TECHNOLOGY OVERVIEW

PASSIVATION TECHNOLOGIES

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PASSIVATION

1.   INTRODUCTION

Passivation of acid-generating material involves oxidizing or protecting the sulfide surface from water and oxygen. Preventing oxidation of sulfides in situ by controlling the environmental conditions for oxidation is potentially a viable alternative to treatment in perpetuity. The generation of acid mine drainage can be likened to a chair, with the four components being the legs (Figure 1-1). Remove any one component (or leg), and the stool does not stand. As a result techniques for reducing metal sulfide oxidation involve removing oxygen, water, bacteria, or the sulfide minerals.
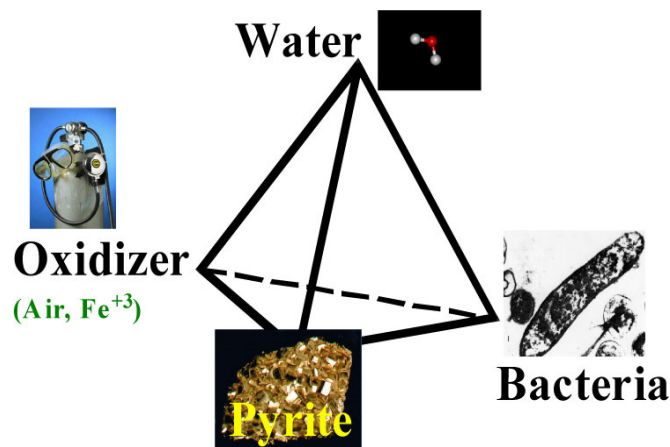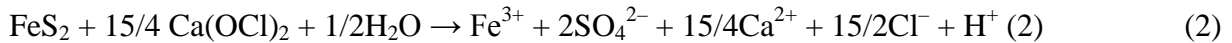

Figure 1-1. Acid rock drainage tetrahedron. (Courtesy Jim Gusek, Golder and Associates)

Since most mine waste already contains sulfides, techniques to coat and/or seal sulfide surfaces to reduce reactivity have been developed. Plastics, polymers, or cementation can be used to seal sulfidic surfaces (Moncrieff 2006). Surface passivation is analogous to galvanizing a nail; the outer layer resists oxidation. Passivated materials generally do not oxidize even if oxidation is an energetically preferential reaction. A variety of chemicals have been used in an attempt to passivate sulfide minerals; the most commonly tested include phosphate, silica, and permanganate.

Reactive mine wastes can be isolated from oxidizing agents (i.e., O_2, Fe^{3+}) by chemically precipitating a ferric coating on the surface of the waste material. This passivation process, sometimes called "microencapsulation," prevents further oxidation of sulfide minerals by blocking the transport of oxidants to the sulfide surface and consuming ferric iron before it can become an oxidant.

The coating can be produced by reacting sulfidic material with low concentrations of an oxidizing agent in the presence of soluble phosphate or silica in a buffered solution. Hydrogen peroxide or calcium hypochlorite has been typically used as oxidizing agents. The oxidizing agent reacts with the sulfide to produce ferric ions:

$$FeS_2 + 15/2H_2O_2 \rightarrow Fe^{3+} + 2SO_4^{2-} + 7H_2O + H^+ \qquad (1)$$
$$FeS_2 + 15/4\ Ca(OCl)_2 + 1/2H_2O \rightarrow Fe^{3+} + 2SO_4^{2-} + 15/4Ca^{2+} + 15/2Cl^- + H^+\ (2) \qquad (2)$$
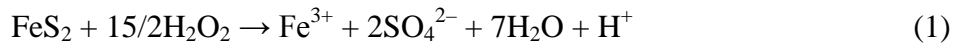
Sodium acetate has been used to buffer the solution at a pH of 5 to 6. At this pH, dissolved ferric iron is unstable and precipitates as ferric hydroxide. If dissolved phosphate is present, it will scavenge ferric ions and ferric phosphate will precipitate:

