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DEVELOPMENT OF A NOVEL THREE-STEP SX PROCESS TO RECOVER COPPER FROM AN ACIDIC SOLUTION

*Robert Minango, Edwin Bwalya, Deogratias Bukunkwe – Chambishi
Baruch Grinbaum – Bateman*

ABSTRACT

Solvent extraction of **Cu** from acidic leach, using an oxime extractant, e.g. LIX 984 or Acorga is a well known and established process.

As the process advances, **Cu** is extracted to the solvent and is replaced by H^+ in the aqueous phase. At high acidity the distribution coefficient of **Cu** between the solvent and the aqueous phase decreases, and eventually relatively high concentration of **Cu** remains in the raffinate, regardless of the number of equilibrium stages. In many processes this phenomenon is immaterial, as the raffinate returns to the leaching and no copper is lost. But when the copper raffinate is used for processing of additional metals, minimal concentration of **Cu** in the raffinate is essential for an effective process.

The recommended process includes three steps:

1. **SX-1:** Standard extraction of Cu with oxime. The resulting raffinate contains about 6-8 g/L Cu and 50 g/L H_2SO_4 .
2. **SX-N:** Extraction of most of the acid into an amine-based solvent, and stripping it with a base, e.g. aqueous ammonia, caustic, Na_2CO_3 etc. The extraction removes no metals, but decreases the concentration of acid from 50 to 10 g/L.
3. **SX-2:** Extraction of the neutralized solution once more with oxime, to remove the residual copper.

Such a process enables one to get down to 100-150 ppm Cu in the final raffinate.

This process was developed and tested in the R&D facility in Chambishi Metals plc, by a joint team of Chambishi & Bateman, using Cognis LIX 984N and real solutions from the plant.

In the laboratory scale, the equilibrium isotherms for SX-1, SX-2 and the neutralization were developed. Computer simulation of the results showed that the optimal configuration is two stages for both extraction and stripping for SX-1. For

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SX-2 2-3 stages of extraction and two stages of stripping are needed. The stripping stages may be common to both SX-1 and SX-2.

The neutralization of SX1 raffinate was tested both by conventional precipitation with lime and by extraction with Alamine based solvent extraction and stripping with a solution of 10% NaOH.

For the SX-N only one stage was needed for both the extraction and stripping.

The bench scale pilot plant was run for both SX-1 & SX-2. The results were very similar to the simulated ones, and the configuration of 2E2S for SX-1 and 3E=2S for SX-2 delivered the required raffinate with less than 150 ppm Cu.

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1. INTRODUCTION

Chambishi Metals plc and Bateman Solvent Extraction (BSX) developed a 3 step SX process for the extraction of Cu from Cu-rich cobalt solutions. A conceptual process flow sheet was developed by Chambishi based on early laboratory and pilot test work conducted by their R&D team. The expenditure on the new SX plant was to be justified by an increase in copper capacity, the ability to produce LME grade cathodes, thus securing a higher price for the copper, and an increase in copper producing capacity.

The process flow sheet envisaged that the extraction of copper should be carried out in three steps:

1. **SX-1:** Extraction of most of the Cu from both the Roaster Leach Liquor (Roaster PLS) and the COSAC pressure leach Liquor (COSAC PLS), reducing the copper in both from 32 g/L to ~10 g/L.
2. Neutralization of the acidic raffinate using either neutralization with lime or **SX-N:** partial extraction of the excess H₂SO₄ with a suitable solvent.
3. **SX-2:** Extraction of the Cu from the neutralized SX-1 raffinate, from both Roaster and Cosac, to achieve a minimum level of Cu in the SX-2 raffinate, which reports to the TM1 Purification plant for cobalt recovery.

2. LIQUID-LIQUID EQUILIBRIA

To simulate the possible variants of the plant, a few sets of liquid-liquid equilibrium experiments, covering the entire range of the process, were carried out. The experiments were done using the variable phase ratio method, as developed by Ashbrook & Ritcey¹.

As the value of the distribution coefficient **D** was known to be rather high, the range of phase ratio (R) was between O:A = 0.5–10, and in few extreme cases – up to 20. All the experiments were carried out at ambient temperature (~25°C), using actual plant solutions and 32% LIX984N in Shellsol 2325 (aromatic level 19%) as solvent. The solvent was loaded and stripped once, to bring it to the normal composition of the barren solvent (BS).

