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GEOCHEMICAL AND FLOTATION STUDIES OF COPPER ORE OF NORTH WAZIRSTAN AGENCY

M Riaz[a], V Hussain[b]*, K Faridullah[a], Mumtaz[a], N Jan[a], K Khan[a]

[a)] *PCSIR Laboratories, Jamrud Road, Peshawar, Pakistan*

[b)] *Department of Geology, University of Karachi, Karachi 75270, Pakistan*

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Important copper deposits of North Wazirstan Agency are confined to Shinkai and Degan Paikhel areas Miran Shah Town. The copper mineralization in these areas is of native and sulphide types as veins, veinlets, stringers and rims around fragments and associated with cupriferous breecia. The cupriferous massive sulphides occur in basalts belonging to obducted ophiollite complex. An average copper contents of 17 ore samples is 0.45%. The flotation results show that maximum liberation of chalcopyrite with gangue minerals occurs at - 63 (240 mesh) size. The complex nature of valuable minerals with gangue does not hinder the separation of copper from the gangue materials. Results show that the copper contents of the ore were enhanced from 0.5% to 24.0% in the concentrate. For ensuring better results about grade and recoveries, further studies on second and third stage flotation are needed.

Key words: Copper mineralization, Sulphide, Ophiolite complex, Froth flotation.

Introduction

The Miran Shah is the head quarter of North Wazirstan in the North West Frontier Province. Important copper deposits have been found at Shinkai near Boya located (longitude 69°, 55° E and altitude 32°, 57° N) at a distance of 19 km from Miran Shah and in the adjoining areas of Deggan and Khaddar Khel (Badshah 1983). A number of chromite and manganese deposits have also been reported from the North Wazirstan Agency. Important occurrences of copper are confined to Shinkai and Deggan Paikhel areas near Miran Shah Town. The mineralization in these areas is characterized as copper native and its sulphides are generally associated with breecia and occurs as veins, veinlets, stringers and rims around fragments (Khan 1998). Present work deals with geochemical and flotation studies of Shinaki copper ore and its associated rocks to assess the economic potential of these deposits.

Geological setting. The Wazirstan plateau overlooks the vast Bannu - D.I. Khan predominant plane in the east, which is part of the desert fringe zones of Indus basin. The eastern abutment of Wazirstan plateau is a thousand feet thick deltaic mass where thin interbedded Cretaceous limestone, shale,siltstone, Eocene limestone and shale are encountered . These rocks are intensely folded and thrust eastward on younger Muree Siwalik - Molsse Group of rocks. The western part of Wazirstan constitutes a complex igneous belt characteristic of tectonic activity at plate scale. The belt represents collision suture zone between Indo - Pakistan plate to the east and Kabul plate to the west. The intense folding of Cretaceous rock at the eastern contact of the igneous complex is indicative of allochthonous emplacement of ophiolites (Badshah 1983).

The igneous belts extend from north east to south west and consists of ultramafic masses, mafic to acidic injections and ultrabasic to basic volcanics. The ultramafic rocks consist of harzbergite, pyoxenite, peridotite and dunite which are generally altered and serpentinized. The intrusives, subordinate on occurrence comprise of diorite, quartz diorite, micro - quartz diorite, granodiobite and gabbro. Volcaic rocks include fine grained porphyritic pillow basalts and andesites with subordinate breecia and minor dacites, tuffs and agglomerates (Badshah 1983).

The ophiolites are generally dismembered and have a complex geological configuration (Afridi *et al*, 1991). On a regional scale, however, the ophiolites can be roughly identified into a basal,part of ultrabasic, an intermediate zone of sheeted dykes or sills and a zone of basaltic and andestie pillow lavas. Presence of jasperites is considered to represent the pelagic sediments hosting manganese oxide deposits. Chromite deposits occur in serpentinized dunites, manganese oxide deposits occur in sediments and cupriferous massive sulphides are hosted in basalts which occur in obducted ophiolitie complex and ophiolitic melange along the collisional suture zone in the Indian and Eurasuian plates.

