

## Interaction of $(\text{NH}_4)_2\text{SO}_4$ and $\text{FeSO}_4$ with metal oxides and ferrites

B.S. Boyanov

*University of Plovdiv 4000 Plovdiv, Bulgaria*

(Received 14 June 1993; accepted 4 January 1994)

### Abstract

The interactions of  $(\text{NH}_4)_2\text{SO}_4$  and  $\text{FeSO}_4$  with the oxides of Zn, Cu, Cd, Mg, Ca, Pb, Fe, Al, individually and mixed ferrites of Zn, Cu, Cd have been investigated using DTA, TGA, X-ray phase analysis and Mössbauer spectroscopy. The temperature ranges over which the obtained sulphates are stable have been determined.

The sulphatization effects of  $(\text{NH}_4)_2\text{SO}_4$  and  $\text{FeSO}_4$  have been compared. Their peculiarities under thermal treatment are presented and the optimum sulphatization temperature intervals have been determined.

### INTRODUCTION

The sulphatization process is one of the effective methods for complex and deep processing of zinc and lead cakes, pyritic calcines and powders of non-ferrous metallurgy [1–4]. Different sulphates,  $\text{H}_2\text{SO}_4$ , spent electrolyte, together with gases containing  $\text{SO}_2$ ,  $\text{SO}_3$  and  $\text{O}_2$ , etc., are used as sulphating agents [1, 2, 5–11].

The study of the solid phase interactions between sulphating agents and the main components of the processed raw material is of great importance for the efficient use of these agents and for achieving a high degree of sulphatization [12–15]. For this purpose an investigation of the reactions of  $(\text{NH}_4)_2\text{SO}_4$  and  $\text{FeSO}_4$  with the main and admixture metal oxides of the treated by-products (copper, zinc and cadmium ferrites and their mixed ferrites) has been carried out.

### EXPERIMENTAL

The interactions between the mentioned sulphates and MeO (Me is Zn, Cu, Cd, Ca, Mg, Pb),  $\text{Me}_2\text{O}_3$  (Me is Fe, Al),  $\text{MeFe}_2\text{O}_4$  (Me is Cu, Zn, Cd) and mixed ferrites of Cu, Zn, Cd ( $\text{Cu}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ ,  $\text{Cu}_{0.5}\text{Cd}_{0.5}\text{Fe}_2\text{O}_4$ ,  $\text{Zn}_{0.5}\text{Cd}_{0.5}\text{Fe}_2\text{O}_4$ ) have been examined using the following methods: DTA and TGA, quasi-isobaric isothermal analysis (a Q Derivatograph, Hungary

was employed), X-ray diffraction analysis (TUR M-62, VEB Transformator- und Röntgenwerk "Herman Matern", Dresden, Germany) and Mössbauer spectroscopy.

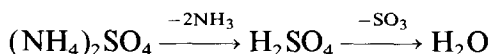
DTA and TGA were carried out under the following conditions: sensitivity of DTA, 1 mV; DTG, 1 mV; TG, 500 mg; heating rate 10 K min<sup>-1</sup>, sample mass, 200 mg (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> (or 500 mg FeSO<sub>4</sub>) + stoichiometric amount of oxide or ferrite. The experiments were performed in air medium. The quasi-isobaric isothermal investigations were accomplished by means of a labyrinth platinum crucible, samples of 100 mg and a heating rate of about 3 K min<sup>-1</sup>.

The X-ray diffraction analysis was carried out using Co K $\alpha$  radiation and an iron target. The Mössbauer spectra are taken on a standard Mössbauer spectrometer operating under conditions of constant acceleration of the <sup>57</sup>Co source in a Pd matrix [16].

## RESULTS AND DISCUSSION

The interaction of (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> with the oxides and ferrites was investigated under dynamic conditions. The thermal decomposition of the sulphate in the presence of MeO, Me<sub>2</sub>O<sub>3</sub> and MeFe<sub>2</sub>O<sub>4</sub> differs essentially from that of pure (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>. Changes of DTA, DTG and TG curves, initial temperature of dissociation (from room temperature up to 260°C for the individual (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>), end temperature, mass of the samples, etc. were observed. This may be well illustrated by the interaction of (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> with zinc compounds, which are the main components of the by-products worked by sulphatization.

