SELECTING SUITABLE METHODS
FOR TREATING MINING EFFLUENTS*

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ABSTRACT

Mining and metallurgical processes, during operations and after decommissioning, may generate effluents such as reclaimed tailings water, acid mine drainage (AMD) and seepage, and process acid streams. Depending on the type of ore and the metallurgical process, these effluents may contain one or more toxic compounds (e.g., acidity or alkalinity, cyanide, ammonia and/or nitrate, heavy metals, total suspended solids (TSS), sulphate) in elevated concentrations requiring treatment before their discharge to the environment or recycle/reuse in the process. Natural oxidation of sulphide minerals present in mining wastes (e.g., tailings and waste rock) at mining sites may generate AMD, which is characterized as a low pH, high acidity effluent containing heavy metals and sulphate. If generation of AMD cannot be controlled and/or prevented, AMD is collected and treated for neutralization of acidity and reduction of metals and TSS to meet regulated water quality standards.

Treatment of mining and metallurgical process effluents can be accomplished by means of physical, chemical and/or biological methods. The mode of process application may vary from the use of either specifically designed, controlled and automated facilities or passive systems. Lime neutralization and precipitation is the most common method used in the mining industry to treat AMD. To reduce the problems associated with disposal and long-term storage of the resulting sludge, the use of a high density sludge process (HDS) has become a preferred option. The use of other chemical reagents, waste or by-products from other industries, and biological sulphate reduction methods can also be considered as viable options for site-specific situations. Recently, several passive treatment systems have been designed and successfully operated, even in the cold North American climate. This paper will discuss available options and provide insights for selecting a suitable method for a given situation using case studies from projects conducted by Golder Associates around the world over the last decade.

MINE EFFLUENT SOURCES: FROM EXPLORATION TO AFTER CLOSURE

Disturbances to the ground start with drilling activities during exploration and continue until the site closure. Generation of poor water quality may start from the beginning of mining activities and may continue many years after the site is decommissioned. Sources of mining effluents that may require treatment include:

Acid Mine (or Rock) Drainage (AMD or ARD)

The management of waste materials such as tailings and waste rocks from mining of sulphidic metal and uranium ores and coal mines poses an environmental challenge to mining companies. Acid generation occurs when sulphide minerals (predominantly pyrite, FeS_2 and pyrrhotite, FeS) contained in the waste material are exposed to oxygen and water (Kuyucak, 2001a, b; Kuyucak, 2002). Following the generation of acid, leaching of oxidized products occurs as rainwater and snowmelt enters the waste pile or dump. If sufficient alkaline or buffering minerals (for example, calcite) are not present to neutralize the acid, the resulting leach water becomes acidic with high concentrations of metal ions such as iron (Fe), manganese (Mn), aluminium (Al), zinc (Zn), copper (Cu), nickel (Ni), lead (Pb), cadmium (Cd), arsenic (As), etc. This water is generally known as acid rock drainage (ARD) or acid mine drainage (AMD). According to its acidity and metal content, AMD can be classified as low, medium, or high strength (Kuyucak *et al.,* 1990). Acid generation can also be observed on roads, bridges, tunnels.

Mine Dewatering - Ammonium and Nitrate

Explosives made of ammonia and nitrate compounds are used for extraction of the ore. Solutions produced from mine dewatering may contain ammonia (NH_4-N), nitrate (NO_3) and, possibly, total suspended solids (TSS) and metal ions in elevated concentrations (Kuyucak, 1998). Careful management and proper disposal is necessary to prevent impacts to surface water and/or ground water resources.

Process Waters – Cyanide and Acids

Different types of chemicals such as cyanide, sulphuric acid, and hydrochloric acid are used for processing of ores and recovery of metals. Cyanide (CN) is used for extraction of precious metals (i.e. gold, silver, and platinum) as well as conditioning of mineral processes such as flotation processes to improve recovery of base metals such as Cu, Pb, and Zn (Kuyucak, 1998).

Mineral Processing and Tailings Reclaim Water - Thiosalts

Grinding and flotation of complex sulphide ores in an alkaline media produces a series of sulphur oxyanions called thiosalts. Thiosalts include thiosulphates, polythionates, sulphide, and sulphate. They represent a delayed acid-generating capacity in mill effluents that results in a drop in pH and, subsequently, an increase in metal and solids concentrations. Treatment of mill effluents to remove/reduce thiosalts is required as current technology has not been able to prevent the production of thiosalts in the grinding and flotation circuits (Kuyucak et al., 2001a; Kuyucak, 2001c).

TREATMENT OBJECTIVES AND APPROPRIATE PROCESS SELECTION

Mining effluents may require treatment by means of a physical, chemical, and/or biological process to minimize or eliminate their potential impact on the environment. Undesirable compounds such as acidity, metals, ammonia/nitrate, cyanide, thiosalts, and TSS are removed or reduced to acceptable levels to comply with regulated water standards. Treatment objectives are usually set based on the regulated standards, which also influence the selection and design of an appropriate treatment process for a given site.

Regulatory Standards

Each country sets standards to regulate the quality of water entering to the environment. Regulatory Water Quality Standards in Canada are set by the federal, provincial and territorial governments requiring monitoring of waters for certain parameters. For

instance, in 1980s, The Ontario Government for the management of persistent toxic substances in industrial direct discharges entering Ontario's waterways launched the Municipal Industrial Strategy for Abatement (MISA) program. Metal mining sector is one of the nine sectors (i.e., pulp and paper, metal casting, iron and steel manufacturing, petroleum, organic chemical manufacturing, inorganic chemical manufacturing, electric power generating, industrial minerals) covered by MISA. According to MISA, daily and monthly maximum levels are set and the water quality must meet criteria for certain parameters and must not be toxic to fish (i.e., *Rainbow trout*) and water flees (i.e., *Daphnia magna*). Mining sites located in the Province of Quebec must meet the water quality standards described by Menviq-Directive 019. Alternatively, site specific standards (e.g., Policy 2, no more than background value) can be set by authorities for a site. World Bank and World Health Organization can also set standards for waters resulting from industrial activities, especially for the projects take place in developing countries.

Additionally in Canada, except Quebec, the provincial governments prepared a Canada-wide Accord on environmental harmonization aiming to achieve the highest level of environmental quality for all Canadians in 1998. Through the Canadian Council of Ministers of the Environment (CCME), ministers set priorities and established workplans for addressing issues of Canada-wide significance and for implementing the commitments set out in this Accord on partnership basis. CCME's water quality task group has developed water quality guidelines mainly for the protection of aquatic life and agricultural water uses.

