

STUDIES ON THE LEACHING OF COPPER FROM COMPLEX COPPER ORES OF CHITRAL

Farzana Rani^a, Izharul Haque Khan^{a*}, Fayyaz Mahmood^a & Muhammad Zafar Iqbal^b

^a Mineral and Metals Research, PCSIR Laboratories Complex, Lahore, Pakistan

^b University of the Punjab, Lahore, Pakistan

(Received 4 August 1993; accepted 6 January 1998)

Mineralogical and chemical studies have indicated potential deposits of complex ores containing minerals of copper, zinc, lead and silver in Dir and Chitral District of Pakistan. Pressure and agitation leaching studies were carried out for the extraction of copper and associated metals under varying parameters by using H_2SO_4 in complex copper ores (average 1.27% Cu), reported to occur in Kaldam Gol area, (District Chitral, NWFP, Pakistan). The maximum recovery of copper obtained at 100°C with 1.87 M H_2SO_4 and 0.5 M HNO_3 for 30 minutes stirring at atmospheric pressure was 35%. On the other hand the maximum recovery of copper with pressure leaching at the same condition at > than 70 atmosphere pressure was doubled i. e. 87%. The conditions for maximum recovery of copper by leaching are presented for these ores.

Key words: Leaching, Agitation, Chalcopyrite, Extraction.

Introduction

The important areas of copper ore deposits in Pakistan are Saindark (Khan *et al* 1988), Chilghazi (Khan and Qazi 1981) and Chitral (Khan *et al* 1981), Dir (Directory of economic minerals 1959) (in NWFP and Baluchistan). The Saindark deposit is typically a large porphyry deposit with dominant chalcopyrite mineral which can be extracted by conventional mineral processing techniques employing froth flotation. Substantial tonnage of copper ore occurs in Saindark as oxidized cover and could not be processed by flotation. The other deposits in the country are small and mostly oxidized which are also amenable to beneficiation. Another difficulty in their economic utilization is their complex nature, being composed of minerals of Zn, Pb, Sb, Ag etc. These deposits have to be treated chemically such as leaching to extract their metal contents.

Vezwa (1970) studied this problem in greater depth on a chalcopyrite pentlandite-pyrrhotite concentrate and showed that the degree of grinding is critical to the achievement of high copper extraction from product that was ground to 93% (-20 μm), the copper extraction was 91% after 8 h at an oxygen pressure of 550 kPa (guage) or (80 lb/in²).

Dugdale and Raymond (1970) first used dilute sulphuric acid and oxygen (Sherrit-Gordon process), and second time used concentrated sulphuric acid (Treadwell process) for leaching of chalcopyrite concentrate. In the Sherrit-Gordon process, chalcopyrite is reacted with dilute sulphuric acid

and oxygen in an autoclave at a temperature of 100°C and an oxygen partial pressure at 40 atm. An important feature of this process is the simultaneous separation of copper from iron (the first is obtained in solution and the latter remains in the solid residue). The Treadwell process was tested on a pilot scale by the Anaconda company, of Tuscon, Arizona. In this process copper sulphide containing ore is treated with concentrated sulphuric acid at 200°C. Copper and iron in the mineral are converted to water soluble sulphates, while the roasted chalcopyrite leached with H_2SO_4 (4.1-11.4%) at 63-96°C with agitation of 678-1182 rpm.

Erbit and Ozel (1983) evaluated that in pressure leaching of chalcopyrite with H_2SO_4 the oxidation rate increased with increasing temperature. The oxidation rate increased to maximum with the increased concentration of the leached charge.

Olive and Boyd (1956) describes the leaching of concentrates and extraction of base metals under drastic conditions of temperature, pressure, particle size and time etc. However, no process has been reported in literature for leaching/extraction of base metals directly from complex ores without prior separation of the base metals. For this purpose the mineralogical and leaching investigations were undertaken on the complex copper ore of Chitral area to determine the nature and mode of occurrence of copper and mechanism for extraction of copper from complex copper ore.

The area of complex sulphide copper ore consists of brown massive diorite having copper mineralization. The samples were procured from a mineral exploring agency working in the area (Sarhad Development Authority).

*Author for correspondence

The chip samples collected from adits, trenches and exposures of sulphide mineralization represented disseminated massive and vein type mineralization in the area. The samples were from both oxidize and sulphide zones.

The percentage of copper in the area under study varies from place to place and bulk samples prepared have an average of 1.27% copper.

