A Pilot Optimisation of Sulphate Precipitation in the High-Density Sludge Process

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Abstract

High sulphate concentrations can cause issues both in a mine's process water recycle and for effluent discharge. This is the case for the Neves-Corvo mine in Portugal. A large study looked at control of sulphate and the part presented here details the optimisation of sulphate removal in the high-density sludge (HDS) process. The HDS process was operated at different pH setpoints, varying sludge recycle rates, and several different reactor retention times for three different water sources. An added step in the process was the addition of carbon dioxide to precipitate calcium carbonate and further minimise the gypsum saturation level. The tests defined optimal HDS conditions to provide improved feed conditions for nanofiltration or for non-scaling process water.

Keywords: Sulphate removal, HDS process, gypsum precipitation, calcium carbonate, nanofiltration, reverse osmosis

Introduction

The Neves-Corvo Mine is located in Baixo (Lower) Alentejo, on the south edge of the Iberian Pyrite Belt. The nearest town is Castro Verde, Portugal. It is operated by Somincor (Sociedade Mineira de Neves Corvo SA), a subsidiary of Lundin Mining. Neves-Corvo is the biggest copper and zinc mine in the European Union and has been in operation since 1988.

Prior to 2014, the mine had experienced problems with site water quality, both internally and in their final effluent. A project was initiated to evaluate commercially available options which could be applied to meet the water needs, both for effluent discharge to the environment and for internal use and consumption as a process water recycle. Within this project, a pilot plant study was completed to evaluate the most economic and efficient process to oxidise thiosalts, precipitate metals, and to reduce sulphate concentrations. The base process of the pilot campaign was the conventional HDS process.

In addition to the HDS process, the pilot test plan included thiosalt oxidation and various sulphate removal techniques such as barium hydroxide precipitation and membrane filtration (both nanofiltration and reverse osmosis). These other tests are discussed in a separate paper (Aubé et al, 2018).

This paper presents the new and extensive tests reviewing all aspects of the HDS process to decrease total dissolved solids in the treated effluent. The HDS process was operated at different pH setpoints, varying sludge recycle rates, and several different reactor retention times. This was done for three different water sources: 1) acid water, 2) process water including thiosalts, and 3) nanofiltration concentrate. The results are detailed in the next sections for these three types of feed waters.

The results of the pilot test were used to design the full-scale treatment plant with confidence. The process setpoints developed in these tests could be applicable to other mine sites around the world for improved HDS treatment and minimisation of the gypsum saturation level and total dissolved solids concentration.

Materials and Methods

The pilot plant was operated on-site at the Neves-Corvo Mine continuously from October to December 2015. As shown in Figure 1, the pilot plant was built inside a 40-foot-

Figure 1: Pilot plant used for the study

long maritime container. The pilot plant was provided by Wood (formerly Amec Foster Wheeler). The two pools near the plant were used to prepare different feed water qualities expected under future mine operating conditions.

The pilot plant consisted of a series of engineered PVC reactors equipped with baffles and risers. Agitation was provided using radial impellers when the reactor was also aerated or axial impellers when there was no gas sparging. The design flowrate of the plant was 2 L/min, but it was sometimes operated at 1 L/min for certain tests. A 150-cm high and 50-cm diameter clarifier with a conical bottom and a rake system was used for solid/liquid separation. The pilot plant was also equipped with a membrane filtration skid for nanofiltration or reverse osmosis.

A programmable logic controller (PLC) system allowed the pilot plant to run unattended for short periods of time and to log key parameters. Reagents, including lime slurry, hydrogen peroxide, ferric sulphate as catalyst, an anionic flocculant, barium hydroxide and carbon dioxide, were fed from reagent storage tanks. Lime feed was controlled by pH and other reagent addition rates were controlled by flow. Air was sparged into reactors when ferrous oxidation was required, and carbon dioxide was used for calcium carbonate precipitation.

Physico-chemical parameters and reagent storage tanks levels were recorded several times per day. The solids content of the different reactor slurries and of the clarifier sludge were measured regularly. Filtered samples were taken twice daily from all reactors to monitor the dissolved concentrations of key elements.

