COST EFFECTIVE CHEMICAL TREATMENT OPTIONS FOR MINE WATER TREATMENT IN THE NORTH

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ABSTRACT

One of the most significant costs for many mines post-production is the cost associated with treating metal laden mine water and acidic drainage. Most sites use simple lime neutralization to treat mine water. While lime neutralization is a very effective treatment method, if not properly applied it can be costly and problematic. Several treatment parameters significantly impact treatment costs, effluent quality, sludge production and the geochemical stability of the sludge produced. Minor modifications to the treatment process can result in a reduction in operating costs, volume of sludge generated, metal release to the environment and liability. This is particularly true when applying treatment processes designed for temperate climates to cold climate conditions.

In some circumstances, simple lime neutralization may not be the best treatment option. The selection of the most effective treatment option will depend on the composition of the mine water, the flow rate and site-specific conditions. A thorough assessment of these parameters is necessary before a treatment process can be selected.

This paper reviews various treatment options available and application of these options to northern sites.

Introduction

Acidic drainage, mine water and other acidic metalliferous effluents are commonly treated in the mining and metallurgical industries using lime neutralization. This centuries old technology is effective in raising the pH of the water and precipitating the metals to below regulatory limits. Upon neutralization, metals precipitate out of the raw water as oxyhydroxides. In northern climates, lime treatment is the most suitable and cost effective option available to treat mine water (Davé, 2003). Since most lime neutralization treatment processes have been developed and applied for temperate climates, modifications to these processes/operations are required to optimize performance in northern climates.

Lime Treatment Chemistry

Although many different biological and chemical technologies exist for treatment of acidic drainage, lime neutralization remains by far the most widely applied method. This is largely due to the high efficiency in removing dissolved metals through neutralization, combined with the fact that lime costs are low in comparison to alternatives. Lime treatment essentially consists of bringing the pH of the acidic drainage to a point where the metals of concern are insoluble (Aubé and Zinck, 2003).

The principle of lime neutralization lies in the insolubility of heavy metals in alkaline conditions. By controlling the pH to a typical setpoint of about 9.5, metals such as iron (Fe), zinc (Zn), and copper (Cu) are precipitated.

Lime dissolution is the first step of the neutralization process. For large treatment systems, quicklime is used. This lime must first be hydrated (slaked) and is normally fed to the process as a slurry. The hydrated lime then dissolves to increase pH. The two following equations illustrate these reactions:

$$CaO + H_2O \rightarrow Ca(OH)_2 \qquad (1)$$

$$Ca(OH)_2 \rightarrow Ca^{2+} + 2OH^- \qquad (2)$$

The increased pH provides hydroxide ions, which precipitate the metals. The following reaction shows the precipitation reaction with Zn as an example:

$$Zn^{2+} + 2OH^- \rightarrow Zn(OH)_2 \qquad (3)$$

Among the metals to precipitate as per the above equation is ferrous iron. Unfortunately, ferrous hydroxides are not as stable as ferric hydroxides when the sludge is exposed to acidic waters or natural precipitation. For this reason, aeration is often applied to oxidize the iron to the more stable form, as per the following equation:

$$Fe(OH)_2 + \frac{1}{2} H_2O + \frac{1}{4} O_2 \rightarrow Fe(OH)_3 \qquad (4)$$

A common by-product of lime neutralization is gypsum. Gypsum precipitation occurs as the mine water is often rich is sulphate and the calcium added from lime will bring the solubility product well above saturation. This reaction is often responsible for scaling in treatment processes.

$$Ca(OH)_2 + H_2SO_4 \rightarrow CaSO_4 \cdot 2H_2O \qquad (5)$$

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O \qquad (6)$$

Treatment Processes

Three typical lime treatment processes are used in the industry and have been described in detail in the literature (Aubé and Zinck, 1999; Vachon, 1987; Kuit, 1980).

Basic. The basic lime treatment involves the addition of lime to the waste stream followed by solid/liquid separation in a settling pond (Figure 1). The lime is added to attain a pH suitable for precipitation of the heavy metals from the waste stream. United Keno Hill Mine (Mayo, YT) and Hudson Bay Mining and Smelting (Flin Flon, MB) apply this treatment process. A higher pH setpoint is often necessary to insure complete precipitation of metals throughout the pond (percent solids 1-5%).

Conventional. In conventional treatment systems mechanically agitated reactors are used and lime addition is controlled by pH. The process provides good effluent quality.