$$Fe^{3+} + KH_2PO_4 \rightarrow FePO_4 + K^+ + 2H^+ \qquad (3)$$

If silicic acid is present in the solution, it will react with the ferric hydroxides, producing an insoluble ferric silicate precipitate that is chemically stable at low pH (Evangelou 1996):
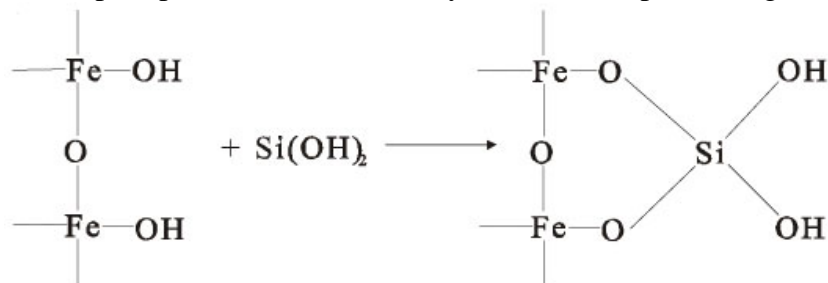
A number of studies have dealt with the feasibility of chemically producing coatings on reactive mine wastes and tailings. Reasonably successful coatings were reported in laboratory studies using phosphates (Evangelou 1994, Georgopoulou et al. 1995, Roy and Worral 1999), silicates (Zhang and Evangelou 1998; Fytas, Bousquet, and Evangelou 1999), and various organic materials (Adams, Ninesteel, and Rauch 1994; Moskalyk 1995). Generally, the presence of coatings on rock and tailing surfaces were confirmed using scanning electron microscopy (SEM), although decreased iron levels in drainage was often cited as evidence of coating formation.

Treatment of acid-generating rock with permanganate and magnesium oxides at a high pH (>12) is a patented process. Maintaining the high pH prevents the permanganate from disproportionating to a weaker oxidant and lowering Eh (De Vries 1996).

The passivation procedure uses the oxidizing ability of potassium permanganate to create an inert manganese-iron oxide on sulfidic rock. The sulfidic rock is treated with a permanganate and magnesium oxide slurry brought up to and held above pH 12. The layer has been shown to resist oxidation in oxidation simulation tests with hydrogen peroxide.

All passivated surfaces still have reactive rock below the surface, and oxidations will return once that passivation layer is removed. Thus, whether passivation is a viable option depends on time, other environmental conditions, and treatment efficiency requirement.

2.   APPLICABILITY

- solid mining waste

- pit wall treatment
- surface applications
- solo technology or in conjunction with others
- multiple contaminants of concern

All of the passivation technologies use a spray-on application, either as a solution (phosphate) or as a slurry (silica). This is one of the few treatment methods that can be used to treat exposed pit walls. Although laboratory and small-scale pilot data are available, there has been no large-scale application of this technology.

3.   ADVANTAGES

- spray-on application
- source control
- may be long-lasting

Since the chemicals are applied as a solution or slurry, they can easily be applied to mine waste that may be difficult to access or treat, such as pit walls. They offer the advantage of stopping the reaction at the source (the sulfide surface) and potentially providing long-term source control.

4.   LIMITATIONS

- not applicable for all cases
- treatment lifetime not known
- initial release of other constituents
- high cost

Since the chemicals are applied with water, the reactions and subsequent effectiveness are limited to the surfaces that can be contacted. This makes treatment at depth or in large stockpiles difficult, since the flow paths in mine waste are tortuous and complex.

Although the passivation compounds are predicted to be very stable, no long-term data are available to predict treatment lifetime.

A phosphate compound and a silica compound were tested for their ability to prevent acid generation and to evaluate application rates and treatment lifetime. Treatment with phosphate delayed but did not prevent oxidation, while the silica treatment has prevented acid generation for over six years (Eger and Antonson 2002, 2004; Eger and Mitchell 2007). With the phosphate treatment, there were elevated levels of phosphate and arsenic in the initial rinse waters. With the silica treatment, pH increased as the amount of treatment chemical increased, since the slurry contained lime in addition to the silica compound.

5.   PERFORMANCE

The effectiveness of passivation chemicals to control release of acid and metals was evaluated at two field sites: Gilt Edge Mine, S.D. (*Final Report: Remediation Technology Evaluation at the Gilt Edge Mine, South Dakota Mine Waste Technology Program Activity 111, Project 29,* 2005 and (http://www.epa.gov/region8/superfund/sd/giltedge/) and the Golden Sunlight Mine, Whitehall, Montana (USEPA 2005). A subsequent, larger-scale treatment was also done at the Golden Sunlight Mine. Most of the discussion and results were taken directly from these reports. Each field program is summarized below.

5.1   Gilt Edge Demonstration

This project consisted of evaluating the use of silica (KEECO), phosphate (EcoBond), Metals Treatment Technologies (MT^2), and permanganate (University of Nevada–Reno [UNR]) to stabilize acidic waste rock. Performance was evaluated as a pilot- scale demonstration by placing treated waste rock into isolated cells at the Gilt Edge Mine, monitoring the leachate collected from the representative cells, and comparing the results to control cells and to rock treated with lime. The leachate was monitored from the spring of 2001 to the fall of 2002. The objective of the treatments was to reduce the contaminants of concern by at least 90% or to South Dakota water discharge limits. The three technology vendors also provided a cost estimate to treat a hypothetical 500,000 yd^3 waste rock pile at the Gilt Edge Mine using the pilot-scale data as a guideline.

