

Investigation of Sulphatization Process in The system $\text{MnCO}_3\text{-MnO}_2\text{-FeSO}_4\text{-O}_2$

Eftimija Hristova, Nikola Nacevski, Goran Nacevski

*Faculty of technology and metallurgy, "Sv. Kiril i Metodij" University,
"Ruger Boskovic" 16, P.O.Box 580 MK - 1001 Skopje, Republic of Macedonia,
E-mail: nacevski@mail.net.mk*

Summary. The paper deals with kinetic of sulphatization of MnCO_3 using activation and substitution with FeSO_4 . Using Differential Thermal Analysis (DTA) and Thermogravimetric (TG) analysis temperature range of activation and substitution with FeSO_4 , where MnSO_4 is a product of reaction, is definite. Several series of sulfuric roasting tests, using different molar ratio $\text{MnCO}_3\text{:FeSO}_4$ between 1:1 and 1:2, were carried out to examine optimal molar ratio. With X-ray analyses temperature range of activation and substitution is detected. Using quantitative analyses optimal molar ratio $\text{MnCO}_3\text{:FeSO}_4$ is determinate. The results of fundamental investigations are implicated for the process of sulphatization of carbonate Mn-ore with FeSO_4 substitution. Chemical and X-ray diffraction phase analyses performed the determination of the phase characteristics of the Mn-ore. For achieving maximal concentration of manganese, optimal particle size of the grain is determinate using granulometric analyses.

Introduction

In Republic of Macedonia there is a reserve of manganese ores, oxide and carbonate ore, which from economical aspect it's not possible to be directly obtained with classical piro-hidrometallurgical methods.

But with previously sulphating roasting of manganese ores with addition of activation agents, respectively with using of activation and substitution of ferrosulphate we can achieve transformation of manganese in mangesulphate, at the same time concentration of manganese in roasted ore.

Previous fundamental investigations of kinetic of reactions from pure MnO_2 and MnCO_3 will be used for process of sulphating roasting of Mn-ores with FeSO_4 as substitutions.

With investigations of kinetic of roasting process, using modern methods of experimental investigation and pure components chemise and mechanize of process of activation and substitution will be define.

Theoretical

On the basis of facts about the behavior of manganese oxides and Fe (II) sulphate at high temperatures, one can assume the course of the reactions (1)-(9) (Table 1).

Eq. No.	Reaction	ΔG_{700} (kJ/mol)	ΔG_{950} (kJ/mol)
1	$6\text{FeSO}_{4(s)} = \text{Fe}_2(\text{SO}_4)_3(s) + 2\text{Fe}_2\text{O}_3(s) + 3\text{SO}_2(g)$	102.07	-16.34
2	$\text{Fe}_2(\text{SO}_4)_3(s) = \text{Fe}_2\text{SO}_3(s) + 3\text{SO}_2(g)$	188.00	54.46
3	$2\text{FeSO}_{4(s)} = \text{Fe}_2\text{SO}_3(s) + \text{SO}_2(g) + \text{SO}_3(g)$	96.69	12.7
4	$\text{SO}_2(g) + 0.5\text{O}_2(g) = \text{SO}_3(g)$	-32.95	-9.61
5	$2\text{MnO}_2(s) = \text{Mn}_2\text{O}_3(s) + 0.5\text{O}_2(g)$	8.86	-17.05
6	$2\text{MnO}_2(s) + \text{SO}_2(g) = 2\text{MnSO}_4(s)$	-236.33	-148.93
7	$\text{Mn}_2\text{O}_3(s) + \text{SO}_2(g) + 0.5\text{O}_2(g) = 2\text{MnSO}_4(s)$	-245.19	-131.88
8	$\text{Mn}_2\text{O}_3(s) + \text{SO}_3(g) = 2\text{MnSO}_4(s) + 0.5\text{O}_2(g)$	-179.28	-112.66
9	$2\text{MnO}_2(s) + \text{FeSO}_4(s) = 2\text{MnSO}_4(s) + \text{Fe}_2\text{O}_3(s) + 0.5\text{O}_2(g)$	106.69	-126.61

