EXTRACTION OF COPPER AT ELEVATED FEED CONCENTRATIONS

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ABSTRACT

A number of flowsheets have been designed and operated, or are currently being considered, to extract copper from leach solutions having much more copper than the 4 g/L levels typically found in heap leach liquors. Dealing with these solutions has required that the envelope for "normal" copper solvent extraction be pushed beyond the usually considered limits. Others have published information on flowsheets to recover copper from leach liquors containing over 25 g/L copper. Secondary solvent extraction circuits are often required to attain satisfactory overall recoveries. This paper reviews some of the issues faced in three pilot plant circuits that were operated by SGS Lakefield Research to produce cathode copper from solutions containing 8 to 20 g/L Cu. The primary objective was to maximize copper extraction using one solvent extraction circuit. The role of feed acidity and the disposition of impurities such as iron and chloride are considered. The challenges of running short SX piloting campaigns are discussed.

INTRODUCTION

Copper solvent extraction was originally developed in the 1960's to recover copper from relatively dilute leach solutions, typically heap leach liquors with copper tenors in the 1 to 4 g/L range. The use of the standard oxime reagents has become an accepted unit operation for this application. In designing circuits to treat 4 g/L copper liquors, a minimum of testwork is generally carried out. The two principal reagent manufacturers, Cognis (LIX reagents) and Avecia (Acorga reagents) have extensive application databases from which they can draw to predict the performance of their reagents with a particular copper SX feed. They both have software to generate equilibrium isotherms used to predict staging requirements. The extraction and stripping kinetics of oxime-based reagents have been extensively investigated and are well understood by the manufacturers. Their databases and the experience of their personnel allows them to recommend and specify reagent schemes, circuit layouts and process design parameters.

In more recent years hydrometallurgy is finding wider application in the treatment of complex ores that contain copper. Very often, the plant will need to process a sulphide concentrate rather than an oxidised copper ore that is readily leached at ambient conditions. It is probably going to be using more aggressive oxidative leaching methods, for example, oxygen pressure leaching. Higher percent solids are employed in the leaching stages both to keep plant sizes as small as practically possible, and to ensure that the heating requirements of the process are being fully met by oxidising the available sulphur. This results in more concentrated leach liquors with higher metal tenors than those produced in heap leaching.

The leaching processes employed produce solutions containing copper and other metal values, for example nickel or PGM, that may be sequentially recovered. Often, the overall economic feasibility of the project requires the recovery of more than one of the metals in solution.

Copper solvent extraction has been adapted to deal with the leach liquors from a number of these flowsheets, some of which have been or are currently operating. The challenges to conventional solvent extraction posed by leach liquors from concentrates have been discussed by Kordosky [1] and Tinkler [2]. Compared with heap leach liquors, the differences can be summarised as follows:
- higher copper tenors, typically over 20 g/L (and even up to 40 g/L);
- more iron in the pregnant leach solution (PLS), and generally wider range of other metals often present at concentrations comparable to copper.

This in turn presents a number of challenges in the design of the flowsheet. A description of the principal ones, which is by no means exhaustive, follows. Many of the factors are interrelated, and will affect other parts of the flowsheet as well each other.

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For each mole of copper extracted, the raffinate acidity is increased by one mole. Extracting 4 g/L Cu completely, adds about 6.2 g/L H_2SO_4. Extracting 20 g/L Cu adds 31 g/L acid. The higher the acidity, the more the extraction reaction is inhibited. Ultimately, with more acid, stripping takes place. A solution is to use a stronger copper extractant, one which will continue to extract copper at higher acidity, but which in turn requires more acid to be stripped.

In order to extract more copper, one can increase the concentration of extractant to give more capacity. This can in turn result in more viscous organic phases, particularly the loaded organic, leading to poorer phase separation performance with increased entrainment losses, and increased impurity transfer to the strip side. One can operate at a higher O/A ratio. In mixersettlers, the best mixing is obtained when the phase ratio in the mixers is close to 1. As well, it is desirable to operate close to O/A = 1 to be able to set the phase continuity. For example aqueous continuous is preferred in the first extraction stage where the loaded organic is produced. Therefore, the minor (aqueous) phase will have to be recycled, and the SX circuit size will be increased significantly. Finally, starting higher up on the isotherm, it is probably necessary to increase the number of stages in the extraction circuit, as compared with a heap leach operation, to attain the extraction desired.

An SX-EW operation is an acid plant. It takes copper out of solution and replaces it with protons which make their way, via the organic extractant, back to the raffinate stream. In heap leach operations the acid is consumed during leaching. In a concentrate leach scenario, it may be more difficult to integrate the acidifed raffinate back into the process, as the acid coming from this stream is not necessarily required or may in fact be detrimental in leaching. Various flowsheets have been developed to deal with high copper leach liquors, and the choice depends on how high the copper concentration is and what else is in the ore or feed.

HIGH COPPER CONCENTRATION FLOWSHEETS

One group of flowsheets has evolved to handle leach liquors with very high copper levels, often over 40 g/L. In this case, the circuit designs do not rely on SX to remove all the copper in one step. The primary extraction circuit takes the bulk of the copper, leaving a raffinate that may contain 8 to 10 g/L. This primary raffinate cannot be discharged because of its copper values. Therefore, it is recycled in the flowsheet to a point where the acidity can be used to do more leaching. An example of this design is the Pasminco Metals circuit described by Tyson et al.[3]. This plant leached a matte in an oxygenated chloride sulphate solution. The PLS contained 40 g/L Cu of which 30 g/L were extracted using 30% Acorga M5640. The 10 g/L raffinate was returned to the secondary leach stage where it was mixed with a stronger acid stream to dissolve more of the matte. The overflow from the secondary leach, carrying the copper and acid from the SX raffinate, was in turn directed to the primary leach where the acidity was consumed by fresh matte feed.