By evaluating the leachate parameters of pH, total dissolved solids (TDS), dissolved arsenic, aluminum, iron, zinc, and sulfate, it was possible to ascertain if the technologies were able to achieve a 90% reduction or the South Dakota discharge limits. The results are summarized in Table 5-1 (USEPA 2004).

Table 5-1. Technology performance summary

Technology	Achieve 90% reduction?			Achieve South Dakota discharge limits?				Cost to treat 500,000 yd^3 of waste rock	Comments
	Al	Fe	Sulfate	pH	TDS	As	Zn		
Presumptive remedy, lime addition	Yes	Yes	Yes	No	Yes	Yes	Yes	$4,774,438	Effective, but pH was elevated above 8.8, and will fail once lime is exhausted.
MT^2	Yes	Yes	No	Yes	No	No	Yes	$4,034,750	Increased TDS, sulfate, and arsenic concentrations.
UNR	Yes	Yes	No	Yes	Yes	Yes	Yes	$3,241,408	Effective and has longer life than lime treatment.

Technology	Achieve 90% reduction?			Achieve South Dakota discharge limits?				Cost to treat 500,000 yd^3 of waste rock	Comments
	Al	Fe	Sulfate	pH	TDS	As	Zn		
KEECO	No	Yes	No	No	No	No	No	$12,682,998	Expensive, and failed during second field season.

Based on the results in Table 5-1, the UNR and lime addition (presumptive remedy) technologies were able to achieve seven of the eight objectives. However, the lime treatment will be exhausted over time because the lime is soluble and will eventually dissolve.

The KEECO and MT^2 technologies may be able to produce favorable results by making dosage adjustments and/or using different treatments; however, additional treatment past the second field season was beyond the scope of this technology demonstration. To confirm whether the modified KEECO and MT^2 treatments would be effective, another technology demonstration would need to be performed.

5.2   Golden Sunlight Mine (GSM) Demonstration

The intent of the demonstration project was to obtain performance data on the ability of four technologies to prevent the generation of acid mine drainage (AMD) from an open-pit highwall:

- EcoBond™ ARD (EcoBond) developed by MT^2 of Denver, Colorado
- magnesium passivation technology (UNR/MgO) developed by the University of Nevada-Reno
- potassium permanganate technology (UNR/KP) developed and patented by DuPont Technology with field applications developed and applied by UNR (the current patent holder)
- a furfuryl alcohol resin sealant (FARS) developed by Intermountain Polymers of Idaho Falls, Idaho

The demonstration was conducted at GSM in an active open-pit gold mine located near Whitehall, Montana. The four technology providers spray-applied their technologies, which were in a liquid form, to a designated 50-foot-high by 50-foot-wide area on the highwall. A background/control plot of the same size was designated and used to evaluate and compare to the four treatment technologies. To evaluate and determine whether the objectives had been achieved, two test procedures were used: humidity cell (HC) testing in the laboratory and a field mine wall sampling method.

Data from the untreated GSM highwall, for both field monitoring and HC laboratory testing, showed that untreated material would produce acid in a natural weathering and oxidizing environment. The same background data from the untreated GSM plot were used for comparison of all the treatment technologies to determine if the technologies were effective in reducing the potential for AMD.

Humidity Cell (HC)Tests

During application of the technologies, each technology provider was required to apply the technology to a specially prepared sample that was sent to McClelland Laboratories, Inc. (MLI) in Sparks, Nevada, where American Society of Testing Materials (ASTM) D5744-96 for Accelerated Weathering of Solid Materials using a Modified HC testing method was conducted. For the HC testing, the technology was allowed to contact the full surface area of the sample being treated for an extended period of time, allowing for the most ideal application conditions. The HC testing results were used to predict whether the untreated and treated samples would produce acid and mobilize metals.

Results from 41 weeks of HC testing indicated and predicted that all technologies were effective in preventing acid production and the mobility of metals. Each technology was compared with the background sample results.

When compared to the background plot for EcoBond technology, the pH was neutral; the electric conductivity was typical for systems exposed to air and indicated minimal metal mobility; iron (Fe), sulfate (SO_4), and acidity production were higher; and calculated ratios were substantially greater than regulatory guidelines. For the two UNR technologies, the pH was slightly greater than 6; the electrical conductivity was typical for systems exposed to air and indicated minimal metal mobility; Fe, SO_4, and acidity production was higher; and calculated ratios were substantially greater than regulatory guidelines. Essentially, no metals were mobilized from EcoBond, UNR/MgO, and UNR/KP cells. The lack of metals mobility indicates that three treatment technologies prevented acid production.

