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Calcination and Pelletizing of Siderite Ore

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Abstract

In the present study, calcination properties of Hekimhan-Deveci siderite (FeCO_3) ore and the effect of calcination process before the pelletization on strength of pellet were investigated and evaluated. Two different calcination processes were followed. One of them is the traditional calcination process and the other one is microwave assisted calcination process which is a new process for siderite ore. The characterization of the calcined and uncalcined siderite ore was done using X-ray diffraction, X-ray fluorescence spectrometry and thermogravimetric analysis. The physical and mechanical properties of pellets which were obtained using the raw siderite and the calcined siderite were compared with each other. As a result of experimental studies, it was found that the calcination process decreased the milling time, causing the significant energy saving and the most suitable calcination process for siderite ore was found as 15 min at 700°C temperature. It was the first time that the calcination process of the siderite ore was achieved by microwave by adding 30 wt% sucrose as a thermal auxiliary. The microwave conditions were determined as 900 W at 3 min. In 3 min, the temperature of the siderite ore increased up to 1100°C and 32.14% weight loss for the sample was achieved.

Keywords: siderite ore, furnace, microwave heating, calcination, pelletizing

1. Introduction

1.1. Importance of the steel and iron industry

The iron and steel industry produces products with desired chemical and physical properties from the melting iron ore in blast furnaces or the melting scrap in arc furnaces by different processes [1]. Changing consumer needs, developments in technology and competition are further increasing the product diversity in the iron and steel sector. Final steel products have numerous types and different application areas. The iron and steel industry, which is the most

important of the heavy industry sectors, supplies raw materials to many important industries such as construction, infrastructure, automotive, white goods and machinery industry. Therefore, it can be said that industrialization of a country is directly related to its strong iron and steel sector and consumption [2]. **Table 1** gives the top 10 countries producing the crude steel in the world.

Today iron constitutes the basic raw material of the industry and plays an important role in the economic development of the countries. The economic development indicators of countries are also determined by per capita iron and steel consumption. **Table 2** shows the consumption of steel per capita.

In the past, iron ore with the characteristics required for blast furnace charging was met directly from iron mines. The need for iron in the industry has increased rapidly and also the reserve of the iron ore which can be directly loaded into the blast furnace has gradually decreased. Therefore recently, the irons ores with low grade have been started to be evaluated. The crude iron ore reserves and its iron content in the world are given in **Table 3**.

The main raw material of the iron and steel industry is iron ore. It must be economical to operate and use a mine as an ore. It is desirable that the blend grade of the iron ores used in the steel industry is at least 57% Fe grade. The iron ore is found in the form of magnetite (Fe_3O_4), hematite (Fe_2O_3), limonite ($\text{FeO}(\text{OH}) \cdot n\text{H}_2\text{O}$), goethite ($\alpha\text{-Fe}^{3+}\text{O}(\text{OH})$), siderite (FeCO_3) and pyrite (FeS_2) minerals in the nature.

1.2. Siderite

The name of the siderite mineral is derived from the word sideros (σίδηρος), meaning iron in Greek. Technically, siderite minerals contains about 48.02% iron (Fe) and be crystal trigonal (hexagonal scalenohedral) system, mostly rhombohedral crystalline; plate, prismatic, massive;

| No | Country | 2011 | 2012 | 2013 | 2014 | 2015 | 2015 (%) |
|----|-------------------|--------|--------|--------|--------|--------|----------|
| 1 | China | 701.9 | 731.0 | 822.0 | 822.8 | 803.8 | 49.60 |
| 2 | Japan | 107.6 | 107.2 | 110.6 | 110.7 | 105.1 | 6.48 |
| 3 | India | 73.4 | 77.2 | 81.2 | 87.2 | 89.0 | 5.49 |
| 4 | USA | 86.3 | 88.6 | 88.8 | 88.1 | 78.8 | 4.86 |
| 5 | Russia | 68.8 | 70.2 | 69.0 | 71.4 | 70.8 | 4.36 |
| 6 | South Korea | 68.5 | 69.0 | 66.0 | 71.5 | 69.6 | 4.29 |
| 7 | Germany | 44.2 | 42.6 | 42.6 | 42.9 | 42.6 | 2.62 |
| 8 | Brazil | 35.2 | 34.5 | 34.1 | 33.8 | 33.2 | 2.04 |
| 9 | Turkey | 34.1 | 35.8 | 34.6 | 34.0 | 31.5 | 1.94 |
| 10 | Ukraine | 35.3 | 32.9 | 32.7 | 27.1 | 22.9 | 1.41 |
| | EU (28 countries) | 177.7 | 168.5 | 166.3 | 169.3 | 166.1 | 10.25 |
| | World | 1538.0 | 1560.1 | 1650.3 | 1669.8 | 1620.4 | 100 |

Table 1. Top 10 countries in world crude steel production (million metric tons) [3].

| Countries/region | 2011 | 2012 | 2013 | 2014 | 2015 |
|-------------------|--------|--------|--------|--------|--------|
| South Korea | 1190.1 | 1135.3 | 1081.7 | 1155.0 | 1155.7 |
| Czech Republic | 663.1 | 639.8 | 641.5 | 678.6 | 723.9 |
| Japan | 546.9 | 541.1 | 558.3 | 574.9 | 535.7 |
| Germany | 561.3 | 507.3 | 517.0 | 530.1 | 523.9 |
| China | 495.4 | 507.3 | 562.0 | 540.6 | 509.0 |
| Australia | 527.1 | 488.1 | 475.1 | 480.4 | 466.2 |
| Turkey | 389.9 | 404.6 | 436.9 | 422.5 | 464.7 |
| Canada | 456.4 | 496.3 | 466.8 | 492.5 | 412.5 |
| EU (28 countries) | 343.0 | 306.2 | 311.1 | 322.0 | 331.6 |
| North America | 267.4 | 285.2 | 276.7 | 311.1 | 282.9 |
| Asia | 256.4 | 261.7 | 282.2 | 277.8 | 266.1 |
| Middle East | 257.6 | 250.3 | 248.8 | 251.9 | 244.4 |
| World | 221.3 | 223.3 | 234.5 | 234.1 | 224.4 |
| South America | 126.4 | 128.0 | 132.3 | 122.8 | 112.4 |
| Africa | 30.1 | 32.8 | 35.4 | 35.4 | 35.7 |

Table 2. Crude steel consumption per capita of the country and regions (kg/person) [3].

medium-fine grained; rarely kidney, oolitic crystal habits. Siderite minerals have transparent-semi-transparent appearance and have different colours like yellowish-brown to greyish-brown, pale yellow to tannish, grey, brown, green, red, black and sometimes nearly colourless; tarnished iridescent at times; colourless to yellow and yellow-brown in transmitted light. The specific weight of siderite mineral is 3.96 g/cm³ and its Mohs hardness is between 3.5 and 4.5. A sample of siderite giving large crystals is given in **Figure 1**.

Massive siderite is commonly found in layered sedimentary beds, especially in mudstones and marls. In addition, it was found as a gangue mineral in hydrothermal ore vein which contains pyrite, chalcopyrite and galenite. It is also found in basaltic volcanic rocks, sometimes in pegmatites and metamorphic rocks.

1.3. Calcination

Calcination is the breakdown of carbonates and hydrates by the effect of temperature in order to obtain oxide form compounds. Calcination not only involves removing of water in the crystal structure, but also removes carbon dioxide or other chemically bound gases such as hydrates, carbonates.

All calcination reactions are endothermic. In terms of thermodynamic rule, the decomposition of a carbonate at a constant temperature is a function of CO₂ partial pressure. The calcination reaction is given in the following Eq. (1) for carbonate compounds.



| Countries | Reserves | |
|-----------------------|-----------|--------------|
| | Crude ore | Iron content |
| Australia | 52.000 | 23.000 |
| Russia | 25.000 | 14.000 |
| Brazil | 23.000 | 12.000 |
| China | 21.000 | 7.200 |
| India | 8.100 | 5.200 |
| Ukraine | 6.500 | 2.300 |
| Canada | 6.000 | 2.300 |
| Sweden | 3.500 | 2.200 |
| United States | 3.000 | 790 |
| Iran | 2.700 | 1.500 |
| Kazakhstan | 2.500 | 900 |
| South Africa | 1.200 | 770 |
| Other countries | 18.000 | 9.500 |
| World total (rounded) | 170.000 | 82.000 |

Table 3. Iron ore reserves and its iron content in the world (million metric tons) [4].

