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Treatment of tailings water for re-use in an antimony mine

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ABSTRACT

The Hillgrove Mine in New South Wales operates a bulk flotation circuit to produce a combined concentrate of stibnite (for antimony) and arsenopyrite (for gold). A build up of inorganic impurities in the tailings storage facility (TSF) water, which is recycled to the flotation circuit, led to poor recoveries of sulphide minerals. This influenced a decision to suspend operations. Hatch develop a membrane process to teat the TSF water so it could again be used in the flotation circuit. Removal of the water from the steady state conditions within the TSF destabilised the chemistry causing the autoprecipitation of metal sulphide species. To produce a sustainable membrane process, a water pre-treatment regime was required to prevent the formation of excessive fouling on the membrane. A regime was developed and the stabilised TSF water was used in bench-scale nanofiltration (NF) tests to produce a permeate stream that achieved good metallurgical recoveries in flotation tests. The process was further proven at pilot scale facilitating the design of a full scale plant for implementation at the Hillgrove Mine.

Keywords: Nanofiltration; Antimony; Tailings; Reverse osmosis; Membrane autopsy; Mopungite

1. Introduction

In 2007 Straits Resources Limited commenced the construction of a processing plant to produce antimony metal, gold bullion and tungsten concentrate at its operations at the Hillgrove Mine in New South Wales. The plant operated a bulk flotation circuit to produce a combined concentrate of stibnite (for antimony) and arsenopyrite (for gold) and an electrowinning (EW) circuit to recover the metal products. It was believed that a build up of inorganic impurities in the tailings storage facility (TSF) water, which is recycled to the flotation circuit, led to the poor recoveries of sulphide minerals. A test involving the replacement of TSF water with potable water in the float circuit produced good metallurgical recoveries and verified the hypothesis. As a result of this test, the avaialble water storage capacity on site approached capacity. These technical and water balance issues influenced a decision to suspend operations unilt a resolution was developed.

Hatch was engaged to develop a sustainable membrane process to enable the TSF water to be re-used in the flotation circuit. Nanofiltration (NF) was selected ahead reverse osmosis (RO) as it removes multivalent species at lower operating pressures and operates at higher fluxes. Tests were conducted at laboratory, bench and eventually pilot scale to produce a sustainable membrane treatment process and a full scale design for implementation at the Hillgrove mine.

The specific objectives of this program were to:

- Understand the chemistry and physical characteristics of the TSF water to determine its propensity to foul under test conditions
- Develop a water pre-treatment regime to prevent membrane fouling

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- Assess the removal of inorganic contaminants from TSF water at bench scale to create a permeate solution that was suitable for use in the flotation circuit
- Conduct pilot trials to verify the bench scale test results and obtain the data required for a full scale plant design

2. Liquor charaterisation

The TSF water is highly concentrated with respect to sulphur compounds, both reduced and oxidised species, in an alkaline brine matrix with minor concentrations of antimony, silica, total organic carbon (TOC) and arsenic. The major sulphur compounds were sulphate, thiosulphate and other unspeciated sulphur compounds. No sulphide was detected. The concentration of compounds varied to some degree each time a sample was collected, however a typical solution analysis showing the major components is shown in Table 1.

The suspended solids ranged in particle size from 6 μm to <0.04 μm, and are predominantly comprised of fine clay particles.

Table 1
Range of concentration values observed for TSF water

Analyte	Units	Min	Max
pH Value	pH Unit	10.2	11.4
Conductivity	mS/cm	15.9	18.5
Total dissolved solids	mg/L	9200	41300
Suspended solids (SS)	mg/L	23	32
Sulfate as S	mg/L	836	1485
Sulfur as S	mg/L	2660	4451
Silicon	mg/L	33.5	181
Chloride	mg/L	1410	4430
Calcium	mg/L	0	8
Magnesium	mg/L	0	12
Sodium	mg/L	2050	3740
Potassium	mg/L	81	118
Antimony	mg/L	323	499
Arsenic	mg/L	3.9	13.1
Silica	mg/L	78.4	393
NO2 + NO3 as N	mg/L	40.5	138
Sulfide as S	mg/L	<0.1	0.2
Thiosulfate as S	mg/L	1037	1676

3. Solution pre-treatment

Upon receipt of the TSF water, the solution was observed to be a pale yellow colour with a slight turbidity. During storage of the TSF water, a reddish precipitate was observed indicating that the TSF water destabilised following removal from the TSF. The oxidation-reduction potential (ORP) of the water was relatively low (–71 mV, $Ag/AgCl_2$) due to the high concentrations of reduced sulphur compounds, particularly thiosulphate. It was hypothesised that exposure to oxygen altered the speciation of the reduced sulphur species, causing the precipitation. The potential to precipitate fouling species following air sparging was considered. In addition, to removing potential foulants, precipitating the salts would reduce the TDS of the solution, lowering the osmotic pressure at the membrane surface. This would improve flux and therefore energy costs associated with pumping.

