

Improved Copper/Iron Selectivity in Solvent Extraction

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BASF Mining Solutions have developed a new generation of copper solvent-extraction reagents that offer significant benefits over the existing reagents available to the industry today. Initial laboratory studies and pilot-plant trials have shown that these new reagents offer the benefits of a dramatic increase in resistance to degradation and are nitration-proof. This paper details a recent pilot-plant campaign at a commercial solvent-extraction plant. The main focus was to evaluate the copper/iron selectivity, copper recovery and net transfer of the new reagent compared with the conventional oxime reagents. The new reagent displays similar copper recovery and net transfer capabilities from typical agitation leach solutions. The pilot-plant results show a step change improvement in copper/iron selectivity in comparison with the existing modified and non-modified hydroxyoxime reagents used on the commercial plant.

INTRODUCTION

Copper solvent extraction (SX) from an acidic aqueous solution is typically accomplished using a hydroxyoxime extractant (Jergensen, 1999; Kordosky, 2000; Szymanowski, 1993). There are three hydroxyoximes from which all standard formulations are derived: 5-nonyl salicylaldoxime (NSAO), 5-dodecyl salicylaldoxime (DSAO) and 2-hydroxy-5-nonyl acetophenone oxime (HNAO). In the case of NSAO, it is necessary to use equilibrium modifiers in order to increase the copper stripped from the extractant (Kordosky & Virnig, 2003). Blends of DSAO, NSAO and HNAO are used to cover a wide spectrum of conditions (Kordosky, 2008). Use of modified aldoximes and reagent blends over the last 30 years has influenced the way copper producers and equipment manufacturers have approached the operation of copper plants.

Existing solvent-extraction reagents cater for typical pregnant leach solutions (PLS) of copper mining systems which do not have significant effects on the reagent. Table I illustrates the range of copper concentration, pH values, temperature and iron concentrations for different leaching operations. As conditions become increasingly aggressive (i.e., higher PLS temperatures in primary sulfide leach or high iron content), current reagents become less capable of functioning according to expectations. One example is the effect of high iron (Fe^{3+}) concentration in PLS and operating SX to achieve high copper recoveries. The ferric is partially chemically extracted and is transferred to electrowinning (EW) during the stripping stage. To avoid a build-up of iron in electrolyte, which negatively affects current efficiency, a bleed of electrolyte is required. This bleed leads to excessive consumption of reagents, such as cobalt added to the EW process, and thus increases operational cost.

Copper ore bodies are typically composed of three distinct zones (Figure 1). Weathering and oxidation convert the copper in the top layers of the orebody to copper oxide minerals, and this represents approximately 10 % of the total copper. A transition from the oxide layer to the supergene area leads to a secondary sulfide zone, containing enriched copper species such as covellite (CuS) and chalcocite (Cu₂S). The secondary sulfide zone represents approximately 25 % of the total copper. The rest of the ore consists of primary sulfide minerals, often chalcopyrite which contains the remaining 65% of the total copper.

Table I. Ranges for various conditions at leaching operations.

Leach Type	Cu (g/L)	pH	Temperature	Fe in PLS
Dump, heap, in situ	<1 - 6	1.3 - 2.2	Ambient	Low - high
Ferric cure, thin layer	3 - 6	1.5 - 2.2	Ambient	Low - high
Vat	5 - 50	1.6 - 2.0	Elevated	Low - high
Agitation	1 - 35	1.4 - 2.0	Ambient or elevated	Low - high
Concentrate	25 - 80	<1.0 - >2.0	Highly elevated	High

