

**MECHANISM OF COPPER CONCENTRATE OXIDATION
IN FLUIDIZED BED REACTOR
AT TEMPERATURES BETWEEN 600-720°C**

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ABSTRACT

Based on the studies of the behaviour of disperse sulphide material in an industrial fluidized bed roasting of copper concentrate, a macromechanism of the process is proposed. Mechanism of copper concentrate oxidation in roasting processes in a fluidized bed reactor has been studied at temperatures between 600°C and 720°C using chemical, XRD and SEM analysis.

Key words: copper, roasting, oksidation, fluidized bed, mechanism

1. INTRODUCTION

In copper production, starting raw materials are sulphide ores and copper concentrates. One of the most significant processes in the treatment of starting raw material is roasting in fluidized layer, since its success affects the succeeding calcine roasting phase. Therefore, the knowledge of mechanisms and kinetics of roasting process of sulphide copper concentrate is of a crucial significance in autogenous processes of smelting of copper [1] and many researchers give their contribution to this topic. So, Bayer and Wiedermann [2] have shown that the oxidation of pure CuFeS₂ starts at 400°C, while addition of alkali salts decreases the starting temperature of oxidation process to 200 °C. Živkovic et al. [3] have investigated the oxidation of a mixture of CuFeS₂ and FeS₂ in non-isothermal conditions at different heating rates in temperature range up to 1000°C. Antic [4] studied kinetics of dissociation and oxidation in natural systems of copper and iron sulphides and iron. The aim of this paper has been to study mechanism of roasting of sulphide copper concentrate in the range from 600-720°C in fluidized bed reactor, in order to prevent sulphatised roasting occurring at temperatures lower than 600°C [5,6] and agglomeration roasting at high temperatures above 800°C.

2. EXPERIMENTAL

Sulphide copper concentrate from copper mine in Bor has been used for experimental investigation of oxidized roasting in fluidized bed reactor in Bor Smelter (Serbia and Montenegro). One fluo-solid reactor, type Dorr-Oliver has been installed there for partial roasting of copper concentrates, within the scope of so-called standard copper recovery procedure. Fluo-solid reactor has been used in our investigations. Partial roasting is performed in fluo-solid reactor with oxidation, i.e desulphurisation level of 40-55% at roasting temperatures of 620 – 650°C. For investigation, samples have been taken for charge, calcine and bed of fluo-solid reactor at the following operating conditions: constant process air flow of 24000 m³_n/h, temperatures 600, 670 and 720 °C and time of charge particle remaining in reaction layer 90 s. To provide required temperatures in reactor, and by its virtue, different level of oxidation for other fixed operating parameters, charging capacity has been changed from 48 to 38t/h. For air feeding, 260 nozzles are used, with 10 openings each, with

mean aperture size of 7,5mm. Roasting temperature regulation was done by adding water with spraying nozzles which are installed at reactor arch, where cooling water flow has been 2 m³/h. From total charge quantity 80-90% of calcine is discharged with process gases which leave the reactor through the opening at the arch and are fed to deducting units. The remaining 10-20% of total charge leaves the reactor as overflow by a special device, so-called "fluoseal".

Chemical composition of dry concentrate has been (in %): Cu-19,64; Fe-29,02; S-33,23; Fe₃O₄-0,15; SiO₂-10,40; CaO-1,55 and remaining minerals 6. Mineralogical composition of this concentrate has been (in %): CuFeS₂-56,71; FeS₂-25,19; Fe₃O₄-0,15; SiO₂-10,40; CaCO₃-1,53 and remaining minerals 6. In the process of fluidized bed roasting wet concentrate is used of the following chemical composition (in %): Cu- 17.68, Fe-26.12, S-29.91, Fe₃O₄-0.13, CaO- 1.40, H₂O-10 and remaining 5.4, where mineralogical composition of this wet concentrate has been (in %): CuFeS₂-51,04; FeS₂-22,67; Fe₃O₄-0,13; SiO₂-9,36; CaO-1,40; H₂O-10 and remaining 5,4.

Sample analysis after sulphide concentrate roasting, with the aim to determine chemical and phase composition has been done by wet chemical method, X-ray diffraction analysis and SEM analysis.

3. RESULTS AND DISCUSSION

Chemical analysis of samples of sulphide copper concentrate after roasting in process air flow of 24000 m³/h at temperatures 600,670 and 720°C is presented in tables 1 and 2.

Table 1. Chemical analysis of samples obtained by charge roasting at 600, 670 and 720°C

Component	Roasting at 600°C (mass %)	Roasting at 670°C (mass %)	Roasting at 720°C (mass %)
Cu	21,78	22,11	22,46
Fe _{sulphide}	23,16	21,75	20,85
S	22,57	20,72	19,02
Fe ₃ O ₄	12,58	15,21 15,21	17,14
SiO ₂	11,53	11,71	11,89
CaO	1,73 1,73	1,75 1,75 1,75 1,75	1,78
remain	6,65	6,75	6,86

Chemical composition of the bed was also analyzed and after completed roasting at 720°C (about 15 % overflow) it was in percentage value: Cu-3,44; Fe (in sulphide form)- 4,03; S-3,02; Fe₃O₄-2,95; SiO₂-42,78; CaO-21,36; Al₂O₃-4,75 and remainder. Mineralogical composition has been in percentage values: CuFeS₂-4,68; Cu₂O-2,05; Fe₃O₄-2,29; Fe₂O₃-3,73; SiO₂-42,48; CaO-21,36; Al₂O₃-4,75 and remainder.

