IMPURITY REMOVAL PILOTING FOR THE TECH PROJECT: MANGANESE, ZINC AND CALCIUM REMOVAL, GYPSUM MANAGEMENT, AND TRANSFORMATION AND PURIFICATION SX FOR PRODUCTION OF HIGH PURITY COBALT SULFATE

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ABSTRACT

The Sulfate Refinery in the Queensland Pacific Metals' TECH Project will treat a crude mixed hydroxide precipitate by sulfuric acid leaching, followed by aluminium precipitation, impurity removal, cobalt solvent extraction, nickel solvent extraction, and crystallization of high purity nickel and cobalt sulfate products. All sulfate refinery circuits were piloted sequentially during 2023 at Lakefield, Ontario by SGS Canada.

This paper focusses on the impurity removal circuit which consists of two solvent extraction (SX) circuits that use di (2-ethyl hexyl) phosphoric acid (D2EHPA®), dissolved in a high flashpoint aliphatic diluent. These two circuits are Impurity Solvent Extraction (ISX) and the Transformation and Purification (TSX and PSX) circuit. In ISX, impurity metals, including manganese, zinc and calcium, are preferentially extracted over cobalt and nickel. Extraction is followed by scrubbing with sulfuric acid prior to sequential manganese stripping and zinc stripping, both with sulfuric acid. A bleed of Zn-stripped organic is directed to iron stripping using oxalic acid. The ISX raffinate is forwarded to cobalt solvent extraction (CSX) for cobalt recovery.

In transformation, a bleed of the ISX stripped organic is transformed into cobalt-loaded organic. In purification, cobalt-loaded strip liquor (LSL) from CSX is contacted counter-currently with the cobalt loaded organic. The impurity metals from the cobalt LSL displace cobalt from the organic and the raffinate (purified cobalt LSL) is forwarded to cobalt sulfate heptahydrate crystallisation. The impurity removal pilot plant design, operation and results are presented. The feed to ISX is calcium-saturated, leading to gypsum formation in parts of the circuit. The paper discusses the strategies for gypsum management developed during piloting. Purification increased the Co:Mn ratio from 540:1 to >600,000:1, the Co:Zn ratio from 6,000:1 to >66,000:1, and the Co:Cu ratio from 12,000:1 to >50,000:1, and the maximum Ca and Fe in purified cobalt LSL feed to crystallisation were determined to be 10 mg/L and 1.5 mg/L respectively.

Keywords: Queensland Pacific Metals, TECH Project, nickel, cobalt, battery metals, impurity removal, solvent extraction, D2EHPA, manganese, zinc, calcium, iron, oxalic acid, gypsum, cobalt sulfate, transformation, purification

INTRODUCTION

Queensland Pacific Metals (QPM) is an ASX listed company and is the 100% owner of the Townsville Energy Chemicals Hub (TECH) Project.

The TECH Project will be a modern and sustainable battery metals refinery, 40 km south of Townsville, in northern Queensland. The TECH Project will produce critical metals for the rapidly emerging lithium-ion battery and electric vehicle sector. Processing high grade nickel laterite ore imported from New Caledonia, the TECH Project will produce nickel sulfate, cobalt sulfate, high purity alumina (HPA) and other by-products – leaving, for the first time ever in the world, almost zero waste products..

QPM is currently in the process of finalising a Definitive Feasibility Study (DFS) for the TECH Project. The parameters for the DFS are to design the TECH Project as a 1.6 million wtpa processing plant. The DFS is due to be completed mid 2024.

Queensland Pacific Metals shareholders include global battery manufacturing leader LG Energy Solution, major Korean conglomerate POSCO and American multinational automotive manufacturing company General Motors. Queensland Pacific Metals has secured binding offtake agreements for the sale of nickel and cobalt with LG Energy Solution, POSCO and General Motors.

The QPM TECH Plant is split into three areas: Front End, Extraction Plant and Sulfate Refinery. Non-Process Infrastructure supports the operation of the three main plant areas.

The Front End of the process covers site storage of ore, ore preparation and storage of residue.

The Extraction Plant uses the DNi Process™ which is essentially a closed-loop leaching process whereby the nitric acid reagent is recirculated via regeneration steps to extract valuable metals from the ore. A hydroxide precipitate of nickel, cobalt, aluminium and manganese, and other residual metals including iron, magnesium, zinc and copper, is the main product from the Extraction Plant that feeds the Sulfate Refinery. By-products from the Extraction Plant include hematite and magnesia.

The Sulfate Refinery uses sulfuric acid to leach the hydroxide precipitate produced in the Extraction Plant. The hydroxide leach liquor produced is purified by aluminium precipitation, impurity removal, cobalt solvent extraction and nickel solvent extraction, followed by crystallization of high purity nickel and cobalt sulfate products. Ammonium sulfate is produced as a by-product from the Sulfate Refinery. The solvent extraction configuration is similar to that used at the Terrafame plant in Finland(1).

SULFATE REFINERY PROCESS OVERVIEW

A simplified block flow diagram of the Sulfate Refinery (SUR) is shown in Figure 1.

The hydroxide precipitate produced in the Extraction Plant is leached using concentrated sulfuric acid to re-dissolve nickel, cobalt, and other impurity metals, producing a PLS stream. The PLS is then treated with limestone slurry in two stages of aluminium removal to precipitate aluminium, chromium, copper, and iron, with co-precipitation of gypsum. Thickening and filtration are used to separate the solids from the process liquor. The washed filter cake solids are directed to Residue Neutralisation, and the aluminium-depleted solution is forwarded to Impurity Removal.

Impurity Removal consists of Impurity Solvent Extraction (ISX) and Transformation and Purification (TSX and PSX). In ISX, impurity metals are preferentially extracted over cobalt and nickel using D2EHPA® and stripped from the extractant using sulfuric acid. In the commercial flowsheet prior to piloting, a bleed of Zn-stripped organic is sent to iron stripping using oxalic acid, and a separate bleed of Zn-stripped organic is sent to impurity transformation. ISX raffinate is sent to Cobalt SX (CSX) for cobalt recovery.

In CSX, cobalt is selectively extracted over nickel, magnesium and ammonia using Cyanex 272 extractant, then selectively stripped from the extractant using sulfuric acid. The cobalt loaded strip liquor is then sent to Purification (TSX and PSX) to further reduce impurities (mainly manganese, zinc and calcium), before reporting to Cobalt Sulfate Crystallisation. In TSX, the Fe-stripped organic from ISX is transformed into cobalt loaded organic. In PSX, the cobalt loaded strip liquor (LSL) from CSX is contacted counter-currently with the cobalt loaded organic. The impurity metals from the cobalt LSL displace cobalt from the organic and the raffinate (purified cobalt LSL) is forwarded to cobalt sulfate heptahydrate crystallisation. The cobalt sulfate heptahydrate produced from the crystalliser is centrifuged, washed, dried and packaged before shipping.

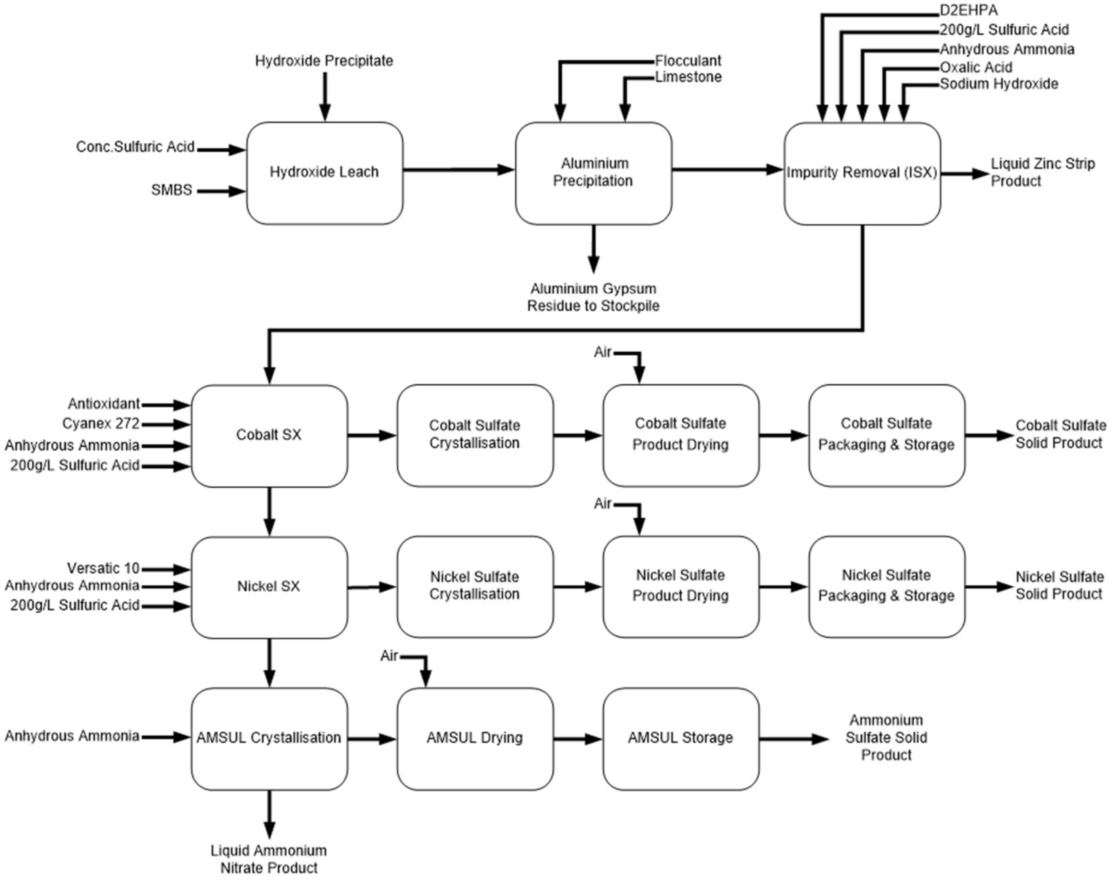

Figure 1: Simplified Sulfate Refinery Block Flow Diagram

The clean raffinate generated from CSX, containing nickel sulfate, magnesium sulfate and ammonium sulfate (AmSul) is forwarded to Nickel Solvent Extraction (NSX). In NSX nickel is selectively extracted over magnesium and ammonium using Versatic 10 extractant, then stripped from the extractant using sulfuric acid. The nickel LSL is filtered and purified before reporting to Nickel Sulfate Crystallisation. The nickel sulfate hexahydrate produced from the crystalliser is then centrifuged, washed, dried and packaged before shipping.

The clean raffinate generated from NSX, containing magnesium sulfate and AmSul, along with ammonium nitrate, is forwarded to AmSul Crystallisation for AmSul and ammonium nitrate production. The AmSul crystals (containing a small amount of magnesium sulfate) produced from the crystalliser are centrifuged, washed and dried before shipping. Ammonium nitrate produced in the crystalliser is sold as a liquid fertiliser.

IMPURITY REMOVAL OVERVIEW

The first part of the impurity removal area is the ISX circuit, for removal of impurity metals (Mn, Zn, Cu, Al, Fe and Ca) from the pregnant leach solution (PLS) to produce a nickel and cobalt enriched solution for the downstream process. The second part of the impurity removal area, Purification, comprises the transformation and purification SX circuits (TSX and PSX), for the removal of residual impurities from the cobalt loaded strip liquor prior to crystallisation.

The extractant is di (2-ethyl hexyl) phosphoric acid, or D2EHPA®, dissolved in a high flashpoint aliphatic diluent. At the design pH, D2EHPA® preferentially extracts key impurity metals over Ni and Co, as well as Mg, in the following extraction order: $Fe^{3+} > Fe^{2+} > Zn^{2+} > Ca^{2+} > Mn^{2+} > Cu^{2+} > Co^{2+} > Mg^{2+} > Ni^{2+}$.

Transformation and purification are considered to be part of the ISX area because these circuits share the same extractant. The D2EHPA® equilibrium pH curve for extraction of various metals is shown in Figure 2. At the design pH, impurity metals displace cobalt from cobalt loaded D2EHPA®.

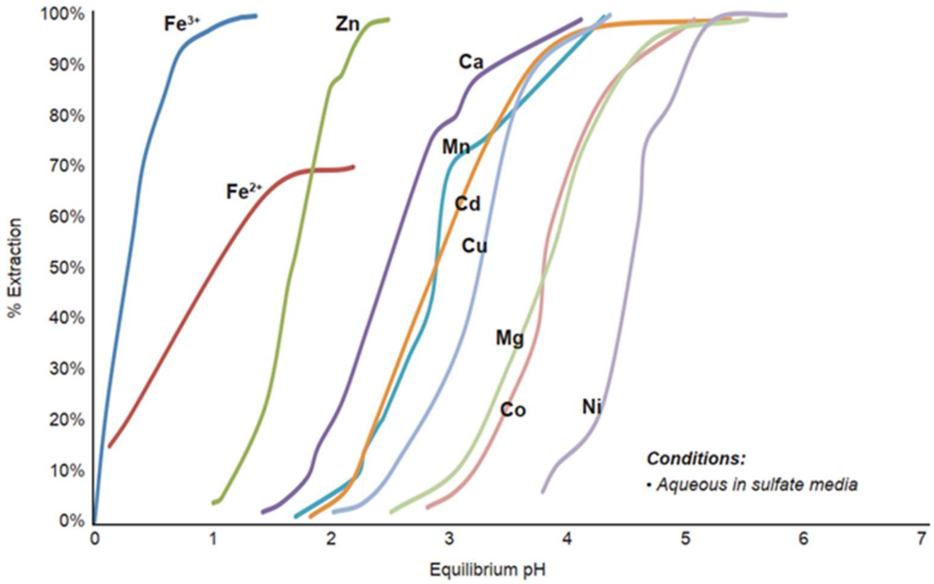

Figure 2: D2EHPA® Selectivity in Sulfate Solutions

ISX Process Description

In ISX, impurity metals are preferentially extracted over cobalt and nickel using D2EHPA® and stripped from the extractant using sulfuric acid. ISX raffinate is sent to CSX for cobalt recovery. A bleed of the stripped organic is directed to Iron Stripping, using oxalic acid, and the Fe-stripped organic is forwarded to TSX. The ISX flowsheet incorporates the following process steps:

Saponification

To ensure efficient impurity transfer from the aqueous to the organic, it is important to maintain an optimum pH during extraction. This is achieved by pre-loading the organic with ammonium ions via contact with gaseous ammonia. The pre-loading reaction is as follows:

$$NH_3\ (g) + H\text{-}D2EHPA(o) = NH_4\text{-}D2EHPA(o)$$

Extraction

In extraction, the PLS is contacted with the organic, which contains a maximum active D2EHPA® concentration of 372 g/L. Increasing the extractant concentration further would increase the organic viscosity which would impact phase disengagement performance in the settlers.

The feed solids content is reduced to 5 mg/L using dual media filters, prior to being contacted counter-currently in four stages with saponified organic. Most of the impurity metals, especially Mn, Zn and Ca, and a small amount of Co, Mg and Ni, are extracted onto the organic at the optimum pH. The raffinate, containing Ni, Co, Mg and ammonium, is filtered and treated before advancing to CSX, whilst the loaded organic exiting the first stage of extraction advances to scrubbing.

The extraction reaction produces AmSul as shown in the following equation for di-valent metal sulfates:

$$MSO_4(a) + 2\ NH_4\text{-}D2EHPA(o) = (NH_4)_2SO_4(a) + M\text{-}(D2EHPA)_2(o)$$

(where M = divalent cation)

Magnesium is not separated in ISX because its equilibrium pH curve is close to that of cobalt (see Figure 2).

