Bulletin

CIM
ICM

Technical Paper

Mineral Processing

Optimization of lime treatment processes

J.M. Zinck, CANMET, Mining and Mineral Sciences Laboratories, Natural Resources Canada, Ottawa, Ontario, Canada, and
B.C. Aubé, Noranda Inc. Technology Centre, Pointe Claire, Québec, Canada

KEYWORDS: Acid mine drainage, Lime neutralization processes, Mineral processing.

Paper reviewed and approved for publication by the Canadian Mineral Processors Division of CIM.

ABSTRACT

Lime neutralization technology is widely used in Canada for the treatment of acid mine drainage and other acidic effluents. In many locations, improvements to the lime neutralization process are necessary to achieve a maximum level of sludge densification and stability. Conventional lime neutralization technology effectively removes dissolved metals to below regulated limits. However, the metal hydroxide and gypsum sludge generated is voluminous and often contains less than 5% solids. Despite recent improvements in the lime neutralization technology, each year, more than 6 700 000 m^3 of sludge are generated by treatment facilities operated by the Canadian mining industry. Because lime neutralization is still seen as the best available approach for some sites, sludge production and stability are expected to remain as issues in the near future.

Several treatment parameters significantly impact operating costs, effluent quality, sludge production and the geochemical stability of the sludge. Studies conducted both at CANMET and NTC have shown that through minor modifications to the treatment process, plant operators can experience a reduction in operating costs, volume of sludge generated, metal release to the environment and liability. This paper discusses how modifications in plant operation and design can reduce treatment costs and liability associated with lime treatment.

Introduction

Treatment of acid mine water via lime neutralization is among the oldest water purification processes used in the metallurgical industry. Despite recent improvements to the traditional neutralization method (Aubé and Payant, 1997; Demopoulos et al., 1995), it is estimated that as much as 6.7 million m^3 of lime treatment sludge is produced annually in Canada (Zinck et al., 1997).

Subtle modifications to the treatment process can significantly decrease costs and improve operational efficiency. Some of these possible modifications are presented here. Theory and examples are included wherever applicable.

Treatment Processes

Three basic lime treatment processes have been described in the literature (Kuit, 1980; Vachon, et al., 1987; GML, 1987; MacDonald et al., 1989) and can be classified as follows:

- Basic: Lime is added directly to the effluent stream. Solid/liquid separation occurs in a sludge settling pond (solids, 1% to 5%).
- Conventional: Mechanically agitated reactors are used and lime addition is controlled by pH. The process provides good effluent quality. Reactor discharge continues to a clarifier, a sludge settling pond or a tailings pond for solid/liquid separation (solids, 3% to 10%).
- HDS: High Density Sludge Processes recycle the clarifier underflow sludge in specific ratios and in a specified reactor for sludge densification. Aeration is often employed. Efficient solid/liquid separation is achieved using mechanical clarifiers. Sludge is disposed of either by on-site storage or it is filtered and transported off site (solids,15% to 30%).

The process itself may significantly affect the treatment costs such as lime consumption (next section). Mixing may have an impact on lime dissolution, precipitate properties, and solid/liquid separation. HDS processes decrease sludge disposal costs and aeration can affect both power and lime efficiency. There can also be significant differences in lime efficiency, depending on the particular HDS process applied (Aubé and Zinck, 1999), but this paper focusses primarily on the optimization of existing processes.

Lime Consumption

Lime Slaking

The term "slaking" refers to the combination of varying proportions of water and quicklime (CaO), to yield a hydrated lime slurry. Quicklime is used at most medium and large operations, as it is the lowest cost alkaline

Janice M. Zinck
is a senior environmental scientist with CANMET's Mining and Mineral Science Laboratories. She holds a Bachelor's degree in chemistry, a Bachelor's degree in geology and a Master's degree in metallurgical engineering from McGill University. Ms. Zinck's area of focus is in the chemical treatment of acid mine drainage, lime neutralization and sludge characterization, stabilization and disposal. She has written over 30 technical papers and holds two patents for the Staged-Neutralization lime effluent process. She is a member of CIM and SME.

Bernard C. Aubé
works as an environmental scientist for Noranda Technology Centre. He holds a Bachelor of Science degree in honours co-op chemical engineering (environmental option) from the University of Waterloo. Bernie has more than eight years' experience in various facets of mining and metallurgical environment, including: water treatment technologies, sludge disposal, hydrogeology, water covers and soil covers for preventing acid mine drainage.

Fig. 1. Particle sizing (50%) and consumption for lime slaked at different temperatures.

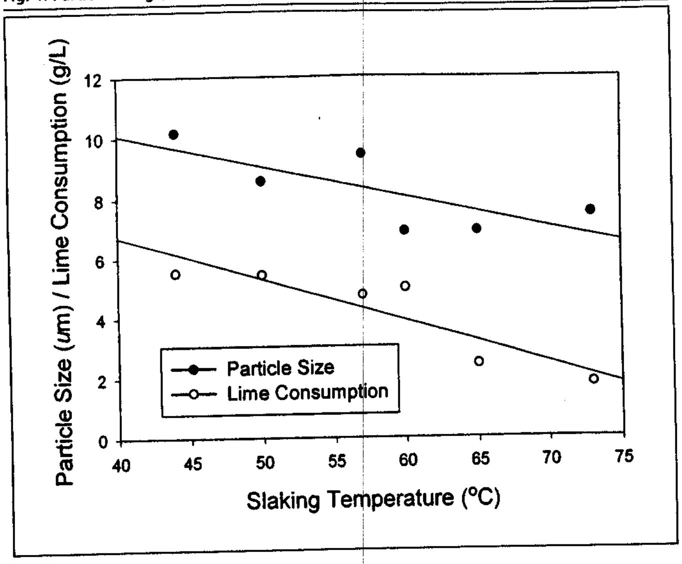


Fig. 2. Particle sizing of Kidd Mining lime (50% passing).