Table 2. Mineralogical analysis of samples obtained by charge roasting at 600, 670,720°C

Component	Roasting at 600°C (mass %)	Roasting at 670°C (mass %)	Roasting at 720°C (mass %)
CuFeS ₂	38,48	22,13	4,11
Cu ₅ FeS ₄	13,35	22,82	33,20
FeS	15,68	19,63	25,02
Fe ₃ O ₄	12,58	15,21	17,14
SiO ₂	11,53	11,71	11,89
CaO	1,73	1,75	1,78
remainder	6,65	6,75	6,86

By analysis of sulphur content in charge before and after roasting oxidation or desulphurization values have been determined at temperatures 600, 670 and 720°C for the total charge value and results are presented in table 3.

Table 3. Calculated values of sulphur content before and after roasting and desulphurization level value at 600, 670 and 720°C

T, °C	Charge volume (kg/h)	Sulphur volume in charge (kg)	Calcine volume (kg)	Sulphur volume in calcine (kg)	Degree of desulphurisation %
600	48000	14356,8 (29,91 %S)	45829,6 (19,63 %S)	8096,3	33,34
670	42000	12562,2 (29,91 %S)	39498,4 (18,06%S)	7133,4	43,32
720	38000	11365,8 (29,91 %S)	35202,7 (16,62%S)	5850,7	48,52

Obtained results show that in sulphide concentrate roasting in air flow the increase in temperature causes the decrease of sulphur content from 29,91 mass percent to 16,62 mass percent for wet concentrate, i.e. oxidation level increases in the range of 600°C to 720°C, at which the required desulphurisation level of 48,52 % is achieved. At the same conditions, as a result of increased oxidation, Fe₃O₄ content in calcine increases from 0,15 to 17,14 mass percent.

X-ray analysis of starting charge has confirmed results of chemical analysis, i.e. it has shown that reactor charge consists of CuFeS₂, FeS₂ and SiO₂. By analysis of calcine at temperatures 600, 670 and 720°C, the existence of the following elements has been established: CuFeS₂, Cu₅FeS₄, Fe₃O₄, FeS, SiO₂, and CaCO₃, in all three cases. Presence of: SiO₂, CaCO₃, CaSO₄, Al₂O₃ has been registered and traces of CuFeS₂ and Cu₂O in bed at 700°C. Results of chemical and X-ray analysis indicate that in roasting process in fluidized bed reactor, CuFeS₂ and FeS₂ are oxidized and converted into more stable sulphides, where conversion of CuFeS₂ does not proceed to the end. By the increase of temperature, the content of Cu₅FeS₄, FeS and Fe₃O₄ increases while one of CuFeS₂ decreases. Disappearance of Fe₂O₃ in calcine, as well as its occurrence in the bed, shows that only in the lower zones of reactor bed there are conditions enabling formation of the highest degree oxide.

SEM analysis results (Figs.1 and 2) of the calcine obtained at 600°C confirm the presence of the agglomerate of different size particles with noticeable pores.

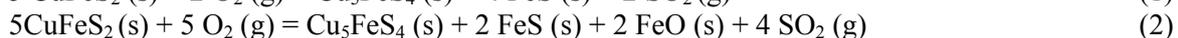
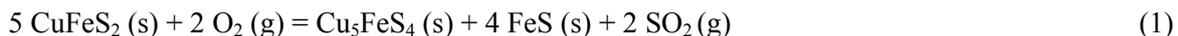


Figure 1. SEM analysis of calcine obtained at 600°C, enlargement 200x



Figure 2. SEM analysis of calcine obtained at 600°C, enlargement 750x

Based on obtained results and all mentioned above, the possible mechanisms of CuFeS₂ oxidation in fluidized layer in temperature range from 600-720°C, is presented as follows:



Values of Gibbs energies in the above mentioned temperature range, for reactions 1 and 2, are as follows: $-\Delta G=503$ to 510 kJ/mole and $-\Delta G= 1328$ to 1317 kJ/mole, respectively, confirming the high probability of their proceeding. This mechanism is confirmed by the cooling water and the air amount calculation in mass and heat balances using HSC program for the CuFeS₂-FeS₂ concentrate roasting process in fluo-solid bed reactor, too [1].

Confirmation of the proposed mechanism could be given using further thermodynamical analysis of isothermal cross-section in the system Cu-Fe-S at 700 °C, presented in Figs 3 and 4 [7]. Isothermal

