

# Copper Extraction from Copper Rolling Mills Scraps using Solvent "Aryl Aldoxime, 2-hydroxy-5-nonylbenzaldoxime" (ACORGA-M5640)

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**Summary:** The performance of ACORGA-M5640 solvent extraction reagent has been experimentally demonstrated for extraction of the copper from scales of copper rolling mills scraps. Initially laboratory scale experiments are performed to evaluate best operating condition for solvent extraction of copper for 6 g/l of copper in feed solution. The conditions at which maximum extraction takes place were established as pH of the feed solution is 2.5, aqueous/organic ratio is 1:3, 30 % of ACORGA-M5640 in 70 % of diluents kerosene; mixing time is 12 min and strength of stripping solution of 2.8N H<sub>2</sub>SO<sub>4</sub>. A pilot plant having three extraction stages and two stripping stages was operated at these conditions. The overall % extraction efficiency achieved in pilot plant is 99.73 % and overall stripping efficiency is 96.92 %. The comparison between extractants ACORGA-M5640 and previously used and ACORGA-P5100 is compared. ACORGA-M5640 has extraction efficiency 4.73 % and stripping efficiency 6.14 % greater than that of ACORGA-P5100.

## Introduction

Liquid-Liquid extraction is a mass transfer operation in which an aqueous solution (the feed) is contacted with an immiscible or nearly immiscible liquid (solvent) that exhibits preferential affinity or selectivity towards one or more of the components in the feed [1]. Two streams result from this contact: the extract, which is the solvent rich solution containing the desired extracted solute, and the raffinate, the residual feed solution containing little solute. Solvent extraction is an industrial method of removing of metallic impurities from liquids. In metallurgy, the term used for separation of pure metals from impure state is sometimes called "winning". The objective of the study was to establish the optimum operating conditions for copper recovery on pilot plant.

The following parameters need to be carefully evaluated when optimizing the design of the extraction processes [2-3].

- 1 Solvent selection
- 2 Operating Conditions
- 3 Mode of Operation
- 4 Extractor Type

Solvents differ in their extraction capabilities depending on their properties and the solute's chemical structure. The "Distribution Coefficient" and "Selectivity" are the most important parameters

that govern solvent selection. The *Distribution Coefficient* ( $m$ ) or *Partition Coefficient* for a component (A) is defined as the ratio of concentration of "A" in extract phase to that in raffinate phase. *Selectivity* can be defined as the ability of the solvent to pick up the desired component in the feed as compared to other components. The desired properties of solvents are high distribution coefficients, good selectivity towards solute and little or no miscibility with feed solution. Also, the solvent should be easily recoverable for recycling [2]. Designing an extractor is usually a fine balance between capital and operating costs. Usually, good solvents also exhibit some miscibility with feed solution. Consequently, while extracting larger quantities of solute, the solvent could also extract significant amount of feed solution. Other factors affecting solvent selection are boiling point, density, interfacial tension, viscosity, corrosiveness, flammability, and toxicity, and stability, compatibility with product, availability and cost [4-5]. The most active ingredient in an extractant is oximes.

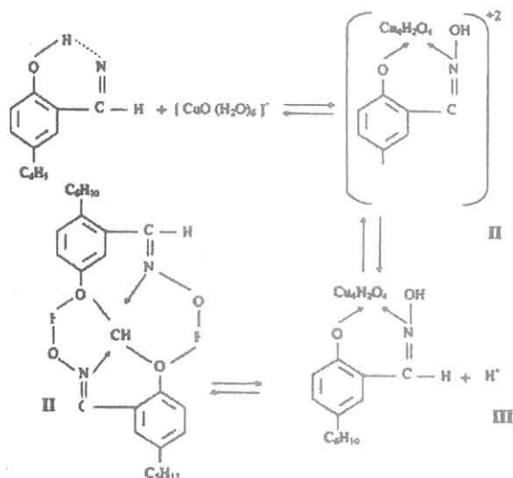
The ketone are termed weak extractants indicating that they will strip readily but have weak affinity for loading copper. In most cases, the ketone alone is too weak to be used as extractant. Depending on the nature of the extraction process, the temperature, pH and residence time are selected for good yield and selectivity. Temperature can also be used as a variable to alter selectivity [6-7].

