

Investigation of Chalcopyrite Cuprum Concentrate Roasting by Thermogravimetric and Differential-Thermal Analysis

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Phase transformations taking place in chalcopyrite cuprum concentrate when heating up in the polythermal treatment schedule were investigated. It is shown that sulfides of copper and iron pass into water-soluble sulfatic phases in the low-temperature interval to 676 °C. These phases transform into oxides at higher temperatures which is unfavorable from the point of view of advanced complex hydrometallurgical method of these metals recovery. The optimum temperature of sulfatizing roasting was determined.

Keywords: CONCENTRATE, CHALCOPYRITE, PYRITE, CALCINATION, POLY THERMAL HEATING, PHASE TRANSFORMATIONS

Introduction

Formation of hardly soluble oxides, including copper ferrite, is inevitable in the calcinated (roasted) products at traditional oxidizing roasting of copper concentrates [1]. Therefore such preparation of the concentrate for copper hydrometallurgy has not found a practical application.

The roasting process of Kadzharansky chalcopyrite concentrate of copper with mineralogical composition, %: 77.24 CuFeS₂, 8.66 FeS₂, 1.62 Cu₂S, 0.55 ZnS, 0.54 PbS, 7.32 SiO₂, 1.70 Al₂O₃, 1.65 (CaO+MgO) was investigated with the purpose to reveal the kinetics and mechanism of joint oxidation of chalcopyrite (CuFeS₂) and pyrite (FeS₂) in order to define the optimum temperature of obtaining sulfated (roasted) product, which is the most suitable for lixiviation and selective extraction of components of value (including iron).

The content of gold and silver in this concentrate is enough (2.6-2.7 g/t Au, 42-44 g/t Ag) in order not to neglect the possibility of their extraction with the use of agglomerated cake of hydrometallurgical process.

Methodology

The kinetics and mechanism of

decomposition and oxidation of concentrate sulfides were studied by thermogravimetric and differentially-thermal analysis methods on derivatograph Q-1500 D (Hungary) in corundum crucibles at continuous increase of temperature at the constant rate 10 °C/min. Aluminum oxide calcined at 1250 °C was a standard sample. All the samples had almost equal values of specific surface area (2.5-4.0 m²/g) to eliminate the effect of different grain size. Analysis of chemical and mineralogical compositions of primary and intermediate products as well as qualitative gas test were conducted by the standard techniques.

Samples for X-ray analysis (for the purpose of latching hard-phase products of reactions on characteristic sections of differential thermal analysis curve) were prepared by means of air hardening of concentrate test charge roasted at different temperatures with soaking 1 hour. X-ray exposure was carried out on X-ray diffraction meter DRON-2.0 in copper k_α radiation. Thermodynamic calculations were accomplished according to data [2-5].

The quantitative magnetic analysis of roasted products (for identification of copper ferrite and magnetite) was carried out by measuring intensity of magnetization [6] of sample on the preliminary graduated ballistic

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magnetometer of special design that allows detection of ferromagnetic phase starting from 0.1 % by weight.

Results and Discussion

Data and results of X-ray phase and magnetic analyses (hereafter) presented in **Figures 1, 2** show that the concentrate undergoes a number of phase transformations caused by oxidation of

sulfides and interaction of solid substances among themselves and with gaseous phase during continuous heating at the presence of oxygen. Various exothermic and endothermic effects on differential thermal analysis curve (DTA) at different temperatures and complicated pattern of sample weight change (curves TG and DTG) are indicative of this. The basic mineralogical compositions of hardened samples as compared to the original concentrate are as follows:

Roasting temperature, °C	Dominant phases
Original concentrate	CuFeS ₂ , FeS ₂ , SiO ₂ (β-quartz)
170	CuFeS ₂ , FeS ₂ , SiO ₂ (β-quartz)
270	CuFeS ₂ , Fe ₂ (SO ₄) ₃ , SiO ₂ (β-quartz)
470	CuSO ₄ , Cu ₂ S (secondary), FeSO ₄ , Fe ₃ O ₄ , SiO ₂ (β-quartz)
670	CuSO ₄ , FeSO ₄ , Fe ₃ O ₄ , Fe ₂ O ₃ , SiO ₂ (α-quartz)
970	CuO, CuFe ₂ O ₄ , Fe ₃ O ₄ , SiO ₂ (α-tridymite)