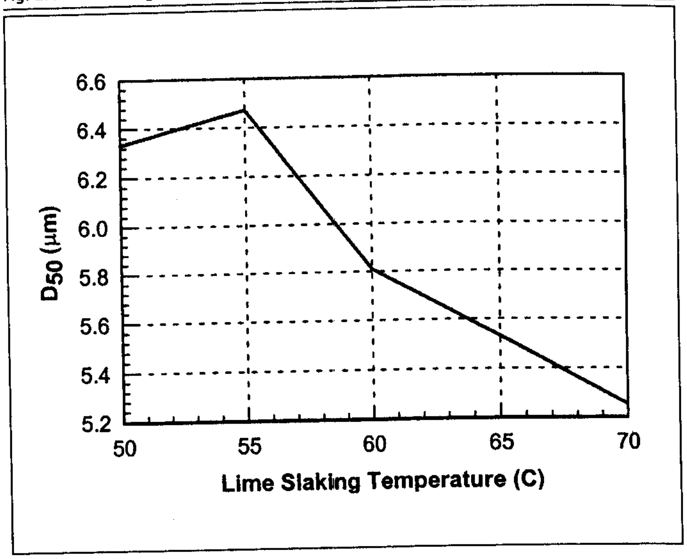


Fig. 3. Particle sizing of Kidd Mining lime (90% passing).

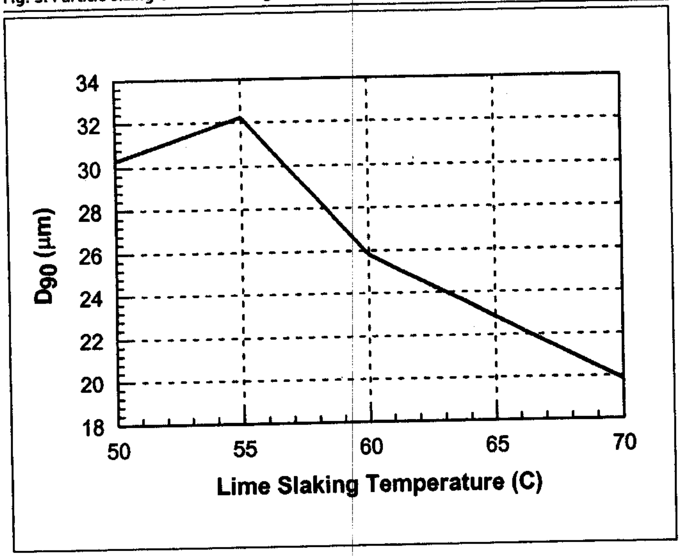
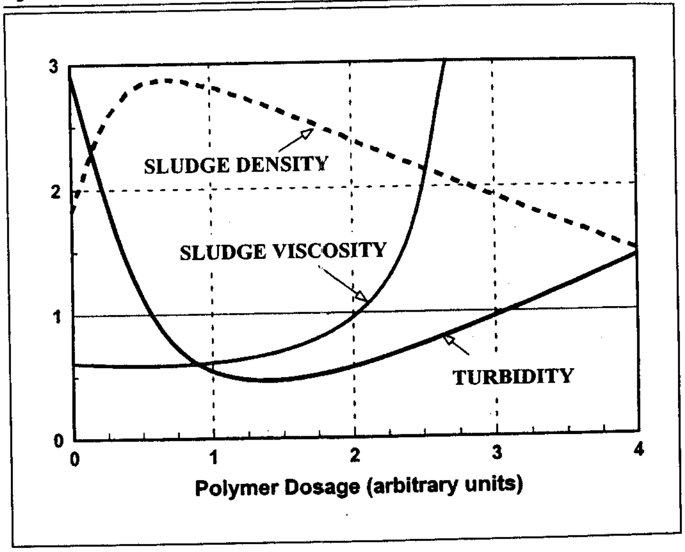


Fig. 4. Effects of flocculant dosage in lime neutralization.



source for AMD 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. The quality of quicklime was beyond the scope of this paper, while temperature and water addition, which are inter-related, are discussed in some detail.

Slaking Temperature — Theoretical

Slaking temperature is typically controlled by the ratio of water added to the lime. It is possible artificially to increase the slaking temperature by using hot water, but the costs would be prohibitive in practice. If excessive quantities of slaking water are used, particularly cold water, "drowning" occurs (EPA, 1983). In this case, the surface of the quicklime particle hydrates quickly, but the mass of hydrate formed impedes the penetration of the water into the centre of the particle, delaying explosion of the particle into microparticles. The rise in temperature is stifled and slaking delayed, resulting in coarser hydrate particles and incomplete hydration. The other extreme occurs when insufficient water is added to the lime, causing the hydrate to be "burned" because of excessive temperatures, 121°C to 260°C; a temperature just below the boiling point of water is optimal. In the former case, much of the hydration water is lost as steam; thus, a considerable number of non-hydrated particles remain. Also, the heat can be so intense that lime particles initially hydrated can be dehydrated.

According to extensive testing (Boynton, 1980), it was found that the surface area was the most significant factor affecting the formation of hydrates. Smaller particle sizes result in a higher surface area, but two similar sizes may differ in efficiency, depending on the form and porosity of the particles. A plate-like, porous particle will exhibit a greater surface area and be more reactive. Some results also showed that to achieve this greater surface area, high temperature and low water addition during slaking is preferable. Tests at 90°C, and a water to CaO ratio of 2.5 yielded 58 300 cm²/g as opposed to 15 314 cm²/g at 4°C and a ratio of 25. These tests also showed that the particle sizes were smaller at higher temperatures. It is also suggested that high-temperature slaking requires cooling to prevent re-crystallization (Boynton, 1980).

