

ENGINEERED PUMPABLE pHOAM™: A NEW INNOVATIVE METHOD FOR MITIGATING ARD¹

James Gusek², Brian Masloff, and John Fodor

Abstract. 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 ferro-oxidans*, 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, sodium thiocyanate, waste milk, and bipolar lipids. 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. Distribution of fine grained limestone on the surface of an acidic mine waste dump is analogous to applying a bandage soaked in antacid to treat an upset stomach. The implementation of up-to-date best management practices has not healed the patient; an equivalent combination of hypodermic needle, cyber knife, and arthroscopic probe is clearly needed.

Using an engineered, flow-able or pumpable foam or pHoam™ as the medicinally analogous “dextrose delivery solution” for solid and/or liquid “geo-antibiotics”, the authors have combined off-the-shelf technologies that have been previously applied in solving geotechnical problems in the mining industry. A patent for the innovative process is pending. This paper discusses method concepts and the advantages it could provide over conventional BMPs.

Preliminary laboratory test results suggest that the delivery of solid and liquid materials into porous, unsaturated rock can provide a variety of ARD-suppressing coatings.

The timing of ARD-suppressing materials’ application to ARD-prone wastes in the mining and processing cycle may govern whether these materials behave as a post-infection medicine or as a vaccine that prevents infection altogether. Field demonstration sites are being sought.

Additional Key Words: acid rock drainage suppression, heavy metals, mining influenced water

¹ For presentation at the 2012 Annual Meeting of the West Virginia Surface Mine Drainage Task Force, Morgantown, WV.

² James Gusek is a senior consultant with Golder Associates Inc., Lakewood, CO 80228, jgusek@golder.com (corresponding author). Brian Masloff and John Fodor are engineers with Cellular Concrete Solutions, LLC, Golden, CO 80401

Introduction

Water pollution associated with mining activity has been a problem for societies probably since pre-historic times although it may have not been recognized at the time. The pioneering hard rock miners in the Colorado Rockies recognized the impacts from poor water quality; the water entering some of their underground workings was so metal-laden and acidic that they could not use it to feed their boilers. In some mines, acid water dissolved iron rails, plating out dissolved copper in the process. In the 16th century, the author G. Agricola in his book *De Re Metallica* noted that water contaminated by mining activities "poisons the brooks and streams, and either destroys the fish or drives them away".

Modern mining activities, both coal and hard rock can generate much the same problem, but with the large volumes of ore and waste rock being excavated and moved, the impacts to the environment are magnified a billion-fold. It is commonly referred to as acid rock drainage or ARD. The sources of water pollution/ARD include draining adits and tunnels, leachate from waste rock and tailings/coal refuse facilities, and water accumulating in or discharging from abandoned pits. Even the construction of highways in geological terrain containing pollution generating rocks has been identified as a problem. The Tennessee Department of Transportation commissioned a guideline document which focused on pollution prevention and ARD mitigation best management practices (Gusek et al., 2008).

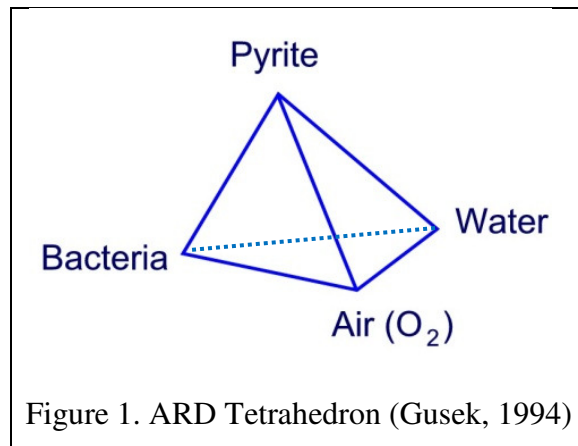
ARD Formation

The formation of ARD is a natural process. In the presence of air, water, and 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 ASMR papers and will not be repeated here. However, it is prudent to revisit the general conditions required for ARD to form.

ARD Tetrahedron Relationship

Considered simply, the elementary ingredients required for the formation of ARD are analogous to the components needed for the burning of combustible materials. To have a fire, one must have air, heat and a fuel source. To have ARD, one needs air, water, and 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. The oxidation of pyrite is an exothermic reaction very similar to conventional combustion. In some extreme cases pyritic mine wastes have actually spontaneously ignited (Li and Parr, 1926), resulting in localized sulfidic air pollution.



The tendency of a given rock or material produce ARD is predicted by a number of standard tests, including acid-base accounting tests, humidity cell tests, and column leach tests.