Raffinate Wash

The raffinate exiting the last stage of extraction is sent to a raffinate wash mixer-settler, where it is contacted counter-currently with diluent. Due to higher solubility of the extractant in the diluent than in aqueous, entrained extractant is transferred from the aqueous into the organic phase. The aqueous is filtered via two dual media filters to further reduce the organic entrainment, further limiting D2EHPA® cross contamination into CSX.

Scrubbing

The loaded organic exiting from the first stage of ISX is scrubbed with acidified process condensate to remove co-extracted Mg, Co and Ni from the organic as well as washing out any entrained AmSul solution. The sulfuric acid concentration of the scrub solution is controlled to achieve the target equilibrium pH exiting the last scrub stage (nominally pH 2). To minimise the Co and Ni loss, the aqueous is recycled back to the ISX extraction stages. The scrubbed organic with reduced Co and Ni content is sent to stripping.

Some gypsum precipitation is anticipated in the latter stages of scrubbing due to the transfer of calcium from the organic into a small aqueous stream.

Manganese Stripping

During manganese stripping, the scrubbed organic is counter-currently contacted with a sulfuric acid solution, which is added to maintain a pre-determined sulfuric acid concentration in the product liquor. At a suitable pH most of the Mn and other metals including Ca, Cu, Mg, Co and Ni are transferred from the organic to the aqueous. The Mn-stripped organic advances to zinc stripping. Gypsum precipitation is expected in manganese stripping due to the transfer of Ca into a small aqueous stream.

Zinc Stripping

During zinc stripping, the organic is counter-currently contacted with a sulfuric acid solution, which is added to maintain a pre-determined sulfuric acid concentration in the product liquor. At the desired acidity, Zn and the remaining metals (except for Fe and Al) are transferred from the organic to the aqueous. In the commercial flowsheet prior to piloting, the stripped organic is split and fed to impurity extraction, iron stripping and impurity transformation. The zinc strip product is a saleable product.

Some gypsum precipitation is anticipated in zinc stripping due to the transfer of Ca into a small aqueous stream.

Iron Stripping

Iron is not quantitatively removed from the organic by sulfuric acid during stripping, potentially leading to iron accumulation in the organic and subsequently inhibiting the extraction of the other metals when the stripped organic is recycled back to extraction. To prevent the accumulation of iron on the organic, a bleed stream of the Zn-stripped organic (less than 10%) is fed to iron stripping. Oxalic acid is used as the stripping agent to remove Fe and the remaining metals from the organic.

This step is conventionally performed using hydrochloric acid, but the extraction plant in the TECH Project is sensitive to chlorides hence the switch to oxalic acid.

Iron Wash

The organic with reduced levels of Fe is washed using process condensate.

Gypsum and crud treatment is performed by a tricanter centrifuge, with the recovered aqueous and recovered organic streams recycled back to the process.

A schematic of the commercial ISX flowsheet as proposed prior to piloting is shown in Figure 3.

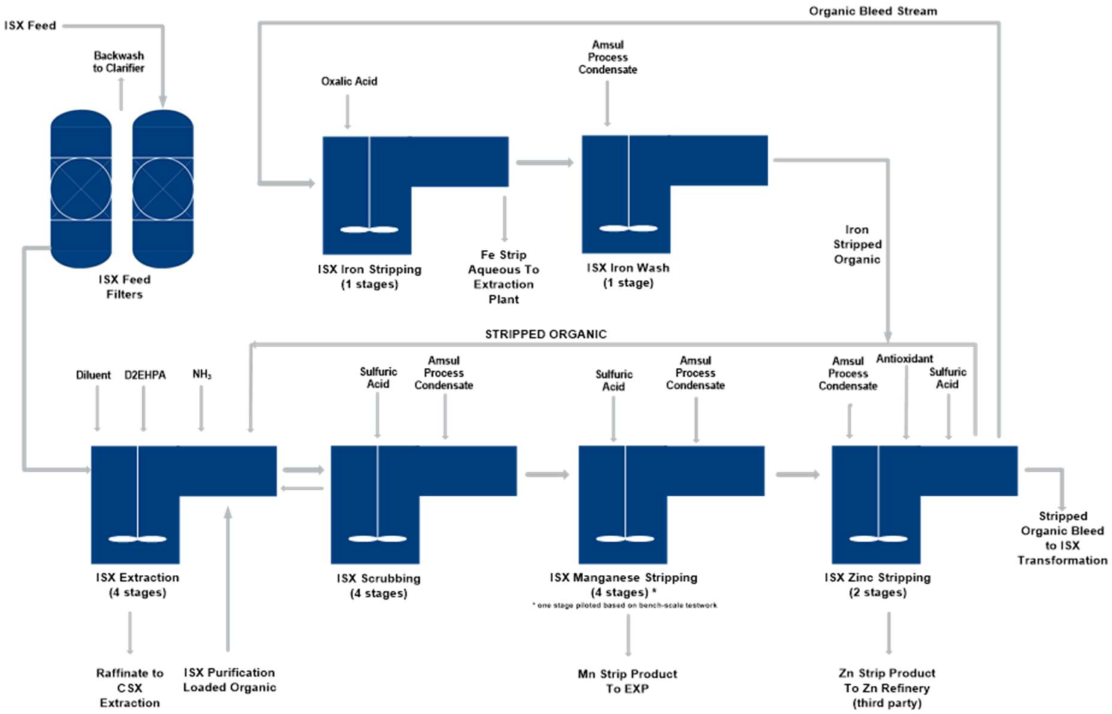

Figure 3: Schematic of the Proposed Commercial ISX Circuit (pre-piloting)

Transformation and Purification Process Description

TSX and PSX utilise the D2EHPA® organic to further purify CSX cobalt LSL ahead of cobalt crystallisation. In TSX, a portion of the ISX stripped organic stream (containing minimal amounts of Zn and Mn) is first preloaded with sodium ions in a saponification stage before contacting a bleed of the purified cobalt LSL. Cobalt displaces sodium to transform the organic into cobalt loaded organic before feeding to PSX.

The PSX step is essential to ensure that there are minimal impurities and organic entrained in the cobalt sulfate crystallisation feed. The cobalt LSL from CSX is contacted with the cobalt loaded organic from TSX. The impurity metals from the cobalt LSL displace cobalt from the organic into the aqueous, thus impurities are removed from the cobalt LSL and replaced by additional cobalt.

The purified cobalt LSL is passed through dual media filters and carbon columns to remove entrained organic before cobalt crystallisation.

The TSX/PSX flowsheet incorporates the following process steps:

Saponification

A portion of the ISX stripped organic is sent to the transformation area, where it is preloaded with sodium ions to maintain the required pH in the system. The preloading reaction is as follows:

$$\text{NaOH(a)} + \text{H-D2EHPA(o)} = \text{H}_2\text{O(a)} + \text{Na-D2EHPA(o)}$$

Transformation

The feed solution, purified cobalt LSL (approx. 120 g/L Co), is contacted counter-currently in four stages with the sodium preloaded organic. At the optimum pH, cobalt displaces sodium and loads onto the organic. The primary objective is the transfer of cobalt from the aqueous to the organic phase. The advance O/A is optimised to achieve this objective.

The transformation reaction is as follows:

$$2\ Na\text{-}D2EHPA(o) + CoSO_4(a) = Na_2SO_4(a) + Co\text{-}(D2EHPA)_2(o)$$

The cobalt loaded organic exiting from the first stage of transformation is forwarded to the purification circuit, whilst the aqueous, containing sodium sulfate, discharges from the last stage of transformation and is combined with the ISX manganese strip liquor.

Purification

The cobalt LSL from CSX contains cobalt sulfate and minor amounts of impurities such as Mn, Zn, Cu and Ca sulfates. The impurity content is further reduced before the cobalt sulfate enriched solution is fed to cobalt crystallisation for cobalt sulfate heptahydrate production. The purification step is necessary to ensure minimal impurity and organic entrainment in the crystalliser feed solution, in order that the cobalt product meets the required specification.

The cobalt LSL is contacted counter-currently in eight stages with the cobalt loaded organic from TSX. At the optimum pH the impurity metals displace cobalt and load onto the organic. The PSX raffinate (purified cobalt LSL), with reduced impurity levels, becomes the feed to cobalt crystallisation.

The key purification reactions are as follows:

$$Co\text{-}D2EHPA(o) + MnSO_4(a) = CoSO_4(a) + Mn\text{-}(D2EHPA)_2(o)$$
$$Co\text{-}D2EHPA(o) + ZnSO_4(a) = CoSO_4(a) + Zn\text{-}(D2EHPA)_2(o)$$
$$Co\text{-}D2EHPA(o) + CaSO_4(a) = CoSO_4(a) + Ca\text{-}(D2EHPA)_2(o)$$
$$Co\text{-}D2EHPA(o) + CuSO_4(a) = CoSO_4(a) + Cu\text{-}(D2EHPA)_2(o)$$

Stripping (pilot plant circuit only)

In the commercial plant the PSX loaded organic returns to the ISX loaded organic tank, combining with the ISX loaded organic feed to scrubbing. In the TSX/PSX pilot plant the organic was recycled within the circuit, with two stages of stripping contacting the impurity loaded organic with a sulfuric acid strip solution. Co, Mn, Ca, Zn and the remaining metal impurities except Fe and Al were transferred from the organic to the aqueous. The stripped organic was returned to saponification.

A schematic of the commercial Purification (TSX and PSX) flowsheet as proposed prior to piloting is shown in Figure 4.

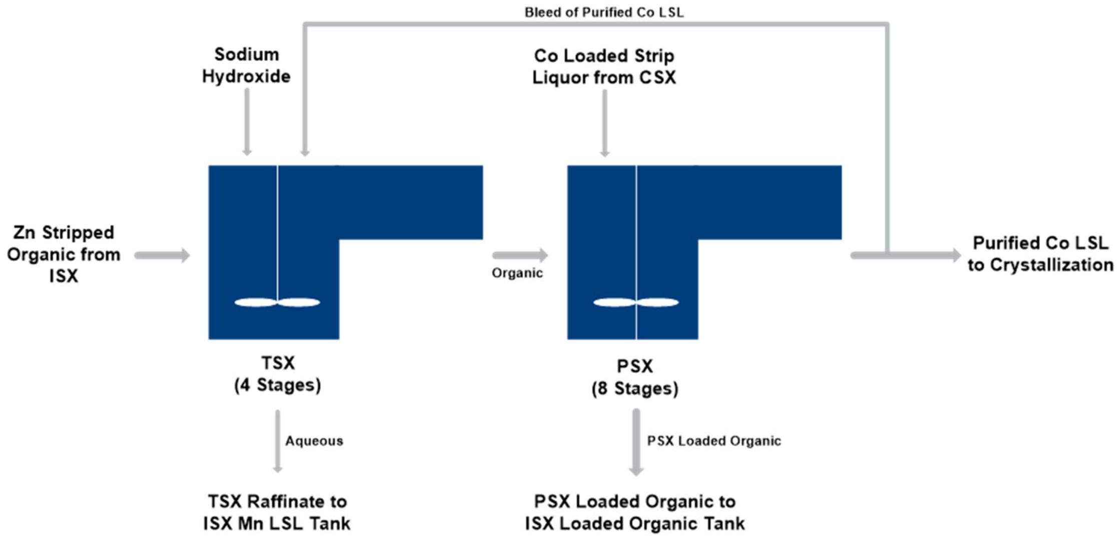

Figure 4: Schematic of the Proposed Commercial TSX and PSX Circuit

PILOTING STRATEGY

The Sulfate Refinery was piloted in 4 stages at SGS, as follows:

- Aluminium Removal (PP1)
- ISX (PP2)
- CSX and NSX (PP3)
- Purification (TSX and PSX) (PP4)

and the product liquor from each pilot plant was stored to feed the subsequent pilot plant.

Since the ISX raffinate is the feed to CSX, and the feed to TSX/PSX is cobalt LSL, the impurity removal pilot plant was run across two campaigns. ISX was run first, to generate feed for the CSX pilot plant, and the TSX and PSX pilot plant was run after the CSX pilot plant had been completed.

PILOT PLANT DESIGN

The results of a comprehensive bench-scale testwork program and the outputs from the SysCAD process model, along with complementary modelling by Syensqo (formerly Solvay), the D2EHPA® manufacturer, were inputs to the pilot plant design.

The ISX pilot plant flowsheet consisted of seven stages: Saponification, Extraction, Scrubbing, Mn Strip, Zn Strip, Fe Strip and Fe Wash. SGS provided a schematic flowsheet for the pilot plant, complete with initial flowrates and initial operating conditions, presented in Figure 5. SGS uses an internal convention of numbering the mixer-settlers in the direction of the organic flow. Notably, the four extraction mixer-settlers are numbered in the reverse order to the project PFD’s, with organic feeding E1 and aqueous feeding E4.

The ISX pilot plant was constructed using jacketed cylindrical glass mixers and settlers of the Hazen-Quinn type, with a nominal volume of 437 mL for the mixers and 2,036 mL for the settlers. The mixers and settlers were mounted at a suitable working height on a frame. The mixers and settlers were interconnected using plastic tubing with plastic compression tube fittings. Settler interface height control was by height adjustment of an external inverted-Y connector on the aqueous advance. The design organic feed rate to Fe Strip was 10% of the primary circulating organic rate. Two smaller mixer-settlers with a nominal volume of 199 mL for the mixers and 823 mL for the settlers were used for Fe Strip and Fe Wash.

The process temperature was maintained at approximately 60°C by recirculating hot water via a distribution manifold through each jacketed mixer and settler. Peristaltic and positive displacement pumps were used for the aqueous and organic flows, and aqueous recycles were pumped using multi-head pumps. Pumps and controllers were generally located above the cells.

One mixing compartment was installed in each stage. The mixing compartment was baffled by four equally spaced indentations moulded into the inside glass wall. Each mixer was fitted with a 51 mm diameter low shear six-blade pump-mix impeller (Figure 6) driven by a variable speed motor. The design mixer speed was 800 rpm and the design tip speed was 2.1 m/sec. Mixer speeds were adjusted during the campaign as required, to maintain pumping and mixing. The two smaller mixer-settlers used for Fe Strip and Fe Wash were fitted with 32 mm diameter impellers. The impellers were of polypropylene construction, and the stainless steel agitator shafts were sheathed in polypropylene tubing welded to the agitator heads.

Loose covers were fitted on all mixers and settlers. The mixer covers were slotted to accommodate removal of the covers without removing the agitator shaft. Each mixer and settler cover was mechanically ventilated via plastic tubing (Figure 7) to a manifold and a central scrubber. A pH electrode and a thermocouple were installed in each mixer via openings in the lids (Figure 7).

In order to prevent transfer of entrained organic with the exiting diluent wash aqueous raffinate stream, a coalescer was installed. The unheated glass coalescer was filled with granular anthracite and was operated not flooded in downflow mode to minimise the risk of cooling and precipitation of metal ammonium sulfate double salts within the coalescer. The feed gravitated onto the top of the carbon and the solution was discharged from the bottom of the column.