* Author for correspondence

Table 1
Chemical evaluation of copper ore (15 samples) of North Wazirstan Agency for major elements % composition of major elements

SiO_2	$[Fe_2O_3]$*	Al_2O_3	CaO	MgO	L.O.I	Total
52.52	14.50	06.20	08.08	10.20	08.60	100.10
60.00	10.30	04.20	08.50	10.25	06.80	100.05
53.20	20.50	07.20	02.50	07.50	08.90	99.80
48.36	25.20	08.70	02.60	08.00	07.10	99.90
60.24	15.30	08.40	01.68	08.00	06.40	100.02
54.40	20.30	09.20	01.68	07.80	06.23	99.61
60.20	17.00	06.20	04.20	06.40	05.80	99.80
58.24	18.40	09.80	08.60	02.40	02.40	99.84
41.04	06.30	07.90	01.12	29.30	13.90	99.56
0.62	00.80	06.90	50.40	00.00	41.05	99.77
04.70	14.30	06.20	23.00	12.40	13.50	100.10
50.98	14.00	08.00	11.20	05.60	10.10	93.88
64.54	14.40	06.30	01.65	08.00	05.00	99.58
54.60	21.10	10.00	01.68	08.40	04.80	99.58
62.40	15.20	09.80	03.36	02.80	06.25	99.58

* Fe_2O_3 as total iron
L.O.I Loss on Ignition at 100˚C

Table 2
Determination of copper content in the ore (28 samples) North Wazirstan Agency

% Composition of elements							
Cu	Co	Mn	Ni	Pb	Zn	Ag	Au
0.150	0.010	0.100	0.050	0.0005	0.060	0.050	<0.001
0.180	0.010	0.150	0.030	0.0000	0.140	0.003	<0.001
0.070	0.000	0.050	0.020	0.0004	0.180	0.002	<0.001
0.160	0.010	0.090	0.010	0.0003	0.020	0.003	<0.001
0.200	0.010	0.180	0.010	0.0000	0.040	0.004	<0.001
0.000	0.010	0.000	0.020	0.0002	0.020	0.001	<0.001
0.000	0.010	0.000	0.010	0.0000	0.020	0.002	<0.001
0.100	0.010	0.000	0.010	0.0000	0.020	0.005	<0.001
0.000	0.010	0.000	0.010	0.0000	0.020	0.005	<0.001
0.100	0.020	0.000	0.270	0.0005	0.020	0.000	<0.001
0.320	0.000	0.130	0.000	0.0001	0.010	0.002	<0.001
0.500	0.010	0.250	0.010	0.0005	0.030	0.000	<0.001
0.060	0.000	0.000	0.000	0.0000	0.020	0.000	<0.001
0.080	0.010	0.000	0.030	0.0003	0.010	0.000	<0.001
0.000	0.010	0.000	0.000	0.0005	0.070	0.001	<0.001

Experimental

Standard procedures (Furman 1963) were applied for chemical evaluation of the representative 15 samples of crude copper ore from North Wazirstan Agency for their major elements. The data obtained (Table I) indicate that the contents of silica (SiO_2) vary from 0.62 to 64.54%, Fe_2O_3 (total) 0.80 to 25.20%, Al_2O_3 4.20 to 9.80%, CaO 1.12 to 23.00% and MgO 0.00 to 29.30%, whereas loss on ignition at 100˚C is in the range of 2.40 to 13.90%. Flame Atomic Absorption Spectrophotometer (Model Z - 8000, Hitachi, Japan) detection limit 0.004 ppm, sensitivity 0.03 ppm and working standards 0.5 ppm to 4.0 ppm was used for the determination of copper in copper ore (Table 3). The copper contents of ore samples range from 0.12 to 0.98% and the average copper content is 0.50%. The minor elements such as Co, Mn, Ni, Pb, Zn, Ag, and Au were also determined using Atomic Absorption Spectrophotometric methods (Table 2).

The X - ray diffraction (XRD) analysis shows that the ore samples contain chalcopyrite, pyrite, and magnetite as major valuable metallic minerals, and brochanite, jasperite, chamosite, namite and quartz as gangue minerals.

