

Experimental Characterization of Magnetite Under Thermal Cycling For Thermocline Energy Storage

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Abstract—the present paper investigates the effect of thermal cycling on magnetite thermo physical characteristics particularly density, heat capacity, thermal diffusivity and thermal conductivity. The purpose was to evaluate the stability of the TESM and to emphasize its suitability for thermocline energy storage for medium temperature. Cycled magnetite was characterized and then compared to raw magnetite. Obtained results have shown that magnetite is a stable filler material, convenient for thermal energy storage. More important, thermal cycling impacts positively the studied material, it permits to get rid for the impurities present in the raw material. Furthermore, thermophysical properties of magnetite increase by applying thermal cycling.

Keywords—magnetite; thermocline energy storage; thermal energy storage material; characterization; thermal cycling.

I. INTRODUCTION

Thermal energy storage systems (TES), presented as a key factor to improve CSP efficiency and deal with problem of solar energy intermittency [1, 2], are commonly classified into three principal categories: sensible heat storage (SHS) systems, latent heat storage (LHS) systems and thermochemical heat storage systems [3, 4, and 5].

Thermocline packed-bed single tank concept fall into the category of sensible heat storage systems, and seems to draw attention recently thanks to its cost effectiveness [6, 7, 8]. Regarding this emergent concept, HTF and TESM play an important role, in this context and to the present time, quartzite [9, 10, 11 and 12] and concrete [12, 13, 14 and 15] have been presented as the most convenient filler material for thermal energy storage. These TESM; by fulfilling the criteria addressed by the international energy agency [16] such as: low commercial cost, large thermal capacity and stability up to 1000°C, etc; have been widely used in the most CSP facilities emerged to date. These materials were distinguished for their thermophysical properties, their mechanical stability and also by being compatible with the most heat transfer fluids commonly used in the CSP applications.

However, magnetite has been lately attracted researchers' attention and thereby; it has been presented as a promising

filler material for thermocline energy storage i.e. the experimental characterization of magnetite up to 1000°C was performed by Grosu et al. [17, 18]. The most relevant thermophysical, mechanical and structural and chemical properties was determined and discussed under static experimental conditions. Through this work, the characterization is extended to the case of thermal cycling, where the chemical and structural composition as well as the thermophysical properties including: density, thermal heat capacity, thermal diffusivity, and thermal conductivity are analyzed under the effect of repetitive thermal cycles.

The considered material is Magnetite. It was supplied by LKAB minerals company (Sweden) and was characterized using two essentials samples geometries. The used samples are illustrated in Fig. 1. The first geometry was a pebble with a volume of approximately 8 cm³. Before thermal cycling the pebbles were cut in half in order to facilitate further the SEM-EDX analysis. The second one was a square sample of approximately 1 cm³, prepared by cutting for further LFA analysis. For the XRD analysis pebbles were crushed to obtain fine powder. Thermal cycling was realized using resistant "Nabetherm" furnace under air atmosphere. Overall, 101 cycles were applied to magnetite samples in the 300°C - 700°C temperature range in order to emphasize the effect of thermal cycling once used in thermocline energy storage process. Numerous techniques were used to ensure this characterization.



Fig. 1. Visual aspect of samples used for magnetite characterization

II. EXPERIMENTAL CHARACTERIZATION OF MAGNETITE UNDER THERMAL CYCLING

The characterization of magnetite under cycling was made based on numerous techniques including SEM, XRD, DSC, etc. Thereafter, the used techniques are presented as well as their specifications.

A. Scanning Electron Microscopy (SEM)

This technique makes it possible to examine the microstructural and morphology of the given sample. In this study, polished half spherical sample of the studied materials are imaged by means of a Quanta 200 FEG SEM, operated in high vacuum mode at 30 kV and with a BSE detector (BSED). More than this, EDX analyses are carried out in order to obtain chemical compositional maps of the different observed sample zones. [18, 20]

B. X-ray powder Diffraction (XRD)

This technique was useful to analyze any structural modifications of magnetite after cycling. Bruker D8 Advance X-ray diffractometer equipped with a LYNXEYE detector using CuK α radiation ($\lambda=1.5418$ Å) and θ -2 θ geometry was applied.