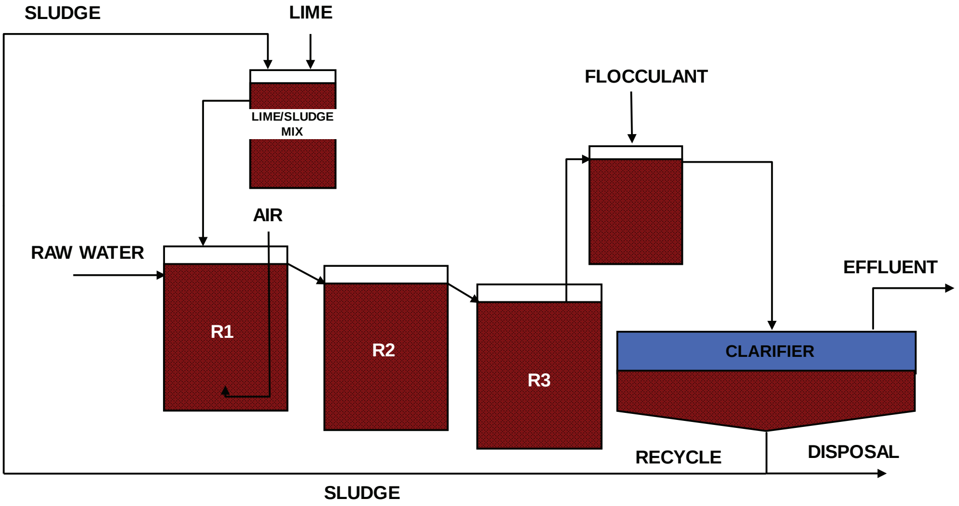

Figure 2: HDS process

Description of Processes

The central component of the pilot plant was an HDS system that allowed enough flexibility to evaluate different retention times, pH setpoints, and sludge recycle flowrates (Figure 2). The HDS process is well-known and described in detail elsewhere (Aubé and Lee, 2015). As a summary description of the HDS process applied here, high-sulphate water was contacted with a mixture of recycled sludge and lime slurry in a reactor. The quantity of lime slurry added in the Lime/Sludge Mix Tank was controlled to maintain the pH of the overflow in the first reactor. Neutralisation reactors were added as needed to provide additional retention time. This formed a slurry consisting of treated water with fresh precipitates combined with recycle sludge solids. This was then flocculated and fed to a clarifier for solid-liquid separation.

To meet the site water objectives, additional process options were evaluated. Notably, a thiosalt oxidation reactor using Fenton's reagent was installed upstream of the HDS for some of the tests. A barium hydroxide reactor was also introduced in the HDS process to precipitate sulphate as barium sulphate for two of the tests. Nanofiltration and reverse osmosis membranes were tested on the feed water upstream of the HDS process and on the HDS effluent. Those distinct process arrangements resulted in different water qualities being evaluated in the HDS section of the process.

Fenton's reagent is a combination of peroxide and iron (Rolia, 1984). These tests, as well as the barium precipitation and membrane filtration tests, are discussed in Aubé et al, 2018.

Acid Water Tests

The first water tested was an acid water source from the tailings area named Cerro do Lobo (CdL). This acid mine drainage (AMD) contains tailings runoff and residual process water from the paste tailings disposal. It is characterised by a low pH near 2.6 and high Fe content averaging 213 mg/L (total). The total sulphate content averaged 4,577 mg/L. This water also contained high Na (983 mg/L), Ca (627 mg/L), and Cl (565 mg/L). The sodium chloride content is mostly from the ore. This salinity significantly affects the equilibrium saturation level of gypsum in the HDS process as the activity (or effective concentration) is decreased for the calcium and sulphate.

