MINERALOGICAL TRANSFORMATIONS IN COPPER CONCENTRATE ROASTING IN FLUO-SOLID REACTOR

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Abstract

This work presents the results of investigation process of copper concentrate roasting in fluo-solid reactor with the aim of studying a transformation degree of primary ore minerals under various technological parameters.

Input material (charge) and roasting products (calcine) were investigated by x-ray diffraction, ore microscopy and chemical analysis. The investigation results have shown that reaction of mineral transformation are not completed, i.e. they are developed only partially (12 - 22%) what is a consequence of insufficient long heating, unsuitable temperature or unfilled other parameters as well as non-uniform grain size.
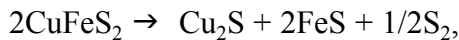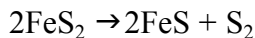
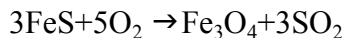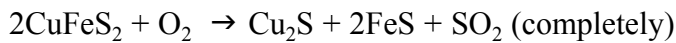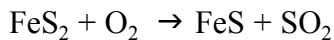*Keywords:* copper, chalcopyrite, roasting

1. Introducing

By introduction of fluo-solid reactor instead of bench furnaces into roasting process, the chemical, kinetics and thermodynamical process conditions were changed, and previously defined models were used for process monitoring and description that did not give satisfied results in new conditions.

Pyrite (FeS_2) and chalcopyrite ($Cu\ FeS_2$) realize sulphur during heating in roasting process and move into more stable sulphides: chalcocite (Cu_2S) and pyrrhotite (FeS). Basic reactions, used for this process description, are [1-3]:

$2FeS_2 \rightarrow 2FeS + S_2$
$2CuFeS_2 \rightarrow Cu_2S + 2FeS + 1/2S_2,$
where elementary sulphur oxidizes into SO_2
$FeS_2 + O_2 \rightarrow FeS + SO_2$
$2CuFeS_2 + O_2 \rightarrow Cu_2S + 2FeS + SO_2$ (completely)
$3FeS+5O_2 \rightarrow Fe_3O_4+3SO_2$

Many scientist were investigated the process of oxidation roasting sulphides of copper row materials, and they were concluded that oxidation of chalcopyrite didn't achieve by de composition on simple sulphides of copper and of iron. The oxidation of chalcopyrite were realised by formation bornite phase [4-13].

However, by analyzing the calcine samples, it was established that a large part of chalcopyrite was untransformed, and that chalcopyrite transformation was developed to bornite and pyrrhotite, but not to chalcocite and pyrrhotite as it was in bench furnaces [4-5].

The aim of those investigations was adefinition of real mineral transformations in the roasting process of chalcopyrite - pyrite concentrate in fluo-solid reactor. The greatest importance in the process of oxide roasting has the mechanism of chalcopyrite ($Cu\ FeS_2$) oxidation, that is degree of stage transformation of this the most important copper mineral.

2. Experimental

Special segment in this work presents a range of experiments of roasting process realized at temperatures of 590^OC, 600^OC, 670^OC, 720^OC, 590^OC and

740^OC. Starting samples for investigation present charge taken from the Smelter Plant in Bor. Charge was undergone to roasting in fluo-solid reactor in the following conditions : flow of process air 24000 - 25000 Nm^3, cooling water flow 1 - 2 m^3/h, where charging capacity varied 45 - 55 t/h, what resulted into various degree of desulphurization as well as various roasting temperature in fixed other fluidization parameters.

After roasting, the samples of calcine and overflow were taken. Sampling crucibles were hermetically closed due to prevention of calcine components oxidation, and for the aim of obtaining as much as possible real results in chemical analysis.

To realize the set task regarding to the quantitative determination of transformation products during roasting, a detail investigation of a large number of samples was carried out by the use of suitable methods : X - ray diffraction, ore microscopy and chemical analysis.