According to eq.(1), dissociation of Fe(II) sulphate is possible at temperatures higher than 677 °C. The reactions presented in eq.(2) and (3) are thermodynamically impossible. The thermal decomposition of Mn(IV) oxide does not occur at the temperatures below 527 °C (eq.(5)). The reactions (6)-(8) are thermodynamically possible with presence of SO₂ and SO₃ gas phases. The sulphatization of MnO₂ with solid Fe(II) sulphate (eq. (9)) was thermodynamically expected at the temperatures higher than 627 °C. Phase stability diagrams in systems Fe-S-O and Mn-S-O are presented in Figs. 1,2.

Phase stability diagrams were obtained by using the PC program HSC 1.12 for thermodynamic calculations. It is seen from Figs.1, 2 that sulphatization of MnO₂ is possible at small area S.

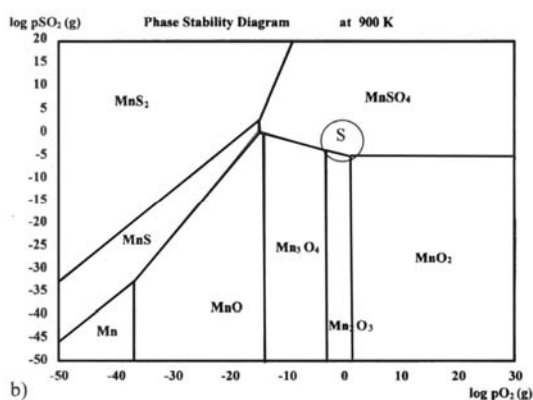
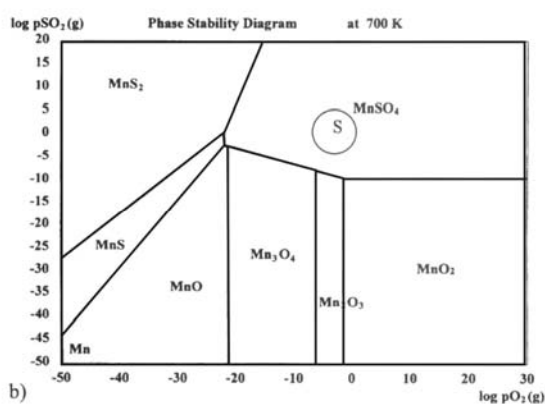
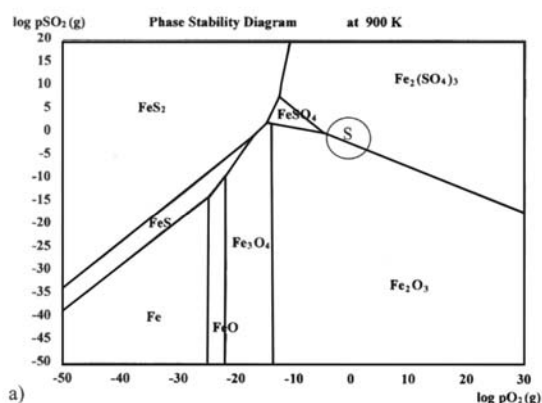
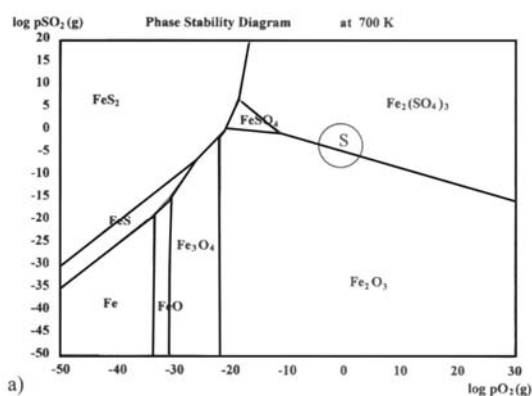


Fig. 1. Phase stability diagrams in system (a) Fe-S-O and (b) Mn-S-O at the temperature of 427 °C (S–sulphatization area).

