Presented and published at "Brazil-Canada Seminar on Mine Rehabilitation", Florianópolis, Brazil, December 1-3, 2003.

# Lime Treatment of Acid Mine Drainage in Canada

Bernard Aubé, P. Eng.
EnvirAubé
361 Aumais, Ste-Anne-de-Bellevue
Québec, Canada, H9X 4A9
aube@enviraube.com

and

Janice Zinck, M.Eng
CANMET-MMSL
Natural Resources Canada
555 Booth Street, Ottawa, Ontario, Canada K1A 0G1
jzinck@nrcan.gc.ca

## Abstract

Although many different biological and chemical technologies exist for treatment of acid mine drainage, lime neutralisation remains by far the most widely applied method. This is largely due to the high efficiency in removing dissolved metals through neutralisation, combined with the fact that lime costs are low in comparison to alternatives. Lime treatment essentially consists in bringing the pH of the AMD to a point where the metals of concern are insoluble. These metals therefore precipitate to form minuscule particles. A subsequent separation of these precipitates is then required to produce a clear effluent which meets regional discharge criteria. The solid/liquid separation forms a sludge which, depending on the applied process, can contain 1 to 30% solids by weight. The different types of lime neutralisation processes, including their respective strengths and weaknesses, are discussed in this paper. The evaluated processes are linked to concrete examples of existing treatment systems throughout Canada.

## The Basics of Lime Treatment

The principle of lime neutralisation 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. Other metals such as nickel (Ni) and cadmium (Cd) require a higher pH, in the range of 10.5 to 11 to effectively precipitate the hydroxides (Figure 1). The greatest difference between the lime treatment processes is the method of separating the solids and the sludge that is formed. The resulting effluent chemistry is very similar for all lime treatment processes.

Lime dissolution is the first step of the neutralisation 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:

$$CaO + H_2O \Rightarrow Ca(OH)_2$$
$$Ca(OH)_2 \Rightarrow Ca^{2+} + 2OH^-$$

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

$$Zn^{2+} + 2OH^{-} \Rightarrow Zn(OH)_2$$

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 oxidise the iron to the more stable form, as per the following equation:

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

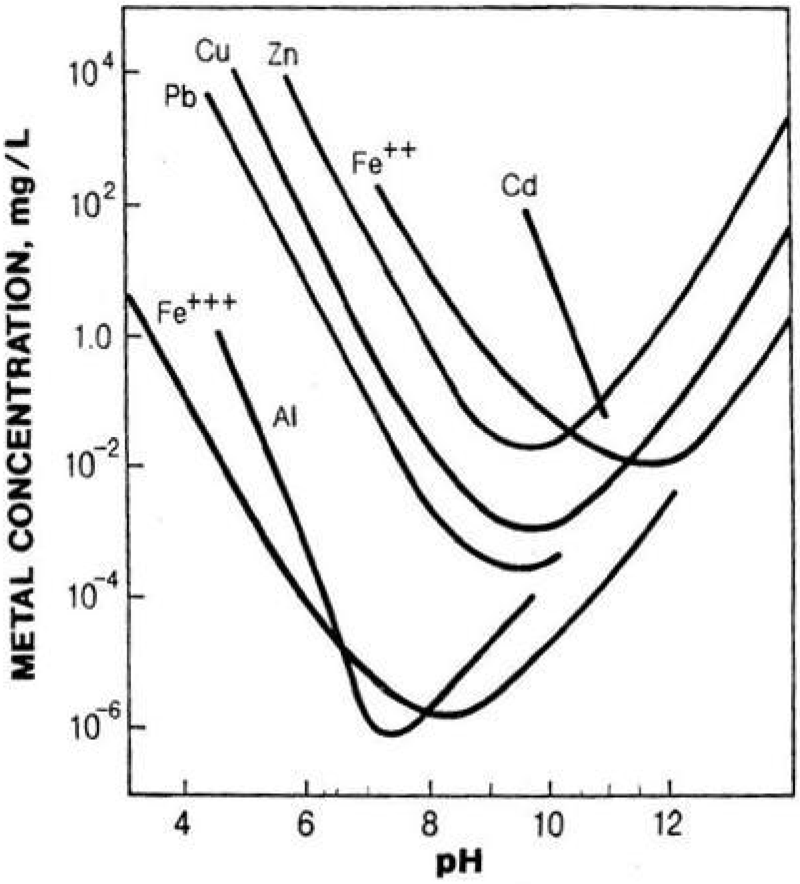


**Figure 1: Metal Hydrolysis**

A common by-product of lime neutralisation is gypsum. Gypsum precipitation occurs as the AMD 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.