CdL water was fed to the HDS process for treatment at pH 10.0 with reactor retention times varying from 0.5 to 4.0 hours. The sludge densification was very efficient, with the minimum target of 20% solids attained within 2.5 days of operation. The highest sludge density attained was 35% solids, without any pumping or viscosity problems. The sludge recycle rate was controlled to maintain a target reactor solids content between 30 and 40 g/L. As gypsum tends to form more readily onto existing gypsum precipitates, higher reactor solid contents serve to offer more precipitation sites onto which the dissolved sulphate and calcium can precipitate. However, the amount of solids to be maintained in the reactor is limited by the flocculation efficiency. If the reactor solids content is too high, the flocculant will not attach to a sufficient fraction of the particles and the clarifier overflow will contain a high total suspended solids (TSS) content. Despite this theory, even at reactor solid contents as high as 45 g/L, the clarifier overflow turbidity and total

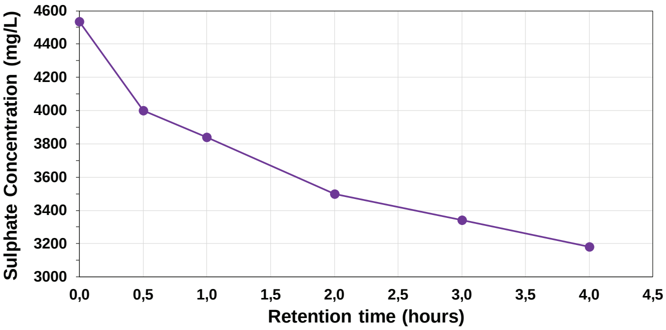

Figure 3 *Sulphate concentration versus retention time for CdL waters*

suspended solids content were low, averaging of 4.2 NTU and 10.7 mg/L TSS. In the best conditions, the TSS was maintained below 4 mg/L.

Figure 3 shows that increasing the retention time up to 4 hours incrementally increased gypsum precipitation and sulphate removal. It is clear that the higher retention time improved sulphate removal as even between 3 and 4 hours retention time, there was an added sulphate removal of 160 mg/L.

The final sulphate concentration attained at Neves Corvo (3200 mg/L) is high in comparison to what is achievable with HDS treatment at other mine sites. This is due to the very high sodium and chloride concentrations of the Neves Corvo waters. This high salinity increases the solubility of all other elements in solution. Despite this comparatively high final concentration, the data clearly indicate that sulphate precipitation as calcium sulphate (gypsum) is improved with increased retention time.

Process Water Tests

A synthetic water was generated on site to simulate future operating conditions. The mixture was composed of 50% CdL water, 30% overflow from the paste tailings thickeners, and 20% mine water. This process water was blended in two 55 m^3 pools and fed to the pilot plant. The water is characterised by a pH that ranged from 2.7 to 3.3, Fe content averaging 94 mg/L and sulphate averaging 3692 mg/L. Thiosalt concentrations averaged 467 mg/L. Ca, Na and Cl concentrations are respectively 702, 906 and 505 mg/L.

Fenton's oxidation (hydrogen peroxide catalysed with ferric sulphate) in the first reactor was used to oxidise thiosalts prior to treatment by the HDS process in subsequent reactors for metals and gypsum precipitation. This process is detailed in Aubé et al, 2018. Essentially, oxidation with Fenton's reagent converts the thiosalts (thiosulphates and other polythionates) to sulphate.

In the HDS portion, three pH setpoints (10.5, 11.0 and 11.5) were tested to evaluate the effect on sulphate removal. Filtered samples from each reactor were analysed to evaluate the progression of gypsum precipitation (Figure 4). This figure shows an increase in sulphate concentration in the Fenton Reactor, despite some gypsum precipitation occurring simultaneously in this reactor. Complete thiosalt oxidation alone would have produced in the order of 800 mg/L of sulphate and the increase in Fenton's Reactor was in the order of 200 mg/L.

Figure 4 shows two important conclusions from the trials: an increased retention time up to 5 hours clearly shows improved gypsum precipitation, and a pH setpoint of 11 improves sulphate removal over pH 10.5 or 11.5. There appears to be only a slight improvement of sulphate removal beyond the 5-hour retention mark, but this is unclear.

