CHARACTERIZATION OF MAGNESIUM SULFATE AS THERMOCHEMICAL MATERIALS FOR SEASONAL HEAT STORAGE

Z. He, **C. C. M. Rindt**, **A. A. van Steenhoven**
Department of Mechanical Engineering, Eindhoven University of Technology (TU/e), 5600 MB Eindhoven, the Netherlands
V. M. van Essen, **R. Schuitema**, **W. G. J. van Helden**
Energy in the Built Environment Unit, Energy research Center of the Netherlands (ECN), 1755 ZG Petten, the Netherlands

Abstract

Heating consumption could be divided into industrial and domestic demands. Solar collectors could produce durable heat in a domestic environment, but most effective in summer and not in winter. A new manner of seasonal storage of solar energy is by means of chemical reactions of thermochemical materials (TCMs), where energy demand in one direction and energy yielding in the reverse direction. The materials in an effective heat storage system must be of fully reversible reactions, high energy density and good durability.

In the present work, magnesium sulfate hepta hydrate ($MgSO_4 \cdot 7H_2O$) with different particle sizes and porosities were characterized using scanning electron microscope (SEM), simultaneous thermal analysis (STA) and cycling behavior test (CBT) to investigate their microstructures and dehydration and rehydration processes. From the obtained results, the effects of particle size and porosity on charging and discharging processes and cycling behavior of $MgSO_4$ are analyzed. The optimal conditions for $MgSO_4$ as seasonal storage materials are discussed.

Introduction

Today the spotlight in the world is on the increasing demand on sustainable and renewable energy sources. Solar energy is one of the most important sources, which could provide durable heat for various applications. However, it is most effective in summer and not in winter when there is a high demand. To accommodate the difference in time between energy production and energy demand, solar heat storage is necessary.

The availability of efficient heat storage technology is one of the key factors for successful usage of sustainable and renewable energies. There are three mainly available ways for solar energy storage: sensible heat, phase change reaction, and thermochemical reaction. Storage based on thermochemical reactions has the highest storage capacity among all the storage media [1]. The basic reaction process for solar energy storage using thermochemical reactions is:

$$\text{C (solid)} + \text{Q (heat)} \Leftrightarrow \text{A (fluid/gas)} + \text{B (solid)}$$

This reaction is considered in thermodynamic equilibrium, where there is no net heat exchange between the reacting substances. The equilibrium temperature is termed as turnover temperature. During summer, the solid C decomposes into the fluid or gas A and the solid B by adding solar heat at a reaction temperature that is higher than the turnover temperature. Materials A and B are stored separately until winter. In winter, A and B are mixed to start the reverse reaction at a temperature that is lower than the turnover temperature, and the heat is released during the reaction.

Due to its higher energy storage density and realization potential, magnesium sulfate is one of the most promising thermochemical materials (TCMs) for solar energy storage [2]. The objectives of the present work are to investigate the effects of particle size and porosity on thermochemical properties of magnesium sulfate hepta hydrate ($MgSO_4 \cdot 7H_2O$) and to give optimal materials conditions of $MgSO_4$ used for solar heat storage.

Experimental Procedure

The raw materials are the magnesium sulfate hepta hydrate powders (VWR International B. V.) with the purity of 99.5%. A Fritsch vibratory shaker and the sievers of 20, 38, 106, 200 and 500 μm were used to obtain the powders with different particle size ranges. To achieve the powder compacts with different porosities, a self-made metallic die was used to press the powders of 106-200 μm into compacts. The porosity was controlled by adding different mass into the die. The calculation of the porosity is shown in ref. 3. The microstructural observation on the powders was made using a JEOL JSM-6330F filed emission scanning electron microscope (SEM). To investigate the mass and heat changes of $MgSO_4$ during dehydration and rehydration, a Netzsch 409 SC simultaneous thermal analysis (STA) machine was employed. 10 mg powders or compacts were used for each run. The materials were initially held at room temperature for 15 minutes and heated to 300 ^{0}C with the heating rate of 1 K/min and held isothermally for 15 minutes, and then cooled down to room temperature with the cooling rate of 5 K/min. Finally they were kept at room temperature for 20 hours. The nominal relative humidity was 40%. 15 g powders were used for the cycling behavior test (CBT). The dehydration was made to heat the materials to 150 ^{0}C for 4 hours in an oven. The rehydration was made to keep the materials at room temperature for 20 hours on the laboratory environment. The processes were repeated to 3 times.

