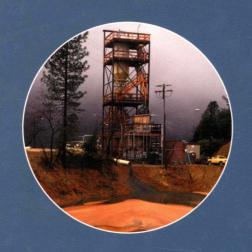




Acid Mine Drainage, Rock Drainage, and Acid Sulfate Soils

Causes, Assessment, Prediction, Prevention, and Remediation







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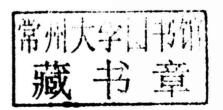
STEPHEN M. TESTA

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Edited by

JAMES A. JACOBS JAY H. LEHR STEPHEN M. TESTA



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ACID MINE DRAINAGE, ROCK DRAINAGE, AND ACID SULFATE SOILS

PREFACE

Acid drainage is a widespread universal biogeochemical process that has existed on Earth for eons, producing acidic waters rich in sulfuric acid and toxic metals, as well as potential resources. Acid drainage occurs at coal mines and is associated with hardrock metal ore deposits, road or building development projects, naturally occurring gossans, or with coastal marine sediments producing acid sulfate soils. Its presence reflects the complex biogeochemical interaction of an oxidizing agent, typically oxygen, which reacts with iron sulfide compounds catalyzed by iron- or sulfuroxidizing microbial organisms, primarily bacteria in the presence of water. Most commonly, pyrite is exposed at the surface through natural processes or a development project, and the oxidation of the iron sulfide compound begins to dissolve, creating the exothermic reactions and by-products described in these pages. This book is a compilation or status report on what is known on the subject of acid drainage, sometimes described in the literature under the topics of acid mine drainage, acid rock drainage, and acid sulfate soils.

Acid drainage occurs in many environments, as discussed in Part I, Causes of Acid Mine Drainage, Rock Drainage, and Sulfate Soils, which focuses on the biogeochemistry of acid mine drainage, rock drainage, and sulfate soils. The telltale dark red to orange river water and sediments are found worldwide in a variety of environmental settings, all associated with sulfide oxidation. Primarily microbially induced, the acid drainage process produces sulfuric acid, creating low-pH conditions in creeks, streams, rivers, and associated water basins.

Acid drainage relating to stream characterization, aquatic and biological sampling, evaluation of aquatic resources, and unusual aspects of sulfide oxidation are discussed in Part II, Assessment of Acid Mine Drainage, Rock Drainage, and Sulfate Soils. As part of the acid drainage process, other toxic

metals become solubilized by the acidic waters, which have been documented to harm aquatic organisms. Large fish kills, up to severe degradation of surface water and groundwater resources, have been well documented in the literature in areas containing acid drainage.

In Part III, Prediction and Prevention of Acid Drainage, we address just how far we have come in predicting acid drainage accurately. The prediction of acid drainage has been challenging. Based on the shallow exposure of copper, gold, silver, and other metal ores, we know that mining in the Rio Tinto area of Spain dates back over 5000 years. Those ores contain iron sulfides that oxidize during mining disturbance when exposed to the oxygen in the atmosphere. Unfortunately, once the process of acid drainage starts, it is virtually impossible to stop the biogeochemical reactions. Various predictive tools and methods, including acid—base accounting, kinetic testing, block modeling, petrology, and mineralogy studies, are described in Part III. Policy, regulation, and brownfield redevelopment are also discussed.

Various passive and active cleanup methods to treat acid drainage once the biogeochemical process begins are described in Part IV, Remediation of Acid Drainage, Rock Drainage, and Sulfate Soils. Reusing the wastes from acid drainage is the best method for sustainable mining and development. Acid drainage and the biogeochemical processes involved can be enhanced and used for resource recovery. In Part V we provide a variety of useful reference appendixes.

We also address several general questions that provide an overview and fundamental understanding of acid drainage:

• Are all sulfur oxidation reactions aboveground?

Not all sulfur oxidation reactions are aboveground. Sulfur oxidation reactions occur in some unlikely places in the subsurface. Understanding water geochemistry and changes in redox conditions is important for water managers who are monitoring and using aquifer recharge systems. Population growth combined with global climate changes requires more astute use and optimization of subsurface aquifers for large-scale water storage systems. In these cases, oxygen-rich surface or treated water can be pumped into subsurface aquifers for storage and reuse. The contact chemistry of injecting highly oxygenated surface or treated waters into reduced pyrite-rich aquifers causes the same acid drainage reactions in the subsurface, frequently liberating arsenic through the production of sulfuric acid and dissolution of the pyrite grains. Examples of aquifer storage and sulfide oxidation, and arsenic mobilization issues from southern Florida are discussed.