X -ray - diffraction analysis of tested samples was carried out on "SIEMENS" device with Cu - anticathode and filtrated emission by Ni-filters at voltage of 40 kV and current intensiuty of 20 mA. The used literature data in comparison of calculated values of interflate distances were taken from card file of ASTM and JOINT COMMITTEE ON POWDER DIFFRACTION STANDARD.

Ore microscopy was carried out on Leitz - Ortolux microscope in reflected light. Quantitative mineralogical content of sample was determined by the use of integration - planimetric method.

Samples were chemically analyzed in the central laboratory of Copper Institute Bor. Copper was determined by the use of many methods : spectrophotometry, atomic-absorption spectrophotometry and electrogravimetry. Sulphur and silicon dioxide were gravimetrically determined, until iron and calcium oxide were volumetrically determined. Magnetite was determined by the use of "Satmagan" magnetic scale.

3. Results and discussion

Based on the results, qualitative and quantitative changes of mineralogical charge content were proved in the roasting process. Pyrite (FeS_2) and a part of

chalcopyrite ($CuFeS_2$) from charge dissociate in the roasting process and move into more stable copper and iron sulphides: bornite (Cu_5FeS_4), pyrrhotite (FeS) and magnetite (Fe_3O_4). A part of chalcopyrite is unchanged during roasting due to a lack of time for its transformation.

Quantitative mineralogical content was determined by the use of Powder Cell analysis (KMS) based on X-ray diffraction analysis (Table 1). Figure 1 presents a difractogram of Charge 3 sample, and Figure 2 presents a difractogram of Calcine 3 sample. Table 2 presents a resulte of partial chemical analysis.

Table 1. Quantitative mineralogical content determined by Powder Cell analysis (KMS)

