

INFLUENCE OF CaF_2 AND CaCO_3 FLUX ADDITIVES ON THE DISTRIBUTION OF GOLD AND PLATINUM BETWEEN MATTE AND SLAG DURING MELTING OF COPPER-NICKEL SULPHIDE MATERIALS

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Abstract

One of the stages of extracting gold and platinum from copper-nickel sulphide materials is their melting in electric furnaces, where the melt is separated into matte and slag. Gold and platinum are concentrated in the matte, but a significant part of them ends up in the slag, which reduces the recovery of metals. The main reason for such losses is the flotation of matte droplets containing gold and platinum with gas bubbles. One of the options for reducing the loss of valuable components is to add fluxes to the initial charge before melting. The influence of calcite and fluorite on the distribution of gold and platinum over the melting products of copper-nickel sulphide materials (matte and slag) has been experimentally studied based on the above theoretical concepts of droplet flotation. When calcite was added to sulphide ore, there was a significant decrease in the sulphur content in the slag - more than 3 times. This led to a decrease in non-ferrous metals in the slag by 2-3 times, gold from 0.45 to 0.29 ppm, platinum from 2.15 to 2.06 ppm. The addition of fluorite to the mixture of copper-nickel-iron matte and model slag significantly reduced the content of sulphur, non-ferrous metals by 1.5-2.5 times, gold was not found in the slag. The decrease in the amount of sulphides in the slag is mainly due to the fact that the listed additives reduce the viscosity of the slag. This leads to acceleration of the coagulation of matte droplets and increases the rate of their settling to the slag-matte boundary.

Keywords: Noble metals, copper-nickel sulphide ore, flotation, flux additives, matte

1. INTRODUCTION

One of the main world reserves of platinum and other precious metals are copper-nickel sulphide ores [1,2]. The extraction of gold and platinum from such ores is a multistage process, including the smelting of the prepared concentrate in ore-thermal furnaces, where the melt is separated into sulphide and oxide components (matte and slag). Gold and platinum are concentrated in matte, but a significant part of them ends up in the slag, which leads to metal losses [3,4]. Losses also occur during depletion smelting in electric furnaces of converter slag and slag of suspended smelting furnaces. Gold and platinum are concentrated in matte drops in the slag. Thus, in order to reduce the loss of valuable components, it is necessary to increase the rates of coagulation and sedimentation of matte droplets in the slag, reducing its viscosity. This is possible by adding fluxes.

The purpose of this work: to search for ways to increase the degree of gold and platinum recovery, experimentally study the effect of calcite and fluorite on the distribution of noble metals over the melting products of copper-nickel sulphide ore (matte and slag) on the basis of the above theoretical concepts of flotation drops.

2. MATERIALS AND METHODS

The material for research is represented by copper-nickel sulphide ore and a mixture of copper-nickel-iron matte and model slag ($\text{CaO} / \text{SiO}_2 / \text{Al}_2\text{O}_3 = 40/40/20$) in a ratio of 3:2. Mineral composition of the ore (wt%): pyrrhotite 42.8, chalcopyrite 20.0, pentlandite 11.3, magnetite 16.0 and silicates 9.9. Platinum content varies from 1.1 to 3.5 g/t, gold 1.4 g/t. Mineral composition of copper-nickel-iron matte (in wt%): troilite 71.4, bornite 11.1, Fe-Ni alloy 7.0, magnetite 4.9. Gold content is 13.1 g/t.

The mineral compositions of the materials and their melting products were determined by X-ray phase analysis on an XRD 7000C X-ray diffractometer. The share of each phase was determined using the program Crystal Impact Match 3. The contents of gold, platinum, copper, nickel, cobalt and were found using the Spectroflame Modula S inductively coupled plasma atomic emission spectrometer, which allows the contents to be determined with an accuracy of 0.1 ppm.

Heating and melting of materials were carried out in corundum crucibles in a resistance furnace with a graphite heater in an air atmosphere at a temperature of 1300 °C. Holding time was 30 minutes, cooling with the oven was 1-2 hours.

