Mitigating Acid Rock Drainage with Land-Applied Biochemical Reactor Effluent

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ABSTRACT
Perpetual treatment of acid rock drainage (ARD) is unsustainable; ARD suppression at its source is the logical strategy to avoid or lessen ARD impacts. Innovative mitigation concepts have been advanced in recent years; the concept of land-applying biochemical reactor (BCR) effluent to suppress ARD is another promising strategic tool. The concept’s elegance lies with the merging of two well-developed mine remediation/processing technologies: BCRs and heap or dump leaching of metal ores. In the proposed innovative approach, organic-rich effluent from a BCR would be land-applied to acid-producing mine waste (e.g., tailings, waste rock, and coal refuse) with solution application methods typically used in heap leach pads. BCR effluent is typically anoxic and contains biochemical oxygen demand, excess alkalinity, dissolved sulfide ion, and dissolved manganese. The process would capitalize on these characteristics to coat mine waste with films of biosolids and/or manganese oxide that would suppress biological and abiotic pyrite oxidation. To the author’s knowledge, this technology has not been implemented in a formal way but anecdotal information suggests that a properly-engineered application could yield significant long term environmental benefits.

Keywords: ARD, bactericide, sustainability, heap leaching
INTRODUCTION

A Medical Analogue

If one can embrace the medical analogue, much of the mining industry currently suffers from a massive bacterial infection. When pyrite-bearing or sulfide-bearing rock formations, tailings, or mine wastes are infected by Acidithiobacillus ferrooxidans, the likelihood of forming acid rock drainage (ARD) is almost guaranteed. The “pharmacy” of antibiotics available is extensive, ranging from solid alkaline amendments like limestone to liquid “medicines” such as sodium lauryl sulfate and sodium thiocyanate. Many of these materials may be in short supply (locally), or carry inconvenient side-effects. The danger of re-infection is a concern that also needs to be addressed. A “probiotic”, naturally-sustainable regimen that introduces a microbial consortium that outcompetes the acidophiles may be the key to why some previous antibiotic applications continue to work for decades. See Gusek and Rastogi, 2015.

Unfortunately, the “geo-medical” teams of geochemists, microbiologists, engineers, and mine managers lack the tools to surgically apply these active ingredients where they are needed most with a minimum of waste. The implementation of up-to-date best management practices has not healed the patient; the equivalent of an intravenous drip of a very inexpensive generic medicine followed by a pro-biotic protocol is clearly needed.

An “Intravenous Drip” for ARD Suppression

The answer to this problem may lie with the merging of two well-developed mine remediation/processing technologies: biochemical reactors (BCRs) and heap or dump leaching of metal ores. In the proposed innovative technology, organic-rich effluent from a BCR would be land-applied to acid-producing mine waste (e.g., tailings, waste rock, and coal refuse) using solution application methods typically used in precious metal heap leach pads.

BCR effluent is typically anoxic and contains biochemical oxygen demand, excess alkalinity, dissolved sulfide ion and manganese. If all these antibiotic and probiotic characteristics can be preserved and the BCR effluent solution can be dispersed over a large area of mine waste (which could be either revegetated or barren), the downward percolating solution should coat the mine waste with a film of probiotic bacteria-supporting biosolids that would suppress biological and abiotic pyrite oxidation. While to the author’s knowledge this has never been implemented, it is believed that heap leach solution application techniques could accomplish this inexpensively. The mine waste ARD source would behave similar to a trickling filter in a waste water treatment plant. ARD might be suppressed for decades, perhaps longer, before a “booster shot” of BCR effluent might be required.

ARD REFRESHER

The formation of ARD is a natural process. In the presence of air, water, and acidophilic bacteria, sulfide minerals such as pyrite oxidize and produce sulfuric acid; concurrently, iron and other metals are released into the water. The problem can be associated with both coal and hard rock operations where previously buried sulfide minerals are exposed to oxygen and water. The descriptions of the bio-geochemical reactions responsible for ARD are found in many technical
papers and will not be repeated here. However, it may be reasonable to revisit the general conditions required for ARD to form.