The analysis of the concentration of **Cu** and **Co** in the aqueous phase was done by ICP

For the solvent no direct analysis was available. The solvent samples were analyzed by stripping twice the **Cu** in the laboratory with 200 g/L H₂SO₄ and analysis of the

¹ (see B. Grinbaum, "An integrated method for development and scaling up of extraction processes", in Y. Marcus, A. Sangupta, "Ion exchange and solvent extraction" vol. **15**, 1– 106, Marcel Dekker, 2002).

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aqueous phase.

The following results were obtained:

2.1 Roaster - Feed to SX-1

PLS: Standard Roast Leach Liquor solution, containing 25 g/L Cu, was spiked to 32.4 g/L Cu using CuSO₄.

The pH of the solution was 1.5, and it contained about 10 g/L free acid as H₂SO₄. The barren solvent (BS) contained 6.0 g/L Cu.

The equilibrium isotherm appears in Fig. 1:

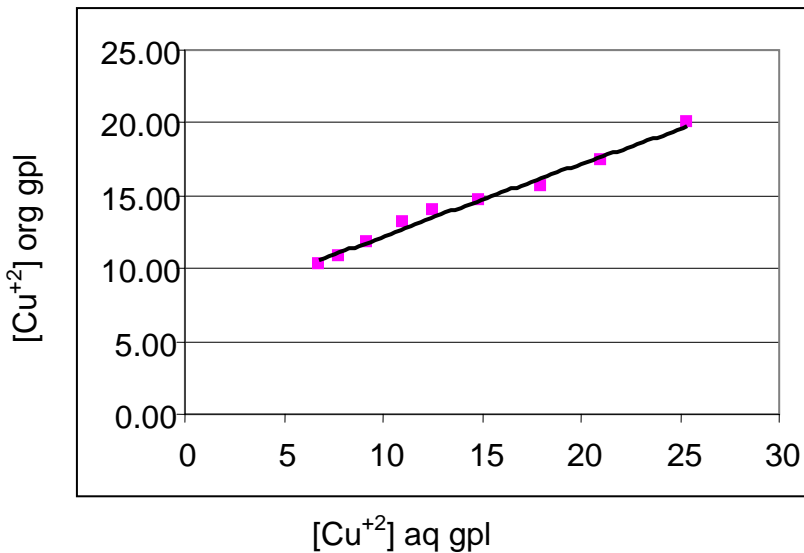


Fig. 1: Equilibrium Isotherm for Roaster SX-1

The line may be well described by a parabolic equation:

$$(1) y = 6.877 + 0.5497x - 0.0017 x^2 \quad R^2 = 0.9818$$

2.2 Roaster Raffinate SX-2

The feed to these experiments was the raffinate of the PLS, which was extracted with solvent in simulation of SX-1 and neutralized to pH=2.2 with lime. It contained 6.8 g/L Cu.

The equilibrium isotherm appears in Fig. 2:

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It may be well described by the parabolic equation:

$$(2) y = 3.0833 + 23.646x - 17.754 x^2 \quad R^2 = 0.9779$$

where all concentration are in g/L **Cu**.

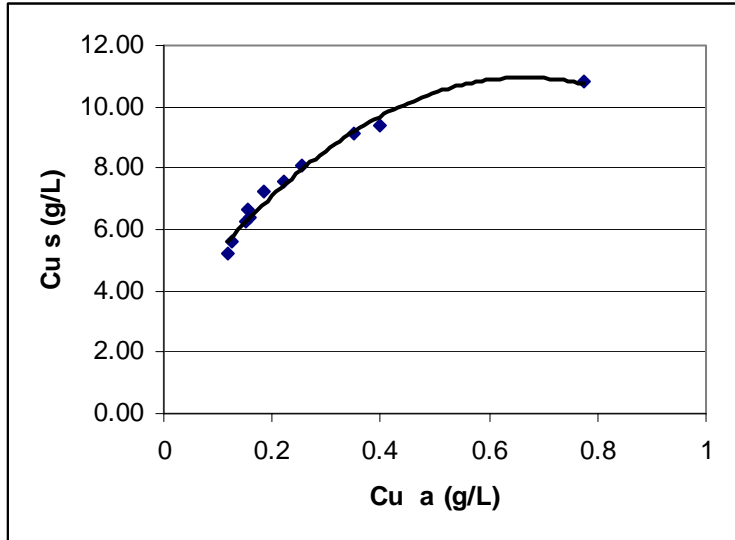


Fig. 2: Equilibrium isotherm for roaster SX-2

The results show that the expected minimum concentration of **Cu** in the raffinate of SX-2 is about 120 ppm (results at limiting conditions represent the best expected results in a multistage plant).

