How does Acid Rock Drainage start?

Quick Facts:

- Sulfide or sulfur must be present for acid to form.
- Acid rock drainage naturally occurs when sulfur/sulfide ores are in contact with water and oxygen.
- Strong acid is made when certain bacteria populate the ore.
- Acid rock drainage may be found at coal mines, hard rock mines, or construction sites that disturb sulfide rock.

Background: The ocean contains sulfate and many trace metals such as gold (Au), copper (Cu), zinc (Zn), mercury (Hg), cadmium (Cd) and so forth. Sulfate (SO_4^{2-}) can become sulfide (S^{2-}) under certain conditions. Dissolved metals, especially divalent metals (Cu^{2+}, Zn^{2+}, Hg^{2+}, etc) bind strongly to S^{2-}, forming metal sulfides. Iron also binds to sulfides, often forming pyrite (FeS_2). Pyrite is common in areas where the ocean once contacted iron soils, and where ocean water has "intruded" into rock through hydrothermal or volcanic processes. A high percent of pyrite is an indication that metal sulfide ore may be in the area. Other types of rock and metal ores, such as carbonates and oxides, may be present in the same area as sulfide rock and ores.

Process: Natural weathering of ore – such as mine tailings, mine waste rock, tunnels or open pit walls – results in the production of a small amount of sulfuric acid (H_2SO_4, also written as $H^+ + SO_4^{2-}$ in equations). This reaction is self-limiting and pH generally does not drop below 4.5.

$$2\ FeS_2 + 2\ H_2O + 7\ O_2 \rightarrow 2\ Fe^{2+} + 4\ SO_4^{2-} + 4\ H^+$$

Bacteria may start to grow on the exposed rock, using the Fe^{2+} (ferrous iron) for energy. These are called iron-oxidizing bacteria. They need Fe^{2+} and oxygen, but get all their carbon from CO_2 in the air. They move electrons from Fe^{2+} to oxygen analogous to the way our cells move electrons from sugar to oxygen to make ATP energy. Humans make end-products of water and CO_2; iron-oxidizing bacteria make end products of water and Fe^{3+}, also called ferric iron.

$$4\ Fe^{2+} + O_2 + 4H^+ \rightarrow 4\ Fe^{3+} + 2\ H_2O$$

Ferric iron is able to act on sulfide rock to make much more acid than natural weathering, and will act even where no oxygen is present, such as under water. When this reaction occurs, pH often drops to 2, and in some places such as Iron Mountain, California, may drop to pH -1.5.

$$FeS_2 + 8\ H_2O + 14Fe^{3+} \rightarrow 15\ Fe^{2+} + 2SO_4^{2-} + 16H^+$$

Many species of iron-oxidizing bacteria are not killed by strong acid, and keep growing and making ferric iron as long as ferrous iron and oxygen are available. A positive feedback loop begins that cannot be stopped, illustrated below, as balanced equations. For this reason, some areas of the world have seen continuous acid production from mines dating back to when the Romans mined for iron[1].

Bacteria: $(4\ Fe^{2+} + O_2 + 4H^+ \rightarrow 4\ Fe^{3+} + 2\ H_2O)$ x 7 to balance electrons

Ferric iron oxidation of pyrite: $(FeS_2 + 8\ H_2O + 14Fe^{3+} \rightarrow 15\ Fe^{2+} + 2SO_4^{2-} + 16H^+)$ x 2 to balance

$$28\ Fe^{2+} + 7\ O_2 + 28\ H^+ \rightarrow 28\ Fe^{3+} + 14\ H_2O$$

$$30\ Fe^{2+} + 4\ SO_4^{2-} + 32\ H^+ \leftarrow 28\ Fe^{3+} + 16\ H_2O + 2\ FeS_2$$

[1] Rosia Montana Project Description. ESG International, Guelph, Ontario, Canada. September 30, 2002.

What are the Impacts of Acid Rock Drainage?

