

TREATMENT OF ACID MINE DRAINAGE BY THE HIGH DENSITY SLUDGE PROCESS

by D.J. Murdock, J.R.W. Fox and J.G. Bensley²

Abstract: The oxidation of sulphide minerals in moist, aerobic conditions leads to the formation of acid and the mobilization of metals. This process is aided by bacterial action and gives rise to acid mine drainage. The most commonly applied technology for chemical neutralization of acid mine drainage is the use of lime which not only neutralizes the acid but also precipitates metals as their oxides or hydroxides. The processes that have been used to date for lime neutralization include simple neutralization, neutralization with aeration to oxidize iron, and neutralization with aeration and sludge recycle. A refinement of the third method, based on aeration and sludge recycle can produce a dense sludge of 20%+ solids with free drainage properties, which rapidly achieves 40% to 50% solids in the impoundment area. Because of these advantages, this method, otherwise known as the high-density sludge (HDS) process, has been selected for treatment of acid mine drainage at several mining operations in Canada and the United States. The stability of the sludge is naturally high but can be further improved by the addition of a slight lime excess before impoundment.

Additional Key Words: acid mine drainage, high density sludge, water treatment, effluent treatment, impoundment.

Introduction

The dissolution of soluble metal compounds from ore, waste rock, and tailings results in metal-contaminated effluent commonly known as acid mine drainage. Properly, acid mine drainage (AMD) refers to water mobilization of sulfide oxidation products. Depending on the type of host rock, sulfide content, and degree of oxidation, such effluents range from near neutral pH with a few milligrams of metal content to highly acidic with metal content measured in grams. The most commonly applied technology in the North American base metal mining industry for the treatment of AMD is chemical neutralization and precipitation using lime. Other technologies may find site-specific application, but there are valid reasons for the dominance of lime treatment. Chemical precipitation is controllable and predictable. Lime is widely available, inexpensive, and easily handled. In some cases, additional reagents are required to fix metals mobilized during sulfide decomposition, including iron salts to remove arsenic and antimony.

The first application of a process in Canada based on neutralization and recirculation of the precipitated sludge was reported by Kuit (1980). The process was installed at the Sullivan Mine of Cominco Ltd. at Kimberley, B.C. As described by Kuit, based on considerable pilot-plant work, a plant had been successfully designed to treat AMD, and the process produced sludge that was substantially denser than that achieved with simple neutralization. At that time, the plant had been operating for only 1 year, but the quality of effluents produced met or fell under the limits set by the Provincial and Federal environmental authorities. It was stated that several years would be required to confirm water management and treatment plant capabilities under the complete range of operating conditions, as well as to confirm the long-term environmental acceptability of the treated sludge.

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² D.J. Murdock, Manager, Process Technologies, J.R.W. Fox, Principal Engineer, Metallurgy, J.G. Bensley, Principal Engineer, Process Control, Cominco Engineering Services Ltd., Vancouver, B.C. Canada

Kuyucak et al (1991) have studied similar variations of the lime neutralization process in a laboratory setting and have reported extensively on the results. These papers are cited here for interested readers but will not be reviewed.

The purpose of this paper is to discuss some of the unique features of the HDS process, to provide an update on the operations and stability of the first plant in Kimberley and provide some practical knowledge on full scale implementation of HDS at several industrial locations.

Process Fundamentals

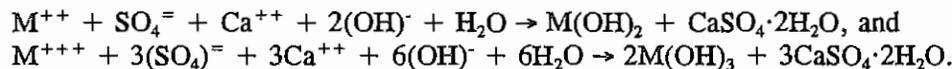
A wide variety of techniques have been considered for the treatment of AMD. Genes et al (1991) presented the following alternatives for the treatment of 400 L/min of acidic drainage from an abandoned lead-zinc mining area in the United States:

- Carbon adsorption.
- Ion exchange.
- Reverse osmosis.
- Electrodialysis.
- Ozonation.
- Engineered wetlands.
- Lime neutralization-precipitation.

Apart from lime neutralization, the only technique that has been applied to any great extent has been engineered wetlands (Norton 1993). Lime neutralization has been the preferred technique for the following reasons:

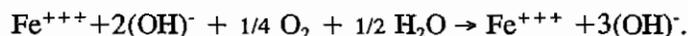
- Capability of treating severe waste rock drainage.
- A wide range of flows can be accommodated.
- Capital and operating costs are moderate.
- It is generally considered the best practical technology.