$$Ca(OH)_2 + H_2SO_4 \Rightarrow CaSO_4 \cdot 2H_2O$$

Another common by-product of lime neutralisation is calcium carbonate. The inorganic carbon for this reaction can either come from the AMD itself or be a result of carbon dioxide from air, which is dissolved during aeration. This carbon dioxide converts to bicarbonate and then partially to carbonate due to the high pH. The carbonate fraction will precipitate with the high calcium content of the slurry to form calcite (calcium carbonate). This calcite can play an important role in the stability of the final sludge product as it provides neutralising potential to the sludge as it is stored. It is also an indicator of the process lime efficiency: more efficient neutralising processes will produce less calcite.

$$Ca(OH)_2 + CO_2 \Rightarrow CaCO_3 + H_2O$$

**Lime Treatment Processes**

The following sub-sections explain the concept and discuss advantages and disadvantages of different treatment processes. The processes are in order of the simplest to the most complex and recent treatment processes. The older methods often use lime less efficiently and do not allow for good control of the treatment system. The more recent processes require a greater capital investment but are considerably more efficient for lime usage and waste production.

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 processes minimise the waste volumes by creating a higher-density sludge. The sludge disposal and lime costs over the long term usually justify a more important capital investment due to significant savings in operating costs.

Pond Treatment

This treatment system entails adding lime in a stream or mixing system and allowing the precipitates to settle in a pond. The pond is often divided into a primary and secondary section. The primary pond serves to accumulate the precipitated sludge and can quickly be filled. These often require yearly dredging of sludge which then requires a storage area. The secondary pond is larger and requires a long retention time with laminar conditions to allow for “polishing” of the effluent.

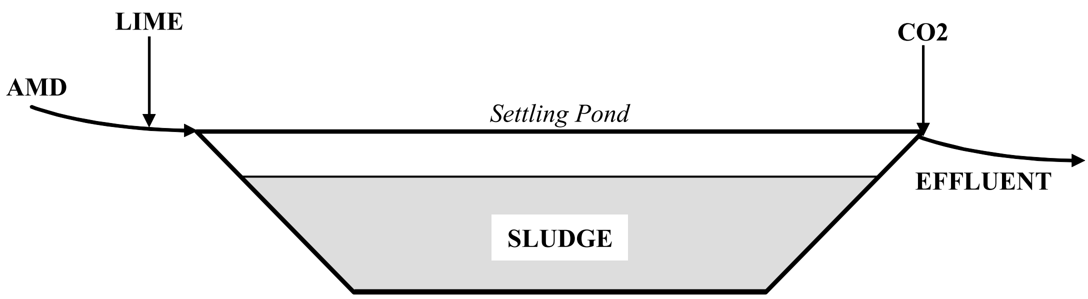


**Figure 2: Pond Treatment**

Pond treatment systems are often chosen for their simplicity and low capital costs when land is available. They can be used to treat very large flowrates and even high concentrations of metals but require a very large surface area when doing so.

Treating AMD in a pond does not allow for much control of the system and thus can be more problematic than other types of treatment systems. For example, it is difficult to treat ferrous iron when present because aeration for oxidation to ferric iron requires proper mixing and contact time. If air is sparged in a pond, the sludge cannot settle. Another example is that the flowrate is normally not controlled when treating in a pond as they are typically designed to use natural depressions along the flow path of the site drainage for treatment. To control the flowrate, an upstream retention pond and either a pumping or a gate system would be required. This would increase the capital requirements and decrease the advantages of such a system. The lack of control typical of such systems reduces treatment efficiency during high flowrates unless other measures are taken to improve the treatment capacity.

Without a feed flowrate control system, the AMD continues to enter the pond even if the lime system is down. This can upset the entire pond and result in a non-compliant discharge. It may also be impossible to shut the system down in times of high wind. Wind effects can cause turbulence in the polishing section of the pond which in turn causes re-suspension of sludges and/or prevents settling of fresh precipitates.

Probably the greatest disadvantage of pond treatment systems is their low lime efficiency. A system that uses in-stream addition without any mechanical mixing may have less than 50% efficiency in lime dissolution. By using an agitator and pH control system, the lime usage efficiency increases significantly. Nevertheless, these systems cannot compare with high-density systems where sludge recycling ensures that unreacted lime be used due to repetitive contact with AMD.

To ensure proper treatment in a pond system, the pH setpoint is often brought up much higher than is necessary for the targeted metal(s). For example, some Zn treatment systems often control the pH to more than 10.5, when HDS systems can efficiently remove Zn from solution at a pH of 9.3. As the local effluent regulations sometimes stipulate a maximum pH of 9.5, the pH must be reduced before final discharge. This is most often done with the addition of carbon dioxide, although some sites use sulphuric acid.

<u>Pit Treatment</u>

Treating AMD in a pit is similar to pond treatment but generally requires pumping into and/or out of the pit. As with pond treatment, mechanical mixing will significantly increase the lime efficiency. There are different means of treating in a pit including batch treatment, a method rarely used in Canada.

