

THERMAL UPGRADING OF MANGANESE ORES PRIOR TO SMELTING

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Abstract

Ferromanganese smelting in electric arc furnaces is an energy-intensive process with corresponding CO₂ emissions and environmental impacts. Upgrading the furnace charge can improve process efficiency and decrease electricity consumption. An oxide manganese ore, consisting mainly of pyrolusite, calcite and goethite, was thermally upgraded by calcination and solid-state reduction. During calcination of the ore at 900-1100°C, carbonates and hydroxides were decomposed and a considerable amount of oxygen was removed. The manganese content of the run-of-mine ore was increased from 39.86% to 47% after calcination. Carbothermic reduction of the ore at 1250°C resulted in almost all of the iron oxide and some of the manganese oxide passing into the metallic form. The results showed that a significant part of the endothermic reactions during the solid-state treatment of the ore can be carried out with low-cost fossil fuels. This leads to enrichment of the electric arc furnace charge, lower electricity consumption in the furnace, lower overall processing costs and a more efficient smelting process.

Keywords: Manganese ore; Thermal upgrading; Calcination; Reduction

1. Introduction

Manganese is one of the most important additives in the iron and steel industry. It acts as both sulphide former and deoxidant. In addition, it improves hardenability, workability, wear resistance and mechanical properties of the iron alloys. Manganese is generally added to the molten alloy in the form of ferromanganese and silicomanganese. About 90 to 95% of the manganese produced is used in steelmaking as ferromanganese [1]. Ferromanganese has conventionally been smelted in blast furnaces. Nevertheless, the blast furnace (BF) have been replaced by electric submerged arc furnace (SAF) over time mainly due to the lower average production cost per ton of the product and the flexibility of the process [2]. However, ferromanganese smelting is still a costly and energy-intensive process that requires high temperatures and a lot of energy to reduce the manganese oxides and produce the desired alloy. The cost of energy required for ferromanganese production can be a significant factor in the overall cost of the process, and fluctuations in energy prices can affect the profitability of the industry.

One solution to the high energy cost of the SAF process may be to heat treat the ore prior to smelting, as in the Rotary Kiln-Electric Furnace (RKEF) process used in ferronickel smelting [3]. The main

concept is illustrated in Figure 1. In the RKEF process the ore is dried, calcined and prereduced in a rotary kiln. The hot calcine from the rotary kiln can be directly charged into the arc furnace. The objective is to carry out part of the energy-intensive smelting process by the low-cost coal in the rotary kiln thereby decreasing the electrical energy consumption in the arc furnace. In addition, calcination [4] and prereduction [5] of the ore in the rotary kiln will eliminate volatile matters and substantial portion of oxygen in the ore, which in turn will provide an enriched charge to the arc furnace and result in a

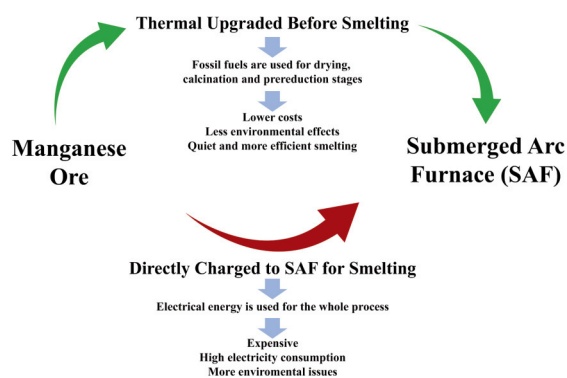


Figure 1. The main concept behind thermally upgrading the ore before smelting

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quieter smelting process. Pre-treatment of manganese ores prior to melting has also been suggested by other researchers [6,7].

A successful heat treatment of manganese ores requires a comprehensive study of the ore behavior upon heating. However, there is only a limited number of recent research [6,8-10] addressing the chemical and mineralogical changes of the ore during heating. Previous studies have focused mainly on the low-grade manganese ores. Manganese ores exhibit significant variations in chemistry and mineralogy, emphasizing the necessity for research on the thermal decomposition of other ores, such as medium-grade ores. This article presents the findings of laboratory-scale research on the calcination and reduction behavior of a medium-grade Turkish manganese ore. The primary objective was to understand how the ore behaves when subjected to thermal upgrading before smelting. This article focuses on the metallurgical aspects of the process, and the energy-related calculations and economic benefits will be covered in another study.

2. Experimental

2.1. Raw materials

The manganese ore used in this research was taken from a reserve located in Kayseri, Turkey. Thirty kilograms of a representative run-of-mine (ROM) ore sample, crushed to -1 cm size, was received. The ore was further crushed to -1 mm and divided by the riffle splitter into batches of about 50 g which were used in the experiments. One batch was finely ground which was used for characterization of the received ore.

