IMPLEMENTATION OF A HIGH DENSITY SLUDGE "HDS" TREATMENT PROCESS AT THE BOLIDEN APIRSA MINE SITE

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ABSTRACT

Lime neutralization is a frequently used method in the mining industry for the treatment of acid waters. These waters contain metal ions such as zinc, manganese, copper, cadmium, lead, etc. The conventional, straight lime neutralization technology generates a Low Density Sludge (LDS) having only 1-2% solids content. This creates sludge disposal difficulties, and results in the loss of potentially large quantities of recovered water, which in turn increases the demand for fresh water requirements for mining/milling activities. The High Density Sludge (HDS) process, on the other hand, is the state-of-the-art technology in North America. It generates a dense sludge with less volume and better particulate properties. Furthermore, the typical gelatinous nature of the sludge changes to a granulated, sand-like texture.

Boliden Apirsa, S.L. investigated the feasibility of an HDS process to increase the treatment capacity of their existing plant, and resolve the issues associated with the LDS process for their Los Frailes project. The project required, given that the production of ore was going to be doubled, a significant increase in water was needed without altering the water reservoir sitting north of the concentrator. In addition, the final effluent quality was a priority issue. First, a pilot-scale study was undertaken in 1996, and parameters critical to the design and performance of the process were determined. The results showed that the HDS process could significantly improve the sludge characteristics by increasing the solids fraction from 1.5 to 12.0%, thereby decreasing the sludge volume to be disposed to the tailings ponds by a factor of 10. A full-scale, HDS lime neutralization treatment plant for an average flow rate of 1500 m^3/hr was designed and was commissioned in early 1998 in collaboration with Golder Associates, Ottawa, Canada. So far, the full-scale treatment plant has been generating a sludge with more than 30% solids content, exceeding its target value of 12% solids. It produces excellent effluent quality, and scaling in the handling equipment is virtually eliminated. The sludge has dense, easily settable granular particles rather than fluffy flocs, yet has low viscosity that facilitates its unassisted gravity flow. The process has resulted in an increase in the treated water volume. The rate of lime consumption per unit volume of water treated also decreased.

The process principles and the steps taken in process development will be discussed and the results obtained to date will be summarized in this communication.

INTRODUCTION

Boliden Apirsa, S.L. has been operating an open pit mine to produce Cu-Pb-Zn concentrates in Aználcollar, Spain. Before the closure of the old Aznalcóllar open pit mine, the company discovered a new reserve Los Frailes in the same area and decided to continue with the mining activities. At the site, tailings resulting from the floatation processes as well as wastewater from the milling processes, the old pit, seepage and surface runoffs were collected in a pond. The water in the impoundment was acidic and contained heavy metals such as iron (Fe), zinc (Zn), manganese (Mn), Lead (Pb), and cadmium (Cd). This water was treated for the purpose of recovery and recycling, by neutralizing the acidity and precipitating metals as their hydroxides with lime (e.g., $Ca(OH)_2$) at the water treatment plant (WTP). A portion of the neutralized "clean" water was recycled back to the process as "reclaim water" and the remaining excess water was discharged to the nearby river. The resulting sludge was disposed into the impoundment along with tailings.

Development of the New "Los Frailes" Project and Requirements

During the development of the new open pit mine Los Frailes project, Boliden Apirsa aimed to increase the production rate compared to the previous production rates used at the site, requiring an increase in the capacity of the dressing plant (or concentrator) for milling and floatation processes. In addition to the mechanical modifications required in the dressing plant, achievement of these objectives would depend on the presence of high quality process water in large quantities including fresh and reclaim water sources. The capacity of the existing WTP at the site had to be increased from 1000 to 1500 m^3/hr for the treatment of more acid water and production of about 50% more reclaim water. Furthermore, the final effluent quality was a priority issue. The existing WTP at the site was operated based on a straight lime neutralization method and it generated low density sludge "LDS" containing 1-2% solids which was characterized by a large volume of fluffy sludge with slow settling properties. The main concern was that, despite the presence of two large clarifiers with 40 m diameter, the existing WTP system could not handle the treatment of increased acid water flows mainly because of poor sludge characteristics. The LDS would decrease the holding capacity of the existing clarifiers, and, consequently, would suppress the treatment capacity of the existing WTP to handle increased feed flows.

