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Solvent Extraction and Electrowinning of Copper from Hot Rolling Mill Scale Liquor

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Abstract. The Acorga M5640 solvent extraction reagent was used for the extraction of copper from hot rolling mill scale liquor. The copper concentration in this liquor ranged between 2 g per litre to 14 g per litre. Ten g per litre Cu and 3 g per litre Fe of the prepared initial feed was used in the solvent extraction and electrowinning unit. Six g per litre Cu in the aqueous solution was used during laboratory scale experimentation because the lower strength was almost completely loaded in the organic extractant, Acorga M5640. The conditions optimized were: organic phase of 30% (v/v) in kerosene and the loaded organic extractant was 5.43 g per litre at 90.5% extraction; pH 2.5; extraction aqueous to organic phase ratio of 5:1 and stripping aqueous to organic phase ratio of 3:1; extraction cycle performance 3 and stripping cycle performance 2; and phase disengagement and equilibration time 10 min. The electrolyte containing sulphuric acid, 35 g per litre in combination with varying amounts of copper sulphate ranging from 25 g per litre to 40 g per litre was used as the strip solution on laboratory scale. Atomic absorption spectrophotometry and electrogravimetric analysis were used for the determination of electrowon copper, which in the present study were 99.89% and 99.78%, respectively. The solvent stability and reliability was excellent, which was also verified by the results achieved during the bench scale study for further use in solvent extraction mixer-settler counter-current unit.

Keywords: Acorga M5640, copper extraction, copper recovery, raffinate copper, solvent extraction, copper electrowinning, waste copper, rolling mill copper scale

Introduction

Copper is among the oldest known metals. Approximately 1.69 million ton of copper will be recovered from Saindak deposits in Balochistan, Pakistan, apart from gold and silver (Shah, 2004). The region of upper Punjab, including Lahore, Gujranwala and Gujarat, has a variety of wire manufacturing industrial units. The waste of this industry includes copper oxide scales. Using solvent extraction process, pure copper can be recovered from this waste.

By and large, the solvent extraction is a hydrometallurgical process in which selective separation of the desired components is achieved and the desired metal is concentrated into a form from which it can be recovered in a high state of purity (Alguacil *et al.,* 2002; Cox, 1992; Ritcey and Ashbrook, 1984). The recovery of copper by solvent extraction was possibly the most significant hydrometallurgical development of the 1960s, which even now is a dominant technology in the industrial chemicals arena (Reddy and Priya, 2005; Aminian and Bazin, 2000; Doungdeetha-Veeratana and Sohn, 1998; Aminian *et al.,* 1997). Solvent extraction of copper was first used commercially in 1968 for the treatment of dilute liquors from dump leach operations. Since then, with the operation of the first commercial plant at the Rancher's Baghdad mine, the total capacity of World's copper production by solvent extraction-electrowinning has increased manifold to 1.65 million ton per annum.

In the early 1970s, ICI developed a reagent known as P-50 to carry out commercial operations using the solvent extraction technique for copper separation. This reagent has proved to be a very strong extractant showing faster kinetics of extraction and relatively higher selectivity than the previously used reagents, namely, LIX 64N and LIX 65N (Lee *et al.,* 1994; Kojima and Miyauchi, 1982), which also resulted in a substantial change in the plant configuration (Banza *et al.,* 2002). The reagent Acorga P5100 was also developed and used commercially for copper extraction at the Kennecott Ray mine plant in Arizona, USA, in 1980. In recent years, it has been replaced with new Acorga reagents, such as M5640 and PT5050, both of which have better selectivity and recovery characteristics (Cox *et al.,* 2004; Lee *et al.,* 2003; Dalton and Steward, 1986). Extensive laboratory scale and commercial operations around the World have demonstrated that Acorga (ester modified reagent M5640) is the most hydrolytically stable formulation available in the market (Alguacil *et al.,* 1998; Szymanowski, 1993). It offers significant savings in operational costs on account of reduced reagent usage, even with commercial initial feed solutions (Dalton and Steward, 1986).