The equilibrium constant of the reaction equals the partial pressure of the CO₂ if the solids activities are equal to one another. Therefore, the complete decomposition temperature of a carbonate compound is the temperature at which the P⁰_{CO₂} pressure equals an atmospheric pressure.



Figure 1. Crystal-shaped siderite sample [5].

The calcination process for siderite ore aims to remove the bound CO_2 in the formation of FeCO_3 . Siderite calcination reactions are given in the following short chemical Eqs. (2)–(4)



During the calcination process, CO_2 composition is removed from the siderite ore structure. So, it lose about 30 wt% of its weight. However, it is necessary to reach a temperature of at least 700°C for this weight loss. The calcination of siderite ore is mostly carried out in rotary kilns. The ore entering the rotary kiln as siderite; leaving the furnace turned into a mixture of hematite, magnetite and maghemite. The distribution of the minerals in this mixture depends on the working temperature of the oven and the duration time. At low temperatures, primarily hematite and then magnetite transformation occurs. However, the mixture is predominantly hematite in every case.

1.4. Traditional and microwave heating methods

Conventional heating principles have been utilized in the heating and/or roasting processes of some raw ores or materials from the past to the present day. There are three basic mechanisms of conventional heating, namely convection, conduction and diffusion. These three heat transfer mechanisms in conventional heating heat the material from the outside to the inside. This method causes large time and energy losses to occur during conduction by conduction into inside of materials. Microwave energy is non-ionizing electromagnetic radiation (radiation) having a frequency in the range of 300 MHz to 300 GHz, with intensive application in the field of communication; only certain frequencies are allowed for industrial, scientific and medical (ISM) applications [6]. Microwave heating is different from conventional heating because it is in the form of electromagnetic energy that can penetrate the depths of the sample [7]. The samples are heated inside to outside in microwave heating systems [8]. The differences between microwave and conventional heating systems and principles are represented in **Figure 2**.

In microwave heating systems, electromagnetic energy is directly converted into heat inside of the material and heating starts inside to outside contrary to the conventional heating. The microwaves propagate at the speed of light and as soon as the source is turned on the electromagnetic wave immediately penetrates to materials and starts to energy conversion. Long heating and cooling phases are not required when the source is turned off, since the heating process is stopped immediately [10].

1.5. Pellets

Pellets are the oval/spherical shaped pieces of ore having high compression strength which are obtained from fines or from finely ground ores by adding various additives like bentonite and whose diameter is generally between 8 and 20 mm as shown in **Figure 3**.

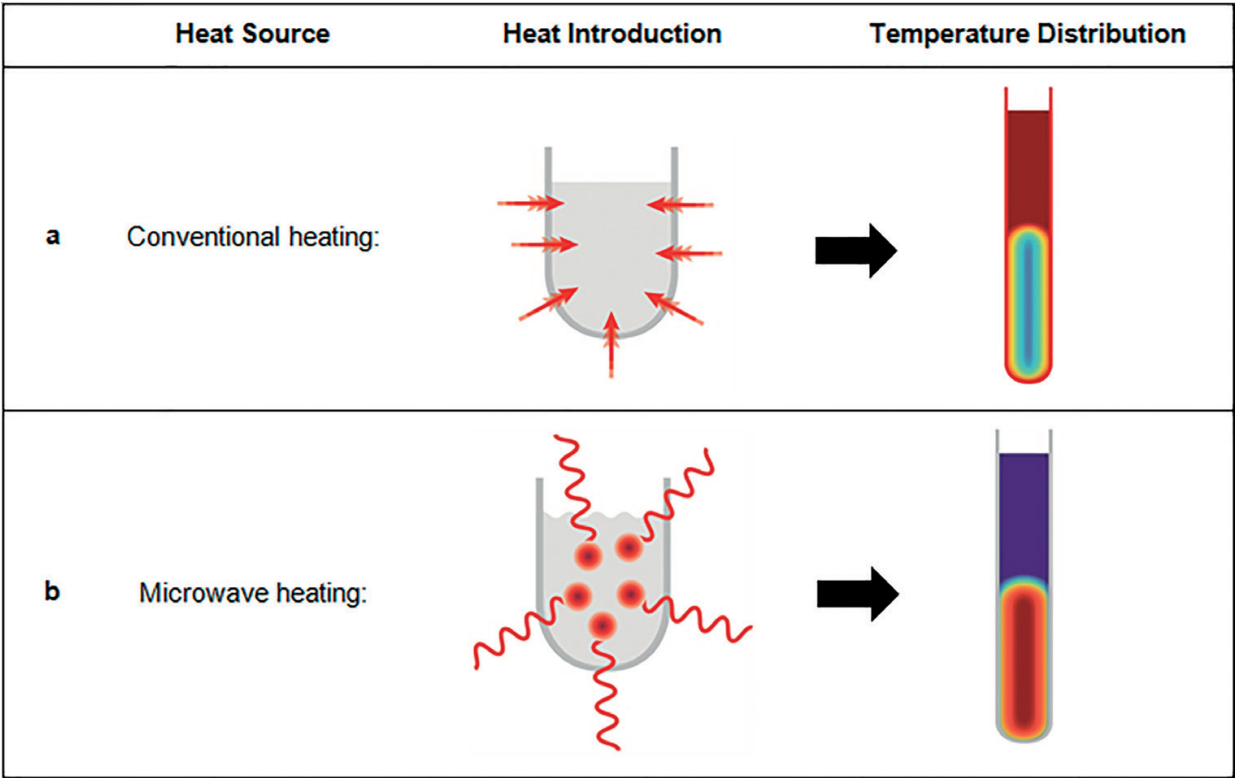


Figure 2. Schematic representation of the comparison of the microwave and conventional heating process [9].

Iron ore pellets can be used as a substitute to sinter and calibrated lump ores in the blast furnace burden. Apart from these pellets can be applied to some non-ferrous metal ores such as lead and chromium ores [11].

Since the 1960s, pelletizing technology has been rapidly developed and provided a quality chargeable material for iron making.

According to 2011 data the world pellet production on the basis of countries and regions is given in **Table 4**.

The purpose of the iron pelletizing process is to convert the iron-rich fine-grained minerals into blast furnace charging material, which is defined as pellet, through agglomeration and hardening. The pellets are rigid and generally spherical shape and must have the following properties to be used in the high-temperature furnace:



Figure 3. The pellets form of iron ore.

| Iron ore, world pelletizing capacity by content and country in 2011 | |
|---|---|
| | Rated capacity gross weight (million metric tons) |
| <i>North America</i> | |
| Canada | 27.5 |
| Mexico | 15.0 |
| United States | 57.4 |
| Total | 99.9 |
| <i>South America</i> | |
| Brazil | 56.0 |
| Chile | 5.3 |
| Peru | 3.5 |
| Venezuela | 11.8 |
| Total | 76.6 |
| <i>Europe and Central Eurasia</i> | |
| Kazakhstan | 8.4 |
| Netherlands | 4.4 |
| Russia | 31.4 |
| Slovakia | 0.4 |
| Sweden | 26.0 |
| Turkey | 1.5 |
| Ukraine | 33.5 |
| Total | 105.6 |
| <i>Asia</i> | |
| Bahrain | 11.0 |
| China | 135.0 |
| India | 24.0 |
| Iran | 12.3 |
| Oman | 9.0 |
| Japan | 3.0 |
| Total | 194.3 |
| <i>Oceania, Australia</i> | 4.3 |
| Grand total | 480.7 |

Table 4. Pellet production in the world and in the region (million metric tons) [12].

- a. must be free from dust and fines.
- b. must show physical strength against breakage during transportation and storage.
- c. must be resistant to crumbling which will occur during various reactions occurring in the blast furnace depending on the heating process.

The ore to be pelletized may be enriched low-grade iron ore or high-grade powder forms ores which cannot be directly charged into the blast-furnace. The pelletizing process consists

of two main parts: raw pellet (green ball) and product pellet. The raw pellet is obtained by mixing the enriched ore with the binders followed by the agglomeration process, the product pellet is obtained by heating and cooling the raw pellet [13].

The pelletizing process occurs in four basic stages, as shown in **Figure 4**. First, the ore and the various additives are mixed to obtain a homogeneous form. The distribution of the materials forming the pellet cake is of great importance in terms of pellet strength. After mixing operation, the mixture is transferred balling discs to obtain pellet form.

This product is called green pellet. Optionally, the process may be ended at this step depending on the needed or, the pellet is transferred to the next device and subjected to the induration to obtain the product pellet as shown in **Figure 5**. After this process, the cooled material is now named the product pellet.

