Differential thermal study of the interactions between sulphates, oxides and ferrites

B.S. Boyanov*

University of Plovdiv, 4000 Plovdiv, Bulgaria

Received 11 October 1996; accepted 21 May 1997

Abstract

The solid state interactions in the $ZnSO_4.7H_2O$-MeO (Me = Cd, Pb, Ca, Mg) and $CuSO_4.5H_2O$-MeO (Me = Zn, Cd, Pb, Ca, Mg) systems, sulphate–ferrite systems, double sulphate systems and triple system $FeSO_4.7H_2O$-$CuSO_4.5H_2O$-$ZnSO_4.7H_2O$ have been studied using DTA, TGA and X-ray diffraction analysis.

The degrees of sulphatization of the studied oxides and ferrites and the phase composition depending on the temperature have been determined. The obtained results are discussed in terms of hydrometallurgical processing of zinc and copper–zinc concentrates. © 1997 Elsevier Science B.V.

Keywords: DTA and TGA; Ferrites; Interaction; Oxides; Sulphates; Sulphatization; X-ray analysis

1. Introduction

The complex character of the processes carried out in the MeS-MeO-MeSO$_4$ (Me = Zn, Cu, Cd, Pb, Ca) systems in the presence of oxygen and Fe_2O_3 requires additional detailed investigations.

The oxidation processes of different MeS in the natural zinc, copper, copper–zinc and lead sulphide concentrates have been studied in detail [1–8]. The MeSO$_4$ dissociation has been a subject of many investigations, mainly by using DTA and TGA [9–13]. Less attention has been paid to the exchange reactions carried out in the oxide–sulphate and ferrite–sulphate systems. They are important for the

processing of the low soluble metal ferrites and utilization of the non-ferrous metals in them. Essential results may be expected about sulphates stabilities and the possibilities of obtaining some of the sulphur input after the roasting of the zinc concentrates combined as soluble sulphates. This is connected with a decrease of the sulphuric acid consumption needed to compensate for the formation of insoluble sulphates during the leaching of the zinc calcine. This question is quite natural when different zinc concentrates (according to their chemical, phase and mineral composition) from different parts of the world are processed together. The results of roasting can be predicted using a computer software [14].

In this connection, the aim of the present work is to investigate the metal sulphates dissociation and the solid-state interactions in the systems, including sulphates, oxides and ferrites.

*Corresponding author. Tel.: 00 359 32 2615 351; fax: 00 359 32 235 049.

2. Experimental

The interactions in the $ZnSO_4.7H_2O$-MeO (Me = Cd, Pb, Ca, Mg) and $CuSO_4.5H_2O$-MeO (Me = Zn, Cd, Pb, Ca, Mg) systems, sulphate–ferrite systems, double sulphate systems and triple system $FeSO_4.7H_2O$-$CuSO_4.7H_2O$ –$ZnSO_4.7H_2O$ have been examined using DTA and TGA and X-ray diffraction analysis.

DTA and TGA (a Q Derivatograph, Hungary) were carried out under the following conditions: sensitivity of DTA, 0.5 mV; DTG, 1 mV; TG, 200 mg; heating rate, $10\,K\,min^{-1}$; sample mass, 200 mg sulphate + stoichiometric amount of oxide or ferrite. A platinum crucible was used. All the studies were performed in the air medium.

X-ray diffraction analysis was carried out with a TUR-M62 apparatus (Dresden, Germany) using CoK_α radiation and an iron target.

The investigated ferrites were synthesised using standard ceramic technology [7,15].

3. Results and discussion

3.1. Interactions of $ZnSO_4.7H_2O$ with MeO (Me = Cd, Pb, Ca, Mg)

A certain amount of $ZnSO_4$ may be obtained during the roasting of zinc sulphide concentrates mainly in the dust separation system. Sometimes in the dust from cyclones and electrostatic precipitators the content of zinc confirmed as a zinc sulphate is about 5–10%.

This zinc sulphate may be obtained directly by ZnS oxidation, by sulphatization of the product of roasting – ZnO, when it is in contact with the furnace gases, containing SO_2 and O_2 or as a result of solid-state interactions [8].

It is important to check the behavior of $ZnSo_4.7H_2O$ in the presence of MeO (Me = Cd, Pb, Ca, Mg). The interest in these oxides is due to the fact that the sulphates of the shown metals are more stable than $ZnSO_4$ and these oxides are always present in the zinc calcine.

