

Acid Mine Drainage

Jerry M. Bigham

School of Environment and Natural Resources, Ohio State University, Columbus, Ohio, U.S.A.

Charles A. Cravotta III

Pennsylvania Water Science Center, U.S. Geological Survey (USGS), New Cumberland, Pennsylvania, U.S.A.

Abstract

Acid mine drainage (AMD) consists of metal-laden solutions produced by the oxidative dissolution of iron sulfide minerals exposed to air, moisture, and acidophilic microbes during the mining of coal and metal deposits. The pH of AMD is usually in the range of 2–6, but mine-impacted waters at circumneutral pH (5–8) are also common. Mine drainage usually contains elevated concentrations of sulfate, iron, aluminum, and other potentially toxic metals leached from rock that hydrolyze and coprecipitate to form rust-colored encrustations or sediments. When AMD is discharged into surface waters or groundwaters, degradation of water quality, injury to aquatic life, and corrosion or encrustation of engineered structures can occur for substantial distances. Prevention and remediation strategies should consider the biogeochemical complexity of the system, the longevity of AMD pollution, the predictive power of geochemical modeling, and the full range of available field technologies for problem mitigation.

INTRODUCTION

Acid mine drainage (AMD) refers to metal-rich sulfuric acid (H_2SO_4) solutions released from mine tunnels, shafts, open pits, and waste rock piles. Similar solutions can be produced by the excavation of roadways through certain rocks, dredging of harbor sediments, or drainage of coastal wetlands.

Spoils and soils exposed to AMD tend to be sparsely vegetated and susceptible to erosion. When AMD enters waterways, increases in pH can result in the precipitation of metal hydroxide sediments, which smother aquatic habitats and clog the gills of fish and other aquatic life (Fig. 1). The corrosion of concrete and metal structures in contact with AMD, such as bridge pilings and pipes, is also greatly accelerated. Once initiated, AMD may persist for decades, making it a challenging problem to solve.

AMD results from the rapid oxidation of iron (Fe)-bearing sulfide minerals such as pyrite (cubic FeS_2), marcasite (orthorhombic FeS_2), pyrrhotite (Fe_{1-x}S , $x = 0$ to 0.2), chalcopyrite (CuFeS_2), and arsenopyrite (FeAsS). These minerals are commonly found in coal and ore deposits and are stable until exposed to oxygen and moisture. Sulfide oxidation produces H_2SO_4 , which can dissolve associated metals. This release of acid and metals can occur locally as a form of natural mineral weathering (Natural Acid Rock Drainage) but is exacerbated by mining because of the sudden, large-scale exposure of sulfides in unweathered rock to atmospheric conditions.

MINE DRAINAGE CHEMISTRY

AMD, in which mineral acidity exceeds alkalinity, typically contains elevated concentrations of sulfate (SO_4), Fe, manganese (Mn), aluminum (Al), and other solutes and may or may not have a low pH^[1] (Table 1). AMD typically has pH from 2 to 6; however, sites, such as Iron Mountain, California, have produced extreme pH values as low as -3.6 .^[2,3] Neutral to alkaline mine drainage (NAMD), with pH from 5 to 8 and a surplus of alkalinity, is common in areas where the surrounding geologic units contain carbonate rocks to buffer acidity^[1,3,4] (Table 1). Because water discharged from mines generally is not at equilibrium with atmospheric conditions, the pH tends to be unstable—the hydrolysis of dissolved Fe, Al, and Mn can decrease the pH, while the outgassing of dissolved carbon dioxide (CO_2) can increase the pH. The “hot peroxide acidity” indicates the ultimate potential for the pH to be acidic or circumneutral and the amount of base required to neutralize the fully oxidized solution.^[4] Given sufficient time for equilibration with the atmosphere and oxidation and hydrolysis of dissolved Fe and Mn, AMD ultimately will have $\text{pH} \leq 4.5$, whereas NAMD ultimately will have $\text{pH} > 4.5$ (Table 1).