### Chemistry of Solvent Extraction of Copper

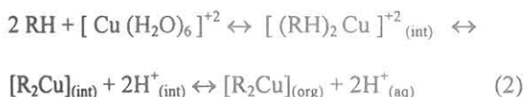
During the loading stage, the overall chemical reaction involved in selective extraction of copper from acidic aqueous sulphate solution by ortho-hydroxy aryl oxime class (aldoxime) in water immiscible organic solvents; "aryl aldoxime, 2-hydroxy-5-nonylbenzaloxime" can be represented as:



Since the aldoxime are very weak acids and exist virtually in unionized form. Therefore the first step appears to be the reaction between aldoxime and hydrated  $\text{Cu}^{+2}$  ions. Where copper forms coordinate with oxygen of  $\text{OH}$  of the phenol followed by the formation of the complex with loss of  $\text{H}^+$  and finally with loss of another  $\text{H}^+$  reaction completes [8-9].



The final complex formed by aldoxime is square planar and is very stable. The driving force in the above sequence of reaction is highly acidic nature of  $\text{H}$  of  $\text{OH}$ ; when  $\text{O}$  is coordinate with copper metal and the stability of the final chelate. The overall reaction in the loading stage can be represented as;



The above reaction occurs at the interface. The position at equilibrium will determine the amount of  $\text{Cu}$  which will be transferred to the organic phase and this depends upon the acidic nature of the intermediate  $[(\text{RH})_2\text{Cu}]^{+2}$ . This means that extractant giving strongly acidic species will transfer more

copper than the extractant forming less acidic complex such as ketoxime.

### Results and Discussion

The effect of concentration of copper in feed have been shown in the Table-1, from 6.0 g/l  $\text{Cu}$  to 18.0 g/l  $\text{Cu}$ . Percentage extraction gradually falls from 88.34 % to 80.13 % respectively. The best operating concentration of copper in feed solution was selected 6 g/l due to high percentage extraction (88.34 %) and less than 1.0 g/l copper in raffinate.

Table 1: Effect of Change in Concentration of copper in feed Solution.

Sr. No.	Copper Conc. in feed, g/l	Organic Loaded Copper, g/l	Raffinate Containing Copper, g/l	% Extraction
1	6	5.30	0.699	88.34
2	8	6.85	1.144	85.69
3	10	8.47	0.615	84.69
4	12	10.02	1.970	83.57
5	14	11.64	2.350	83.19
6	16	13.20	2.798	82.51
7	18	14.44	3.559	80.22

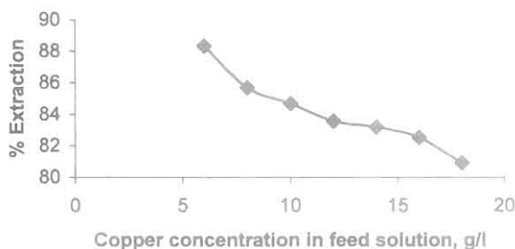


Fig. 1: Effect of Concentration of Copper in feed Solution.

The higher concentration from 6g/l shows more than 1.0 g/L  $\text{Cu}$  in raffinate and less % extraction. Other constant parameters were pH 2.5, Aqueous/ Organic ratio 1:1, percentage of organic in diluents was 20 %, and mixing and phase separating times were 10 and 15 minutes respectively.

In Table-2, the effect of pH variation on extraction has been given. Seven solutions were prepared. The pH of the solutions was 1.0, 1.5, 2.0, 2.5, 3.0, 3.5 and 4.0 respectively. Results have shown that percentage extraction increases from pH 1.0-2.5 (i.e. 81.98%-88.34%). After pH 2.5 it gradually decreased from pH 3.0-4.0 (87.28%-85.16). It has been clear from above discussion that optimum pH is 2.5, because at this pH highest percentage extraction has been achieved. Other constant parameters were concentration of feed solution 6 g/l, aqueous/organic ratio 1:1, room temperature, mixing and phase

separation times were 10 and 5 minutes respectively extractant 20% ACORGA-M5640 in 80% kerosene. Extraction percentage will increase continuously up to the pH of 2.5 and then decreases with increase in pH.

