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THERMODYNAMIC ANALYSIS OF THE SULPHATIZATION PROCESSES TAKING PLACE IN A DUST-GAS FLOW FROM FLASH SMELTING FURNACE

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ABSTRACT

Analytical studies of the physicochemical interactions and isothermal equilibriums in Cu-Fe-S-O system were conducted at temperatures 1623K, 1373K and 973K by software HSC Chemistry ver.7.1 modules: Reaction Equations and Lpp diagrams.

The thermodynamical stability of the phases in Cu-S-O and Fe-S-O systems were determined under certain conditions. The tendencies of their variation upon injection of "sulphatizing air" in the volume of the dust-gas flow output of flash smelting furnace (FSF) uptake were also studied. It was established that the formation of cuprum sulphate and iron ferric sulphate is thermodynamically possible only at temperatures lower than 973 K. The results predicted on the basis of the analytical investigation were confirmed by chemical and X-ray analyses of dust samples taken from the convective part of the waste heat boiler (WHB).

Keywords: FSF, dust-gas flow, sulphatization, copper and iron oxides, WHB.

INTRODUCTION

Over half of all copper produced worldwide is currently obtained by means of flash smelting of copper sulphide concentrates (the Outokumpu process) [1, 2]. This is an autogenous process, which uses the heat, generated during sulphide oxidation, to heat and smelt the charge. The technological gas, generated during the process is rich in sulpher dioxide (from 20 % to 70 %) and contains from 3 % to 15 % of the feed material. This dust-gas flow goes through cleaning facilities (WHB and electrostatic precipitators) for heat reduction and dust particles removal prior to its introduction to sulphuric acid production.

The abrupt changes in the thermodynamic and aerodynamic conditions during the transition of the dust-gas flow from the smelting furnace uptake through the waste heat boiler (WHB) result in formation of thick and hard to break build-ups [3, 4]. They cause serious problems concerning the smelting furnace operation, drop of power supply and even breakdowns. Removal of the formed build-ups in WHB is extremely labor-consuming, dangerous and leads to loss of time and resources. According to Ranki-Kilpinen [5] and Nurminen [6], this problem can be partially solved by injecting the so-called "sulphatizing air" to the dust-gas flow at the uptake output of the smelting furnace. It facilitates the formation of cupric and ferrous sulphates.

In terms of thermodynamics, the process of sulphatization depends on two basic parameters: the temperature and the partial pressures of oxygen and sulfur dioxide in the gas phase. The aim of this work is to carry out a thermodynamic assessment of the influence of these two parameters on the processes of sulphate formation on the ground of copper and iron sulphides and oxides present in the dust-gas flow upon injection of an additional volume of "sulphatizing air" to the smelting furnace uptake and WHB.

EXPERIMENTAL

It is found that the dust-gas flow which goes through the smelting furnace uptake contains particles of non-reactive chalcopyrite, copper sulphide, iron sulphide, copper and iron oxides, and metal copper droplets. Depending on the furnace load and the degree of oxygen enrichment, the temperature of the discharged flow varies between 1623K and 1673K. After injection of "sulphatizing air" in the course of the transition from the uptake to WHB, the temperature of the dust-gas flow drops. It is assumed that the temperature is ca 1373 K at WHB input; it decreases to 973 K at the end of the radiation section, and then to 623 K at the output of WHB convective section.

Methodology of study

Professional software for thermochemical calculations, HSC Chemistry ver.7.1 [7] was applied in this study. Two modules of this software were used: Reaction Equations for computation of Gibbs energy and Lpp-Diagrams for calculating and drawing of the studied systems phase diagrams: Cu-S-O and Fe-S-O. They can be used to describe the processes of sulphate formation of copper and iron particles present in the dust-gas flow going through the smelting furnace uptake, the radiation section and convective sections of WHB.

The analytical study comprised two stages:

- assessment the effect of temperature on the thermodynamic probability of the possible physico-chemical interactions running in Cu-Fe-S-O system;

Table 1. Gibbs energy of the chemical interaction taking place in dust-gas flow of the uptake of FSF and WHB, kJ/mol$_{O2}$.