The options to handle the increased feed flows would include:

- construction of a third clarifier in addition to the existing two;
- implementation of a new treatment process at the site which could generate denser and less voluminous sludge with rapid settling properties;
- combination of adding a new clarifier and implement a new treatment system.

The first option presented shortfalls; although it would be sufficient to meet the treatment needs, it could not produce high quality reclaim water in large quantities due to LDS. In addition, since the amount of the treated water would not be increased, it would result in consumption of a large quantity of lime. As a result, the second option appeared to be more viable.

Water management at the Boliden Apirsa site

Before the tailings pond dam failed in April 1998, the Aznalcóllar tailings (North and South) ponds were used for the disposal and storage of tailings, sludge and wastewater from different sources. As mentioned above, the wastewater collected in the ponds was treated and reclaimed. The excess portion was discharged to the Agrio River. The quality of the treated water, in terms of pH and metal concentrations, have been continuously monitored to meet the limits set by the Spanish Environmental Authorities.

Following the dam failure, the site water management plan has been modified. Currently, the old Aznalcóllar pit has been employed for disposal and storage of tailings, sludge and wastewater, instead of the tailings ponds. Similar to the previous practice, wastewater from all sources including the water from the Aznalcóllar pit and surface runoff and consolidation water from the old tailings pond area have been treated for their recovery and reuse in the dressing plant. Figure 1 illustrates the site water management plan.

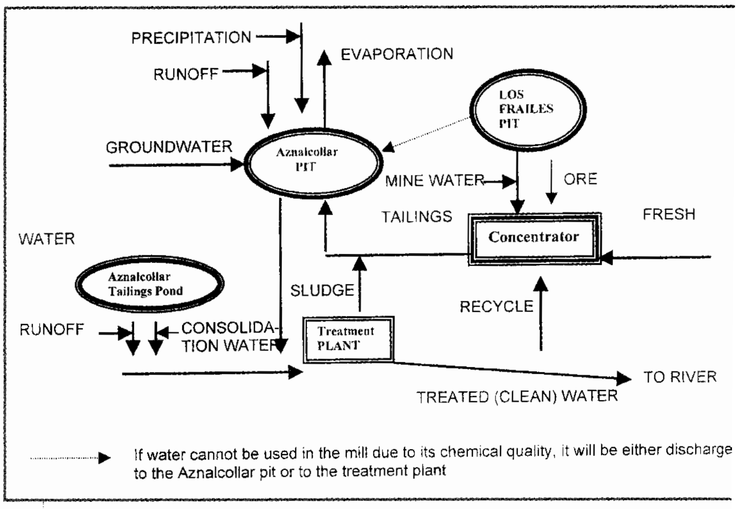

Figure 1. Water Management at the Boliden Apirsa Site.

Approach for the development of new Water Treatment Plant (WTP)

Boliden Apirsa, S.L. first evaluated the capability of the high density sludge "HDS" lime neutralization process as an alternative to the ongoing low density "LSD" process to improve sludge characteristics. A pilot-scale test was undertaken at the site in June 1996, to demonstrate the capability of the process to produce high density sludge and, if successful, to determine process design parameters and unit operation requirements for adaptation of the HDS process to the existing system. Based on favourable pilot-scale results, the company decides to implement the HDS process for treating an average flow rate of 1500 m^3/hr acid water

In this paper the basic principles of the lime neutralization process and the HDS method as well as the pilot test and the results obtained are described. In addition, process design parameters and unit operation, implementation of the process to the Boliden Apirsa site and the results obtained from the plant to date are discussed.