A proposed reaction between thiosulphate and oxygen is shown in Eq. (1), however in practice, the oxidation of thiosulphate is a very complicated process, in which it has been postulated that one sulphur atom is oxidised to sulphate via sulphite, while the other is cleaved and reduced to form a polythionate species such as trithionate or tertrathionate and/or sulphur(0) [1]. The prediction of sulphur behaviour according to such pathways was outside the scope of this work, so a more empirical approach was undertaken. Approximately 5 L of the TSF water was air sparged overnight using an aquarium pump and glass frit. The precipitate that formed (Fig. 1) was filtered off using a 0.45 μm polysulfone membrane and collected for XRD analysis. The filtrate was submitted for metal and metalloid analysis by ICP. During the test, the solution pH dropped from pH 10.2 to pH 9.6. The significant analyte depletions are shown in Table 2. The XRD analysis of the solids indicated that the solids were amorphous and only returned tentative peak assignments.

$$H_2O + Na_2S_2O_3 + 2O_2 = Na_2SO_4 + H_2SO_4 \quad (1)$$

The concentrations of sulphur (15%) and antimony (52%) were depleted by significant amounts according to ICP analyses (Table 2), implying that an amorphous antimony sulphur compound was responsible for the red precipitate.

The filtrate from the precipitated TSF water was very clear, however after several hours of storage further precipitate was observed. Although air sparging removed an antimony/sulphur compound, the instability of the

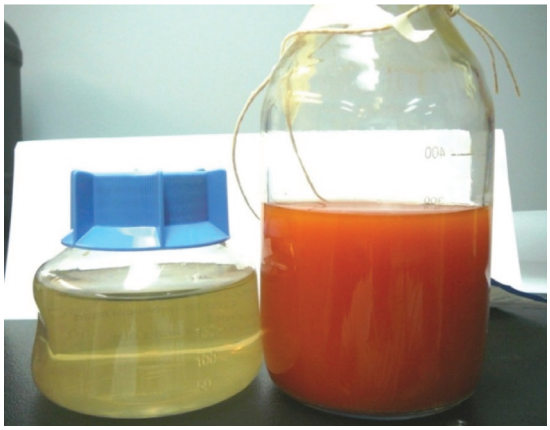

Fig. 1. TSF water before and after air sparging.

Table 2
Significant analyte depletions following air oxidation

Analyte	Units	TSF feed	Air oxidised TSF	% depletion
Sulphur	mg/L	2660	2250	15
Antimony	mg/L	323	155	52

filtrate still posed the risk of fouling during membrane filtration.

The pH of the solution dropped during the air oxidation, so another empirical test was conducted to see if the observed precipitation was:

- due to the oxidised sulphur species
- due to the resulting change in pH
- reversible upon acid addition according to Le Chatellier's principle

HCl was added drop wise into a 100 mL subsample of the TSF water and a second 100 mL sample containing the precipitate. No dissolution of the red precipitate occurred upon acid addition. However, upon immediate addition of the acid to the TSF water, the red precipitate appeared. It was concluded that the antimony sulphur compound was produced indirectly from exposure to air as a result of the reducing pH.

A further test was conducted using dropwise addition of NaOH. If the solution is destabilised by acid addition, it followed that the solution could be stabilised following caustic addition, increasing the solubility of the reduced sulphur compounds. Following addition of the NaOH to the sample in which the precipitate had formed, the precipitate immediately re-dissolved to produce the pale yellow colour of the feed liquor. The pH increase required to achieve this was 0.5 units above the initial solution pH of 10.2. Increasing the feed pH by caustic addition was used to prevent the antimony sulphur compounds from fouling the NF membranes.

4. Bench-scale nanofiltration tests

The NF membrane tests were conducted to achieve a volume recovery of 70% (hydraulic limitation), starting from an initial feed volume of 1 kL. The TSF liquor used for this test was at pH 11.5 upon arrival and was adjusted to pH 12.0 using 50% NaOH to prevent precipitation of antimony sulphur compounds on the NF membrane. The test was conducted in batch mode using a single 4" diameter spiral wound NF membrane (8 m^2 surface area) with the retentate being returned to the feed tank until 70% of the feed volume was filtered through to the permeate tank. Pre-filtration was via 20 µm, 5 µm and 1 µm microfiltration (MF) cartridge filters placed in series.

