

TECHNOLOGY OVERVIEW

IN SITU TREATMENT OF MINE POOLS AND PIT LAKES

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IN SITU TREATMENT OF MINE POOLS AND PIT LAKES

1. INTRODUCTION

In situ treatment of mine pools and pit lakes is an emerging technology for treating mine influenced water (MIW). The technology consists of the injection or placement of substances, including alkaline materials and organic carbon substrate, with nutrients directly into the mine pool or pit lake to neutralize the MIW and to produce anaerobic conditions to precipitate metals in place. The chemistry and biochemistry of these applications are briefly presented here, but more detailed descriptions of the processes are covered in the bioreactor and chemical precipitation technology overviews.

Injection of a carbon source such as molasses or alcohol with nutrients and sometimes an alkaline source, such as lime, can create conditions favorable to the precipitation of dissolved metals in place. The addition of a carbon source promotes the existing bacterial microbes to use in sequence oxygen, nitrate, ferric iron, manganese, and sulfate as electron acceptors for growth and results in the formation of a strongly anaerobic (sulfate-reducing) environment; i.e., a sulfate-reducing bioreactor is formed. Some metals are less soluble in their reduced form, including selenium, chromium and uranium. These oxidized metals can be removed from the water as solids through the biological process as previously described. The metal removal will occur sequentially between ferric iron and sulfate. Once a sulfate-reduction stage is achieved, the microbiological chemical reaction produces sulfide gas, which combines with dissolved metals to precipitate as metal sulfides of very low solubility. The sequence of metal sulfides precipitation is generally $Pb > Zn > Cu > As > Cd > Fe > Mn$.

The main components of pyrite oxidation and generation of acid rock drainage (ARD) are oxygen and ferric iron. To know the amount of carbon source to be added (the carbon demand), all the organic carbon sinks preceding the metal of concern need to be calculated and summed along with the metal of concern. In many cases the bulk of the cost of in situ treatment is involved in managing oxygen (Harrington 2002).

Alkalinity is produced as the carbon substrate is metabolized, causing an increase buffering capacity of the MIW, which may also lead to an increase in the pH of the MIW. Carbon dioxide may also be produced and evolve from the mine pool into the unsaturated zones of the mine workings, displacing oxygen and reducing pyrite oxidation in the lower parts of the mine workings above the mine pool.

Injection of alkaline materials, such as coal combustion by-products or lime, into a mine pool or pit lake can raise the pH of the MIW. The rise in pH then promotes the equilibrium precipitation of dissolved metals as hydroxides and carbonates. However, some metals have higher solubility at high pH levels.

In situ treatment of solid mining waste in the form of residual minerals in mine walls, tailings, or waste rock involves the application of amendments such as potassium permanganate, phosphate or biosolids, and carbon substrate to stabilize the metals in place and reduce the formation of

leachate or inhibit the migration of metals. This is the subject of a number of the case studies as identified in this technology overview. However, these are discussed in other technology overviews, including phosphate and other amendments, passivation, and biologic source treatment. In situ treatment is covered in INAP (2009) and Gusek and Figueroa (2009). The latter reference classifies in situ treatment as semipassive.

A somewhat related technology that could be classified as an in situ abiotic source treatment is termed “rapid filling” (Gusek and Figueroa 2009). Soon after the closure of a pit or underground mine containing sulfide minerals, the pyrite oxidation process can be reduced by allowing surface water to enter the mine rapidly, thus blocking the oxygen from contacting the minerals. This process is discussed in a case study of the Island Copper Mine of North Vancouver Island, British Columbia, Canada (Gusek and Figueroa 2009). Some 1 million metric tons of acid-generating waste rock was placed in the pit (which was the lowest land elevation at the time); then a channel connecting Rupert Inlet was constructed, allowing sea water to fill the pit rapidly. Fresh water was allowed to fill the upper portions of the pit, creating a permanent density contrast so that overturning would not occur. The water column reduces the formation of acid rock drainage through oxygen depletion. This process does not affect the ferric iron, which also creates acid rock drainage, but at circum-neutral pH, ferric iron has such a low solubility that it is not a problem either.