Results and Discussion

After being sieved, the powders with different particle size ranges were obtained. Figure 1 shows the SEM images of the classified powders.

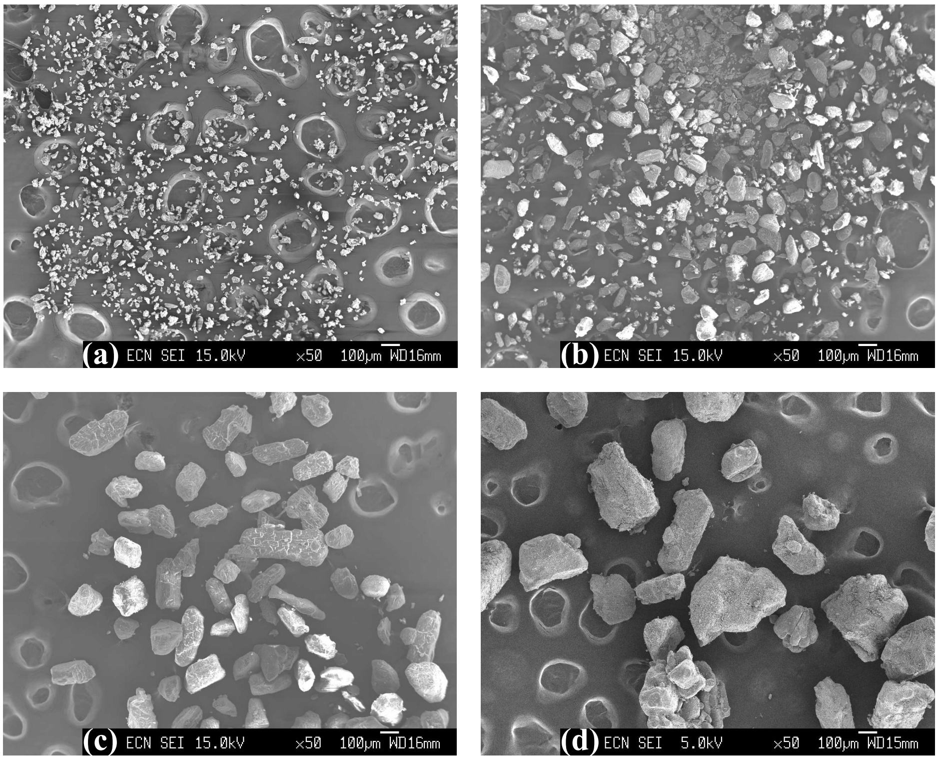

Figure 1 SEM images of the powders with different particle sizes [(a) 20-38 μm (b) 38-106 μm (c) 106-200 μm (d) 200-500 μm]

The STA results of the powers with different particle sizes and the compacts with different porosities are shown in Figure 2. Based on the mass change and heat change of the materials, three reactions occurred during dehydration: from heptahydrate to hexahydrate at 40 ^{0}C, from hexahydrate to monohydrate at 70 ^{0}C, and from monohydrate to anhydrate at 270 ^{0}C. At room temperature, the anhydrate took up the water molecular during rehydration and converted to hexahydrate finally. The reactant and the products occurred during dehydration and rehydration, heptahydrate, hexahydrate, monohydrate, and anhydrate, are believed to be the only members that exist on earth as thermodynamically stable minerals [4]. For the powders with different particle sizes, the effect of particle size is mainly displayed on the rehydration process. Compared to larger particles of 200-500 µm, the smaller particles of 38-20 µm obtained more water molecular during rehydration, which could be attributed to higher reactive activity of the smaller particles. On the other hand, shorter diffusion path due to smaller particles could improve the reaction rate of the rehydration processes [5]. With respect to Figure 2(c), the water uptaking of the porous compacts initially is slower than that of powders, but later on the uptaken amount increased fast for the porous compacts and finally they achieved more water than the powders. Compared to other porosity, the porous compact with 20% porosity obtained more water molecular during rehydration, which indicates an appropriate microstructure.