AMD forms by complex biogeochemical processes involving oxidation–reduction, hydrolysis, precipitation, and dissolution reactions as well as microbial catalysis.^[2] The entire sequence is commonly represented by Reaction 1, which describes the overall oxidation of pyrite by oxygen in the presence of water to form solid iron hydroxide

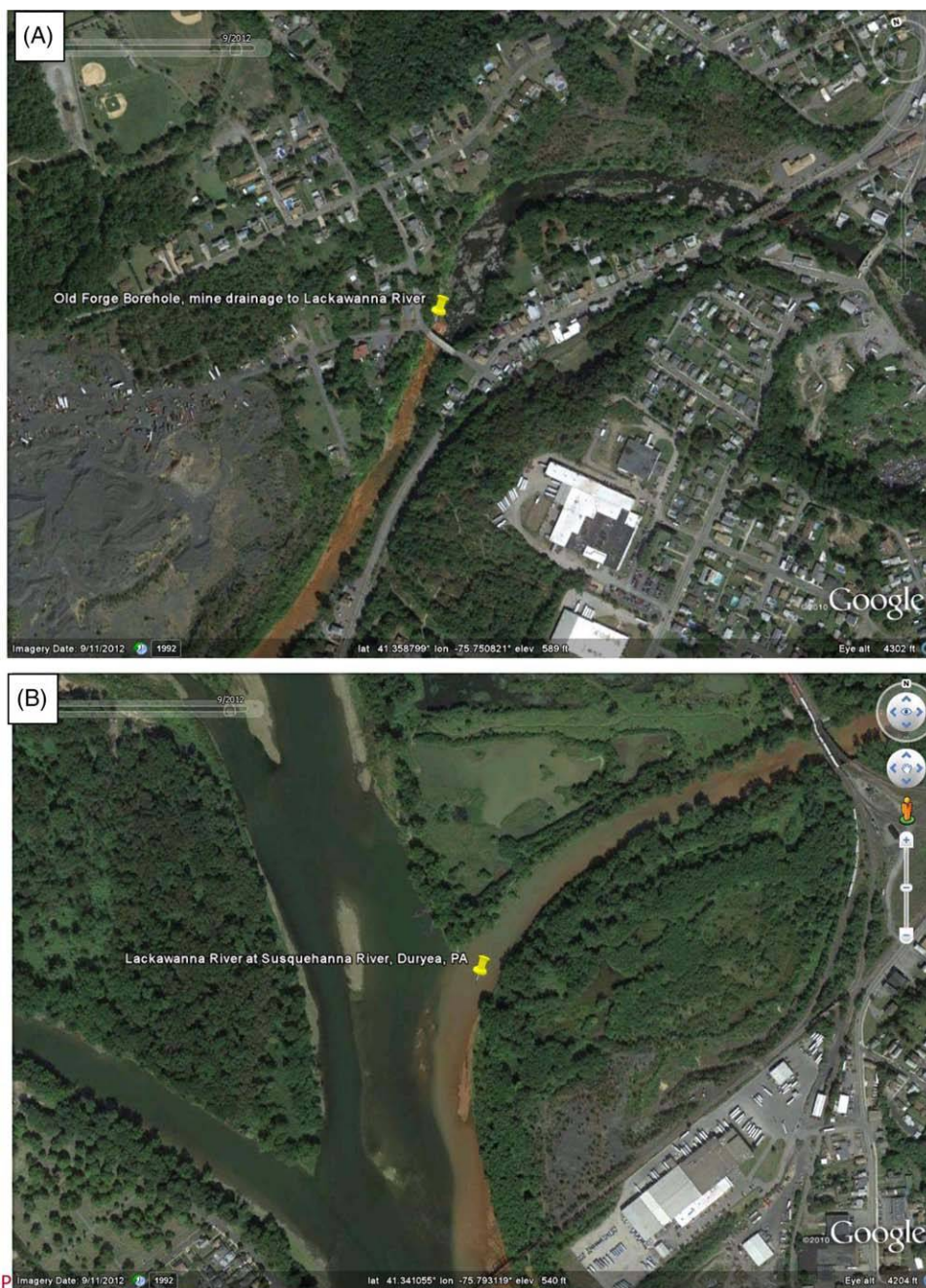
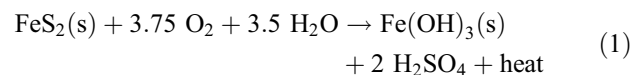


