A PATHWAY TO WALK-AWAY?

30-Year Old Bactericide Technology to Suppress Acid Rock Drainage Needs to Be Revisited

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INTRODUCTION
Mine water treatment, either actively or passively, is unsustainable. Clearly, inexpensive suppression of acid rock drainage (ARD) at its source is required for the mining industry to avoid being saddled with ARD treatment in perpetuity. Geomembrane caps and covers, co-disposal, and other strategies address the physical aspects of ARD mitigation and control but they ignore the most important driver of ARD generation: microbial kinetics that represent one of four vertices on the ARD Tetrahedron (Figure 1). If one or more corners of the tetrahedron are disrupted or removed, ARD will not form. To date, most ARD control strategies have addressed pyrite, water, and air. The microbial community consisting of the common bacteria *acidithiobacillus-ferrooxidans* [ATBFO] has largely been ignored.

Patented controlled-release *ATFBO* bactericide pellets formulated in the 1980s, coupled with surface-applied bactericide, were used at dozens of ARD-prone sites across the USA and internationally. In the late-1990s, usage of this technology virtually ceased when the sole vendor of the bactericide products closed its doors. The primary goal of these products was facilitating revegetation on acid generating mine wastes. Decreasing ARD flows, metals/acidity loadings, and sulfate concentrations were secondary benefits. At the time, government agencies and mining companies alike viewed bactericide applications as temporary remedies. Three decades of positive performance data at some bactericide-treated sites suggest otherwise.

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With the right follow-up, the bactericide technology can work for much longer than the three months typically cited in the technical literature which is still being quoted (e.g., as in the INAP GARD Guide, Section 6.6.4.5). Perhaps this misperception is the main reason that the GARD Guide (2018) devotes relatively little of its focus (317 words in four paragraphs) on the use of bactericides for suppressing ARD.

While the technology of bactericide application is not new, 30-plus years of hindsight shows that it is not enough to kill the ATBFO; the acidophilic microbial community needs to be replaced with a pro-biotic heterotrophic community that outcompetes it for the process to “stick” (Figure 2). Neutral rock drainage (NRD) also appears to form due to microbial activity as shown by research at the Antamina Mine in the Peruvian Andes (Dockrey, et al., 2014). At this site, the pyrite bearing but non-acid-generating (NAG) mine waste contains significant carbonate content and while the resulting mining influenced water is net alkaline, it contains elevated levels of zinc, nickel, copper, and manganese.

The essence of this ARD-disrupting technology is that bactericides, coupled with organic matter to support competing bacteria, can suppress ARD permanently and sustainably. Other modern mining technology innovations can be merged into the strategy to increase its practicality and effectiveness. These include: heap leach application of bactericide solutions, geophysical identification of pyritic waste “hot spots,” and specialized grouting with innovative transport media such as foam or temporary grout made with common guar gum. ARD inhibitor delivery with agricultural drones has also been considered. Recent innovations in revegetation technology such as amending soils with biochar and pro-biotic soils can also contribute to ARD suppression on the sustainability side of the situation.

All these methods can be used with bactericides and naturalistic reagents (such as waste milk) to temporarily suppress ARD in tailings, waste rock, pit walls, etc. until modern vegetation best management practices (BMPs) can sustainably provide the necessary follow-up conditions to render the situation PERMANENT. Implementing this proven technology on a case-by-case basis would be the first key step on a practical “Pathway to Walk-Away” for mining companies and government agencies.

**KEYWORDS**
Acid Rock Drainage (ARD) suppression; ARD source control; microbial inhibition; anionic surfactant bactericides; probiotic organic acids

**BACKGROUND**
The bacterial component of ARD formation was first recognized in the early 1950s and subsequent research that appears to peak in the 1980s and 1990s revealed that many common surfactants such as sodium lauryl sulfate (SLS), sodium dodecylbenzene sulfonate (SDS), alkyl benzene sulfonate (ABS), biosolids, and other organic materials significantly inhibited bacterial activity with respect to ATBFO which had been initially identified as Thiobacillus-ferrooxidans.
In particular, Kleinmann and Erickson (1983) published a compendium of research findings on this topic in US Bureau of Mines (USBM) Report of Investigation No. 8847. In the mid- to late-1980s and the decade following, bactericide usage focused on facilitating revegetation of pyritic coal mine wastes (e.g., coarse coal refuse) and minimizing acidic drainage from pyritic shale partings in surface mine backfill. A summary of the advances and state of the art was provided by R. Kleinmann in Brady, Smith, and Schueck, eds., 1998 (Chapter 15).