Paste slakers, which use paddle torque for water addition, operate at temperatures of 90°C to 95°C. The capital cost of these slakers is greater than that of a slurry slaker but temperature control is better and slaking efficiency is assured during proper operation. Slurry slakers typically feed the quicklime at a constant rate and control the water addition with a PID loop on a set temperature. With both types of slakers, the resulting slurry is typically diluted, stored in a vessel, then fed to the process to control pH. This dilution, immediately following slaking, will cool the hydrated particles and prevent re-crystallization.

TABLE 1. Slaker performance at Noranda operations

Site	Slaker type	Slaking temperature °C	Particle size D_{50}	Particle size D_{90}	Slurry solids (%)
Geco	paste	90 to 92	5.26	21.9	26.3
Mattabi	paste	90 to 92	5.89	22.9	12.7
Horne	slurry	70	5.23	21.3	21.1
Brunswick	slurry	65	6.53	26.3	15.5

Slaking Temperature — Laboratory Tests

A series of tests were conducted at CANMET to determine the effect of temperature on slaking at the laboratory scale. Lab-grade quicklime was slaked at six different set temperatures ranging from 44°C and 75°C, collecting the resulting slurry and then using it to neutralize 1 litre of synthetic AMD (pH 2.35). The mass of hydrate used for neutralization was calculated from the slurry density and volume needed for the neutralization to pH 10. The particle sizing of the hydrates was determined using a Microtrac laser scattering particle size analyzer. The temperature was controlled with the addition of water.

The results (Fig. 1) show that smaller calcium hydroxide particles are formed when the hydration occurs at a higher temperature. The smaller particle size results in a larger surface area and, therefore, better utilization of the lime for neutralization. The highest slaking temperature did not result in the smallest particle size but did show the greatest neutralization efficiency. This may be explained by the theory that efficiency is not only related to particle size, but to the active surface area. The particles slaked at high temperature may have been more porous, and thus more reactive or may have aggregated prior to particle size analysis.

Attempts made to duplicate these results on an industrial scale proved unsuccessful.

Slaking Temperature — Kidd Mining Division

In order to define the effect of slaking temperature at the full scale, some tests were undertaken at Kidd Mining Division of Falconbridge Limited. Kidd operates a slurry slaker and stores the resulting hydrate in their lime slurry storage tank. A dosing system is used to control pH in a neutralization reactor, followed by solid/liquid separation in a large settling pond. The slaker was operating at 55°C prior to the tests and was decreased to 50°C for the first sample, then samples were taken in order of temperature: 55°C, 60°C, and 70°C. The size of the resulting particles is shown in Figures 2 and 3.

There was little time allowed for the slaking system to reach steady state during the testing and this may have affected the precision of the results. Although the temperature was allowed to reach the desired setpoint, some of the solids from the previous slaking temperature may have remained in the slurry at the slaker overflow. The compressed sampling schedule may therefore show the effects of the previous slaking temperature: the 50°C sample was partially slaked at 55°C, the 55°C at 50°C, the 60°C at 55°C, and the 70°C sample at 60 °C. This may partially explain why the 55°C sample contains larger particles than does the 50°C sample.

Figures 2 and 3 nevertheless reveal that a considerably smaller particle size is formed at the highest slaking temperature. Figure 2, with the 90% passing particle size, shows that a significant number of particles (>10%) are above the 30 micron size when the slaking temperature is 55°C or less. If the slaking temperature is increased to 70°C, there is less than 10% of the particles larger than 20 microns. It is these large particles that represent the unavailable lime. Larger particles may become coated with metal hydroxides during the neutralization process or may simply not dissolve entirely. In either situation, these large particles will settle with the sludges and increase costs both in lime consumption and increased sludge volume. Slaking at the higher temperature should, therefore, increase lime efficiency and decrease sludge production.

Slaking Temperature — Site Comparison

Table 1 shows the measured particle sizes from other operations within Noranda Inc. Comparing these sizes to the results from Kidd shows that the test at 70°C was representative of slurry slaker performance at other sites. Comparisons within Table 1 do not account for the lime quality (different suppliers) and grit removal, but the results show that Brunswick Mine, with a slaking temperature of 65°C, resulted in coarser particles than the paste slakers. The lime slaking at 70°C at the Horne smelter seemed comparable to paste slaking. Dissolution efficiency and surface area were not measured for these slurries.

The last column in Table 1 presents the solid content of the lime slurry, as used in the process. For paste slakers, the slurry is diluted following hydration. The slurry density is, therefore, controlled entirely by the dilution water. As shown in the laboratory tests, slaking lime at 70°C results in a slurry density of approximately 30% solids, and this was done with tap water at 13°C. When slaking in winter in the full scale, the fresh water used may be considerably colder and, therefore, result in a higher density of slurry prior to the final dilution. There is a secondary dilution for slurry slakers as well, prior to storage.

Experience in pH control with lime has shown that the higher solid contents such as at Geco (26%) and the Horne (21%) are less problematic than lower solid contents. The sites with lower density lime slurry more often experienced problems with plugging at elbows and valves in the lime distribution system. The plugging problems seem to be caused by settled grits which sometimes bypass the grit removal system. This can be explained by the fact that lime slurry with a high solid content will have a higher density and viscosity and thus retain grits in suspension. As the costs of downtime can be high a lime slurry, density of 20% to 25% is recommended.

Control pH

The control pH can play an important role in lime dissolution efficiency. In the treatment of Zn, a minimum pH of approximately 9.0 is required for hydroxide precipitation to meet the MMLER 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.

Kidd Mining Division applies conventional treatment for removal of Zn. Settling of Zn hydroxides occurs in a large pond and the sludge is dredged on a yearly basis and then stored on site. The old sludge was found to have a paste pH above 11 and contain over 20% Ca. The total inorganic carbon (TIC) content of 5.5% meant that there was about 27% carbonate, or 45% calcite. A mass balance with respect to Ca suggested that 18% of it was included in the calcite, 1% was associated to sulphate in the form of gypsum, and the remaining 1% was likely residual unreacted lime.

