

## HYDROMETALLURGICAL PROCESSING OF COPPER ORE

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A hydrometallurgical method has been proposed for the 99% extraction and recovery of copper from indigenous copper ore using 5% solutions of trioctylamine in benzene after acid leaching of the ore with 7.5M HCl. Various parameters, such as, the effect of temperature, acid concentration and digestion time have been optimised. The process developed has been made more cost effective by recycling used solvent.

**Key words:** Hydrometallurgy, Copper, Trioctylamine, Solvent extraction.

### Introduction

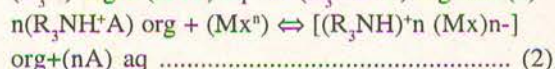
Although solvent extraction and hydrometallurgy have been employed for the separation of metal ions in aqueous solution for many years (George and Frieser 1957), their application in industrial processes for the recovery of metals is relatively recent. Until 1960, alkylamine was used as liquid extracting agent for various anionic species of metal ions (Mahlman *et al* 1954; Moore 1955). A number of research papers have also been published in recent years concerning the extraction of copper metal, but most of them are related to the characterisation, thermodynamics, mechanism and coordination of the metal in the form of its chelates and complexes (Furman *et al* 1949; Hague *et al* 1951; Gahler 1954; Taylor 1954; Friedberg 1955; Allen 1956; Stpeniak-Biniakiewicz and Swymanowski 1979; Komosrawa and Yamada 1980; Jianhu and Zhanyau 1990). However very little information is available on the application of these methods to the processing of minerals and ores. The present paper describes the extraction and recovery of copper with tertiary amine from oxide type of copper ore of North Waziristan Agency FATA DC Pakistan.

### Experimental

**Sample preparation.** The sampling of ore was carried out by the geologist of FATA DC 1 Kg of the original sample was broken into pieces with the aid of a hammer, then pulverised to 150  $\mu\text{m}$  size in a ball mill. The resulting material was further reduced to the mass of about 100 g using two stages grinding, coning and quartering. The final sample was sieved to the particle size  $<150 \mu\text{m}>125\mu\text{m}$  so that the homogene-

ity of the analyte be retained and a minimum amount of the sample could also be used for the analyses.

**Procedure.** 0.5 g of the powdered ore was weighed, transferred to a 100 ml Pyrex glass beaker containing about 25 ml of 10 M HCl. The contents were leached over a steam bath at 80°C for 6 h, and baked twice on water bath for the removal of silica. The resulting solution (leachate) was cooled to room temperature and filtered through Whatman (12.5 cm.) filter paper into a 100 ml volumetric flask. Added more 10 M HCl and diluted with distilled water so that the final solution concentration was 7.5 M HCl. 10 ml of the leachate was transferred to a 100 ml separating funnel, and 5 ml of 5% trioctylamine in benzene added to it. The two phases were shaken on a vibroshaker for 2-2.5 min, then allowed to separate and the organic amine phase was drained into a dried small beaker. Fresh 5 ml of 5% trioctylamine in benzene solution was added to the aqueous phase left in the separating funnel and the extraction was repeated (double extraction/ extraction in portions) in the manner described above. The two organic phases (5 ml + 5 ml) were mixed and stripped (back-washed to aqueous phase) with an equal volume of 0.10 M HCl solution. The resulting stripped solution and the aqueous phase left after double extraction of copper were analysed for copper contents using atomic absorption spectrophotometer (Hitachi Z-8000) in the flame mode for determining the percentage extraction as well as recovery of copper. The overall reaction between copper (M) and tertiary amines ( $\text{R}_3\text{N}$ ) may be represented by the following equations.



Where  $\text{R}_3\text{N}$  = Tertiary amine;  $\text{H}^+\text{A}^-$  = An inorganic acid and

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(MX)<sup>n-</sup>=Anionic complex, where, M is a metal ion and X is a ligand.