Fig. 2. Phase stability diagrams in system (a) Fe-S-O and (b) Mn-S-O at the temperature of 627 °C (S–sulphatization area).

Experimental

Fundamental investigations of sulphatization process for pure components (MnCO_3 , MnO and FeSO_4) in the function of temperature were performed. Using the equipment “Q-DERIVATOGRAPH” produced by MOM (Ungaria), the weight change of the sample (TG), the rate of weight change (DTG) and the enthalpy change (DTA), under next experimental conditions: mass of sample: 100 mg, DTA sensor control - 1mV, DTG sensor control - 1mV and TG sensor control - 1mg, are measured simultaneously for: MnCO_3 , MnO_2 , FeSO_4 , $\text{MnCO}_3 + \text{FeSO}_4$, $\text{MnO}_2 + \text{FeSO}_4$ and MnSO_4 . Results are presented in fig. (3)– (8).

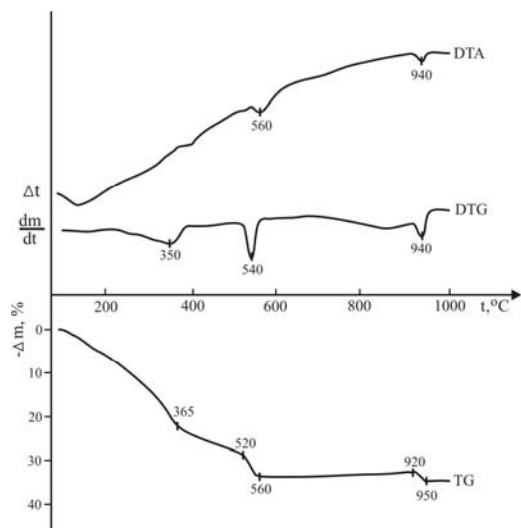


Fig. 3. DTA-DTG-TG traces for sample of MnCO₃

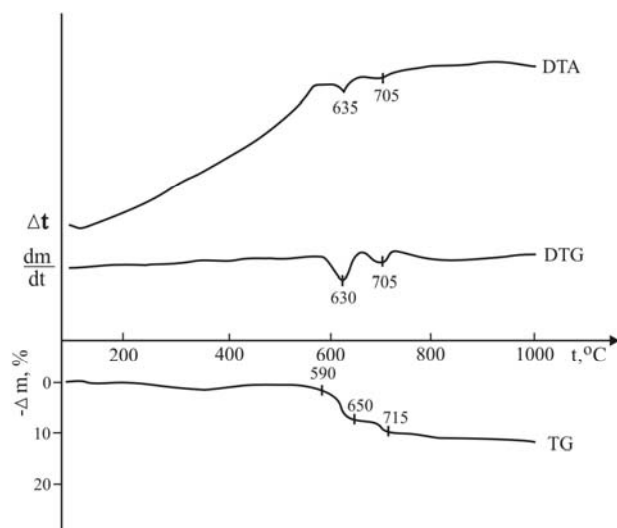


Fig. 4. DTA-DTG-TG traces for sample of MnO₂