Materials and Methods

Equipment/Apparatus. The equipment/apparatus used in the studies were Z-8000 polarized zeeman atomic absorption spectrophotometer, X-rays diffractometer siemens D-5000, Pyrex glass apparatus, Bomb digester.

Chemicals. Sulphuric acid, Nitric acid, Hydrochloric acid, Hydrofluoric acid and Perchloric acid used were of A. R. grade (E.Merck).

Procedure. The chemical evaluation of minor elements was carried out on atomic absorption spectrophotometer. The mineralogical investigation was done by using X-ray diffractometer.

Major elements were determined by standard chemical methods. For the determination of minor elements, 2-3 g rock was dissolved in HF-HClO₄-HNO₃ and diluted with 20% HCl solution in 100 ml volumetric flask. The results of chemical analyses and XRD data of ores are reported in Tables 6 and 7.

Ore Samples Preparation. The representative ore samples received from exploratory mines were about 20 kg each. Total number of representative samples received were 17 from

Rahat Gol, Puritgol, and Kaldam Gol areas. The ore was subjected to crushing in Jaw and Roll crushers. A sample weighing 1.00 kg was ground in a Teema mill to about -200 mesh size for chemical analysis, X-ray diffraction and leaching studies. Different mesh size samples from -30# to -150# were prepared after sieving.

Leaching Experiments. Laboratory scale experiments were carried out in a Bomb digester for pressure leaching and a Pyrex beaker of 250 ml capacity for agitation leaching. Bomb comprises a 50 ml stainless steel pressure vessel with a screw lid and fitted with a Teflon liner. When heated to 150-180°C it could withstand pressure of 80-90 atmosphere. Ore of different mesh sizes e.g. -30#, -50#, -100#, -150#, and -200# was used for leaching purposes.

The experiments were conducted by taking 1 to 5 g sample and leaching with H₂SO₄ under pressure and at atmospheric pressure by heating upto 100°C at different parameters such as acidity, use of HNO₃ as oxidizing agent, pressure, temperature, liquid: solid ratio, mesh size and time period etc. The samples were analyzed for copper, iron and free sulphuric acid by using standard analytical methods. All the leaching tests were carried out at approximately 100°C.

Results and Discussion

Ore samples of 200 mesh size were selected to study the leachability of the ore using 0.375 M, 0.75 M, 1.87 M, 3.75 M sulphuric acid and at a tentatively selected liquid: solid ratio of 2.5: 1 for a period of 90 min. at 100°C and 0.5 M HNO₃ was added as an oxidant, in a bomb digester. The results (Fig. 1) indicate that by increasing the acid concen-

Table 1
Effect of acid concentration

Wt. of ore	=	1 g				
Liquid/solid ratio	=	2.5/1				
Ore size	=	Minus 200 mesh				
Leaching time	=	90 min.				
Oxidizing agent (HNO ₃)	=	0.45 molar				
Temp.	=	100°C				
Pressure	=	>/70 atm.				
			Leaching solution			
Initial H ₂ SO ₄ + HNO ₃ Conc.			Cu ext. Fe ext. Final			H ₂ SO ₄ + HNO ₃ H ₂ SO ₄ : consumed g/1 conc. : Cu
	%	g/1	%	g/1	+HNO ₃	
65.20	40.89	1.76	45.00	5.890	35.00	17.60
102.00	65	3.28	51.28	6.72	45.00	17.37
212.40	76	3.88	76.00	10.08	145.33	17.28
396.40	83	4.20	94	12.32	320.00	18.19

tration, the extraction of copper increased. For 0.375 M H_2SO_4 the copper extraction was 41% while for 3.75 M H_2SO_4 (368 gm^{-1}) the copper extraction reached to 83% of the total copper. It was possible to get 100% leaching by increasing the acid concentration but that was un economical. By using the 0.75 M (102 gm^{-1}) H_2SO_4 copper extraction reached to 65%. By increasing the acid concentration to nearly twice the copper extraction increased by only 10%. It was observed that after 0.75 M the rate of leaching slowed down (Table 1).

