Abstract

The rapid assessment of potential acid and metal mobility from mine-waste materials is an area of growing need as the effects of inactive mining sites are evaluated and mitigated across the country and globally. We developed a statistically based, cost-effective sampling strategy to provide a foundation for screening and prioritizing mine-waste piles on a regional or watershed scale. The sampling strategy entails collection from each waste pile of a multi-increment sample (consisting of at least 30 increments (i.e., subsamples)) of the less than 2 mm (minus 10 mesh) fraction of surficial material. One waste-pile sample collected using this sampling strategy contains as much information about average properties as do 30 individual grab samples at \( \frac{1}{30} \) of the analytical cost. Issues of heterogeneity and sampling errors are addressed by this sampling strategy.

The USGS Field Leach Test (FLT) is a simple and fast (15-minute) leaching procedure for the screening of mine-waste materials and serves as an effective indicator of waste-material geochemistry and leachability due to rainfall and snowmelt runoff. When used in conjunction with the sampling strategy described above, the FLT can be performed easily in the field, can provide on-site pH and electrical conductivity information (for field prioritization), and can furnish adequate samples for desired elemental analyses. This test is based on the premise that the most chemically reactive material in weathered mining waste consists of relatively soluble components in the fine-grained fraction of the mine-waste material. Mineralogical examination of the mine-waste material to determine its influence on acid generation and metal release is an additional important characterization tool.

Colleagues at the U.S. Geological Survey and the Colorado School of Mines have developed a simple decision tree (Mining Waste Decision Tree, MWDT) to
determine if a mine-waste pile poses a potential toxicity risk to the aquatic environment. Implementation of the MWDT incorporates the sampling strategy and FLT discussed above, as well as some other simple physical assessments and chemical tests. The MWDT has proven to be an effective tool for screening large numbers of mine-waste piles and extensive areas of contamination. It works particularly well for severe situations (leachate pH less than 5) where aquatic toxicity is based primarily on acidity and metal geoavailability; that is, the release of elements from earth materials. However, recent applications have shown that the MWDT is also useful at marginal sites (pH greater than or equal to 5) where additional leaching and toxicity tests are necessary to evaluate potential metal bioavailability to aquatic biota.

Introduction

Acid rock drainage (ARD) and metal leaching are among the most costly and potentially environmentally damaging issues facing the mining industry (Price, 2005). Special problems are caused by abandoned mines that have not been properly rehabilitated because society must bear the costs of either unmitigated environmental damage or rehabilitation (National Research Council, 1997). Thousands of historical mine-waste piles are present on abandoned and inactive mining sites in the United States and around the world. Release of dissolved metals, acidic solutions, and particulates from these piles creates possible contamination problems for receiving waters and ecosystems.

The rapid assessment of potential acid and metal release from mine-waste materials is an area of growing need as the effects of abandoned and inactive mining sites are evaluated and mitigated across the country. Basic screening-level investigations can provide important information for land-management decisions, and findings from such investigations can define the scope for more detailed investigations. Key indicators of acid generation and metal release should be addressed in the basic screening. Indicators that can be readily measured in the field include leachate pH, electrical conductivity, and some leachable metal concentrations. Other indicators that involve laboratory analyses include additional leachable metal concentrations, mineralogy (including identification, quantification, and mode of occurrence of sulfide and carbonate minerals), and bulk chemistry (including key environmental elements, total sulfur, and inorganic carbon). Discussion of screening-level procedures are found in Herron, et al. (2001), Price (1997, 2005), Price and Errington (1998), Smith et al. (2000a, 2002, 2003), Stewart et al. (2006), and U.S. Environmental Protection Agency (2001).

A screening-level approach that applies field-based, inexpensive sampling and characterization procedures is presented here, and can be used for screening and prioritizing mine-waste piles on a regional or watershed scale. Also discussed is a simple decision tree (Mining Waste Decision Tree, MWDT; Wildeman et al., in press) that determines if a mine-waste pile poses a potential toxicity risk to the aquatic environment.
Sampling Strategy for Characterizing Mine-Waste Piles

Many site-characterization activities, remediation efforts, and regulatory tests require collection of a "representative" sample. In the case of mine-waste piles, sample collection can be a difficult task due to the compositional, spatial, and particle-size heterogeneity of the mine-waste material. We developed a statistically based, cost-effective sampling strategy for mine-waste piles to aid in reconnaissance screening and prioritization of sampling sites (Smith et al., 2000b). This strategy minimizes sampling error while providing an intermixed sample representing the average properties of a given mine-waste pile. It entails collection of a multi-increment sample from individual piles and allows for regional or watershed-based assessments. Even though this sampling strategy requires a bit more effort than the collection of grab samples, the statistical foundation and overall reduction in analytical costs makes this strategy feasible and advantageous.