• Can acid drainage be a resource?

Acid mine drainage resources such as the various forms of vitriol have been known for millennia. The ubiquitous bright yellow staining found in rivers and creeks as a result of naturally occurring sulfur oxidation was undoubtedly noted by prehistoric man. The Rio Tinto acid mine drainage area in southern Spain presents an example of a long-term, ongoing environmental challenge with enormous resource potential. Even miners working around 3000 B.C. and later alchemists were aware of the magical and reactive characteristics of the acidic waters of the Rio Tinto. Rio Tinto, the "red river," was named for the dark reddish orange mine drainage that empties into the waterway. For about 5000 years, the acid drainage from Rio Tinto, rich in sulfuric acid and metals, was used as a resource by the many civilizations that controlled the mines. Called "oil of vitriol" by medieval European alchemists, this chemical was used for tanning leather and dying cloth. The acid mine drainage chemicals were also used in early medicines, especially for treating the eyes. Although associated as a waste product with acid drainage, sulfuric acid is still greatly valued and produced synthetically in chemical plants. Sulfuric acid is currently one of the world's largest-volume industrial chemicals and is used in numerous manufacturing processes.

Today, bioleaching or biomining methods use changes in redox conditions to mobilize metal cations from insoluble ores by biological oxidation and complexation processes. An important bacterium of acid mine drainage which is also used in the bioleaching mining process is *Acidithiobacillus ferrooxidans*, which oxidizes ferrous iron (Fe²⁺) and generates ferric iron (Fe³⁺), an oxidant. This microbe, common to acid mine drainage environments, is used in the bioleaching process to leach copper from low-grade mine tailings and waste mining rock. DNA studies indicate a large list of iron- and sulfur-oxidizing bacteria and archaea capable of withstanding extremes in pH and temperature while obtaining energy from the iron and sulfur oxidation processes. The earlier scientific literature refers to iron- and sulfur-oxidizing bacteria, and the primary transformations described in this book are

still performed by these microbes. However, more recently, microbiology researchers using detailed genetic testing techniques refer to richer, more complex, and more diverse acid mine drainage microbial communities. In one study, these communities contain microbial eukaryotes consisting of both fungi and protists that can create biofilm structures in the areas colonized by the microbial community. According to researchers, these biofilm structures can affect the abundance of both the more abundant aerobic bacteria and archaea and the microbial community composition through a variety of previously unknown interactions and complex mechanisms. Clearly, our understanding of the microbiology of acid mine drainage is evolving, which provides improvements in our resource recovery options. The optimization of the biogeochemical process in metal resource recovery has increased copper recovery rates and reduced the operating costs of mining companies using this enhanced mining method, called bioleaching. Future hardrock mining operations will require the expertise of multidisciplinary teams of mining engineers, mining geologists, geochemists, microbiologists, hydrogeologists, environmental specialists, wildlife biologists, and others to maximize resource recovery while minimizing environmental degradation. Case studies provide examples of various treatment technologies. The cold-mix asphalt process can use mine tailings and mining wastes to create valuable recycled products to be used locally. The asphalt product prevents the metals from leaching and stops the acid generation process when used properly.

Shale gas fracturing, currently employed in Pennsylvania and several other states, requires millions of gallons of water per well. Recycling of acid mine drainage for hydraulic fracturing will divert some of the more than 300 million gallons of mine drainage water that flows into Pennsylvania's rivers and streams each day. Acid mine waters are also being considered a valuable resource in West Virginia, Pennsylvania, Maryland, and other states where treated and recycled water is used in aquaculture projects to grow striped bass, rainbow trout, char, yellow perch, and catfish. These recent projects demonstrate the value of some of the resources derived from acid drainage.

How long has acid drainage occurred on Earth?

The sulfur oxidation reactions catalyzed by the iron- and sulfur-oxidizing microorganisms have been on the planet for eons, but they did not occur within the first few million years after formation of the planet, about 4.6 billion years ago. The early Earth atmosphere contained no free oxygen. The dating of the earliest biogeochemical processes associated with sulfur oxidation and the generation of acid drainage depends on the presence or absence of pyrite grains in nonmarine sedimentary rocks. Sulfur-reducing microbial communities may represent some of the earliest bacteria on Earth and may have existed near the dark, hot, nutrient-rich waters of hydrothermal vents in the oceans. The iron- and

sulfur-oxidizing communities of bacteria and archaea developed later with the ability to obtain energy from the iron- and sulfur-oxidation process.