No	Reaction	Uptake of FSF ΔG_t, kJ/mol T=1623 K	WHB, ΔG_t kJ/mol Radiation section Input T=1373 K	 Radiation section Output T=973K	 Convective section T=623K
	i)oxidation of copper sulphides				
1	$2CuFeS_2 + 6O_2 = Cu_2O*Fe_2O_3 + 4SO_2$	-207.39	-223.61	-251.36	-272.31
2	$Cu_2S + 2O_2 = Cu_2SO_4$	-41.46	-87.33	-159.01	-224.31
3	$Cu_2S + 1{,}5O_2 = Cu_2O + SO_2$	-146.02	-158.88	-189.67	-216.40
4	$Cu_2S + O_2 = 2Cu + SO_2$	-167.02	-175.59	-195.13	-210.84
5	4Cu + O2 = 2Cu2O	-98.13	-133.46	-191.09	-242.50
	ii) oxidation of iron sulphides				
6	$3FeS + 5O_2 = Fe_3O_4 + 3SO_2$	-218.49	-248.84	-275.23	-299.91
7	$2FeS + 3{,}5O_2 = Fe_2O_3 + 2SO_2$	-219.23	-242.04	-272.82	-301.23
8	$FeS + 2O_2 = FeSO_4$	-127.36	-172.77	-246.78	-313.04
	iii) interaction between copper and iron compounds				
9	$2Cu_2O + Cu_2S = 6Cu + SO_2$	-65.53	-50.43	-22.78	6.51
10	$Cu_2O + FeS = Cu_2S + FeO$	-133.69	-127.60	-114.01	-53.66
11	$Cu_2O + Fe_2O_3 = Cu_2O*Fe_2O_3$	-12.34	-16.46	-22.76	-28.51
12	$Cu_2O + Fe_3O_4 = 2CuFe_2O_4 + FeO$	20.39	12.75	0.07	-10.06
13	$Cu + Fe_2(SO_4)_3 = CuSO_4 + 2FeSO_4$	-90.21	-80.75	-64.49	-53.66
	iv) interaction of copper and iron oxides with the gas phase				
14	$2SO_2 + O_2 = 2SO_3$	105.47	59.51	-14.72	-80.45
15	$Cu_2S + SO_2 + 3O_2 = 2CuSO_4$	15.29	-44.71	-140.79	-228.77
16	$Cu_2O + 2SO_2 + 1{,}5O_2 = 2CuSO_4$	246.06	69.47	-91.92	-241.15
17	$2Cu_2O + 4SO_3 + O_2 = 4CuSO_4$	318.84	89.39	-246.33	-562.55
18	$2Cu_2O+2SO_2 + O_2 = 2Cu_2SO_4$	272.10	127.34	-67.04	-248.01
19	$Cu + O_2 + SO_2 = CuSO_4$	106.81	20.78	-116.71	-241.49
20	$FeS + 2{,}5O_2 + SO_2 = FeSO_4 + SO_3$	-124.81	-126.31	-196.25	-259.40
21	$2Fe_2O_3 + 4SO_2 + O_2 = 2FeSO_4$	515.79	270.87	-23.34	-324.55
22	$Fe_3O_4 + 3SO_2 + O_2 = 3FeSO_4$	378.34	173.04	-73.60	-325.33
23	$2FeSO_4 + SO_2 + O_2 = Fe_2(SO_4)_3$	197.08	101.53	-52.27	-187.82

- calculation and drawing of equilibrium phase diagrams of Cu-S-O and Fe-S-O systems in coordinates LogP_{O2} vs. LogP_{SO2} at temperatures and pressures typical for FSF furnace uptake and WHB.

Computation of Gibbs energy

In terms of physical chemistry, the reactions running in the smelting furnace uptake and WHB were conditionally divided to four groups: i) oxidation of copper sul-

