

KINETICS AND MECHANISM OF ARSENIC SULFIDES OXIDATION

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Abstract

The kinetics of oxidation process of realgar and orpiment natural mineral mixture was studied under non-isothermal conditions. The proposed reaction mechanism and chemical transformation investigated by SEM-EDX, XRD and thermal analysis, are discussed. Using mathematical modeling on results obtained during analysis in non-isothermal conditions, activation energy of this process was determined.

Keywords: Thermal analysis; Activation energy; Realgar; Orpiment.

1. Introduction

Though known since ancient times [1,2] the As-S system is a subject of interest for numerous researchers. The reason for this is the insufficient consideration of the mechanisms of the oxidation reactions occurring in this system, as well as a lack of

complete databases with thermodynamic and kinetic parameters describing the oxidation processes of compounds from this system. It should also be mentioned that the literature data for temperatures significant for describing the oxidation mechanism differ depending on the source [3].

Knowing the behavior of the arsenic

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sulfides is important from the aspect of their genesis, mostly because arsenic sulfides are common constituents in almost all mineral deposits of nonferrous ore bodies. Knowing the As transport in the active geothermal field is important to understand the potential form of occurrence of its sulfide minerals. Reaction path modeling in the As-S system was investigated by Claverlay et al [4]. The object of their investigation was zonal mineral precipitation of As sulfide and As transport in an active geothermal field. Features relative to natural genesis were revealed as well as the synthesis of arsenic sulfides.

Since most of the arsenic sulfides present in the nonferrous ores is difficult to remove using differential flotation procedures, most of the arsenic is remaining in final concentrate which will be further processed using pyrometallurgical treatment [5]. Since most of the arsenic compounds are highly evaporative their potential to leave the reactor during pyrometallurgical processing is considerably high [6], this is why the other aspect, which is of same importance as the arsenic sulfides genesis, is understanding the behavior of arsenic sulfides during the pyrometallurgical treatment of nonferrous concentrates [7,8]. Since ecological aspects of technological processes are becoming the most important parameters, which should be considered during evaluation of existing or development of new technologies for pyrometallurgical nonferrous metals extraction [9,10], toxicity of arsenic and its compounds is another reason why their behavior should be completely familiar [11,12]. To understand the behavior of arsenic sulfides in complex metallic systems

such are: Cu-As-S, Zn-As-S, Fe-As-S, or their combination, it is important to obtain relevant data considering the thermal behavior of the As-S system under oxidative conditions. A number of authors studied natural as well as synthetic realgar (As_2S_2), also present in the literature with the formula AsS or As_4S_4 . The degree of dissociation of arsenic sulfide (AsS) was determined by measuring the vapor pressure change with temperature [13]. The sulfide was synthesized by heating chemically pure elements at 500–600 °C for 2 h. After homogenization under vacuum at 300–320°C, the compound contained 70.18% of As. The mechanism of oxidation of the most important compounds in As-S system were presented in [3,14].

The present research consists of a kinetic study of the non-isothermal oxidation of natural mixture containing the realgar and orpiment mineral forms. The main aim was to determine the kinetic parameters, as well as the mechanism of oxidation of this mixture, as the base for further investigations of their behavior in the complex metallic systems, characteristic for the nonferrous metallurgy.

2. Experimental

A sample of natural mineral mixture, from the Trepča mine, ore body Stari Trg, Serbia, was used in the investigation. X-Ray analysis was performed in order to characterize the starting sample. The phase composition was determined using a Siemens X-ray diffractometer with a Cu anticathode and Ni filter at a voltage 40 kV and current of 18 mA. Analyses, including

energy dispersive X-ray fluorescence (EDXRF) coupled with scanning electron microscopy (SEM), were used to determine the composition of the starting samples. Energy Dispersion X-ray Fluorescence analysis was done on Canberra equipment with the radioisotopes: Cd-109 (22.1 keV) and Am-241 (59.5 keV).

The non-isothermal oxidation process was investigated using the results of differential thermal analysis (DTA). A thermal analysis Derivatograph 1500 (MOM Budapest) was used, operating under the following conditions: air atmosphere, heating rate of 20 °C/min and $T_{\max} = 1273$ K.

