

KINETICS OF ROASTING OF COPPER AND IRON SULFIDES WITH SODA IN A VIBRATORY BOILING LAYER

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Preliminary Note – Prethodno priopćenje

The kinetics of the roasting of iron and copper sulfides in a pulsating layer was studied, and the kinetic parameters of the processes were determined. The determination of the order of the roasting reactions and activation energy in the $\text{MeS} - \text{Na}_2\text{CO}_3 - \text{O}_2$ system is based on the differential method. Using the dependences of the degree of conversion of copper and iron sulfides in the reactor of the vibratory pulsating layer at a pulsation frequency of 50 Hz and a pulsation amplitude of 0,1 - 0,5 mm, the values of the apparent activation energy in the temperature ranges of 500 - 550 - 600 °C were obtained for FeS 1,60 - 1,64 and for Cu_2S 1,44 - 2,41 J* mol^{-1} (CO_2).

Key words: metal sulfide, copper sulfide, iron sulfide, sulfatization, leaching.

INTRODUCTION

Pyro and hydrometallurgical processing of sulfide concentrates, which contain heavy non-ferrous metals Cu, Zn, Pb, as well as iron and gangue components in the form of silica, calcium and magnesium oxides, is associated with the using of operations of oxidative or sulfatizing roasting in the technological scheme.

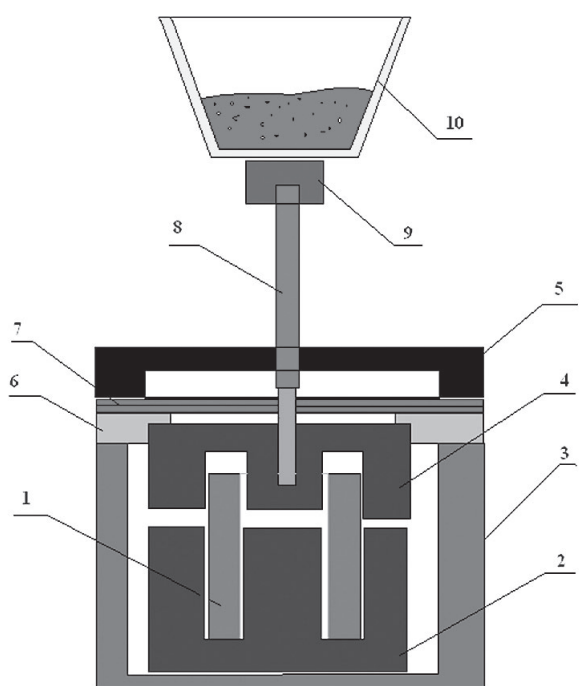
Roasting is a preparatory operation before melting on matte or crude metal in pyrometallurgy and is necessary for the partial or sufficiently complete removal of excess sulfur sulfides into gases that need to be processed to produce sulfuric acid. In hydrometallurgy, oxidative roasting with the removal of sulfur in gases promotes the partial formation of water-soluble metal sulfates and makes up for the loss of sulfuric acid in production.

When roasting sulphides with soda ash in an oxidizing atmosphere, sulfur is converted to sodium sulfate, silica partially forms sodium silicate, and heavy non-ferrous metals form oxides. At temperatures above 700 - 750 °C, an alkaline melt is formed which corrodes the lining of the kiln or melting unit. Previous experiments proved the possibility of a fairly complete desulfurization of copper, lead and zinc sulfides at temperatures of 600 - 700 °C. For roasting a charge containing soda, tubular furnaces and fluidized bed boilers are acceptable that mix the charge and, accordingly, allow oxygen to flow into the reaction zone. However, these processes have disadvantages associated with the energy consumption for the rotation of tubular furnaces, with dust removal, the need for strict control of operating parameters during roasting in a fluidized bed.