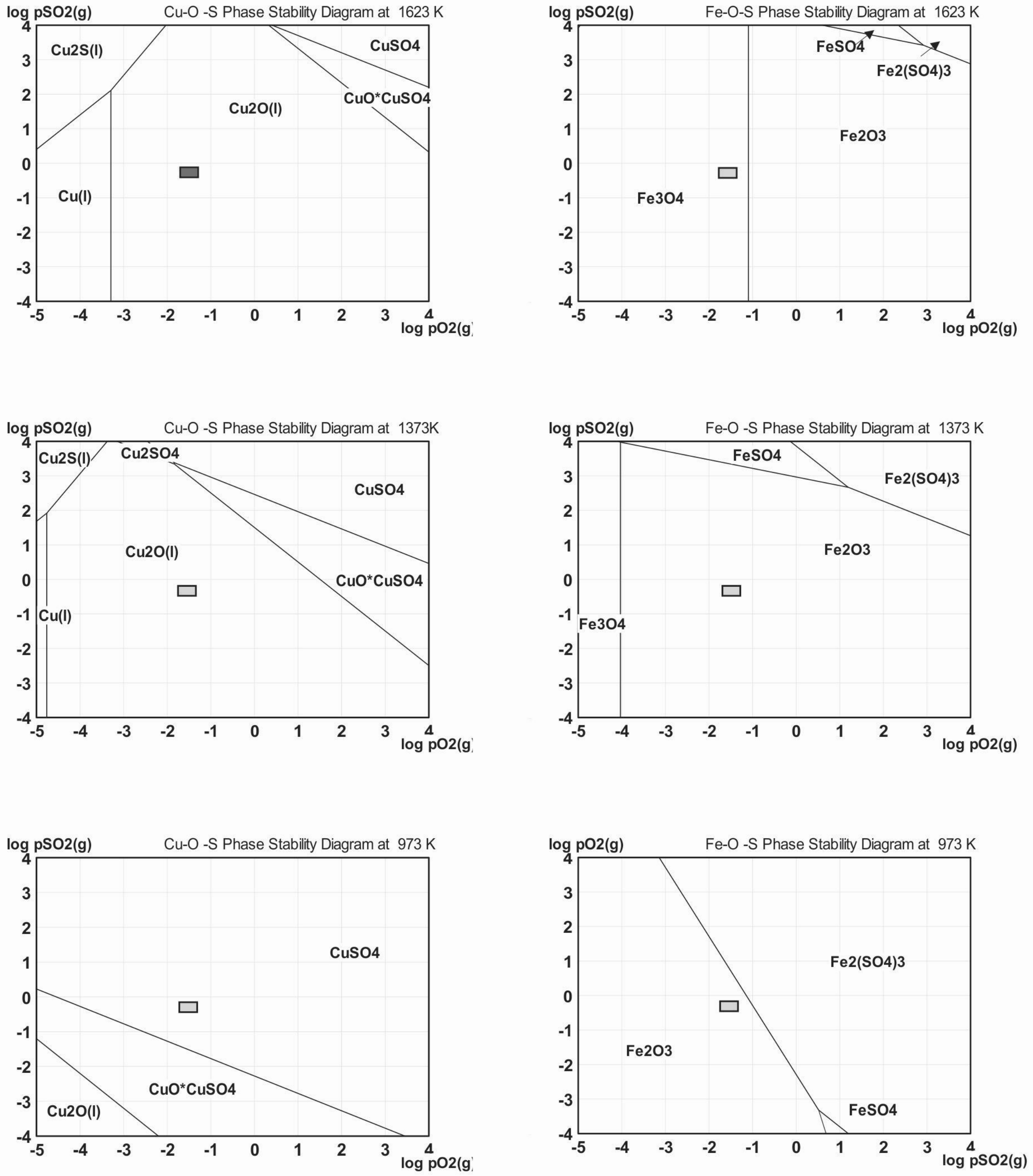

Fig.1. Equilibrium compositions in the Cu-S-O and Fe-S-O systems at temperatures typical for the uptake of FSF (a, d) and inlet and outlet of the radiation section of WHB: input (b, e) and output (c, f) - ▭ the area of real P_{O2} and P_{SO2} values in dust-gas flow at minimum and maximum charge load.

Table 2. Technological parameters of FSF and volumes of „sulphatizing air" injected in the FSF uptake.

Charge of FSF, t/h		Reaction shaft of FSF		Uptake of FSF Sulphatizing air, Nm^3/h	Amount gas from output of FSF, Nm^3/h
		Air, Nm^3/h	Oxygen, Nm^3/h		
Min	85	30442	11900	5324	21009
Max	154	59014	22300	8250	75816
Average	130	46800	18676	6755	38339

phides ($CuFeS_2$, Cu_2S) to oxides (Cu_2O, $CuSO_4$, Cu_2SO_4) and spinels ($CuFeO_2$, Cu_2FeO_4); ii) oxidation of FeS to sulphates ($Fe_2(SO_4)_3$, $FeSO_4$) and oxides (FeO, Fe_3O_4, Fe_2O_3); iii) interaction between copper and iron compounds and iv) copper and iron oxides interaction with the gas phase.