The results obtained (Fig. 1) prove that the dissociation process of (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> [10] is a step process that takes place according to the following scheme:



Increasing the temperature above 700°C leads to dissociation of SO<sub>3</sub> to SO<sub>2</sub> and O<sub>2</sub>.

The mechanism of thermal decomposition of (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> is complicated and connected with the formation of intermediate compounds [8, 9, 17–20]. The aim of this work is to investigate the possibility of using (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> as sulphatization agent. On the basis of the results obtained it seems that (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> will be active within the range 340–430°C.

The thermal decomposition of (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> in the presence of ZnO starts at 145°C and has a step character (Fig. 2). The results obtained indicate that a chemical interaction occurs between ZnO and SO<sub>3</sub> forming ZnSO<sub>4</sub>. On the DTA curve an endothermic effect is observed at 745°C, corresponding to the phase transition  $\alpha$ -ZnSO<sub>4</sub>  $\rightarrow$   $\beta$ -ZnSO<sub>4</sub> [17], after which ZnSO<sub>4</sub> decomposes to ZnO and SO<sub>3</sub> and an intermediate product (ZnO · 2ZnSO<sub>4</sub>) is

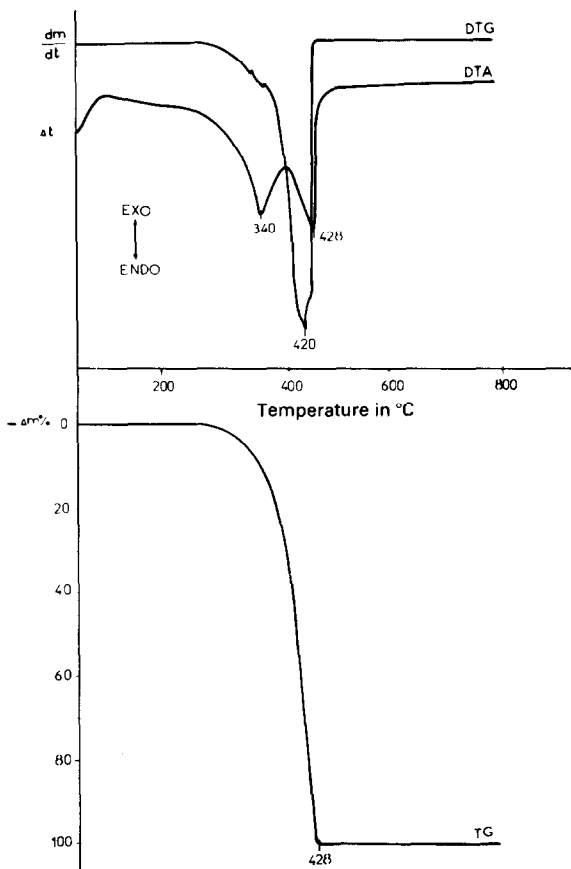


Fig. 1. Derivatogram of  $(\text{NH}_4)_2\text{SO}_4$ .

formed endothermically at about  $860^\circ\text{C}$ . The thermal decomposition of  $\text{ZnSO}_4$  is completed at  $990^\circ\text{C}$ , which is confirmed by the calculations and the shape of the TG curve.

During the interaction of  $(\text{NH}_4)_2\text{SO}_4$  with  $\text{ZnO}$ , ammonia and water are liberated up to  $470^\circ\text{C}$ ,  $\text{SO}_3$  interacts with  $\text{ZnO}$  almost stoichiometrically and  $\text{ZnSO}_4$  is formed. On the basis of the investigation under dynamic conditions it is found that only  $\text{ZnSO}_4$  occurs within the range of  $470\text{--}700^\circ\text{C}$ .

In the case of the interaction of  $(\text{NH}_4)_2\text{SO}_4$  with  $\alpha\text{-Fe}_2\text{O}_3$  and  $\text{ZnO}$  (molar ratio 1:1:1) the results obtained are similar to those for the  $(\text{NH}_4)_2\text{SO}_4\text{-ZnO}$  system. When  $\text{ZnO}$  and  $\alpha\text{-Fe}_2\text{O}_3$  form ferrite however, some differences are observed (Fig. 3).