Table 2: Effect of change in pH of feed Solution

Sr. No.	pH	Organic Loaded Copper g/l	Raffinate Containing Copper, g/l	% Extraction
1	1.0	4.91	1.08	81.98
2	1.5	5.04	0.95	84.10
3	2.0	5.17	0.83	86.22
4	2.5	5.30	0.69	88.34
5	3.0	5.24	0.73	87.28
6	3.5	5.21	0.79	86.75
7	4.0	5.11	0.89	85.16

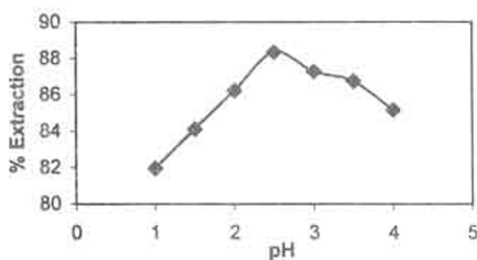


Fig. 2: Effect of pH variations in feed Solution

In Table-3, effect of change in aqueous/organic ratio has been shown. The quantity of the aqueous phase was remained constant in each case but quantity of organic changed from 1 to 4 times. Increasing the quantity of organic increased percentage extraction. Percentage extraction was increased from 1:1 to 1:3 but at 1:3.5 and further it remained almost constant. So optimum aqueous/organic ratio is 1:3 where % extraction is 92.58%. Other parameters were remained constant i.e., concentration of feed solution 6 g/l, pH =2.5, room temperature, mixing time 10 minutes, extractant composition 20% ACORGA-M5640 in 80% of Kerosene. Table-4 shows the effect of change in percentage of organic in diluent. By changing percentage of organic in diluent from 10% to 30% shows relative increase in percentage extraction i.e. 83.04% to 90.46%.

Table 3: Effect of change in Aqueous/Organic Ratio:

Sr. No	Aqueous/Organic Ratio	Organic Loaded Copper, g/l	Raffinate Containing Copper, g/l	% Extraction
1	1:1	5.3	0.69	88.34
2	1:1.5	5.36	0.635	89.40
3	1:2	5.42	0.57	90.46
4	1:2.5	5.49	0.51	91.52
5	1:3	5.55	0.45	92.58
6	1:3.5	5.55	0.45	92.58
7	1:4	5.54	0.45	92.47

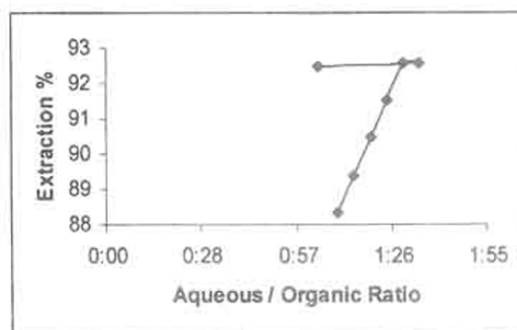


Fig. 3: Effect of Aqueous/Organic Ratio

Table 4: Effect of Change in %age of Organic in Diluent.

Sr. No.	% of Organic in Diluent	Organic Loaded Copper, g/l	Raffinate Containing Copper, g/l	% Extraction
1	10	4.98	1.01	83.40
2	15	5.11	0.89	85.18
3	20	5.30	0.69	88.34
4	25	5.36	0.64	89.40
5	30	5.42	0.57	90.46
6	35	5.39	0.61	89.93
7	40	5.39	0.61	89.93

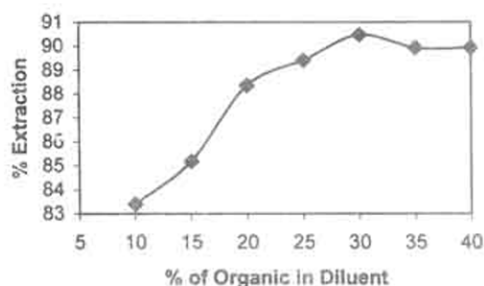


Fig. 4: Effect of % Change of Organic Diluent

Beyond 30%, at 35% and 40% percentage extraction decreased from 90.46% to 89.93% and remained constant for further percentages of organic in diluent.

