

Prepared in cooperation with the Tennessee Department of Transportation

Bibliography for Acid-Rock Drainage and Selected Acid-Mine Drainage Issues Related to Acid-Rock Drainage From Transportation Activities

Open-File Report 2015-1016

U.S. Department of the Interior U.S. Geological Survey

Cover. (Front and back) Photographs showing roadcut staining caused by acid-rock drainage in Hickman County, Tennessee.

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By Michael W. Bradley and Scott C. Worland

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Abstract

Acid-rock drainage occurs through the interaction of rainfall on pyrite-bearing formations. When pyrite (FeS₂) is exposed to oxygen and water in mine workings or roadcuts, the mineral decomposes and sulfur may react to form sulfuric acid, which often results in environmental problems and potential damage to the transportation infrastructure. The accelerated oxidation of pyrite and other sulfidic minerals generates low pH water with potentially high concentrations of trace metals. Much attention has been given to contamination arising from acid mine drainage, but studies related to acid-rock drainage from road construction are relatively limited. The U.S. Geological Survey, in cooperation with the Tennessee Department of Transportation, is conducting an investigation to evaluate the occurrence and processes controlling acid-rock drainage and contaminant transport from roadcuts in Tennessee. The basic components of acid-rock drainage resulting from transportation activities are described and a bibliography, organized by relevant categories (remediation, geochemical, microbial, biological impact, and secondary mineralization) is presented.

Introduction

Acid-rock drainage (ARD) occurs through the interaction of rainfall and groundwater on pyrite-bearing formations, which often results in environmental problems and potential damage to the transportation infrastructure. There is a need to better understand the chemical, geologic, hydrologic, and bacterial factors that prevent and control acid production in runoff from roadcuts during and after highway construction. Pyrite (FeS₂) and similar minerals containing sulfur and trace metals are present in a number of rock formations throughout Middle and East Tennessee and can be particularly important in the black shale of the Highland Rim and Valley and Ridge provinces, shale and coal formations along the Cumberland Plateau, and shale and other metamorphic rocks in the Blue Ridge (fig. 1). When exposed to oxygen and water, pyrite (FeS₂) may decompose to form sulfuric acid (eq. 1). When released into the environment, sulfuric acid can cause ecological problems and damage to transportation infrastructures. Pyrite-bearing formations exposed in a road cut may contribute to acidic runoff having a pH less than 4 and containing elevated concentrations of iron and other metals.

$$12FeS_2+45O_2+34H_2O \rightarrow$$

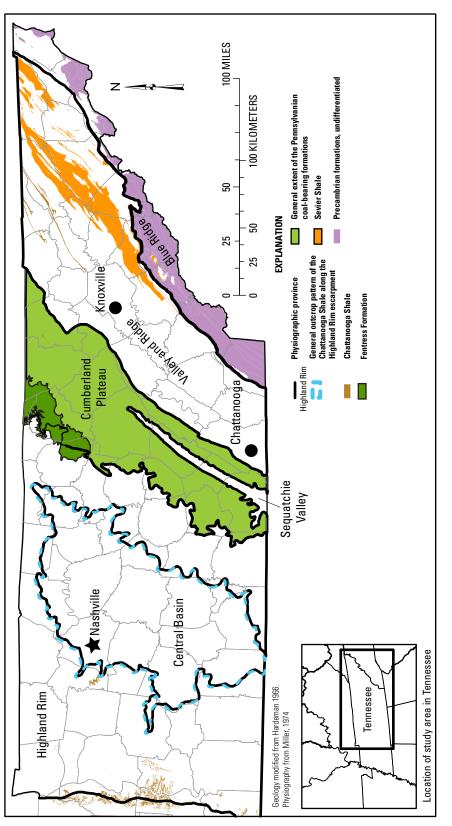
$$4[H_3OFe(SO_4)_2Fe(OH)_3]+16H_2SO_4$$

$$(1)$$

The resulting acid drainage and dissolved metals can be transported to surface water or, under dry conditions, may form deposits of sulfur salts and entrained metals on the surface of roadcuts. These secondary sulfate minerals (SSMs) are readily dissolved during subsequent precipitation, possibly further loading runoff with mobilized metals and acidic water.

In Tennessee, ARD has been observed along roadcuts associated with the Chattanooga Shale and may also be associated with the Sevier Shale, the Fentress Formation and Pennsylvanian coal deposits, and sulfide-bearing Precambrian igneous and metamorphic rocks, especially the Anakeesta Formation (fig. 1). The Chattanooga Shale crops out along the Highland Rim escarpment in Middle Tennessee and along strike belts in East Tennessee. The Fentress Formation and equivalent formations and Pennsylvanian coal deposits crop out along the escarpments of the Cumberland Plateau. The Precambrian igneous and metamorphic formations crop out along the Blue Ridge Mountains in East Tennessee.