For practical purposes one may assume that **150 ppm is the lowest limit for design of an extraction plant.**

2.3 Cosac extraction

As the concentration of **Cu** in the Cosac PLS is similar to the roaster PLS, the isotherm for its extraction is similar to the Roaster one:

The equilibrium isotherm appears in Fig. 3:

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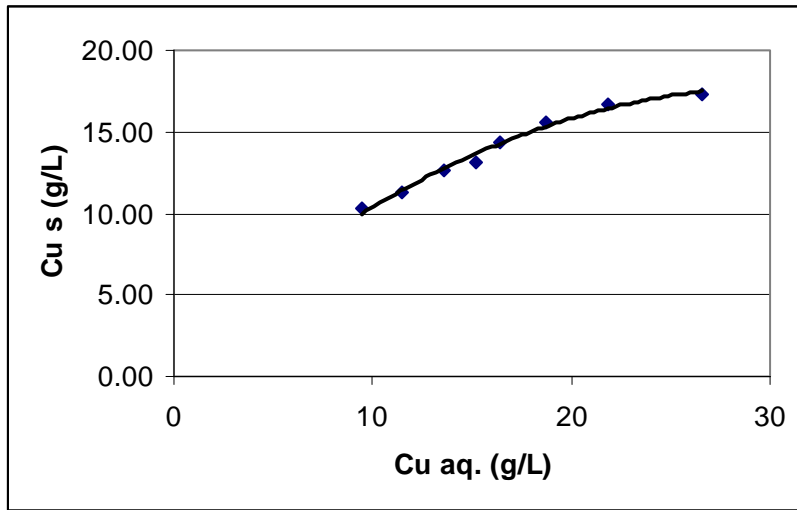


Fig. 3: Equilibrium isotherm for Cosac SX-2

It may be well described by the parabolic equation:

$$(3) y = 1.4424 + 1.0702x - 0.0176 x^2 \quad R^2 = 0.9869$$

where all concentration are in g/L **Cu**.

The results are very similar to the Roaster SX-1 extraction, and show that a similar configuration for its extraction is required.

2.4 Stripping

The stripping was tested by loading a batch of solvent to 16 g/L **Cu** and stripping in variable phase ratio, using spent electrolyte with 35 g/L **Cu** and 180g/l H_2SO_4 . The equilibrium isotherm appears in Fig. 4:

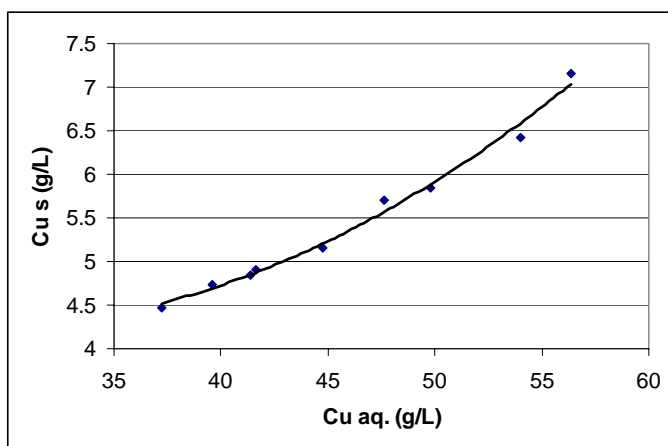


Fig. 4: Equilibrium isotherm for Stripping of loaded organic

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The values may be well described by the parabolic equation:

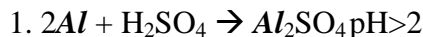
$$(4) y = 6.9454 - 0.195x + 0.0035 x^2 \quad R^2 = 0.9889$$

2.5. Neutralization with Alamine 336

A novel process for decreasing the acidity of the raffinate from 50 to ~10 g/L H₂SO₄ is to extract the excess acid with a basic extractant, e.g. Alamine 336. After stripping of the acid from the solvent with a base, the Alamine may be reused for further extraction. This process enables very accurate removal of acid, by the means of simple pH control. As the extraction of acid is simple acid-base reaction, one equilibrium stage is enough for both the extraction and the stripping. This method is simpler and with less losses of metals than the lime neutralization.