Optimized percentage of organic in diluent is 30% of organic in diluent. At 30%, the extraction was maximum that is 90.46%. Table-5 shows the effect of change in mixing time on extraction. By increasing mixing time from 2 minutes to 12 minutes shows relative increase in percentage extraction from 68.21% to 89.93%. By increasing further time no more increase in percentage extraction has been achieved. So the optimum mixing time is 12 minutes.

Table 5: Effect of Change in Mixing Time.

Sr. No.	Mixing Time (minutes)	Organic Loaded Copper, g/l	Raffinate Containing Copper, g/l	% Extraction
1	2	4.09	1.91	68.21
2	4	4.41	1.59	73.51
3	6	4.72	1.27	78.81
4	8	5.05	0.95	84.10
5	10	5.30	0.69	88.34
6	12	5.39	0.60	89.93
7	14	5.39	0.60	89.93

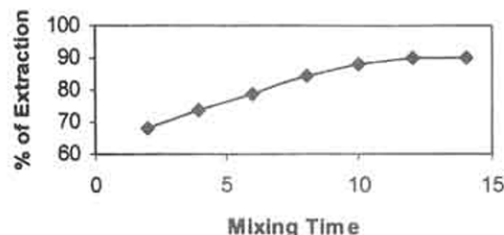


Fig. 5: Effect of changing Mixing Time on Extraction

Table-6 shows the stripping behavior. By increasing percentage of  $H_2SO_4$  in water from 0.8 N to 2.8 N shows relative increase in percentage stripping from 82.22 % to 90.45 % respectively. Further increase of percentage of  $H_2SO_4$  in water shows no further stripping. So the optimized strength of stripping solution is 2.8 N of  $H_2SO_4$ .

Table 6: Stripping Behavior Using Modifier

Strength of Stripping Solution ( $H_2SO_4$ )	Loaded Organic, g/l	Aqueous Solution with Cu, g/l	Stripping %
0.8N	5.3	4.32	81.54
1.2N	5.3	4.44	83.96
1.6N	5.3	4.57	86.35
2N	5.3	4.64	87.55
2.5N	5.3	4.70	88.75
2.8N	5.3	4.76	89.95
3.3N	5.3	4.76	89.95

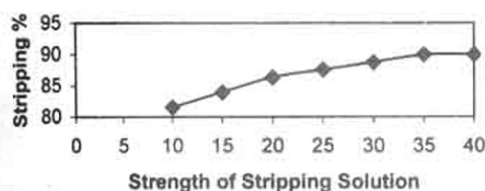


Fig. 6: Stripping Behavior

All the best operating conditions were applied to pilot plant, which has 3 extraction stages and 2

stripping stages. Extraction was 99.73 % and over all stripping percentage was 96.92 %.

Table-7: Comparison of ACORGA-M5640 &amp; P5100 at Pilot plant

Extractant	Extraction %	Stripping %	No. of Extracting Stages	No. of Stripping Stages
P 5100	95	90.78	3	3
M5640	99.73	96.92	3	2

ACORGA-M5640 has extraction efficiency 4.73 % and stripping efficiency 6.14 % in excess to ACORGA-P5100.

## Experimental

The study was conducted on two stages

### A) Laboratory Scale Work

The following parameters were studied at laboratory scale:

#### 1. Effect of change in concentration of copper in feed solutions

Seven different solutions of copper sulphate concentrations; 2g/l, 4g/l, 6g/l, 8g/l, 10g/l, 12g/l and 14g/l were prepared. The pH of all solutions was maintained at 2.5. Mixing 20 ml of ACORGA-M5640 in 80 ml of kerosene formed 20 % organic solution. 100 ml of feed solution containing 2g/l of copper was taken in separating funnel. 100 ml of 20 % organic solution was added to it (aqueous/ organic ratio 1: 1). This mixture was shaking in separating funnel for about 10 minutes. Copper was loaded from feed solution to organic solution and observed by changing color, which was brown and turned into black. The mixture was then allowed to settle for about five minutes in separating flask. The raffinate was then analyzed chemically by iodometric titration to estimate the concentration of copper.