The interactions between $ZnSO_4.7H_2O$ and MeO evaluate the obtained derivatograms of their mixtures and compare them with the derivatogram of the pure $ZnSO_4.7H_2O$ [16].

3.1.1. $ZnSO_4.7H_2O$-CdO system

At the interaction of $ZnSO_4.7H_2O$ with CdO the following peculiarities were observed:

1. The dehydration process begins at a temperature which is 70°C higher than the pure $ZnSO_4.7H_2O$.
2. Three steps of dehydration are established for the system studied but $ZnSO_4.7H_2O$ had only two steps.
3. The endothermal effect at 745°C which is a result of $\alpha \rightarrow \beta$ transition of $ZnSO_4$ is not observed.
4. At 1000°C the total mass loss is 52.5% which is 16.5% lower than the value obtained for the pure $ZnSO_4.7H_2O$. The results show that a solid-state interaction has been carried out and $CdSO_4$ has been obtained. The phases ZnO, $CdSO_4$ and CdO were found in the sample at 1000°C according to the calculations made and carried out by X-ray diffraction analysis. A part of CdO is sulphatized and the degree of sulphatization (η) at 1000°C is 59% (Table 1).

3.1.2. $ZnSO_4.7H_2O$-PbO system

In the case of the interaction of $ZnSO_4.7H_2O$ with PbO the results obtained for the dehydration process are similar to those for $ZnSO_4.7H_2O$. The crystallized water molecules liberate entirely at 350°C.

According to the TG curve a small decrease in the sample mass was observed at a temperature higher than 880°C but it is essentially smaller for $ZnSO_4$. At 1000°C $-\Delta m = 46\%$, which means that 23% of zinc sulphate mass has reacted with PbO and $PbSO_4$ and ZnO have been obtained.

The calculations indicate that 82.3% of the initial PbO has combined at 1000°C with the liberated SO_3 from $ZnSO_4$ and $PbSO_4$ obtains.

Indirect confirmation for $PbSO_4$ obtaining at the interaction in the studied system is the presence of an endothermal-effect at 865°C which is a result of $\alpha \rightarrow \beta$ transition in $PbSO_4$. This means that the exchange reaction $ZnSO_4 + PbO \rightarrow ZnO + PbSO_4$ begins and proceeds at a temperature lower than 865°C.

3.1.3. $ZnSO_4.7H_2O$-CaO system

A change in the dehydration character was observed at the interaction of $ZnSO_4.7H_2O$ with CaO. The step kind of the crystallization water liberation was not well observed.

Table 1
Results from DTA and TGA study of the sulphate–oxide and sulphate–ferrite systems

N	System	Mass loss at 1000°C, −Δm,%	Degree of sulphatization (η, %) at temperature		Phases at temperature
			1000°C		1000°C
1	$ZnSO_4.7H_2O$-CdO	52.5	59.0		$CdSO_4$, CdO, ZnO
2	$ZnSO_4.7H_2O$-PbO	46.0	82.0		$PbSO_4$, ZnO, PbO
3	$ZnSO_4.7H_2O$-CaO	57.5	41.4		ZnO, CaO, $CaSO_4$
4	$ZnSO_4.7H_2O$-MgO	48.5	73.8		$MgSO_4$, ZnO, MgO
			850°C	1000°C	850°C
5	$CuSO_4.5H_2O$-ZnO	67.0	67.3	0	$ZnSO_4$, ZnO, CuO
6	$CuSO_4.5H_2O$-CdO	47.0	90.4	62.3	$CdSO_4$, CuO, CdO
7	$CuSO_4.5H_2O$-PbO	38.0	93.5	84.2	$PbSO_4$, CuO, PbO
8	$CuSO_4.5H_2O$-CaO	51.5	49.9	48.3	CuO, CaO, $CaSO_4$
9	$CuSO_4.5H_2O$-MgO	52.0	78.7	47.2	$MgSO_4$, CuO, MgO
				1000°C	1000°C
10	$ZuSO_4.7H_2O$-$CdFe_2O_4$	61.0	59.4/960°C	28.8	ZnO, $CdFe_2O_4$, $CdSO_4$, Fe_2O_3
11	$CuSO_4.5H_2O$-$CdFe_2O_4$	60.0	56.1/850°C	21.8	CuO, $CdFe_2O_4$, $CdSO_4$, Fe_2O_3
12	$CuSO_4.5H_2O$-$ZnFe_2O_4$	66.0	15.6/850°C	0	CuO, $ZnFe_2O_4$

The theoretical mass loss (71.6%) for a full dissociation of the initial $ZnSO_4.7H_2O$ does not reach up to 1000°C. The value obtained is 57.5% which means that 41.4% of the initial CaO is combined as $CaSO_4$.