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The purity of extracted copper was determined employing electrogravimetric method of analysis (Robert and Dennis, 1968; Belcher and Gordon, 1963), which is an ASTM (E53-02) recommended technique to determine the purity of copper (ASTM, 2004).

Materials and Methods

Chemicals and reagents. Acorga M5640 (a trademark of Avecia Ltd.) introduced by Imperial Chemical Industries (ICI) was used by diluting it to the desired concentration in kerosene oil (Alguacil *et al.,* 2002). The active substance of the reagent is 5-nonyl salicylaldoxime, which also contains a fatty ester as modifier (Szymanowski, 1993). The basic oxime substance, including the selectivity of copper over iron, increases its resistance to hydrolysis and decreases formation of a fine dispersion that impedes phase disengagement in the settler (Szymanowski, 1993; Dalton and Steward, 1986).

The extractant was contacted with a series of solutions of copper sulphate ranging in concentration between 2 and 14 g per litre Cu in the aqueous initial feed. Extraction and stripping were carried out using separatory funnels with thermostatically controlled temperature at 25 °C and mechanically shaken with reciprocating shaker (OSK 9611, Ogawa Seiki, Japan; Catalogue Science and Education, 2000) at the rate of 200 times per min for 10 min. Extraction phase ratio of aqueous to organic phase of 5:1, and the stripping phase ratio of aqueous to organic phase of 3:1 was used. The pH of the aqueous solution was adjusted with nitric acid solution as it degrades oximes, which have high selectivity for copper over iron. For the estimation of the copper loading, the organic phase was washed, prior to extraction, with distilled water until it was acid free (pH of the raffinate, 5.5 to 6.0).

Deodourized kerosene oil Shellsol D70, UK was used as the diluent (Banza *et al.,* 2002). The selected diluent was suitable, having the density (at 20 °C) of 0.786 g per litre, boiling range of 212-295 °C, flash point of 96 °C, and aromatic contents as $<2\%$.

The modifier used was 99% tri-*n*-butyl phosphate (Merck, Germany), which was used to improve the reagent modification and phase disengagement performance.

Sampling and sample preparation. The waste liquor (hot rolling mill scale liquor) was collected directly from the plant. Coning and quartering procedure for sampling was followed for obtaining truly representative samples. The composite sample was packed in double sealed thick polyethylene packs to be subsequently used for the preparation of varying amounts of pregnant leach solution, ranging in composition from 2 to 14 g per litre Cu.

Instrumentation and procedure. The pH (pH meter model # 8520, Hanna Instruments, operateable in the temperature range of 0-100 °C) of the solution was adjusted at 2.0 initially, but all later studies were carried out at 2.5, as this pH value was found to be optimum. A calibrated stopwatch (Timex, USA) was used to measure the time interval during the extraction and stripping phase disengagements. All studies were carried out at 25 °C.

The pilot plant (counter-current mixer-settler unit) contained 10 mixer-settler compartments, aided with a stirring mechanism, which was driven by motors rotating at 2000 rpm. The driving mechanism was coupled with reduction gears to control the stirring speed in the mixer. The unit, alongwith the electrowinning apparatus fitted with the cell, was operated with a power supply of 115 voltage. The flow rate was controlled by raising Y-type fittings, up or down, for level control. This unit was also supplemented with plastic tubes, fittings and diaphragm pumps. Solvent extraction and stripping of copper performance was conducted as shown in the process flow-sheet diagram (Fig. 1).

Electrowinning apparatus. The apparatus consisted of a rectangular plastic vat fitted with bus bars, electrodes, and an electrical transformer (HBS Corporation, USA) with a capacity of 1.1 kilowatt, 0 to 10 volts, aided with regulators. It was used for electrodeposition of copper from concentrated leach solution. The copper stripped from cathodes was collected for its estimation.

Analytical testing methods. Electrogravimetric analysis was carried out using electrolytic analyzer OSK 2000 (Catalogue Science and Education, 2000) to determine quantitively the electrowon copper having the minimum purity of more than 99%. The instrument works on the principle of electrogravimetric method of analysis which is an analytical test method recommended as ASTM E53-02 for the determination of purity of copper (ASTM, 2004).