- i. Mixing
- ii. Agglomeration
- iii. Induration
- iv. Cooling

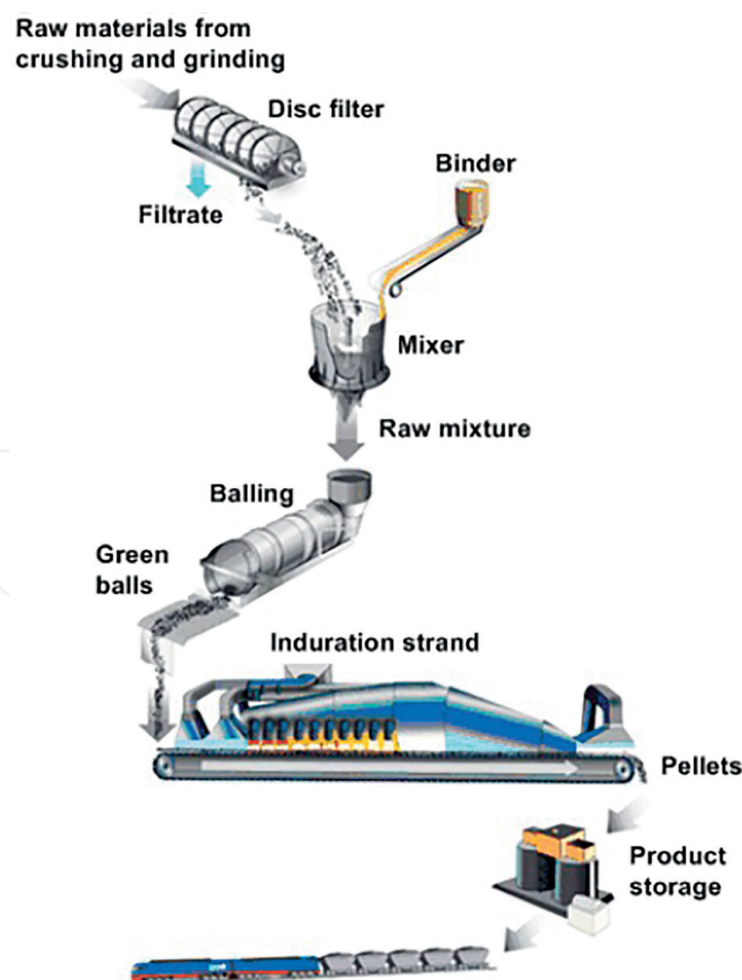


Figure 4. Schematic of a pelletizing plant with wet grinding [14].

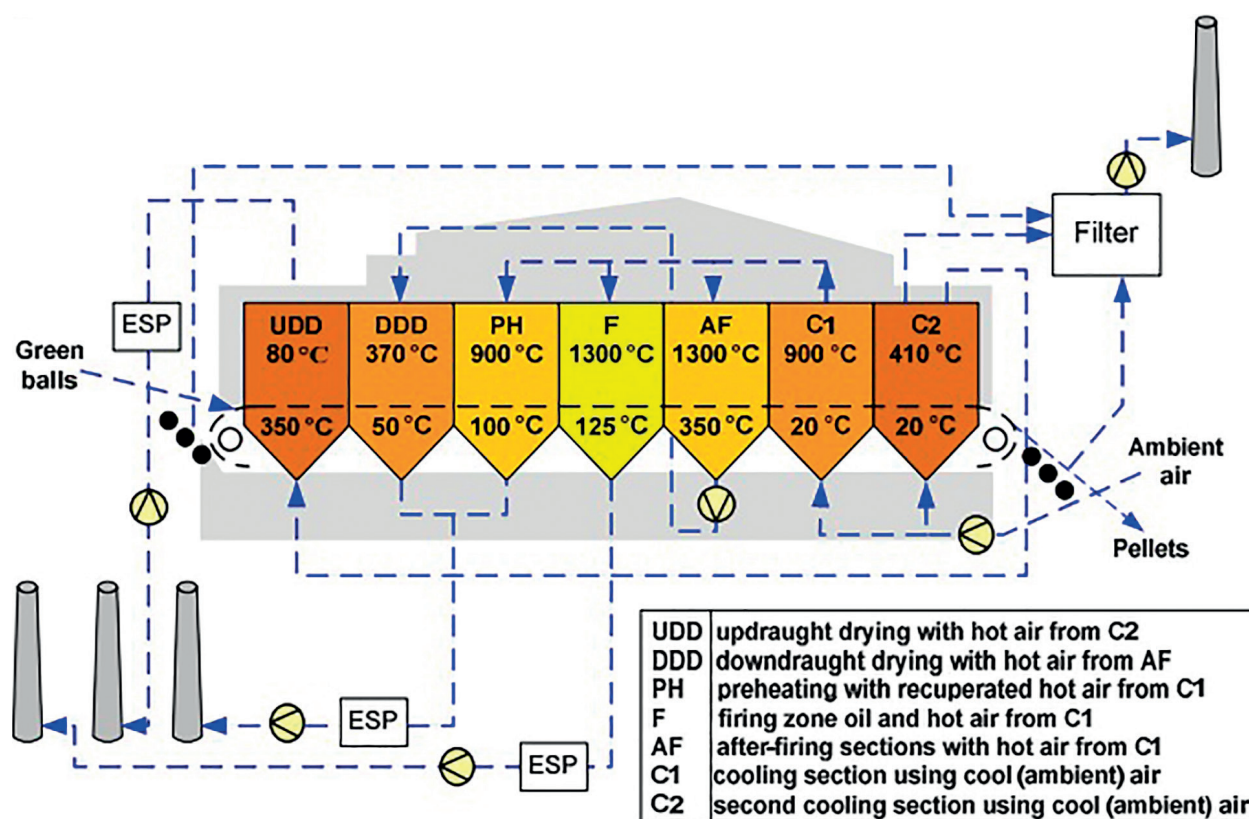


Figure 5. Schematic of the straight grate process [14].

In the process of obtaining the product pellet, the principle is that the material be heated at a recrystallization temperature according to the compound type. The recrystallization temperature for siderite is about 1300°C. If this temperature level is exceeded too much, liquid phase formation is occurred and undesirable sintering process starts.

2. Materials

2.1. Ore and chemicals

In this study, siderite ore was obtained from the Deveci district of Hekimhan Malatya Province. **Figure 6** shows the pictures of the raw siderite ore and the calcined siderite ore used in the study. The elemental analyses of raw siderite ore is given in **Table 5**.

In addition, the bentonite which was used during the pelletizing process was also obtained from Hekimhan/Malatya. Its density is 2.60 g/cm³ and colours are white, grey, yellow, pink and green. Bentonite, a volcanic mineral formed by the decomposition of volcanic ash in situ and composed of montmorillonite clay mineral of large size which absorbs water and is used commercially in drilling mud, catalyst, paint, plastic filling works [15].

In the microwave experiment part, sucrose—C₁₂H₂₂O₁₁ (Merck 99.5%) and urea CH₄N₂O (Merck 99.5%) was used as a thermal auxiliary and consolidate purposes, respectively.



Figure 6. Raw siderite (on the left) and calcined siderite (on the right).

3. Experimental part

3.1. Milling operation

The raw siderite ore used in the study was sieved and weighed. The results of the sieve analysis are given in **Figure 7**. When the graph was examined, it was determined that P_{80} (80% of the feed passed through the sieve) was 7.9 mm and d_{50} (50% of the feed passed through the sieve) was 5.6 mm.

The raw siderite ore was both directly grounded and calcined before grinding operation. During this calcination process, CO_2 is removed by the effect of temperature, causing the capillary cracks in the ore, as a result fragmentation and crumbling is occurred. This situation is evident in the cumulative undersize graph given in **Figure 8** showing that calcination process slightly decreased the particle size of the siderite.

| Component | Concentration (%) |
|------------------|-------------------|
| Fe_2O_3 (Fe %) | 53.21 (37.25) |
| MgO | 18.88 |
| Al_2O_3 | 0.25 |
| SiO_2 | 4.42 |
| SO_3 | 0.84 |
| K_2O | 0.81 |
| CaO | 9.87 |
| MnO | 11.39 |

Table 5. Chemical analysis of raw siderite ore sample.