Sustainability Considerations

Treatment processes can be designed to produce an effluent and sludge of adequate quality to be recycled and reused for other uses, including mining processes, agricultural water for irrigation and livestock, recreational water, hydro-electric generation, and process water for industries found in the vicinity of the mining site. Golder Associates Ltd. (Ottawa) performed pilot studies at the Kingsmill Tunnel Site in Peru in collaboration with the Peruvian Water Works Company (Sedapal). The study treated

AMD with a high density sludge process (HDS) for its potential use as a supplemental source of drinking water for the City of Lima. The results of physical, chemical, biological, and toxicological tests were compared to both the Peruvian Drinking Water Quality Standards and the U.S. EPA standards. The treated AMD was found to be acceptable as a supplement to drinking water resource (e.g., lake and river). The project could also be economically viable generating revenue from the sale of the treated AMD (Kuyucak et al., 2003; Kuyucak et al., 2004). Boliden implemented a HDS process to the Apirsa site in Spain to be able to obtain a water quality that could be recycled back to the mining/mill processes thereby reducing the need for fresh water use (Kuyucak et al., 1999).

Value recovery from the metal hydroxide and/or metal sulphide sludge has also been investigated (Hedin, 2006; Kuyucak et al., 1994; Rao et al., 1994). Metal laden wastes can be sent to smelters or metal manufacturing processes as a secondary feed material. In addition, the use of sludge in back fill materials have been practiced (Kuyucak et al., 2001b).

TREATMENT OPTIONS

Heavy metals such as iron, zinc, copper, lead, cadmium, aluminium, and manganese found in acid mine waters become insoluble and precipitate in solution at a certain pH level when they react with a chemical reagent to form a metal complex (Kuyucak, 2001d; Kuyucak, 1995a). Factors governing the metal-removal process include: the type of chemical reagent used, pH of the water, oxidation/reduction and hydrolysis reactions, the presence of biotic and abiotic catalysts, and the retention time of the water.

Various methods and processes are available for AMD treatment. A selection of these process is described below.

Active methods – Neutralization and Precipitation Processes

AMD effluent can be effectively neutralized with a reagent (e.g., calcium or sodium hydroxide and calcium or sodium carbonate) to precipitate metals. Neutralization / pre-

cipitation processes are often performed in a treatment plant consisting of pumps, mixed (and aerated) reactors and/or clarifier/thickener and are particularly feasible for treating large volumes of highly contaminated waters due to its simplicity and low cost.

Metal hydroxides precipitate out of solution when they reach their solubility limit (Kuyucak 1995 a, b). This occurs at a certain pH, above and below which metal hydroxides are more soluble. Lime neutralization is efficient for the treatment of common heavy metals (Cu, Zn, Cd, Mn, Pb, Fe^{2+}) as their solubility is low at a pH greater than 9 and they precipitate. Depending on the solubility of the specific metal hydroxides, neutralization processes may be inefficient to reduce metals to desired low levels. For instance, ferric iron (Fe^{3+}) and aluminium are hydrolyzed and precipitate out at pH levels less than 5. The relationship between metal solubility and pH is illustrated in Figure 1. Neutralization/precipitation processes can achieve reduction of concentrations to certain levels of selected metals as summarized in Table 1.

Table 1:   Removal of metal ions by neutralization/precipitation

Metal	pH	Concentration Acheivable	Comment
Cr	7-8	<0.5 µg/L	reduction of Cr^{6+} to Cr^{3+}
Cu & Zn	9-10	<0.1 mg/L	
Pb & Fe^{3+}	9-10	µg/L range	
Cd & Ni	>10	< 1mg/L	hindered by high Fe concentrations
Mn	>10	<1 mg/L	strong oxidation required

In some cases, pH adjustment is ineffective, or not quite effective. Therefore, other precipitation reagents such as S^{2-} compounds and/or emerging technologies (ion exchange, membrane separation, solvent extraction, etc.) for metal removal should also be considered to meet the required standards.

Contaminants such as As, Sb, Mo and Se are usually require additional chemicals (H_2O_2, $FeCl_3$ or $Fe_2(SO_4)_3$, Na_2S, CO_2) as adjuncts to lime process (Kuyucak and Payant, 1996). For instance, stringent final effluent limits for controlling dissolved metals and suspended solids, sodium sulphide (Na_2S) and more sophisticated S/L separation equipment such as sand filters are employed (Kuyucak and Payant, 1996). Na_2S (e.g. 5 mg/L) is added in lime neutralization at pH 10.5 to lower Cd to less than 0.01 mg/L in the treated tailings water of the Samatosum treatment plant, Kamloops, British Columbia. Dynasand filters were installed to separate solids to produce a final effluent quality with low turbidity and containing metals below 0.1 mg/L total for each the heavy metals (i.e. Zn, Pb, Mn, Cd) could be achieved with help of sand filters.

A common method for removing Hg is by sulphide precipitation, resulting in an effluent of 10-20 μg Hg /L. Co-precipitation with iron can lower Mo to < mg/L. Ion exchange (IX) appears to be an alternative method to achieve low Hg and Mo levels, 1 to 5 μg/L and 2 mg/L, respectively. Recently selective IX resins are available on the market for removal of metal ions such as Cu, Zn, As, Se, and NO_3. Oxidation of As^{3+} to As^{5+} is necessary to remove As from effluent prior to lime, sulphide and ferric iron precipitation. If chromium is in the form of Cr^{6+}, a more toxic and untreatable form, it has to be first reduced to Cr^{3+} and then neutralized for its removal as $Cr(OH)_3$. Reducing reagents may contain sulphide or xanthate compounds.

Lime Neutralization Processes, High Density Sludge (HDS) Method and Critical Process Parameters

In lime neutralization processes, the use of lime as quick lime (CaO) or hydrated lime ($Ca(OH)_2$), is often preferred over other alkaline reagents, particularly for treating acidic effluents (i.e., ARD) in large quantities, due to its high reactivity and abundance (Kuyucak, 2001 a, d). Acid is neutralized and metals, such as $Fe^{(2+/3+)}$, Zn, Cu, Al, and Pb, are precipitated in the form of metal hydroxides. The resulting mixture of $CaSO_4$ (gypsum) and metal hydroxide is called "sludge." The principal reaction in lime neutralization can be expressed as follows (Eq. 1):

$$Ca(OH)_2 + Me^{2+}/Me^{3+} + H_2SO_4 <\text{--}> Me(OH)_2/Me(OH)_3 + CaSO_4 + H_2O \qquad (1)$$

Air is frequently used to oxidize the ferrous (Fe^{2+}) iron to ferric iron (Fe^{3+}) during precipitation because ferric iron sludges are chemically more stable than ferrous iron sludges. Other methods may include chemical (e.g., hydrogen peroxide) and biological (e.g., iron and/or sulphur oxidizing bacteria *Thiobacillus sp.*) methods (Rao et al., 1995). The sludge produced is allowed to settle in clarifiers/thickeners. When the solid content is less than 1 mg/L, sand bed filters are employed for polishing to meet the required level of suspended solids in the final effluent. The supernatant is then discharged to the receiving stream and the settled sludge is disposed of in specifically designed ponds.

