Metal Leaching in Mine-Waste Materials and Two Schemes for Classification of Potential Environmental Effects of Mine-Waste Piles

By David L. Fey and George A. Desborough

Chapter D4 of
Integrated Investigations of Environmental Effects of Historical Mining in the Basin and Boulder Mining Districts, Boulder River Watershed, Jefferson County, Montana

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Professional Paper 1652–D4

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Chapter D4

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Abstract

Surface waste material was collected from 19 metal-mining-related dumps at 10 sites in the Boulder River watershed study area. Leach and acidity analyses of waste material provided a foundation for the development of two classification schemes for evaluating the potential environmental effect of mine-waste piles. Mineralogical and geochemical analyses of a vertical core of tailings at a mill site showed a distinction in the amount of deposit-related elements between surface and buried waste material.

Mineralogy of bulk surface samples was determined primarily by X-ray diffraction. Anglesite and jarosite were present in about 80 percent of the waste piles. Sphalerite and arsenopyrite, both common primary minerals in the mineral deposits, were not present in the mine-waste samples. Goslarite (a zinc sulfate) and scorodite (iron arsenate) were identified in the field. Total-digestion inductively coupled plasma–atomic emission spectroscopy (ICP-AES) elemental and X-ray diffraction analyses of a core from the Buckeye flotation tailings revealed that most of the pile contained oxidized tailings composed of secondary minerals produced during weathering and sparse to no original sulfide minerals; the bottom of the core contained a layer of primary sulfide minerals. Comparison of concentrations in the sulfide and oxidized layers in this core demonstrated that significant leaching of deposit-related trace elements had occurred in the oxidized layer, with some elements migrating downward.

The surface samples were subjected to two leaching techniques to determine the concentration of water-soluble, deposit-related trace elements in the dump materials. Net acid production, an indication of the ability of a material to produce acid when oxidized over a long period of time, was also determined. The sum of the concentrations of deposit-related elements (Ag+As+Cd+Cu+Pb+Zn) in these leachates, when plotted against either the leachate pH or the net acid-production value, provided two schemes for classifying these mine wastes. Metal-mining wastes in the study area had classifications ranging from low potential to high potential for causing environmental degradation. The leach and acidity tests showed that material with net acid potential greater than 20 pounds $CaCO_3$ per ton equivalent will release high concentrations of iron, arsenic, cadmium, copper, lead, and zinc, and produce leachates with low pH.

The two classification schemes derived from the chemical and waste-pile-size data provide a means to compare the potential of the waste piles in a watershed to cause environmental degradation. These methods are meant to provide numerical means of evaluating and comparing wastes, but do not incorporate such factors as proximity to ground or surface water, presence of surface water, or draining adit water flowing over or infiltrating into the piles. These factors must be considered by land managers along with the classification results.

Introduction

Metal-mining-related wastes in the Boulder River watershed study area cause detrimental effects on water quality because of acid generation and toxic-metal solubilization (Nimick and Cleasby, this volume, Chapter D5; Cannon and others, this volume, Chapter E1). Mining-related wastes also contribute to contamination of streambed sediment through the fluvial transport and deposition of tailings and the settling of metal-rich colloidal material (Church, Unruh, and others, this volume, Chapter D8).

Veins enriched in base and precious metals were explored and mined in the Basin, Cataract, and High Ore Creek basins for a period of more than 70 years. Extracted minerals included galena, sphalerite, pyrite, chalcopyrite, tetrahedrite, and arsenopyrite. Most of the metal-mining waste sites in the study area were identified and described by the Montana Bureau of Mines and Geology (Metesh and others, 1994; Metesh and others, 1995; Marvin and others, 1996). In 1997, we collected composite surface samples from sites in the Basin and Cataract Creek basins to identify, characterize, and classify waste sources.

Purpose and Scope

The purpose of this chapter is to describe various geochemical and mineralogical studies to help understand and assess the potential geochemical effect of mine-waste piles in the Boulder River watershed study area. Material from the surface of waste piles was sampled and analyzed to determine the minerals and elements present in waste piles. A core was collected from one waste pile to determine whether surface samples have different trace-element composition and mineralogy from samples collected at depths. Finally, chemical and physical attributes of waste piles were combined to construct two classification schemes to rank the potential environmental hazard of runoff from mine-waste piles. The goals of this part of the Boulder River watershed study were to:

- Characterize the mineralogy and geochemistry of mine wastes

- Demonstrate the geochemical differences between surface and subsurface material in mine-waste piles

- Develop a classification scheme or schemes to assess the potential environmental effect of runoff from mine waste

- Apply the classification schemes to the sampled mine-waste piles.

Sample Collection and Preparation

Bulk Surface Samples

Mine-waste samples (exploration waste, dump material, or mill tailings) were collected from the surface of 19 waste piles at 10 sites in the Boulder River watershed study area. Surface material was collected for analysis because it is what is exposed to air, rain, and snowmelt runoff infiltration. Material from each site was collected from 30 or more randomly selected 3-ft cells across the top and sides of a dump to a depth of approximately 3 in. using four to six randomly selected 2–3 oz scoops per cell. This collection method is designed to reduce the sampling error (also called the fundamental error; Smith and others, 2000). Samples were dry sieved in the field to obtain a minus-0.08 in. (<2 mm) fraction. The minus-0.08 in. fraction was deemed to be the most reactive to water in short-term exposures. Coarser material was discarded. The resulting composite sample typically contained 2–4 lb of mine waste. The minus-0.08 in. fraction was split in the laboratory using a Jones splitter. One fraction was further split into a ½ lb sample that was used for (1) bulk chemical analysis (after sieving to minus-80 mesh (<190 μm) and grinding to minus-200 mesh (<75 μm)); (2) X-ray diffraction (XRD) analysis to determine mineralogy; (3) analysis of heavy-mineral concentrates to identify high-density minerals; (4) leaching tests to determine amounts of soluble deposit-related elements; and (5) net acid production (NAP) tests (after grinding to minus-200 mesh (<75 μm)).

Two-Inch Diameter Vertical Core

At the Buckeye mill tailings site, we also drove a 2-in. PVC pipe about 6 ft through the thickest part of the tailings. In the laboratory, core samples were described and subdivided into subsamples (by depth) according to visually identified differences in mineralogy, organic content, and apparent oxidation zones. The subsample material was sieved to minus-100 mesh (<150 μm), analyzed for bulk chemistry, and examined with XRD for mineralogy. Analyses from this core illustrate the leaching of trace elements as sulfidic waste weathers; they are discussed in more detail in the section on effects of weathering on dump surface material and in Cannon and others (this volume).

Location of Mine-Waste Sites

We sampled and analyzed material from selected sites likely to have moderate to high impact on the environment, and to which we had access (either public land or private land with permission). We did not sample all possible waste sites, and so the rankings derived from the classification schemes discussed herein serve as applied examples of those schemes, and not a definitive ranking of all mine-waste sites in the study area.

