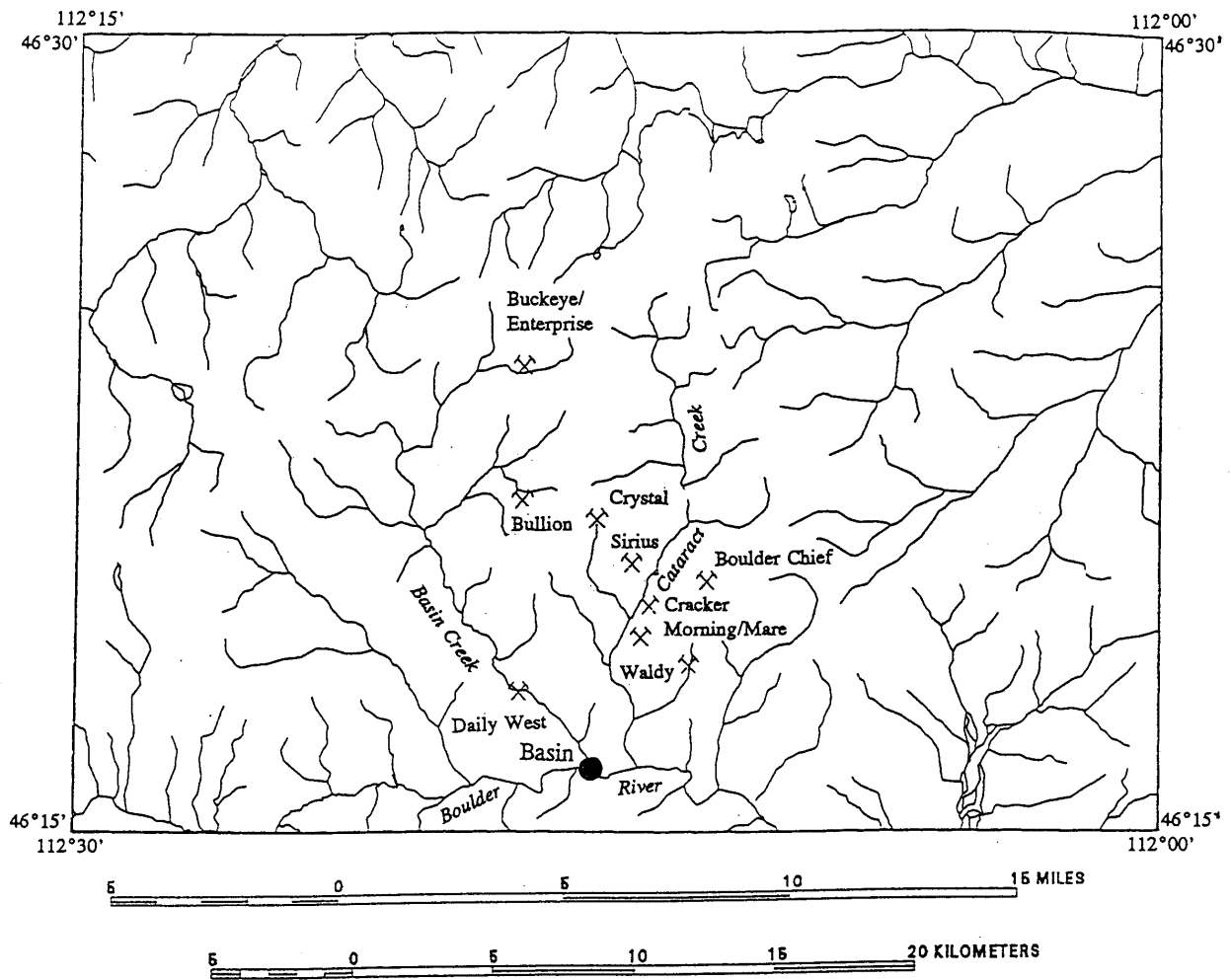


Figure 1. Location of mining-related waste piles studied in the Basin and Cataract Creek drainages, northern Jefferson County, Montana.