Data were collected at room temperature between 25° and 80° in 2 θ with a step size of 0.02°C and counting time of 8 s per step. The EVA program was used to determine the phase composition of the material [21, 22].

C. Densitometry

Density of the studied material was determined by means of Archimed method with water. Detailed protocol is available in reference. [17, 19, 21, 23]

D. Differential Scanning Calorimetry(DSC)

DSC is remains a compelling technique used in thermal characterization [24, 25]. It permits the direct measurement of thermal capacity (Cp) [18]. Measurements of cycled magnetite were taken applying 10 C.min⁻¹ dynamic heating rate between 40°C and 500°C under nitrogen atmosphere with a flow of 50 ml/min.

The study was performed under controlled room conditions by using aluminum crucibles containing 70 mg of cycled magnetite; experiments were carried out by using DSC Q2500 device.

E. Laser Flash Apparatus (LFA)

Thermal diffusivity of cycled magnetite was measured from 30°C to 800°C under argon atmosphere with a flow of 50ml/min. The square pieces described above were used for this technique.

The samples were coated with graphite to ensure irradiation absorbance and enhance emissivity. To conduct this test holders samples (10×10×2.95mm) were used in a laser flash apparatus (LFA457 NanoFlash from Netzsch). Thermal conductivity was obtained using the following equation $\lambda=\alpha\rho C_p$. [21, 22], where ρ is density.

III. CYCLED MAGNETITE CHARACTERIZATION RESULTS

This section concerns results obtained through cycled magnetite characterization. It focuses on geochemical composition, thermal and thermophysical properties of cycled magnetite. A comparison between raw magnetite and cycled magnetite is hence established.

A. Geochemical composition:

Through this analysis the filler material stability is examined. Raw magnetite and cycled magnetite have similar chemical composition, which was previously presented [18]. Both samples are mostly formed by Fe with some inclusions of Mg, Al, C and Si, which can be seen from SEM-EDX analysis presented on Fig. 2.

The sample after cycling does not demonstrate any significant morphological differences, apart from rare localized formation of dendritic structures which signifies the formation of Hematite phase.

The XRD analysis (Fig. 3.) shows the presence of crystalline phases of hematite Fe₂O₃, magnetite Fe₃O₄ and siderite CFeO₃. No significant differences were observed after the cycling suggesting stability of the material.

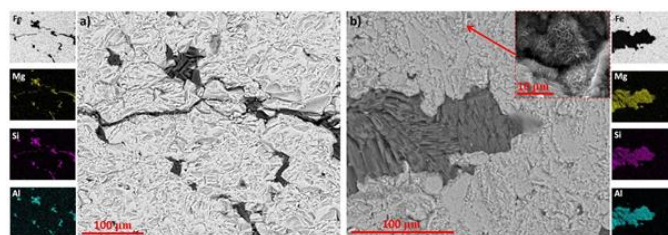


Fig. 2. SEM-EDX analysis of a) raw Magnetite and b) cycled Magnetite

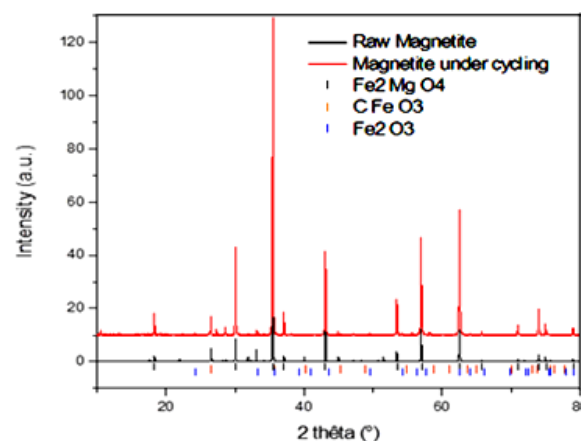


Fig. 3. Experimental X-ray powder diffraction profile of raw magnetite and cycled magnetite

B. Density

TABLE I summarizes the principal density measurement results from dry mass, suspended mass and saturated mass of samples. It is found that the bulk density of raw and cycled magnetite is 4962kg/m³ and 5081kg/m³, respectively.

