

PILOT-PLANT STUDY OF SULFURIC ACID EXTRACTION FROM A NICKEL ELECTROLYTE USING ALAMINE 308

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Abstract

The solvent extraction of sulfuric acid from a nickel spent electrolyte stream at Anglo Platinum's Base Metals Refinery could replace the precipitation process that is currently the main outlet for sulfur from the flowsheet. The tertiary amine extractant, Alamine 308, exhibited excellent chemical characteristics for the selective recovery of H₂SO₄ from the electrolyte and did not suffer from the phase-disengagement problems that had been previously experienced with other tertiary amines. The acid-loaded organic phase is stripped with ammonium hydroxide, producing ammonium sulfate: the sulfate concentration of the loaded strip liquor can therefore be upgraded compared to the feed liquor. A saleable by-product, ammonium sulfate, is produced. Results of a pilot-plant trial on the optimisation of the solvent-extraction process are presented.

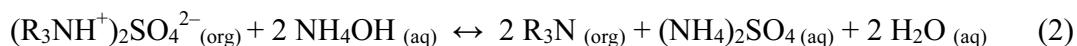
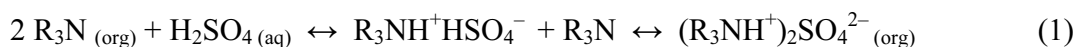
INTRODUCTION

The flowsheet of Anglo Platinum's Base Metal Refinery (BMR) (Rustenburg, South Africa) involves sulfuric acid leaching of sulfide smelter products followed by solution purification and electrowinning (EW) of nickel and copper [1, 2]. At present, the only outlet for sulfur is *via* the production of Na₂SO₄, which is crystallised following neutralisation of nickel spent electrolyte (SE) with NaOH to precipitate Ni(OH)₂. The cost of producing sodium sulfate far exceeds its resale value. Of the various alternative processes to remove sulfur considered for this flowsheet, the most viable is the use of solvent extraction (SX) [3].

Tertiary amines have been employed for acid removal from other electrolytes. Tumilty patented H₂SO₄ extraction from cobalt electrolytes using 10 vol.% Alamine 336 to improve cobalt EW efficiency [4]. Gottlieb *et al.* investigated the recovery of H₂SO₄ from copper tankhouse electrolyte bleeds with 40 vol.% tris(2-ethylhexyl)amine, which would allow acid to be returned to the circuit without the accompanying impurities which accumulate in the closed SX-EW loop [5, 6].

Although reasonable extraction of H₂SO₄ from the nickel electrolyte can be achieved with various extractant functionalities (including amines, alcohols, and phosphine oxides), the recovered acid is considerably more dilute than the initial acid content of the feed and cannot be substantially upgraded by distillation or evaporation due to azeotrope formation. A promising alternative is removal of H₂SO₄ from the nickel SE using a tertiary amine extractant (Equation 1) and its recovery as ammonium sulphate

(Equation 2)—a product saleable as fertilizer in the agricultural industry.



In 2007, this process was tested in a pilot-plant campaign using Alamine 336, a tri-octyl/decyl amine, as the extractant [7]. Using three extraction stages, sulfuric acid was recovered with >99% extraction efficiency and stripped in two stages to yield a loaded strip liquor (LSL) containing ~300 g/l $(NH_4)_2SO_4$. To reduce the impurity deportment to the LSL, the selectivity of the extractant for sulfate over borate anions (added as boric acid to the electrolyte to maintain cathode quality in EW) was exploited by operating close to the loading capacity of the organic phase, resulting in the preferential loading of sulfate and restricting the co-extraction of borate.

Although excellent extraction efficiency and selectivity of extraction were measured in this trial [7], excessive physical entrainment of both the aqueous and organic phases was measured in the extraction, scrub, and strip circuits and contributed to impurity deportment to the LSL. Measures taken to minimise the entrainment losses, such as installation of coalescers and picket fences and reduction of the extractant concentration, were not effective. It was necessary to install an organic coalescer on the raffinate line to recover organic back to the circuit and an aqueous coalescer on the loaded organic line to reduce the deportment of aqueous phase to the strip and scrub circuits. Furthermore, only operation under aqueous-continuous mixing conditions gave acceptable bulk phase-disengagement times whereas organic-continuous mixing resulted in phase-separation times in excess of 10 min.