The dissociation of  $(\text{NH}_4)_2\text{SO}_4$  starts at a higher temperature ( $210^\circ\text{C}$ ). Part of the  $\text{SO}_3$  obtained does not participate in the sulphatization process of the ferrite. Data from DTA, TGA and X-ray analysis of samples, heated to different temperatures show that  $\text{Fe}_2(\text{SO}_4)_3$  and  $\text{ZnSO}_4$  are formed almost simultaneously. The decomposition of  $\text{Fe}_2(\text{SO}_4)_3$  leads to the evolu-

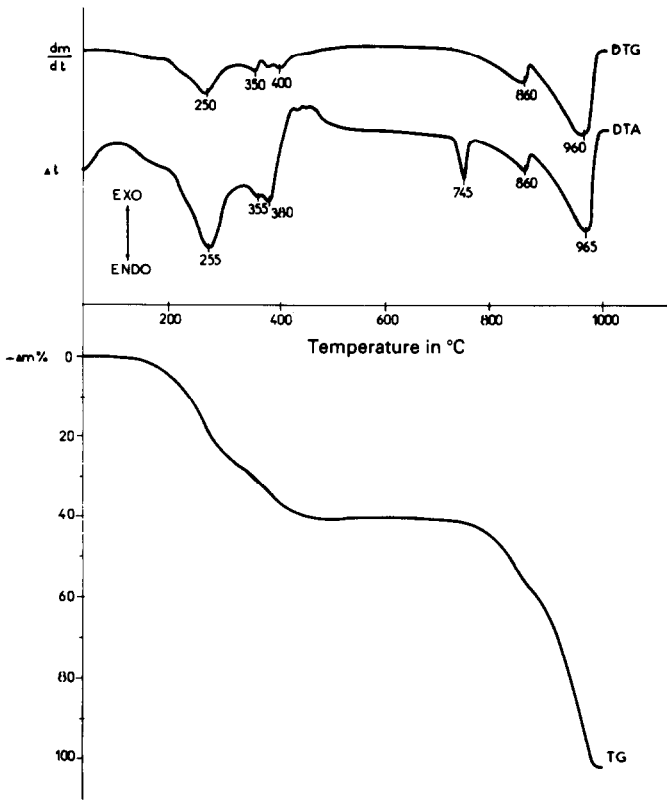


Fig. 2. Derivatogram of the  $(\text{NH}_4)_2\text{SO}_4\text{-ZnO}$  system.

tion of  $\text{SO}_3$ , which contributes to the formation of  $\text{ZnSO}_4$  or slows down its dissociation.

The results indicate that no intermediate product of  $\text{ZnO} \cdot 2\text{ZnSO}_4$  is formed during the decomposition. An essential difference in comparison with the  $(\text{NH}_4)_2\text{SO}_4\text{-ZnO}$  system is the completion of dissociation at the considerably lower temperature of about  $890^\circ\text{C}$ .

The processing of the Mössbauer spectra shows that the values of the isomer shift (IS), quadrupole splitting (QS) and intrinsic magnetic field ( $H_{\text{eff}}$ ) of the iron containing phases in the initial sample and the samples heat-treated up to 590, 710 and  $1000^\circ\text{C}$  agree with those presented in our earlier work [16]. On the basis of Mössbauer spectroscopy data and X-ray diffraction analysis results we have come to the conclusion that the phases  $\text{ZnFe}_2\text{O}_4$ ,  $\text{ZnSO}_4$  and  $\text{Fe}_2(\text{SO}_4)_3$  are present in the sample heat-treated up to  $590^\circ\text{C}$ . The sulphates have an undefined amount of water of crystallization absorbed from the air. By increasing the temperature up to  $710^\circ\text{C}$  the phase  $\text{Fe}_2\text{O}_3$  is observed. The iron combined in the heat-treated sample as oxide and ferrite is about 79% and 21%, respectively. The amount of iron forming