As can be deduced, density of magnetite has increased by 2.4 % after thermal cycling.

Such a slight density variation is within the uncertainty brought of some inhomogeneity of natural material and perhaps some sample oxidation from Magnetite Fe_3O_4 to Hematite $\alpha\text{-Fe}_2\text{O}_3$. Additionally, one should not exclude the possibility of decomposition of some organic impurities in raw natural material after the cycling.

TABLE I DENSITY MEASUREMENT RESULT FOR DRY MASS, SUSPENDED MASS AND SATURATED MASS OF MAGNETITE

Temperature (°C)	21,9
Average dry mass (g)	17,05
Average suspended mass (g)	13,595
Average saturated mass (g)	16,95
Average bulk density raw magnetite (kg/m ³)	4962
Average bulk density cycled magnetite (kg/m ³)	5081
Theoretical density cycled magnetite (kg/m ³)	4945

C. Capacity

Capacity (C_p) remains one of the most relevant thermophysical properties for a TESM. Raw and cycled magnetite heat capacity variation for different temperatures between 50°C and 500°C are respectively plotted in Fig. 4. As can be seen, specific heat for raw magnetite depend significantly on the temperature and varies according to the range of temperature considered here from 0.64 J/g.K to 1.01 J/g.K with an correspondent average value of 0.825 J/g.K. Whereas, for cycled magnetite, it ranges from 0.74 J/g.K to 1.03 J/g.K with an correspondent average of 0.885 J/g.K. We can firstly deduce a significant difference between raw magnetite and cycled magnetite; cycled magnetite present higher values than raw magnetite.

Moreover, capacity has a notable dependence to temperature; as can be confirmed by the literature [20] and demonstrated trough DSC results, this property increases with the temperature. Taking into account the structural and elemental analysis presented above, the difference between the heat capacity of the raw and the cycled magnetite can be devoted to the decomposition of some impurities, which was demonstrated before [18].

This result is very important because it shows that according to the heat capacity, the magnetite performance for thermocline storage applications can be increased over the time and then, the aging effect after several cycles of use cannot make degrading this thermal storage property [18].

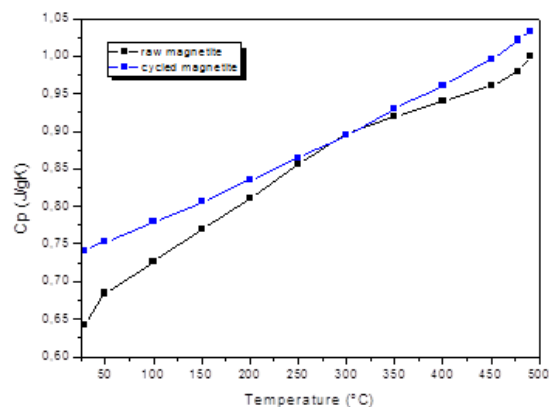


Fig. 4. Measured Heat capacity of raw and cycled magnetite versus temperature

D. Thermal diffusivity:

Fig. 5. presents the thermal diffusivity versus temperature ranged between 50°C and 550°C for both raw and cycled magnetite. The obtained diffusivity is varying between 1.40 mm²/s at room temperature and 0.30 mm²/s at 550°C. As can be seen, for the magnetite, no significant difference can be detected between magnetite before and after cycling, suggesting that Magnetite to Hematite transformation was limited upon thermal cycling. On the other hand, thermal diffusivity decreases with the increase of temperature. This tendency is in a good agreement with literature for other TESM [26].