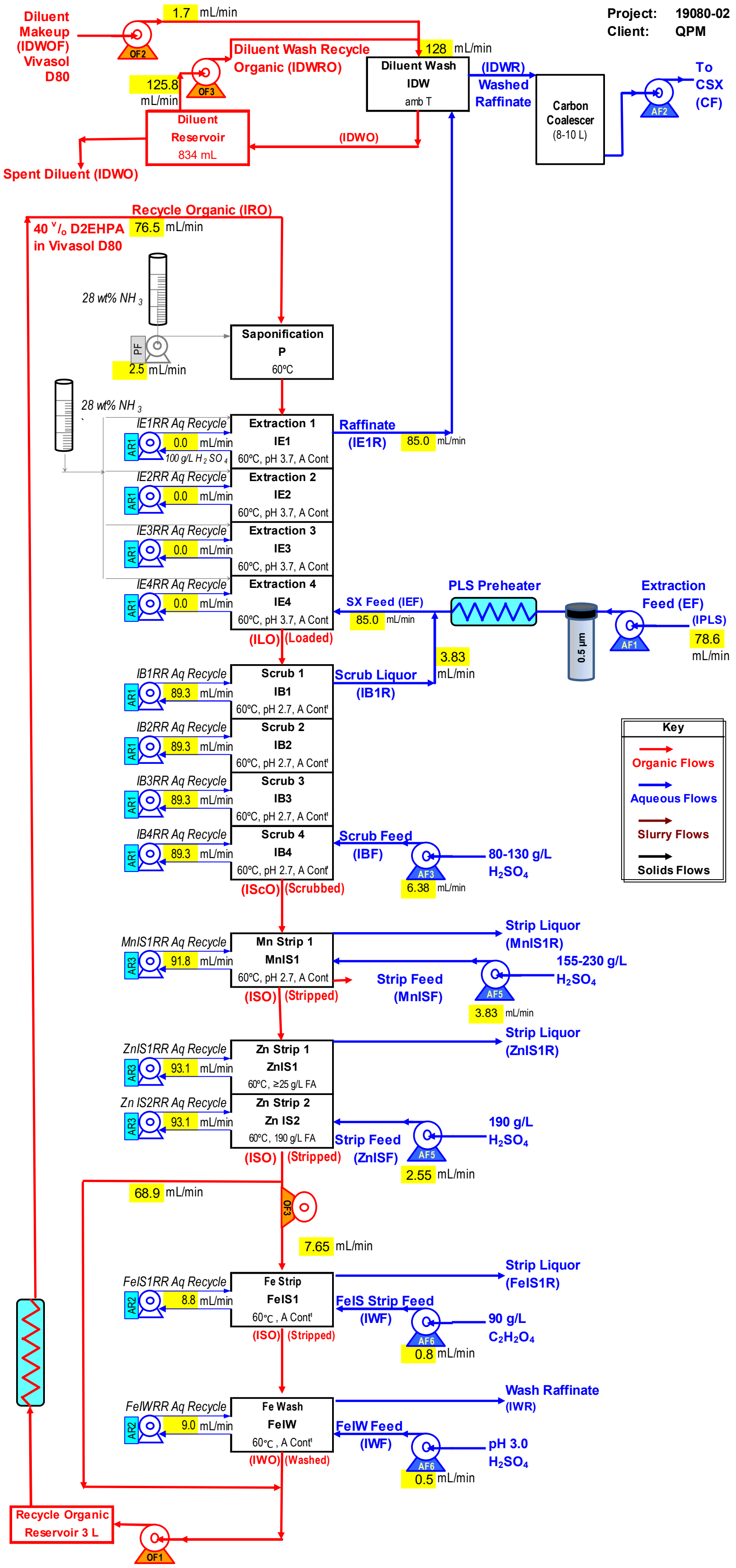

Figure 5: ISX Pilot Plant Schematic (source: SGS)

Figure 6: Photograph of 51 mm Six-Blade Low Shear Pump-Mix Impeller

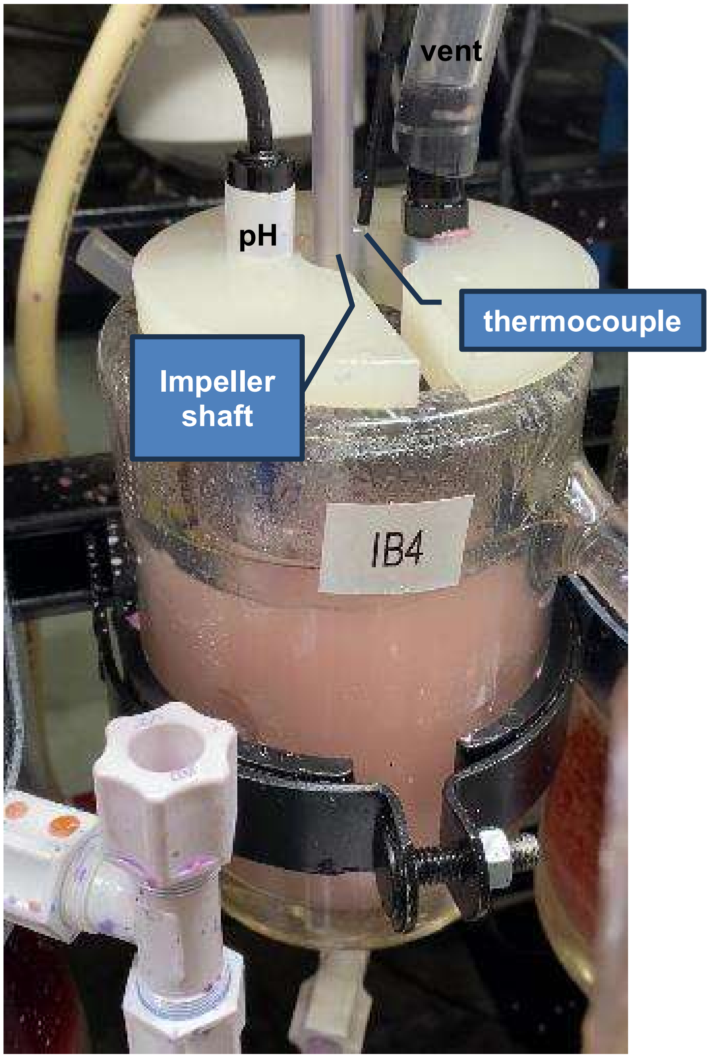

Figure 7: ISX Scrub 4 Mixer, showing clear plastic vent tubing connected to the slotted cover

A photo of the ISX pilot plant at SGS is shown in Figure 8.

Figure 8: Photograph of the ISX Pilot Plant at SGS Canada

The TSX and PSX pilot plant flowsheet consisted of a saponification stage, four stages of Transformation (TSX) to preload the organic extractant with cobalt, followed by eight stages of Purification (PSX), and two stages of stripping using sulphuric acid. Stripping is not a feature of the commercial TSX/PSX process, since commercially the PSX loaded organic returns to the ISX loaded organic tank. SGS provided a schematic flowsheet for the pilot plant, complete with initial flowrates and operating conditions, presented in Figure 9. SGS use an internal convention of numbering each mixer-settler in the direction of the organic flow. Notably, the four Transformation mixer-settlers are numbered in the reverse order to the project PFD’s.

Equipment of sufficient size for metallurgical validation of the flowsheet, and with materials of construction suitable for the solution matrices, was used for the TSX and PSX pilot plant. The SGS pilot plant was constructed using jacketed cylindrical glass mixers and settlers of the Hazen-Quinn type, with a nominal volume of 199 mL for the mixers and 823 mL for the settlers. The mixers and settlers were interconnected using plastic tubing with plastic compression tube fittings. Settler interface height control was by height adjustment of an external inverted-Y connector on the aqueous advance. The organic saponification mixer was a jacketed glass cylindrical mixer with a nominal volume of 562 mL

The process temperature was maintained at approximately 60°C by recirculating hot water via a distribution manifold through each jacketed mixer and settler. Peristaltic and positive displacement pumps were used for the aqueous and organic flows, and aqueous recycles were pumped using multi-head pumps. Pumps and controllers were generally located above the cells.

One mixing compartment was installed in each stage. The mixing compartment was baffled by four equally spaced indentations moulded into the inside glass wall. Each mixer was fitted with a 32 mm diameter low shear six-blade pump-mix impeller (similar to the 51 mm impeller shown in Figure 6) driven by a variable speed motor. Mixer speeds were adjusted during the campaign as required to maintain pumping and mixing, typically between 800 and 1,200 rpm. The impellers were of polypropylene construction, and the stainless steel agitator shafts were sheathed in polypropylene tubing welded to the agitator heads.

Loose covers were fitted on all mixers and settlers. The mixer covers were slotted to accommodate removal of the covers without removing the agitator shaft. Each mixer and settler cover was mechanically ventilated via plastic tubing to a manifold and a central scrubber.

To prevent transfer of entrained organic with the exiting Purification aqueous product stream, a coalescer was installed. The coalescer was filled with granular anthracite and was operated flooded, in up-flow mode.

A photo of the Purification (TSX/PSX) pilot plant at SGS is shown in Figure 10.

The raffinate from TSX and the strip liquor (S1R) was collected in pails while the PSX raffinate (P1R) was passed through a heated carbon coalescer and then collected in pails, as shown in the pilot plant schematic (Figure 9). As with ISX, the stages were numbered according to the flow of organic throughout the circuit.

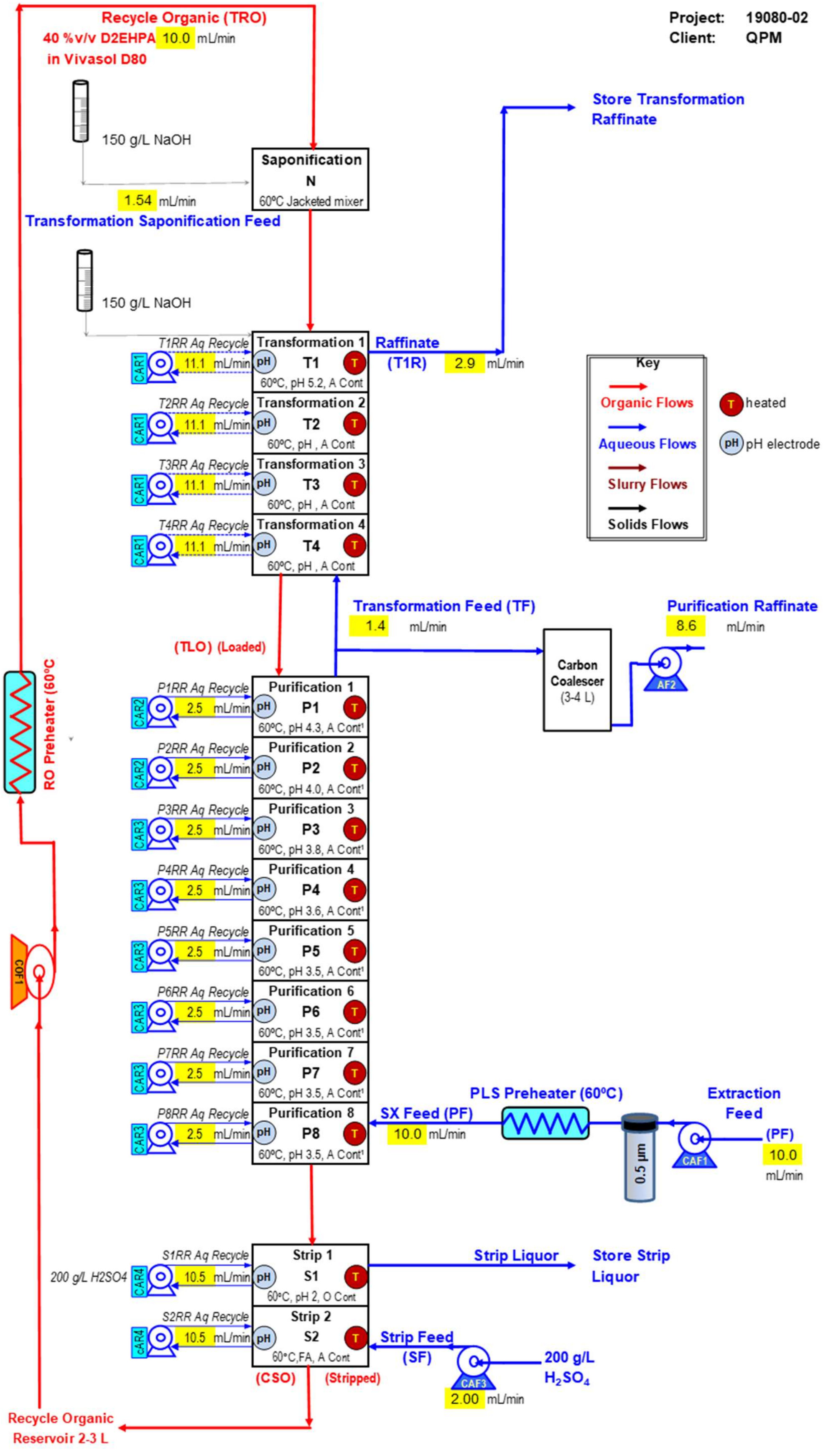

Figure 9: Transformation and Purification Pilot Plant Schematic (source: SGS)

Figure 10: Photograph of the Purification (TSX and PSX) Pilot Plant at SGS Canada

CONTINUOUS PILOT PLANT OPERATIONS

The key objective of the ISX and TSX/PSX continuous pilot plants was the metallurgical confirmation of the commercial plant design. The ISX pilot (PP2) plant was operated for 24 hours per day, for ~231 hours, over the period May 23 to June 2, 2023. Following the subsequent CSX and NSX pilot plant, the TSX/PSX pilot plant (PP4) was operated for 24 hours per day, for ~183 hours, over the period July 12 to 20, 2023.

ISX Pilot Plant Operation and Results

Feed Preparation

The feed for the ISX pilot plant was the product liquor from the preceding Aluminium Removal pilot plant. There were two feed solutions prepared, Extraction Feed 1 (EF-1) was fed from startup on May 23 and then Extraction Feed 2 (EF-2) was introduced after 74 hours on May 26.

EF-1
1200 L of feed solution (sufficient for 10 days operation) was prepared by the addition of metal sulfate salts (Al, Ni, Fe, Zn, Cu) to Aluminium Removal product liquor as required. Fe was added as Fe(II) sulfate. EF-1 was homogenised and stored at ambient temperature in 2 x 600 L IBCs. EF-1 was used as feed during the initial 74 hours of operation. The chemical composition of EF-1 which was unavailable prior to startup of the ISX continuous pilot plant was found to be significantly above target for Ca (37%) and Zn (10%), and below target for Mg (15%).

EF-2
800 L of feed solution (sufficient for 7 days operation) was prepared by blending 600 L of EF-1 with 200 L of ISX raffinate product and adding metal sulfate salts as required to achieve a feed composition closer to the targets. EF-2 was homogenised and stored at room temperature in one IBC.

Initially the feed solution (EF-1) was not diluted as the concentrations of nickel and cobalt post aluminium removal were lower than expected in ISX feed. However, the solution was calcium saturated, with a calcium concentration 37% higher than expected for ISX. The high calcium tenor resulted in significant gypsum precipitation throughout the scrub, manganese strip and zinc strip stages, causing frequent blockages and very unstable operation. The commercial plant design employs a 10% dilution via a calcium-free aqueous recycle stream from the downstream plant. It was therefore decided on day 3 to dilute the ISX feed by 10% using raffinate from the first few days of operation, the composition of which closely resembled the modelled recycle stream. Concentrations of manganese and zinc in the adjusted feed were then spiked to reflect the values expected in ISX feed. The compositions of the solutions are listed in Table 1.

Table 1: ISX Continuous Pilot Plant Aqueous Feed Compositions

	Concentration g/L		
Component	**EF-1**	**EF-2**	**Target**
Al	0.005	0.003	0.005
Ca	0.706	0.477	0.491
Co	6.274	5.874	6.286
Cu	0.031	0.022	0.035
Fe	0.005	0.003	0.005
Mg	7.080	6.631	8.349
Mn	4.522	4.307	4.339
N	not available	6.15	7.27
NO_3	tba	26.2	tba
Na	0.516	0.508	0.596
Ni	60.40	58.35	57.34
S	41.70	41.95	41.37
Zn	1.106	0.983	0.991

The feed solution composition used for the continuous pilot plant simulated a maximum Mg impurity case rather than the nominal Mg case (4.51 g/L Mg). Precipitative Ca stripping was anticipated in Scrubbing (minor), Mn strip (majority) and Zn strip (minor).