The widespread use of electromagnetic vibrators has significantly improved the technological processes of transportation of bulk materials, briquetting of charges. In the field of obtaining composite materials from powders by thermosynthesis in a vibrating layer, the works of V. G. Lyulko et al. [4-5] were published. The authors of these works noted that vibrational fluidization provides a multiple increase in the volume of the layer and its highly porous structure, reduces viscosity and eliminates screening of particles. By specially developed methods of vibration exposure, it is possible to destroy cohesive bonds of particles, increase the relative velocity of motion, create additional flow turbulence, and thereby increase the area and multiplicity of interfacial interaction with the gas medium, significantly intensify the processes of heat and mass transfer. The uniform distribution of temperature and filter gas, the active mixing of the dispersed material create favorable conditions for obtaining end products of uniform composition and properties. Analysis of plant designs (vertical and horizontal type, through-flow, cycle, etc.) and their experimental testing made it possible to create an experimental installation of a universal type for carrying out physicochemical and kinetic studies of the heat treatment of powders in a vibrating layer when changing the parameters of vibrational fluidization (amplitude 2 - 4 mm ; frequency - 23, 33, 42, 50 Hz), temperature-time factors: temperature up to 1 100 °C; time from 5 minutes to several hours; gaseous medium - oxidizing, reducing, neutral, as well as vacuum (low 10 Pa).

The possibility of intensive mixing of finely dispersed material in the reactor of the vibratory pulsating layer and conducted studies on the oxidation of sulfide materials in a pulsating layer by an electromagnetic vibrator were tested.

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1 - electromagnetic coil; 2 - motionless core; 3 - case; 4 - movable core; 5 - housing cover; 6 - gaskets; 7 - leaf springs; 8 - rod-tube; 9 - mounting sleeve; 10 - crucible with a charge of the charge.

Figure 1 Laboratory electromagnetic vibrator for mixing the charge

EXPERIMENTAL

Initial materials: copper sulfide - Cu_2S and iron sulfide FeS grade h, sodium carbonate (b / c sodium carbonate) according to GOST 83 - 79 grade (h).

A diagram of the laboratory setup of a vibrating pulsating layer for roasting sulfide materials are shown in Figure 1.

The analysis of gases on CO_2 was carried out on a Gasochrome-1 chromatograph and on CO_2 , CO , O_2 on a MAG-6-T multi-channel gas analyzer, X-ray spectral analysis of materials on a SPARK-1 spectrophotometer; the differential method was used to study the kinetics of roasting materials in a pulsating layer at 500 - 600 °C.

The temperature in the furnace was measured and maintained at a given level by a thermocouple and an IRT-5301 regulator meter. The temperature in the reaction zone was measured by an additional thermocouple and a digital instrument DT-838. A portion of the materials was weighed on an electronic balance VLT-510-P (capto).

Air for sulfide oxidation reactions was supplied by a microcompressor through a rod-tube, air flow rate was measured by rotameters calibrated by a foam flowmeter.

When you turn on the electromagnetic vibrator, the charge layer with a mass of $(10 - 15) \cdot 10^{-3}$ kg goes into an intense mobile state providing mixing of the entire volume. Air can be supplied to the surface of the mixture, or to the material layer through a ceramic spray in the center at the bottom of the crucible.

RESULTS AND DISCUSSION

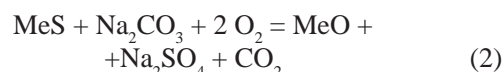
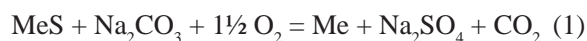
The mixing mechanism of the charge and related phenomena. Depending on the power supplied to the vibrator and the air supply to the layer, there are phenomena of an increase in the speed of movement of particles in the layer along circular paths, and at some parameters of the flow rate of the blast, particle size, and amplitude of the vibration, charge particles are removed from the layer. Therefore, when creating a roasting unit for practice, the selection of optimal parameters is necessary. The dust removal of the charge from the reactor can be significantly reduced by using a metal mesh - a bump stopper covering the top of the reactor.

