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Technical Communication

The Passive Prevention of ARD in Underground Mines by Displacement of Air with a Reducing Gas Mixture: GaRDS

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Abstract. There are few effective remedial strategies capable of reducing or preventing pollutant loads from underground mines. The Gas Redox and Displacement System (GaRDS) is a new approach devised for stabilising sulphide minerals by manipulating the atmosphere in mining voids. This prevention technique offers the potential for passive, low cost, and effective control of acid drainage from underground mines at sites where flooding is not feasible. GaRDS utilises reducing gas mixtures generated by anaerobic bacterial activity to displace oxygen without impeding drainage from the workings. These gas mixtures halt sulphide oxidation and acid generation, and can precipitate secondary sulphides from the accumulated drainage water.

The GaRDS technique has significant advantages for mine operators who wish to temporarily close a mine, implement a low-cost, passive acid drainage prevention strategy, and retain the option of reopening the mine if metal prices increase. It is fully compatible with conventional ARD closure strategies for underground mines, and is expected to rapidly improve drainage water quality emerging from enclosures and prevent further sulphide oxidation. A field demonstration of the GaRDS technique has commenced at an adit in an historical mining district in Australia (Zeehan Mineral Field in Tasmania). The aim is to develop a generic technology that will find widespread application to both existing and historical acid drainage problems and prevent future problems arising at mine closure.

Key words: Acid mine drainage, prevention, reducing atmosphere, underground mines.

Introduction

Most strategies for preventing acid rock drainage (ARD) involve covering the sulphidic rock mass to slow the diffusion of atmospheric oxygen (Ritchie, 1994). By reducing the rate of oxygen supply, the sulphide oxidation rate slows, therefore decreasing the rate of acid drainage generation. Depending on the quality of the cover, this approach may succeed in ameliorating the ARD. Another strategy reported by Tasse et al. (1994) involved the creation of an oxygen intercept barrier over a tailings dam consisting of a thick (1 m) layer of organic matter, mostly woodchips. The upper section of the organic layer consumed oxygen by bacterial oxidation producing CO_2, whilst the wetter base underwent bacterial degradation producing CH_4 and CO_2.

The use of organic matter successfully stopped oxygen diffusing into the tailings; however, the organic matter was consumed at a high rate and would require successive replenishment. In addition, contamination of the drainage water with organic leachates and potential methylation of heavy metals may be problematic for direct application of organic matter.

Treatment of ARD at coal and metal mines is often based on the assumption that prevention is not technically or economically feasible. While remediation of waste rock involves a range of challenging issues that are the subject of widespread investigation, underground workings receive far less attention. This dearth of viable remedial strategies for underground workings has led to what is a common problem throughout the world today: numerous highly polluting legacies of a previous era of mining with few options for low-cost remediation.

At present, the use of controlled flooding using carefully designed bulkheads capable of holding substantial water pressures is essentially the only option available for improving water quality from underground workings. This approach is very effective in reducing ARD in particular situations, but has a number of disadvantages. For example:

- The risk of catastrophic bulkhead failure is a major deterrent to regulators and mining companies.
- The decision to proceed with a bulkhead requires extensive hydrogeological and geotechnical knowledge of a site. Both investigations are generally time consuming and expensive.
- Flooding cannot be used in all cases because the resulting hydraulic head is too high to permit bulkhead installation in some situations.
- Due to the need for rigorous design specifications, bulkhead installation costs are routinely very high.
- Due to the complexity of natural hydrologic systems, there is no guarantee that bulkheads will be successful.
- Bulkhead installation often leads to multiple point source leakage of ARD, thereby compromising control of drainage.

In situations where mine flooding is not an option, collection and treatment of ARD is the only alternative to pollution at present. Treatment is commonly a high cost option, and is required for tens to hundreds of years. In an attempt to address the dearth of cost effective remedial options for underground workings, Earth Systems and ANSTO have devised a new and highly innovative ARD avoidance methodology that addresses the shortcomings of the flooding approach, and provides a generally applicable, low-cost solution. The Gas Redox and Displacement System (GaRDS) approach separates degrading organic matter from the drainage stream and overcomes potential drainage contamination by dissolved organics. Direct contact between air and degrading organics is also avoided to reduce oxidation losses. This novel approach is based on using the highly reduced gas mixtures generated by natural bacterial degradation of organic matter to passively displace oxygen (i.e. air) from adits, shafts, and the unsaturated fractured rock mass surrounding the subsurface voids. By maintaining highly reducing conditions, the sulphides can be stabilised. The passive displacement of air by a reducing gas mixture does not require any power supply or pumps.