Fig. 1 (A) Discharge from the Old Forge Borehole (41.3591–75.75137), which drains a flooded underground coal mine in northeastern Pennsylvania, imparts a characteristic orange–brown turbidity to the Lackawanna River due to voluminous precipitates of iron hydroxide minerals. (B) Confluence of the Susquehanna River (at left) and Lackawanna River (at right) near Duryea, Pennsylvania (41.3412–75.7930), nearly 3 miles downstream from the Old Forge Borehole.

Source: Google Earth image dated 9/11/2012.

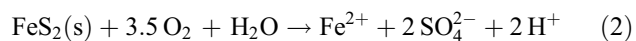
$[\text{Fe}(\text{OH})_3]$ and H_2SO_4 with the spontaneous release of energy as heat.



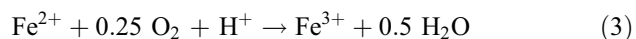
Chemolithotrophic microbes, described in more detail below, utilize the energy from the oxidation of Fe and sulfur (S).

Pyrite and related iron sulfide minerals contain both Fe and S in reduced oxidation states. When exposed to oxygen and water, the S moiety is oxidized first, releasing H_2SO_4 and Fe^{2+} to solution (Reaction 2). The rate of oxidation is dependent on environmental factors such as

temperature, pH, Eh, and relative humidity as well as mineral surface area and microbial catalysis.



Reaction 2 can be strictly abiotic or mediated by S-oxidizing bacteria.^[5] The Fe^{2+} is subsequently oxidized by oxygen, as described by Reaction 3.

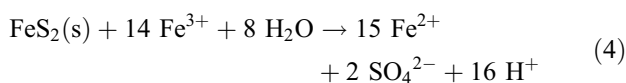


If acidity generated by Reaction 2 exceeds the buffering capacity of the system, the pH eventually decreases. Below

Table 1 Summary of mine drainage chemistry for 140 abandoned coal mines in Pennsylvania, 1999.^[1]

	AMD (hot acidity ≥ 10 mg/L; N = 88)	NAMD (hot acidity < 10 mg/L; N = 52)
	Median (range)	Median (range)
pH, fresh (units)	4.1 (2.7 to 6.2)	6.2 (5.2 to 7.3)
pH, aged (units)	3.2 (2.2 to 4.6)	7.8 (4.7 to 8.6)
Alkalinity (mg/L as CaCO ₃)	0 (0 to 190)	125 (8 to 510)
Hot acidity (mg/L as CaCO ₃)	124 (10 to 1590)	-52 (-417 to 7.5)
Cl (mg/L)	4.9 (0.1 to 460)	20.5 (0.7 to 270)
SO ₄ (mg/L)	560 (34 to 2000)	475 (96 to 1400)
Ca (mg/L)	85 (3.3 to 410)	100 (11 to 320)
Mg (mg/L)	41 (3.6 to 210)	37 (8.5 to 140)
Na (mg/L)	6.9 (0.69 to 460)	63 (0.89 to 500)
K (mg/L)	2.6 (0.5 to 12)	3.2 (0.78 to 6.3)
Silica (mg/L)	20 (6.4 to 67)	15 (5.8 to 22)
Fe (mg/L)	41 (0.046 to 512)	23 (0.049 to 101)
Al (mg/L)	7.7 (0.014 to 108)	0.022 (0.007 to 1.5)
Mn (mg/L)	3.4 (0.39 to 74)	1.5 (0.02 to 9.2)
As (mg/L)	0.0010 (< 0.00003 to 0.064)	0.0052 (< 0.00003 to 0.015)
Cu (mg/L)	0.0039 (0.00045 to 0.19)	0.0008 (0.0004 to 0.017)
Ni (mg/L)	0.145 (0.02 to 3.2)	0.0225 (0.0026 to 0.12)
Pb (mg/L)	0.00067 (< 0.00001 to 0.011)	< 0.00001 (< 0.00001 to 0.00068)
Zn (mg/L)	0.27 (0.011 to 10)	0.0088 (0.0006 to 0.25)