3.1.4. $ZnSO_4.7H_2O$-MgO system

The results obtained for this system are similar to those for the $ZnSO_4.7H_2O$-CaO system. The difference is that the $ZnSO_4$ dissociation degree is lower and MgO sulphatization degree is 73.8% at 1000°C.

3.2. Interactions of $CuSO_4.5H_2O$ with MeO (Me = Zn, Cd, Pb, Ca, Mg)

For the processing of copper–zinc raw materials it is important to study the interaction between $CuSO_4$ and different metal oxides.

3.2.1. $CuSO_4.5H_2O$-ZnO system

A small enlargement of the dehydration temperature interval is observed at the thermal treatment of the mixture of $CuSO_4.7H_2O$ and ZnO (Fig. 1). A third step of dehydration can be seen at temperature above 275°C, which is connected with a gradual mass decrease. The liberation of the crystallisation water molecules from the $CuSO_4.5H_2O$-ZnO system is complete at about 400°C, while for the pure $CuSO_4.5H_2O$ this temperature is 270°C (Fig. 2).
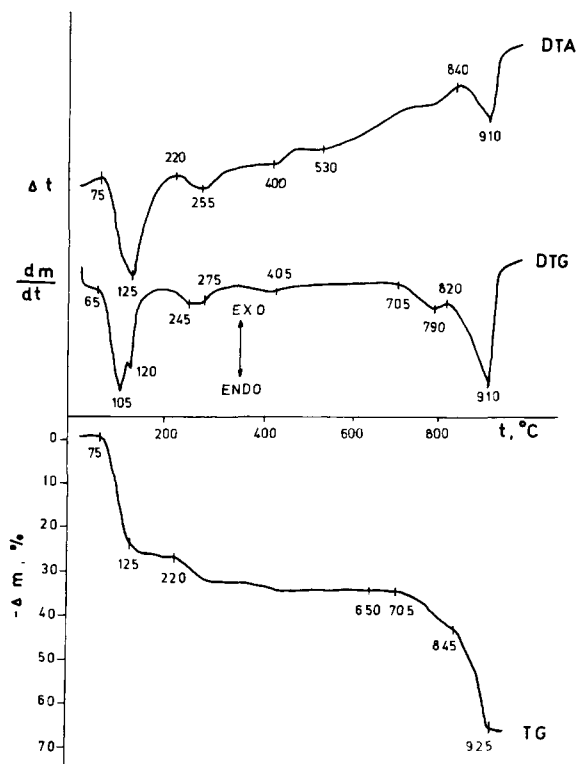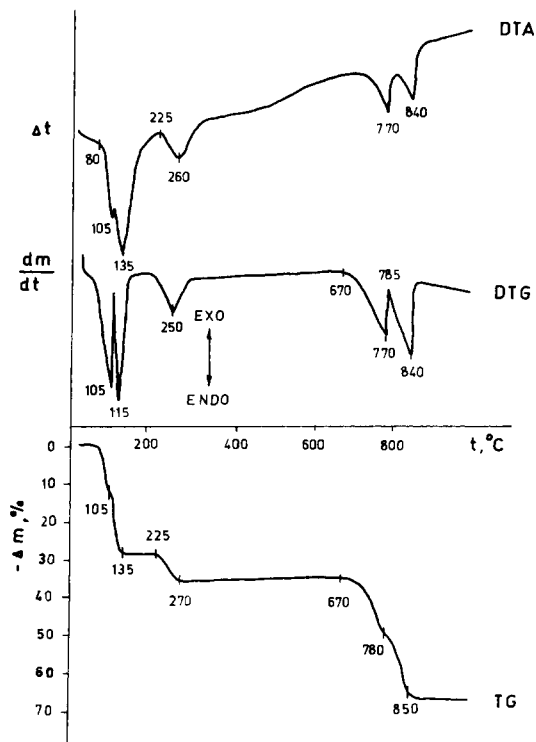

Fig. 1. Derivatogram of the $CuSO_4.5H_2O$-ZnO system.