Runoff contaminated with ARD from roadcuts can be treated similar to acid-mine drainage (AMD), that treatment can be costly and must be maintained. Over the past 20 years, scientists and engineers have experimentally altered environmental conditions to stimulate microbial remediation in contaminated aquifers (Bradley 2003; U.S. Environmental Protection Agency, 2004). Chemical supplements, such as peroxide-compounds that increase oxygen levels to stimulate aerobic fuel biodegradation (King and others, 2005), or lactate and molasses that stimulate iron- or sulfur-reducing bacteria to enhance reductive dechlorination, have been injected





into aquifers to stimulate contaminant remediation (Byl and Williams, 2000; Byl and others, 2002; Byl and Painter, 2009). These strategies, used to manipulate biogeochemical processes in the subsurface, have been very successful in the bioremediation of organic and metal contaminants. However, minimal research has been conducted in the application of this microbial engineering strategy to control ARD at roadcuts in areas prone to pyrite oxidation and acid formation. The U.S. Geological Survey (USGS), in cooperation with Tennessee Department of Transportation, conducted an investigation to identify the geochemical, bacterial, and hydraulic factors controlling acid production from pyrite-bearing rock and to evaluate methods to control acid production and contaminant transport from roadcuts in Tennessee. The primary objectives of the investigation are to (1) evaluate engineering and hydrologic controls to reduce formation of acid and metal transport, (2) define mechanisms and sources for transport of water and oxygen into pyrite-bearing formations and the formation of acid runoff, and (3) identify chemical or environmental conditions that reduce the biological production of acid from pyrite, with an emphasis on beneficial microbial communities that reduce pyrite oxidation. One component of the investigation was a detailed literature search and review for ARD covering peer reviewed journals, academic theses and dissertations, and government reports on ARD.

Purpose and Scope

The purpose of this report is to present the results of the literature search and selected reviews conducted for the investigation and to provide a bibliography for ARD issues and processes, ARD and transportation systems, and relevant references for AMD. The bibliography includes 210 references for books, journal articles, conference proceedings, reports, and master's theses and doctoral dissertations. Most references are presented in simple citation form; seven of the most relevant are annotated in brief summaries.

Methods and Sources

The references included in this bibliography were compiled from a series of computer searches from various databases and search engines. Available on-line search engines included the USGS Publications Warehouse (http://pubs.er.usgs.gov/), Google Scholar (http://scholar.google.com/), ACORN and WorldCat through the Heard Library, Vanderbilt University (http://www.library.vanderbilt.edu), and the USGS National Geologic Map Database (http://ngmdb.usgs.gov). Databases such as GeoRef and others also were searched through the USGS Library (http://library.usgs.gov/). The references were indexed by major topic, ARD, AMD, or geologic formation. The USGS National Geologic Map Database—Geologic Lexicon (http://ngmdb.usgs.gov/Geolex/search) was searched for additional information and references on specific geologic formations. The acid drainage literature was further evaluated for the application to background information, remediation activities, geochemical processes, microbial activity, ecological impact, secondary mineralization and other ARD or AMD associated topics.

Selected Annotated Citations

The literature review identified seven research papers related to ARD, transportation, SSM, or remediation that were found to be particularly helpful. The selected references are listed below with annotations summarizing the reports and stating the relevance of the material to ARD processes.

Hammarstrom, J.M., Brady, Keith, and Cravotta, C.A., 2005, Acid-rock drainage at Skytop, Centre County, Pennsylvania, 2004: U.S. Geological Survey Open-File Report 2005–1148, p. 50, accessed July 11, 2014, at http://pubs.usgs.gov/of/2005/1148/.

Relevance: Hammarstrom and others (2005) is one of the few reports that deal exclusively with ARD caused by road construction. The report provides a case study with excellent examples of the phenomena and processes present at an ARD impaired road construction site.

Summary: Hammarstrom and others (2005) investigated the ARD arising from road construction activity on Interstate 99 in Skytop Pennsylvania. The area contained exposed pyrite and associated zinc-lead sulfide minerals beneath a 10-meter (m) gossan along a 40- to 60-m deep roadcut through a 270-m long section of the Ordovician Bald Eagle Formation. The pyritic sandstone from the roadcut was crushed and used locally as road base. Acidic (pH < 3), metal laden seeps and runoff from the roadcut had to be remediated, causing a delay in road construction. Storm events followed by dry periods promoted oxidative weathering and dissolution of primary sulfides, which resulted in intermittent deposition of secondary sulfur salts (copiapite, melanterite, and halotrichite). The salts rapidly decreased the pH of deionized water to below 2.5 during laboratory tests. The salts sequestered metals and acidity between rainfall events, and contribute pulses of contamination during subsequent rain events.