At roasting temperatures and the composition of the charge leading to the formation of a small amount of liquid phases, high-temperature granulation of the fired material with the formation of spherical granules is observed. In experiments on roasting sulfide mixtures containing silica, the formation of granules is observed at temperatures above 700 - 725 °C due to the formation of liquid phases of sodium silicate and soda. High-temperature granulation does not interfere with the oxidation of sulfides and reduces the loss of charge with dust.

When studying the kinetics of roasting sulfides of copper and iron in a pulsating layer in order to prevent sintering of the material, the mixture was diluted with an inert material - alumina.

Kinetics of sulfide oxidation in a pulsating layer. Earlier, experiments were carried out on roasting granular materials with soda under the conditions of a filter layer [1, 2], and at this stage, for comparison, the kinetics of roasting of iron and copper sulfide in a pulsating layer were studied, and kinetic parameters of the processes were determined.

Methods for studying the kinetics of chemical processes and determining kinetic parameters are described in the literature [1, 2]. To process the experimental data on sulphide roasting, a differential method was chosen to determine the order of the roasting reaction in the system, $\text{MeS} - \text{Na}_2\text{CO}_3 - \text{O}_2$ in which processes with the formation of metals, oxides, sodium sulfate and CO_2 evolution proceed in parallel:



The process parameters were evaluated by the carbon dioxide content of CO_2 and their quantity: the degree of decarbonization of soda, the degree of desulfurization of metal sulfide, or the degree of sodium sulfatization. Calcined soda does not decompose upon heating in the temperature range of interest with the release of CO_2 .

The kinetics of burning iron sulfide FeS and copper Cu_2S in a mixture with Na_2CO_3 was studied at 500, 550 and 600 °C, air flow $(5 - 8) \cdot 10^{-3} \text{ m}^3$ and power on the