It was established that the mass loss at 1000°C (66–67%) for the pure $CuSO_4.5H_2O$ and the double system
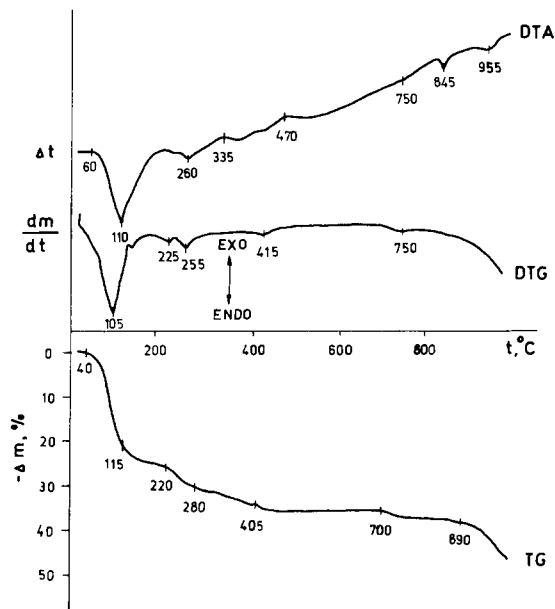
Fig. 2. Derivatogram of $CuSO_4.5H_2O$.

Fig. 3. Derivatogram of the $CuSO_4.5H_2O$-CdO system.

$CuSO_4.5H_2O$-ZnO is approximately close to the theoretical values. On the basis of the obtained results a conclusion can be made that the exchange reaction has not been carried out during the thermal treatment of the system. But there is an increase of the end temperature of dissociation from 850°C for the pure $CuSO_4$ up to 925°C for the mixture $CuSO_4$-ZnO (Fig. 1).

The sample mass remains constant above 925°C. This shows that there is a temperature range in which $CuSO_4$ and $ZnSO_4$ exist simultaneously and $CuSO_4$ dissociates up to 850°C and the $ZnSO_4$ dissociation process continues up to 925°C.

On the basis of the data obtained an assumption can be made about the solid-state reactions in the studied system up to 850°C:

1. Dehydration of $CuSO_4.5H_2O$
2. Dissociation of $CuSO_4$
3. Exchange reaction between $CuSO_4$ and ZnO: $CuSO_4 + ZnO \rightarrow CuO + ZnSO_4$
4. Beginning of $ZnSO_4$ dissociation

Above 850°C $CuSO_4$ is probably dissociated completely and the phases observed in the system are CuO, $ZnSO_4$ and ZnO. The sulphatization degree of ZnO at this temperature is 67.3%.

3.2.2. $CuSO_4.5H_2O$-CdO system

The dehydration process in the $CuSO_4.5H_2O$-CdO system (Fig. 3) is similar to that for the $CuSO_4.5H_2O$-ZnO system (Fig. 1). After dehydration the first mass loss is observed at temperature about 700°C. The mass remains almost constant in the temperature interval 770–860°C. Intensive decrease of the mass begins above 890°C and $-\Delta m = 47\%$ at 1000°C.

The mass loss at the final dissociation temperature for pure $CuSO_4$ (850°C) is 38%.

The calculations show that the sulphatization degree of CdO at 850°C is 90.4%. At 1000°C this degree decreases to 62.3% as a result of the dissociation of the obtained $CdSO_4$.