Atomic absorption spectrophotometer (Hitachi Z-8000, Japan) was used to determine copper. Standard solutions of the elements to be determined were employed to construct a calibration curve from which the contents of test solutions (impurities) were determined by using ASTM standards B 170-99 (ASTM, 2004).

Results and Discussion

Bench scale studies. ***(a) The effect of copper concentration in the feed.*** The effect of Cu-concentration in the initial feed (range: 2.0-14.0 g per litre) was studied at pH 2 and aqueous to organic phase ratio of 1:1(Table 1). It may be noted from the given data that the percent efficiency of copper extraction

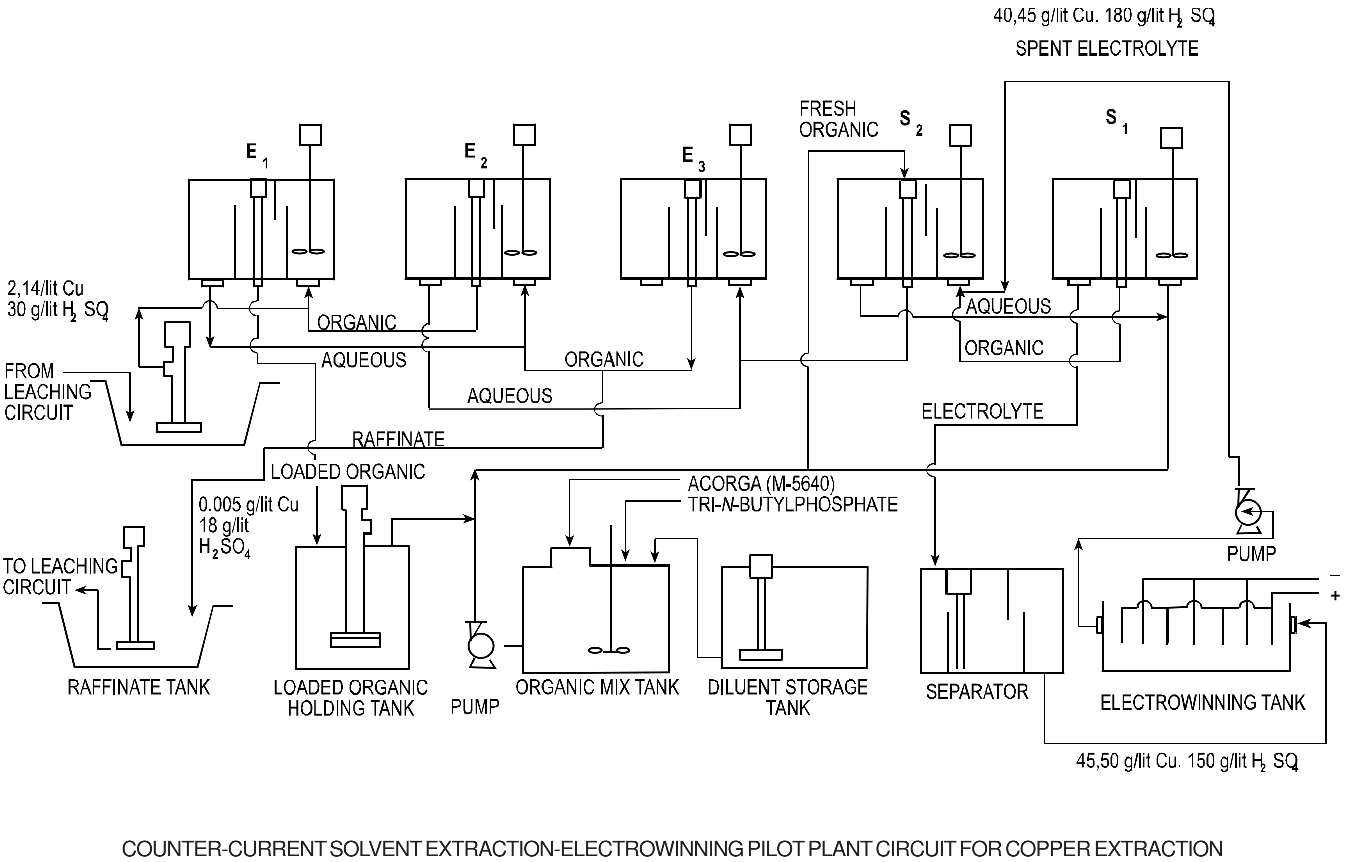

Fig. 1. Process flow-sheet for the extraction and electrowinning of copper from hot rolling mill scale liquor waste; E_1, E_2, E_3 = extraction cells; S_1, S_2 = stripping cells.