Coal was used as the reductant. Its size was reduced to -1 mm to ensure homogeneous mixing of coal and ore. Chemical analysis of the coal is given in Table 1.

Table 1. Chemical analysis of the reductant coal (wt.%)

C	Volatile matter	Sulphur	Moisture	Ash (mainly SiO ₂)
76.06	17.64	0.33	1.77	4.2

2.2. Characterization of the ore

The finely ground ore was analyzed using Bruker S8 TIGER Series 1 XRF device. To analyze manganese with different oxidation numbers separately, small amounts of ground ore was digested with HCl:HClO₄:HNO₃ acid solution with gradual temperature rise during digestion. The solution was analyzed by AAS for Mn²⁺ and Mn⁴⁺. Mineralogical analysis of the ore was conducted using the Rigaku SmartLab SE XRD device. Differential thermal analysis (DTA) and thermogravimetric analysis (TGA) were performed on a TA SDT 650 device to

study the ore's thermal behaviour.

2.3. Calcination of the ore

A muffle furnace was used for calcination experiments. The ore was dried overnight before calcination. Fifty grams of -1 mm dried ore was charged into an alumina crucible and heated to constant weight in air at predetermined temperatures (300-1100°C). For each temperature, weight loss was plotted against time. Weight loss during calcination was recorded by removing the sample from the furnace, weighing it, and then placing it back in the furnace. Calcined samples were ground and analyzed by XRD to determine the mineralogical changes during calcination.

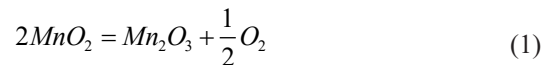
2.4. Reduction of the ore

A horizontal tube furnace was used for reduction experiments. The ore was calcined at 950°C for 60 min. prior to the reduction. In the reduction experiments, 30 g of dry calcine was thoroughly mixed with specific amount of coal and charged into an alumina crucible. Theoretically required amount of coal was calculated assuming that all Mn₃O₄ and Fe₂O₃ in the calcined ore would be reduced to MnO and Fe, respectively. It was assumed that the reduction took place by the reaction of solid carbon with these oxides. Six experiments were conducted at various temperatures between 900 and 1250°C. The aim was to reduce the sample as much as possible without significantly sintering it. Excessive sintering is industrially undesirable as it causes agglomeration on the furnace wall. Metallization of iron in the reduced samples was measured using bromine-methanol method [5].

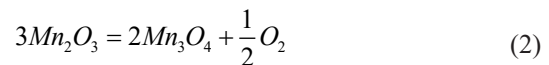
3. Results and Discussion

3.1. Thermodynamic considerations of calcination¹

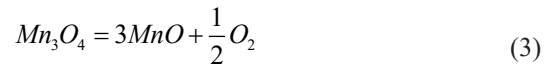
Calcination generally involves thermal decomposition of the compounds in the presence of air. Possible decomposition reactions during the calcination process are listed below:



$$\Delta G^\circ = 81.72 - 0.1081T \text{ (kJ)}$$



$$\Delta G^\circ = 97.12 - 0.0749T \text{ (kJ)}$$

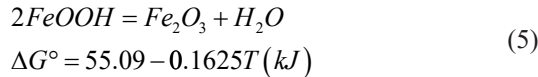


$$\Delta G^\circ = 225.55 - 0.1166T \text{ (kJ)}$$

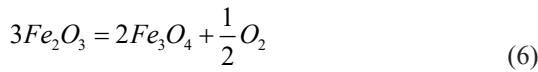




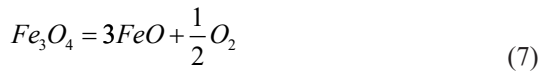
$$\Delta G^\circ = 386.95 - 0.0763T \text{ (kJ)}$$



$$\Delta G^\circ = 55.09 - 0.1625T \text{ (kJ)}$$



$$\Delta G^\circ = 245.11 - 0.1488T \text{ (kJ)}$$



$$\Delta G^\circ = 292.93 - 0.1197T \text{ (kJ)}$$



$$\Delta G^\circ = 268.59 - 0.0613T \text{ (kJ)}$$

¹All thermodynamic data was extracted from Ihsan Barin's book "Thermochemical data of pure substances" [25]

Of these, dehydroxylation of goethite, Equation 5, generally takes place below 350°C [11]. Goethite transforms into hematite (Fe₂O₃) during dehydroxylation process. Decomposition of other oxides is discussed in more detail below.

Equilibrium oxygen pressure for these reactions was plotted against temperature (Figure 2). The intersection of the P_{O₂} = 0.21 atm line with these curves gave us the minimum temperature required for these reactions. From these data, MnO₂ converts into Mn₂O₃ at 440°C and then to Mn₃O₄ at 946°C in air. These data are reasonably close to theoretically calculated 510 and 915°C [12] and experimentally determined 500 and 900°C [13] by other researchers. According to these results, MnO₂ will transform into Mn₃O₄ at common calcination temperatures (usually up to 1150°C) and ambient atmosphere. However, MnO can form at temperatures above about 1560°C.