Active Ingredients That Can Suppress ARD Production

Researchers and practitioners of water pollution mitigation have identified various active ingredients that can be applied to potential water pollution situations both within the mining industry (including ARD production) and in similar conditions (e.g., road construction). Many of these concepts have been successfully demonstrated on laboratory scale, but only a few have been tried at actual sites. The active ingredients include liquids, solid particles, gases, and living microbes; they are all designed to disrupt the ARD Tetrahedron relationship (Figure 1) and thereby prevent or suppress ARD. Examples of each active ingredient type follow.

Liquid Active Ingredients

Olsen, et al. (2006) provides a comprehensive discussion of ARD-suppressing liquid reagents which is summarized and expanded here. Examples of liquid active ingredients include: sodium lauryl sulfate, a common surfactant identified as a bactericide that mitigates the oxidation of the mineral pyrite, bi-polar lipids (Zhang et al., 2003), and sodium thiocyanate appear to have a similar effect. Sodium hydroxide and hydrated lime solutions can adjust the pH of acidic pore water in contact with pyritic rocks and thus suppress ARD-generating bacterial activity.

Additional examples of liquid active ingredients include solutions of dissolved potassium permanganate (KMnO_4) which has been shown to coat particulate mine waste materials with a layer of manganese dioxide and isolate pyritic rock from air and water and thus suppress ARD formation. Waste milk has been show to encourage a bio-film of bacteria that out-compete the

suite of acid-generating bacteria (Jin et al., 2008 and ITRC, 2011). Solutions of dissolved phosphate have been shown to complex with dissolved iron and starve bio-oxidation of pyrite through disruption of the kinetics of ARD formation. However, use of this active ingredient has undesirable consequences if it is not properly controlled because it is a microbial nutrient. Silicate-based liquid active ingredients that coat the surfaces of pollution-prone materials have also been developed (e.g., Keeco Mix (Mitchell et al., 1999)).

While not practical in typical situations, waste paint might be used to suppress pyrite oxidation and prevent ARD.

Solid Active Ingredients

Examples of solid active ingredients include:

- limestone, dolomite, cement kiln dust, steel slag, sodium bicarbonate, fly ash and other coal combustion by-products, and various pozzolanic materials which can provide acid-neutralizing alkalinity to pyritic rocks and mine wastes which are prone to produce ARD;
- slow-release bactericides (Rastogi et al., 1986) such as the commercial product ProMac™ which can suppress pyrite oxidizing bacteria;
- organic materials such as cellulose, wood, paper, bio-solids, animal and vegetable protein whose decay can create conditions that suppress pyrite oxidation and ARD; and
- processed peat, natural peat, zeolite minerals, manganese oxides, and similar man-made products such as resins known to adsorb heavy metals.

Additional examples of solid active ingredients include: zero valent iron, nano-scale iron, powdered iron oxy-hydroxides, and powdered copper. These materials have the ability to chemically alter dissolved pollutants and as a result, detoxify them.

Gaseous Active Ingredients

Examples of gaseous active ingredients include: carbon dioxide or nitrogen which can displace oxygen in the pore spaces in unsaturated, particulate mine wastes and thereby suppress ARD production; and hydrogen sulfide which also may have a similar effect as well as immobilizing heavy metals that may be in solutions in contact with particulate mine wastes. While using gaseous ARD suppressing materials is theoretically possible, their use to date has

been minimal. Oxygen depletion through encapsulation or total, permanent immersion in weakly oxygenated water is a passive approach to ARD management.

Microbial Active Ingredients

Examples of microbial active ingredients include common materials that typically include bacterial suites including the bacteria *Desulfovibrio*, which under certain conditions and in the presence of other cellulose-degrading bacteria can out-compete *Acidithiobacillus ferro-oxidans* and thus suppress ARD (Zhang et al., 2003). Common microbial source active ingredients may include municipal sewage bio-solids, composted animal manure, and organic soils harvested from natural wetlands.

Table 1 below summarizes some common ARD-suppressing materials available and what vertex of the ARD Tetrahedron they are known to suppress, but delivering these to large volumes of materials or areas has been problematic, especially if the materials are deposited or encountered in an unsaturated condition.

Table 1 – Summary of Materials Known to Suppress ARD

Basic ARD Ingredient	The “Geo-Medicines”	Anticipated ARD-Suppressing Reaction
Air	Fresh or composted wood chips, sawdust, or cellulose Mushroom compost Animal & vegetable protein Municipal sewage bio-solids Paper products	Consumes oxygen by organic decay
	Nitrogen Carbon dioxide	Displaces air/oxygen
Water	Potassium permanganate solutions Keeco Mix (micro-silicate) Bentonite clay Paint (latex or oil-based) or other water-resistant coating material	Coats reactive surfaces to render them impermeable
	Chitorem™	Add organic matter and alkalinity
Sulfides	Limestone Dolomite Kiln dust Sodium bicarbonate Fly ash Flue gas desulfurization Pozzolanic materials (cement)	Neutralize acidity/add alkalinity