| Sample	chalcopyrite %	magnetite %	bornite %	pyrrhotite %	pyrite %	quartz %	anhydrite %	calcite %
Charge 1	42.3				29.95	27.74		
Calcine 1	56.6	21.49	7.91	14				
Overflow 1						12.71	12.47	74.82
Charge 2	26.86				17.63	55.52		
Calcine 2	75.96	12.12	1.55	10.33				
Overflow 2						26.14	8.87	64.99
Charge 3	68.61				16.75	14.64		
Calcine 3	66.81	18.69	3.48	11.03				
Overflow 3						38.67	6.34	54.99
Charge 4	67.73				15.32	16.95		
Calcine 4	67.29	20.03	5.59	7.09				
Overflow 4						39.55	1.42	59.02
Charge 5	57.88				18.68	23.44		
Calcine 5	64.13	15.66	12.26	7.95				
Overflow 5						50.75	9.73	39.52
Charge 6	49.96				15.66	34.38		
Calcine 6	69.73	15.65	4.28	10.35				
Overflow 6						56.49	5.23	38.27
Charge 7	41.51				23.79	34.7		
Calcine 7	61.54	19.77	3.68	15.01				
Overflow 7						42.84	10.61	46.56
Charge 8	54.35				17.08	28.58		
Calcine 8	65.57	11.22	9.92	13.29				
Overflow 8						46.07	8.27	45.02
Charge 9	58.12				25.13	16.74		
Calcine 9	62.68	16.88	6.17	14.28				
Overflow 9						39.45	9.76	50.79
Charge 10	39.38				25.3	35.33		
Calcine10	58.96	14.24	10.01	16.79				
Overflow10						59.02	5.32	35.66
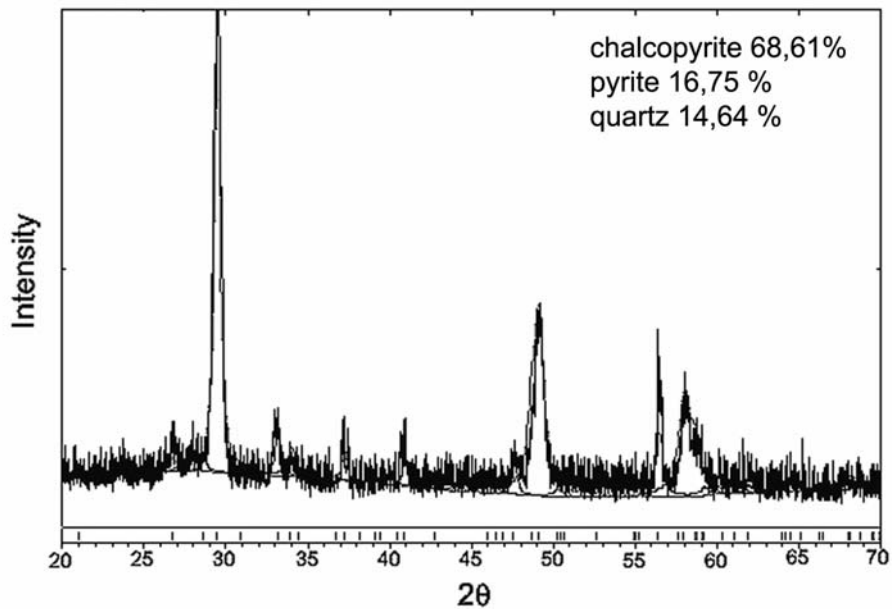
Figure 1. Difractogram of Charge 3 sample
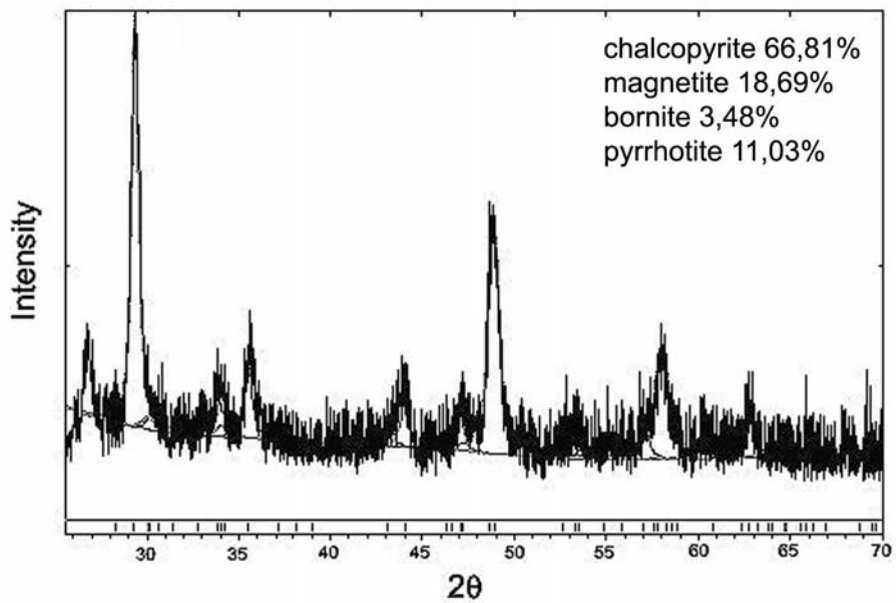
Figure 2. Difractogram of Calcine 3 sample