Hematite, formed by the dehydroxylation of goethite, does not undergo any transformation up to

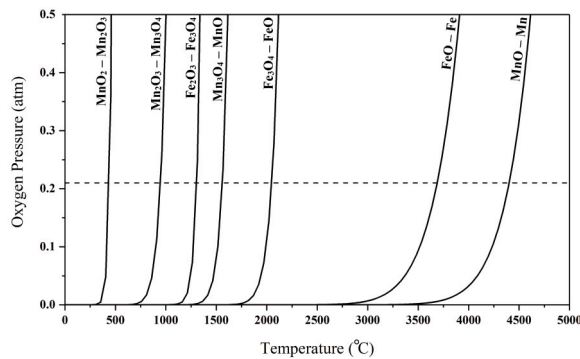


Figure 2. Equilibrium oxygen pressure for various transformations

about 1300°C, where it turns into magnetite (Fe₃O₄). This temperature is above common calcination temperatures and therefore iron will be found in the calcined ore as magnetite. To summarize, the main transformations expected during calcination are dehydroxylation of goethite to form hematite and decomposition of MnO₂ to Mn₂O₃ and then to Mn₃O₄.

3.2. Thermodynamic considerations of reduction

Carbothermic reduction of oxides takes place mainly through their reaction with the surrounding CO. On the other hand, in the presence of solid carbon in the system, the Boudouard reaction plays a key role in controlling the furnace atmosphere, i.e. partial pressure of CO and CO₂. Therefore, the reduction reactions and the Boudouard reaction should be considered simultaneously.

The main reduction reactions that can take place during the reduction are shown in Figure 3-a. This figure also shows the variation of the equilibrium CO pressure with temperature for these reactions. Figure 3-b, adapted from Figure 3-a, shows the predominance area diagram of Fe-Mn-O system. This figure shows the T and PCO required to obtain any of the oxide combinations. During the reduction process, the furnace atmosphere, mainly determined by the Boudouard reaction, roughly follows the path indicated by the dashed line on the figure. According to this diagram, MnO₂ present in the ROM ore (or Mn₃O₄, if the ore is calcined before reduction) can be reduced to MnO even at relatively low temperatures. It is reported that manganese containing other minerals like braunite and cryptomelane are also transform into Mn₃O₄ and then to MnO [12]. Therefore, no matter what the starting material is, the final product will be MnO. Metallic manganese cannot be achieved under these circumstances. Further reduction of MnO to metallic Mn require temperatures above 1400°C [10]. Under a reducing atmosphere, hematite will be readily reduced to magnetite. Reduction of magnetite to ferrous oxide (FeO) will be thermodynamically possible above about 530°C (point A on the figure). Ferrous oxide will be reduced to metallic iron above about 750°C (point B on the figure). To summarize, the reduced sample is expected to be composed of mainly MnO and metallic iron.

3.3. Ore characterization

Chemical analysis of the ore is given in Table 2. The ore was a medium-grade with about 40 wt.% of Mn and 6.6 wt.% of iron. The main gangue minerals were the oxides of silicon and calcium.

The XRD pattern of the ROM ore is shown in



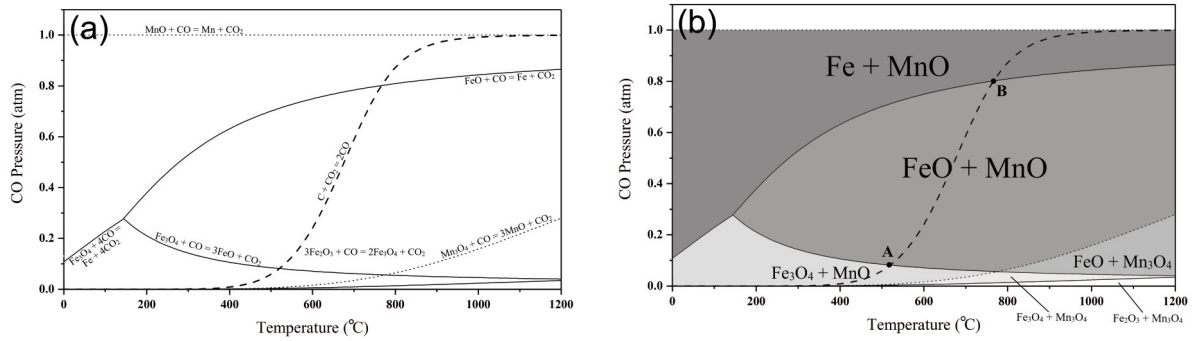


Figure 3. (a) Equilibrium CO pressures for different reactions at different temperatures, (b) predominance area diagram for Mn-Fe-O system

