Journal of Thermal Analysis and Calorimetry, Vol. 59 (2000) 869–875

KINETICS OF THERMAL DECOMPOSITION OF PLUMBO-JAROSITE

M. Özacar[1*]*, A. Alp*[2] *and A. O. Aydin*[1]

[1]Department of Chemistry, Science and Arts Faculty, Sakarya University, 54100 Serdivan-Sakarya
[2]Department of Metallurgy, Engineering Faculty, Sakarya University, 54040 Esentepe Campus-Sakarya, Turkey

(Recevied December 6, 1998; in revised form June 15, 1999)

Abstract

An investigation was carried out on the kinetics of thermal decomposition of plumbo-jarosite. The kinetic models of dissociation of the compounds in the ore were identified. The results of the kinetic studies and the mechanism of the process are discussed. The thermal decomposition of plumbo-jarosite occurs in three stages: the first up to 763, the second up to 1023 and the third up to 1223 K, the corresponding activation energy values being 62.2, 60.3 and 98.0 kJ mol^{-1}, respectively.

Keywords: decomposition, kinetics, plumbo-jarosite

Introduction

Plumbo-jarosite is a mineral in the jarosite group, which have the general formula $AB_3(XO_4)_2(OH)_6$; plumbo-jarosite has the formula $Pb[Fe_3(SO_4)_2(OH)_6]_2$ [1, 2]. This mineral exists in substantial deposits in Mugla, Elazig, Amasya, Içel and Nigde in Turkey. Recent studies on plumbo-jarosite dealt with geological and analytical aspects [3, 4].

The mineral from Bolkardagi was earlier calcined and reacted with sulphuric acid, hydrochloric acid, acetic acid, potassium hydroxide and sodium chloride solutions in order to determine its solubility [4]. This mineral has been shown to contain 2.14%, SiO_2, 1.8% CaO and 1.72% MgO as impurities. The thermal decomposition of the mineral has been investigated by DTA and TG, and X-ray diffraction methods have also been carried out [5].

The objective of the present study was to establish the kinetics of thermal decomposition of the mineral plumbo-jarosite under atmospheric conditions.

Experimental

The plumbo-jarosite sample used in these studies was obtained from Bolkardagi-Nigde. The material was cleaned and ground to 200 mesh. The H_2O, PbO, SiO_2 and

---

* Author for correspondence: e-mail: mozacar@hotmail.com; fax: 00-90-264-2762059

1418–2874/2000/ $ 5.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

SO_3 components in the sample were analysed by gravimetry. CaO, MgO and Fe_2O_3 were estimated by complexometry with EDTA [6]. The chemical composition of the ore is given in Table 1.

Table 1 The chemical composition of the ore plumbo-jarosite

Components/%								Total
SiO_2	PbO	Fe_2O_3	CaO	MgO	SO_3	H_2O	Other	
2.14	21.79	42.72	1.80	1.72	21.39	8.20	0.24	100.0

The kinetic measurements were carried out isothermally in the temperature ranges 437–763 K (first stage), 763–1023 K (second stage) and 1023–1223 K (third stage). The measurements allowed appropriate selection of the kinetic equations and determination of the parameters of the processes.

Results and discussion

The starting material for the first stage of the decomposition was plumbo-jarosite dried to constant mass at 378 K. Samples were subjected to thermal decomposition under atmospheric conditions at temperatures of 473, 523, 573, 623, 673 and 723 K.

In the second stage, the starting material was plumbo-jarosite after decomposition by ignition to constant mass for 5 h at 763 K. Samples of this material were subjected to thermal decomposition at temperatures of 773, 823, 873, 923, 973 and 1023 K.

In the third stage, the starting material was plumbo-jarosite ignited previously for 5 h at 1003 K. The kinetic measurements were made at 1023, 1073, 1123, 1173 and 1223 K.

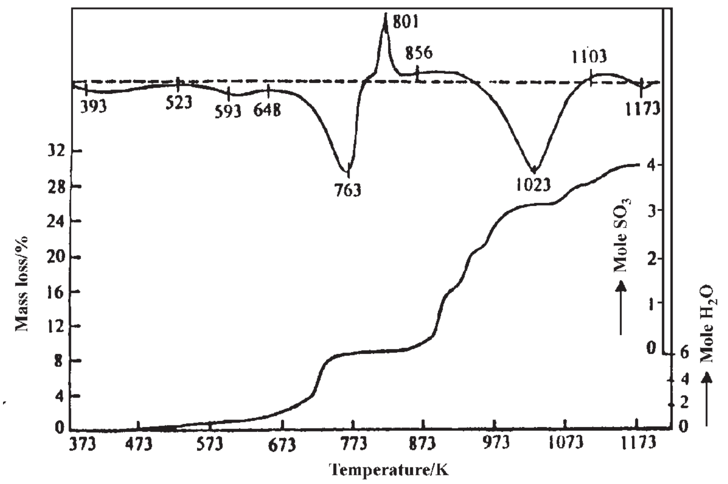

Fig. 1 TG-DTA curves of plumbo-jarosite

The reactions that occur during the thermal decomposition of plumbo-jarosite $[PbSO_4.Fe_2(SO_4)_3.4Fe(OH)_3]$ in these three stages are

