

KINETICS AND MECHANISM OF PYRITE OXIDATION

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ABSTRACT

This paper reports the results attained by experimental research for determination of the mechanism of the pyrite oxidation process under non-isothermal conditions. Kinetic parameters of the process were determined according to the relationships of Kissinger and Ozawa.

INTRODUCTION

The subject of pyrite oxidation has been studied mostly by thermal analysis methods, and various different results are given in the literature. Paulik et al. [1] and Berg et al. [2] report exothermic effects on the DTA curve in the course of pyrite oxidation: the first at a temperature of 450–480 °C, the second at 530–570 °C and the third at 630–690 °C. These transformations are interpreted in different ways [3], but without exact details, thus indicating that the process mechanism has not been defined adequately.

Experimental results on determination of the oxidation mechanism of natural pyrite from a deposit of copper-bearing mineralization at Bor (Yugoslavia) are presented in this paper. Kinetic parameters for the previously defined mechanism were determined under non-isothermal process conditions.

EXPERIMENTAL DETAILS

To obtain the results presented in this paper, a sample of well crystallized pyrite from a natural deposit with 0.5% of quartz and 0.4% of Cu was used.

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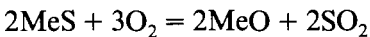
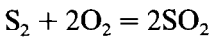
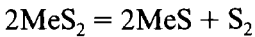
The experiments were carried out on the Derivatograph 1500 thermoanalytical device (developed by the Hungarian company MOM) in an air atmosphere, and mineralogical characterization was effected on Siemens X-ray equipment with a Cu anticathode and an Ni filter at an average voltage of 40 kV and electrical current intensity of 18 mA.

RESULTS AND DISCUSSION

Figure 1 shows the X-ray diagram for the examined pyrite sample, which exhibited cubic crystallization with clearly defined reflections which matched well with those of an ASTM standard. Some impurities of quartz and copper sulphides are present at trace level, and therefore not recorded on the X-ray diagram.

The pyrite sample was comminuted in an agate mill to a particle size below 74 μm . The sample so prepared was used for oxidation in an air atmosphere at different heating rates. The obtained DTA, TG and DTG curves are presented in Fig. 2. The results indicate that exothermic effects are obtained at temperatures of 450, 490 and 550 $^{\circ}\text{C}$ at a heating rate of 10 $^{\circ}\text{C min}^{-1}$.

Starting from a general mechanism of the sulphide oxidation process



on the basis of the results obtained for the pyrite oxidation process, as shown in Fig. 2, at a temperature of 460 $^{\circ}\text{C}$ the first (I) exothermic effect on

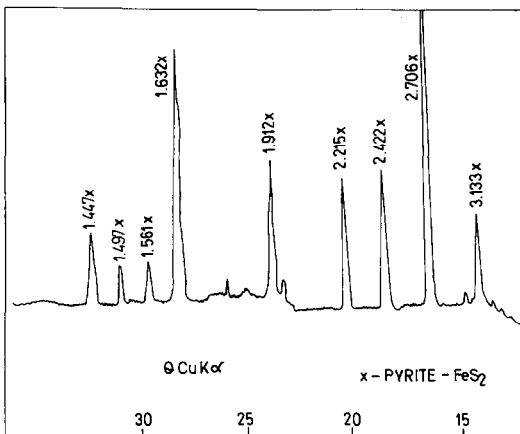


Fig. 1. X-ray diagram for the pyrite sample examined.

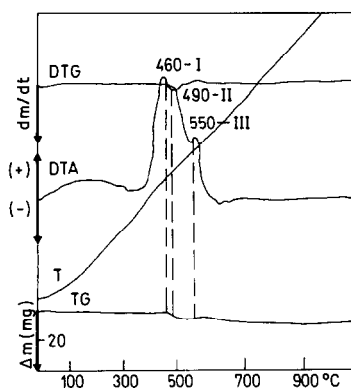
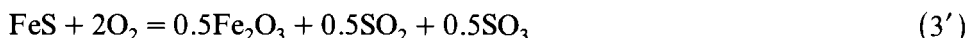
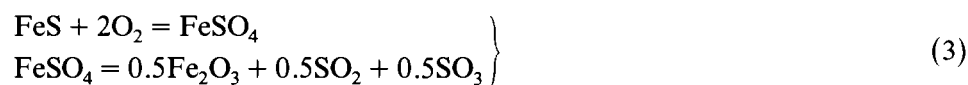
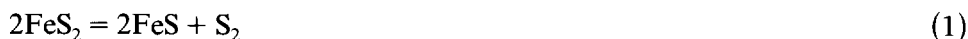


