



Applied Mineralogy of Anthropogenic Accessory Minerals

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Abstract. The term “accessory minerals” is applicable to an expanding range of mineral resources, including rare minerals of anthropogenic deposits and mineral metallurgical wastes. Typical accessory minerals of sedimentary rocks, metallurgical slags and calcines include sulphide minerals of iron, copper, and zinc. This work covers certain chemical transformations of accessory sulphides contained in the wastes of the metallurgical industry. Note that similar behaviors of sulphides may also be observed in the thermal processing of coal. It is shown that, in terms of thermodynamics, thermal processing of products containing precious metals enables application of various methods for generating artificial covellite with silver and gold content through the use of accessory sulphide minerals.

Keywords: Accessory minerals · Precious metals · Thermal processing · Thermodynamics

1 Introduction

Accessory minerals, in the classical sense, are minerals contained in rocks in small quantities (less than 1%). It may be assumed that the term is also applicable to an expanding range of mineral resources, including rare minerals of anthropogenic deposits and mineral metallurgical wastes. Typical accessory minerals of sedimentary rocks, metallurgical slags and calcines include sulphide minerals of iron, copper, and zinc, often containing precious metals.

This work covers certain chemical transformations of accessory sulphides contained in the wastes of the metallurgical industry. Note that similar behaviors of sulphides may also be observed in the thermal processing of coal. Process mineralogy (Bradsow 2014), recently expanded to include thermal processes (Rubin et al. 2014), is the critical tool when studying the behavior of accessory sulfide minerals.

2 Methods and Approaches

The traditional technology used for the processing of zinc concentrates obtained in flotation concentration of polymetallic sulphide ores envisages oxidizing roasting of the zinc concentrate, in which the main mineral, ZnS sphalerite, is converted into zinc

sulphate $ZnSO_4$. The inevitable impurities of pyrite FeS_2 and chalcopyrite $CuFeS_2$, present in the zinc concentrates, are also oxidized into the corresponding simple sulfates and oxides at temperatures above 770 °K (Naboichenko et al. 1997). At present, fluidized bed furnaces are predominantly used for oxidizing roasting, with the oxidation process occurring in a hot gas flow in a suspended state.

Despite the obvious benefits, such as high yield and roasting rates, fluidized bed furnaces also have certain disadvantages, including partial underburning of sphalerite due to the rapid formation of a poorly gas-permeable zinc sulfate film on its surface. This inevitably leads to underburning of fine inclusions in sphalerite grains of other sulfide minerals, primarily chalcopyrite. Chalcopyrite is the most common impurity in sphalerite, which is due to the high similarity of the structures of their crystal lattices. It is known that chalcopyrite is most frequently found in the sphalerite structure in the form of very fine grains, down to emulsion shots (Betekhtin 2008). The behavior of chalcopyrite inclusions in sphalerite is significant for subsequent stages of processing of the calcined concentrate.

After the oxidizing roasting, the resulting zinc calcine is subjected to staged sulfuric acid and aqueous leaching of zinc sulfate and oxide-sulfate with the recovery of a zinc sulfate solution to be subsequently used for zinc metal precipitation by electrolysis. Acid and neutral zinc sulfate leaching is performed at temperatures of up to 80–100 °C, additionally enabling chemical transformations of insoluble calcine components on the grain surfaces. The insoluble cake obtained after leaching includes a certain amount of underburned sulphide minerals containing precious metals, primarily silver. It was previously demonstrated (Otrozhdennova et al. 1997; Geikhman et al. 2003) that sulphide minerals remaining in the cake may be flotation concentrated, yielding a froth product containing up to 18% of sulfide sulfur and up to several kilograms of silver per ton.

We have studied the composition of concentrates obtained by flotation concentration of the cake generated after zinc sulphate leaching at three metallurgical enterprises in different countries. The studies were performed using a Camscan scanning microscope, an Analysette laser microanalyzer, a Geigerflex X-ray phase spectrometer, optical microscopy tools, etc.

It was found that there was no fundamental difference in the material composition of such concentrates at different metallurgical plants. This is explained by the similarity of the ore bases and of the metallurgical treatment structures used at the mining enterprises analyzed. Sphalerite (70–80%) is the main mineral found in the composition of the concentrates, followed by such spinel-structure minerals as $MeFe_2O_4$, covellite, oxide compounds of zinc and iron (several percent), and traces of chalcosite.