Batch treatment is done by allowing contaminated water into the pit to a level just below that which would allow seepage out of it. At this point, the pit water is contacted with lime through either recirculation of the pit water or uniform distribution of lime. Once the target pH is attained, the sludge is allowed to settle quiescently to the bottom. The clear supernatant is then pumped out and neutralised with sulphuric acid or carbon dioxide if necessary. Once the pit level is brought down to just above the sludge bed, the procedure is re-started.

At Falconbridge's Raglan Division (SMRQ – Société Minière Raglan du Québec), a Ni mine in Northern Québec, pit treatment is completed by pumping neutral drainage to a tank, where pH is controlled by adding hydrated lime to a pH of about 11 (Figure 3). For better solid/liquid separation, ferric sulphate and a flocculant can be added for coagulation and flocculation, respectively. The treated slurry is then discharged underwater at one end of the pit to promote settling of the fresh particles. A clear supernatant is pumped out from the opposite end of the pit. The effluent is then neutralised to pH 9.2 using sulphuric acid prior to release (Aubé and Arseneault, 2003). In the spring, when the pit water is contaminated, it is possible to recirculate the water and treat the entire pit volume before pumping from other sources.

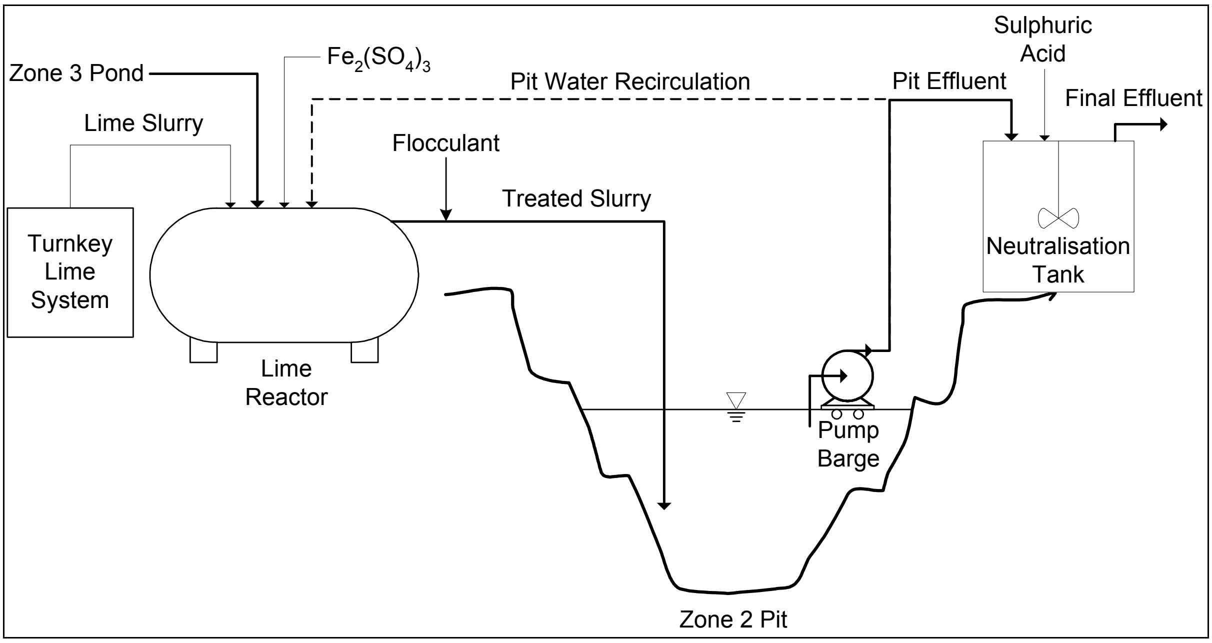


**Figure 3: Pit Treatment Process at Raglan**

One of the keys to this system is that the pit is pumped out using a floating barge. This ensures that only the clean surface water is pumped out, regardless of the level in the pit. As the pumping rate into and out of the pit varies, the level in the pit also varies.

Some of the same disadvantages exist for pit treatment as for pond treatment, including the potential for re-suspension in high winds. An additional disadvantage is the potential for uncontrolled addition of contaminated water from the pit walls and from seepages entering the pit. Even if the pH is sufficiently high to cause precipitation, minuscule particles may form which do not settle easily. If possible, all inputs to the pit should be collected and neutralised prior to entering the pit.

In-line Treatment and Co-deposition

Another alternative for operating mines is the addition of lime and AMD to the tailings line as it is pumped to the tailings deposition area. This allows for a single storage area and minimises the space needed for sludge deposition. The sludge will combine with the tailings solids and fill in the voids between the tailings.