Most of this calcite was not formed during the neutralization process, but would have likely been stored as unreacted lime, and reacted over time with the carbon dioxide from air to form calcite. This suggested very poor utilization of lime in the process and triggered further investigation. The control pH in the reactor outlet was 11. This pH was set mostly by experience, but also to maintain a high pH throughout the pond and to ensure sufficient buffering capacity to treat small seeps entering into the settling pond. At least one area was known to allow a small flow of Zn-containing water to drain into the pond. When treating for Zn, the optimum pH is 9.7. For the best treatment efficiency at Kidd, the goal should be to obtain a pH of 9.5 to 10 at the overflow of the pond.

The pH setpoint was decreased to 10.5 and this goal was met to satisfaction. By reducing it to 10.5, the efficiency of lime dissolution is increased significantly. The actual change in treatment efficiency may be determined following dredging.

Cost of Carbonate Formation

The inorganic carbon system can significantly affect the lime efficiency in heavy metal treatment. Dissolution of carbon dioxide and precipitation of calcite consume lime intended for production of metal hydroxides. AMD typically has a pH below 5 and, thus, whatever inorganic carbon is present will be in the form of dissolved CO_2 prior to treatment. Another source of carbonate in water treatment is carbon dioxide dissolving from air. Either source starts as carbon dioxide and would consume two hydroxyl ions prior to precipitation with Ca to form calcite. The following equations illustrate this reaction:

$$\text{CO}_2(g) + \text{H}_2\text{O} \Rightarrow \text{HCO}_3^- + \text{H}^+$$

$$\text{HCO}_3^- \Rightarrow \text{CO}_3^{2-} + \text{H}^+$$

$$\text{Ca}^{2+} + \text{CO}_3^{2-} \Rightarrow \text{CaCO}_{3W}$$

$$\text{Ca}^{2+} + \text{CO}_2(g) + \text{H}_2\text{O} \Rightarrow \text{CaCO}_3 + 2\text{H}^+$$

Or, if we include lime addition and dissolution:

$$\text{Ca(OH)}_2 + \text{CO}_2 = \text{CaCO}_3 + \text{H}_2\text{O}$$

Each mole of calcite formed therefore consumes one mole of lime for neutralization. By applying the molecular weights of calcite (100 g/mol) and quicklime (56 g/mol), and assuming a cost of $100/tonne for quicklime, each tonne of calcite produced costs approximately $56 in lime. If hydrated lime were used at an assumed cost of $120/tonne, calcite costs could then be estimated at $89 per tonne produced. For an average-size treatment plant, about 3500 dry tonnes of sludge can be produced in a year, which means that each 1% increase in average calcite content of the sludge will cost $1,960 in quicklime alone. The calcite content of sludge can vary from 1% to more than 40%. This does not include site-specific sludge disposal costs, as detailed later in this paper.

Mixing

Mixing is an important parameter in sludge production. Benefits of higher agitation rate include better dispersion of added lime and recycled sludge, improved aeration resulting in faster oxidation rates of ferrous iron when necessary, and efficient mixing so larger particles remain suspended. Disadvantages include increased energy requirements and possible particle attrition.

Conventional Treatment Systems (No Sludge Recycle)

In reactor systems without sludge recycling, such as conventional treatment, increased solution velocity serves to increase particle/sludge density and settling rate. Increasing the agitation speed in reactors without sludge recycle serves to increase sludge density by accelerating the diffusion of metal ions to the precipitating hydroxide surface, resulting in particle growth. Rapid mixing tends to rework fragile porous flocs into dense, compact aggregations as void spaces are reduced (Zinck, 1993). These denser aggregates settle more quickly than the larger, porous particles/flocs formed at low mixing speeds (Zinck et al., 1998b).

Rapid mixing in conventional systems improves lime dissolution and retards local regions of high levels of supersaturation in the reactor where particle nucleation (rather than growth) can occur. This leads to the production of gelatinous, fine-grained sludges with poor S/L separation characteristics. This is typical of what occurs in basic treatment systems (no mechanical mixing); lime dissolution is poor and gelatinous sludges are produced as metal hydroxides are precipitated under high supersaturation conditions with very little or no particle growth occurring.

HDS Treatment Systems (Sludge Recycle)

Laboratory tests in CSTRs (6 L, 7.5 cm ID) found that at lower agitation rates (Reynolds Number ~8000) porous particles with floc-like characteristics form and particle growth is limited. However, in a process where sludge is recycled (HDS), rapid mixing and high hydrodynamic shear (Reynolds number ~19 500) were found to be detrimental to the formation of large compact particles, as particle abrasion and particle growth processes occur counterproductively. Because of the high particle population in the HDS reactor, the high hydrodynamic shear causes particle collisions and attrition resulting in the presence of fines which hinder sludge settling and reduce effluent clarity. Optimum mixing conditions in a recycled CSTR system were found to correspond to a Reynolds Number of approximately 13 700. Under this mixing speed, solution velocity is sufficient to enhance particle growth and lime dissolution while limiting the number and force of inter-particle collisions occurring in the reactor.

