



# A Pilot Comparison of Sulphate Removal Technologies at Neves Corvo

Bernard Aubé<sup>1</sup>, Moacir Lamares<sup>2</sup>, Stéphan Lone Sang<sup>3</sup>

<sup>1</sup>*Envirobay Inc., Sainte-Anne-de-Bellevue, Québec, Canada*

<sup>2</sup>*Sociedade Mineira de Neves-Corvo, S.A., Portugal*

<sup>3</sup>*Wood Environment & Infrastructure Solutions, Montréal, Québec, Canada*

## Abstract

The process water at Neves Corvo mine contains high sulphate and thiosalt concentrations, as by-products from the milling and flotation process. The pilot study described in this paper established the most cost effective options for treating thiosalts and sulphates at this site. A prefeasibility study was previously completed to compare existing and proposed sulphate treatment technologies. Only the most promising technologies were studied in the pilot test. Membrane nanofiltration and reverse osmosis were tested extensively, in conjunction with the high-density sludge (HDS) process for pre-treatment and for treatment of the membrane concentrate. Barium sulphate precipitation tests were also completed in conjunction with the HDS process. Thiosalts were successfully oxidised using Fenton's Reagent.

**Keywords:** Sulphate removal, HDS process, nanofiltration, reverse osmosis, barium hydroxide

## Introduction

The Neves-Corvo Mine is located in Baixo (Lower) Alentejo, on the south edge of the Iberian Pyrite Belt in Portugal. The nearest town is Castro Verde. It is operated by Sominor (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. Internal quality requirements were identified as a need for non-scaling water with a pH within the range of 7.0 to 10.0, and non-hazardous.

The Neves Corvo discharge is regulated both by final effluent concentration limits and stricter environmental guidelines to be met in the Oeiras River. The most critical parameters of concern include sulphate ( $\text{SO}_4^{2-}$ ), chloride (Cl<sup>-</sup>), and thiosalts for toxicity. The

sulphate effluent discharge limit is 2000 mg/L and the more stringent receiver guideline that could apply during dry periods is 250 mg/L. Chloride is an issue only during these dry periods, with a guideline of 250 mg/L. In this paper, the term thiosalts is used to represent thiosulphate  $\text{S}_2\text{O}_3^{2-}$  and other polythionates ( $\text{S}_X\text{O}_6^{2-}$  where  $3 \leq X \leq 10$ ). Concentrations of thiosalts were reported as thiosulphate and a target of 10 mg/L was established to ensure that pH depression in the receiver was prevented.

Within this project, a pilot plant study was completed to evaluate the most economic and efficient processes to oxidise thiosalts, precipitate metals, and to reduce sulphate concentrations.

## Raw Water Qualities

In order to design a system that would meet the needs in coming years, two synthetic water qualities called "CdL Sim" and "CdM Sim" were tested during the pilot plant study (Table 1). These synthetic waters were generated on site from existing available water sources. The simulated water was created using tailings water, overflow from the paste tailings



thickeners and mine water (underground de-watering). The proportion of each was determined based on projected future water conditions as predicted by a site water reticulation model.

**Table 1** Raw water qualities

Average Concentration (mg/L)	CdL Sim	CdM Sim
Sulphate	3537	2800
Thiosalt	501	1180
pH	2.7 – 3.3	5.2 – 6.1
Fe	98	0.62
Ca	677	766
Na	885	805
Cl	511	555

### Pre-Feasibility Study

The first phase of the study included a pre-feasibility study (PFS) of different sulphate treatment technologies. Five different technologies were considered as potential components of the required treatment complex. These were the high density sludge (HDS) system, Fenton's oxidation process, barium precipitation, an ettringite process, and membrane treatment. Various combinations and permutations of these treatment technologies were then considered as individual reticulation scenarios, and two levels of flowrates were considered for each. A total of 22 scenarios were thus considered. Each was engineered to a pre-feasibility level in order to develop the Process Flow Diagrams, preliminary Process and Instrumentation Diagrams, preliminary General Arrangements, equipment lists, and associated capital and operation costs.

Detailed water and mass balance modelling suggested that to meet all the site requirements for water, it was necessary to oxidise the thiosalts, treat acidity via HDS and apply one of the three retained sulphate removal technologies. Using the PFS-level cost esti-

mates developed for all 22 scenarios, three specific treatment trains were retained for cost comparison in Table 2. These are:

- Fenton's oxidation, HDS process, followed by ettringite precipitation;
- Fenton's oxidation, HDS process, followed by barium sulphate precipitation;
- Fenton's oxidation, HDS process, followed by membrane treatment.