Piloting

The organic was saponified using ammonia and fed to the first of 4 extraction stages (IE1). In Saponification the design advance O/A was 31:1 and the design flow rate targets of 76.5 mL/min ISX recycle organic (IRO) and 2.47 mL/min saponification feed (PF) were intentionally not changed during the pilot plant campaign. The saponification results summarised in Figure 11 show the target advance O/A was not attained consistently. Steady state operation of saponification was not achieved during the first nine operating days due primarily to uncontrolled variability in the PF flow rate. During each day the ambient air temperature at the ammonia solution drum increased due to solar heating of the adjacent exterior wall of the building. The ammonia solution began to gasify inside the plastic tubing, affecting the solution flow rate. Gasification of the ammonia solution was not an issue overnight when the ambient air temperature was cooler.

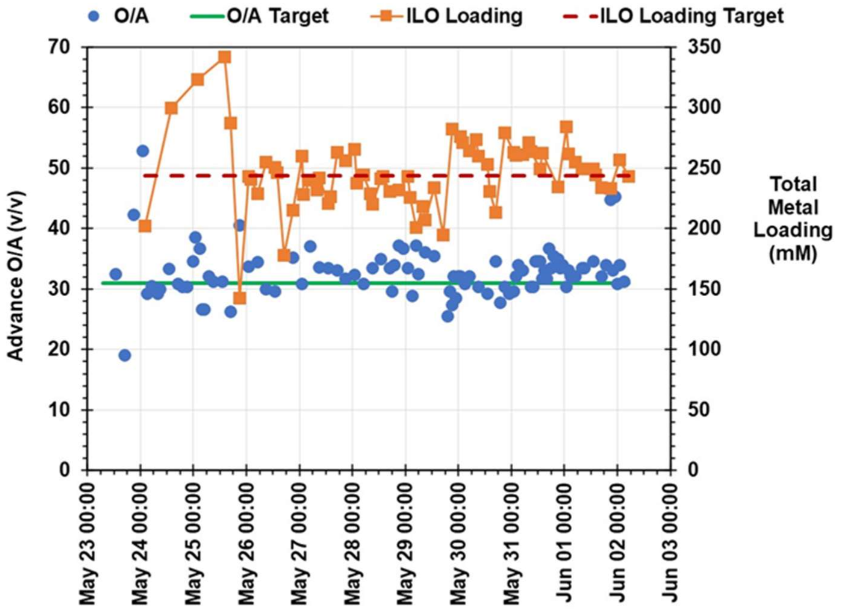

Figure 11: ISX Organic Saponification Advance O/A and Total Metal Loading in Impurity Loaded Organic

A short-term upset during May 25 was caused by third phase formation in the saponification settler. Total metal loading in ISX loaded organic (ILO) was calculated using the results of four-hourly back-stripped assays. The total metal loading trend shown in Figure 11 is not consistent. The total metal loading in ILO was also affected by initial high levels of Zn and Mn in recycle organic. In particular, Zn in IRO increased to almost 6 g/L during May 24-25 (Figure 12).

Figure 13 shows the measured advance O/A in extraction, which was adjusted by changes to the extraction feed flowrate in an effort to control the circuit. The setpoint target is identified by the orange line. Assay trends for the extraction raffinate (CSX feed) are plotted in Figure 14. Mn in the extraction raffinate ranged from 1.7 to 190 mg/L. There were periods when Mn was consistently less than 10 mg/L, and it was less than 5 mg/L about 20% of the time. Periods of high Mn (and Zn) in the recycle organic contributed to high Mn in the raffinate, particularly early in the campaign. Ca ranged from 1.7 to 18.4 mg/L and averaged 3.9 mg/L for the campaign. Cu ranged from <0.1 to 7.5 mg/L and averaged less than 1.5 mg/L overall. Zn was generally below detection limit (2 or 4 mg/L) and only those samples above detection limit are included in the figure below.

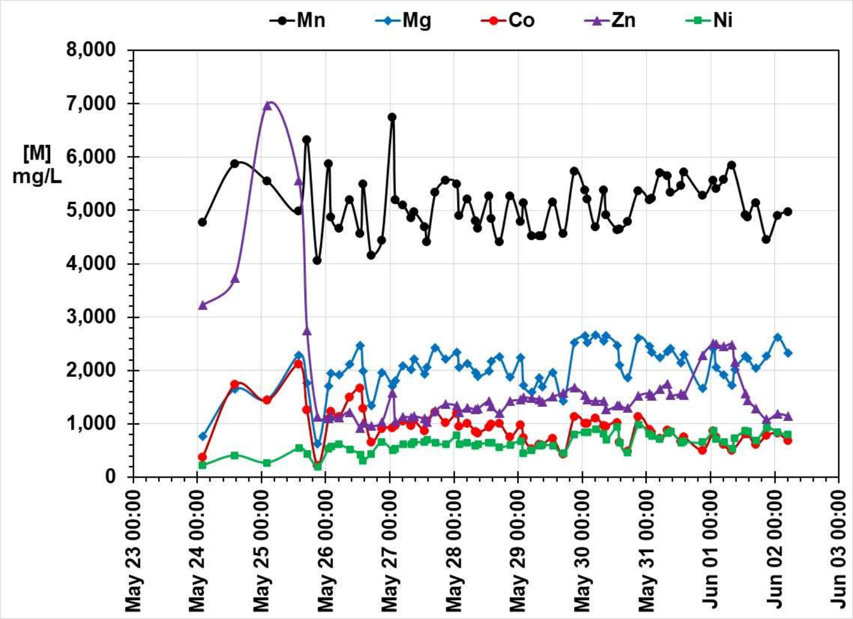

Figure 12: ISX Loaded Organic (ILO) Composition

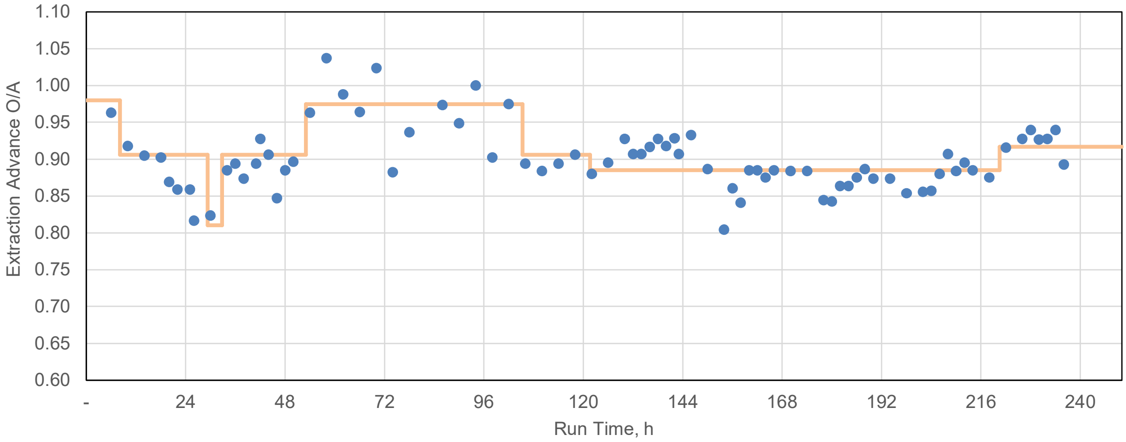

Figure 13: ISX Extraction Measured Advance O/A

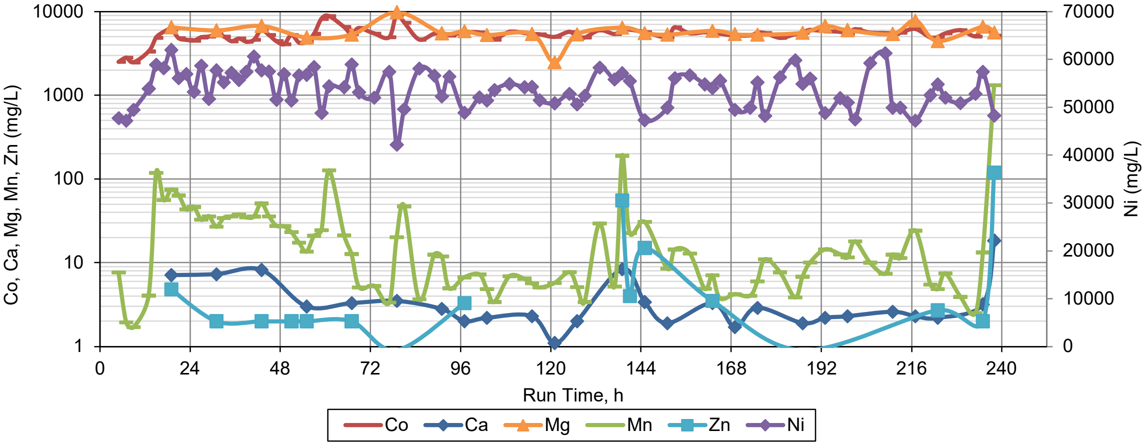

Figure 14: ISX Extraction Raffinate (IE1R) Assay Trends

ISX loaded organic (IE4O) assays are plotted in Figure 15, including both organic analysis by back-stripping (hollow symbols with line) as well as direct organic assays (filled symbols and no line). The data illustrate that the back-strip analyses generally aligned well with the direct organic assays.

Total metal loading ranged from 214 g/L to 271 mmol/L from hour 72 onwards and averaged 243 mmol/L during that period with minor variation. Mg loading increased at around hour 154, which aligns generally with a decrease in the advance O/A, and Ni loading also increased around this time. Zn loading increased around hour 200, corresponding to an increase in Zn in the recycle stripped organic.

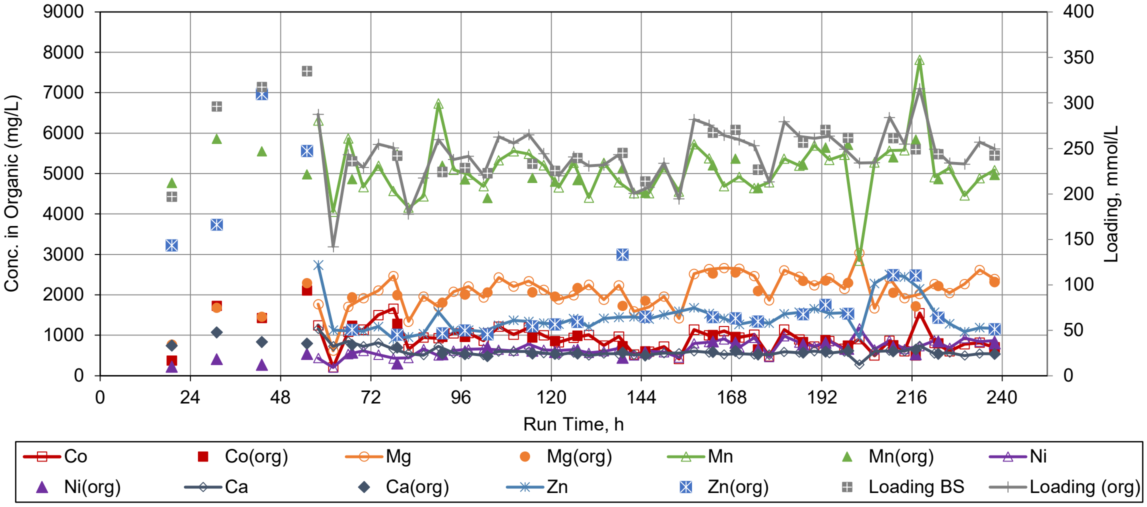

Figure 15: ISX Loaded Organic (IE4O) Assay Trends

Recorded pH measurements for IE mixers are shown in Figure 16. The measured IE1 mixer pH (blue dots) is observed to be close to the value of 2.75 indicated by Syensqo's predictive modelling.

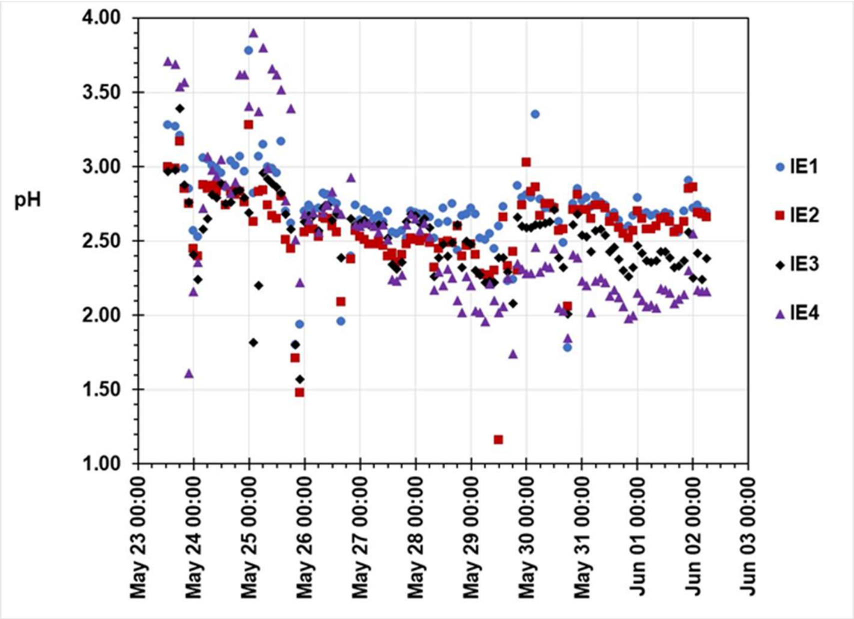

Figure 16: pH Measurements in ISX Extraction Mixers

The loaded organic advanced to 4 stages of scrubbing. In the early stages of the campaign precipitative Ca stripping by the sulfuric acid scrub solution took place in the 3rd and 4th scrubbing stages (IB3 and IB4) (see Figure 17 and Figure 18). IB4 was the stage with the lowest mixer pH. Vacuum filtration of the IB4 aqueous recycle stream (IB4RR) stream (IB4 is the fourth scrubbing stage with the lowest mixer pH and the greatest risk of precipitative Ca stripping by the sulfuric acid scrub solution) was implemented on May 27 to minimise gypsum crud accumulation in the IB4 settler (Figure 19). The equipment readily facilitated this as the aqueous discharge is from the bottom of the settler.

Figure 17: Gypsum from Scrub 3 Settler, May 25

Figure 18: Gypsum from Scrub 4 Settler, May 25

Figure 19: Gypsum Crud in ISX Scrub 4 Settler

The scrub feed sulfuric acid concentration was intentionally varied during the campaign as shown in Figure 20. In the first instance, acid concentration was increased to increase Ni and Co scrubbing efficiencies and later decreased to decrease Ca scrubbing efficiency sufficiently to prevent gypsum precipitation in IB4.

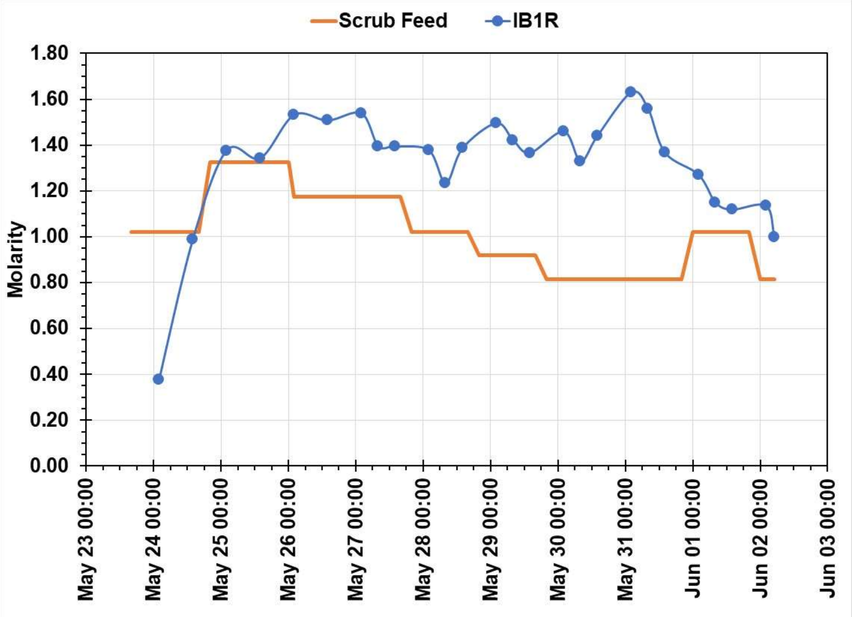

Figure 20: Molarities of ISX Scrub Feed Acid and Total Metals in IB1R

Starting at hour 158 the pH in IB4 was directly controlled by the addition of 200 g/L sulfuric acid and at hour 178 the Scrub Feed (IBF) was stopped with all scrub solution (as 80 g/L H_2SO_4) added via pH control in IB4. The pH trends in scrubbing are plotted in Figure 21.