The potential use of Alamine is not new. It was studied by A. Eyal since 1982 (see e.g.²). The biggest advantage of Alamine is its strong alkalinity that enables carrying out the entire extraction in one stage, with lowering the acidity of the raffinate as far as needed. Its main disadvantages are: the stripping must be done with a base (even hot water cannot remove the acid from the solvent), third phase is created and the phase separation is poor. The latter two problems are solved satisfactorily by addition of high alcohol, e.g. Isodecanol, as modifier and working at temperature above 40°C.

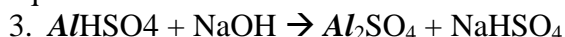
Alamine 336 can extract acid according to two equations:



In the intermediate region of $1 < \text{pH} < 2$ both species coexist.

As the neutralized raffinate should be at pH 1.5-2, both Al₂SO₄ and AlHSO₄ are expected in the solvent.

The sulfate may be recovered by stripping with a base, e.g. NaOH, according to the equations:



For the sake of simplicity, the creation of water is excluded from the equations.

Please note that in this article Al stands for Alamine 336 and not for aluminium.

2.5.1. Extraction

The first set of experiments was to determine the amount of solvent that is needed to bring the Chambishi SX-1 raffinate to the desired acidity. The raffinate used had relatively high acidity – 60 g/L H₂SO₄.

² A. Eyal et al., "Recovery and Concentration of strong mineral acids from dilute solutions through LLX", Solvent Extraction and Ion Exchange 9, 195-236 (1991)

The results are listed in Table 1:

No.	Sol (mL)	Aq.(mL)	pH	H ₂ SO ₄ (g/L)	R (O:A)	Acid in S (calc)		%loading (calc)	
						g/L	M	as HSO ₄ ⁻	as SO ₄ ⁼
0	Raffinate		0.59	60					
1	250	250	1.1	26	1.0	34.0	0.35	66.1	132.3
2	300	230	1.3	16	1.3	33.7	0.35	65.6	131.2
3	375	210	1.7	11	1.8	27.4	0.28	53.4	106.7
4	475	190	2.4	5.1	2.5	22.0	0.23	42.7	85.4
5	565	170	3	3.1	3.3	17.1	0.18	33.3	66.6

Table 1: Extraction of Chambishi SX-1 with Alamine-based solvent

The conclusion is that the recommended phase ratio for extraction of H₂SO₄ from the raffinate is in the range O:A= 1.5-2, depending both on the acidity of the raw raffinate and the required acidity of the neutralized raffinate.

The process was carried out at 50°C. The extraction was very quick (below 1 minute is required for the equilibrium) and the phase separation was fair. The loaded organic was opaque, and contained 2.5% water. The solvent remained opaque for a few days and even after centrifugation for 15 minutes.

2.5.2. Stripping

The most convenient option is stripping with NaOH. The aqueous product is a concentrated solution of Na₂SO₄, at almost neutral pH.

In the first experiment 200 ml (170 g) of loaded solvent were mixed with 150 ml (182 gram) of 30% Na₂SO₄ solution at 50°C (as in a continuous process some Na₂SO₄ solution is always present in the aqueous phase, the concentrated solution of Na₂SO₄, was added in order to simulate the real conditions). The neutralization was done by slow addition of 10% aqueous NaOH.

The change of the pH in the aqueous phase and % of stripping of the sulfate, as a function of the addition of the base are shown in Fig. 1:

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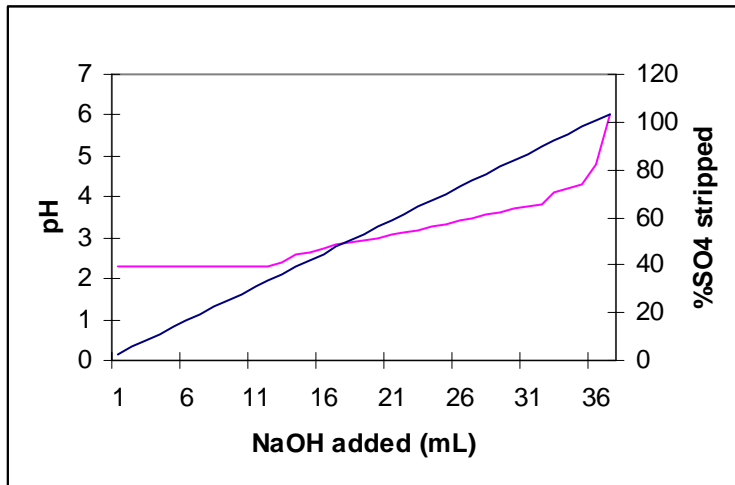