3. Results and Discussion

Results of the X-ray analysis of the starting sample are presented in Fig. 1, while the results of the X-ray analysis of the sample heated at 700°C are presented in the

Fig. 2.

The peaks of the starting sample diffractogram (X-ray), Fig. 1, are in the area characteristic for minerals realgar and orpiment; besides those two main minerals only quartz and pyrite (FeS_2) were detected. Figure 2 is presenting the results of X-ray analysis for the investigated samples heated at 700°C. On this diffractogram the products of oxidation were detected. Arsenic sulfides were oxidized to As_2O_3 and pyrite to Fe_2O_3 .

Results of the SEM-EDX analysis are presented in the Figure 3, while the results of the chemical composition of two spots indicated in Figure 3, are presented in the Table 1.

The results presented in Table 1 show that the starting sample, in point 2, contain 67.5% As which is in stoichiometry range of As_2S_2 (realgar) [3]. The composition of point 1, when sulfur from FeS_2 is subtracted, is equivalent to the As_2S_2 (realgar) and As_2S_3 (orpiment) mixture. Two investigated spots

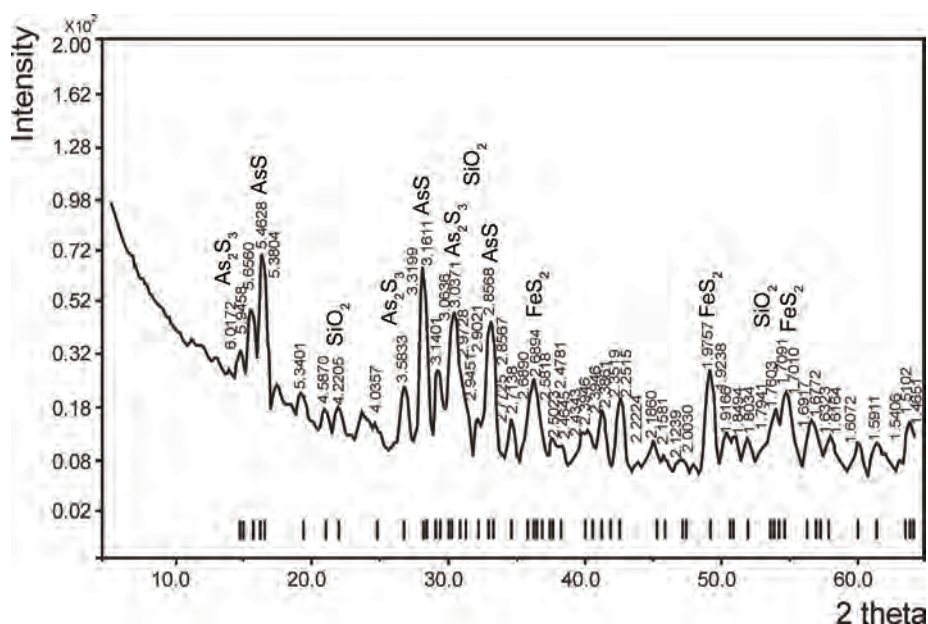


Fig. 1. Results of the X-ray analysis of the starting sample

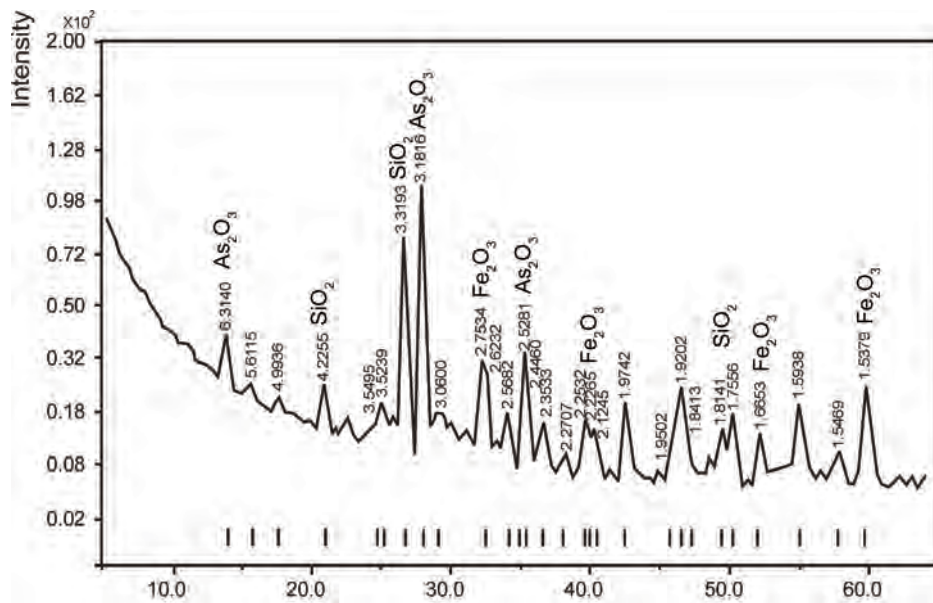


Fig. 2. Results of the X-ray analysis of the sample heated at 700°C

didn't revealed SiO_2 content. Since SiO_2 is present in the sample, according to the results of X-ray analysis, only possibility is that it is located in white polygons in Fig. 3, which were not subjected to spot analysis.

Results of DTA analysis are presented in Fig. 4. The DTA results show the existence of a first set of two connected exothermal peaks in the temperature range 260–330 °C. The third and fourth exothermal peaks starts at 580°C and ends at 745°C and they are also connected as second set of peaks. Both sets of exothermal peaks are representing two parallel processes. First set of exothermal