Target Population

The target population for the mine-waste pile sampling strategy is the surficial (down to 15 cm depth) material dry-sieved to less than 2 mm (minus 10 mesh), but this statistical approach also can be applied to other target populations (e.g., drill cores or trenching). The target population is limited to surficial material because of ease of collection and the assumption that surficial material is the most likely material to impact runoff from snowmelt and rain storms. The less-than-2-mm fraction was chosen out of necessity to reduce the sampling error by decreasing the maximum particle size (see discussion below). The less-than-2-mm fraction encompasses the most reactive material in mine-waste piles (Smith et al., 2000b). Used in combination with leaching studies, the less-than 2 mm fraction may tend to slightly overestimate the leachability of the material as a whole, but this size-fraction cutoff does not appear to miss any leachable phases (Smith et al., 2000b). Also, Price and Kwong (1997) recommend a separate analysis of the less-than-2-mm fraction when evaluating the weathering effects of waste-rock piles.

Sampling Errors

The sampling strategy is designed to address sampling errors related to heterogeneity. We adopted an approach of particulate sampling developed by Pierre Gy (Gy, 1998; U.S. Environmental Protection Agency, 1999). Pitard (1993) provides a detailed discussion of sampling errors. The fundamental sampling error (FSE) generally is the main source of sampling error and is the result of the compositional heterogeneity of particles. The FSE cannot be eliminated, but it can be estimated prior to sampling. The upper limit of the FSE should not exceed $\pm 16\%$ (Pitard, 1993, p. 356), and it is preferable that it be $\leq \pm 5\%$. Based on estimates of FSE, steps can be taken to minimize it and thus minimize the overall sampling error. Important factors in the FSE include heterogeneity, maximum particle size, and sample mass.

If the mass of the population is greater than ten times the mass of the sample, the FSE can be estimated by the following equation:
\[ FSE^2 = \frac{c_l f g d^3}{M_S} \]  

(1)

where
- \( FSE^2 \) is a relative variance
- \( M_S \) is the sample mass (g)
- \( c \) is the mineralogical factor
- \( l \) is the liberation factor
- \( f \) is the shape factor
- \( g \) is the granulometric factor
- \( d \) is the maximum particle size (cm)

The mineralogical factor, \( c \), is the maximum heterogeneity generated by the constituent of interest in the target population. It can be estimated by dividing the approximate density of the material (g/cm\(^3\)) by the average concentration of the constituent of interest (ppm as a fraction of 1), and assumes complete liberation of the constituent of interest. The \( c \) factor can have a wide range of values, primarily depending upon the concentration of the constituent of interest. The liberation factor, \( l \), is a correction factor for \( c \) that takes into account incomplete liberation of the constituent of interest. Values for \( l \) range from 0, when there is no liberation, to 1, when there is complete liberation. Values for the shape factor, \( f \), vary from 0.2 for flakes to 10 for needles, with a value of 1 for cubes. A value of 0.5 is often used for \( f \) and represents a roughly spherical shape (Pitard, 1993). This spherical shape corresponds with our observation of the majority of shapes in the less-than-2-mm fraction of mine-waste materials. The granulometric factor, \( g \), is a correction factor when all the particles are not the same size. Noncalibrated material has a value of 0.25, and calibrated material has a value of 0.55.

The FSE was reduced in the mine-waste pile sampling strategy by decreasing the maximum particle size to 2 mm.

The amount of sample mass collected was determined according to the approach of Pitard (1993) and Gy (1998). The FSE equation shown above can be used to determine the total sample mass necessary to minimize the FSE to an acceptable level. For a FSE of 5%, the above equation can be rewritten as:

\[ \frac{0.0025}{M_S} = \frac{312.5 (0.2)^3}{M_S} \quad \text{or} \quad M_S = \frac{312.5 (0.2)^3}{0.0025} = 1000 \text{ g} \]  

(2)