Fig. 5: Stripping of sulfate and the pH vs. the amount of NaOH

From the data it is clear that the change in the pH, along most of the range, is linear to the recovery of the sulfate, and that the process can be easily controlled by setting the set point at pH4-4.5. Under these conditions >90% of the stripping is achieved, without any real danger of getting into the alkali region.

2.5.3 Validation of the process

In order to prove that the recommended process is valid, a batch of PLS was neutralized with fresh solvent. The solvent was stripped with 10% NaOH, as described above, until pH 6-7.

The resulting solvent was used to strip a fresh batch of PLS, and then neutralized in the same manner. The procedure was repeated 3 times.

After the third iteration, the pH of the neutralized PLS was 2, exactly as it was after the first one, and the amount of NaOH used for neutralization was also same in both cases.

3. SIMULATION

The isotherms, reported in Chapter 2, were used to simulate the behavior of the plant.

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3.1 Roaster SX-1

Using both the equation (1) the following results were obtained:

No. stages	Phase ratio	Cu in BS (g Cu/L)	Cu in:	
			Raff. (g Cu/L)	LO (g Cu/L)
1	3	4.5	10.7	11.75
1	4	4.5	8.22	10.58
1	4	5.0	8.88	10.91
2	3	4.5	4.35	13.58
2	3	5.0	5.1	13.80
2	3	6.0	6.85	14.18
2	2	4.5	10.6	14.83
2	2.5	4.5	6.68	14.44

The conclusion is straightforward:

The optimal configuration is 2 Extraction stages, with phase ratio near to O:W=3.

Assuming that the stripped organic will be no more than 4.5 g/L at all times, and that raffinate of 6.5 g/L Cu is required, the phase ratio may be reduced to 2.5.

3.2 Roaster SX-2

The simulation shows that using R=3 and stripped solvent of 4.5 g/L, 2 stages are sufficient to obtain product with less than 150 ppm Cu in the raffinate.

Note that due to the asymptotic character of the input data the simulation was more complicated than for SX-1, as constraint functions had to be introduced to ensure that the raffinate does not violate the experimental results, i.e. does not drop below 120 ppm Cu.

3.3 Cosac Extraction

As the isotherm for the Cosac was very similar to that of the roaster SX-1, the same equilibrium isotherm was used for it, and accordingly the inevitable conclusion is that 2 extraction stages are needed to bring the Cosac raffinate to the required 6.5 g Cu/L.

3.4 Stripping

Using equation (4), it was found that two stages are needed to obtain the required stripping to 4.5 g/L Cu in the stripped solvent, while the concentration of the stripping raffinate is a function of the phase ratio, and may be varied as wished.

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4. PILOTING OF SX-1

4.1 Equipment

The experiments were carried out using bench-scale pilot units of Chambishi R&D department. Each unit consisted of a mixer with volume of 1 liter and a settler with volume of ~7 liter and settling area of 540 cm². The mixers had an option of internal recycle for the heavy (i.e. aqueous) phase. The amount of the recycle was difficult to control, and it was a direct function of the speed of the mixer.

To assure residence time of 3 minutes in the mixer, and assuming a net phase ratio of 1:1 in the mixer, the flow rate of the solvent was set to 167 mL/min. The flow rate of the aqueous feed was set as to keep the required phase ratio of O:A 3:1 in extraction and O:A 1.7:1 in stripping.

4.2 Raw Materials

400 L of PLS, 300 L of the Weak Electrolyte (WE) and 100 L solvent were prepared.

The solvent contains ~32% LIX984N in Shelsoll 2325.

The PLS was standard roaster solution, spiked with CuSO₄ to 32 g/L Cu and ~12 g/L Acid.

The weak electrolyte contained 35 g/L Cu and 180 g/L Acid.