Basic ARD Ingredient	The “Geo-Medicines”	Anticipated ARD-Suppressing Reaction
Sulfides (Cont).	Steel slag Lime solution Sodium hydroxide solution Ammonia solution	
Bacteria	Sodium lauryl sulfate (aka shampoo) (Kleinmann, 1982) Alkyl-benzene sulfonate (aka laundry detergent) Milk Bi-polar lipids Potassium Humate (Leonardite) Sodium thiocyanate solution Phosphate solution	Bactericide
	Composted animal manure Municipal sewage bio-solids Natural soils from wetlands	Inoculate ARD-prone rock with beneficial bacteria (Jin et al., 2008)

Limitations of Conventional Active Ingredient Application

Many of these pollution mitigation strategies and methods were patented but have not been widely applied despite their potential to solve a specific ARD problem. The primary reason for this aspect relates to the inability of practitioners to feasibly deliver and apply active ingredients to large volumes of potentially-ARD-generating materials. When active ingredients are carried in a conventional suspension or slurry (for solids) or a conventional solution (for liquids), there is much waste and little if any hydrologic control. This is especially true when the liquids are injected into permeable materials such as a pile of mine waste rock or coarse coal refuse.

For example, the injected fluids are drawn by gravity toward the bottom of the pile with little horizontal dispersion; multiple injection boreholes with close spacing may be required to effectively deliver the active ingredients to the waste horizon target. Excess fluids drain out the bottom of the pile and may be difficult or impossible to capture and recycle. However, the process has been demonstrated (see Fisher Coal Mine below).

Case Studies of Conventional Active Ingredient Application

1996 – Fisher Coal Mine, PA

A pumped injection technique for suppressing ARD is well-documented in Plocus and Rastogi (1997) which required four deep injection wells [16 m (53 ft) deep] and 25 shallow injection wells 3 m (10 feet) deep to treat only about 1,200 m² (0.3 acres) of a coal mine waste pile in Pennsylvania. In order to implement their injection plan, pumping equipment with a pressure capacity of 20.7 megapascals (3,000 psi) was required. The active ingredients they used were a 20% solution of sodium hydroxide followed by a 2% solution of sodium lauryl sulfate, injected sequentially. While the process worked and the treatment appears to still be working 16 years later (Plocus, 2011), the technology was not considered practical.

1996 – Fran Coal Mine, PA

Schueck et al. (1996) reported on treating pods of pyritic material in a backfilled surface coal mine pit with FBC ash grout in three ways:

- 1) injection grouting only,
- 2) capping only, and
- 3) both capping and grout injection.

Based on the water chemistry results from monitoring wells, Option 3 worked the best followed by Option 1. Schueck et al. (1996) reported:

The inability to control final grout placement is a major drawback of the injection process... Because the grout is a viscous fluid, it will tend to flow into high permeability zones when pumped into spoil under pressure. If the permeability within the [pyritic rock] pod is low, the injected grout may flow away from the pod instead of filling the voids within the pod as intended or else the well will accept very little grout. When this happens, AMD abatement will be limited or will not occur at all.

2003 - Neves Corvo Copper-Tin Mine, Portugal

Verburg et al. (2003) reported the results of a 30-week monitoring humidity test cells filled with pyritic mill tailing paste to evaluate various ARD-prevention strategies. They found that “the bactericide-amended samples demonstrate consistently higher values for paste pH and lower values for SC [specific conductance] than the other samples, both in the short term and long

term”. The results further demonstrated that the application of the bactericide had a beneficial effect (i.e., preventing growth and bacterial activity) during all stages of acid generation at this site. The effects of the bactericide application persisted throughout the 30-week monitoring period. Contrary to the findings of Plocus described above, the authors believed that “under operational or post-closure conditions, periodic or continuous application of a surfactant-type bactericide is generally required to maintain effectiveness”. This belief may be related to the perceived difficulty in evenly applying a bactericide to tailings in an operational environment.

2006 – Sequatchie Valley Coal Mine, TN

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, the Western Research Institute (Jin et al., 2008 and ITRC, 2011) injected a mixture of undiluted waste/returned milk and a bacterial inoculum (biosolids) into mine waste that had been reclaimed and revegetated. The goal of the process was to establish a bio-film of bacteria (>70 species) on the pyritic waste that would out-compete acido-thiobacillus ferro-oxidans and thereby prevent ARD. A brief description of the multiple event injection process follows (Jin et al., 2008).

A total of 3,000 gal of ES [biosolids] and 9,000 gallons of returned milk were injected from day 35 to 116 of the study and an additional 9,000 gal of returned milk was injected approximately 1 year later from day 430 to 511. Returned milk was injected as soon as it was collected from stores by the dairy so milk was not stockpiled and injected at one time but over a few months.