Fig. 2. DTA, TG and DTG curves for pyrite treated in an air atmosphere at a heating rate of $10^{\circ}\text{C min}^{-1}$.

the DTA curve occurs, but no change of sample mass is observed at this point on the TG curve. This clearly indicates that dissociation of the pyrite has taken place, whereby extracted elementary sulphur remains on the surface of the pyrite particles. After that, oxidation of sulphur begins, and causes the occurrence of the second peak (II) on the DTA curve. At the same time there is a loss of mass on the TG curve owing to SO_2 gas extraction. It is important to note that process II starts before the end of process I, so there is a partial overlap on the DTA curve. In the course of further heating at a temperature of 550°C , the third exothermic peak (III), which corresponds to sulphate formation, occurs on the DTA curve. Sulphate formation is indicated by an increase of the mass of the examined sample on the TG curve and by its further transformation into Fe_2O_3 , with extraction of gaseous components of SO_2 and SO_3 . This process is shown by the overall reaction (3'). The process mechanism of pyrite oxidation can be thus presented as



The pyrite sample examined was subjected to oxidation in an air atmosphere at different heating rates from 7°C to $20^{\circ}\text{C min}^{-1}$ under the same conditions, and the results obtained for the maximum dependence on the heating rate in the DTA curve are shown in Fig. 3.

The experimental results obtained for pyrite oxidation at different heating rates were treated according to the methods developed by Kissinger [4] and Ozawa [5] in order to determine kinetic parameters for the processes I, II

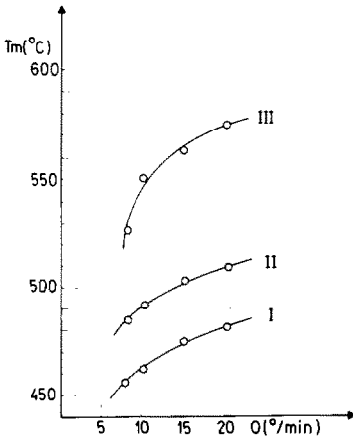


Fig. 3. Dependence of T_m on heating rate for the processes taking place in the course of pyrite oxidation.

and III that take place in the course of pyrite oxidation in an air atmosphere. Figure 4 shows the dependences $\ln(\phi/T_m) = f(1/T_m)$ and $\ln \phi = f(1/T_m)$, where ϕ is the heating rate and T_m is the temperature of the maximum on the DTA curve.

On the basis of these results, the corresponding values for activation energy E and the integration constants C and C_1 have been calculated for the studied processes of natural pyrite oxidation which were presented in Table 1.

The results obtained indicate that, in the course of pyrite oxidation, dissociation of a hexagonal FeS troilite structure and sulphur monoclinic structure takes place. This leads to vacancies at Fe positions within the formed troilite structure. The defective troilite structure so formed is more unstable compared with the pyrite cubic lattice, which facilitates its

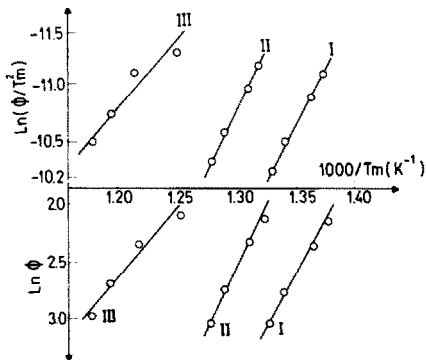


Fig. 4. Dependences $\ln(\phi/T_m) = f(1/T_m)$ and $\ln \phi = f(1/T_m)$ for the pyrite oxidation processes.

TABLE 1

Calculated values for activation energy E and integration constants for the processes of pyrite oxidation

Process	Method			
	Kissinger		Ozawa	
	E (kJ mol ⁻¹)	C	E (kJ mol ⁻¹)	C_1
I	160	4.2×10^6	182	9.2×10^{13}
II	406	7.9×10^{22}	490	9.4×10^{34}
III	95	18.69	114	2.2×10^8

oxidation and the insertion of oxygen in vacant places within the troilite lattice. Sulphur oxidation, as a typical exothermic process, has an increased value of the activation energy E ; a subsequent troilite oxidation to Fe_2O_3 , with intermediate formation of FeSO_4 , causes a decrease in values of the activation energy due to the gradually more marked diffusion resistances which are caused by transformations within the lattice, since the Fe_2O_3 structure is identical with the corundum lattice structure.

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