Depending on site factors, lime neutralization facilities can vary greatly in degrees of sophistication. They range from the simple addition of lime to the tailings pipe lines to plants consisting of reactors, clarifiers, and sludge dewatering equipment as depicted in Fig. 2. The metal concentration of the water and the sophistication of treatment process affect the sludge percent solids content ("sludge density"). As a result, sludge densities may vary from 1-30% solids. To minimize the formation of a voluminous, the process parameters are set to optimum to obtain denser sludges. Major process parameters affecting sludge characteristics include: the rate of neutralization; the rate of oxidation; the Fe^{2+} to Fe^{3+} ratio; the concentration of ions; aging, recycling of settled sludge; temperature; and crystal formation.

The current state-of-the-art lime neutralization process for treating AMD and other acidic waters is called the "High Density Sludge (HDS)" process that is capable of producing more compacted sludges than traditional methods of liming Kuyucak et al., 2001a, d). In the HDS process, more than one reactor is used to perform the neutralization (Fig. 2). A portion of the sludge generated is recycled from the clarifier underflow to the process and is used along with lime as the alkaline reagent. Neutralization reactors are aerated to oxidize Fe^{2+} and pH is continuously monitored. The neutralized AMD with metal precipitates is then flocculated with a polymer and a clarifier/thickener is used to facilitate solid/liquid (S/L) separation.

The solid content in the resulting sludge is significantly higher (e.g. 10-30%) as opposed to the case not involving sludge recycle. Sludge recycling can be facilitated by either using it alone to partially neutralize AMD or after mixing with lime. The way of practise is site specific and usually multiple step neutralization methods result in better success for high strength AMD. It can be determined by conducting pilot tests for design purposes.

A two-step lime neutralization process developed by Kuyucak and Sheremata (1995) is illustrated in Figure 2 (e.g. Type IV treatment). In this process, pH of the influent is raised to 4-5 with recycled sludge in the first reactor and, in the second reactor, pH is set to an optimum pH sufficient to precipitate metals of concern. Aeration is provided to the reactors for oxidation of Fe to produce chemically more stable sludge (Kuyucak et al., 1995). This process has been applied to Noranda Mineral's Geco Mine in 1995 in Marathon, Ontario, Canada (Geco Process). A similar two-step process was implemented to the Kristineberg site in Sweden. A three-step HDS neutralization method was implemented to the Falun site in Sweden where SO_4, Fe^{2+} and Zn concentrations are as high as 45, 16 and 3 g/L, respectively. Specific design parameters for the Falun site were determined based on the water quality and available information without conducting bench or pilot tests. Some parameters were modified during commissioning of the plant to optimize the treatment efficiency.

The HDS plants are reasonably well automated, such that operation requires minimum labour and attention. A Programmable Logical Control (PLC) system has been used to control the process. The performance of the system can be monitored from a computer screen and process parameters such as sludge recycle rate, acid water flow rate and pH can be set or changed directly from the automated controls. The process is mainly controlled by two parameters: pH and sludge level in the clarifier. When the sludge level reaches the high set point the sludge purge pump automatically starts and the sludge is purged until the low level is reached. Sludge purge can be done manually as well. In addition, clarifier rake torque and effluent turbidity, and the sludge density as kg/m^3 are measured in the clarifier and in the sludge recycle line, respectively.

Golder has conducted several pilot tests and designed implemented several HDS processes including conventional and multiple step neutralization methods Kuyucak et al., 1999, Kuyucak 2001b; Kuyucak et al., 2003; Kuyucak et al., 2004; Kuyucak et al., 2005). Almost all HDS systems reduce the SO_4 content in the acid water to levels lower than theoretical solubility limit of gypsum (i.e., 2000 mg/L $CaSO_4$) and gypsum precipitates often form white colour crystal particles which are visible to naked eye. At two sites, the sludge is further dewatered with a drum "vacuum" filter its solids content increases to more than 50%. At the Kristineberg site in Sweden the dewatered sludge is backfilled to the mine for ultimate disposal and storage after being mixed with tailings. The Falun HDS system has been successfully operated since 2000, generating sand-like granulated sludge with 60-70% solids content which is landfilled. The quality of effluent generated in these facilities often surpasses the permitted effluent quality objectives.

The recent tendency in the mining industry is to use the HDS method or to upgrade the existing plants to the HDS because, in addition to the improved sludge characteristics and effluent quality, the HDS offers a number of cost advantages. It increases the quantity of the recovered water and, in another term, the quantity of lime used per unit of water treated decreases.   Scaling in the process is significantly reduced and the process control is reasonably well automated requiring less maintenance and labour.

In-Line Lime Treatment

Neutralization and aeration were combined into a single step by injecting a caustic reagent into the port of a jet pump. Overall cost of the process including capital, operating and maintenance was also found to be much lower than the conventional mechanical aerators (Kuyucak, 1995). The in-line method was recommended to neutralize low strength AMD containing Zn, Cu, Pb, Mg and Fe^{2+} (38, 0.96, 0.4, 17 and <200 mg/L, respectively).

Alternative Neutralizers

Limestone (CaCO₃) Neutralization

Under controlled conditions, higher density sludges can be obtained from neutralization of AMD using $CaCO_3$, as opposed to lime. Limestone can remove acidity and precipitate iron. Limestone in AMD dissociates and CO_2 gas evolves, as shown below:.

$$CaCO_{3(s)} + H_2SO_{4(aq)} <---> CaSO_{4(s)} + H_2O + CO_2(g) \qquad (3)$$

$$CaCO_{3(s)} + Fe_2(SO_{4(aq)})_3 + 3H_2O <---> 3CaSO_{4(s)} + 2Fe(OH)_{3(s)} + 3CO_{2(g)} \qquad (4)$$
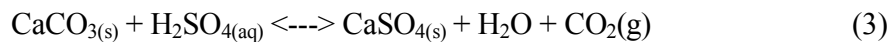
Released CO_2 gas forms carbonate ion which acts as a buffer and sets an upper limit on pH (max pH 6.5) and also affects the rate and amount of lime consumption. The precipitates may settle very slowly because of their small particle size. Removal of a broad range of metals and ferrous iron cannot be achieved since they require higher pH levels than 6.5. A combination of limestone-lime treatment process, was suggested for removal of a wide range of metal ions (Kuyucak, 1995).