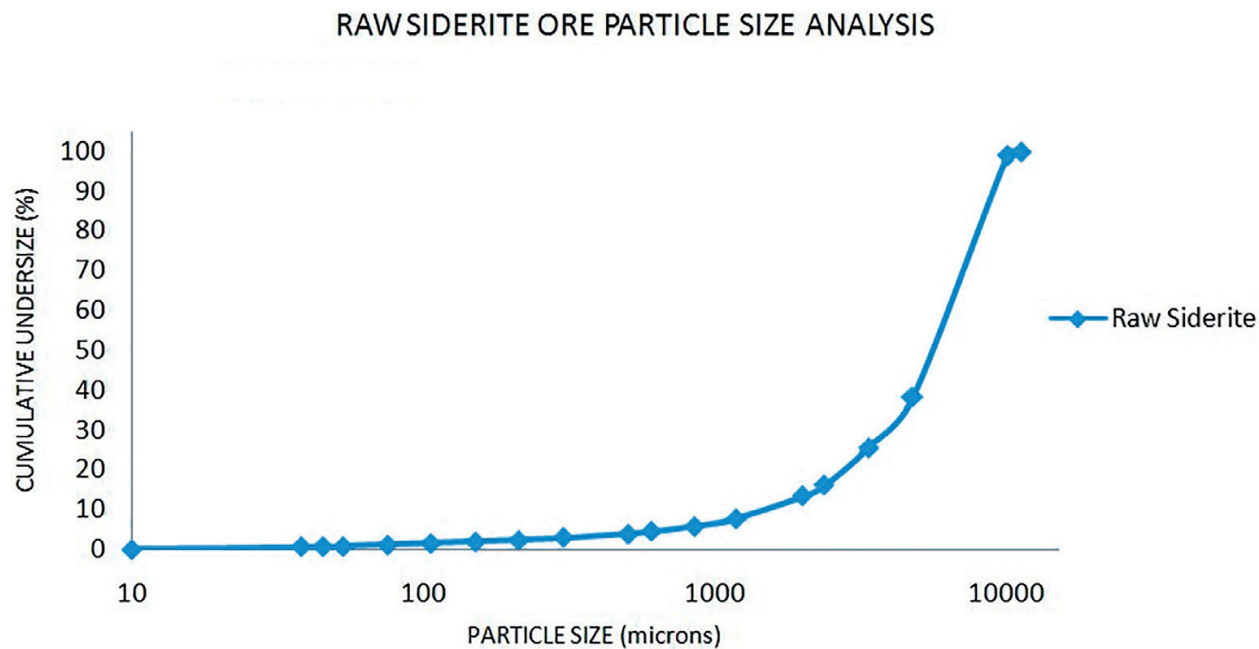


Figure 7. Cumulative undersize graph of raw siderite.

Grinding operation was done by a laboratory-type ball mill not only to examine the grindability properties of the siderite ore but also to produce fine fractions required for pelletizing. **Figure 9** shows the undersize graphs of raw siderite ore grounded at different times.

As milling media, four different sizes of balls were charged with diameters of 20, 25, 30 and 40 mm and milling parameters are given in **Table 6**.

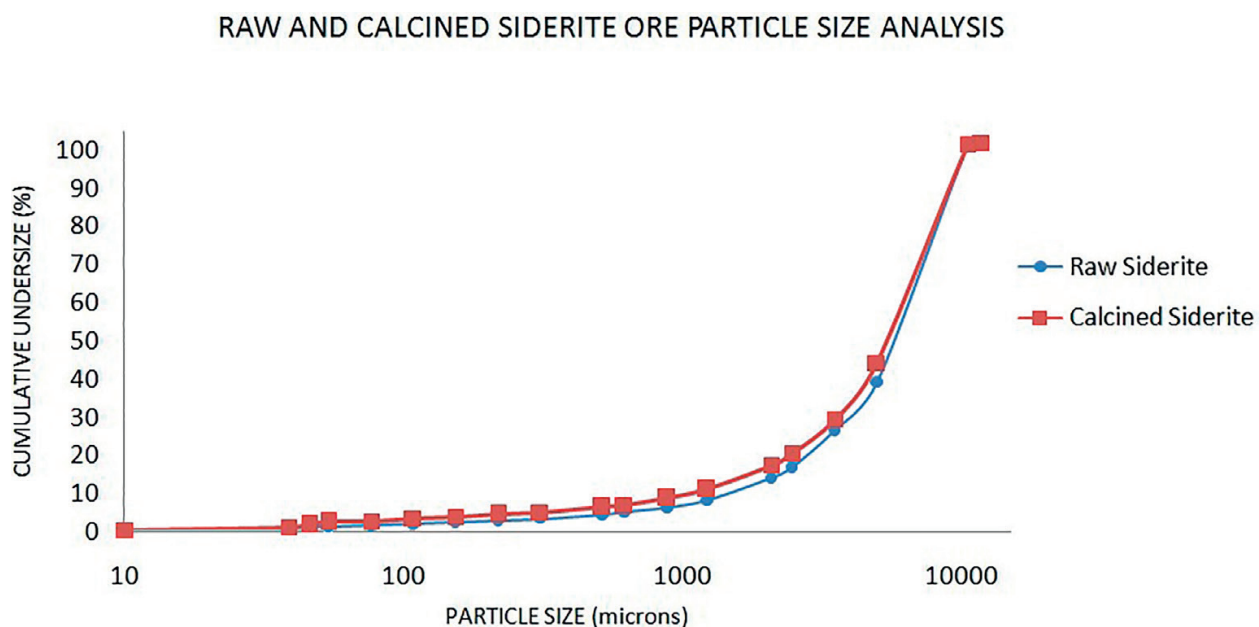


Figure 8. Comparison of raw and calcined siderite cumulative undersize graphs.

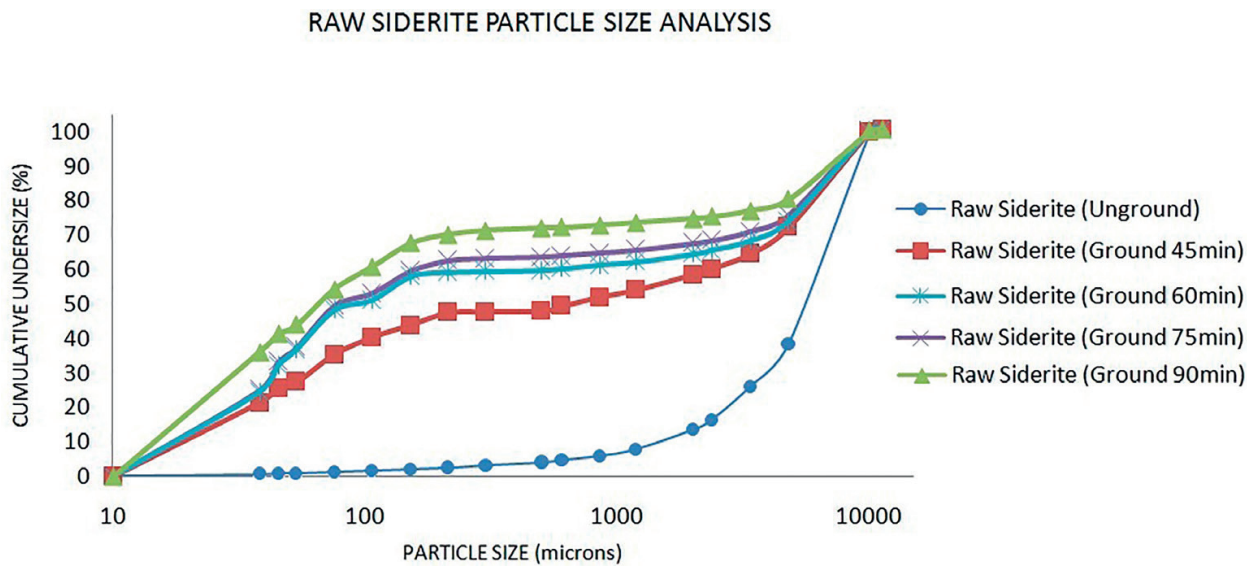


Figure 9. Cumulative undersize graphs of raw siderite ore that milled at different times.

The raw siderite was also calcined and then subjected to grinding. The cumulative undersize curves of calcined siderite ore are given in **Figure 10**.

Aforementioned, the cracking occurs in the siderite structure due to CO_2 escaping from its body during the calcination process. A similar situation is also in the grinding process. The calcined siderite was ground much easier than raw siderite when the raw and calcined siderite were grounded at the same conditions (90 min) as shown in **Figure 11**.