In this calculation, we assume a density of 1.5 g/cm\(^3\) and a concentration of \( \geq 30 \text{ ppm} \), which yields a \( c \) value of 50,000. We also assume that \( l = 0.05 \) (incomplete liberation), \( f = 0.5 \) (spherical), \( g = 0.25 \) (noncalibrated), and \( d \), the maximum particle size, is 2 mm (0.2 cm). As seen in this equation, a FSE of 5% can be achieved by collecting at least 1,000 g of less-than-2-mm material. If a larger maximum particle size is desired, then a larger sample mass must be collected. Also, for constituents of interest that are present in trace amounts, a larger sample mass or a smaller maximum particle size must be used to achieve the same FSE.
Another sampling error that was addressed in the mine-waste pile sampling strategy is the grouping and segregation error (GSE), which occurs because not all particles are randomly distributed. The GSE can be minimized by collecting random samples and by collecting multiple increments (i.e., subsamples), with an increment defined as a group of particles collected from a population with a single operation of the sampling device. Pitard (1993, p. 187) states that a sample should be made up of at least 30 increments.

**Sampling Procedure**

Multi-increment sampling involves collecting increments from different parts of the mine-waste pile and mixing them together. This more accurately reflects the average concentration of the component of interest than does any single-point sample. This approach reduces bias and improves accuracy over single-point sampling without the expense of additional laboratory analysis.

The strategy entails collection of a surficial (down to 15 cm depth) multi-increment sample from each mine-waste pile that consists of at least 30 increments. The mine-waste pile is divided into at least 30 cells of roughly equal surface area. Increments of roughly equal mass (at least 100 g) are randomly collected from each cell with a stainless steel trowel, successively placed in a plastic bucket, and mixed to create one multi-increment mine-waste pile sample. Particles greater than about 1 cm are excluded during the initial collection procedure. The sample is air-dried and dry-sieved to less than 2 mm (minus 10 mesh). If samples are collected wet, they should be air dried and efforts made to break up clods prior to sieving. The resulting less-than-2-mm sample should weigh at least one kilogram. If a mine-waste pile is too steep to sample all cells, at least 30 increments can be randomly collected at predetermined distances along transects.

In this sampling strategy, we focus on the average properties of a given mine-waste pile. Hence, collecting more sample mass is the same as collecting a larger number of samples in terms of error, but not in terms of cost. One 30-increment mine-waste-pile sample collected using this sampling strategy contains as much information about average properties as 30 individual grab samples at $1/30$ of the analytical cost.

**Screening Procedures for Prioritizing Mine-Waste Piles**

**U.S. Geological Survey Field Leach Test (FLT)**

Leaching tests continue to be one of the primary screening procedures used to evaluate, characterize, and prioritize mine-waste materials (Al-Abed et al., 2006). They are conducted to identify and estimate the amounts of soluble constituents that can be released from waste-rock materials during rainstorms and snow melt. However, many established leaching tests are complicated, time consuming, and require specialized equipment. The USGS Field Leach Test (FLT) can be easily performed in the field or in the laboratory, can provide on-site pH and electrical conductivity information, and can furnish leachate samples for metal analyses. The FLT is described in detail by Hageman (2005) and Hageman and Briggs (2000), and has been applied at a number of sites (Hageman, 2004; Hageman et al., 2005). The test involves combining 50.0 g of less-than-2-mm mine-waste material (collected using the sampling strategy previously
described) with 1.0 L. of deionized water in a capped one-liter polyethylene bottle. The mixture is vigorously shaken for five minutes, and then allowed to settle for 10 minutes. The pH and electrical conductivity can be measured in the field, and subsamples can be filtered (using a syringe and a 0.45 μm filter) and preserved for analysis of chemical constituents. Hageman and Briggs (2000) demonstrated that geochemical trends generated by the FLT correlate favorably with results from the Synthetic Precipitation Leaching Procedure (SPLP, EPA method 1312; U.S. Environmental Protection Agency, 2004b).

Mineralogy

Mineralogical examination is essential to understanding the weathering processes, mineral habit, and reactive minerals that result in ARD and metal leaching from mine-waste piles (Diehl et al., 2006a; Diehl et al., 2006b, these proceedings; Enviromine, 2006b; Hammarstrom and Smith, 2002). Sulfur and carbonate mineralogy and abundance, and mode of occurrence of chemical elements and reactive minerals are usually the focus of mineralogical investigations. In addition, silicate and aluminosilicate minerals that may have long-term ARD neutralizing potential (e.g., chlorite, biotite, anorthite, and olivine) can be identified and quantified. Blowes and Jambor (1990) developed a mineralogically based sulfide alteration index to quantify the degree of oxidation of mine-waste materials. It is a useful exercise to categorize mine-waste materials using such an index to be able to compare relative degrees of oxidation between samples and sites.