increased gradually from 88.35 % to 90.46 % with an increase in the initial feed concentration from 2.0 g per litre to 6.0 g per litre copper. At the miximum Cu extraction of 90.46%, when the initial feed concentration was 6.0 g per litre, the raffinate yield was 0.572 g per litre copper. Above 6.0 g per litre in the initial feed range of 2.0 to 14.0 g per litre studied, the percent extraction of copper showed a downward trend.

(b) The effect of pH variation of the initial feed. The copper extraction by Acorga M5640 being dependent on the initial acidity of the aqueous solution, studies were carried out to determine the influence of pH on copper extraction, from the initial feed Cu concentration of 6.0 g per litre. The effect of pH variation from 1.0 to 2.5 in the initial feed solution showed that increase in the extraction of copper occurred from 81.98 % to 88.34 %, when the pH was changed from 1.0 to 2.5, but declined progressively when the pH was raised to 3.0 and above up to 4.0, from 87.28% to 85.16% (Table 2). Thus, the optimum copper extraction was achieved at pH 2.5 at the equilibrating contact time of 10 min.

The copper extraction data, as related to Cu concentration and pH of the initial feed solution, are useful in the designing of equipment as these are important critical factors to evaluate the overall throughput, the equipment dimensions, and capital costs. It may be noted that equilibrium was generally reached within 10 min of contact, as indicated by the dark-brown colour of copper-loaded solvent, which made a clear indication between the phases.

(c) The effect of aqueous-organic phase ratio. The observations on the effect of aqueous-organic phase ratio on copper extraction have been given in Table 3. It may be noted that copper extraction increased slowly from 88.34 % to 92.58 % with a change in the aqueous to organic phase ratio from 1:1 upto 5:1. Further increase in the aqueous to organic pahse ratio of upto 7:1 showed a decline in the extraction. It is concluded, therefore, that the most suitable and economical aqueous-organic phase ratio was found to be 5:1.

The copper equilibrium isotherm was obtained with an organic solution of 30% (v/v) Acorga M5640 in kerosene oil and aqueous solution of 6 g per litre copper at the initial pH of 2.5, using the continuous aqueous to organic phase volume variation procedure. Ten min equilibration time was followed. The results obtained are given in Table 3. It was observed that the maximum loading of 5.55 g per litre was reached after three extraction cycles at the aqueous to organic pahse ratio of 5:1, beyond which it showed a decreasing trend.

(d) The effect of different concentrations of the organic phase on extraction efficiency. The observations obtained on the effect of different concentrations of the organic phase on extraction efficiency have been recorded in Table 4. The aqueous to organic phase ratio used was 5:1. The copper extraction was observed to increase from 83.0% to 90.5% as the concentration of the organic phase increased from 10% to 30% (v/v), whereas the percentage of copper extraction decreased with further increase in the organic phase concentration up to 40 % in kerosene (v/v).

(e) The effect of copper stripping from loaded organic. The effect of stripping behaviour of loaded organic with sulphuric acid and then with acid and copper sulphate is shown in Table 5. Changing the concentration of sulphuric acid from 10 g per litre to 40 g per litre yielded the maximum stripped solution of 90.45% at the acid concentration of 35 g per litre. Using the selected acid concentration of 35 g in combination with variable amounts of copper sulphate from 25 g per litre to 45 g per litre of the solution showed an increasing trend in the stripped solution. The maximum stripped solution of 92.35% was achieved using 35 + 40 g per litre solution of sulphuric acid + copper sulphate, which resulted in optimum output.