The costing was completed by obtaining actual quotes for all major equipment, then adding factors for installation (when missing), civil (including concrete, structural, buildings), electrical, automation, and process piping. Engineering and construction management costs were estimated, and a 30% contingency was added to the total. Table 2 shows the results of capital, operating, and net present value costs (CAPEX, OPEX and NPV) of the three treatment trains retained.

The ettringite process costs were estimated in cooperation with a process supplier of good reputation in the mining industry. This process was found to have the highest capital costs and also a very high operating cost, due to the numerous reagents required and the management of large volumes of sludge. For this reason, it was eliminated and not tested at the pilot scale.

Barium sulphate precipitation was very expensive for operation, simply due to the high cost of the barium hydroxide reagent and its limited availability. The capital cost of using barium precipitation, on the other hand, was low as the process step could be integrated in an HDS plant, which was needed regardless of the approach. It was therefore considered worth testing in order to properly define best operating conditions and dosages as a back-up option or on a temporary basis.

Membrane filtration following Fenton and HDS showed the lowest net present value costs. It was determined that membrane filtration would be a viable sulphate removal

**Table 2** Estimated cost of different treatment options (flowrate of 400 m<sup>3</sup>/h)

Proposed Treatment	Total CAPEX (€)	OPEX (€/year)	NPV <sub>8%,20years</sub> (M€)
Fenton + HDS + Barium	≈ 11 000 000	≈ 6 980 000	≈ 80
Fenton + HDS + Membrane	≈ 18 800 000	≈ 3 440 000	≈ 50
Fenton + HDS + Ettringite	≈ 48 800 000	≈ 6 030 000	≈ 108



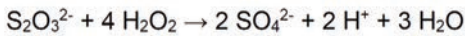
technology to meet the needs at Neves Corvo. Tests were planned with different nanofiltration and reverse osmosis membranes.

## Equipment and Methods

The pilot plant was operated on-site at the Neves-Corvo Mine continuously from October to December 2015. A detailed description of the metal hydroxide and gypsum precipitation section of the plant is available in Aubé et al, 2018. In this paper, the specific processes other than HDS are described.

### Thiosalt Oxidation

Prior to the pilot plant trials, thiosalt oxidation testing using the Fenton reaction was completed at the bench level and also in another smaller pilot trial at a very low flowrate. This reaction uses hydrogen peroxide ( $H_2O_2$ ) as an oxidizing agent. A metal catalyst in slightly acidic conditions (pH 4.0) such as iron can improve efficiency and reduce reaction times. Thiosalts are oxidized to sulphuric acid. In this trial, ferric sulphate was added as a catalyst when needed. The thiosalt oxidation formula is the following:



The thiosalt oxidation tests were integrated as part of the HDS treatment in the first reactor, as shown in Figure 1. Due to acid formation during the oxidation process, alkalinity had to be added during the oxidation

stage. In most tests, pH control was achieved by recycling the clarifier underflow sludge from the HDS neutralisation to this first reactor (R1). The speed of the pump feeding sludge to R1 was controlled on a pH setpoint of 4.0. This meant that no lime was required to control pH in this reactor and the sludge also served to provide seed particles for precipitation. This served to increase particle size, sludge density, and prevented scaling in this reactor. This recycle can also serve to assist in catalysing the reaction as the sludge already contains iron. The remainder of the recycled sludge was directed to the Lime/Sludge Mix Tank to be combined with lime prior to controlling the pH of the HDS process reactor to setpoints ranging from 10 to 11.5.

The thiosalt oxidation part of the process is important in this discussion on sulphate removal as the product of oxidation is sulphate, specifically sulphuric acid. This means that one process step required for water treatment at Neves Corvo includes the formation of additional sulphate, while others are focused on its removal.

