

## **DTA AND TGA STUDY OF $\text{MeSO}_4$ ( $\text{Me} = \text{Fe}, \text{Co}, \text{Ni}$ ) DISSOCIATION IN THE PRESENCE OF COKE**

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### **Abstract**

*$\text{MeSO}_4$  ( $\text{Me} = \text{Fe}, \text{Co}, \text{Ni}$ ) dissociation is investigated in order to estimate the effect of temperature, time and presence of coke as reducer on the degree and mechanism of dissociation. It is proved that the presence of coke decreases the dissociation temperature considerably and increases the degree of  $\text{MeSO}_4$  dissociation.*

*Based on the obtained experimental data, a mechanism of the processes is proposed. The obtained results can be used in the industrial production of non-ferrous metals for explaining the processes that take place in the reduction of zinc and lead cakes in order to achieve favorable environmental, technical and economic results.*

*Keywords:* DTA; TGA; sulfates; dissociation; coke

### **1. Introduction**

Iron always accompanies zinc in the initial sulfide concentrates and sometimes its concentration can reach 10-12 %. Its basic disadvantage is the possibility of ferrites formation  $\text{Fe}_2\text{O}_3$  with  $\text{MeO}$  ( $\text{Me}=\text{Zn}, \text{Cd}, \text{Cu}, \text{etc.}$ ) [1], which are insoluble in diluted solutions of sulfuric acid. For the sulfatization

of ferrites and other insoluble compounds, containing precious metals,  $\text{FeSO}_4$  can be used [2-5]. So it is necessary to investigate its dissociation under various conditions.

Nickel is an obstructive element in zinc electrodeposition but always accompanies it in natural raw materials [6]. Its presence in the form of a sulfate or oxide increases the quantity of the nickel passing into the solution.

Nickel and cobalt accompany in measurable quantities the copper raw materials much more often [7]. In some technological schemes it is possible to obtain their sulfates which dissociate in a subsequent thermal treatment. That is why it is interesting to examine their behaviour in the presence of the most frequently used solid fuel – coke.

Cobalt, like nickel, is also an obstructive element in zinc electrodeposition, as it always accompanies zinc in natural raw materials [6,8]. The two elements are found in the zinc calcine in the form of sulfates and oxides, which increases the quantity of the impurities passing into the solution.

The dissociation of  $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$  and  $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$  is important for the final phase, under which the two elements can be present in the zinc cake that goes to wealzing.

The dissociation of different metal sulfates [9-14] has been studied mainly in an oxidizing or inert atmosphere. There are too little data, however, for their behaviour in a reducing environment, which is important from both theoretical and practical point of view.

Therefore, the present study using DTA and TGA is aimed to examine the behaviour of  $\text{MeSO}_4$  (Me = Fe, Co, Ni) in the presence of coke in various ratios to the sulfates. The data obtained and those published earlier should be interpreted in terms of raw materials containing different sulfates.

## 2. Experimental

The sulfates studied have a purity of p.a. The coke characteristics and derivatogram are displayed in [15]. Fraction of 0.12 mm was used. The mass ratio  $\text{MeSO}_4 : \text{C}$  in the mixtures studied is 1:1, 1:3, and 1:5.

DTA and TGA (a Q Derivatograph, Hungary) were carried out under the following conditions: sensitivity of DTA, 1 mV; DTG, 1 mV; TG, 200 mg;

heating rate,  $10^\circ \text{ min}^{-1}$ ; sample mass 200-300 mg sulfate, coke or their mixture. All the studies were performed in the air medium. A ceramic crucible was used.

Calculations, based on the chemical composition, are made for different ratios of  $\text{MeSO}_4 : \text{C}$  in the tested samples. The degree of dissociation of  $\text{MeSO}_4$  is calculated on the basis of the obtained TG curves.

X-ray diffraction analysis was carried out with a TUR-M62 apparatus (Dresden, Germany) using  $\text{CoK}_\alpha$  radiation and an iron target.