Conductivity and pH were monitored throughout the test and samples were collected for solution analysis at a 70% recovery level. A summary of the analalytical data is shown in Table 3. The rejection calculations were based on the ratio of feed and permeate concentrations. Greater than 96% rejections were achieved for the key compounds, including sulphur species, antimony and arsenic, at 70% recovery. The TDS rejection was 86%. The relatively high conductivity in the permeate is associated with the transmission of sodium hydroxide.

Although an excellent rejection of key species was demonstrated, the critical test to determine if the process offered value to the customer was a comparison of the NF permeate with potable water as a feed stream for flotation. TSF feed and NF permeate were submitted for flotation tests using a standard Hillgrove Mine ore. The solution pH for the TSF feed and the NF permeate were reduced to pH 7 prior to the tests without prefiltration of precipitated solids. The tests were conducted in triplicate and the average values are reported in Table 4. Sb recovery represents the stibnite float and Au recovery represents the arsenopyrite float. The tests that were conducted using the NF permeate produced favorable recoveries of antimony and gold when compared to the potable water tests. The untreated TSF water produced very poor results.

Table 3
Summary of analyte rejection data for NF process

Analyte	Unit	TSF feed	NF retentate	NF permeate	% rejection
TDS	mg/L	16000	45100	2180	86
Sulfur as S	mg/L	4176	38000	57	99
Sulfate as S	mg/L	1263	4462	19.7	99
Antimony	mg/L	499	3121	19	96
Arsenic	mg/L	3.86	22.1	0.03	99
Silica	mg/L	393	958	98.1	75
Thiosulfate as S	mg/L	1197	8094	20.5	98
pH	units	12	11.6	11.9	N/A
Conductivity	mS/cm	15.9	35.5	6.3	60

Table 4
Summary of recovery data from flotation tests

Test	Sb recovery (%)	Au recovery (%)
Base case – potable water	99	94
TSF water	7.5	15
NF permeate	97	95

5. Pilot-scale nanofiltration tests

The pilot trials were conducted on site at the Hillgrove mine. TSF water was pumped to an MF plant with 50 m^2 of membrane surface at a nominal pore size of 0.1 µm. The MF permeate was effectively clear of suspended solids (SDI = 0.5) and was fed to the NF feed tank. The filtration configuration used in the trials was a tapered three stage system comprised of 6 x 4" NF membranes and 18 x 2.5" NF membranes (total surface area of 91 m^2).

Caustic soda was added to the NF feed tank to raise the pH by ~0.5 units to stabilise the liquor and prevent precipitation of antimony sulphur species. The feed rate to the NF plant was ~2 kL/h and the target recovery level was 85%.

The analyte rejection characteristics at 85% recovery are shown in Table 5. Considering the recovery level of 85% was well higher than the 70% used in the bench-scale trial, the rejections were again very good with a TDS rejection of 87% based on the ratio of feed to permeate concentration.

The vast majority of the filtration was completed in the first stage, with significant membrane resistance observed in stages 1 and 2. A membrane autopsy was conducted on the membranes following the trial. An obvious scale was present on the membranes in stages 2 and 3. The thin layer of fouling was very reflective and appeared to be highly crystalline. This scale was removed from the membrane surface (Fig. 2) and analysed using SEM and EDS technology (Figs. 3 and 4). The surface fouling in stage 2 was highly crystalline and, based on the EDS results, appears to be an oxide of antimony. The membrane material contributed to the peaks associated with carbon, sulphur and oxygen [2].

The key elements detected on the NF membrane scale were antimony and oxygen. An XRD analysis was conducted on the scale to verify the EDS analysis and

Table 5
Summary of analytical data from NF trial

Analyte	Unit	TSF feed	NF retentate	NF permeate	% rejection
TDS	mg/l	13000	77260	1660	87
Sulfur as S	mg/l	12900	84317	297	98
Silica	mg/l	352	1610	130	63
Conductivity	mS/cm	14.0	76.2	2.6	82

Fig. 2. Scale scraped from the NF membrane.

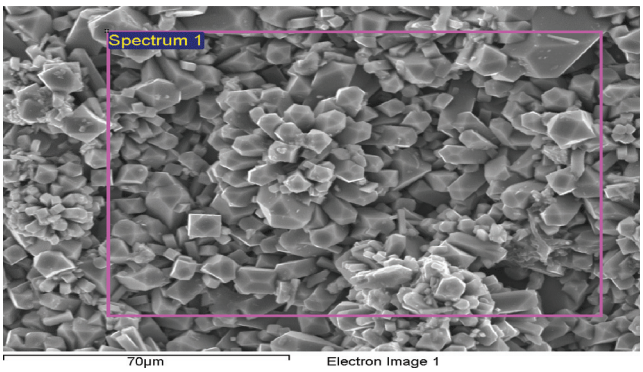

Fig. 3. SEM image of scale present on the NF membrane.