Magnesium Hydroxide (Mg(OH)₂)

$Mg(OH)_2$ can result in a lower volume and more dense metal hydroxide sludge when it is properly applied in the neutralization system. $MgSO_4$, which is more soluble than $CaSO_4$, forms in the process and $Mg(OH)_2$ can also remove metals through surface adsorption. However, the rate of neutralization is slow and the buffering capability of $Mg(OH)_2$ prevents the pH from exceeding 9. Depending on the pH requirements, it can be used in conjunction with NaOH. $Mg(OH)_2$ is usually employed in treatment plants, such as Canadian Copper Refinery (CCR) in Montreal east, where the disposal cost of sludges generated is high, in order to reduce sludge disposal costs (Kuyucak et al., 1990).

Sulphides

Sulphide precipitation (Na_2S) has been used to treat wastewaters from metal finishing industries; it is not routinely used to treat AMD. Solubilities of metal sulphides are usually several orders of magnitude less than metal hydroxides (Kuyucak et al., 1991a, b; Kuyucak,

1995). Na_2S, FeS, $(NH_4)_2S$, BaS or H_2S can be used as reagents. Sulphide precipitation results in better metal removal in effluents which contain phosphate, ammonia, organics, surfactants, chelators and Cr^{6+}. Metal sulphide complexes offer some advantages over hydroxide precipitates because they are less voluminous and are chemically more stable, being less susceptible to changes in pH as long as they are stored under anaerobic conditions.   In addition to the noxious H_2S evolution from the system, settling and separation of fine and colloidal metal precipitates from the treated water pose potential problems and S/L separation may require a filtering system such as sand filter. Due to its higher cost in comparison to the cost of lime neutralization, its application is limited to site specific conditions. Biologically generated sulphide precipitation processes have been investigated as an alternative treatment method (Yanful et al., 1991; Kuyucak, 2000).

Sodium Hydroxide (NaOH)

It has high reactivity and results in less voluminous sludge. This is expensive and the resulting sludge does not settle well, requiring filtering in most cases.

Ammonia (NH₃)

Its use is mainly preferred by coal mining industries due to its high solubility and less sludge production properties. It is usually injected near the bottom of ponds or inlet water as gaseous anhydrous ammonia (Kuyucak, 2000). Some hazards are associated with handling of ammonia as well as some uncertainty concerning potential biological reactions.

Others (Waste/By-Products of Industries)

Some waste or by-products of industries such as fly ash, kiln dust, paper pulp, and red mud (bauxite residue), respectively, from power plants, crude oil combustion gasification processes, paper production, and aluminum extraction have potential as a lime substitute for the treatment of AMD. Metal contaminants present in these compounds may raise some concerns as well as their neutralization potential and reaction rates may be low and slow as compared to lime (Kuyucak, 2000; Zinck and Griffith, 2006).

Coagulation/Flocculation for Better TSS Removal (Solid/Liquid Separation)

Fine particles (precipitates) in suspension are coagulated and flocculated to form compact aggregates ("flocs") and, subsequently, to improve S/L separation or sedimentation where coagulants such as inorganic Al^{3+} or Fe^{3+} salts help to discharge or destabilize the electronegative colloids and then flocculants (i.e., organic "polymers") bridge the neutral particles. Type of polymer and dosages, the temperature of the system, the viscosity and chemical characteristics of the pulp, and external stirring are critical parameters (Kuyucak, 2000). Since fish gills are negatively charged the use of cationic polymers or their residual quantities in water may result in some concerns. A basin or a clarifier (e.g., regular circular or lamella) can be used for setting/separation process.

pH Adjustment for Meeting Final Effluent Quality Requirements

Following neutralization at a higher pH, the pH of the final effluent is returned to an acceptable range (6.5-8.5) with either sulphuric acid or CO_2. The use CO_2 may be more beneficial since it increases alkalinity and buffering capacity of waters. Due to its low cost, if an increase in the water alkalinity is not required or an increase in SO_4 levels is not of a concern, sulphuric acid is preferred.

Sludge Dewatering Options

Lime treatment plants generally utilize one basin for the dual purpose of effluent clarification and sludge thickening. Except very site specific applications (e.g., reduce transportation and landfill costs, potential metal recovery in smelters), dewatering via filters has not been widely practised in the mining industries. It has been found that the technique of freeze-dewatering be an efficient alternative and a single freeze-thaw cycle could reduce the volume of sludge by 90% (Kuyucak, et al., 1991a, b). A feasible rate of freezing can be obtained by manipulating the depth of the sludge. Golder incorporated a simple freeze/thaw dewatering system to the design and implementation of an HDS treatment plant to the Ottawa Airport. A sludge with about 70% S content could be obtained.
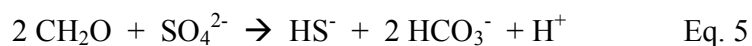
Sludge Stability and Fixation

During storage of the sludge, heavy metals may become solubilized and released in the water in the sludge pond and into ground and surface waters. The possibility of metal mobilization is determined by a "leaching test" (e.g. EPA Toxicity Characterization of Leaching Protocol "TCLP", Synthetic Precipitation Leaching Protocol "SPLP", etc.). Depending on sludge characteristics and site specific requirements, sludge is stabilized by mixing it with cement and/or lime prior to its disposal (Kuyucak, 1995; MacDonald and Webb, 2005; Zinck, 2006).

Biological and Passive Processes

Sulphate reducing bacteria based processes can be employed either in controlled reactors as an active biological process or passive systems. The most common passive treatment systems are sulphate reducing bacteria based processes, anoxic limestone drains, constructed anaerobic and aerobic wetlands, and biosorption. The performance of individual systems is a function of both quality and quantity of the raw mine drainage. Experience has demonstrated that the influent flow rate, contaminant concentrations, pH and alkalinity (or acidity) are all extremely important to system performance. And, in addition to temperature, the capacity of the biological treatment system is significantly affected by the changes in pH.