Quick Facts:

- Sulfuric acid dissolves metals in rock, which then precipitate when they reach neutral water downstream.
- When iron precipitates, it armors the stream bottom.
- Metals may remain bioavailable even after precipitation.
- High salinity from sulfates in acid drainage corrodes pipes, limiting industrial and agricultural use.

Impacts near the mine: As sulfuric acid is made, it dissolves rock around it, releasing metals that were previously bound up as solid ore. For instance, chalcopyrite ($CuFeS_2$) releases dissolved Cu^{2+} and Fe^{2+}; arsenopyrite (FeAsS) releases dissolved arsenic (As^{3+} or As^{5+}) and Fe^{2+}; galena (PbS) releases dissolved lead Pb^{2+}; cinnabar (HgS) releases dissolved mercury Hg^{2+}; feldspar rocks (aluminum silicates with calcium, magnesium, or sodium) release dissolved Al^{3+}, K^+, Ca^{2+}, Mg^{2+}. In this way, elements that make up the rock and mineral ore are released in a dissolved form into groundwater or surface water. The water color may be dark green, the color of ferrous iron, if there is little oxygen in the water, or red, the color of ferric iron, in oxygenated water. If there is a lot of copper in the water, it may take on a glacial green-blue color.

Initially when acidic water leaves a mine area, the streams or ponds it enters are impacted by low pH and anoxic kill flora and fauna in the watershed near the discharge.

Impacts downstream: Downstream, dilution and buffering occur. As mine discharge contacts neutral pH natural waters, metals begin to precipitate. The primary metal of concern is often iron, in abundance from dissolution of pyrite. As it precipitates in oxygenated water, it forms iron hydroxides, primarily $Fe(OH)_3$, which is a yellow-orange color. This sticks to the bottom of the stream or pond, and eventually "armors" it like cement. Plants and animals living in sediment die, and a domino effect may occur whereby other aquatic life dependent on sediment life becomes impacted.

Aluminum forms white streamers and gelatinous precipitates as it moves from the dissolved Al^{3+} form to the solid $Al(OH)_3$ form. This milky white material can clog the gills of fish, suffocating them.

Precipitated metal complexes are generally less bioavailable than dissolved metals or sorbed metals, but once they enter sediment, cycling can occur. Deeper sediments provide a "reduced" atmosphere, different than an oxygenated atmosphere, which can release metals or change their form. This is particularly dangerous when mercury has deposited. When elemental mercury (Hg^0) is eaten only 0.01-7% is absorbed, the rest will pass out of the intestines[1]. However, under reduced sediment conditions in areas where certain bacteria live (sulfate-reducers and others), the mercury is complexed to organic molecules, especially methyl groups ($CH_3 - Hg^+$). Plants, invertebrates, fish, and animals are able to absorb mercury in this form. At the sediment/water interface, metals may cycle between solid metal precipitates and dissolved metal ions as redox conditions change. Dissolved metals can be taken up directly by aquatic life, or bind loosely (sorb) to particles in water where they are available to filter feeders. Some metals, such as copper, are toxic in very low concentrations (parts per billion). Metals initially dissolved from acid rock drainage may enter the food chain downstream of a discharge area this way.

Salinity: Sulfate is often released in very high concentrations from mine discharge. The maximum contaminant level (MCL) for sulfate is 500 mg/L, and releases in acid mine discharge are often near 2,000 mg/L and can be over 20,000 mg/L. This is corrosive to pipes that carry water, makes industrial use of the water difficult, and the water cannot be used for irrigation.

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[2] Doull, J, CD Klaassen, and MO Amdur. 1980. Casarett and Doull's Toxicology: the basic science of poisons. 2nd edition. Macmillan Publishing Co., Inc. New York.

Can Acid Rock Drainage be Predicted?

Quick Facts:

- Geology, climate, and hydrology are important to ARD generation and vary between sites.
- The rate of release of acid producing and alkaline producing material may not be the same.
- Models often underestimate the potential for acid generation at hard rock mine sites, and models are not re-evaluated to determine if predictions were correct.