LIME NEUTRALIZATION AND HIGH DENSITY SLUDGE PROCESS

Characteristics of mining water and lime treatment

Effluents discharged from mining and metallurgical operations may contain heavy metals such as iron (Fe), zinc (Zn), copper (Cu) and lead (Pb), and sulphate (SO_4). These waters can be treated for the neutralization of acidity, precipitation of heavy metals and removal of SO_4 using lime neutralization (Kuyucak, 1995 and 1998). Lime is used as either quicklime (CaO) or hydrated lime ($Ca(OH)_2$). The lime treatment of acid mine water is presented by the following equation, where metal cations in solution react with the hydroxide ions and precipitate as metal hydroxides. SO_4 ions form insoluble gypsum complexes ($CaSO_4 . xH_2O$) with calcium ions. The resulting precipitate, called "sludge" consists of metal hydroxides and gypsum. The sludge has to be handled with care for its disposal and long-term storage.

$$M^{2+} + SO_4^{2-} + H^+ + Ca^{2+} + 2\,OH^- \longrightarrow M(OH)_2 + CaSO_4 + H_2O$$

Iron in mining effluents may exist as Fe^{2+} (ferrous) or Fe^{3+} (ferric). Due to its lower solubility and the chemically more stable nature of ferric hydroxide ($Fe(OH)_3$), ferrous iron is oxidized to ferric state (Chusnie, 1984; Kuyucak et al., 1991a). The oxidation of iron in solutions is usually obtained by aeration.

Lime neutralization methods

Basic technology

A lime neutralization system typical of basic technology commonly used in the mineral industry is depicted in Figure 2.

The acid water is first mixed with lime slurry directly in a pond or in a mechanically agitated and aerated neutralization tank (US EPA, 1983; MEND/CANMET, 1994). In tank application, single stage or two-stage neutralization may be employed depending on the characteristics of the acid water and the neutralization chemicals. Then, a flocculant may be added to the neutralized water to promote settling. A clarifier or a settling pond is used for solid-liquid (i.e., sludge) separation. The overflow, i.e., treated water, is discharged to the environment or is recycled back to the process.

Although this technology is widely practised, it generates low density sludge with 1%-2% solids requiring a large volume for settling/clarification ponds or clarifiers and large areas for sludge disposal and storage. The amount of water recovered is low due to the large low density sludge volume generated.

High Density Sludge Method (HDS)

This is a mechanical technique used to improve the physical properties of the sludge. The major differences between basic lime neutralization and the HDS methods can be seen by comparing Figure 2 to Figure 3. As shown in Figure 3, a portion of the underflow sludge is recycled back to the treatment process (Knocke and Kelley, 1987; Yamabe, 1990; Kuyucak, 1998). The recycled sludge is used in the process along with lime in dry or slurry form. The neutralization of the water and oxidation of Fe^{2+} take place in the chemical oxidation reactors (or neutralization tanks). Flocculant is added to the neutralization tank overflow to enhance the settling. The flocculated slurry flows into a clarifier/thickener ("HDS Thickener"). The overflow from the clarifier is discharged to the environment or is reclaimed. Excess underflow sludge is disposed as sludge wastage. The process can be adapted to conventional equipment.

Benefits of the HDS process

The HDS process is considered as the state-of-the-art lime neutralization method which offers attractive potential for minimizing waste sludge volumes. In North America, it has been proven successful (MEND/CANMET, 1994) for generating a denser sludge that contains >10%S, yet flows by gravity due to its low viscosity. The particles are more granular and hydrophobic in nature, tending to attract heavy metals and repel water, and settle rapidly and drain readily to achieve high solids content (~30-40% solids) during their disposal. The need for a large clarifier is reduced. Due to the small sludge volume, the cost of

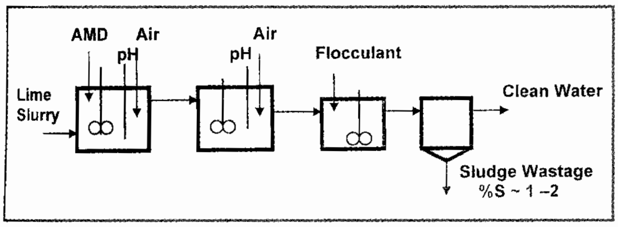

Figure 2. Lime addition to neutralization reactors: Basic-Conventional Method.