X-ray diffraction (XRD) methods can be used in an initial screening to identify mineral phases in mine-waste samples. This information can be combined with bulk chemical analysis to account for residence sites of environmentally important chemical elements and accessory mineral phases. However, weathered mine-waste material commonly contains a significant portion of non- or poorly crystalline material that is not detectable by XRD techniques. Also, many of the important mineralogical processes that relate to ARD generation and leachable metals occur at the microscopic scale. Hence, it is generally necessary to supplement XRD methods with microanalysis techniques to identify and quantify pertinent mineral phases and to determine the mode of occurrence of chemical elements in minerals. Microanalysis techniques, such as scanning electron microscopy (SEM) and elemental X-ray maps, can greatly enhance the understanding and interpretation of mineralogical weathering processes. These techniques are discussed in detail by Diehl et al. (2006b, these proceedings).
Potential for Acid Generation

Determining the potential for mine-waste piles to generate acid can be approached in a number of ways. The use of analogous mineral deposit types (geoenvironmental models) to compare a mine site of interest with the environmental characteristics of geologically and mineralogically similar sites can be very useful in the screening phase (Plumlee, 1999; Plumlee et al., 1999). This approach also can lend insight into the types of acid-base accounting (ABA) tests that should be performed at the screening level and for more detailed characterization (Schmiermund et al., 2006; Schmiermund and Ranville, 2006).

Static ABA is a screening procedure to predict if a mine-waste material will produce ARD. It compares the acid production potential (AP) with the acid neutralization potential (NP). AP and NP determinations involve static procedures or calculations that do not take into account rates of reactions. The ultimate ARD potential is calculated from the ratio of NP to AP (neutralization potential ratio, NPR) or the subtraction of AP from NP (net neutralization potential, NNP), and then by applying various corrections or safety factors. Price (2005) states that the inherent uncertainties in AP and NP determinations may limit the utility of the NNP calculation for forecasting long-term reaction rates.

A number of procedures have been developed to determine AP and NP. Overviews of some of these procedures can be found in Enviromine (2006a), Miller et al. (1997), Price (1997, 2005), Price and Errington (1998), Sobek et al. (1978), Stewart et al. (2006), and U.S. Environmental Protection Agency (2001, 2004b). Individually, each test method has limitations in how accurately it can predict AP and NP. It is good practice to use a combination of test methods to define NPR and identify samples that require further investigation. An initial AP estimate commonly is calculated from the total sulfur concentration. An initial NP estimate commonly is determined by using the Sobek or modified Sobek method (Sobek et al., 1978), which involves addition of hydrochloric acid to a sample, heating, and back-titrating the mixture with sodium hydroxide to determine the amount of unreacted hydrochloric acid.

Net Acid Production. Many of the ABA methods were originally designed for coal-mine waste or for fresh waste material. For the weathered material that is typical of historical mine-waste piles, it is advantageous to adopt a method that incorporates the potential acid production of secondary and tertiary minerals and the potential acid-consuming capacity of host-rock minerals (e.g., carbonates, aluminosilicates, and silicates). We adopted a slightly modified version of the Net Acid Production (NAP) method of Lapakko and Lawrence (1993) for historical mine-waste piles. In this method, acid generation and acid neutralization reactions occur simultaneously, and the end result is a direct measurement of the net amount of acid generated by the entire sample. A 1.0 g sample of pulverized (minus 200 mesh) waste material is digested with a heated solution of 30% hydrogen peroxide, cooled, and filtered. The main difference between this method and the commonly used Net Acid Generation (NAG) test (Miller et al., 1997) is the addition of hydrogen peroxide until all the reactions have gone to completion, which can be important for samples containing large quantities of sulfide minerals, or samples containing organic matter or manganese. The acidic filtrates are titrated to pH 7, and the NAP is calculated in terms of kilograms CaCO\textsubscript{3} per metric ton of waste. Fey
et al. (2000) demonstrated that mine-waste piles segregate into different groups when NAP is plotted against leachable metals. This approach can be used to rank the potential of mine-waste piles to degrade water quality.