4.3 Results

The recommended configuration consisted of two extraction and two stripping stages.

The summary of all the runs appears in Table 2 in the next page.

4.4 Description of the Experiments

4.4.1 Flow rates:

The initial flow rates in the extraction were 167 mL/min for the solvent and 56 mL/min for the aqueous feed, to ensure residence time of 3 minutes for the solvent in the mixer. When the phase ratio was increased to 4, the flow rates were 167 and 40 mL/min respectively.

In the stripping the flow rate of the solvent was always equal to the flow rate in the extraction. The flow rate of the aqueous was kept constant at 100 mL/min.

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Date	Time	Config.	Cu concentration (g/L)						H ₂ SO ₄ (g/L)				Remarks
			PLS	LO	SS	ER	SE	SR	PLS	ER	SR		
11.12.04	17:00	1E,2S	34.98	9.12		9.6	35.7	42.2	14	47.5	170	Fresh Solvent	
	23:00		35.31	10.41	4.79	16.04	35.85	46.42	12	42.5	170	Closed circuit	
12.12.04	12:00		30.95	11.52	5.05	11.6		46.01	11	42.4	163	PLS from Cosac	
13.12.04	0:00	2E, 1S	30.93	12.89	5.72	12.19	32.87	45.59	10		159		
14.12.04	6:00	2E, 2S	34.15	14.7	6.44	11.88	35.72	48.91				Low Hz (~29)	
	12:00		34.83	15.5	5.64	11.58	36.32	51.36				pH _{ER} =0.66	
15.12.04	22:00		33.90	12.56	5.45	8.71	36.00	46.21				R=4, Hz=31	
16.12.04	14:30		34.96	12.28	5.14	8.03	34.96	45.47	11.5	51.5		pH _{ER} =0.63	
	22:00		34.55	11.72	5.68	7.86	36.2	46.69	12	55.5		R=4, Hz =33	
17.12.04	13:00		34.55	11.48	5.22	6.57	35.10					pH _{ER} =0.59	

Table 2: Summary of Runs of the SX-1 Extraction Pilot Plant

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4.4.2 Mixing Intensity

The work started with relatively low speed of the mixers, to ensure the desired recycle ratio and avoid foaming. Initially the VFDs of the mixers were set to 29 Hz.. At this speed the mixing seemed reasonable and no foam was observed. The recycle ratio in the extraction battery was sufficient, i.e. $R=1$ in the mixer. The pH in the E2 mixer was 0.66.

When the results showed poor raffinate quality – 11.5 g/L Cu, to compare with 4 g/L Cu as predicted by the simulator or 4.5 g/L as obtained by shaking the content of the second mixer for 3 minutes and separating phases – the speed was increased to 31 Hz. This decreased the Cu in the raffinate to 8 g/L, but caused some suction of air through the feed inlet to the mixer. The resulting foam did not accumulate nor harm the phase separation. The pH dropped accordingly to 0.63.

The mixing was gradually increased, and the mass transfer improved accordingly. Finally the speed was increased up to 39 Hz. Now the recycle flow was too high, and the recycle line was choked. The resulting phase ratio was about 2. The mixing improved, and the pH of the raffinate dropped from 0.63 to 0.59. The foaming was not critical, and apparently did not increase significantly the entrainment.

The resulting Cu was 6.57 g/L, i.e. within the process demands. After sampling of the dispersion from the mixer and shaking for 3 minutes, the concentration of the raffinate dropped to 6.23.

In the stripping there was no problem of mass transfer during the experiments, and there was no need to change the speed of the mixers.

These results indicate that high mixer speed is essential to achieve high mass transfer in the extraction. It did not come as a surprise, as the extraction of Cu is known to have poor mass transfer characteristics.

5. PILOTING SX-2

The equipment described for SX-1 above was reconfigured to four stages of Extraction and two stages of Stripping. The simulation based on the laboratory experiments had indicated only two stages of extraction and two stages of stripping, however, four extraction stages were erected, just to be on the safe side. The PLS flow rate was the same as used for SX-1, i.e. 167 L/min, to allow 3 minutes residence time in the mixer. Initially the phase ratio was set at $O:A = 3:1$ (as was at SX-1). Later it was decreased to 2.5.