During this test, the sludge density generally varied between 20 to 30% solids. The reactor solid contents often exceeded the maxi-

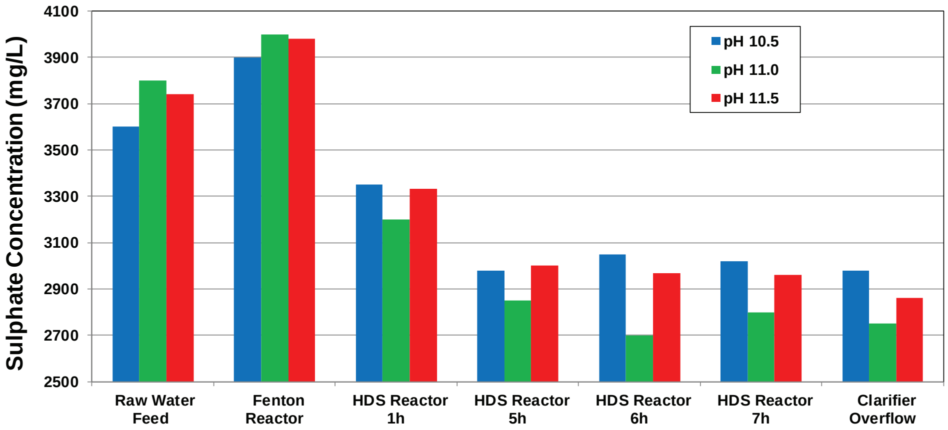

Figure 4 *Sulphate concentrations throughout the Fenton-HDS process*

mum target of 40 g/L, even going beyond 60 g/L at times. Despite this, the clarifier overflow remained clear and the TSS was maintained well below the target with an average of 8.4 mg/L.

Nanofiltration Concentrate Tests

Nanofiltration tests were conducted to remove sulphate to low levels, meeting strict guidelines of 250 mg/L for discharge (Aubé et al, 2018). The results presented here are from a test where the sulphate-rich concentrate issuing from membrane filtration was treated using HDS. Prior to nanofiltration (using an NF270 membrane), the process water had been treated via Fenton-HDS, as per the previous section, removing metals and thiosalts. Therefore, the concentrate treatment in this 5-hour HDS test was focused specifically on sulphate removal.

The nanofiltration concentrate fed to the HDS process had an average pH of 4.7 with sulphate at 4500 mg/L, Ca at 856 mg/L, Na at 1000 mg/L and Cl at 462 mg/L. As the water fed to the nanofiltration membrane had previously been treated by the Fenton-HDS process, the thiosalts and Fe contents were low (37 and 1 mg/L, respectively). A key factor to consider is that an anti-scalant (SpectraGuard 250) had been added during the nanofiltration tests. As an anti-scalant is designed to inhibit precipitation, it could affect gypsum formation in the HDS process.

The sludge produced from this process was white and consisted almost entirely of gypsum. It had reached 20% solids content after only 3 days. Two pH setpoints were operated during this test and it appeared that the final sulphate concentration was approximately 100 mg/L lower when operating at pH 11.5 over pH 11.0. It is unclear if the anti-scalant had a significant impact, as the final concentrations attained, though higher than for other tests, are also affected by the higher salinity of the concentrate. A clear and consistent increase in sulphate removal was shown for increased retention times up to 3 hours, beyond which only a marginal increase was measured (67 mg/L).

Reducing Calcium Concentration

Gypsum precipitation, the source of scaling problems, is a function of both sulphate and calcium concentrations. In order to provide an improved water quality for either a membrane feed or for re-use at the mine, decreasing calcium would be a significant benefit. Also, the optimum pH setpoint in the HDS process was defined as pH 11.0, which is above the maximum water quality objective of 10.0. Trials were conducted using carbon dioxide sparging in a final reactor with a 30-minute retention time, prior to the clarifier and solid/liquid separation, to see if both pH reduction and some calcium removal could be simultaneously attained.