2. APPLICABILITY

In situ treatment technologies for MIW are applicable to the following:

- mine pools, pit lakes, and impacted groundwater
- solo technology or in combination with other treatments
- easy accessibility
- treatment of multiple contaminants of concern, including metals, cyanide, and uranium
- treatment of high or low volume of material

In situ treatment technologies for MIW can be applied in pit lakes and mine pools depending on the site-specific characteristics. A few examples are presented below.

2.1 Tide Mine Pool Example

A proof-of-principle demonstration project was conducted at the abandoned Tide Mine in western Pennsylvania from June 2004 to February 2005 (Houston et al. 2005). An aerobic acidic mine pool (with pH of 2.5–3 and net acidity of 300 mg/L CaCO₃) which had active pyrite oxidation and acid rock drainage (ARD) producing high dissolved solids and metals concentrations that discharges about 100 gpm into an adjacent stream was converted into an anaerobic sulfate-reducing bioreactor with addition of alkaline material sodium hydroxide (NaOH), organic carbon such as molasses and alcohol, and an injection of CO₂ gas into the unsaturated zone above the mine pool. With the conversion to an anaerobic system, the chemistry of the approximately 6 million gallon mine pool changed dramatically as measured at the discharge. The pH increased to about 6; the DO was less than 2; alkalinity was 150 mg/L CaCO₃, and the oxidation-reduction potential (ORP) dropped to highly negative value. Aluminum and

ferric iron decreased to nondetect. Ferrous iron increased to a peak, then began decreasing with the onset of sulfide gas production (i.e., precipitation of FeS solid in the mine). The baseline metals concentrations were 7 mg/L Fe(III), 40–50 mg/L Fe(II), 15 mg/L Al, and 3 mg/L Mn.

The alkaline material and molasses were mixed and circulated through the mine pool for three months. A hydraulic residence time of 18 days was calculated, which gave a mine pool estimate of about 2 million gallons, about three times less than the original estimate, indicating that stagnant zones probably exist.

The injection of CO₂ gas into the beach zone of the mine produced a dense anaerobic blanket of CO₂-enriched air on top of the mine pool in the unsaturated zone and broke the chimney effect of rising, hot, oxygen-depleted air produced from pyrite oxidation reactions. Without the chimney effect, the draw and inflow of new oxygen-enriched air, which contributed to ongoing pyrite oxidation, was terminated.

With the elimination of ferric iron and dissolved oxygen through the conversion to a sulfate-reducing anaerobic environment along with the creation of a dense anaerobic blanket of CO₂-enriched air on the top of the mine pool in the unsaturated zone, the pyrite oxidation process and ARD production were basically terminated. The improved water quality at the discharge was maintained with passive addition of alcohol through the rest of the project.

2.2 Barite Hill Pit Lake Example

At the abandoned aerobic pit lake of the Barite Hill gold and silver mine in South Carolina, the Green World Science (GWS) patented process owned by Arcadis was selected and employed as a cost-effective, innovative Superfund remedy (Harrington et al. 2009). The Barite Hill mine was a cyanide heap leach operation with pyrite-rich waste rock and an open pit produced 1990–1994. Prior to going bankrupt, the mine operators conducted some reclamation, including addition of alkaline material to the naturally filling pit. This step neutralized the pit water, but the alkalinity was consumed with additional acid loading as the pit continued to fill and the pH dropped again. It was producing gas emissions of SO₂ and was expected to spill over into the adjacent creek and impact the environmentally sensitive Strom Thurmond Lake. The Barite Hill mine became a Superfund site with the bankruptcy of the operating company, and the remedy (minimum waste rock backfill, lime neutralization, and carbon addition) was selected through the EPA Superfund procedure. The remedy involved the addition of soluble organic carbon to transform the 60 million gallons of acidic (pH 1.5–2.3) water with high metals concentrations (Al, As, Cd, Cu, Fe, Mn, Ni, Se, and Zn) into an anaerobic sulfate-reducing bioreactor where good quality water is produced through metal sulfide precipitation.

