Engineered Pumpable pHoam™: A New Innovative Method for Mitigating ARD

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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.

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 (3).

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.

There are four generally-accepted chemical reactions that drive the production of acid drainage whereby pyrite (FeS_2) is oxidized in a step-wise fashion:

$$1)\ FeS_2 + 7/2\ O_2 + H_2O \rightarrow Fe^{2+} + 2\ SO_4^{2-} + 2\ H^+$$

$$2)\ Fe^{2+} + 1/4\ O_2 + H^+ \rightarrow Fe^{3+} + ½\ H_2O$$

$$3)\ Fe^{3+} + 3\ H_2O \rightarrow Fe\ (OH)_3 + 3\ H^+$$

$$4)\ FeS_2 + 14\ Fe^{3+} + 8\ H_2O \rightarrow 5\ Fe^{2+} + 2SO_4^{2-} + 16\ H^+$$

Below a pH of 4.5, reaction numbers one, two and four appear to be catalyzed by the action of natural bacteria, *Acidithiobacillus ferro-oxidans* and related microbes, which accelerates the pyrite oxidation process and lowers the pH even further.

Hydrogen ions (H^+) and ferric ions (Fe^{+3}) catalyze the oxidation of other metal sulfides that may be present, releasing additional metals such as copper, lead, zinc, cadmium, mercury, and manganese into contacting waters.

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 corner. 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, resulting in localized sulfuric air pollution.

The tendency of a given rock or material to 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 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 ARD. Examples of each active ingredient type follow.

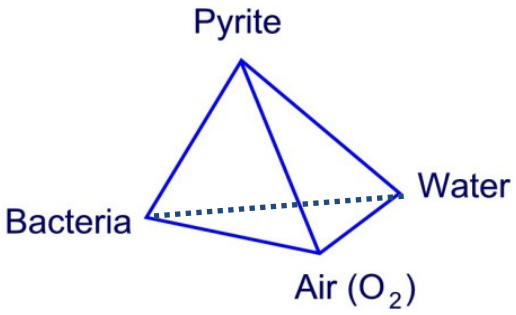

Figure 1. ARD Tetrahedron (2)

Liquid active ingredients

Olsen, et al. (7) provides a comprehensive discussion of ARD-suppressing liquid reagents which is summarized and expanded here. Sodium lauryl sulfate, a common surfactant identified as a bactericide that mitigates the oxidation of the mineral pyrite is an example of a liquid active ingredient for ARD suppression. Bi-polar lipids (10) 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 (6). Solutions of dissolved phosphate have been shown to complex with dissolved iron and starve bio-oxidation of pyrite through disruption of the kinetics of equations 2, 3, and 4 as previously discussed. 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 (7)).

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 (9, 11) 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 (ZVI), 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. For example, ZVI has been shown to remove chromium from electroplating waste (4).

Gaseous active ingredients
Examples of gaseous active ingredients include: carbon dioxide or nitrogen which can displace oxygen in the pore spaces in 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 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 (13). Common microbial source active ingredients may include municipal sewage bio-solids, composted animal manure, and organic soils harvested from natural wetlands.

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 pollution problem. The primary reason for this relates to the inability of practitioners to feasibly deliver and apply active ingredients to large volumes of potentially-polluting 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.

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. This is well-documented in Plocus and Rastogi (9) who 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 m^2 (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 (10), the technology was not considered practical.

A similar injection/treatment process was implemented at the Sequatchie Valley coal mine in Tennessee using waste milk by the Western Research Institute (5).

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. ARD-suppressing active ingredients 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 pHoam™ to distinguish it from common foams used in other industrial applications, including fire-fighting.

The proposed pHoam™ 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 pHoam™ of pre-determined "stability", can flow omni-directionally or bi-directionally from a single injection point as an advancing front. The density of the

pHoam™ composites will typically be less than 320 kg/m^3, which should lower injection pressures and increase the injection duration and coverage from each injection point.

pHoam™ 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 pHoam™ 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 Kohlhass (1):

> *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 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.

