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INVESTIGATION INTO THE SULPHIDATION PROCESS OF MINERAL AND ANTHROPOGENIC COPPER RAW MATERIALS WITH ELEMENTAL SULFUR

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ABSTRACT

The object of this research is the sulphidation of both the mine tailings from the Zhezkazgan concentrating mill (ZhCM) and the mixed copper ore deposits of Bozschakol. The composition of ZhCM tailings and Bozschakol ore deposits were analysized by X-ray Diffraction. The sulphidation process was carried out from 300°C to 800°C to investigate the influence of heat on the sulphidation process. The results showed that 300°C – 400°C was the best temperature for sulphidation. In addition, the effect of changing the mass percentage of sulphur during sulphidation process was discussed. Reusing mine tailings to extract valuable metals and decrease environmental hazards is also investigated in this article.

Key words: Flotation, Mine tailings, Sulphidation, Chalcopyrite, X-ray Diffraction.

INTRODUCTION

The copper industry is one of the key industries of Kazakhstan. Kazakhstan has significant reserves of copper ores, one-tenth of the world reserves. The basic raw materials for the production of copper are now in short supply. Alternative raw materials could be sub-standard copper ores, unmined reserves and tailings. A large proportion of these non-traditional sources of raw materials for copper production consist of a high percentage of impure and oxidized components.

The problem is refining the process and solving technological problems, to allow profitable mining of low-grade ores[1]. A more efficient method is needed for the processing

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of complex ores and mine tailings of copper ores. Studies to recycle oxidized materials provide both hydrometallurgical and pyrometallurgical processing. The most promising methods transform the oxidized forms of non-ferrous metals (oxides, carbonates, sulfates, molybdates, etc.) to sulphidated ores. About 85% of copper ores are enriched by flotation, this method is still under development in Kazakhstan. The purpose of this article is to study the applicability of flotation to sulphide rich and oxidized copper sources both natural and man-made. The object of the research is the mine tailings of the Zhezkazgan concentrating mill (ZhCM) and the mixed copper ore deposits of Bozschakol. The technology of copper minerals' sulphidation is studied in the work of researchers Ertseva et al.[2-4] and Padilla et al.[5] But these studies look at sulphidation of the copper sulphide mineral - chalcopyrite at 350-520^{0}C:

$$5CuFeS_2 + 2S \longrightarrow Cu_5FeS_4 + 4FeS_2 \quad \ldots(1)$$

$$5CuFeS_2 + 4S \longrightarrow Cu_5FeS_6 + 4FeS_2 \quad \ldots(2)$$

$$5.5CuFeS_2 + 4.5S \longrightarrow Cu_{5.5}FeS_{6.5} + 4.5FeS_2 \quad \ldots(3)$$

$$CuFeS_2 + S \longrightarrow CuS + FeS_2 \quad \ldots(4)$$

The purpose of chalcopyrite sulphidation is to improve the efficiency of the leaching process by pirrita copper sulfide in the system $NaCl$-H_2SO_4-O_2.

In our case, it was necessary to sulphidate oxidized copper minerals together with rare metals using a flotation method and collecting both the rare metal sulphides and copper sulphides. Converting the metal ore's surfaces to sulphides makes them hydrophobic and improves their enrichment by flotation. Sulphidation of chalcopyrite in ores – helps with the separation of copper and iron sulfides, and increases the selective extraction of copper from raw materials.

Characteristic of raw materials

Copper ore of Boschekul deposit

Boschekul - The largest copper deposit in Kazakhstan contains copper, molybdenum and porphyry ores. The ores of copper are generally in the form of oxidised compounds, with a sulfide content lower than the oxide content. Quantitative analysis determined the precise masses of the oxides and the sulfides of copper (Table 1).

The sample analyzed below had an unusually high copper content of 0.76% compared to the average of 0.36%, 64% of the copper in the ore analyzed was in the form of oxides.

Table 1 - Phase analysis of copper in ore of Bozschakol deposits

Cu oxidized minerals	Cu secondary sulfides	Cu primary sulfides	Σ Cu
0.486	0.21	0.056	0.75

X-ray analysis established the presence of the following minerals: quartz, clinochlore, muscovite, albite, pyrite and chalcopyrite (Fig. 1).