### 3. Results and discussion

#### 3.1 Dissociation of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O} + \text{coke}$

The derivatogram of pure  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  is shown in Fig.1 and the derivatogram of the mixture of  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  and coke – in Fig.2.

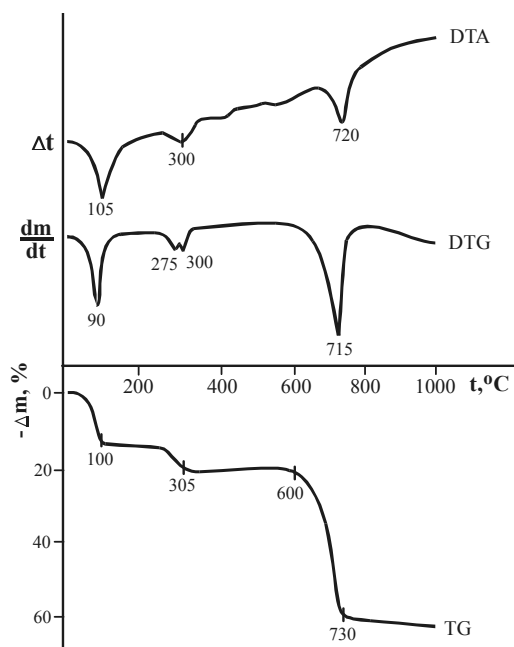


Fig. 1. Derivatogram of  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$

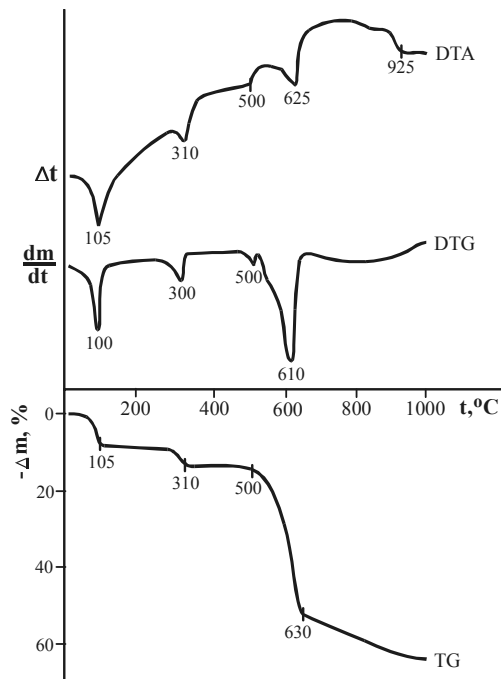


Fig. 2. Derivatogram of  $FeSO_4 \cdot 7H_2O + coke (FeSO_4 : C = 1 : 5)$

From these two derivatograms, it is obvious that up to a temperature of about 310 °C dehydration takes place following the same mechanism. After the completion of a process, the mass of the samples, under the temperature of the solid fuel combustion, remains constant. From the derivatogram of the mixture, it is obvious that after that temperature, decreasing of the sample mass is observed, which is connected with two different rates of the process. But in the pure  $FeSO_4$  dissociation takes place with a maximum of the endothermal effect at 720 °C.

Table 1 presents the data for the mass change of the samples during their thermal treatment. The symbols used in the table are:  $\Delta m_1$  - loss of mass of pure  $FeSO_4 \cdot 7H_2O$  + loss of mass of coke ( $FeSO_4 : C = 1 : 5$ );  $\Delta m_2$  - loss of mass of the mixture of  $FeSO_4 \cdot 7H_2O$  and coke (1:5);  $\Delta m_3$  - loss of mass of the mixture of  $FeSO_4 \cdot 7H_2O$  and coke (1:3);  $\Delta m_4$  - loss of mass of the mixture of

Table 1. Change of sample mass of  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ +coke (mass %)