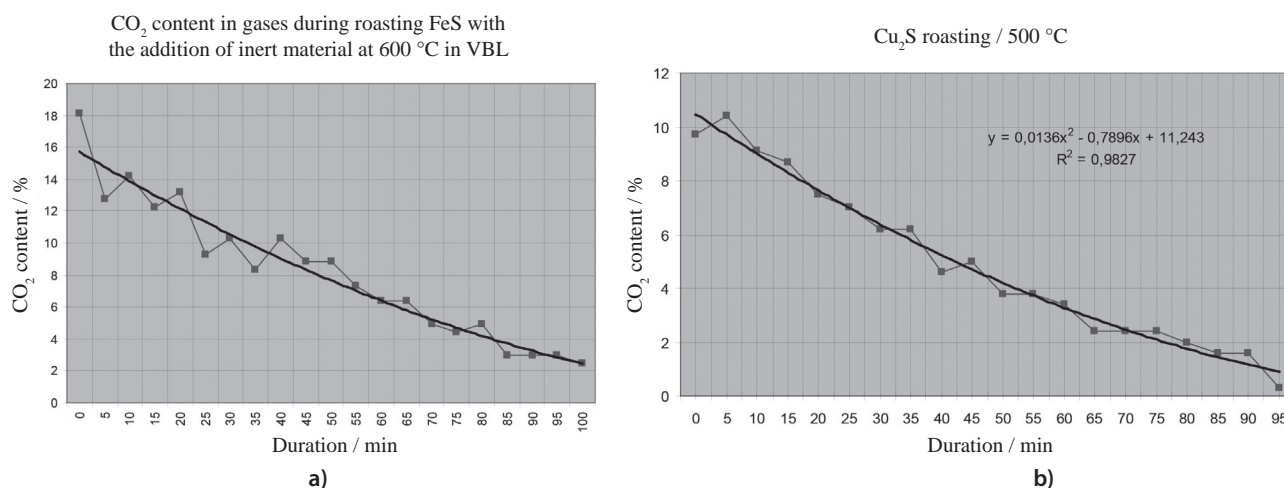


Figure 2 Dependence of CO₂ content on the roasting duration: a) FeS; b) Cu₂S

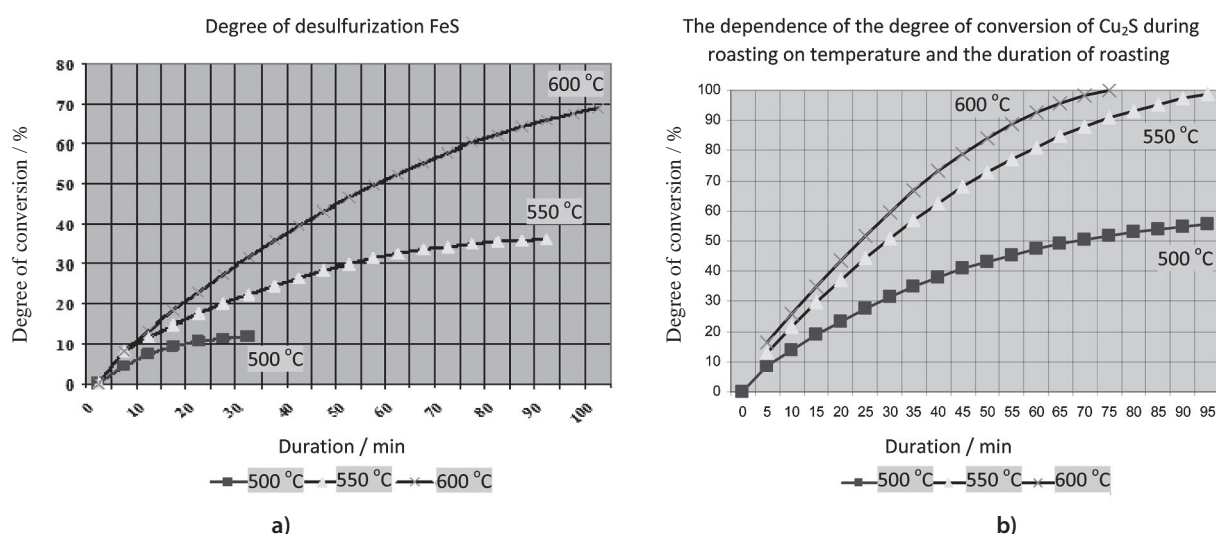


Figure 3 Dependence of the degree of roasting of sulfides on temperature and the duration of roasting in a vibrating pulsating layer: a) FeS; b) Cu₂S

vibrator 30 - 40 W. Weighed FeS was $5,0 \cdot 10^{-3}$ kg., And soda Na₂CO₃ $6,0 \cdot 10^{-3}$ kg. The mass of an inert diluent (alumina) is equal to the mass of a sample of sulfide.

Graphically, the change in carbon dioxide content in the reactor exhaust gas at an air blast flow rate of $7,4 \cdot 10^{-3}$ m³ / h is shown in Figure 2.

According to the results of parallel experiments, the change in the degree of conversion (degree of desulfurization) of iron sulfide FeS and copper sulfide Cu₂S in the reactor of the vibratory pulsating layer at a pulsation frequency of 50 Hz and a pulsation amplitude of 0,1 - 0,5 mm is shown in Figure 3.

Using the average speed of the process as a function of duration, we plotted the dependence $\ln V = f(\ln C)$, then, using the slope of the straight line and the segment cut off on the ordinate axis, the n-orders of the complex reaction and the logarithm of the rate constant, $\ln K$, were determined. The reaction rate and carbon dioxide concentration calculated for comparability in fractions of a unit. This data representation is not tied to the number of components, it allows you to get kinetic results that can be used for various reactors while maintaining the flow coefficients.

$\ln K$ was calculated and the order of the reactions shown in Table 1 was determined, and the logarithm of the constant of the calcination rate of FeS and Cu₂S in the pulsating layer versus the reciprocal temperature were plotted as shown in Figure 4.