Reactor discharge is sent to sludge settling ponds or tailings ponds for solid/liquid separation (percent solids 3-10%). This type of process is used at Falconbridge (Sudbury) and INCO (Sudbury, Ontario).

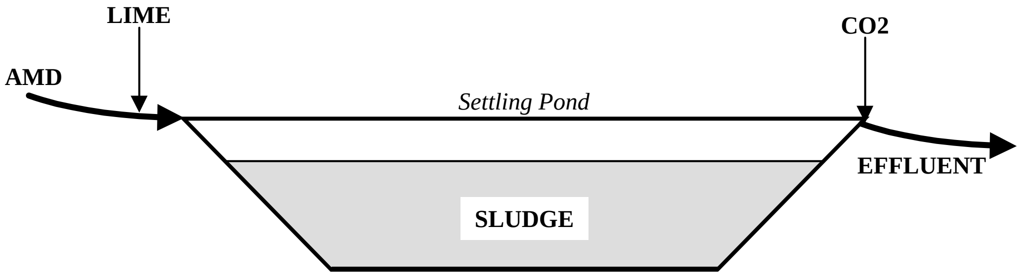

Figure 1 - Basic Lime Treatment (Aubé and Zinck, 1999)

High Density Sludge Process. Figure 2 describes the standard High Density Sludge (HDS) process. In this process, the acidic drainage is generally fed into a Rapid Mix Tank (RMT), where it is contacted with a lime/sludge slurry to bring the pH of the combined slurry to 9 or 9.5. The RMT is often used to offer better pH control in the process, but is not necessary. The retention time in this vessel varies normally from 2 to 10 minutes. The Lime Reactor (LR) has a retention time typically ranging from 30 to 90 minutes.

Air is normally sparged in the LR for ferrous oxidation. The Floc Tank (FT) is used to contact the polymer with the precipitates for floc formation. A portion of the sludge from the clarifier underflow is recycled to the lime/sludge mix tank (L/S).

The feed rate and a pre-determined ratio of solids recycled to solids formed control the sludge recycle rate. The lime addition is controlled to maintain pH at the desired setpoint, measured either in the RMT or the LR (percent solids 15-30%). The High Density Sludge technology is used at various sites in Canada including Teck Cominco’s Kimberley site (British Columbia) and Red Dog site (Alaska), La Mine Doyon (Quebec) and Geco (Manitouwadge, Ontario)

The metal precipitates created during all processes are wastes typically identified as sludge. This sludge must be disposed of in an environmentally acceptable manner. As sludge disposal costs can be important, the most advanced lime treatment processes minimize the waste volumes by creating a higher-density sludge. As such, the higher capital requirement associated with more sophisticated treatment systems is quickly off-set by lower operating and sludge disposal costs.

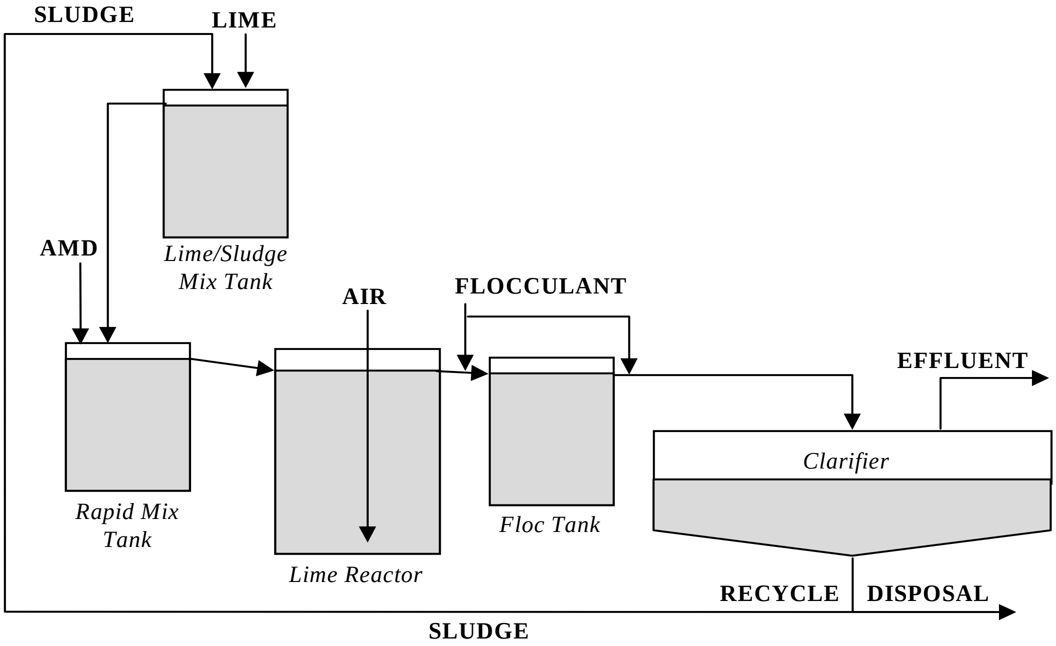

Figure 2. Conventional high density sludge process (Aubé and Zinck, 1999).