Metesh and others (1995) inventoried 37 waste sites from historical records in the Basin Creek basin and visited 28. They sampled 14 sites. Of those 14, we visited and sampled 5 sites. Our sampling plan was based on assessing which sites were likely to contribute adversely to the quality of water and sediment in the study area. Some sites were deemed too small, too distant from any surface water (for example, the Morning mine), or too inaccessible for remediation (Hector mine). Other sites showed no significant impact on nearby streambed sediment (for example, Lady Lieth and Winter's Camp mines), and so were not sampled. Metesh and others (1995) inventoried 57 sites in the Cataract Creek basin, visited 54, and sampled 27. We collected samples at five sites, using the criteria just listed to screen sites. The Crescent mine is accessible only by foot, and although it has visible mine discharge, it had negligible effect on sediment in upper Cataract Creek, based on streambed sediment analyses (Church, Unruh, and others, this volume). Similarly, effect on sediment of Hoodoo Creek (tributary to Cataract Creek) from the Blue Diamond–Occidental mine was minimal. The Phantom mine-waste pile on Cataract Creek was very small (200 tons). One site not sampled but which should have been was the Morning Glory tailings. This site is on the west bank of Cataract Creek and contained approximately 6,000 tons of material (Metesh and

others, 1995). However, Metesh and others (1995) concluded that the pile did not appear to contribute to the degradation of Cataract Creek, and that the mineralogy of the material suggested little potential for metals to be released.

We collected 19 bulk surface samples from mine-waste piles at 10 mine sites located in the Basin and Cataract Creek basins (fig. 1). The estimated sizes of the waste piles are in table 1.
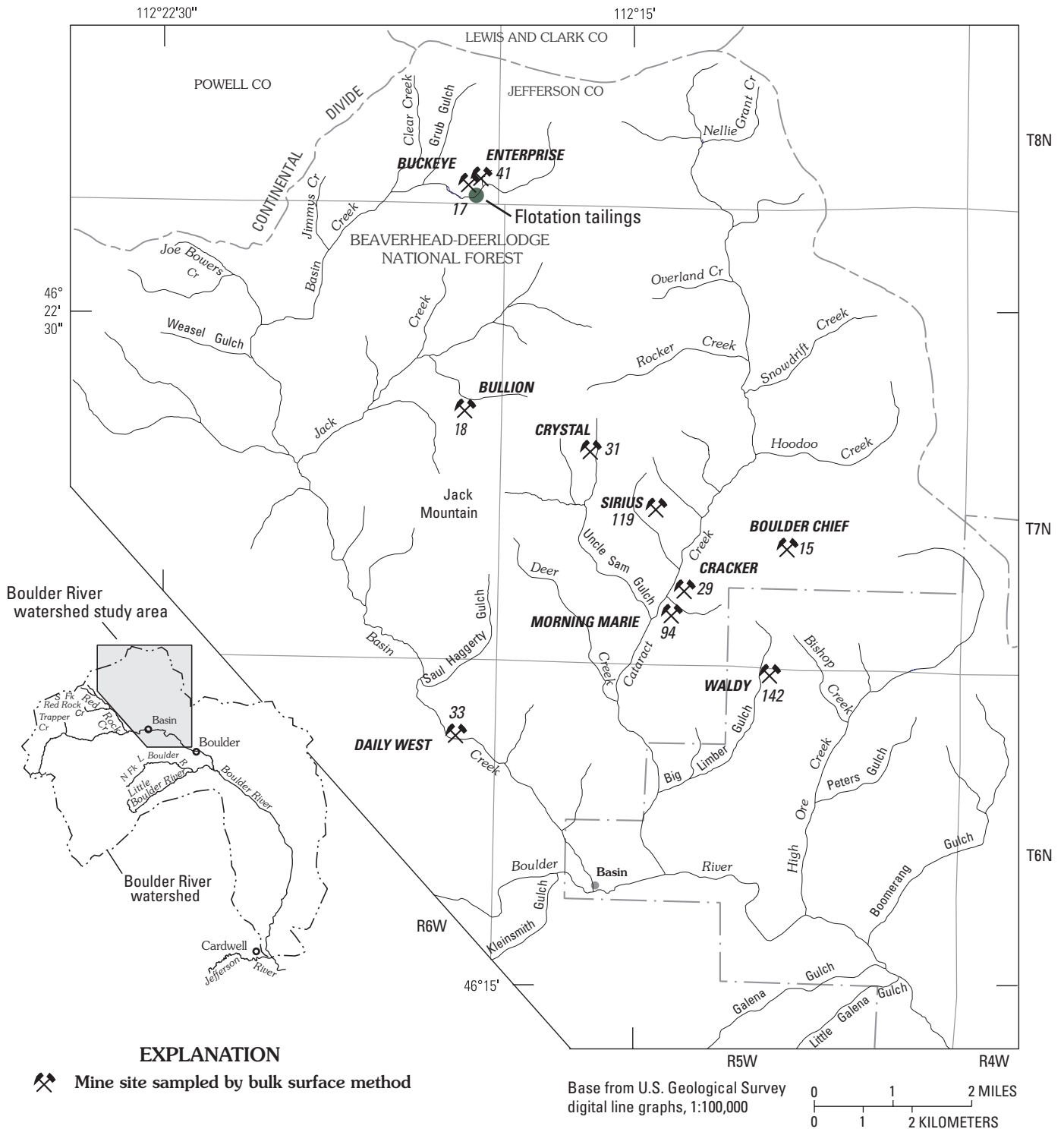

Figure 1.   Boulder River watershed study area, and localities of bulk surface mine-waste samples (sites numbered as in Martin, this volume, Chapter D3).

Table 1. Site numbers, site names, sample descriptions, and estimated size of mine-waste piles sampled in the Boulder River watershed study area.

[Site numbers are from Martin (this volume, table 1)]

Site No. and name	Sample description, bulk surface sample	Estimated size (tons)
41 Enterprise mine	Brown waste from Enterprise mine	5,000
17 Buckeye mine	Light-gray waste from Buckeye mine	10,000
	Light-gray tailings from flat near creek	8,400
18 Bullion mine	Uppermost dump, upper adit	6,000
	Middle dump, middle adit	7,000
	Lower dump, lower adit	12,000
	Small dump near lowest adit	500
	Upper tailings impoundment	1,200
	Lower tailings impoundment	3,600
15 Boulder Chief mine	Waste above adit from open cut	3,500
	Waste from below mine adit	3,500
142 Waldy mine	Waste dump at adit	700
94 Morning Marie mine	Waste piles from adit	1,000
29 Cracker mine	Waste from adit	4,000
33 Daily West mine	Yellow waste near creek bed	300
119 Sirius mine	Waste dump at adit	5,000
31 Crystal mine	Altered rock along east side of open cut	20,000
	Altered rock along west side of open cut	10,000
	Waste at ore bins near creek	4,000

In the Basin Creek basin, we visited the following sites and collected samples as noted:

- Buckeye mine area near the head of Basin Creek; two samples

- Enterprise mine area (just upstream of the Buckeye mine on Basin Creek); one sample

- Bullion mine area, above a small tributary to Jack Creek (the Bullion mine tributary); six samples

- Daily West mine, along Basin Creek about 3 mi upstream from the town of Basin; one sample.

In the Cataract Creek drainage basin, we visited the following sites and collected samples as noted:

- Crystal mine, near the head of Uncle Sam Gulch (tributary of Cataract Creek); three samples

- Sirius mine; one sample

- Morning Marie mine, along Cataract Creek upstream of Uncle Sam Gulch; one sample

- Cracker mine, along Cataract Creek upstream of Uncle Sam Gulch; one sample

- Boulder Chief mine, about 1½ mi east of Cataract Creek and 1½ mi south of Hoodoo Creek; two samples

- Waldy mine, in Big Limber Gulch about 2 mi upstream from Cataract Creek; one sample.