Temperature t, °C	$-\Delta m_1$ $\Delta m_{\text{FeSO}_4} + \Delta m_{\text{coke}}$ 1:5	$-\Delta m_2$ ( $\text{FeSO}_4$ +coke) 1:5	$-\Delta m_3$ ( $\text{FeSO}_4$ +coke) 1:3	$-\Delta m_4$ ( $\text{FeSO}_4$ +coke) 1:1
450	0	0	0	0
500	1.15	1.53	1.27	0.47
550	2.67	5.73	4.64	1.42
600	4.58	24.05	16.46	6.60
650	9.16	39.31	43.04	17.92
700	23.28	40.84	44.30	35.38
750	40.08	43.51	45.99	44.81
800	42.37	45.42	47.26	45.28
850	44.27	47.33	48.10	45.75
900	46.18	49.24	48.52	46.23
950	47.70	50.0	48.95	47.17
1000	48.09	50.76	48.95	47.17

$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  and coke (1:1).

Fig. 3 shows the curves of the sum of the mass change for the individual  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  and coke (curve 1), and their mixture (curve 2).

It is evident that the loss of about 25-30 % of the mixture mass of  $\text{FeSO}_4$  and coke is reached at a temperature about 70-80 °C lower than the one of individual  $\text{FeSO}_4$  heating. That is why in this case the acceleration of the dissociation process in the presence of solid fuel is less compared to that of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  or  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$  [16]. This is mainly due to the lower dissociation temperature of  $\text{FeSO}_4$ .

### 3.2 Dissociation of $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ + coke

Fig. 4 presents the derivatogram of pure  $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ , while in Fig. 55 derivatogram of  $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$  and coke ( $\text{NiSO}_4$ : coke=1:5) are given.

It is evident that the dissociation process takes place in different ways for the two samples. Before the temperature of coke combustion, dissociation takes place, following one and the same mechanism. The dehydration of  $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$  is a three-stage process. Calculations show that at a temperature

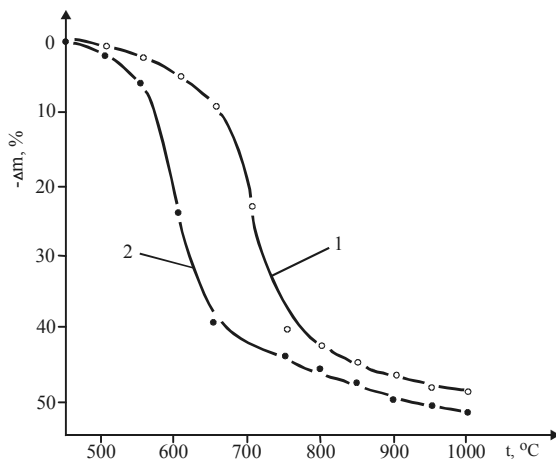


Fig. 3. Mass change of  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  and coke: individually treated (1) and their mixture (2)