3.2.3. $CuSO_4.5H_2O$-PbO system

The derivatogram of the $CuSO_4.5H_2O$-PbO system (Fig. 4) shows a small dehydration change compared with the pure $CuSO_4.5H_2O$ which is mainly expressed by the higher temperature of its complete performance.
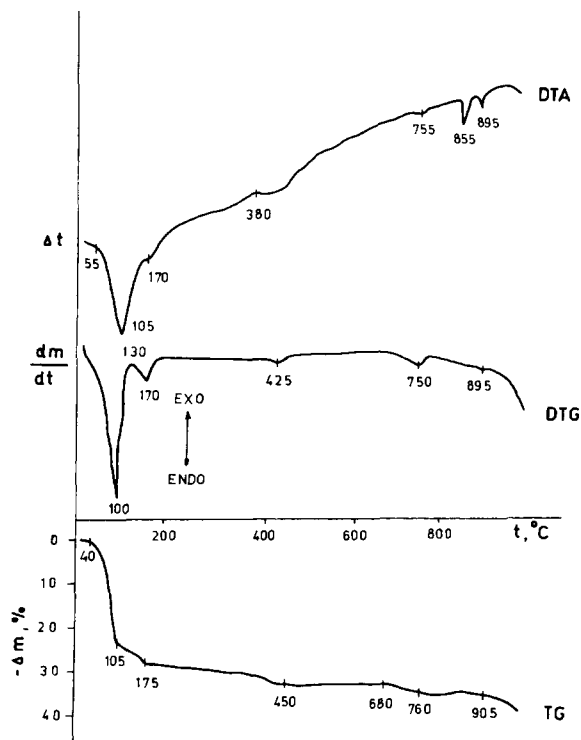
Fig. 4. Derivatogram of the $CuSO_4.5H_2O$-PbO system.
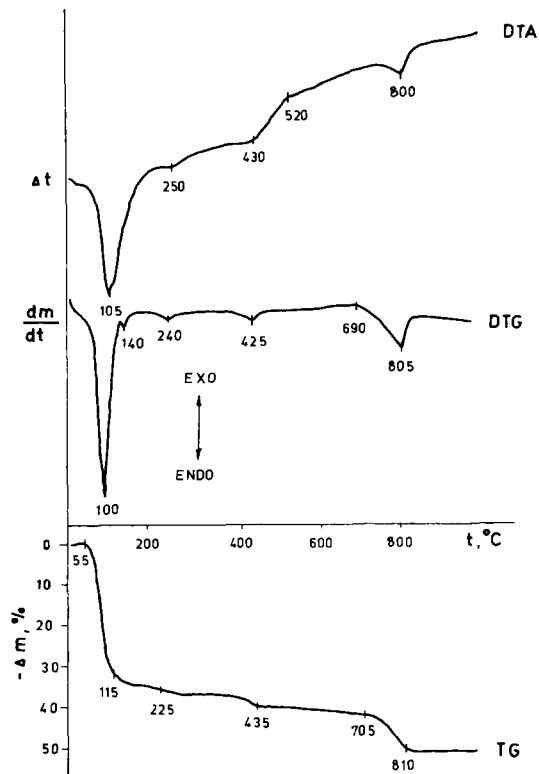
Fig. 5. Derivatogram of the $CuSO_4.5H_2O$-CaO system.

Above 680°C a certain decrease in the sample mass is observed up to 760°C which may be due to partial $CuSO_4$ dissociation. In the temperature interval 670–905°C, the liberated SO_3 combines completely with PbO and $PbSO_4$ is formed. The $PbSO_4$ dissociation process begins at 905°C. The total mass loss in the $CuSO_4.5H_2O$-PbO system is 38% at 1000°C.

The sulphatization degree of PbO is quite high – 93.5% at 850°C and 84.2% at 1000°C.

3.2.4. $CuSO_4.5H_2O$-CaO system

After the $CuSO_4.5H_2O$ dehydration up to 435°C in the presence of CaO, the dissociation process of the anhydrous $CuSO_4$ leads to SO_3 liberation, which interacts with CaO (Fig. 5). The mass decrease is completed at 810°C which is 40°C lower than that for the individual $CuSO_4$. Because of that, above 810°C there is no great change in the sulphatization degree – 49.9% at 850°C and 48.3% at 1000°C.

3.2.5. $CuSO_4.5H_2O$-MgO system

Magnesium oxide is sulphatized by $CuSO_4$ and the degree of sulphating of MgO is 78.7% at 850°C and 47.2% at 1000°C. The data show that MgO sulphatizes at 850°C in an essentially greater degree compared with CaO.

On the basis of the results obtained, the degree of sulphatization (η) of the oxides studied by $CuSO_4$ at 850°C can be written in the following series:

$$\eta_{PbO} > \eta_{CdO} > \eta_{MgO} > \eta_{ZnO} > \eta_{CaO}$$

At 1000°C this series changes and is of the following kind:

$$\eta_{PbO} > \eta_{CdO} > \eta_{CaO} > \eta_{MgO} > \eta_{ZnO}$$

These data indicate that ZnO, which is one of the main components of zinc and copper–zinc calcines, sulphatizes at a little above 850°C because of the thermal instability of the obtained $ZnSO_4$.