Perhaps the best known mill currently handling a concentrated copper solution through a solvent extraction circuit is Western Metals' Mt. Gordon Operation in Australia [4, 5, 6]. This plant uses oxygen pressure leaching to dissolve the copper values from their chalcocite orebody. It was the first commercial application of pressure oxidation to leach copper from a sulphide ore. The plant flowsheet has been complicated by various phases of expansion, but essentially involves oxygen pressure leaching of the ore in SX raffinate. Pressure leaching is followed by a train of atmospheric leach tanks where ferric ion is consumed and leaches a few additional percent of copper.

Copper is extracted from the pregnant leach solution in Mt. Gordon's primary SX circuit having two extraction and two strip stages and using a 23% Acorga M5640 extractant mixture. The copper concentration is reduced from 35 g/L to 10 g/L. As the raffinate is recycled to leaching, the contained copper is not lost, and the acidity of the raffinate is used in the leaching step.

To maintain the water balance, a bleed must be taken from the raffinate. Copper is extracted from this bleed with a smaller secondary SX circuit using a side-stream of the stripped organic from the primary circuit. The loaded organics are combined and stripped together. Overall recovery of leached metal is not reported in the literature, but ore to metal copper recoveries in excess of 90% are claimed, along with leach recoveries of 93%, which would imply that the recovery of dissolved copper is on the order of 96-97% through the SX/EW circuits.

More recently, Dynatec Corporation have reported in a number of articles [7, 8, 9] on the flowsheet development that they have been involved in for the Las Cruces massive sulphide ore situated near Seville, Spain. The Las Cruces flowsheet is somewhat more complex than the Mt. Gordon's, in order to deal with the particularities of the ore. Like Mt Gordon, the ore is pressure leached, but the Dynatec circuit includes a two-stage countercurrent leach with an atmospheric leach preceding the pressure leach.

The Las Cruces flowsheet also incorporates two SX circuits, somewhat like at Mt. Gordon, with the secondary SX treating a raffinate bleed stream. Copper, typically assaying in the 22±2 g/L Cu range, is extracted from the PLS coming from the atmospheric leach using a 30% solution of Acorga M5640 reagent. The primary circuit employs three extraction stages, one scrub and two strip stages. The main task of the scrub stage is to reduce iron transfer. The raffinate, at 1.5 to 4 g/L copper, still contains too much of this element to be considered dischargeable. Furthermore, the raffinate contains 45±2 g/L sulphuric acid, and as such is a useful source of acid for the pressure leach step. Therefore, the bulk of the raffinate is directed to the second stage pressure leach which is carried out on the first stage atmospheric leach residue. Primarily determined by the water balance, a bleed of 20 to 25% of the raffinate is taken and first sent through the secondary SX circuit to extract more copper. This circuit employs the same strength extractant but has only

single extraction and strip stages. The secondary raffinate is reported to contain in the range of 0.3 to 2 g/L copper. The overall performance of the circuit is very much dependent on how much of the free acidity is consumed in the primary leach, and on the copper concentration to primary SX. It is reported that during the piloting campaigns, when the primary SX feed contained 20 g/L Cu and 14 g/L H_2SO_4, overall copper recovery exceeding 99% (of the copper put into solution from the ore) could be attained.

Another flowsheet that employs two successive solvent extraction circuits to handle a high concentration pregnant leach solution SX feed produced by two-stage leaching has been described by Sole [10] reporting on the piloting results from the circuit tested for the Konkola Deeps Expansion Project in the Anglo American Research Laboratories. Here, the orebody contains both sulphide and oxide zones. The sulphide leach circuit produced a PLS containing 60 g/L Cu. This was sent to a primary solvent extraction circuit that removed 50 g/L Cu using a 32% extractant strength. Both Acorga M5640 and LIX 984N were tested. All of the primary circuit raffinate, still high in copper (~10 g/L) and acid (~80 g/L H_2SO_4), was used to leach the oxide ore, thus consuming the acid. The oxide ore PLS containing about 6 g/L Cu, was routed to a second SX step employing 16% extractant to produce a final raffinate with a copper tenor that averaged 0.25 g/L over the piloting campaign.

All of these flowsheets have found ways to deal with the relatively high concentrations of acid in the raffinate, by recycling the raffinate back to the process to consume this acid. Pressure leaching was used in two of the examples mentioned as an effective way of consuming this acidity. In the other two, the acidity was consumed in atmospheric leaching steps. All the flowsheets have also found ways to deal with the relatively high copper levels in the primary SX raffinates while at the same time maintaining good overall copper recoveries. Mt. Gordon and Las Cruces produce raffinates from which a bleed stream is taken to a secondary scavenger SX circuit. In the Konkola Deeps circuit, the oxide ore consumes the acidity allowing a second SX circuit to operate at much more favorable conditions enabling production of low copper raffinates. In the Pasminco circuit, the copper left in the discharged stream is precipitated out and recycled to the lead plant from where it eventually would get back into the copper circuit in the copper lead matte feed.