Optimization of Lime Treatment

Several parameters can be adjusted to optimize the lime neutralization process whether in a basic system or an automated HDS system. One of the key parameter to optimize is lime consumption, as it can lead to excessive costs and high reagent utilization if the process is not efficiently controlled. Improved lime utilization depends on several factors, the most important of which include lime slaking, mixing and pH control.

The term slaking refers to the combination of varying proportions of water and quicklime (CaO), to yield a hydrated lime slurry (as represented in Equation [1]). Quicklime is used at most medium and large operations as it is the lowest cost alkaline source for mine water neutralization. Factors affecting the efficiency of the lime slurry include the reactivity, particle size and gradation of the quicklime, the quantity of water used for slaking, the slaking temperature, and agitation. Controlling the slaking process, particularly the temperature, can reduce lime requirements by more than half (Figure 3).

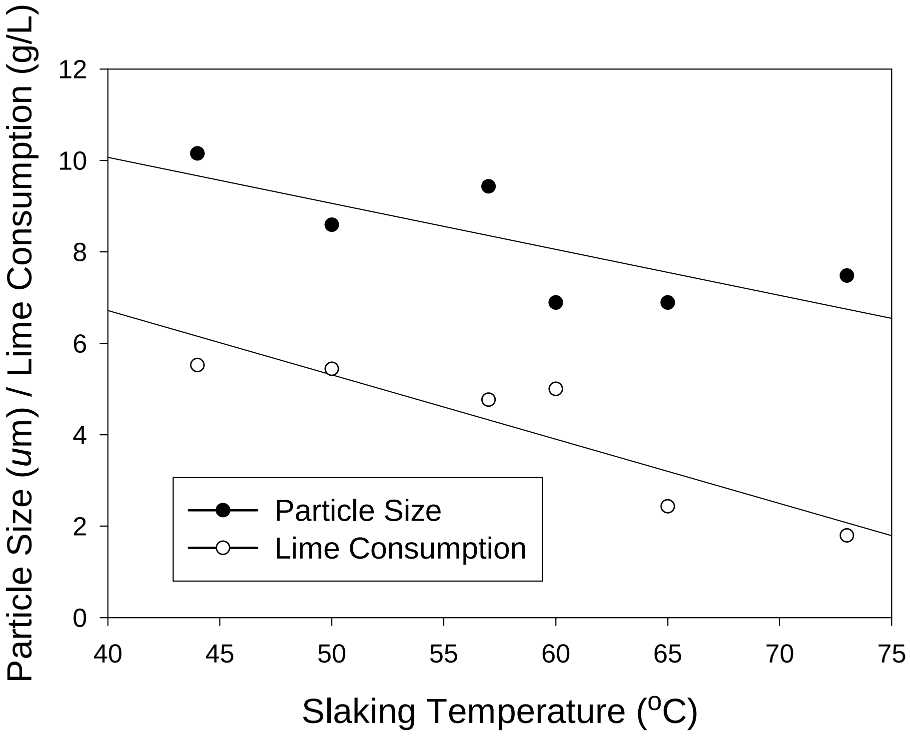

Figure 3: Particle sizing (50%) and consumption for lime slaked at different temperatures (Zinck and Aubé, 2000).

Hydrated lime is only slightly soluble in water. However, two factors that enable lime to be such an effective base, despite its low solubility in water, are: (1) the fineness of the hydrated lime particle size and (2) the double hydroxyl groups that result from each molecule of lime that dissociates in water. As such, mixing is another important factor that controls lime consumption and treatment effectiveness. With inefficient mixing the lime particles do not dissolve but instead become coated by precipitating hydroxides and gypsum. If the lime does not mix well with the waste stream it cannot effectively raise the pH and remove the metals.