All the chemicals used in these investigations were analytical grade. Trioctylamine (5% solution) was freshly prepared for each experiment (in thiophene free benzene). All the aqueous solutions were prepared in distilled water unless otherwise stated. The acid strength of solutions in different instances was adjusted with 10 M HCl, that was further diluted for maintaining the requisite acid concentration.

## Results and Discussions

**Effect of acid concentration.** Fig 1 represents the % leaching /recovery of copper as a function of hydrochloric acid concentration in the range 0.1-10M HCl. It can be seen that

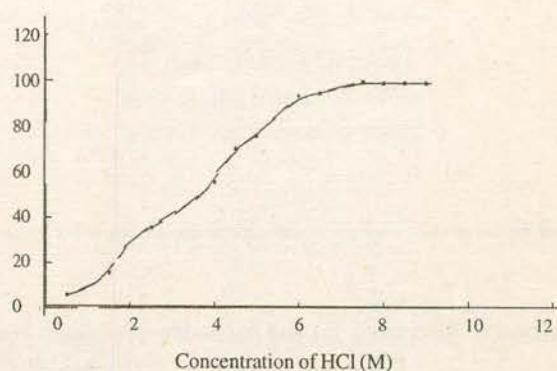
**Table 1**

Chemical evaluation of copper ore of North Waziristan Agency

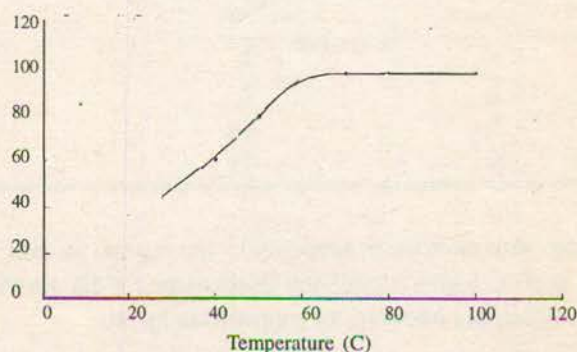
S.No.	Major & Trace contents	% Composition
1.	SiO <sub>2</sub>	50.98
2.	Fe <sub>2</sub> O <sub>3</sub>	14.00
3.	Al <sub>2</sub> O <sub>3</sub>	08.00
4.	CaO	11.20
5.	MgO	05.60
6.	Loss On Ignition	10.10
7.	Cu	00.50
8.	Co	00.01
9.	Mn	00.25
10.	Ni	00.00
11.	Pb	00.00
12.	Zn	00.02
13.	Ag	00.00
14.	Au	00.00
	Total	100.66

the % recovery of copper increases steeply with increase in the molar concentration of HCl. The % leaching recovery of copper becomes quantitative at 7.5M HCl and reaches to a maximum of 99%. However, the effect becomes constant after 8.0M HCl concentration and the curve tends to levels off.

**Effect of temperature.** Fig 2 illustrates the effect of temperature on % leaching/recovery of copper. The studies have been carried out by varying the temperature range from 25 to 100°C. The effect shown in Fig 2 represents a general



**Fig 1** Effect of acid concentration on leaching of copper from its ore.



**Fig 2** Effect of Temperature on acid leaching of copper from its ore.

**Table 2**

Comparative results of methodologies used for acid leaching of the ore

S.No.	Leaching methodologies	Present in ore	Leached % %Copper	% Leaching
1.	Direct acid leaching with 7.5 M HCl at 80 ° C	0.50	0.480	96.00
2.	Acid leaching with 7.5 M HCl and baking once at 80°C	0.50	0.490	98.00
3.	Acid leaching with 7.5 M HCl and baking twice at 80°C	0.50	0.415	99.00

**Table 3**  
Methodologies used for the recovery of copper from acidic aqueous solutions with used and regenerated solvents (TOA/Benzene)

