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Metal Mine Rock and Waste Characterization Tools: An Overview

K. Lapakko

Minesota Department of Natural Resources, US

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METAL MINE ROCK AND WASTE CHARACTERIZATION TOOLS: AN OVERVIEW

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Kim Lapakko, ADTI-MMS
Minnesota Department of Natural Resources
Division of Lands and Minerals
500 Lafayette Road, St. Paul, MN 55155-4045
kim.lapakko@dnr.state.mn.us

1. INTRODUCTION

Effective and efficient remediation of abandoned metal mine wastes requires tailoring remedial designs to the quality (and quantity) of drainage from the mine waste. Mine wastes that generate problematic drainages may require robust measures, whereas mine wastes that generate environmentally benign drainage may require no remediation whatsoever. The quality of drainage from mine wastes is a function of mine waste composition, which is variable even within a mine site. Furthermore, mine waste drainage quality is variable with time and drainages that appear innocuous today may acidify in the future. Therefore, to remediate abandoned mine wastes effectively and efficiently, the present drainage from mine wastes must be determined and the future quality must be predicted.

The objectives of this presentation are to identify categories of tools available for characterizing mine wastes and predicting drainage quality, and to enumerate some of the specific tools within these categories. The analytical focus of these tools ranges from screening large areas of abandoned mine wastes to determining compositions of individual mineral grains. The presentation which follows is not intended to provide a complete catalogue of tools or to describe those tools presented in detail. A list of references is provided to identify more detailed information on topics of interest. A brief summary of mine waste drainage chemistry is provided to assist the subsequent discussion.

2. MINE WASTE DISSOLUTION

2.1. Acid Generation

The following discussion focuses on mineral dissolution reactions that influence mine waste drainage quality. The reactions presented result in acid production, acid neutralization, and trace metal release. Within the discussion, some of the solid phases of interest in mine waste characterization are identified. Detailed discussion of aqueous geochemistry fundamentals and geochemistry of acid mine drainage is presented by Nordstrom (1999), Nordstrom and Alpers (1999), Smith (1999) and Smith and Huyck (1999).

There are three general types of acid release from mine wastes: iron sulfide oxidation, dissolution of soluble iron sulfate minerals, and the dissolution of less soluble sulfate minerals of the alunite/jarosite series. The oxidation of iron sulfide minerals such as pyrite (FeS_2) and pyrrhotite

($Fe_{1-x}S$, $0.7 < x < 1.0$) is responsible for the majority of acid production by mine wastes (Stumm and Morgan 1981). Equations 1 and 2 represent pyrite and pyrrhotite oxidation by oxygen (after Stumm and Morgan 1981; Nelson 1978). In addition to acid (H^+), sulfate is also released to solution, and its presence in mine waste drainage is typically the first indicator of sulfide mineral oxidation. The iron product presented is ferric hydroxide, although formation of intermediate aqueous ferric hydroxyl species (e.g. $Fe(OH)_2^+(aq)$, $Fe(OH)_3(aq)$) will also result in acid production.

$$FeS_2(s) + (15/4)O_2(aq) + (7/2)H_2O = Fe(OH)_3(s) + 2SO_4^{2-}(aq) + 4H^+(aq) \qquad (1)$$

$$Fe_{1-x}S(s) + [(9-3x)/4]O_2(aq) + [(5-3x)/2]H_2O = (1-x)Fe(OH)_3(s) + SO_4^{2-}(aq) + 2H^+(aq) \qquad (2)$$

Ferric iron can also oxidize sulfide minerals (reactions 3, 4). The amount of acid generated as a result of the iron sulfide oxidation is the same as that for oxidation by oxygen. The additional acid generated is due to precipitation of the aqueous ferric iron (left side of equation) as ferric hydroxide (equation 5).

$$FeS_2(s) + 14Fe^{3+}(aq) + (19/2)H_2O + 15/4O_2(aq) =$$
$$15Fe(OH)_3(s) + 2SO_4^{2-}(aq) + 46H^+(aq) \qquad (3)$$

$$Fe_{1-x}S(s) + (8-2x)Fe^{3+}(aq) + [(9-3x)/4]O_2(aq) + [(53-15x)/2]H_2O =$$
$$(9-3x)Fe(OH)_3(s) + SO_4^{2-}(aq) + (26-6x)H^+(aq) \qquad (4)$$

$$Fe^{3+}(aq) + 3H_2O = Fe(OH)_3(s) + 3H^+(aq) \qquad (5)$$

The rate of iron sulfide oxidation and attendant acid production is dependent on solid-phase compositional variables and microbial activity, as well as the availability of oxygen and water. Oxidation rates vary among sulfide minerals, and it is often reported that reactivity decreases in the order marcasite > pyrrhotite > pyrite (e.g. Kwong and Ferguson 1990). However, different reactivity rankings have been reported by other authors and may be a function of reaction conditions, trace element concentrations of the minerals, and crystal-morphology characteristics, among other factors (Jambor 1994; Plumlee 1999). For a given sulfide mineral, the oxidation rate increases with the available surface area. For example, the oxidation of framboidal pyrite, with a high associated surface area, is reported to be much more rapid than that of euhedral pyrite (Pugh et al. 1984; White and Jeffers 1994).

Whereas the abiotic rate of pyrite oxidation by oxygen decreases slightly as pH decreases, the overall abiotic rate increases as pH decreases into a range where ferric iron becomes the dominant oxidant (Williamson and Rimstidt 1995). Nordstrom (1982) reported that as "pH decreases to 4.5, ferric iron becomes more soluble and begins to act as an oxidizing agent." As pH further decreases, bacterial oxidation of ferrous iron becomes the rate limiting step in the oxidation of pyrite by ferric iron (Singer and Stumm 1970), which is the only significant oxidizing agent in this pH range (Nordstrom 1982; Singer and Stumm 1970; Kleinmann et al. 1981). In laboratory tests the pyrrhotite oxidation rate in the pH range of 3.5 to 4.05 was roughly six to seven times that in the range of 5.35 to 6.1, and the higher rate was attributed to bacterially mediated oxidation (Lapakko and Antonson 1994). Data presented by Nordstrom and Alpers (1999) suggest that the bacterially mediated rate of pyrite oxidation by ferric iron is roughly two to three orders of magnitude faster than the abiotic oxidation by oxygen at pH 2.