3.3. Interactions between sulphates and ferrites

In the zinc hydrometallurgy the process of ferrites formation and the ways of their dissolving are of great importance. In this connection, the ferrites formed during the concentrate roasting in a fluid bed furnace can be transformed to water-soluble compounds of the metals included in them.

3.3.1. $ZnSO_4.7H_2O$-$CdFe_2O$ system

During the thermal treatment of this system some differences are established compared with the pure $ZnSO_4$: the initial temperature of dissociation increases; $ZnSO_4$ does not dissociate completely at 1000°C (the value obtained is 61.0%, while the theoretical value is 71.6%); some retardation of the dissociation process is observed.

At temperature 960°C, which is the end dissociation temperature for the individual $ZnSO_4$, there is some amount of SO_3 non-liberated from the $ZnSO_4.7H_2O$-$CdFe_2O_4$ system. It is probably connected as sulphate, formed at its interaction with $CdFe_2O_4$.

Due to the instability of $FeSO_4$ and $Fe_2(SO_4)_3$ above 800°C, the sulphatization process can proceed between CdO from the ferrite and SO_3 from $ZnSO_4$.

The calculations made indicate that the sulphatization degree of $CdFe_2O_4$ at 960°C and 1000°C is 59.4% and 28.2%, respectively. These data confirm that $CdFe_2O_4$ can be sulphatized at the conditions shown but the temperature affects this process very strongly. The increase of the temperature with only 40°C decreases the $CdSO_4$ content in the system twice.

3.3.2. $CuSO_4.5H_2O$-$CdFe_2O_4$ system

This dissociation process in the system is carried out in two very clearly expressed stages with the temperature between them at 825°C. At the temperature of complete dissociation of $CuSO_4$ (850°C) the total mass loss is 49% which corresponds to a 54.0% degree of sulphatization of CdO from $CdFe_2O_4$. This degree decreases with an increase in the temperature as a result of $CdSO_4$ dissociation and reaches a value of 21.8% at 1000°C.

3.3.3. $CuSO_4.5H_2O$-$ZnFe_2O_4$ system

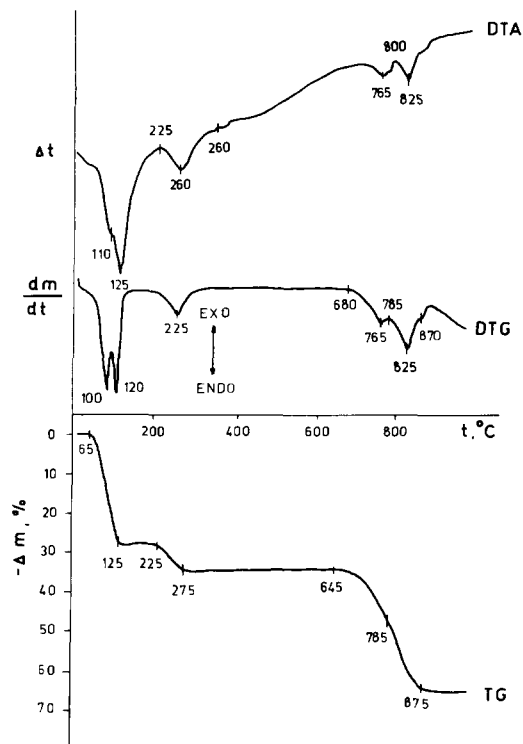This system and the interactions in it are very important for the practice because of the great per-

Fig. 6. Derivatogram of the $CuSO_4.H_2O$-$ZnFe_2O_4$ system.

centage of $ZnFe_2O_4$ formed at the roasting of zinc and copper–zinc concentrates.

According to the DTA curve of the $CuSO_4.5H_2O$-$ZnFe_2O_4$ system (Fig. 6) the dissociation process is performed in three steps. The TG curve shows that the dissociation is completed at 875°C and this temperature is only 25°C higher than the end temperature of the pure $CuSO_4$.

The results obtained show that $ZnFe_2O_4$ is sulphatized by $CuSO_4$ but the degree of sulphatization of the process is too low. It is only 15.6% at 850°C and there are not sulphate phases at 1000°C. The newly formed $ZnSO_4$ is so instable that it dissociates completely at a temperature above 875°C.

The experiments performed and the obtained results confirm ferrite stability. It is necessary to establish optimal conditions (temperature, duration, sulphating agent, medium) for their conversion into water soluble compounds so that the degree of sulphatization is higher than 85%.