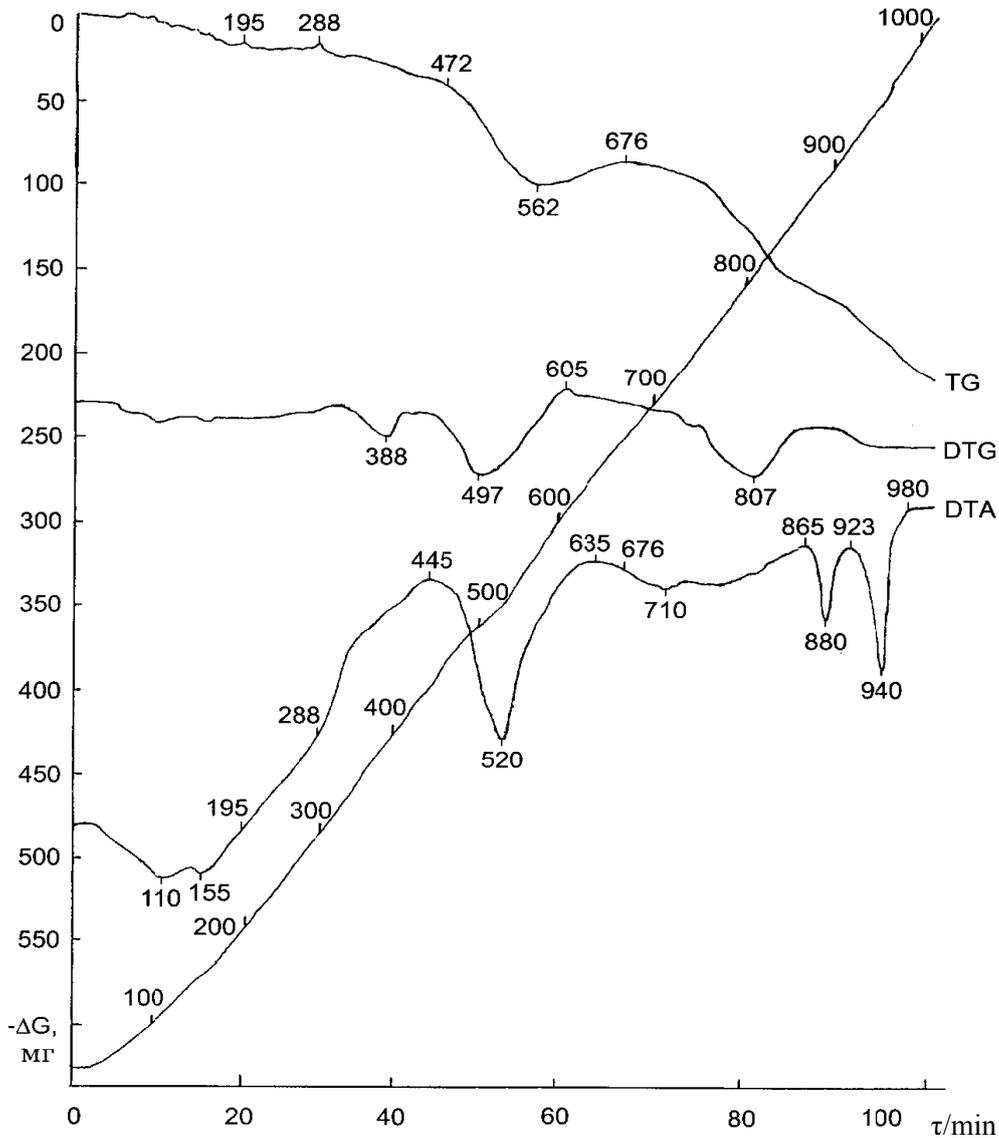
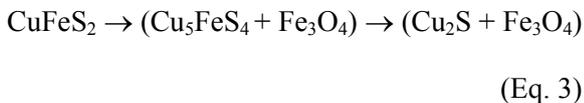


Figure 1. Derivatogram recorded at roasting of chalcopyrite cuprum concentrate

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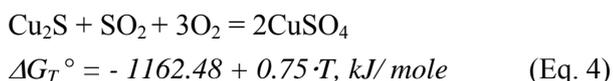
containing in the concentrate. The other (bigger) part of chalcopyrite in the same interval of temperatures according to [7] transforms as follows:



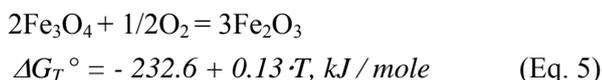
Therefore, there are phases Cu_2S (secondary) and Fe_3O_4 (Figure 2, diffraction maxima 4) along with solidphase reaction products (1) in the sample roasted at 470 °C with soaking 1 hour. The presence of Fe_3O_4 in the sample was confirmed also by quantitative magnetic analysis.