$$\text{at 473–763 K: } 4Fe(OH)_3 \rightarrow 2Fe_2O_3+6H_2O \quad (1)$$

$$\text{at 763–1023 K: } Fe(SO_4)_3 \rightarrow Fe_2O_3+3SO_3 \quad (2)$$

$$\text{at 1023–1223 K: } PbSO_4 \rightarrow PbO+SO_3 \quad (3)$$

The TG-DTA curves of the thermal decomposition of plumbo-jarosite are given in Fig. 1 to explain the mechanism suggested by Eqs (1)–(3). As may be seen from Fig. 1, the mechanism suggested by Teberdar *et al.* [5] is confirmed by the results obtained from the TG-DTA curves for plumbo-jarosite.

The transformation degree was determined from the relation

$$\alpha=\frac{\Delta m_t}{\Delta m_{max}}$$

where Δm_t mass loss of the sample after time t, and Δm_{max} maximum loss in mass of the sample in the given stage of decomposition.

Figures 2–4 present the results obtained in 3 experimental series corresponding to the individual stages of thermal dissociation of plumbo-jarosite: the preliminary dehydration of $Fe(OH)_3$ at 473–763 K, the decomposition of $Fe_2(SO_4)_3$ at 763–1023 K, and the decomposition of $PbSO_4$ at 1023–1223 K.

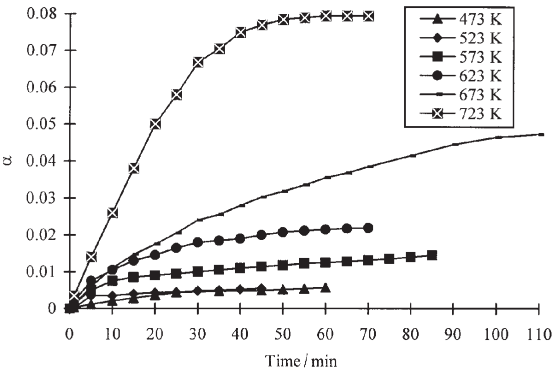

Fig. 2 Kinetic curves of first stage of thermal decomposition of plumbo-jarosite

The calculations showed that the results of the kinetic studies on the thermal dissociation of plumbo-jarosite may be described in all three stages with the aid of the equation derived by Jander [7–10]:

$$[1-(1-\alpha)^{1/3}]^2=kt \quad (1)$$

or that of Ginstling and Brounstein:

$$1-2/3\alpha-(1-\alpha)^{2/3}=kt \quad (2)$$

where α – degree of transformation, t – time in min and k – rate constant in min^{-1}.

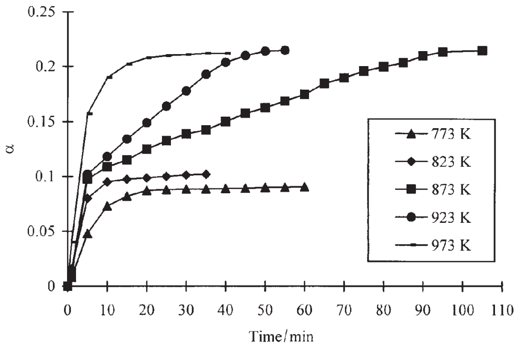

Fig. 3 Kinetic curves of second stage of thermal decomposition of plumbo-jarosite