The near-complete precipitation of the metals as hydroxides in the neutralization process proceeds according to the following reactions:



As implied by the equations above, the products of these reactions are metal hydroxide precipitates and calcium sulfate (gypsum). It is hypothesized that if the sulfate concentration of the wastewater is high enough, there will be sufficient gypsum produced to exceed its solubility and it will precipitate with the sludge. The presence of the gypsum increases the buffering capacity of the sludge and may be partially responsible for the sludge's improved chemical stability. Wasserlauf (1987), Higgs (1990) and Kuyucak (1991) have all studied this issue and found gypsum does indeed exist in the sludge although at ambient temperatures, treated solutions are often supersaturated in gypsum. These findings tend to support the author's hypothesis.

Complete oxidation of the ferrous hydroxide to the more stable ferric hydroxide is required for optimum process chemistry, as follows:



Incomplete ferrous oxidation during treatment can result in chemical instability of impounded sludge and redissolution of heavy metals. Simplified lime treatment flowsheets are shown in figure 1. For the most part, metal hydroxides are compatible with effluent objectives. However, the supplemental addition of iron salts and/or minor

sulfides can compensate for most deficiencies in metals removal by lime. The first scheme shown in figure 1 essentially involves the addition of lime and mixing the solids with the tailings discharge. This process is low in cost and was successfully applied at Heath Steele Mines in New Brunswick (Busse 1974). The process is also used at Equity Silver Mines Ltd. in British Columbia (Gormely 1989). Although this process can produce acceptable effluent quality, the precipitated sludge produced is voluminous, rarely exceeding 2.5% solids, and difficult to handle. Sludge stability is questionable, and redissolution of precipitated metals is a concern. Furthermore, the volume of sludge produced can approach the volume of the original effluent treated.

The second scheme requires an independent plant for lime reaction and aeration to oxidize Fe^{++} to Fe^{+++} , followed by a clarifier or settling pond. Chemical stability of the sludge is improved, but given the low density, disposal is still a concern.

These disadvantages are largely overcome by using the third scheme, the HDS process, which produces a thickener underflow sludge of 20%+ solids with free drainage properties, which rapidly achieves 40% to 50% solids. The stability of the sludge can be further improved by the addition of a slight lime excess before impoundment.

The effective removal of base metals in a stable form in the HDS process is caused by the formation of a precipitate of calcium and coprecipitate with iron on the surface of a recycled particle. The stability of the precipitates is favorably influenced by a high-iron-to-total-metal ratio. Simple recycle is not enough to change metal ratios, and in extreme examples iron may have to be added, or the storage site for sludge produced must allow for the possibility of longer term instability. In all cases the oxidation of ferrous to ferric iron is the principal oxygen-consuming cation reaction. Anions containing sulfur (such as thiosulfate) and arsenic (as arsenite) may also require oxidation. However, if air is sparged into the reactor for oxidation, the oxygen transfer may well be controlling the reaction and hence the reactor tank sizing. Oxygen transfer will be dominant in agitator design and power requirements.

Design plant throughput is influenced by the volume of water to be treated: for example, seasonal changes will determine runoff, much of which may have to be treated. Increased flow may be accompanied by a dilution of contaminants, both acid and metal, and the resulting plant influent may require reduced oxidation and/or residence time.

High-Density Sludge Process

A simplified flowsheet for the HDS process is shown in figure 2. The main features of the process have been reported previously by a variety of authors such as Kuit (1980) and can be summarized as follows: A combination of lime and recycled sludge is added to the sludge-lime mix tank at the head of the process. This mixture is discharged to the rapid mix tank, to which is also added the influent. Thereby achieving a partial neutralization. This mixture is fed to the main lime reactor where a combination of aggressive aeration and high shear agitation ensures optimum process chemistry and clarifier performance. The discharge from the lime reactor is treated with flocculant prior to entering the flocculant mix tank. The clarifier separates the treated effluent from the sludge, a portion of which is recycled to the head of the process.