3.4. Dissociation of the sulphate systems

The double systems $FeSO_4.7H_2O$-$ZnSO_4.7H_2O$, $FeSO_4.7H_2O$-$CuSO_4.5H_2O$, $CuSO_4.5H_2O$-$ZnSO_4.7H_2O$ and the triple system $FeSO_4.7H_2O$-$CuSO_4.5H_2O$-$ZnSO_4.7H_2O$ were investigated by DTA and TGA. The aim of this study was to check the mutual influence of the sulphates on the dissociation process. The results made the following summaries possible:

1. DTA and TGA curves show that the dissociation process of the sulphates is carried out in more than two stages which are a result of the relative sequence of sulphates dissociation.
2. The presence of sulphate with lower temperature of dissociation decreases the end temperature of dissociation of the more stable sulphate present in the system.
3. At the co-attendance of iron, copper and zinc sulphates in the oxidation roasting products of zinc and copper–zinc concentrates their end dissociation temperature decreases to lower than 900°C. This confirms that the dust from cyclones and electrostatic precipitators of the fluid bed furnace will have higher content of sulphur combined as sulphates compared with the calcine from the overflow. The reason for this is the lower temperature in these apparatuses and the possibility of carrying out the sulphatization process between the oxides, ferrites and the furnace gases, containing SO_2 and O_2 and solid-state interactions between the formed sulphates and the oxides and ferrites from dust.

4. Conclusions

1. The solid-state interactions between $ZnSO_4.7H_2O$ and MeO (Me = Cd, Pb, Ca, Mg) lead to the obtaining of $MeSO_4$ in different degrees depending of the nature of the metal oxide and the temperature.

2. The obtained series according to the values of the sulphatization degree (η) in the systems $CuSO_4.5H_2O$-MeO (Me = Zn, Cd, Pb, Ca, Mg) at 850°C has the following kind: $\eta_{PbO} > \eta_{CdO} > \eta_{MgO} > \eta_{ZnO} > \eta_{CaO}$; at 1000°C: $\eta_{PbO} > \eta_{CdO} > \eta_{CaO} > \eta_{MgO} > \eta_{ZnO}$.
3. The ferrites $ZnFe_2O_4$ and $CdFe_2O_4$ can be sulphatized by $CuSO_4$ and $CdFe_2O_4$ by $ZnSO_4$ but $ZnFe_2O_4$ is more stable than $CdFe_2O_4$ and its η has a lower value compared with that for the cadmium ferrite.
4. Optimal temperature interval for obtaining a high degree of sulphatization of the studied oxides and ferrites is 850–900°C.

References

[1] G.I. Sergeev, Kompleksnoe Izpolzovanie Mineralnogo Syria, 3 (1990) 64.
[2] C. Malinovski and K. Malinovska, Thermochim. Acta, 246 (1994) 141.
[3] L.S. Getskin and V.I. Yarygin, Tsv. Metally, 7 (1986) 24.
[4] A.V. Finkelshtein and L.B. Bruk, Tsv. Metally, 7 (1992) 13.
[5] F.R.A. Jorgensen and E.R. Segnit, Trans. Inst. Min. Metal., 90 (1981) 10.
[6] F. Ajersch and M. Benlyamani, Thermochim. Acta, 143 (1989) 221.
[7] R. Dimitrov and B. Boyanov, Rud. Metal. Zbornik, 30 (1983) 211.
[8] R. Dimitrov and B. Boyanov, Thermochim. Acta, 64 (1983) 27.
[9] J. Staszko, J. Mozejko and M. Olszak-Humienik, J. Therm. Anal., 45 (1995) 1109.
[10] H. Tanaka, M. Kawano and N. Koga, Thermochim. Acta, 182 (1991) 281.
[11] D.W. Jonson and P.K. Gallagner, J. Phys. Chem., 75 (1971) 1179.
[12] Zhong Qin, J. Therm. Anal., 45 (1995) 211.
[13] B. Pacewska and J. Pysiak, J. Therm. Anal., 37 (1991) 1389.
[14] R. Dimitrov, B. Boyanov and M. Sandalski, Metallurgiya (Sofia), 6 (1985) 15.
[15] B. Boyanov, J. Therm. Anal., 44 (1995) 707.
[16] B. Boyanov, Thermochim. Acta, 240 (1994) 225.