Effect of Time. Ore was leached with 1.87 M H_2SO_4 for different time periods, 15 min :20 min, 60 min and 180 min as shown in Fig.2. Keeping all other conditions constant, the

Table 2
Effect of time

Wt. of ore	=	1 g		
Liquid/solid ratio	=	2.5 / 1		
Ore size	=	Minus 200 mesh		
H_2SO_4 conc	=	1.78 molar		
Oxidizing agent (HNO_3)	=	0.45 molar		
Temp.	=	100°C		
Pressure	=	>/70 atm.		
Leaching solution				
Time	Cu extd.		Fe extd.	
min	%	g/l	%	g/l
15	57.72	2.932	68.96	8.96
30	67.32	3.42	76.52	10.08
60	69.68	3.54	76.52	10.08
90	76.00	3.908	76.52	10.08
180	8.141	4.152	76.52	10.08

Table 3
Effect of oxidizing agent (HNO_3)

Wt. of ore	=	1 g		
Liquid/solid ratio	=	2.5/1		
Ore size	=	Minus 200 mesh		
Leaching time	=	30 min.		
H_2SO_4	=	1.87 M		
Temp.	=	100°C		
Pressure	=	>/70 atm.		
Leaching Solution				
HNO_3	Cu extd.		Fe extd.	
Molar (M)	%	g/l	%	g/l
0.135	52	2.64	8.96	68.37
0.27	61	3.1	8.96	68.37
0.45	67.32	3.42	10.08	76.52
1 M	79.00	4.013	10.08	76.52
Nil	41.00	2.04	8.96	68.37

maximum amounts of copper extracted were 81% in 180 min. and minimum 58% in 15 min and 67.32% in 30 min: 89.69% in 60 min. thus the optimum copper recovered was in 30 min. of time period (Table 2).

Effect of Oxidizing Agent. Ore was leached in presence of different concentrations of HNO_3 as 1 M, 0.5 M, 0.27 M and 0.135 M as oxidizing agent, while the other conditions remained the same 79% of copper could be extracted in presence of 1 M HNO_3 while only 67.20% could be extracted with 0.5 M HNO_3 . The optimum extraction of copper was obtained at 0.5 M concentration of HNO_3 as oxidizing agent shown in Fig. 1 (Table 3).

Table 4
Effect of liquid/solid ratio

Wt. of ore	=	1 g		
Liquid/solid ratio	=	2.5/1		
Ore size	=	Minus 200 mesh		
Leaching time	=	30 min.		
H_2SO_4	=	1.87 M		
Temp.	=	100°C		
Pressure	=	>/70 atm.		
Oxidizing agent	=	0.45 molar		
Leaching solution analysis				
Liquid/solid	Cu extd.		Fe extd.	
ratio	%	g/l	%	g/l
1/1	54.85	2.784	0.7956	17
1.5/1	58.71	2.982	1.5912	34
2.5/1	63.83	3.242	3.229	69
3.5/1	62.90	3.195	3.229	69

Table 5
Effect of particle size

Wt. of ore	=	1 g		
Liquid/solid ratio	=	2.5/1		
Leaching time	=	30 min.		
H_2SO_4 conc.	=	1.87 M		
Temp.	=	100°C		
Pressure	=	>/70 atm.		
Oxidizing agent	=	0.45 molar		
Leaching solution analysis				
Particle size	Cu extd.		Fe extd.	
	%	g/l	%	g/l
-30	36.53	1.876	59.626	10.00
-50	37.80	1.92	59.62	10.00
-100	53.26	2.704	77.00	14.4
-150	67.71	3.44	77.00	14.4
-200	67.40	3.42	77.00	14.4

Effect of Liquid: Solid Ratio. A series of experiments were performed using -200# ore with 1.87 M H₂SO₄ to determine the effect of liquid : solid ratio which was varied from 1:1 to 3.5:1. The leaching was done for 30 min. and the copper was determined at the end of each run. The results given in Fig 4. indicate that extraction was 54.84 % at 1:1, 58.71% at 1.5:1, 63.83 percent at 2.5:1 and 62.90 % at 3.5:1. The results indicate that increasing the liq.: solid ratio above 1:1 causes only a slight improvement in the copper extraction. It was found that a liq:solid ratio of 2.5:1 offered a reasonable operating condition for -200 mesh ore (Table 4).

Effect of Particle Size. A number of tests were conducted to find out a particle size range which could give maximum

Table 6

Results of chemical analysis of Chitral copper ore

SiO ₂	76.64	%
CaO	7.4	%
Loss on ignition	6.79	%
Fe ₂ O ₃	4.68	%
Al ₂ O ₃	0.28	%
Cu	1.27	%
Pb	2907	ppm
Sb	1284	ppm
As	750	ppm
Mn	602	ppm
Zn	84.3	ppm
Sn	6.6	ppm
Ag	14.64	ppm
Au	0.45	ppm

Table 7

Results of x-ray diffraction study of the copper ore.