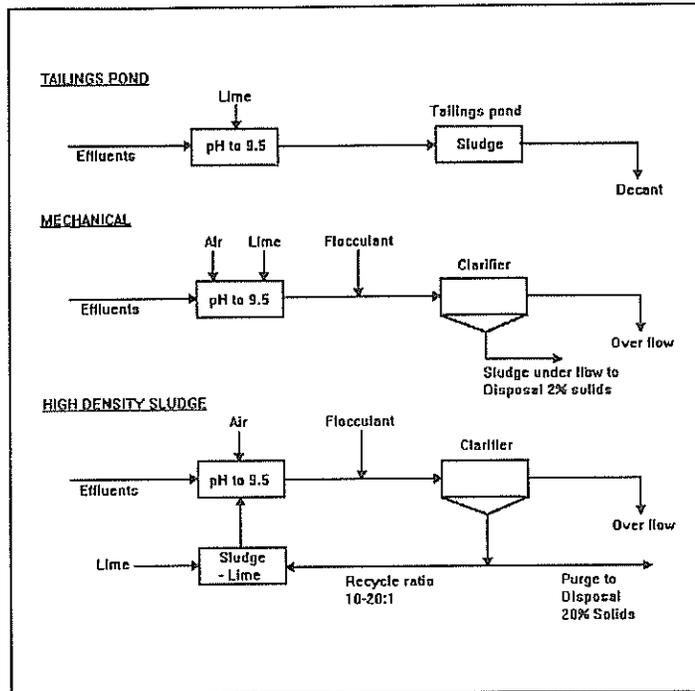


Figure 1. Lime neutralization treatment alternatives.

The HDS process is normally run at a pH between 9 and 9.5, as most metals encountered in the process precipitate at or below this concentration of hydroxide ions. This pH is also required for ferrous iron oxidation. Oxidation of ferrous to ferric iron takes place quite rapidly at this pH, and oxygen is the most usual oxidizing agent. There is no reason why other agents cannot be used for oxidation, although all the plants built by the authors so far have used air for oxidation.

The process itself depends upon sludge recycle from the treated effluent, and in most plants this has been achieved in a thickener style clarifier, which offers a pumpable sludge as the separated solids product. Clearly, recycle from a settling pond presents some material-handling problems, as do filter-style clarifiers, but both could be used.