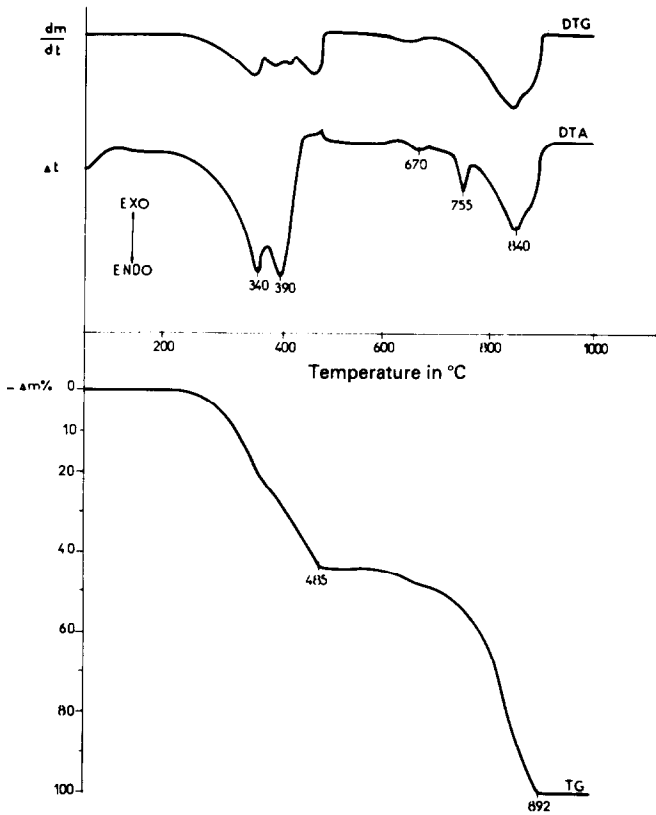
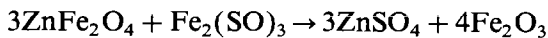
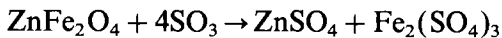


Fig. 3. Derivatogram of the  $(\text{NH}_4)_2\text{SO}_4\text{-ZnFe}_2\text{O}_4$  system.

ferrite increases up to 34% at  $1000^\circ\text{C}$  and at this temperature the phases  $\text{Fe}_2\text{O}_3$ ,  $\text{ZnFe}_2\text{O}_4$  and  $\text{ZnO}$  can be identified.

On the basis of the results obtained it may be assumed that the mechanism of the sulphatization is



The presence of cadmium in the  $(\text{NH}_4)_2\text{SO}_4\text{-Zn}_{0.5}\text{Cd}_{0.5}\text{Fe}_2\text{O}_4$  system (Fig. 4) causes the sulphatization process to be more complicated and the degree of sulphatization is 81.1% at  $500^\circ\text{C}$ . By increasing the temperature above  $600^\circ\text{C}$  the consecutive dissociation of the obtained sulphates is observed very clearly; iron sulphate  $\text{Fe}_2(\text{SO}_4)_3$  decomposes within the temperature range  $600\text{--}700^\circ\text{C}$ ,  $\text{ZnSO}_4$  within the range  $700\text{--}850^\circ\text{C}$ , and  $\text{CdSO}_4$  above  $850^\circ\text{C}$ .

Similar investigations of sulphatization of the mentioned oxides and ferrites have been carried out with  $(\text{NH}_4)_2\text{SO}_4$  and also with  $\text{FeSO}_4$ .

