MASS TRANSFER DURING SULFUR EXTRACTION

FROM ORES

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A study was made concerning the kinetics of sulfur extraction from ores with kerosene, for the purpose of determining the limiting process stage at temperatures within 120-140°C. The diffusion coefficients within this temperature range have been determined.

The process of extracting a solid substance from porous particles is widely used in various branches of industry: chemical, mining, and hydrometallurgical.

Of interest is the method of extracting sulfur from ores which has been widely used abroad, especially where the sulfur content in the raw material ranges from 8 to 30%.

The excellent solubility of sulfur in various solvents, especially in such an inexpensive one as naphtha, makes it feasible to produce a high-quality (99.8% pure) substance by a 95-99% complete extraction.

The industrial implementation of these processes is closely tied to theoretical studies of the kinetics governing the mass transfer and to an understanding of the material transfer mechanism.

Most studies concerned with the problems of mass transfer in a solid-liquid system deal with the mechanism of material transfer from the solid phase to the liquid phase. Meanwhile, the most important practical systems consist of a solid inert material with the extractable substance distributed in its pores. The process of extraction from porous materials is more complex, of course, because it includes both a material transfer within pores (intramolecular diffusion) and a material movement from the surface of porous particles to the main mass of liquid (external diffusion). Although the material transfer is diffusive in both cases, its mechanism is not the same.

The authors' purpose in this study was to explore the kinetics of sulfur extraction from ores and, on this basis, to determine the diffusion coefficient for pores.

According to the theory of heterogeneous processes, the mechanism of sulfur extraction from ores comprises the following sequence: 1) dissolution of sulfur; 2) migration of the dissolved substance to the solid-liquid interphase boundary (internal diffusion); and 3) transfer of the dissolved substance from the solid surface to the main mass of liquid (external diffusion). Depending on the nature of the extractable substance and of the solvent, on the pore structure, and also on the process conditions, the extraction rate will be governed by one of these three stages. It is necessary to determine which stage limits the process, therefore, because there one will search for ways to improve the yield, for it one will select the appropriate apparatus, etc.

The method in [1] was used for establishing the mechanism of sulfur extraction from ores. The gist of this method is a correlation of test points with various curves based on the equation

$$1 - \varphi_0 + \varepsilon \left(\frac{1}{6} - \frac{\varphi_0^2}{2} + \frac{\varphi_0^3}{3}\right) = \left(1 + \varepsilon \frac{1}{6}\right) \frac{t}{T} .$$
 (1)

L'vov Polytechnic Institute, L'vov. Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 23, No. 2, pp. 304-307, August, 1972. Original article submitted December 13, 1971.

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Fig. 1. Determination of the diffusion coefficient $\Phi = f(t)$ at various temperatures: 1) 100°C; 2) 110; 3) 117; 4) 120; 5) 130; 6) 140. Time t (min).

Here

$$\varepsilon = kR/D$$
.

It follows from Eq. (1) that the critical parameter which determines the extraction mechanism is ε . Thus, as $\varepsilon \rightarrow 0$, the process is governed by the kinetic stage (chemical conversions constitute the slow stage) and the equation becomes

$$1 - \varphi_0 = \frac{t}{T} \ . \tag{2}$$

When $\varepsilon \to \infty$, the process becomes diffusion kinetic (the inflow and the outflow of reagents constitute the slow stage) and the equation becomes

$$1 - 3\varphi_0^2 + 2\varphi_0^3 = \frac{t}{T} \,. \tag{3}$$

Experiments for the purpose of accumulating test data on the extraction kinetics were performed with lumps of sulfur ore from the Rozdol'sk deposits, after they had been comminuted down to a 3-5 mm fraction. The average diameter of the test particles was 4 mm. The sulfur content in the ore was 16.7%.

We will assume that the ore particles containing the extractable substance in its pores were spherical in shape. During extraction there occurred a gradual contraction toward the center of a sphere with the radius r_0 and full of the extractable substance.

The test procedure was as follows.

Into a vessel wrapped in a heating jacket and containing 6 liters of kerosene we poured a measured quantity of ore particles. The contents of the vessel were then fast mixed with stirrer blades (n = 350 rpm).

The tests were performed at constant temperatures within the 100-140°C range. The temperature was maintained constant throughout each test by passing a thermostaticized liquid through the heating jacket.

At definite time intervals, samples were taken from the vessel for subsequent filtering and cooling down to $t = 20^{\circ}C$. The sulfur extract from the sediments was weighed.

The test results are shown in Fig. 1.

We will assume now that internal diffusion is the limiting stage of the extraction process. Then, according to (3), the quantity $\Phi = 1/6 - \varphi_0^2/2 + \varphi_0^3/3$ must be a linear function of time t. It is evident from Fig. 1 that this is, indeed, so. It appears feasible, therefore, to determine the diffusion coefficients from the slope $(\tan \alpha)$ of the straight lines, considering the equation derived in [2]:

$$\frac{\beta\rho_{0}}{\Delta c}\left(\frac{1}{6}-\frac{\varphi_{0}^{2}}{2}+\frac{\varphi_{0}^{3}}{3}\right)=\frac{Dt}{R^{2}}$$
(4)

When $c_S \gg c$, Eq. (4) yields

$$tg\,\alpha = \frac{Dc_s}{\rho_0 R^2 \beta}\,.\tag{5}$$

The diffusion coefficient as a function of the temperature, $D = f(\theta)$, is shown in Fig. 2.

As the temperature rises, according to Fig. 2, the diffusion coefficient first increases very slightly and then, within 117-120°C, it jumps up. The anomalous changes in the diffusion coefficient correspond to temperatures at which solid sulfur becomes liquid and, thus, the mechanism of material transfer changes.

In order to explain the mechanism of material transfer within porous particles, test data are shown in Fig. 3 along with theoretical curves which have been plotted on the basis of Eqs. (2) and (3), respectively.



Fig. 2. Diffusion coefficient as a function of the temperature.

Fig. 3. Kinetics of sulfur extraction from ores with kerosene: 1) 100°C; 2) 110; 3) 117; 4) 120; 5) 130; 6) 140. Theoretical curves: I) according to Eq. (2); II) according to Eq. (3).

A comparison between experimental and theoretical data indicates that the process of sulfur extraction from ores is intradiffusive.

The dimensionless radius φ_0 corresponding to some definite instant of time t is found from the equation of material balance

$$G_0\left(1-\varphi_0\right) = Wc. \tag{6}$$

It follows from the preceding discussion that at temperatures above 120°C sulfur diffuses fast through a porous ore structure filled with kerosene. This can be utilized for a highly efficient extraction of sulfur on an industrial scale.

NOTATION

K	is the reaction rate constant;
R	is the radius of spherical particle;
$\varphi_0 = r_0 / R$	is the dimensionless radius;
r_0	is the radius of sphere containing the extractable substance;
r	is the radial coordinate;
D	is the diffusion coefficient;
t	is the time coordinate;
Т	is the time of complete extraction, corresponding to $\varphi_0 = 0$;
ρ_0	is the density of ore;
G ₀	is the total mass of extractable substance in porous particles;
W	is the volume of solvent in the vessel;
c	is the concentration of dissolved sulfur in the vessel;
β	is the sulfur content per unit mass of ore;
$\Delta \mathbf{c} = \mathbf{c}_{\mathbf{S}} - \mathbf{c}$	is the motive force;
cs	is the saturation concentration;
θ	is the temperature.

LITERATURE CITED

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