Sulphate Reducing Bacteria "SRB" Based Processes

Under reducing and anaerobic conditions, and in the presence of organic carbon nutrient sources, sulphate reducing bacteria (SRB) can convert AMD sulphate to sulphide. As a respiration product by SRB, CO_2 produces bicarbonate alkalinity, increasing pH, while sulphide forms insoluble metal complexes, as illustrated by Eq. 5 and 6.

$$2\,CH_2O \;+\; SO_4^{2-} \;\rightarrow\; HS^- \;+\; 2\,HCO_3^- \;+\; H^+ \qquad \text{Eq. 5}$$

$$Me \;+\; H_2S \;\rightarrow\; MeS \qquad\qquad\qquad\qquad \text{Eq. 6}$$

As the use of SRB in engineered lagoons, in open pits and flooded mines were investigated world wide, especially over the last two decades (Kuyucak and Germain, 1994a, b; Kuyucak and Germain, 1995; Kuyucak 2002). Their use in controlled reactor was implemented by Budelco (The Netherlands) at full-scale to remove metals and SO_4 from underground mine water in early 1990s and recently several new developments are underway to be either pilot-tested or implemented at mining sites to treat AMD and recover metal values for sale or use (Bratty et al., 2006). In active processes, ethanol and/or natural gas are the main nutrient sources. Parameters critical to the success of the process are temperature, nutrients, alkalinity, retention time, bacterial population, contaminants present in ARD and loading rates (flow, acidity and metals). In passive systems, organic materials such as straw, sawdust, wood shavings, manure, are added into the system to provide a slow release of nutrients to bacteria. Sometimes, limestone and soil are also added into the nutrient mixture to increase alkalinity and, subsequently, enhance the activity of SRB.

In some circumstances, these processes have been proven to be feasible alternatives to conventional lime neutralization/precipitation and sulphide precipitation methods (Kuyucak, 2000; Gusek, 2004; Kuyucak et al., 2006). Properly functioning passive treatment systems can produce compliance level effluents with no additional costs other than the initial construction and limited periodical maintenance. Even if supplementary chemical treatment is required to meet effluent limits at some sites, it still can be cost effective. They are particularly ideal for decommissioned sites and treatment of seepage where the temperature, flow rate and chemical composition do not fluctuate and remain optimal all year round. Alkalinity required for removing acidity and metals can be generated by two naturally occurring processes: the dissolution of limestone or other carbonate rocks; and bacterial sulphate reduction which also generates sulphide to precipitate/remove metals.

In passive systems such as wetlands, although minor removal of base metals by co-precipitation, adsorption and uptake reactions may occur under aerobic conditions, base metals such as cadmium (Cd), lead (Pb), nickel (Ni) and zinc (Zn) are not effectively removed when AMD is a net-acidic. Base metal ions including ferrous iron (Fe^{2+}) in net-

acidic AMD can   anaerobic (i.e., sulphate reducing bioreactors) When aerobic systems also works in conjunction to create complete, integrated treatment systems. Removal of aluminium (Al) occurs by precipitation which is dependent on pH and alkalinity levels in the treatment media, as ferric iron (Fe^{3+}) hydrolysis and iron hydroxide precipitation reactions take place when pH levels are >4.5. In passive treatment systems, reduction in manganese (Mn) levels is usually marginal (Kuyucak, 2002; Kuyucak *et al.,* 2006).

A recent project designed and implemented by Golder to a decommissioned mining site in Val d'Or in Quebec, Canada in 2004 requiring collection and treatment of seepage with typical ARD characteristics in a short period of time proved that passive systems can be a cost-effective alternative to active systems. The site was remote and had extreme winter conditions (i.e., -20ºC for greater than 6 months of the year) and no power. The application of a chemical (active) treatment was unfeasible due to significant required resources in both capital and time. The site-specific passive treatment facility included a seepage collection system, anaerobic and aerobic cells, and a limestone filter. A suitable organic nutrient mixture for the anaerobic fermentation and cultivation of sulphate reducing bacteria (SRB) were prepared from locally available materials (e.g., wood chips, manure, limestone, hay) and preconditioned. The treatment facility was installed and commissioned in October 2004. The results to date indicate that a properly designed and implemented passive system can produce water quality in compliance with the provincial government regulations. Parameters critical for successful operation of the system included: nutrients and organic substrate biodegradation; anaerobic/reducing conditions; hydraulic loading and metal loading rate changes; storm water impact; hydraulic design of the system (i.e., to avoid short-circuiting and channelling); gas lock-up; and temperature (Kuyucak, 2006). Variations in these parameters create significant design challenges. It has been revealed that passive systems are more sensitive to low temperatures at start-up than during operation and should be started at relatively high ambient temperatures (i.e., during warmer months) for optimum performance. Starting up the passive treatment system in warm weather gives the SRB (i.e., *Desulfibrio* populations) and associated microorganisms a chance to build up population density before they encounter cold water under cold temperature conditions. The SRB-hosting

organic substrate should be protected against freezing conditions by covering it with a thick soil layer (i.e., >0.6m). Burying the organic substrate with bacteria to conserve heat and prevent freezing was an approach used by several system designers and operators (Kuyucak *et al.,* 2006).

Wetlands

Organic and inorganic compounds, and suspended solids can be removed using wetlands. A wetland is usually composed of two distinctive zones: Oxidation Zone, which is vegetated with aquatic plants, and Reducing Zone, which is the sedimentation zone rich in SRB, denitrifying and Mn reducing bacteria. Plants play a filter role, take up metals and help the oxidation processes to occur, while bacteria act as catalyzers for chemical reactions.

Anoxic Limestone Drains (ALD)

An ALD system generally consists of an excavated seepage interception trench backfilled with crushed limestone and covered with plastic and clay-soil to keep air out. ALD basically provides an increase in alkalinity. Oxidation of Fe^{2+} and formation of ferric oxyhydroxides, which armour the limestone and prevent an increase in alkalinity, are thus avoided. Designs of ALD are reported to be site-specific. Usually, an ALD system is followed by a wetland for oxidation and precipitation of iron and other contaminants.

Open Limestone Trenches

Trenches are typically most effective for polishing/conditioning relatively low strength and neutral AMD. Acid water flows in a trench containing a layer of limestone where alkalinity and buffering capacity in the acid water are increased. Alkaline water flows into an open air (or aerated) basin for oxidation and precipitation of metals (e.g. $Fe^{2+/3+}$, Al, Zn, Cu. A process consisting of aeration, mixing and open limestone trenches that was designed and implemented by Golder to a decommissioned Barrick Gold site in Val d'Or, Quebec has been operated successfully year round since 1997. The system generates an effluent quality that meets Menviq standards, especially for parameters including pH, Ni, Cu and Fe.