Acid drainage on the Earth's surface has been occurring naturally for eons. Iron sulfides, pyrite in particular, are common in organic-rich sediments, forming below the surface where hydrogen sulfide gas produced by sulfate-reducing bacteria reacts with iron dissolved in oxygen-depleted waters. Crystalline pyrite occurs in igneous and hydrothermal deposits as well. Even though pyrite and iron sulfides are common in rocks, they are almost never found in sediment grains formed when surficial rocks erode and create sedimentary deposits. This is because the pyrite would have been oxidized by the exposure to atmospheric oxygen as it is exposed and eroded on the surface of the Earth. Preserved pyrite found in sedimentary deposits is not common in modern nonmarine sediments after the Precambrian because sulfate levels tend to be very low, and free oxygen levels in the atmosphere allowed for generally aerobic conditions in surface waters. Therefore, the time at which pyrite and other oxygen-sensitive minerals, such as siderite (iron carbonate) and uraninite (uranium dioxide), are found in sedimentary rocks at a time of deposition reveals when the amount of oxygen in the atmosphere and surface ocean was small. The level of oxygen in the atmosphere is estimated to have an upper limit of about 1% of present-day 20.9% oxygen levels, and the oxygen level might have been much lower. About 2.2 to 2.3 billion years ago, the oxygen content in the atmosphere and oceans increased dramatically, probably associated with oxygen production by cyanobacteria: bluegreen algae. After that time, pyrite, siderite, and uraninite have not been present as sediment grains on the surface of the Earth. Since pyrite would still have been available and eroded from surface source rocks over geologic time, the absence of pyrite as sediment grains some 2.2 to 2.3 billion years ago indicates the oxidation of iron sulfides and the beginning of sulfur oxidation on Earth and the earliest formation of the biogeochemical processes that produce acid drainage.

• What is the extent of acid drainage on Earth?

Based on the presence of the elements sulfur, oxygen, and iron in the solar system and the universe beyond, similar sulfide oxidation reactions, induced chemically or catalyzed by microbes, may possibly to occur elsewhere in the solar system. In this book we describe the oxidation of sulfides and the ensuing consequences of these reactions: prediction,

prevention, and remediation once these seemingly irreversible reactions start. Currently, acid mine drainage microbial communities are being documented in countless environmental settings on every continent, including Antarctica. Some of these are nonextreme environments with regard to temperature and pressure, and might be grass pasture soils or even agricultural soils. Examples of extreme environments where acid mine drainage microbial communities exist include high-temperature, high-pressure environments such as petroleum reservoirs and deep oceanic hydrothermal vents. The same sulfur streaks as those seen in the Rio Tinto area can also be seen in extreme environments such as on Ellesmere Island in the Canadian High Arctic, where research suggests that dark red smears are the result of sulfur-oxidizing metabolism by aerobic bacteria. Based on the literature, acid mine drainage microbial communities are relatively diverse and widespread on Earth.

• Is sulfur oxidation likely to occur outside Earth?

Acid drainage caused by sulfide oxidation is a universal process that is likely to be found in other locations in the solar system and beyond, possibly abiotically (using chemistry without microbes) or biotically with iron- or sulfuroxidizing microbes. Iron-oxidizing microbes are more likely to be found than aerobic life forms in the search for life on other moons and planets, because free oxygen in oceans or in an atmosphere is not likely to exist unless it has been produced by microbes, as on Earth. In fact, it is possible that these same reactions might occur in places beyond Earth where these elements and compounds react together. Billions of years ago, sulfur-oxidizing reactions may have occurred on Mars. Europa, a moon of Jupiter, and Titan and Enceladus, two moons of Saturn, are believed to have liquid water. Several researchers have noted that the luminous white surface of Europa is stained dark red, possibly representing sulfur-rich deposits that could be by-products of sulfur oxidation.

In summary, acid drainage and sulfur oxidation are widespread and have a large impact on Earth's resources and are associated with environmental challenges. This book has brought together scientists and engineers who have independently researched acid mine drainage, acid rock drainage, and acid sulfate soils, to summarize our current knowledge in one volume.