The technology was implemented in a 4 ha (10 acre) area exhibiting a seepage of about 0.12 m³/min. (30 gpm). Ground water upstream of the test plot exhibits typical ARD characteristics, depressed pH (5.5 to 6.0 s.u.); the seepage downstream of the test plot exhibits a pH of 6.8 to 8 about four years after the initial injection event (ITRC, 2011). This promising process was recently patented (Jin et al., 2012).

A Revised Theory of Bactericide Field Effectiveness

It has been long held that highly-soluble bactericides offer only a temporary ARD mitigating benefit and lose their effectiveness because they are washed away by percolating rain and snowmelt (Verburg et al., 2003). How then, does one explain the 16-year endurance of the

bactericide application at the Fisher coal mine by Plocus and Rastogi? A revised theory of field effectiveness of bactericides is proposed: early bactericide applications were successful but only temporary because the acidophilic community may have been decimated and pockets of acidophilic thiobacillus ferro-oxidans survived in rock particle crevices to provide the inoculum for re-infection.

To counter this phenomenon, slow-release commercial bactericides like ProMac™ were developed. As the bactericide component, sodium lauryl sulfate, was eluted from the ProMac™ by rainfall events and the spring freshet, it was thought that the "I-V" drip delivery would keep the acidophilic community in check until the positive biogeochemical benefits of surface revegetation efforts kicked in. This may have worked in many cases which might be a future investigation topic for others. However, long-term documented effectiveness of bactericide application to suppress ARD was never proven; the mining community and researchers addressing the ARD problem found answers in abiotic acid-base accounting ratios and numerical thresholds. Indeed, there appear to be only two case studies providing evidence that long term application of bactericides or similar anti-bacterial measures work: the aforementioned Fisher and Sequatchie coal mines. What could have possibly made them successful?

Despite the completely different ARD-suppressing reagents involved (i.e., bactericides and waste dairy products), the two factors for success appear to be:

- 1) temporary but complete saturation of the geophysically-targeted acidic mine waste with the bactericide solutions, and/or
- 2) Multiple injections of ARD-suppressing reagents.

Bactericides and Dairy Products are Colloidal Suspensions

It is interesting to note that both anti-bacterial surfactants (e.g., sodium lauryl sulfate) and milk are classified as suspensions of colloids, not true solutions. Thus, the active ingredients within the liquid phase form “micelles” or nano-scale clusters of molecules (Zsigmondy, 1917 and Shaw, 1980). This phenomenon can be visually observed as the “cloudiness” of colloidal fluids compared to the clarity of true solutions. Unfortunately, this clustering phenomenon could theoretically affect the biological toxicity of the treatment if the injected fluids were diluted (as in the case of the Fisher Mine). The micelles of reagents would be distributed like raisins in a

pie rather than uniformly dispersed. An ARD-suppressing reagent delivery method that avoids this restriction could be quite beneficial.

Foam: An Innovative Active Ingredient Delivery Method

Foam is a two-phase fluid consisting of a gas component surrounded by a thin fluid phase that is developed with a soluble surfactant or soap. In senescence, the interiors of the colloidal micelles previously described are filled with gas and the specific surface of active ingredient (e.g., bactericide) is greatly increased while the amount of water required to saturate a target treatment zone are proportionally decreased. Research efforts are underway to use this engineered material to deliver ARD-suppressing liquid-phase active ingredients (e.g., bactericides, etc.) which can be entrained in or are a part of the foam structure. In addition, solid phase ARD-suppressing ingredients such as limestone, lime, steel slag, biosolids, or cement kiln dust can be entrained and suspended in the foam structure. Such mixtures comprised of ARD-suppressing components are hereafter referred to as pHoamTM to distinguish it from common foams used in other industrial applications, including fire-fighting.

The proposed pHoamTM method solves the active ingredient delivery problem by increasing the mobility and surface area of solutions or mixtures of active ingredients without sacrificing hydrologic control. Active ingredients suspended or contained in a pHoamTM of pre-determined "stability", can flow omni-directionally or bi-directionally from a single injection point as an advancing front. The density of the pHoamTM composites will typically be less than 320 kg/m³, which should lower injection pressures and increase the injection duration and coverage from each injection point.

pHoamTM Stability

The term "stability" used here refers to the general characteristics of the mixture with regard to longevity of the foam structure, its density, water content, and fluidity. For example, a pHoamTM could be designed to be thick enough to resist being drawn by gravity to the bottom of a given zone being treated and would advance in three dimensions, as a bulb. It could also completely fill an underground mine adit or coal mine entry. It would be expected to penetrate any roof falls as long as the collapsed material was permeable.