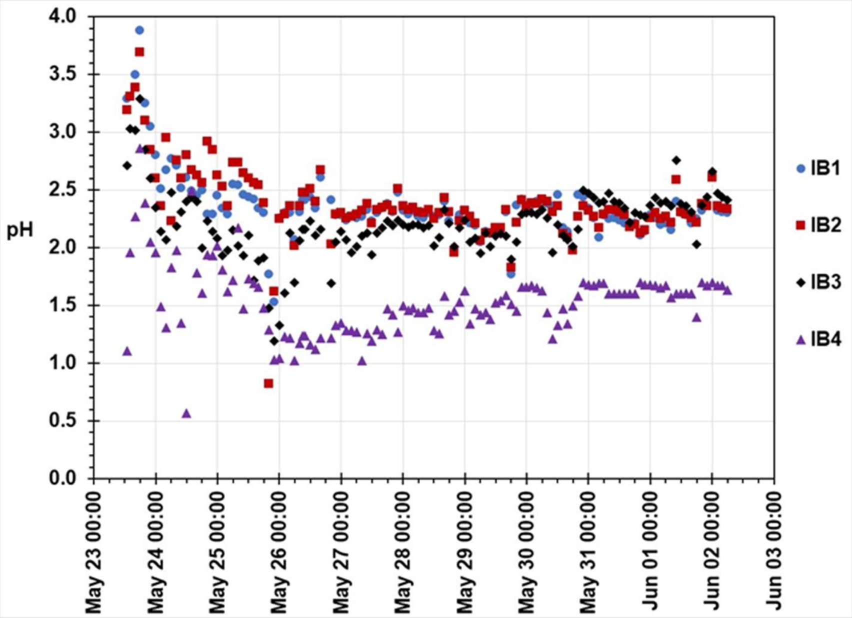

Figure 21: pH Measurements in ISX Scrub Mixers

No further gypsum precipitation was observed in IB4 after the implementation of pH control. Figure 22 shows the filter paper on the IB4 aqueous recycle filter on June 1, completely free of solids 48 hours after last being replaced. Ca tenors in IB4 recycle aqueous before and after the implementation of pH control are shown in Figure 23. Figure 24 shows the Scrub 2 and 3 settlers on May 28.

Figure 22: Scrub 4 (IB4) Settler Gypsum Filter after 48 hours, May 31

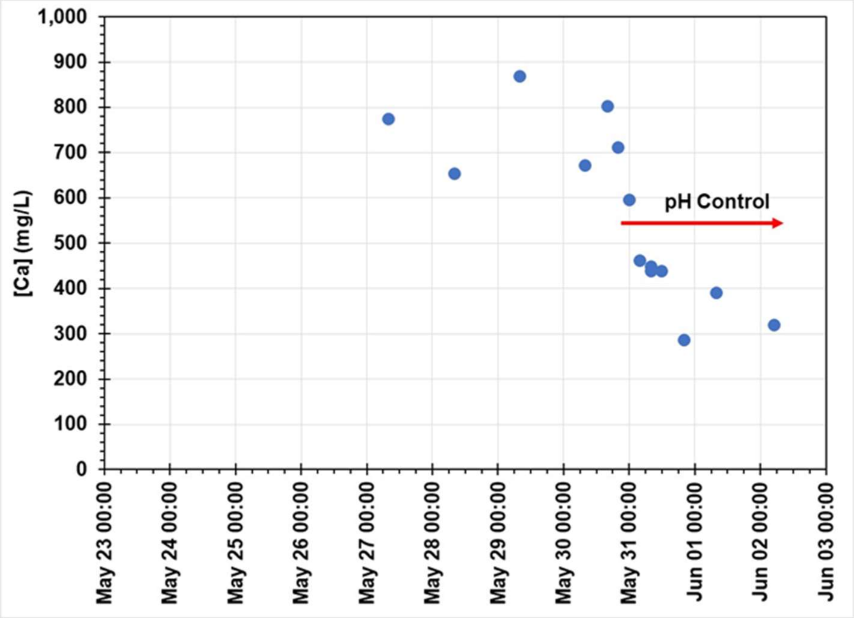

Figure 23: Ca in ISX Scrub Stage 4 Aqueous Recycle (IB4R)

Figure 24: ISX Scrub 2 and 3 Settlers, May 28

The primary objectives of scrubbing were to achieve high scrub efficiencies for Ni and Co, while minimising Zn, Ca, Mn and Cu scrubbing and avoiding gypsum precipitation in the scrubbing mixers. The trends for Ni, Co, Mg, Ca, Cu and Mn scrubbing efficiencies are shown in Figure 25. Ni scrubbing efficiency >99.5% and Co scrubbing efficiency >90% were achieved consistently. From May 27 onwards, Mn scrubbing efficiency was <5% and Cu scrubbing efficiency was <20%. Ca scrubbing efficiency at 30 to 70% was too high following start up, largely due to the loaded organic variability. The change to pH control for scrub feed acid addition on May 30 resolved this issue and Ca scrubbing efficiency was reduced to <10%. In general, the scrubbing section achieved the process objectives quite well, and confirmed the Syensqo predictive modelling.

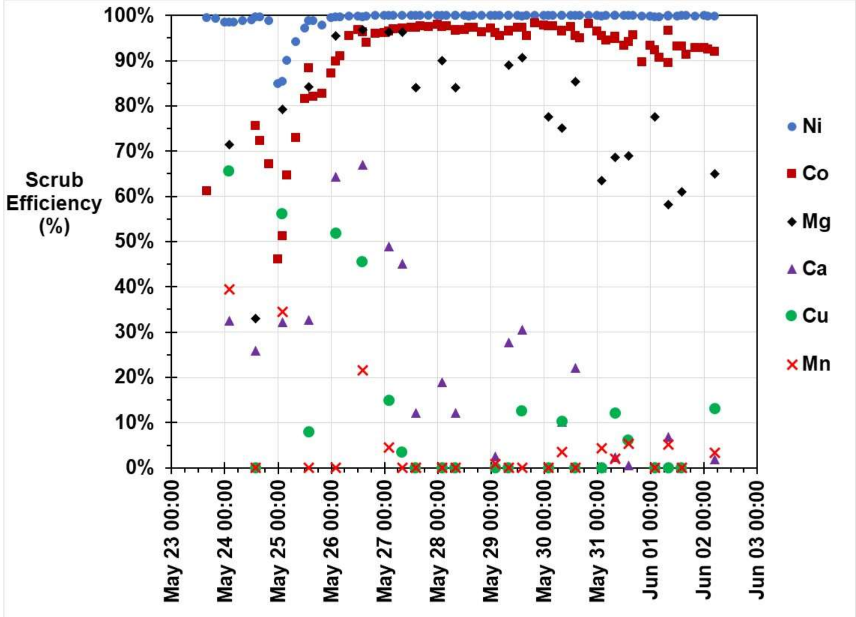

Figure 25: ISX Scrubbing Efficiency

The scrubbed organic advanced to a single stage of Mn Stripping. The Mn Strip objectives were to strip approximately 80% Mn and 10% Zn from the organic, and to achieve precipitative stripping of the majority of the Ca. At the design advance O/A of 20:1, the solubility of Ca in the sulfuric acid strip solution is significantly exceeded (maximum 20 x 600 = 12,000 mg/L); gypsum precipitates in the mixer and largely settles to the floor of the settler. Filtration of the Mn strip (MnIS1) aqueous recycle was implemented on May 25 to minimise accumulation of gypsum crud in the settler (Figure 26 and Figure 27). Gypsum collected from Mn strip on May 29 is shown in Figure 28.

Figure 26: ISX Manganese Strip Gypsum, May 25

Figure 27: ISX Mn Strip Gypsum Filter

The Mn strip feed acid concentration was increased from 155 g/L to 200 g/L and then 230 g/L to target higher Mn tenor and decreased water content of Mn strip product (MnIS1R) solution (Figure 29).

Figure 28: Partially Air-dried ISX Mn Strip Gypsum, May 29

Commencing on May 31, 4-hourly rush analysis of back-stripped Mn-stripped organic (MnIS1O) commenced to improve process control, and 30 mg/L Ca in Mn-stripped organic was targeted in order to avoid gypsum precipitation in Zn strip (Figure 30).

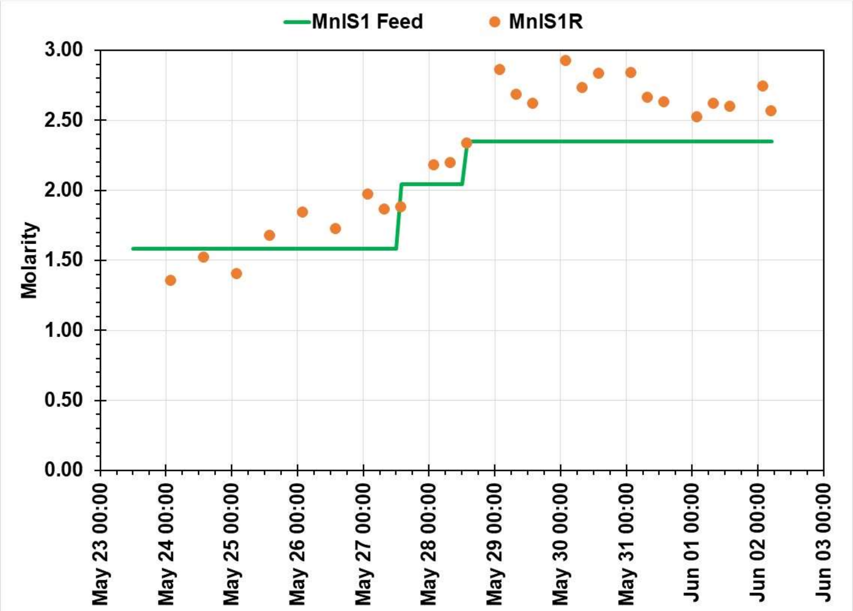

Figure 29: Molarities of ISX Mn Strip Feed Acid and Total Metals in Mn Strip Aqueous

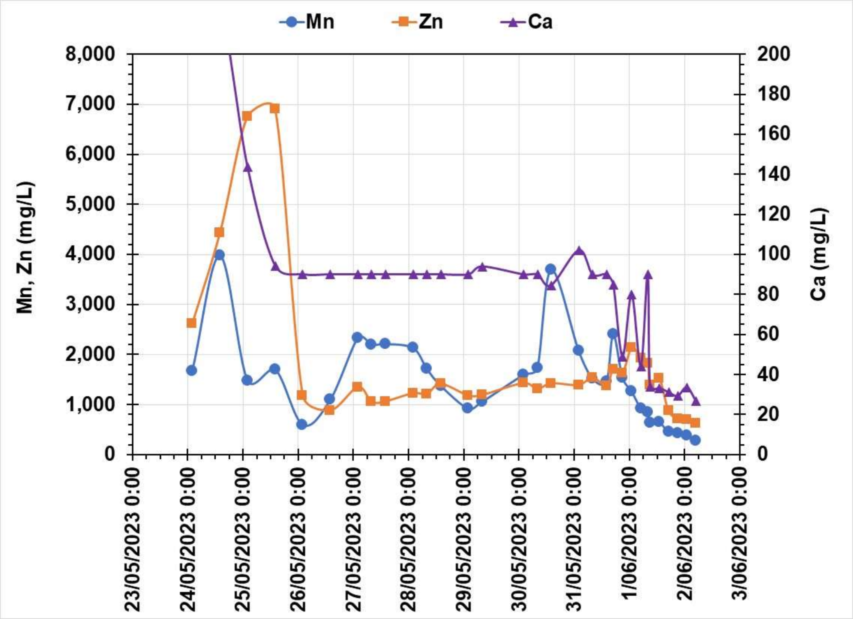

Figure 30: ISX Manganese-Stripped Organic (MnIS1O) Composition

Gypsum scale was observed to adhere to wetted stainless steel and polypropylene surfaces. Scale was not observed to adhere to any wetted surfaces (walls, floor) in the glass settler. The scale growth rate on the polypropylene pump-mix impellers in MnIS1 mixer (and IB4 mixer) was such that the impeller stopped pumping and required removal and cleaning each two days. The appearance of the scale accumulation on a 51 mm diameter pump-mix impeller is shown in Figure 31.

The scale growth rate on wetted stainless steel in MnIS1 mixer was investigated over the period May 27 to June 2. A stainless steel coupon was prepared by bending 6.4 mm tubing. The appearance of scale accumulation on the stainless steel coupon is shown in Figure 32. The coupon was inserted in MnIS1 mixer for up to a day at a time, to quantify the scale growth rate.

Figure 31: Gypsum Scale on an ISX Pump-Mix Impeller

Figure 32: Gypsum Scaling on 316SS Tube Coupon in Mn Strip

As might be expected, scale growth was shown to be proportional to the free acid concentration (Figure 33). At higher acidity, Ca is stripped into a smaller volume of strip feed aqueous resulting in higher Ca tenors.

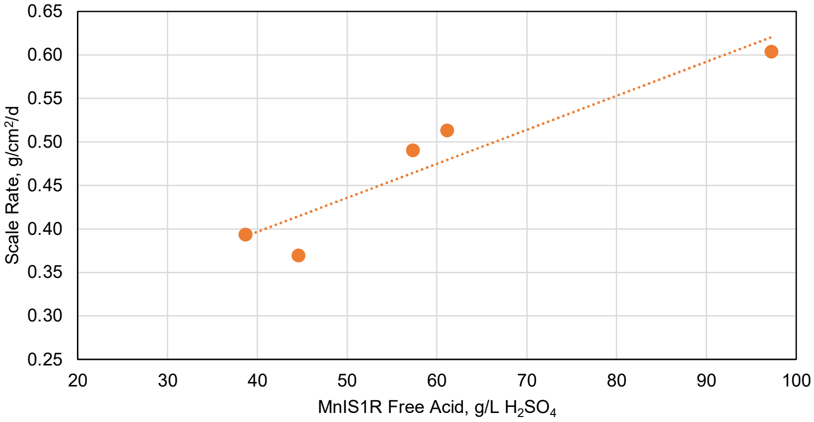

Figure 33: Effect of Free Acid on Scaling Rate in MnIS1

The trends for the Mn content of the key organic streams exiting each stage in the ISX circuit are shown in Figure 34. The Mn content of scrubbed loaded organic was around 5,000 mg/L and the design target was 80% Mn stripping efficiency in Mn Strip, equivalent to 1,000 mg/L Mn in Mn-stripped organic (MnIS1O). This target was achieved only occasionally between May 23 and June 1. While the design target of 80 g/L Mn in Mn strip aqueous product was exceeded, this was at the cost of under-stripping Mn. The sampling schedule included direct analyses of MnIS1O samples each 12 hours but the turnaround time for these assays was several days. It was not possible to consistently achieve the 80% Mn stripping efficiency target without timely MnIS1O assay results. Following the implementation of additional 4 hourly RUSH assays of back-stripped MnIS1O at 17:00 on May 31, the Mn and Zn contents of MnIS1O were controlled to <1,000 mg/L during the final 24-hour period of the campaign.