Aeration

Theory

Ferrous iron, when exposed to oxygen, will oxidize to ferric iron at a rate determined by the ferrous iron concentration, the dissolved oxygen (DO) concentration, and the pH of the solution. At pH values greater than 6.0, the reaction rate can be defined by the following equation:

$$\frac{-d\,(\text{Fe}^{2+})}{dt} = k\,(\text{Fe}^{2+})(\text{O}_2)(\text{OH}^-)^2$$

The reaction is first order with respect to the ferrous iron and the dissolved oxygen concentrations. This means that the oxidation rate decreases as the concentration of either decreases. The reaction rate is second order with respect to the hydroxyl ion (OH^-) concentration, which means that the reaction rate increases 100 times for each one-unit rise in pH above pH 6.0. The rate of ferrous iron oxidation can be classified as extremely slow at a pH of less than 3.0, slow in the pH 3 to 6 range, moderate to fast in the pH 6 to 8 range, and rapid above this point. Even if the raw water has a high oxidation potential and the DO is saturated, the ferrous conversion may occur very slowly at the typically low pH. For this reason, most of the iron fed to a water treatment plant (WTP) is in the ferrous form.

The most widely accepted iron oxidation reaction at alkaline pH is as follows (Aubé and Payant, 1997):

$$\text{Fe(OH)}_2 + \tfrac{1}{2}\,\text{H}_2\text{O} + \tfrac{1}{4}\,\text{O}_2 = \text{Fe(OH)}_3$$

The stoichiometry of this reaction shows that 0.25 oxygen moles are needed to oxidize 1 mole of ferrous hydroxide. AMD near 10°C will often be saturated in oxygen and therefore contain about 11 mg/L — enough to oxidize about 77 mg/L of ferrous iron. Add on to that the oxygen transferred from the surface of the reactor and, depending on the diameter to height ratio and the surface turbulence, another 25 mg/L can be oxidized.

Aeration in Operations

At Noranda Inc., Heath Steele Division in New Brunswick, the WTP was designed with two 40 HP blowers, one for operation and the other as a backup. Tests conducted without air showed that up to 300 mg/L of ferrous iron are oxidized without additional aeration. The WTP blowers are now shut down, and the plant operates without aeration. No difference has been found in the treatment efficiency or sludge characteristics following the blower shutdown.

Other treatment plants within the Noranda group have also been operated without aeration and found that the oxidation potential of the raw water alone was sufficient to convert the ferrous iron to ferric following the pH increase. The Mattabi Division WTP treats more than 140 mg/L of Fe without aeration, and treatment plants at Brunswick Mining and Waite Amulet can oxidize almost 100 mg/L Fe without aeration.

Although some sites may contain high concentrations of iron and do not need aeration, this is not always the case. At Geco Division, the ferrous concentrations in the raw water can be as high as 1000 mg/L, and aeration is necessary for ferrous oxidation.

The risk of not oxidizing the iron is that the resulting sludge may be unstable relative to iron. This has not been investigated in detail, as the ferrous content of the sludge may be apt to oxidize considerably faster than it would dissolve. The typical control pH of 9 to 10 will precipitate ferrous iron to within MMLER limits, so that treatment is not a serious concern for most sites. It can be asserted that a small fraction of ferrous in the sludge will not significantly affect stability. The effect of predominantly ferrous hydroxide sludge has not been investigated and should be prevented until further investigation.

It is recognized that the degree of iron oxidation in the absence of aeration is dependent on the site-specific raw water chemistry. Therefore, in order to determine whether aeration is needed in an existing plant, the best method is to turn off the aeration and measure the ferrous concentration at the exit of the neutralization step. In a planned construction, simple neutralization of a representative sample of feed, and measurement of residual ferrous is the best indicator. Seasonally, oxidation is most difficult in the spring when ponds are often ice-covered and iron concentrations are high.

Aeration Costs

The primary cost of aeration is in the blower power consumption. For example, a 40 HP blower operating 24 hours per day for a year will cost about $13k/yr in power consumption at $0.05/kWh. A second cost is in the mixing system, as proper aeration requires that a high-shear radial impeller be used to break-up the air bubbles and increase the surface area for oxygen dissolution. These mixers typically draw more than twice the power than would an axial agitator used solely to maintain the precipitates in suspension.

A hidden cost is also included in the dissolution of carbon dioxide from air, which will increase lime consumption and sludge production. The cost of producing calcite, as detailed above, is approximately $56/tonne for a site using quicklime as the neutralizing agent. Although air contains only 0.03% carbon dioxide, the dissolution rate of CO_2 is considerably faster than oxygen. If aeration is not necessary, these additional lime costs and associated additional sludge disposal costs must also be considered.

The capital costs of aeration include the purchase price of a blower, the air distribution system, and the radial agitator. Often a second blower is added as a backup, and either a separate building is constructed or a room is insulated for sound due to the high decibels put out by a blower. This can put the cost of a set of blowers above $100k.

Solid-Liquid Separation

In lime neutralization, the contaminants of concern are generally heavy metals. These are precipitated by increasing the pH with lime. The precipitates generally consist of metal hydroxides, gypsum, unreacted lime and calcite. To meet effluent targets, the precipitates must be efficiently separated from the treated water. Gravity separation is the method of choice in the industry. The precipitates are settled to form a treated effluent and a sludge.

Factors that affect the settling ability of lime sludges include: final pH, particle surface charge, degree of mixing, surface areas of sludge particles, recycling, solids population in the reactor, flocculant usage and method of neutralization. The operator has control of many of these factors, but a compromise must often be made. The final pH, for example, is most often controlled by the raw water chemistry and the effluent targets. If, for example, Zn is the major contaminant, the pH must be brought up to at least 9.0, and ideally to 9.7.

Surface area and particle charges are typically factors of raw water chemistry and the treatment process. The solids population of the reactor can also be described as the solid content of the slurry. In an HDS Process, the recycle rate affects this parameter directly. In most water treatment plants, a clarifier (or clari-thickener) is used for solid/liquid separation. The operator can optimize clarifier efficiency through better control of flocculation, as discussed in the following section.

Theory of Flocculant Addition

The flocculant type and concentration have a major impact on sludge properties and typically account for 2% to 5% of treatment costs. Flocculation aids in clarification by promoting the formation of flocs which settle more rapidly.