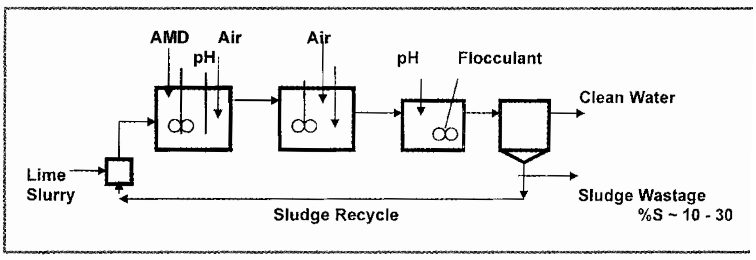

Figure 3. High Density Sludge "HDS" Process.

waste sludge pumping and treatment per unit volume of treated water (i.e., more water is recovered for the same quantity of lime consumed) is reduced. Scaling in the process equipment is eliminated or minimized. The sludge is chemically and physically more stable (i.e., less metal leachability and less disturbance by wind) during its subsequent disposal/storage in an impoundment.

HDS Process principles and critical parameters

The high %S and reduced sludge volume obtained in the HDS method are attributed to the controlled neutralization and oxidation rates, absorption of metals by ferric iron precipitates and better crystal formation due to saturated concentrations of gypsum (Burkhart and Voigt, 1986). A relation between gypsum crystallization, its size and morphology to %S of metal hydroxide sludges have been established with SEM analyses (Kuyucak et al., 1991a, b). The recycled gypsum particles play a "seed" role and promote particle growth and crystal formation. Parameters critical for the process performance briefly include:

- Neutralization rate
- Oxidation rate and the ratio of Fe^{2+}/Fe^{3+}
- Sludge recycling rate
- Crystallization
- Aging of the sludge

PILOT STUDIES AT BOLIDEN APIRSA SITE

Water quality

The quality of the water that was treated during the pilot studies and the limits set by the Spanish Environmental Authorities for the treated water are shown in Table 1.

Parameter	Acid Water (mg/L)	Limits (mg/L)
pH	3.5	5.5 - 9.5
Copper (Cu)	16.71	<0.2
Iron (Fe)	113.4	<2
Zinc (Zn)	573.2	<3
Lead (Pb)	2.67	<0.2
SO_4	5276	<2000

Table 1. Acid water quality and limits at the time of process development.

Equipment

A small pilot equipment setup was designed and constructed at the site. The process flowsheet and important parameters associated with the operation were as given above in Figure 3. The equipment consisted mainly of five tanks of different sizes and a clarifier. All tanks were instrumented with appropriate mixers and aerated as required. The process control was manual for pH adjustment. Only acid water and lime slurry were pumped into the reactors. Gravity flow was used for the flows between reactors and the clarifier, and for the discharge from the clarifier.

The lime slurry and recycled sludge were blended in the sludge/lime mix tank at the head of the process. This mixture was discharged to the rapid-mix tank, which achieved partial neutralization of the acid water entering the process. The principal treatment took place in two neutralization tanks which provided a retention time of 60 min for a combined flow of 1 L/min acid water and recycled sludge (i.e., 25% of inflow rate). The pH was controlled in the neutralization tanks in the range of 9.5 to 10.5, which was sufficient to reduce metals to below the regulated standards. The slurry from the neutralization reactors was treated with a dilute flocculant solution prior to entering the gently agitated floc-mix (or flash-mix) tank. This vessel ensured good floc formation prior to clarification.

Chemicals

A slurry of 5% hydrated lime ($Ca(OH)_2$) was prepared as a source of the alkaline reagent. A synthetic polymer (Nalco 677SC) of 0.05% strength was used to provide 3 mg/L of flocculant concentration in the process.