The Gibbs energy values referring to the physicochemical reactions, running in the dust-gas flow in the smelting furnace uptake and along the length of WHB were calculated using the HSC Chemistry ver.7.1 (module Reaction Equations) software. They are listed in Table 1.

The analysis of the results showed that reaction (1) referring to oxidation of the chalcopyrite to copper spinel and reactions (3 and 4) of oxidation of copper sulphide to metallic copper and copper oxide were the most probable one in the furnace uptake. Furthermore, the probability of $Cu_2O*Fe_2O_3$ formation grew with temperature decrease. Reaction (10) of copper resulphidation in case of contact of smelted Cu_2O and FeS particles was also highly probable. The probability of formation of cupric sulphates in correspondence with reactions 2 and 18 was much lower. The highly negative Gibbs energy values referring to oxidation reactions 6 and 7 (FeS transformation to Fe_3O_4 and Fe_2O_3) showed that they would run with priority when compared to reactions of $FeSO_4$ formation (reactions 8, 13 and 20).

Iron oxides formation was the most probable reaction in WHB radiation section. The thermodynamic probability of cupric and ferrous sulphates formation increased simultaneously with the processes of oxidation of copper and iron sulphides as the temperature decreases below 973 K. This was particularly favored by the interaction with the gas phase containing SO_2, SO_3 and O_2 (reactions 15, 17 and 20).

The formation of cupric sulphates (reactions 15 - 19) and ferrous sulphates (reactions 8, 21, 22, 23) was the most probable reaction among the other processes running in WHB convective section where the temperature decreased from 973 K down to 623 K at the output.

Calculation and drawing of Lpp-diagrams

The oxygen partial pressure in the gas phase was the main thermodynamic parameter affecting the degree and rate of oxidation and sulphatization reactions. Lpp module of HSC Chemistry ver.7.1 software was used to determine the effect of this parameter on the equilibrium compositions of Cu-S-O and Fe-S-O systems. Only the compounds whose formation was verified by the thermodynamic calculations carried out were taken into account in diagrams drawing.

RESULTS AND DISCUSSION

Lpp phase diagrams of both systems studied are shown in coordinates $LogP_{SO_2}$ vs. $LogP_{O_2}$ (Fig. 1). They are drawn for temperatures, typical for the smelting furnace uptake (1623 K) and for the radiation section of WHB (1373 K and 973 K). The phase Lpp diagrams for the convective section of WHB (T = 623 K) are not shown, since only cupric and ferrous sulphates are present in the ranges of $LogP_{SO_2}$ and $LogP_{O_2}$ studied.

The field that corresponds to the minimum and maximum values of partial pressures of SO_2 and O_2, after "sulphatizing air" injection in the volume of the dust-gas flow at the transition of the furnace uptake and WHB, are specified on the diagrams presented. These values are calculated based on the operational data for flash smelting of copper sulphide concentrates (Tables 2 and 3) to copper matte at the minimum and maximum furnace load. These values are: $P_{SO_2} = 0.18$ and $P_{SO_2} = 0.39$ atm for sulphur dioxide, and $P_{O_2} = 0.053$ and $P_{O_2} = 0.023$ atm - for oxygen. They are plotted by rectangles on the Lpp diagrams.

The analysis of the phase equilibriums in Cu-O-S and Fe-O-S systems shows that Cu_2O, Fe_3O_4 and Fe_2O_3 are stable phases at temperatures typical for the smelt-

Table 3. Chemical composition of the technological gas from FSF, in vol. %.

Values	SO_2	SO_3	N_2	O_2	CO_2	CO
Min	18	1	79	1	1	0
Max	39	4	46	6	3	2
Average	32	2	59	4	2	1

ing furnace uptake (1623 K) and for WHB input (1373 K), even after "sulphatizing air" injection. The presence of these phases as well as of copper spinels (cuprospinel, delaphosphite, and magnetite) is found in earlier studies [8] of built-ups samples collected from WHB radiation section.

The area of cupric and ferrous sulphates stability increases considerably with temperature decrease. $CuSO_4$ and Fe_2O_3 are already stable phases at 973 K (at the output of WHB radiation section). $CuSO_4$ and $Fe_2(SO_4)_3$ are the only stable phases at the end of WHB convective section (T = 623 K) taking into account the full range of P_{SO_2} and P_{O_2} values.