3. RESULTS AND DISCUSSION

The main reason for the loss was the flotation of matte droplets containing gold and platinum by gas bubbles that appear as a result of the decomposition of sulphides during the melting of copper-nickel sulphide materials [5]. From the point of view of physical chemistry, flotation means the floating of bodies of higher density than a liquid on its surface under the action of interfacial tension forces. In the process of flotation, the bubble must overcome the matte-slag interface and hold the matte drop while floating up in the slag. For the bubble to float up with a matte drop in the slag, two conditions must be met:

- 1) The drops are held on the bubbles by surface tension, which can be called the coupling force. In order for the drop not to separate from the bubble, the adhesion force of the matte drop to the bubble must be greater than its gravity.
- 2) The buoyancy force applied to the bubble must be greater than the gravity of the drop. Otherwise, the drop will sink.

With decreasing droplet size r , the adhesion force decreases in proportion to r , and the gravity is proportional to r^3 . The prevalence of surface forces over gravity is characteristic of all dispersed systems. Therefore, micron droplets of matte will almost always float. In the slag, there is a collision of matte droplets and, as a result, coagulation. For example, a bubble with a volume of V_g is capable of lifting gold droplets whose volume V_{Au} does not exceed $1/19 \cdot V_g$. In our experiments, the gold content was about $4 \cdot 10^{-6}$ g/g of the melt, the radius of the initial particles was 3 μm , the radius of the bubbles reached 1 mm, and the thickness of the melt was 5 cm. In this case, the bubble on its way upward must collect and bring to the surface of the melt about 44 thousand gold droplets. Then they are combined by coagulation. As a result, large droplets are formed (up to 300 microns in diameter). The bubble float speed in the oxide melt according to the Stokes formula is high and amounts to about $6.7 \cdot 10^{-3}$ m/s. Thus, the flotation of dispersed droplets in melts proceeds at high rates and leads to their significant enlargement, in contrast to the flotation of solid particles. In the latter case, only the formation of fragile associations is possible. The rate of coagulation of droplets, by analogy with colloidal systems, is proportional to temperature and inversely proportional to the viscosity of the slag and the concentration of droplets. The resulting large droplets will settle in the slag and end up in the matte again. The deposition rate is inversely proportional to the viscosity. A schematic of the process at the slag-matte boundary is shown in **Figure 1**. Thus, in order to reduce the loss of valuable components, it is necessary to increase the rate of coagulation and sedimentation of matte droplets in the slag, reducing its viscosity. This is possible by adding fluxes.

Two fluxes were selected for the experiments - calcite (CaCO_3) and fluorite (CaF_2). The choice of fluxes is justified as follows.

In the metallurgical production of non-ferrous metals, technologies with the addition of calcite in the form of limestone are known [6]. Calcite releases large amounts of CO_2 gas when heated. Despite the fact that gas bubbles lead to the removal of gold- and platinum-containing sulphide droplets from the matte melt into the slag [5], they also contribute to the enlargement of dispersed droplets in the slag. CaO formed during the decomposition of calcite lowers the melting point of the slag and its viscosity. CaO also leads to partial desulphurization of the matte. Fluorite is currently used in ferrous metallurgy. Slags with this component have low values of surface tension, melting point and viscosity [7].