peaks is presenting the parallel oxidation of two arsenic sulfides to As_2O_3 . Most of the produced arsenic oxide is evaporating as As_4O_6 . Since there is amount of crystalline As_2O_3 detected at X-ray diffractogram obtained at 700°C, it can be concluded that small amount of this compound remains captured in the core of the investigated samples grains. The second set of exothermal

peaks is also presenting the combination of two processes. First process, which culminates at 584.3°C is representing evaporation of remaining arsenic sulfides and their oxidation in gaseous phase to As_4O_6 [3], while the second process is

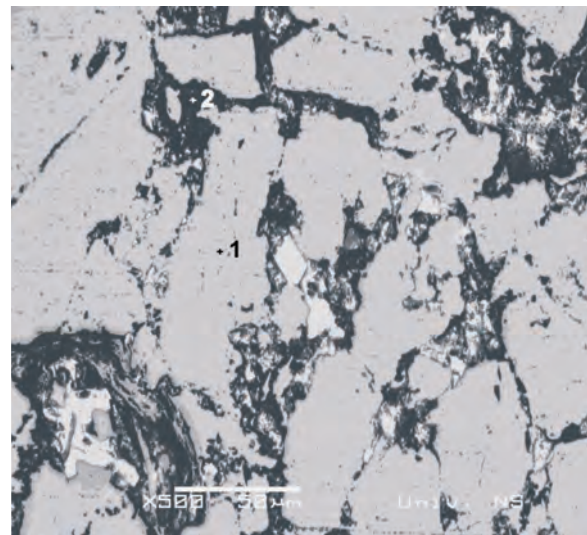


Fig. 3. SEM-EDX analysis of the starting sample (1 and 2 are points included in spot analysis of the sample)

Table 1. Results of the chemical composition obtained using spot analysis of the sample

Spots	Spot composition, %			
	As	S	O	Fe
1	65.03	28.42	4.51	2.03
2	67.5	32.5	-	-

representing oxidation of pyrite to Fe_2O_3 and it culminates at 645.4°C [14,15].

According to the character of the investigated process in the investigated As–S–O system, which results in the corresponding shape of the DTA–TG–DTG curves, Fig. 4, it is possible, using the non-isothermal model of Borchardt and Daniels [16], to determine the activation energy of oxidation, in both characteristic temperature ranges. First temperature range is $260\text{--}330^\circ\text{C}$, with two characteristic peaks, and the second one is $580\text{--}745^\circ\text{C}$, also with two characteristic peaks. Using equation $k_i = T_i/A - a_i$, which is the essence of the Borchardt and Daniels model (where A is the area of the peak present on the

DTA–TG–DTG curve, a_i – the areas of the peaks segments and T_i – the temperature interval of the segments) the rate constants k_i were determined for different temperature intervals. According to this data, an Arrhenius diagram was constructed, Fig. 5. and Fig. 6.