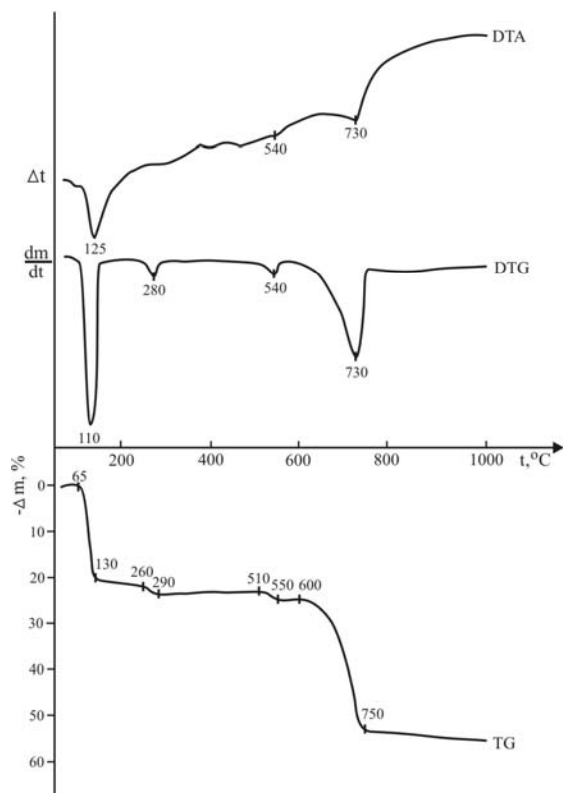


Fig. 5. DTA-DTG-TG traces for sample of FeSO₄

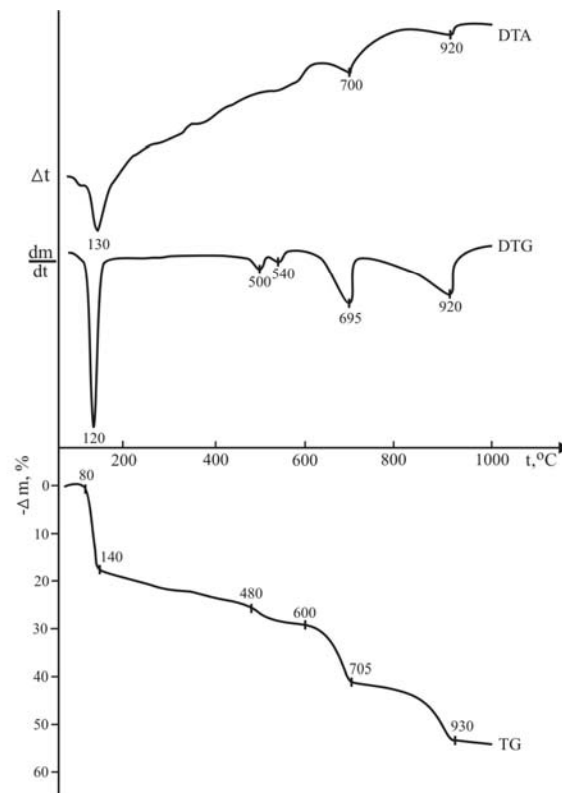


Fig. 6. DTA-DTG-TG traces for sample of MnCO₃+FeSO₄

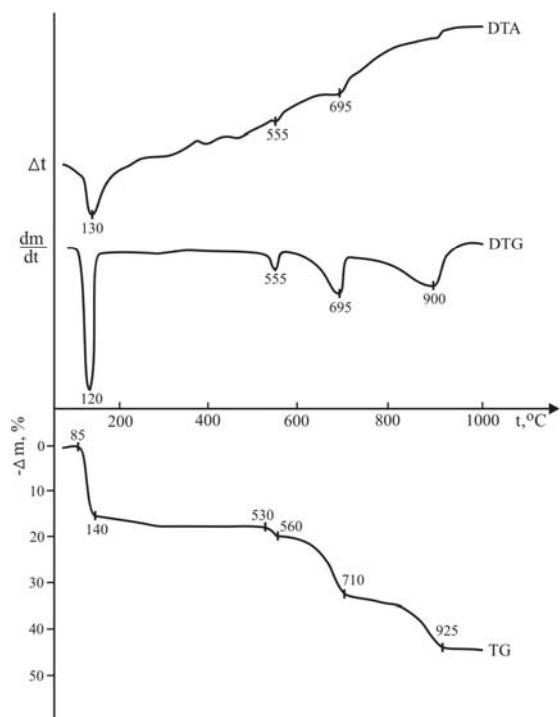


Fig. 7. DTA-DTG-TG traces for sample of $\text{MnO}_2+\text{FeSO}_4$

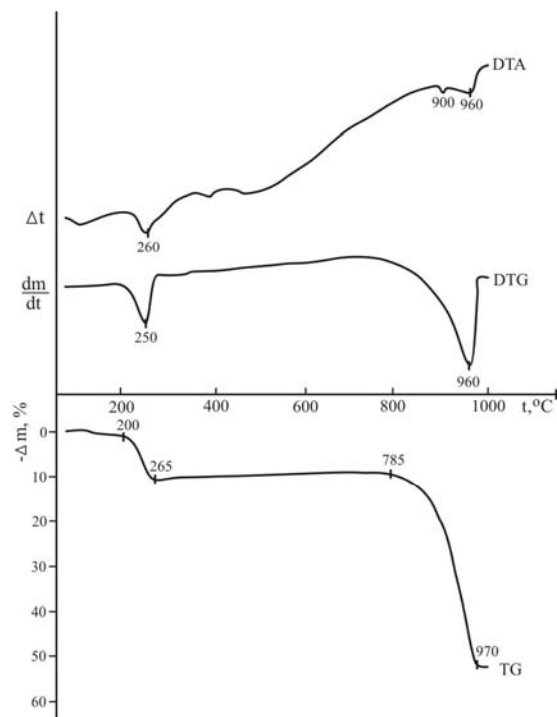


Fig. 8. DTA-DTG-TG traces for sample of MnSO_4

The DTA-DTG-TG trace for the MnCO_3 sample (fig.3.) shows endothermic peaks confirming dissociation of MnCO_3 to MnO_2 and then to Mn_3O_4 as final product. The DTA-DTG-TG trace for the MnO_2 sample (fig.4.) shows endothermic peak at 650°C confirming transformation $\text{MnO}_2 \rightarrow \text{Mn}_3\text{O}_4$. The DTA-DTG-TG trace for the ferrosulphate sample (fig. 5) shows endothermic peaks at 110°C , 280°C , 540°C and 730°C confirming the removal of water, transformation $\text{FeSO}_4 \rightarrow \text{Fe}_2(\text{SO}_4)_3$ and thermal dissociation of $\text{Fe}_2(\text{SO}_4)_3$ with Fe_2O_3 as final product. It is seen from fig.6 and fig.7 that endothermic peaks of DTA-DTG-TG trace for sulphatization of MnCO_3 to MnO_2 are in close temperature interval, where, peak at 695°C confirming transformation of manganese in manganesulphate and peak at 920°C confirming dissociation of MnSO_4 and transformation to Mn_2O_3 (fig. 8).

Chemical analyses of ferrosulphate as sulphatization agent is given in table 2.

Table 2. Chemical analysis of ferrosulphate

Comp.	$\text{FeSO}_4\cdot\text{H}_2\text{O}$	Fe^{3+}
%	96.13	0.57

In order to investigate the composition of the product of thermal treatment of sulphatization agent ferro sulphate, depending on temperature 450-700 °C, series of experiments were performed. The thermal treatment residue was leached in water to dissolve Fe^{2+} and Fe^{3+} . The quantity of dissolved components in relation to temperature is presented in Table 3.