Monitoring and analyses

The clarifier overflow (i.e., treated water) was monitored for pH, metals and SO_4, with samples taken daily at Boliden Apirsa's analytical laboratory. Metal concentrations were analyzed by an atomic absorption spectrophotometer and SO_4 concentrations were determined by the standard gravimetric method. Thickened sludge from the clarifier underflow was sampled at four hour intervals and was analyzed for its %S and chemical composition. Sludge settling rates were determined on the samples taken from the clarifier inlet by recording the interface distance between the clarified water and settling solids vs. time in a graduated cylinder.

Parameters for pilot evaluation

The process was first designed and operated to determine the capability of the process. The primary objective of the pilot test was "Proof of the Concept". Then, once the process reached a state at which a sludge had about 9-10% solids, the characteristics of the sludge generated by straight liming were compared to those produced by the HDS process. In addition, the rate of lime consumption, flocculant consumption, sludge production and the frequency for purging the sludge were investigated. Design and scale-up parameters were obtained for the implementation of a commercial scale HDS process to the site.

PILOT TEST RESULTS

The results obtained from the pilot tests showed a substantial increase in sludge %S and a decrease in sludge volume (Table 2). Based on the pilot test results it was calculated that the treatment of 1500 m^3/hr acid water would result in about 432 m^3/hr of sludge at 1.5% S. This quantity could be lowered to about 43 m^3/hr at 10% S or to 22 m^3/hr at 20% S.

Test	Sludge density (%S)	Settling Velocity (m/h)	Final Effluent (mg/L)	Zn	Fe	Cu	Pb	SO_4	pH
LDS	1.75	0.7	F	0.08	0.05	0.02	0.00	2892	-
			UF	0.34	0.17	0.06	0.00	2962	9.7
HDS	11.9	0.8	F	0.02	0.00	0.00	0.00	2098	-
			UF	0.05	0.05	0.01	0.00	1985	9.77

LDS: Straight liming - simulation of the existing treatment process with the pilot test setup; F: Filtered; UF:Unfiltered
Table 2. Pilot test results.

The effluent quality (i.e., clarifier overflow) for the unfiltered samples was better than that produced with the LDS process. For instance, Zn concentrations were found to be 0.34 for LDS and 0.05 mg/L for the HDS process. The SO_4 concentration was lowered from 5276 in the acid water to less than 2000 mg/L with the HDS process whereas the LDS process could not decrease it less than 2900 mg/L. After 24-h of operation, the LDS process showed heavy scaling in the form of a thick white crust at the walls of the neutralization reactors and the clarifier. There was no scaling in the equipment when the HDS process was employed.

The chemical analysis of the sludge samples confirmed that SO_4 was incorporated into the sludge as gypsum. It was evident from the data given in Table 3 that the amount of gypsum contained in the sludge samples was increased as the sludge %S increased. The SO_4 contained was increased from 54.8% to 74.5%, when the sludge %S rose from 1.7% to 11%. Reduced scaling with the HDS process observed can be attributed to inclusion of SO_4 in the sludge as gypsum rather than precipitating on the surface of the equipment. The colour of the sludge generated by the HDS process was dark brown, the sludge particles were rounded and had a sand-like texture.

% Solids	Zn	Cu	Fe	Gypsum*
4.5	8.26	0.37	1.75	54.8
6.35	7.4	0.3	1.51	62.57
9.3	7.5	0.33	1.54	64.5
10.96	7.4	0.33	1.63	70.95
7.49	7.49	0.33	1.48	72

* All results are in %
Table 3. Relationship between % solid and gypsum content of the sludge.

In spite of its "thixotropic" nature, the sludge could easily flow by gravity from the clarifier underflow, at which point the %S was more than 10. The settling velocities ranged between 0.6 - 1 m/hr. Higher velocities were observed for the sludge samples with good physical characteristics (i.e., particle size, texture). Based on the successful results of the pilot test, it was decided to implement the HDS process on the site.

