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HIGH OXIDATIVE PROCESS FOR DEAD ROASTING OF POLYMETALLIC SULFIDE CONCENTRATES

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ABSTRACT
The ore bodies: Coka Marin, Tenka and Blagojev Kamen, in Eastern Serbia, contain polymetallic sulfide minerals rich in precious metals: silver and gold. Basically, these minerals contain: chalcopyrite, $CuFeS_2$, pyrite, FeS_2, as well as lead and zinc sulfide. Oxidation roasting of sulfide compound is the first stage of processing sulfide concentrates. The laboratory tests indicate the possibility of achieving a high degree of desulfurization, over 95%, under application of enriched air and a temperature of about 900 ^oC. The mechanism of oxidative roasting is interesting, too, because it is based on the transfer of oxygen through the iron oxides, magnetite Fe_3O_4, primarily. Also, this paper points out the technological and economic aspects of applied technology of processing of polymetallic concentrates.
Keywords: sulfide polymetallic concentrates, dead roasting mechanism

1. INTRODUCTION
In Serbia, few potential ore bodies of sulfide polymetallic concentrate located in the East region. It is calculated about 8-10x10^6 t of this ores in reserve. Presently in Serbia only copper sulfide concentrates is treated in the smelter plant and a small amount of the others concentrates, rich in lead and zinc, is utilized by conventional process of copper smelting. Many problems with presence of lead and zinc in the smelting and converting is generated. In this way, this article should found the best solution for processing this concentrates in a next time.

2. THERMODYNAMIC PRINCIPLES OF HIGH OXIDATIVE PROCESS FOR ROASTING POLYMETALLIC SULFIDE CONCENTRATES
The principle of roasting lies in the tendencies of the metal sulfides to form stable oxides during the oxidation process. At the start of roasting process some complex sulfides as pyrite, FeS_2, and chalcopyrite, $CuFeS_2$, are decomposed under the condition temperature of the process. These reactions are follows [1]:

$$2CuFeS_2 \rightarrow Cu_2S + 2FeS + S_{lab} \qquad \Delta G^o_{900C} = +46{,}70\,\frac{kJ}{mol}. \qquad (1)$$

$$FeS_2 \rightarrow FeS + S_{lab} \qquad \Delta G^o_{900C} = -2{,}72\,\frac{kJ}{mol} \qquad (2)$$

In this way released labile sulfur is oxidized to SO_2 gas as follow:

$$S_{lab} + O_2 \rightarrow SO_2 \qquad \Delta G^o_{900C} = -294{,}31\,\frac{kJ}{mol} \qquad (3)$$

During the oxidation process are possible and the following reactions:

$$ZnS + \frac{3}{2}O_2 = ZnO + SO_2 \qquad \Delta G^o_{900C} = -355{,}05\frac{kJ}{mol} \qquad (4)$$

$$3FeS + 5O_2 = Fe_3O_4 + 3SO_2 \qquad \Delta G^o_{900C} = -1303{,}46\frac{kJ}{mol} \qquad (5)$$

$$3Fe_3O_4 + FeS = 10FeO + SO_2 \qquad \Delta G^o_{900C} = +72{,}72\frac{kJ}{mol} \qquad (6)$$

$$PbS + \frac{3}{2}O_2 = PbO + SO_2 \qquad \Delta G^o_{900C} = -318{,}38\frac{kJ}{mol} \qquad (7)$$

$$Cu_2S + 2O_2 = 2CuO + SO_2 \qquad \Delta G^o_{900C} = -286{,}39\frac{kJ}{mol} \qquad (8)$$

According to Yazawa [2], at this temperature, when roasting proceeds at a P_{SO2} of 0,1 atm, first came to the oxidation of zinc sulphide and then, very quickly, and the formation of iron oxide to magnetite, Fe_3O_4. Then, PbS and Cu_2S are also possible oxidized. If charge consists of $CuFeS_2$ with small quantity of FeS, at these temperatures, under insufficient oxygen, the roasting process results in the formation of magnetite and a bornite solid solution. Quite differently, the products of the dead roast in excess oxygen vary widely with temperature; and are $CuFe_2O_4$ and CuO at 827°C and $CuFe_2O_4$ at 1000°C. In the case concentrates rich in pyrite, FeS_2, at this temperature, the decomposition sulfur pressure of pyrite to pirrhotite is nearly atmospheric so the FeS is oxidized to Fe_3O_4 and the final stable product upon further oxidation is Fe_2O_3. Practically, as shows the Fig.1, during oxidation magnetite formed process vary. The question is what the real explanation that after rapidly rising in the start, the magnetite decreased in the rest of time the oxidation process. One of the possible answer is theirs consumption for oxidation the other parts of sulfide minerals.