The High Ore Creek basin is also in the study area. However, we did not collect samples from the Comet mine, the largest mining operation in that drainage, because it was scheduled for remediation.

Figure 2.   View of lower (largest) waste dump at Bullion mine, looking north. Distance across dump is about 200 feet (60 m). Loading chute seen at center of picture. Mill was below dump, to the north.

Geochemistry and Mineralogy of Mine Wastes

Mineralogy

Minerals in the bulk surface samples of mine waste were determined by X-ray diffraction (copper radiation) of 2-oz samples of the minus-0.08-in. (<2 mm) fraction after pulverizing in a Spex mill to minus-200 mesh (<75 μm). Both anglesite and jarosite were present in about 80 percent of the samples. Whereas anglesite is chemically simple ($PbSO_4$), jarosite may be chemically complex. Studies of members of the alunite-jarosite family of minerals by Scott (1987) showed that the general formula for jarosite is $AB_3(XO_4)_2(OH)_6$; the large cation (A) may be Na, K, Ag, NH_4, H_3O, Ca, Pb, Ba, Sr, or Ce, and the B sites may be occupied by Al, Fe, Cu, or Zn. The anion (XO_4) may be SO_4, PO_4, AsO_4, SbO_4, CrO_4, or SiO_4. For our samples, the dominant X-ray diffraction pattern was that of the jarosite family, with SO_4 as the major anion with some possible AsO_4 substitution where arsenic was abundant. The major cations appeared to be K, Pb, and H_3O based on scanning electron microscopy and energy-dispersive X-ray fluorescence analysis.

Heavy-mineral concentrates were obtained by mechanical panning of a 1-oz fraction of each minus-0.08 in. (<2mm) split in order to concentrate high-density minerals such as pyrite, galena, and sphalerite. These minerals were identified by X-ray diffraction, X-ray fluorescence, and optical microscopy. Although sphalerite (ZnS) and arsenopyrite (FeAsS) are common primary hydrothermal minerals in the ore deposits of the study area (Billingsley and Grimes, 1918), we found no arsenopyrite in the heavy-mineral concentrates from any sample and only trace amounts of sphalerite in one sample.

White botryoidal crusts of goslarite ($ZnSO_4 \cdot 7H_2O$) were found underneath an overhang on the largest waste pile at the Bullion mine (fig. 3). Thus, we suspect that zinc resides chiefly in this soluble zinc sulfate, and possibly in gunningite ($(Zn, Mn)SO_4 \cdot H_2O$). Scorodite, a highly water-soluble iron arsenate ($FeAsO_4 \cdot 2H_2O$), was abundant on the surface of one waste pile at the head of Jack Creek, about 1 mile north of the Bullion mine. Scorodite is the most commonly occurring oxidized secondary mineral derived from arsenopyrite. The absence of primary zinc- and arsenic-bearing minerals and the presence of these two secondary minerals suggest that most of the zinc- and arsenic-bearing primary sulfide minerals had been converted to more soluble sulfate or arsenate phases by weathering. This weathering took place since the cessation of mining, a period of 50–100 years.

Figure 3. Soluble salt goslarite ($ZnSO_4 \cdot 7H_2O$) coating mine waste, Bullion mine. This easily dissolved mineral formed in place from leaching of zinc from waste pile; it was protected here from rain by an overhanging cut in the waste pile. Field of view in photograph is about 1 ft across.

Mixed-Acid Digestion Method

A mixed-acid digestion technique was used to provide bulk analyses of surface mine-waste samples and the core subsamples. We used the results to illustrate the geochemical difference between dump surface material (mostly oxidized) and material at depth (partially oxidized or unoxidized). A 0.2 g portion of material was subjected to a mixed-acid digestion using, in sequence, HCl, HNO_3, $HClO_4$, and HF acids (Crock and others, 1983; Briggs, 1996). The resulting solution was analyzed for 40 elements using inductively coupled plasma–atomic emission spectroscopy (ICP-AES). The digestion dissolves sulfides and most silicates and oxides; resistant or refractory minerals such as zircon, spinels, and some tin oxides are only partially dissolved. Samples of standard reference material (SRM) were digested and analyzed with the mine-waste samples. These standards were SRM-2704, SRM-2709, SRM-2710, and SRM-2711, available from the National Institute of Standards and Technology. Analytical results for the bulk surface materials are in Fey, Desborough, and Finney (2000), and results for the 2-in. core from the Buckeye site are in Cannon and others (this volume) and the database (Rich and others, this volume, Chapter G). A statistical summary of mean values, median values, and standard deviations for multiple analyses of the reference materials, and comparisons with certified values appear in Fey, Unruh, and Church (1999).

Passive Leach Method

A passive leach procedure was also applied to the bulk surface mine-waste materials, and the results were used in one of the waste classification schemes discussed herein. A 100-g sample was exposed to 2 L of laboratory deionized water (pH of 5.0±0.2) in an open 4-L beaker. Samples were left at rest for 1 hour and then gently stirred for 5 seconds to prevent stratification of the leachate. The pH of the leachate was measured after 24 hours, and then a 60-mL sample of the leachate was filtered through a Gelman 0.45-μm filter using a disposable 60-mL syringe (Desborough and Fey, 1997), acidified with six drops of ultra-pure HNO_3, and refrigerated prior to analysis by ICP-AES. The data for the passive leach procedure are in Desborough and Fey (1997).

EPA-1312 Leach Method (Synthetic Precipitation Leach Procedure–SPLP)

This procedure was used on the bulk surface mine-waste materials, and the results were used in one of the waste classification schemes discussed below. A 100-g sample of mine waste was placed in a 2.3-L polyethylene bottle. Two liters of an extract solution were added, resulting in a 1:20 sample/extract ratio, with 300 cm^3 of headspace. The extract solution was made from deionized water acidified to a pH of 4.2 with

a 1-percent aqueous solution of 60/40 v/v H_2SO_4/HNO_3. The capped bottles were placed on an end-over-end (tumbling) rotating agitator at 30 rpm for 18 hours. The leachates were then pressure filtered through a 0.7-µm filter (USEPA, 1986). A 100-mL aliquot of filtered solution was acidified with ultra-pure HNO_3 and analyzed for 25 elements by ICP-AES (Briggs and Fey, 1996) and for sulfate (as sulfur) by ICP-AES. Specific conductance and pH were determined on the unacidified bulk filtered leachate. All data are in Fey, Desborough, and Finney (2000).

Net Acid Production (NAP) Method

This test was applied to the bulk surface mine-waste materials, and the results are used in one of the classification schemes herein. A 1.0-g sample of pulverized, minus-200 mesh material was digested with a solution of 30 volume-percent hydrogen peroxide to oxidize pyrite and pyrrhotite, thereby producing sulfuric acid (Lapakko and Lawrence, 1993). The produced acidic solution reacted with the bulk sample, releasing additional acidity from water-soluble salts (present as a result of wetting-drying cycles on the mine-waste pile). The solution also reacted with acid-consuming minerals such as carbonates, biotite, chlorite, and epidote. The solutions were heated to near-boiling for 1 hour, cooled, and filtered. The filtrate was then titrated to a pH of 7 with 0.1M NaOH. A calculated net acid production (NAP) is expressed in terms of lb-equivalent $CaCO_3$ per ton of mine waste. This NAP is meant to represent the net long-term or total potential of a material to produce acid over an unspecified period of weathering. The NAP analyses are in table 2.