Alternatively, the pHoam™ mixture could be designed with a high “slump” (using a term familiar to those dealing with concrete designs) that would fan out generally in two dimensions, following a horizontal plane as in the case of covering a relatively flat tailings surface or following the floor of an open pit or pit bench or mine adit/entry.

pHoam™ longevity can be manipulated to a desired time required for maximum treatment or travel through the material treated. For example, if a pHoam™ were to be applied to acidic mine waste on a truck load by truck load basis, the pHoam™ structure might only need to persist for an hour or less, as long as the pHoam™ permeates the entire load. Conversely, pHoam™ injected into a waste rock dump might be designed to persist for several days to allow maximum penetration.

The water content of pHoam™ can be adjusted to produce a relatively dry pHoam™ which barely changes the moisture content of the rock mass being treated. When the bubble structure collapses, the entrained moisture will coat the nearby rock particles. If the rock mass has a relatively high field capacity, a soil characteristic, compared to the moisture content of the pHoam™, little if any leakage from the treated mass should result. The active ingredients, both liquid and solid, should remain within the waste mass and not flow or rinse out.

Conversely, a high water content pHoam™ might be used to rinse out undesirable target contaminants from the mine waste. For example, a high water content pHoam™ could rinse out retained nitrate contamination derived from blasting agent residue in a waste rock dump that would otherwise require an extended period to be flushed out by pulses of infiltration of rain or snow melt.

The Physics of pHoam™

As discussed by Blauer and Kohlhas (1974):

Generally, foams are dispersions of a relatively large volume of gas in a relatively small volume of liquid. When the volume of liquid is considerably greater than that of gas, the gas bubbles are, as a rule, spherical and their mutual interaction is weak. These systems are known as "gas emulsions." In a true foam, the bubbles are so crowded that their shape is deformed, usually polyhedral.

Since the pHoam™ is mostly comprised of a gas phase with very little liquid (e.g. foam might be formulated to be 10% water and 90% gas), the liquid is more likely to be retained as a coating on the rock particles when the foam structure de-stabilizes. If a solid phase is present in the pHoam™, it is more likely to be deposited on the surfaces of the mine waste instead of being carried away by gravity drainage in a conventional slurry suspension. Polymer additives can also be used in conjunction with pHoam™ composites. The polymer can bond the active ingredients to the mine waste.

Also, as the solid phase is a relatively small volumetric component of the pHoam™ mass, it is difficult to completely fill the pore spaces between the permeable mine waste particles. This is a desirable condition, as it allows multiple events of active ingredient injection; i.e., a “booster shot” of antibiotics is required if the active ingredients are consumed and require replenishment.

The particle size distribution of the mine waste will certainly influence pHoam™ designs. Consider the heterotrophic nature of a typical mine waste dump (Figure 2). Due to the natural particle size segregation associated with end-dumping from trucks over the edge, a zone of larger waste particles will be typically found at the toe of each lift. These high-permeability zones can act as preferred pathways for air and water which will promote ARD formation. Injected pHoam™ would also follow these preferred pathways, depositing ARD-suppressing reagents where they could provide the highest benefit. Fine-grained zones adjacent

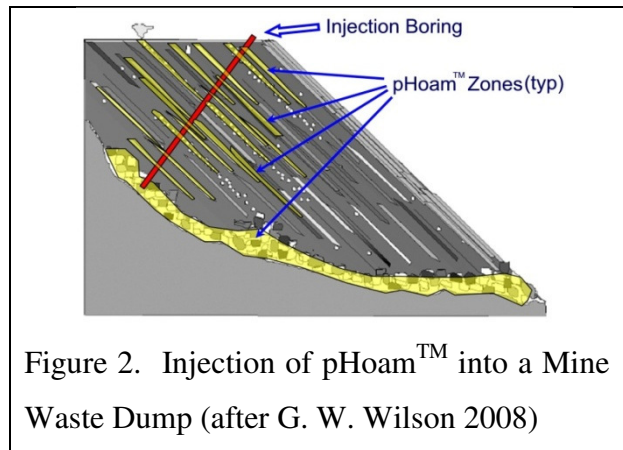


Figure 2. Injection of pHoam™ into a Mine Waste Dump (after G. W. Wilson 2008)

to coarser zones would tend to “wick” the liquid phase of active ingredients into the matrix and retain it with capillary force. The wicking could be facilitated by the decreases in surface tension provided by the surfactant component of the pHoam™. It is likely that solid phase ARD-suppressing reagents would be deposited adjacent to the finer-grained zones as a “rind” of beneficial treatment.

The “Cyber-Knife” Effect

It is well known that pyrite oxidation is exothermic. This reaction can result in elevated temperatures in mine waste and in the worst situation, actual combustion. Common sense suggests that when foam or pHoam™ approaches materials with elevated temperatures, the foam/ pHoam™ bubble structure will collapse as the liquid component evaporates. This feature could potentially give pHoam™ a “heat-seeking missile” capability that could automatically deliver more ARD-suppressing active ingredients to a mine waste site in the zones where it is needed the most. Hot zones in the mine waste would become “sinks” for pHoam™ bubble disintegration and resultant preferential deposition of more active ingredients compared to cooler zones nearby. Adopting the medical analogy, this is similar to a cyber-knife application to a specific diseased target organ without the need for an equivalent MRI image.