Pilot plant studies. The results of the optimized conditions obtained during the bench scale studies were scaled-up on the pilot plant, and the observations obtained are given in Table 6. For this purpose, aqueous solutions of different copper concentrations, ranging between 2 and 14 g per litre copper, were prepared and the pH was adjusted to 2.5 with nitric acid. The organic extractant Acorga M5640, 30% (v/v) in kerosene, was used and the equilibration time given was 10 min. The initial feed solution was run using a diaphragm pump, while the organic phase was run counter-currently through flow meter (Cole-Parmer P-03219-29, USA). The loaded organic phase was stripped with spent solution from the electrowinning apparatus, while the concentration-leached solution was fed through the stripped line resulting in high percentage of copper in the aqueous phase. The flow was controlled using the Y-type fitting, up or downward. The copper deposited on the stainless steel plates was collected and analyesd chemically (electrogravimetric analysis) and by atomic absorption

Table 1. The effect of copper concentration in the initial feed on the percentage of Cu extraction

Copper concentration in initial feed (g per litre)	Loaded organic (g per litre)	Raffinate copper (g per litre)	Extraction (%)
2.0	1.767	0.233	88.35
4.0	3.555	0.445	88.87
6.0	5.428	0.572	90.46
8.0	6.855	1.145	85.69
10.0	8.474	1.526	84.74
12.0	10.028	1.972	83.57
14.0	11.647	2.353	83.19

pH = 2.0; temperature = 25 °C; aqueous : organic phase ratio = 1:1; best extraction at initial feed concentration = 6.0 g Cu per litre

Table 2. The effect of pH variation of the initial feed on the percentage of Cu extraction

pH	Loaded organic copper (g per litre)	Raffinate copper (g per litre)	Extraction (%)	Equilibration time (sec)
1.0	4.919	1.081	81.98	570
1.5	5.046	0.954	84.10	582
2.0	5.173	0.827	86.22	590
2.5	5.300	0.700	88.34	598
3.0	5.237	0.763	87.28	609
3.5	5.205	0.795	86.75	608
4.0	5.110	0.900	85.16	603

initial feed concentration = 6.0 g per litre copper; temperature = 25 °C; aqueous : organic phase ratio = 1:1; best extraction obtained at pH 2.5

Table 3. The effect of aqueous to organic phase ratio on the percentage of Cu extraction

Aqueous phase : organic phase ratio	Loaded organic copper (g per litre)	Raffinate copper (g per litre)	Extraction (%)
1.0 : 1.0	5.30	0.699	88.34
2.0 : 1.0	5.36	0.635	89.40
3.0 : 1.0	5.42	0.572	90.46
4.0 : 1.0	5.49	0.508	91.54
5.0 : 1.0	5.55	0.445	92.58
6.0 : 1.0	5.55	0.445	92.58
7.0 : 1.0	5.54	0.451	92.47

initial feed concentration = 6.0 g per litre copper; pH = 2.5; temperature = 25 °C; extraction cycles 3; best aqueous : organic phase ratio obtained = 5:1

spectrophotometry (Hitachi Z-8000 spectrophotometer, Japan). The stainless steel cathode plates were coated on the edges with epoxy resin to avoid the overlaying of copper on the edges of the plates. The maximum ratio of net iron to copper selectivity achieved was 1988, with the maximum overall copper extraction efficiency of more than 96% (Table 6).

It is evident that the concentration of organic extractant Acorga M5640 affects the copper extraction. The data obtained indicated the maximum copper enrichment in the aqueous phase of 10 g per litre copper in the initial feed concentration in contact with the organic phase of 30% (v/v) Acorga M5640. The result of two-stage counter-current stripping carried out at organic : aqueous pahse ratio of 3:1, with the stripping feed of 1.8 molar sulphuric acid, indicated a maximum copper stripping efficiency of more than 98%. The reason behind the better copper extraction and stripping efficiency on pilot plant scale study may be attributed to the better controls and minimum losses, with no formation of polynuclear complexes in the organic solution.