Depending on the application, two definitions of polymer dosage are commonly used in the mining industry. The first definition, most often used in operations, is defined in ppm, or in mg of dry polymer added per litre of treated effluent (or plant feed). This definition is easily used to set a dosage in the plant and calculate the yearly consumption of flocculant. An automated treatment plant may have the option of setting the flocculant feed rate as a direct function of the plant flowrate to maintain the dosage following changes in treatment rate.

The second definition relates the mass of polymer used to settle a specific mass of sludge. This is typically defined in mg of polymer per g of sludge, or g per tonne. The second definition better describes the actual process of flocculation and, thus, is a better basis for comparison. This definition can be used in scientific studies or pilot tests. The second definition of dosage requires that the solid content of the flocculated slurry be known.

Optimum dosage depends on the application but normally lies in the range of 2 g/t to 200 g/t of dry material flocculated. Industries surveyed report flocculant dosages varying from 1 to 20 ppm (Zinck et al., 1997, Aubé and Payant, 1996). An inverse relationship exists between solids content of the slurry and optimal polymer dosage, when calculated as a mass ratio (mg/g). At low solids content, a large excess of polymer is required to enmesh the relatively few particles. At high solids content, as for HDS processes, flocculation will occur at a lower dosage (Benefield et al., 1982).

Determination of optimal polymer dosage for a specific treatment plant is critical. The polymer dosage will affect the effluent quality, the sludge settling rate, the sludge viscosity, and the final sludge density. The following paragraphs examine each of these relationships independently. These discussions apply particularly to treatment processes where polymer is added prior to solid/liquid separation in a clarifier. These relationships are partly derived from theory, pilot testing, and site experience. It is important to note that all of these relationships depict the standard expectations, and do not necessarily apply to all types of polymers. Polymers typically used in lime neutralization are high to very high molecular weight polymers with a slight to moderate anionic charge.

Effluent Quality

The primary purpose of flocculation is to agglomerate the finer particles and enhance settling in order to obtain a clear effluent. The clarification efficiency can be measured via turbidity, suspended solids content, or the concentration of a metal included in the suspended solids. A minimum dosage of polymer is required to meet effluent targets. With higher dosages, the effluent may continue to meet these targets until the settling rate becomes so high as to cause high shear on the particles and break up. Particle break-up is greater when very high molecular weight polymers are used.

A conceptual rendition of this relationship is shown in Figure 4. Assuming that the minimum effluent quality targets are met at the arbitrary turbidity unit of 1, it is possible to meet these targets at a range of about 0.7 to 3 dosages. The best effluent quality is attained at dosages of 1.25 to 1.5. This curve is typical of many operations but may vary depending on the process and polymer of use.

Sludge Viscosity

Sludge viscosity is affected primarily by the process and the physico-chemical properties of the precipitates (Aubé and Payant, 1997), but over-flocculation can also have a significant impact. At low to medium polymer dosages, there is little or no effect of polymer on viscosity, but beyond a given threshold, the viscosity increases significantly. The physical theory for this occurrence is that the polymer strands begin to enmesh and are difficult to pull apart. It is quite common for this threshold to be within the range of acceptable effluent quality, as depicted in Figure 4.

Sludge Density

High-density sludge could be formed without flocculation, if effluent clarity were not a concern. Experience has shown that flocculation enhances densification at low dosages, but the settled density may decrease as the polymer dosage is increased. As with most polymer effects, this one is highly dependent on the polymer of use. Polymers with higher charges will tend to repel each other more and decrease the sludge density more significantly as the dosage is increased. A conceptual depiction of this relationship is also included in Figure 4.

Sludge Settling Rate

The sludge settling rate generally increases with increasing polymer dosage. There is a maximum attainable settling rate beyond which the floc interaction will hinder settling (Benefield et al., 1982; Zeta-Meter, 1993). In Figure 4, the settling rate is not depicted, but the maximum would be expected above two polymer dosage units. Depending on the polymer of choice, the best settling rate may be too high and therefore be partly responsible for the turbidity increase at higher dosage.

Site Implications

These numerous effects of polymer addition offer some contradictory basis for determining the optimum polymer dosage. Suppliers will generally depend on the settling rate to recommend a dosage to the operator, but the fastest settling may result in high turbidity or sludge viscosity.

TABLE 2. Effect of flocculant concentration on particle size distribution (Zinck et al., 1998a)

Percol E10 dosage (mg/g)	Solids content (mg/L or ppm)	Settling rate (%)	Viscosity (m/hr)	Sludge distribution (cP)	Particle size (µm, D_{50})
0.06	2.4	34.06	5.10	23.7	54.0
0.10	4.4	30.35	5.94	26.9	56.6
0.18	8.0	32.12	11.33	21.8	69.9
0.24	10.8			S/L separation difficulties	

Generally speaking, the most common mistake made by operators in solid/liquid separation is over-dosing of polymer. Assuming that the effects of Figure 4 are representative of an actual water treatment plant, operators are likely to be dosing in the 2 to 2.5 range. This dosage may consistently meet effluent targets, result in an acceptable sludge density, but cause occasional problems with sludge viscosity. A second disadvantage is that the polymer costs are unnecessarily high.

The optimum dosage for this system is actually in the 1 to 1.5 range. At this dosage, the effluent turbidity is at its best, the sludge viscosity and density are excellent, and the flocculant costs are low. Operating below 1 may be acceptable, but small plant upsets or a dilute batch of polymer could put the operator out of compliance.

For the operator, it may be safest to define the optimum polymer concentration using pilot testing, but this is expensive, time-consuming and not always representative. To determine the optimum polymer dosage in an operating plant, it may be necessary to decrease the polymer feed until the clarifier effluent quality is affected, then turn it back up 5% to 10%.