Potential Application Situations – Medicine or Vaccine?

When does ARD-prone rock get infected? Conventional wisdom suggests that freshly-excavated rock containing pyrite has a relatively small acidophilic population when it is being excavated from a working face in a mine. Prolific infection with acidophilic bacteria does not appear to be instantaneous and sometimes months may pass before low-pH ARD is exhibited in runoff and/or seepage. The whole point of adding alkalinity to satisfy acid-base accounting based ARD-suppression criteria is to allow the amendments to collectively behave as a preventive “vaccine” to suppress acidophilic bacterial activity. Wilson (2008), in his discussion of cover installations on waste rock, suggests that ARD prevention as the waste is placed should help to minimize future ARD treatment liability.

It is uncertain how long a bactericide needs to be contact with the target organism to be effective. However, from a pHoam™ perspective, a diluted pHoam recipe whose bubble structure decays in less than an hour (i.e., one with a relatively low “stability” as previously discussed) might be analogous to a “weakened virus” that would deal with human or animal disease. This is a topic that could benefit from future research.

Logic would therefore suggest that the amount of ARD-preventing “pHarmaceuticals” may be less (and therefore less expensive to apply) as a preventive vaccine compared to the amounts needs to “medically” address a larger, more-established and problematic acidophilic microbial

community. In other words, applying an ARD preventive vaccine may be much more cost effective than waiting until mine closure to address this issue. To be effective, however, vaccination efforts must be thorough as even small volumes of un-vaccinated ARD-prone rock could eventually re-infect adjacent treated areas.

Equipment

The production of pHoam™ uses common construction equipment including tanks, mixers, compressors, reagent feeders and piping. Foam generation equipment typically has no moving parts. For example, a photo of an in-line static mixer is shown in Figure 3. A schematic layout of a pHoam™ system for treating a heap leach pad is provided in Figure 4; while the equipment spread may appear simple, the innovation in the technology lies in designing the pHoam™ with the desired stability that matches the ARD-suppression situation.

Because up to 90% of the pHoam™ composite is a gas, large volumes of mine waste (or mine voids) can be treated using minimal amounts of water and active ingredients.



Figure 3. Static mixer used to combine solid and foam components to create pHoam™

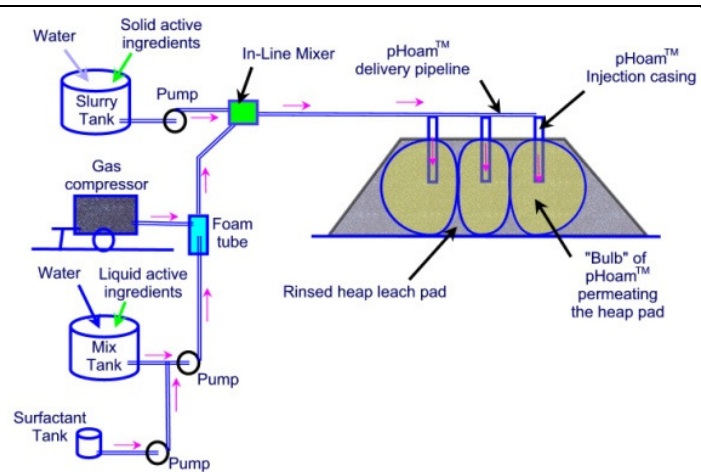


Figure 4. Example pHoam™ System Schematic Layout

Laboratory Test Work

Static Test Coating of Coarse Grained Rock

Practitioners in the petroleum industry have been injecting foams into porous media since the 1970's as evidenced in the technical literature (e.g., Blauer and Kohlhas, 1974) but the geological settings were significantly different from those faced by the mining industry. To validate the technology with regard to ARD-suppression, the authors conducted several laboratory scale demonstrations. The first demonstration validated that a pHoam™ mixture could be developed to coat large particles of rock with a thin layer of fine-grained limestone with little water. Figures 5A through 5B compare the initial pHoam™ application on the left with the limestone-coated rocks about an hour later on the right. Figure 5C is a close-up photo of the rock surface with a safety pin for scale; the rock in Figure 5D exhibits a coating (estimated <1mm thick) on the treated surface.



pHoam™ Injection into Coarse-Grained Rock Filled Column

The authors next filled a 150 mm diameter 2.1 meter long clear plastic tube with test gravel (nominal diameter 25mm particles) after inserting a garden hose tremmie pipe into the sealed bottom of the pipe. The tube was positioned at a reclining angle of about 20 degrees on a sawhorse support. The pHoam™ injection rate was on the order of 0.75 liters per second (12 gpm). The void space in the tube was estimated to be about 15 liters (40% voids). The pHoam™ advanced in a steady front from the bottom to the top of the tube in about 20 seconds after which the pHoam™ feed was suspended. However, the pHoam™ continued to expand and fill voids in the gravel after the feed was suspended. See Figure 6.