'd'	Intensities	Minerals
4.97	4.40	Malachite, Azurite, Galena
3.69	2.40	Malachite, Azurite
2.45	5.30	Malachite, Azurite
4.7073	1.49	Chlorite
4.448	4.94	Illite, Muscovite
2.2427	27.11	Qtz.
3.3347	100	Qtz., Muscovite
2.8944	10.43	Qtz. Dolomite
3.0179	7.25	Tetrahedrite, Chalcopryrite, Cuprite
1.8162	10.07	Tetrahedrite, Qtz.
2.1242	5.90	Cuprite
2.97	4.52	Galena
1.67	4.32	Hematite

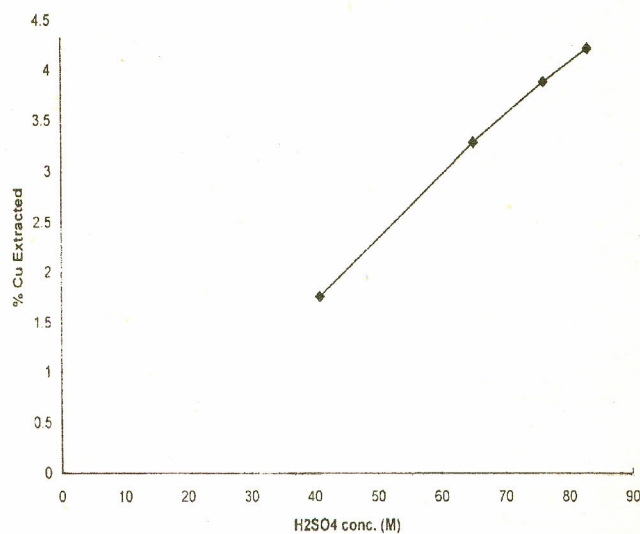


Fig 1. Effect of acid concentration.

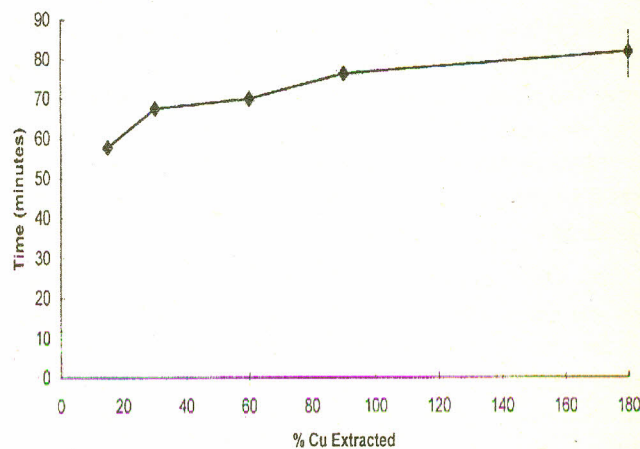


Fig 2. Effect of time.

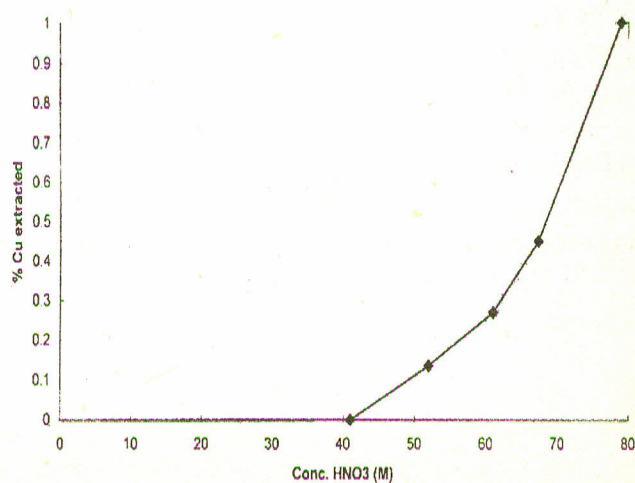


Fig 3. Effect of HNO₃ concentration.