Pilot testing

The effect of flocculant dosage was studied using a 288 L/day mini HDS pilot plant at 10% sludge recycle (volume recycle/volume AMD) (Zinck et al, 1998b). Percol E10, a high molecular weight polymer with a slight anionic charge was added at four incremental concentrations, as shown in Table 2. Chemical and physical characteristics of the recovered sludge and effluent were determined. Settling rates were determined on slurry collected from the outlet pipe of the Polymer Mixing Tank.

As shown in Table 2, the settling rates increased with increasing polymer dosages up to 8.0 ppm. A significant increase occurred when the dosage was raised from 4.4 to 8.0 ppm. At the highest concentration tested, 10.8 ppm, donuting was encountered in the clarifier and the test was discontinued. The term "donuting" applies when the sludge bed turns with the clarifier rakes, and new sludge simply flows out through a hole formed in the middle of the existing sludge bed (Aubé and Payant, 1997). Without sufficient time for densification, low-density sludge is produced.

TABLE 3. Comparison of treatment and disposal costs

Item	Conventional treatment	HDS-type process
Sludge solid content (%)	5	25
Sludge density (t/m3)	1.05	1.20
Sludge disposal costs ($/a)	$266,667	$46,667

Donuting occurs both in pilot plants and full-scale plants. In both cases, it is the viscosity of the sludge that causes it to agglomerate and stick to the rake blades instead of flowing to the centre of the clarifier. In this case, the high sludge viscosity can be attributed to the increase in polymer dosage, as all other process parameters remained unchanged.

Particle size distribution showed a pronounced increase in bimodality as flocculant concentration increased. The bimodal particle size distribution consists of two peaks. The first peak, at a smaller size fraction (-8 µm), corresponds to individual particles. The second peak, a larger size faction (~75 µm), consists of agglomerated particles. The second peak became more distinct when the flocculant concentration was increased as the mid-size particles were agglomerated into larger particles at increased flocculant dosages.

Sludge Disposal

Sludge Volume

Sludge disposal can account for a significant proportion of the overall treatment costs. Taking the example of 3500 dry tonnes of sludge produced per year, and assuming a cost of $\$4/\text{m}^3$ for disposal in an engineered impoundment (Senes, 1994), there is a significant reduction in disposal costs with a higher sludge density (Table 3).

The actual cost of disposal varies significantly from site to site, depending primarily on availability of storage space. The sludge also continues to densify following field emplacement. Freeze-thaw and long-term settling can more than double the storage density of sludge. The final sludge solids content depends mostly on the initial density and the disposal method.

At Noranda Inc., Geco Division, for example, sludge stored on a tailings beach at 20% to 30% solids was found to contain up to 60% solids a year later. Underwater disposal at Mattabi Division resulted in sludge originally discharged at approximately 15% to densify to 22% solids. At Brunswick Mining Division, low-density sludge disposed of at surface more than five years earlier was only at 10% solids. The comparison between Geco and Mattabi shows that the disposal method can have a significant impact, as drainage of the sludge is beneficial. The old Brunswick sludge was allowed to drain at least partially, but the water retention of low-density sludge is apparent.

These examples show that, although densification occurs in storage, the long-term density is highly dependent on the initial solid content of the sludge. The sites mentioned showed densification in the order of 1.5 to 3 times the initial solid content, depending on the disposal method. The initial density resulting from a given AMD depends primarily on the process (Aubé and Zinck, 1999), but also on optimizing process parameters such as polymer dosage (mentioned above) and sludge recycle rate. These parameters are site-specific and must be defined either by piloting the treatment process or by controlled experiments in the plant. Densification in storage is enhanced by favouring drainage, freeze-thaw, and evaporation.

Sludge Stability

In most cases lime sludges appear stable with respect to metal leaching. However, several factors can impact on the long- and short-term stability of these materials. These factors include: available excess alkalinity, iron to base-metal ratio of sludge, sludge ageing, degree of sludge crystallinity and disposal environment. Of these factors, the operator can control the disposal scenario and can impact the excess alkalinity. Crystallinity depends primarily on the process, and the chemistry of the sludge is affected by the AMD composition.

Sludge stability has been studied extensively (Zinck et al., 1997; Zinck et al., 1998a). Further discussions on the effect of treatment process on long term sludge stability can be found in Aubé and Zinck (1999).

Labour Costs

Labour costs can, in some cases, represent the highest individual cost of treating AMD. Generally, the labour requirements are inversely proportional to the level of automation. A plant with an automatic call-out system, including automated shutdown and re-start sequences, can be left unattended either off-day shift or for entire weekends, as well. Of primary importance for automated treatment is turbidity and pH monitoring of the effluent. One of these parameters can normally indicate when an effluent is approaching compliance limits.

Automatic shutdown procedures may be more difficult in open channels using gravity treatment, as it may not be possible to stop the release of water in order to allow the time needed for repair. Shutdown procedures work well for HDS plants where the feed is normally pumped to the plant or the gravity-feed is controlled by an automatic valve that can be closed. Parameters other than pH and turbidity that may be used to trigger a shutdown include the recycle and feed flowrates, the tank levels in the lime and polymer storage vessels, the clarifier sludge level, and the rake torque.

Downtime

For start-up, fine tuning, and process upsets, many water treatment plants have the option of bypassing (or diverting) the effluent back to the raw water holding facility. This is a useful option, but it is often abused. It is important for the plant operator to understand that the treated water diverted to the raw water holding facility costs just as much to treat as released effluent, but it must be treated again. For example, a 10000 L/min. plant, treating water at \$0.50 per m^3 would cost \$7,200 to by-pass the plant effluent for one day.

A possible alternative is to shut down the plant, correct the situation, and then re-start the treatment process once the problem is rectified. This option does not save on labour costs, but it does save on reagent and partial power costs. The cost of downtime can be calculated by adding the operator time, the fraction of power which is continuously used (i.e. heating in winter), and any liability that can be incurred by not being able to treat.