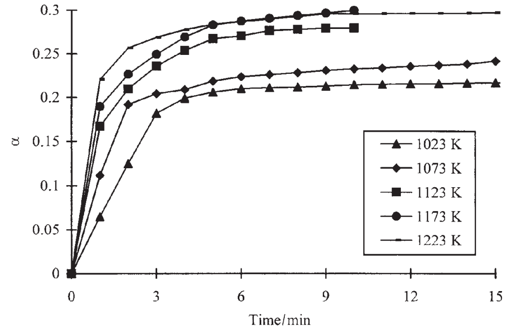

Fig. 4 Kinetic curves of third stage of thermal decomposition of plumbo-jarosite

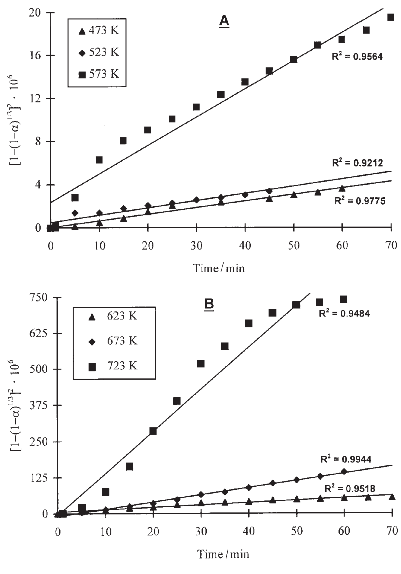

Fig. 5 Plot of $[1-(1-\alpha)^{1/3}]^2$ *vs. t* for first stage of decomposition of plumbo-jarosite

The Jander equation was compared with the Ginstling and Brounstein equation by using the method of Sharp *et al.* [11] for the experimental data. It was found that the Jander equation was the better kinetic model for the thermal decomposition of plumbo-jarosite.

The variations in $[1-(1-\alpha)^{1/3}]^2$ with time for different temperatures are shown in Figs 5–7. The values of k were calculated from the slopes of each straight line by using the linear regression (least squares) analysis method. The values of k obtained from Figs 5–7 are given in Table 2.

The change in ln$k$ with $1/T$ is shown in Fig. 8. The removal of 6 moles of H_2O as seen in reaction 1 and Fig. 1, due to the dehydration of $Fe(OH)_3$, continues up to 763 K. The values of the activation energy (E) and pre-exponential factor (A) from the Arrhenius diagram (Fig. 8) for the first stage are 62.231 kJ mol^{-1} and $0.203 \cdot 10^{-3}$ min^{-1}, respectively.

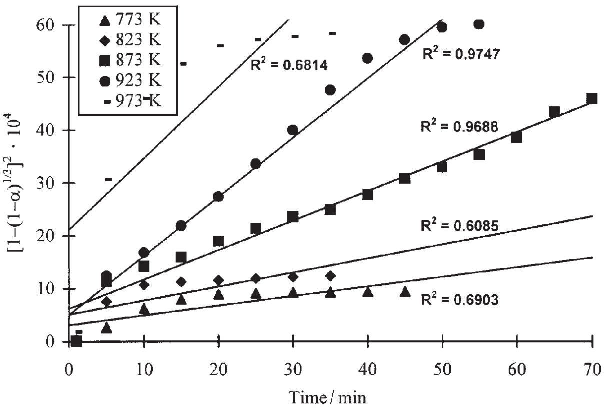

Fig. 6 Plot of $[1-(1-\alpha)^{1/3}]^2$ *vs.* t for second stage of decomposition of plumbo-jarosite

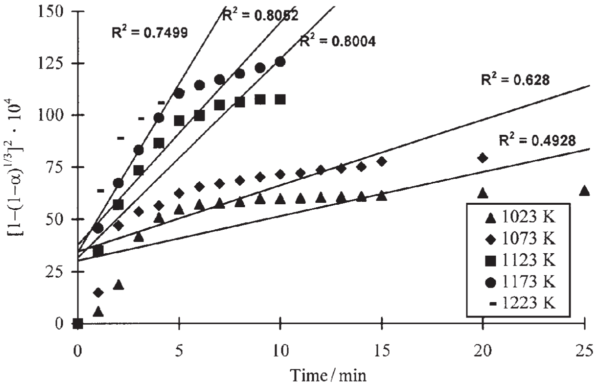

Fig. 7 Plot of $[1-(1-\alpha)^{1/3}]^2$ *vs.* t for third stage of decomposition of plumbo-jarosite

Table 2 Rate constants of dehydration and desulphuration of plumbo-jarosite

	Temperature/K	Jander equation
		Rate constant k/min^{-1}
First stage	473	$6.363 \cdot 10^{-8}$
	523	$6.395 \cdot 10^{-8}$
	573	$2.641 \cdot 10^{-7}$
	623	$8.453 \cdot 10^{-7}$
	673	$2.470 \cdot 10^{-6}$
	723	$1.528 \cdot 10^{-5}$
Second stage	773	$2.108 \cdot 10^{-5}$
	823	$2.839 \cdot 10^{-5}$
	873	$5.629 \cdot 10^{-5}$
	923	$1.145 \cdot 10^{-4}$
	973	$1.443 \cdot 10^{-4}$
Third stage	1023	$1.665 \cdot 10^{-4}$
	1073	$2.417 \cdot 10^{-4}$
	1123	$7.418 \cdot 10^{-4}$
	1173	$8.169 \cdot 10^{-4}$
	1223	$9.288 \cdot 10^{-4}$

The rate of the process is controlled by the diffusion of a gaseous reaction product (H_2O) through the layer of solid product formed on the substrate grains [12, 13]. The activation energy value reveals that the process is controlled by diffusion.