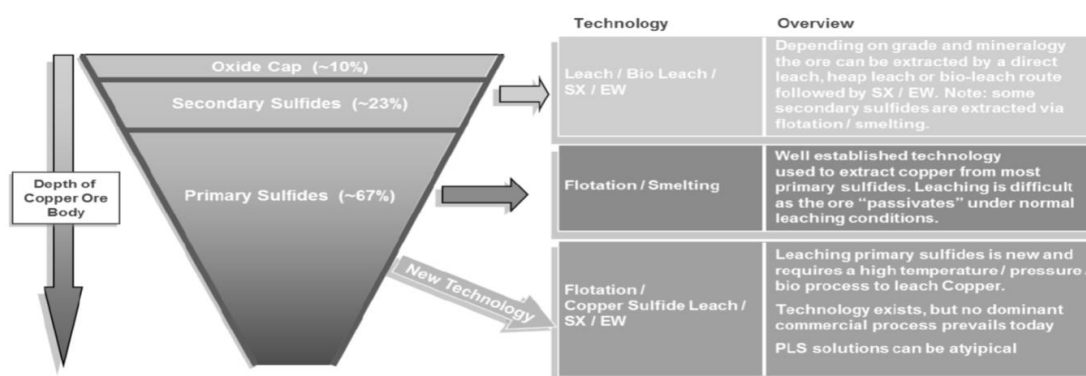


Figure 1. Copper production processes from various ore reserves.

SX/EW was developed to treat oxide ores, which were considered to be waste. It was discovered that secondary sulfides could also be leached. In the presence of dilute acid, half of the copper in chalcocite can be leached. The remainder can be recovered slowly by a bacterially assisted oxidative system. This discovery led to a substantial portion of the global copper production being converted to SX-based processes, with the balance of primary sulfides being concentrated and sent for smelting.

There are numerous technologies that have been developed for the leaching of primary sulfide ores (Dreisinger, 2006). While there are as many conditions as there are processes, the high temperature of the resulting PLS solution is ever-present. Through long-term laboratory temperature studies and plant data from sulfide leaching systems, BASF determined that there is a substantial increase in reagent degradation at elevated PLS temperatures. This is true of neat reagents, unmodified reagent blends and modified reagents (Bender *et al.*, 2013).

BASF has developed a new generation of SX reagents that have a much greater stability at higher temperatures. In addition, these reagents have approximately an order of magnitude higher copper selectivity over iron and cannot be nitrated (all current reagents can be nitrated under nitrating conditions). These novel reagents have been tested in static and continuous laboratory experiments. BASF has also completed various customer pilot-plant trials. The following data are based on the information from a pilot-plant trial run at a commercial SX plant that uses both modified and non-modified hydroxyoximes.

PILOT-PLANT PARAMETERS

The pilot plant used during the trial consisted of four mixer-settler stages constructed of stainless steel. Figure 2 shows a photograph of the pilot plant in operation at the commercial plant. Each mixer had a variable speed drive to control the impeller speed. Watson Marlow peristaltic pumps were used to feed and control the PLS, spent electrolyte and organic solution flows. A 60-litre plastic container served as a loaded organic tank.



Figure 2. Pilot plant in operation at the commercial plant.

Table II illustrates the various parameters and operating ranges of the pilot plant during the trial. The pilot plant was set up inside the commercial plant SX area to ensure that plant solutions were easily accessible.

Table II. Pilot-plant parameters and operating ranges.

No of stages	4	
Primary mixer volume	8	L
Secondary mixer volume	8	L
PLS flow	130 - 160	L/h
Organic flow	170 - 210	L/h
Total Mixer residence time	2.5 - 3.2	min
Impeller tip speed	5.5 - 6.5	m/s
Settler Flux	1.8 - 2.2	m ³ /m ² /h
Organic depth	40 - 50	mm
Aqueous depth	140 - 150	mm
Organic space velocity	0.47 - 0.57	cm/s

PLANT CONFIGURATION AND SOLUTIONS

Plant Configuration

The commercial plant has a BASF Split Circuit™ configuration with high-grade (HG) PLS reporting to a 2 extract, 2 strip (2E-2S) staged SX plant. The low-grade (LG) PLS reports to a 2 extract, 1 parallel, 1 strip (2E-1P-1S) staged SX plant. Figure 3 illustrates the two SX configurations. The pilot plant was

first configured and run as a HG circuit for four days. On completion of the HG circuit run, the pilot-plant staging was changed to the LG configuration and ran for four days with LG PLS.