The particle size determination of major valuable metallic minerals chalcopyrite, pyrite and magnetite are given in (Table 4). Other minor metallic minerals were found with very low contents. Liberation studies were conducted to obtain liberated chalcopyrite with gangue minerals. The maximum liberation of chalcopyrite with gangue minerals occurs at - 63 microns (240 mesh) size. After undertaking chemical analysis of 28 samples for their copper content, all these samples were combined (28 kg) and crushed in jaw crusher to obtain a suitable feed for grinding. The grinding and powdering was carried out using a laboratory rod mill (Model WEDAG Westfalia, Bochum) and electric sieve shaker (Endecott, Model 2 MK II, London). Regrinding method was carried out to achieve the desired mesh of liberation of chalcopyrite in the ground product.

A series of flotation tests were carried out to determine the effect of collector, potassium propyl xanthate (kpx) concentration and activator sodium sulphide (Table 5). The commercially available kpx was recrystallized twice from acetone by addition of petroleum ether and dried under vacuum to avoid any atmospheric oxidation. Analytical reagent grade sodium sulphide was used to study the effect of activator in flotation. Solutions were made with distilled water (Khan 1998). All the flotation tests were carried out by using laboratory flotation machine (Denver, England) in a litre cell at 25% (weight / volume) pulp density. The impeller speed was kept constant at 1200 rmp throughout the flotation tests. 25 g powdered (240 mesh) copper ore was conditioned prior to its flotation with 60 g / ton sodium sulphide activator for five minutes and subsequently with collector for five minutes. The effect of various concentrations of collector are given in Table 5. The desired value of pH (9 - 10) was adjusted with lime water and was kept constant throughout the flotation tests, 2 - 3 drops of frother (cynamide, aero froth 65) was used for flotation. Time

Table 3
Determination of copper content in the ore (28 samples) of North Wazirstan Agency

S. No	Sample No.	Cu (%)	Rock / ore
1	P3 - 1	0.03	Associated rock
2	P3 - 2	0.05	Associated rock
3	P3 - 3	0.04	Associated rock
4	P3 - 4	0.02	Associated rock
5	P3 - A1	0.27	Ore
6	P3 - A2	0.33	Ore
7	P3 - A3	0.07	Associated rock
8	P3 - A4	0.09	Associated rock
9	P3 - B1	0.94	Ore
10	P3 - B2	0.41	Ore
11	P3 - B3	0.05	Associated rock
12	P3 - B4	0.64	Ore
13	P3 - C1	0.59	Ore
14	P3 - C2	0.30	Ore
15	P3 - C3	0.40	Ore
16	P3 - C4	0.49	Ore
17	P3 - D1	0.22	Ore
18	P3 - D2	0.21	Ore
19	P3 - D3	0.19	Ore
20	P3 - D4	0.17	Ore
21	P3 - E1	0.98	Ore
22	P3 - E2	0.42	Ore
23	P3 - E3	0.05	Associated rock
24	P3 - E4	0.12	Ore
25	P3 - F1	0.25	Ore
26	P3 - F2	0.08	Associated rock
27	P3 - F3	0.38	Ore
28	P3 - F4	0.10	Associated rock

batch method was used during each flotation test and the products were obtained after 5 minutes each . The flotation time was normally noted to be less than 15 min. The copper concentrate, middling and tailing obtained were dried and assayed for copper contents by atomic absorption spectrophototmetric technique (Rao *et al* 1976; Xiang and Yen 1998).

Results and Discussion

The copper content in the North Wazirstan Agency copper ore ranges from 0.12 to 0.98% and the average copper content of 28 samples is 0.48%. Other minor elements are not present in significant quantity. The major valuable metallic minerals are chalcopyrite, pyrite and magnetite, other minerals such as galena, sphalerite etc. and found with low contents. Therefore, size determination was made only on chalcopyrite, pyrite and