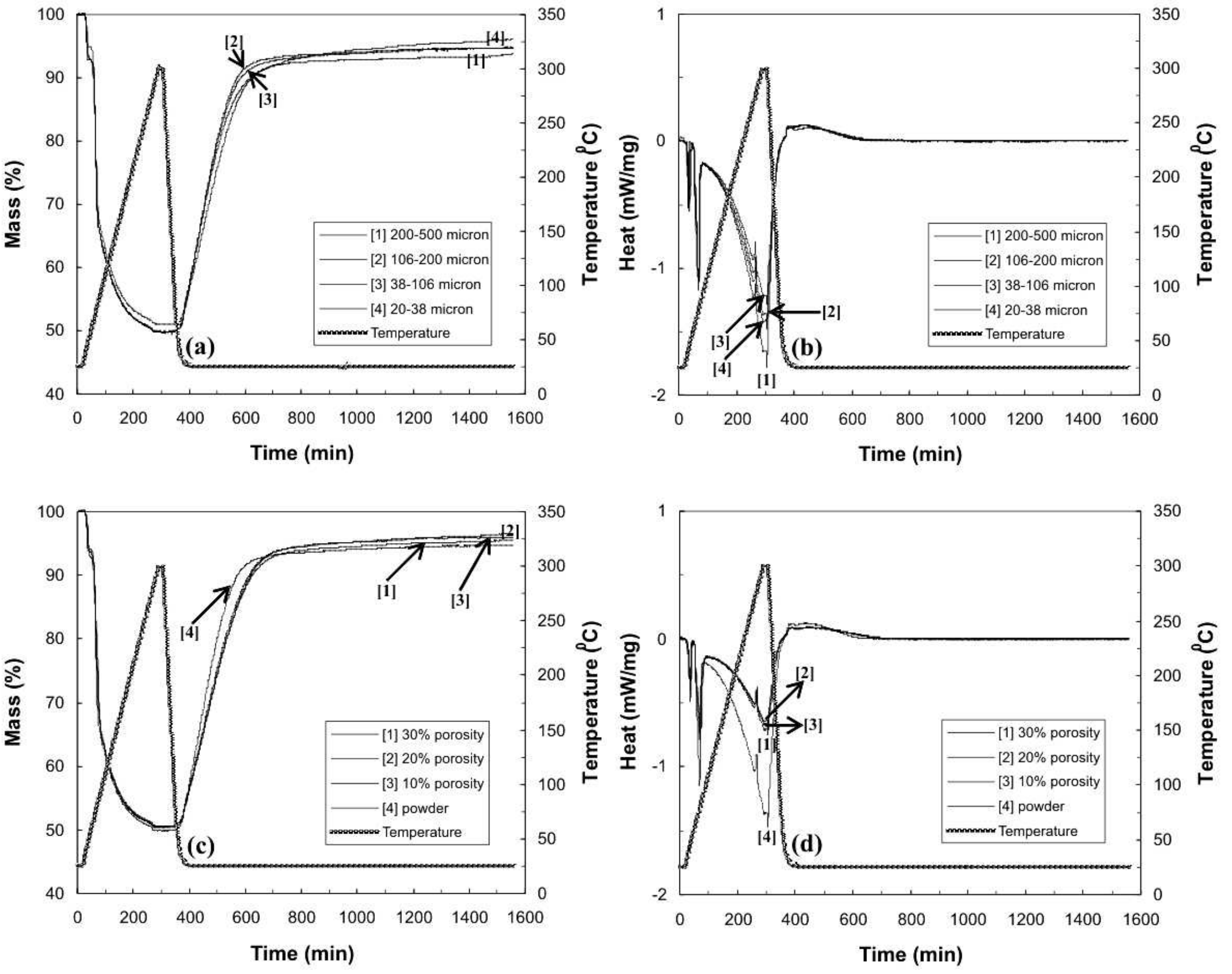

Figure 2 STA results of the powders with different particle sizes [(a) mass change (b) heat change] and the compacts with different porosities [(c) mass change (d) heat change]