ARD Tetrahedron

Considered simply, the elementary ingredients required for the formation of ARD are analogous to the components needed for the burning of combustible materials. To start a fire, one must have air, heat, and a fuel source. To generate ARD, one needs air, water, a pyrite source, and the bacteria to speed reactions that would otherwise occur slowly: consider an "ARD Tetrahedron" concept (see Figure 1), with each requirement positioned at a vertex. If any of the primary ingredients are missing, isolated, or chemically neutralized, fire/ARD will not form. Pyrite will oxidize in the absence of acidophilic bacteria; however, these bacteria are reported to accelerate the kinetics of pyrite oxidation by an order of magnitude (Baldi, et al. 1992).

![ARD Tetrahedron](image)

Figure 1 ARD Tetrahedron (Gusek, 1994)

Baseline Testing

The tendency of a given rock or material to produce ARD is predicted by a number of standard tests, including acid-base accounting, humidity cells, and column leach testing. Based on this author’s experience, the microbial component of ARD production in these tests is rarely assessed. Even more rarely, probiotic measures such as the application of waste milk to create heterotrophic biofilms that outcompete acidophiles (Jin et al. 2008) have only recently been considered as viable technologies.

However, the concept of introducing competing bacteria is not new. Sobek, Benedetti, and Rastogi (1990) suggested that a probiotic process would complement the application of a slow-release acidophilic bactericide, sodium lauryl sulfate:

“Inhibiting or destroying thiobacilli can significantly slow the rate of acid production. Anionic surfactants, organic acids and food preservatives (Onysko et al. 1984) act as bactericides and kill these bacteria; however, bactericides degrade over time and are lost because of leaching and runoff. To overcome the inherent short duration effectiveness of spray applications, controlled release systems to provide the bactericide slowly over a long time period were developed (Sobek et al. 1985).

Control of acid generation for prolonged periods greatly enhances reclamation efforts and can reduce reclamation costs by reducing the amount of topsoil needed to establish vegetation. Three natural processes resulting from strong
vegetative cover for three years or more can break the acid production cycle. These processes are:
1) A healthy root system that competes for both oxygen and moisture with acid-producing bacteria;
2) Populations of beneficial heterotrophic soil bacteria and fungi that are re-established, resulting in the formation of organic acids that are inhibitory to T. ferrooxidans (Tuttle et al. 1977); and
3) The action of plant root respiration and heterotrophic bacteria increase CO$_2$ levels in the spoil, resulting in an unfavorable microenvironment for growth of T. ferrooxidans.”

Sobek, Benedetti, and Rastogi viewed antibacterial application as a method to reduce the volume of topsoil to revegetate potentially acid generating or PAG waste. They believed that at least three years of acidophilic bacterial suppression was sufficient to accomplish this goal.

The 21st century ARD-focused community of geochemists may be aware of how acidophilic bacteria promote ARD but they may not understand its kinetic importance. An informal survey suggests that inclusion of acidophilic inoculum, bactericides, and nutrients to support competing bacteria in humidity cell and column leach tests is rarely attempted because the effects of bactericides have always been considered temporary. As Sobek, Benedetti, and Rastogi (1990) suggest, that might be true but the limitation might be overcome by substitution of heterotrophic bacteria and fungi into the ARD generation zone coupled with a slow-release bactericide.

**BIOCHEMICAL REACTOR TECHNOLOGY REFRESHER**

Sulfate reduction in biochemical reactors (BCRs) has been shown to effectively treat ARD containing dissolved heavy metals, including aluminum, in a variety of situations. The chemical reactions are facilitated by the bacteria *Desulfovibrio* in BCRs as shown schematically in Figure 2 and the photo in Figure 3. However, a consortium of bacteria contribute to this effort as discussed in Seyler et al. (2003).

![Figure 2 Down-flow Biochemical Reactor Schematic](image1)

![Figure 3 A Typical Biochemical Reactor](image2)

The key conditions for sulfate reducing bacteria (SRB) health are a pH of 5.0 (maintained by the SRB itself through the bicarbonate reaction and/or the presence of limestone sand), the presence of a source of sulfate (typically from the ARD), and organic matter (from the substrate). BCRs have
been successful at substantially reducing metal concentrations, nitrate concentrations, and favorably adjusting pH of metal and coal mine drainages.

As discussed in Blumenstein & Gusek (2010), typical BCR effluent contains biochemical oxygen (BOD)/dissolved total organic carbon (TOC), and sulfide in varying concentrations. Ironically, when compared to the context of this paper, these are referred to as “nuisance” parameters that need to be addressed in order to allow the discharge of a BCR effluent to a natural receiving stream that might be impacted by BOD and the depressed dissolved oxygen characteristics of raw BCR effluent.

