TECHNOLOGY OVERVIEW

CHEMICAL PRECIPITATION

August 2010

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ITRC (Interstate Technology & Regulatory Council). 2010. *Chemical Precipitation.* Washington, D.C.: Interstate Technology & Regulatory Council, Mining Waste Team. www.itrcweb.org.

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CHEMICAL PRECIPITATION

1. INTRODUCTION

Chemical precipitation is a conventional technology used to treat mining-influenced water (MIW), including acid mine drainage, neutral drainage, and pit lake water. Chemical precipitation processes involve the addition of chemical reagents, followed by the separation of the precipitated solids from the cleaned water. Typically, the separation occurs in a clarifier, although separation by filtration or with ceramic or other membranes is also possible. Chemical precipitation can also be used in pit lakes or other water bodies, in which case the precipitated solids can simply remain in the bottom of the pool.

Precipitation can be induced by the addition of an alkali, sulfide, coagulant, or other reagent that will bond with dissolved metal ions. Alkali sources include caustic sodium hydroxide (NaOH), hydrated lime ($Ca(OH)_2$), quick lime (CaO), limestone ($CaCO_3$), and magnesium hydroxide ($Mg(OH)_2$). Sulfide reagents used to cause precipitation of contaminants include iron sulfide (FeS), sodium hydrosulfide (NaHS) (Wellington-Oro Water Treatment Plant), sodium sulfide (Na_2S), calcium sulfide (CaS), and biogenic sulfide generated in situ by sulfate reduction. Coagulants can include alum $KAl(SO_4)_2$, iron hydroxide ($Fe(OH)_3$), or ferric chloride ($FeCl_3$). Carbonates can also be used in chemical precipitation, including sodium carbonate (Na_2CO_3), calcium carbonate ($CaCO_3$), or CO_2 under pressure (Toby Creek Mine).

Additional methods reported are neutralization using the Rotating Cylinder Treatment System (RCTS) (Leviathan Mine, Sunshine Mine, Cement Creek, American Tunnel, Inactive Copper Mine in Vermont, Zortman Landusky), $FeCl_3$ for arsenic removal (Lava Cap Mine), use of CO_2 under pressure (Toby Creek Mine), and a limestone/steel slag system (Ohio Mines). Advantages of steel slag are low cost and less degradation over time than limestone alone. The steel slag produces extreme alkalinity and can precipitate manganese and other trace metals. Some metals may be removed by co-precipitation with iron or aluminum oxyhydroxide species.

The technologies discussed in this guidance are based on representative case studies. Additional information about this technology and other acid drainage treatments can be found in the GARD Guide (INAP 2009).

- **Hydroxide Precipitation.** Raising the pH with the use of alkaline agents causes certain dissolved metals (e.g., cadmium, copper, iron, lead, manganese, and zinc) to precipitate as hydroxides. A polymer may be added to enhance flocculation, and the solution may be transferred to a clarifier to separate the solids from the cleaned overflow effluent. The resultant metal-hydroxide sludge extracted from the bottom of the clarifier usually contains a large percentage of bound water, limiting the potential for reuse, and is disposed of as a solid waste. The amount of sludge generated can be reduced by employing a high-density sludge (HDS) treatment technique. In HDS processes, the precipitated hydroxide sludge is recycled to a conditioning tank, where it is mixed with the alkali reagent. The sludge/alkali slurry is then metered into the MIW to raise the pH and cause additional metal precipitation. This reconditioning of the sludge provides for precipitation sites for the dissolved metals to bond, increasing the overall density of the sludge in the clarifier underflow.

Limestone is economical and less corrosive than the other two forms of lime; however, it is limited by its slow dissolution rate, and its efficiency can be adversely affected by armoring, which is the formation of an impervious coating. These two issues may be addressed by using fluidized-bed reactors and the addition of CO_2, as used at both Toby Creek and Friendship Hill. Additionally, the maximum pH achievable with limestone (8–8.5) is much lower than with lime (>12). Thus, only metals that achieve the desired solubility at or below pH 8 can be effectively targeted.

- **Sulfide Precipitation.** The addition of a sulfide induces precipitation of dissolved metals as metal sulfides. This treatment is very effective for many metals, including zinc and cadmium. It is less effective for some contaminants such as manganese. If the MIW is acidic, pH adjustment may be required prior to the sulfide precipitation. Benefits of sulfide precipitation include a reduction over hydroxide precipitation of the quantity of sludge generated. The sludge is more easily reprocessed to recover the metals and may offset the cost of treatment. However sulfide precipitation is not viable for all situations as the generation of excess hydrogen sulfide (H_2S) may be a nuisance or safety concern.