Table 3. Dependence of $\text{FeSO}_4 \cdot \text{H}_2\text{O}$ dissociation degree on temperature

T (°C)	Fe^{2+} (g/dm ³)	Fe^{3+} (g/dm ³)	Fe^{2+} (%)	Fe^{3+} (%)	Fe_2O_3 (%)*
450	9.3	6.0	57.2	36.9	5.9
500	3.2	9.0	19.7	53.3	25.0
600	3.3	7.6	20.3	46.7	33.0
700	0.1	4.6	0.6	28.3	71.1

*Calculated from $(\text{Fe}^{2+} + \text{Fe}^{3+}) - \Sigma \text{Fe} = \text{Fe}_2\text{O}_3$

According to Table 3, Fe^{2+} oxidizes to Fe^{3+} and $\text{Fe}_2(\text{SO}_4)_2$, producing the SO_2 and SO_3 gas phase.

Experimental results of sulphate roasting process of MnCO_3

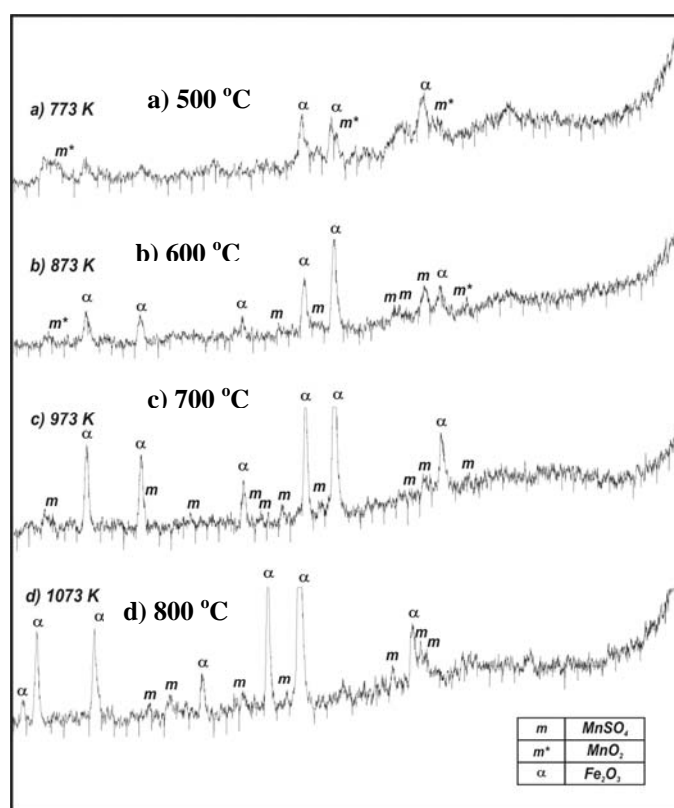
Sulphatization process of MnCO_3 with ferrosulphate as sulphatization agent was investigated with several series of tests under next conditions: molar ratio phase $\text{MnCO}_3/\text{FeSO}_4$: 1/1; 1/1.2; 1/1.5; 1/2, time of roasting 15 min - 90 min, and constant temperature (700 °C). The testing samples were prepared by homogenization of MnCO_3 and FeSO_4 , and roasted in quartz tube heated in an electro furnace. Achieved results are shown in table 4.

Based on data obtained in table 4, can be concluded that under constant temperature of roasting (700°C) maximal grade of sulphatization is achieved when molar ratio phase $\text{MnCO}_3/\text{FeSO}_4$ is 1/1.5 and time of roasting 60 min.

The XRD patterns of $\text{MnCO}_3/\text{FeSO}_4$ mixture in 1/1.5 molar ratio phase, as product of thermal treatment at different temperatures: 500°C (a); 600°C (b); 700°C (c) and 800°C (d) are shown at fig. 9.