pH 3, Fe³⁺ solubility increases and a second mechanism of pyrite oxidation becomes important (Reaction 4).

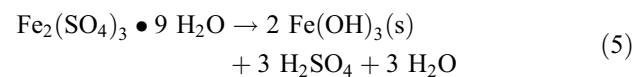


In this case, pyrite is oxidized by Fe³⁺ resulting in the generation of even greater acidity than when oxygen is the primary oxidant. Pyrite decomposition is thus controlled by the rate at which Fe²⁺ is converted to Fe³⁺ at low pH.^[6] At pH < 5 , Fe²⁺ oxidation by Reaction 3 is very slow unless catalyzed by populations of acidophilic, Fe-oxidizing bacteria^[6,7] that oxidize Fe²⁺ as a means of generating energy. In doing so, they supply soluble Fe³⁺ at a rate equal to or slightly greater than the rate of pyrite oxidation by Fe³⁺. Pyrite oxidation then regenerates Fe²⁺ (Reaction 4) creating a cyclic situation that leads to vigorous acidification of mine drainage water.

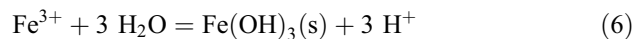
MINE DRAINAGE MINERALOGY

Sulfide mineral oxidation typically takes place in humid air above the groundwater table or at the land surface, where reactants are present and variably soluble products including secondary sulfate minerals may accumulate. Commonly observed secondary sulfates associated with weathered pyrite include melanterite (FeSO₄ • 7H₂O), rozenite (FeSO₄ • 4H₂O), szomolnokite (FeSO₄ • H₂O),

copiapite (Fe^{II}Fe^{III}₄(SO₄)₆(OH)₂ • 20H₂O), and coquimbite (Fe₂(SO₄)₃ • 9H₂O).^[3,8,9] Such secondary SO₄ minerals can also form by the evaporation of AMD during dry periods. Dissolution of these relatively soluble “acid sulfate” minerals by infiltrating water or runoff can result in the rapid release of “stored acidity.”^[3,9] For example, H₂SO₄ is a product of the dissolution of coquimbite (Reaction 5).



The Fe³⁺ released by dissolution of such SO₄²⁻ minerals may interact with pyrite (Reaction 4) or hydrolyze and precipitate as a variety of insoluble Fe minerals, generally represented as [Fe(OH)₃] (Reaction 6).



These rust-colored (yellow-to-red-to-brown) solids can impart turbidity to the water or coat streambeds and aquatic plants and, thus, are often the most obvious indicators of mine drainage contamination. The actual mineralogy of the precipitates is determined by solution parameters such as pH, SO₄, and metal concentration and can vary both spatially and temporally. Some of the most common mine drainage minerals are goethite (α-FeOOH), ferrihydrite (Fe₅HO₈ • 4H₂O), schwertmannite [Fe₈O₈(OH)₆SO₄], and jarosite [(H₃O, K, Na)Fe₃(OH)₆(SO₄)₂].^[10] Goethite is a crystalline oxyhydroxide that is relatively stable over

a wide pH range and may represent a final transformation product of other mine drainage minerals.^[10,11] Ferrihydrite is a poorly crystalline ferric oxide that forms in higher pH (> 6.5) environments. Schwertmannite is commonly found in drainage waters with pH ranging from 2.8 to 4.5 and with moderate to high SO₄ contents. Schwertmannite may be the dominant phase controlling Fe and trace metal concentrations in most AMD.^[12] Jarosite group minerals form in more extreme environments, often with pH < 3, very high SO₄ concentrations, and in the presence of appropriate cations such as sodium (Na) and potassium (K).^[10]