3. EXPERIMENTAL TEST

To verify the thermodynamic calculations and assumptions, dead roasting laboratory tests were carried out at Mining and Metallurgy Institute Bor. The sulfide polymetallic concentrates, which composition are summarized in Table 1, was roasted under oxygen enriched air atmosphere (57-65 $\%O_2$) in the horizontal rotation converter at temperature of 900°C.

Table 1. The chemical composition of three types of concentrates[3]

Concentrate	Cu	Fe	S	Au	Ag
	(%)			(g/t)	
Coka Marin	7.1	12.6	31.01	21.5	124.0
Tenka	5.5	17.3	33.20	4.0	180.0
Blagojev Kamen	2.3	22.9	31.24	614.0	498.7

The great benefit of the concentrates is high content of precious metal, silver and gold. The effect of time for oxidation complex sulfides was studied, the sulfur elimination ratio i.e. the level of desulfuration (%), during roasting process summarized and plotted in Fig. 1.

As the Fig.1 shows, the first 20 minutes of oxidation process carried out very fast and due to the increased magnetite, Fe_3O_4, and sulfur eliminated up to 80 %. It is means that formed calcine saturated with magnetite. Desulfuration carried out slowly and magnetite decreased after this period. It is explained as magnetite consumption from incoming sulfides content in the minerals. At last, it is evident that labile sulfur, as product of decomposed complex sulfides, oxidized very fast to SO_2, while oxidation sulfur from Cu_2S is not sufficient under the condition of roasting process.

The validity of the thermodynamic calculations and practical data of experimental tests show that by a temperature of 900 ^{o}C and oxygen enriched air atmosphere produced calcine with a small amount of sulfur (4-5 %).

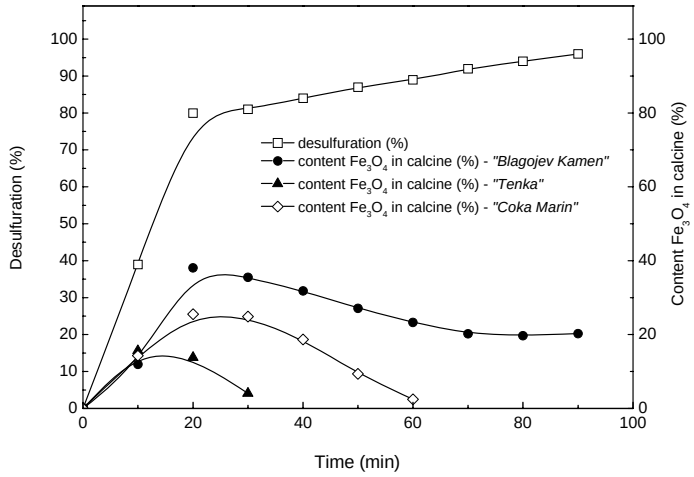

Figure 1. The effect of time during oxidation process on the sulphur elimination ratio ($S_{eliminated}/S_{total}$, %)

The effect of extra heat from exothermical reaction oxidation of sulphur is shown in Fig.2. This effect is more expressed if higher amounts of oxygen involved in the process.

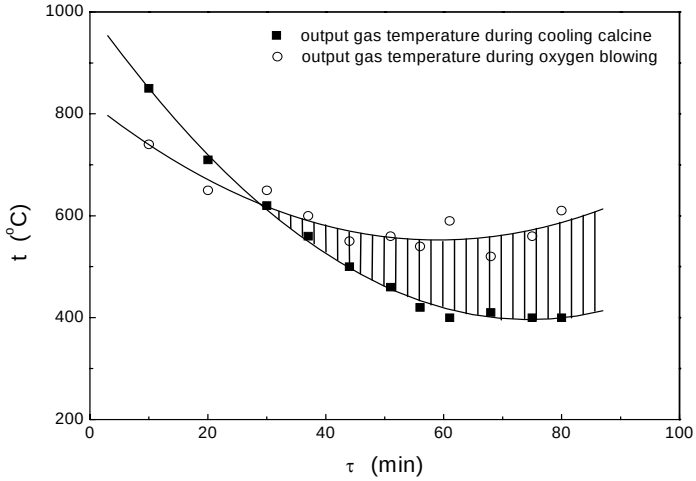

Figure 2. Extra heat from exothermical reaction oxidation of sulphur

4. CONCLUSIONS

Laboratory experiments have fully confirmed the thermodynamic calculations and assumptions and serve as basic information for a practical work and processing polymetallic sulfide concentrates. In Serbia, higher precious metal price and interest rates as a great reason that these types of concentrate will be very actual in the next time.

5. REFERENCES

[1] HSC Chemistry Ver.2.03, Outokumpu Research, Oy.Pori, Finland
[2] A. Yazawa, Metallurgical Transactions B, Vol. 10 B, 1979.
[3] Copper Institute Laboratory Bor, Annual Report, 2001, Serbia.