Factors affecting acid generation: The percent of sulfur or sulfide in rock may be quoted as indicative of the potential to generate acid, but many other factors are important in the final chemistry. As little as 0.2% sulfide may result in ARD depending on site conditions. The mass of sulfide and the mass of neutralizing rock such as carbonates and silicates need to be accurately estimated at different sections of the mine site. Rates at which sulfide oxidizes to acid versus rates that alkaline producing rocks dissolve need to be considered. For instance, if carbonates react quickly and are depleted while sulfide continues to make acid, acid will eventually be generated in the mine discharge. This change in rates may not be observed for decades. Different pyrite structures oxidize at different rates, making predictions particularly difficult. Under a microscope, if the pyrite mineral structure is shaped like clusters of raspberries ("framboidal") it oxidizes quickly; if it is made up of crystal-like clusters ("crystalline"), it oxidizes slowly.

Other factors that are important to whether, and how fast or how soon, ARD will present include the hydrology of the area, climate, particle size, and heterogeneity of rock.

Static and Kinetic Testing: A common method used to determine acid generating potential is Acid-Base Accounting (ABA) or "static" testing. This was developed to predict acid generation at coal mines, and is generally accurate for coal operations. This laboratory method estimates the potential for sulfide rock to generate acid (acid potential =AP) and the potential for neutralizing rock to consume acid (neutralizing potential =NP). The ratio of NP/AP is referred to as the net neutralizing potential (NNP). The ratio alone cannot provide full information on whether a site will develop ARD, any more than the percent sulfur/sulfide alone can– predictions need to be based on more than one factor. . A ratio of more than 1:1 is sometimes used to indicate that ARD will not develop, but sites with ratios as high as 5:1 have been known to develop ARD. Instead the ratio should be used as a guideline to determine what sections of the mine need to go through "kinetic" testing designed to better imitate site conditions. In general, rock with a ratio of 1:1 or higher should go through kinetic testing.

Kinetic testing may involve any of several different methods, with the "humidity cell" test being one of the more common. Kinetic tests involve larger sample sizes over longer periods of time than static tests. Variables may be adjusted, such as frequency and amount of wetting, particle size, and whether or not the sample is inoculated with bacteria. There is no single standard method for kinetic testing, nor a standard for interpretation. The purpose of the test is to confirm static test results, and estimate rates of acid generation and actual drainage water quality.

The parameters chosen for the test can be highly influential on the results. For instance, how representative the samples collected for the test are, how many samples are collected, how representative particle size and rock mixing are, the analytical method chosen, and the parameters for controlling the test (temperature, bacterial inoculation, wetting, and so forth).

Accuracy of Predictions: ABA predicts coal mine discharge well; in one study it was determined that predictions were correct 96% of the time[3]. However, the mineralogy at hard rock mines is much more complex, and predictions nearly always fail. In one study that looked in detail at 25 mines, all of which predicted they would not develop acid mine drainage, 89% did in fact generate acid[4].

Factors affecting prediction accuracy: Predicting chemical reactions in complex mineral systems is difficult because many site-specific factors need to be considered in the model. The results of static and kinetic testing need to be analyzed with the mineralogy, hydrology, and environment in mind, as well as an understanding of intended ore processing and mine waste management plans, water and gas transport within the exposed rock, and heterogeneity of potentially reactive areas. Testing cannot assume that acidity and alkalinity will be released in parallel, nor that they will be released similarly under different pH conditions; carbonate consumes acid more quickly at lower pH than at neutral pH. Models then need to be proofed by returning to sites to determine if the model was accurate, and if not, what factors may be confounding the results. In fact, neither mining companies nor regulators do the long term ground-proofing to determine model accuracy.

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[3] Skousen, J, J Simmons, LM McDonald, and P Ziemkiewicz. 2002. Acid-Base Accounting to Predict Post-Mining Drainage Quality on Surface Mines. J Env Quality 31: 2034-2044.

[4] Maest, A and J Kuipers. 2005. Comparison of Predicted and Actual Water quality at Hardrock Mines: the reliabilityof predictions in Environmental Impact Statements.

Can Acid Rock Drainage be Treated?