As can be seen from the above graph, the size fraction of both raw siderite and calcined siderite is quite different with each other after the same milling operation. In the graph, the size of d_{50} grain for the raw siderite is 66 μm while calcined siderite for d_{50} is found as 54 μm . Although there are minor differences in the small size fraction, the raw and the calcined siderite are not noteworthy in scale. However, it is not possible to mention about fractions of large grain size from the same situation. The value of P_{80} for the raw siderite is 4.75 mm while for the calcined siderite this value is 110 μm . P_{80} value of the calcined siderite is about 43 times smaller than that of the raw siderite. Thus, the grinding effect of the calcination process increases as the size increases. Moreover, calcined siderite has reached these grinding values with a feed of 40% higher than the raw siderite volume.

| Ball diameter (mm) | Ball mass (g) | Charge (piece) | Real and bulk density (g/cm ³) | Ball charge ratio (% volume) | Feed (g) | Feed ratio (% volume) | Calcined siderite feed (% volume) |
|--------------------|---------------|----------------|--|------------------------------|----------|-----------------------|-----------------------------------|
| 20 | 32.78 | 30 | 7.82–4.57 | 32 | 3000 | 20 | 28 |
| 25 | 64.00 | 20 | | | | | |
| 30 | 110.70 | 20 | | | | | |
| 40 | 262.34 | 17 | | | | | |

Table 6. Grinding parameters.

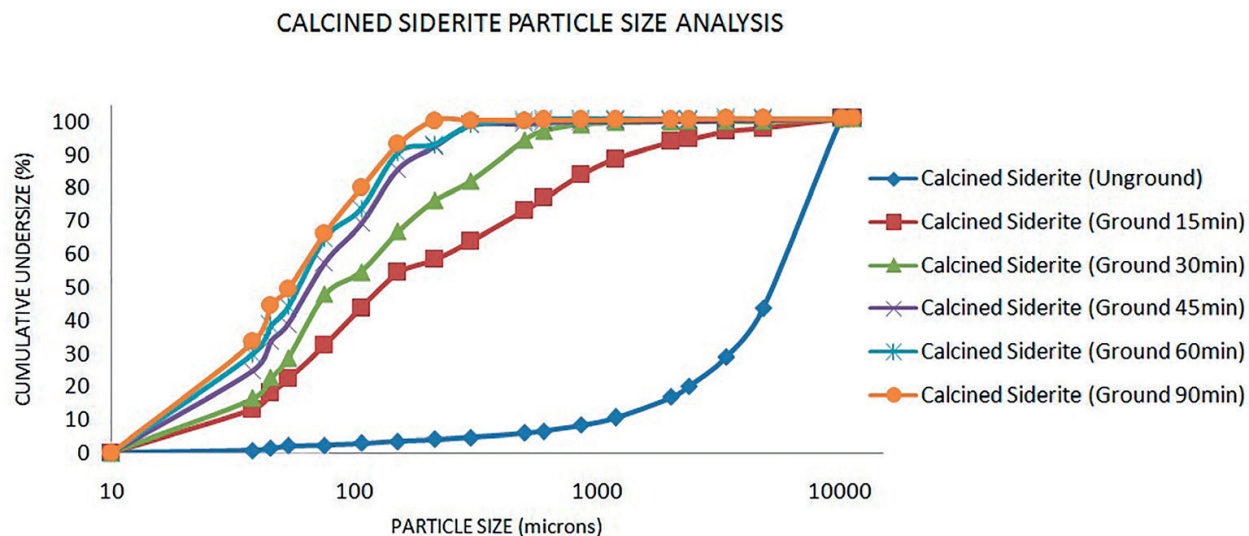


Figure 10. Cumulative undersize graphs of calcined siderite ore, which were milled at different times.

Minimizing the size of raw materials such as ores and rocks also seriously damages the machinery and milling equipments, as well as the enormous energy consumption. Today, about 40% of the energy consumed in mining operations is spent for size reduction. It takes 3.3% of the total electricity energy consumed in the world. This demonstrates the importance of energy efficiency in size reduction processes [10, 16].

In this respect, the production of the fine material required for the production of the pellet should be done after the calcination step. In this way it will be possible to save a great deal of energy and extend the life of grinding machines. This is only one of the advantages to be achieved as a result of making changes in the pellet production process.

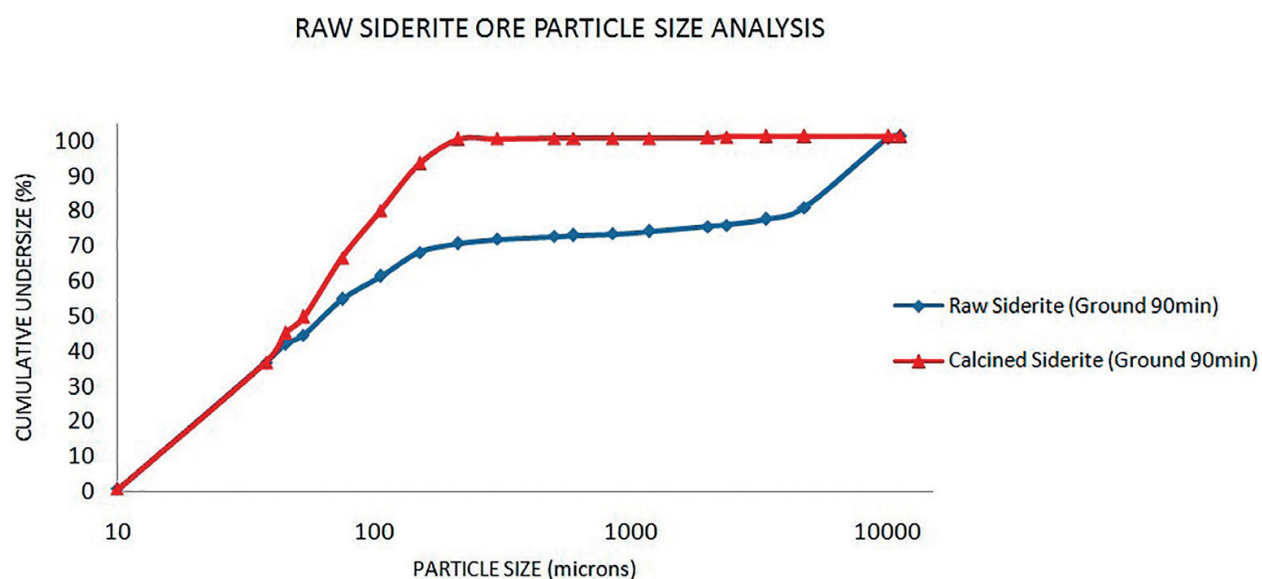


Figure 11. Cumulative undersize graphs of raw and calcined siderite at equidistant times.

3.2. Calcination experiments

Thermogravimetric analysis (TGA) was used to determine the weight loss of raw siderite exposed to temperature and the result is given in **Figure 12**. Calcination experiments of siderite ore were carried at temperatures of 465-500-550-600-650-700-750-800°C. In these experiments; the effects of two different sizes, large (−14 + 4.35 mm) and small (−300 μm), calcination temperatures and duration time on the calcination yields were investigated.

The optimum calcination temperature was determined as 700°C based on the calcination experiments and the TGA graph (**Figure 12**). The weight loss depending on the duration time at 700°C is given in **Figure 13**. In the same graph, the effects of size were also investigated.

In the calcination experiments, weight loss of the siderite ore was found to be 31.01 wt%. According to above graphs, it was found that the CO₂ in the siderite was completely removed from the body in terms of weight loss (calcination loss: 31.04%) at the temperature of 700°C and for 15 min and these calcination conditions were selected as a reference conditions and applied in subsequent experiments. No remarkable difference was recorded for the weight loss and magnetic susceptibility balance (**Table 7**) after 15 min at 700°C. It is therefore unnecessary to keep the calcination time longer than 15 min.

Also at this point it was found that the material grain size had no effect on the calcination process (except when it has a heat capacity that is too high to slow the heat transfer too much). The large particle size is also advantageous because it easily provides a comfortable circulation of hot air flow.