In terms of their elementary chemical composition, the concentrates were represented by zinc 45–48%, total sulfur 20–22%, sulfur sulfide 17–19%, iron 11–14%, silica 2.5–4%, and copper 3–4%. The silver content was 0.2–0.4% (2–4 kg/t); the gold content was 10–15 g/t.

3 Results and Discussion

The most important finding is the presence of copper sulphide covellite CuS in the flotation concentrate, in which the bulk of silver is concentrated. The availability of silver-containing films of copper sulfides (without their identification) on the surfaces of sphalerite contained in the zinc cake flotation concentrate has been indicated previously (Otrozhdennova et al. 1997). We have established that covellite forms distinct substances on the sphalerite surface. No native silver was found in the samples. Gold is present in the form of fine grains containing silver and copper. The gold sample is 700–930. Copper-containing metals in the source zinc concentrate entering the roasting process are represented almost exclusively by chalcopyrite, including its aggregates with sphalerite.

Two main methods of covellite formation in the metallurgical processing of zinc may be considered in this regard. The first is the interaction of dissolved copper sulfate with the sphalerite surface in sulfuric acid leaching of zinc calcines, with the formation of covellite films in the course of the resulting exchange reaction and with the transition of zinc ions into the solution. The second possible source of covellite is the transformation of fine chalcopyrite inclusions contained in sphalerite grains with the migration of the resulting covellite to the sphalerite surface due to the strong differences in the structures of their crystal lattices. None of these methods has been subjected to special experimental verification. Given that even isomorphous substitution of copper with silver can occur in chalcopyrite, despite the difference in the electron spiral radii of silver of 1.26 Å and copper of 0.96 Å, it may be assumed that silver-containing covellite may be generated using these methods, especially considering the effects produced on such processes by associated minerals.

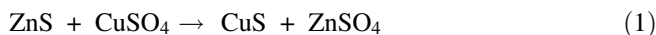
Let us consider the thermodynamic feasibility of the two hypothetical processes of formation of man-made covellite. In the below calculations of the free energy of the processes and their enthalpy and entropy increments, known reference data are used for reactions (I) and (II). These calculations show that reaction (I) can occur spontaneously, which is facilitated by the entropy effect, and reaction (II) requires external energy inputs, which does not contradict the conditions of respective production processes (Tables 1 and 2).

Table 1. Thermodynamic characteristics

Substance	ΔH^0 , kJ/mol	S_{298}^0 , J/mol K	C_p , kJ/mol K
ZnS	-206	57.7	46.0
CuSO ₄	-771.4	109.2	98.9
CuS	53.1	66.5	47.8
ZnSO ₄	-982.8	110.5	99.2
Реакция	-58.5	10.1	2.1

Table 2. Thermodynamic characteristics

Substance	ΔH^0 , kJ/mol	S_{298}^0 , kJ/mol K	C_p , kJ/mol K
CuFeS ₂	-194.93	124.9	95.67
CuS	53.10	66.5	47.8
FeS	-100.00	60.3	50.5
Реакция	41.8	1.9	2.63



$$\Delta H_{798}^0 = \Delta H_{298}^0 + \int_{298}^{798} \Delta c_p dT = -58.5 \cdot 10^3 + 2.1 \cdot (798 - 298) = -57.45 \text{ kJ/mol}$$

$$\Delta S_{798}^0 = \Delta S_{298}^0 + \int_{298}^{798} \frac{\Delta c_p}{T} = 10.1 + 2.1 \cdot \ln \frac{798}{298} = 12.17 \text{ J/molK}$$

$$\Delta G_{798}^0 = \Delta H_{798}^0 - 798 \cdot \Delta S_{798}^0 = -57450 - 798 \cdot 12.17 = -67.2 \text{ kJ/mol}$$



$$\Delta H_{798}^0 = \Delta H_{298}^0 + \int_{298}^{798} \Delta c_p dT = 43, 15 \text{ kJ/mol}$$

$$\Delta S_{798}^0 = \Delta S_{298}^0 + \int_{298}^{798} \frac{\Delta c_p}{T} = 4, 4 \text{ J/molK}$$

$$\Delta G_{798}^0 = \Delta H_{798}^0 - 798 \cdot \Delta S_{798}^0 = 39, 56 \text{ kJ/mol}$$

4 Conclusions

In terms of thermodynamics, combined thermal processing of products containing precious metals enables application of various methods for generating artificial covellite with the participation of accessory sulphide minerals. Respective statements may be useful for both metallurgical processes and thermochemical processing of hard coals, which always contain impurities of sulphide minerals.

Acknowledgements. The work was carried out with the support of the Russian Science Foundation (project No. 17-17-30015).

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