In the second stage, the effect of diffusion is much more distinct, probably in consequence of the increased thickness of the layer of solid reaction product (Fe_2O_3).

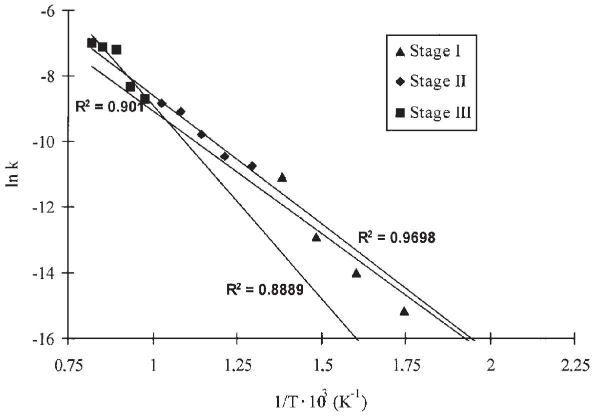

Fig. 8 Plots of ln$k$ *vs.* $1/T$ for decomposition of plumbo-jarosite

The values of the activation energy (E), 60.338 kJ mol^{-1}, and pre-exponential factor (A), 0.235·10^{-3} min^{-1}, may be accounted for by the diffusional nature of the process.

The desulphuration of $PbSO_4$ occurs in the third stage of the decomposition of plumbo-jarosite. The activation energy (E) and pre-exponential factor (A) are 98.019 kJ mol^{-1} and 0.178·10^{-3} min^{-1}, respectively. The rate of the process is controlled by diffusion (or at least by diffusional kinetics), because of the third stage having a higher activation energy than those of the other stages.

Conclusions

Total dehydration had occurred by 763 K. $Fe_2(SO_4)_3$ and $PbSO_4$ were transformed to Fe_2O_3 and PbO by the liberation of SO_3 in the temperature ranges 763–1023 and 1023–1223 K, respectively.

The resultant product, which contains $PbO\cdot 3Fe_2O_3$ and small amounts of SiO_2, CaO and MgO as impurities may be used as a pigment because it displays different colours depending on the decomposition temperature. Additionally, sulphur trioxide obtained during the decomposition can be used in the production of sulphuric acid or sulphates.

From the results obtained, it may be concluded that the decomposition of the mineral plumbo-jarosite involves the diffusion phase, i.e. the resistance to the diffusion of reaction gas product through the laminar layer of gas which envelopes the particles of solid reagent limits the rate of the process.

References

1 H. Gülensoy and I. A. Şengil, J. Chem. Ind., 31 (1989) 116.
2 J. O. Knizek and H. Fetter, J. Am. Ceram. Soc., 25 (1946) 355.
3 G. A. Khan, I. A. Yakubovic, N. P. Panteleeva and B. A. Agranat, SSSR, Sb. Mosk. Inst. Stali Splavov, 53 (1969) 96.
4 T. Teberdar, H. Gülensoy and A. O. Aydin, J. Sci. Technol., University of Marmara, 3 (1984) 209.
5 T. Teberdar, H. Gülensoy and A. O. Aydin, J. Sci. Technol., University of Marmara, 2 (1985) 76.
6 H. Gülensoy, The basis of complexometry and complexometric titrations, Fatih Publishing House, Istanbul 1984, p. 109 and 133.
7 J. Madarász, G. Pokol, C. Novák, H. Moselhy and S. Gál, J. Thermal Anal., 40 (1993) 1367.
8 Y. Deutsch, Y. Nathan and S. Sarig, J. Thermal Anal., 42 (1994) 159.
9 D. Dollimore, Thermochim. Acta, 203 (1992) 7.
10 A. R. Salvador and E. G. Calvo, Thermochim. Acta, 203 (1992) 67.
11 J. H. Sharp, G. W. Brindley and B. N. Narahari Achar, J. Am. Ceram. Soc., 49 (1966) 379.
12 J. Pysiak and B. Pacewska, J. Thermal Anal., 19 (1980) 89.
13 Z. D. ivković and B. Dobovisek, J. Thermal Anal., 12 (1977) 207.