Table 4
Results of particle size determination of principal minerals

Average size	Chalcopyrite %		Pyrite %		Magnetite %	
µm	Ind.	Cum	Ind.	Cum	Ind.	Cum
1.286	2.330	-	-	-	4.26	-
1.000	5.620	7.95	7.88		7.95	12.21
0.503	13.230	21.18	17.73	25.61	8.49	20.70
0.253	18.950	40.13	31.49	57.10	11.89	32.59
0.128	17.200	57.33	20.96	78.06	20.72	53.31
0.060	24.700	82.03	16.01	94.07	27.23	80.54
0.020	14.490	96.52	5.18	99.25	14.89	95.43
0.005	3.480	100.00	0.75	100.00	4.57	10.00

Table 5
Effect of potassium propyl xanthate concentration on the flotation studies of copper ore (containing 0.48% Cu)

Collector dosage g / ton	Flotation fraction	%Cu	% Recovery	Cum. % recovery	Cum. % grade
	Conc. 1	14.00	52.00	42.00	14.00
50	Conc. 2	9.34	23.56	65.56	10.50
	Middling	6.00	7.44	73.00	9.70
	Tailing	0.56	17.00	100.00	1.70
	Conc. 1	19.00	54.36	36.36	19.00
100	Conc. 2	9.10	22.25	58.61	12.02
	Middling	5.00	10.24	78.85	8.35
	Tailing	0.43	13.15	100.00	1.47
	Conc. 1	20.00	56.25	34.24	20.00
150	Conc. 2	16.00	21.09	85.33	17.00
	Middling	5.52	11.79	87.12	10.00
	Tailing	0.30	10.88	100.00	1.93
	Conc. 1	21.00	47.23	47.23	21.00
200	Conc. 2	18.00	25.88	73.11	15.25
	Middling	6.10	18.08	91.19	11.00
	Tailing	0.20	6.31	100.00	2.00
	Conc. 1	22.92	58.03	58.03	22.91
250	Conc. 2	9.40	11.26	69.29	15.72
	Middling	6.20	8.72	78.01	12.82
	Tailing	0.40	21.99	100.00	1.71
	Conc. 1	24.00	51.65	61.65	24.00
300	Conc. 2	15.00	39.06	90.71	17.87
	Middling	3.70	4.00	94.71	14.21
	Tailing	0.11	5.29	100.00	1.82
	Conc. 1	23.00	66.22	66.22	23.00
400	Conc. 2	1.48	21.19	86.45	1.35
	Middling	3.30	4.98	91.30	12.89
	Tailing	0.24	8.61	100.00	2.31
	Conc. 1	20.15	45.20	45.20	20.15
600	Conc. 2	12.23	18.09	63.29	15.94
	Middling	4.85	5.82	69.11	12.61
	Tailing	1.19	30.89	100.00	3.18

magnetite. Particle size of chalcopyrite is found in a rather wide range with 0.060 mm fraction accounting for 82.03% - 0.06 mm fraction about 18%. If one stage grinding was used to liberate all chalcopyrite particles, a considerable part of chalcopyrite and other minerals would be overground, which would not only need more equipment and energy consumption but also cause difficulties in its flotation. Therefore, a stage grinding with coarser one to discard tailing followed by regrinding of rough concentrate has been recommended.

Sulphide minerals are among the simplest to float but commercially very important. There were the earliest group of minerals treated in this way and have been the subject of numerous researchers (Leija 1982; Critechley and Riaz 1991; Riaz *et al* 2001). The North Wazirstan Agency copper deposits are porphyry copper sulphide ore, containing predominantly chalcopyrite and pyrite. Therefore, a lime circuit was used in these studies to keep the pH in the range of 9 - 10. Use of lime was preferred as it acts as depressant for iron sulphide gangue minerals.

A series of flotation tests were conducted with different collector dosages, keeping all other flotation parameters constant. The increase of collector concentration upto 300 g / ton of the ore increases the copper content in concentrate with improved percent recovery and grade. Best flotation results were obtained with 300 g / ton of collector concentration with enhanced copper content from 0.5% to about 24%. The increased concentration of collector over this value affects the chalcopyrite flotation adversely. The results obtained by froth flotation technique indicate that it is possible to obtain good separation of chalcopyrite from the gangue materials. Despite the complex nature of the ore, the upgradation is quite satisfactory. For obtaining better grade and recoveries, further studies for two stage flotation are recommended.

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