In conventional and HDS processes, mixing is less of an issue than in basic systems. Many treatment operations are simplistic and primitive. In these systems lime is often added into a make shift reactors or directly to the waste stream without adequate mixing. In remote sites the challenge is to provide effective mixing with minimal maintenance. An ideal option for these sites is the use of static mixing systems.

Static mixers are applied in-line and utilize cross-stream mixing and flow splitting to achieve very rapid blending. They allow for effective mixing without consuming energy and can easily be retrofitted into existing lines. CANMET-MMSL is currently investigating the application of static mixers to basic treatment systems.

Control of the setpoint pH can also play an important role in lime dissolution efficiency. In the treatment of Zn, a minimum pH of approximately 9 is required for hydroxide precipitation to meet the MMER limit of 0.5 mg/L. At some sites, the pH control is set at 11, as this results in consistently acceptable Zn levels in the effluent. The pH of lime slurry is typically between 12 and 12.7, and this represents $Ca(OH)_2$ saturation. If the control pH of the slurry approaches this value, the lime efficiency decreases sharply. In addition, if the control pH is set too high there is risk of amphoteric metals redissolution.

Issues with Cold Climate Treatment

Significant challenges must be overcome when treating water in northern climates. These include potential freezing problems, slow hydrolysis reaction kinetics and a very high influx of water during spring thaw.

One potential problem is line freezing, particularly at the beginning and end of the treatment season. The most troublesome areas are the pump suction and some low points along the line (Aubé and Arseneault, 2003). In extreme temperature conditions, treatment operations should be designed in such a way as to minimize temporary shutdowns and equipment freeze-ups. Another issue with freeze-ups is that frozen lines can rupture resulting in accidental mine water/sludge spills. Redundancy should be built into these treatment operations in case of shut down or operational problems.

At lower temperatures, hydrolysis reaction kinetics are very slow and as a result precipitate crystallinity is poor. In addition, as the solubility of lime increases with decreasing temperature, in poor mixing regimes the likelihood of local areas of supersaturation increases. As a result, the sludge that is generated is often voluminous and difficult to settle. Since acceleration of the reaction kinetics is not an option, reaction mechanisms should be controlled to encourage particle growth and enhance precipitation. Control of process parameters such as mixing and pH setpoint control can go a long way to improve not only treatment efficiency but sludge properties.

In temperate climates, a significant fraction of the spring thaw infiltrates the ground where it is stored for a more gradual release. In the north, permafrost conditions do not allow for water infiltration as frozen soils have very low permeability. As a result the snowmelt reports as essentially 100% runoff.

Other Options

Many of the sources of mine water in Northern Canada that require treatment contain little iron or the ferrous iron in solution precipitates rapidly upon contact with the air prior to lime addition (neutral mine drainage). In iron rich systems ferric hydroxides form during treatment at pH~3. Ferric hydroxide (ferrihydrite) is a gelatinous precipitate which has a tremendous capacity to adsorb other metals. As such in iron rich systems, metals such as Zn, Cd, As, and Cu are much more readily removed than in iron-limited systems where there is no substrate for adsorption.

Ferric Sulphate

The presence of trace metals such as arsenic, zinc and cadmium in the mine water can pose treatment challenges specifically if the amount of iron present in the waste stream is limited. In these cases, the addition of ferric sulphate can significantly improve metal removal by surface adsorption and co-precipitation. Actual removal performance varies with waste streams and contaminants present.

This method is completed by manual addition of ferric sulphate distributed throughout the surface of the pond or injection in-line. The iron sulphate quickly dissolves and causes the iron to re-precipitate as ferric hydroxide. The ferric hydroxide (ferrihydrite) serves to agglomerate the zinc hydroxide precipitates and also to adsorb any Zn remaining in solution. The larger particles formed by the combination with ferric hydroxides then settle much faster than the smaller $Zn(OH)_2$ particles alone.