Effects of Weathering on Dump Surface Material

In this study, we collected surface samples at 10 waste sites. Factors that can influence the resulting analytical values are numerous. One factor is the surface inhomogeneity of the material sampled. We addressed that factor by collecting many subsamples from at least 30 cells across the surfaces of waste piles and mixing them into one composite sample. Another factor leading to variation is inhomogeneity on a vertical scale within a waste pile. The surface zone typically is composed of oxidized material that has been exposed to the environment for 50 years or more. The concentrations of deposit-related trace elements are usually lower in surface waste material than in material from deeper inside a pile due to accelerated weathering and leaching at the surface. Other concerns related to differential weathering of dumps include slope aspect (north-facing or south-facing) and top versus sides, but we did not address these particular distinctions in this study. Material from below the surface is less likely to be completely oxidized, and material from deep within a pile can contain a large proportion of the original sulfide minerals. Hence, surface sampling is likely to produce a sample biased towards lower metal content, but one that represents the material that determines the chemical composition of surface runoff. Deep sampling would provide a sample that yields a higher metal content and that better represents the long-term potential for future metal release. However, deep sampling is both technically difficult and expensive. We collected a 6-ft long core from the thickest part of the Buckeye tailings, and through geochemical analyses, we show the distinction between surface sampling and depth sampling. The *processes* of element mobility and dispersion of metals represented by this core are discussed in Cannon and others (this volume).

Production records from Roby and others (1960) indicate that ore was last produced at the Buckeye mine in 1939. Rossillon and Haynes (1999) suggested that reprocessing of ores using flotation took place in the early 1940s, resulting in the waste we investigated from the flood plain near the Buckeye mine. Thus, the study of this core examines the results of a 60-year experiment, showing the effect of annual saturation and weathering of mine wastes in a temperate environment. The 2-in. core provided an opportunity to examine the tailings chemistry vertically from the present surface to a depth of about 6 ft. Throughout most of the flood-plain area that is covered by waste, the tailings were thin (generally less than 2 ft thick) and oxidized. The 6-ft core encountered a layer of unoxidized sulfidic tailing about 20 in. thick at a depth of 3 ft (fig. 4). The sulfide zone was near the bottom of the tailings deposit, resting on stream-deposited sand and gravel in a buried wetland. Although some initial inhomogeneity may have existed in the deposition of these reprocessed tailings, they all were likely deposited as sulfidic material; the difference in chemistry between the oxidized and sulfidic tailings now likely reflects the relative mobility of metals as they were weathered and oxidized from the original sulfide minerals. We analyzed, by mixed-acid digestion and XRD, 26 subsamples from this core: 14 from the upper, oxidized zone, 8 from the sulfide zone, and 4 from the contaminated flood-plain sediment beneath the tailings. We distinguished the zones in the core by visual inspection, descriptions of the core intervals, and mineralogy of the subsamples. The oxidized zone contained no visible sulfides and no pyrite based on XRD (although traces of sphalerite were found by XRD of samples concentrated by panning). The sulfide tailings zone had visible sulfides, and pyrite was identified by XRD. Sample descriptions, mineralogy by XRD, and concentrations of selected elements in mixed-acid digestions are in table 1 of Cannon and others (this volume).

The analyses for silver, lead, copper, zinc, cadmium, and arsenic are summarized in the box plot in figure 5. The median values are instructive to demonstrate the relative mobilities of the elements. The median silver values for the oxidized and the sulfide tailings were nearly identical (67 ppm vs. 70 ppm). This indicates that silver was not mobile in this surficial weathering environment. Lead shows a 33 percent decrease from the sulfide to the oxidized zone (15,000 ppm

Table 2. Site numbers, names, pH of passive leach, net acid production (NAP), sum of five trace elements (As+Cd+Cu+Pb+Zn) in both leaches; iron, sulfate, and specific conductance of EPA-1312 leach, and classification scores of wastes by Method 1 and Method 2.

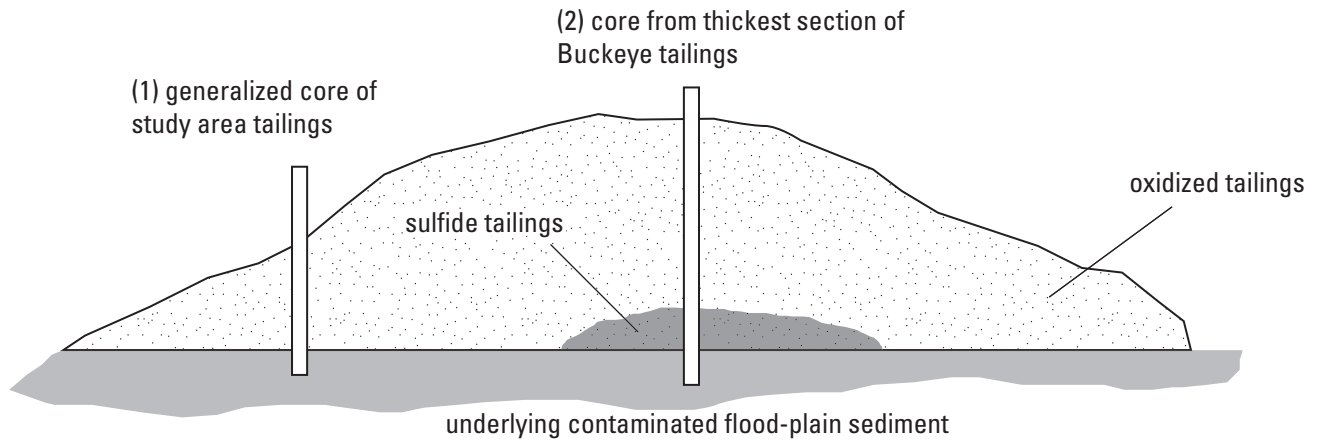| Site Site No. and name	pH, passive leach standard units	NAP, lb/ton	Specific conductance, 1312 leach µS/cm	Sulfate, 1312 leach mg/L	Sum of metals, passive leach µg/L	Sum of metals, 1312 leach µg/L	Dissolved iron, 1312 leach µg/L	Rank by Method 1 scale 1-9	Rank by Method 2 scale 3-10
41 Enterprise mine	3.75	12	106	16	100	330	190	5	5
17 Buckeye mine	3.33	42	240	44	2,500	11,000	1,700	8	10
	3.25	10	210	37	13,000	13,000	1,200	9	9
18 Bullion mine	2.94	34	597	120	4,100	5,700	9,700	8	10
	3.08	36	315	130	6,000	7,100	5,400	9	10
	3.74	8	230	85	3,600	5,400	130	7	8
	3.62	8	107	21	42	190	120	4	3
	3.92	6	60	8.8	150	480	210	4	4
	3.90	6	61	7.9	230	650	360	5	5
15 Boulder Chief mine	6.78	0	119	15	41	66	80	3	5
	3.23	12	333	67	6,600	11,000	1,000	9	9
142 Waldy mine	6.60	4	202	55	27	28	33	2	4
94 Morning Marie mine	3.65	6	96	18	100	200	22	4	4
29 Cracker mine	3.46	26	185	47	7,800	14,000	34	9	8
33 Daily West mine	2.75	68	1,090	280	36,000	34,000	22,000	7	8
119 Sirius mine	3.33	16	240	55	2,000	9,400	620	8	7
31 Crystal mine	5.93	0	87	31	750	710	190	6	5
	4.76	2	60	24	270	260	26	5	5
	3.84	8	78	29	1,800	3,100	37	6	6

Figure 4.   Generalized cross section of tailings sampled by cores at Buckeye flotation mill. Tailings consisted predominantly of oxidized waste material and were sampled as per core number 1. At thickest part of Buckeye flotation tailings, a sulfide layer remaining at depth was sampled as per core number 2. Copper, zinc, cadmium, and arsenic can migrate and are removed by annual flooding of the site during spring runoff (Cannon and others, this volume).

vs. 10,000 ppm). This means that some lead was lost from the oxidized tailings (Cannon and others, this volume). Note that anglesite (lead sulfate, a weathering product) was present in all of the oxidized tailing samples.