Quick Facts:

- Active and passive treatment techniques are available and may be used in combination.
- No one method works for all sites; flow volume and metal concentration are important in choosing a method that will work.
- Treatment is often required in perpetuity, so the cost of treatment can be very high.

Background: Treatment of ARD requires that acid be neutralized, dissolved metals removed, and sulfate concentrations reduced. Mine water discharge quality varies tremendously between sites. The volume of flow, timing of flow, types and concentrations of metals, cost, and site accessibility are the primary factors influencing the method chosen for remediation.

Treatment methods: Methods are generally classified as “active”, “passive”, or “semi-passive”. When flow volumes are high and/or metals are found in high concentration, an active method needs to be employed. The most common active method is adding lime to the mine water in a controlled manner. The lime, $Ca(OH)_2$, reacts with the acid, sulfate, and metals to make gypsum, $CaSO_4$, and metal hydroxides. The metal hydroxides precipitate, forming a sludge. Depending on the nature of the sludge and the site, sludge may be disposed of on-site, sprayed onto land (“land application”), or taken to a hazardous waste landfill. This may involve significant costs. Lime treatment also requires staff to be on site every day; because treatment will likely be required “in perpetuity” (for as long as acid is generated), operation and maintenance expenses can be quite high. In some areas, buildings need to be constructed and heated for the equipment and staff. In addition to cost, it can be difficult to remove some elements – particularly arsenic, selenium, and manganese. Sulfate generally remains near 1600 mg/L, and EPA maximum contaminant level (MCL) for sulfate are 500 mg/L.

Passive systems can be utilized for seeps, small volumes, and discharge with metal loadings that not extraordinarily high. Most passive systems involve a natural or man-made wetland or bioreactor. Wetlands contain anaerobic sediment in which sulfate-reducing bacteria (SRB) live. SRB convert sulfate in mine discharge water to sulfide – essentially reversing the process of natural weathering. When sulfide is present, dissolved metals, especially divalent metals, will bind and precipitate as dense metal sulfide sludge, removing the dissolved metals from the water. Because SRB use sulfate, sulfate is removed from the water to some extent, although generally not to as low as EPA MCL. While these systems offer an attractive “walk-away” solution, they are limited in the situations in which they will work effectively. SRB do not grow well in low pH water, so mine discharge may need to have the pH adjusted. In addition, SRB require carbon, but will not utilize cellulose or plant material; they consume small chain carbons such as ethanol, methanol, ethylene glycol, acetic acid, and so forth. Supplements such as hay, mushroom compost, manure and so forth are often added to man-made wetlands or bioreactors to stimulate bacteria that break this material down into smaller chains that SRB can utilize. This is inefficient, with SRB generally making up only about 1% of the total bacterial population in these systems. In addition, wetlands will need to have sludge removed from them.

Other passive techniques include aeration channels to oxidize iron and precipitate it in a controlled manner, and mixing limestone ($CaCO_3$) with waste rock to fill an open pit. Aeration channels need to have the base rock replaced frequently, and the long term efficacy of mixing limestone with waste rock will depend on many factors, similar to the issues faced in predicting ARD.

A semi-passive technique is one in which a pond area is built and designed specifically to encourage sulfate-reducing bacteria. In this, the mine water pH needs to be adjusted above pH 4.5 by pumping in sodium hydroxide and a preferred carbon needs to be dosed in. Because pumps are required, staff must visit the site on at least a weekly basis to monitor pumps and re-supply reagents. The sulfide sludge produced is more dense than the hydroxide sludge produced during liming, so sludge removal expenses may be reduced in addition to reduction in staff expenses. Sulfate discharge may be lower than at liming sites, although not as low as the EPA MCL.

A remediation method may combine any number of techniques, and mix passive and active systems.

Does remediation work? Lime treatment is generally effective for most metals, although removal of the metalloids arsenic and selenium can be problematic. There are occasionally issues with year-round access to the treatment site, and if liming is not consistent and year-round, the watershed will be impacted. The efficacy of passive techniques over the long term is yet to be determined.