Table 2. Chemical analysis of the manganese ore sample (wt.%)

Mn	Mn ⁴⁺	Mn ²⁺	Fe	SiO ₂	Ca	Al ₂ O ₃	Mg
39.86	37.77*	2.66*	6.631	6.29	9.296	0.789	0.391
K ₂ O	Na ₂ O	Pb	P	S	Zn	Moisture	L.O.I
0.384	0.118	0.34	0.107	0.11	0.009	2.65	16.16

* The slight difference with the total Mn is due to the analysis methods. Mn²⁺ and Mn⁴⁺ were analyzed by AAS while the total Mn was analyzed by XRF

Figure 4. The ore was mainly composed of pyrolusite (MnO₂) and calcite (CaCO₃). Goethite and quartz were also present in smaller quantities. According to the literature [4,8-10,12,14,15], bixbyite, braunite, hausmannite, cryptomelane, rhodochrosite, tephroite, rhodonite and manganite are the other mostly reported Mn-bearing minerals in Mn ores. In most of the cases, gangue minerals are mainly calcite and quartz.

Although Mn²⁺ detection (see Table 2) indicates the presence of Mn-bearing minerals other than MnO₂, they were not detected by XRD. It can be attributed to their presence in amounts below the detection limit of XRD or their peaks being covered by other high-intensity peaks. Another reason can be the dissolution of manganese within the structure of other minerals [9].

DTA and TGA curves of the ore are shown in

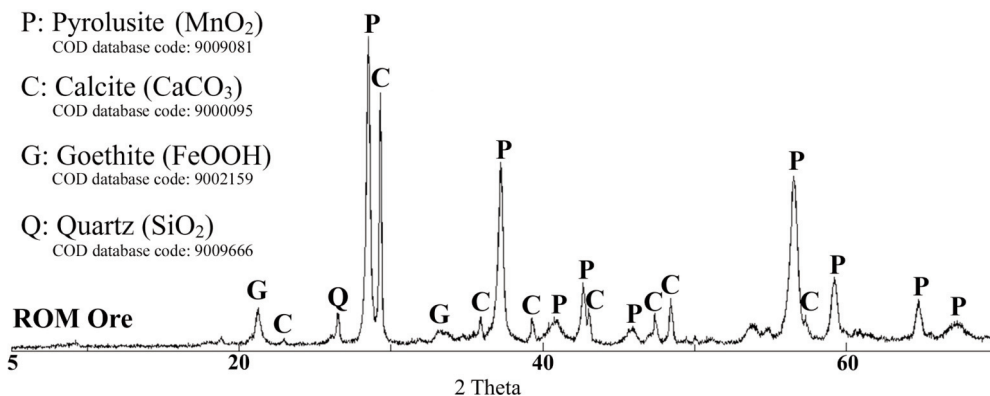


Figure 4. XRD pattern of the manganese ore sample

Figure 5. Three weak endothermic peaks at about 100, 350 and 450°C together with three intense peaks between 600 and 800°C were recorded. Sample weight decreased mildly up to 600°C but decreased significantly between 600 and 800°C. Sample weight remained almost unchanged up to 950°C and again began to decrease at higher temperatures. The low-temperature endothermic peak at about 100°C was related to the evaporation of free water. It was difficult to discuss about the nature of the other effects using only the current diagram.

For this reason, calcination experiments were conducted at different temperatures and XRD was used to identify any possible reactions taking place during the course of heating.

3.4. Calcination of the ore

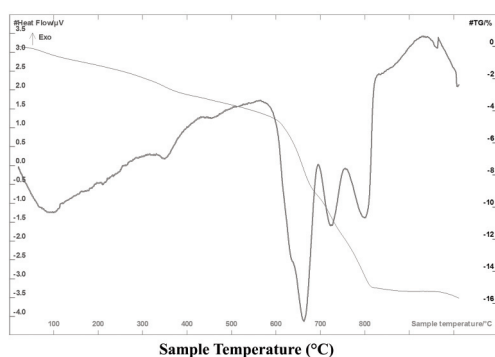


Figure 5. DTA/TG analysis of the manganese ore sample

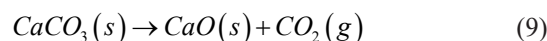
The XRD pattern of the calcined samples are shown in Figure 6. Comparing the XRD pattern of the sample calcined at 300°C and that of the ROM ore (see Figure 4), it was concluded that the main fraction of the goethite dehydroxylated at this temperature according to Eq. (5). The remainder dehydroxylated when the temperature increased to 400°C as the characteristic peaks of goethite completely disappeared at this temperature.

Although no change was detected between 400 and 500°C from XRD (see Figure 6), the weight of the sample continued to decrease in between. This weight loss may be attributed to the dehydroxylation of clay minerals present in minor quantities in the ore. Accordingly, the endothermic peaks at 350 and 450°C in the DTA pattern can be related to the dehydroxylation of goethite and clay minerals, respectively.