IMPLEMENTATION OF THE FULL-SCALE PROCESS TO THE APIRSA SITE

Process description

The new treatment system was designed by Golder Associates (Ottawa, Canada) to treat an average flow of 1500 m^3/hr acid water with a peak capacity of 2000 m^3/hr. Boliden's engineering group (Contech AB, Skelleftea, Sweden) carried out the detailed engineering design, construction and instrumentation of the plant in collaboration with the Boliden Apirsa site personnel.

The system, except the lime/sludge mix tank, has been arranged in two parallel units to provide flexibility for maintenance, downtime operations and peak flow conditions as illustrated in Figure 4. Key unit operation segments of the process scale up included: lime slurry unit and slurry feed control; reactors with ample retention time and equipment for agitation, oxidation and aeration; clarification and thickening; and process control. Aeration was obtained from air compressors. Although all the system was constructed new, the clarifiers and the lime slurry preparation unit were upgraded by modifying a few components (i.e., mixing system, feed well, rake and launder) to lower the overall operating cost of the plant. The process uses a slurry of hydrated lime ($Ca(OH)_2$) as it was in the past. Except for the flocculant preparation and process control units, the treatment plant was placed outdoors and designed in a cascade form. All reactors, except the sludge/mix tank, were made of concrete and were installed with appropriate mixing and aeration devices. Lime slurry, acid water, flocculant and recycled sludge have been added to the system with the help of pumps, as the rest of the system operates based on gravity flow.

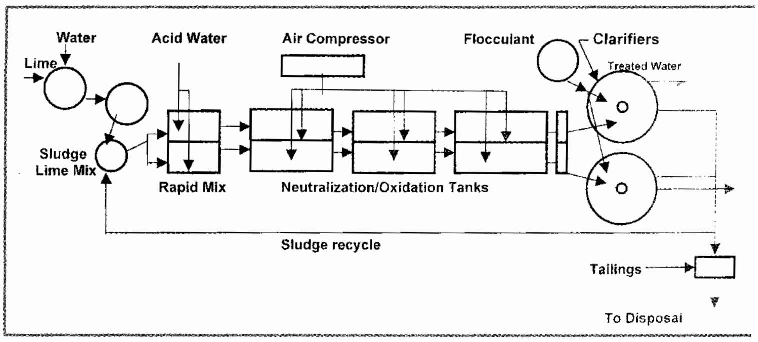

Figure 4. Boliden Apirsa HDS lime neutralization treatment plant.

Process start up

During the plant start up, one unit of the treatment plant (or half of the system) was used. The other half continued to be operated with the old method. With this system, the target feed flow rate would be 750 m^3/hr. During the early stage of the start up, sludge level measurements, acid water flow settings and sludge purge were performed manually. Operational conditions such as sludge recycle rate, sludge purge rate and sludge depth in the clarifier were optimized during the commissioning of the plant. Flow meters and pumps were calibrated. Pumps and agitators were checked for their power consumption. The type and concentration of polymer were verified and the location of polymer addition was modified. The system was deliberately shut down and re-started. Both manual and automatic re-start systems were checked for their performance.

Process control and sludge disposal

The plant has been reasonably well automated, such that operations require minimum labour and attention. A PLC (Programmable Logical Control) 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, air blow 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. The pH is measured at the outflow of the first neutralization tank and the signal from the pH probe operates the outflow of the lime slurry tank. The pH measurement at the output of the second reactor ensures the completeness of the neutralization and oxidation processes. The sludge level indicator sensor controls the sludge level in the clarifier. A high and low level is set for the sludge in the clarifier and monitored by the sensor. 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. The effluent turbidity in the clarifier is also monitored with the help of a sensor. All values can be observed from the computer screen.

The sludge is disposed along with tailings to the tailings disposal impoundment, such as a pond or pit. The sludge purging takes place for about 6 hours every few days, i.e., 2 or 4 days depending on the flow rate and chemical composition of the acid water treated.