Table 1 Results of roasting of FeS and Cu₂S for calculations according to the Arrhenius equation

T/°C	T/K	1/T*10 ⁴	FeS		Cu ₂ S	
			Ln K	n	Ln K	n
500	773	12,937	3,0404	0,701	3,9455	0,932
550	823	12,151	2,889	0,816	3,809	1,083
600	873	11,455	2,7517	0,673	3,607	1,057

In contrast to the process of roasting iron sulfide, which stops at 500 °C in 20 - 25 minutes, when roasting copper sulfide, carbon dioxide is released for the selected weights and experimental conditions for 90 - 120 minutes. Correspondingly, the degree of conversion of copper sulfide during roasting according to sulfide-soda-sulfate technology is significantly higher compared to iron sulfide, and the results of experiments on roasting in a pulsating layer confirm the previously obtained

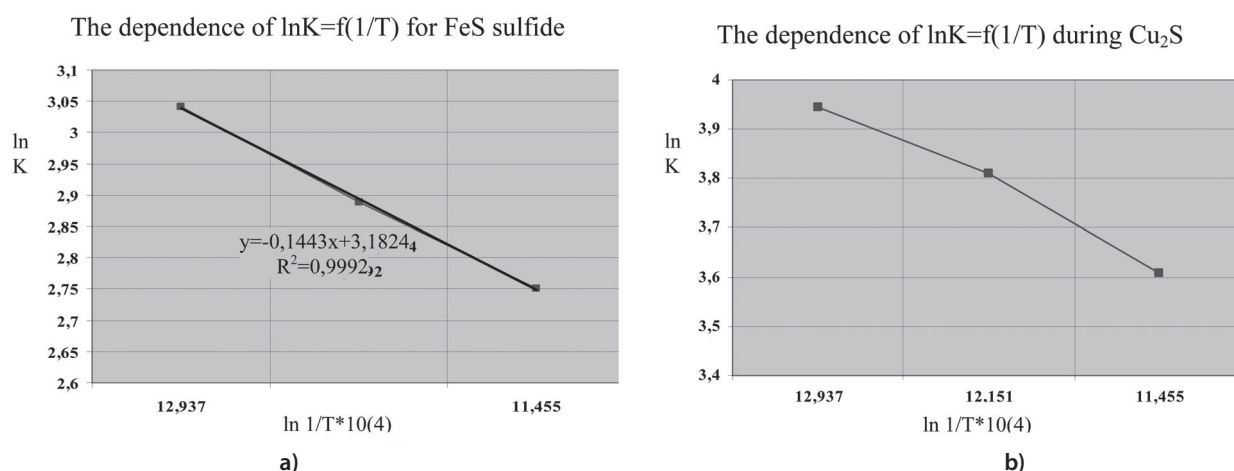


Figure 4 Dependence of the logarithm of the roasting rate constant of a) FeS and b) Cu₂S in the pulsating layer on the reciprocal temperature.

results for roasting sulfides and granular charges of sulfide concentrates in the filter layer.

Similar to the oxidation of iron sulfide, the oxidation of copper sulfide in the presence of soda is limited by diffusion. An increase in temperature also increases the speed of the process and the degree of conversion, but also in the conditions of a pulsating layer, the diffusion of reagents and primarily the oxidizing agent determines the speed of the roasting process as a whole.

Intensification of roasting is possible by increasing air flow or increasing the oxygen content in the blast, but it is necessary to exclude sintering and melting of the cinder due to the excess heat of exothermic reactions in the layer.

Therefore, for various scales of roasting, the operating parameters including the ratio of the amount of charge and oxygen-containing blast should be determined from the heat balance for the roasting apparatus used.

CONCLUSION

The kinetics of roasting of the main components of copper concentrates — iron and copper sulfides with weighed portions of sulfides $5 \cdot 10^{-3}$ kg, air flow rate $(5-8) \cdot 10^{-3}$ m³/h with dilution of the sample with an inert material (alumina) was studied. The obtained values of the apparent activation energy in the temperature range 500 – 550 - 600 °C indicate the diffusion mechanism of sulfide burning in the presence of sodium carbonate. The use of a vibropulsing layer provides intensive mix-

ing of the charge during roasting, preventing sintering. In this case, the dust removal from the layer did not exceed 0,5 %.

Acknowledgements

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Note: The responsible for English language is Bekzat Abdikerim, Almaty, Kazakhshtan