A disadvantage to this system is often a lack of pH control, depending on how the lime and AMD are added. If the AMD can be first pumped to the mill, it can then be combined with the tailings and the lime to precipitate the metals prior to pumping to the tailings pond. When this is done, the pH can be controlled in a mix tank and the lime utilisation can be adequate. If, on the other hand, the lime is added to the tailings and the AMD is combined to this stream, pH control is very difficult. Typically, when this is done, an excess amount of lime is added to ensure that the minimum pH is attained. This type of treatment system is therefore inefficient.

There is also the possibility of sludge re-dissolution if the tailings continue to oxidise, but there is very little information on the effects of mixing sludge and tailings. Some studies have shown that the sludge helps decrease the permeability of the tailings and may therefore help maintain saturation and inhibit oxidation. If the tailings are already acid, the same study shows that partial re-dissolution is probable.

Conventional Treatment Plant

The conventional treatment plant is one where the AMD is neutralised in a mix tank with controlled addition of lime to attain a desired pH setpoint (Figure 4). The slurry is then contacted to a flocculant and fed to a clarifier for solid/liquid separation. The sludge is collected from the bottom of the clarifier and either pumped to a storage area or pressure-filtered to increase its' density prior to transport. The clarifier overflow can normally be released directly, but often a sand filtration system or polishing pond is used to reduce residual suspended solids.

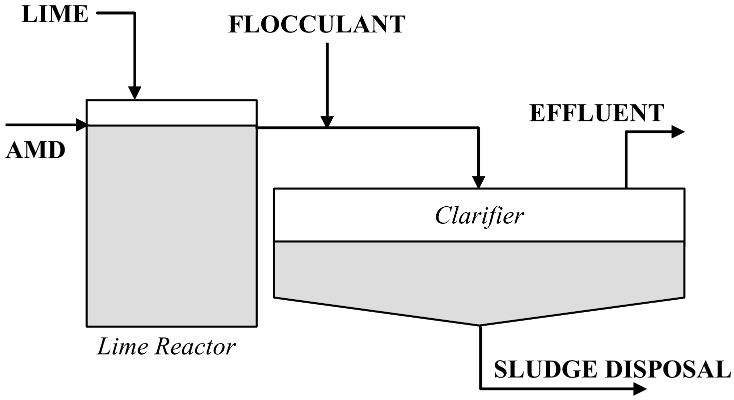


**Figure 4: Conventional Treatment Plant**

This process normally has a better lime efficiency than the pond or pit treatment processes, although it still is not nearly as efficient as HDS processes where sludge is recycled. The fact that the feed is pumped to the plant and that the process can be well instrumented, means that this type of treatment is well controlled. If upsets occur, the feed can be stopped and the release of non-compliant effluent is easily prevented.

The conventional treatment plant has rarely been used in recent years as recycling sludge is a small additional step and provides significant advantages. The most important is that the sludge formed by a conventional treatment plant is of less than 5% solids, while an HDS process will most often create a sludge of more than 20% solids. A sludge of such low density requires significant pumping and storage, particularly if the metal concentrations in the AMD are high. High metal concentrations result in high solids formation and increased sludge production.

Another advantage to recycling sludge was already mentioned: lime efficiency. The conventional process is a once-through open process, while the closed HDS processes promote dissolution of unused lime through repeated contact with the AMD. A third significant advantage concerns scaling on the reactor walls and conduits to the clarifier: if the AMD contains high sulphate concentrations, gypsum scaling can occur following addition of Ca from lime. If the pH setpoint is high (for treating Ni or Cd), calcium carbonate (calcite) scaling can occur. By recycling sludge in HDS systems, the precipitation of gypsum or calcite occurs on the surface of existing particles instead of reactor surfaces.

HDS Process

The high density sludge (HDS) process is the standard in the AMD treatment industry today (Figure 5). Instead of contacting lime directly to the AMD as in the previously described processes, this system contacts recycled sludge with the lime slurry for neutralisation. To do this, the sludge from the clarifier bottom is pumped to a "Lime/Sludge Mix Tank" where sufficient lime to neutralise the AMD to the desired pH setpoint is also fed. This forces contact between the solids and promotes coagulation of lime particles onto the recycled precipitates. This mixture then overflows to the Rapid Mix Tank (RMT) where pH is controlled. The neutralised slurry then overflows to the Lime Reactor (LR) where the precipitation reactions occur. Aeration is often added to this reactor to oxidise ferrous iron to ferric. The fact that the lime and recycled particles are combined forces the precipitation reactions to occur on the surface of the existing particles, thereby increasing their size and density. The slurry then overflows to a Floc Tank to contact the particles to a flocculant and properly agglomerate all precipitates and promote efficient settling in the clarifier. As per the conventional treatment plant, the clarifier overflow can either be discharged or polished prior to discharge.

