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CALCINATION OF THE TURKISH MANGANESE ORE FROM DENÎZLÎ-TAVAS REGION

The production of steel and high demand for ferro-manganese used in the Turkish iron and steel industry increases every year. In Turkey, there are some important ore reserves of manganese, especially in the Denîzlî-Tavas region. However, this carbonated ore body has relatively low content of manganese which is about 31% Mn. The aim of this work was to calcine the fore-mentioned ore to increase its manganese content and so make it more suitable to carbothermic reduction in a furnace for ferro-manganese production. The main parameters studied were temperature of calcination, duration of calcination and size of ore. The results showed that, although a temperature of 700 °C was enough to calcine a sample ground finely to –74 microns, for the calcination of an ore crushed to about 1 mm grain size a temperature of 900 °C and 1 hour duration would be more suitable industrially. Under these conditions, the weight loss of the sample was about 15.5% and its manganese content increased to 36%.

INTRODUCTION

Research was initiated in the Middle East Technical University, Metallurgical and Materials Engineering Department with the ultimate purpose of using the Turkish manganese ores for the production of ferro-manganese in an already existing iron blast furnace or in an electric arc furnace that will be constructed newly (Emeksiz, 1993; Îmer, 1997). Turkey has some manganese ore bodies scattered around the country. The ore body found in the Denîzlî-Tavas region is the largest with the ore reserve of 2.68 Tg. However, the ore is of carbonate type with a relatively low content of manganese, about 31% Mn, and it falls in a group called ‘ferruginous’(10–35% Mn). Therefore, the purpose of this work is to calcine the mentioned ore to remove its carbon dioxide and crystalline water and to make it more suitable to carbothermic reduction as ferro-manganese.

Manganese ores are usually calcinated since they have crystalline water in their structure. In addition, if the ore has rhodocrosite type carbonates, it will give off carbon dioxide together with combined water. A minimum temperature for

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decomposition of various carbonates and hydroxides at 1 atm total pressure can be obtained from $\log p$–$1/T$ type of diagrams (Rosenqvist, 1974). It can be seen from such diagrams that minimum temperature for decomposition of rhodocrosite ($MnCO_3$) under atmospheric pressure is about 400 °C. If there is also manganite ($Mn_2O_3{\cdot}H_2O$) in the ore, the minimum temperature for its decomposition will be above 200 °C. Therefore, it is expected that calcination will start above 200 °C.

In literature, aside from theoretical works on the subject, there were no calcination studies encountered on carbonate type of ores containing relatively low manganese. However, literature survey showed that the reduction of such ores by carbon at various temperatures had been studied previously (Brandstatter,1981; Hansen,1993). It was evident that calcination reactions would take place while ore was heated to the working temperature.

EXPERIMENTAL

Characterizaton of the sample

A 50-kg representative ore sample was procured from Ereðli Iron and Steel Works of Turkey which owns the mining rights of the manganese ore body in the Denîzlî-Tavas region. This bulk sample was crushed and ground to 1mm size, successively, to get samples of about 50 g for chemical and mineralogical analyses. The complete analysis of Denîzlî-Tavas ore is given in Table 1. In this table, the ignition loss was more than necessary stoichiometric carbon dioxide to combine with manganese as manganese carbonate, indicating that there was also some combined water in the structure of the ore.

Table 1. Chemical composition of Denîzlî-Tavas manganese ore

Element	wt. %	Compound	wt. %
Mn	30.34	SiO_2	18.72
Fe	5.56	CaO	7.32
S	1.48	Al_2O_3	3.52
Zn	0.34	MgO	2.41
Ni	0.30	K_2O	0.65
Cu	0.11	TiO_2	0.53
P	0.13	Na_2O	0.19
Pb	0.07	Ignition Loss	15.10
As	0.09	(IL)	

The Thermogravimetric Analysis (TGA) and Differential Thermal Analysis (DTA) of this manganese ore was also done. The thermogravimetric analysis showed that weight loss started already at 60 °C due to evaporation of mechanically held water. The total weight loss was 18.8%. On the other hand, the peaks on the DTA curve indicated the presence of an extensive endothermic reaction around 160 °C relatively less endothermic reactions at temperatures of 420, 520 and 810 °C, and, a strongly endothermic reaction at 1150 °C. The reaction around 160 °C was probably due to evaporation of chemically bound water. The other reactions were probably due to decomposition of carbonates. The difference of 3.7% between the TGA weight loss and ignition loss given in Table 1 appeared to be due to usage of a wet sample during TGA analysis.