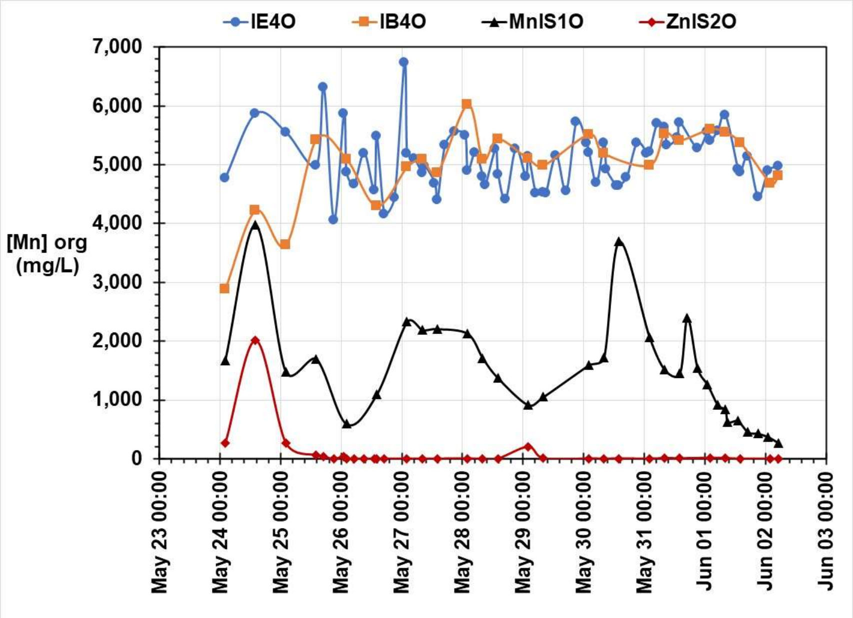

Figure 34: Mn Contents of Key Organic Streams Exiting Each Stage in ISX

In Zn strip, the Mn-stripped organic was contacted in two counter-current stages with sulfuric acid solution. The key objective was to strip 100% of the remaining Zn, Ca, Mn, Cu, Mg, Co and Ni from the organic to the aqueous phase.

During the initial part of the campaign significant gypsum precipitation was experienced in the first stage of Zn stripping (ZnIS1) as shown in Figure 35 and Figure 36. It was demonstrated over several days that it is possible to avoid gypsum precipitation in Zn strip by ensuring the Ca content of Mn-stripped organic is sufficiently low to avoid Ca saturation in the ZnIS1 mixer.

Figure 35: Gypsum Scaling on ZnIS1 Impeller

The results of the bench scale Zn stripping isotherm test were not available until after completion of the ISX pilot plant campaign. The pilot plant identified that the nominal advance O/A in Zn stripping was 6:1. Previously this was expected to be 20 to 30:1. The organic flow rate target was fixed for the duration of the campaign and the Zn strip feed (ZnISF) flow rate target was adjusted on multiple occasions during the campaign in response to process results. The advance O/A based on manually measured organic and ZnISF flow rates is shown in Figure 37.

Figure 36: Zinc Strip Gypsum, May 25

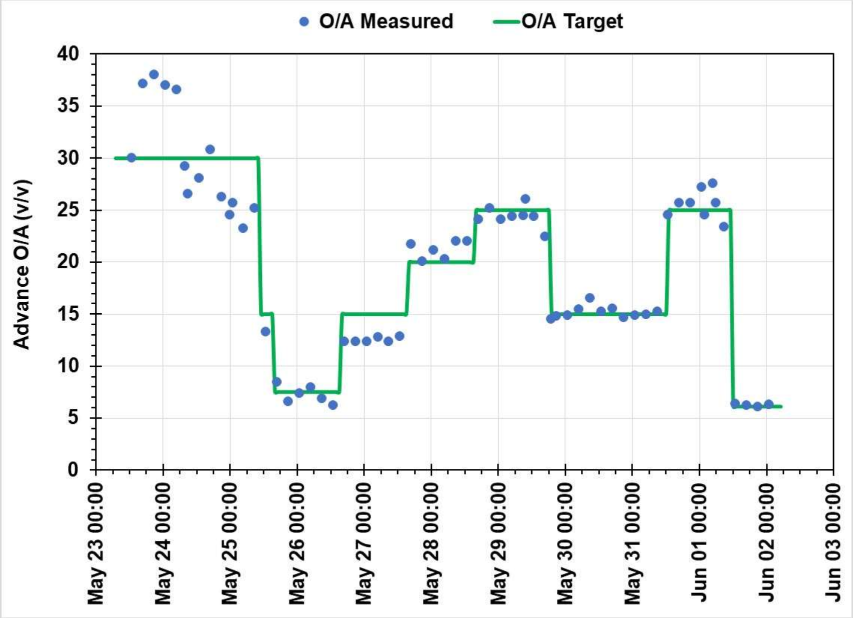

Figure 37: ISX Zn Strip Advance O/A

The design Zn stripping target was 100% stripping of Zn (and Mn). The trends for the Mn and Zn contents of ZnIS2 organic are shown in Figure 38. For much of the campaign the design target was not met.

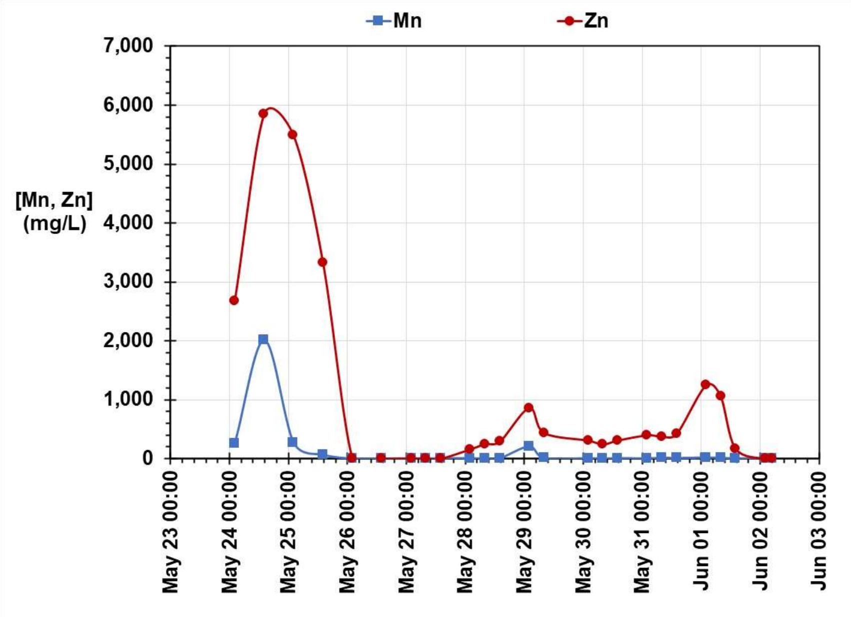

Figure 38: ISX Zn Stripped Organic Composition

A 10% bleed of the Zn-stripped organic was directed to two counter-current stages of Fe stripping (FeIS1 and FeIS2), using a 90 g/L oxalic acid strip feed solution. It is more commonplace for an Fe strip of D2EHPA® to be performed using hydrochloric acid, however the upstream Extraction Plant is sensitive to chlorides, hence the selection of oxalic acid. The key objective of Fe stripping was to strip sufficient Fe from the organic to prevent build-up in the ISX circuit.

The trend for the Fe content of the organic feed stream to Fe stripping is shown in Figure 39. The Fe content increases to 80 mg/L during the first few days of the campaign and then declines to a steady state range of 50 to 60 mg/L. This indicates that the rate of Fe stripping was equal to the Fe loading rate in extraction.

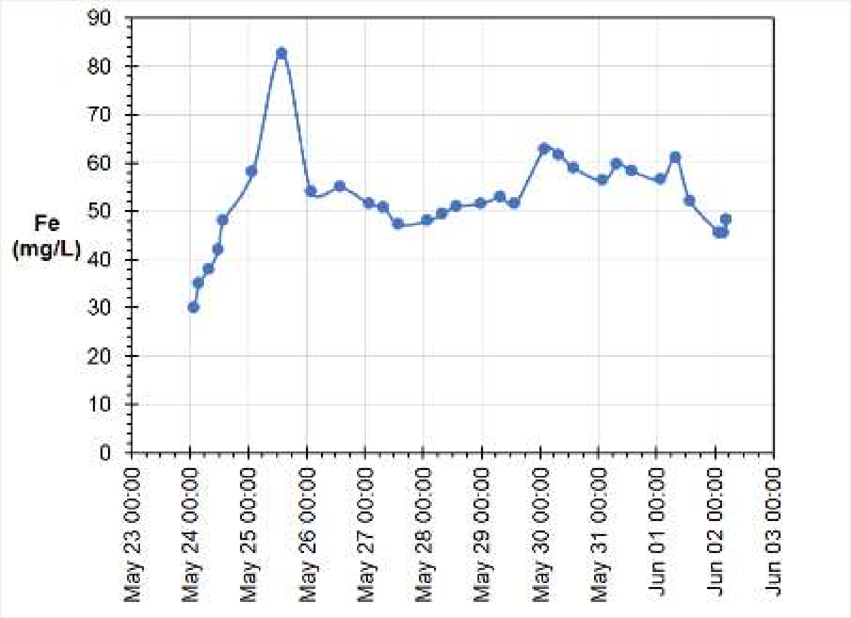

Figure 39: Fe Content of Zinc-Stripped Organic

The trends for Fe stripping efficiency and free oxalic acid in Fe strip raffinate (FeIS1R) are shown in Figure 40. A good correlation between Fe stripping efficiency and the free oxalic acid concentration is evident.

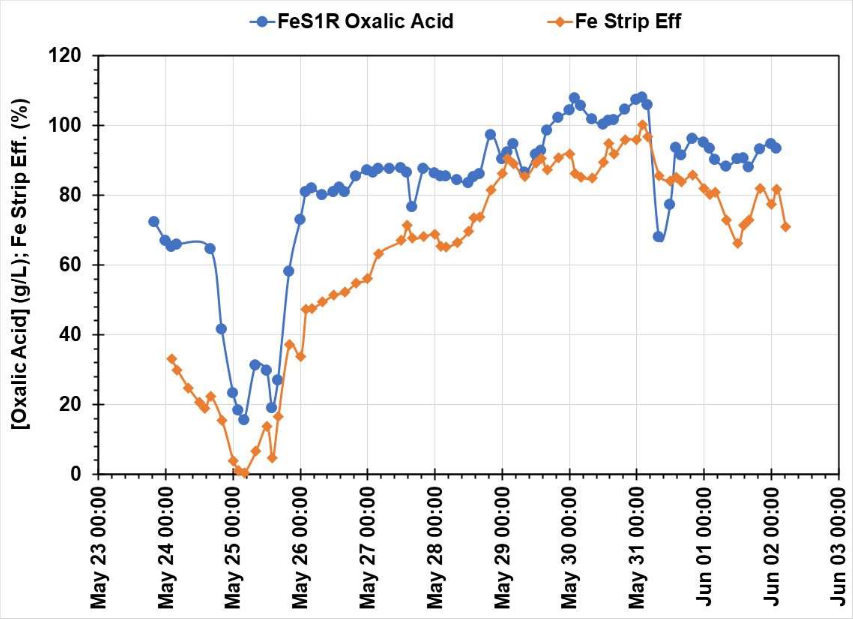

Figure 40: ISX Fe Stripping Efficiency & FeIS1R Free Oxalic Acid

The ISX continuous pilot plant experienced precipitation of mixed metal oxalate solids (Zn/Mn) in the Fe strip mixer and settler due to under-stripping of divalent metals in the Zn strip (Figure 41). Chemical analysis confirmed the solids were Zn and Mn oxalates (both insoluble) formed when the Zn-stripped organic contained slightly elevated levels of unstripped Zn and Mn.

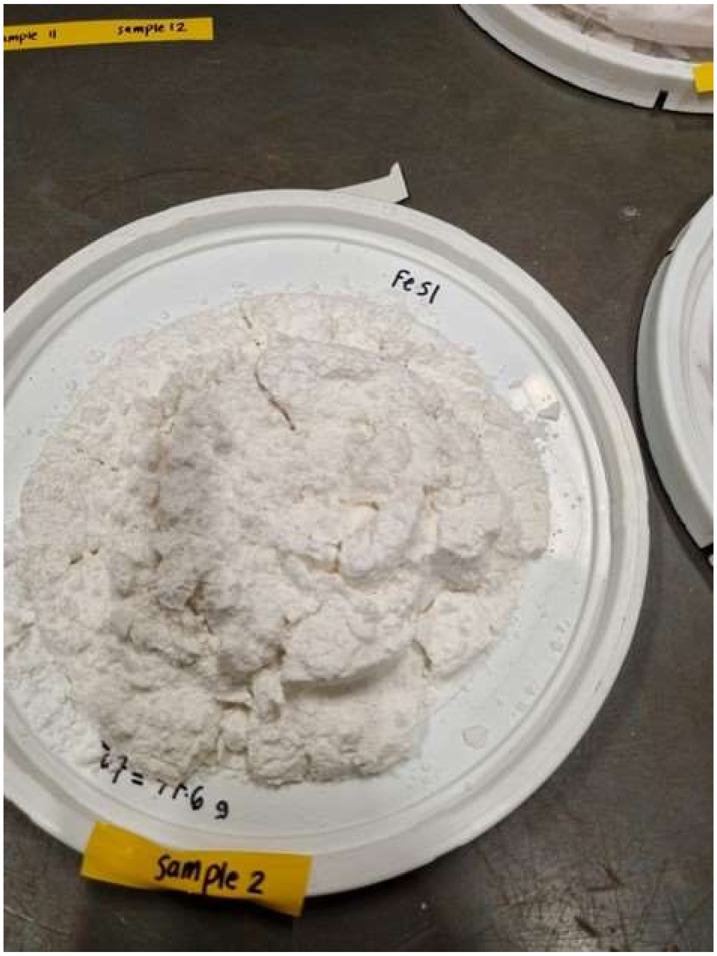

Figure 41: Solids Removed from ISX Fe Strip Settler, May 27

It was subsequently decided to add a third Zn strip stage to the commercial flowsheet, on the Zn-stripped organic bleed stream to Fe strip, with the full Zn strip acid feed flow contacting that 10% bleed stream to ensure quantitative stripping. Two bench-scale acid strip contacts were conducted on separate samples of pilot plant Zn-stripped organic to confirm the design.

The continuous pilot plant campaign proved the technical feasibility of Fe stripping using oxalic acid. An Fe stripping efficiency of 90% could be achieved in a single stage using 90 g/L oxalic acid strip solution and an advance O/A of 10:1.

Purification (TSX and PSX) Pilot Plant Operation and Results

Feed Preparation

For TSX and PSX, a synthetic Transformation aqueous feed solution was prepared from reagent grade cobalt sulphate salt for use during start up, until Purification raffinate was available. The composition is listed in Table 2. The organic feed was a fresh solution of 40% v/v D2EHPA® in VivaSol D80, to replicate ISX stripped organic.

The available quantity of cobalt LSL from the CSX continuous pilot plant was 16 L, sufficient for ~24 hours feed to PSX. Enough synthetic cobalt LSL solution was prepared to feed Purification for the remainder of the planned eight days test duration. The synthetic feed solution composition was intended to replicate the expected CSX cobalt LSL composition arising from the maximum design concentrations of Zn, Ca, Mn, Cu and Fe in ISX raffinate (CSX feed), as shown in Table 3. The composition of both purification feed streams (synthetic and CSX cobalt LSL) are listed in Table 2. The CSX pilot plant cobalt LSL contained significantly elevated concentrations of Ni and Mg that would not be expected in the commercial purification feed stream, but which persisted due to upsets experienced during CSX pilot plant operations.