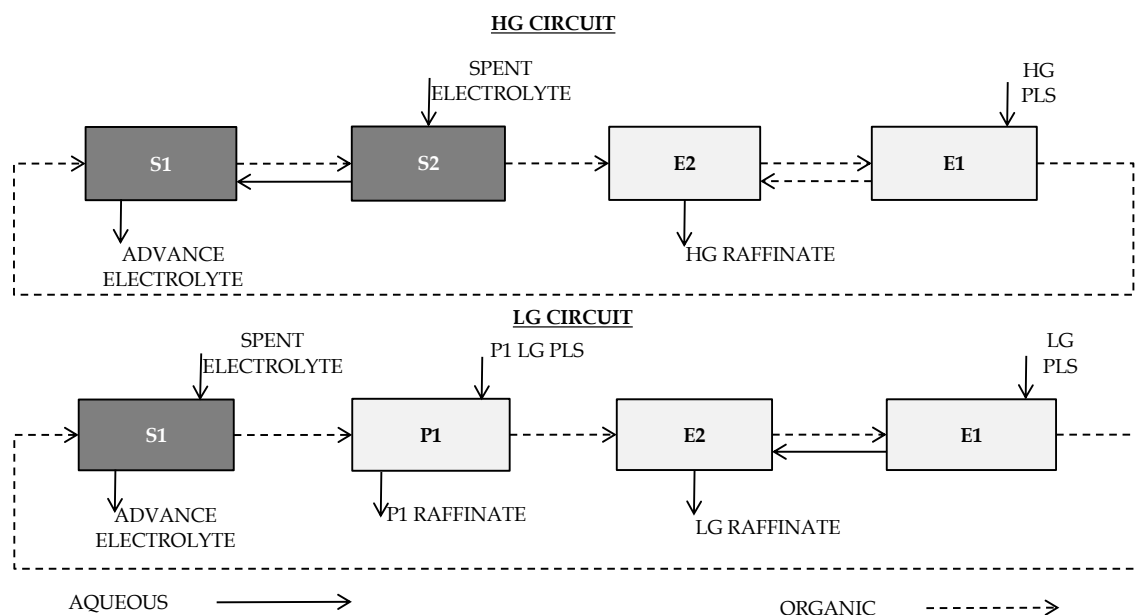


Figure 3. Commercial and pilot plant SX configurations.

Plant Solutions

Plant solutions (PLS and spent electrolyte) directly from the commercial plant were used in the pilot-plant trial. The solution bleeds were taken close to the entry points of the commercial SX plant. This ensured that the pilot plant was fed with very similar PLS and spent electrolyte solutions compared with the commercial plant. Table III shows the concentration range of PLS and spent electrolyte for the two circuits. It should be noted that the PLS grades tended to vary over short periods of time, even within a shift. This made operation of the pilot plant difficult, as operators were not able to respond to these changes in grade.

Table III. PLS and spent electrolyte concentrations.

Circuit		PLS			Spent Electrolyte		
		Cu (g/L)	Fe (g/L)	pH	Cu (g/L)	Fe (g/L)	Acid (g/L)
HG SX	Range	3.7 - 4.2	4.1 - 4.9	1.3 - 1.7	39.3 - 42.7	14.1 - 15.6	161 - 188
	Average	4.1	4.3	1.5	40.2	14.9	175.7
LG SX	Range	1.0 - 1.4	3.3 - 3.7	1.3 - 1.7	40.4 - 44.7	13.6 - 16.2	172 - 200
	Average	1.2	3.5	1.5	42.3	14.9	187.3

The major differences in the circuits were the extractants used. The HG commercial circuit used a HNAO/NSAO blend, from BASF, and the LG commercial circuit used a modified HNAO/NSAO blend from a competing manufacturer. The new generation reagent from BASF was used in both HG and LG pilot-plant circuits. Fresh extractant was used for the pilot-plant campaign. While it would have been ideal to operate a side-by-side comparison using fresh extractants (both incumbent and new), this was not possible due to the availability of only one pilot plant. In addition, trying to compare a pilot-plant campaign with one reagent followed by another campaign with a different reagent is not entirely feasible due to the wildly fluctuating PLS grades and characteristics that an agitation leach system typically produces. Table IV indicates the extractant concentration, as volume percent, dissolved in Shellsol 2325 or BP Mining Solvent.