### Membrane Filtration Tests

The pilot plant was equipped with a membrane filtration skid including a 100-mm diameter (4”) stainless steel vessel of 1013 mm (40”) in length for operating at a maximum pressure of 2050 kPa (300 psi) and a nominal flowrate of 50 L/min. The raw water was pumped through a pre-filter using a centrifuge

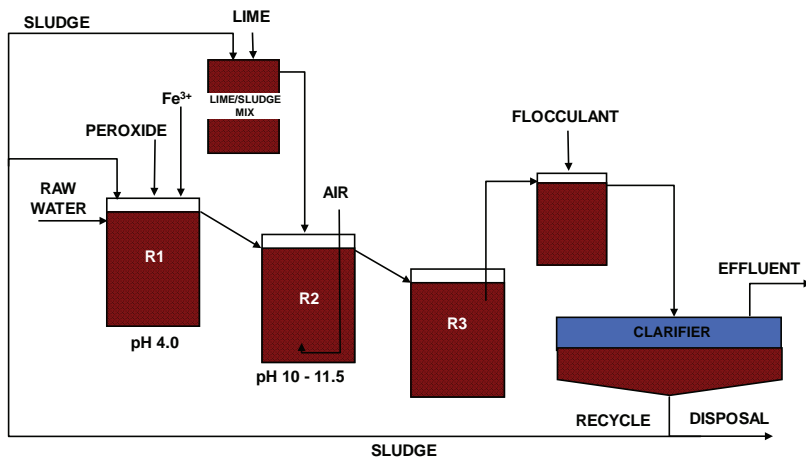


Figure 1 Flowsheet for Fenton's Reagent combined with HDS



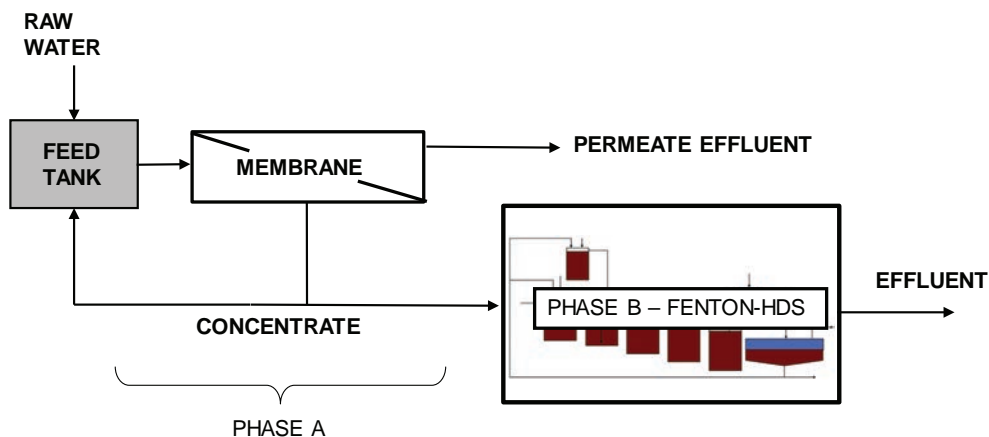


Figure 2 First continuous membrane test configuration

gal pump, prior to the booster pump feeding the membranes. The resulting pressures, flows, and conductivities were monitored continuously. A 100-L reservoir was used for Clean-In-Place (CIP).

Both batch tests and continuous tests were completed using this skid. For the batch membrane testing, two 1000-L totes were required; one was filled with 1000 L of raw water and the second tote served for permeate collection. An initial one-time dosage of an antiscalant was added (at 3.7 mg/L) to the feed tank in order to minimise the potential for membrane fouling from scale formation. Permeate was routed to the graduated permeate storage tank and the concentrate was recirculated to the feed tank. Four different membranes were tested in the batch tests, including two reverse osmosis membranes, BME-4040 and ESPA2-LD-4040 and two nanofiltration membranes: NF90-4040 and NF270-4040.

The objectives of the first continuous test were to confirm the constant permeate water quality for continuous operation of the membrane and to evaluate membrane fouling over time, as well as define the needs for concentrate treatment. The process was configured as shown in Figure 2, with CdM Sim as the membrane feed water. The continuous operation of the membrane was set to represent only 50% recovery rate to minimise fouling of the membrane due to gypsum precipitation. As that recovery rate cannot be achieved in a single pass with the filtration skid used,

partial recirculation of the concentrate was applied. The pilot membrane system was fed at a rate of 20 L/min with 2.5 L/min in permeate production. Therefore, to operate at a 50% recovery rate, 5.0 L/min of raw water was fed and the concentrate bleed was also set to 2.5 L/min. Most of the concentrate (15 L/min) was returned to the feed tank to be mixed with the raw water. The concentrate bleed was then sent to Fenton-HDS treatment, as discussed in Aubé et al, 2018.