Table 2: TSX & PSX Pilot Plant Aqueous Feed Composition

Component	Concentration (mg/L)			
	Synthetic Transformation Feed	Purification Feed		
		Synthetic	CSX Co LSL	Design
Al	< 0.4	< 0.3	1.5	0
Ca	3.9	44	12	39
Co	122,000	124,308	132,667	117,499
Cu	< 0.1	37	11	0.7
Fe(III)	< 4	6.0	2.5	24
Mg	2.79	27	3,533	8
Mn	0.98	202	246	98
Na	< 3	<2	16	0
Ni	20.4	39	1,530	12
S	75,700	69,854	77,667	64,821
Zn	< 2	32	22	39

Table 3: Maximum Impurity Design Basis for Purification Feed

ISX Raffinate					Purification Feed (Co LSL)		
Co	6,000	mg/L			Co	120,000	mg/L
Zn	2.0	mg/L	Co/Zn w/w	3,000	Zn	40	mg/L
Ca	2.0	mg/L	Co/Ca w/w	3,000	Ca	40	mg/L
Mn	10.0	mg/L	Co/Mn w/w	600	Mn	200	mg/L
Cu	2.0	mg/L	Co/Cu w/w	3,000	Cu	40	mg/L
Fe	0.3	mg/L	Co/Fe w/w	20,000	Fe	6	mg/L

Piloting

In TSX organic saponification, the feed organic (TRO) was contacted with an aqueous NaOH solution to pre-neutralise the target fraction of the organic extractant (initially 50% n/n). The advance O/A was controlled to a target of 6.5:1 to achieve this. The saponification target was reduced from the design value of 50% to 40% n/n Na loading when third phase formation occurred at startup on July 12.

NaOH solution addition was split between the saponification (N) and transformation stage 1 (T1) mixers after 16:00 on July 16 to eliminate third phase formation, as follows:

- 150 g/L NaOH solution addition to the saponification mixer at 35% n/n Na loading in saponified organic (NO) (40% v/v D2EHPA® basis)
- 100 g/L NaOH solution addition to T1 mixer under pH control at setpoint 4.0.

Figure 42 shows the organic saponification advance O/A based on manually measured organic and NaOH flowrates. The advance O/A was intentionally varied to achieve process targets, either Na loading in saponified organic (NO) or operating pH in the T1 mixer.

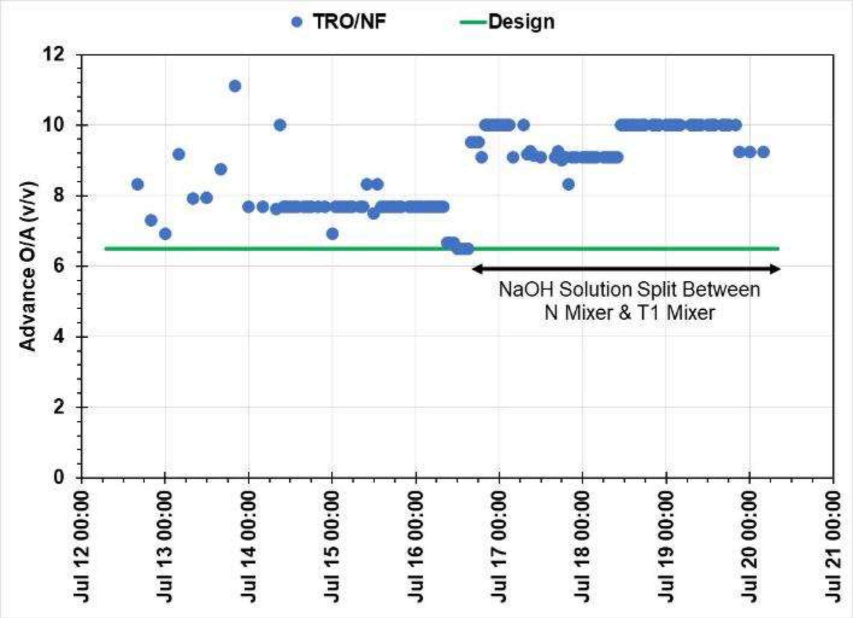

Figure 42: TSX Organic Saponification Advance O/A (40% v/v D2EHPA® Basis)

Trends for Na loading in NO and Co loading in transformation loaded organic (TLO) are shown in **Error! Reference source not found.**. The Na content of NO was under-reported during July 12 to 15 due to third phase formation. From July 16 onwards, 35% n/n Na loading was targeted in NO.

In Transformation, the feed solution (synthetic purification raffinate at 120 g/L Co) was contacted in four counter-current stages with saponified organic. The key objective was to maximise transfer of Co from the aqueous to the organic phase. The advance O/A was optimised to achieve this objective. Transformation feed was changed from the synthetic Co solution used for startup to Purification raffinate (P1R) early on July 13.

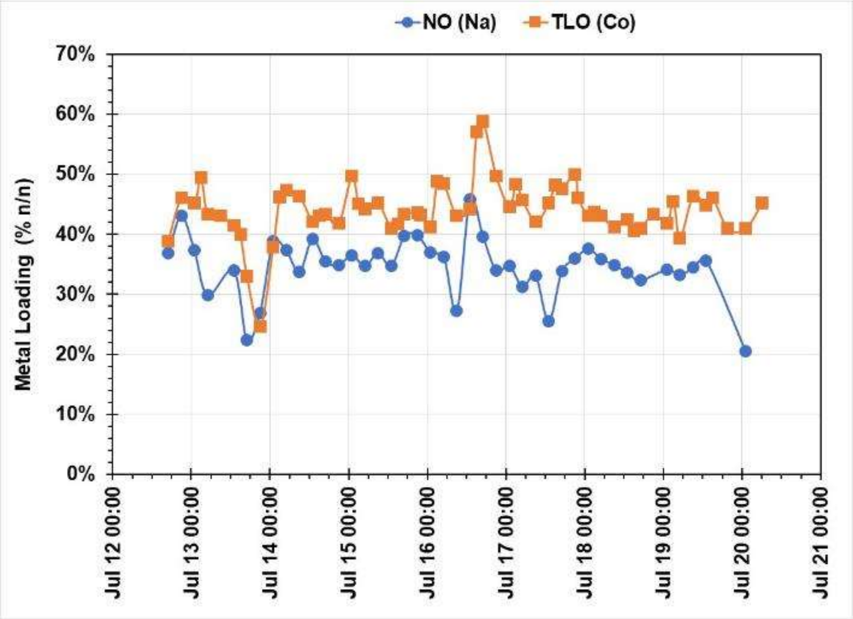

Figure 43: TSX Metals Loading in NO and TLO (40% v/v D2EHPA® Basis)

Advance O/A was used as the primary control tool in Transformation. TRO and transformation feed (TF) flow rates were varied to increase/decrease Co loading in TLO. Figure 44 shows the TSX advance O/A based on manually measured TRO and TF flow rates.

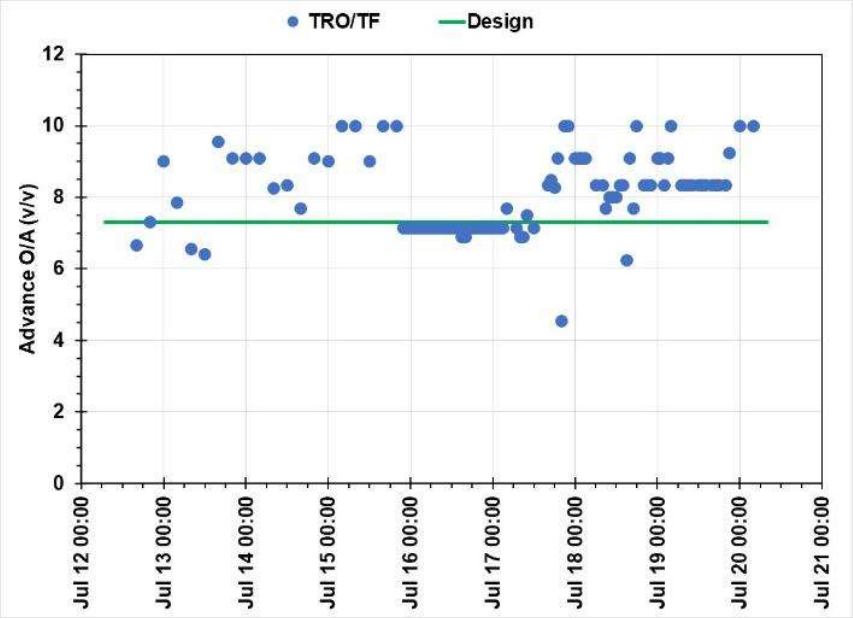

Figure 44: TSX Transformation Advance O/A

During July 15 the Co content of transformation raffinate (T1R) was near the design target of 300 mg/L and trending lower, and T1 mixer pH was between 4.0 and 4.2. These process results indicated that pH 4.0 could be a suitable setpoint for T1 mixer pH control. As discussed above, NaOH solution was added to T1 mixer under pH control (setpoint 4.0) from July 16 onwards.

Figure 45 shows the T1R Co trend. Upsets corresponding with each full profile (FP) sampling were observed, as the sample volumes of organic and aqueous abstracted from each TSX settler (~30 mL) were significant relative to the TSX feed rates (~10 mL/min organic and ~1.2 mL/min aqueous), resulting in temporary loss of interstage advance flows.

Each TSX mixer-settler was prefilled prior to startup using synthetic TF (120,000 mg/L Co). Due to the long aqueous transit time in TSX of ~ 48 hours, 72 hours of continuous operation was required to displace the prefill Co inventory through the circuit. The Co content is maintained at or below the design value of <300 mg/L from July 16 onwards.

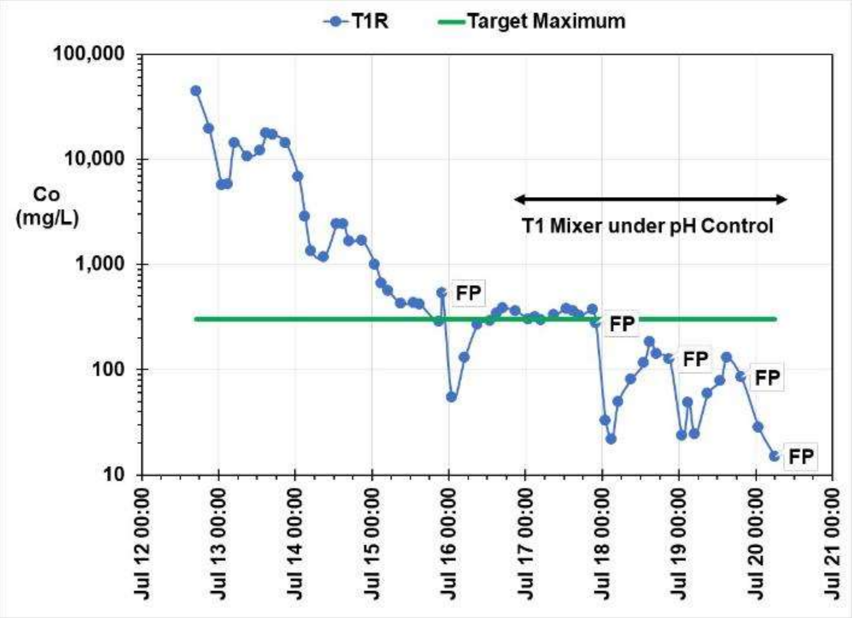

Figure 45: TSX Transformation Raffinate Cobalt Content

TLO Co loading is shown in Figure 46. The design Co loading value of 16,500 mg/L (50% n/n, 40% v/v D2EHPA® basis) was not consistently attained. Referring to the Co loading operating isotherm in Figure 47, it is apparent that the Co loading is limited to a maximum of about 14,500 mg/L when using the saponification approach with TF containing 120,000 to 140,000 mg/L Co.

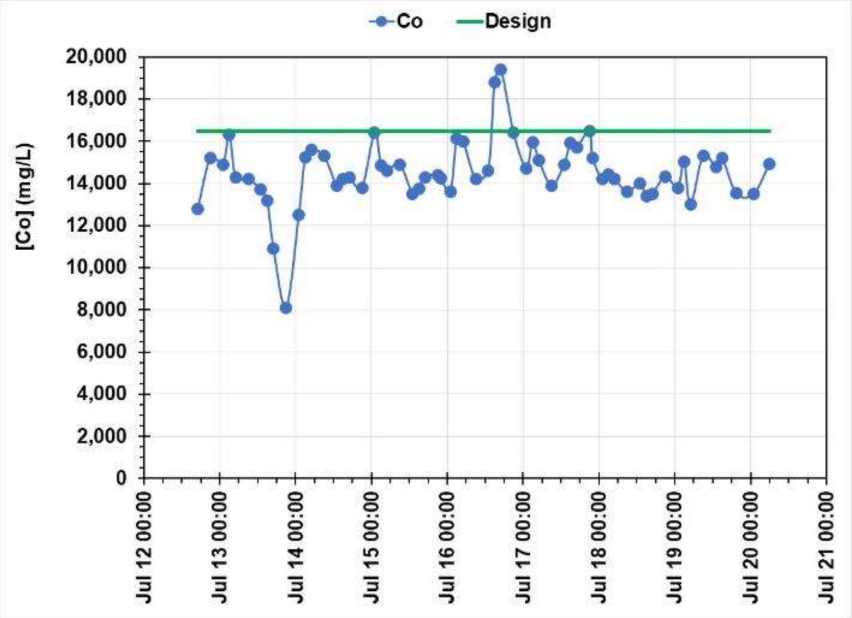

Figure 46: Co Content of TSX Transformation Loaded Organic

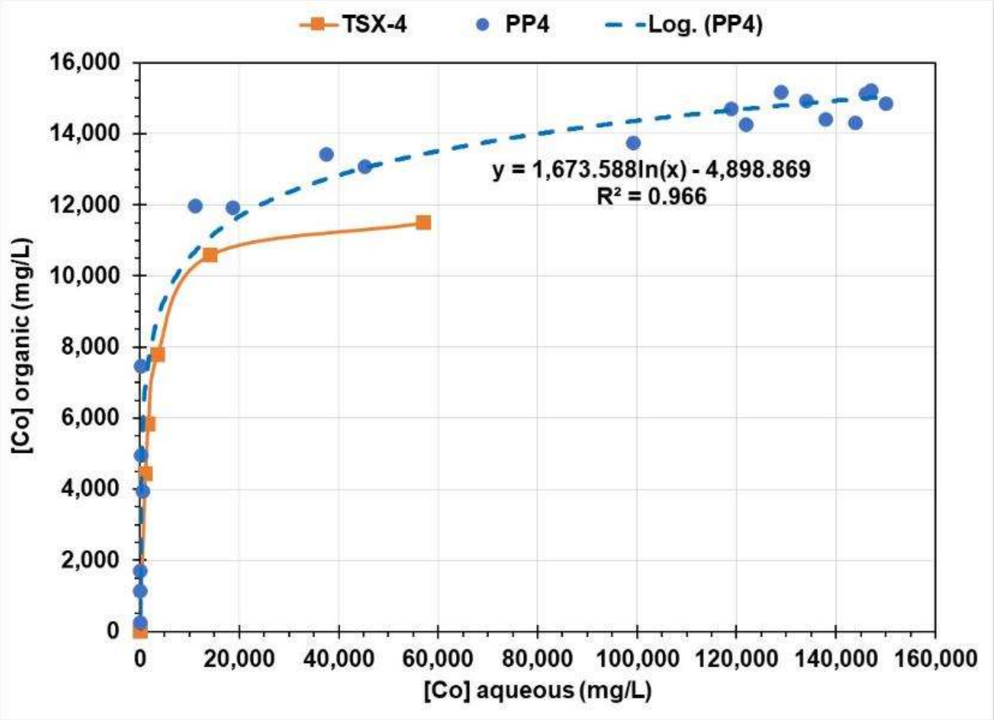

Figure 47: TSX Transformation Cobalt Loading Operating Isotherm

In Purification, the feed solution is contacted with Co pre-loaded organic in eight counter-current stages. The key objective was to maximise the transfer of Fe, Al, Zn, Ca, Mn and Cu impurities from the aqueous to the organic phase. The advance O/A was optimised to achieve this objective.