Figure 6. Gravel in column is encapsulated with pHoam™ after feed was suspended

A similar test was conducted with a 50 mm (2-inch) diameter column filled with 1.5 kg of relatively dry pea gravel (moisture <1%). The voids in the column were completely filled with a pHoam™ generated with 72 mL of liquid containing a sodium lauryl sulfate surfactant. The pHoam was designed to be stable for 12 to 18 hours. As a result of the application/injection, the moisture content was increased by about 4.8%. The final apparent moisture content of about 5.8% was less than the field capacity of the material, so the liquid content of the pHoam™ appeared to evenly coat the pea gravel after the bubble structure collapsed.

Costs

It can be safely projected that the more “stable” the pHoam™ mixture is, the more expensive it will be due to increasing surfactant requirements. Preliminary cost estimating model results suggest that treatment costs will be primarily influenced by:

1. surfactant type - there are natural, protein-based surfactants that may double as oxygen-depleting active ingredients
2. surfactant strength - a short-lived ARD pHoam™ “vaccine” formulation may not require as much surfactant as one designed to persist for several days and travel great distances (several hundred meters) in a “medicinal” formulation being injected into a thoroughly-infected mine waste mass (e.g., mine waste or coal refuse dump)
3. Cost of solid active ingredients (e.g., biosolids, alkalinity sources)
4. Cost of liquid active ingredients (e.g., water-soluble organic materials or alkalinity sources or non-surfactant bactericides)

Labor and equipment costs per tonne or cubic meter of mine waste treated are expected to be less than 20 percent of the total. The preliminary cost estimating model results were strongly influenced by the values assumed for the active ingredients.

For example, some municipalities currently pay over US\$316 per dry tonne to dispose of biosolids [20% solids by weight] produced from waste water treatment plants (Carollo Engineers 2008). If biosolids, which are predominantly comprised of organic carbon, are found to be a suitable solid-phase ARD suppressing material, and a municipality was willing to pay a mining company a fraction of its current disposal cost, the “credit” from this income stream could significantly offset surfactant, labor and equipment costs and final cost of ARD prevention using the pHoam™ technology may be very low and *sustainable*. In an ideal situation, the mining company (or any other public, private, and non-profit entity) utilizing the pHoam™ process to deliver ARD-suppressing materials that others consider a waste might actually turn a small profit. Of course, as soon as the municipality discovers that there is a market for their biosolids/waste material, the price may escalate. Procuring multiple sources of a given active ARD-suppressing ingredient well in advance would be advised.

If biosolids’ application as an ARD-suppressing material is practical, why has it not already been used? The answer, as with any other material in the “ARD pHarmacy”, is likely that a

practical way of delivering it to coat large volumes of mine waste has not been available. Perhaps this situation is no longer true.

Summary

The pHoamTM ARD-suppression technique is an emerging technology and the potential advantages of treating large volumes of mine waste with little water have yet to be fully developed. The technology could find application at both active and abandoned mines, either underground or surface, and could address mine wastes such as tailings, waste rock and even backfill in pits that have been fully revegetated without re-disturbance. The design of pHoamTM applications will be site specific, and will depend on the grain size, geochemistry, and in-place permeability of the mine waste, among other factors. It does not appear to be appropriate for application in fully-saturated or flooded conditions although pHoamTM with a density heavier than water is possible.

Future Study and Technology Development

Much study remains to advance the pHoamTM ARD-suppression technique from an emerging technology to a best management practice. As such, the authors are seeking demonstration sites that ideally exhibit the following conditions:

- Has research funding available
- Contains mine waste that is fully characterized, mapped, and is acid generating
- Is an active mine site/plant with a steady, consistent stream of acid-prone waste (e.g., coarse coal refuse or coarse tailings) that could be evaluated in test piles or lined test containers
- Is relatively small in scale (0.5 to 1 hectare) (1 to 2 acres)
- Is relatively accessible by conventional construction equipment
- Is amenable to “dissection” after pHoamTM application
- Has documented ARD impact
- Is on publicly-owned land (USFS, USBLM, USEPA Superfund)
- Is not a part of or contingent upon ongoing litigation

To quote a Latin proverb: *Nihil simul inventum est et perfectum*. [Nothing is invented and perfected at the same time.]