As potential alternatives to Alamine 336, the physical and chemical performances of other tertiary amines, including tris(2-ethylhexyl)amine (TEHA), Alamine 308, and Alamine 310, were evaluated in bench-scale studies. TEHA was eliminated from consideration because it is not commercially available and Alamine 310 exhibited similar problematic physical characteristics to Alamine 336. The physical performance of Alamine 336 did not improve with the addition of isodecanol as a modifier. Alamine 308, or tri-isooctyl amine, with isodecanol as a modifier, performed well and was selected for further pilot-scale testing.

The results of a 20-day pilot-plant trial, treating ~34 l/h of nickel SE are reported. The main objective was to verify the physical performance of the Alamine 308 extractant with isodecanol as modifier under continuous operating conditions. Additionally, the acid extraction was optimised and $(NH_4)_2SO_4$ concentration of the LSL maximised, while minimising transfer of nickel and boron. The deportment of nickel to the product is important because of limits on that element in fertilizer specifications, whereas the recovery of H_3BO_3 to electrowinning has cost-savings implications.

PILOT-PLANT EQUIPMENT AND EXPERIMENTAL METHODS

The circuit configuration for the pilot plant is shown in Figure 1, with photographs of the pilot-plant setup in Figures 2 and 3. The circuit comprised four extraction, one scrub, and two strip stages. Mixer settlers (7 L mixing volume and 0.13 m² settling area) were configured for counter-current flow of the aqueous and organic phases. Solutions were pumped into the plant *via* peristaltic pumps; inter-stage solution transfer was by means of pumping impellers. The pH of each stage was monitored using pressurised pH electrodes (Hamilton) and the pH of the strip circuit was controlled by pH controllers linked to aqueous ammonia dosing pumps. To optimise mixer organic-to-aqueous volumetric ratios (O:A), aqueous recycles were employed. The terminal mixers of the extraction and strip circuits (E4 and S1) were run under organic-continuous mixing conditions to minimise organic losses to the aqueous outlet streams.

The nickel SE (feed to SX), supplied by Anglo Platinum BMR, assayed 36 g/l H₂SO₄, 40 g/l Ni, and 1.7 g/l B. The organic phase comprised 10 vol.% Alamine[®] 308 (Cognis) and 5 vol.% isodecanol (Protea Mining Chemicals) in the aromatic diluent ShellSol[®] A150 (Shell Chemicals). Demineralised water was used as the scrub and strip liquors, with 25% m/m NH₄OH solution added directly into the strip mixers to maintain the required strip pH profile. Flowrates, pH, and other relevant operational variables were measured hourly. All streams were assayed 4-hourly for acid concentration (by titrimetric analysis) and 8-hourly for nickel, sodium, and boron (by inductively coupled plasma optical emission spectroscopy).

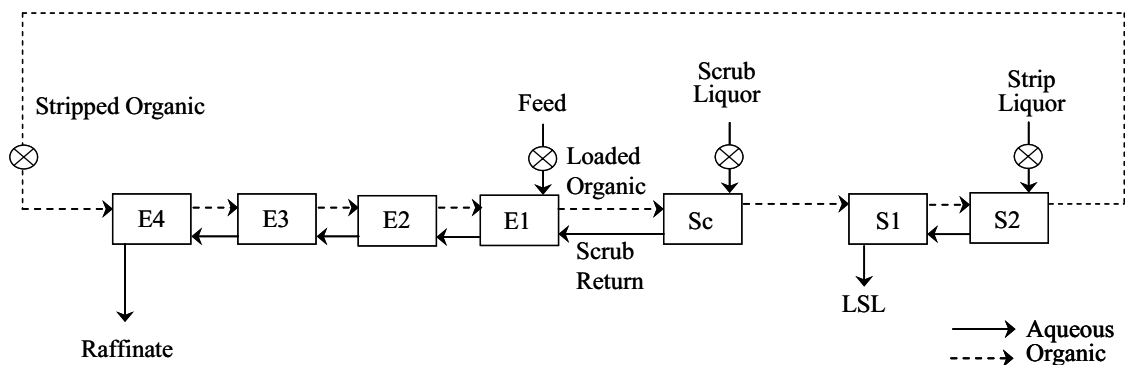


Figure 1. Pilot-plant circuit configuration.



Figure 1. Front view of pilot plant, showing mixer settlers and stripped organic holding tank and the loaded strip liquor tank on right.