Biosorbents

Biological materials such as sawdust, sphagnum moss or algae can be used as adsorbents (or biosorbents) in treating mining effluents. A bed of biosorbents can be placed where the seepage occurs. When it is saturated by metals, the proponents suggest it can either be disposed of (with tailings or recycled to a smelter), or washed with an appropriate eluate for recovery of metals (Kuyucak, 1990; Kuyucak and Volesky 1990; Kuyucak 2002; Volesky and Kuyucak, 1988; Gusek, et al., 2006).

CONSIDERATION FOR DESIGN AND IMPLEMENTATION OF APPROPRIATE TREATMENT PROCESSES

Process Selection (i.e., Lime Precipitation, Active, Passive, etc.)

An appropriate treatment process for a given site is selected based on the quality and quantity of the mining water, type of parameters that require removal/reduction, treated water quality objectives and capital and operational costs. Theoretically, the quantity of chemicals required for the treatment of water can be estimated based on the chemical analysis of the water providing information for the concentration of metal ions and total acidity. The quantity of sludge to be generated can also be calculated with the help of the concentration of metals, TSS, acidity and SO_4.

While assessing the suitability of passive systems, availability of space at the site is as important as the quality and quantity of the water to be treated. The type and process units of a passive system are decided based on the alkalinity or acidity levels as well as the type of metal ions to be removed/reduced. For instance, if the water contains net alkalinity and neutral to alkaline pH levels containing Fe and Al with metal ions in low concentrations (e.g., Cu, Cu, Ni), an aerobic wetland could provide a feasible treatment where Al and Fe can precipitate as a result of hydration reactions and Al and Fe hydroxides can serve adsorption site for removal of metal ions. If the water contains net acidity and requires removal/reduction of metal ions, the use of a limestone and SRB-based treatment system would be necessary where alkalinity can be produced and metals can be removed as metal sulphides.

Conducting Tests and Evaluating Treatability

Desktop evaluations are usually followed by bench-scale treatability tests where treated water can be produced and its quality can be evaluated. The optimal pH range and the quantity of the chemical reagent required for treating per unit volume of the water being treated are determined. Suitable type of polymer flocculant which is added into the neutralized water to enhance the settling/separation of precipitates and optimal flocculant dosages are identified with the help of bench-scale treatability tests as well as sludge settling rates and sludge production rates. Optimal retention time for reactions to occur and need for auxiliary processes such as oxidation with air or chemicals can also be investigated.

Pilot tests aim to simulate the selected process at a large scale to obtain treated water and sludge. If the process is available commercially, the commercial process could be scale-down and instrumented to automate the process as much as possible. The quality of the treated water and sludge generated are examined and the overall treatment efficiency is evaluated. Scale up and design parameters are defined and specifications of process units and equipment are identified as well construction requirements. Conducting a pilot scale test may particularly be beneficial when the use of a new "emerging" technology is considered or the water quality to be treated is not a typical type or the quality of the treated water requires evaluations for its use and toxicity.

Golder has built a pilot system, a down-size of HDS process, and fully-automated with the help of a PLC. Several pilot studies such as Boliden Apirsa (Spain), Kristineberg (Sweden), and Kingsmill Tunnel (Peru) were conducted as shown in Figure 4.

Design and Implementation: Design should consider flexibilities for construction, operation and maintenance. Equipment with a critical role in the process should be duplicated (e.g., ARD influent pumps, sludge recycling and disposal pumps, pH probes, etc.) and selected from robust/durable materials. The system should be equipped with

proper alarms and device to stop operation when required. The use or adaptation of equipment available at the site should be considered to reduce capital costs where possible. Rake in the clarifier/thickeners serving a HDS process should be designed properly to handle heavy mass. Designing Boliden Apirsa HDS treat plant in two identical units provided flexibilities for maintenance and operation of the system.

Thiosalts in Mill "Tailings Reclaim" Water

The rate of thiosalt oxidation to sulphate and the production of acid are extremely slow at normal temperatures and in the absence of catalysts and strong oxidants. However, the rapid oxidation of thiosalts observed in many river systems suggests that biological and/or chemical catalysts are often present. It has been found that ultraviolet (UV) of sunlight is effective in degrading thiosalts.

Some methods aim to increase buffering capacity of waters to be able to prevent the pH from potential decrease by adding an alkaline buffering reagent that can increase alkalinity levels in the water and control the pH rather than treating the water. For instance, addition of sodium bicarbonate ($NaHCO_3$) or neutralization of water with sodium carbonate has been practiced. Increasing the water pH to 10-11 and then dropping the pH to regulated limits by sparging carbon dioxide are also employed as a relatively cost-effective method with a marginal success at some mining and metallurgical processing sites (Kuyucak, 2005, Kuyucak 2001c, Kuyucak 2001a). Carbonate-based method may function satisfactorily for low thiosalts concentrations (e.g., < 100 mg/L).

Treatment methods are usually based on the degradation principles of thiosalts from mill effluents. Many of the methods have been evaluated only in laboratory scale tests and a few of them have been pilot tested or full-scale applied. The treatment options include: Chemical oxidation including hydrogen peroxide (H_2O_2), chlorine (Cl_2) and ozone (O_3); Membrane and electrochemical processes including reverse osmosis (RO), electrodialysis (ED) and electro-oxidation; Air oxidation including alkaline oxidation, Cu-catalyzed air

oxidation and SO_2-air oxidation; Biological oxidation including the use of biological contactors, activated sludge and packed columns where degradation of thiosalts and the oxidation of sulphite to sulphate occurs with the help of sulphur oxidizing bacteria such as *Thiobacillus ferrooxidans* and *Thiobacillus thiooxidans* and other methods such as anaerobic microbiological sulphide reduction or reduction by metals and sea disposal.

For instance, Golder evaluated and designed/implemented an effective method to Boliden Apirsa (Spain) site. Addition of H_2O_2 to only a portion of the treated effluent coming from a HDS lime neutralization process before its discharge to the environment was found to be the most cost-effective method due to low capital cost of the process. In addition to low investment cost, it was easy to prove its effectiveness to obtain permit and the delivery and construction time was short enough to meet the short deadline for when the treatment needed to be in operation. Furthermore, since the HDS process originally designed in two identical units to provide easiness for maintenance and operation, the modifications needed in the HDS water treatment plant were also insignificant.

The analysis of thiosalts which is reasonably complicated and time consuming was one of the major draw backs interfered with conducting tests and developing the process. Golder found a direct relationship between the COD levels and thiosalts concentrations in the treated final effluent. The analysis of COD is relatively simple and rapid. During the studies at the Boliden Apirsa site in Spain, to be able to meet the regulated COD limit of 30 mg/L in the final effluent, the concentration of thiosalts had to be less than 52 mg/L.