Table 4. The effect of different concentrations of the organic phase on the efficiency of Cu extraction

Organic phase (%, v/v)	Loaded organic copper (g per litre)	Raffinate copper (g per litre)	Extraction (%)
10.0	4.980	1.019	83.00
15.0	5.110	0.890	85.16
20.0	5.300	0.699	88.34
25.0	5.360	0.635	89.40
30.0	5.420	0.572	90.50
35.0	5.396	0.604	89.93
40.0	5.396	0.604	89.93

initial feed concentration = 6.0 g per litre copper; pH = 2.5; temperature = 25 °C; aqueous : organic phase ratio = 5:1; best organic phase concentration obtained = 30 % in kerosene (v/v)

Table 5. The effect of copper stripping behaviour of the loaded organic*

Stripping solution	Strength of stripping solution (g per litre)	Loaded copper (g per litre)	Aqueous copper (g per litre)	Stripped solution (%)
Sulpuric acid				
	10	10.05	8.264	82.22
	15	10.05	8.450	84.12
	20	10.05	8.640	86.02
	25	10.05	8.830	87.92
	30	10.05	8.890	88.55
	35	10.05	9.090	90.45
	40	10.05	9.090	90.45
Sulpuric acid + copper sulphate				
	35+25	10.05	9.090	90.45
	35+30	10.05	9.150	91.08
	35+35	10.05	9.210	91.71
	35+40	10.05	9.280	92.35
	35+45	10.05	9.240	92.03

* stripping cycles 2; organic : aqueous phase ratio = 3:1; best strength of the electrolyte stripping solution = sulphuric acid 35 g per litre + 40 g per litre copper sulphate solution

Table 6. Pilot plant studies on the influence of change in copper concentration in the initial feed on copper extraction and copper to iron selectivity

Copper concentration in the initial feed (g per litre)	Loaded organic (g per litre)	Copper raffinate (g per litre)	Copper extraction efficiency (%)	Sulphuric acid [M**]	Selectivity of copper over iron	Copper stripping efficiency (%)	Cathodic copper estimation	
							electro-gravimetric	AAS*
2.0	1.811	0.189	90.56	1.8	1625	92.4	98.59	98.71
6.0	5.661	0.339	94.35	1.8	1900	95.7	99.71	99.85
10.0	9.626	0.374	96.26	1.8	1988	98.8	99.77	99.89
12.0	11.390	0.610	94.92	1.8	1910	97.3	99.78	99.87
14.0	13.040	0.960	93.13	1.8	1855	94.2	99.78	99.89

*atomic absorption spectrophotometric; ** molarity; extraction aqueous : organic phase ratio = 5:1; stripping organic phase : aqueous phase ratio = 3:1; initial iron concentration = 3 g per litre; extraction stages = 3; stripping stages = 2; pH = 2.5

The electrogravimetric analysis of the electrowon copper indicated cathodic copper ranging from 98.59% to 99.78% for the initial copper concentration ranging from 2 to 14 g per litre, whereas the analysis by atomic absorption spectrophotometric technique indicated cathodic copper variation from 98.71% to 99.89%.

Conclusion

The bench and pilot plant scale studies have clearly demonstrated that Acorga M5640 is a very selective commercial solvent and extraction reagent, which offers a promising alternative for the removal of copper metal from metal containing waste streams like hot rolling mill scale liquor and from other hydrometallurgical applications. In particular, the ester modified Acorga M5640 showed significant improvement in the recovery of Cu and selectivity over iron. The observed loadings were relatively higher than those obtainable with LIX series coupled with reduced losses of the organic extractant on account of its low volatility (Cupertino *et al.,* 1999). Another advantage of this solvent is that with conventional leaching liquors, the modified aldoxime reagent demonstrated faster phase disengagement characteristics, which was about 10 min compared to 80-100 min with LIX series solvents. The extraction of copper with Acorga M5640 increases with the rise in pH value, reaching maximum at pH 2.5 (30%, v/v, Acorga in kerosene). The results of the two-stage stripping assimilation for 9.626 g per litre of copper-loaded organic phase carried out at the organic-aqueous phase ratio of 3:1, with 1.8 molar sulphuric acid solution, gave the maximum copper stripping efficiency of 98.8%.

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