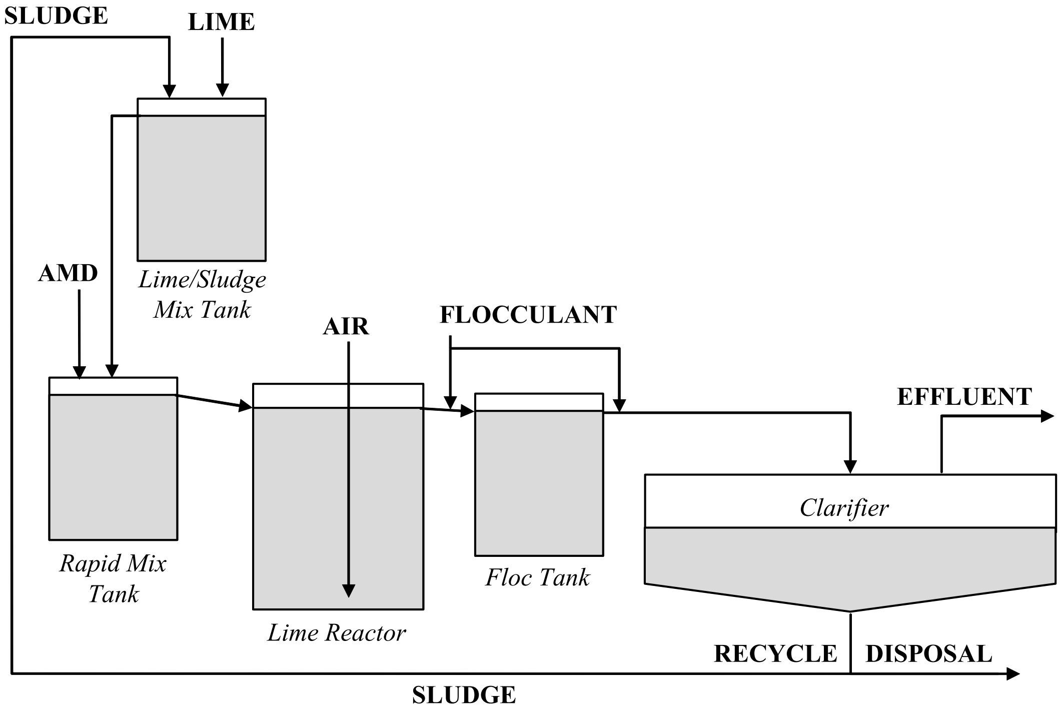


**Figure 5: HDS Process**

The HDS process as shown in Figure 5 contains a Rapid Mix Tank (RMT) and a Floc Tank (FT). This process is applied at numerous mine sites throughout Canada. Figure 6 shows a recent variant of the HDS process (Aubé, 1999) applied at Noranda Inc., Heath Steele Division. The Heath Steele Process is identical in concept and provides the same physical and chemical advantages as the HDS process, but without two of the four reactors. With today's advanced process control systems, a Rapid Mix Tank is not necessary for pH control. Tests were completed in a pilot scale showing that there is no advantage to using this reactor (Aubé, 2004)

The Floc Tank was also removed, as it is possible to ensure proper flocculant contact by providing turbulence in the conduit leading from the Lime Reactor to the clarifier. A trough with baffles may be sufficient to ensure proper contact with the small particles. As is often the case even when a Floc Tank is used, the flocculant is also added in the clarifier feed well. The Heath Steele treatment plant has been operating successfully since 1997 (Aubé, 1999).