Using the diagram in Figs. 5-6, the activation energy was calculated and found to be 101 kJ/mol and 110 kJ/mol , for the first characteristic set of exothermic peaks. The values of 77 kJ/mol and 68 kJ/mol were calculated for the second set of exothermic peaks, which are all in the kinetic domain according to the classical kinetic theory [17,18].

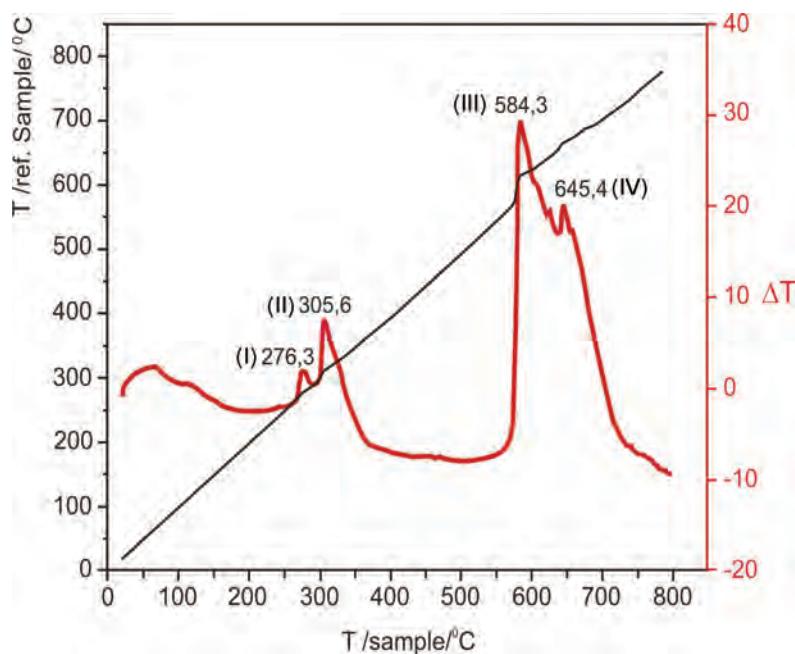


Fig. 4. Results of the DTA analysis of the starting sample

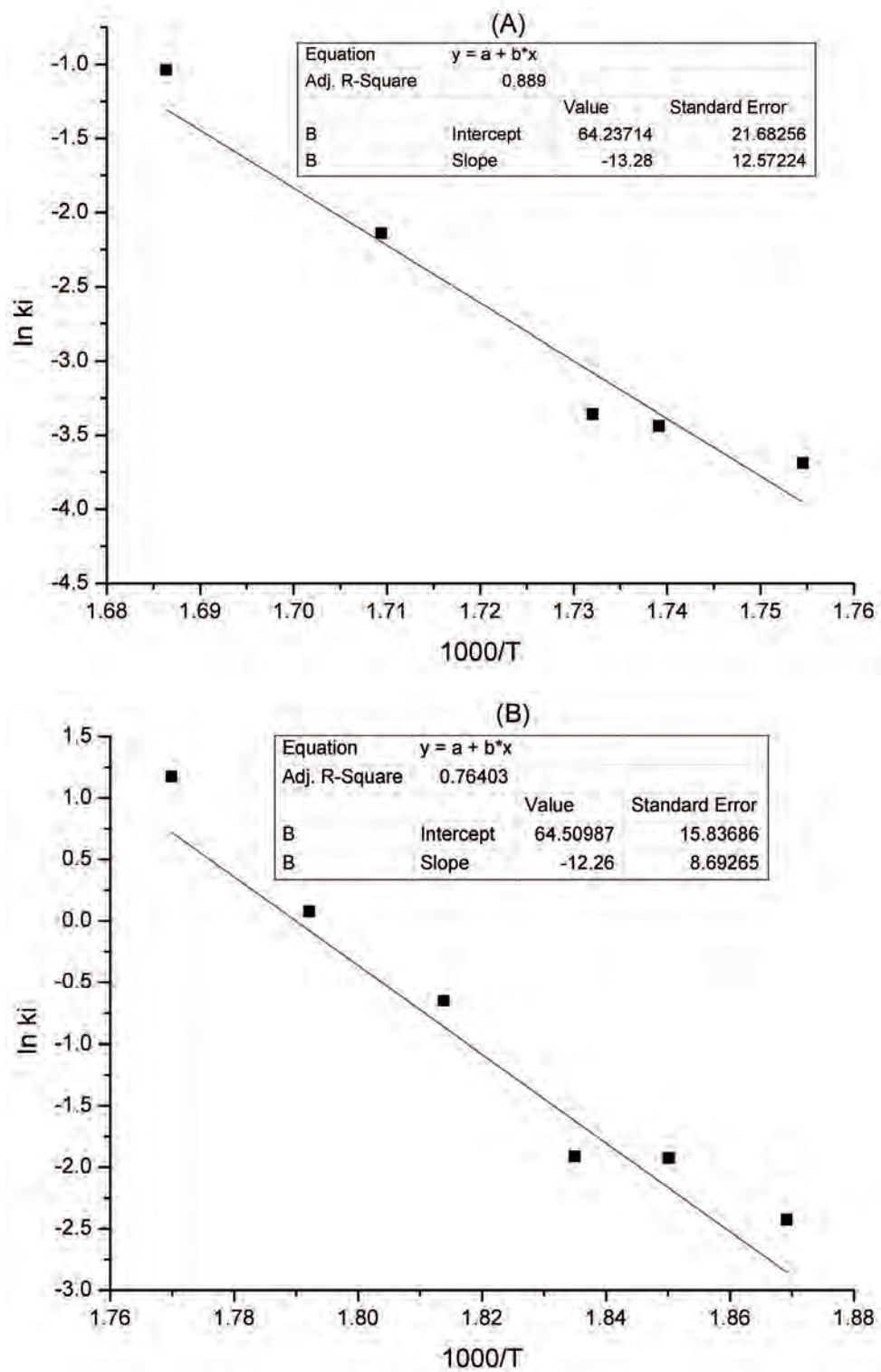


Fig. 5. Arrhenius diagrams for the investigated process
(a) first, (b) second peak on the DTA curve