A careful examination of the XRD patterns of samples calcined at 600 and 700°C revealed that the characteristic peaks of pyrolusite weakened as temperature rose and only a very small peak remained when it reached 700°C. At this temperature a new phase, bixbyite (Mn_2O_3), came to existence. Therefore, the strong peak at about 675°C and associated large weight loss in the DTA pattern were related to the transformation of MnO_2 to Mn_2O_3 [9] according to Equation 1.

Examination of the XRD patterns of samples calcined at 700, 800 and 900°C indicated that calcite began to decompose above 700°C. A complete decomposition of calcite was not achieved below

900°C. Calcite decomposes to give CaO and CO_2 according to the reaction below:



Although no other transformation could be detected from the XRD analysis, there were two endothermic peaks at about 720 and 800°C in the DTA pattern. One possible explanation may be that the decomposition of calcite was achieved via a two-step process.

Although decomposition reactions have been reported [14,16] to be completed at 900-950°C, thermodynamic calculations have shown that Mn_2O_3 converts to Mn_3O_4 at approximately 950°C. This is in line with other reports [15] in the literature. Therefore, one more calcination test was carried out at 1100°C. The temperature was chosen high enough to ensure complete decomposition. The XRD analysis of the sample revealed that Mn_2O_3 transforms into Mn_3O_4 (Equation 4).

Calcination of the ore at 900°C and 1100°C resulted in 14% and 16% mass loss respectively. The calcined ore contained about 47% Mn and 7.8% Fe. This means that the calcination will result in the corresponding enrichment of the ore, which is in accordance with the literature [4,7,14]. Temperatures higher than 1100°C are not suggested for calcination as thermodynamically no other decomposition will take place.

3.5. Reduction of the ore

Efficient production of FeMn depends on the degree of solid state prereduction [2]. Reduction experiments, as listed in Table 3, were conducted to study the reduction behavior of the ore. Reduction time was chosen to be 60 min. and kept constant in all experiments. Based on the literature [16] and previous experience [5], reduction reactions finish before 60 minutes, and longer times have no effect on the reduction process. In the first set of experiments (No. 1 – No. 3) it was tried to keep the coal amount at the minimum level and a reducing gas (CO) was sent to the furnace instead. Although reduction reactions were expected to enhance above 1000°C [5,10], metallization of iron was low and about 67% at

Table 3. List of the reduction experiments

Exp. No.	Temperature (°C)	Calcined ore (g)	Coal (g)	Atmosphere	Time (min.)
1	900	30	4.35	CO (50 cc/min.)	60
2	1000	30	4.35	CO (50 cc/min.)	60
3	1100	30	4.35	CO (50 cc/min.)	60
4	1100	30	8.7	CO (50 cc/min.)	60
5	1150	30	8.7	N_2 (50 cc/min.)	60
6	1250	30	8.7	N_2 (50 cc/min.)	60