The nanofiltration membrane used for this test was the NF90-4040. The membrane pressure was adjusted to maintain the permeate flowrate at 2.5 L/min. Over time, the fouling of the membrane required higher pressures. Once the high pressure setpoint of 1250 kPa (180 psi) was reached, the membrane system underwent a Clean In Place (CIP) sequence. Following the cleaning, the membrane was restarted at a lower pressure, typically around 1050 kPa (150 psi).

The second continuous membrane test had a similar configuration, but with a different feed water and with pre-treatment, as shown in Figure 3. The feed water for the membrane section was the effluent from a Fenton-HDS treatment with 3.5 hours of retention time in the HDS reactors, and calcium carbonate precipitation using carbon dioxide in the final reactor. The pre-treated water was allowed to age for a minimum of 2 days prior to being fed to the membrane skid, simulating a pond between the process steps.

Apart from the tests carried out by Wood,



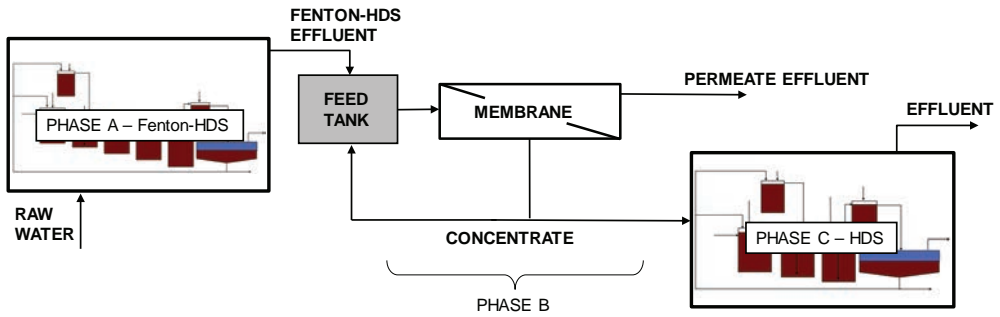
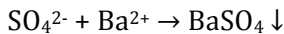


Figure 3 Membrane treatment of pre-treated water through Fenton-HDS, with concentrate treatment

a membrane supplier was also on-site for extensive testing of both nanofiltration and reverse osmosis membranes. A summary of the results from all the continuous tests are described under the “Results and Discussion” section.

### Barium Sulphate Precipitation

Sulphate is known to precipitate readily with barium as per the equation below. This reaction was completed using barium hydroxide monohydrate as the reagent. The amount of barium hydroxide added was calculated based on a targeted residual sulphate concentration of 1900 mg/L in the final effluent. While barium chloride is less expensive than barium hydroxide, it was not chosen for use in this project because Neves Corvo also have constraints for chloride concentrations in the effluent.



A barium hydroxide slurry was used for dosing with two different process configurations being tested. Configuration #1, as shown in Figure 4, combined the Fenton’s oxidation, HDS, and the barium treatment steps simply by adding a reactor where both the barium hydroxide slurry and carbon dioxide were dosed. This configuration used a single clarifier, which means that a single sludge from the HDS and barium precipitation reactions was produced in the clarifier and was recirculated back to the front end of the process.

In Configuration #2, as shown in Figure 5, an independent Fenton-HDS process was operated and the clarifier overflow was conveyed to the barium treatment process. With each process having its own dedicated reactors and clarifiers, two different types of sludge were produced. Sludge from each clarifier was recirculated back into the respective process.

In both configurations, a barium hydrox-

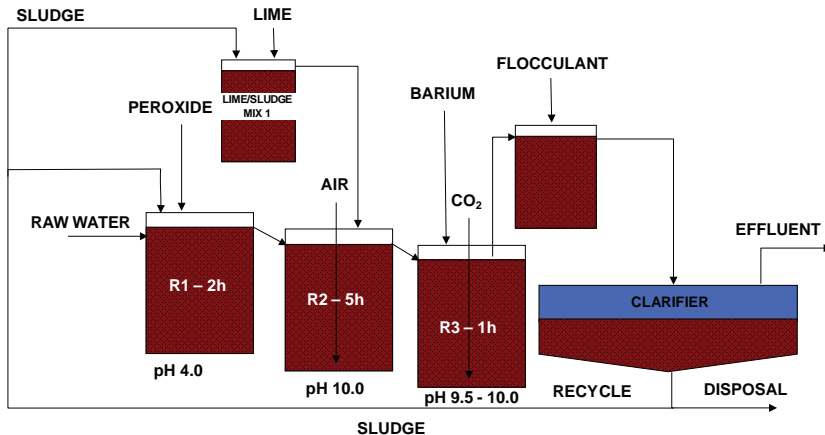


Figure 4 Barium sulphate precipitation: Configuration #1, with a single clarifier