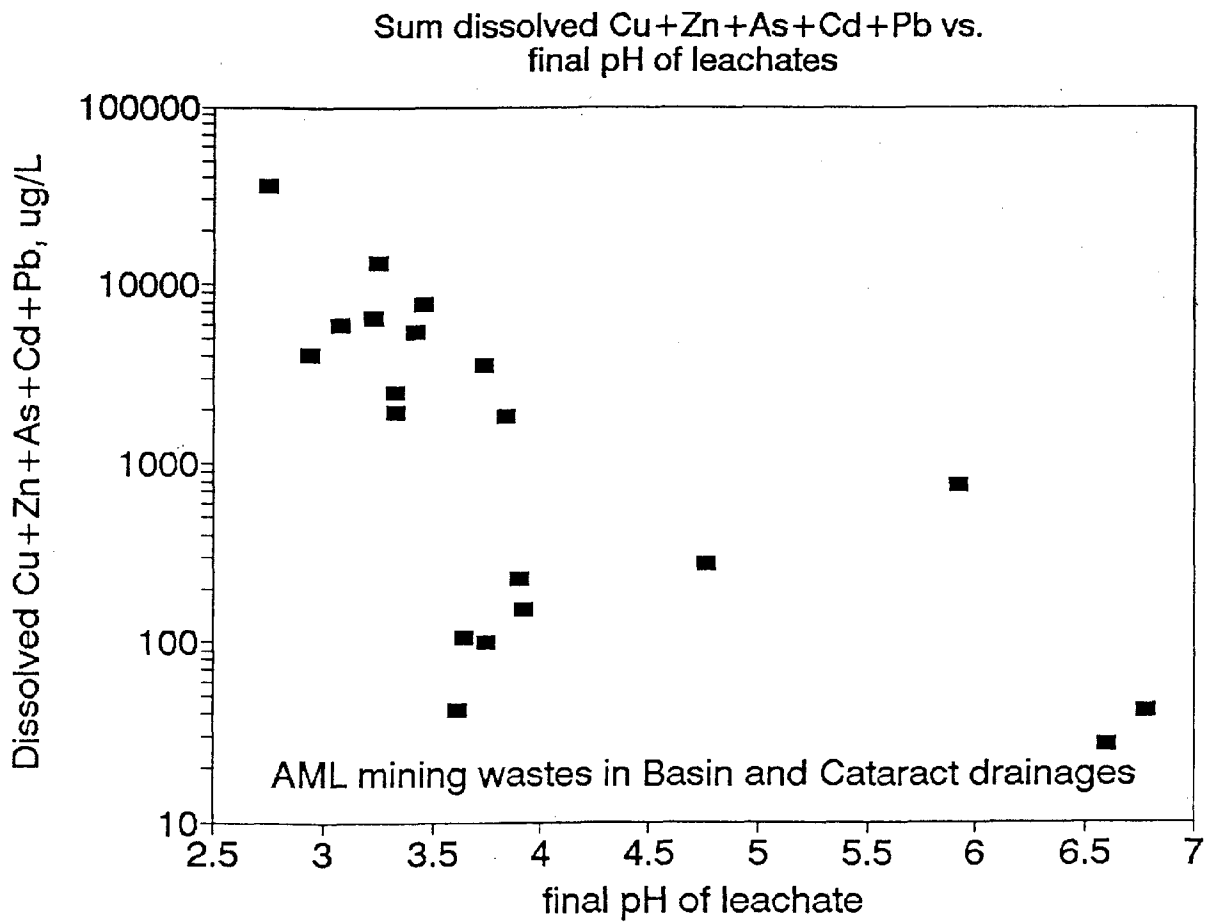


Figure 2. Relations of the concentration of certain dissolved toxic metals in leachates to the pH of the leachate.