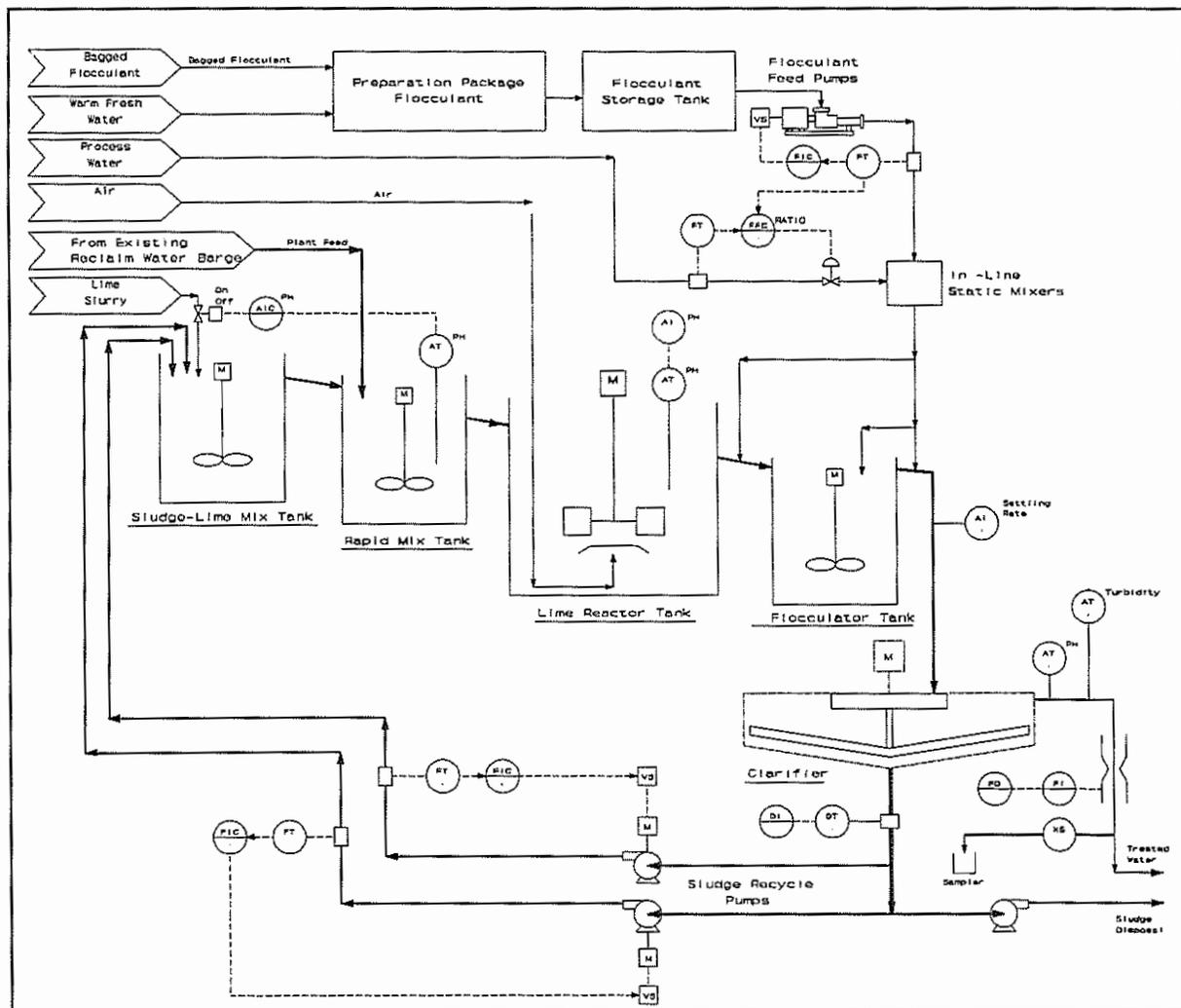


Figure 2. Simplified HDS process flowsheet.

Design Parameters and Plant Features

Some general comments on the materials of construction and design parameters are as follows:

Untreated water supply — All pumps in contact with this water should be 316 SS because of the acid pH of the water. Any surge tanks should also be 316SS. Pipelines are best in high density polyethylene. Scaling conditions of the water must be evaluated so that pipeline descaling can be provided if required. The propensity of water to cause scale in pipelines is governed by the concentration of scale forming compounds such as sulfates and

carbonates. Analysis for these compounds in conjunction with their respective solubility curves and information on typical temperatures and pH's expected will provide insight regarding the extent of scaling problems to be expected. The process water flow rates and contaminant levels must be fully known in order to develop a proper design.

Sludge-lime mix tank — This vessel is normally made of carbon steel since the vessel contents are at a high pH. The agitator must be able to supply adequate mixing power to get sufficient shear in the vessel.

Rapid mix tank — This vessel must be made of 316 SS because of the corrosive nature of the untreated water being put into the tank. The agitator and shaft should be 316SS or rubber covered.

Lime reactor — This tank can be either concrete or mild steel. Concrete is preferred because of the high power input requirements of the agitator. The final selection is dependent on an economic analysis and the need to prevent freezing in the plant. The agitator gear reducer must be of a very heavy duty design to handle the difficult process requirements of keeping solids in suspension, dispersing the air into small bubbles, and contacting the air, water and solids. Designing for a low-maintenance requirement is also an important factor.

Flocculent mix tank — This vessel can be concrete or mild steel. The agitation is gentle to avoid breaking any of the flocs produced.

Clarifier — This vessel can be either steel or concrete. Site objectives and location will form part of the economic evaluation to determine steel or concrete. This vessel is not a thickener but a clarifier, and so thixo-posts are required rather than shoes to move the sludge. The introduction of the flocculated feed into the clarifier must be gentle to avoid breaking up the flocs. The clarifier overflow must be properly collected to reduce the problems of freezing.

Sludge disposal — This may require pumping over a long distance. The line loss characteristics of the sludge must be known to properly size the pumps required. Proper startup and shutdown of this batch pumping operation are important to avoid plugging or freezing during wintertime operation. The sludge lines can be HDPE or steel.

The principal control parameters for the HDS process are also illustrated in figure 2. The pH in the rapid mix tank is the primary parameter used to control lime addition to the sludge-lime mix tank. Optimum operation is achieved through time-proportional control of a pinch valve, which taps a small proportion of the slurry circulating in a loop from the lime slurry storage tank. The pH in the lime reactor is monitored and may be used to adjust the set-point of the primary pH control loop based on operating parameters such as feed rate, metals loading, and sludge recycle rate.