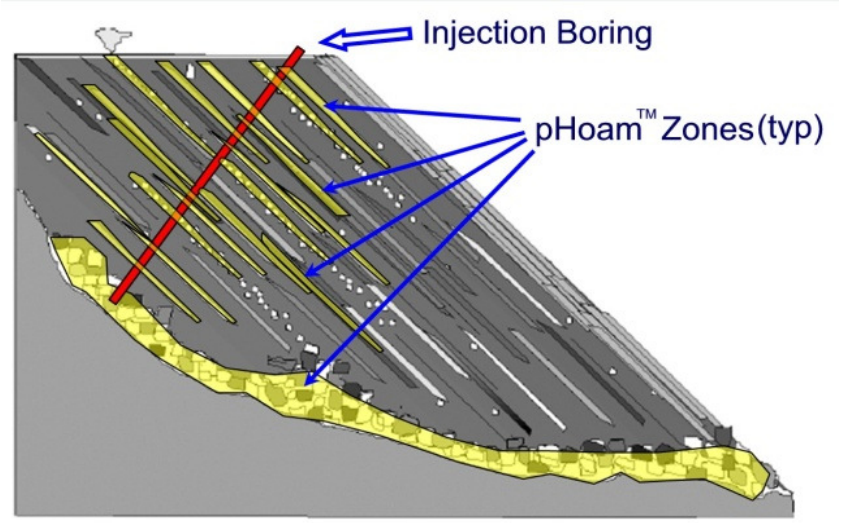

Figure 2. Injection of pHoam™ into a Mine Waste Dump; After (12)

The "heat-seeking missile" effect

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 collapse and resultant preferential deposition of more active ingredients compared to cooler zones nearby.

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. While the gas would typically consist of common air, nitrogen-rich/oxygen-depleted gas mixtures might be considered for addressing the oxygen vertex of the ARD Tetrahedron (Figure 1).

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

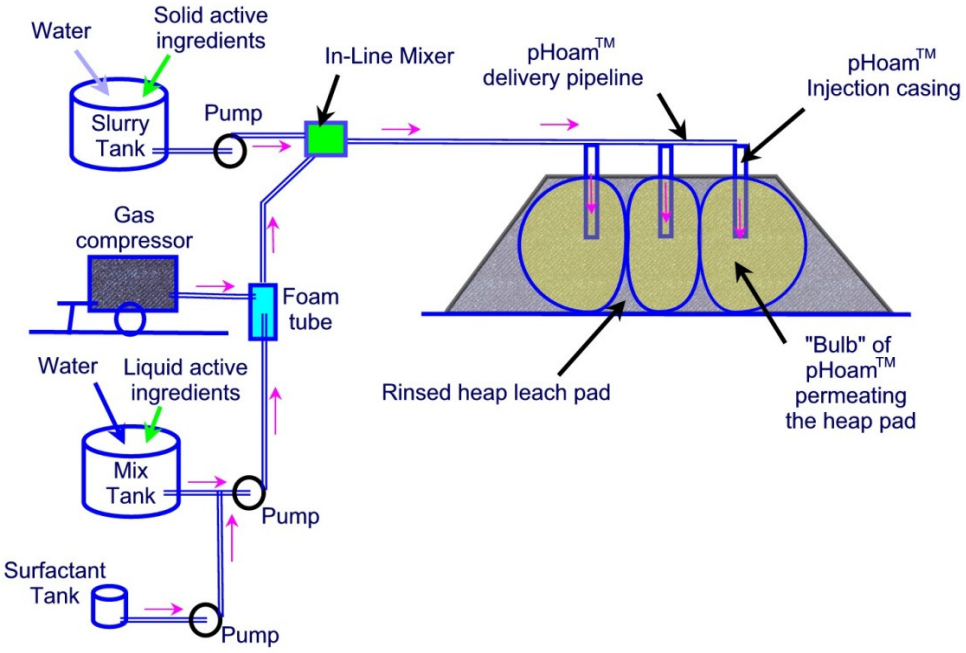

Figure 4. Example pHoam™ System Schematic Layout

Laboratory test work

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 Kohlhass (1)) 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.

A – pHoam™ applied to test rock

B – test rock after about 1 hour

C – test rock surface pre-pHoam™ application

D – test rock surface post-pHoam™ application

Figure 5. Laboratory application of pHoam™ to a clean gravel test rock

Test injection into porous medium

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

Summary

The pHoam™ 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 pHoam™ 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 pHoam™ with a density heavier than water is possible.

Future Study and Technology Development

Much study remains to advance the pHoam™ ARD-suppression technique from an emerging technology to a best management practice. Humidity cell testing is underway and the preliminary results will be presented as soon as they are validated. Furthermore, the authors are seeking demonstration sites that ideally exhibit the following conditions:

- Contains mine waste that is fully characterized, mapped, and is acid generating
- 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 pHoam™ application
- Has documented ARD impact
- Is on public-owned land (USFS, USBLM, USEPA Superfund)
- Has research funding available
- Is not a part of or contingent upon ongoing litigation

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