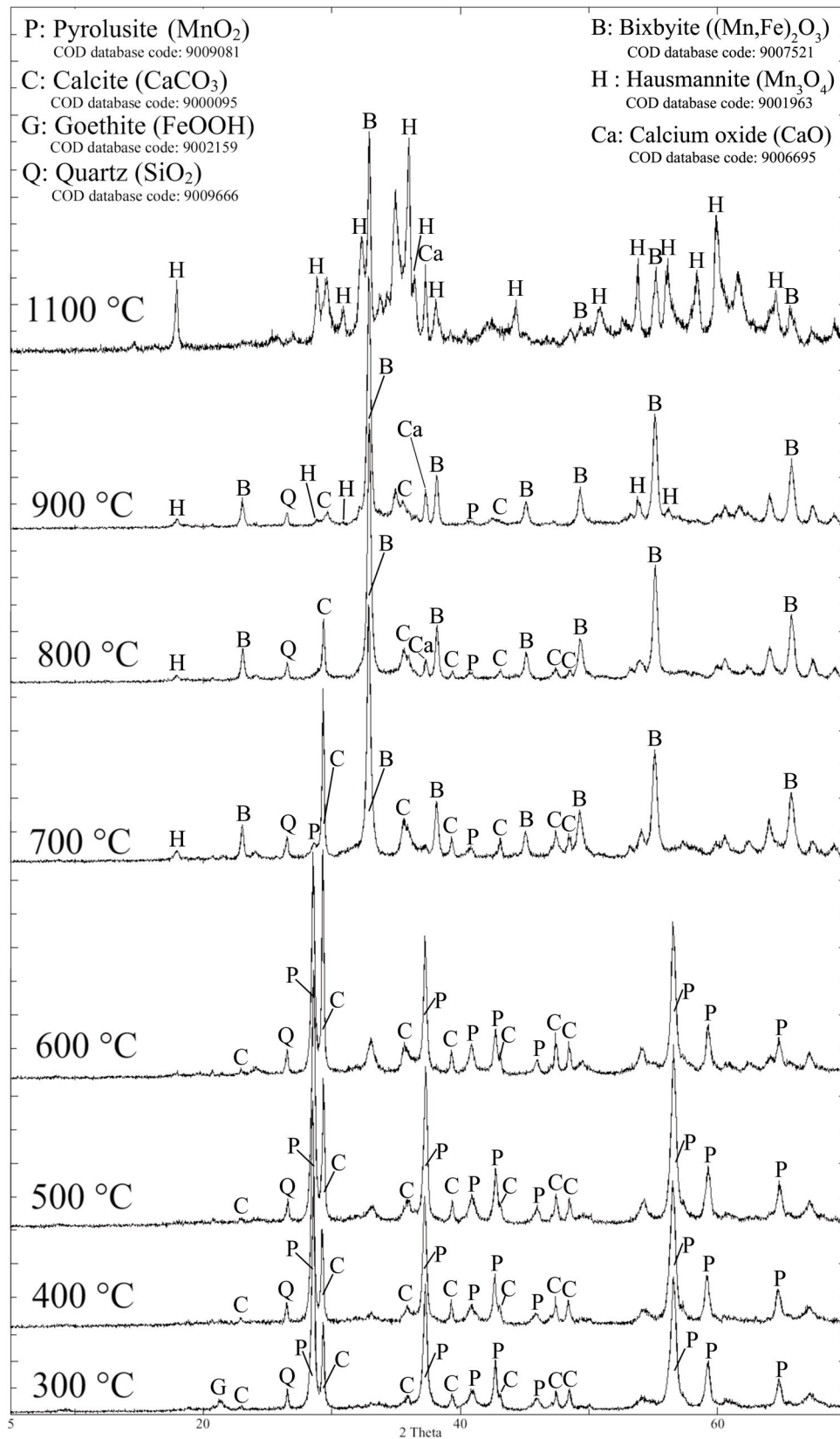
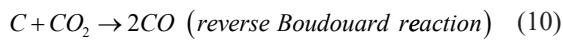


Figure 6. XRD pattern of the samples calcined at different temperatures

1100°C. This showed that the coal addition below the theoretical value was insufficient.

In the next experiment, No. 4, coal amount was increased to the theoretically calculated level to encourage reduction reactions. However, metallization of iron was not acceptably high and remained at about 82%. This was mainly attributed to the usage of CO gas. High CO partial pressure hinders the gasification of carbon via the reverse Boudouard reaction which plays a key role in reducing the ore. High CO partial pressure shifts the following reactions to the left.



Where M can be either Fe or Mn. Increasing the partial pressure of CO results in more unreacted coal, retards reduction process and even causes reoxidation of metallic phases [17-19]. Therefore, an inert atmosphere was used instead of CO in the subsequent experiments.

The next experiment (No. 5) was carried out at 1150°C and under an inert gas (N₂). Metallization of

iron was about 93% and there was no sign of sintering in the sample. The ultimate aim of the reduction experiments was to reach as much reduction as possible without sintering. Sintering is industrially unwanted as it causes accretion on the furnace (rotary kiln for example) wall. The temperature was increased to 1250°C (Exp. No. 6), resulting in a metallization degree of 96%. The preliminary result showed that sintering started to happen at this temperature suggesting that this is the maximum temperature to reduce the ore in solid state without considerable sintering. This result agreed with the literature [20].

The XRD patterns of the reduced samples are shown in Figure 7. Sample reduced at 900°C was composed of manganosite, iron, knebelite, calcite and cementite. Unreacted coal was also detected as graphite at this sample. These phases mainly continued to exist at higher temperatures and only their proportions seemed to change with temperature. The exceptions were graphite and calcite whose characteristic peaks disappeared above 900°C and 1150°C, respectively. This seems to contradict the results of calcination experiments, in which calcite degraded substantially at 900°C. This can be attributed to the presence of CO₂ in the furnace