Calcination experiments were also carried out in a microwave oven. Microwave oven application offers great advantages especially for short heating and calcination time [17]. In microwave

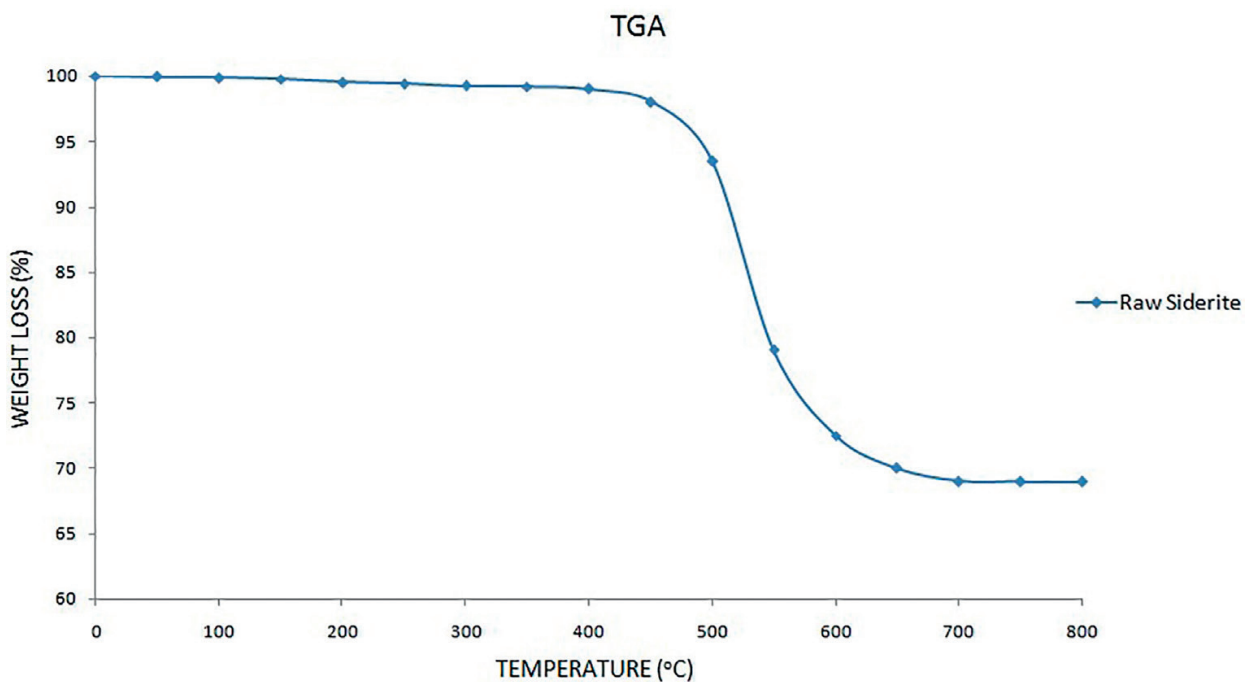


Figure 12. Thermogravimetric analysis (TGA) of siderite ore.

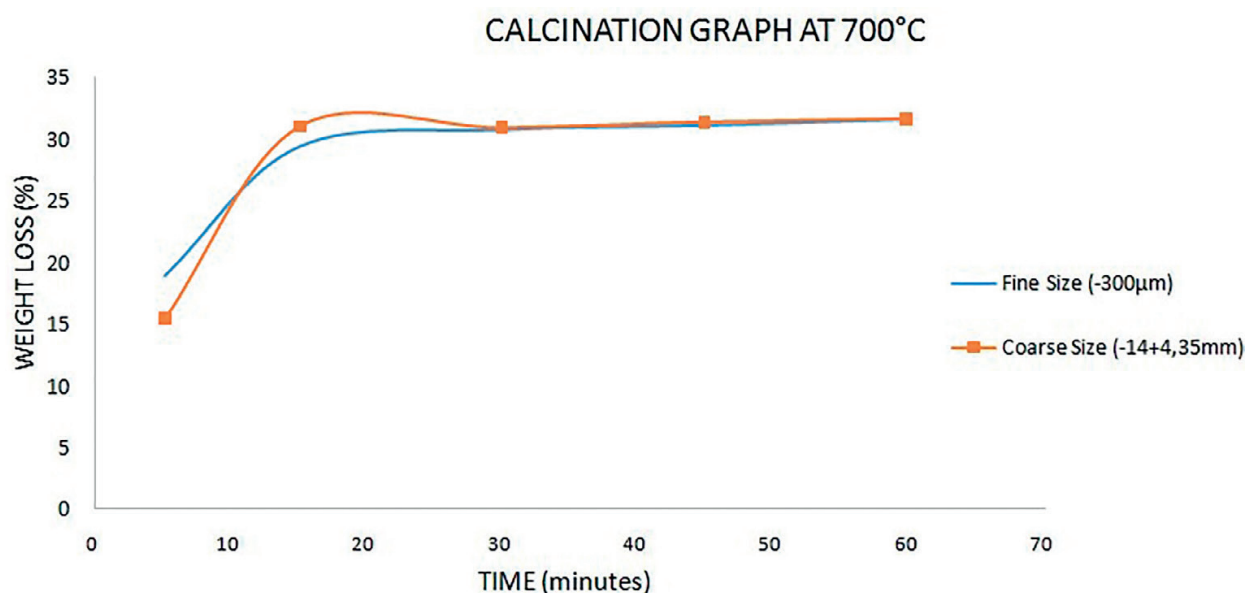


Figure 13. Calcination graph of raw siderite ore at 700°C.

heating method, 32.14% weight loss of the siderite was detected. In microwave calcination operation, the siderite ore was mixed with the sucrose (30 wt% by weight of siderite) and the mixture was put into the microwave oven. After 3 min, the temperature of the mixture was detected as 1100°C. In the microwave heating method, sucrose was used as thermal auxiliary to heat siderite ore. The calcination results, showing the weight loss versus time, of the electrical furnace and the microwave furnace are given in **Figure 14**. Apart from the partial reduction in the magnetic susceptibility balance, the microwave oven has no disadvantages over the electrical furnace. On the contrary, higher weight loss was achieved.

Calcination procedures which were carried out using the electrical furnace and the microwave oven were achieved. The results showed that necessary weight losses and high iron content in the calcined samples were obtained and the calcination process in electrical furnace and microwave oven caused the hematite transformation which was provided the magnetic properties. The chemical structure of the raw siderite and the calcined siderite in the electrical furnace and the microwave oven were checked using Rigaku Miniflex 600 XRD (Cu K α (40 kV, 15 mA, λ : 1.54051 Å). Comparison of the XRD patterns (**Figure 15**) showed that by addition of sucrose the siderite can be calcined by using microwave oven in 3 min.

| Sample no | Calcination temperature (°C) | Magnetic susceptibility ($\times 10^{-8} \text{ m}^3/\text{kg}$) |
|-----------|------------------------------|--|
| 1 | 465 | 1708.16 |
| 2 | 500 | 17690.50 |
| 3 | 600 | 19780.03 |
| 4 | 700 | 19530.93 |
| 5 | 1100 (microwave method) | 15410.03 |

Table 7. Magnetic susceptibility balance values.

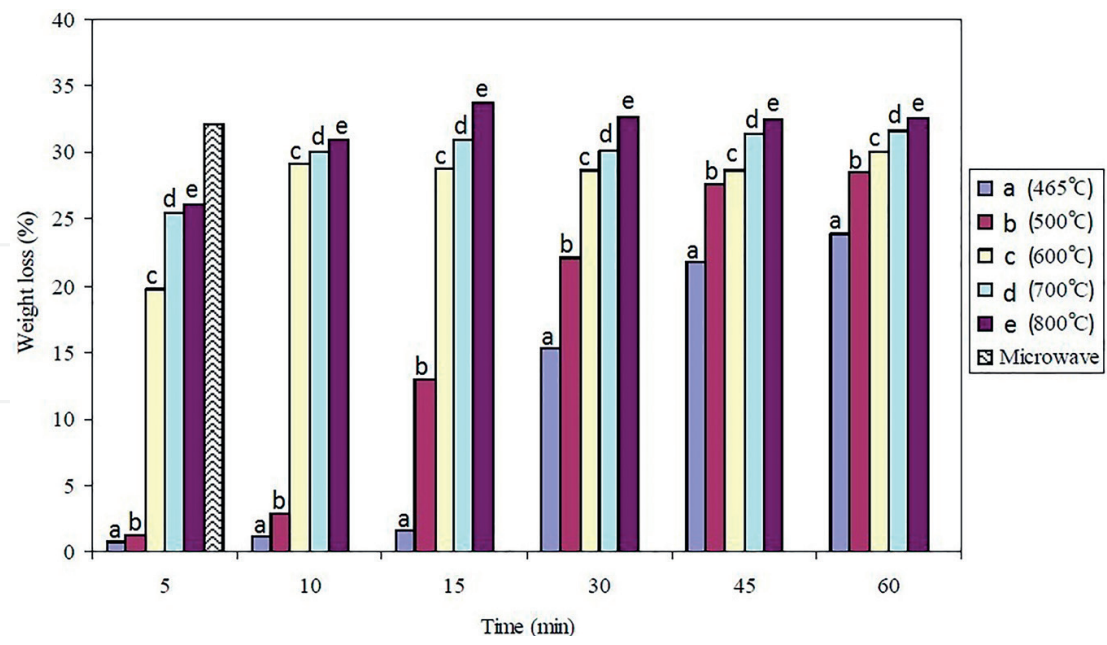


Figure 14. The weight loss versus time obtained from the electrical furnace and the microwave oven.