Mineralogical analysis of the Denîzlî-Tavas ore was done by combining results of microscopic examination of some typical samples in epoxy and as thin sections, and studying the X-ray diffraction patterns of powdered samples with a computerized Rigaku X-ray diffractometer. This analysis gave the following results:

- The ore mineral found most abundant in the ore was rhodochrosite ($MnCO_3$), either free or locked in calcite, and with colour varying from light pink to dark brown. Its weight percentage was between 20–25%.

Table 2. The mineralogical composition of Denîzlî-Tavas manganese ore

Mineral	Weight, %*
Rhodochrosite	21.0
Manganite	16.0
Psilomelane	12.0
Pyrolusite	5.0
Bixbyite + Hausmannite + Braunite	3.0
Calcite	13.1
Quartz	18.7
Pyrite	2.8
Al_20_3	3.5
MgO	2.4

*Total is 97.5%. Rest, which is 2.5%, is the sum of other elements or oxides given in Table 1.

- The second ore mineral was dark gray coloured manganite ($Mn_2O_3xH_2O$). This mineral was also encountered as fine, light gray-white-coloured and amorphous manganese hydroxide, disseminated extensively in gangue minerals. Its abundance was in the range 15–20 wt. %.
- The third important ore mineral was light gray-coloured psilomelane (nearly MnO_2 – there might be some K, Ba, Pb, Fe, Cu, Zn in its structure). It appeared to be in carbonated or siliceous gangue, together with pyrolusite. It was 10–15 wt. % of the ore.

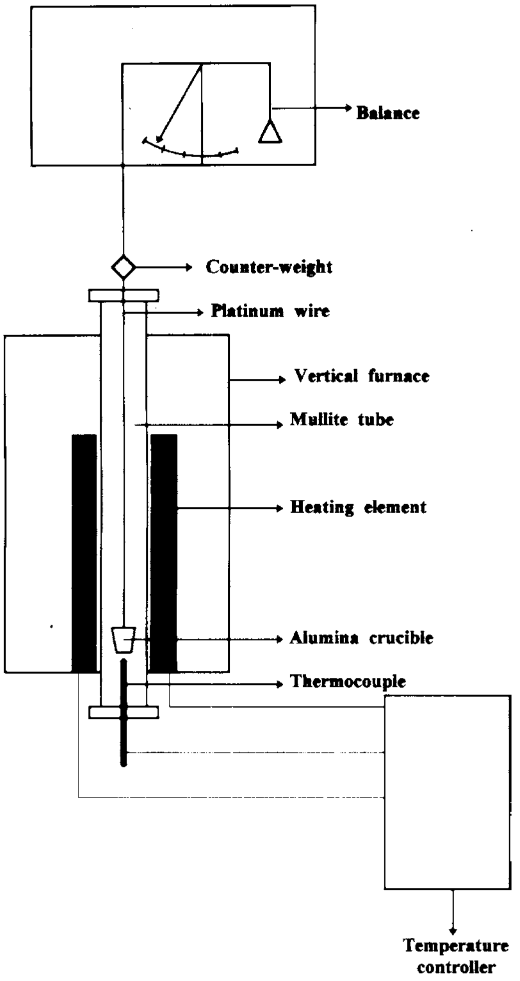

Fig. 1. Schematic representation of thermal balance set-up

- White coloured pyrolusite (MnO_2) was also present. Together with psilomelane.
- It also showed a colloform aggregate, with these two minerals forming kidney-shaped concentric layers. The amount of pyrolusite was in the range 5–6 wt. %.
- There were also some ore minerals as bixbyite ($(Mn,Fe)_2O_3$), hausmannite (Mn_3O_4) and braunite ($3(Mn,Fe)_2O_3.MnSiO_3$).The total of these was about 3 wt. %.
- In addition, there were, in small quantities, minerals of jacobsite ($(Mn,Fe)_3O_4$), hematite (Fe_2O_3), lepidocrosite ($FeO(OH)$), goethite ($HFeO_2$), limonite ($FeO(OH)\cdot nH_2O$), pyrite (FeS_2), rutile (TiO_2) and marcasite (FeS_2).
- The main gangue minerals in the ore were calcite ($CaCO_3$) and quartz (SiO_2). The weight percentages of these were about 10% and 18–20%, respectively. Considering the mineralogical analysis of Denîzlî-Tavas ore together with its chemical analyses, the resulted approximate mineralogical composition is as shown in Table 2.