MINE DRAINAGE MICROBIOLOGY

The most studied bacterial species in mine drainage systems belong to the genus *Acidithiobacillus* (formerly *Thiobacillus*).^[13] Species such as *Acidithiobacillus thiooxidans* and *Acidithiobacillus ferrooxidans* are important in S and Fe oxidation in acid drainage; however, many other microorganisms, such as *Leptospirillum* species, may also be involved.^[3] Bacteria have been found in close association with pyrite grains and may play a direct role in mineral oxidation,^[5] but they most likely function indirectly through oxidation of dissolved Fe²⁺ as described previously. In low pH systems (< 3), *A. ferrooxidans* can increase the rate of Fe oxidation as much as five orders of magnitude relative to strictly abiotic rates.^[6,7]

Fe-oxidizing bacteria are chemolithotrophic, meaning they oxidize inorganic compounds, such as Fe²⁺, to generate energy and use CO₂ as a source of carbon. Fe oxidation, however, is a very low energy yielding process compared to heterotrophic processes. It has been estimated that the oxidation of 90.1 moles of Fe²⁺ is required to assimilate 1 mole of C into biomass.^[14] Thus, large amounts of Fe²⁺ must be oxidized to achieve even modest growth.

In addition to mediating Fe oxidation, bacteria may play an additional role in mineral formation. Bacterial cells in mine drainage systems are often partially encrusted with mineral precipitates.^[15] Bacterial cell walls provide reactive sites for the sorption of metal cations, which can accumulate and subsequently develop into precipitates using the bacterial surface (living or dead) as a template.^[16]

ENVIRONMENTAL IMPACTS OF MINE DRAINAGE

AMD from mine openings, such as tunnels or shafts, or from mine spoil can impact aquatic environments substantial distances downstream. Chemical precipitates can smother streambed habitats, obstruct water flow, dramatically increase turbidity, and ruin stream aesthetics. Dissolved metals and acidity can also be toxic to plants and animals.

Besides Fe, dissolved Al is common in AMD. The primary source of Al is the acid dissolution of aluminosilicates found in soil, spoils, tailings deposits, and gangue material.^[10] At moderate concentrations (<1 mg/L), Al can be toxic

to plants, and colloidal Al precipitates can clog or irritate the gills of fish and other aquatic organisms causing suffocation. Al occurs as a dissolved species at low pH but rapidly hydrolyzes at about pH 5 to form “amorphous” feldspars [Al₄(SO₄)(OH)₁₀ · 4H₂O] or gibbsite [Al(OH)₃].^[3,10] Al precipitates are white in color but are readily masked by associated Fe compounds.

Elevated concentrations of trace elements such as arsenic (As), copper (Cu), nickel (Ni), lead (Pb), and zinc (Zn) may be released during the oxidation of sulfide minerals and be present in AMD and NAMD solutions (Table 1). These elements can play a role in mineralization processes by forming coprecipitates with iron sulfate and hydroxide minerals^[9,17] but occur primarily as sorbed species with the hydroxides.^[8,12] Mine drainage precipitates can retain both anions and cations, depending on pH. While coprecipitation and sorption function to immobilize trace elements by removing dissolved ions from solution, this effect may not be permanent. Dissolution of precipitates and shifts in pH can result in the release of sorbed species, providing a latent source of pollution.^[18]

DEALING WITH MINE DRAINAGE

Successful control of mine drainage usually involves varying degrees of prevention and treatment.