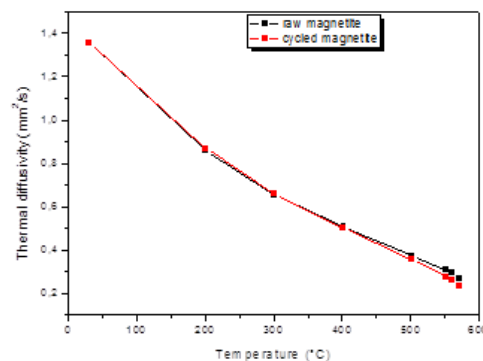


Fig. 5. Measured thermal diffusivity of raw magnetite and cycled magnetite

E. Thermal conductivity:

Thermal conductivity is defined as the ability of the material to conduct heat. In this study thermal conductivity is calculated indirectly based on thermal diffusivity and heat capacity measurement using the relation $\lambda = \alpha \rho C_p$.

Results of thermal conductivity for raw magnetite and cycled magnetite are provided in Fig. 6. The value for raw magnetite is ranged between 2.5 W/m°C and 4 W/m°C with an average value of 3.25 W/m°C. Whereas, it varies between 2 W/m°C and 7 W/m°C for cycled magnetite with an average value of 4.5 W/m°C. As we can observe, thermal conductivity has the same trend as thermal diffusivity. More important,

cycled magnetite conductivity is significantly higher than raw magnetite for temperatures lower than 350°C, for higher temperatures, no significant difference can be observed.

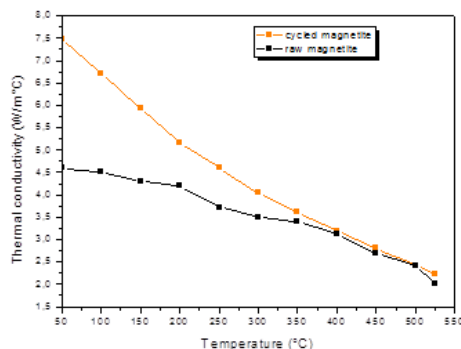


Fig. 6. Measured thermal diffusivity of raw magnetite and cycled magnetite

Hence, we can deduce that applying thermal cycling to raw magnetite leads to a noticeable enhancement of this parameter. It can be explained by magnetite oxidation to hematite, which has no significant effect on the heat capacity, but rather pronounced effect on the thermal conductivity. Particularly, the predominance of hematite which has a high thermal conductivity increases the thermal conductivity of the cycled magnetite [18]. This increase in thermal conductivity can be very profitable in terms of improving heat exchange inside the TESM particle to obtain a homogeneous particle temperature and then to improve the heat exchange between the HTF and the TESM.

IV. CONCLUSION

Through this paper, magnetite under cycling, as a new thermal energy storage material candidate, has been subject to an experimental characterization. This characterization was addressed in the frame of SIROCCO project and has involved: characterization of cycled magnetite, cycling effect on magnetite properties and thermal and thermophysical characteristics of the TESM.

After 101 thermal cycles, an experimental characterization of magnetite was performed in terms of suitability for thermocline energy storage and cycled magnetite was compared to raw magnetite. Hence, thermal and thermophysical properties mainly density, heat capacity and conductivity of the TESM have been discussed.

From the obtained results for the TESM, the following conclusions can be extracted:

- Magnetite demonstrates an excellent thermo-physical properties, thereby, it can be considered as a beneficial TESM for thermocline energy storage;
- Thermal cycling has a positive impact on magnetite characteristics, for medium temperature range of thermocline energy storage i.e. it allows to get rid from impurities present in the natural rock and also permits to enhance its properties.

Nevertheless, it is important to bear in mind that this material was supplied by 'LKAB Minerals Company, Sweden' and that other suppliers are available such as: 'Martin and Robson magnetite, South Africa', 'Panjiva, India', etc. which may slightly affect the obtained results.

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