The development of controlled-release pellets containing SLS was one key advance in the ATBFO bactericide technology since the publication of USBM RI No.8847 in 1983. The commercially available product called “ProMac” which evolved through two formulations (Kleinmann in Brady et al., 1998) was typically applied in the following manner:

1. The exposed mine waste surface received agricultural lime or other alkaline amendments to neutralize stored acidity;
2. A 2% solution of SLS was sprayed on exposed pyritic mine waste with a hydroseeding unit;
3. Slow-release ProMac pellets were applied; these dissolved at various rates to basically deliver an SLS solution with a steady concentration of about 465 mg/L dissolved in infiltrating rainfall or snowmelt (Sobek et al., 1990); and
4. A final lift of topsoil or plant growth media as thin as 100 mm was placed and revegetated.

The revegetation step appeared to be a key step in the success of ATBFO suppression process; otherwise, SLS reapplications as frequent as three times per year were recommended (Kleinmann, op cit.). Verburg et al. (2003) observed positive results with the application of a 1% SLS solution to suppress ARD formation in a metal mine tailing containing 60% by weight pyritic sulfur. Verburg et al. observed the following trend: “… the supernatant from the bactericide-amended samples without exception has the highest values for pH and lowest values of specific conductance, acidity, and sulfate with each material group [tested].” After 30 weeks of observation, the positive effects of SLS application were still evident but were rightly considered temporary.

Other non-surfactant organic amendments were found to be effective in suppressing ATBFO including:

- Composted sewage sludge (Pichtel & Dick, 1990)
- Water-soluble extract from composted sewage sludge (Pichtel & Dick, 1990)
- Composted paper mill sludge (Pichtel & Dick, 1990)
- Spent brewery grain (Lindsay et al., 2010)
- Pyruvic acid (Pichtel & Dick, 1990)
- Waste milk/dairy products (Jin et al., 2008 & 2012)

In theory, any biodegradable organic matter, including biochemical reactor (BCR) effluent could be effective in suppressing ATBFO (Gusek, 2015). When biodegradable organic matter is included in the design, the ATBFO suppression effects may last longer than SLS, SDS, or ABS alone, but they should still only be considered temporary. A robust plant community is recommended to sustainably suppress ATBFO in the long term. This means that the vegetative community on the land surface above closed underground mines or pit walls has a greater importance on the longevity of bactericide treatments.
HOW SURFACTANT-BASED BACTERICIDES WORK

The ATBFO organism functions well in aqueous environments exhibiting pH values <2.0. To survive in this hostile environment, the microbes cloak themselves in a thick oily protein membrane which employs several protective mechanisms, including proton “pumps,” that allow the cells to maintain a circumneutral internal pH. Surfactants disrupt the protein membrane resulting in the flooding of the cell protoplasm with the surrounding acidic fluid. In effect, the microbe “stews in its own juices” and is destroyed. It is impossible for an ATBFO cell to develop resistance strategies as do other common microbes in response to exposure to antibiotics. See Figure 3.

Probiotic Bacteria Substitution Facilitated by Organic “Bactericides”

Darwinian forces can also be employed to suppress ATBFO activity. If organic nutrients are available to a suite of introduced heterotrophic microbes, these microbes can out-complete the ATBFO consortium for resources (i.e., oxygen and iron) and ATBFO populations are thus decimated. As previously cited, common municipal biosolids and organic acids have been shown to suppress ATBFO activity (Pichtel and Dick, 1990). The proteins in waste milk can provide a similar effect (Jin, et al., 2008). The EPA has used biosolids on at least five Superfund sites but only one, the California Gulch Site in Colorado, exhibited acidic drainage issues due to the presence of pyrite (EPA Clue-In, 2011).

However, while the biosolids may have provided a temporary inhibitory effect, the subsequent success of the vegetation on these sites appears to have played a major role in the sustainability of the overall process. That is, the organic acids generated by seasonal plant root degradation provide another antibacterial reagent that can suppress ATBFO (Tuttle, et al., 1977). The organic acids induce a weakening in the ATBFO cell wall and its contents leak out (Figure 4).

In a net alkaline geochemical environment that exhibits neutral rock drainage, reducing conditions induced by the presence of organic matter can dissolve the iron mineral Schwertmannite, which has been identified as an ideal substrate/media for ATBFO colonies (Dockrey, et al., 2014). Consequently, an organic amendment strategy has the additional potential of robbing ATBFO of critical microbial habitat.

When these various inhibitory mechanisms are combined, the “probiotic” effect from microbial consortia that outcompete ATBFO may be the key to why the benefits of some previous SLS and SDS applications appear to persist for decades.

Waste milk and dairy products fall into a special category because of the casein protein they typically contain, even in powdered form. Casein is pH sensitive; it transforms into curds and whey at a pH of about 4.6. This “heat seeking missile” like characteristic can result in the passivation of pyrite surfaces, nearby accumulations of ATBFO acidic salts, and/or Schwertmannite in a biofilm of curds/cheese. This “cheese-ball” effect immobilizes organic matter where it is needed the most, in the proximity of pyrite in the mine waste mass, where it can exclude oxygen and support heterotrophic bacteria thus disrupting two vertices of the ARD Tetrahedron and perhaps passing the “tipping point” into sustainability as discussed below.