The remedial action began in the fall of 2007 with the creation of a spillway from the pit lake to the adjacent creek to regulate the water level. The other actions included subaqueous placement of about 50,000 cubic yards of high-pyrite waste rock with some lime addition, neutralization of the pit using carbide lime from a local source, and carbon addition (molasses) to produce an acidic neutral water with low metals concentrations. Soil capping of waste rock above the water level was also implemented to reduce future pyrite oxidation.

The treated water met maximum contaminant levels (MCLs), criterion maximum concentrations (CMCs), and criterion continuous concentrations (CCCs) for all but selenium and cadmium, which were slightly above the CCCs. Notably, copper and zinc were reduced from 287 and 40.2 mg/L to 0.010 and 0.020 mg/L, respectively.

About 1,860 tons of hydrated and water saturated lime along with 400 tons of very soluble organic carbon compounds (molasses and alcohols) was added directly into the pit lake in January through May 2008 via a custom-designed aerated batch delivery system. With excess addition of carbon and lime along with the other actions to inhibit pyrite oxidation and acid loading, the remedy is expected to be permanent with periodic monitoring and addition of carbon and lime. The cost of the remedy was estimated at \$2.6 million, which was 79% to 88 % less than traditional remedies for pit lakes.

2.3 Sweetwater Uranium Pit Example

At the Sweetwater uranium mine in Wyoming, over 1.25 billion gallons of uranium- and selenium-contaminated pit lake water were treated with 1.1 million pounds of GWS organic carbon and nutrients (Harrington 2002). The uranium and selenium concentrations were reduced to standards of 5 mg/L and 0.05 mg/L, respectively. The treatment was conducted in the winter when a layer of ice covered the pit. This condition reduced the O₂ loading, which was greater than 80% of the carbon demand. The selenium and uranium were biologically reduced to insoluble forms as electron acceptors in the water at about 3°C.

2.4 Red Oak Mine Pool Case Study

Alkaline injection into a mine pool at Red Oak, Oklahoma produced neutral water with reduced metals concentrations (Red Oak case study; Canty and Everett 2004; Winfrey, Canty, and Nairn 2008). In December 2001 about 2,500 tons of fluidized-bed combustion (FBC) ash was injected into the acidic pool, estimated to be about 3.1 million cubic feet in volume. The initial conditions were pH = 4.75; alkalinity = 0; and Fe, Mn, and Al = 179, 6.7, and 3 ppm, respectively. Immediately after injection, the pH rose to 12.45, and alkalinity was 1,340 ppm with concentrations of Fe, Mn, and Al less than 1 ppm. The pH decreased to about 7.5, and the alkalinity dropped to about 65 ppm over time. Fe and Mn increased, but Al stayed below 1ppm. The alkaline injection technology (AIT) was successful in producing a net alkaline water in which dissolved iron was removed in an aeration pond prior to discharge into the adjacent stream. The ecological environment of the stream showed remarkable improvements during the post-injection period of 24 months.

Of the toxic metals that may be present in the FBC ash, only selenium was above the regulatory standards. This technology can be used alone or in combination with SAPs, thus reducing the size requirements and complication imposed by Fe³⁺ and Al³⁺.

2.5 Copper Basin Site Example

At the Copper Basin site in Tennessee both in situ and ex situ treatment with hydrated lime have been employed at the pit lake to treat North Potato Creek (which flows through the upper levels of the pit and discharges into Ocoee River) and highly acidic mine water from the lower levels of the pit lake (Faulkner et al. 2005). The neutralized solution is added to the pit lake for retention

and clarification to protect the Ocoee River from receiving North Potato Creek acid mine drainage. The effluent from the pit lake after treatment met all applicable water quality standards. However, monitoring with contingency plan is required.

The pit lake was evaluated for its potential for overturning, which could then result in a release of acidic waters with high metals concentrations from the deeper depths of the pit into the Ocoee River. It was determined that overturning was not possible due to the density contrast between the water in the shallow levels and the deep levels. However, monitoring is required.