Table IV. Organic extractant concentrations.

Extractant	HG SX	HG pilot plant	LG SX	LG pilot plant
	HNAO/NSAO	New Generation	Modified HNAO/NSAO	New Generation
Maximum Cu loading (g/L)	13.5	14.6	14.1	15.5
Reagent concentration (v/v %)	25.5	26.1	25.9	27.7

COMMERCIAL AND PILOT-PLANT OPERATING RESULTS

To compare the results from the pilot-plant campaigns with those of the commercial plant, the pilot-plant organic-to-aqueous advance ratios (O:A) were maintained at similar values to those of the commercial plant. The objective of the pilot-plant campaign was to operate both the HG and LG circuits under similar conditions to the commercial plant and to mimic the results obtained in the commercial plant. The new generation reagent concentration formulation was targeted to achieve a high copper recovery and thus a low copper raffinate. Normally, this reagent concentration would be too high for the PLS grades that ultimately reported to both the pilot and commercial plants during the duration of the piloting campaign. The commercial plant was experiencing low PLS copper grades and was targeting a high copper recovery. Inadvertently, this increased the iron co-extraction due to the large amount of excess reagent available. The slightly higher new generation reagent concentrations used, in the respective pilot-plant circuits, would therefore lead to higher recovery and would better illustrate the improved copper/iron selectivity. Tables V & VI show the relative operating conditions for both the pilot plant and commercial plant for the respective circuits.

Table V. HG SX – Pilot plant vs. plant data.

	HG Pilot plant	HG Plant
PLS - Cu (g/L)	4.06	3.50
Raffinate - Cu (g/L)	0.30	0.34
Extract O:A	1.26	1.33
Strip O:A	2.96	3.50

Table VI. LG SX – Pilot plant vs. plant data.

	LG Pilot plant	LG Plant
PLS - Cu (g/L)	1.22	1.12
Series / Parallel Raffinate - Cu (g/L)	0.03 / 0.07	0.08 / 0.12
Series / Parallel Extract O:A	1.55 / 1.88	1.32 / 1.99
Strip O:A	3.28	3.47

One measured and two calculated parameters were compared for each circuit, namely: iron concentration in loaded organic, copper/iron selectivity and copper recovery.

Copper/iron selectivity was calculated as per Equation 1:

$$\text{Cu:Fe} = ([\text{Cu}]_{\text{loaded organic}} - [\text{Cu}]_{\text{stripped organic}}) / ([\text{Fe}]_{\text{loaded organic}} - [\text{Fe}]_{\text{stripped organic}}) \quad [1]$$

Recovery (%) was calculated as per Equation 2:

$$\text{Recovery \%} = ([\text{Cu}]_{\text{PLS}} - [\text{Cu}]_{\text{Raffinate}}) / [\text{Cu}]_{\text{PLS}} \times 100 \quad [2]$$

High-Grade Circuit Results

The figures in this section display the calculated results of the HG pilot plant compared to the HG commercial plant. All results were calculated based on a four-hourly sample analysis over a period of four days.

Copper/Iron Selectivity

Figure 4 shows the Cu:Fe selectivity ratios and the Fe concentration in the loaded organic for the HG pilot-plant circuit compared to the HG commercial plant circuit.