Fortunately, the BOC/TOC cited above are also probiotic nutrients that can support a microbial community that can occupy and quickly displace the niche occupied by the acidophiles.

It is noteworthy that BCRs do not remove manganese. Thus, any dissolved manganese present in the BCR present is available to create encapsulating and metal adsorption-capable films of MnO₂ (“desert varnish”) under certain aerobic conditions.

**HEAP LEACH TECHNOLOGY REFRESHER**

Heap leaching technology was described by Agricola in the 16th century as a method for recovering alum for tanning of animal hides (Kappes, 2002). In America, a similar technology was used in Vermont in the early-1800’s at the Elizabeth Mine for recovery of Copperas, or hydrated ferrous sulfate, that was used for curing and setting colors in hides and pelts, dye and ink manufacturing, and for treating timber (Hammarstrom et al. in Slack, 2001). Modern gold and silver heap leaching practices matured in the western USA in the early 1970s and are now used world-wide.

The recovery of metals from ore heaps or marginal mine waste dumps involves the application of a “barren” leach solution (typically sodium cyanide in the case of precious metals and sulfuric acid in the case of copper) to dissolve the metals to yield a pregnant or “preg” solution that is recovered by gravity and processed for the metal(s) of interest. After the metals are recovered from the preg solution, the resulting barren solution is recycled back to the heap to leach more metals. Several holding and process ponds are involved as shown in Figure 4.

Kappes (2002) provides an overview of the heap leaching process; design aspects related to the application of BCR effluent to mine wastes follow.

Solution distribution piping that is typically installed on top of the heap or dump is a leaching design feature of special interest with regard to ARD suppression. There are four mainstream methods for applying barren solution (Kappes, 2002):

- Drip emitters,
- Wobbler sprinklers,
- Reciprocating sprinklers, and
- High rate evaporative sprinklers.

To preserve the anoxic and geochemically reducing characteristics exhibited by BCR effluent, reciprocating and evaporative sprinklers would logically be avoided. The oxidation of BCR effluent as it traveled from the sprinkler head to the PAG rock surface or tailings surface would result in a deposit of biosolids and noxious odor.

Drip emitters or wobbler sprinklers would allow the well-buffered, soluble TOC containing solution to infiltrate into and percolate through the mine waste where ARD-suppressing biofilms should form along preferential pathways. This approach would be especially attractive in situations where the mine waste repository surface had already been revegetated. BCR effluent
would percolate through the plant growth medium and some buffering and organic matter addition would certainly bolster the productivity of the vegetative community.

A typical leach pad solution distribution system is comprised of a series of header pipes and sub-header pipes connected to a series of lateral pipes or hoses into which the drip emitters or wobbler sprinklers are installed. Whether or not the distribution piping is removed prior to a leach pad’s or waste repository’s receiving a fresh lift of ore-grade material will vary depending on site-specific economics. It may be more cost effective to abandon a piping network in place rather than expending the time and labor effort to dismantle, move, and reinstall it elsewhere on the site.

![Figure 4](image.png)

**Figure 4** Heap Leach Pad Schematic (After Chamberlain & Pojar, 1984)

As subsequently discussed, it is unlikely that a BCR effluent solution distribution system would be abandoned in place due to the relatively temporary (compared to a “resource recovery” operation) deployment over an ARD-producing zone in the mine waste repository (which might include pit walls). Rather, the solution distribution system would be designed to be modular and easily transferred in a sequential fashion to where it would be needed next at the site.

If a heap leach pad contains PAG rock, it is probably only a matter of time before ARD becomes an issue. Cellan, et al. (1997) described the construction of a “Biopass” system at the closed Santa Fe gold mine in Mineral County, Nevada. The installation included retrofitting a geomembrane-lined solution pond into a BCR. The effluent from the BCR flowed by gravity through a buried pipeline to a leach field. The proposed ARD-suppressing process would differ from the Cellan et al. concept by recycling the effluent from the retrofitted pond(s) back to the source of the ARD. Of course, this will alter the water balance of the leach facility and a “circulating load” of mining influenced water would need to be managed. A new water balance estimate would be design necessity if BCR effluent is applied to the PAG waste in this fashion.

Faulkner (2015) described a “nuisance” condition where elevated BOD-containing BCR effluent from a newly commissioned unit was land-applied to a waste rock dump that exhibited elevated selenium concentrations. The selenium concentrations in the dump seepage co-incidentally decreased in response to the BCR effluent application. It is too early to say if the decreased selenium levels will persist after the land application activity was suspended.
VACCINATION VS MEDICATION?

