Characterization of desert sand for its feasible use as thermal energy storage medium

Miguel Diago, Alberto Crespo Iniesta, Thomas Delclos, Tariq Shamim, Nicolas Calvet*

Institute Center for Energy (iEnergy), Department of Mechanical and Materials Engineering, Masdar Institute of Science and Technology, Masdar City, P.O. Box 54224, Abu Dhabi, United Arab Emirates.

Abstract

Desert sand samples were thermally analyzed and their suitability for use as sensible heat thermal energy storage (TES) media is evaluated. Mass loss during heating was monitored with a thermal gravimetric analyzer (TGA) linked to a Fourier transform infrared spectrometer (FTIR). This technique showed that the relative mass loss rate of all the samples is comparable and that carbon dioxide is produced during their degradation. The calcite content of each sample is estimated assuming full calcination during the process. Additionally, larger fractions of the samples were heated in a high temperature electric furnace. This experiment showed that some samples tend to agglomerate at high temperatures, thus rendering their use as heat transfer fluid media questionable. Furthermore, color change from lighter tones to whiter tones is observed. This effect may impact the radiative properties of the samples, especially their solar absorptivity values. Finally, the average heat capacity in the 150-1100 °C temperature range was measured with a differential scanning calorimeter. The average heat capacity for all the samples was 926.1 J kg⁻¹ K⁻¹.

© 2015 The Authors. Published by Elsevier Ltd. This is an open access article under the CC BY-NC-ND license (http://creativecommons.org/licenses/by-nc-nd/4.0/).

Peer-review under responsibility of Applied Energy Innovation Institute

Keywords: Thermal energy storage; Concentrated solar power; Sand; Thermal stability

1. Introduction

Efforts are being made to increase the share of renewable energy use in the energy portfolio [1]. In line with the strategies laid out by other nations, the government of the United Arab Emirates (UAE) has declared the objective of meeting at least 7% of its energy needs with renewable energy by 2020 [2]. Among various choices available, solar energy is a very important option in this region [3].

For solar energy, one of the challenges that needs to be addressed is the hourly mismatch between production and demand. TES solutions have already been proposed to obtain a levelled power production for longer duration [4]. Among them, systems based on sensible heat storage on solid particles that act as solar collectors and heat storage media have been presented in the past [5]–[8]. Usually the material of choice is restricted to silicon carbide or sintered bauxite particles which can be repeatedly heated up to 1000-1200 °C without significant degradation [9].

The following study assesses the possibility of substituting that media with raw sand from the desert of the UAE, which is cheaper [10] and widely available. Mass loss due to calcination, agglomeration phenomena and heat capacities on six desert sand samples are investigated. This is continuation of the work presented previously [11], [12].
2. Material and methods

2.1. Material selection

Six sand samples from selected locations in the desert of the UAE were studied. The samples were collected in the Abu Dhabi and Dubai emirates. At a first glance, the most striking difference between them is the color, which varies from light cream to red tones. Figure 1 presents a collection point map.

![Figure 1. Sand samples collection sites. Locations indicated with (×).](image)

2.2. Method of characterization

All the sand samples were subjected to a thermal gravimetric and Fourier-transform infrared spectrum study (respectively abbreviated as TG and FTIR). Additionally, an electric furnace was used to study agglomeration effects on the samples and a differential scanning calorimeter was used to measure the heat capacity of the sand samples after the heat treatment in the furnace.

2.2.1. TG analysis

The TG analysis was performed on a Netzsch TG 449 F3 Jupiter setup using alumina crucibles to hold the sample. The data obtained from the TG analysis was post-processed on Netzsch Proteus 5.2.1 software.

All the TG analyses were done under a protective atmosphere of nitrogen set at a constant flow rate of 20 mL/min for the full length of each measurement. For all cases, the temperature program was set to hold 1100 °C for one hour after heating at a constant rate of 10 °C/min.

2.2.2. FT-IR analysis

The decomposition gases generated during the heating process were simultaneously analyzed on a coupled Bruker Optics Vertex 80V spectrometer. The FTIR results were managed under the OPUS 7.0 suite.

The decomposition gases of each sample were submitted through a heated duct at 150 °C to the infrared spectrometer. A fast Fourier analysis was performed in the wavenumber range 650-4500 cm\(^{-1}\) and the absorbance values stored as a function of time.

2.2.3. Agglomeration analysis

All the samples were heated up to 900 °C in an electrical furnace 310P from Nabertherm. The controller was set up to reach the final temperature in 30 minutes and to hold it for one hour.