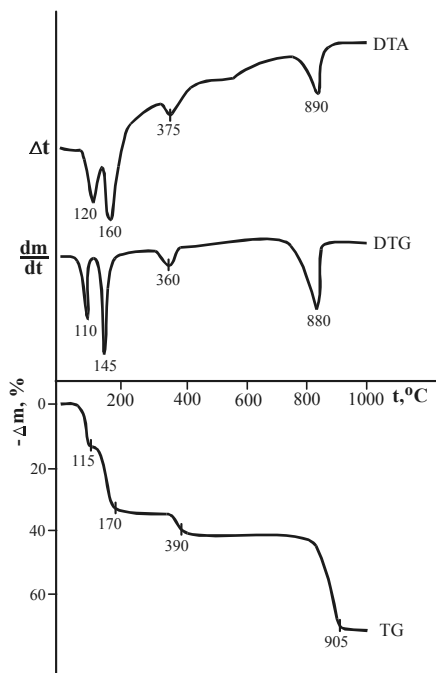


Fig. 4. Derivatogram of  $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$

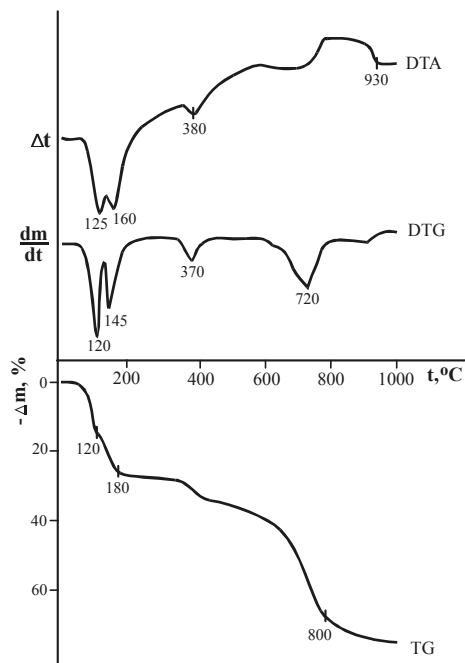


Fig. 5. Derivatogram of  $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$  + coke ( $\text{NiSO}_4:\text{C}=1:5$ )

of about 115°C two molecules of water are dismissed, and further another three molecules at about 170°C – 180°C. The last sixth water molecule is discharged at a temperature of 390°C. After that temperature the mixture of  $\text{NiSO}_4$  and coke sharply decreases its sample mass. At the same time in the pure  $\text{NiSO}_4$  dissociation takes place with a maximum of the endothermal effect at 890°C, while the thermal effect of this process in the mixture of  $\text{NiSO}_4$  and coke is not clearly expressed. The end temperature of the dissociation of pure  $\text{NiSO}_4$  is 925°C, and in the presence of coke it decreases.

The data for mass change during the thermal treatment of the samples are presented in table 2. The symbols used in the table are:  $\Delta m_1$  - loss of mass of pure  $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$  + loss of mass of coke ( $\text{NiSO}_4 : \text{C} = 1:5$ );  $\Delta m_2$  - loss of mass of the mixture of  $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$  and coke (1:5);  $\Delta m_3$  - loss of mass of the mixture of  $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$  and coke (1:3);  $\Delta m_4$  - loss of mass of the mixture

Table 2. Change of sample mass of  $\text{NiSO}_4 \cdot 6\text{H}_2\text{O} + \text{coke}$  (mass %)

Temperature t, °C	$-\Delta m_1$ $\Delta m_{\text{NiSO}_4} + \Delta m_{\text{coke}}$ 1:5	$-\Delta m_2$ ( $\text{NiSO}_4 + \text{coke}$ ) 1:5	$-\Delta m_3$ ( $\text{NiSO}_4 + \text{coke}$ ) 1:3	$-\Delta m_4$ ( $\text{NiSO}_4 + \text{coke}$ ) 1:1
450	0	0	0	0
500	1.13	1.13	0.84	0
550	3.02	3.02	2.09	0.47
600	4.52	5.28	3.77	1.41
650	6.04	10.57	6.28	1.88
700	7.92	20.75	10.46	3.29
750	9.81	31.69	25.10	5.16
800	12.75	35.47	36.40	9.39
850	21.51	37.74	37.24	20.66
900	37.36	39.62	37.66	31.92
950	40.38	40.38	38.08	32.39
1000	41.51	40.75	38.08	32.86

of  $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$  and coke (1:1).

The curves of the sum of the mass change for the individual samples of  $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$  and coke (curve 1) and their mixture (curve 2) are presented in Fig.6.