Other alternatives include capital investments that would prevent the need for diversion. These could include a large polishing pond for removing peaks of suspended solids, an improved flocculation system, enhanced pH control, or even increased retention time in the treatment process. An economic analysis can be made on the return on investment assuming that by-pass time is minimized. Most often, simple understanding of the cost implications can significantly reduce the incidences and duration of effluent diversion.

Another means of minimizing downtime is in preventative maintenance (PM). A scheduled, detailed PM program may seem time-consuming and, thus, expensive, at first, but the cost savings over the long term can be significant. By applying the above calculations for cost of downtime, and estimating both the cost of the PM and the economy in length/occurrence of plant shutdowns, a return on investment can be calculated.

Conclusions

There are many factors that affect the efficiency of lime neutralization processes. This paper discussed a few of the most significant factors, particularly those affecting the cost efficiency of treatment. Industrial experience, theoretical analysis, and laboratory testing were used to define some of the better practices for process optimization. Following is a list of findings that can be applied at most sites.

1. Lime slaking efficiency increases with temperature, up to the boiling point of water.
2. Lime slurry feeding is facilitated at higher densities (20% to 25% solids).
3. Whenever possible, a lower pH setpoint will result in better lime efficiency.
4. The need for aeration should be determined as it is often unnecessary and expensive.
5. Polymer dosages should be re-examined regularly to prevent over-dosing.
6. Sludge density should be maximized to decrease long-term disposal costs.
7. Effluent re-circulation (by-passing or diverting) is expensive and should be prevented.
8. A rigorous preventative maintenance schedule can decrease downtime and result in a significant return on investment.

References

AUBÉ, B.C. and PAYANT, S., 1996. Engineering and Process Summary of the Treatment Pilot Program at Heath Steele, Noranda Technology Centre, May.

AUBÉ, B.C. and PAYANT, S.C., 1997. The Geco Process: A new high density sludge treatment for acid mine drainage. In Proceedings of the Fourth International Conference on Acid Rock Drainage, May 31-June 6, Vancouver, British Columbia.

AUBÉ, B.C. and ZINCK, J.M., 1999. Comparison of AMD Treatment Processes and their Impact on Sludge Characteristics. In production, Sudbury '99, September 1999.

BENEFIELD, L.D., JUDKINS, J.F., and WEAND, B.L., 1982. Process Chemistry for Water and Wastewater Treatment. Prentice-Hall, Inc., New Jersey.

BOYNTON, R.S., 1980. Chemistry and Technology of Lime and Limestone. 2nd edition. John Wiley and Sons, Inc., New York.

DEMOPOULOS, G.P., ZINCK, J.M., and KONDOS, P.D., 1995. Production of Super Dense Sludges with a Novel Neutralization Method. *In* Waste Processing and Recycling in Mineral and Metallurgical Industries II. *Edited by* S.R. Rao, L.M. Amaratunga, G.G. Richards and P.D. Kondos. Vancouver, British Columbia, Aug. 20-24, p 401-411.

GIONET, MELLOR, LIEBICH ASSOCIATES LIMITED (GML), 1987. Generation and Stability of Canadian Mine/Smelter Treatment Sludges. DSS Contract No. 15SQ. 23440-5-9161, GML Project 7227-R-1, July.

KUIT, W.J., 1980. Mine and tailings effluent treatment at Kimberley, B.C. operations of Cominco Ltd. CIM Bulletin, Vol. 73, No. 824, p. 105-112.

MacDONALD, R.J.C., KONDOS, P.D., CHEVIER, S., RUBINSKY, P. and WASSERLAUF, M., 1989. Generation of, and disposal options for canadian mineral industry effluent treatment sludges. *In* Tailings and Effluent Management Symposium, August 20-24, Halifax, Nova Scotia.

EPA, 1983. Design Manual, Neutralization of Acid Mine Drainage. U.S. Environmental Protection Agency Office of Research and Development Industrial Environmental Research Laboratory, University of Kentucky, EPA-600/2-83-001. Jan.

SENES CONSULTANTS LIMITED, 1994. Acid Mine Drainage — Status of Chemical Treatment and

Sludge Management Practices. DSS Contract No. 015SQ.23440-3-9140, June.

VACHON, D., SIWIK, R.S., SCHMIDT, J. and WHEELAND, K., 1987. Treatment of acid mine water and the disposal of lime neutralization sludge. *In* Proceedings of Acid Mine Drainage Seminar/Workshop, Halifax, Nova Scotia, Environment Canada, March 23-26, 1987. p. 537-564.

ZETA-METER, INC., 1983. Everything you want to know about Coagulation & Flocculation ..., Zeta-Meter, Inc. Staunton, Virginia. Fourth Edition. April.

ZINCK, J.M., 1993. An Investigation into the Hydrolytic Precipitation of Iron(III) from Sulphate-Bearing Effluents, M.Eng. Thesis, McGill University.

ZINCK, J.M., WILSON, L.J., CHEN, T.T., GRIFFITH, W., MIKHAIL, S. and TURCOTTE, A.M., 1997. Characterization and Stability of Acid Mine Drainage Treatment Sludges. Mining and Mineral Sciences Laboratories Report 96-079 (CR), MEND Report 3.42.2, May.

ZINCK J.M., HOGAN, C.M. GRIFFITH, W.F. and LAFLAMME, G., 1998a. Effect of Process Parameters and Ageing on Sludge Density and Stability. MMSL Report 97-085 (CR), March. MEND Report 3.42.2b.

ZINCK, J.M., HOGAN, C.M. and GRIFFITH, W.F., 1998b. Effect of process parameters and aging on sludge density and stability. *In* Waste Processing and Recycling in Mineral and Metallurgical Industries II. *Edited by* S.R. Rao, L.M. Amaratunga, G.G. Richards and P.D. Kondos. Calgary, Alberta. August.