INTERMEDIATE COPPER CONCENTRATION FLOWSHEETS

There has been somewhat less published about copper solvent extraction circuits dealing with feed copper concentrations in the 8 to 20 g/L range. This paper will present the experience obtained at SGS Lakefield in three different piloting campaigns which fall into this category. In each case, the raffinate was recycled to another part of the pilot plant flowsheet. However, unlike the situations discussed above for the high copper feed flowsheets, it was an objective of these copper SX circuits to maximise copper extraction and to produce raffinates that carried well below 1 g/L Cu, and to do this with a single copper SX circuit.

It must first be noted, that in all three cases, no bench-scale testwork had been budgeted for or carried out. While this may not be an ideal scenario for the person charged with designing the circuit, it is a reality of commercial testing. The solvent extraction circuits were designed and constructed based on literature data. This was augmented in the later two cases, by modeling simulation to predict circuit performance that was furnished by the reagent supplier. The copper circuits were part of larger integrated flowsheets that were being tested. As such, the copper circuits were largely viewed as "knowns", having a service function to provide the rest of the circuit with recycle streams and in two cases, to provide the client with cathode copper samples.

The three pilot campaigns corresponding to project work on three different ores for three clients, are identified as G3M, PMMN and LXOX. Table I lists some general characteristics for the three pilot campaigns. These campaigns were all of relatively short duration as had been specified by our clients. The conditions upstream of the SX circuit were being changed. Therefore, the feed to the SX circuit was varying almost continuously throughout each campaign. This presented an additional challenge to the operators who had to be supported by timely analytical results.

Table 1 General Characteristics of Circuits Operated

CIRCUIT IDENTIFIER	GSM	PMMN	LXOX
Cu in SX feed (g/L)	8.5-9.7	13-28	13.5-17.5
Total Operating Time (h)	16[1], then 31[2]	240	300
Cathode Copper Produced	No[1], Yes[2]	Yes	Yes
Raffinate Recycled to Circuit	Yes[1], No[2]	Yes	Yes

[1] operated in large cells; [2] operated in small glass cells

One way to try to stabilise the SX circuit feed conditions is to accumulate larger homogeneous feed batches and campaign these through the circuit. However, this is often not possible because with a relatively short piloting schedule for the overall flowsheet, every attempt is made to minimise solution holdup in the circuit. Longer holdup just increases the time required to fill the circuit, for any operating changes to make their way through the circuit, and for steady-state to be reached. For any of the three campaigns discussed, it would be difficult to claim that the SX circuit was ever operating under truly stable feed conditions. A fine balance must be maintained between minimising SX feed inventory and making sure that feed to the SX circuit is not interrupted by shortages or upstream shutdowns causing SX circuit stoppages.

G3M Circuit: The G3M project undertook the development of a flowsheet to treat a copper gold ore that contained both sulphide and oxide zones. The overall process that was eventually settled on was flotation of the sulphide ore, pressure leaching of a blend of the sulphide concentrate with the oxide ore, copper SX/EW and gold recovery from the leach-neutralisation residues by cyanidation.

Two different leaching flowsheet configurations were tested during the relatively short piloting period. The flowsheet that was ultimately recommended for further testwork resembled the Las Cruces circuit without the secondary solvent extraction. The SX raffinate was recycled to an atmospheric leach stage preceding the autoclave.

The solvent extraction circuit was initially set up to operate in conjunction with the rest of flowsheet. Larger fiberglass mixer-settlers were employed with two extraction and one stripping stage. The circuit had been designed on the basis of a feed containing 9 g/L Cu at a pH of 2. The organic selected was 12% LIX 984 (Cognis) in Isopar M (Exxon) aliphatic diluent.

This extractant is an unmodified 1:1 blend of 5-dodecylsalicylaldoxime and 2-hydroxy-5- nonylacetophenone oxime. The circuit was operated at ambient temperature (~20ºC). The feed that ultimately arrived at the solvent extraction circuit contained 9.5 g/L Cu at a pH of 1.5. It quickly became evident that raffinates below 1 g/L were not being produced by this circuit. The organic strength was increased to 15% and operating phase ratios were adjusted. A second run was performed in the larger mixer-settler units with slightly altered conditions. The operating conditions and results for these two initial runs are compared in Table 2 for conditions as they were at the end of each run.

One major change was that the feed pH was increased over 2 with $Mg(OH)_2$. Because of other changes in the circuit taking place, the level of Mg in the SX feed actually decreased despite the addition of $Mg(OH)_2$. The acidity of

the strip feed was also increased to promote stripping. This led to an improvement in copper recovery from 83% to 90% which was better but not sufficiently high to produce a raffinate that could be discharged.

At this point in the test campaign, the trial of the rest of the circuit was completed. SX feed solution was set aside and run through a continuous SX circuit that was set up using smaller glass mixer-settlers. The organic phase from the larger circuit continued to be used for all subsequent testwork. The principal objectives were to produce lower raffinates and to examine the effect of operating phase ratios and staging on the overall extraction. The main change made to the circuit design was to increase staging to three extraction and two strip. It was anticipated that the feed to SX coming from leaching would be hot enough to heat the SX system to about 45ºC and the effect of higher operating temperature was also examined in these runs. Operating conditions and results can be compared in Table 3.

The switch to more extraction and stripping stages decreased the raffinate copper concentration from around 1 g/L to below 0.2 g/L. Extractions as high as 98% were obtained with O/A = 4 in extraction. Changing the extraction phase ratio was very effective in controlling the amount of copper in the raffinate, as the data in Table 3 show. The result for net copper transfer in run 3-5 agrees with that reported by Kordosky [1] at similar extraction recovery.