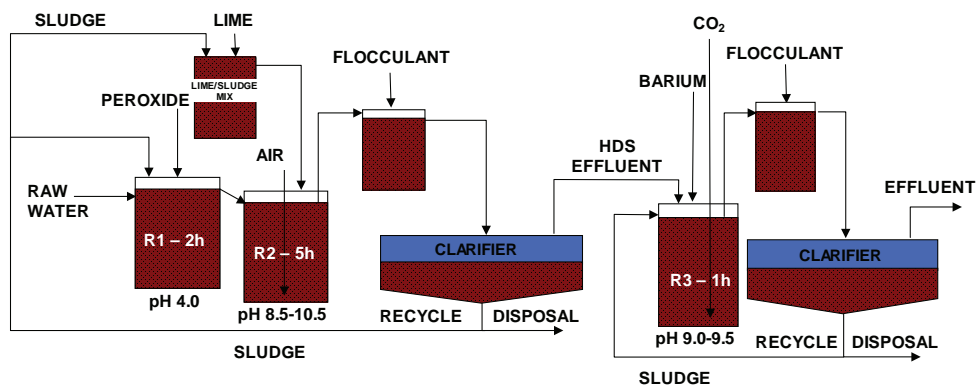


Figure 5 Barium sulphate precipitation: Configuration #2, with two clarifiers

ide monohydrate slurry was added in a reactor with a 1-hour retention time, in which carbon dioxide was also added to control pH to a range of 9.0 to 10.0. The slurry was then pumped to a flocculant tank before flowing to a clarifier.

## Results and Discussion

Although many of the tests combined different processes, for simplicity, the results are presented one technology at a time.

### Thiosalt Oxidation

Thiosalt oxidation with hydrogen peroxide catalysed with ferric sulphate was successful. Residual thiosalt concentrations below 25 mg/L were achieved at 90% stoichiometric hydrogen peroxide addition. Residual thiosalt concentrations as low as 10 mg/L were achieved in the pilot test at stoichiometric addition of hydrogen peroxide (100%). It was found that pH control to 4.0 is an important operational parameter in order to maintain process efficiency. When pH increases above 4.0, the Fenton reaction kinetics are greatly reduced. Below pH 2.5, the risk of hydrogen sulphide generation increases; it is a hazardous gas that needs to be carefully monitored and controlled.

The preferred operating conditions were a retention time of 2 hours, a pH setpoint of 4.0, and a stoichiometric addition rate of peroxide to thiosalts concentration. Recycling the sludge is beneficial to the process: it prevents scaling since new gypsum precipitates will form on existing sludge particles; it can be used to maintain the pH in the reactors;

it provides more catalyst when there is Fe in the sludge; and it maintains the Fenton reaction. One test without sludge and only lime addition showed major scaling in the reactor, while it was negligible with a sludge recycle.

### Membrane Filtration Tests

Batch membrane tests were completed using two reverse osmosis membranes (BME-4040 and ESPA2-LD-4040) and two nanofiltration membranes (NF90-4040 and NF270-4040). Test results showed that the target sulphate concentration of 250 mg/L could be met with the NF membranes at lower feed pressures. For the continuous tests completed by Wood, these two NF membranes were used.

As mentioned, a supplier also completed some testing on site using one nanofiltration (HL4040FM) and one reverse osmosis (AK-4040FM) membranes.

These membranes were selected as they were expected to ensure that local discharge limits were respected. Table 3 presents the concentration of the feed and permeate from each membrane. The metal concentrations in the permeate for NF90 were all below the discharge limits. Thiosalts were also rejected by the NF90 with a residual concentration of 17 mg/L for a 98.6% rejection. To prevent acidification in the environment, a thiosalts concentration of less than 10 mg/L could be necessary, depending on the alkalinity of the effluent and the receiver.

The NF270 was less efficient with sulphate treatment (210 mg/L in the permeate). Chloride concentrations in the permeate were shown to be higher than in the concentrate.