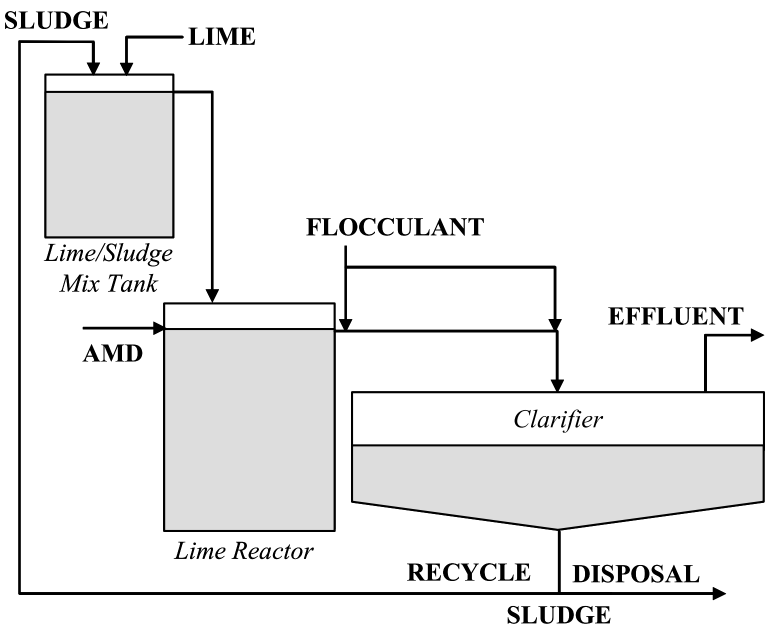


**Figure 6: Heath Steele Process**

Geco HDS Process

In 1995, a new treatment plant was constructed and optimised at the Noranda Inc., Geco Division that did not apply the any of the traditional neutralisation methods. The Geco HDS Process does not have a Lime/Sludge Mix Tank, in contrast with other HDS processes (Aubé and Payant, 1997). The clarifier sludge is recycled to the first reactor (R#1) where it is contacted directly to the AMD (Figure 7). This reactor has a retention time of at least 30 minutes to allow for partial dissolution of the sludge and precipitation of the metals in AMD. At the actual treatment plant, a Rapid Mix Tank is used but, like the Floc Tank, this reactor is optional. The pH is controlled in the RMT by direct lime addition. Reactor 2 (R#2) has a 40 minute retention time for precipitation reactions and oxidation of ferrous iron to ferric iron. Following flocculant addition, the slurry is fed to a clarifier for solid/liquid separation.

The sludge from the Geco plant has reached over 30% solids in the first year of operation. In a survey of sludge qualities, the sludge sampled from this plant was the only one to have a crystalline component (Aubé and Zinck, 1999). All other sludge samples, whether high-density or not, were found to be completely amorphous. Geco’s sludge also showed the lowest neutralising potential. This may seem like a disadvantage for long-term stability, but it also means that the process is more lime-efficient. A high neutralising potential indicates either the presence of unreacted lime or formation of excess calcium carbonate in the system. By contacting the sludge directly to the AMD in the Geco process, unreacted lime is consumed and carbonates are dissolved.

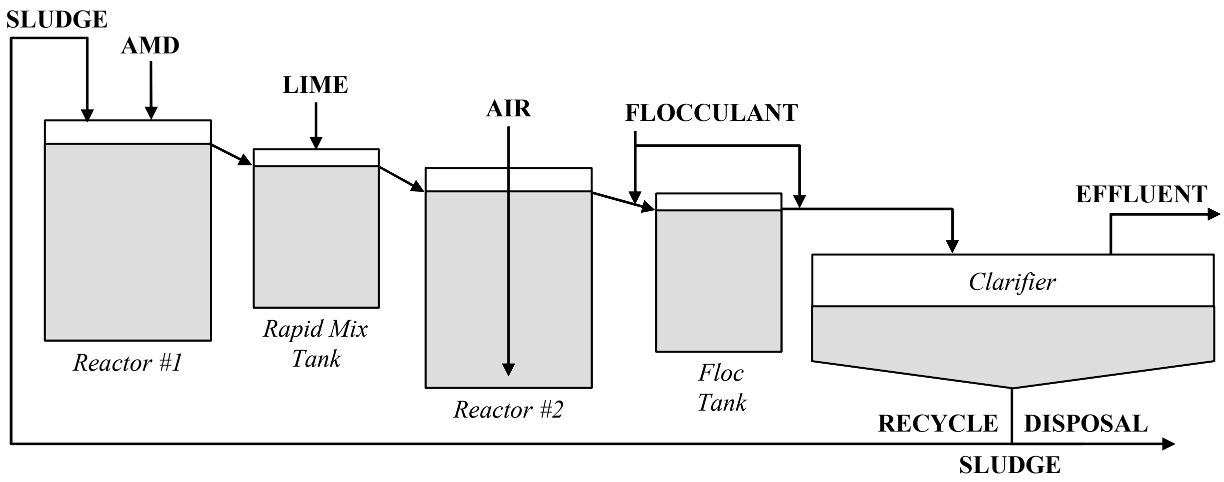


**Figure 7: Geco Process**

One advantage of the Geco Process over the HDS Process is the fact that it does not have a Lime/Sludge Mix Tank. This vessel requires considerable maintenance as it is a viscous mixture with a high scaling potential. Operators must frequently clean out this vessel in order to use the entire vessel and prevent the overflow from clogging up. As the sludge is contacted directly to the AMD in the Geco Process, this removes the need for such a high-maintenance reactor.

