



Natural Magnetite for thermal energy storage: Excellent thermophysical properties, reversible latent heat transition and controlled thermal conductivity



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ABSTRACT

Thermal energy storage (TES) has gained growing interest in the area of renewable energy due to its great potential for increasing the efficiency of concentrated solar power (CSP) plants. One of the central issues is the development of a working body with desirable properties, namely, thermal conductivity; heat capacity; density; price; availability; and eco-friendliness. This study reports the thermophysical characterization and proposes a reliable and industrial appropriate treatment route for natural Magnetite to obtain a material possessing not only a combination of the above properties, but also the possibility of easy control (programming) of thermal conductivity in a wide range of values. The combination of such properties is exceptional and crucially advantageous for TES applications like packed-bed heat storage systems.

1. Introduction

Magnetite (Fe_3O_4) is a prominent natural material whose properties have attracted attention since antiquity. Its usage for practical applications has been documented due to its magnetic properties as far back as the 8th century [1]. Today, the range of applications is impressive ranging from drug delivery, magnetocytolysis [2], and magnetic resonance imaging [3,4] to cancer therapy [5], hyperthermia [6], nanocomposites, ferrofluids [7,8] and more [9]. Magnetite has many advantages such as availability, low cost, ecological friendliness and non-flammability, yet it has been mentioned only briefly as a potential material for Thermal Energy Storage (TES) [10] as well as part of iron ore [11]. Furthermore, it has not been studied extensively for TES applications perhaps due to its low thermal conductivity, which is a critical property in this field. On the other hand, the iron oxide, Hematite ($\alpha\text{-Fe}_2\text{O}_3$), noted to have much higher thermal conductivity, was used as part of composite TES materials such as concrete [12,13] and the composites consist of natural materials [14]. It is indicated in [12,13] that iron oxide is used, however, considering that it is obtained as by-product from strip steel production it is a reasonable assumption that it is Hematite. In this paper, we propose a simple treatment route for natural Magnetite for beneficiation from high and controlled thermal conductivity and increased energy density due to reversible antiferromagnetic phase transition. This would provide a cheap, largely available, ecologically friendly material with excellent and tunable

thermophysical properties for TES applications, particularly for packed-bed thermocline storage systems, which have received considerable attention as a promising new TES configuration [15–18] using different combinations of heat transfer fluids with or without TES materials as air with alumina [15,16] or steatite in [18], Hitec molten salt in [19] and thermal oil with pebble in [20].

TES is highly topical due to its great potential for increasing the efficiency and to level off daily demand and supply of Concentrated solar power (CSP) plants [21–23]. The simple concept that excess heat present at CSP plants during sunlight hours can be stored and transformed into electricity during night time or cloudy periods, raises challenging ensemble of requirements for the properties of TES materials: thermal conductivity, high heat capacity and density, excellent stability, compatibility with HTF in the operation temperature range, non-flammability, non-toxicity, availability and low cost. The latter in particular is becoming a crucial parameter for reaching high competitiveness in the field of renewable energy [23].

Apart from thermo-chemical energy storage systems, there are two main methods for storing heat [21,22]: (i) by means of a heating-cooling cycle which takes advantage of materials with high heat capacity – sensible heat storage; and (ii) by taking advantage of the enthalpy of reversible phase transitions of different nature, which are associated with additional heat supply to the material upon heating and its release upon cooling – latent heat storage. Today, materials with heat capacity in the range of 0.5–2.0 J/K g are considered acceptable

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for sensible TES.

Typically, thermal conductivity plays a major role in obtaining an efficient steep thermocline system. While higher values are beneficial during charging and discharging periods, lower values are preferential for maintaining a steep thermocline zone to avoid its deterring during idle periods. For these reasons, optimum value may sometimes be required for each specific packed-bed system [24].

The values of thermal conductivity are reported in the range of 0.3–100 W/K m [25–28] and whilst very high values are reported for expensive or rare materials, the thermal conductivity is rarely higher than 5 W/K m for low-cost materials [25–28].

In this paper, an evaluation of Magnetite for a new area of application – Thermal Energy Storage – is investigated taking advantage of its excellent thermophysical properties for sensible TES combined with exceptional ability to simply program its thermal conductivity in a wide range of values and, additionally, benefit from the latent heat related to its antiferromagnetic transition at high temperature. Considering the aforementioned advantages of natural Magnetite, it may be considered as a very promising candidate for TES applications, especially for packed-bed systems, in a wide temperature range (up to at least 1000 °C).