Figure 2. Rear view of pilot plant, showing mixing boxes, dosing lines, pH controllers, and pumps.

RESULTS AND DISCUSSION

Physical Performance

The physical appearance of the Alamine 308 organic phase in this campaign was translucent and the streams in both the aqueous and organic overflow weirs of the mixer-settler boxes were visually clear of the opposite phase. The introduction of picket fences into the settlers reduced the dispersion band widths and it was not necessary to include either aqueous or organic coalescers. In contrast, during the campaign using Alamine 336 [7], aqueous phase in the organic weirs and an organic layer in the aqueous weirs were detected. The Alamine 336 organic phase in the extraction settlers had a green tint (due to entrained aqueous Ni SE), while the aqueous phase in the strip settlers was milky and organic droplets were visible on the walls of the settlers.

Nickel and sodium cations are not chemically extracted by tertiary amine (anion exchanger) extractants so their deportment through the circuit is assumed to occur only by physical means. The nickel deportment was therefore used as a measure of the aqueous-in-organic entrainment of the system. Under optimised conditions, the Alamine 308 loaded organic phase contained 82% less nickel than the corresponding Alamine 336 system, confirming that aqueous-in-organic entrainment was significantly less in the Alamine 308 system.

The mixers in the Alamine 336 campaign could only be operated under aqueous-continuous mixing conditions for phase disengagement times to be acceptable: under organic-continuous mixing, the dispersion band extended to fill the entire settler due to the excessively slow rate of phase disengagement. In this Alamine 308 campaign, however, the mixers could readily be operated organic-continuous, and the E4 and S1 mixers were operated in this mode for the entire campaign with no difficulty. Some foaming in E4 and S1, experienced at start-up, was eliminated by adjusting the aqueous recycle flowrates so that the mixer O:A values were approximately unity.

Extraction Circuit Performance

The extraction circuit comprised four extraction stages. With the exception of stage E4, which was operated organic-continuous, all the extraction stages operated under aqueous-continuous conditions.

The theoretical loading of acid as the sulfate anion (Equation 1) was calculated as 11 g/l H₂SO₄, while theoretical loading as bisulfate was calculated as 22 g/l. The measured acid loading at 98% extraction efficiency averaged 16.2 g/l during the campaign, indicating that some loading of bisulfate does occur. A decrease in extraction efficiency to 90% increased the measured acid loading on the loaded organic to 18.2 g/l, indicating that, as would be expected, an increase in loading as the bisulfate anion occurs as capacity on the organic phase decreases.

The selectivity of the tertiary amine extractant for sulfate over borate anions was again evident and was enhanced by adjusting the extraction efficiency to limit the organic-phase capacity available. Figure 4(a) shows the acid and boron profiles across the circuit at 90% extraction efficiency. The high acid concentration in the extraction circuit,

particularly in E4 and E3, restricted capacity on the organic phase and resulted in the preferential loading of sulfate/bisulfate in the E2 and E1 stages and, consequently, a loaded organic phase that contained less boron. Excess capacity on the organic phase (Figure 4(b)) when operating at 98% extraction efficiency resulted in lower acid concentrations in the E4 and E3 stages and allowed for the co-loading of boron which is then carried over as an impurity to the scrub and strip stages.