Table 4. Results from sulphate roasting as a function of molar ratio phase and time

N° sample	Time (min)	MnCO ₃ /FeSO ₄	m (MnCO ₃) (gr.)	m (FeSO ₄) (gr.)	C _(Mn⁺⁺) (mg/dm ³)	grade of sulphatization (%)
1	15	1/1	1.00076	2.68050	1598.82	83.51
2	30	1/1	1.00036	2.68042	1591.06	83.14
3	60	1/1	1.00063	2.68002	1674.48	87.47
4	90	1/1	1.00078	2.68005	1564.15	81.70
5	15	1/1.2	0.92042	2.95005	1250.00	70.99
6	30	1/1.2	0.92052	2.95003	1257.02	71.38
7	60	1/1.2	0.92079	2.95002	1222.69	69.41
8	90	1/1.2	0.92002	2.95021	1272.45	72.30
9	15	1/1.5	0.75004	3.02004	1413.22	98.49
10	30	1/1.5	0.75024	3.02040	1459.03	98.86
11	60	1/1.5	0.75054	3.02011	1527.32	99.78
12	90	1/1.5	0.75024	3.02001	1525.32	99.47
13	15	1/2	0.58288	3.31229	963.90	86.44
14	30	1/2	0.58142	3.13119	920.14	82.73
15	60	1/2	0.58010	3.13022	946.45	85.28
16	90	1/2	0.58070	3.13132	935.46	84.21

**Fig.9** XRD patterns of MnCO₃/FeSO₄ mixture roasted at: 500 °C (a); 600 °C (b); 700 °C (c) and 800 °C (d)

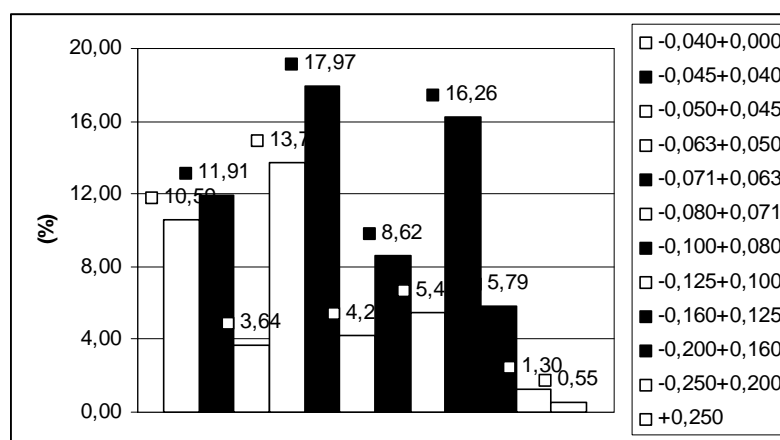
For sample (a) roasted at temperature of 500 °C there are indications for presence of MnO_2 (m^*) so the process of sulphatization is not started. But, in sample (b) roasted at temperature of 600 °C it can be observed diffraction lines of MnSO_4 (m) which leads us to conclusion that sulphatization process is started. For sample (c) there are no indications of presence of MnO_2 , and also we can see the strongest diffraction lines for determination for presence of MnSO_4 .

Characterization of carbonate Mn ore

The complete research is done with an average sample of carbonate Mn ore: chemical analyses of Mn ore (table 5), granulometric analyses (fig.10) and DTA-DTG-TG analyses (fig. 11).

Table 5. The results of chemical analysis of carbonate Mn-ore

Comp.	Mn	Fe	SiO_2	CaO	MgO	S	Al_2O_3	CO_2
%	28.54	2.13	12.72	6.51	4.05	0.27	2.55	27.64



Mn (%)											
1	2	3	4	5	6	7	8	9	10	11	12
35.275	34.42	34.8	34.8	36.97	38.67	38.67	39.52	40.8	43.77	45.0	42.5
	5	5	5	5	5	5	5	0	5	5	

Fig.10 The granulometric distribution map of the sample of carbonate Mn-ore

The granulometric distribution map and chemical analysis of Mn (%) for all fractions show that the optimal particle size of the grain with maximal concentration of manganese is in range - 0.250+0.200 mm.