Table 2. Results of partial chemical analysis

	CA					
Sample	**Cu %**	**SiO$_2$ %**	**Fe %**	**Cao %**	**S %**	**Fe$_3$O4%**
Charge 1	14.76	10.42	26.44	5.77	34.85	0.34
Calcine 1	16.97	15.85	33.23	1.32	20.3	10.66
Overflow 1	1.1	7.2	2.105	45.005	0.8	0.44
Charge 2	12.86	16.26	25.97	3.19	29.55	0.39
Calcine 2	14.93	20.57	30.07	1.32	18.89	8.99
Overflow 2	0.795	17	1.73	41.56	0.6	0.54
Charge 3	19.41	11.37	29.18		32.72	0.27
Calcine 3	20.68	16.53	30.58		19.5	10.31
Overflow 3	4.165	20.65	5.005	33.14	0.6	3.1
Charge 4	18.8	11.17	27.37	3.16	29.7	
Calcine 4	21.32	14.53	33.51	1.67	19.9	11.57
Overflow 4	6.12	32.84	7.68	24.37	4.18	2.27
Charge 5	19.88	11.46	30.72	1.79	31.48	
Calcine 5	22.72	14.14	30.86	1.45	21.08	8.61
Overflow 5	1.93	33.97	2.51	30.74	1.18	0.52
Charge 6	18.8	12.77	26.72	2.57	31.38	
Calcine 6	19.96	13.41	29.04	1.58	19.5	8.07
Overflow 6	1.22	29.69	3.77	31.74	1.28	0.52
Charge 7	15.8	13.06	26.67	2.83	33.07	
Calcine 7	16.1	20.64	30.35	2.46	19.6	9.39
Overflow 7	1.68	29.99	2.57	33.08	0.39	0.64
Charge 8	16.96	11.02	27.23	2.33	32.08	
Calcine 8	18.8	13.89	31.97	1.75	20.88	9.31
Overflow 8	0.98	23.33	1.26	38.44	0.79	
Charge 9	15.7	12.28	26.3	2.66	31.88	
Calcine 9	18.4	14.32	31.89	1.5	21.47	9.39
Overflow 9	1.08	25.93	1.45	30.07	0.69	0.12
Charge 10	15.34	12.25	27.64	3.75	33.07	
Calcine 10	18.06	13.84	32.67	1.52	22.06	9.34
Overflow 10	0.95	22.7	1.26	36.43	0.44	

Having in mind that grain size of sulphide copper concentrate has great role in the process of oxidation roasting in fluo-solid reactor, a granulometric content of sample was analyzed.

It was found out that coarse fractions are fragmented in fluo-solid reactor and redistributed towards smaller diameter particles, Figure 3.

To calculate a transformation degree for each grain class separately, and then for the whole sample, an integration of ore saamples Calcine 1 and Calcine 5 was carried out. Agreements with the KMS results are satisfied

what is seen in Table 3, where 12.78% of chalcopyrite is transformed in Calcine 1 sample, until 21.48% of chalcopyrite is transformed in Calcine 5 sample. That points out that the reactions of mineral transformation are partly developed.
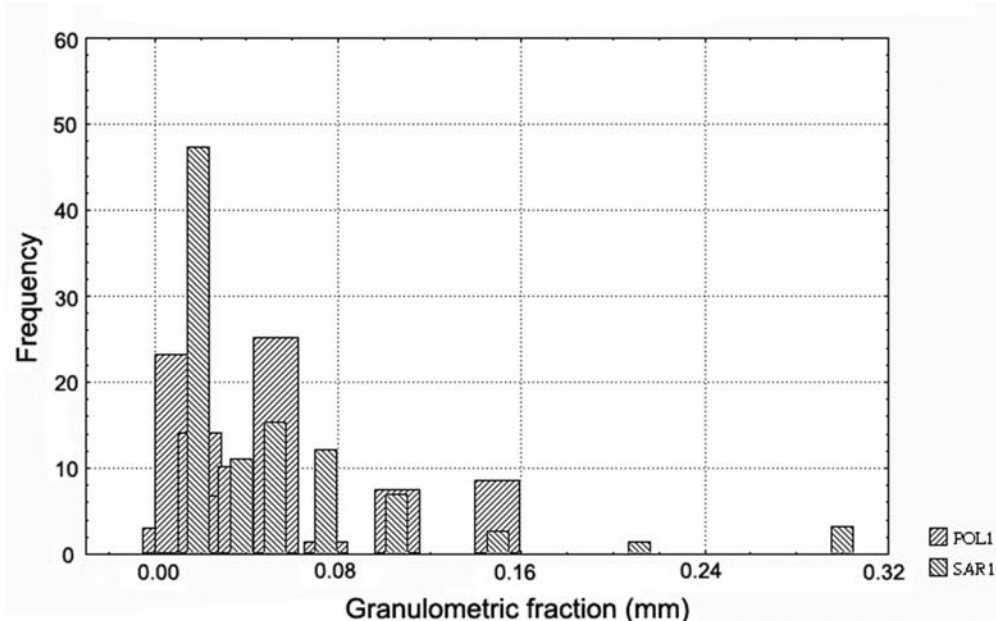

Figure 3. Distribution diagram of Charge 1 and Calcine 1

Tables 4 and 5 give the results of integration with transformation degree.