  The Town of Breckenridge in Summit Hill, Colorado operates a water treatment plant which uses sulfide precipitation to treat acid mine drainage water that is contaminated with zinc and cadmium (USEPA Region 8 n.d.). The dissolved metals are precipitated and recovered for commercial use. The treated water meets Colorado water quality standards. The process reportedly does not produce any odors or any special-handling waste. Treatment removes more than 90% of cadmium and more than 99% of zinc from the mine drainage. Average cadmium and zinc concentrations at the untreated mine discharge were 59 μg/L cadmium and 123,000 μg/L zinc. The treated water has cadmium and zinc concentrations below 4 μg/L and 225 μg/L, respectively. The site was remediated under EPA's superfund program. Additional details are at USEPA Region 8 (n.d.).

- **Surface Pool Water.** As opposed to the continuous-flow treatment schemes discussed above, pooled water (i.e., pit lakes, mine pools) can be treated with chemical precipitation in a batch mode. Often the treatment is a hybrid involving both hydroxide and sulfide precipitation. An alkali is added to increase pH and cause some precipitation of dissolved metals. A carbon source is also added to encourage growth of sulfate-reducing bacteria and induce sulfide precipitation as well.

2. APPLICABILITY

Chemical precipitation technology is applicable to the following situations:

- mining-influenced water
- high or low volume of material

- solo technology or in conjunction with others
- multiple contaminants of concern

Chemical precipitation is a flexible permanent technology that can address metal contamination in MIW at mine sites. This technology can be used in conjunction with other treatments or by itself, depending on site conditions. The treatment system can be designed to deal with a variety of site conditions. The optimal process and its efficiency depend on several factors, including flow rate or volume, contaminants and their concentrations, other water parameters, discharge criteria, site access, and sludge disposal options.

Chemical precipitation is a standard treatment technique used across the United States and around the world. At least 12 case studies were received, and all show that it was successful. Additional lab-scale technology studies were also reported.

3. ADVANTAGES

Chemical precipitation has the following advantages:

- permanent
- immediate results
- efficient
- easily implemented
- easy to monitor

Chemical precipitation offers many advantages as a treatment alternative. It is able to meet stringent discharge criteria. It has been used effectively for many years. The design of the treatment process can be customized and thus can be used in a variety of situations. Chemical precipitation is a long-term remedy that can address both acute and chronic risks to human and ecological receptors. It provides a relatively rapid effect in the reduction of contamination in downgradient surface water bodies. Advances in remote monitoring have increased the ability for chemical precipitation to be used in locations previously prohibitive.

- **Hydroxide Precipitation.** The addition of alkali reagents to treat MIW has many positives. Virtually all metals can be removed to well below discharge criteria. Each alkali has its own advantages. Sodium hydroxide is available as a liquid and is easily delivered into the system. Calcium-based reagents provide a source of hardness into the environment, reducing the toxicity of residual dissolved metals to environmental receptors. Quick lime and limestone are both very inexpensive chemicals. Hydrated lime does not require slaking to activate. The appropriate choice of reagent depends on site-specific criteria.

- **Sulfide Precipitation.** The main advantage of sulfide precipitation over hydroxide precipitation is in the quantity and type of sludge generated. Metal sulfides sludges are generally denser than metal hydroxide sludges and contain less bound water. Metals can be easily extracted and reprocessed. Sulfide can also be generated on site by the reduction of sulfates. This is typically done with the use of sulfate-reducing bacteria (SRB). The SRB can work directly in the treatment system with MIW containing sulfates or in a bioreactor designed to generate the sulfide for delivery as a reagent.

4. LIMITATIONS

- high cost
- not applicable for all cases
- requires operation and maintenance (O&M)
- requires power
- may generates a waste product

Disadvantages or limitations of chemical precipitation include the traditionally active nature of the process. Chemical reagents need to be procured, energy inputs and manual oversight are required, and a waste stream is generated. These can equate to a relatively high cost for treatment.

- **Hydroxide Precipitation.** Depending on the volume of water necessary for treatment, the cost of this technology can be high. Metal hydroxide sludge typically contains water bound in the chemical matrix and results in a large volume of waste requiring disposal Generation of large volumes of sludge may be problematic if there is not room available. Increased costs from energy use occur when attempting to drive off excess moisture. Lined impoundments must be considered if there is potentially hazardous waste that can migrate from the sludge disposal site. The waste product may contain free liquids or fail testing by the Toxicity Characterization Leaching Procedure (TCLP) and may necessitate subsequent disposal at an approved hazardous waste facility, incurring more costs.