Calcination experiments

In the calcination experiments, the parameters that could be changed and, ought to be determined are temperature, duration of experiments, and particle size of ore. Therefore, the experiments were done in this work with the purpose of determining the optimum values of these parameters.

Two different set-ups were used during calcination experiments; one of them was Cahn 1000 electrobalance with a weight measurement sensitivity of ±10 mg (sensitivity is dependent on the weight of the sample) and with a furnace that can be heated to maximum 1200 °C, while the other one was a thermal balance with a furnace that can be heated to maximum 1500 °C and made in METU. The electrobalance used was a standard instrument with a flow-through tube hanging from top and argon as protective gas, so, since it was not very much different from thermal balance, its set-up was not given here. The thermal balance set-up is shown in Fig. 1.

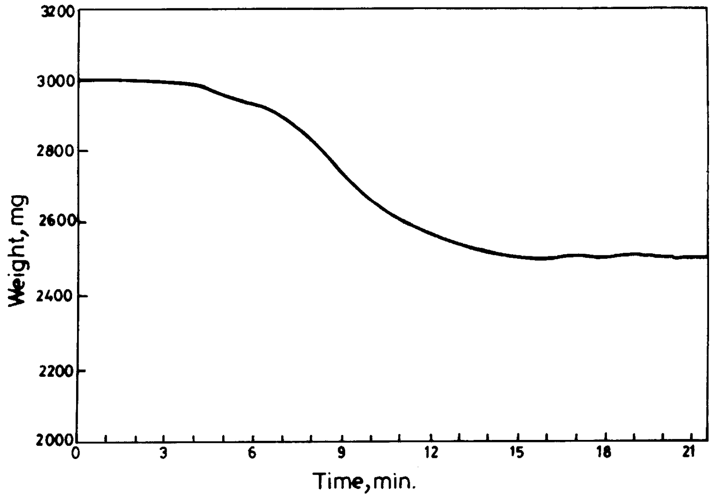

Fig. 2. Weight versus time plot, $T = 900$ °C, under argon

Electrobalance measurements

Manganese ore samples of about 3 grams ground to –200 mesh were filled in alumina crucibles with 2 cm diameter and 3 cm length and weighed with an accuracy of ±1 mg using a standard laboratory balance. Then, for each experiment one crucible was fixed to the end of a platinum wire with 50 cm length and lowered down to the hottest zone of the furnace. The wire was hanged from the other end to the electrobalance, alumina furnace tube was installed and gas flow connections were done to make it gas-tight. Heating was started after purging the furnace tube with argon at a rate of 50 cc/min for about 5 minutes. Under lowered argon flow, the furnace reached the desired temperature in about 5 minutes. The weights were recorded immediately after the beginning of heating at intervals of 0.5 minutes. Since electrobalance was connected to a computer, recording of the weights was done automatically and then these values were used to plot computer graphs. An example for recorded weights is given in Table 3. The curve plotted using these values is shown in Fig. 2. The effect of temperature on total weight loss during calcination of Denîzlî-Tavas manganese ore under argon gas can be seen from Table 4 and Fig. 3.