*Table 3 Summary of membrane test results*

Membrane	NF90-4040		NF270-4040		HL4040FM		AK4040FM	
	Feed	Permeate	Feed	Permeate	Feed	Permeate	Feed	Permeate
Sulphate	2800	39	3167	210	2700	31	2782	<10
Thiosalts	1180	17	23	4.2	1144	94	1179	3.3
Ca	815	8.0	703	42	799	23	818	1.3
Na	883	36	877	333	908	408	896	14
Cl	555	49	510	529	518	610	538	37

This phenomenon is called the “Donnan effect” which is the consequence of the movement of monovalent ions in the membrane to maintain the ionic balance in the solution – essentially, the permeating sodium pulled the chloride through the membrane. Similar results were obtained with HL4040FM, which is a nanofiltration membrane from the previously mentioned supplier.

As expected, the RO membrane (AK-4040FM) produced the best permeate quality and met all the discharge limits. However, it required higher pressures and showed a greater fouling potential, requiring more frequent cleaning.

As two of the NF membranes increased the chloride concentrations in the permeate, these were discounted for potential full-scale application. Overall, the results obtained from these tests suggest that NF90 could be a potential option for a full-scale system as the concentrations met all the required criteria for discharge at lower pressures than any RO membranes. If a thiosalt removal rate of 98.6% was found to be insufficient, some oxidation could also be provided either upstream or downstream of the nanofiltration.

### *Barium Sulphate Precipitation*

As described previously, two different configurations of barium addition were tested: one combining the HDS and the barium treatment steps using a single clarifier (Configuration #1, Figure 4) and the other maintaining separate HDS and barium treatment processes, each with its own dedicated reactors and clarifiers (Configuration #2, Figure 5). In both cases, the barium consumption rate was stoichiometric to the amount of sulphate removed. The final sulphate concentration could be controlled as required, to a target of less than 2000 mg/L (note that these tests

focused on attaining the higher of the two sulphate limits as it is proposed to be applied only during the wet season).

The difference between the tests lies in the sulphate concentration prior to barium dosing. In Configuration #1, with a single clarifier, the sulphate concentration in the reactor prior to barium addition averaged 3600 mg/L. With a separate complete HDS treatment prior to barium addition, the sulphate concentration was 3250 mg/L and could be optimised to a lower level.

In the optimised HDS treatment (Aubé et al, 2018), sulphate concentrations of less than 3000 mg/L were achieved. This could not be done in Configuration #1 as the recycled sludge contained a significant fraction of barium sulphate. For the HDS process to remove sulphate as calcium sulphate, the recycled sludge must consist mostly of gypsum to provide precipitation sites. This means that Configuration #2, with two clarifiers, could meet the same target concentration of sulphate (<2000 mg/L), with 40% lower consumption of barium than for Configuration #1.

This process is most readily applicable to higher sulphate concentration targets, as a high barium dosage could result in residual barium concentrations in the treated effluent. That said, the results from both tests indicated that dissolved barium concentration in the effluent was less than 0.15 mg/L. Total Ba concentrations in Configuration #1 and #2 averaged 1.4 mg/L and 0.84 mg/L, respectively. These results indicate that most of the residual Ba was in the suspended solids and a polishing step such as a settling pond or a filter could decrease the residual concentrations further.

The barium precipitation process was also shown to produce very high sludge densities as both configurations attained sludge solids



contents exceeding 40% solids. Despite these very high densities, the sludge rheology was such that conveying the sludge did not pose any viscosity problems.

Since it is proven that Barium hydroxide can stoichiometrically reduce sulphate concentrations, it could be used as a back-up option, but operating costs remain much higher than with membrane filtration due to reagent costs.

## Conclusion

The tests described in this paper include thio-salt oxidation by Fenton’s Reagent, barium sulphate precipitation and membrane filtration for sulphate removal. All tests were successful.

Thiosalt oxidation was most efficient at a pH of 4.0, in a reactor with a two-hour retention time and recycled HDS sludge used for pH control. Under these conditions, the peroxide consumption was slightly less than the stoichiometric requirement to meet the treatment target.

Barium sulphate precipitation was stoichiometric to meet the sulphate target of 2000 mg/L. It is best to dose the barium in a separate process after a complete HDS process to minimise the sulphate concentration prior to barium dosage, thereby minimising barium reagent consumption.

Nanofiltration membranes could be used to meet the target of 250 mg/L sulphate. Due to chloride limits and the Donnan effect, the preferred membrane was the NF90. Although reverse osmosis membranes produced a better permeate, higher feed pressures were required and more frequent cleaning was needed.

Overall, the most effective treatment train for controlling thiosalts and high sulphate concentrations at Neves Corvo was shown to be Fenton’s oxidation combined with the HDS process, followed by nanofiltration.

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