Copper, zinc, and cadmium all show dramatic differences between the sulfide and oxidized tailings zones. The median copper value for the sulfide tailings was 2,800 ppm, whereas it

was only 88 ppm in the oxidized tailings. The median copper value from a premining baseline core taken at site 7B from the meadow south of Basin Creek was 29 ppm (Church, Unruh, and others, this volume, table 3); the oxidized tailings zone in our core contained barely three times the copper concentration over the local background. These results show that the majority of copper originally present in the tailings
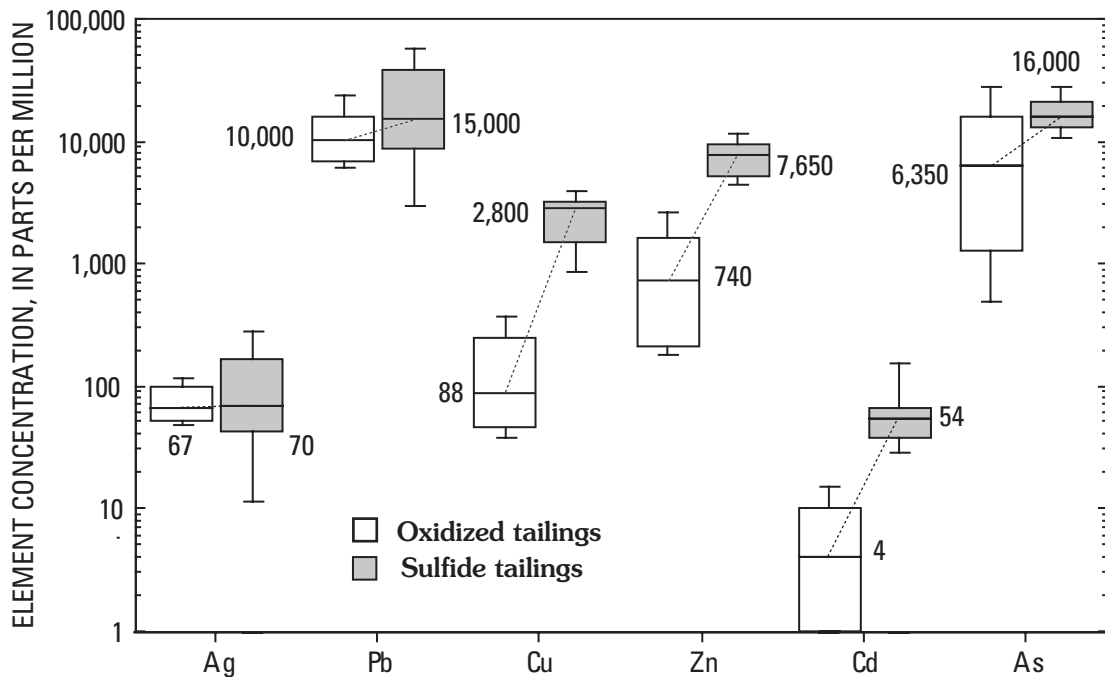

Figure 5.   Box plots of silver, lead, copper, zinc, cadmium, and arsenic concentrations in tailings core from Buckeye mine site. Upper bar represents 90th percentile of population; upper line of box represents 75th percentile; middle line represents 50th percentile (median); lower line represents 25th percentile; lower bar represents 10th percentile. Numbers by the boxes are median values. Plot shows that silver is essentially immobile, lead is slightly mobile, and that copper, zinc, cadmium, and arsenic can be mobilized by near-surface weathering processes.

was leached from the oxidized zone. The median values for zinc were 7,650 ppm and 740 ppm, respectively. The zinc concentration in the oxidized tailings was only 10 percent of the concentration in the sulfide tailings, so we conclude that zinc, like copper, was weathered out of and dispersed from the upper tailings. The local background concentration for zinc, also taken from the core at site 7B, was 190 ppm. Cadmium is geochemically similar to zinc and showed a similar response. The median value for cadmium in the sulfide tailings was 54 ppm, whereas in the oxidized tailing it was 4 ppm. Similar to zinc, the cadmium concentration in the oxide tailings zone was about 10 percent the concentration contained in the sulfide tailings zone. It is important to note that the trace-element concentrations in the sulfide tailings zone probably do not represent the original concentrations, as some losses from weathering may have occurred in the sulfide tailings zone as well. For example, anglesite (lead sulfate, a weathering product) was also present in most of the sulfide tailings subsamples, indicating that weathering processes were active in the subsurface sulfide tailings zone.

Arsenic concentrations in the oxidized zone were highly variable, but the median value was lower than in the sulfide zone. The median values were 6,350 and 16,000 ppm, respectively. The lowest concentration of arsenic in the oxidized tailings was only 500 ppm. Concentrations of arsenic in the contaminated flood-plain sediment below the sulfide tailings were relatively high (about 2,000 ppm). Together, these observations suggest that much but not all of the arsenic had been leached from the oxidized tailings, that arsenic was somewhat mobile in the sulfidic tailings, and that some of the mobilized arsenic accumulated in the flood-plain sediment.

These geochemical results demonstrate two important issues. First, surface material on mine-waste piles has undergone weathering by surface processes. Second, collection of surface samples leads to analyses that underestimate the deposit-related metals in the mine-waste dumps (except silver, which appears to be chemically immobile).

Classification Schemes for Mine-Waste Piles

One of the objectives of collecting and studying mine waste from the study area was to develop and apply a classification method, based on chemical and physical parameters, to help land managers prioritize mine-waste sites in terms of removal or remediation. Values for total-metal content, water-soluble metals, mineralogy, net acid production, pH of leach solutions, and size all are important in describing a particular material's tendency to affect water that it contacts. Over the course of the study, we developed two methods to classify mine-waste piles in the Boulder River watershed study area.

The first method (Method 1) was described in Desborough and Fey (1997) and utilized the pH of the passive leach solutions, the sum of dissolved deposit-related elements (ΣDE)

($\Sigma As+Cd+Cu+Pb+Zn$ in µg/L) in the passive leach solutions, and the estimated size (in tons) of the waste dump. Four classes were defined for the acidity component: for pH > 6.0, class 0; for pH between 4.5 and 6.0, class 1; for pH between 3.5 and 4.5, class 2; and for pH <3.5, class 3. Similarly, for the sum of dissolved elements, four classes were defined: for ΣDE <500 µg/L, class 0; for ΣDE between 500 and <1,000 µg/L, class 1; for ΣDE between 1,000 and 5,000 µg/L, class 2; and for ΣDE >5,000 µg/L, class 3. The size factor has three classes: for size <500 tons, class 1; for size between 500 and 2,500 tons, class 2; and for size >2,500 tons, class 3. These size classes were defined for this study; other watersheds may have waste piles with far greater ranges in size. The sum of the class numbers for each parameter (pH, ΣDE, size) gives a classification number between 1 (low potential for water-quality degradation) and 9 (high potential). The classification numbers based on Method 1 for the waste piles are listed in table 2.