3. ADVANTAGES

In situ treatment has the following advantages:

- lower cost compared to other treatments of MIW
- minimizes and also reduces ARD
- small infrastructure footprint, which requires small land requirements
- limited visual impacts and site disruption
- rapid results
- wide range of applicability, e.g., climate
- ease of construction and maintenance

The in situ treatment of MIW is a low-cost remedial alternative that meets remediation objectives as seen in the Barite Hill Mine (Harrington et al. 2009). The remedial goals can be achieved rather quickly—within a few months to a year—depending on the size of the site and the amount of material needed.

The ability to minimize or reduce the formation of acid rock drainage is a primary advantage of the in situ treatment technologies. This may require intermittent long-term addition of carbon source or alkaline materials to maintain the desired environments. In situ treatments do not require large amount of land for implementation. The pit lake and the underground mine voids provide the necessary space for precipitated metals, so no disposal is required.

In situ treatment can take place in most climates (Harrington 2002), although in extreme cold climates additional insulation may be required. Biological activity may be slowed in cold environments, but it does not stop. Also groundwater temperatures, especially from deep sources, do not dramatically change seasonally, thereby having minimal impact on biological activity. In general, in situ methods are the least invasive and most cost-effective option for treating contamination in pit lakes and mine pools. Continued research regarding the longevity and flexibility of in situ treatment will ultimately define its impact.

4. LIMITATIONS

- need for detailed site characterization limits applicability
- limited information regarding variation in treatment materials
- adequate delivery of the additive, substrate, and inoculums

- longevity unknown
- monitoring required with contingency plan

To know the amount of amendment needed, detailed characterization of the site is needed. Sometimes critical information may be lacking. In some cases of mine pool treatment, the underground mine workings are already flooded, and the subsurface conditions are unknown since adequate mine maps may be unavailable. Also at pit lakes it should be assessed whether or not lake overturning is a possibility and what would be the consequences of overturning were to occur. There is a wide and significant variation in the treatment materials and material to be stabilized. Even though there are some recent full-scale applications, more sites must be exposed to these treatments to define their value, versatility, and longevity.

Due to the newness of the in situ treatment technologies for mine pools and pit lakes, the longevity and need for continued addition of amendments are still unknown. In some cases a “bank” of iron sulfide (FeS) can be precipitated to protect the metals of concern from redissolving into the water by adding excess organic carbon. This bank of iron sulfide called “mackinawite” is not acid producing upon oxidation. Consequently, if oxygenated conditions are reestablished, the FeS consumes oxygen before it can affect the metals of concern.

Because the inexact extent of the mine pool, its stagnant zones, the amount of acid loading, etc., the exact amount of amendments needed to treat the MIW to meet the objectives is an estimate that is difficult to ascertain. Ongoing oxygen input and its reactive products represent the largest carbon demand for a sustainable treatment. Means to reduce oxygen input will reduce treatment costs. Future acid loading is difficult to estimate, and the carbon demand from previously precipitated metals is difficult to estimate as well. Therefore, to obtain the proper application rates, conservative assumptions should be made. This step may lead to overestimating the amendment requirements and additional costs.

5. PERFORMANCE

The success of an in situ treatment system relies on site-specific conditions. Reports on the case studies and examples from the references indicate that in situ treatment systems hold significant promise at meeting water quality standards, including MCLs, CMCs, and CCCs. Very high concentrations of dissolved metals and acidity have been successfully treated.

In the Barite Hill mine (Harrington et al. 2009), neutralization of the pit using carbide lime from a local source and carbon addition (molasses) produced an acidic neutral water with low metals concentrations that meet MCLs, CMCs, CCCs for all but selenium and cadmium (which were slightly above the CCCs). Notably copper and zinc were reduced from 287 and 40.2 mg/L to 0.010 and 0.020 mg/L, respectively.

For the Sweetwater Uranium mine (Harrington 2002) the uranium and selenium concentrations were reduced to the regulatory standards of 5 mg/L and 0.05 mg/L, respectively. The treatment was conducted in the winter when a layer of ice covered the pit.