These weathering reactions produce acidic, iron- and sulfate-rich waters which can 1) react with sulfide minerals and accelerate their oxidation, 2) evaporate partially or totally to precipitate hydrated iron-sulfates and other minerals, and/or 3) contact host rock minerals, which react to neutralize some or all of the acid. Acidic flow which is not neutralized within the mine waste will exit as acid rock drainage (ARD).

Hydrated iron-sulfate and trace-metal sulfate minerals (Table 1) precipitate during the evaporation of acidic, metal- and sulfate-rich water within mine-waste materials and store acid and metals released by sulfide mineral oxidation. The stored acid and metals can be subsequently released by additional flow through the mine waste (e.g. rain events, snow melt). The more common hydrated iron-sulfate minerals that occur as efflorescent salts on the surfaces of weathering pyrite include melanterite, rozenite, szomolnokite, romerite and copiapite ($FeSO_4{\cdot}7H_2O$, $FeSO_4{\cdot}4H_2O$, $FeSO_4{\cdot}H_2O$, $Fe^{2+}(Fe^{3+})_2(SO_4)_4{\cdot}14H_2O$, and $Fe^{2+}(Fe^{3+})_4(SO_4)_6(OH)_2{\cdot}20H_2O$, respectively; Alpers et al., 1994). According to Nordstrom (1982) and Cravotta (1994), these efflorescent salts are highly soluble and provide an instantaneous source of acidic water upon dissolution and hydrolysis. They are partially responsible for increased acidity and metals loadings in the receiving environment during rain events. Their cumulative storage and incremental release may help explain the lag from mine-waste placement to AMD-formation, particularly in arid climates.

As an example, equations 6, 7 and 8 summarize the step-wise dissolution of melanterite. The net result of equations 6 through 8 is summarized in equation 9, which shows a net production of two moles of acid for each mole of melanterite dissolved. Cravotta (1994) showed that a similar aqueous dissolution of romerite produced six moles of acid for each mole of romerite dissolved.

$$FeSO_4{\bullet}7H_2O\mathit{(s)} = Fe^{2+}\mathit{(aq)} + SO_4^{2-}\mathit{(aq)} + 7H_2O\mathit{(aq)} \tag{6}$$

$$Fe^{2+}\mathit{(aq)} + (1/4)O_2\mathit{(g)} + H^+\mathit{(aq)} = Fe^{3+}\mathit{(aq)} + (\tfrac{1}{2})H_2O\mathit{(aq)} \tag{7}$$

$$Fe^{3+}\mathit{(aq)} + 3H_2O\mathit{(aq)} = Fe(OH)_3\mathit{(s)} + 3H^+\mathit{(aq)} \tag{8}$$

$$FeSO_4{\bullet}7H_2O\mathit{(s)} + (1/4)O_2\mathit{(g)} = Fe(OH)_3\mathit{(s)} + SO_4^{2-}\mathit{(aq)} + (9/2)H_2O + 2H^+\mathit{(aq)} \tag{9}$$

The alunite-jarosite mineral group consists of sulfate minerals which are less soluble than the efflorescent sulfate salts (Table 1). According to Nordstrom (1982), the evaporative concentration of efflorescent iron sulfates leads to the precipitation of the more common iron minerals such as goethite and jarosite. Similar reaction of efflorescent aluminum sulfates will produce alunite. Alpers et al. 1994 reported that jarosite is slightly soluble and can, therefore, contribute acid according to equation 10. For example, preliminary leach studies on natural and synthetic jarosites conducted by the USBM showed a drop in pH from 6 in the deionized water leachant to 3 or 4 after contact with the jarosites. It should be noted, however, that there is a wide variety of these minerals and their reactivity is also variable. For example, Alpers (2000) speculated that a pure jarosite or hydronium jarosite may buffer pH in the range of 1.5 to 3.

$$KFe_3(SO_4)_2(OH)_6\textit{(s)} = K^+ + 3FeOOH\textit{(s)} + 2SO_4^{2-}\textit{(aq)} + 3H^+\textit{(aq)} \tag{10}$$

2.2. Acid Neutralization

The balance between the rates of acid production by iron-sulfide mineral oxidation and host-rock mineral neutralization will determine the acidity of mine-waste drainage. The most effective minerals for neutralizing acid are those containing calcium carbonate and magnesium carbonate, including calcite, magnesite, dolomite, and ankerite ($CaCO_3$, $MgCO_3$, $CaMg(CO_3)_2$, and $CaFe(CO_3)_2$, respectively). Equation 11 represents the dominant acid-neutralizing reaction of calcite ($CaCO_3$) above pH 6.4, whereas equation 12 is the dominant reaction below pH 6.4 (Drever, 1988):

$$CaCO_3\textit{(s)} + H^+\textit{(aq)} = HCO_3^-\textit{(aq)} + Ca^{2+}\textit{(aq)} \tag{11}$$

$$CaCO_3\textit{(s)} + 2H^+\textit{(aq)} = H_2CO_3\textit{(aq)} + Ca^{2+}\textit{(aq)} \tag{12}$$

Of the carbonate minerals, calcite ($CaCO_3$) dissolves most rapidly (Busenberg and Plummer 1986). Relative to calcite, the rate of dolomite [$(Ca,Mg)CO_3$] dissolution is about an order of magnitude slower (Busenberg and Plummer 1982) and the rate of magnesite ($MgCO_3$) dissolution is about four orders of magnitude slower (Chou et al. 1989). The rate of siderite dissolution under anoxic conditions is reported to be three orders of magnitude slower than that of calcite (Greenberg and Tomson 1992). However, iron and manganese carbonates do not provide net acid neutralization under oxidizing conditions, due to oxidation of the released iron or manganese, the subsequent hydrolysis and precipitation of these metals, and the consequent acid production (e.g. equations 7, 8).