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PART I

CAUSES OF ACID MINE DRAINAGE, ROCK DRAINAGE, AND SULFATE SOILS

ACID DRAINAGE AND SULFIDE OXIDATION: INTRODUCTION

JAMES A. JACOBS AND STEPHEN M. TESTA

Since antiquity, and escalating on a large scale at the beginning of the industrial revolution, the extraction of coal, iron ore, and other minerals and metals from the Earth has had a significantly adverse impact on the environment. Acid mine drainage (AMD) or acid rock drainage presents one of mining's most serious threats to surface water and groundwater.

INTRODUCTION

The presence of acid mine drainage has the potential, and under certain conditions has actually devastated rivers, streams, and aquatic life for a very long time. Mineral resources such as coal, and metal ores such as gold, silver, and copper, are often rich in sulfide minerals, reflecting rock or sediment environments generally high in sulfur content and low or devoid of free molecular oxygen. Once exposed to water and air during mining, pyrite and other iron sulfide rocks release sulfuric acid in the presence of extremely acidophilic microorganisms. These complex interactions occur in microbial communities of autotrophic and heterotrophic bacteria and archaea which catalyze iron and sulfur oxidation, determining the release rates of metals and sulfur to the environment as acid mine drainage (Baker and Banfield, 2003). Even eukaryotic life forms (fungi and yeasts, protozoans, microalgae, and rotifera) may be part of microbial communities present in low-pH environments. Although the primary aerobic iron- and sulfur-oxidizing bacteria have been studied for decades, more recently, DNA analysis and genetic studies have identified some archaea, and even a few eukaryotes, to be present in the microbial community in the extremely low-pH acid mine drainage environments studied (Baker and Banfield, 2003). The ecology and biodiversity of acid mine and rock drainage microbial communities have been well documented by Baker et al. (2004, 2009) and Rawlings and Johnson (2002, 2007).

Once the sulfuric acid is created, the pyrite dissolves in drainage water, releasing associated metals and metalloids such as aluminum or arsenic into the surrounding environment. Wherever iron sulfides are exposed, such conditions can occur: open pits, underground excavations, leach pads, and tailing and waste rock piles.

Contaminated water flowing from abandoned coal mines is one of the most significant contributors to water pollution in former and current coal-producing areas. Acid mine drainage can have severe impacts on aquatic resources, can stunt terrestrial plant growth and harm wetlands, can contaminate groundwater, can raise water treatment costs, and can damage concrete and metal structures. In the Appalachian Mountains of the eastern United States alone, more than 7500 miles of streams are affected. The Pennsylvania Fish and Boat Commission estimates that the economic losses on fisheries and recreational uses are approximately \$67 million annually. While most modern coal-mining operations must meet strict environmental regulations concerning mining techniques and treatment practices, there are thousands of abandoned mine sites in the United States.

Treatment of a single site can result in the restoration of several miles of affected streams. Acid runoff from the Summitville mine in Colorado, a designated federal Superfund site, killed all biological life in a 17-mile stretch of the Alamosa River. Acid and metals in runoff from the mining of

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molybdenum at the Questa mine in New Mexico adversely affected biological life along 8 miles of the Red River. The effect on the environment can be severe. Streams and surface water bodies with a pH of 4.0 or lower can be devastating to fish, animals, and plant life. Once started, the process becomes very difficult to stop and can occur indefinitely, requiring mitigation and water treatment long after mining ends—in perpetuity. Along with countless other mines throughout the world featuring serious long-term environmental impacts, acid drainage at the Golden Sunlight mine is estimated to continue for thousands of years.

Common iron sulfide minerals, primarily pyrite (FeS₂), but also marcasite (FeS₂), arsenopyrite (FeAsS), and chalcopyrite (CuFeS₂), are exposed to the oxygen in the atmosphere during mining, excavation, or through natural erosion processes, and the compounds react with oxygen and water to form sulfate, resulting in acid drainage. This acidity results from the action of extremely acidophilic bacteria, which generate their energy by oxidizing ferrous iron [Fe(II) or Fe²⁺] to ferric iron [Fe(III) or Fe³⁺] using oxygen for cellular respiration. The ferric iron, in turn, dissolves the pyrite to produce soluble ferrous iron and sulfate. The ferrous iron is then available for oxidation by the aerobic acidophilic microbes, which scavenge dissolved oxygen in the pore space or water column. This biogeochemical cycle continues until the iron sulfide mineral (e.g., pyrite) is dissolved.