At the Red Oak case study site, the AIT was successful in producing a net alkaline water with low metals concentrations in which dissolved iron was removed in an aeration pond prior to discharge into the adjacent stream. The ecological environment of the stream showed remarkable improvements during the post-injection period of 24 months.

With the conversion to an anaerobic system at the Tide mine (Houston et al. 2005), the chemistry of the approximately 6 million gallon mine pool changed dramatically as measured at the discharge. The pH increased to about 6; the dissolved oxygen was less than 2; alkalinity was detected at 150 mg/L CaCO₃; and the ORP dropped to highly negative value. Aluminum and ferric iron decreased to nondetect, and ferrous iron increased to a peak, then began decreasing with the onset of sulfide gas (i.e., precipitation of FeS solid in the mine). The baseline metals concentrations were 7 mg/L Fe(III), 40–50 mg/L Fe(II), 15 mg/L Al, and 3 mg/L Mn.

6. COSTS

Relative to active treatment technologies, in situ treatment systems can be inexpensive compared to other MIW treatment technologies. The cost of the remedy at the Barite Hill mine example was estimated at \$2.6 million, which was 79%–88% less than traditional remedies for pit lakes. This cost works out to \$.043/gallon treated. The amount is high since it includes other costs associated with management of high-pyrite-containing waste rock, including subaqueous disposal, high wall reclamation, and capping.

Cost factors involve the amount, availability, application, and transport of amendments. Managing oxygen is reportedly the highest cost item. Since mine pools and pit lakes contain such large volume of MIW, the amount of amendment for treatment is also large.

Other costs factors to be considered include mobilization and use of heavy equipment at remote and or steep sites, local availability and quality of the materials required for treatment, the potential need for operation in extreme cold conditions, and requirements for long-term monitoring.

There is no reported cost of installing the in situ treatment systems for the case studies. However, for the alkaline injection of the FBC ash at the Red Oak site, the major cost factors included the hauling of the material to the site, installation of the injection wells, and injecting the alkaline slurry.

7. REGULATORY CONSIDERATIONS

Construction of in situ treatment systems may require approvals and/or permits from one or more regulatory authorities (federal, state, and/or local), depending on the site location and the applications being proposed. It should also be noted that if any surface water is being impacted, a National Pollutant Discharge Elimination System permit may be required at the final point of discharge. At Superfund sites these permits are not required, but the treatment must meet the substantive requirements (i.e., applicable or relevant and appropriate requirements).

Sometimes the materials being used for treatment may be considered pollutants, such as the FBC ash used in the Red Oak case study to raise pH in the mine pool. The CCB may contain metals that could be released at high-pH conditions. Only selenium was of concern at this site. In cases involving injection to remediate groundwater, the underground injection control (UIC) regulations cover this application.

Projects have to deal with one or more of the following acts or agencies, depending on the specifics of the site:

- Clean Water Act (CWA)
- Comprehensive Environmental Response Compensation, and Liability Act (CERCLA)
- Surface Mining Control and Reclamation Act (SMCRA)
- UIC Regulations
- U.S. Environmental Protection Agency (USEPA)
- state agencies
- local governments

8. STAKEHOLDER CONSIDERATIONS

Because of their simple construction, limited operation and maintenance requirements, and generally minor post-construction surface visual impacts, in situ treatment systems do not suffer from most of the stakeholder issues that may apply to other AMD treatment technologies. However, project- and site-specific stakeholder considerations must be taken into account when selecting and designing an effective treatment system.

The case studies did not report encountering any public issues or concerns with in situ treatment systems projects. However, since the contaminants are precipitated within the mine pool or pit lake during in situ treatment, it may be possible for the metals to redissolve due to changes in the environmental conditions and cause a release in the future. Until more examples of this technology are in place for decades, extended monitoring should be a requirement.

9. LESSONS LEARNED

The reported lessons learned were that establishing a good working relationship with a network of communication and cooperation among the stakeholders are critical to the success of the project.

10. CASE STUDIES

Table 10-1. Case study using in situ treatment for mine pools and pit lakes
[Red Oak Site, an abandoned underground coal mine in Latimer Co., southeast OK](#)

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