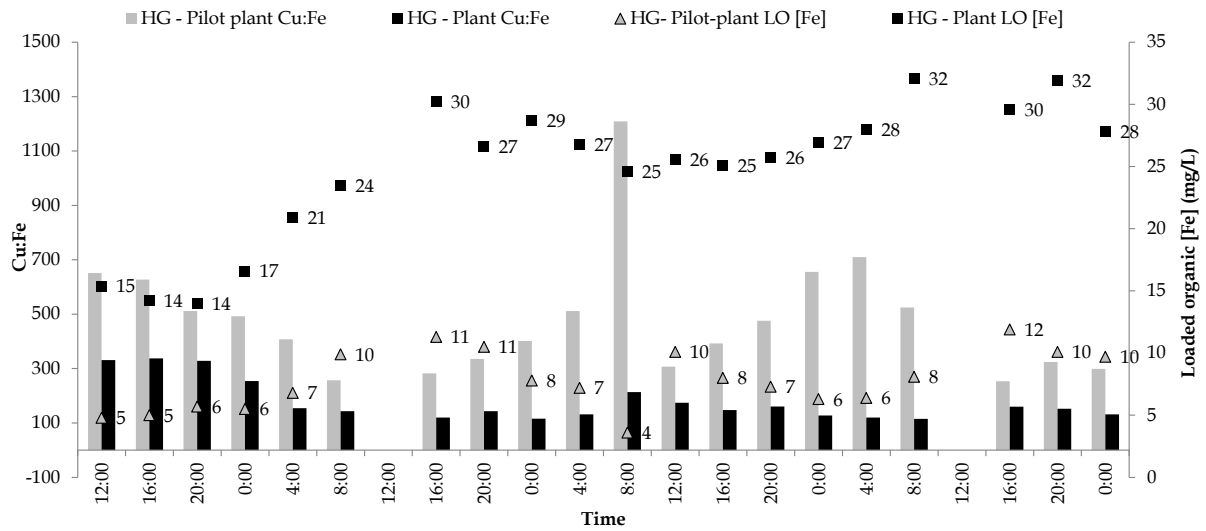


Figure 4. HG circuit Cu:Fe selectivity ratios and [Fe] in loaded organic.

Copper Recovery

Figure 5 displays the calculated recovery of copper for the HG pilot plant and HG commercial plant circuit.

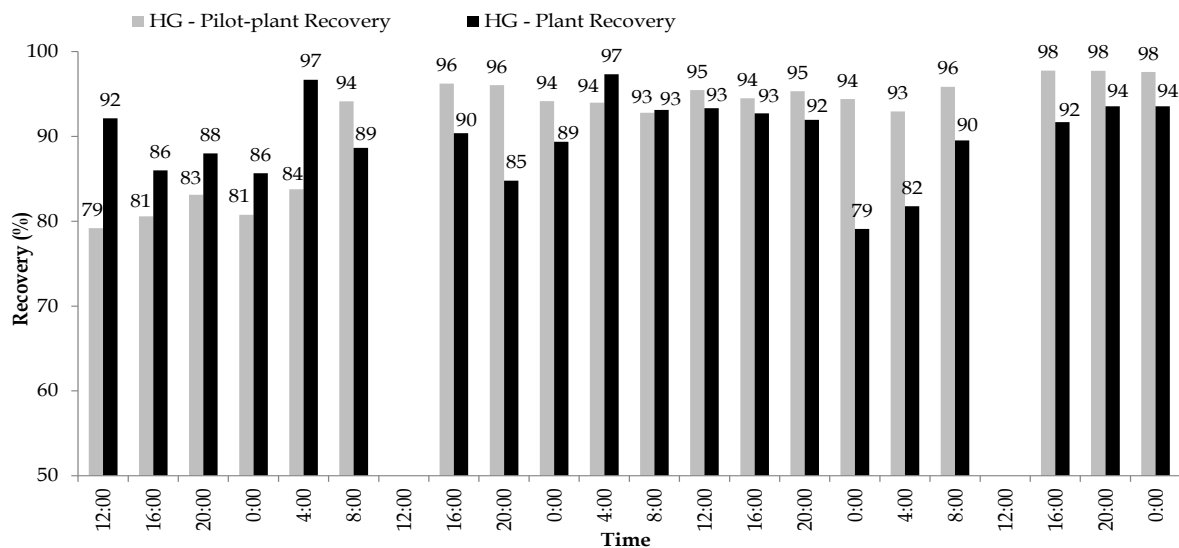


Figure 5. HG circuit recovery results.