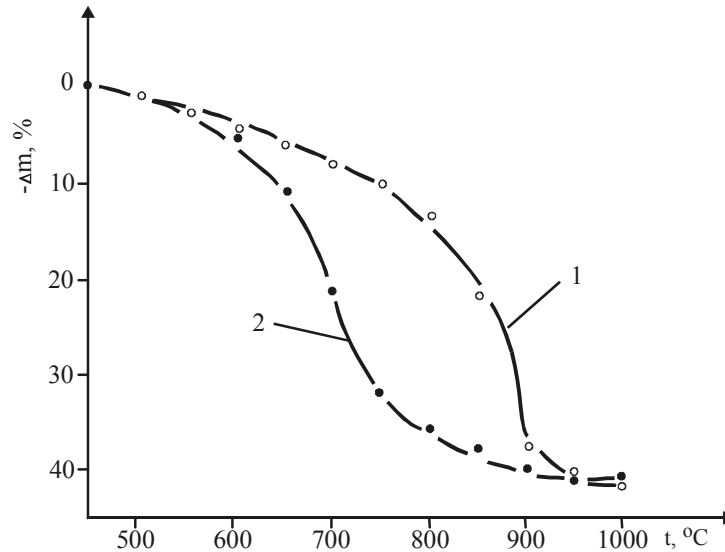


Fig. 6. Mass change of  $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$  and coke: individually treated (1) and their mixture (2)

The figure shows that the acceleration of the dissociation process with the presence of solid fuel in the sample is significant. Loss of mixture mass of about 20 % in  $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$  and coke is reached at a temperature 150°C lower than the one of individual thermal treatment of  $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ .

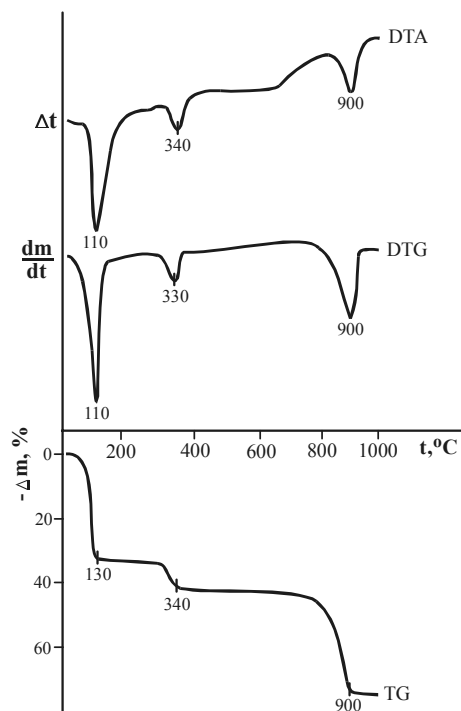
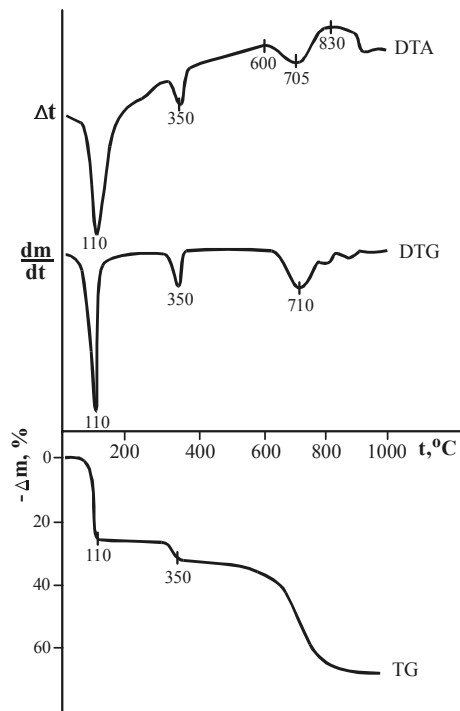
### 3.3 Dissociation of $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ + coke

Fig 7 displays the derivatogram of pure  $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ , while that of the mixture of  $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$  and coke is shown in Fig.8. The two derivatograms reveal the following:

1. The process of dehydration in both cases takes place in a two-stage mechanism. In the first stage at 110-130°C the six molecules of water are dismissed and at a temperature of 340-350°C (second stage of the process) the last seventh molecule is discharged.

2. In the mixture of  $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$  and coke, a sharp decrease of the sample mass is noticed, which occurs at a temperature about 180°C lower than the temperature of dissociation of the anhydrous  $\text{CoSO}_4$ . The process takes place



Fig.7. Derivatogram of  $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ Fig.8. Derivatogram of  $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$  + coke ( $\text{CoSO}_4:\text{C}=1.5$ )

very intensively, which can be seen from the endothermic effect at 705 °C on the DTA curve and at 710 °C on the DTG curve. The data in Table 3 and Fig.9 are also indicative of the intensity of the dissociation process.