Table 2 G3M Circuit 2E 1S Large Mixer-Settler Conditions and Results

RUN			1	2
Stages	Extraction		2	same
	Stripping		1	same
Advancing O/A Ratios	Extraction		3.9	4
	Stripping		1.9	2
Mixing Time	Extraction	(min)	2.6	2.7
	Stripping	(min)	2.2	same
Temperature	(ºC)		~20	same
Organic Phase (LIX 984/IsoparM)		(v/o)	15/85	same
Extraction Feed	Cu	(g/L)	9.6	same
	pH		1.5	2.3
	Fe	(g/L)	0.95	0.62
	Mg	(g/L)	20	10.5
	Mn	(g/L)	2.9	1.5
Raffinate	Cu	(g/L)	1.6	0.95
	pH		1.2	1.1
Strip Feed	Cu	(g/L)	30	31
	H_2SO_4	(g/L)	165	180
Organic Copper	Loaded	(g/L)	4.6	5.2
	Recycle	(g/L)	2.5	2.7
Copper Recovery		(%)	83	90
Net Transfer	(g Cu/L/(v/o extractant))		0.14	0.17

Table 3 G3M Circuit 3E 2S Small Mixer-Settler Conditions and Results

RUN			3-2	3-5	4-4
Stages	Extraction		3	same	same
	Stripping		2	same	same
Advancing O/A Ratios	Extraction		4.1	2	3.3
	Stripping		2.1	2.1	2.1
Mixing Time	Extraction	(min)	2.3	2.0	2.2
	Stripping	(min)	2.0	2.0	1.9
Temperature	(^{o}C)		~45	same	same
Organic Phase (LIX 984/IsoparM)		($^{v}/_{o}$)	15/85	same	same
Extraction Feed	Cu	(g/L)	8.9	8.6	9.3
	pH		2.1	2.3	2.4
	Fe	(g/L)	2.2	2.1	3.5
	Mg	(g/L)	1.7	1.7	1.9
	Mn	(g/L)	12.3	13.1	14.2
Raffinate	Cu	(g/L)	0.16	0.8	0.28
	pH		1	1.2	1.1
Strip Feed	Cu	(g/L)	36.5	37	35.5
	H_2SO_4	(g/L)	178	178	171
Organic Copper	Loaded	(g/L)	5.8	8.1	6.2
	Recycle	(g/L)	2.9	3	2.6
Copper Recovery		(%)	98	91	97
Net Transfer	(g Cu/L/($^{v}/_{o}$ extractant))		0.19	0.34	0.24

Physically, the circuit operated very well. Phase separations were rapid and there was no evidence of increased organic deterioration at the higher operating temperature, although it must be stated that with the relatively short operating time, none would really have been apparent. With only 15% LIX 984 in the extractant, there did not appear to be any qualitative difference in phase separation performance at the two temperatures used.

The piloting campaign was not designed to examine some of the other parameters, for example iron transfer, that might be important in operating a commercial circuit. It did demonstrate that the copper extractant, selected without any screening work, was effective and that conditions could be tailored to produce the desired extraction levels.

PMMN Circuit: The PMMN flowsheet was developed to recover a range of metals from a sulphide bulk concentrate. The principal pay metals are copper,

nickel, gold and platinum group precious metals (PGM). The flowsheet is an application of the PLATSOL® Process [11] that has been developed at SGS Lakefield Research. The key unit operation in the PLATSOL® Process is oxidative pressure leaching of the sulphide concentrate with chloride salts to promote dissolution of the gold and PGM. The pilot plant was operated for 10 days (24h/d) with copper SX/EW running continuously during this time. The SX unit operation was fully integrated with the rest of the flowsheet, and the copper SX raffinate was recycled to the leach circuit, with a portion being set aside for Ni/Co recovery that was to be carried out in a separate piloting campaign. Over 44 kg of cathode copper were produced.

The copper SX circuit was set up using fiberglass mixer-settlers which are shown in the overview in Figure 1 and in a close-up in Figure 2. Mixer volumes are about 2 L, settlers close to 6 L. The circuit was constructed with two extraction and two strip stages. One scrub stage was installed to control chloride and entrained impurity transfer from the extraction feed. It used de-ionized water acidified to pH 1.2 at an advance O/A phase ratio of 20/1. The organic phase was 30$^{v}/_{o}$ LIX 984 (Cognis) in Orfom SX-7 (Chevron Phillips) diluent which is an approximately 80/20 aliphatic/aromatic mixture. The same batch of organic was used throughout the campaign with some fresh makeup for volumes removed in sampling. The SX circuit operated at ~40ºC, both to promote phase separation, and because this was the expected temperature from the heat balance on the flowsheet. Mixing time was 3-4 min per stage.

The objectives of the copper circuit were to produce a raffinate around 0.3 g/L Cu and to control the transfer to electrowinning of the chloride in the PLS introduced in the PLATSOL® leach. The leach liquor also contained significantly higher concentrations of dissolved metals than normally found in a copper heap leach solution as indicated in Table 4, so the selectivity of copper SX both in terms of chemical rejection of other metals, and with respect to good phase separation to avoid entrainment of extraction aqueous, was of paramount importance.