Dissolution of silicates such as plagioclase-feldspars (e.g. anorthite in equation 13, Busenberg and Clemency 1976) and olivine (e.g. forsterite in equation 14, Hem 1970) can also neutralize acid. However, their rates of dissolution and consequent acid neutralization are slow relative to the carbonate minerals (Nesbitt and Jambor 1998). For example, White et al. (1999) noted that "at near neutral pH, the dissolution rate of calcite is approximately 7 orders of magnitude faster than the dissolution of plagioclase feldspar." Nonetheless, silicate mineral dissolution can maintain neutral conditions if the rate of acid production is quite slow (Lapakko and Antonson 1994; Lapakko et al. 1997; Lapakko and Antonson 2002). The effectiveness of silicate minerals in neutralizing acid increases with increasing mineral surface area which, in turn, increases with increasing mineral content and decreasing grain size.

$$CaAl_2Si_2O_8\textit{(s)} + 2H^+\textit{(aq)} + H_2O\textit{(aq)} = Ca^{2+}\textit{(aq)} + Al_2Si_2O_5(OH)_4\textit{(s)} \tag{13}$$

$$Mg_2SiO_4\textit{(s)} + 4H^+\textit{(aq)} = 2Mg^{2+}\textit{(aq)} + H_4SiO_4\textit{(aq)} \tag{14}$$

2.3. Trace Metal Release by Trace Metal Sulfide Oxidation

Trace metals are metals which occur at low average concentrations in the earth's crust but can be present at elevated levels in mineralized areas. Trace metals commonly occur as sulfide minerals, the oxidation of which releases the trace metal from the highly insoluble sulfide phase (e.g. reaction 15). Once released to solution, there are several types of reactions that can influence the migration and fate of these minerals. Smith and Huyck (1999) present a series of diagrams for the generalized relative mobility of elements under different environmental conditions, for use as an initial estimate of metal behavior in surficial environments. At a regional scale, generalizations frequently can be used to estimate broad trends in metal mobility. However, as the scale becomes increasingly finer, estimating metal behavior generally becomes increasingly difficult (Smith and Huyck 1999).

In general, metals may remain in solution or be removed in secondary phases. For removal from solution, trace metals may precipitate as oxides, hydroxides, or carbonates, be adsorbed by surfaces such as iron oxyhydroxides (Smith 1999), or coprecipitate with other solid phases. In acidic solutions trace metal removal is limited, and elevated trace metal concentrations are often associated with these solutions. However, circumneutral drainages can also contain elevated concentrations of trace metals such as nickel, copper, cobalt (Lapakko 1993a), zinc, manganese (Smith and Huyck 1999), molybdenum (Brown 1989), arsenic, and antimony. Concentrations of molybdenum, arsenic, and antimony in particular can be elevated even as pH increases above 7.

Oxidation of arsenic and antimony sulfides can produce acid, as can oxidation of the iron sulfide fraction of mixed sulfide minerals such as chalcopyrite (Plumlee 1999). Other trace metal sulfide oxidation will produce acid if and only if the metal released hydrolyzes (reaction 16) or precipitates as a hydroxide, oxide, or carbonate (reaction 17). For most trace metals this will occur only at pH levels above 6, and as pH decreases below this level the secondary phases will dissolve. Consequently, they do not generally contribute to acid production observed at lower pH levels.

$$\mathrm{ZnS}(s) + 2\mathrm{O_2}(aq) = \mathrm{Zn^{2+}}(aq) + \mathrm{SO_4^{2-}}(aq) \tag{15}$$

$$\mathrm{Zn^{2+}}(aq) + \mathrm{H_2O}(aq) = \mathrm{Zn(OH)^{+}}(aq) + \mathrm{H^{+}}(aq) \tag{16}$$

$$\mathrm{Zn^{2+}}(aq) + 2\mathrm{H_2O}(aq) = \mathrm{Zn(OH)_2}(s) + 2\mathrm{H^{+}}(aq) \tag{17}$$

2.4. Key Solid-Phase Factors Controlling Mineral Oxidation and Dissolution

Whereas the acid-producing and acid-neutralizing mineral contents, and the balance of these contents, influence mine waste drainage quality, there are several subtle mineralogical factors which are also influential. Individual minerals may be entirely liberated from the rock matrix, occur interstitial to other minerals (partially liberated), or as inclusions within other minerals. The extent of liberation affects availability for reaction. For example, acid-producing or acid-neutralizing minerals included within minerals such as quartz will be essentially unavailable for reaction.

Oxidation of sulfide minerals and dissolution of carbonate minerals are surface reactions and, therefore, the rates of these reactions are dependent on the reactive surface area. Reactivity decreases as mineral surfaces are covered with coatings, such as iron oxyhydroxides, whereas the concentration of lattice defects tends to increase reactivity. Mineral surface area is dependent on the extent to which the mineral is liberated from the rock matrix, mineral grain size, and the "roughness" of the mineral surface.

3. GEOENVIRONMENTAL MODELS

Geoenvironmental models provide an initial assessment of potential water quality impacts based on characteristics of the mineral deposit. An initial compilation of geoenvironmental models is given in du Bray (1995). A geoenvironmental model has been defined as a "compilation of geologic, geochemical, geophysical, hydrologic and engineering information pertaining to environmental behavior of geologically similar mineral deposits 1) prior to mining, and 2) resulting from mining, mineral processing, and smelting" (Plumlee and Nash 1995). Plumlee et al. (1994) noted that "a detailed understanding of mineral deposit geology and geochemical processes, which control element dispersion into the environnment, is crucial for the effective prediction, mitigation, and remediation of the environmental effects of mineral resource development." In developing a geoenvironmental model, information from the field of economic geology is compiled and translated from the language of economic geology and mining engineering to the language environmental science (Seal et al. 2000).

Key descriptors in an environmental model are deposit type, related deposit types, deposit size, host rocks, surrounding geologic terrane, wall rock alteration, nature of ore, mining and ore processing methods, deposit trace element geochemistry, primary mineralogy and zonation, secondary mineralogy, soil and sediment signatures, topography, hydrology, drainage signatures, climatic effects and potential environmental concerns (Plumlee 1999; Plumlee et al. 1999). Thus, sites can be initially assessed by determining site characteristics and comparing them with previously determined relationships between similar characteristics and their potential for adverse impacts on water quality.

4. NON-INVASIVE TECHNIQUES

Non-invasive techniques are summarized in Smith et al. (2000a; 2000b). Imaging spectroscopy and geophysical methods are identified as non-invasive techniques for screening large areas for abandoned mine wastes. These tools can be used to locate mine wastes and assist in prioritizing sites for further characterization. Imaging spectroscopy can be used to identify minerals generated by sulfide-mineral weathering that are exposed on the earth's surface. The Airborne Visual and Infra-Red Imaging Spectrometer (AVIRIS) when flown at an altitude of 20 km can cover a path 10.5 km wide with resolution to 17 meter pixels (Smith et al. 2000a). The data generated are digested using the USGS Tetracorder (Clark et al. 1990). Manual spectrometers allow this technology to be applied readily in the field.

Swayze et al. (2000a; 2000b) used AVIRIS in conjunction with the USGS Tetracorder to map iron-bearing products (jarosite, goethite, hematite) of sulfide-bearing mine waste weathering. Jarosite appeared to be the best indicator of acidic conditions. Dalton et al. (2000) applied the same technology to determine the presence of both acid-generating and acid-neutralizing minerals in a watershed with sulfide mineralization.