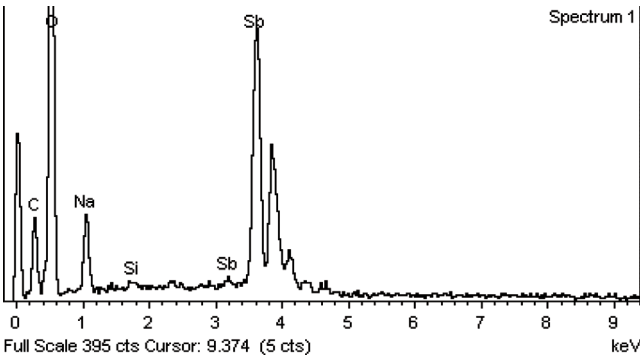

Fig. 4. EDS trace of scale present on the NF membrane.

determine the compound(s) present in the scale (Fig. 5). The mineral mopungite ($NaSb(OH)_6$) was determined, a rare sodium antimony oxide, as well as minor traces of quartz.

The detection of mopungite on the membrane as a significant scale required the development of a cleaning regime or method for preventing the mineral from depositing on the membrane. The mineral mopungite is soluble in hot water [3] and an empirical approach was

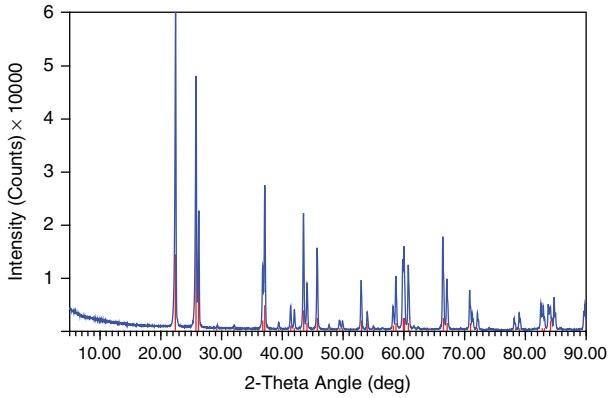

Fig. 5. XRD trace showing the presence of mopungite and quartz[3].

used to determine if hot water washing presents a suitable cleaning regime. Approximately 10 g of mopungite was scraped from the surface of the membrane and 1 g was placed in a solution of water. The water was gradually heated to 65°C, the temperature at which the solid material appeared to dissolve at a discernable rate. The change in solution conductivity was observed to verify dissolution of the solids. The conductivity increased by 300 mS/cm and the solids appeared to dissolve. Following this, a section of a scaled membrane was soaked in water at 65°C for 20 min and a section of like membrane was soaked in water at ambient temperature for the same period of time. The surfaces of the membranes were compared and there was a distinct reduction in the degree of scaling on the membrane exposed to the hot water.

The recommended operating temperature for the membranes used in the pilot trials is 45°C, however the temperature is limited by the materials used to construct the membranes and not the membrane surface. An equivalent membrane is available that offers an operating temperature of 65°C with a short term cleaning temperature of 80°C. It was concluded that the full scale design would include the higher temperature tolerant membranes to allow hot water cleaning. In addition, the feed tank should be heated to reduce the propensity of the mopungite to precipitate on the membrane surface.

6. Conclusions

Straits Resources' Hillgrove Mine was temporarily suspended due to contaminated process water affecting its flotation circuit recoveries. These technical issues and related water balance issues had to be resolved to recommence its operations.

TSF water precipitates antimony sulphur species upon contact with air or on contact with acid, and

therefore has a high propensity to cause fouling on a membrane surface. To prevent such fouling, addition of caustic to the feed liquor was used to increase the solubility of the fouling species. The contaminated TSF water was successfully treated using nanofiltration membranes at bench scale, producing a permeate that achieved very good metallurgical float recoveries.

The process was further developed during continuous pilot trials conducted at the Hillgrove mine site. During these trials, a significant increase in membrane resistance was observed. Following a membrane autopsy, it was determined that the scaling species was a rare sodium antimony oxide known as mopungite. Mopungite is soluble in hot water so a cleaning regime using hot water flushes was designed to prevent permanent fouling. The pilot scale tests produced data that facilitated the design of a full scale sustainable membarne plant for implementation ot the Hillgrove Mine.

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