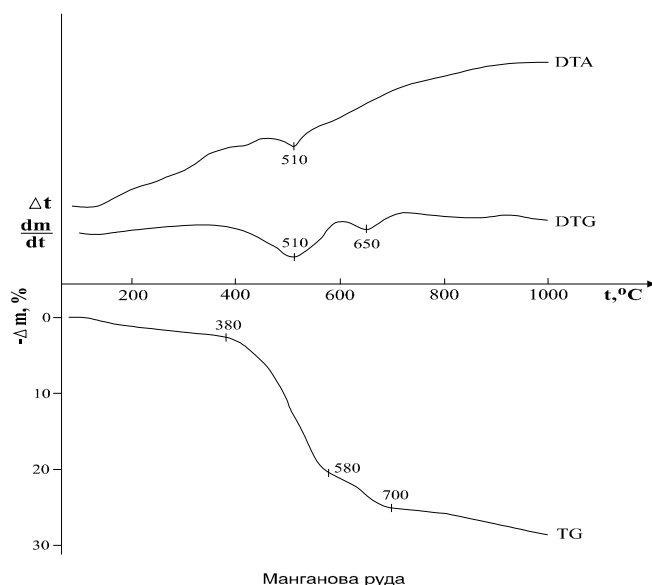


Fig. 11 DTA-DTG-TG traces for sample of carbonate Mn ore

The DTA-DTG-TG trace for the carbonate Mn ore sample (fig.11.) shows two endothermic peaks confirming dissociation of MnCO_3 to MnO_2 .

Conclusion

On the basis of experimental data the following could be concluded:

- Using Differential Thermal Analysis (DTA) and Termogravimetric (TG) analysis are definite phase transformations of MnCO_3 and FeSO_4 , and from the other hand temperature range of activation and substitution with FeSO_4 as a sulphatization agent - 695°C , (where MnSO_4 is a product of reaction).
- Process of sulphatization of MnCO_3 with FeSO_4 , under constant temperature of roasting 700°C , maximal grade of sulphatization (99.86 %) is achieved when molar ratio phase $\text{MnCO}_3/\text{FeSO}_4$ is 1/1.5 and time of roasting 60 min.
- With X-ray diffraction (XRD) patterns, the temperature of substitution and forming of MnCO_3 (700°C) is proved.
- Granulometric distribution map with chemical analysis of Mn (%) for all fractions and DTA-DTG-TG trace for the carbonate Mn ore confirming dissociation of MnCO_3 to MnO_2 at the temperature of 650°C with optimal particle size in range - $0.250+0.200$ mm, where maximal concentration of manganese is in the carbonate Mn ore.

References

1. F. Paulik, I. Paulik, L. Erdei, Teoreti~ni osnovi na derivatografskite izsleavania, NHT, Plovdiv, 1985,
2. M. Braun, D. Dollimor, A. Galvei, Reakcii tverdi~h tel, MIR, Moskva, 1983,
3. Zivkovic Z, Savovic C. Principles of metallurgical thermodynamics, Tech. Fac Bor; Bor, Yugoslavia: 1997
4. Zivkovic Z, Dobrovisek B. Differential Thermal Analysis, Tech. Fac Bor; Bor, Yugoslavia: 1984
5. R. Vracar, D. Sinadinovic, N. Vidakovic, Z. Kamberovic, Sulphatization of manganese slime from zinc electrolyses with ferrosulphate, Scandunavian Journal of Metallurgy, Munksgaard, **261-267**, 27 (1998)
6. M. Spasic, D. Vucorovic, I.Ilic, R.Vracar, Mining and Metallurgy, **201-220**, 9 (1966)
7. M. Saeed, N. Nusrat, K. M. Bahatty, V. Madan, J. Pak, Sci Ind Res, **376-379**, 29(5) (1986)
8. M. Tugatepe, O. Murat, A. Kujulu, Z. Baban, A. Kasgos, Chem. Acta Turc, **1-15**, 13(1) (1985)
9. G. Haralampiev, Teoria na metalurgi~nite procesi, Tehnika, Sofija, 1987