Table 3. Weight losses as function of time in experiment No.1 as determined by electrobalance. Argon atmosphere, T= 900 °C

Time min	Weight mg	Time min	Weight mg	Time min	Weight mg	Time min	Weight mg
0	3003.5	5.5	2942.0	11	2602.1	16.5	2500.6
0.5	3003.6	6	2935.1	11.5	2581.1	17	2500.6
1	2999.6	6.5	2918.5	12	2564.1	17.5	2503.0
1.5	3000.6	7	2899.0	12.5	2550.4	18	2496.7
2	3000.6	7.5	2863.4	13	2537.7	18.5	2504.5
2.5	2999.1	8	2827.7	13.5	2523.0	19	2503.5
3	2997.6	8.5	2774.5	14	2512.3	19.5	2503.5
3.5	2996.7	9	2730.1	14.5	2499.1	20	2497.3
4	2993.7	9.5	2691.0	15	2502.5	20.5	2497.3
4.5	2972.3	10	2651.9	15.5	2498.6	21	2497.3
5	2959.1	10.5	2631.0	16	2495.2	21.5	2497.3

Initial weight: 3003.5 mg, final weight: 2497.3 mg, weight loss: 506.2 mg, loss%: 16.9.

Table 4. Total weight losses detected by electrobalance
Sample particle size –200 mesh

Experiment No.	Temperature °C	Total weight loss, mg	Total weight loss, %	Weight loss after 20 min, %
1	900	506.2	16.9	16.9
2	600	424.8	11.5	10.5
3	1000	831.1	17.8	17.8
4	400	230.0	5.05	4.45
5	850	760.6	16.71	16.71
6	300	124.0	2.79	2.77
7	700	629.4	14.16	13.26

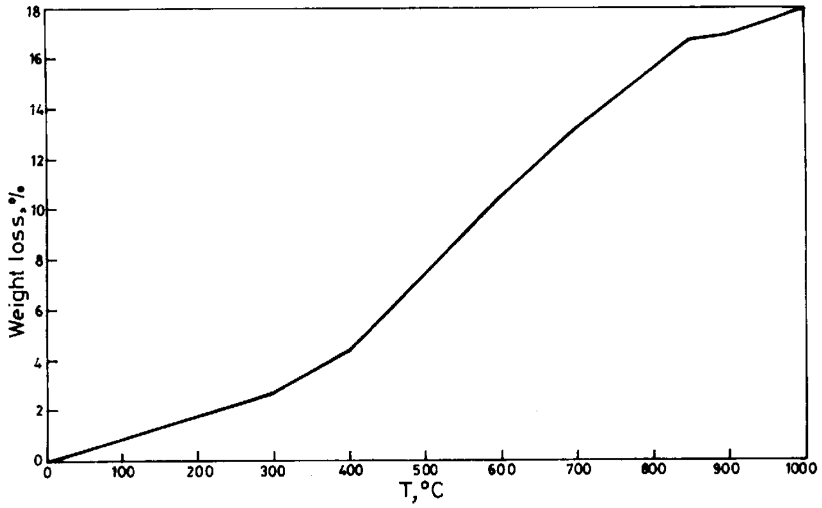

Fig. 3. The variation of weight loss in electrobalance with temperature for a fixed calcination time of 20 min

Thermal balance measurements

The calcination experiments in electrobalance did not exactly represent industrial conditions since it was necessary to use argon gas to protect sensitive parts of electrobalance and since calcination started before the temperature of the furnace was constant (it was difficult to hang the crucible containing the sample at a high temperature). Therefore, it was necessary to construct a new thermal balance set-up. The sample was suspended from top, as in electrobalance. The difference was that the sample crucible was held in a relatively cold upper region of the furnace during heating and lowered to the hot zone of it only when a steady working temperature was obtained. The weight measurement sensitivity of this thermal balance was about ±1 mg.

Before starting the experiments the hot zone of the furnace was found by determining the temperature profile of it. For this purpose, the temperature of the furnace was set to 1000 °C by controller, a Pt–Pt 13% Rh thermocouple wire was lowered down the furnace tube and temperature measurements were done in intervals of 5 mm by moving thermocouple up and down. By this way, the length of the hot zone of the furnace and variation of temperature in this zone were found to be 4cm and ±8 °C, respectively. Besides, the measured temperature of the hot zone of the furnace was compared with the temperature indicated by the controller and calibrated, taking 0 °C as reference.

In the experiments without any protective gas flow, the temperature of the hot zone of the furnace was initially set to the desired value, and then, 5–8 gram sample placed in an alumina crucible with dimensions 2 cm ϕ by 5 cm length, was lowered to this zone at the end of a platinum wire. This wire was hanged from the other end to the thermal balance.