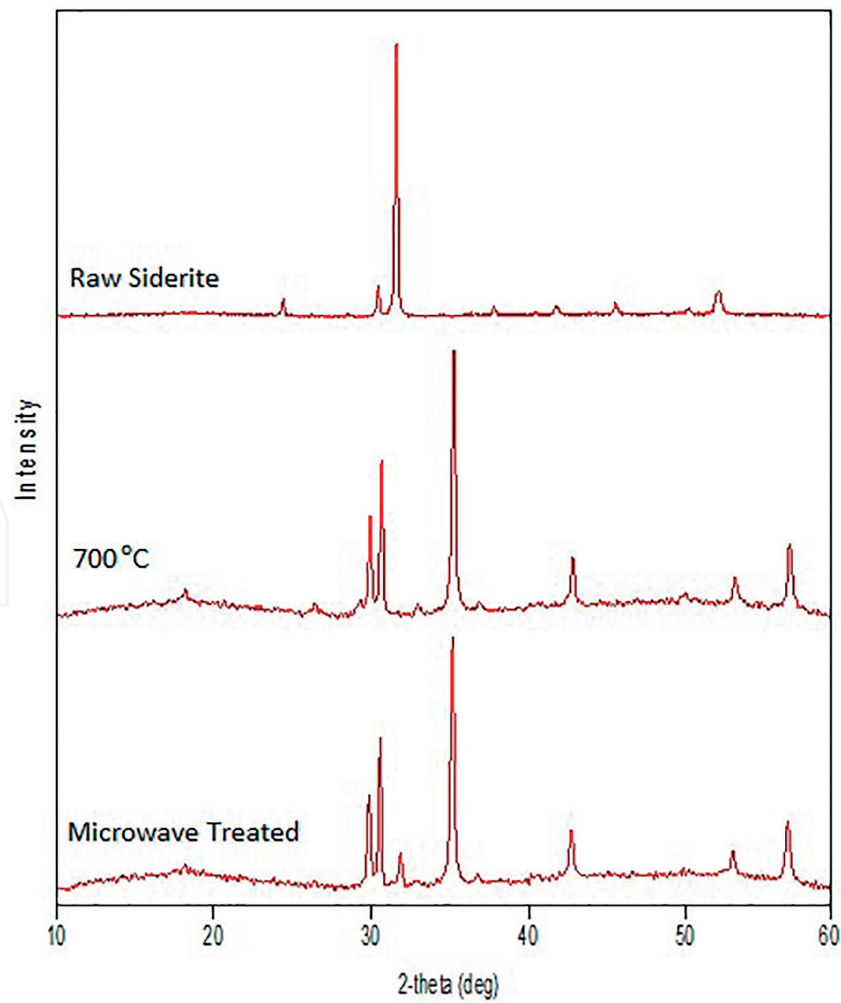


Figure 15. XRD patterns of the raw and the calcined siderite.

3.3. Pelletizing experiments

The green pellets were obtained by pelletizing machine which has a disc diameter of 60 cm and an angle of 50° and operated at a speed of 20 rpm. Pellets were produced by adding bentonite in proportions of 8, 10, 12% by weight into the raw and calcined ore. The mixture conditions are given in **Table 8**. The best pellet strength results were obtained for the calcined siderite sample with 10% bentonite addition which had been subjected to 90 min in mill.

Figure 16 indicates the raw pellets which were obtained from the raw and calcined siderite.

Examples of product pellets which were obtained using the electrical chamber furnace are given in **Figure 17**. After heating process, there was no visual difference observed between the pellets made with the raw siderite and the calcined siderite.

The SEM images belonging to the pellets obtained by mixing the siderite and 10 wt% bentonite are given in **Figure 18**. Trigonal crystals were observed in the SEM images, indicating the recrystallized hematite minerals. It can be said that the pellet heating process is performed at the proper temperature.

The resulting product pellets were subjected to a compressive strength test at a constant loading rate of 10 mm/min according to ISO/TC 102/SC 3 ISO 4700: 2015 coded standards of the International Organization for Standardization. The data obtained in the test result are presented in **Table 9**. According to the results, the pellets with the highest compressive strength obtained from the raw material added with 10% bentonite and milled for 90 min after being calcined.

The compressive strengths of the obtained pellets are shown on the graph in **Figure 19**. As it can be seen in the graph pellets obtained from calcined ores have more strength than that obtained from uncalcined ore. The improvements in the milling parameters of the calcined

| Sample type | Clay ratio (%) |
|--|----------------|
| Raw siderite (90 min milling) | 8 |
| | 10 |
| | 12 |
| The calcined siderite (60 minutes milling) | 8 |
| | 10 |
| | 12 |
| The calcined siderite (90 minutes milling) | 8 |
| | 9 |
| | 10 |
| | 11 |
| | 12 |

Table 8. Raw materials and clay rates used in pelletizing.



Figure 16. The pellets obtained from the raw and calcined siderite.

siderite ore was further reduced the size distribution in the raw material, making it possible to do more durable pellets. The smaller the size distribution in a raw material, the more resistant the pellets to be obtained from it [18].

The most basic way to increase the specific surface area is milling operation. In the previous sections, we have mentioned that grinding is not a very economical process in terms of both machine-equipment and energy costs, and that work should be done in large grain sizes as possible. For this reason, in order to investigate the possibility of using large grain size materials for pellet production, an urea (30% by weight) was added into the raw siderite with the size of the $-150 + 75 \mu\text{m}$, which cannot be pelletized by conventional methods. The mixture was put into the microwave oven with a frequency of 900 W for 5 min. The photo of the pellets is given in **Figure 20**.

The pellets which were obtained by this method had very high porosity. It is very advantageous to use large-sized material as pellet raw material. For example, with the aid of a sieve to be used after grinding, the product can be divided into two different fractions. The small size fractions may be fed to the conventional pelletizing plant and the large size may be fed into the microwave pelletizing plant.



Figure 17. The products pellets.