The key challenge in operating this copper SX circuit is shown in Figure 3. The SX feed copper concentration ranged from 12 g/L to 28 g/L with one batch near the end of the run having only 8 g/L Cu. To cope with the changing feed conditions, the extraction O/A ratio was adjusted frequently as the campaign progressed. To cope in turn with the

Table 4 PMMN SX Circuit Feed – Other Elements

COMPONENT	Ni	Co	Zn	Fe$_{Total}$	Mg	Cl
CONCENTRATION RANGE (G/L)	13-17	0.5-0.9	1.6-3.8	3.4-14.5	2.5-5.5	6-7

changing loading on the organic phase, the strip O/A ratios had to be adjusted to maintain stable operation in EW. While the feed pH did vary as the data in Figure 3 show, the variation in terms of free acidity at these pH levels is small and had much less of an effect on the extraction performance than the change in copper concentration in the feed.
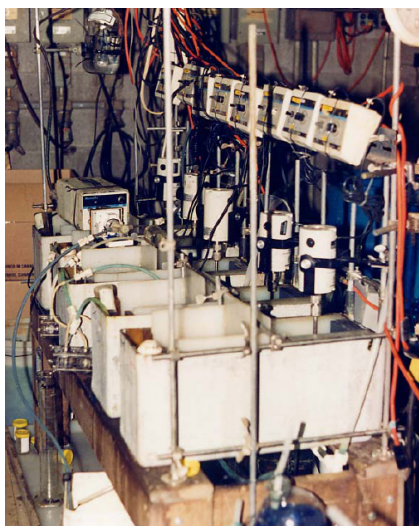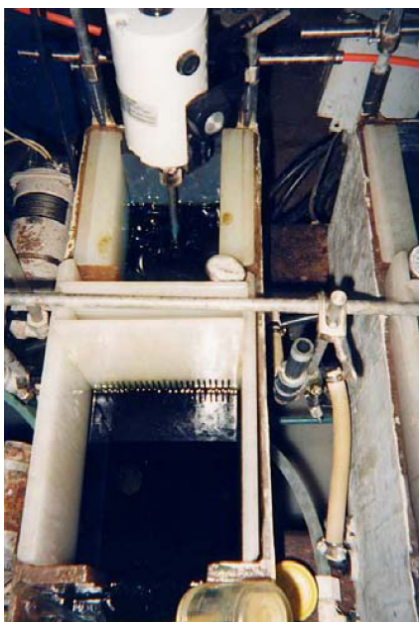

Figure 1 Cu SX Circuit Overview

Figure 2 Strip Stage Close-up

Figure 4 shows the copper loading on the organic phase as the run progressed. When the organic phase was overloaded, copper extraction decreased. Good results, better than 95% copper extraction, typically corresponded to net copper transfer values in the 0.30 to 0.37 g/L Cu per % extractant range.
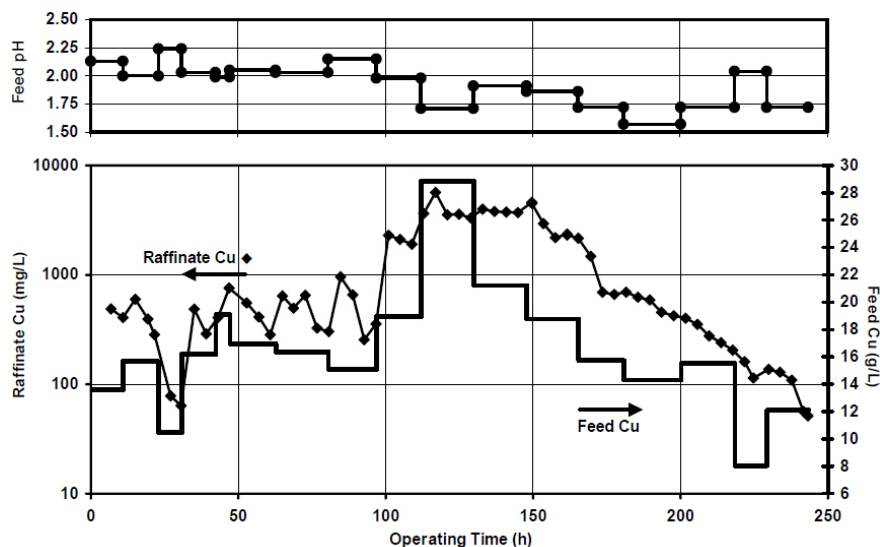
Figure 3 PMMN Circuit Feed Conditions and Raffinate Response
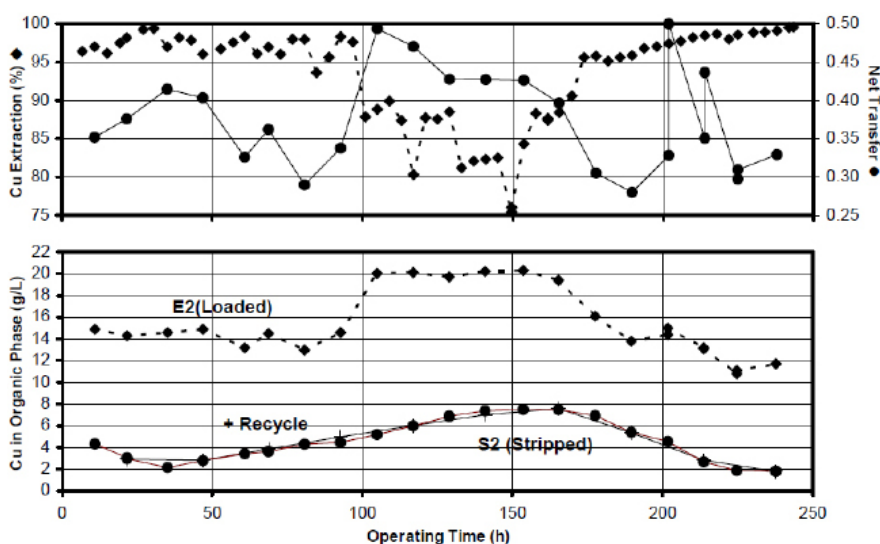
Figure 4 PMMN Organic Cu Trends and Cu Extraction
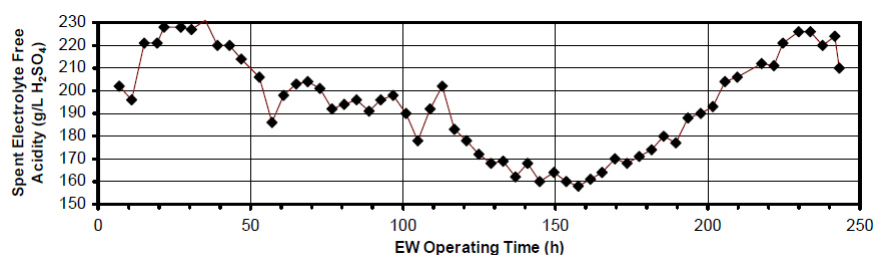
Figure 5 PMMN Circuit Spent Electrolyte (Strip Feed) Acidity