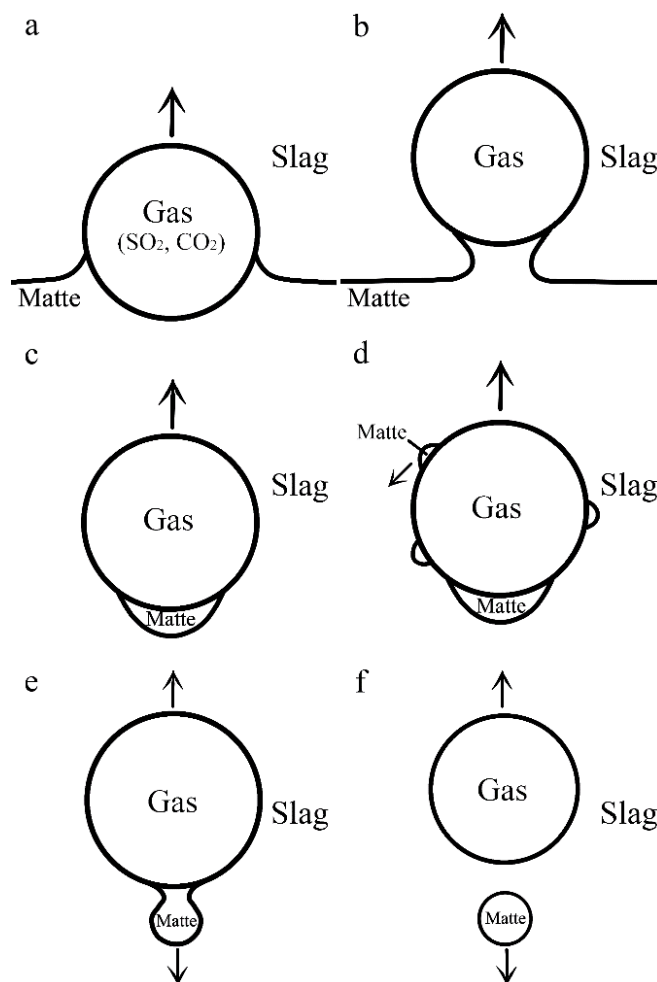


Figure 1 Stages of passage of a gas bubble through the matte-slag interface: a - exit of a gas bubble to the matte-slag interface; b - transition of a gas bubble through the matte-slag interface; c - floating up of a gas bubble with a sulphide drop; d - collection by the gas bubble of other dispersed matte droplets encountered on its way; e - separation of the enlarged sulphide droplet from the gas bubble; f - deposition of a sulphide droplet and floating of a gas bubble

In order to predict changes in the phase composition, an analysis of possible chemical reactions in copper-nickel sulphide ore was carried out using the Equilibrium Compositions module of the HSC Chemistry 6.1 software package under reducing conditions (with a carbon content of 1.8 wt%) with varying contents of calcite and fluorite. It was found that gold and platinum during heating in the range of 0-1300 °C can be in the following form: metallic forms of Au and Pt, sulphide PtS, intermetallic compounds AuCu, PtFe, PtFe₃, PtNi (**Figure2**).

Non-ferrous metals are mainly present in the sulphide form. The addition of calcite and fluorite does not significantly change the system: all the listed forms of occurrence of gold, platinum and non-ferrous metals are preserved, only their contents change. The proportion of oxide compounds Cu and Ni changes insignificantly.

The experiments were carried out with the addition of CaCO_3 and CaF_2 in the amount of 10% of the charge weight: the first was added to the copper-nickel sulphide ore, the second was added to the mixture of copper-nickel-iron matte and model slag. The products of material melting - matte and slag - were analyzed for the content of S, non-ferrous metals (Cu, Ni, Co), gold and platinum. The data are shown in **Tables 1** and **2**. The main proportion of sulphide droplets was observed on the surface of the slag.