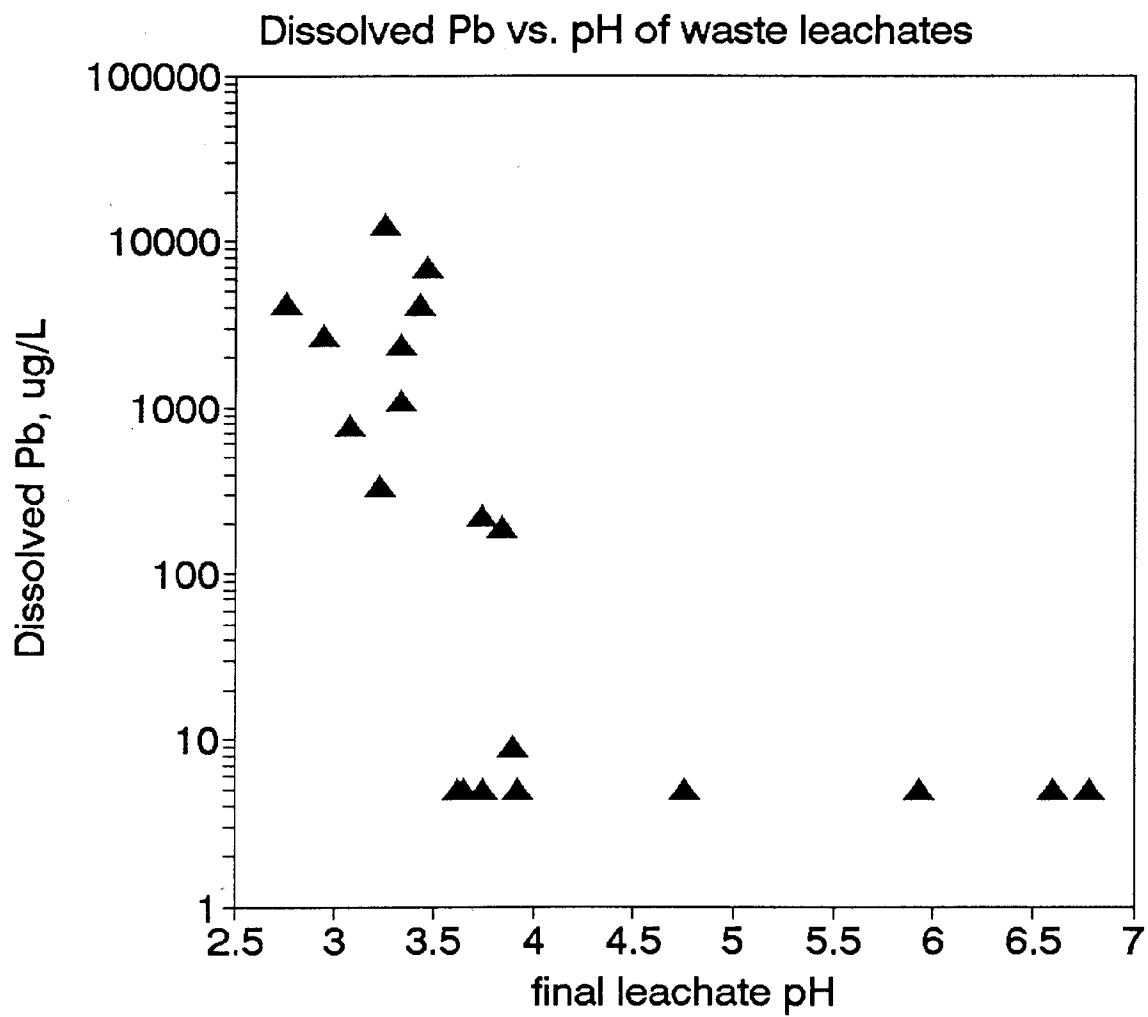


Figure 3. Relations of dissolved Pb to the final pH of the waste leachates.