- **Sulfide Precipitation.** The process must be designed and maintained so that the mass balance of H_2S is consumed by precipitating metal sulfides. This can be a delicate balance between influent sulfur/sulfide sources and monitoring system parameters. Monitoring units must be in place for potential release of H_2S. In the case of biogenic metal sulfide precipitation, high H_2S level can create a toxic environment for the bacteria, rendering them unable to function properly. It can be difficult to remove all metals if proper conditions are not attained and maintained. Metal sulfides precipitate in a reduced environment. It is essential to maintain the oxidation-reduction potential at a sufficiently reduced value.

5. PERFORMANCE

Chemical precipitation is a proven, large-scale technology that offers permanent results. It is applicable for many mine drainage sites and can be used solo or in conjunction with other treatment technologies. Chemical precipitation has demonstrated achievement of stringent water quality limits in acid mine discharges and has reduced/eliminated migration of metal contaminants to downgradient water bodies, wetlands, and watersheds. The performance and results are specific to initial water quality and site limitations. Each site must be fully characterized physically and chemically to ensure that the right technology(s) are being used and state regulations are met.

6. COSTS

Chemical precipitation is generally considered a high-cost treatment. Impacts to cost result from variables, including flow rate, contaminants being treated, quantity and characteristic of sludge generated, variability of contaminant concentrations, reagents used, labor demand, etc.

Reagent cost will greatly impact O&M costs of treatment. In September 2000, the National Lime Association reported a comparison of costs. Sodium hydroxide was reported to cost $228 to neutralize 1 ton of sulfuric acid. Magnesium hydroxide was $179. Calcium hydroxide cost $66, while calcium oxide was the lowest of the reagents compared at $37.

The Wellington-Oro Treatment Plant operates at a low of 50 gpm to a high of 150 gpm, treating for zinc and cadmium at a pH of 6.4. The capitol cost associated with this plant is approximately $4.3 million. It has not been in operation long enough to report O&M costs.

7. REGULATORY CONSIDERATIONS

A National Pollution Discharge Elimination System (NPDES) permit may be required under the Clean Water Act. An active and ongoing treatment process may require oversight of a certified operator. Additionally, the quantity of chemicals and sludge contained on site may trigger regulation under the Resource Conservation and Recovery Act (RCRA). Disposal of the waste sludge must comply with applicable regulations. Additional treatment mechanisms should be considered when the primary treatment system cannot achieve regulatory standards or state regulators will not agree to alternative abatement standards for individual cases.

8. STAKEHOLDER CONSIDERATIONS

Chemical precipitation is a well-accepted technology which offers permanent results for metal contaminants removal and achieves stringent discharge limits that are protective of public health and the environment.

The Wellington-Oro site was identified a potential Superfund site in 1989, which eventually galvanized a community-based team to review treatment options at the site. This resulted in a unique settlement agreement that enabled the land to be purchased for public open space, while providing for treatment of contaminated water emanating from the site.

9. LESSONS LEARNED

In some cases, an effective industry/regulatory working group with regular meetings, intervening conference calls, and general correspondence greatly assist with constructive feedback and generate public cooperation towards design/implementation of the remediation project. Once projects are approved, technologies can be improved upon and enhanced for other applications.

10. CASE STUDIES

Table 10-1. Case studies using chemical precipitation (full scale).

Multiple Ohio sites
Copper Basin Mining - Lower Potato, TN
I-99 Remediation, PA
Iron Mountain Mine (Copper), CA
Leviathan Mines, CA
Fire Road Mine, New Brunswick, Canada
Copper Basin of TN
Unnamed site, Alpine, CA
Sunshine Mine, ID
Inactive Copper Mine, VT
Zortman Landusky - Swift Gulch Site, MT
Wellington-Oro Water Treatment Plant
Lava Cap Mine, CA
Toby Creek, PA
Friendship Hill, PA
Argo Tunnel, CO
Cement Creek, CO
American Tunnel, CO

11. REFERENCES

INAP (International Network for Acid Prevention). 2009. *The Global Acid Rock Drainage (GARD) Guide*. www.gardguide.com/index.php?title=Main_Page.

USEPA (United States Environmental Protection Agency) Region 8. n.d. "Superfund Program: French Gulch." www.epa.gov/Region8/superfund/co/frenchgulch.