Outline of Technique

Underground mining introduces air directly into zones of sulphide-bearing rock, and the receding water table associated with tunnelling and dewatering causes air to be drawn into fractures within the rock mass surrounding the mine workings. Both of these processes result in dramatically enhanced sulphide oxidation. The oxidation products are subsequently dissolved by infiltrating rainwater, and acidic and metal-rich water collects in the underground voids and exits from adits.

The flooding of underground mines via bulkhead installation aims to return groundwater to pre-mining levels and thereby minimise further sulphide oxidation. GaRDS aims to passively displace air from the mining voids and fractured rock mass above the water table by introducing biogas to the mine once all shafts and adits have been closed. The biogas is comprised of carbon dioxide and methane (CO_2 and CH_4) produced by anaerobic bacteria breaking down crude organic matter. This is the same process that produces landfill gas from putrescible waste at municipal landfills. A range of different types of organic matter will be suitable, and it may be possible in some situations to find synergies with the waste disposal strategies of local communities (sewage and/or putrescible waste handling). GaRDS works in two ways, physically displacing oxygen and chemically reversing the acid-generating reactions and stabilising the acid-producing minerals.

As a first step, all man-made exits (e.g., adits, shafts, drillholes, etc.) must be sealed with low-cost barriers displaying low gas permeability to dramatically lower gas diffusion into or out of mine workings. At the topographically lowest exit to the mine workings, a barrier configuration will allow all drainage out, whilst the mine remains substantially sealed to gas flow.

As CO_2 and CH_4 gas production progresses, oxygen and nitrogen initially contained within underground workings will be expelled through fractures in the unsaturated zone. This will eventually lead to a situation where the atmosphere within the voids and rock fractures is almost exclusively CO_2 and CH_4 (i.e. $CO_2 \simeq 49\%$, $CH_4 \simeq 49\%$, residual gases will include: CO, H_2, H_2S, NH_3, N_2, O_2, C_2H_6...etc). Eventually, it is expected that small volumes of both CO_2 and CH_4 will evolve from the fractured rock mass at the ground surface. Under these circumstances, oxidation of sulphides in the unsaturated zone and mining voids will have been effectively terminated. The relatively high density of CO_2 will ensure that oxygen is effectively displaced from all accessible voids and fractures.

In most settings, sulphide oxidation at mine sites is controlled by ambient oxygen concentrations. The key oxygen source is air, and other components of air are effectively inert with respect to sulphide oxidation. This is not the case with the system proposed here. GaRDS generates gases that are not inert with respect to either oxygen or sulphides. For example, CH_4 can react with oxygen to produce CO_2, and CO can react with oxygen to produce CO_2. Minor concentrations of H_2S will also be a potential oxygen consumer, further lowering trace amounts of ambient oxygen to stabilise sulphides. H_2S is also expected to encourage the precipitation of secondary pyrite by reacting with available aqueous ferrous iron.

Geochemistry of the GaRDS Approach

The general equilibrium depicting the oxidation of iron sulphide is as follows:

$$FeS_2 + 3.5\ O_2 + H_2O = Fe^{2+} + 2\ SO_4^{2-} + 2\ H^+$$

The GaRDS approach is to remove oxygen from this equilibrium, and thereby prevent it from proceeding. Although acid products formed prior to oxygen displacement will take some time to be flushed through the fractured rock mass and mine voids, no further sulphide oxidation will occur when the reducing gas mixture dominates the mine environment.

The Eh-pH diagram (Figure 1) depicts the Fe-S-C-O-H system at 25°C, and is a good model for the key components of an ARD environment.