Characteristic diffraction maxima of chalcocite on this diffractogram most likely refer to not only secondary Cu_2S , but also to primary one which due to insignificant amount (1.62 %) was not revealed on diffractograms of both original concentrate and samples roasted at 170 and 270 °C. Total velocity of oxidizing reactions of pyrite and chalcopyrite is maximum at ~ 497 °C (see DTG curve). Mainly sulfurous gas molecules were observed in this area in roasted products by means of gas analysis.

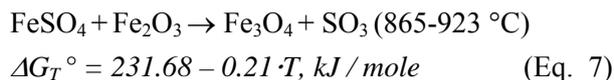
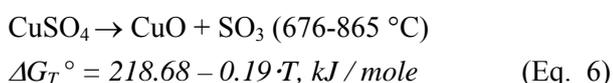
The next exothermic effect in the range from 520 to ~ 676 °C and corresponding growth of sample weight are obviously caused by chalcocite oxidation reaction to divalent copper sulfate:



Divalent sulfates of copper and iron as well as magnetite and hematite were observed in the sample roasted at 670 °C with soaking 1 hour by X-ray structure magnetic analyses. Undoubtedly, the latter is a product of magnetite partial oxidation by air oxygen:



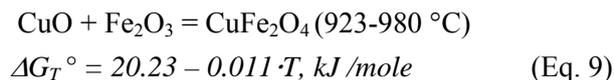
The second stage ($T > 676$ °C) accompanied with intensive weight loss and three endothermic effects on DTA curve includes decomposition processes of sulfates of copper and iron:



Dissociation of SO_3 in gaseous phase:



And also reaction of copper ferrite formation:



Therefore, only phases CuFe_2O_4 , CuO and Fe_3O_4 are detected in the sample roasted at 970 °C with soaking 1 hour.

It is possible to notice that here copper ferrite (nonstoichiometric type of solid solution $\text{Cu}_{1+x}\text{Fe}_{2-x}\text{O}_4$ is possible, where $x \leq 1$) is an inheritor of original chalcopyrite. Congenital transition of chalcopyrite in spinel ferrite phase occurs inside of grains, through the intermediate phases CuSO_4 , FeSO_4 , Fe_3O_4 , CuO and Fe_2O_3 . And as here cuprous oxide and ferric oxide are not in the mechanical mixture in the form of separate particles and are mixed on a molecular level, there are almost perfect conditions for intensive formation of ferrite through a solidphase diffusion. For the same reason the formation of CuFe_2O_4 (or $\text{Cu}_{1+x}\text{Fe}_{2-x}\text{O}_4$) progresses in the very narrow temperature interval (see endothermic effect on DTA curve in the range 923-980 °C).

The course of β -quartz transformation into α -quartz (573 °C [8]) and α -quartz into α -tridimit (870 °C [8]) is clearly visible on diffractograms. When heating the concentrate, any interaction of SiO_2 with intermediate roasted products was not revealed.

As for ZnS and PbS present in the original concentrate, these sulfides also obviously transform in the corresponding sulfates, and then at higher temperatures sulfates are decomposed with precipitation of oxides. However, due to their small amount diffraction maxima are not shown in X-ray diffraction images.

The total weight change at 1000 °C approximately matches the sum of calculated amount of evolved gas and moisture.

Conclusions

1. The formation of copper ferrite hardly soluble in sulfate, ammoniacal and other solutions

is inevitable in the roasted product at deep roasting of chalcopyrite copper concentrate.

2. Roasting before hydrometallurgical processing of chalcopyrite copper concentrate should be carried out at temperatures not above 676 °C in order to produce soluble sulfatic roasted product. The optimum temperature of roasting is 650 ± 20 °C. Duration of concentrate holding at optimum temperature depends on the furnace type and air delivery pattern in the reaction zone.

References

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Исследование обжига халькопиритового концентрата меди методом термогравиметрического и дифференциально-термического анализа

Саргсян Л.Е., Оганесян А.М.

Исследованы фазовые превращения, происходящие в халькопиритовом концентрате меди при нагревании в политермическом режиме. Показано, что в низкотемпературном интервале до 676 °C сульфиды меди и железа переходят в водорастворимые сульфатные фазы, которые при более высоких температурах превращаются в оксиды, что нежелательно с точки зрения применения комплексного гидromеталлургического метода извлечения этих металлов. Установлена оптимальная температура сульфатизирующего обжига.