Prevention

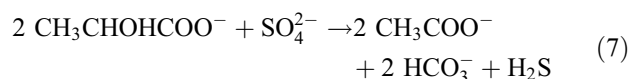
Prevention techniques include sealing mine shafts to prevent discharge, burying or submerging spoil piles to reduce contact by oxygen, remining and recycling of waste materials to eliminate the sulfide minerals, and the addition of bactericides to limit catalysis by Fe-oxidizing bacteria. These techniques often have limited success. Sealing of mines is extremely difficult due to fractures and the permeability of surrounding rocks. Covering spoil with soil material can decrease the degree of sulfide oxidation by limiting exposure to oxygen, but establishment of a vegetative cover is necessary to prevent erosion from reexposing the spoil. Submerging mine waste in water may be effective where oxidation has not initiated; however, previously formed oxidation products can be dissolved with acidity, metals, and SO₄ released to solution (Reaction 5). Remining and recycling may not be economically viable. Inhibition of Fe-oxidizing bacteria with bactericides can decrease sulfide mineral oxidation and reduce metal mobility; however, reapplication is necessary and adequate distribution to all affected areas is difficult. In addition, target bacteria may develop resistance and beneficial bacteria may be harmed.^[5]

Treatment

The traditional approach to treatment of AMD involves neutralization of acidity by the addition of alkaline chemical agents such as caustic soda (NaOH) or hydrated

lime [Ca(OH)₂]. This method is effective in rapidly increasing pH and precipitating dissolved metals; however, it requires continuous oversight and produces large amounts of metal-rich sludge that require disposal. Alternative remediation strategies focus on low-maintenance treatment methods. For example, diverting AMD through limestone drains coupled with settling ponds or aerobic wetlands have shown some promise as passive remediation technologies.^[19] In these systems, drainage is channeled through either oxic or anoxic limestone substrates to neutralize active acidity. Dissolved metals are then allowed to hydrolyze and precipitate in ponds or wetland cells. A major difficulty is the coating of limestone surfaces by precipitates of Fe and Al that may eventually obstruct flow. When drainage is naturally net alkaline, engineered aeration systems can be effective in promoting CO₂ outgassing, which increases pH and the rate of abiotic Fe(II) oxidation, with the rapid removal of dissolved Fe by mineral precipitation.^[20]

Compost wetlands are designed to stimulate the development of anaerobic microbial populations, particularly SO₄-reducing bacteria. The bacteria use the compost as an organic substrate and remove SO₄ from solution either by converting it to hydrogen sulfide (H₂S), which is lost to the atmosphere, or by forming insoluble iron sulfides (Reactions 7 and 8).



Bicarbonate is formed as a by-product of SO₄ reduction and functions to buffer acidity. These systems have also shown limited success in the field because the SO₄ removal rates are usually low (<10%), and pH often remains unchanged or decreases within the system.^[11] Nevertheless, bioreactors involving SO₄ reduction can be effective for removing potentially toxic trace elements such as Zn and Cu that form sulfide precipitates.