Hammarstrom, J.M., Seal, R.R., II, Meier, A.L., and Kornfeld, J.M., 2005, Secondary sulfate minerals associated with acid drainage in the eastern US: Recycling of metals and acidity in surficial environments: Chemical Geology, v. 215, no. 1, p. 407–431.

Relevance: Hammarstrom and others (2005) presents a straightforward introduction to secondary sulfur mineral salts that are often present at ARD impaired road construction sites.

Summary: Hammarstrom and others (2005) presented the results of laboratory experiments conducted with secondary sulfate minerals (sulfur salts) commonly associated with ARD. The secondary minerals are produced when metal-sulfide

minerals experience chemical and mechanical weathering. The salts form following rain events and subsequent drying. Dissolution experiments revealed a decrease in pH from 6.0 to <3.7 units and an increase in dissolved aluminum (>30 milligrams per liter [mg/L]), iron (>47 mg/L), sulfate (>1,000 mg/L), and base metals (2 to >1,000 mg/L). Locations with winter-long snowpack, such as Vermont, exhibited the highest metal loading during spring runoff. In warmer locations, such as Virginia, metal loads peaked during the summer months.

Huckabee, J.W., Goodyear, C.P., and Jones, R.D., 1975, Acid rock in the Great Smokies: Unanticipated impact on aquatic biota of road construction in regions of sulfide mineralization: Transactions of the American Fisheries Society, v. 104, no. 4, p. 677–684.

Relevance: Huckabee and others (1975) address the negative impact of road construction ARD on aquatic ecology. Although other papers explore similar phenomena, this paper is unique in describing that the ARD and subsequent ecological impact is the direct result of pyritic material from the Annakeesta Formation as a result of road construction.

Summary: A highway construction project in the Great Smoky Mountains National Park resulted in a fish kill on a stream in the park. The stream drained an area of roadbed fill that contained iron sulfide minerals. The pH below the fill was significantly lower than the pH upstream. Brook trout were eliminated from the stream for about 8 kilometers (km) downstream from the fill and this stream reach remained devoid of fish for over 10 years. Huckabee and others (1975) conducted survival experiments with brook trout and salamanders. Trout were placed in mesh baskets below and above the fill. After 2 days, all of the fish below the fill had died, and all of the fish above the fill survived. The results were similar for survival tests conducted with salamanders. The study suggested that brook trout could not tolerate the stream conditions with a depressed pH. Iron and sulfide precipitates coated the stream bed for 2 km downstream of the fill. The researchers conducted similar tests with fish and salamander on small streams that flowed over a natural exposure of the pyrite-bearing Anakeesta Formation. The results showed the negative effect of natural ARD on aquatic ecology.

Kwong, Y.T.J., Whitley, G., and Roach, P., 2009, Natural acid rock drainage associated with black shale in the Yukon Territory, Canada: Applied Geochemistry, v. 24, no. 2, p. 221–231.

Relevance: Kwong and others (2009) provides a background for understanding natural ARD. The authors explore the potential acid production from pyritic materials naturally present in watersheds.

Summary: Kwong and others (2009) investigated the sediment and water geochemistry associated with natural ARD originating from black shale formations in the Yukon Territory, Canada. Tributary streams contained water having a pH of 3.0, and concentrations of 150 mg/L zinc, 39 mg/L

nickel, 2.8 mg/L copper, and 9.1 mg/L arsenic. The small tributary streams having anomalous acidity and metal contents contributed only a small fraction of contaminant loadings to the major water sources in the area, and the authors proposed considering metal loadings on a watershed scale rather than on a stream-by-stream basis. Dilution, neutralization, sorption, co-precipitation, and microbial mediation were identified as the major mechanisms attenuating aqueous transport of potentially deleterious metals.

Keith, D.C., Runnells, D.D., Esposito, K.J., Chermak, J.A., Levy, D.B., Hannula, S.R., Watts, M., and Hall, L., 2001, Geochemical models of the impact of acidic groundwater and evaporative sulfate salts on Boulder Creek at Iron Mountain, California: Applied Geochemistry, v. 16, nos. 7–8, p. 947–961.