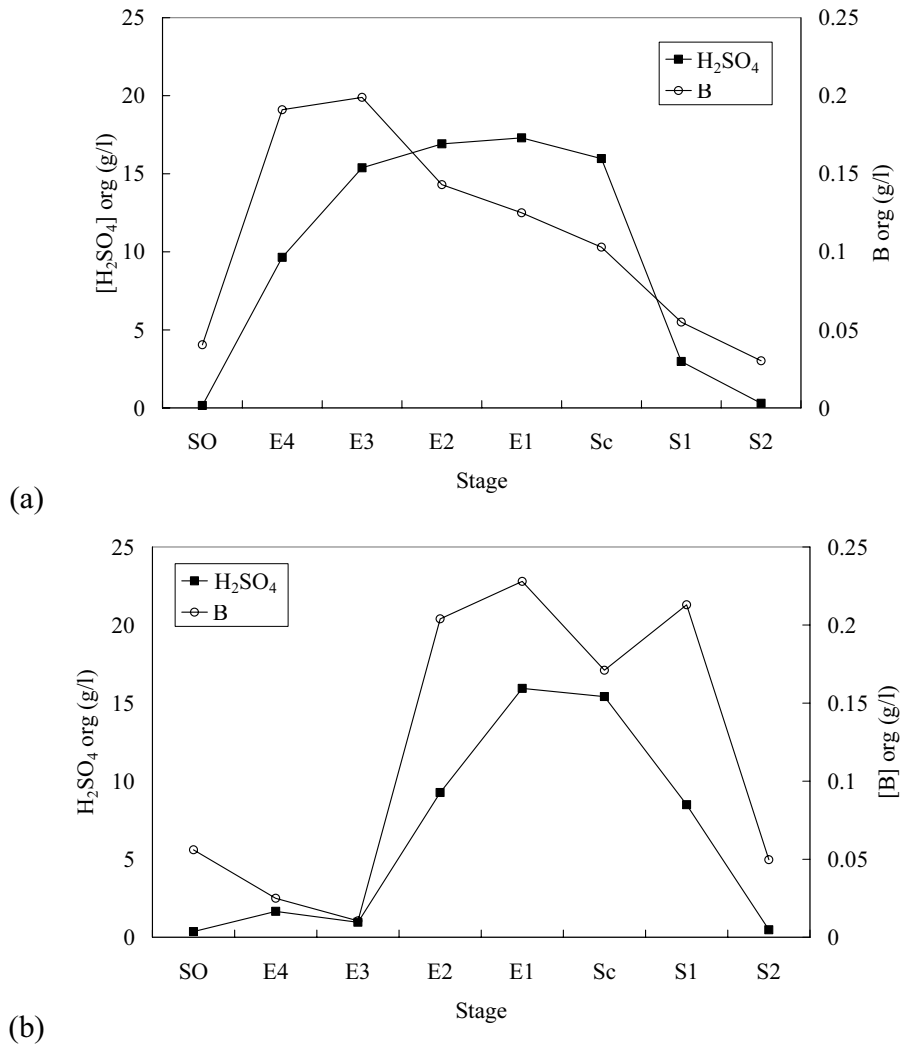


Figure 4. Acid and boron profiles across the circuit at (a) 90% and (b) 98% extraction efficiency.

Scrub Circuit Performance

The scrub circuit used demineralised water as the scrub liquor which was acidified from Day 17 by direct dosing of 98% H₂SO₄ into the mixer. This stage was intended to perform both chemical scrubbing and physical washing of impurities from the loaded organic (E1 org) before it entered the strip circuit. Because the loaded scrub liquor was returned to the extraction circuit, the advance O:A was maintained as high as possible at ~21 to avoid dilution of the raffinate. Some scrubbing of acid from the loaded organic (between 0.5 and 1 g/l) did occur in the scrub stage but this was returned to the extraction circuit so does not represent a loss. Figure 5 shows the profiles for (a) boron, which is chemically extracted, and (b) nickel, which is physically entrained in the organic phase.