The data in Table 5 and Fig. 4 are given as examples to the weights detected as function of time for a constant temperature of 900 °C. The final experimental results of thermal balance measurements are shown in Table 6. The effect of particle size of the ore on calcination behaviour can be also seen clearly from this table.

Table 5. Weights measured by thermal balance in experiment No.11, in air, $T = 900$ °C, particle size = –200 mesh

Time min	Weight mg	Time min	Weight mg
0	5084	11	4270
1	4988	12	4270
2	4782	13	4270
3	4608	14	4270
4	4438	15	4270
5	4361	16	4270
6	4320	17	4270
7	4266	18	4270
8	4270	19	4270
9	4270	20	4270
10	4270		

Empty crucible: 10272 mg, crucible + sample: 15356 mg, sample weight: 5084 mg, final weight: 4270 mg, weight loss: 814 mg, loss, %: 16.01.

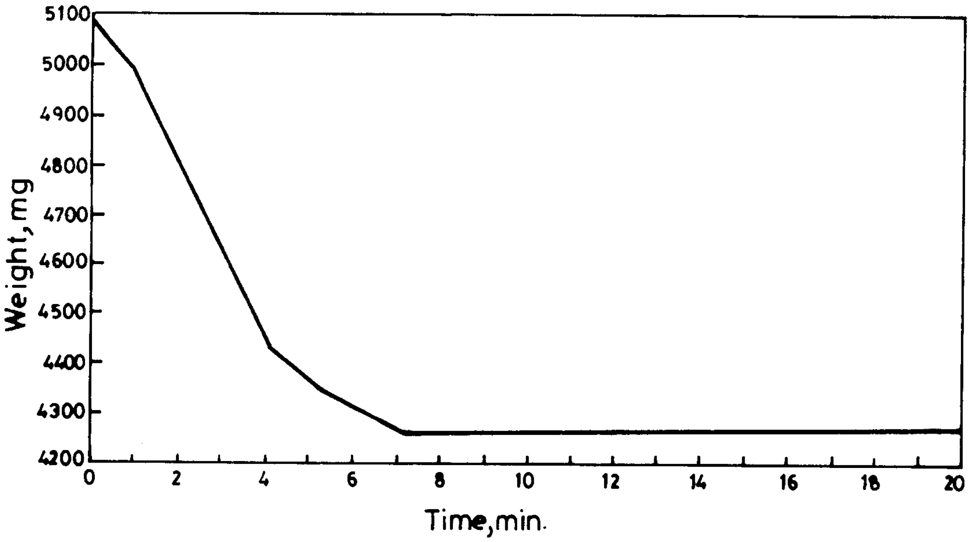

Fig. 4. Weight versus time curve for experiment No.11 done by thermal balance, in air, $T = 900$ °C

Table 6. Total weight losses in experiments done by thermal balance

Experiment No.	Temp. °C	Particle size mesh	Tot. weight loss, mg	Tot. weight loss, %	Const. weight time, min
8	700	–200	669	13.37	28
9	800	–1 mm	1179	15.89	55
10	800	–20 +28	847	15.52	42
11	900	–200	814	16.01	8
12	900	–20 +28	905	15.06	9
13	900	–1 mm	1247	15.99	14

RESULTS AND DISCUSSION

The calcination experiments carried out by means of electrobalance under an inert argon gas and using very finely ground sample showed that at the temperature range of 900–1000 °C the calcination was complete in 15 to 20 minutes, with H_2O and CO_2 in the structure being expelled. Under these conditions, complete calcination of the ore resulted in an average weight loss of 16.5%. Complete calcination could be also realized below 900 °C, e.g. at 850 °C. However, in such a case it would take longer time, about one hour for completion of calcination reactions. The effect of particle size was not determined by using the electrobalance.