A second ranking method (Method 2) has been developed that considers the effects of (1) the net acid production (NAP), (2) the sum of dissolved deposit-related elements (also $\Sigma As+Cd+Cu+Pb+Zn$) in the leach solution following the EPA-1312 leach method, (3) the concentration of dissolved iron in the EPA-1312 solution, and (4) estimated size. This ranking method was described in Fey, Desborough, and Church (2000). The approach is similar to Method 1, which utilized element concentration data from the passive leach. The difference is that Method 2 does not consider the pH of the passive leach solution (a short-term snapshot of hydrogen ion activity mostly resulting from the dissolution of water-soluble salts) as the "acidity parameter," but rather utilizes the total long-term net acid production (NAP), as determined by the hydrogen-peroxide oxidation of sulfides in the sample.

There are two chemical components to Method 2: a plot of ΣDE from the EPA-1312 leach solutions against the NAP, and a plot of dissolved iron from the EPA-1312 leach solutions against the NAP. A plot of the NAP, expressed as lb $CaCO_3$ per ton, versus the ΣDE from the EPA-1312 leach solutions was developed from data for about 110 mine-waste samples collected from the Animas River study area in Colorado, and the Boulder River watershed study area (Fey, Desborough, and Church, 2000). Only the samples from the Boulder River study area are shown here (fig. 6). We delineated four classes of samples: Group 1, which has low NAP (<20 lb $CaCO_3$/ton) and <1,000 µg/L ΣDE; Group 2, which has low NAP and moderate ΣDE (between 1,000 and 5,000 µg/L); Group 3, which has low NAP and high ΣDE (>5,000 µg/L); and Group 4, which has high NAP (>20 lb $CaCO_3$/ton) and high ΣDE (>5,000 µg/L). No samples plotted in the lower right-hand area in the diagram of high NAP and low ΣDE.

The second chemical indicator considered in Method 2 was the dissolved iron content of the EPA-1312 leach solutions. Iron is an important constituent in the mine wastes and the leach solutions because considerable amounts of pyrite (or its oxyhydroxide weathering products) are found in many mine wastes. Fey, Desborough, and Church (2000) showed that samples from the Boulder River watershed study area can

contain as much as 0.05 percent of their iron in water-soluble form. Dissolved iron in water results in well-defined acute and chronic toxicity, regardless of alkalinity (Colorado Department of Health, 1984). Therefore, we added dissolved iron as one of parameters in the ranking criteria. Because the dissolved iron concentration of a leachate can overwhelm the signal from the ΣDE, we plot it on a separate figure (fig. 7). We classified the data points into three groups: Group 1, having NAP less than 20 lb CaCO$_3$/ton and dissolved iron less than 1,000 µg/L; Group 2, having NAP less than 20 lb CaCO$_3$/ton and dissolved iron greater than 1,000 µg/L; and Group 3, having NAP greater than 20 lb CaCO$_3$/ton and dissolved iron greater than 1,000 µg/L. Figure 7 shows these classes. Only one out of twenty-one samples plotted in the lower right hand portion of the diagram, representing the unusual condition of relatively high acidity and a low dissolved iron concentration. This sample was from the Cracker waste pile.

The size classes were the same as for Method 1: for size <500 tons, class 1; for size between 500 and 2,500 tons, class 2; and for size >2,500 tons, class 3. Figures 6 and 7 combine to show that if the NAP is above 20 lb CaCO$_3$/ton, the mine waste is likely to produce high concentrations of dissolved trace elements in leach solutions.

Method 2 sums the class numbers for the sum of dissolved metals and NAP (four classes), dissolved iron and NAP (three classes), and the size (three classes). The sum of these three criteria then yields an estimate of a mine-waste pile's potential to adversely affect water quality, with a rank of 3 indicating little potential and a rank of 10 indicating the highest potential. The classification numbers based on Method 2 for the waste piles are listed in table 2.

Classification of Mine-Waste Piles in the Boulder River Watershed

We apply here both classification schemes to the bulk surface samples that we collected from mine sites in the Boulder River watershed study area (fig. 8). The sample sites are depicted with symbols of three different colors, representing the relative potential for the materials to affect water quality.
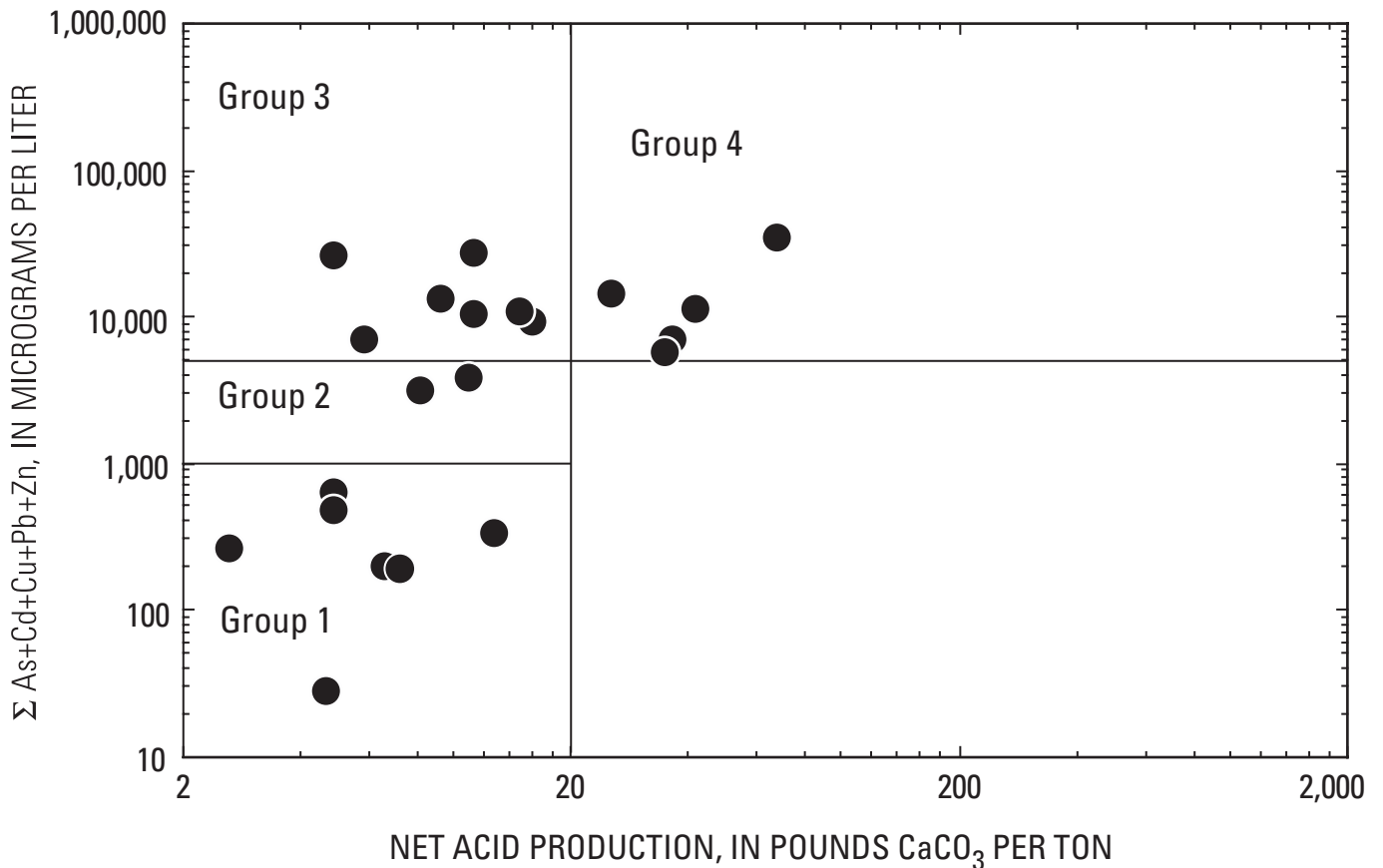