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5.1. Raw Material

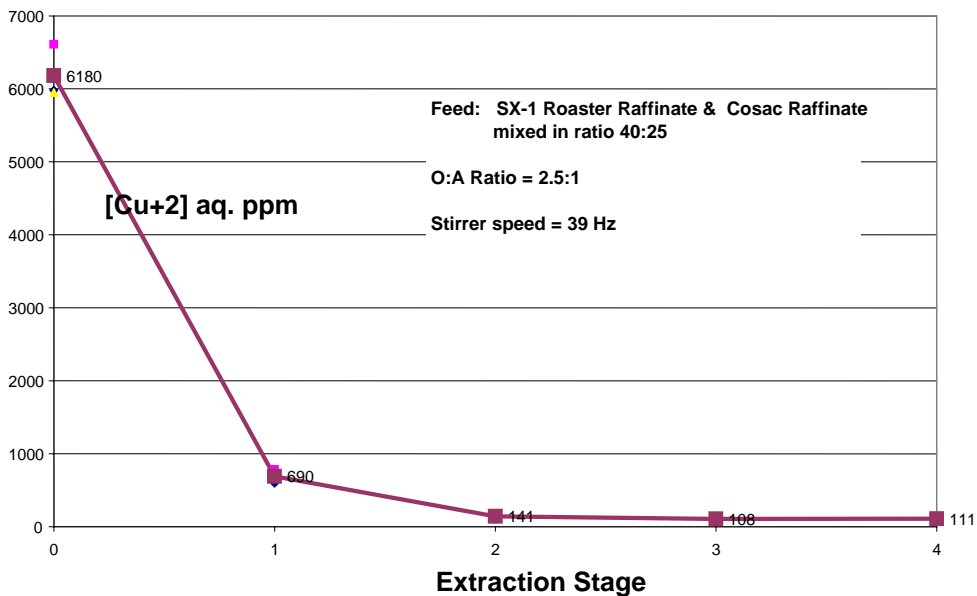
The raw material for the SX-2 pilot runs was a mixture of Cosac & Roaster SX-1 Raffinate. The mixture had been neutralized batch-wise with lime to 5 – 6 gpl H₂SO₄.

5.2 Results

The initial runs were done using a O:A ratio of 3:1. The results obtained were excellent, with the raffinate from Stage 2 averaging about **80 ppm Cu**. These results were partly attributed to the low **Cu** tenor (27 g/L) and high acidity (190 g/L H₂SO₄) in the Weak Electrolyte strip feed.

The conditions were adjusted to strip ratio O:A = 2.5:1, Weak Electrolyte Cu to 30 g/L and acid to 180 g/L H₂SO₄. The raffinate copper tenor averaged 140 ppm after the second stage and 110 ppm Cu after both the third and fourth stages. The fourth stage is obviously not required.

Fig 5 below illustrates these results.



6. CONCLUSIONS

1. The recommended process enables recovery of copper down to 110 ppm Cu in the raffinate. The value of 150 ppm is recommended for design purposes.
2. To achieve this result, the feed to SX-2 should contain not more than 6.5 g/L Cu and 10 g/L acid, at pH=1.5-2.0
3. The raffinate of both the roaster and the Cosac PLS can be extracted down to 6.5 g/L Cu, using two stages of MS. The acidity of the raffinate is about 50 g/L H₂SO₄.
4. The stripping caused no problems; and two stages will be able to strip all the copper within the range set by the designers.
5. The recommended configuration for the process should be:
 - SX-1 extraction for Cosac & Roaster solution: 2 extraction & 2 stripping stages.
 - SX-N for neutralization of the raffinate with Alamine 336: 1 extraction & 1 stripping stage.
 - SX-2 for combined roaster & Cosac neutralized raffinate: 2-3 extraction and 2 stripping stages.
6. The stripping stages may be common for both plants.
7. The phase ratio in extraction over the entire plant should be O:W=2.5-3.
8. The stripping can increase the concentration of the **Cu** in the aqueous electrolyte by 10-20 g/L. The design target of increasing it from 30 to 45 g/L **Cu**, using 2 stages, was proven
9. The feasibility of this configuration for both SX-1 and SX-2 extraction and stripping was proved experimentally in a continuous bench-scale pilot plant at the Chambishi site.
10. Less than 100 ppm of Co was extracted to the solvent and lost in the strip solution.
11. The recommended method for neutralization of the raffinate is extraction of the acid with Alamine.

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