As agreements for the whole sample are excellent, transformation degree per classes is not in agreement with the confirmed rule that it is inverse proportional to the grain size. This disagreement is the result of quantity increase of completely untransformed chalcopyrite grains towards lower classes. Untransformed grains reach maximum concentration in the finest classes. Due to this, their transformation degree is the lowest.

When it is having in mind that fragmentation of starting material - charge is carried out during process in fluo-solid reactor, then this phenomena is easy undestandable. It is seen from granulometric content of charge and calcine that distribution is moved towards finer classes, calcine is concentrated in lower fractions, what was statistically processed.

Chalcopyrite is much more than products of its transformation such as its concentration in lower granulometric classes disturbs a view on transformation degree per classes. Transformation degreee in coarse grain fractions is much more lower. Small number of grains in coarse fractions contribute to this as it could increase an error.

Table 3. Transformation degree obtained based on quantitative mineralogical content and integration of ore samples

Sample	% transformation	
	KMS-PCW	integration
Calcine 1	12.26	12.78
Calcine 5	16.05	21.48

Table 4. Results of Calcine No. 1 integration

% fractions	grain size (ì m)	% transformation
2.96	0 - 10	0.21
23.3	10 - 20	1.78
14.08	20 - 30	1.11
6.73	30 - 40	0.55
10.2	40 - 50	1.02
25.1	50 - 60	4.74
	60 - 70	
1.5	70 - 80	0.47
	80 - 90	
	90 - 100	
16.13	over 100	2.90
Transformation degree chalcopyrite		**12.78**

Due to this, transformation degree in class could be evaluated based on untransformed chalcopyrite grains and pure grains of bornite, chalcocite or digenite. Determination of transformation degree in class could be obtained based on partly transformed chalcopyrite grains. Although those grains are also fragmentated and present the fragments of some coarse ones, they only hold an information on transformation degree of chalcopyrite into bornite in some classes. Since there is a probability that they are fragments of coarse grains, a large number of measurements is required for reliable result.

Table 5. Results of Calcine No. 5 integration

% fractions	grain size (ì m)	% transformation
14.10	0 - 10	0.66
16.20	10 - 20	1.16
12.20	20 - 30	0.99
8.50	30 - 40	1.00
11.10	40 - 50	1.58
11.30	50 - 60	3.81
	60 – 70	
12.00	70 - 80	7.49
	80 - 90	
	90 - 100	
14.60	over 100	4.79
Transformation degree chalcopyrite		**21.48**

The results of partial chemical analyses of charge and calcine samples roasted at various temperatures are given in Table 6. It is noticed an increase of magnetite content, and decrease of sulphur content with temperature increase, until copper content is practically unchanged.

The results point out that desulphurization degree and magnetite quantity (Figure 4) are increased with roasting temperature increase. Then, it could be said that chalcopyrite content is decreased with roasting temperature increase, and magnetite and bornite content is increased, what is seen from difractogram in Figure 5.

Based on minerals contents obtained by the use of Rietveld analysis (KMS) a relation of bornite and chalcopyrite (Figure 6) was determined depending on temperature. It is noticed that bornite content has linear increase with temperature.

The following diagram gives an effect of grain size on transformation degree (Figure 7). It could be said that a transformation level of chalcopyrite into bornite is exponentially decreased with grain size increase, that is transformation degree is higher in finer grains and reaction is faster.