The results of calcination experiments done by thermal balance and given in Table 6 showed that for complete calcination of Denîzlî-Tavas manganese ore ground to 74 microns particle size a time of 15 minutes was enough at a temperature of 900 °C. The weight loss under these conditions was, on the average, 15.5%. The calcination time was very much dependent on temperature; at a definite particle size, this time decreased with increasing temperature. The minimum temperature necessary for completion of calcination in an industrially suitable time, was 700 °C. At this temperature, depending on the particle size, the time for complete calcination varied from 20 minutes to one hour. Therefore, it appeared that the variation in particle size was more effective at relatively lower temperatures. For example at 800 °C, complete calcination of a very finely ground (about 74 microns) ore took 18 minutes, while this duration was about 60 minutes for an ore sample with a particle size of about 1 mm. This means that the complete calcination time increased by a factor of 3. On the other hand, for a temperature of 900 °C, complete calcination of very fine ore took about 9 minutes while it took 15 minutes for an ore sample with about 1mm particle size; the increase in complete calcination time was only by a factor of 1.5.

The experimental results also showed that the total weight loss readings done under argon using electrobalance and thermal balance differed by about 1% (absolute value). There may be two reasons for this behaviour. Firstly, the sample used in thermal balance may oxidize towards the end of the experiments, resulting in some increase in weight. Secondly, the mechanically held water in the sample may evaporate while it is kept in the upper part of furnace as it is heated to the working temperature. As can be seen in Table 1, the analysis of dry sample for ignition loss gave a value of 15.1% and this seemed to support the second possibility. If the weight loss after calcination at 900 °C was taken as about 15.5%, the manganese content of ore, which was 30.34% (Table 1) originally, would increase to about 36%.

X-ray diffraction analysis of samples calcined at various temperatures showed that below 950 °C manganese oxide was present in the calcine as Mn_3O_4 whereas above this temperature as Mn_2O_3. Therefore, the temperature of calcination could be adjusted such that the form of manganese oxide in the calcine would be suitable to the ferro-manganese production process which might follow.

CONCLUSIONS

1. To predict the behaviour of Denîzlî-Tavas manganese ore during calcination, mineralogy of it was studied and manganese carbonate (rhodochrosite) and manganese hydroxide(manganite) were found to be most abundant. Iron in the ore was in the form of various minerals of iron oxides. The DTA and TGA analyses of samples showed that during heating manganite decomposes releasing H_2O and rhodocrosite, giving off CO_2.

2. The minimum temperature necessary for calcination of this ore was found to be 700 °C. However, at this temperature the complete calcination time varied between 20 minutes and 1 hour, depending on the particle size of the ore. Under industrial conditions this time might be as long as 2 hours. Therefore, as a result of this work, it was proposed to carry out calcination at 900 °C, and the calcination time (with a good stirring) should be minimum 1 hour, and particle size of ore should be about 1 mm. In that case, the manganese content of ore which was about 31%, would increase to above 35% and calcine would be more suitable for reduction smelting, as far as charge composition was concerned. In addition, it was determined that below a calcination temperature of 950 °C the manganese oxide in the calcine was present as Mn_3O_4,whereas above this temperature as Mn_2O_3, which might effect the subsequent carbothermic reduction process.

3. Under the optimum conditions given above, an industrial pilot test could be run using a rotary furnace fired with natural gas. Similar tests could be also done under a gaseous atmosphere with composition similar to the ferro-manganese electric arc furnace exit gases, which would act both as fuel and carrier of sensible heat. The particle size of ore could be around 1 mm.

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Produkcja stali i duże zapotrzebowanie na żelazo-mangan przez turecki przemysł żelaza i stali rośnie każdego roku. Turcja posiada kilka dużych złóż manganu, w tym złoże Denîzlî-Tavas. To węglanowe złoże rudne ma względnie niską zawartość manganu, która wynosi około 31%. Celem tej pracy było prażenie rudy dla podwyższenia zawartości manganu i uczynienia jej bardziej podatną na karbotermiczną redukcję w piecach produkujących żelazo-mangan. Badano takie główne parametry procesu jak temperaturę i czas prażenia w powiązaniu ze składem ziarnowym rudy. Stwierdzono, że temperatura wynosząca 700 °C była wystarczająca do wyprażenia rudy rozdrobnionej do –74 mikrony, ale ruda o uziarnieniu około 1 mm wymagała temperatury 900 °C i czasu prażenia 1 godziny. W tych warunkach straty prażenia wynosiły 15.5%, a zawartość manganu wzrastała do 36%.