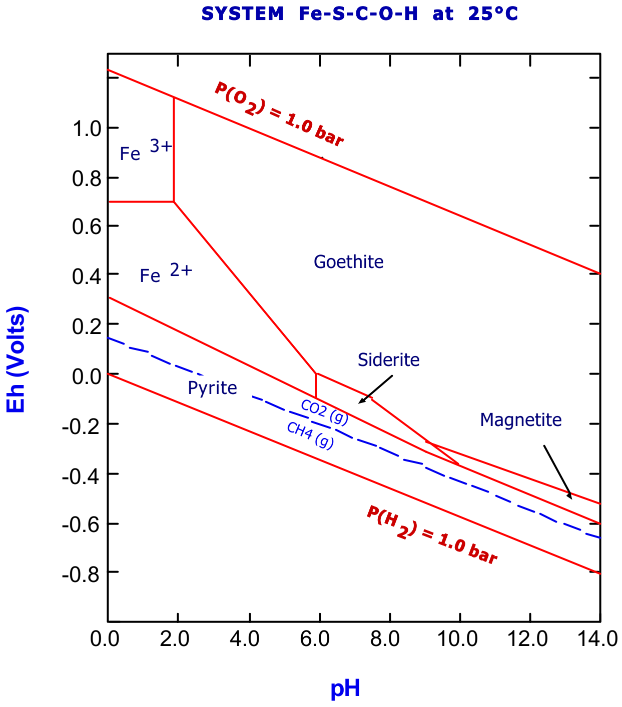

Figure 1. An Eh-pH diagram for the Fe-S-C-O-H system at 25°C. Log a $Fe^{2+} = -4.0$ and log a $SO_4^{2-} = -3.0$. The CO_2 (g)-CH_4 (g) boundary and the siderite field are based on an atmosphere comprising approximately 0.5 bars CO_2 and 0.5 bars CH_4 partial pressure.

Carbon is included in the system to model the impact of the reducing gas mixture. The CO_2 - CH_4 boundary is shown to demonstrate that an atmosphere dominated by equal partial pressures

(0.5 bars) of these gases lies in the stability field of pyrite. Pyrite and other metal sulphides will remain completely stable in the presence of the reducing gas mixture. Maintaining low mine-void oxygen concentrations with a reducing gas mixture is the critical feature essential for the success of a GaRD System.

Short Term Water Quality Issues

A by-product of pyrite oxidation and acid generation that remains in some underground workings is ferric hydroxide precipitate. This compound forms as soluble ferrous iron undergoes oxidation when mine water reacts with atmospheric oxygen. Soluble sulphate initially complexed with the ferrous iron leaves the underground workings as dissolved sulfate. The residual ferric hydroxide, although not present at all sites, is expected to have a minor impact on discharge water quality after a GaRD System is implemented. This impact is expected to continue until the ferric hydroxide is completely mobilised or converted to another iron compound.

Stored ferric hydroxide in the mine voids will be reduced to soluble iron by CH_4 and H_2 and some may be transported from the workings in the decant water. Such processes may be represented by the following reactions:

$$Fe(OH)_3 + CH_4\ (aq) = Fe^{2+} + CO_3^{2-} + 3.5\ H_2$$

$$Fe(OH)_3 + 2\ Fe^{3+} + 1.5\ H_2 = 3\ Fe^{2+} + 3\ H_2O$$

Some of the aqueous ferrous iron will be immobilised within the mine void as siderite ($FeCO_3$) as gaseous CO_2 reacts with water containing elevated iron concentrations:

$$CO_2 + H_2O = HCO_3^- + H^+ = H_2CO_3$$

$$Fe^{2+} + HCO_3^- = FeCO_3 + H^+$$

$$Fe^{2+} + CO_2 + H_2O = FeCO_3 + 2\ H^+$$

It is possible that elevated ferrous iron concentrations will exit underground workings until all of the ferric hydroxide stored in the workings from past sulphide oxidation has been consumed (i.e., converted to siderite or mobilised from the workings in the decant water). At sites with considerable stored ferric hydroxide, a pond may be required near the adit exit to precipitate and store iron bearing precipitates that form as the solution reacts with air.

Slightly acidic water is expected to form within a mine void due to carbonic acid formation (H_2CO_3). The drainage water will rapidly evolve CO_2 (i.e. degas) as it exits the mine, and will consequently become less acid or even slightly alkaline. This process will also assist the precipitation of any iron that is mobilised.

Predicted Benefits of GaRDS

There are several advantages to the proposed GaRDS technique relative to the installation of bulkheads. These include:

- Long term minimisation or prevention of acid drainage from underground workings.
- No large-scale pre-feasibility investigation required.
- Rapid and low-cost to install.
- Very low recurrent costs, especially relative to conventional chemical treatment systems.
- Can be applied to most underground workings or portions thereof that cannot be flooded.
- Minimal risk associated with operation.
- Remediation is passive and potentially self-healing.
- Only a small mass of degrading solid organic matter is required to fill (non-floodable) airspace (ie. adit + shaft + fracture volume) due to solid to gas conversion.
- In some cases, the GaRDS approach could be combined with sewage disposal strategies.
- Reprecipitation of metal sulphides likely at some sites.
- Performance of the system can be judged by the quality of the water emanating from the workings (e.g., total acidity over time will decrease).

Sites Where GaRDS May Be Inappropriate

The volume of gas, and therefore the mass of organic matter, needed to maintain reducing conditions in underground workings will vary significantly from site to site. It will primarily be a function of the volume of mine + overlying pore space void, and the permeability of the rock mass overlying the mine void. Sites with competent weathered rock and soil horizons overlying the mine void (ie. low gas permeability covers) will minimise the loss of gases through the fractured rock mass. This will, in turn, minimise the consumption of organic matter and thereby lower operating costs.