Continuing with the medical analogy, vaccination to suppress ARD should ideally occur shortly after pyritic waste is either excavated or placed. Thus, vaccination would occur before the acidophilic bacterial community has a chance to mature. The medical sage advice of Benjamin Franklin, “an ounce of prevention is worth a pound of cure”, is especially appropriate but it might be updated for a mine site application to read: “a tonne of ARD prevention is worth a hectare of passive treatment”.

The advantages of pursuing this preventive protocol include:

- Closer control of ARD-suppressing solution application (focused only on PAG waste zones identified by geophysics, mining records, field testing, or other methods),
- Lower cost because the levels of stored acidity in the PAG waste (if it is fresh) should be low,
- Better management of ARD issues throughout the mine life instead of waiting until closure and attempting to gain control of a “Stage 4” geo-bacterial condition, and
- Lower costs of active treatment during operations.

The application of geo-medicines to suppress ARD on legacy sites that have been “cooking” for years offers a special challenge. This is the analogous “medication” scenario. As the surfactant-based bactericides such as sodium lauryl sulfate are organic compounds, they are susceptible to degradation when exposed to acidic conditions on the acidified mineral surfaces. In this author’s opinion, any bactericide should be applied in a solution that is well-buffered and contains enough alkalinity to protect the bactericide’s molecular integrity from the stored acidity in the mine waste. This suggests that medicating a “thoroughly-infected” mine waste material will be more expensive than the implementing vaccinating protocol described above for the same material.

The preference to engineer a “silver bullet” process to suppress ARD with bactericides and probiotic nutrients in a single “cocktail” application is a strong one. It will save costs and time. However, unpublished data suggests that some acidophilic bactericides are also toxic to probiotic bacterial communities. This finding suggests that a sequential application strategy may have a better chance of success in producing the desired outcome: decimation of the acidophilic community and its replacement with a self-sustaining heterotrophic community perpetually supported by organic acids from the healthy vegetation on the surface of the site.

Expected ARD Suppression Mechanisms

The percolating BCR effluent should contain at least five characteristics known to suppress ARD:

1. Dissolved organic carbon (measured as BOD or TOC),
2. Bicarbonate alkalinity,
3. Reducing oxidation reduction potential (ORP) of – 100 mv or less,
4. Low dissolved oxygen [DO] (<1 mg/L),
5. Dissolved sulfide ion, and
6. Dissolved manganese.

The alkalinity and low DO in the BCR effluent should decimate the acidophilic community. The sulfide ion and reducing ORP conditions should facilitate precipitating any dissolved ferrous iron
the solution encounters as a monosulfide (FeS). The BOD present in the solution should be oxidized and form a coating of biosolids on the mine waste particle surfaces. This biofilm layer should support a microbial community that outcompetes the acidophilic community and thereby suppress ARD formation. Based on the slow degradation of organic matter in municipal landfills, the beneficial effects of these combined mechanisms could persist for decades.

The benefits of manganese dioxide MnO$_2$ deposition would occur deeper in the rock/waste “column” under oxidizing conditions. The MnO$_2$ would tend to coat exposed rock surfaces along the preferential flow pathways. This reaction would only occur at circum-neutral pH such as that provided by well-buffered BCR effluent.

The proposed ARD suppression method is more appropriate to surface mining situations such as:

- Heap leach facilities,
- Tailing storage facilities,
- Waste rock repositories,
- Coal refuse disposal sites (fine and coarse refuse), and
- Pit walls.

Space limitations prohibit more detailed discussions on how BCR effluent application with heap leach pad drip emitters might be implemented in the above situations. However, it must be stressed that the long-term success of the proposed technology depends on the ultimate establishment of a robust vegetated cover to create a perpetual “probiotic” almost walkaway ARD remedy. Again, this “marriage” of BCR and heap leaching technologies is conceptual; to the author’s knowledge, it has never been implemented.

**MEDICATION CASE STUDIES**

The application of BCR effluent to suppress ARD is a promising concept. Anecdotal information suggests that there may be sites in the USA where it is being evaluated. Consequently, only two case studies in the literature appear to be available to suggest that the concept could work with an appropriate level of design effort.