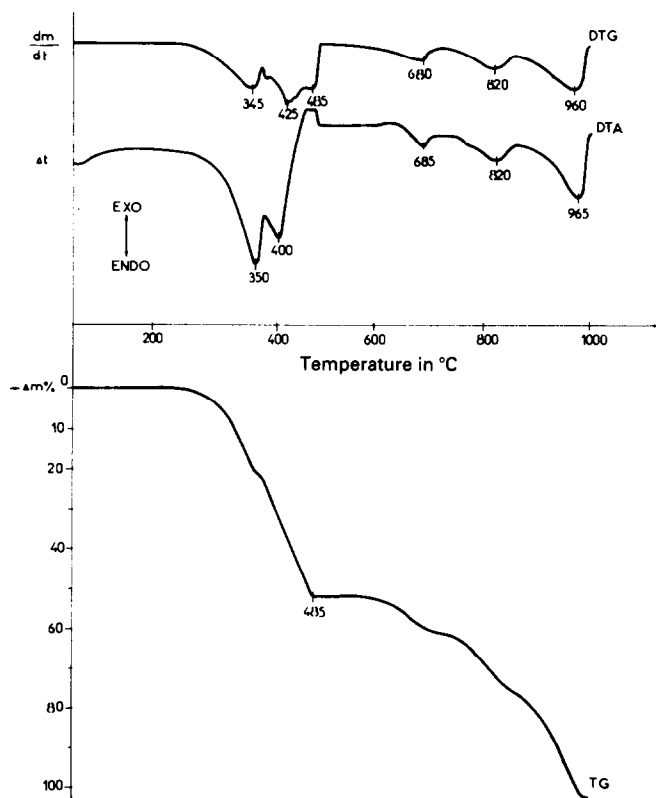


Fig. 4. Derivatogram of the  $(\text{NH}_4)_2\text{SO}_4\text{-Zn}_{0.5}\text{Cd}_{0.5}\text{Fe}_2\text{O}_4$  system.

#### COMPARISONS AND CONCLUSIONS

From the results obtained (Figs. 5 and 6) the following comparisons and conclusions could be drawn.

Sulphatization with  $(\text{NH}_4)_2\text{SO}_4$  takes place at a lower temperature than with  $\text{FeSO}_4$ . Almost all sulphates are obtained in measurable extent ( $\eta/\%$ ) at temperatures up to  $650^\circ\text{C}$ , whereas with  $\text{FeSO}_4$  this is possible upon its complete dissociation above  $700^\circ\text{C}$ .

The behaviour of  $\text{CdO}$  is similar regardless of the sulphating agent used. The decomposition of the formed  $\text{CdSO}_4$  begins above  $900^\circ\text{C}$ , which means that the degree of sulphatization of this valuable component in some by-products of non-ferrous metallurgy will be about 85–90%.

The application of  $\text{FeSO}_4$  results in a very high degree of sulphatization of  $\text{PbO}$  and in partial decomposition of the  $\text{PbSO}_4$  obtained above  $900^\circ\text{C}$ . When  $(\text{NH}_4)_2\text{SO}_4$  is used as a sulphating agent its dissociation probably occurs at a temperature which is lower than that required for the complete sulphatization of  $\text{PbO}$ . The experimental results indicate that the presence of  $\text{PbO}$  increases the consumption of sulphating agent. It is difficult to

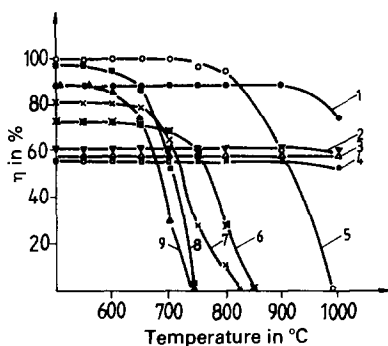


Fig. 5 (left). Sulphates obtained in the  $(\text{NH}_4)_2\text{SO}_4 + \text{MeO}$  ( $\text{Me}_2\text{O}_3$ ) systems depending on the temperature: 1,  $\text{CdSO}_4$ ; 2,  $\text{PbSO}_4$ ; 3,  $\text{CaSO}_4$ ; 4,  $\text{MgSO}_4$ ; 5,  $\text{ZnSO}_4$ ; 6,  $\text{Al}_2(\text{SO}_4)_3$ ; 7,  $\text{CuSO}_4$ ; 8,  $\text{Fe}_2(\text{SO}_4)_3$  (from  $\alpha\text{-Fe}_2\text{O}_3$ ); 9,  $\text{Fe}_2(\text{SO}_4)_3$  (from  $\gamma\text{-Fe}_2\text{O}_3$ ).