For the FARS technology, the pH ranged between 4 and 5, the electrical conductivity was typical of systems exposed to air and indicated some metals mobility for Fe and SO_4. The FARS-treated sample did prevent AMD but not as well as the other three technologies. Because the FARS technology has binding/stabilizing capabilities, the FARS HC sample had to be broken apart to allow it to fit into the HC test cells, which exposed rock surfaces that otherwise would have been covered.

Residual Wash Sampling Tests

After the technologies were applied to the GSM highwall, a mine wall/residual wash water sampling test method that was developed for the Canadian Mine Environment Neutral Drainage Program was implemented. The sampling test included information where the total metals loading per unit area and the pH of the highwall in the field were calculated and measured, respectively. This method allowed the technologies to be evaluated under field conditions and field-designed application rates.

Field results for the mine wall sampling show that for the EcoBond, UNR/MgO, and UNR/KP plots, the pH was as low as the pH of the background plot. This means that the pH was <4 and the range of average percent metals reduction was between -211% and 82% (see Table 5-2). The FARS recorded pH was steady at pH 4–4.5, extending for the full demonstration, and the percent metals reduction ranged 75%–91% compared to the background results.

Table 5-2. Percent reduction of total metals from the treated technology plots compared to the untreated plot (Plot A)

Metal	FARS	EcoBond	UNR/MgO	UNR/KP
A1	75	20	38	62
Cu	85	-211	26	76
Fe	85	24	-16	30
Mn	84	49	82	51
Ni	90	48	50	72
Zn	91	-40	75	76

Note: A large negative number for the percent metals reduction indicates high metals mobility; a high positive number indicates a low mobility.

In the field, physical stabilization of the highwall was observed on only the FARS technology plot. The other three technologies provided chemical passivation of the wall but not physical stabilization.

6.   COSTS

Theoretical costs for highwall treatments varied from $6/yd^3 for the permanganate to over $24/yd^3 for the silica treatment (Gilt Edge demonstration project). In a comparison of FARS, UNR/MgO, UNR/KP, and EcoBond processes, costs were broken down to include materials, installation, and oversight. Mobilization and shipping costs appear to be primarily dependent on distance and not on the special equipment or other needs. The core cost elements are listed in Table 6-1. Unit costs varied $2–$8 per square foot.

Another factor that affects the cost of applying these technologies includes the size of the plots. The cost to implement a technology on a small test plot is usually higher than applying the technology to a large area. Costs for highwall treatment with permanganate were <$1.50/ft^2, more than 50% less than in the small demonstration project (Golden Sunlight Demonstration project).

Table 6-1. Costs to treat highwall, Golden Sunlight technology demonstration

Technology	Material	% of total	Install	% of total	Oversight	% of total	Total	Unit cost*
FARS	$3,600	68%	$1,695	32%	(1)	0%	$5,295	$2.12
UNR/MgO	$3,780	41%	$2,948	33%	$2,394	26%	$9,155	$3.65
UNR/KP	$3,780	41%	$2,948	33%	$2,394	26%	$9,122	$3.65
EcoBond	$10,250	54%	$5,884	31%	$2,910	15%	$19,044	$7.63
*Basis: 2,500 ft^2								
(1) Oversight assumed to be part of the installation cost.								

7.   REGULATORY CONSIDERATIONS

Passivation is a new technology, and the lack of large-scale, long-term data creates regulatory barriers. Although some of the initial data suggest that treatment can be effective, there are very limited data on long-term performance. In addition, several studies have indicated that there is an initial release of other constituents that would need to be evaluated. Techniques to control and possibly treat this release may be needed and regulatory approval obtained in advance of any release of these constituents.

8.   STAKEHOLDER CONSIDERATIONS

Since this is a new technique with limited data, stakeholders are likely to be wary of its applicability and effectiveness.

9.   LESSONS LEARNED

9.1   Stockpile Treatment

The effectiveness of passivation technology is a function of the contact of the treatment chemicals with the sulfide mineral surfaces. Application to existing waste rock stockpiles is unlikely to be successful without moving the material and treating it in smaller batches or lifts. The actual dose of the chemical is an important variable affecting both performance and cost.

9.2   Highwall Treatment

Problems were encountered in the experimental program which affected the evaluation of the technologies. Several mine wall sampling ports were lost when mine wall movement caused the highwall to become unstable. The loss of the sampling ports had the potential to affect the overall results. Due to the instability of most highwalls, additional sampling ports should be included. In addition, there was a possibility that airborne particulates and runoff from untreated areas affected the field results. This needs to be considered in future applications.

10.   CASE STUDIES

Table 10-1. Case study used in this technology overview

Golden Sunlight Mine

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