GaRDS implementations may not be appropriate at sites where there is extensive collapsed ground (e.g., around some coal mines), or where the cost of providing relatively low permeability gas barriers is prohibitive (e.g., multiple connected workings in historical mining districts with adits, shafts, glory holes, pits, etc.).

Synergy with the Neutral Barrier Technology

In the fractured rock mass above a mine void, the interaction of CO_2 gas with various aqueous species is expected to result in the precipitation of a range of secondary minerals such as siderite (as previously discussed), rhodochrosite ($MnCO_3$), malachite/azurite (e.g., $Cu_2(OH)_2CO_3$), smithsonite ($ZnCO_3$) and possibly even ankerite ($Ca[Fe,Mg,Mn],(CO_3)_2$) calcite ($CaCO_3$), dolomite ($Ca,Mg(CO_3)_2$) and magnesite ($MgCO_3$). The precipitation of assorted carbonate minerals in rock fractures will have the feedback effect of lowering permeability and thereby reducing water infiltration and gas diffusion from the mine. GaRDS is effectively a self-sealing approach, and therefore employs key aspects of the Neutral Barrier Technology (Waring and Taylor, 1999). This natural tendency to precipitate mineral carbonates could be enhanced by addition of lime and limestone to the surface to intercept drainage passing into the mine void. As a result, the low permeability seal over the mine is likely to improve with time, reducing the consumption of organic matter and lowering operational costs.

Natural Analogues

Clay-capped putrescible landfills are excellent non-mining analogues for the GaRD System. In these environments, substantial volumes of roughly equal proportions of CO_2 and CH_4 are generated by anaerobic activity, resulting in the displacement of air from the vadose zone above the organic waste. Monitoring of landfill gas composition at sites across the world indicates that oxygen levels are routinely less than 1.0 vol.%, and commonly less than 0.1 vol.%. This indicates that pore gas displacement/reaction by biochemically generated CO_2 and CH_4 is highly effective in some subsurface environments. Abundant metal sulphide precipitation is also typical of most putrescible landfills.

The underground coal mining industry also provides a rare natural analogue to the GaRD System. Coal bed gas emissions dominated by CO_2 and CH_4 are filling underground mining voids in a defunct South African coal mine, and appear to be responsible for preventing acid generation from exposed pyrite by displacing air and reducing ambient oxygen levels to less than 5-6 vol.%. Mine water discharge is near neutral to slightly alkaline with low to moderate sulphate concentrations, strongly supporting the role of the reducing gas mixture in pyrite stabilisation.

Conclusions

GaRDS offers a new methodology for passively preventing the formation of ARD in underground mines that does not involve the installation of pressure bulkheads. This approach is expected to operate in two ways. First, by physically displacing oxygen from mine void or pore spaces, sulphide oxidation will be effectively terminated. Second, by encouraging highly reducing conditions, it will be possible to chemically reverse the acid-generating reactions that dominated prior to installation of GaRDS. Once all residual acid sulphate products have been expelled from the mine void and overlying pore spaces, aqueous sulphate concentrations are predicted to return to background levels.

Reducing gas mixtures can be generated passively by the anaerobic decomposition of organic matter. Synergies may be found between local communities that generate organic wastes and mine operators / regulators who need to provide solutions to ARD prevention. Such synergies will significantly reduce GaRDS operating costs.

Typical weathered rock horizons at most mine sites will ensure that gas release from above mine voids will be negligible, thereby mitigating concerns about high operational costs, greenhouse gas emissions and explosive risk. Although not described here, the explosive risk of CH_4 in the presence of elevated oxygen concentrations both within and exterior to the mine has been addressed. Simple site characterisation, installation and operation strategies have been devised to overcome risks and concerns related to the use of biogenic CH_4.

GaRDS offers a flexible approach to ARD prevention, and can be implemented temporarily or for long-term mine closure. GaRDS could be readily deactivated (within days) if a mine needs to be reopened due to improved metal prices.

In principle, the GaRDS technique can be extended to include sulphidic waste rock dumps that have already been covered, to augment pollution control performance. A low-cost combination of the Neutral Barrier Technology (Waring and Taylor, 1999) to lower infiltration, and GaRDS to passively slow or stop sulphide oxidation is likely to become a preferred remediation approach for easily sealed underground mines. Eventually it may be applied to inherently more permeable/leaky systems such as covered waste rock dumps.

It is expected that the current field implementation at a site in Tasmania, Australia, will demonstrate a generic technology that will find widespread application to acid drainage issues, and prevent future problems arising at mine closure.

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