Figure 3 shows the CBT results of the powders with different particle sizes. With respect to Figure 3(a), it is noted that the mass decreased after dehydration and the mass increased to some extend after rehydration for one cycle. The decreased mass after dehydration kept constant for each run, which indicates a completed lost of water after the powders were isothermally held for 4 hours at 150 ^{0}C. After rehydration, the actual increased mass is strongly dependent on the humidity of the environment. In general, higher humidity leads to higher mass. To investigate the effect of particle size on the cycling behavior more clearly, the mass change between the current and the last steps was taken into account, as shown in Figure 3(b). The mass change between the current and the last steps increased as particle size reduced, which indicates more thorough reactions of dehydration and rehydration for smaller particles.

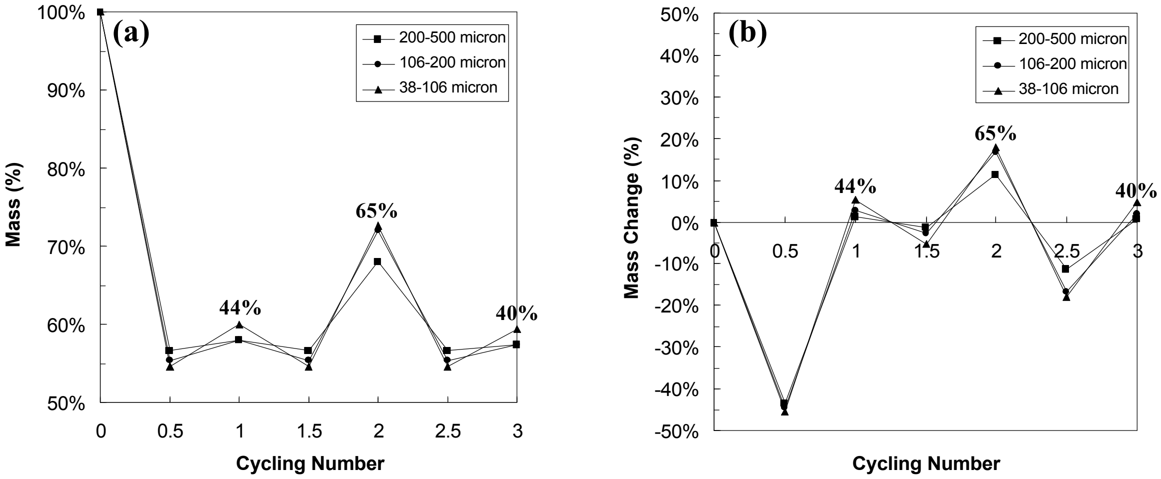

Figure 3 CBT results of the powders with different particle sizes [(a) mass compared to the initial powders after one step (b) mass change between the current and the last steps]

Based on the present results, the particle size and the porosity do have the effects on thermochemical properties of $MgSO_4$. However, it should be noted that these effects are not so remarkable, which might be attributed to the experimental scale of the sample sizes, which is not great.

Conclusions

Three reactions occurred during dehydration: from heptahydrate to hexahydrate at 40 ^{0}C, from hexahydrate to monohydrate at 70 ^{0}C, and from monohydrate to anhydrate at 270 ^{0}C. At room temperature, the anhydrate took up the water molecular during rehydration and converted to hexahydrate finally.

The actual increased mass after dehydration was strongly dependent on the humidity. In general, higher humidity led to higher mass.

The powders with smaller particle size showed more thorough reactions of dehydration and rehydration.

Compared to other porosity, the porous compact with 20% porosity obtained more water molecular during rehydration.

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