The steady drop in strip feed acidity over the first 100 h of the run, as seen in Figure 5, only added to the problem caused by the marked increase in extraction feed copper (Figure 3) in that the lower acidity led to a steady rise in the recycle organic copper concentration, as less copper was stripped Figure 4. When the high copper feed was encountered, the deterioration in circuit performance was accelerated. Once the feed copper concentration decreased to about 16 g/L and the strip feed strength was increased, copper extraction increased (Figure 4), despite the slight continuing decline in the feed pH.

With the significant amounts of other metals in solution, as well as the chloride, the selectivity of the extractant

was of interest. The only element that was observed to be accumulating in the strip liquor leaving the stripping stage was iron. The data are plotted in Figure 6 and a best-fit line is also shown. The slope of this line corresponds to an accumulation rate of 1.9 mg/L per hour of operation which in turn equates to about 6 mg Fe transferred per liter of organic to strip.

Chloride transfer was not observed, as the chloride levels in the strip liquor remained below 10 mg/L for the duration of the piloting campaign. The scrub stage was effective in controlling chloride transfer, which would be through entrainment of aqueous with the loaded organic. Therefore, it was concluded that the iron transfer was not from entrained aqueous, but rather from extracted iron. Some iron in the electrowinning aqueous is desirable. The level is usually controlled in commercial operations by the EW electrolyte bleed. However, if on further investigation and longer piloting, it had been established that the rate of iron transfer was too high, a different extractant choice could reduce iron transfer. It is generally accepted that ester modified aldoximes such as Acorga M5640 (Avecia) have higher Cu/Fe selectivity [1].

The piloting work for the PMMN project established that a single copper solvent extraction circuit could attain raffinate levels around 0.3 g/L from feeds in the 12 to 16 g/L Cu range. The circuit was flexible in being able to respond to changing feed copper concentrations with changes in extraction phase ratios. It should also be possible to use stronger extractants, those that extract at higher acidity, to further reduce raffinate copper levels.

LXOX Circuit: The LXOX piloting project treated a copper ore that also contained some copper sulphides. The test flowsheet incorporated an atmospheric acid leach of the ore, solid liquid separation to produce the copper SX feed, washing of the residue in a CCD circuit with SX raffinate, flotation of a sulphide concentrate from the washed CCD residue and oxidative pressure leaching of the sulphide concentrate. The acid and ferric ion produced in the
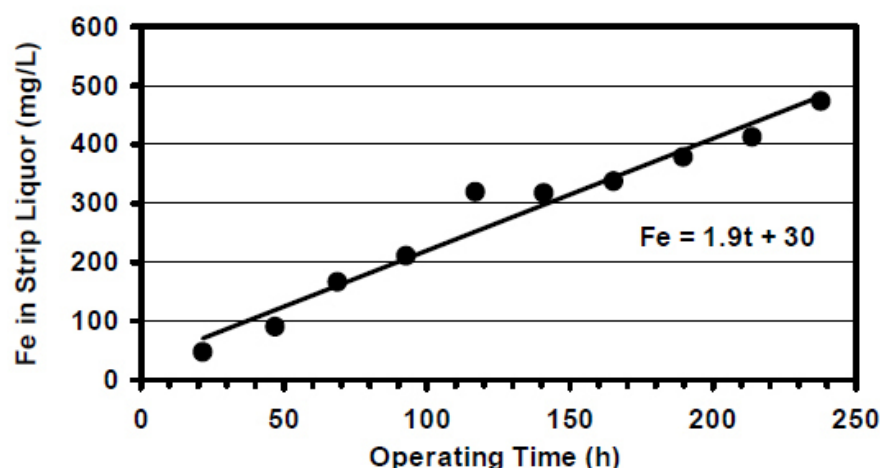

Figure 6 Iron Accumulation in the PMMN Strip Liquor

pressure leach step was to be consumed in the atmospheric leach. The principal source of soluble copper loss in this flowsheet is with the flotation tailings. As noted, SX raffinate was used to wash the leach residue in the CCD circuit. Entrained solution leaving the CCD circuit with the washed residue as part of the CCD underflow would have as much copper as the SX raffinate, and this would be, for the most part, lost in the flotation step, exiting with the flotation tailings.