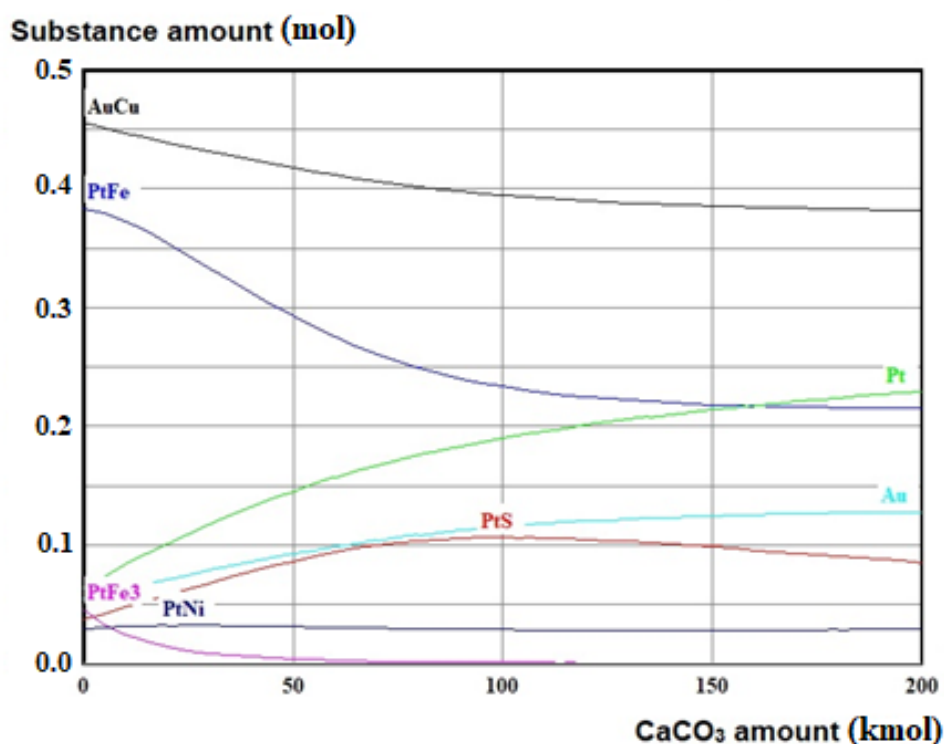


Figure2 Equilibrium composition of copper-nickel sulphide ore depending on the change in the amount of CaCO_3 (from 0 to 200 kmol) at the temperature of 1300 °C

Table1 Content of sulphur, non-ferrous and noble metals in matte and slag after melting the charge without and with the addition of CaCO_3

Component	Content of components in wt%			
	Without CaCO_3		CaCO_3 in the amount of 10%	
	Matte	Slag	Matte	Slag
Cu	4.66	0.38	4.68	0.15
Ni	4.28	0.45	4.39	0.14
Co	0.11	0.02	0.11	0.008
Pt	$4.1 \cdot 10^{-4}$	$2.15 \cdot 10^{-4}$	$3.8 \cdot 10^{-4}$	$2.06 \cdot 10^{-4}$
Au	$1.77 \cdot 10^{-4}$	$0.45 \cdot 10^{-4}$	$1.83 \cdot 10^{-4}$	$0.29 \cdot 10^{-4}$
S	30.5	4.60	28.7	1.13

Table2 Content of sulphur, non-ferrous and noble metals in matte and slag after melting a charge from a mixture of Cu-Ni-Fe matte and model slag without and with the addition of CaF₂

Component	Content of components in wt%			
	Without CaF ₂		CaF ₂ in the amount of 10%	
	Matte	Slag	Matte	Slag
Cu	7.02	0.1	7.25	0.05
Ni	4.98	0.03	5.12	0.01
Co	0.15	0.005	0.16	0.002
Au	13.1·10 ⁻⁴	0.75·10 ⁻⁴	13.5·10 ⁻⁴	Not detected
S	29.8	0.41	30.9	0.34

When CaCO₃ was added to sulphide ore, the entire mixture melted at a temperature of 1260-1270°C, which is 10-20 °C less when melting the ore without adding flux. **Table 1** shows that there was a significant decrease in the sulphur content in the slag - more than 4 times. This, in turn, led to a decrease in non-ferrous metals in the slag by 2-3 times, gold from 0.45 to 0.29, platinum from 2.15 to 2.06%.

The addition of fluorite to the mixture of copper-nickel-iron matte and model slag lowered the melting point of the mixture to 1210-1220 °C (the melting temperature of the mixture without adding CaF₂ is 1270 °C). According to **Table 2**, Fluorite reduced the content of sulphur, non-ferrous metals by 1.5-2.5 times, gold was not found in the slag. The influence of CaF₂ on the amount of platinum in the slag has not been established, probably due to the insufficient accuracy of its determination by the method used.

Thus, the studies carried out have shown that the addition of calcite and fluorite to the charge increases the extraction of non-ferrous metals, gold and platinum into the matte. This is due to the fact that the listed additives reduce the viscosity of the slag. A decrease in viscosity leads to an acceleration of the coagulation of sulphide droplets carried into the slag during flotation, and increases the rate of their settling to the slag-matte boundary, where they merge with the matte mass.

4. CONCLUSION

The stages of the passage of a gas bubble through the matte-slag interface are considered. The flotation of micron matte droplets in the slag is inevitable and leads to the loss of valuable components. To reduce losses, it is necessary to increase the rate of coagulation of drops and their deposition in the slag, reducing its viscosity. This is possible by adding fluxes. It was found that the introduction of CaCO₃ and CaF₂ (in an amount of 10 wt% each) into the initial charge during melting of copper-nickel sulphide materials onto matte made it possible to reduce the content of sulphide droplets in the slag and, accordingly, valuable metals, gold and platinum.

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