Influence of the calcination temperatures on thermal properties of natural iron ore for heat energy storage

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Abstract. If the iron ore is used as solar heat storage material, it can greatly reduce the cost of thermal storage in concentrating solar power plants due to its lower cost. Therefore, in this paper, we made a foremost investigation on the temperature dependence of the thermal properties of the natural ore. With the help of the X-ray diffraction, scanning electron microscopy and differential scanning calorimeter, thermal properties of the samples were measured and analyzed.

1. Introduction
The development of green and sustainable energy storage technologies is of great importance to cope with the excessive depletion of non-renewable fossil fuel and the state of global warming. One typical example in this area is the solar energy application, which can be easily found in many aspects of our daily life. However, the extensive utilization of solar energy is mainly limited due to its intermittence and instability. For mitigating these issues, thermal energy storage (TES) has been emphasized. As prominent natural materials, iron ores, including magnetite, hematite (H) and maghemite (M), etc., have been mentioned as a potential material for TES due to their many advantages, such as availability, low cost, ecological friendliness, etc. For example, recently in 2017, Yaroslav. Grosu et al. made detailed investigations on the thermal properties of natural magnetite, and they consider it as promising material for energy storage application. In 2018, basing on effective evaluation on the thermophysical properties of BOF-Slag, magnetite and river rock, they further point out that magnetite has excellent energy density and high thermal conductivity compared with other ceramic materials considered for TES applications [1, 2]. For hematite, it was reported earlier in 1971 that its thermal conductivity value can attain 6.0 W·m⁻¹·k⁻¹, much higher than that of magnetite [3]. However, the current literature reports indicated that there are few studies on the relationship between the thermophysical properties and calcined temperature for iron ore. Considering that iron ore often needs to be shaped and sintered before further application, we made an investigation on the temperature dependence of the thermal properties of the natural ore. The purpose of this study is to try to optimize natural iron ore’s performance as thermal storage material by identifying the sintering technique.
2. Experimental procedure

2.1. Sample preparation
Natural iron ore from Liaoning, China, and aluminum powder from Oriental Chemical factory, was used as the original material. The chemical compositions of natural iron ore measured by X-ray fluorescence spectrum analysis are given in Table 1. Scanning electron microscopy (SEM) picture of both natural iron ore is given in Figure 1. Depending on the SEM result, it is easily concluded that the average particle size of the used iron ore is tens of microns. The pattern of natural iron ore performed by X-ray diffraction (XRD) is also presented in Figure 1. The XRD result is consistent with the analysis shown in Table 1 and the natural iron ore is confirmed to be mainly maghemite.

Table 1. Chemical compositions of natural iron ore.

| Composition | Fe$_2$O$_3$ | SiO$_2$ | Na$_2$O | MgO | Al$_2$O$_3$ | CaO | MnO | K$_2$O | SO$_3$ | TiO$_2$ | Cl | P$_2$O$_5$ |
|-------------|-------------|--------|---------|-----|-------------|-----|-----|--------|--------|--------|----|---------|
| Content (wt.%) | 79.26 | 12.21 | 0.20 | 3.57 | 3.49 | 0.58 | 0.24 | 0.17 | 0.12 | 0.08 | 0.05 | 0.03 |

![Figure 1. SEM pictures (a) and XRD pattern (b) of the natural iron ore.](image)

2.2. Characterization techniques and methodology
The microstructure and the morphology of the resultant samples were characterized by means of SEM (JSM7401). The crystalline phase compositions of the resultant samples were defined by XRD (Bruker D8 Advance) using Cu Kα radiation and a scan speed of 6 °/min. The densities of the samples were experimentally measured by Archimedes drainage method. The heat transfer properties were investigated by Laser thermal conductivity meter (LFA467 Netzsch, Germany). The phase change properties of samples were characterized using a differential scanning calorimeter (DSC, Netzsch STA449F5) in the nitrogen atmosphere with a heating rate of 10 °C/min from 25 °C to 800 °C. The specific heat capacities of the samples were experimentally measured by specific heat ratio method using sapphire as standard sample with a temperature range from 25 °C to 600 °C.
Figure 2. Sketched picture of both (a) preparation process and (b) sintering technique.

Figure 3. Both SEM pictures and density curve of the samples sintered at different temperatures in air. (a) density curves (b)-(f) SEM pictures. (b)-800°C; (c)-850°C; (d)-900°C; (e)-950°C; (f)-1000°C.
3. Results and discussions

The influences of the temperature on the samples’ densities are shown in Figure 3. Figure 3(a) indicates no obvious changes are found in all the samples’ densities despite the increased temperature, which indicates a relative high density could be obtained at a lowered calcination temperature for the natural iron ore. Obviously, this is helpful to reduce the production cost. The fractured SEM pictures of the samples sintered at different temperatures in air are displayed in Figure 3(b)-(f). The calcination temperatures have no significant effects on the fractural morphologies. This is consistent to the result shown in Figure 3(a).