S. No.	Methods for regeneration of used solvents	Number of uses	Conc. of copper (ug)		% Recovery of copper.
			Added	Recovered	
1.	Direct application of the used solvents without being washed.	I	20	19.10	95.50
		II	20	19.10	95.50
		I	20	19.60	98.00
2.	solvents after washing once Application of the used with distilled water.	II	20	19.50	97.50
		III	20	19.40	97.00
3.	Application of the used solvents after washing twice with distilled water.	I	20	19.80	99.00
		II	20	19.80	99.00
		III	20	19.74	98.70
		IV	20	19.70	98.50
		V	20	19.70	98.50

**Table 4**

Methodologies used for the recovery of copper from copper ore with used and regenerated solvents (TOA/Benzene)- % Cu in copper ore=0.50

S. No.	Number of applications of regenerated and used solvents	% Copper recovered from the ore	% Recovery of copper
1.	I	0.49	98.00
2.	II	0.49	98.00
3.	III	0.48	96.00
4.	IV	0.47	94.00

increase with increase in temperature and reaches its maximum at 80°C which is optimum temperature for the quantitative %leaching /recovery of copper from its ore.

*Effect of leaching time.* Fig 3 depicts the % leaching or

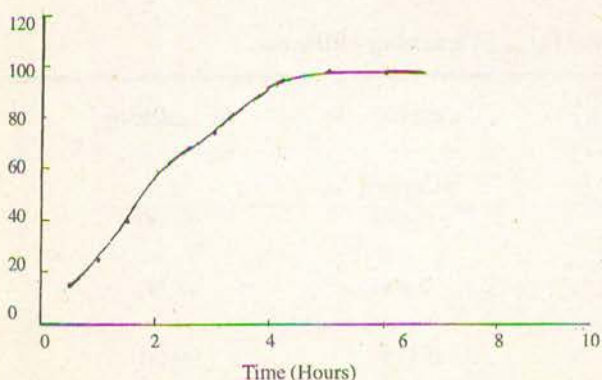


Fig 3 Effect of digestion time on acid leaching of copper from its ore.

recovery of copper from its ore as function of acid digestion time from 0.50 to 8.0 h at a constant temperature of 80°C. Complete digestion of the ore takes place in 6 h after that the graph tends to level off.

*Acid leaching methodologies.* The acid leached solution obtained from acid digestion (with 7.5M HCl) of the copper ore at 80°C was baked (once and twice) over waterbath for 6 h. The resulting dried masses were dissolved in few ml of 7.5M HCl solution, filtered through Whatman (12.5 cm) filter paper in a 100ml flask and discarded the residues. To each filtrate in the volumetric flask was added the requisite ml of 10M HCl and diluted with distilled water so that the final HCl concentration was 7.5M. The resulting solutions were analysed for copper content. The comparative studies are illustrated in Table 2.

*Application of the used and regenerated solvents (Trioctylamine/Benzene) for the recovery of copper from*

*acidic aqueous solutions & copper ore.* The exhausted and regenerated organic solvent was applied as such and also after washing twice with distilled water, for the recovery of copper from the acidic aqueous solutions (of known concentrations) and indigenous copper ore. The minor differences in % recovery during the successive applications of the regenerated solvent may be due to the exhaustion and/or its wastage during repeated applications. The data obtained are summarised in Table 3 and Table 4.

### Conclusion

It is concluded from the investigations, that, copper metal makes a colourless chloro complex with HCl at a specific molar (7.5M) concentration. The chloro-complex formed, being anionic in nature is quantitatively extracted into the liquid anion exchanger "trioctylamine" because even trace of copper content could not be found in the aqueous phase left behind after the extraction of copper into the organic phase (5% trioctylamine in benzene). It is also evident from these studies that, the extraction and recovery of copper depends on the acid (HCl) and solvents [TOA(trioctylamine)/Benzene] concentrations, temperature and acid digestion. The method developed may also be promoted as useful and economical industrial tool.

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