Low-Grade Circuit Results

Similar to the HG results, the LG results were also calculated based on a four hourly sample analysis over a period of four days.

Copper/Iron Selectivity

Figure 6 shows the Cu:Fe selectivity ratios and the Fe concentration in the loaded organic for the LG pilot-plant circuit compared to the LG commercial plant circuit.

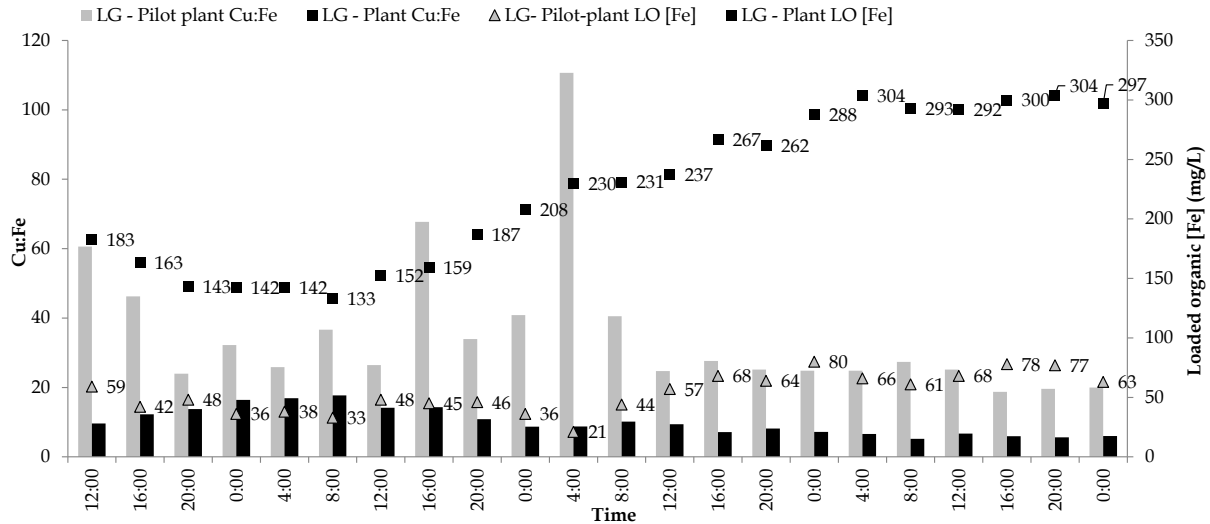


Figure 6. LG circuit Cu:Fe selectivity ratios and [Fe] in loaded organic.

Copper Recovery Series Stage

Figure 7 displays the calculated recovery of copper for the series extraction stages of the LG circuits.