Airborne geophysical surveying (radiometric, magnetic, electromagnetic) can also be used to augment geological mapping data for location of abandoned mine wastes and preliminary ranking of sites with regard to potential water quality impacts. These techniques can be applied to map subsurface lithology, structure, and ground water flow. B. Smith et al. (2000) described application of these techniques at both regional (e.g. state) and local (e.g. watershed) scales. Overviews of geophysical techniques are provided by Campbell and Fitterman (2000) and Campbell et al. (1999).

5. TOOLS TO ASSESS MINE WASTE REACTIVITY

5.1. Mine Waste Sampling

Mine waste characterization approaches described in sections 5 through 7 involve testing of individual samples. The collection of samples and subsequent testing must be based on clearly defined objectives. Collecting representative waste rock samples from abandoned mine lands can be complicated, "due to the compositional, spatial, and size heterogeneity of the waste material" (Smith et al. 2000c). Sampling theory and practice are addressed by Pitard (1993), and sampling specifically related to tailings (MEND 1989; Runnels et al. 1997) and waste rock (MEND 1994; Runnels et al. 1997, Smith et al. 2000c) has also been addressed. With regard to proposed mines, waste characterization must describe the compositional variation within and among the various rock units and tailings types identified in the mine plan. Drill core, bulk samples and test shaft samples can be used to represent waste rock, and bench scale test or pilot plant products can provide tailings samples (Lapakko 1990). Appropriate samples can be selected from this collection and subjected to tests selected to address program objectives.

5.2. Balance of Acid Production and Acid Neutralization (Static Tests)

Static tests are short term (usually measured in hours or days) and relatively low cost tests developed to provide an estimate of a mine waste's capacity to produce acid and its capacity to neutralize acid. These tests measure only the capacities for acid production and neutralization and do not consider 1) the availability of acid-producing and acid-neutralizing minerals or 2) differences between the respective dissolution rates of acid-producing and acid-neutralizing minerals. Thus, these tests are commonly used as a screening tool, and their implications are subject to further verification. These tests are discussed in detail by White et al. (1999).

The most commonly-used static test is known as acid-base accounting (ABA; Ferguson and Erickson 1988). Variations of ABA used in North America include standard ABA (Sobek and others 1978), modified ABA (Coastech Research Inc. 1989; Lawrence 1990; Lawrence and Wang 1996), and the B.C. Research Initial Test (BCRI, Bruynesteyn and Duncan 1979). These static tests quantify the potential of mine waste samples to produce and neutralize acid. They quantify acid producing potential (AP) using either total sulfur or sulfide-sulfur content to estimate the quantity of acid-producing minerals present. The total sulfur content will overestimate the actual AP of samples containing substantial non acid-producing sulfate minerals (e.g. barite or gypsum). On the other hand, the sulfide-sulfur measurement will underestimate the actual AP of samples containing substantial acid-producing sulfate minerals (e.g. melanterite or jarosite). Knowledge of the mine waste sulfate mineralogy will indicate if the sulfate minerals present, if any, are acid producing and allow selection of the more appropriate AP quantification.

Existing techniques, such as those using a combustion furnace (e.g LECO furnace) with subsequent quantification of the sulfur dioxide evolved, are capable of accurately determining total sulfur and, therefore, the maximum acid production potential. The American Society of Testing and Materials (ASTM) includes ASTM E-1019, ASTM E-395-70, ASTM E-1915-97 among these methods (ASTM 2000a). Sulfide-sulfur is often determined by treating the sample to remove a specific sulfur phase, and using a determination of total sulfur on the original and treated sample to determine the change in sulfur content resulting from the extraction. Minerals which present problems include barite and members of the alunite-jarosite series. Sulfur analyses are discussed in greater detail in section 6.2.1.1.

Different static-test methods can produce markedly different neutralization potentials (NP) for the same sample (Lapakko 1994a). Protocol variables which may contribute to these differences include mine-waste particle size (tailings are typically run "as received"); "digestion" variables such as the acid used, amount of acid added (i.e. digestion pH), temperature, and duration; and the endpoint pH of the "back titration", if a back titration is used. The most influential of the protocol variables are particle size, extent of acid addition, and the back titration endpoint. The extent to which protocol variables will affect the measured NP is dependent on the sample mineralogy. The effects of individual silicate minerals on NP is presented by Jambor et al. (2000). If static tests are used for NP determinations on a lithology, values should be compared with mineralogical determinations of calcium and magnesium carbonate content to determine the accuracy of static test measurements.

The Net Acid Production (NAP) (Coastech Research Inc., 1989) and Net Acid Generation (NAG) (Miller et al. 1990) tests are based on the principle that hydrogen peroxide accelerates the oxidation of iron sulfide minerals. The acid consequently produced dissolves neutralizing minerals present, and the net result of the acid production and neutralization can be measured directly. This test does not require sulfur determinations and is, therefore, more readily conducted in a field laboratory than other static tests. Fey et al. (2000) used a hydrogen peroxide based procedure, a modification of the NAP test to account for acid production by iron sulfide minerals as well as acid released from soluble acidic salts. The NAP values derived, in conjunction with the sum of five leachable metals or leachable iron was used to rank the potential quality of drainage from different waste rock samples.

5.3. Presence of Soluble Salts

Paste pH is a common and simple field test used to assess the presence of soluble acid salts on mine wastes. Most methods use a 1:1 weight ratio of distilled water to air dried solids, with measurements of the mixture made by a pH meter calibrated at pH 4.00 and 7.00. Sample mass and equilibration time of the water-solids mixture prior to pH measurement vary among methods (Hammarstrom and Smith 2000). The procedure described by MEND (1990) determines pH of a mixture of 10 g rock (-60 mesh) and at least 5 mL distilled water (water addition is adequate to saturate, but not cover, the rock). The Acid Concentration Present test is slightly more involved but supplies an estimate of acidity present rather than simply pH (Bucknam 2000). A mixture of 20.0 g rock (-200 mesh) and 50 mL deionized water is agitated, the initial pH is recorded, and the mixture is titrated to pH 7 with NaOH.