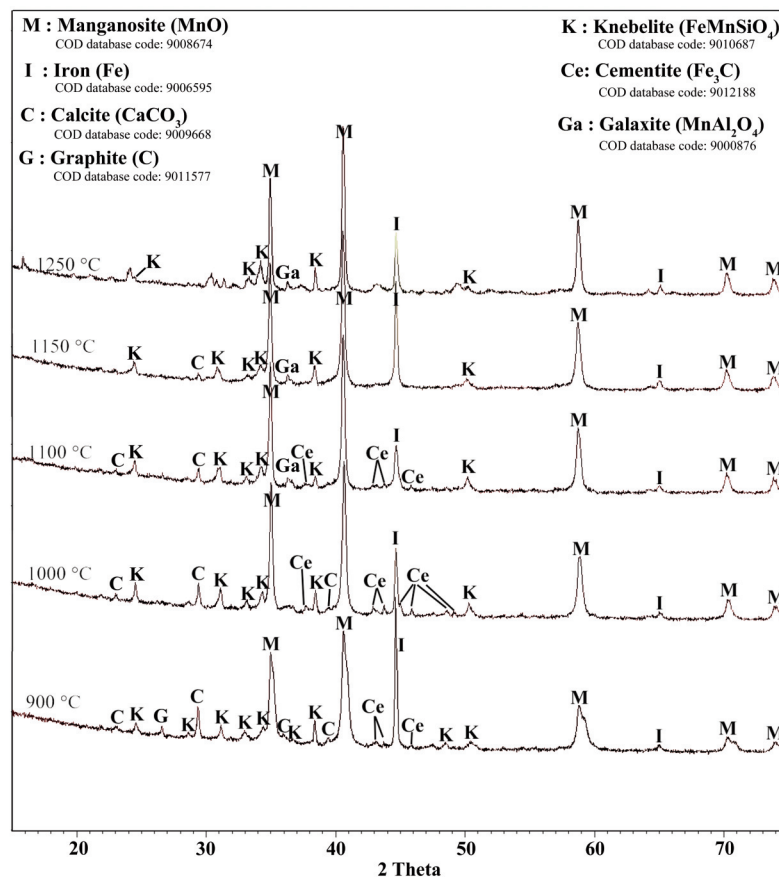


Figure 7. The XRD patterns of the reduced samples

atmosphere in the reduction process, which shifted the decomposition reaction to the left. Above 1100°C, a new phase, galaxite, formed in the reduced sample. According to the XRD pattern of the sample reduced at 1250°C, one or more phases were formed at this temperature. However, they could not be identified, probably due to the fact that some of their main characteristic peaks overlapped with other high-intensity peaks. Further discussion of the XRD results will be presented in the following section.

3.6. Microstructural study under SEM

SEM micrographs of a sample reduced at 1250°C are shown in Figure 8. Although the microstructure was not the same throughout the sample, it was mainly composed of four different phases marked by numbers on Figure 8-e. Elemental analysis of these phases determined by EDS is given in Table 4. The most common phase, marked with number 1, was rich in Mn and O, and probably corresponded to MnO identified by XRD. The phase number 2 was an Fe-Mn alloy containing 20-30 wt.% Mn. This phase sometimes contained high amounts of phosphorus, which was most likely sourced from coal used as a reductant. This phase probably corresponded to the Fe

phase identified by XRD. The third most common phase, number 3, was rich in Si, Ca, Mn and O. This may be related to the unidentified peaks in the XRD pattern. The coexistence of MnO and an oxide phase (slag) in reduced manganese ore has also been reported in the literature [17,21]. The phase number 4 was an Al, Mn and O rich phase and probably corresponded to galaxite identified by XRD.

Considering the elemental analysis of the metal

Table 4. EDS point analysis of the various phases present in the reduced ore (wt.%)

Phase No	Mn	Fe	P	O	Si	Ca	Al
1	70-80	-	-	20-30	-	-	-
2	20-35	55-75	10-15	-	-	-	-
3	~ 32	-	-	~ 38	~ 14.5	~ 12.5	-
4	~ 20	-	-	~ 52	-	-	~ 25

phase, it is seen that manganese was reduced, contrary to what was stated in the previous thermodynamic discussion. Previous discussion was about the reduction of pure MnO in the presence of solid carbon in the system. However, MnO can also be dissolved in the oxide phase and more complex interactions occur

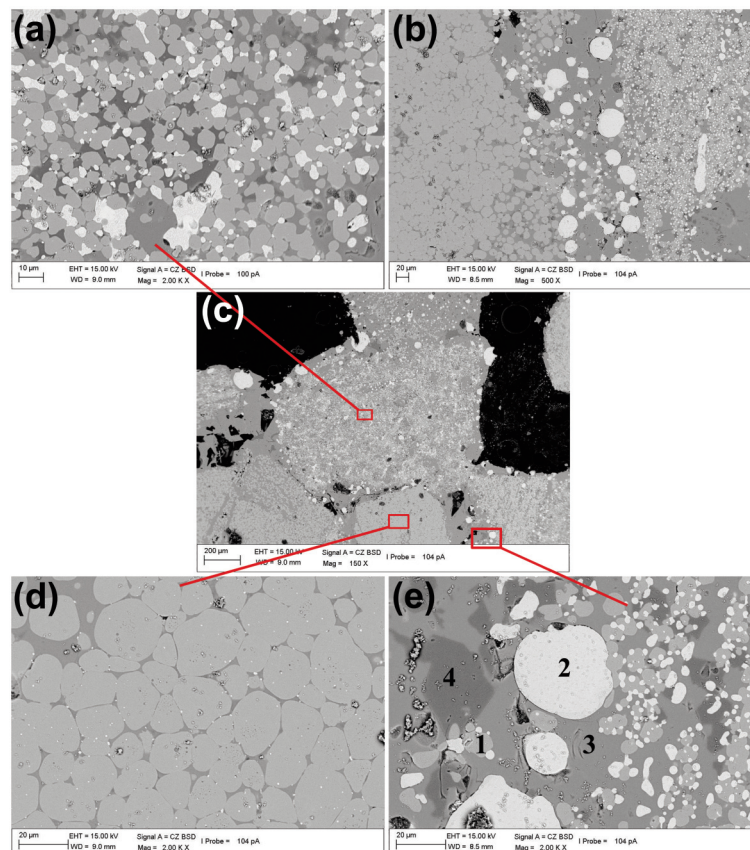
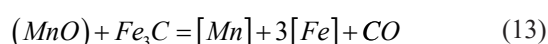