*Table 6. Results of partial chemical analyses of Charge and Calcine
at various temperatures*

Component	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	Sample 6
Cu (%)	19.64	20.48	20.42	19.16	20.22	20.32
S (%)	33.23	24.99	24.89	21.66	18.82	18.72
Fe (%)	27.42	31.14	31.28	31.14	31.97	32.12
CaO (%)	1.55	2.12	2.10	1.23	2.26	2.60
Fe_3O_4 (%)	0.15	5.86	6.36	12.16	15.32	15.42
SiO_2 (%)	10.40	13.08	12.46	13.80	12.72	16.34

Sample 1 - Charge of No.2 reactor
Sample 2 - Calcine of No.2 reactor at temperature of $590^O C$
Sample 3 - Calcine of No.2 reactor at temperature of $600^O C$
Sample 4 - Calcine of No.2 reactor at temperature of $670^O C$
Sample 5 - Calcine of No.2 reactor at temperature of $720^O C$
Sample 6 - Calcine of No.2 reactor at temperature of $740^O C$

4. Conclusion

Based on carried out investigations for mineral transformation into fluo-solid reactor, the results were obtained as a base for the following conclusions:

- In the roasting process of charge, pyrite and a part of chalcopyrite dissociate and transform into more stable copper and iron sulphides: bornite and pyrrhotite, and a part of chalcopyrite is unchanged.

- With temperature increase, chalcopyrite content decreases, and magnetite and bornite content increases.

- With temperature increase and desulphurization degree, a character of clacopyrite transformation into bornite and pyrottite is unchanged and those changes are only   quantitative.

- Real granulometric content in the roasting process is very changeable. Chalcopyrite grains are fragmented and fill fine grain size fractions. A small number of them stay in coarse fractions and due to this there is an impression that transformation level of chalcopyrite - bornite is lower in fine grain size fractions. Due to this, distribution of unchanged chalcopyrite per fractions has to be taken only as a measure for total transformation in the whole sample, and not   per fractions.

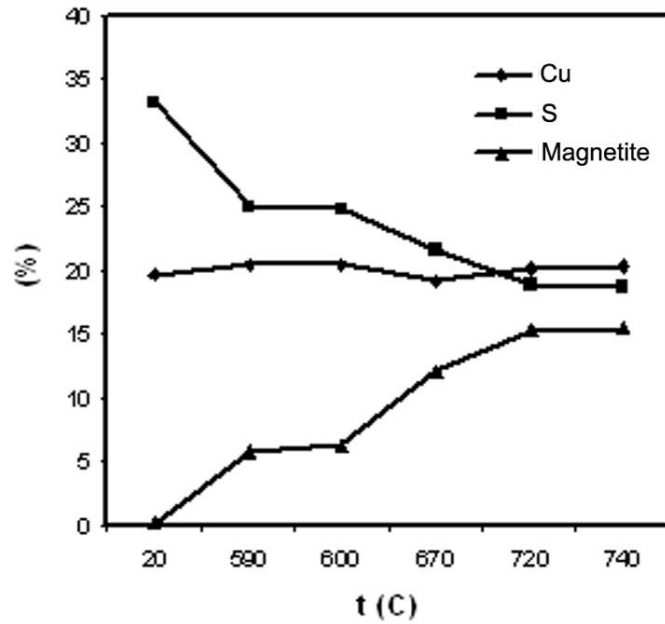- Reactions of mineral transformations are not complete, i.e. they are

Figure 4. Diagram of copper (Cu), sulphur (S) and magnetite content in Charge and Calcine at various temperatures
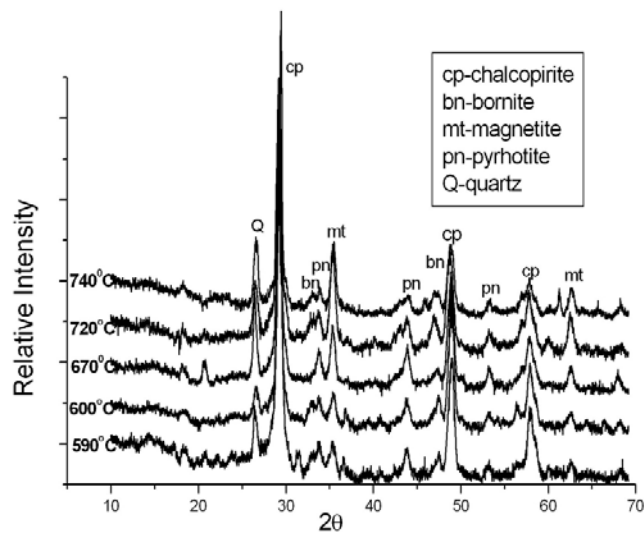