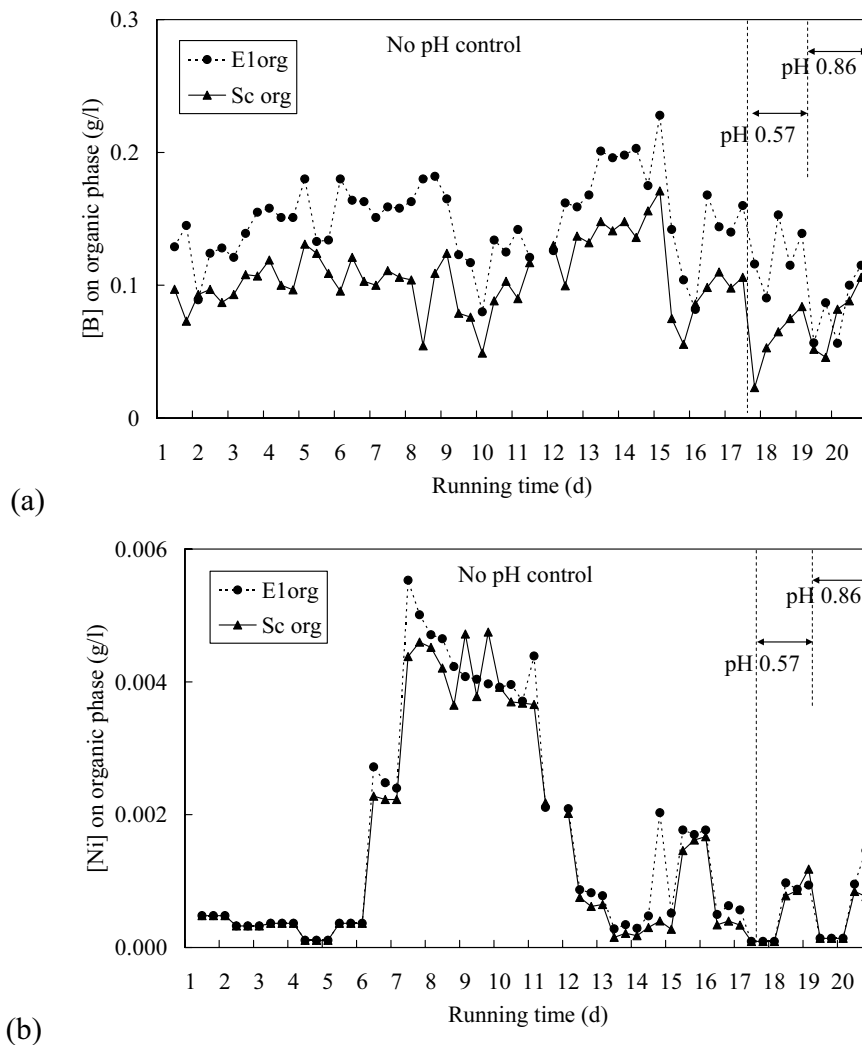


Figure 5. Effect of the scrub circuit and pH control of the scrub mixer on the mass flow of (a) B and (b) Ni in the loaded and scrubbed organic phases.

Boron was scrubbed from the loaded organic phase and reduced from an average concentration of 0.15 g/l to 0.11 g/l ($\Delta B = 0.040$ g/l) when no pH control was applied. The average amount of boron scrubbed from the loaded organic (ΔB) increased to 0.044 g/l when the scrub mixer pH was adjusted to 0.57 and reduced to 0.035 g/l when the pH was increased to 0.86. It seems that pH adjustment of the scrub liquor increases the reagent requirements of the process but does not result in a significant decrease in the boron concentration in the loaded organic; the runtime, however, may have been insufficient to achieve steady-state results. The philosophy of adjusting the pH of the scrub circuit to increase the scrubbing efficiency needs to be considered in conjunction with the product purity required and possible added selectivity that crystallisation of the LSL product stream could introduce.

Nickel on the loaded organic is not removed in the scrub circuit, indicating that it is not effective as a wash stage. The overall nickel transfer in the loaded organic is generally low, at 0.001 g/l Ni under optimised conditions, and a wash stage would not be required to reduce the value further.

Strip Circuit Performance

The ammonium sulfate concentration in the LSL product stream as a function of the advance O:A is shown in Figure 6. The strip O:A was continually increased during the campaign (by decreasing the strip liquor flowrate). Since the pH profile of the strip circuit was adjusted by the addition of 25% NH_4OH to each mixer, this introduced an additional aqueous stream to the strip circuit and, in effect, decreased the measured O:A ratio. Under the highest O:A tested, the NH_4OH flowrate was almost equal to that of the strip liquor itself, so there is little opportunity to further increase this parameter. Although the concentration of NH_4OH used for pH adjustment could be increased, concern exists regarding the potential detrimental effects of high localised ammonia concentrations or soap formation. Alternatively, gaseous ammonia could be used and injected into the mixer feed lines to avoid dilution of the product liquor.

The LSL was recycled back to the strip circuit as strip liquor from Days 8 to 16 in an attempt to progressively increase the ammonium sulfate concentration of the product. The circuit configuration during this LSL recycle period is shown in Figure 7. An average $(\text{NH}_4)_2\text{SO}_4$ concentration of 444 g/l was achieved during this period. No problems were experienced with phase disengagement or precipitation in the strip circuit, leaving room to potentially increase this concentration further, up to the $(\text{NH}_4)_2\text{SO}_4$ solubility limit of 700 g/l. The average $(\text{NH}_4)_2\text{SO}_4$ concentration achieved when the LSL was not recycled was 265 g/l, which is comparable to the LSL concentration of 293 g/l achieved during the Alamine 336 trial [7]. A notable disadvantage of recycling the LSL is that an increase in the impurity concentrations, particularly boron, of the product liquor concomitantly occurs, as shown in Table 1. The aqueous phase concentrations for boron in the scrub and strip circuits (Figure 8) clearly show the increase during the LSL recycle and decrease once the LSL recycle was discontinued.