The oxidation of pyritic sulfur is a heat-generating reaction. In coal seams the pyrite oxidation reaction is sufficiently exothermic that mined-out areas in underground coal mines in high-sulfur-content coal seams have been documented to have had spontaneous combustion. The heat generated from the oxidation of pyritic sulfur can increase the temperature of the surrounding coal, increasing the rate of oxidation and causing coal degradation to occur (Smith et al., 1996). Excluding oxygen from the air in mined-out areas is the theoretical solution to spontaneous combustion related to pyrite oxidation, but in practice it is difficult to hermetically seal mined-out areas to exclude oxygen. Heat from the reaction can occur not only in subsurface mines but also in mine waste rock piles, where the heat is dissipated by thermal conduction or convection. Stability analysis of mine waste rock indicates that convective flow can occur because of the high porosity of the material. Convection cells formed in waste rock would draw in atmospheric air with oxygen and continue to drive the oxidation reaction. Convection gas flow due to the oxidation of sulfide minerals depends on the maximum temperature in the waste rock. The maximum temperature depends on the ambient atmospheric temperature, the strength of the heat source, and the nature of the upper boundary. If the sulfide waste is concentrated in one area, as is the case with encapsulation, the heat source may be very strong (U.S. Environmental Protection Agency, 1994). Due to the exothermic nature of the oxidation process, removing the oxygen from the pore spaces of sulfur-rich

waste rock piles can minimize the chance for oxidation and combustion.

The hot exothermic reactions produce sulfuric acid—rich solutions which contain high concentrations of metals, frequently iron, aluminum, arsenic, lead, copper, cadmium, manganese, and zinc. Although this reaction can occur abiotically, it appears that most of the oxidation of sulfide minerals on Earth over the past more than 2 billion years since oxygen has been present in the atmosphere has occurred as a result of aerobic microbial-catalyzed processes on the reaction surfaces of iron sulfide minerals in the presence of atmospheric oxygen and water.

EARLY EARTH ATMOSPHERE

According to Cloud (1968), Knoll and Holland (1995), Baker and Banfield (2003), and Knoll et al. (2012), the environmental conditions of the early Earth were anoxic prior to the appearance of oxygen-producing bacterial photosynthesis. Before photosynthesis evolved in microbes, Earth's atmosphere had no free oxygen (O_2). In the Precambrian, early anaerobic sulfate-reducing microbes used the sulfate (SO_4^{2-}) rather than free oxygen for respiration, and hydrogen sulfide (H_2S) was produced as the waste product (Schidlowski et al., 1983).

DNA-based studies of microbes populating mining environments containing acid mine drainage have provided insights into the diversity of acidophilic, metal-tolerant species. The broad distribution and ubiquitous nature of acidophiles associated with pyrite oxidation and acid mine drainage includes numerous nonextreme environments, including arid southwestern U.S. soil, Wisconsin agricultural soil, and grass pasture rhizospheres, to name a few locations. The extreme environments where acidophiles were identified included high-temperature petroleum reservoirs, a mid-Atlantic hydrothermal vent, a Yellowstone National Park hot spring, Antarctic sea ice and water, deep subsurface paleosol, and the Iron Mountain mine near Mt. Shasta, California. As well as acidophilic prokaryotes, such as iron- and sulfuroxidizing bacteria and archaea, eukaryotic life forms (fungi and yeasts, protozoans, microalgae, and rotifera) may be active in environments where the pH is below 3, such as in waters produced by acid drainage. More information on bacteria, archaea, and eukaryotic life forms may be found in articles by Baker and Banfield (2003) and Rawlings and Johnson (2002). Microbial populations not only play a key role in acid drainage, but have also been identified in microbialinduced corrosion and in bioleaching for metal resources. Significantly improved understanding and control of diffusion processes on mineral surfaces in the nanoenvironment will help to minimize acid mine drainage, increase structural corrosion protection of industrial facilities, and raise yields of metal resource recovery in bioleaching processes.

Acid drainage, most of which is the result of isolated point sources of pyrite and other sulfide minerals that are exposed to water and oxygen in the atmosphere, can be removed through erosion within a few thousand to a few million years. With the large acidophile diversity and the limited duration of active acid drainage processes, many of which are isolated point sources, lateral gene transfer is a mechanism by which some AMD survival genes could be introduced to create new acid- and metal-tolerant lineages of organisms. There is no evidence to suggest that AMD organisms evolved from nonextremeophiles when local acidic environments appeared (Baker and Banfield, 2003). Mielke et al. (2003) have shown that acidic conditions can eventually develop through microbial activity by Acidithiobaccilus ferrooxidans, even though the initial pH conditions for microbial-induced pyrite oxidation were neutral.