Synthetic feed solution was used for most of the campaign. CSX cobalt LSL was added over a 24-hour period, followed by a final 9-hour period, again using the synthetic feed solution, during which the aqueous inventory in the eight PSX mixer-settlers corresponding to CSX cobalt LSL was displaced.

The results of the bench-scale purification isotherm tests indicated that Cu extraction was the limiting criterion. The McCabe-Thiele diagram showed that Cu could be reduced from 40 mg/L to 2.2 mg/L with 8 stages using an advance O/A of 0.8:1. The PSX pilot plant was intentionally started with an advance O/A target of 1:1, to be conservative. Once process results confirmed the Purification stage was working well, the advance O/A target was reduced from 1:1 to 0.8:1 on July 16. Most Cu assays were below the lower reporting limit during the operating period at 1:1 PSX advance O/A target, however Cu in purification raffinate (P1R) was greater than the product maximum limit for about 36 hours during the operating period at 0.8:1 PSX advance O/A target.

It was subsequently established that the advance O/A calculated using the measured TRO feed rate to Saponification was misleading. In a typical 24-hour period, there were 21 organic samples withdrawn from the circuit between Saponification and P8, which effectively decreased the PSX advance O/A. In comparison only three samples of PF solution were collected each 24 hours. The ratio of the Cu contents of purification feed (PF) and purification loaded organic (P8O) were compared. The average Cu content of the synthetic PF solution was 37 mg/L so at an advance O/A of 1:1 and <1 mg/L Cu in P1R the expected Cu content of P8O would be expected to be close to 37 mg/L. However the P8O Cu trend showed a gradual increase to >50 mg/L Cu. The PSX effective O/A (calculated from the PSX Cu metallurgical balance) averaged 0.77:1 during the latter 48-hour period when the PSX O/A target was 1:1, and averaged 0.66:1 in the following 48-hour period when the PSX O/A target was 0.8:1.

This explains why the Cu impurity concentration was above the P1R product maximum limit. The PSX advance O/A was effectively ~0.8:1 during the period when the PSX advance O/A target was 1:1, and the PSX O/A was effectively <0.7:1 during the period when the PSX advance O/A target was 0.8:1. It has therefore been concluded that Cu Purification was successfully achieved at the design PSX O/A of 0.8:1 (Figure 48).

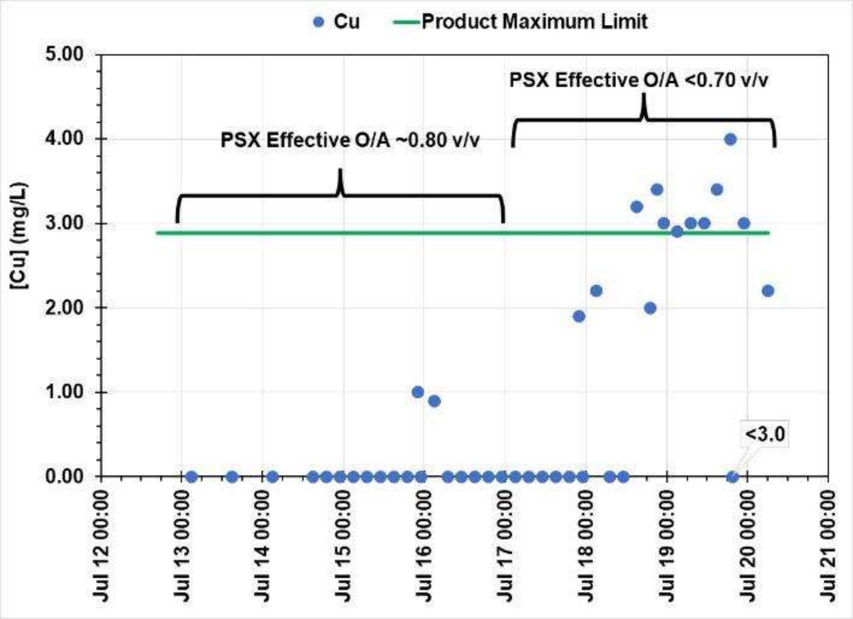

Figure 48: PSX Purification Raffinate Cu Content

Other impurities such as Mn and Ca were reduced to well below the target values for the duration of the Purification pilot campaign (Figure 49 and Figure 50). Na Purification was successful, with all P1R assay results below the product maximum limit. The majority of Zn, Fe and Al assays (for P1R progress samples) were below the reporting limits for those elements, demonstrating successful Zn, Fe and Al Purification.

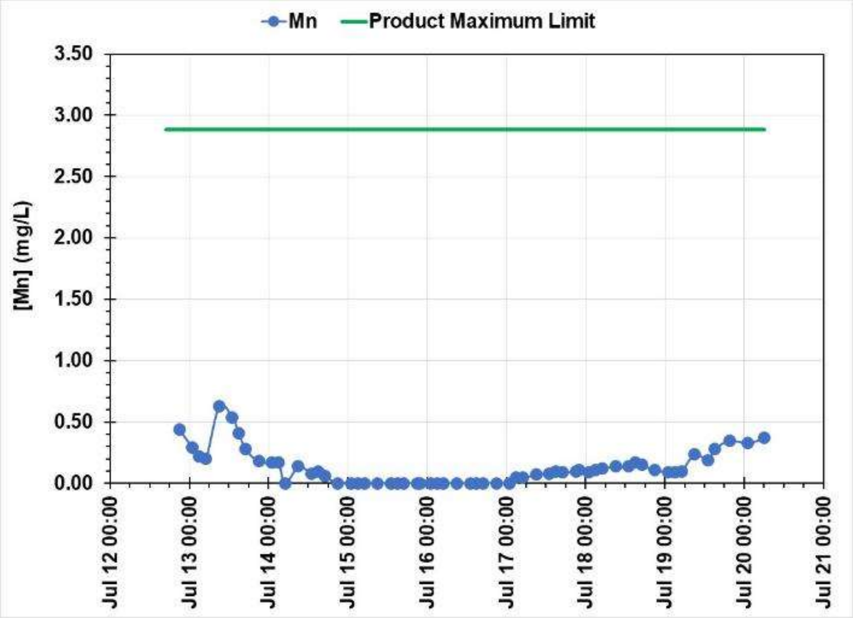

Figure 49: PSX Purification Raffinate Mn Content

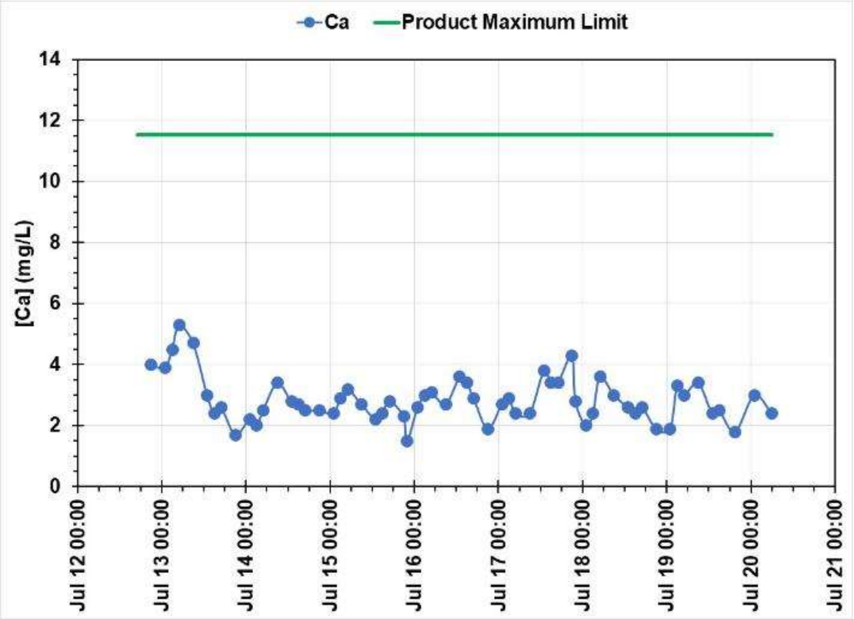

Figure 50: PSX Purification Raffinate Ca Content

The composition of each Purification raffinate pail (purified Co LSL) is shown in Table 4. Pails 1 to 5 are produced from synthetic PF and Pail 6 is produced from CSX cobalt LSL. The maximum limits shown in Table 4 are derived from QPM's maximum impurity specification for the cobalt sulfate heptahydrate product. Ni and Mg are not able to be separated from the feed solution by PSX, and the P1R results that are above the product maximum limits for those elements arise from operational issues during the preceding CSX continuous pilot plant.

Table 4: Composition of PSX Purification Raffinate Pails

Pail #	1	2	3	4	5	6	Product Maximum Limit
Component (mg/L)	**Jul 14 16:13**	**Jul 15 20:12**	**Jul 17 05:05**	**Jul 18 07:09**	**Jul 19 07:57**	**Jul 20 06:28**	
Al	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	2.9
Ca	3.8	< 0.9	< 0.9	1.6	2.2	< 0.9	11.4
Co	129,000	133,000	138,000	133,000	129,000	132,000	119,077
Cu	< 2	< 2	< 1	< 2	2.6	2.6	2.9
Fe	< 0.3	< 0.4	< 0.6	< 0.4	1.4	1.3	2.9
Mg	9.6	9.5	9.1	9.9	10.2	1 580	11.4
Mn	0.21	< 0.04	< 0.04	0.08	< 0.20	0.21	2.9
Na	< 2	< 2	< 2	2	< 5	20	57
Ni	16	18	18	18	18	857	229
Zn	< 2	< 2	< 2	< 2	< 2	< 2	2.9

As it was operated separately from the ISX pilot plant, the TSX/PSX pilot plant also included a stripping stage so that the organic could be recirculated. In the commercial plant the organic returns to the ISX Loaded Organic Tank for treatment in the ISX scrubbing and stripping circuits.

CONCLUSIONS

The ISX pilot plant outcomes validated many aspects of the design and identified opportunities for improvements to the process design criteria in several facets of the circuit. Key findings included the following:

- Confirmed four extraction and four scrubbing stages.
- Confirmed that only a single manganese stripping stage is required (reduction from four stages previously).
- Gypsum precipitation can be isolated to the manganese stripping area by pH control in scrubbing and management of the acidity in manganese and zinc stripping.
- Target raffinate quality was achieved for extended periods of time, producing a raffinate (CSX feed) with <10 mg/L Mn and <2 mg/L of Zn, Ca and Cu.
- Reduction of magnesium was achieved, effectively increasing the Co:Mg ratio in raffinate compared to feed, positively impacting downstream CSX operation.
- The preliminary commercial plant design included separate organic feed streams from the ISX Zn-stripped organic tank to Fe stripping and TSX. It is now proposed to configure Fe strip and TSX in series so that the feed organic to TSX is Fe-stripped organic with a very low Fe content.
- A sulfuric acid strip of the organic bleed to Fe Strip has been added ahead of Fe Strip. This would be effectively a third zinc stripping stage, utilising the total incoming Zn Strip acid feed flow to quantitatively strip any residual Zn and Mn from the small organic bleed flow advancing to Fe Strip, to prevent metal oxalate precipitation.
- The number of Fe stripping stages has been increased to two in series. This is expected to provide 99% Fe stripping efficiency and improved oxalic acid reagent efficiency.

The updated ISX schematic for the commercial plant is shown in Figure 51.

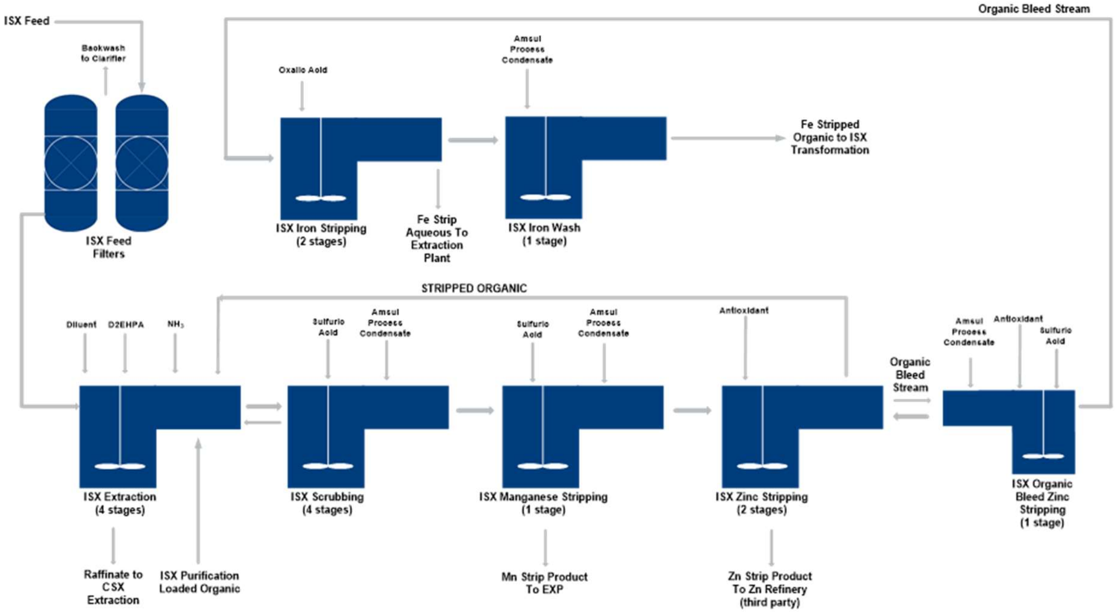

Figure 51: Schematic of the Proposed Commercial ISX Circuit after Piloting

The Purification pilot plant was successful in confirming design values for achieving a purified cobalt LSL feed to crystallisation in the commercial plant, and flagged improvements to the process design criteria in several facets of the circuit. Key findings included the following:

- Purification substantially reduces the impurity content of the cobalt LSL feed to crystallisation. The Cobalt LSL Co:Mn ratio was improved from 540:1 to 600,000:1. the Co:Zn ratio from 6,000:1 to >66,000:1, and the Co:Cu ratio from 12,000:1 to >50,000:1.

- Maximum Ca and Fe in PSX raffinate (Cobalt LSL feed to crystallisation) were determined to be 10 mg/L and 1.5 mg/L respectively.
- Confirmed 4 transformation and 8 purification stages.
- The organic loading in saponification was revised from 45-50% n/n Na loading to 35% n/n.
- The maximum achievable Co loading is about 13.5 g/L (41% n/n) using the saponification approach and 120 g/L Co in Transformation feed. This is equivalent to an advance O/A of ~9:1.
- Control to pH 4.0 using 100 g/L NaOH is required on the last stage of transformation. An equilibrium pH value of approximately 4.0 is required to achieve the raffinate target of <300 mg/L Co.
- The organic stoichiometric load in TSX is increased from 20% n/n to 40% n/n (max 45%).
- The equilibrium pH in P8 is revised from 3.5 to 2.0-2.4.

Overall, the ISX and Purification pilot plant achieved their objectives.

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The views of the author do not necessarily represent those of Queensland Pacific Metals.

REFERENCES

1. Arpalahti, A. (2023). “2023 Update on The Terrafame Nickel Operation”. Proceedings of the ALTA Nickel-Cobalt-Copper Conference, Perth, Australia, May 1-3, 2023.