From the derivatograms of  $3\text{CdSO}_4 \cdot 8\text{H}_2\text{O}$  and its mixture with coke it is noticeable that in the two samples up to about 450 °C the process follows the same mechanism. Two-stage dehydration takes place at temperatures of 90 - 100 °C and 200 - 215 °C respectively. After dehydration the sample mass remains the same up to about 450 °C.

The anhydrous  $\text{CdSO}_4$  remains stable in a very wide temperature interval (250 - 950 °C) and at 800 - 840 °C phase transitions according to the following scheme are observed:



The  $\text{CdSO}_4$  dissociation process begins only after 950 °C. It is evident from the derivatogram of the mixture of  $\text{CdSO}_4$  and solid fuel that the dissociation starts after about 450 - 500 °C and takes place at a significant rate. The thermal effects that follow the reaction are not clearly stated.

The curves of change in the sample masses of individual  $\text{CdSO}_4$  and coke (curve 1) and their mixture (curve 2) are presented in Fig. 10.

It is evident that the degree of dissociation in the presence of solid fuel is higher by about 10% compared to the degree of dissociation of pure  $\text{CdSO}_4$ .

Table 3. Change of sample mass of  $\text{CoSO}_4 \cdot 7\text{H}_2\text{O} + \text{coke}$  (mass %)

Temperature t, °C	$-\Delta m_1$ $\Delta m_{\text{CoSO}_4} + \Delta m_{\text{coke}}$ 1:5	$-\Delta m_2$ ( $\text{CoSO}_4 + \text{coke}$ ) 1:5	$-\Delta m_3$ ( $\text{CoSO}_4 + \text{coke}$ ) 1:3	$-\Delta m_4$ ( $\text{CoSO}_4 + \text{coke}$ ) 1:1
450	0	0	0	0
500	1.15	0.76	0.42	0
550	3.08	1.92	1.69	0
600	5.0	3.85	2.97	0.47
650	6.54	6.92	4.66	0.94
700	8.85	15.77	7.63	1.89
750	11.15	26.92	14.41	3.30
800	14.62	32.69	17.37	4.72
850	20.78	35.77	23.73	8.96
900	38.46	37.69	34.32	21.69
950	39.23	38.08	36.44	32.08
1000	39.23	38.08	36.86	32.55

Because of the higher temperature of  $\text{CdSO}_4$  decomposition compared to that of the other studied sulfates, up to about 700 °C curves 1 and 2 are almost identical. Above this temperature the effect of the burning fuel on the dissociation is significant and the loss of mass on curve 2 is considerably greater. At 1000 °C,  $\text{CdSO}_4$  dissociation is not complete which is why curves 1 and 2 at this temperature do not coincide. This fact shows that in a reducing process with the presence of  $\text{CdSO}_4$ , its dissociation is greatly intensified when solid fuel is present, and the reducing of  $\text{CdO}$  will be greatly intensified.

The obtained results for the dissociation of the studied  $\text{MeSO}_4$  (Me=Zn, Cu, Pb, Cd, Fe, Co, Ni) [15,16] in the presence of solid fuel are the grounds for making the following general conclusions:

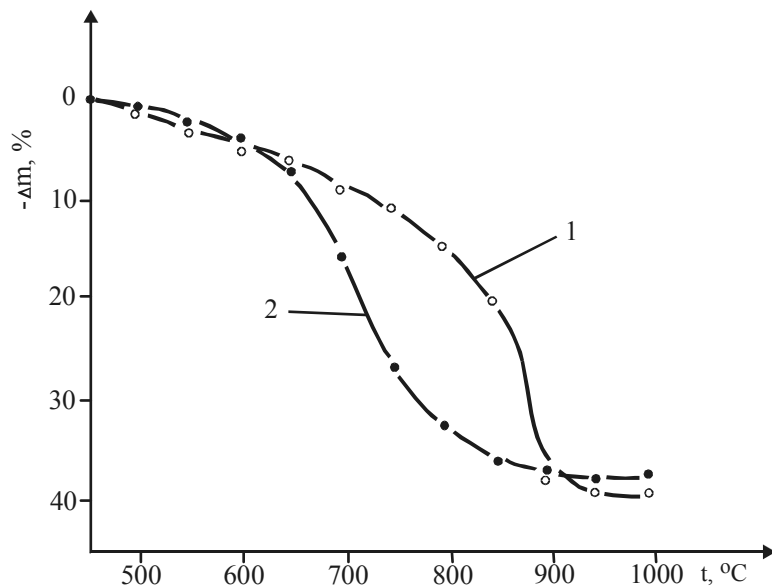


Fig.9. Mass change of  $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$  and coke: individually treated (1) and their mixture (2)

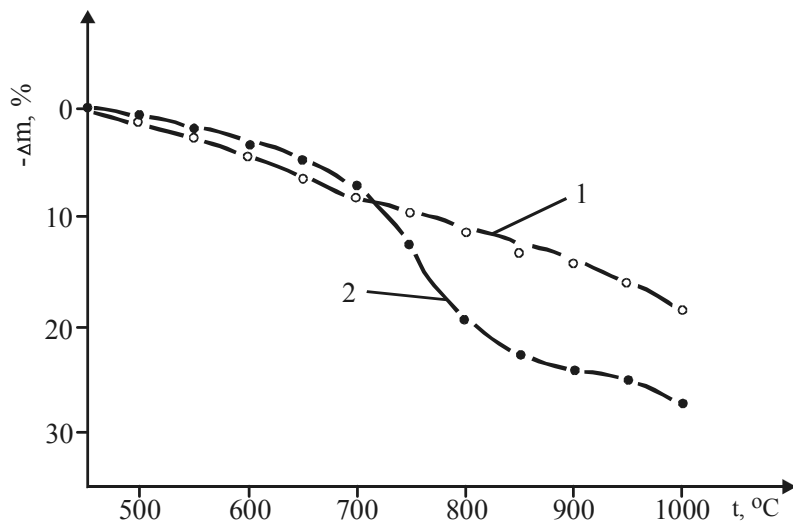


Fig.9. Mass change of  $3\text{CdSO}_4 \cdot 8\text{H}_2\text{O}$  and coke: individually treated (1) and their mixture (2)

1. The dehydration of  $\text{MeSO}_4$  that usually takes place up to a temperature of about 300 - 350 °C is not influenced by the presence of solid fuel, because of the low value of the temperature (before coke combustion). The mechanism of the dehydration process in both cases remains the same.

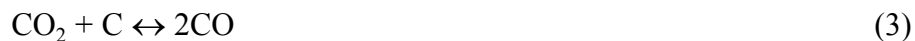
2. Above 450 °C, when coke combustion starts [15], the character of the dissociation process of the already obtained anhydrous sulfates changes significantly. It can be noticed in all sulfates that the dissociation process withdraws to lower temperatures, becomes more intense and that the type of curves, obtained by DTA and TGA, changes.

3. The character of the solid fuel effect on the dissociation of  $\text{MeSO}_4$  is approximately the same for all of them, except  $\text{CdSO}_4$ . Because of the higher temperature of dissociation of  $\text{CdSO}_4$ , the dissociation process at 1000 °C is not complete.

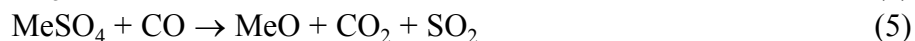
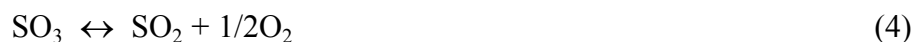
4. According to the decrease in the dissociation temperature, the solid coke has the most significant effect on  $\text{CuSO}_4$ , followed by  $\text{ZnSO}_4$ ,  $\text{NiSO}_4$ ,  $\text{CoSO}_4$  and the slightest effect on  $\text{FeSO}_4$ .