Figure 6. Net acid production (NAP) of waste samples versus the sum of dissolved concentrations of As+Cd+Cu+Pb+Zn from EPA-1312 leach solutions. NAP is a measure of long-term acid producing potential of waste material. Samples with NAP greater than 20 lb/ ton CaCO$_3$ equivalent generally have the sum of metals greater than 5,000 µg/L for mine wastes from the type of polymetallic vein deposit in the Boulder River watershed.
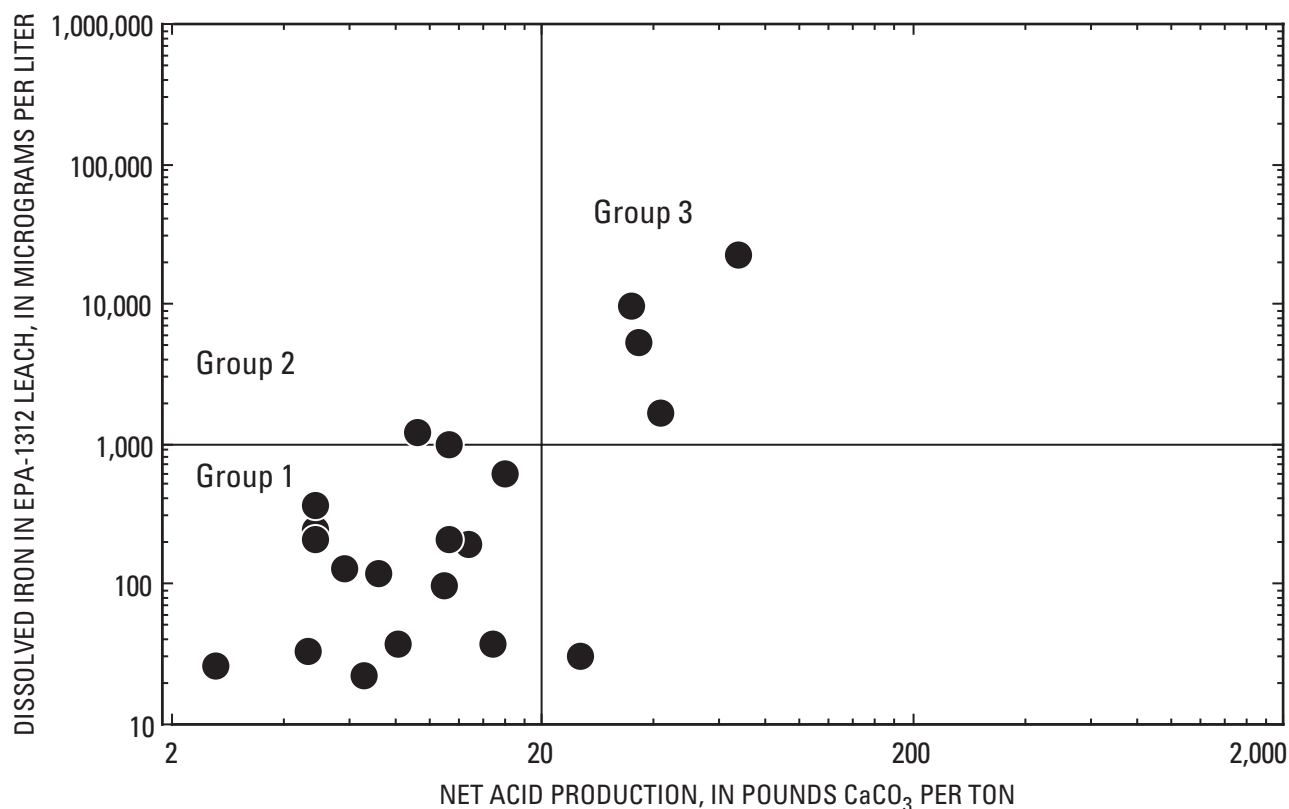
Figure 7.   Net acid production (NAP) of waste samples versus dissolved iron from EPA-1312 leach solutions. Samples with NAP greater than 20 lb/ ton CaCO$_3$ equivalent generally have dissolved iron greater than 1,000 µg/L for wastes from the type of polymetallic vein deposit in the Boulder River watershed.

In this illustration, the size of the waste pile has been incorporated into the color of symbol used.

The classification results reveal that the Buckeye mine-waste pile had the highest potential for affecting the nearby environment. With Method 1 this pile scored 8 on a scale of 1 to 9. On the basis of Method 2 the Buckeye mine-waste pile scored 10 on a scale of 3 to 10. Flotation tailings from the reprocessed gravity tailings of the Buckeye mine, deposited on the north side of Basin Creek, also presented a significant problem. These tailings scored 9/9 and 8/10, respectively, on the basis of Method 1 and Method 2. The waste pile at the Enterprise mine, near the Buckeye mine/mill complex, scored a moderate 5/9 and 5/10.

At the Bullion mine, there were three large waste piles, termed the upper, middle, and lower waste sites. The upper and middle waste piles scored high. On the basis of Method 1, they scored 8/9 and 9/9; using Method 2, both scored high, 10/10. The lower waste pile of the Bullion mine complex was the largest, and also scored high. Its classification scores were 7/9 and 8/10. During a rainfall event on August 2, 1999, overland flow was observed at the Bullion mine site. After an initial decrease, dissolved zinc concentrations increased by about three fold in the Bullion Mine tributary, presumably from the dissolution of easily soluble zinc salts (Lambing and others, this volume, Chapter D7). This observation confirms

that mine-waste piles can have a direct, short-term effect on water quality in receiving streams.

In addition to the three large waste piles, two former tailings impoundments were farther downstream along Bullion Mine tributary. These tailings were different from the unmilled mine wastes in the three large dumps; the difference is reflected in the classification scores. The tailings had been leached of much of their original metal content (table 2), and so their classification scores were moderate. The upper tailings impoundment scored 4/9 and 4/10, and the lower tailings impoundment scored 5/9 and 5/10. A small (500 ton) dump near the two former tailings impoundments had classification scores of 4/9 and 3/10.

Along Uncle Sam Gulch, waste from ore bins upstream from the adit at the Crystal mine scored moderately high (6/9 and 6/10). Material collected from the large exploration cut in the hilltop above the mine had very low acidity and low leachable metals. The scores for this surface material were 6/9 and 6/10 (east side) and 5/9 and 5/10 (west side). After a rainfall event on August 4–5, 1999, zinc concentrations in Uncle Sam Gulch increased by a factor of about 1.8 (Lambing and others, this volume).