**SUCCESSFUL BACTERICIDE CASE HISTORIES—HAS IT BEEN DONE BEFORE?**

While the concept of permanently suppressing ARD using an anti-bacterial strategy sounds too good to be true, it has been documented at some mine sites. However, this can be a challenge because many projects were completed 20 to 30 years ago and the sites have dropped from public and regulatory oversight. A lack of digital data on these sites adds an additional layer of documenting challenge. However, the reader is referred to a paper (Gusek, 2016) in which seven case histories of success are documented.
• Route 43, Jefferson County, OH
• Branchton Coal Refuse Disposal Area, Butler County, PA
• North Fork Coal Mine, Wise County, VA
• Dawmont Coal Refuse, Harrison County, WV
• Norton Coal Refuse, Randolph County, WV
• California Gulch Superfund Site, Lake County, CO
• Fisher Coal Mine, Indiana County, PA (See also Gusek & Plocus, 2016)

A PATHWAY TO WALK AWAY
A “Walk-Away” mine land reclamation/remediation scenario is the holy grail of any mining company or government agency. To achieve this status, a site must require: 1) little to no maintenance, 2) infrequent inspection, and 3) little or no long-term monitoring while simultaneously being returned to a land use that is a benefit to society.

Case histories previously documented and others demonstrate that walk-away successes are possible even in situations where pyritic waste has already been intensely involved in microbial/ATBFO activity. However, a “silver bullet,” one-size-fits-all approach will not be successful unless it is followed by the development of a robust vegetative cover that delivers a steady dosage of antibacterial organic acids. Each site may have its own set of “tipping points” whereby the acidophilic population is sufficiently decimated to the point that sustainable organic-acid delivering BMPs provide long-term ARD suppression for walking away. This “pre-conditioning” concept warrants additional research.

The science and engineering behind revegetation of disturbed mine land is well-documented in three-decades of the proceedings of the American Society of Mining and Reclamation (see www.asmr.us). However, the sequential applications of organic and inorganic amendments that suppress ATBFO activity have yet to be combined in a manner that pre-conditions a problematic site past the “tipping point” to reap the benefits subsequent vegetation. Design considerations for site pre-conditioning follow.

Controlled Application of Antibacterial Reagents
With the lack of ProMac or similar controlled release technologies, alternative SLS delivery methods are required. Fortunately, heap leaching practices for gold and silver ore matured in the western USA in the early 1970s and are now used world-wide. This concept was described by Gusek (2015) for the application of BCR effluent or waste milk (organic bactericides) but it might also be used for the controlled delivery of inorganic/surfactant bactericides such as SLS. Antibacterial reagents can also be delivered using temporarily stable foams as described by Gusek et al. (2012). The reagents can be solid, liquid, or gaseous. As SLS is a common foaming agent, the foam itself is antibacterial.

However, one must consider the strength of the bactericide solution in any controlled delivery design. Elevated concentrations of SLS, for example, may adversely affect desirable heterotrophic bacterial communities as well as ATBFO (Clark, 2015). Also, excessive SLS concentrations can adversely affect aquatic organisms. This design consideration supports the concept of prolonged application of low dosage bactericides; it is probably another reason that the slow release pellets worked as well as they did.

2. Addition information (Gusek, 2017) on some of these sites can also be downloaded from the ASMR website.
Advances in Revegetation Technology
While much has been accomplished with regard to revegetating drastically disturbed lands, advancements continue. Examples could include genetically-modified plants that might capitalize on soil characteristics that are typically toxic to natural plant species to gain a vegetative foothold in challenging environments. Also, the use of biochar (Harley, 2011) as a soil amendment has potential to increase soil cover production by sequestering plant nutrients/fertilizers in a way that is not easily rinsed out by precipitation events but is still extractable by plants. Establishing a robust vegetative cover should accelerate site recovery and suppress ARD more quickly than waiting for natural plant community succession. Some vendors (Theisen, 2018) are offering biotic soils that are applied with a hydroseeder.

Merging of Different Technologies
The engineer’s toolbox of ARD suppressing technologies has increased in breadth since the introduction of bactericides about three decades ago. Unfortunately during this period, the ARD suppression “industry” per se appears to have acquired a “vendor” perception where a specific product is advocated for nearly every situation. As ARD has been termed a worldwide bacterial infection (Gusek, 2012), it seems that another medical analogue is appropriate: some ARD suppression practitioners might be analogous to medical doctor specialists who are proficient at healing patients with a specific malady rather than primary care physicians who view a patient holistically. From an engineering perspective, remediation of ARD requires a 21st century “general practitioner” who can merge the available technologies into a coordinated assault on the ATBFO community at a given site or in a given situation.