The probability of the processes of sulphate formation running in this section of WHB is checked by chemical and XRD analyses of collected dust samples. The dust elemental composition is identified by means of complexometry and atomic absorption spectrometry (AAS). There are also other elements present in the samples, such as As, Bi, Ni, Co and Mn, (in quantities of ca 2 %) as well as oxygen, connected with Cu, Fe and other elements. The chemical analysis of the dust is shown in Table 4.

It is notable that over 90 % of dust sulphur is in a sulphate form. Moreover, a significant part of the iron is in the form of magnetite (75 %). According to Tz. Markova et al. [9], the presence of magnetite in the dust

Table 4. Chemical composition of the dust from convective section of WHB, in mass %.

Load, t/h		Cu	$Fe_Σ$	Fe_3O_4	Pb	Zn	$S_Σ$	$S_{Sulphate}$	SiO_2	CaO
Min	85	19.94	19.55	20.26	4.94	3.11	7.75	6.84	8.99	0.72
Max	154	26.17	30.21	22.60	7.34	4.37	13.02	11.93	11.12	1.05
Average	130	23.86	24.81	21.20	6.07	3.39	10.88	9.79	9.98	0.94

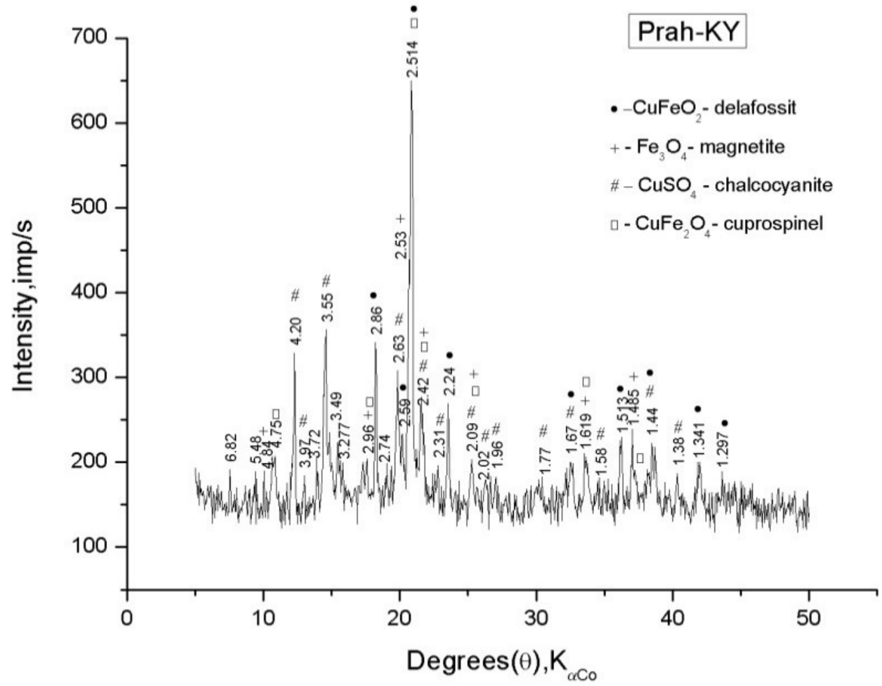

Fig. 2. XRD patterns of the sample of dust from convective section of WHB.

catalyzes the copper oxides sulphatization processes.

Fig. 2 shows a typical X-ray diffraction of the dust samples collected from the convective section of the boiler. The analysis was performed using a DRON-3M diffractometer with CoKα radiation (λ = 1.7890 Å).The presence of chalcocyanite, delafossit, cuprospinel and magnetite in the dust confirms totally the results of the analytical study carried out.

CONCLUSIONS

Sulphatization of copper and iron sulphides cannot not be expected in case of "sulphatizing air" injection to the dust-gas flow in the course of transition between the uptake and WHB. This is due to the high temperature at the input in the radiation section of the boiler.

The thermodynamic calculations carried out lead to the conclusion that the processes of copper and iron sulphate formation are both probable at temperatures lower than 973 K, but the probability of cupric sulphates formation is higher. This conclusion is verified by the chemical and XRD analyses of dust samples collected from the convective section of the boiler.

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