#### 2. Effect of pH variation

Seven solutions were prepared in seven different glass bottles, each had 6 g/l of copper but different pH 1.0, 1.5, 2.00, 2.5, 3.00, 3.5, 4.0 respectively, was maintained by adding  $H_2SO_4$  or NaOH. Experiment was performed by taking 100 ml of feed solution containing 6 g/l of copper, pH 1.0 and equilibrated with 100 ml of 20 % of organic solution in separating funnel. The aqueous to organic ratio was 1: 1. The mixture was shaking and then mixture is to settle in separating flask. After 5 minute phase disengagement was happened; organic and aqueous phases, then analyzed chemically by iodometric titration to estimate the concentration of copper.

metric titration to estimate the concentration of copper.

### 3. Effect of change in aqueous/organic ratio

To study the effects of change in aqueous/organic ratio on extraction, different ratios of aqueous/organic used are 1:1, 1:1.5, 1:2, 1:2.5, 1:3, 1:3.5 and 1:4. Feed solution contained 6 g/l of copper, pH 2.5 and 20% by volume of organic solution. The procedure was same for each experiment as described for change in concentration of copper.

### 4. Effect of change in percentage of in diluents

Percentage of organic extractant (ACORGA-M5640) in diluent (kerosene) was changed in each experiment. The percentage of in diluents in experiment was 10 %, 15 %, 20 %, 25 %, 30 %, 35 % and 40 % respectively. The remaining parameters in each experiment were constant which include 6 g/l of copper in feed solution, pH 2.5, and aqueous/organic ratio 1: 1. For each experiment the procedure was same as demonstrated for change in concentration of copper. Chemical analyses were done by iodometric titrations.

### 5. Effect of changing the mixing time

Experiments were performed by changing mixing time at room temperature, but the remaining parameters were same as above. Extractant composition is 20 % ACORGA-M5640 in 80 % of Kerosene. The procedure was same as describe in "change in concentration of copper". Percentage extraction was noted against each mixing time.

### 6. Stripping behavior

Copper loaded organic solution contains 10.05 g/l of copper. To strip out the copper from loaded organic solution, seven different stripping solutions were prepared. Stripping solution was prepared by adding different percentage of  $H_2SO_4$  in water (10 % stripping solution means 10 ml of  $H_2SO_4$  in 90 ml of water). The percentage of  $H_2SO_4$  in water in experiments was 0.8 N, 1.2 N, 1.6 N, 2 N, 2.5 N, 2.8 N and 3.3 N respectively.

In the first experiment loaded organic and stripping solution were equilibrated in separating flask with the ratio of 1: 1. 5ml of modifier Tri-n-butyl phosphate was also mixed. The mixture was shaking for about 10 minutes and copper was stripped out from loaded organic solution to aqueous phase. This was observed due to change in color of loaded organic and aqueous stripping solution was

changed from brown color to black color due to formation of  $CuSO_4$ . Phase disengagement was quite visible and organic came at the surface and pregnant solution (stripping solution contain pure  $CuSO_4$ ) remained at the bottom. Organic and pregnant solutions were then separated, and pregnant solution was analyzed chemically by iodometric titration to estimate the concentration of copper in it. From this, percentage of stripping was calculated.