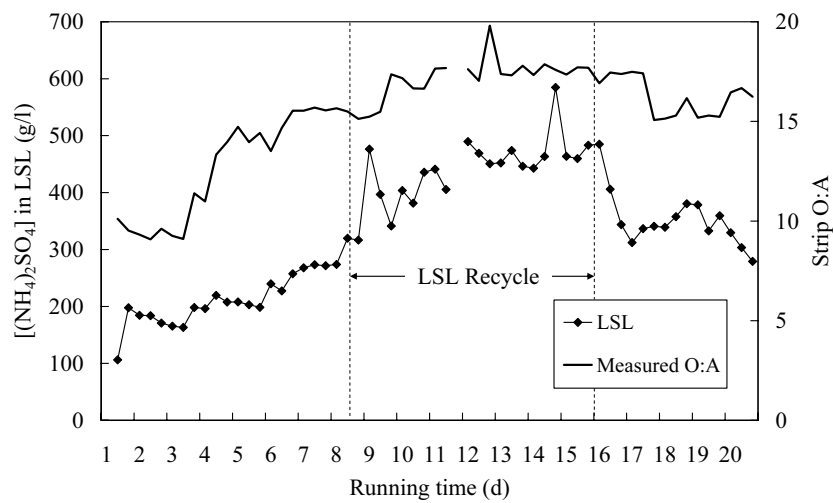


Figure 6. Ammonium sulfate concentration of the LSL as a function of the strip O:A ratio.

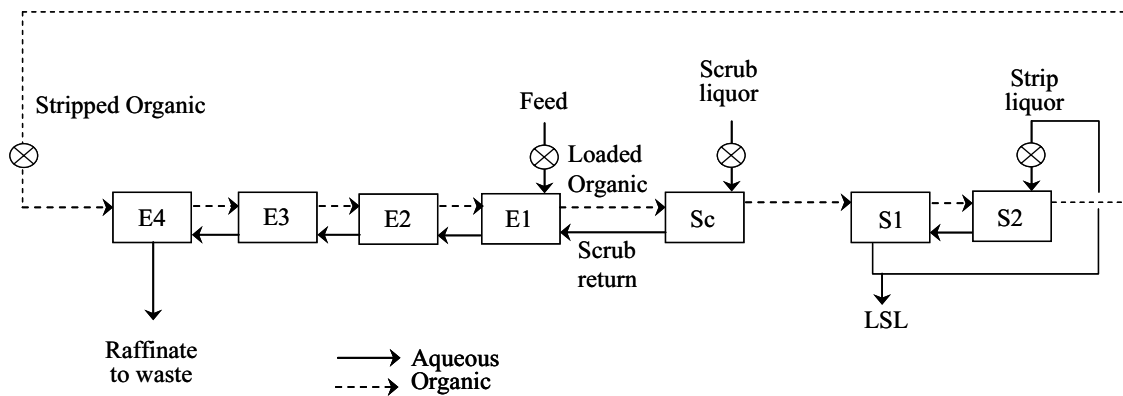


Figure 7. Pilot-plant circuit configuration during LSL recycle.

Table 1. Average impurity deportment to LSL.

Component	Impurity concentration in LSL (g/l)	
	During LSL recycle	No LSL recycle
(NH ₄) ₂ SO ₄	444	265
B	2.3	1.6
Ni	0.03	0.02
Na	0.04	0.03