REFERENCES

- Cravotta, C.A., III. Dissolved metals and associated constituents in abandoned coal-mine discharges, Pennsylvania, USA – 2. Geochemical controls on constituent concentrations. *Appl. Geochem.* **2008**, *23* (2), 203–226.
- Nordstrom, D.K.; Blowes, D.W.; Ptacek, C.J. Hydrogeochemistry and microbiology of mine drainage: An update. *Appl. Geochem.* **2015**, *57*, 3–16.
- Nordstrom, D.K. Mine waters: Acidic to circumneutral. *Elements* **2011**, *7* (6), 393–398.
- Kirby, C.S.; Cravotta, C.A., III. Net alkalinity and net acidity I: Theoretical considerations. *Appl. Geochem.* **2005**, *20* (10), 1920–1940.
- Lu, X.; Wang, H. Microbial oxidation of sulfide tailings and the environmental consequences. *Elements* **2011**, *8* (2), 119–124.
- Singer, P.C.; Stumm, W. Acidic mine drainage: The rate determining step. *Science* **1970**, *167*, 1121–1123.
- Kirby, C.S.; Thomas, H.M.; Southam, G.; Donald, R. Relative contributions of abiotic and biological factors in Fe(II) oxidation in mine drainage. *Appl. Geochem.* **1999**, *14* (4), 511–530.
- Jambor, J.L.; Nordstrom, D.K.; Alpers, C.N. Metal-sulfate salts from sulfide mineral oxidation. In *Sulfate Minerals; Crystallography, Geochemistry and Environmental Significance; Reviews in Mineralogy and Geochemistry*; Alpers, C.N., Jambor, J.L., Nordstrom, D.K., Eds.; The Mineralogical Society of America: Washington, DC, 2000; Vol. 40, 303–350.
- Hammarstrom, J.M.; Seal, R.R., II.; Meierb, A.L.; Kornfeld, J.M. Secondary sulfate minerals associated with acid drainage in the eastern US: Recycling of metals and acidity in surficial environments. *Chem. Geol.* **2005**, *215* (1–4), 407–431.
- Bigham, J.M.; Nordstrom, D.K. Iron and aluminum hydroxysulfates from acid mine waters. In *Sulfate Minerals; Crystallography, Geochemistry and Environmental Significance*; Alpers, C.N., Jambor, J.L., Nordstrom, D.K., Eds.; Reviews in Mineralogy and Geochemistry; The Mineralogical Society of America: Washington, DC, 2000; Vol. 40, 351–403.
- Gagliano, W.B.; Brill, M.R.; Bigham, J.M.; Jones, F.S.; Traina, S.J. Chemistry and mineralogy of ochreous sediments in a constructed mine drainage wetland. *Geochim. Cosmochim. Acta.* **2004**, *68*, 2119–2128.
- Webster, J.G.; Swedlund, P.J.; Webster, K.S. Trace metal adsorption onto an acid mine drainage iron(III) oxy hydroxy sulfate. *Environ. Sci. Technol.* **1998**, *32*, 1361–1368.
- Kelly, D.P.; Wood, A.P. Reclassification of some species of *thiobacillus* to the newly designated genera *Acidithiobacillus* gen. nov., *Halothiobacillus* gen. nov. and *Thermithiobacillus* gen. nov. *Int. J. Syst. Evol. Micr.* **2000**, *50* (2), 511–516.
- Ehrlich, H.L. *Geomicrobiology*, 3rd Ed.; Marcel Dekker, Inc.: New York, 1996; 293–295.
- Clarke, W.; Konhouser, K.O.; Thomas, J.; Bottrell, S.H. Ferric hydroxide and ferric hydroxysulfate precipitation by bacteria in an acid mine drainage lagoon. *FEMS Microbiol.* **1997**, *20* (3–4), 351–361.
- Konhouser, K.O. Diversity of bacterial iron mineralization. *Earth-Sci. Rev.* **1998**, *43*, 91–121.
- Carlson, L.; Bigham, J.M.; Schwertmann, U.; Kyek, A.; Wagner, F. Scavenging of As from acid mine drainage by schwertmannite and ferrihydrite: A comparison with synthetic analogues. *Environ. Sci. Technol.* **2002**, *36* (8), 1712–1719.
- Lee, G.; Faure, G.; Bigham, J.M.; Williams, D.J. Metal release from bottom sediments of Ocoee Lake No. 3, a primary catchment area for the Ducktown, Mining District. *J. Environ. Qual.* **2008**, *37* (2), 344–352.
- Cravotta, C.A., III; Trahan, M.K. Limestone drains to increase pH and remove dissolved metals from acidic mine drainage. *Appl. Geochem.* **1999**, *14*, 581–606.
- Cravotta, C.A., III. Monitoring, field experiments, and geochemical modeling of Fe(II) oxidation kinetics in a stream dominated by net-alkaline coal-mine drainage, Pennsylvania, U.S.A. *Appl. Geochem.* **2015**, *62*, 96–107.