2. Methods

2.1. Material

Natural Magnetite used in this work was supplied by LKAB minerals company (Sweden). The raw material and samples treated in the furnace at 400, 800 or 1000 °C for 1–21 days under air atmosphere were investigated. The material is presented in pebbles of approximately 1 cm³. The names of the samples corresponding to the particular conditions of treatment are presented in Table 1. The raw Magnetite-p powder sample was obtained by grinding the raw Magnetite bulk material. The Magnetite 1000-p powder sample was obtained by 1000 °C treatment of raw Magnetite-p powder for 1 day. The size of the grains of the powder sample was in the order of tenth of microns, which was verified by SEM technique.

2.2. Characterization techniques and methodology

2.2.1. Inductively coupled plasma – optical emission spectroscopy (ICP-OES)

The chemical composition of the Magnetite was studied by ICP-OES with a Perkin Elmer Optima 2000 OV. For these measurements, fine powder of the sample was obtained and fused with 99.9% lithium metaborate in high purity graphite crucibles and later dissolved with diluted HNO₃ (trace metal grade nitric acid and ultrapure Milli-Q®

Table 1
Treatment conditions for different samples of Magnetite.

Sample name	Treatment time (days)	Treatment temperature (°C)	Form
Raw Magnetite	–	–	Bulk
Raw Magnetite-p	–	–	Powder
Magnetite 400	1	400	Bulk
Magnetite 800	1	800	Bulk
Magnetite 1000-p	1	1000	Powder
Magnetite 1000-1	1	1000	Bulk
Magnetite 1000-2	2	1000	Bulk
Magnetite 1000-7	7	1000	Bulk
Magnetite 1000-21	21	1000	Bulk

Table 2

Chemical composition of temperature treated Magnetite obtained by ICP technique.

Compound (%)							
Fe ₂ O ₃	SiO ₂	MgO	Al ₂ O ₃	K ₂ O	Na ₂ O	MnO	CaO
96.5	2.2	0.4	0.3	0.1	0.1	0.1	< D.L.

D.L. is detection limit.

water were used to prepare the dissolution). The solution obtained was directly analyzed by using the accepted standard practice reported in ref. [29], which includes high-temperature treatment. The analysis was carried out for the major and trace elements (Al, Ca, Fe, Mg, Mn, Si, Na and K).

2.2.2. Scanning electron microscopy (SEM)

The samples were imaged by means of a Quanta 200 FEG scanning electron microscope operated in high vacuum mode at 30 kV and with a back scattered electron detector (BSED). In addition, energy-dispersive X-ray spectroscopy (EDX) analyses were carried out in order to obtain chemical composition maps of the different observed samples zones.

2.2.3. X-ray power diffraction (XRD)

X-ray powder diffraction technique was used for the structural analysis by means of a Bruker D8 Advance X-ray diffractometer equipped with a LYNXEYE detector using CuK α radiation ($\lambda=1.5418$ Å) and θ - 2θ geometry. Data were collected at room temperature between 25° and 80° in 2θ with a step size of 0.02° and counting time of 8 s per step. The EVA program was used to determine the phase composition of the material.

2.2.4. Densitometry

Bulk and skeletal densities were measured using cubical samples of around 10 mm side length. A high-precision balance and caliber were used to calculate the apparent density while the helium pycnometer AccuPyc II 1340 from Micromeritics was used to determine the skeletal density.

2.2.5. Differential scanning calorimetry (DSC)

The heat capacity (C_p) of the investigated materials was measured in the 25–500 °C temperature range by the DSC technique (Thermal Analysis Q2000 model) using the modulated heating ramp dynamic method [30], which allows a direct measurement of the C_p . The modulation amplitude and period have been fixed to ± 1 K and 120 s, respectively. The selected continuous heating rate was 2 K/min. The instrument was previously calibrated using sapphire as standard material. Around 25 mg of bulk samples, previously polished to ensure a good thermal contact, were placed inside high-conductive aluminum holder sample which then were hermetically closed. The experimental error of this technique is below 3%.

The enthalpy of phase transition was measured in the 25–710 °C temperature range with the same apparatus using the standard DSC approach.

2.2.6. Laser Flash Apparatus (LFA)

The thermal conductivity (λ) values were obtained in indirect way from the thermal diffusivity (α), density (ρ) and heat capacity (C_p), according to the following equation: $\lambda=\alpha\cdot\rho\cdot C_p$.

The thermal diffusivity of the studied materials was obtained by using the Laser Flash Apparatus (LFA) method [31], using a LFA-457 from NETZSCH. Square samples with a side length of 10 mm and a thickness of 2 mm were used. In order to minimize the experimental error, a graphite film prime was added over the samples and the reference surfaces.

LFA technique was also used for indirect C_p measurement of

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