The target pH for calcite precipitation requires a balance between the amount of car-

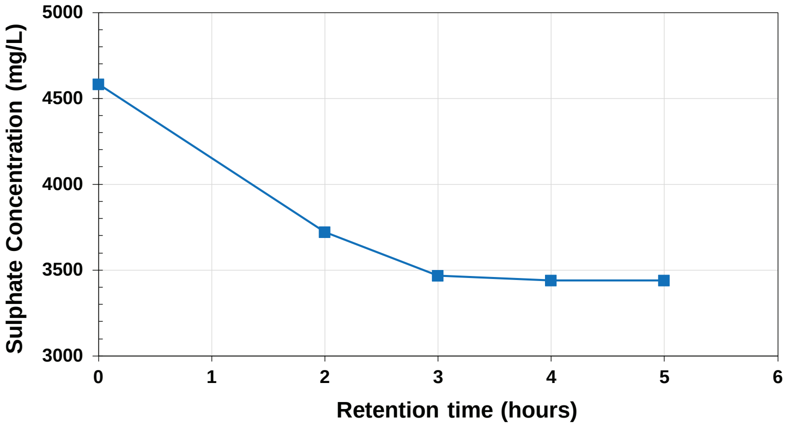

***Figure 5** Treatment of nanofiltration concentrate with respect to retention time*

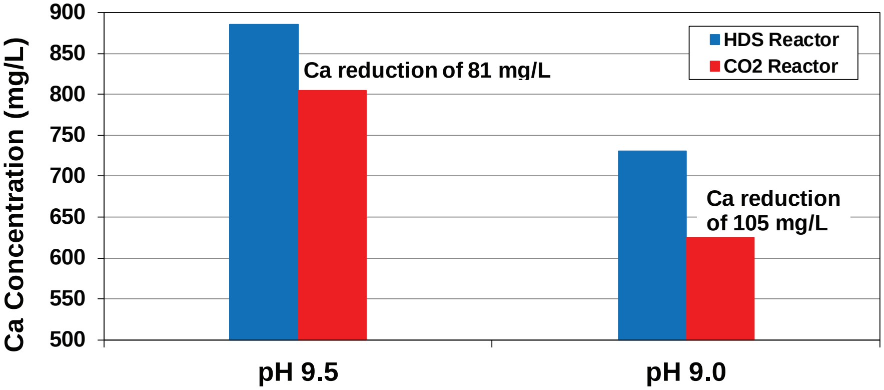

Figure 6: *Calcium removal with carbon dioxide sparging*

bon dioxide added and the form in which it is present. Precipitation only occurs with the CO_3^{2-} form, which is predominant at high pH values. At a pH of 9.0, less than 5% of the total inorganic carbon is in CO_3^{2-} form while at pH 9.5, almost 10% is in the desired form. The results shown in Figure 6 indicate that both these pH setpoints decreased Ca concentrations significantly, with pH of 9.0 showing a slightly better removal with a 105 mg/L difference.

Conclusions

Results of this pilot campaign clearly showed that sulphate removal through gypsum precipitation improves with retention time. Significant added precipitation was shown in all cases for the first 3 hours and marginal improvement beyond 4 hours and up to 7 hours retention.

For treatment of acidic water, a setpoint pH of 11 performed best for sulphate removal. When treating a nanofiltration concentrate, pH 11.5 was slightly better over a setpoint of 11.0.

The pilot results clearly indicated that higher concentrations of gypsum solids in the reactors improved sulphate removal. The tests showed increased sulphate precipitation and a clear effluent with reactor solid contents of up to 60 g/L.

Sparging carbon dioxide in the process as a final step before the clarifier serves to both decrease the final effluent pH and reduce the final calcium concentration, thus producing a treated effluent with lower scaling potential. A setpoint pH of 9.0 showed better results than pH 9.5.

References

Aubé, B., Lamares, M, Lone Sang, S., 2018 "A Pilot Comparison of Sulphate Removal Technologies at Neves Corvo". Paper presented at the 11th ICARD | IMWA | MWD 2018, Pretoria, South Africa.

Aubé, B., Lee, D.H., 2015. "The High Density Sludge (HDS) Process and Sulphate Control", Paper presented at ICARD-IMWA 10th International Conference on Acid Rock Drainage and International Mine Water Association Annual Conference, April 21-24, 2015, Santiago, Chile.

Rolia E., 1984. "Oxidation of Thiosalts with Hydrogen Peroxide", Report CANMET Canada Centre for Mineral and Energy Technology".