At another site in Canada, Golder Associates Ltd. has used a combination of lime and soda ash (Na_2CO_3) to add buffering capacity while neutralizing the water. Replacing the old practice where increasing the pH to 11 and dropping it to pH <9 with CO_2 with this method resulted in significant savings in the lime consumption and, subsequently, overall treatment costs.

Removal of Sulphate (SO$_4$)

There exist several methods for removal/reduction of SO$_4$ from waters. These methods include: precipitation with barium (Ba); ion exchange (IX); biological sulphate reduction (SRB process) and aluminium hydroxide (Al(OH)$_3$) precipitation (Kuyucak et al., 2003; Kuyucak et al., 2004). In general, these methods are not used widely for the treatment of mining effluents. Even if they show technical feasibility, their application may not be economically feasible, especially for large flows. When required, treatment of a small fraction of the water which will be discharged to the environment can be considered. Management of brine from IX and reverse osmosis (RO) membrane based systems adds additional costs to the process.

Removal of Total Dissolved Salts (TDS)

Dissolved salts other than sulphates (calcium, magnesium, etc.) may also be present in ARD. The expected concentration range for total dissolved salts (TDS) is generally in the order of 100 mg/L to 30 000 mg/L. These levels can lead to a reduction in the quality of potable surface and ground water supplies and therefore these compounds require removal/reduction from the ARD before it reaches the natural environment or water resources. Recently, RO has received consideration.

Removal of Cyanide, Ammonia, and Nitrate (NH$_4$-N/NO$_3$)

Ammonia may be found in mining effluents because of the hydrolysis of cyanate and/or the dissolution of blasting agent (e.g., ammonium nitrate fuel oil mixture) residues. The rate of cyanate hydrolysis is relatively rapid at pH levels less than 6 or at elevated temperatures. Since free ammonia can form soluble amine complexes with heavy metals such as copper, zinc, silver and nickel, the presence of ammonia may inhibit precipitation of these metals at pH values above 9 which is known to be an effective range for the precipitation of metal hydroxides (Kuyucak, 1998; Kuyucak, 2002). Nitrate is the end-

product of the cyanide oxidation process and forms as a result of chemical or biological oxidation of ammonia. Reactions are presented with Equations 7 and 8.

Aerobic (for CN, NH_3, thiosalts)
Nitrification: $NH_3 + O_2 \rightarrow NO_3$ Eq. 7

Anaerobic (for NO_3)
Denitrification: $NO_3 + C_{org} \rightarrow N_2 \uparrow + CO_2 \uparrow$ Eq. 8

The widely used method for removal of cyanides and ammonia is natural degradation in holding ponds. When cyanides are biologically or chemically oxidized, they are then converted to ammonia and carbon dioxide. Then, natural degradation of ammonia involves the transpiration of dissolved ammonia gas from the wastewater. The removal is enhanced by increasing pond area, increasing pH and by allowing for more contact with air. A biological process unique to Homestake Mining in South Dakota decomposes metal-cyanide complexes and efficiently oxidizes cyanides to ammonia which is further oxidized by bacteria ("nitrification") to nitrate (Eq. 7).

The potential processes for removal of nitrates and nitrites include: biological denitrification where nitrates/nitrites are reduced to nitrogen gas (Eq. 8), ion exchange and reverse osmosis where nitrates/nitrites are removed from the water and are obtained in a very concentrated form requiring further disposal methods. As wetland filtration has a limited use, anaerobic passive systems containing organic materials such as woodchips and denitrifying bacteria have been practiced for denitrification of nitrates.

On-line ammonia and nitrate monitoring devices are available on the market. Their installation on the process lines can reduce the non-compliance situations.

Removal of Cyanide

Residues and wastewater streams containing cyanide and cyanide compounds have to be treated to reduce the concentration of total cyanide and free cyanide below the regulated limits.

A variety of cyanide related compounds can form in solutions resulting from cyanidation, natural attenuation or treatment processes. These compounds include thiocyanate (SCN^-), cyanate (OCN^-), ammonia (i.e., free ammonia NH_3 or ammonium ion NH_4^-) and nitrate (NO_3^-).

Natural degradation reactions can render cyanide non-toxic (carbon dioxide and nitrogen compounds). These natural reactions have been utilised by the mining industry as the most common means of attenuating cyanide. However, the rate of natural degradation is largely dependent on environmental conditions and may not produce an effluent of desirable quality in all cases year round and the environmental regulations have become more and more stringent with respect to cyanide in the recent years. Technologies including chemical, biological, electrochemical and photochemical methods have been developed for removal/reduction of cyanide and cyanide compounds below the regulated limits in wastewaters.

Cyanide is treated to "destroy" it, generally by converting it into compounds that are in-soluble and so cannot be taken up by organisms. Cyanide destruction plants must be re-liable all the time and provisions should be made for recycling of solutions that do not meet the discharge criteria during plant upsets. Installation of a continuous on-line moni-toring device is very useful. The process should not produce undesirable by-products and should be able to destroy harmful by-products of the cyanide destruction process such as ammonia and metals should also be removed. The effluent treatment process should be appropriate to site-specific climatic conditions (e.g., temperature, precipitation), solution chemistry and discharge requirements. The capital and operational costs should suit the mining production conditions such as production rate and life expectancy.

Despite its wide use in the last two decades, the use of alkaline chlorination process has become limited. Unique methods, such as Homestake biological process and the Hemlo / Golden Giant copper and iron sulphate precipitation process, are mainly developed and used by the same companies. The Inco SO_2/Air Process has been receiving worldwide

attention. The application of hydrogen peroxide has also been increasing. Investigations for the development of new processes have been ongoing. In arid climates, evaporation is used to obtain zero discharge.