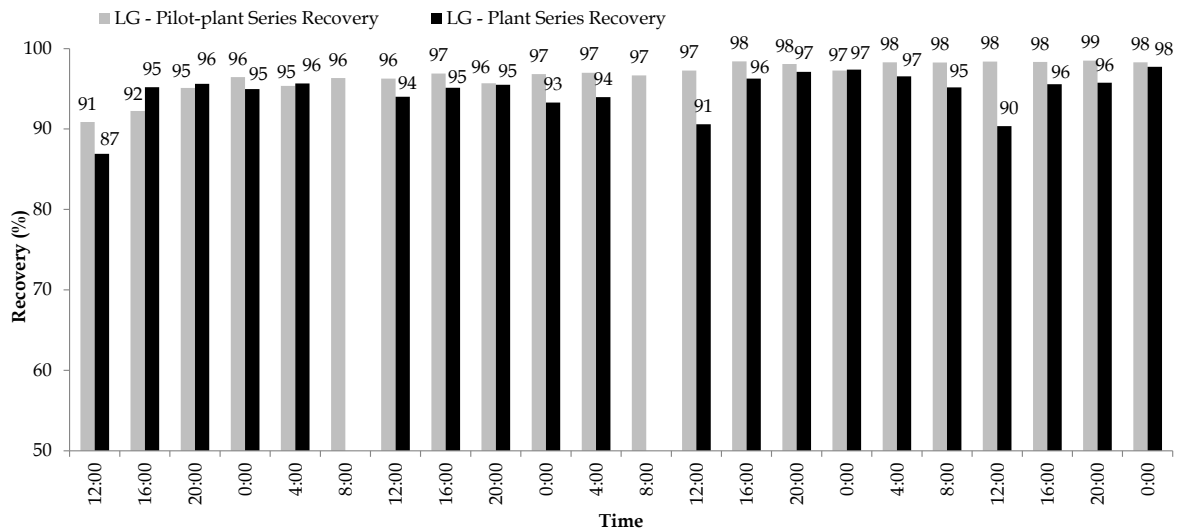


Figure 7. LG series circuit recovery results.

Copper Recovery Parallel Stage

Figure 8 displays the calculated recovery of copper for the parallel extraction stage of the LG circuits.

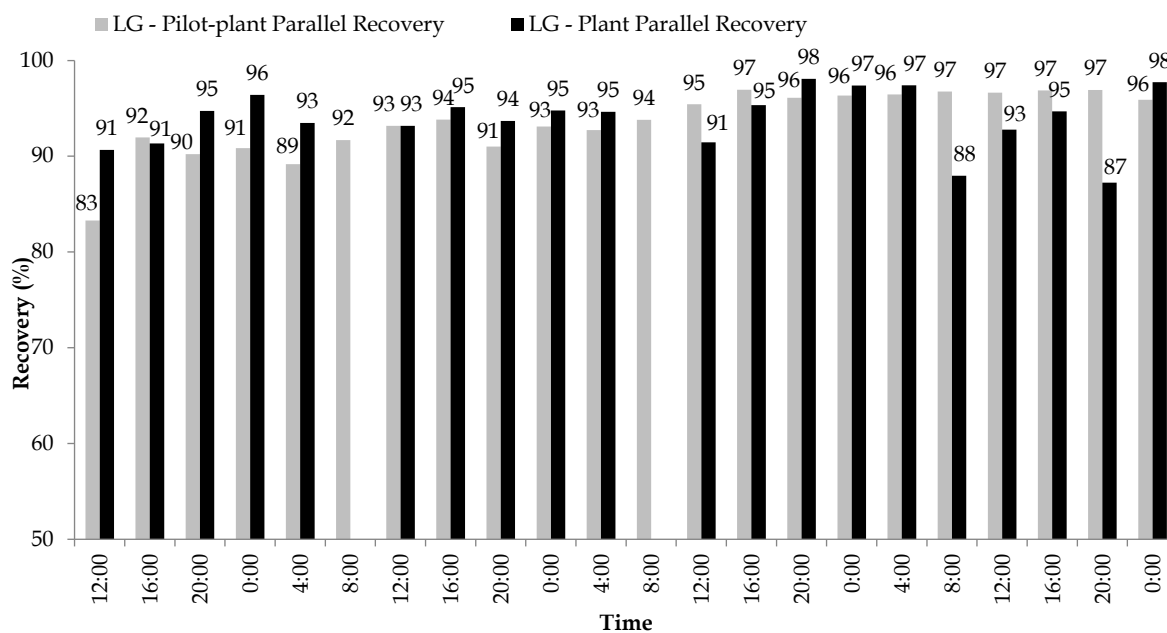


Figure 8. LG parallel circuit recovery results.

DISCUSSION

HG Circuit

Table VII below summarises the results of the HG circuit. The copper/iron selectivity ratio for the pilot plant was consistently 2 to 3 times higher than that of the commercial plant. It should be noted that a plant organic extractant is generally less selective than fresh organic extractant and, had selectivity improvements been observed in the order of only 10 or 20 %, then the trial results would have been insignificant. However, the new extractant exhibited a significant difference in selectivity, which far overrides any inherent selectivity benefit a fresh reagent would have over the same reagent formulation present in a used plant organic. Generally, there is an inverse relationship between copper recovery and net transfer. As can be seen in Table VII, the net transfer (per volume % reagent) is lower for the pilot plant due to the fact that higher recoveries were targeted by increasing the reagent concentration.