Although acid generation has received the most attention, leachable metals are a potential source of toxicity in metal mine waste drainage, and several tests have been developed to assess their presence. Among these tests are the U.S. Environmental Protection Agency (1994) Toxicity Characteristic Leaching Procedure (TCLP, Method 1311) and Synthetic Precipitation Leaching Procedure (SPLP, Method 1312). The TCLP was designed to simulate leaching in sanitary landfills and involves leaching with acetic acid, which has a strong capacity to leach lead. It is required under the Resource Conservation and Recovery Act (RCRA) to define a hazardous waste. The SPLP more closely approximates conditions in a waste rock dump (Smith 1997) and substantial data on SPLP testing of mine wastes have been generated (Hammarstrom and Smith 2000). This test has been designated as American Society for Testing and Materials (ASTM) method D 6234-98, Standard Test Method for Shake Extraction of Mining Waste by the Synthetic Precipitation Leaching Procedure (ASTM 2000a). A third test is the Nevada Meteoric Water Mobility Procedure (MWMP). This test is conducted in columns (I.D. = 6 in.) and allows for both larger masses and particle sizes of rock to be tested. This method is currently in the ASTM review process.

Hageman and Briggs (2000) describe a field leach test which provides an indication of the extent of readily soluble salts, including those which are acidic and/or contain trace metals, stored in mine waste dumps. Such a tool can be used for screening by qualitatively characterizing waste rock dump material. Fifty grams of material less than two mm in diameter is placed in one liter of deionized water, shaken vigorously for five minutes, and allowed to settle for 10 minutes. Aliquots are analyzed for pH and specific conductance in the field, and others are filtered and preserved for subsequent analyses for dissolved components. Test results were comparable to those for the Synthetic Precipitation Leaching Procedure (U.S. Environmental Protection Agency 1994).

5.4. Metal Partitioning

The concentration of a trace metal in a mine waste does not necessarily reflect its potential for release. The phase in which trace metals exist determines how readily available they are for release to the environment. Sequential extractions are used to operationally define the ease with which constituents are released to solution from the solid phase. For mine wastes, Leinz and others (1999, 2000) developed a series of extractions to partition the following phases: water soluble, ion exchangeable, associated with carbonates, associated with manganese oxides and amorphous iron oxides, associated with crystalline iron oxides, occurring in sulfide minerals, and occurring as or in silicate minerals. Additional information on extraction techniques and their application is also available in the literature (Tessier et al. 1979; Chao and Zhou 1983; Chao 1984; Ribet et al. 1995; Kelsey et al. 1996; Harrington et al. 1998).

6. TRADITIONAL GEOCHEMICAL ANALYSES

6.1. Introduction

There are numerous analytical tools available to accurately determine the mine-waste solid phase characteristics which control drainage quality. Chemical analyses can estimate the content of acid-producing and acid-neutralizing minerals, and accurately quantify trace metals contents in mine waste samples. Furthermore, chemical analyses can determine whole rock composition that, in conjunction with x-ray diffraction analysis, can be used to determine mineralogic composition. Mineralogic analyses are necessary to determine most of the factors identified in the previous section.

6.2. Chemical Analyses

This section is intended to identify methods used by geochemical laboratories to analyze mine waste samples for (1) elements and compounds present in minerals which generate and neutralize acid, (2) trace metals, and (3) whole rock constituents which, in conjunction with x-ray diffraction analyses, can be used to quantify mineralogical composition. Procedures selected are dependent on the mine waste sample mineralogy. Consequently a knowledge of this mineralogy as well as expertise in chemical analyses is required to select appropriate techniques. Accuracy required and cost must also be considered. It should be noted that appropriate sampling and sample preparation techniques are essential to obtaining reliable data. Although these topics are beyond the scope of the present report, techniques for sampling abandoned mine wastes are presented by Smith et al. (2000a) and methods of rock sample preparation are discussed by Crock et al. (1999).

6.2.1. Sulfur and Carbonate Analyses

Of particular importance are acid-producing sulfur species and acid-neutralizing carbonate species. Acid-producing sulfur species include sulfide associated with iron sulfide minerals and sulfate associated with jarosite, alunite and efflorescent sulfate minerals. Trace metal sulfides will contribute to drainage acidity if, and only if, the associated trace metals precipitate as hydroxides, oxides, or carbonates. These minerals are of interest because they can contribute trace metals to drainage. Jarosites and alunite must be distinguished from non-acid-producing sulfate minerals such as gypsum and anhydrite. Calcium and magnesium carbonate minerals are important because their dissolution can neutralize acid. It is necessary to distinguish these minerals from carbonates of iron and manganese which, under oxidizing conditions, will yield no net acid neutralization.

Except where noted, the methods presented for sulfur and carbonate analyses employ a high temperature combustion furnace and are among those used by Newmont Mining Corporation (Bucknam 1999). Additional discussion of other analytical methods for sulfur and carbon methods is presented by Crock et al. (1999), with details presented by Arbogast (1996) and Jackson et al. (1987). CANMET, Natural Resources Canada, also has a manual of analytical methods (CANMET 2000).

6.2.1.1. Sulfur Determinations

Given the different forms in which sulfur can occur in metal mining wastes and their different potentials for acid production, an analytical scheme to speciate sulfur would be most beneficial. Tuttle et al. (1986) developed such a scheme to quantitatively recover acid-soluble sulfate, sulfur associated with monosulfide minerals, disulfide minerals and organics from oil shales and associated rocks. Development of a similar approach for metal mining wastes is presently in progress at the US Geological Survey (USGS) and a publication on this work is anticipated in 2002 (Briggs 2001).

Total sulfur can be determined by igniting the sample in a high temperature combustion furnace at 1500 to 1700°C and the resultant gas phase is analyzed for sulfur dioxide, as described in ASTM method E1915-97 (ASTM 2000a). Accelerators are used to quantitatively convert all forms of sulfur to sulfur dioxide. A halogen trap should be used to prevent interference from chlorine and fluorine gas generated during combustion. These gases can interfere with the sulfur dioxide measurement, leading to overestimation of the total sulfur content. Additional ASTM methods for total sulfur include D 4239-00, D 3177-89 and D5016 (ASTM 2000a). It should be noted that methods D4239-00, D3177-89 and D5016 have been formally tested only on coal and coke or their ashes, and interlaboratory testing is required to determine their applicability to metal mine wastes.