<u>Staged-Neutralization Process</u>

The Staged-Neutralization (S-N) process applies crystallization principles to enhance sludge crystallinity and reduce sludge volume (Demopoulos, 1995). This process has been patented in the both the United States and Canada (Demopoulos et al., 1997; Zinck et al., 2001). The Staged-Neutralization process involves neutralizing in a series of steps to control the level of supersaturation during metal precipitation. The process uses recycled sludge in the first two reactors to partially neutralise the AMD. The sludge addition rate should be controlled to reach a desired pH, as illustrated in Figure 8. In the third and fourth reactors, lime is used to bring the slurry to the desired pH. A flocculant is then added to agglomerate the precipitates and enhance settling. The process design for Staged-Neutralization is solution specific. The number of reactors required and the target pH in each reactor is based on the metal type and concentration in the mine water to be treated as well as the degree of sludge density desired.

Laboratory tests have shown that chemical overgrowth, not mechanical aggregation, is the primary precipitation mechanism. In laboratory and pilot trials, the physical properties of the sludge were greatly improved; densification increased from 25% solids with recycling to over 50% solids under supersaturation controlled recycling. The sludge produced from this process settled faster than that from existing plants by a factor of about three (12 m/h as opposed to 4 m/h with most sludges). Unlike most treatment plants in operation, the sludge contained a crystalline iron compound rather than only amorphous precipitates.

This process has yet to be applied in the full scale. Although excellent sludge properties and low lime consumption would be expected, the capital costs would be higher than other processes as four full-size reactors are needed to properly apply the S-N Process.

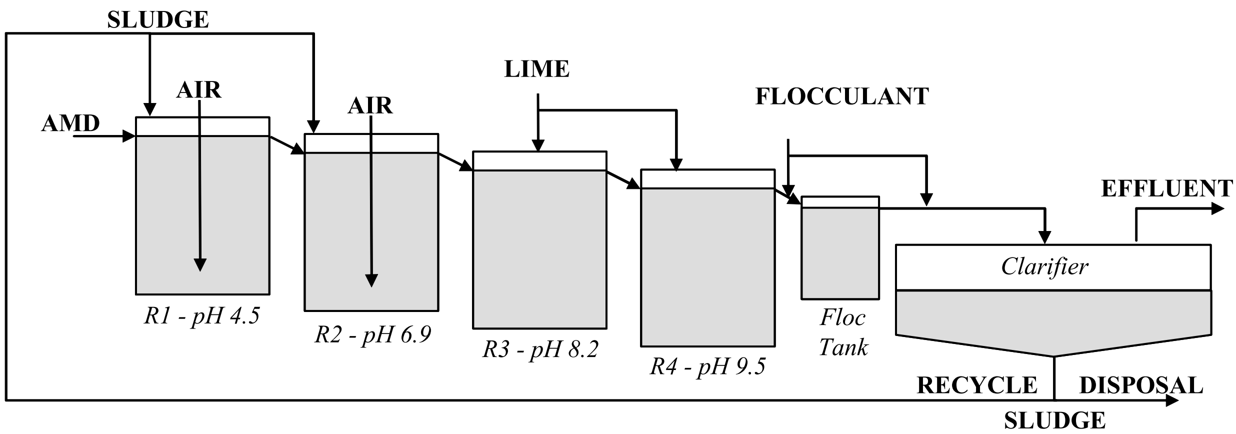


**Figure 8: Staged-Neutralisation Process**

## Comparisons Between Processes

In order to compare the treatment processes, pilot trials have been completed. Two pilot campaigns are summarised here: one completed by Noranda Inc. Technology Centre at Heath Steele Division and one completed by CANMET using their pilot plant facilities. Also used to compare processes are sludge analyses completed by both CANMET and Noranda. The results and conclusions from these tests are summarised in the following sections.

Heath Steele Pilot Tests

Pilot tests completed after the Geco plant was commissioned compared the HDS Process with the Geco Process (Aubé, 2004). These showed similar sludge qualities as far as density and viscosity. For effluent quality, there was a slight edge to the Geco Process. The Geco Process was also found to use a little less lime for neutralisation. The sludge stability was determined using leach tests, and these showed a slight advantage to the HDS process.

A detailed analysis of results showed that the Geco process uses residual lime, magnesium hydroxide and particularly calcium carbonate formed in the process to partially neutralise the AMD in the first reactor. Some of the calcium carbonate and Mg is re-precipitated in the second reactor, but the total remaining alkalinity in the sludge is lower than that of the HDS Process. This means that the Geco Process would produce a less alkaline sludge, but it also means that it uses less lime.

This therefore represents the foremost trade-off between the Geco Process and the HDS Process: the Geco Process uses less lime but the HDS produces a more stable sludge. The decision between the two processes therefore lies in the needs of the site. If the AMD contains mostly Fe and lower concentrations of Zn, Ni, and Cd, the sludge stability will not be significantly affected and the less-expensive Geco Process should be chosen. If the sludge contains some of these more soluble heavy metals and must be stored in a sensitive area, the HDS process can be applied.