Table VIII shows the average copper and iron concentrations of loaded and stripped organic for both HG circuits. It is clear, from Figure 4 and Table VIII, that the amount of iron extracted in the pilot-plant circuit is significantly lower than that of the commercial plant.

Table VII. HG SX – Pilot plant vs. plant data results summary.

	HG Pilot plant	HG Plant
Cu:Fe	482	178
Recovery (%)	92	90
Net transfer (g/L Cu/vol %)	0.122	0.140

The copper recovery across the pilot plant was consistently higher than that of the commercial plant. The first 16-hour period (see Figure 5) of the pilot-plant circuit run was the only period where the recovery was lower than that of the commercial plant. This was due to the organic recycles being fully

opened in error during start-up. This reduced the efficiency of the stripping section, resulting in a higher stripped organic concentration, leading to a lower recovery.

Table VIII. Loaded and stripped organic concentrations for HG circuits.

Loaded organic	HG Pilot-plant	HG Plant
Cu (g/L)	7.9	6.1
Fe (mg/L)	7.8	24.7
Stripped organic	HG Pilot-plant	HG Plant
Cu (g/L)	4.9	2.5
Fe (mg/L)	0.3	2.7

LG Circuit

The summary of the LG circuit results are displayed in Table IX. The copper/iron selectivity ratio for the pilot plant was consistently more than 3 times higher than that of the commercial plant. Table X shows the average copper and iron concentrations of loaded and stripped organic for both LG circuits.

Table IX. LG SX – Pilot plant vs. plant data results summary.

	LG Pilot plant	LG Plant
Cu:Fe	36	10
Recovery (%) - series / parallel	97 / 94	95 / 94
Net Transfer (g/L Cu / vol %)	0.050	0.068

The copper recovery of the LG pilot-plant circuit was, on average, slightly higher than that of the LG commercial plant circuit. As discussed previously, this can be attributed to the higher reagent concentration in the pilot plant. The resulting copper net transfer per volume percent extractant of the new generation reagent was lower than that of the incumbent modified HNAO/NSAO blend in the plant for the same reason. It is also clear, from Figure 7 and Table X, that the amount of iron extracted in the pilot-plant circuit is significantly lower than that of the commercial plant.

Table X. Loaded and stripped organic concentrations for LG circuits.

Loaded organic	LG Pilot-plant	LG Plant
Cu (g/L)	6.9	4.1
Fe (mg/L)	53.5	223.5
Stripped organic	LG Pilot-plant	LG Plant
Cu (g/L)	5.5	2.3
Fe (mg/L)	4.5	17.6

CONCLUSIONS

- The new generation solvent-extraction reagent provided adequate results in terms of copper transfer in both extract and strip stages. As expected, the overall copper recoveries for both HG and LG pilot-plant circuits were higher compared with the commercial plant.

- The HG circuit iron concentration in the loaded organic, for the new generation reagent, was 60% lower compared with the HNAO/NSAO reagent blend, even though copper recoveries were higher.
- The LG circuit iron concentration in the loaded organic, for the new generation reagent, was more than 70% lower compared with the incumbent modified HNAO/NSAO reagent blend in the commercial plant.
- The iron bleed across the electrolyte, due to the partial chemical extraction of iron, could be reduced by as much as 4 times when using the new generation reagent under the same plant conditions.
- The main aim of the pilot campaigns was to demonstrate that the new generation extractant was capable of extracting and stripping copper with a similar efficiency compared with the incumbent commercial extractants. This aim was met and illustrates that the new generation extractant offers a viable alternative to the conventional oxime-based extractants available, while at the same time offering a step change improvement in Cu:Fe selectivity.

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