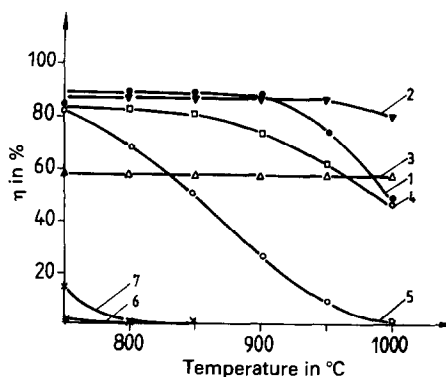


Fig. 6 (right). Sulphates obtained in the  $\text{FeSO}_4 + \text{MeO}$  ( $\text{Me}_2\text{O}_3$ ) systems depending on the temperature: curves 1–7 as in Fig. 5.

utilize the  $\text{PbSO}_4$  obtained through the well-known hydrometallurgical methods of sulphatization product processing.

The explored compounds sulphatize  $\text{CaO}$ , which is available in the raw material; the extent of this process is about 55–60%  $\text{CaSO}_4$  obtained at lower temperature. In the  $(\text{NH}_4)_2\text{SO}_4\text{--CaO}$  system the  $\text{CaSO}_4$  is more stable than  $\text{CaSO}_4$  formed during the sulphatization process with  $\text{FeSO}_4$ .

The magnesium oxide is sulphatized more completely when using  $\text{FeSO}_4$  and the  $\text{MgSO}_4$  formed partially dissociates above  $850^\circ\text{C}$ . In the presence of  $(\text{NH}_4)_2\text{SO}_4$  as sulphating agent,  $\text{MgSO}_4$  is formed which is more stable and hardly dissociates at all at temperatures up to  $1000^\circ\text{C}$ .

Zinc oxide in the by-products is either free or combined as ferrite, silicate, etc. In the light of the results obtained here it may be concluded that  $(\text{NH}_4)_2\text{SO}_4$  sulphatizes  $\text{ZnO}$  more completely than  $\text{FeSO}_4$ . The extent of  $\text{ZnO}$  sulphatization at  $800^\circ\text{C}$  is of the order of 95%, whereas when  $\text{FeSO}_4$  is used it is about 70%. The effect of using  $(\text{NH}_4)_2\text{SO}_4$  decreases for sulphatization of iron-containing by-products because of the formation of iron sulphate as an intermediate product in the process.

Copper oxide causes the greatest difficulties during the sulphatization process as regards the establishment of conditions for its change into a sulphate at a low extent of iron sulphatization. The  $\text{CuSO}_4$  formed has a slightly higher dissociation temperature than  $\text{FeSO}_4$ , which may be used to obtain copper sulphate and for the transition of iron into water-insoluble  $\text{Fe}_2\text{O}_3$  at the same time.

The behaviour of  $\text{Al}_2\text{O}_3$  is similar to that of  $\text{CuO}$ , but it increases the consumption of sulphating agent. The copper and aluminium sulphates

obtained by the use of  $(\text{NH}_4)_2\text{SO}_4$  are more stable and sulphatization takes place at a lower temperature.

In the case of sulphatization of ferrites and mixed ferrites by  $(\text{NH}_4)_2\text{SO}_4$ , up to a temperature of about  $700^\circ\text{C}$  the systems contain sulphates of useful components and of iron. Above that temperature, dissociation may be assumed to be due mainly to the sulphates obtained.

Zinc ferrite is sulphatized more completely by  $(\text{NH}_4)_2\text{SO}_4$  and intensive dissociation of  $\text{ZnSO}_4$  occurs at temperatures higher than  $750^\circ\text{C}$ . About 45% of zinc is in sulphate form when  $\text{FeSO}_4$  is used as the sulphating agent.