The main operating targets of the SX circuit were to make low copper raffinates, while at the same time producing high-grade cathode copper. The LXOX pilot plant SX/EW circuit operated for 13 days (24h/d), fully integrated with the up-and-down-stream unit operations. The pilot plant produced over 105 kg of cathode copper grading over 99.98%.

The mixer-settler circuit used for the LXOX campaign was built with the same units as those depicted in Figures 2 and 3. However, the circuit was installed with three extraction stages, one scrub and two strips. In this circuit, the scrub feed solution was a mix of spent and rich electrolytes and de-ionised water, blended to match a compositional target that had been calculated from the process mass balance model. It was fed to the scrub stage at an advance O/A ratio of 40/1, and scrub liquor exiting this stage was recycled to the leach circuit.

Two organic phases were used during the piloting campaign. The run

started with a fill of $35^v/_o$ LIX 622N (Cognis) which is ~60% 2-hydroxy-5-nonylsaliclyaldoxime plus ~20% tridecanol modifier, in Escaid 110 (Exxon) aliphatic solvent extraction diluent. At 166 h of operation, roughly half way through the campaign, all the organic was drained from the circuit and replaced with $34^v/_o$ Acorga M5640 (Avecia), an ester modified aldoxime reagent, again in Escaid 110 diluent. Both LIX 622N and Acorga M5640 are classed as strong copper extractants, as compared with the aldoxime/ketoxime blends such as LIX 984 in that they have greater extraction capacity at higher feed acidity (typically pH closer to 1). The SX circuit with both organics was operated at ~40°C in extraction, somewhat cooler in stripping (~35°C).

A stronger extractant was selected for this circuit because, as stated, the primary objective was production of a raffinate as low in copper as possible. As with the PMMN circuit, the SX feed was continuously changing with changing upstream conditions as that part of the circuit was optimised. Furthermore, approximately 2/3 of the way through the campaign, the leach feed was changed from one ore composite to a second with different mineralogical and chemical properties. However, unlike the PMMN SX feed solution, the only impurities in the LXOX SX feed present in g/L amounts were Fe which ranged from 15 to 17 g/L and Al at 4.5-5.5 g/L through the campaign. Therefore, the objective job of the scrub stage was to limit iron transfer.

Figure 7 maps the evolution of SX feed copper and acidity levels over the course of the piloting campaign. Feed copper concentrations ranged from 12.5 to 17.5 g/L in the early part of the run, steadying into a narrower 14.5 to 17 g/L range in the latter half. Feed acidity decreased steadily through the run with the pH rising gradually from less than 1 but never exceeding more than 1.3 except in the very first batch of feed. In terms of free acid, this represented a range of ~15 g/L H_2SO_4 near the beginning of the campaign to values close to 6 g/L in the later stages of the run.

With the high feed copper levels, and relatively high feed acidity, it was difficult to keep the raffinate copper below 1 g/L. It cannot be said that one reagent was more effective than the other in this regard, because feed as well as operating conditions (strip feed acidity, O/A ratios) were different enough from the first half of the run to the second to prevent comparisons of reagent performance with respect to copper extraction.

Strip feed (spent electrolyte) acidity is plotted in Figure 8. During the run, the acidity increased progressively. This helped the loading capacity by improving stripping, although this parameter did not seem to be as important as the amount of copper in the feed. The copper concentrations on the loaded and recycle organics were fairly constant through the LIX 622N operating period as Figure 9 illustrates, despite the changes in extraction feed. During the Acorga period, the organic copper loadings decreased steadily as strip feed acidity increased.

The results of this pilot plant campaign illustrate the effect of progressive adjustment of operating conditions once the feed conditions had more or less stabilised. It was ultimately possible to improve extraction over 95%, and had the campaign run longer, it is likely that raffinate levels would have continued to decrease improving overall extraction. The PMMN circuit used a weaker extractant, but was dealing with lower feed acidity. It was able to attain extractions over 95% at somewhat higher net copper transfer values than
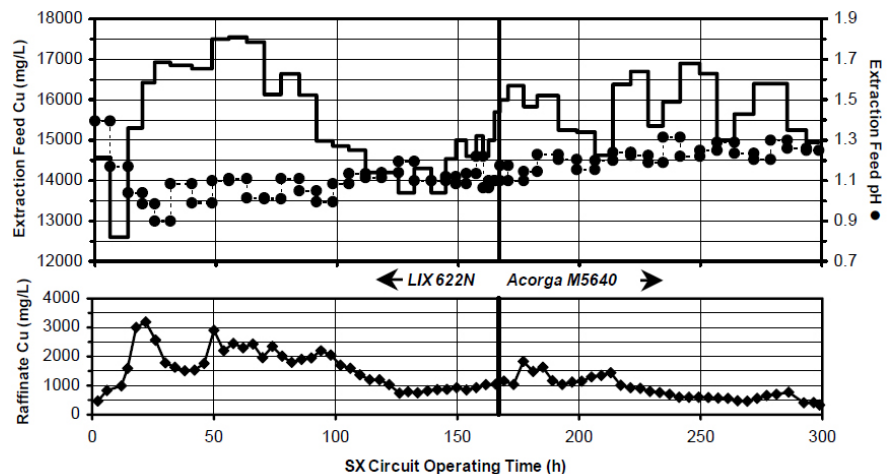