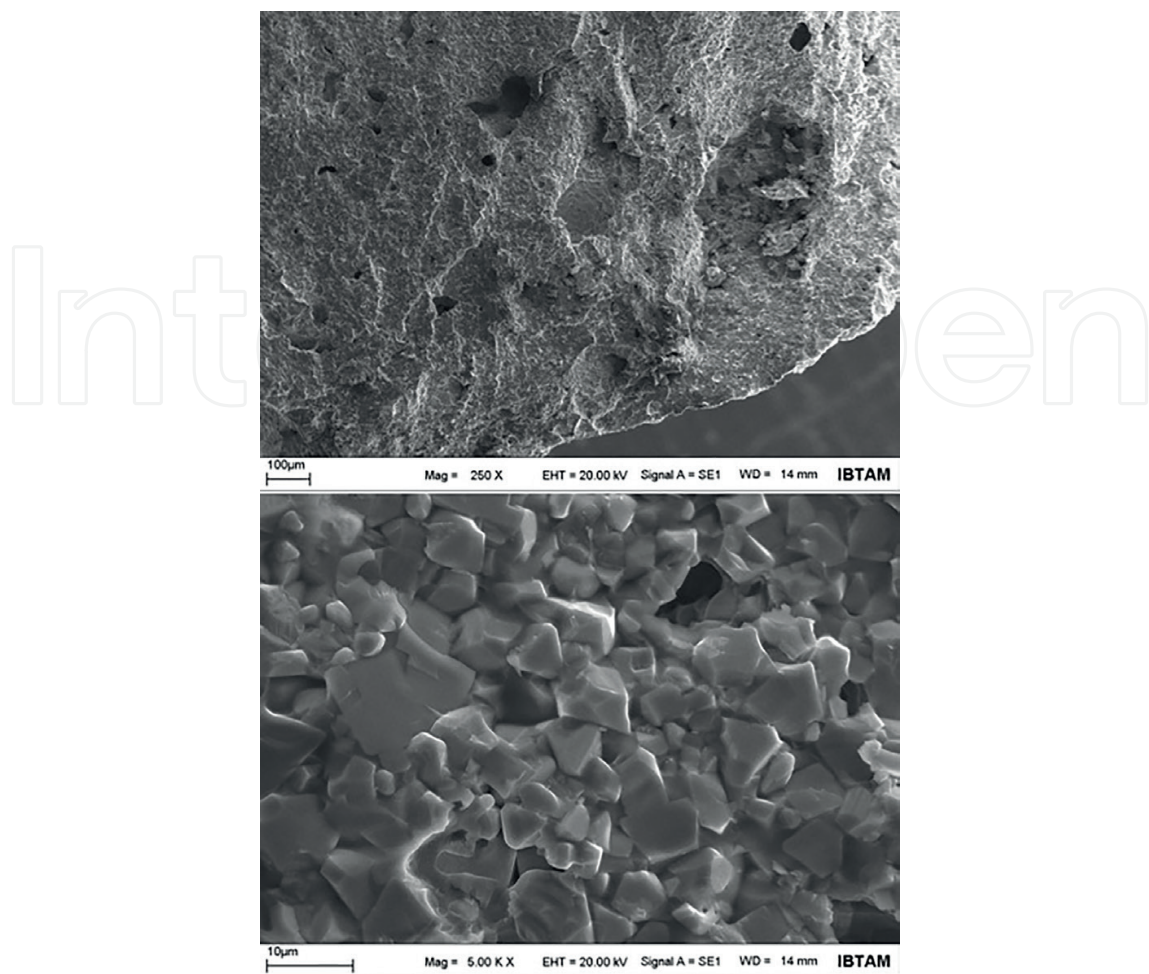


Figure 18. SEM images of the pellets.

| Sample type and grinding time | Clay ratio (%) | Density (g/cm ³) | Pellet diameter (mm) | | | | |
|-------------------------------|----------------|------------------------------|----------------------------|-----|-----|-----|-----|
| | | | 9 | 10 | 11 | 12 | 13 |
| | | | Compressive strength (kgf) | | | | |
| Raw siderite 90 min | 8 | 4.05 | 129 | 146 | 153 | 179 | 199 |
| | 10 | 3.77 | 155 | 164 | 179 | 191 | 211 |
| | 12 | 3.52 | 139 | 152 | 160 | 167 | 200 |
| Calcined siderite 60 min | 8 | 4.38 | 139 | 147 | 156 | 168 | 189 |
| | 10 | 4.28 | 159 | 162 | 166 | 176 | 205 |
| | 12 | 4.06 | 149 | 154 | 165 | 182 | 213 |
| Calcined siderite 90 min | 8 | 3.86 | 155 | 159 | 164 | 169 | 198 |
| | 9 | 3.84 | 174 | 190 | 192 | 200 | 207 |
| | 10 | 3.84 | 199 | 215 | 225 | 232 | 268 |
| | 11 | 3.81 | 149 | 183 | 205 | 230 | 258 |
| | 12 | 3.75 | 142 | 144 | 146 | 156 | 171 |

Table 9. Pellet compression strengths according to pellet diameters and clay rate.

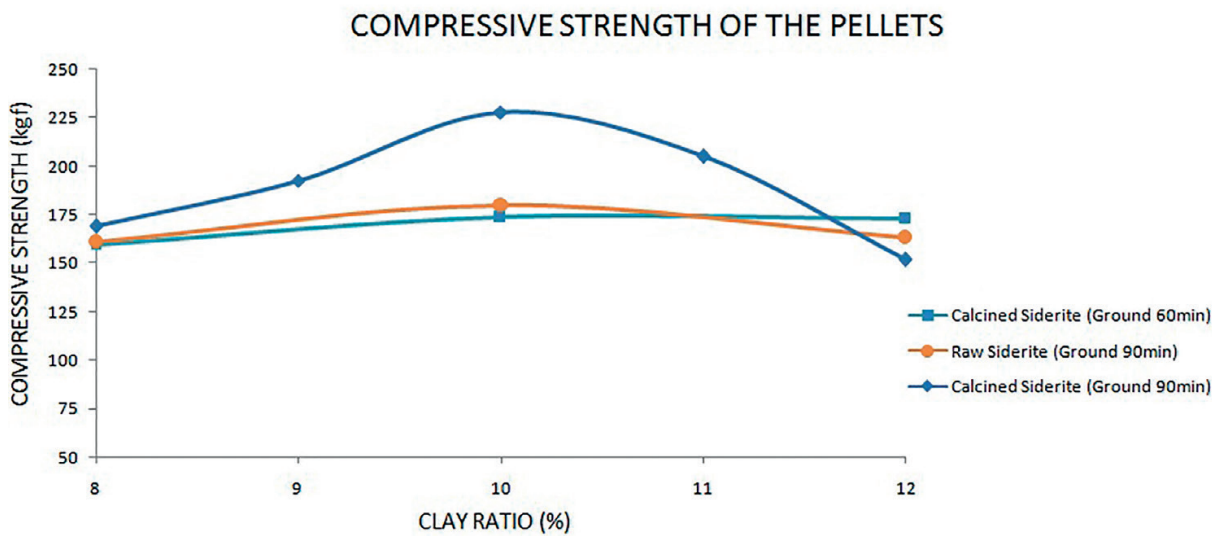


Figure 19. The effects of the bentonite ratio on the compressive strength of the pellets.



Figure 20. 30% by weight urea-added pellet obtained by microwave irradiation.

4. Conclusions

The raw siderite samples from the Hekimhan/Deveci region were subjected to calcination treatments at different temperatures (465, 500, 550, 600, 650, 700, 750, 800°C) for various duration time (5, 10, 15, 30, 45, 60 min) using the electrical furnace. Both the results of the experiments and the thermogravimetric analysis (TGA) showed that the most suitable calcination process was decided as 700°C for 15 min. The raw siderite (45, 60, 75, 90 min) and siderite calcined at 700°C (15, 30, 45, 60, 90 min) were milled. Significant behavioural differences between the two materials were identified. Calcination makes the grinding process much easier. The raw pellets were prepared

by adding different bentonite ratios (8, 9, 10, 11, 12%) to the raw siderite and the calcined siderite which were milled for 90 and 60 min, respectively. The raw pellets were heated at a temperature of 1300°C which is the recrystallization temperature of hematite. Recrystallization was confirmed by SEM images and the process was confirmed to be successful. The product pellets were tested for compressive strength. The highest level of pellet strength was determined from the material obtained by grinding calcined siderite for 90 min. This pellet, which has a maximum strength value of 268 kgf, has an average durability of 28% higher than the pellet made of the raw siderite.

The results obtained in this study are listed below:

1. Calcination treatment caused big difference in the grinding behaviours of the ore. It has been found that the milling of the ore after calcination is much easier than the raw siderite.
2. The 31.01% weight loss material that was obtained from the calcination process with the conventional heating method will have great benefits from cost of transportation both in the plant and outside of the plant.
3. It has been determined that the most suitable calcination process for siderite ore is to be carried out at 700°C for 15 min.
4. The calcination process increased the Fe content from 37.25 to 55.61%.
5. The raw siderite was treated by microwave radiation (P: 900 W, f: 2.45 GHz) but neither heating nor weight loss was detected.
6. The addition of the 30 wt% sucrose into the raw siderite before the irradiation of microwave increased the temperature up to 1100°C in a 3 min. The XRD result showed that the calcination was successfully accomplished in 3 min by microwave. However, in terms of magnetic susceptibility balance, microwave-derived calcined siderite has lower values of about 23% than the conventional method.
7. Pellets obtained from calcined ores have more strength than that obtained from uncalcined ore. The highest compressive strength was obtained with addition of 10% bentonite and ground for 90 min. The highest compressive strength of this pellet is determined as 268 kgf. This pellet is about 28% more durable than the others.
8. As it is known, the strength of the pellets, which are blast furnace charging materials, determines the charge amount of the furnaces. The material charge to the blast furnaces is such that the pellets at the bottom end are not broken. More durable pellets were obtained in the present study.
9. Pellets with the addition of 30 wt% urea admixture into the coarse size of $-150 + 75 \mu\text{m}$ the siderite ore were obtained using microwave. This method is promising in terms of the reducing the grinding costs.

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