If sludge stability is an important issue, lime can be added to the sludge as it is pumped to the storage area. Either process can therefore be applied in this situation as the overall lime consumption will essentially be the same for a given sludge stability.

CANMET Pilot Tests
In another pilot study, the HDS process, the Geco HDS process and the Staged Neutralization process were compared in terms of treatment efficiency, costs and environmental performance (Zinck and Griffith 2000). While all the HDS processes effectively treated the low-strength Fe-Zn rich acidic drainage solutions, there were subtle differences in their performance. For example, the Staged-Neutralization process produced the densest sludge followed by the Geco Process. As a disadvantage, the viscosity of the S-N was much higher than either the HDS or the Geco sludge. The settling rate for both the Geco and the S-N process sludges were faster than the HDS process sludge.

Lime consumption was lowest with the S-N process followed by Geco and HDS process. This is expected as the AMD is neutralised in a single large step for the HDS Process, while the Geco Process uses two steps and the S-N process applied four. The step-wise neutralisation will effectively utilise any residual alkalinity in the sludge and improve lime efficiency by controlling the level of supersaturation in each reactor.

Sludge Survey
A study of treatment sludges sampled from various water treatment plants has shown that substantial differences can be related to the treatment process and raw water composition (Aubé and Zinck, 1999). This study suggests that sludge densities, excess alkalinity, long-term compaction properties, metal leachability, crystallinity and cost efficiency can be affected by the neutralisation process and specific process parameters. The study also showed that the sludge density and dewatering ability is not positively correlated with particle size as previously suggested in numerous studies. The treatment process comparisons include sludge samples from basic lime treatment, the HDS Process, and the Geco Process.

The sludge densities, pH and Eh varied significantly between the different treatment processes. Most HDS plants generate sludges between 20 and 35% while pond and conventional treatment sludges are normally in the range of 2 to 7% solids. Pond treatment processes typically have poor pH control and as such, the paste pH of the sludge often exceeded 10. More efficient high-density sludge plants tend to produce sludge with less neutralisation potential and a higher degree of crystallinity than sludge produced from basic treatment. This indicates lower lime consumption, but less buffering capacity in the sludge.

**Conclusions**

There is no shortage of selection when in comes to choosing an active treatment method for mine water. As discussed in this paper each process has its advantages and disadvantages. The appropriate choice is site-dependent and should be based on the treatment challenges. For example, if sludge disposal volume is an important concern than one of the HDS processes should be selected. For improved lime efficiency, the Geco or Staged-Neutralization process should be considered. If capital investment is a concern and a large surface area is available, then perhaps pond treatment would be an effective treatment option. In special cases where an unused open pit is available, pit treatment may be the least expensive option.

**References**

Aubé, B., 2004. “La production de boues à haute densité dans le traitement des eaux acides minières”. Master’s thesis (to be submitted), Université de Montréal – École polytechnique. {English Title: “High Density Sludge Production in Acid Mine Drainage Treatment”}

Aubé, B., and Arseneault, B. 2003. “In-Pit Mine Drainage Treatment System in a Northern Climate” In Proceedings for “Sudbury 2003 Mining and the Environment Conference”, May 25-28 2003. (available at http://www.enviraube.com/images/raglan.pdf)

Aubé, B. 1999. "Innovative Modification to High Density Sludge Process" Proceedings for Sudbury ’99, Mining and the Environment II.

Aubé B. and J.M. Zinck, 1999. "Comparison of AMD Treatment Processes and their Impact on Sludge Characteristics". Proceedings for Sudbury ’99, Mining and the Environment II.

Aubé, B.C., Payant, S.C., 1997. "The Geco Process: A New High Density Sludge Treatment for Acid Mine Drainage" Proceedings of the Fourth International Conference on Acid Rock Drainage.

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. (Eds. S.R. Rao, L.M. Amaratunga, G.G. Richards and P.D. Kondos), Vancouver, B.C. Aug. 20-24, 1995. pp 401-411.

Demopoulos, G.P., Zinck, J.M. and Kondos, P.D., 1997. Multiple Stage Precipitation of Heavy Metals From Acidic Aqueous Solutions., U.S. Patent # 5,672,280. September 30, 1997

Zinck, J.M. and Aubé, B.C. 1999. "Optimization of Lime Treatment Processes". Proceedings of the 31st Annual Canadian Mineral Processors Conference.

Zinck, J.M. and W.F. Griffith, 2000. “An Assessment of HDS-Type Lime Treatment Processes-Efficiency and Environmental Impact” In: 5th International Conference on Acid Rock Drainage, Denver, Colorado, May 21-24, 2000

Zinck, J.M., Demopoulos, G.P. and Kondos, P.D. , 2001. “Improved precipitation process for acidic mineral effluent treatment”, Canadian patent # 2,149,493. March 20, 2001.