CONCLUSIONS

Since the site conditions, the quality of water to be treated, cost of reagent and degree of treatment requirements may vary from site to site, treatment costs are site specific. Some processes may require up front high capital costs and may provide lower operational costs (e.g., reagent cost, energy and maintenance requirements), while some processes can be implemented to a site with small capital costs, but operation using these methods might be expensive. During the project planning stage, cost-benefit analyses should be conducted for potential alternative treatment methods to determine the most appropriate process for the given site.   Conducting treatability studies using bench and pilot scale tests are useful to determine critical process parameters and design and scale up parameters.
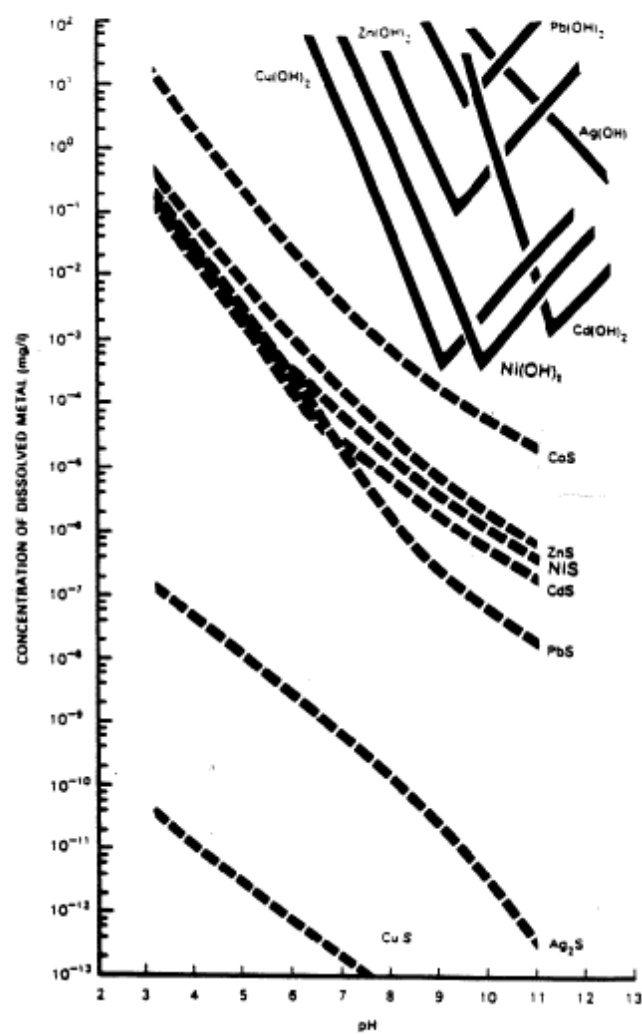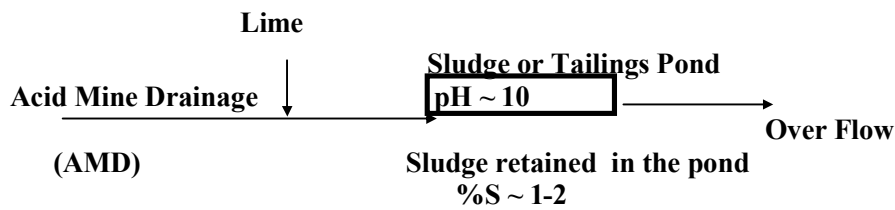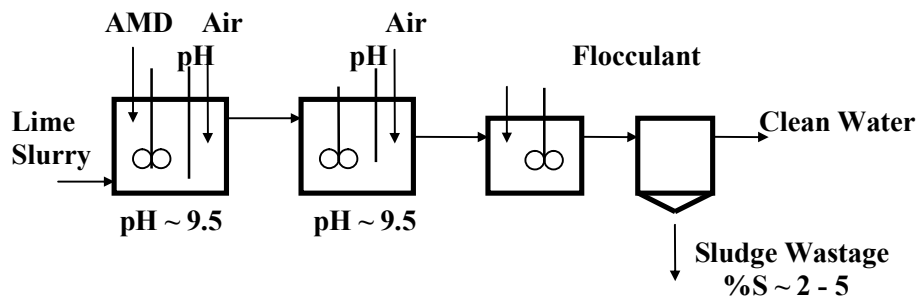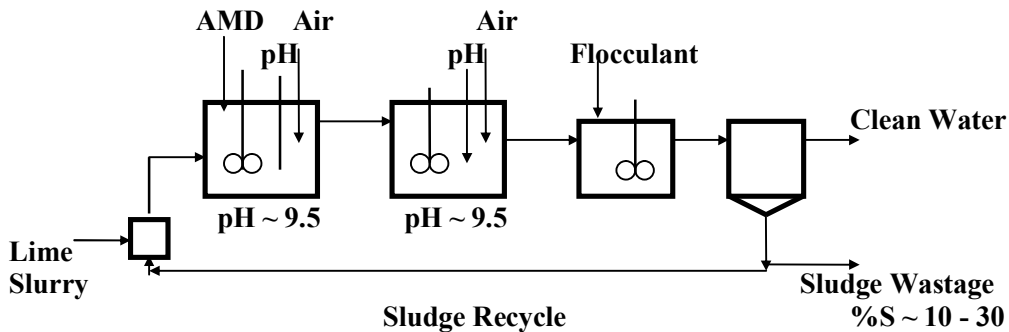
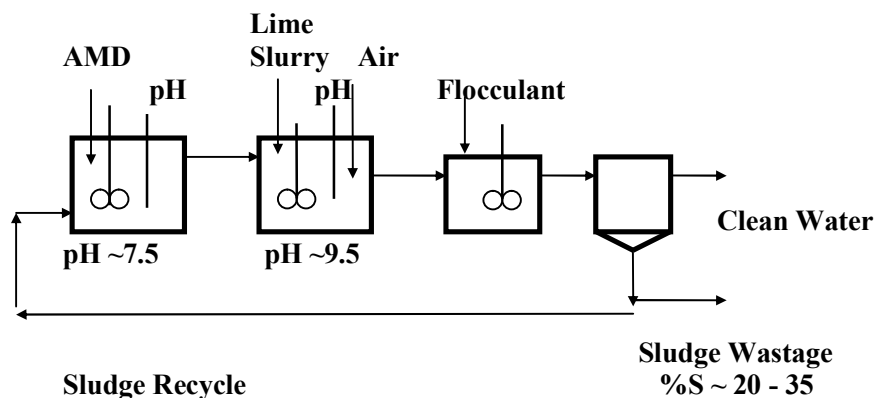Figure 1 - Comparison of Solubilities of Metal Hydroxides and Sulphides as a Function of pH

Type I - Lime addition to acid water: Conventional Method.

Type II - Lime addition to neutralization reactors: Conventional Method.

Type III - Sludge recycled into lime slurry: High Density Sludge "HDS" Process (Boliden-Apirsa Treatment Plant, Golder Associates, Ottawa, Canada).

Type IV - Sludge recycle into acid water: Two-Step "HDS" Process (Boliden Kristineberg Treatment Plan, Golder Associates, Ottawa, Canada).

Figure 2. Types of Lime Neutralization Processes and the Resulting Sludge Densities.

Figure 3: Drum vacuum filter dewatering metal hydroxide sludge from HDS processes at the Falun site, Sweden.

Figure 4: Pilot HDS Treatment Unit

Acknowledgements

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