Relevance: Keith and others (2001) modeled the potential of ARD to degrade streams during storm events. Although the study was in a location of extensive ARD contamination, the effect of rain events (temporal variability) and the transport processes (spatial variability) involved are important to any study of ARD.

Summary: Keith and others (2001) modeled the hydrogeochemical "rinse-out" of metals and acidity during the first major storm of the wet season at Boulder Creek and Iron Mountain, California. The heavy loading of metals and acidity arises from the dissolution of accumulated evaporative sulfate salts (SSM). For Boulder Creek, 20 percent of the dry-season baseflow was composed of acidic metal-bearing water. Modeling results suggested that even a relatively modest amount of sulfur salts can maintain the pH of surface streams near 3.0 during rainstorms. On a weight basis, it was determined that Fe-sulfate salts are capable of producing more acidity than other sulfate salts.

Orndorff, Z.W., and Daniels W.L., 2004, Evaluation of acidproducing sulfidic materials in Virginia highway corridors: Environmental Geology, v. 46, p. 209–216.

Relevance: Orndorff and Daniels (2004) provide a practical approach to an initial evaluation of ARD related to road construction. The sulfide hazard map is intended to provide information about pyrite-bearing formations and the potential need to adopt best management practices during construction along transportation corridors.

Summary: Orndorff and Daniels (2004) constructed a statewide sulfide hazard rating map for Virginia. Geologic formations associated with roadcuts producing ARD were characterized by calcium carbonate equivalence (from potential peroxide activity tests) and total sulfur. The authors considered occurrences from different geologic settings, including those in the Coastal Plain, Piedmont, Valley and Ridge, Appalachian Plateau, and Blue Ridge physiographic provinces. Formations with high acid producing potential did not always exhibit the most severe ARD, because the production of ARD at a given site was not only dependent on the acid-producing potential, but also on the proximity and

volume of surface water, drainage design, and the presence of ARD-neutralizing material.

Nordstrom, D.K., and Southam, Gordon, 1997, Geomicrobiology of sulfide mineral oxidation, *in* Banfield, J.F., and Nealson, K.H., eds., Geomicrobiology: Interactions between microbes and minerals: Washington D.C., Reviews in Mineralogy, Mineralogical Society of America, p. 361–390.

Relevance: The book chapter by Nordstrom and Southam (1997) is an excellent resource for exploring the biogeochemistry involved with ARD. The chapter provides a technical foundation of the oxidation reactions, reaction rates, and the catalyzing influence of microbiology on the chemical breakdown of sulfide minerals.

Summary: Nordstrom and Southam (1997) provide background for the biogeochemistry involved in pyrite oxidation. Microbes are often the only form of life found in waters impaired by ARD. Lithotrophs derive their metabolic energy from the oxidation of inorganic compounds, such as iron and sulfur. The most common lithotroph involved in the oxidation of pyritic materials is the bacterial genus, Thiobacillus. The presence of the lithotroph T. ferroxidans is described by Nordstrom and Southam (1997) as increasing the oxidation rate of iron by five orders of magnitude and having a significant effect on the weathering of pyrite. When the surface of pyrite interacts with acidic solutions, the iron is leached from the surface leaving a sulfur-rich surface. Bacteria attach themselves onto this sulfide surface and solubilize the surface through enzymatic oxidation (direct mechanism). Microbes also catalyze the oxidation of aqueous ferrous iron to ferric iron. Sulfide is then oxidized by the ferric iron (indirect mechanism).

Bibliographic Citations

The literature review focused on ARD and transportation issues and included references on ARD remediation, geochemical processes, and biochemical processes. The original literature review was expanded to include the formation and dissolution of secondary sulfate minerals (SSMs) associated with ARD because of the presence of SSM at roadcuts in Tennessee and the potential for ARD contaminant transport from the SSM. Additional references on AMD that were applicable to the microbial conditions, biogeochemical processes and applicable remediation methods were also included as part of the literature review.

The bibliography is divided by primary subject in the reference, either ARD or AMD, and subdivided by selected topic: remediation, geochemical, microbial, ecological impact, and secondary mineralization. References that did not fit the selected topics were grouped as "Other." The AMD references are not comprehensive, but include references that are most relevant to the understanding on the ARD processes and remediation. Selected references on the geology of pyrite-bearing formations in Tennessee are also included in the bibliography.

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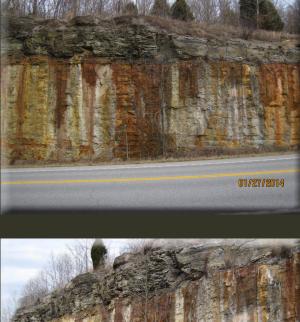
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