Flocculant may be added at various locations prior to the flocculator tank and in the feed to the clarifier. Flocculant flow is measured prior to dilution and controlled to an operator determined set-point. An on-line settling rate analyzer is commercially available that can be used to determine the settling characteristics of the clarifier feed and thus speed up the establishment of optimum flocculant requirements, in addition to monitoring the effects on clarifier overflow turbidity. Monitoring of clarifier underflow density is essential. This parameter combined with sludge recycle flow rate determines recycle mass flow, the control of which is paramount in achieving optimum process performance. Duplication of the sludge recycle circuit with the use of variable-speed pump controllers and automatic line-flush sequencing has been found to provide good operating flexibility.

Clarifier overflow turbidity and pH are monitored, and can be used to shut down plant feed in the event that they exceed operational limits. Final discharge flow is monitored and grab samples are taken automatically for analysis and reporting. Fresh water consumption can be reduced through the use of treated water (from clarifier overflow) for lime slaking, flocculant dilution, and line flushing.

In order to minimize labor costs, various automatic sequences for equipment operation can be included that are controlled through programmable logic controllers. For example, operation of lime slakers can be automated based on the drawdown of slurry from the lime slurry storage tank, and flocculant preparation can be similarly controlled. At remote sites where the plant is mainly unattended, an automatic power on-restart sequence (which can restart the plant in the event of a brief power interruption) has been found to be beneficial.

Case Studies

Cominco Ltd., Kimberley BC, Canada

This plant was one of the first applications of the HDS process in Canada. The plant was started up in 1979 and has been operating more or less continuously since that time. The plant treats on average 11,500 L/min of AMD at a pH of 4.0. The normal maximum that the plant is designed to treat is 18,000 L/min, which can be forced to 27,000 L/min. Some comparative data are presented in tables 1 and 2, which show the design basis originally selected and the performance achieved shortly after startup, compared with that achieved during the 12-month period from June 1992 to May 1993. The values shown for 1992-93 are the averages of the monthly composite performance.

Table 1. Kimberley HDS plant, comparative plant performance.

Species, ppm	1979		1992-93	
	Influent	Effluent	Influent	Effluent
Iron	250	<1.0	144	0.02
Zinc	22	<0.2	28	0.01
Lead	5	<0.1	4.9	0.02
Suspended solids	75	<15	73	10
pH	4.5	9.5	4.0	9.3

Table 2. Typical comparative operating parameters, per unit volume of water treated.

	1980	1992-93
Lime consumption, g/L	1.0	.5
Flocculent consumption, g/m ³	3.0	2.1
Sludge production, g/m ³	1.3	.66

Trends in treated water flow, soluble zinc concentration in the treated water (plant effluent in figure 3 below) and soluble zinc concentration from water wells surrounding the sludge impoundment site for the period June 1992 to May 1993, are shown in figure 3. The soluble zinc content of the well water provides an indication of the extent to which heavy metals are re-released by the sludge over time and therefore, a measure of long-term sludge stability.

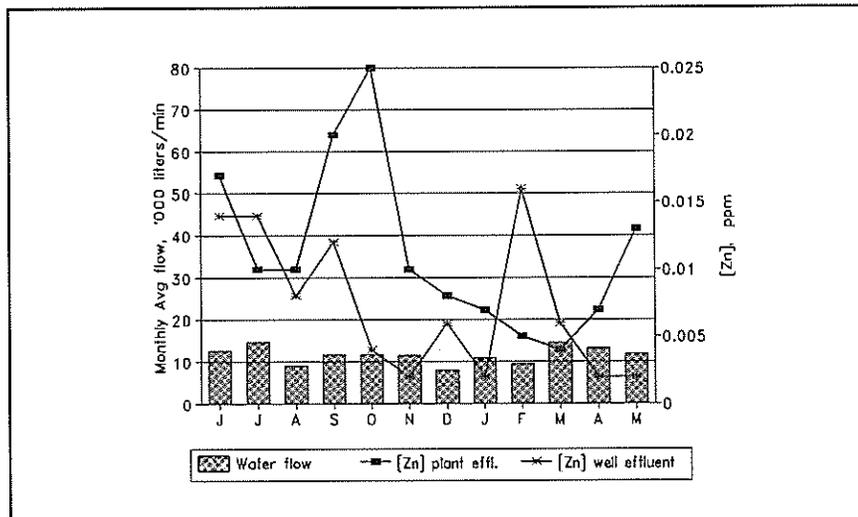


Figure 3. Kimberley plant performance and sludge stability, June 1992 to May 1993

The data plotted in figure 3 shows conclusively that after 13 years of operation, the plant still produces an effluent that contains metal concentrations substantially below current government regulations. Regulations in Canada for zinc are a maximum of 0.5 to 1 ppm in discharged effluent. Furthermore, the low content of metals in the well water from around the impounded sludge indicates that, to date, re-release of the metals to the ground water is not occurring, due to sludge stability.