This assault might include:

- a primary application of SLS bactericide to decimate the ATBFO community followed by
- an application of waste milk or other organic amendment (with inoculant) to establish a competing heterotrophic bacterial community finally followed by
- the establishment of a vibrant and sustainable vegetative cover to maintain the heterotrophs.

If properly designed and engineered, this could be a promising “Pathway to Walk-Away” for sites plagued with chronic ARD.

Economic Comparisons
Comparing the cost of perpetual mine water treatment (even passively) with a one-time application of ARD-inhibitors can be complicated by the incremental cost of revegetation which is required in virtually every mine closure plan. While the purchase cost of some ARD-inhibitors such as sewage sludge may be zero, transportation costs to the site may be prohibitive. Each situation will be different.

The ARD inhibiting reagents are remarkably inexpensive. For example, the reagent cost (in 1995) at the Fisher Site as detailed in Gusek and Plocus (2016) was $8,400. Kleinmann and Erickson (1983) reported that sodium lauryl sulfate (SLS) had been applied to a 4.45 ha inactive coal refuse pile in southern West Virginia, USA at a material cost of about $US500/ha. SLS is the active ingredient in shampoo and it can be obtained in powder form virtually anywhere in the world. Assuming inflation of about 5% per annum for 35 years, the 2018 estimated material
cost for the Kleinmann and Erickson site would be about $2,750/ha. If one assumes that the application cost is about equal to the material cost, this value doubled is about US$6,200 per ha. No water treatment data for the site is available.

Powdered milk is a sustainable product that is globally available. In 2018, a milk over-supply situation exists in the US due to changing consumer habits, trade wars, and other factors (Shanker & Mulvany, 2018). This challenge for the dairy industry may be an opportunity for the mining industry. For example, slightly out-of-specification powdered milk is available in the US for about US$2.20 per kilogram. A typical powdered milk reconstitution recipe calls for 96 grams of powdered milk per liter of water. A 2% strength diluted milk suspension (1.92 grams of milk powder per liter) would cost about US$ 4.42 per m$^3$ or $0.017$ per US gallon. As previously discussed, this probiotic, ARD-inhibiting liquid could be delivered to acidic mine waste (either vegetated or barren) using heap leach technology. If the site is already vegetated, this application might be a one-time event. Data from site specific laboratory tests and field demonstrations would provide the design basis. In summary, given favorable dairy product market conditions, diluted waste milk that might be otherwise fed to animals (e.g., pigs) or dumped on pastures might find a new beneficial use and a new sustainable market for dairy farmers might be created.

If one considers that in-perpetuity (mathematically) would be 100 years in the future and one further assumes a discount rate of 5 percent, the break-even cost of a one-time, year-zero application of ARD inhibitors would be 19.85 times the annual cost (assuming no inflation) of perpetual treatment. In other words, if perpetual treatment cost $1 million per year for a century, one could break even by “investing” $19.85 million in ARD suppression at the site. Modest inflation would skew the break-even value upward, of course, but the economic benefits are clear: investing significantly less than the break-even cost in ARD prevention measures that would minimize or eliminate long term treatment costs is probably a good idea.

**SUMMARY**

The use of bactericides and probiotic inhibitors (combined) is an established, sustainable strategy for suppressing the oxidation of pyrite and the production of both acid rock drainage and neutral rock drainage. The strategy is based on sound science and engineering. Alone, the beneficial effects of bactericides such as anionic surfactants are temporary; overdosing would not improve the outcome and this approach and could actually harm the environment.

Probiotic inhibitors such as applied organic wastes alone are also a temporary remedy. The organic matter will eventually be consumed, albeit slowly, the ATBFO community will rebound, and ARD/NRD production will return.

Based on case studies, a sequential ARD inhibition strategy appears to hold the most promise where:

- The *ATBFO* community is **decimated** with anionic surfactant bactericides,
- Introduced organic matter and an inoculum produces a new bacterial community that **out-competes** the weakened *ATBFO* microbial suite, and
- The new organic-based bacterial community is supported and **sustained** by the organic/humic acids generated by surface vegetation.

This ARD-suppressing sequence of **Decimate, Out-Compete, and Sustain** involving the combined use of bactericides, probiotic inhibitors, coupled with sustainable vegetation could
provide a “walk-away” remedy for many mine sites at a cost much less than perpetual mine water treatment. Using off-the-shelf technology, the mining industry can advance toward a walk-away remedy for ARD that will improve the bottom line for many sulfide ore projects (both legacy and planned), and preserve its social license to mine.

REFERENCES CITED