Other sulfur species are often determined by treating the sample to remove a specific sulfur phase, and using a determination of total sulfur on the original and treated sample to determine the change in sulfur content resulting from the extraction. For example, Newmont Mining Corporation (Bucknam 1999) determines sulfide content by heating the sample at 550°C for one hour to convert sulfide to sulfur dioxide (pyrolysis). The sulfide content is determined as the difference between total sulfur in the sample and in the residual, as described in ASTM method E-1915-99 (ASTM 2000a). Sulfide minerals vary in their pyrolysis loss under these conditions, with chalcopyrite ($CuFeS_2$) and galena (PbS) reporting only minor losses, leading to underestimation of the sulfide content. Some sulfates such as sulfuric acid, jarosite, and iron sulfates may be partially decomposed, leading to overestimation of the sulfide content.

In an alternate method Newmont digests the sample with sodium carbonate to remove sulfate minerals and the residual is analyzed for total sulfur (Bucknam 1999). The residual sulfur is assumed to be present as sulfide and the difference between the two analyses is assumed to be the sulfur originally present as sulfate. Orpiment (As_2S_3) and realgar (AsS) will dissolve to some degree during the digestion, leading to underestimation of the sulfide content. Jarosite and alunite may not totally dissolve in the digestion, leading to overestimation. Inclusion of this method as part of ASTM E-1915 (ASTM 2000a) has been proposed and, to assess its reliability, the method is scheduled for interlaboratory testing. A method which estimates pyritic sulfur as the difference between hydrochloric acid residual and nitric acid residual sulfur contents is also being evaluated for inclusion in this method.

As is clear from the previous two methods, the fractionation of sulfur-bearing minerals is subject to interference. Consequently, when encountering samples from a given lithology, Newmont will use several different methods and take the rock mineralogy into account before selection of a specific method to determine sulfide (or other sulfur species). Due to the uncertainty in determining what sulfur fractions are removed by a given extraction strategy, analytical results are sometimes reported operationally, that is, in terms of the extraction procedure. Acid soluble sulfate is one such example (Crock et al. 1999; Arbogast 1996). One split of the sample is analyzed for total sulfur. A second split is leached with 0.1 N HCl and the residue is analyzed for total sulfur. The difference between the two sulfur values is acid soluble sulfate.

Two sulfate species which are particularly difficult to determine are barite and members of the alunite-jarosite group. Barite can be solubilized using sodium carbonate fusion and/or chemical determinations of barium content can be used to estimate barite content. The alunite-jarosite group is diverse in composition and reactivity and, consequently, extractions for the chemical analysis of this group are not standardized. Newmont uses a hot sodium carbonate digestion to solubilize these minerals, but questions the validity of this method, particularly on advanced argillic alteration lithologies (Bucknam 2000). Some forms of barite also may be problematic, underscoring the importance of considering sample mineralogy when selecting chemical analytical methods.

6.2.1.2. Carbon Determinations

ASTM E-1915-97 (ASTM 2000a) is one method for determination of total carbon content (carbon present as carbonate, organic carbon, and graphite). The sample is ignited in a furnace at 1500 to 1700°C in an oxygen atmosphere (operate instrument according to manufacturer's instructions). The gas generated is filtered and analyzed by non-dispersive infrared absorbtiometry to determine the amount of carbon dioxide generated by combustion of all forms of carbon in the solid. There are no significant interferences.

As was described for determination of sulfur species, carbon species are often determined by treating the sample to remove a specific carbon phase, and using a determination of total carbon on the original and treated sample to determine the change in carbon content resulting from the extraction. Parallel to their method of sulfide determination, Newmont uses pyrolysis to determine carbonate content (Bucknam 1999). The sample is heated at 550ºC for one hour to drive off organic carbon as carbon dioxide (and sulfide sulfur as sulfur dioxide). The carbonate carbon is estimated as the total carbon in the residue, and tends to be slightly low due to some loss of carbonate during pyrolysis. This method has the advantage of allowing determination of carbonate and sulfide contents with the same preparatory step.

Hammack (1994) indicated that the difference in temperatures at which carbon species decompose can be used to speciate carbon. Transition metal carbonates (e.g. siderite, $FeCO_3$, and rhodochrosite, $MnCO_3$) decompose, yielding CO_2, in the range of 220ºC to 520ºC. Whereas calcite decomposes slightly between 300ºC and 500ºC, most decomposition occurs above 550ºC. Dolomite decomposes at 800ºC to 900ºC.

A second method used by Newmont to determine carbonate content is referred to as "Acid Insoluble Carbon" (Bucknam 1999). The sample is digested with hot 20% HCl, dried, and rinsed three times with distilled water to remove residual chloride, which can interfere with the subsequent analysis for total carbon. The residual solid is analyzed for total carbon and assumed to be organic carbon. The digestion is assumed to dissolve all carbonates present and the residual solid contains only organic carbon, which includes graphite. The carbonate carbon content is the difference between total carbon and acid insoluble carbon.

To non-quantitatively screen for the presence of calcite, the sample is subjected to digestion in 10% acetic acid at 90ºC for 30 minutes (Acetic Acid Soluble Calcium, Bucknam 1999). An aliquot of the solution is taken and diluted to volume. The sample is preserved with 2% HCl, lanthanum (1%) is added to inhibit matrix effects, and the solution is analyzed for calcium using flame atomic absorption spectrophotometry. Newmont uses this method to estimate the calcite content of some lithologies.

6.2.2. Total Major (whole rock), Minor and Trace Metals

6.2.2.1. Introduction

Analytical techniques for determining metal concentrations in rock samples can be generally categorized as nondestructive or destructive. Nondestructive techniques analyze the sample directly, leaving it intact. In contrast, destructive techniques dissolve the sample and the resultant aqueous solution is submitted for analysis by one of several methods.

6.2.2.2. Nondestructive Techniques

Two nondestructive techniques discussed by Crock et al. (1999) are instrumental neutron activation analysis (INAA) and X-ray fluorescence spectrometry (XRF). Some XRF techniques fuse the sample into a lithium borate glass and would, therefore, be considered destructive (Seal 2000). INAA involves irradiation of samples in a neutron flux to produce radionuclides of the elements present. The resultant radioactivities are measured by gamma-ray spectroscopy to determine the elemental concentrations present. The method has a short count alternative which determines concentrations of 24 elements and a long count alternative which determines 40 elements.

Two alternative XRF methods are described by Crock et al. (1999). Both methods subject the sample to short wavelength X-rays which induce emission of longer wavelength X-rays from the sample. The elements present and their concentrations are determined by identification of their characteristic X-ray spectra. The sensitivity and detection limits for both methods are dependent on the rock matrix. Wavelength dispersive XRF (WDXRF) is used to determine contents of elements with atomic numbers less than or equal to 26, generally referred to as major elements or whole rock constituents, although it can be used for elements of higher atomic numbers. Energy dispersive XRF (EDXRF) is used for determination of elements with atomic numbers greater than 26. It has the additional benefit of being transportable for field use.