Brunswick Mining and Smelting, Bathurst, N.B., Canada

The Brunswick Mining and Smelting Company operates a mine in the Province of New Brunswick, Canada. The ore contains considerable amounts of pyrite as well as the valuable sulfides of copper, lead, and zinc. Mining operations on current reserves are planned for another 30 years. A water treatment plant based on the HDS process was commissioned in the fall of 1993.

The topography of the property is such that although tailings and waste dump seepage could be conveniently collected, the catchment area for contaminated surface runoff was quite large and hydrological studies indicated that the 100-year event was expected to produce 750,000 L/min from the potentially contaminated catchment area, although a normal peak of 40,000 L/min was expected during spring runoff.

At the average feed rate of 22,000 L/min, metals at 150 ppm Fe, 100 ppm Zn, and pH 3.5 are expected with the worst case designed for 40,000 L/min with 230 ppm Fe, 200 ppm Zn and pH 2.0. The main HDS plant is designed to accept flows up to 60,000 L/min but at these flows metal loadings would be below the peak (and close to the average quoted above). Flows above 60,000 L/min may be possible but at very significantly reduced metal loadings.

At time of writing (November 1993) the plant was functioning well at a feed rate of 30,000 L/min producing a sludge of greater than 20% solids. Treated water discharge was meeting design specifications. The plant started treating water at reduced flows in order to make sludge for recycle. When sludge reached 12% solids, full operation was instituted. It took about 1 week to reach 18% solids in full operation, and 20% was exceeded by the second week.

Glenbrook Nickel Co., Coos Bay, OR, U.S.A.

The Coos Bay facility imports lateritic nickel ore from offshore. Water collected on the site includes runoff from ore storage piles. Although this water is close to neutral (pH 6.5) it contains soluble copper, nickel, and chromium at 1-ppm levels, as well as iron at several parts per million. The water had to be treated prior to discharge into the estuary of a salmon river.

A laboratory program determined that the metals presented no particular treatment problem, with the exception of chromium. Removal was effected by the addition of an iron salt and liming. Chromium removal required that a ferrous iron salt be added to the effluent prior to the addition of limed recycled sludge. The resulting mixture was aerated, flocculated and settled in a Delta stack clarifier, and the clarifier overflow was either discharged directly to the estuary, or clarified through a mixed-bed clarifier.

It is postulated that the ferrous iron addition reduced hexavalent chromium to its insoluble trivalent state and that this material was then co-precipitated onto the recycled sludge with the iron, which was then all oxidized to ferric. If ferric iron was added to the system, the chromium remained in solution, although nickel, iron and copper were removed. The sludge was disposed of by adding it to the lateritic nickel ore and shipping it to the smelter.

Tiwest, Kwinana, W.A., Australia

Tiwest is a titanium pigment plant treating mainly natural rutile in an acidic chloride digestion system. The iron-containing waste streams were previously neutralized with lime and thickened to about 6% solids. The Tiwest plant was operating a straight lime neutralization plant for the treatment of effluent from various waste waters emanating from its chloride based titanium pigment plant. Densities of the sludges were less than 6% and storage space was becoming a problem. Cominco Engineering Services Ltd. was retained to carry out test work and demonstrated in the mini-pilot plant sent to Australia that sludges of 20% solids could be made.

A flowsheet was produced that utilized as much as possible of the existing plant, in essence the only new requirement was the reactor tank where aeration of the slurry took place. Other modifications to the plant took place, such as the piping in of a slurry recycle line, and the utilization of tankage from the old liming plant as mix and reactor vessels. The gas dispersion agitator selected was of the "gas shear turbine" type, which has a significantly lower power requirement than the Rushton design. The plant has been running successfully since April 1992.

Conclusions

Based on applications in Canada and elsewhere, the HDS process has been shown to be an effective and economical method for the treatment of AMD. Experience to date suggests that the associated sludge is both dense and stable, and that no significant re-release of the precipitated metals to the environment takes place. The applicability of the technology is not limited to the treatment of mine drainages only, but the technology can be effectively applied to other industrial effluents that have significant quantities of dissolved heavy metals.

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