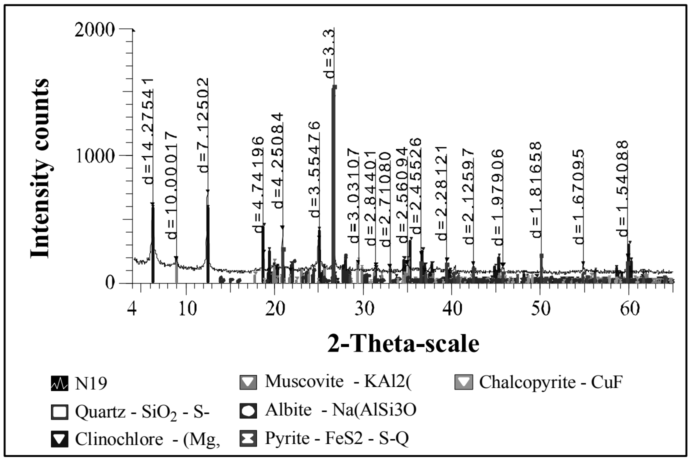

Fig. 1: X-ray analysis (X-ray fiffraction) of Bozschakol ore

Copper sulfide in the ore is in the form of chalcopyrite and semi-quantitative analysis showed it to be 3.8% by mass. The sample was also found to have a high alumina content.

The results are semi-quantitative X-ray analysis of crystalline phases.

The name of the phase	Formula	Concentration (%)
Quartz	SiO_2	52.9
Clinochlore	$(Mg,Fe)_5Al(Si_3Al)O_{10}(OH)_8$	25.2
Muscovite	$KAl_2(AlSi_3O_{10})(OH)_2$	7.3
Albite	$Na(AlSi_3O_8)$	5.8
Pyrite	FeS_2	5.1
Chalcopyrite	$CuFeS_2$	3.8

Mine tailings ZhCM

ZhCM has significant copper and rhenium content in its tailings. ZhCMs mine tailings are difficult to enrich because of a complex chemical and mineral composition and the tailings are not amenable to conventional processing. The mineral composition of the tailings is predominantly calcite, quartz and bornite, and partially extracted ores (chalcopyrite and chalcocite). The chemical composition of the waste contained in these by mass percentage is: total sulphides = 2.5; S = 0.9; Fe = 1.9; Cu = 0.15; Pb = 0.04; Zn = 0.03; Re = 0.61 x 10^{-4}; Mo = 0.0001.

A sample from ZhCM's mine tailings was analyzed and found to have a copper content of 0.41% above the average of 0.15%. The analyzed tailings had 70% of the copper in the form of copper sulphides (Table 2) and 30% as copper oxides.

Table 2: Phase analysis of copper in the mine tailings of ZhCM

Cu, simple oxides	Cu, complex oxides with other metals	Cu secondary sulfides	Cu primary sulfides	Σ Cu	Cu_{total}
0.035	0.034	0.19	0.15	0.41	0.41

X-ray analysis established the presence of the following minerals: quartz, clinochlore, muscovite, albite and calcite (Fig. 2). ZhCM's mine refuse is also high in alumina content.

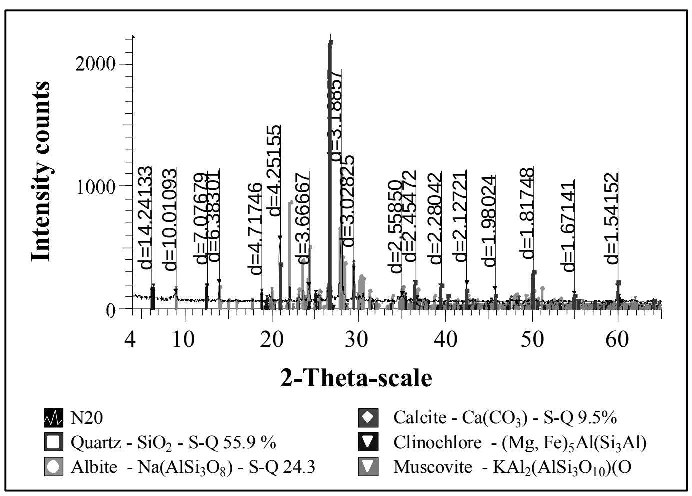

Fig. 2: XRD of mine refuse of ZhCM

Method of sulfidation

Sulphidation was carried out in a crucible furnace with selit heaters. The temperature was controlled by chromel-alumel thermocouples. A layer of sulfur was first placed into a crucible and then the powdered ore/tailings were placed on top. This allowed an efficient sulphidation because of the interaction of the solid ore/tailings with a gas. Sulfur in the form of a sublimate percolates through the ore layer thus sulphidating the oxidized ore. 85% of the ore had a particulate diameter of 0.074 mm. Grinding of the raw materials to this size produced efficient flotation. Sulphidation was carried out with 5-15% sulphur at temperatures between 300-800^{0}C.