The level of agglomeration of each sample was assessed by laying the sand on a flat surface and observing the presence of conglomerates. Pictures were taken immediately after laying the sample on a clear surface.

2.2.4. Heat capacity measurement

The heat capacity of the sand samples after their heat treatment in the electric furnace was measured with a DSC device (Netzsch DSC 404 F1). The samples were heated up to 1100 °C at a constant heating rate of 20 °C/min under a protective atmosphere of nitrogen flowing at 20 mL/min. Finally, the heat capacity of each sample was calculated through the ratio method using a disc of sapphire as a reference [13], [14].
3. Experimental results

3.1. TG analysis

The experimental data was reported by the device as the temporal mass change of the sample during the duration of the experiment. Additionally, and in parallel, the exhaust gases from the sample were screened using infrared spectroscopy.

A significant variation in mass was observed in all the experiments. Figure 2 is a representation of the evolution of the relative mass change to the initial mass as a function of the temperature. The value for the initial mass was assumed to be the mass of the sample at 150 °C in order to discard possible moisture remaining in the sand.

![Figure 2. Evolution of calcinated mass in each sand sample](image)

The decomposition pattern of all the samples is comparable. This suggests that the elements that decompose in each sample are similar in nature. Moreover, the different relative amounts of sample that is decomposed can be accounted to the variable mass fraction of the element that decomposes in the range of temperatures under study.

All the samples were subjected to an identical thermal cycle for a second time, although no further mass loss was observed. This indicates that all the samples are thermally stable up to 1100 °C and that, unless agglomeration occurs as shown below, they can be potentially used as TES media.

3.2. FT-IR analysis

The spectroscopic infrared analysis of all the samples is found to be comparable. In these spectra, only the peaks corresponding to the vibration modes of carbon dioxide (CO₂) are observable [15].

3.3. Bulk heat treatment study

3.3.1. Agglomeration

Some samples were found to agglomerate after being heated to high temperatures in the electrical furnace. Conglomerates of varying size were clearly observable when some samples were laid on a flat surface after the heat treatment. Figure 3 displays an example of agglomeration on sample 1.

Agglomeration was noticeable on all samples with the exception of samples 2 and 6. In these samples, only a change of color was observed. The flowability (i.e., the ease with which they were extracted from the furnace crucible) was comparable to the existing before the heating treatment.

For all cases, it was found that the agglomeration was easily undone with gentle vibration.

![Figure 3. Agglomeration on sample 1 after treatment at 900 °C](image)
3.3.2. Color change

The color of all the samples was found to shift to whiter tones after the heat treatment. Sample 2 was found to suffer the greatest change. Figure 4 compares its color before and after the heat treatment.

![Figure 4. (a) Sample 2 before the heat treatment; (b) Sample 2 after the heat treatment.](image)

3.4. Heat capacity

The heat capacities from all the samples as read from the DSC are reported in Table 1 as average values between 150 °C and 1100 °C. Additionally, the evolution of the measured heat capacity for sample 3 is reproduced in Figure 5.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Average ( C_p ) (J kg(^{-1}) K(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>864.6</td>
</tr>
<tr>
<td>2</td>
<td>876.1</td>
</tr>
<tr>
<td>3</td>
<td>903.6</td>
</tr>
<tr>
<td>4</td>
<td>1017.2</td>
</tr>
<tr>
<td>5</td>
<td>878.3</td>
</tr>
<tr>
<td>6</td>
<td>1016.6</td>
</tr>
</tbody>
</table>

![Figure 5. Evolution of calculated heat capacity of sample 3 after heat treatment in the electrical furnace.](image)

The peak in the heat capacity that appears in Figure 5 the temperature of 573 °C corresponds to the solid phase transition in quartz from the \( \alpha \) to the \( \beta \) phase [16], [17].

4. Results discussion

4.1. Calcium carbonate content

The results of the TG analysis can be used to estimate the calcium carbonate content of all the samples. For this, it needs to be assumed that the CO\(_2\) detected by the FTIR instrument corresponds exclusively to the decomposition product of the calcination of the calcium carbonate present mainly as calcite. This assumption is in line with previous findings reported in the literature on the qualitative analysis of sand samples from the desert of the UAE [18]-[21].

The calcination reaction, following \( \text{CaCO}_3 (s) \rightarrow \text{CaO} (s) + \text{CO}_2 (g) \), is assumed to be complete and irreversible. The irreversibility assumption is supported by the removal of the carbon dioxide with a current of nitrogen from the reaction site as soon as it is released from the sample.