6.2.2.3. Destructive Techniques

Acid digestion, sintering, and fusion are destructive techniques used to dissolve rock samples, and the resultant solution is analyzed by one of several techniques (Chao and Sanzolone 1992; Crock et al. 1999). An aqua regia (hydrochloric and nitric acids) digestion has been used by commercial laboratories to attack sulfides, as well as some oxides and silicates, to determine trace metal concentrations. A "near total" low-temperature, atmospheric-pressure digestion using a combination of hydrofluoric, hydrochloric, nitric and perchloric acids (Crock et al. 1983) is also employed by some of these laboratories. Relative to sintering and fusion, this approach has the advantage of limiting potential trace element contamination from the sintering and fusion fluxes. Furthermore, there is less dilution of trace element concentrations when the sample is solubilized, allowing more accurate quantification.

Certain minerals (spinels, beryl, tourmalines, chromite, zircon, monazite, niobates, tungstates, topaz, cassiterite) are resistant to acid digestion and must be subjected to sintering or fusion and subsequent acid digestion to bring them into solution. Most of these minerals will be solubilized by use of a sodium peroxide sinter. However, alternative fluxes may be required to solubilize specific minerals (Sulcek and Povondra 1989). Common fusion reagents are lithium metaborate, sodium and/or potassium hydroxide, sodium carbonate, and alkali persulfates. The benefits of sodium peroxide sintering over fusion are that it decomposes zircon, does not attack the graphite crucible as much as fusion, and can be more effectively removed from the crucible than a fusion melt (Lamothe 2001). Furthermore, sodium peroxide sintering is the only reliable method of solubilizing rare earth elements (Lichte et al. 1987), although these elements can also be determined by INAA.

Whereas sintering and fusion, with subsequent digestion, can solubilize a wider variety of minerals, their use has disadvantages in the subsequent analysis. Crock et al. (1999) cite disadvantages of these methods as elevated salt concentrations in the digestate, greater dilution requirements, and contributions of elements in the sintering and fusion reagents to the digestate. They are generally more appropriate for determination of whole rock components than trace elements.

The most common methods for analysis of digestates are flame atomic absorption spectroscopy (F-AAS), graphite furnace-atomic absorption spectroscopy (GF-AAS), inductively coupled plasma-atomic emission spectroscopy (ICP-AES), and inductively coupled plasma-mass spectrometry (ICP-MS) (Hall 1995). The first two methods analyze solutions for a single element at a time, whereas the ICP methods analyze solutions for multiple components simultaneously. Crock et al. (1999) provide detection limits for these methods and discuss their advantages and disadvantages.

6.2.3. Mineralogical Analyses

The mineralogical techniques most commonly applied to mine waste samples are optical microscopy, X-ray diffraction (XRD) and scanning electron microscopy (SEM). Jambor and Blowes (1998) reported on the application of traditional mineralogical techniques to analysis of sulfide-bearing mine wastes. The authors noted that XRD "provides an easy and reliable method of identifying the common carbonate minerals." The integrity of mineralogic results is improved by subjecting polished thin sections to analysis by XRD (to obtain diffractograms), transmitted-light microscopy (for petrographic description) and reflected-light microscopy (to define "ore" mineralogy). Optical microscopy is recommended in addition to XRD in order to verify mineral identifications, resolve any ambiguous or overlapping XRD data, and to identify minerals unidentified by XRD due to their low content or poor crystallinity. References for additional information on XRD include Klug et al. (1974) and Azaroff and Buerger (1958).

It should be noted that XRD cannot identify amorphous minerals, such as oxyhydroxides of iron, aluminum and aluminosilicates, which are commonly associated with acidic drainage. It can, however, be used to determine the amount of amorphous material present using the Rietveld Method (Young 1993). The USGS is presently developing a sequential extraction scheme to determine the composition of amorphous materials in mine wastes (Sutley 2001).

Analyses can be further augmented by scanning electron microscopy (SEM), which can achieve magnification roughly 100 times that of an optical microscope. Adding an X-ray spectrometer to the SEM allows chemical analysis of small areas of interest. Two types of X-ray spectrometry are energy-dispersive (EDS) and wavelength-dispersive X-ray spectrometry (WDS), the latter of which is also referred to as electron-probe microanalysis (EPMA). EDS is less expensive and has detection limits about an order of magnitude higher than those for EPMA (Gill 1997).

SEM and X-ray spectrometry are "essential to obtain compositional data for solid-solution minerals, to obtain information on fine-scale features such as alteration rims, and to verify the identification of grains too fine-grained to be unambiguously identified by optical microscopy" (Jambor and Blowes 1998). This is of particular value in ascertaining the composition of complex carbonate minerals to detemine the extent of acid-neutralizing components. A variety of approaches to determining ore and the associated environmental mineralogy are presented by Cabri and Vaughan (1998). Applications of mineralogical techniques to determine reactions within mine wastes and to assess mine waste remediation in dry climates is presented by Esposito (1999) and Whitney et al. (1995), respectively.

7. KINETIC TESTS

Kinetic tests are tests in which mine-waste samples are subjected to dissolution, often with the objective of empirically estimating the potential quality of drainage from the mine waste. These tests are also used to assess the relative potentials of mine waste samples to produce acidic drainage, rather than to simulate field drainage quality (White and Lapakko 2000) and, in some cases, to determine rates of mineral oxidation and dissolution. Although these tests do not precisely simulate dissolution in the field, and results are subject to interpretation, they represent a useful tool when no field data are available on the mine waste of interest. A number of kinetic tests have been used for dissolution testing of mine wastes (e.g. Caruccio 1968; Lapakko 1988; Lawrence 1990; Ferguson and Morin 1991), some of which are listed below. Several studies provide comparisons among kinetic test results (Coastech 1989; Bradham and Caruccio 1991; Lapakko 1993b; Lawrence 1995).