Discussion of the experiments results

It is possible to sulfidate up to 75% of the copper in the ore at a temperature of 300^{0}C as research with feedstocks from Boschekul with elemental sulfur shows in Table 3. Sulfur is consumed at 10-15% by weight of the ore. Further increases in the temperature of sulfidation to 400^{0}C and above lead to the loss of sulfur in the gas phase and it failed to react with the components of the ore. At 300^{0}C the content of copper sulphide reached 72-75% compared to 35.37% at 400^{0}C. Increasing the mass percentage of sulphur in the reactants from 5 to 15% increased the sulphide content of copper sulfide. Further increases in the mass of sulphur in the reactants does not lead to a significant improvement in sulfidation, so the results of these experiments are not given in the table.

Increasing the temperature to 600-800^{0}C increased the copper oxide content, at this temperature the copper sulfide content was lower than in the original ore.

Chalcopyrite decomposes to simple sulphides of copper and iron. In the temperature range 565-590^{0}C β- tetragonal chalcopyrite stucturally transforms to cubic form. At 565-590^{0}C chalcopyrite thermally decomposes to form intermediates of bornite and pyrrhotite, but at 700^{0}C bornite further decomposes into simple sulfides. The decomposition of chalcopyrite at temperatures of 600-700^{0}C prevents air penetrating the sulfide particles, so only sulfide decomposition products are formed. After most of the labile sulfur from the decomposition of chalcopyrite is used up, then it becomes possible for atmospheric oxygen to access the surface of ore and oxides form.

The sulfidation of ZhCM mine tailings follows a similar pattern to that of Boschekul. The optimum temperature for sulfidation of copper is in the 300-400^{0}C temperature range (Table 4). The percentage of copper sulfide produced was higher when Bozschakol tailings were used than when ZhCM tailings were used.

Table 3: Sulphidation results of Boschekul ore deposits with elemental sulfur

Temp. (^{0}C)	Consumption of sulfur (%)	Exit cinder (%)	Copper cinder (%)		Copper sulfide in ore (%)	Copper sulfide in cinder (%)
			Oxidized	Sulfide		
300	5	102.4	0.39	0.34	35.37	46.58
300	10	104.2	0.37	0.52	35.37	72.22
300	15	110.6	0.17	0.53	35.37	75.71
400	5	102	0.41	0.32	35.37	43.84
400	10	104.6	0.4	0.31	35.37	43.66
400	15	104.6	0.5	0.28	35.37	35.90
600	5	99.6	0.74	0.059	35.37	7.38
600	10	99.6	0.77	0.03	35.37	3.75
600	15	97.8	0.75	0.02	35.37	2.60
800	5	97.6	0.63	0.182	35.37	22.41
800	10	97	0.67	0.144	35.37	17.69
800	15	97	0.68	0.14	35.37	17.07

Table 4: Sulphidation results of ZhCM mine tailings with elemental sulfur

Temp. (^{0}C)	Consumption of sulfur (%)	Exit cinder (%)	Copper cinder (%)		Copper sulfide in mine refuse (%)	Copper sulfide in cinder (%)
			Oxidized	Sulfide		
300	5	100.4	0.06	0.35	83.13	85.37
300	10	100.8	0.05	0.36	83.13	87.80
300	15	109	0.021	0.37	83.13	94.63
400	5	100.2	0.06	0.35	83.13	85.37
400	10	100.6	0.05	0.36	83.13	87.80
400	15	100.6	0.026	0.37	83.13	93.43
600	5	100.4	0.34	0.023	83.13	6.34

Cont…

Temp. (^{0}C)	Consumption of sulfur (%)	Exit cinder (%)	Copper cinder (%)		Copper sulfide in mine refuse (%)	Copper sulfide in cinder (%)
			Oxidized	Sulfide		
600	10	100.4	0.323	0.027	83.13	7.71
600	15	101.2	0.32	0.028	83.13	8.05
800	5	99.4	0.32	0.042	83.13	11.60
800	10	99.4	0.311	0.049	83.13	13.61
800	15	99.6	0.33	0.05	83.13	13.16

At elevated temperatures, chalcopyrite decomposes. Chalcopyrite decomposition is greater in the ZhCM mine tailings than the Boschekul ores. Sulfidation of the tailings was easier than for the raw ore because the ZhCM mine tailings were already partially processed.

It was not possible to establish whether rare metals like molybdenum and rhenium were successfully sulphidated, because of their low content in the ore. But it was possible to determine in the subsequent flotation of copper sulfide.

CONCLUSION

Successful sulfidation of the copper oxides was shown experimentally in the Boschekul ores and mine tailings at 300-400^{0}C. The main factor influencing the degree of sulfidation was consumption of sulfur, over the range of 10-15% by weight of raw materials. Higher temperatures adversely affected the sulfidation process due to decomposition of chalcopyrite in the system, which increased the copper oxide content.

Optimal conditions of sulfidation were found and it enabled the production of copper at low temperatures and recycling of anthropogenic sulfur.

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