ACID DRAINAGE DEPOSITS

Acid drainage deposits are found throughout the world in a variety of settings, including both natural environments and anthropogenic land disturbances such as highway construction and mining, where acid-forming sulfide minerals are exposed at the surface of the Earth (Jennings et al., 2008). Whether acid drainage occurs at coal mines, in hardrock metal ore deposits as a result of construction projects, in naturally occurring gossans, or in coastal marine sediments containing potential acid sulfate soils, it involves the complex interaction of an oxidizing agent, typically oxygen, with iron sulfide compounds, primarily pyrite, catalyzed primarily by acidophilic, metal-tolerant iron- and sulfur-oxidizing bacteria in the presence of water. Aerobic oxidation of iron, commonly called rust, does occur chemically without microbial involvement. The complete redox cycle with Fe(III) and Fe(II) shuttles electrons back and forth in energy transfer by microbial populations using different terminal electron acceptors. In a microbial process related to acid mine drainage, microbial-induced corrosion of iron and steel infrastructure affects nearly all industries, including water and sewage collection in cast iron pipes and the distribution of natural gas and oil in steel pipes. Building and bridge steel used for structural purposes undergoes constant microbialinduced corrosion attack if the steel and iron components are exposed to conditions favoring microbial activity.

Although abiotic oxidation of ferrous iron with oxygen can occur chemically at mine sites under suitable conditions, the majority of sulfuric acid generation related to pyrite oxidation is initiated and greatly accelerated by iron- or sulfuroxidizing bacteria. Sulfide oxidation catalyzed by bacteria and other microbes may have reaction rates six orders of magnitude (i.e., 1 million times) greater than the same reactions in the absence of microbial communities (Evangelou and Zhang, 1995). Acid drainage generation is a complex

biogeochemical process involving oxidation and reduction (even on the same mineral surface), hydrolysis, precipitation, and dissolution reactions as well as microbial catalysis (Nordstrom and Alpers, 1999). Early microbial research regarding bacteria and the acid drainage process originally identified *T. ferrooxidans* as the main iron-oxidizing bacteria. After genetic research and better laboratory procedures were developed to examine the presence of various microbes associated with the production of acid drainage, it is now known, based on DNA-based studies, that numerous other iron- and sulfur-oxidizing microbial species exist, which include bacteria and, to a lesser extent, archaea. In some cases, even small populations of prokaryotic organisms may also be present. Significant variations in the species diversity of microbial communities can exist between different sample locations. More detailed information on microbial communities in acid mine drainage may be found in the work of Baker and Banfield (2003).

The longevity of acid drainage proves that once pyrite oxidation catalyzed by microbial communities begins, it is virtually impossible to control the acid drainage without significant engineering effort. Consequently, many ancient pre-Roman mining sites are still producing acid drainage. Dioscorides, a Greek physician of the first century A.D., noted the presence of vitriol, an acidic liquid produced near copper ore deposits on Cyprus (Karpenko and Norris, 2002). The mine drainage was sulfuric acid associated with the oxidation of iron sulfide minerals with copper and other trace metals.

For European alchemists during the Middle Ages, sulfuric acid associated with metal mine drainage was called *oil of vitriol*. Vitriol was used in the production of acids, medicines, and leather dyes and is the source of the word *vitriolic*, which in common conversation means caustic speech or criticism that is extremely bitter. Vitriol is now known to consist of hydrated sulfates of iron, copper, and even magnesium and zinc, which are all secondary minerals associated with weathering of metallic sulfide deposits, commonly known at the time as pyrites.

Not only are sulfur-rich precipitates signs of acid drainage, but the formation of sulfuric acids also liberates associated metals, such as iron, aluminum, arsenic, zinc, lead, nickel, and copper, among other metals, into surface water and groundwater. Even mineral prospectors looked for the naturally occurring "yellow boy" signature of iron hydroxide in creek beds as evidence of nearby sulfur-rich metal ores. Although naturally occurring acid drainage exists, most major challenges relate to coal or metal mining, and the resulting damage to aquatic organisms, fish kills, and the environment as well as the destruction of water and plant resources is significant in certain parts of the world. It should be noted that not all coal or metal mines produce acid drainage, and not all acid drainage is produced by mines.