**Antibiotic Case Study in Pennsylvania, USA**

Plocus and Rastogi (1997) sequentially injected solutions of caustic soda (NaOH) and sodium lauryl sulfate at the Fisher Coal Mine in Pennsylvania USA in 1995. The PAG rock zone in a backfilled coal pit had been identified using geophysical techniques. The site was fully revegetated at the time of the two-step caustic/bactericide application through a network of shallow and deep injection boreholes that mimicked the pattern typically found in a heap leach pad. The effects of the injection process were dramatic. See Gusek and Plocus (2015). Chemistry of a toe seep at the site improved enough within 30 days that chemical treatment of the ARD was no longer required. In 2014, almost two decades later, this is still the case. The seepage chemistry is suitable enough to be polished in an aerobic passive treatment system. Bond release for the site is pending.

**Probiotic Case Study in Tennessee, USA**

An injection/treatment process similar to the one described by Plocus and Rastogi was implemented at the Sequatchie Valley coal mine in Tennessee. In this case, waste milk and a bacterial inoculum (biosolids) were injected into mine waste that had been reclaimed and revegetated. The project, completed by the Western Research Institute (Jin, et al., 2008 and ITRC, 2014) was undertaken to establish a bio-film of bacteria on the pyritic waste that would out-compete Acidithiobacillus ferrooxidans and thereby prevent ARD. While details are lacking, the technology was implemented in a 4 ha area exhibiting a seepage of about 0.12 m$^3$/min. (30 gpm).
Ground water upstream of the test plot exhibits typical ARD characteristics, depressed pH (5.5 to 6.0 standard units); the seepage downstream of the test plot exhibits a pH of 6.8 to 8 about four years after the initial injection event (ITRC, 2014). Plans are underway to evaluate this technology in a more con-trolled manner at the Sequatchie site.

It is interesting to note that this probiotic application did not include a specific bactericide as implemented by Plocus and Rastogi. This might be due to how the casein protein in milk behaves when it contacts an acidic environment: by curdling into a globular mass. One could theorize that this property imparts a “heat-seeking missile” effect to the patented process of using dairy products to suppress ARD. The milk proteins should selectively coat rock surfaces that are acidic. Regardless, conventional wisdom suggests that BCR effluent (with its high dissolved organic matter content) would be more similar to milk than to the two ARD-mitigating solutions that Plocus and Rastogi used sequentially at the Fisher site. Similar to milk’s behavior, when BCR effluent encounters oxidizing conditions on a rock surface, a film of organic biosolids should be selectively deposited.

PRELIMINARY “MEDICATION” COST MODEL

Ultimately, the cost of implementing this ARD mitigation alternative would need to be compared to the costs of perpetual treatment. As a starting point, a drip irrigation cost estimating spreadsheet available from the University of Delaware Agricultural Extension (U. of D., 2014) was used to develop the cost of installing a drip irrigation system on a hypothetical 8.1 ha ARD “medication” situation site. The irrigation system was sized with a drip row spacing of about 1 meter to apply about 152.4 cm of BCR solution for over the span of a year. This would amount to about 33.8 m$^3$ per day or 12344 m$^3$ per annum. The capital cost of the installation was about US$14500. The annual operating cost was estimated to be about US$19000, most of which was labor. Factoring in the useful life of the various capital components yielded an annual fixed cost of US$7200 to yield a total annual cost of about US$26000.

Gusek and Schneider (2010) cited a projected BCR unit treatment cost of US$0.31 per m$^3$ of effluent spread over the assumed 20-year BCR lifespan. This would amount to about US$4000 per year. Combining the drip sprinkler and BCR cost yielded an annual cost of about US$30000 per year or about US$3700 per ha or US$1500 per acre. Of course, the actual volume of BCR effluent required, its application rate, and duration may need to be adjusted for site-specific conditions which would be based on small scale field tests.

CONCLUSIONS

The re-purposing of BCR effluent to suppress ARD formation is a scientifically sound concept. It has never been implemented but if it works as expected, ubiquitous ARD suppressing materials such as wood chips, spoiled hay, straw, and animal manure could be locally procured to reduce costs and provide sustainable supplies that would be naturally grown, not manufactured. Carbon sequestration may be a small side benefit of the process. The upside potential of this innovative merging of two common mining technologies could provide a paradigm shift in mine remediation strategy that has incalculable benefits to society world-wide. This emerging technology could be another step on the “pathway to walkaway” with regard to mine closure.
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