CSP² FACT SHEET

FORMATION, IMPACTS, AND REMEDIATION OF ACID ROCK DRAINAGE

TERMS:

Acid rock drainage: Water that contains sulfuric acid as a result of sulfide/sulfur ore coming in contact with water and oxygen.

Bioavailability: Metal in a form that can be taken up and absorbed into the tissues or fluids of an animal or plant, with minimal excretion.

Carbonate: Rock containing CO_3^{2-}, usually bound to K^+, Ca^{2+}, and/or Mg^{2+}. Upon contact with acid, carbonate forms bicarbonate (HCO_3^-) or water and CO_2. By removing hydrogen ions (H^+) from solution, pH increases.

Humidity Cell Test: The protocol calls for 200 g of ore crushed to -2.38 mm and put in a plastic container. Over a 7 day cycle, dry air is passed over the sample for 3 days, humid air for 3 days, then 200 ml of deionized water is used to rinse it on the 7th day. The test is usually conducted for ten weeks. The purpose is to determine the rate of reactions of acid generating and acid consuming rock.

Iron-oxidizing bacteria: Bacteria that gain energy by transferring electrons from Fe^{2+} (ferrous iron) to oxygen, making end products of Fe^{3+} (ferric iron) and water. Electron transfer sets up an electron transport gradient that is used to make ATP energy. Example species/genus are *Acidothiobacillus ferrooxidans*, *Leptospirillum ferrooxidans*, and *Metallogenium*.

MCL: Maximum contaminant level – an enforceable EPA standard for drinking water contamination.

Reduced environment: A "redox" (reduction-oxidation) scale measures the "electron-richness" of a zone. Areas rich in electrons, or "reducing potential" are called reduced environments, and are in contrast to oxidized areas. In reduced zones, such as anaerobic sediments, metal ions change forms. Fe^{3+} becomes Fe^{2+}, As^{5+} becomes As^{3+}, Hg^{2+} becomes Hg^+ or Hg^0, and so forth. Complexes may dissolve and release free dissolved ions; e.g. $Fe(OH)_3$ is Fe^{3+} and three OH- ions bound together and this complex dissolves when Fe^{3+} is reduced to Fe^{2+}.

Sulfate-reducing bacteria (SRB): Anaerobic bacteria natural to wetlands that get energy by transferring electrons from carbon molecules (such as ethanol) to sulfate, with waste products of CO_2 (or small metabolic acids such as acetic acid) and sulfide. The free sulfide waste is available to bind dissolved metals to form a metal sulfide precipitate. Some example genuses are *Desulfovibrio*, *Desulfobacter*, *Desulfococcus,* and *Desulfobacterium.*

Sulfide mine: General term referring to a mine in which minerals are found bound to sulfides, or in an area with pyrite (FeS_2). Other ores may also be present, including neutralizing rock such as carbonates and silicates.

FOR FURTHER INFORMATION:

1. *Sulfur percentage that generates acid*
   Li, M.G. 2000. Acid rock drainage prediction for low-sulphide, low neutralization potential mine wastes. Proceedings from the Fifth International Conference on Acid Rock Drainage, ICARD 2000, p 567-580. Society for Mining, Metallurgy, and Exploration, Inc.

2. *Acid generating potential testing methods, and problems with them*
   US EPA. 1994. Acid Mine Drainage Prediction. Document EPA530-R-94-036.
   Sherlock, EJ, RW Lawrence, and R Poulin. 1994. On the neutralization of acid rock drainage by carbonate and silicate minerals. Environmental Geology 25 (1): 43-54.

3. *Prediction reliability*
   Maest, A and J Kuipers. 2005. Comparison of Predicted and Actual Water Quality at Hardrock Mines: the reliability of predictions in Environmental Impact Statements.
   Maest, A and J Kuipers. 2005. Predicting Water Quality at Hardrock Mines: Methods and Models, Uncertainties, and State-of-the-Art.

4. *ARD treatment methods*
   Skousen, JG and PF Ziemkiewicz. 1996. Acid mine drainage control and treatment. 2nd edition. National Mine Land Reclamation Center and West Virginia University. Morgantown, WV.