The approximated mass fraction of calcium carbonate in a sample can be directly estimated as a function of the mass change measured in the TG instrument. The calculation is shown in equation (1).
In equation (1), \( m_{\text{sample}} \) refers to the initial mass of the sample, \( \Delta m \) is the mass change measured by the instrument and \( M_{\text{CaO}} \) and \( M_{\text{CaCO}_3} \) are the molar weights of calcium oxide and calcium carbonate respectively. \( x_0^{\text{CaCO}_3} \) indicates the estimated initial mass fraction of calcium carbonate.

Table 2 shows the mass fraction estimations obtained with this method.

<table>
<thead>
<tr>
<th>Sample</th>
<th>( m_{\text{sample}} ) (mg)</th>
<th>( \Delta m ) (mg)</th>
<th>( \Delta m / m_{\text{sample}} )</th>
<th>( x_0^{\text{CaCO}_3} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>62.5</td>
<td>-15.79502</td>
<td>-25.3%</td>
<td>0.574</td>
</tr>
<tr>
<td>2</td>
<td>74.7</td>
<td>-20.81301</td>
<td>-27.9%</td>
<td>0.633</td>
</tr>
<tr>
<td>3</td>
<td>95.0</td>
<td>-13.75801</td>
<td>-14.5%</td>
<td>0.329</td>
</tr>
<tr>
<td>4</td>
<td>85.7</td>
<td>-15.05191</td>
<td>-17.6%</td>
<td>0.399</td>
</tr>
<tr>
<td>5</td>
<td>47.5</td>
<td>-11.27400</td>
<td>-23.7%</td>
<td>0.539</td>
</tr>
<tr>
<td>6</td>
<td>70.3</td>
<td>-11.02787</td>
<td>-15.7%</td>
<td>0.357</td>
</tr>
</tbody>
</table>

4.2. Agglomeration issues

Sand agglomeration at high temperatures is a problem that may affect the operation of the system. Conglomerates can block the flow of sand through the particle solar receiver, as was the case at times during the prototype trials [11]. Moreover, agglomeration is also a concern for sand storage, where conglomerates can also be formed at high temperature and potentially prevent the discharge of the storage tank.

Few references were found in literature about this issue. However, it appears that it can be explained by the formation of low melting point (500 – 700 °C) eutectics by the impurities present in the sand such as calcium, aluminum and magnesium [22].

4.3. Heat capacity

The sand samples tested in this work present a heat capacity similar to that found in silicon carbide (934.6 J kg\(^{-1}\) K\(^{-1}\) reported by Flamant et al. [23]) or the aluminosilicate proppants used in the falling particle solar receiver developed in Sandia Laboratories (up to 1084.1 J kg\(^{-1}\) K\(^{-1}\) as reported by Siegel et al. [24]).

These values are however lower than the heat capacity of the traditional molten salt known as solar salt (60 wt% NaNO\(_3\), 40 wt% KNO\(_3\)) reported in the order of 1550 J kg\(^{-1}\) K\(^{-1}\) [25].

5. Conclusion

Several sand samples from the eastern region of the desert of the UAE were thermally analyzed. Mass loss was observed in all of them after one cycle at high temperature, indicating decomposition of an element tentatively assumed to be calcite. The repetition of the thermal cycle did not lead to further mass loss, which means that all the sand samples are thermally stable up to 1100 °C after the first cycle.

Testing with larger batches of sand in a furnace at 900 °C indicated that some samples tend to form agglomerates. This is a concern for the design of a hot sand storage system or sand bed solar receivers, as this effect could disturb the flow of sand through different parts of the device. However, it was also found that these agglomerates are extremely weak and that gentle shaking successfully dissolves them.

The heat capacities of the heat-treated samples was then measured between 150 and 1100 °C and averaged. The results were in line with the heat capacities measured in other materials used for solar thermal energy storage.

Finally, color change in the sand samples was observed during the furnace testing. All samples became whiter in different degrees. This has possibly an effect on the radiative properties of the samples, especially on the solar absorbance, and will be studied in future work.

Acknowledgements

This work is part of the SANDSTOCK project ongoing at Masdar Institute of Science and Technology. This research is supported by the Government of Abu Dhabi to help fulfill the vision of the late President Sheikh Zayed bin Sultan Al Nahyan for sustainable development and empowerment of the UAE and humankind.
References