Figure 4 displays the XRD patterns of the obtained samples at 850°C. Besides the diffraction peaks of both M and H, the tiny diffraction peaks of oxides including Al2O3 and SiO2 are also found. Further XRD analysis indicates the phase transformation of the pure natural iron ore from maghemite to hematite in the calcination process. The fact that maghemite, γ-Fe2O3, which is ferromagnetic iron (III) oxide phase with cubic structure, would convert to the hematite with corundum structure (α-Fe2O3) at proper temperatures in the air has been reported by many researchers [4]. This transition is a thermal activated process, which can be affected by many factors, such as pressure, internal defects, preparing methods, particle size, impurities, vacancies in structure, pretreatment, etc. [5]. As an important research method, doping technique is often used to modify both the microstructure and chemical composition of maghemite (γ-Fe2O3) for improving its thermal stability in phase transformation. For example, many doped metal oxide ions have been reported to be able to suppress the transformation of γ-Fe2O3 to α-Fe2O3 [6-7]. In our research, similar phase transition was also found. Due to the impurities in iron ore, as shown in Table 1, the phase transition process of iron ore differs from that of pure Fe2O3. Moreover, further research on doping elements also shows that the doping element, such as aluminum, would have significant effects on the phase transformation of iron ore. We will continue to try these research activities in the near future.

Figure 4. XRD patterns of the samples sintered at 850 °C in air.

Figure 5. DSC/TG curves of the air-sintered samples.

In order to find the possible effects of the calcinations temperatures on the thermal properties of iron ore, the samples calcinated at different temperatures were detected by DSC/TG technique and the results are given in Figure 5. Since the curve shape of the 900 °C-sample is very similar to that of 950 °C-sample, only the measured curve of 900 °C-sample is given in Figure 5. The same choice was also made for the curves of the 800-850 °C-samples. It is easily found that all the TG curves are almost flat despite of various temperatures, which suggests the chemical stability of the composites in the measurement process. Figure 5 also reveal that there are four typical peaks in DSC curves. A broaden peak is situated at temperature range of 300-400°C while a tiny peak is at 677°C. Besides, another two peaks at 573 and 576°C, in spite of being not very obvious, also can be found in Figure 5(see the
The broad exothermic peak situated in the temperature range of 300-400 °C should be connected to the phase transition from maghemite to hematite. It has been reported that silicon dioxide would have phase transition from α to β-SiO$_2$ phase at 573 °C [8, 9]. Therefore, the circled peaks should have close relations with impurities in iron ore, such as SiO$_2$, since the content of SiO$_2$ in the used precursors is as high as 12%. The peak at about 677 °C should be attributed to the antiferromagnetic transition of Hematite, which has been reported to be about 690 °C by literature [10]. Figure 5 shows that the calcination temperatures have a significant impact on the phase transition process. For example, as the calcination temperature increases, the broaden peak tends to disappear, while the rest peaks tend to increase. This indicates impossible mutual reactions and redistribution of impurities in iron ore. However, further research becomes necessary.

Depending on the above measured results, a more suitable calcination temperature for iron ore should be 1000 °C. Therefore, the temperature dependence of both specific heat capacities and thermal conductivities is displayed in Figure 6. The samples were prepared in air with the calcined temperature as 1000 °C. Figure 6 (a) indicates the specific heat value increases almost linearly with the increased temperatures. The rapidly growth is found around 600 °C and then a broad peak starts to be formed with temperature increasing from 600 to 670 °C. Figure 6 (b) is the temperature dependence of the thermal conductivity for the samples sintered at 1000 °C. As shown in Figure 6 (b), all the thermal conductivity values tend to decrease with the increased temperature. The averaged value of the sample is about 2 W/(m·K) at room temperature. In general, many factors, such as temperature, microstructure, composition, etc., can affect both the specific heat capacity and thermal conductivity [11, 12]. Among these factors, temperature is obviously more important. The specific heat capacity would increase with increased temperature since the increased temperature can lead to intensely thermal motion of the atom, and further increase the entropy value. In this case, the lattice vibration is the main contributor to the increment in specific heat capacity [13]. However, it is the opposite for thermal conductivity. Thermal conductivities of majority of oxides tend to reduce with increased temperature and then become constant or start to increase at a certain temperature [14-16]. These analyses are consistent to our experimental results shown in Figure 6.

![Figure 6. The temperature dependence of both specific heat capacities (a) and thermal conductivities (b).](image)

4. Conclusions
This paper has investigated the influences of the calcination temperatures on thermal properties of natural iron ore for heat energy storage. Research in areas, such as sintering behavior, microstructure, specific heat capacity, thermal conductivity, etc., have been conducted. The results show that the samples sintering in air can realize better improvements in thermal properties. A more suitable calcination temperature for iron ore should be 1000 °C. And with the sample calcined at 1000 °C, the specific heat capacity with a value of about 0.8-1 J/g·K and thermal conductivity with a value of
about 2 W/(m·K) can be obtained, which can satisfy the requirements of industry. However, further studies still become necessary for performance improvement.

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