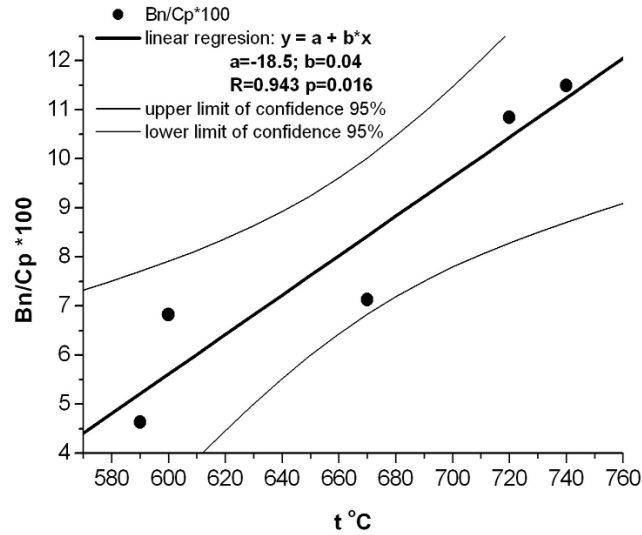*Figure 5. Difractogram of Calcine samples at various temperatures: 590°C, 600°C, 670°C, 720°C and 740°C*

Figure 6. Diagram of bornite and chalcopyrite relation for temperature from 590^oC - 740^oC (Cp - chalcopyrite (Cu FeS$_2$) , Bn - bornite (Cu$_5$FeS$_4$))

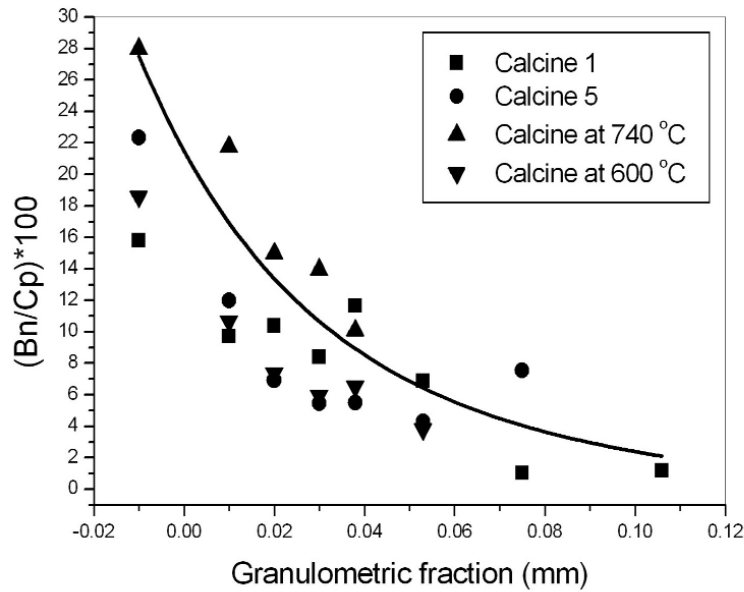*Figure 7. Effect of grain size on transformation degree (Cp - chalcopyrite (Cu FeS$_2$) , Bn - bornite (Cu$_5$FeS$_4$))*

only partly developed (12 - 22%) what is the result of insufficient time, unsuitable temperature or unfilling the other parameters as well as for example a grain size.

-    Uncomplete transformation disturbs both the technological process and has ecological importance due to a fact that a large part of sulphur does not go to the Sulphuric Acid Plant but into the vicinity and polluts it. Due to those reasons, a production optimization is required as well as permanent control of Charge and Calcine.

Acknowledgement

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