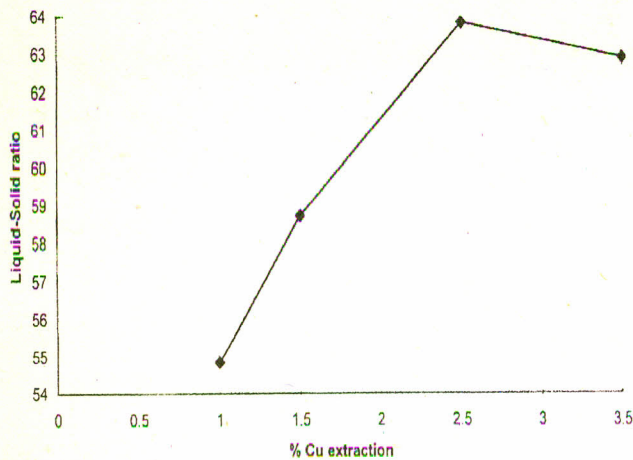


Fig 4. Effect of liquid-solid ratio.

copper extraction. The ore was pulverized to obtain samples passing through -30, -50, -100 and -150 mesh size. Leaching tests were performed at a liq:solid ratio of 2.5:1 using 1.87 M H_2SO_4 and 0.5 M H_2SO_4 and 0.5 M HNO_3 for a time period of 30 min at 100°C temp and under >70 atm. pressure. The effect of particle size on the leachability of copper (Fig. No 5) shows that ore sample of -150 mesh size gives optimum extraction. Further decrease in the size indicates that the copper extraction becomes constant or is decreased (Table 5).

X-Ray Diffraction Study. The X-ray diffractogram of the ore was taken after grinding to - 200 mesh. The X-ray diffraction results showed a number of lines due to a number of mineral phases in the composite ore; the 'd' values and intensities obtained by XRD are given in table No.7. The mineral components identified are quartz, Muscovite, Tetrahedrite, Cuprite, Malachite, Azurite, Chalcopyrite, Galena, Hematite and Chlorite.

Conclusion

The Chitral complex copper ores were found to contain an average of 1.27% copper and 4.68% Fe. The other elements such as Pb, Sb, As, Mn, Zn, Ag and Au were also found but in minor quantities.

The maximum extraction of copper from complex copper ore was found to be 87.00% with 1.87 M H_2SO_4 in presence of 0.5 M HNO_3 at 100°C, at 70 atm pressure after 30 min-

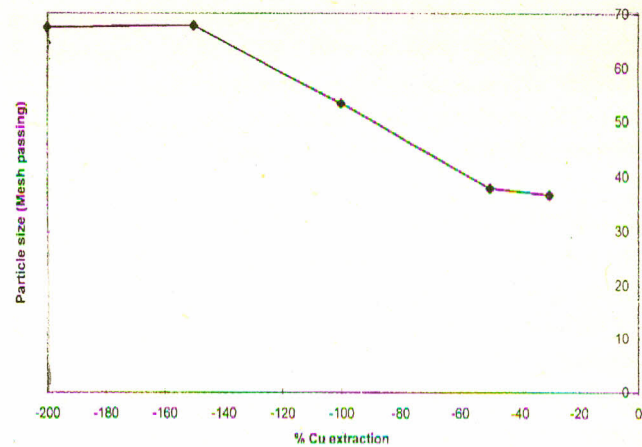


Fig 5. Effect of particle size.

utes with liquid:solid ratio of 2.5:1 and particle size of -150 mesh.

References

- Khan I H, Qazi M A, Sheikh N A, Ahmad S, Mahmood F 1988 R&D work on Saindak copper ore by PCSIR Labs. Lahore.
- Khan I H, Qazi M A 1981 Evaluation and beneficiation studies on Chitral copper ores. PCSIR Labs. Complex Lahore.
- Khan I H, Mahmood F, Naeem M 1991 Geochemical, mineralogical and beneficiation studies on Chitral copper ore. MMRC, PCSIR Labs. Complex Lahore.
- Directory of economic mineral 1959 *Geological Survey of Pakistan*.
- Vezwa 1970 Acid pressure leaching penta landite-chalcopyrite, pyrholite conc. *Tech. Bull. TB 129 20* PPS Ottawa Ont. Canada.
- Dugdale, Raymond H 1970 *Copper and iron extraction from chalcopyrite*. Arcond Co. Ger. U.S. Appl. 22 Jan. 170, 28 pp.
- Erbil, Ozel 1983 Recovery of copper from chalcopyrite concentrate using ferric chloride leaching. *Dogaseri B,7* (1) 45-9 (Turkish).
- Olive R A C, Boyd 1956 *Quantitative chemical analysis, 11th ed* 342-4, 349-51 Edinburgh, TWEEDALE Count London 39-A, Welbeck St. Wol.