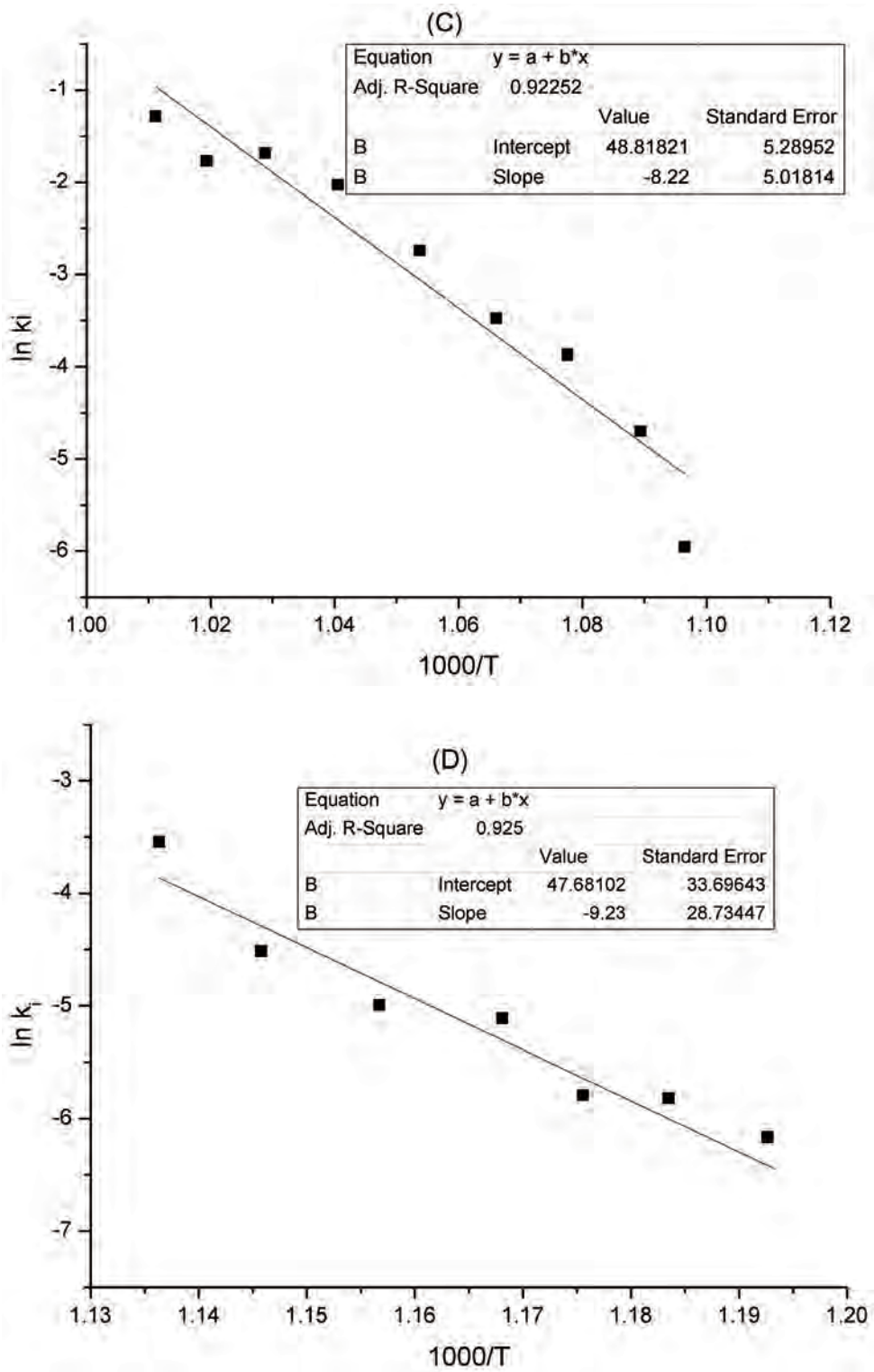


Fig. 6. Arrhenius diagrams for the investigated process (c) third and (d) fourth peak on the DTA curve

4. Conclusions

In the first part of this paper, analysis of arsenic sulfide mixture, obtained from the Trepča mine, Serbia, was performed. According to the mineralogical investigations, coupled with SEM EDX analysis, this mixture of arsenic sulfides was determined to be mixture of realgar and orpiment minerals. In the second part of the paper, the oxidation of this mixture was analyzed in the non-isothermal conditions, based on the DTA results. According to this analysis, oxidation of investigated samples is happening in two characteristic stages. First stage is beginning at 260 and it ends at 330°C. In this stage, oxidation of two arsenic sulfides is carried out. Both As_2S_2 and As_2S_3 are oxidized to As_2O_3 . Since As_2O_3 is highly evaporative, it mostly evaporates in the form of As_4O_6 (g). Small amount of this compound is remaining captured in the core of the investigated samples grains, even at higher temperatures, as revealed using X-ray at 700°C. The second stage of oxidation is beginning at 580°C and it ends at 745°C. At this stage there are also two characteristic peaks. First peak, at 584.3°C, is presenting sublimation of remaining arsenic sulfides and their oxidation in the gaseous phase, and the second one is corresponding to oxidation of FeS_2 to Fe_2O_3 .

According to the Borchard and Daniels method, activation energies of arsenic sulfide mixture oxidation process, described above, are placing all the reactions in the kinetic area.

Oxidation of arsenic sulfides is happening fast with very high values of activation energies. Sublimation of arsenic sulfides and

FeS_2 oxidation are to some extent slower processes, nevertheless, those processes are also happening in the kinetic area.

The results presented in this paper should be useful as the addition to the data base considering kinetic parameters of the arsenic sulfides oxidation process, which is the subject of interest for large number of researchers around the world.

Also, these results are the bases for further investigations of arsenic sulfides behavior, as the part of nonferrous metals concentrates, during their pyrometallurgical treatment.

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