The rate of adsorption varies with temperature, which can be a factor at northern sites. Small changes in temperature can have a significant impact on the affinity of zinc for the ferrihydrite surface; equilibrium sorption capacity decreased by 3–4 orders of magnitude as temperature fell from 25 to 4°C for all pH values (Trivedi et al., 2004). Zinc sorption onto ferrihydrite, is governed by pH as well as by temperature and Fe/Zn ratio

Manganese Oxidation

Manganese has similar properties to iron in that as an oxyhydroxide it has a tremendous adsorption capacity. As such, the transport and fate of heavy metal pollutants in natural waters is strongly affected by Fe and Mn oxide precipitation and dissolution. In addition to adsorption, heavy metals are also incorporated in the Fe and Mn oxide matrix as impurities when precipitation occurs or when new mixed metal/Fe and metal/Mn coprecipitates are possible. Consequently, the cycling of redox conditions and the associated precipitation and dissolution of Fe and Mn oxides can lead to the cyclical uptake and release of heavy metal pollutants. Compared to iron, the oxidation of Mn(II) is at least 10 times slower at circumneutral pH. Only for pH greater than 8 does the reaction rate become significant. Unlike the iron oxidation/hydrolysis reaction, MnOOH will precipitate to any great degree only after the pH has been raised by lime neutralization. By controlling and optimizing the redox conditions, natural Mn in the mine water can be precipitated, coprecipitating Zn and other metal contaminants.

Site Application Examples

United Keno Hill

The Keno Hill Mining District of the Yukon Territory is historically the second largest silver producer in Canada. More than 65 silver vein deposits and prospects have been identified in a belt about 8 km wide and 22 km long. Although mining has ceased since 1989, there remains active exploration in the area and public concern regarding metal-rich discharges from some of the abandoned mine workings. In particular, drainages from the Galkeno 300 and 900 adits are characterized by high dissolved zinc concentrations (approximately 100 and 10 mg/L Zn, respectively). Lime treatment has been used as the primary process for zinc removal. Previous studies by Indian and Northern Affairs Canada, the Yukon Territorial Government (YTG) and CANMET-MMSL suggest that the current lime treatment systems on site work but not very efficiently or consistently (Fiset et al., 2003). Optimum zinc removal and lime utilization are treatment challenges at this site.

The Galkeno 900 sludge characterized by CANMET-MMSL in 2001 (Fiset et al., 2003) showed poor lime utilization efficiency and a very high neutralization potential (911 kg $CaCO_3$ equiv/tonnes). Overdosing of lime through ineffective slaking practices, insufficient mixing and poor pH control usually lead to high NP values. This site could benefit from simple treatment modifications including optimization of the lime slaking process, installation of static/in-line mixers and ferric sulphate addition. The Galkeno 300 site discussed by Kwong and Zinck (2005) could significantly reduce treatment costs by optimizing Fe(II)/Mn(II) oxidation/precipitation and subsequent co-precipitation. Combining the Galkeno 300 and 900 streams may also serve to be beneficial.

Faro Mine

The Faro mine commenced mining of massive sulphides from an open pit mine to recover a zinc/lead concentrate in the late 1960s, at a rate of 8,000 tpd. Tailings were deposited in tailings impoundments in the Rose Creek Valley. In 1981 the mine was closed but re-opened in 1986 under new ownership and the milling capacity was increased to approximately 13,000 tpd. In 1991, the Faro pit was mined out and mining continued in the Faro underground mine as well two new open pits were opened on the Vangorda Plateau. In 1992 the discharge of tailings to the valley impoundments was discontinued and tailings were placed in the Faro open pit. Economic failure of Curragh Resources resulted in the mine closing in 1992. Mining was resumed in 1995 under the ownership of Anvil Range Mining.

The mine water at the Faro mine is treated by a process designed to simulate a modified high density sludge process. The mill was retrofited to treat the water, dewater and recycle the slurry. In 2001, fresh sludge was collected directly from the recycle line at the plant and characterized. Results showed that the sludge consisted primarily of $CaCO_3$ and the neutralization potential (NP) was very high (849 kg $CaCO_3$ equiv/tonnes), one of the highest reported in the literature (Zinck et al., 1996; Aubé and Zinck, 1999). The very high NP value measured indicates that the lime neutralization process is not efficient with respect to lime utilization. As discussed above, overdosing of lime through ineffective slaking practices, insufficient retention time and poor pH control usually lead to high NP values. The high flows at this site and the low iron content of the raw water makes it more challenging to treat. Ferric sulphate addition and a treatment process audit may be beneficial in this case.

Conclusions

Lime neutralization is a cost effective method to treatment metal contaminated solutions. However the application of this relatively simple method needs to be customized depending on the site particularly in northern climates. Depending on the nature of the mine water lime neutralization may need to be complimented with the addition of ferric sulphate. However other cases, simple control the redox conditions during treatment to encourage coprecipitation/ adsorption of heavy metals such as Zn with Fe/Mn oxyhydroxides may be all that is necessary. Other process modifications such as improved slaking, enhanced mixing and better pH control could result in considerable treatment cost reductions.

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