Results obtained during the plant start up and today

The process start up took about three weeks of intense work. First the system was operated based on the optimal parameters found during the pilot tests and observations and tests were done at every component of the process. Then, modifications to improve and optimize the performance of the plant and the treatment efficiency of the process were implemented as required. The work done and results obtained are summarized below.

Activity (week #)	Feed flow (m^3/hr)	Sludge %S	Settling rate (m/hr)	Metal ions (mg/L)					
				Cu	Pb	Zn	Fe	Mn	SO_4
Acid water	–	–	–	18	4	470	95	100	4863
Objectives	1500*	>10*	>0.8*	0.04(d)	0.05(t)	1(t)	2(t)	1(t)	<2000
Bench test	1 L	1.2 – 1.7	0.6	0.01	0.1	0.03	0.00	0.00	>3000
Week 1	150-250	>9	>0.8	0.15 [0.00]	0.07 [0.07]	3.12 [0.03]	0.52 [0.00]	0.33 [0.00]	2004 [1983]
Week 2	500	18-20	>0.9	0.13 (0.00)	0.09 (0.09)	2.96 (0.05)	0.00 (0.00)	0.29 0.03	2095 (2015)
Week 3	750	16-18	>0.9	0.17 (0.00)	0.15 (0.00)	2.67 (0.08)	0.22 (0.02)	0.27 (0.02)	2235 (2109)
Steady-state**	1500	30	>0.9	<0.003	<0.003	0.006	0.02	0.003	~2000

[ ] Filtered samples; ( )Rested samples; (d) Dissolved; (t) Total (unfiltered sample); *Objectives set by Boliden; **At steady-state, all metal analyses are done on non-filtered samples (by Denga S.A. Madrid, May 21, 1999 sample).

Table 4. Results obtained during the plant start up.

At the end of the first week, about 10% solids content was obtained in the clarifier underflow. The initial settling rate of the sludge was about 0.8 m/hr. The results obtained for sludge %S and the effluent quality as well as acid water quality and objectives are presented in Table 4, on a weekly basis for the first three weeks. The effluent quality on unfiltered samples had high suspended solids (SS) and, consequently, contained elevated levels of metals (e.g., Zn, Fe) whereas the metals were either very low or below the detection limits in the filtered samples. The SO_4 concentrations were about 2000 mg/L.

At the end of the second week, about 20 %S was achieved. The sludge was easily flowing by gravity and had a particulate granular texture visible to the eye. The sludge initial settling rates were always above 0.9 m/hr. However, the effluent was still high in SS. Instead of filtering, to understand whether the reason for high SS was physical or chemical, the effluent samples were left still for about two hours in the bottle ("Rested Samples") before analysis. The decant from the rested samples was analyzed and the results were compared with those obtained from the original clarifier overflow samples. Metal levels in the rested samples were well below the regulated limits, being either very low or below detection limits of the equipment used for analysis. This indicated that the cause for the high SS in the effluent was physical, and settling conditions in the clarifier needed improvements (i.e., better flow distribution and less turbulence). To correct the cause, a drop-box was designed and installed in the clarifier feed-well.

In the third week, the system performed well and the clarifier handled the high flow rates as required. The sludge recycling rate was optimized. The sludge purge was practiced. The equipment had no scaling at all at the end of the third week. However, the quality of the effluent was similar to that obtained in the second week in that it retained similar levels of SS, showing that the clarifier feed-well would require further modifications.

About one month later, the process gradually reached its steady-state. Following the final modifications on the clarifier, it has produced an excellent effluent quality and sludge with about 30%S which could easily flow by gravity.

CONCLUSIONS

A full-scale treatment plant based on the High Density Sludge HDS process was implemented at the Boliden Apirsa site. It has been generating a sludge with more than 30% solids content, exceeding its target value of 10% solids. It produces excellent effluent quality and scaling in the handling equipment is virtually eliminated. The sludge has dense, easily settleable granular particles rather than fluffy flocs, yet has low viscosity that helps its unassisted flow by gravity. The process has resulted in an increase in the treated water volume. The rate of lime consumption per unit volume of treated water has also decreased.

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