Kinetic Tests

- Commonly used laboratory tests
  - Humidity cell (Caruccio 1968)
  - Modified humidity cells (Lawrence 1990)
- Less commonly used laboratory tests
  - Large scale humidity cells (Brodie et al. 1991)
  - Columns (e.g. Bradham and Caruccio 1991)
- Rarely used laboratory tests
  - Wet-dry cycle test (e.g. Lapakko 1988, 1993b)
  - Shake flask test
  - Soxhlet test (Singleton and Lavkulich 1978)
  - Elevated temperature test (modified from Renton et al. 1988)
- Field tests
  - Tubs (Bradham and Caruccio 1991)
  - Test piles (Lapakko 1994b)

Kinetic tests generally accelerate weathering beyond that observed in the field. It has been noted that some natural conditions, such as those typical of tropical areas (e.g., surface temperatures that exceed 40°C, compounded by tropical rainfall), are more conducive to weathering than those commonly employed in kinetic tests. Under such extreme temperatures, iron-sulfide mineral oxidation would increase. Critical components of accelerated-weathering tests include an abundant supply of oxygen, and a sufficient volume of water to help flush a large percentage of the reaction products from the sample being tested. Effects of weathering in the kinetic tests can be observed more quickly than in the natural environment, even under extreme conditions, due to factors such as the relatively large fraction of rock mass exposed to oxygen and the large volume of water (per unit mass of rock) available for transport of reaction products. Acceleration of weathering is desirable to reduce the time ordinarily required to generate empirical dissolution data for evaluating the potential of mine waste to produce problematic drainage. Even under conditions of accelerated weathering, samples may produce neutral drainage for several years prior to acidifying, and this "lag time" can be affected by the particle size selected for testing (Lapakko et al. 1998)

Although many kinetic tests have been employed (see above), it is only recently that efforts have begun to provide well-defined protocols and quantify the intralaboratory and interlaboratory replication of test results (White and Lapakko 2000; Lapakko and White 2000). These efforts include a test that was designated as ASTM method D 5744-96 in 1996 (ASTM 2000b). Important considerations in conducting any kinetic test are 1) define test objectives; 2) select a method appropriate for the objectives; 3) characterize the solids to be tested with respect to particle size, chemistry and mineralogy; 4) take care in splitting solids; 5) analyze intial rinse (the first rinse of the experiment) samples for a multitude of components to determine potentially problematic constituents; 6) regularly analyze for indicators of acid production and acid neutralization, although frequency may be decreased over time; and 7) determine extent and rates of mineral dissolution to assess the relevance of data to long term environmental behavior. Mineralogical analysis of leached solids and geochemical equilibrium modeling will aid in determining reactions responsible for the observed drainage quality.

7. SUMMARY

A variety of categories of tools are available for characterizing materials related to metal mining. An initial assessment of water quality for a specific site can be made by examining water quality from sites of similar characteristics. Application of airborne imaging specroscopy or geophysical methods assists mapping of abandoned mine wastes and aids in screening large areas. Field and laboratory tools are available to estimate the balance of acid-producing and acid-neutralizing components, the extent of readily soluble components, and the leachability of trace metals. More sophisticated geochemical techniques will more accurately quantify chemical and mineralogical composition. Finally, dissolution tests are available to determine the relationship between solid-phase composition and drainage quality.

8. RESEARCH NEEDS

1. Assess the accuracy of existing chemical analytical methods for determining sulfur present with alunite-jarosite and develop alternative methods if necessary.
2. For various lithologies, establish relationships between neutralization potential determined by static tests and that present as calcium carbonate and magnesium carbonate (See Lapakko 1994a; Jambor et al. 2000).
3. Conduct long-term dissolution tests to determine the relationship between solid-phase compositional variations within individual lithologies and drainage quality.
4. Provide field verification data for methods designed to predict mine waste drainage quality.
5. Determine the influence of arid conditions on the accuracy of predictive tools such as kinetic tests.

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Table 1. Selected sulfate minerals from Alpers et al. 1994.

Selected Soluble Iron-Sulfate Minerals		Some Soluble Sulfate Minerals		Less Soluble Sulfates: some minerals of the alunite group	
Mineral	Formula	Mineral	Formula	Mineral	Formula
Fe^{II}		epsomite	$MgSO_4.7H_2O$	jarosite	$KFe_3^{III}(SO_4)_2(OH)_6$
melanterite	$Fe^{II}SO_4.7H_20$	hexahydrite	$MgSO_4.6H_2O$	natrojarosite	$NaFe_3^{III}(SO_4)_2(OH)_6$
ferrohexahydrite	$Fe^{II}SO_4.6H_20$	goslarite	$ZnSO_4.7H_2O$	hydronium jarosite	$(H_3O)Fe_3^{III}(SO_4)_2(OH)_6$
siderotil	$Fe^{II}SO_4.5H_20$	bianchite	$ZnSO_4.6H_2O$	ammoniojarosite	$(NH_4)Fe_3^{III}(SO_4)_2(OH)_6$
rozenite	$Fe^{II}SO_4.4H_20$	gunningite	$ZnSO_4.H_2O$	argentojarosite	$AgFe_3^{III}(SO_4)_2(OH)_6$
szomolnokite	$Fe^{II}SO_4.H_20$	gypsum	$CaSO_4.2H_2O$	plumbojarosite	$Pb_{0.5}Fe_3^{III}(SO_4)_2(OH)_6$
halotrichite	$(Fe^{II})Al_2(SO_4)_4\ .22H_20$	anhydrite	$CaSO_4$	alunite	$KAl_3(SO_4)_2(OH)_6$
Mixed Fe^{II}-Fe^{III}		retgersite	$NiSO_4.6H_2O$	natroalunite	$NaAl_3(SO_4)_2(OH)_6$
copiapite	$Fe^{II}Fe_4^{III}(SO_4)_6(OH)_2.20H_2O$	chalcanthite	$CuSO_4.5H_2O$	ammonioalunite	$(NH_4)Al_3(SO_4)_2(OH)_6$
bilinite	$Fe^{II}Fe_2^{III}(SO_4)_4.22H_2O$	alunogen	$Al_2(SO_4)_3.17H_2O$	osarizawaite	$PbCuAl_2(SO_4)_2(OH)_6$
romerite	$Fe^{II}Fe_2^{III}(SO_4)_4.14H_2O$	mirabilite	$Na_2(SO_4).10H_2O$	beaverite	$PbCuFe_2^{III}(SO_4)_2(OH)_6$
voltaite	$K_2Fe^{II}_5Fe_4^{III}(SO_4)_{12}.18H_2O$	thenardite	$Na_2(SO_4)$		
Fe^{III}					
coquimbite	$Fe_2^{III}(SO_4)_3.9H_2O$				
kornelite	$Fe_2^{III}(SO_4)_3.7H_2O$				
rhomboclase	$HFe^{III}(SO_4)_2.4H_2O$				
ferricopiapite	$Fe_5^{III}(SO_4)_6O(OH).20H_2O$				