Literature Cited

- Blauer, Roland E., and C. A. Kohlhas, 1974. "Formation Fracturing with Foam," Presented before the 49th annual fall meeting of the Society of Petroleum Engineers of AIME held in Houston, Tex., Oct. 6-9, 1974.
- Carollo Engineers, 2008. City of Riverside [CA] Wastewater Collection and Treatment Facilities Integrated Master Plan; Volume 8: Solids Treatment and Handling; Chapter 7: Solids Disposal, Final Report, February, 2008.
- Gusek, J.J., "Avoiding and Remediating Acid Rock Drainage" presented at Latin American Mining Opportunities, Randol at Vancouver '94, Oct. 30-Nov. 2, 1994.
- Gusek, James J., Harry Moore, Vanessa Bateman, James Ozment, Leonard Oliver, Deedee Kathman, Jacob Waples, Thomas Rutkowski, Wilson Bowden, and Andrea Reither, 2008. "A New Guidance Document for Mitigating Impacts from Acid-Producing Rock Formations in Tennessee Road Construction Projects". Presented at the 59th Annual Highway Geology Symposium, Santa Fe, New Mexico. May 6-9, 2008.
- Interstate Technology Regulatory Council (ITRC) website, Sequatchie Valley Coal Mine project accessed 28-Oct-11 (http://www.itrcweb.org/miningwasteguidance/cs31_sequatchie.htm)
- Jin, Song, P. H. Fallgren, J. M. Morris, & J. S. Cooper, 2008. Source Treatment of Acid Mine Drainage at a Backfilled Coal Mine Using Remote Sensing and Biogeochemistry. *Water Air Soil Pollution* 188:205–212.
- Jin, Song, P. H. Fallgren, J. M. Morris, 2012. Treatment and prevention systems for acid mine drainage and halogenated contaminants. United States Patent No. 8,105,489. January 31, 2012.
- Li, S. H. and S. W. Parr, 1926. The Oxidation of Pyrites as a Factor in the Spontaneous Combustion of Coal. *Ind. Eng. Chem.*, 1926, 18 (12), pp 1299–1304.
- Mitchell, Paul, James Rybock & Amy Wheaton, 1999. Treatment and Prevention of ARD Using Silica Micro-Encapsulation. Paper presented at the 1999 National Meeting of the American Society for Surface Mining and Reclamation, Scottsdale, AZ, August 13-19, 1999. Vol. II, pp 657-651.

- Olson, Gregory J., Thomas R. Clark, Terry I. Mudder, Mark Logsdon, 2006. "Toward Source Control of Acid Rock Drainage". Paper presented at the 7th International Conference on Acid Rock Drainage (ICARD), March 26-30, 2006, St. Louis MO. R.I. Barnhisel (ed.) Published by the American Society for Mining and Reclamation. . pp 2170–2187.
- Plocus, Van G. and Vijay Rastogi, 1997. Geophysical Mapping and Subsurface Injection for Treatment of Post-Reclamation Acid Drainage. Paper presented at the 1997 National Meeting of the American Society for Surface Mining and Reclamation, Austin, Texas, May 10-15, 1997. pp 34-42.
- Plocus, Van. 2011, pers. comm.
- Rastogi, Vijay, R. Krecic, A. Sobek and M. Shellhorn, 1986. ProMacTM Systems for Reclamation and Control of Acid Production in Toxic Mine Waste, Poster Paper in Proceedings of the 7th Annual West Virginia Acid Mine Drainage Task Force Symposium. April 1-2, 1986. <http://wvmdtaskforce.com/proceedings/86/ras/86ras.htm>
- Schueck, Joseph, M. DiMatteo, B. Scheetz, and M. Silsbee, 1996. Water Quality Improvements Resulting From Fbc Ash Grouting of Buried Piles of Pyritic Materials on a Surface Coal Mine. Paper presented at the 1996 Annual Meeting of the West Virginia Acid Mine Drainage Task Force, Morgantown, W.Va., April 2, 3, 1996.
- Shaw, Duncan J. 1980. Introduction to Colloid and Surface Chemistry. Colchester and London: Butterworth & Co Ltd. 273 pp.
- Verburg, Rens, B. Johnson, M. Fordham, and M. Logsdon, 2003. A Rapid and Cost-Effective Method for Bench Screening of Geochemical Performance and Disposal Options for High-Sulfide Tailings. Presented at the 6th International Conference of Acid Rock Drainage (ICARD), Cairns, QLD, Australia, July 12-18, 2003. pp 739-749.
- Wilson, G.W. 2008. Why are we still struggling [with] acid rock drainage? *Geotechnical News*. 26(2):51-56.
- Zhang, Xiang, Michael J Borda, Martin AA Schoonen, and Daniel R. Strongin, 2003. Pyrite Oxidation Inhibition by a Cross-Linked Lipid Coating. *Geochemical Transactions* 2003, 4:8.
- Zsigmondy, Richard, 1917. The Chemistry of Colloids. New York: John Wiley & Sons, Inc. 288 pp.