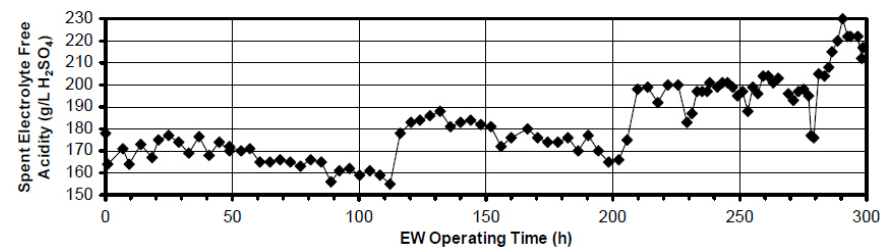Figure 7 LXOX Circuit Feed Conditions and Raffinate Response

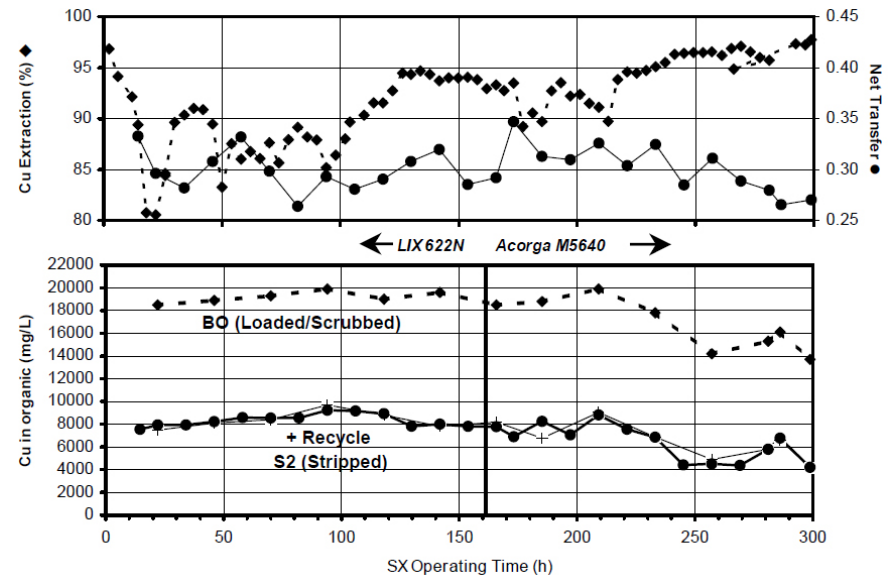Figure 8 LXOX Circuit Spent Electrolyte (Strip Feed) Acidity

Figure 9 LXOX Organic Cu Trends and Cu Extraction

the LXOX circuit, implying a more efficient use of the extraction capacity. However, comparisons of the two circuit are difficult to make because neither one ever operated at true steady-state conditions, and there were other significant differences in the makeup of the feed solutions. As well, there was less scope for changing the extraction O/A in the LXOX circuit compared to the PMMN operation

because of the former's tighter integration with the rest of the pilot plant circuit.

As noted, iron was the major impurity element of concern in the SX feed. Figure 10 is a plot of the iron concentration in the EW electrolyte over the course of the campaign. At approximately 230 operating hours, the electrolyte was diluted to lower the

copper concentration and this resulted in the step change seen in the graph.

The data indicate that there appear to be different iron transfer rates for the two reagents that were used. With LIX 622N, the electrolyte picked up iron at a rate of 2.7 g/L per hour of operation. This corresponds to ~15 mg of Fe transferred per L of organic into the strip circuit. For the latter part of the run with Acorga M5640, the transfer rate was approximately 7 mg/L of organic. These values are net of the iron being bled out of the circuit with the scrub feed electrolyte bleed. The result is consistent with the reported greater selectivity over iron for modified aldoximes [1]. They are higher than the value obtained in the PMMN pilot circuit. While the iron in the PMMN feed ranged over a broader span the average concentration was still less than half than that present in the LXOX SX feed. In the PMMN circuit, a reduction step for PGM recovery preceded copper SX, while in the LXOX circuit the liquor came from an oxidative leach. For the little they extract, ferric ion is favoured over ferrous by copper extraction reagents. More aggressive scrubbing of the loaded organic for example at a lower O/A ratio or with a scrub feed containing more copper and/ or less iron, would probably have helped to limit iron transfer in the LXOX circuit. Other measures, such as a reduction loop in the scrub stage may have also been beneficial [12].

Physically, the LXOX circuit operated well with both reagents. Phase separation was good, despite increased organic phase viscosity resulting from higher extractant concentrations.

CONCLUSIONS

The examples discussed in this paper illustrate just how robust a process copper extraction with modern solvent extraction reagent has become. The reagents were able to cope with wide variations in feed conditions, and by adjusting operating conditions, it was, in most cases, possible to attain the low raffinate targets and to produce high purity copper. A single copper circuit can handle copper concentrations up to 18 g/L without undue difficulty.

Higher concentrations may require the secondary extraction circuits that have been tested in other situations, but the practical limits for single circuits have not yet been entirely established. Copper solvent extraction circuits can function in a service role in short integrated pilot plant campaigns. However, such campaigns will not furnish good SX operating and design data, and the process engineer will do better to consult the extensive databases and operating experience of the principal reagent manufacturers. Evaluation and comparison of copper extraction reagents is not possible in short and unstable operating campaigns, only in much longer campaigns under constant feed and operating conditions. Less is known about extraction in circuits that introduce high levels of other elements such as chloride or iron with the copper feed. It was found that chloride is quite effectively controlled by scrubbing. The data presented indicate that iron may be of concern in some scenarios and measures need to be tested to make sure that it is being controlled at acceptable levels. More work and longer piloting runs are required to determine whether these impurity elements have any longer term effect on reagent stability, degradation and crud formation.

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