The Sirius mine had low acidity, moderately high summed metal content, and low dissolved iron. Its scores were 8/9 and 7/10. The Cracker mine dump was close to Cataract
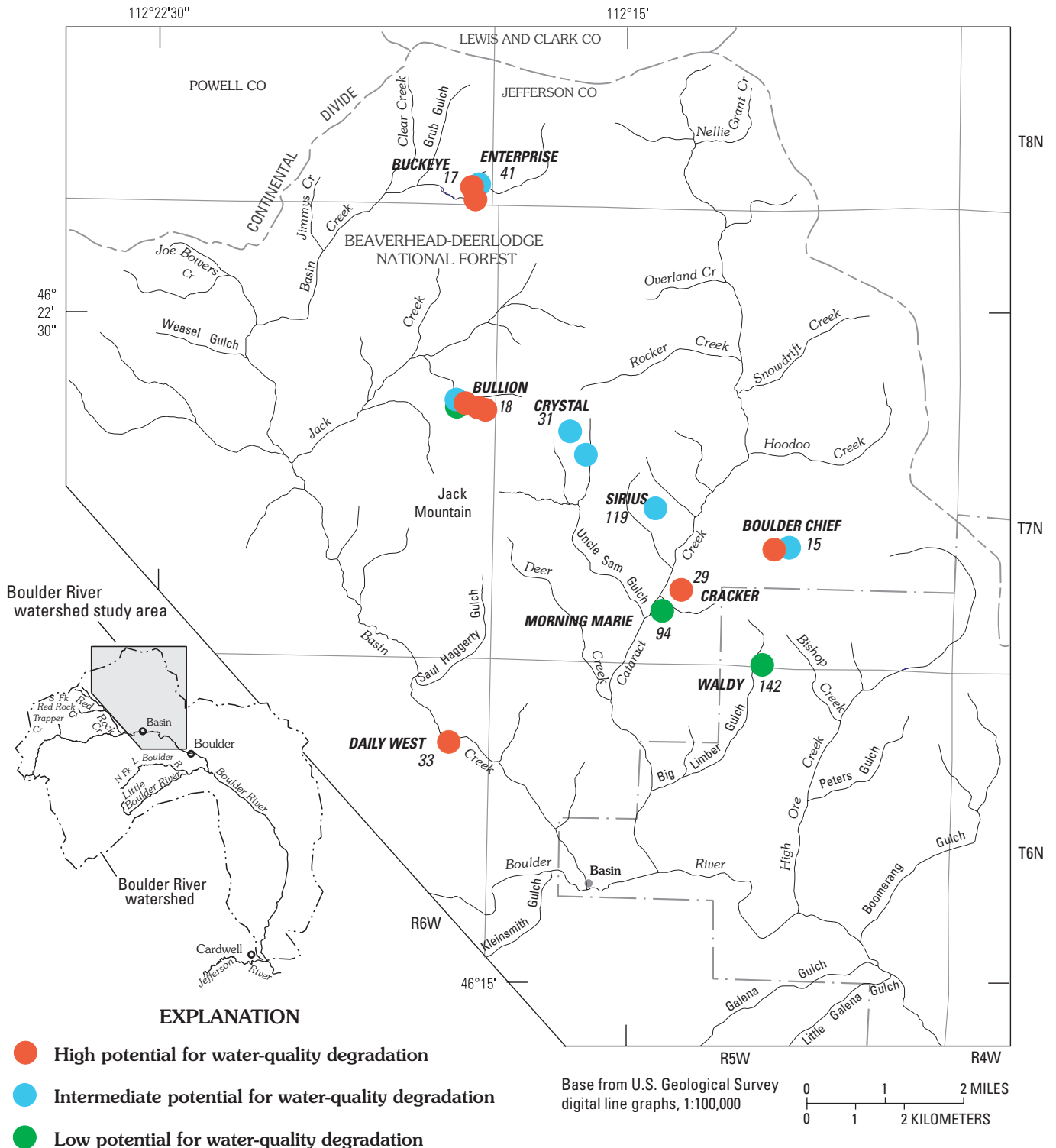
Figure 8.   Boulder River watershed study area with mine-waste piles ranked by water-quality degradation potential. Green sites, low potential; blue sites, intermediate potential; red sites, highest potential for water quality degradation. This ranking using chemical data and size does not incorporate nonquantified data such as presence of draining adits, surface water in contact with dumps, or distance to streams. Sites numbered as in Martin, this volume.

Creek, contained moderately large tonnage (4,000 tons), and had low dissolved iron but high summed dissolved trace elements. The classification scores were 9/9 and 8/10. The Daily West dump, despite its small size, has the most available soluble acid and metals of any of the wastes studied in this report. In addition, the waste pile is located in the flood plain of Basin Creek. The classification scores were high (7/9 and 8/10) but would have been higher if the dump were larger.

The waste from below the adit of the Boulder Chief mine was classified high, with scores of 9/9 and 8/10. This site was situated more than ½ mi from the nearest first-order tributary, and Cataract Creek was more than 1 mi away. However, the metal-loading study for Cataract Creek detected input from the Boulder Chief mine (Kimball and others, this volume, Chapter D6).

The waste piles from both the Morning Marie (Cataract Creek) and Waldy (Big Limber Gulch) mines were small, and had low acidity, low dissolved summed metals, and low dissolved iron. The scores from the two classification methods were 4/9 and 4/10 for the Morning Marie waste pile and 2/9 and 4/10 for the Waldy waste pile.

An important factor not included in this numerical ranking model is the proximity to a stream of a particular waste dump. Assigning a numerical value to this factor is difficult, as several aspects may influence the severity of the impact from waste material. Water draining from an adit and over a waste pile, or surface water flowing over or through the waste and directly into a nearby creek constitutes a direct flow path for impact of that waste pile on stream water. This should be a primary, non-numerical factor to be considered in ranking waste dumps for removal. Proximity to a stream or body of water is also important, as storm or snowmelt runoff can easily transport acid and dissolved metals or metal-sorbing colloidal materials directly to surface water. In two studies of waste-material impact on surface water in the Animas River, Colo., watershed, Nash (1999a, 1999b) emphasized the importance of field observations of these kinds of flow paths. Knowledge of local ground water, the influence of fracture control on ground-water flow, and waste permeability is also important.

Summary and Conclusions

Metal-mining waste was collected by bulk surface sampling at 10 sites in the Boulder River watershed study area. Mineralogical analyses revealed that 80 percent of the samples contained anglesite and jarosite. Primary sulfide minerals were rare: only trace amounts of sphalerite and no arsenopyrite, although these minerals had been reported as abundant by early reports. The minerals goslarite (a zinc sulfate) and scorodite (iron arsenate) were found in the field. Mineralogical and whole-sample analyses of core samples from the thickest part of the flotation tailings at the Buckeye site demonstrated the relative mobilities of six deposit-related elements over a 60+ year period of annual weathering cycles. Silver is essentially chemically immobile, lead is

nearly immobile, and copper, zinc, cadmium, and arsenic can be mobilized in the surface weathering environment.

Two classification methods for mine-waste piles were developed. These schemes were based on geochemical data derived from two leach methods and waste-pile size. The geochemical parameters were pH and soluble metal content (As+Cd+Cu+Pb+Zn) from a passive leach, and NAP, soluble metal and soluble iron content from an EPA-1312 leach. Applying these methods to the Boulder River watershed study area reveals that waste piles from the Buckeye mine/mill, the Bullion mine/mill, the Daily West mine, the Cracker mine, and the Boulder Chief mine had high potential for environmental degradation. Wastes from the Crystal mine and the Sirius mine had an intermediate potential, and wastes from the Morning Marie and the Waldy mines had low potential for environmental degradation.

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