Copper and cadmium ferrites have approximately the same behaviour upon sulphatization, both with  $(\text{NH}_4)_2\text{SO}_4$  and  $\text{FeSO}_4$ . A difference in the degree of sulphate dissociation is observed at  $500\text{--}600^\circ\text{C}$ . It is about 20% lower when  $(\text{NH}_4)_2\text{SO}_4$  reacts with the ferrites, probably due to the simultaneous sulphatization of  $\text{CuO}(\text{CdO})$  and  $\text{Fe}_2\text{O}_3$  on account of the lower dissociation temperature of  $(\text{NH}_4)_2\text{SO}_4$ . With increased temperature, an additional amount of  $\text{CuO}(\text{CdO})$  is sulphatized by the iron sulphate formed.

The presence of cadmium in the mixed ferrites increases the temperature of  $\text{SO}_3$  liberation, whereas copper decreases it.

In the course of their interaction with  $(\text{NH}_4)_2\text{SO}_4$  the stability of the ferrites decreases in the following sequence:  $\text{CuFe}_2\text{O}_4$ ,  $\text{CdFe}_2\text{O}_4$ ,  $\text{ZnFe}_2\text{O}_4$ . The optimum temperature range for their sulphatization is  $600\text{--}650^\circ\text{C}$ . The extents of sulphatization of  $\text{ZnFe}_2\text{O}_4$ ,  $\text{CdFe}_2\text{O}_4$  and  $\text{CuFe}_2\text{O}_4$  are about 90%, 80% and 70%, respectively.

The experimental data discussed above may be used in zinc, copper and cadmium production for improving the results of hydrometallurgical processing of different by-products, containing non-ferrous metals.

## REFERENCES

- 1 V.K. Karra and P.K. Jena, *Trans. Indian. Inst. Met.*, 5 (1973) 18.
- 2 A.P. Snurnikov and V.F. Larin, *Tsvetn. Met.*, 6 (1969) 29.
- 3 P. Saikkonen and J. Rastas, *Finn. Chem. Lett.*, 3–4 (1985) 101.
- 4 I. Palencia, F. Carranza and M. Garcia, *Hydrometallurgy*, 23 (1990) 191.
- 5 V.N. Gaprindashvili, R.M. Duduchava and N.D. Mamagaeshvili, *USSR Patent No.* 382717, 1973.
- 6 A. Lenchev and M. Karavasteva, *Izv. VUZ, Tsvetn. Metal.*, 1 (1982) 36.
- 7 B. Boyanov, R. Dimitrov and N. Dobrev, *Tsvetn. Met.*, 5 (1986) 34.
- 8 T. Nagaishi, S. Ishiyama, Y. Yashimura, M. Matsumoto and S. Yoshinaga, *J. Therm. Anal.*, 23 (1982) 201.
- 9 T. Nagaishi, S. Ishiyama, M. Matsumoto and S. Yoshinaga, *J. Therm. Anal.*, 29 (1984) 121.
- 10 P.K. Sahoo, S.K. Bose and S.C. Sircat, *Thermochim. Acta*, 31 (1979) 303.
- 11 P.K. Sahoo, S.K. Bose and S.C. Sircat, *Thermochim. Acta*, 31 (1979) 315.
- 12 A.A. Milner, O.T. Popovich, N.N. Kii and E.V. Klimenko, *Khim. Tekhnol. (Kiev)*, 3 (1989) 37.
- 13 R.K. Basu, P. De and B.K. Dutta, *Indian J. Technol.*, 27 (1989) 355.



- 14 J.S. Dennis and A.N. Hayhurst, *Chem. Eng. Sci.*, 45 (1990) 1175.
- 15 Y. Pelovski, W. Pietkova, I. Gruncharov, B. Pasewska and J. Pysiak, *Thermochim. Acta*, 205 (1992) 219.
- 16 R. Dimitrov, B. Boyanov and S. Nikolov, *Thermochim. Acta*, 34 (1979) 149.
- 17 M. Brown, D. Dollimore and A. Galwey, *Reaktsii Tverdykh Tel*, Mir, Moscow, 1983, p. 260.
- 18 C.E. Baily, *J. Chem. Phys.*, 5 (1983) 2740.
- 19 T.I. Konkoly, *Thermochim. Acta*, 60 (1983) 149.
- 20 S. Ahmed, A.M. Shaman, A. Ibrahim and F. Hanna, *Phys. Status Solidi A*, 115 (1989) 145.