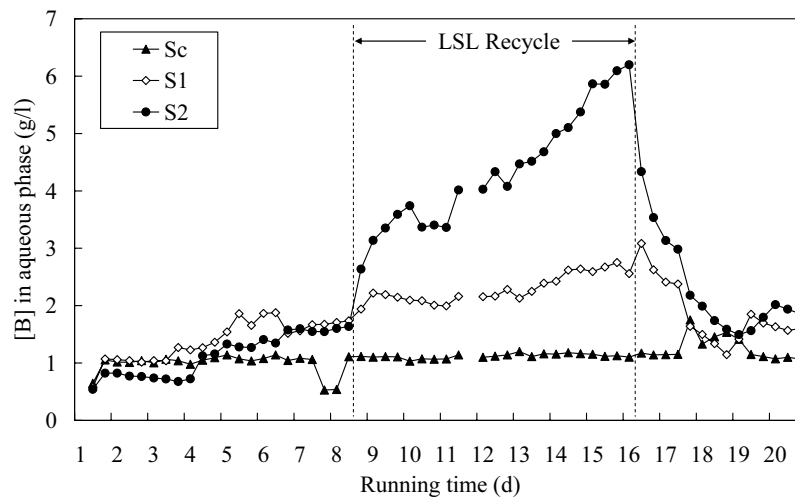


Figure 8. Boron concentration of the aqueous scrub and strip stages during the campaign.

Product Purity

Table 2 presents typical analyses of the various process streams under optimised conditions, indicating the product purity achieved in this trial. Crystallisation of the LSL gave a white crystalline product that was identified by x-ray diffraction as $(\text{NH}_4)_2\text{SO}_4$. Chemical analysis indicated that some further purification of the product occurs during the crystallisation process. The impurity department of a bench-scale crystallisation of the pilot-plant LSL is shown in Table 3: most of the boron and nickel report to the mother liquor while sodium is equally distributed between the crystals and mother liquor. It is likely that even higher purities could be achieved on optimisation of the crystallisation process.

The specifications for fertiliser-grade ammonium sulfate target a limit of 0.3% B (as calcium borate) and 180 mg/kg Ni [8]. Calcium borate is preferred as other forms of borate, such as sodium borate, can potentially be toxic if overdosed whereas calcium borate remains safe due to its slow-release property. The ammonium sulfate product crystallised from this process may require additional purification for boron: although the total boron content met the specification at 620 mg/kg B, it is probably as present as ammonium borate. Nickel is not expected to be problematic, as this product analysed 7 mg/kg Ni, confirming that additional selectivity is introduced by the crystallisation step. Further purification of the LSL by ion exchange ahead of crystallisation could be considered, particularly to remove boron present as ammonium borate.

Table 2. Compositions of process streams under optimised conditions*.

Component	Feed	Raffinate	Loaded Organic	Scrubbed Organic	Stripped Organic	LSL
H ₂ SO ₄ (g/l)	36.0	4.02	19.2	19.1	0.51	203 [#]
B (g/l)	1.70	1.44	0.10	0.08	0.008	1.6
Ni (g/l)	40.0	38.0	0.001	0.001	0.001	0.02
Na (g/l)	49.6	45.6	< 0.01 [‡]	< 0.01 [‡]	< 0.01 [‡]	0.03

* 10 vol.% Alamine 308 and 5 vol.% isodecanol in ShellSol A150; extraction O:A = 1.9; strip O:A = 15; no LSL recycle.

[#] equivalent to 265 g/l (NH₄)₂SO₄.

[‡] value at the detection limit in organic phase.

Table 3. Impurity department during crystallisation.

Component	Relative department (% of total impurity)	
	(NH ₄) ₂ SO ₄ crystals	Mother liquor
B	3.5	96.5
Ni	14	86
Na	59	41

CONCLUSIONS

The physical performance of Alamine 308 with isodecanol as a modifier is superior to Alamine 336 in the extraction of acid from Ni SE, without a compromise in the chemical performance. Alamine 308 showed similar selectivity for sulfate over borate as was seen in the Alamine 336 system. The impurity department to the loaded organic phase can be reduced by adjusting the extraction efficiency, thereby operating close to the loading capacity of the organic phase. There is thus a trade-off between maximising extraction efficiency and minimising impurity transfer. The scrub stage facilitated removal of some boron from the loaded organic phase but did not wash the entrained aqueous nickel carry-over effectively. The product liquor concentration was upgraded to 444 g/l (NH₄)₂SO₄ by recycling the LSL to the strip circuit as strip liquor, however this was at the expense of increasing the impurity loading on the stripped organic that then influenced the department of impurities throughout the circuit. The average (NH₄)₂SO₄ concentration when not recirculating the LSL was 265 g/l. High quality (NH₄)₂SO₄ crystals were produced on crystallisation of the LSL.

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After completing her Masters degree at the University of Stellenbosch, Karen joined Anglo Platinum's Research Centre where she was involved in various platinum group metals research projects. She joined the Extractive Metallurgy group when Anglo Research was formed where her main area of interest is solvent extraction.