In  $\text{CdSO}_4$  above 850 °C, the dissociation in the presence of solid fuel is greater by about 10% in comparison with the anhydrous  $\text{CdSO}_4$ , and this value is maintained up to 1000 °C.

5. The probable mechanism of the processes taking place in the mixtures of  $\text{MeSO}_4$  and solid fuel can be shown in the following reactions:



$t > 700 \text{ }^\circ\text{C}$



6. The intensification of the dissociation process of  $\text{MeSO}_4$  in the presence of solid fuel in pyrometallurgical processing of sulfate-containing products in reducing environment would lead to withdrawal of the processes to a lower

temperature. This leads to formation of metal oxides products, which can be reduced to the corresponding metals comparatively more easily than other compounds. At the same time, formation of metal oxides (especially when  $\text{PbO}$  and  $\text{SiO}_2$  are present), can lead to obtaining low-temperature melting eutectics, partial melting of the material, worsening of its reduction, forming of crust on the fireproof brickwork.

#### 4. Conclusions

1. It was established that in the system  $\text{MeSO}_4$  – solid fuel the temperature of dissociation of all studied sulfates decreases (by about 100-200 °C). Based on the effect of coke on the dissociation process (rate of dissociation –  $u$ ), the studied sulfates can be arranged in the following order:  $u_{\text{CuSO}_4} > u_{\text{ZnSO}_4} > u_{\text{NiSO}_4} > u_{\text{CoSO}_4} > u_{\text{FeSO}_4}$ . The dissociation of  $\text{CdSO}_4$  is not complete up to 1000 °C.

2. On the basis of the obtained experimental data, a probable mechanism of the processes that take place is proposed.

3. The use of fuel decreases the sulfate content in the lead and zinc cake. This is of great importance to the choice of optimal conditions for carrying out the agglomeration and wealz processes. In the agglomeration of lead raw materials the adding of a small quantity of solid fuel would lead to an increase in the portion of the processed sulfate-containing semi-finished products.

#### References

1. R.Dimitrov and B.Boyanov, *Rudarsko-Metalurski Zbornik*, 31 (1984) 67.
2. A.P.Snurnikov and V.F.Larin, *Non-ferrous Metals*, 6 (1969) 29 (in Russian)
3. A.P.Snurnikov and V.F.Larin, *Non-ferrous Metals*, 7 (1969) 34 (in Russian)
4. B.S.Boyanov, *Thermochimica Acta*, 302 (1997) 109-115.
5. B.Boyanov, R.Dimitrov and N.Dobrev, *Non-ferrous Metals*, 5 (1986) 34 (in Russian)

6. V.Karoleva, Metallurgy of Non-ferrous Metals, *Tekhnika*, Sofia, v.2, 1986, p.299 (in Bulgarian)
7. R.I.Dimitrov, B.S.Boyanov, Ya.P.Balabanov and G.N.Korudanov, *Non-ferrous Metals*, 5 (1983) 12 (in Russian)
8. L. Muresan, G. Maurin, L. Oniciu and D. Gaga, *Hydrometallurgy*, 43 (1996) 345.
9. M.E.Brown, D.Dollimore and A.K.Galwey, Solid State Reactions, *Mir, Moscow*, 1983, p.357 (in Russian)
10. Y.Pelovski, V.Petkova, I.Dombalov, and I.Grancharov, *J.Therm.Anal.*, 36 (1990) 1727.
11. H.Tagawa, *Thermochimica Acta*, 80 (1984) 23.
12. H.Tagawa and H.Saijo, *Thermochimica Acta*, 91 (1985) 67.
13. H.Tagawa and K.Kawabe, *Thermochimica Acta*, 158 (1990) 293.
14. H.Tanaka, M.Kawano and N.Koga, *Thermochimica Acta*, 182 (1991) 281.
15. B.Boyanov and R.Dimitrov, *Thermochimica Acta*, 322 (1998) 69.
16. B.Boyanov, Dissociation of  $\text{MeSO}_4$  (Me = Zn, Cu, Pb) in the presence of coke, *J.Therm.Anal.Cal.* (in print)