### B) Pilot Plant Study

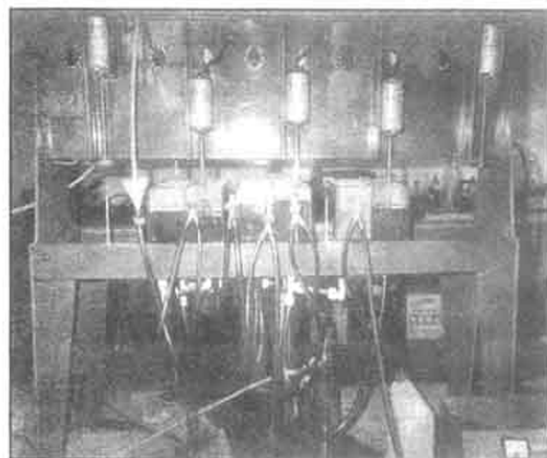


Fig. 7: Solvent Extraction Pilot Plant

The best operating conditions that 'studied at laboratory scale were applied to pilot plant. The plant was run first with water to check the pilot plant whether its parts were in working position or not. The plant was then run with acidic leach copper sulphate solution to extract the copper by using extractant ACORGA-M5640. Aqueous feed solution from feed tank goes to the mixer unit of extraction stage 1. Fresh organic solution is fed to the mixer unit of the extraction stage three. As the process is counter current, raffinate of the extraction stage 1 is the feed solution of the extraction stage 2 and the loaded organic from stage 2 is added to the mixer unit of the extraction stage 1. Similarly, Raffinate of the extraction stage 2 is the feed solution of the extraction stage 3 and the loaded organic from stage 3 is added to the mixer unit of stage 2. Final raffinate from extraction stage 3 goes to raffinate tank. Loaded organic from stage 1, after full extraction of copper, goes to storage tank, from where it goes to stripping section. Stripping solution from stripping tank goes to the mixer unit of the stripping stage 2. Loaded Organic after stripping from stage 1 enters the mixer unit of stripping stage 2.

Table 8: Experimental Pilot Plant Study on Extractant ACORGA-M5640

Feed Solution	Extract Phase	Raffinate Phase	Overall Extraction %	
Cu conc. in feed, g/l	Cu conc. in loaded organic, g/l	Cu conc. in raffinate, g/l	99	
6	5.98	0.016		
Stripping Solution Strength	Cu in Stripped Solution, g/l	% Extraction	No. of Extraction Stages	No. of Stripping Stages
2.8N H <sub>2</sub> SO <sub>4</sub>	5.8	96.92	3	2

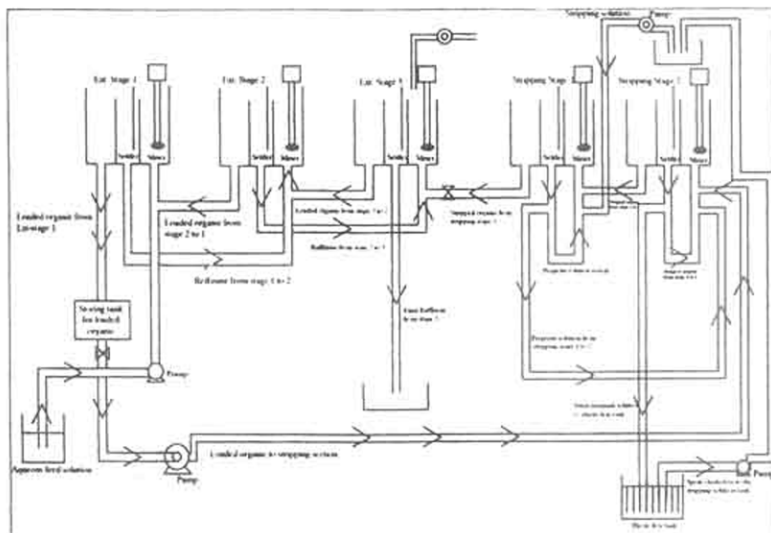


Fig. 8: Schematic Diagram of Solvent Extraction Plant

The stripped aqueous CuSO<sub>4</sub> solution from settler unit of the stripping stage 1 goes to the mixer unit of stripping stage 2 and also recycles to its mixer unit. The stripped aqueous CuSO<sub>4</sub> solutions from settler unit of the stripping stage 2 goes to the electrolytic tank and also recycle to its mixer unit. Stripped organic from stripping stage 1 goes to mixer unit of the extraction stage 3. In electrolytic tank, copper is deposited on the cathode same as in electroplating phenomena and H<sub>2</sub>SO<sub>4</sub> is formed, which is recycled to stripping tank. The schematic diagram of pilot plant is shown Fig. 8.

### Conclusions

There are a number of factors affecting extraction performance, the best operating conditions for solvent extraction of copper from copper rolling mills scraps are as follows:

- 6 g/l of copper in feed solution
- 2.5 pH
- Aqueous / organic ratio will be 1:3

- 30 % diluent organic phase
- Mixing time 10 minutes
- 2.8 N H<sub>2</sub>SO<sub>4</sub>

When these operating conditions were applied to pilot plant which has three extraction stages and two stripping stages, 99.73 % extraction and 96.92 % stripping were reported. Pure copper (99.73 %) was deposited on cathode by electrolysis of stripped aqueous copper sulfate solution. ACORGA-M5640 showed 4.74 % more extraction and 6.14 % more stripping than ACORGA-P5100. The study could often be an iterative cycle involving laboratory testing followed by pilot plant study. In most industrial extractors, there is usually a good scope for optimizing solvent usage.

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