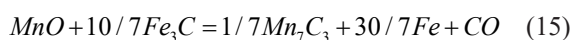
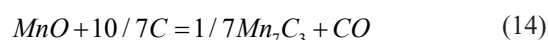
Figure 8. Low (c) and high (a,b,d,e) magnification SEM photographs from different spots of a reduced ore sample

within the reduced sample. Two possible mechanisms are discussed below that may explain reduction of manganese oxide to elemental manganese. The first and most possible explanation would be the reduction of pure MnO [22] or MnO dissolved in the oxide phase [22] by dissolved carbon [23] or iron carbide [24] according to the following reactions:



This is in line with the XRD results, which show that above 1000°C cementite is involved in a reaction, weakening its characteristic peaks. Dissolved carbon was also present in the metal phase, but as the sample was covered with a carbon film before EDS analysis, the detected carbon was not included in the elemental analysis given in Table 4.

The second mechanism proposed in the literature [20] is the reduction of manganese oxide to form manganese carbide according to the following reactions:



This mechanism is less likely than the previous one. Enough carbon must be present in the system for manganese carbide to form. However, in our case, carbon was added only enough for the reduction of iron oxide (see experimental section). In addition, manganese carbide was not detected by XRD.

4. Conclusions

A Turkish manganese ore was characterized and then subjected to calcination and solid-state reduction experiments. The ore was oxide-type medium-grade with 39.86 wt.% Mn and 6.63 wt.% Fe. Pyrolusite was the main Mn-bearing mineral while iron was present as goethite. The main gangue mineral was calcite. Calcination of the ore at 1100°C increased ore grade to about 47 wt.% by removal of volatiles and a part of the oxygen. Calcined ore contained hausmannite and bixbyite. Reduction of the ore with coal at 1250°C resulted in the formation of a Fe-Mn alloy, MnO and slag. Almost all of the iron oxide together with a part of the manganese oxide was reduced to metallic iron.

The results revealed that manganese ore can be thermally upgraded before smelting. A considerable portion of the energy-consuming decomposition reactions and reduction reactions can be carried out outside the electric furnace. Cost-effective fossil fuels can be used instead of expensive electricity reducing the overall cost of the process. In addition,

considering the low efficiency of coal-fired power plants (about 33%), using fossil fuels directly for thermal treatment of the ore will reduce CO₂ emissions and environmental problems.

Data availability

The study did not report any data.

Conflict of interest

The author declares no conflicts of interest.

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TERMIČKI TRETMAN RUDA MANGANA PRE TOPLJENJA

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Apstrakt

Dobijanje ferromangana u elektrolučnim pećima je energetski intenzivan proces sa odgovarajućim emisijama CO₂ i uticajem na životnu sredinu. Predtretman šarže peći može poboljšati efikasnost procesa i smanjiti potrošnju električne energije. Oksidna ruda mangana, sastavljena pretežno od piroluzita, kalcita i goetita, termički je prečišćena kroz kalcinaciju i redukciju u čvrstom stanju. Tokom kalcinacije rude na 900-1100°C, karbonati i hidroksidi su razgrađeni, a značajna količina kiseonika je uklonjena. Sadržaj mangana u rudi povećan je od 39.86% na 47% nakon kalcinacije. Karbotermička redukcija rude na 1250°C rezultirala je prelaskom skoro svih oksida gvožđa i nekih oksida mangana u metalni oblik. Rezultati pokazuju da se značajan deo endotermnih reakcija tokom termičkog tretmana rude može izvesti uz upotrebu jeftinih fosilnih goriva. Ovo dovodi do obogaćivanja šarže električne peći, smanjenja potrošnje električne energije u peći, smanjenja ukupnih troškova obrade i efikasnijeg procesa topljenja.

Ključne reči: Ruda mangana; Termičko prečišćavanje; Kalcinacija; Redukcija