**Mining Waste Decision Tree**

Wildeman et al. (in press) have developed a simple Mining Waste Decision Tree (MWDT; figure 1) to determine potential aquatic metal toxicity from mine-waste materials. The MWDT has both a chemical and a physical component; the chemical component addresses the availability of potential contaminants from a mine-waste material, and the physical component addresses the ability to deliver those contaminants to the watershed. The chemical component of the MWDT uses simple physical and chemical tests to determine whether effluent from mine-waste material poses a potential toxicity threat to the aquatic environment, and incorporates the sampling strategy and leaching test (FLT) described above. The MWDT has been used at a number of sites and appears to be a robust method for performing a rapid, low-cost assessment of a site or region prior to more extensive regulatory work.
Figure 1. The Mining Waste Decision Tree (MWDT), a simple assessment scheme to determine potential aquatic metal toxicity from mine-waste materials (modified from Wildeman et al. (in press)).
The MWDT makes a distinction between leachates or waters with pH values less than 5 and those greater than 5. The MWDT assumes potential aquatic toxicity from cationic metals (such as Al, Cd, Cu, Ni, Pb, and Zn) when pH values are less than 5 because these metals generally are largely dissolved and minimally complexed with organic or inorganic ligands. Judgments about probable toxicity come from comparison of the leachate metal concentrations to aquatic toxicity standards (e.g., U.S. Code of Federal Regulations, 2000; U.S. Environmental Protection Agency, 2004a). Although this serves the purpose of a general screening tool, a number of other factors (such as degree of leachate dilution upon entering a receiving water, the actual water-rock ratio in the mine-waste pile, and toxicity-mitigating factors) must be considered if a more complete toxicity assessment is desired. Under acidic conditions, metal binding by dissolved organic carbon (DOC) is reduced because the metal-binding sites are mostly protonated. In mining-impacted systems, iron oxyhydroxides generally precipitate at pH values less than 5, but aluminum oxyhydroxides do not; thus, Al is in the dissolved phase (Nordstrom and Alpers, 1999). Also, sorption of metal cations onto iron oxyhydroxides is generally minimal at pH values less than 5 (Smith, 1999). In addition, there is minimal carbonate alkalinity at pH values less than 5, so survival of aquatic species is difficult due to the lack of both pH buffering and metal-carbonate complexation. Because these metals are present as dissolved, uncomplexed aquo ions, they generally are readily bioavailable (Pagenkopf, 1983). Hence, because these factors promote metal toxicity to aquatic organisms, the MWDT considers leachate metal concentrations to be a sufficient predictor of potential aquatic metal toxicity at pH values less than 5.

Conversely, when pH values are greater than 5, potential aquatic toxicity depends on factors in addition to the metals released from the leaching tests. Hence, leachates and waters with pH values greater than 5 warrant further examination of their chemical composition and potential aquatic toxicity. For example, alkalinity and DOC can influence metal speciation through complexation and can reduce bioavailability. Hardness cations (e.g., Ca and Mg) can compete with metals for biological uptake sites and can also reduce bioavailability (Pagenkopf, 1983). These mechanisms are incorporated into the MWDT through the use of toxicity tests (e.g., Adams, 2006; Blumenstein, 2006; Blumenstein et al., 2005; Moehle et al., 2006; Ranville et al., 2006) or toxicity modeling on the leachate or site-associated water (Ranville et al., 2006; Smith et al., 2006). Use of the Biotic Ligand Model (see Gorsuch et al., 2002) is a promising modeling tool to predict aquatic toxicity (U.S. Environmental Protection Agency, 2002; Ranville et al., 2006; Smith et al., 2006).

Summary

Basic screening-level investigations of mine-waste piles can provide important information for land-management decisions, and findings from such investigations can define the scope for more detailed investigations. We have briefly discussed a sampling strategy and several procedures that lend insight into key indicators of acid generation and metal release from mine-waste piles. These approaches can be used for screening and prioritizing mine-waste piles on a regional or watershed scale. Also discussed is a simple decision tree (Mining Waste Decision Tree, MWDT) that can be
used to determine if a mine-waste pile poses a potential toxicity risk to the aquatic environment.

Acknowledgments

The mine-waste-pile sampling strategy was developed during the U.S. Geological Survey Solid-Phase Sampling Workshop. We acknowledge the helpful input from workshop participants in developing the strategy. We thank Anne McCafferty and Dave Smith for their helpful review comments on this paper. This work was funded by the U.S. Geological Survey Mineral Resources Program, and Colorado School of Mines funding was received through U.S. Environmental Protection Agency Grants R 82951501-0 and R 82950001.

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