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Use of Natural Syrian Zeolitic Tuff in Solar Thermal Applications

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We focus our attention in this work, from experimental point of view, on the applicability of natural Syrian zeolitic tuff in storing thermal solar energy. Several samples of different zeolitic content were taken from different heights of the borehole. These samples were used in this study. It was found that, when the heating temperature is below 100°C, the effect of Syrian natural zeolitic tuff' storing energy is quite good. The obtained results clearly show that the tentative idea of utilizing natural zeolitic tuff to store solar heat energy is feasible. Zeolitic content and grain sizes are the main affecting factors. As the operating temperature of the conventional flat-plate solar collectors generally is below 100°C, the aforementioned conclusion has important significance.

Key words and phrases: zeolitic tuff, thermal energy, energy storage, long-term storage.

Introduction

Energy storage unit is one of the major components of any solar system. The dependence of the solar collector performance on temperature makes the whole system performance sensitive to temperature. The energy storage may be in the form of sensible heat of a liquid or solid medium as heat from fusion in chemical systems or as chemical energy in reversible chemical reaction. The choice of storage media depends on the nature of the process. For water heating, energy storage as sensible heat of stored water is logical while, if air heating collectors are used, storage in sensible or latent heat effects in particulate storage units is indicated.

The major characteristics of a thermal energy storage system are [1]: (a) its capacity per unit volume; (b) the temperature range over which it operates; (c) the means of addition or removal of heat and the temperature differences associated therewith; (d) temperature stratification in the storage unit; (e) the power requirements for addition or removal of heat; (f) the containers associated with the storage system; (g) the means of controlling thermal losses from the storage system; and (h) its cost. However, large-scale solar heating systems that supply energy to district heating systems require large-scale facilities to store summer energy for winter use. Bankston [2] provides a review of seasonal storage solar heating systems. A good candidate for long period energy storage could be materials that undergo a change of phase in a suitable temperature range and chemical reactions.

Materials that undergo a change of phase in a suitable temperature range could be useful for energy storage if several criteria can be satisfied. These criteria are:

1. The phase change must be accompanied by a high latent heat effect;
2. The phase change must be reversible over a very large number of cycles without serious degradation;
3. The phase change must occur with limited supercooling or superheating;
4. Means should be available to contain the material and transfer heat into it and out of it;
5. The cost of material and its containers must be reasonable.

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Glauber's salt ($Na_2SO_4.H_2O$) was the earliest phase change storage material to be studied experimentally for house heating applications [3]. After that a lot of phase change materials, such as $Fe(NO_3)_2.6H_2O$, $CaCl_2.MgCl_2.H_2O$, $AlSO_4.10H_2O$, $MgCl_2.6H_2O$ and $CrCl_2.6H_2O$ was treated experimentally.

An ideal thermochemical reaction for energy storage is an endothermic reaction in which the reaction products are easily separable and do not undergo further reactions. Thermal decomposition of metal oxides and hydroxides has been extensively studied for energy storage (see for example [4–6]). However, technical and economic questions, related to the practical applications of this kind of energy storage, are yet to be answered for all the possibilities of chemical energy storage.

Zeolite has extremely nonlinear adsorption isotherms to water. The feature of adsorbing and desorbing water makes zeolite a new type of material for storing solar energy and to be taken off from it. When zeolite is heated, water molecules in it escape, and heat energy is stored in it in the meantime. When water molecules are adsorbed again, the heat energy in zeolite is released. Therefore, we focus our attention in this work, from experimental point of view, on the applicability of natural Syrian zeolitic tuff in storing thermal solar energy.

1. Experimental arrangement

The investigated, in this work, samples have been prepared from grounded Syrian natural zeolitic tuff which contains mainly about 50% of zeolite of three types (analcime, phillipsite and chabazite). The mineral composition of the studied samples is given in the Table 1. The samples were ground using a planetary ball mill (Retsch PM400) for 20 minutes with the speed of 350 rpm. Then we sieved the powder using a group of sieves with meshes ranging from 20 microns to 2000 microns. We studied 10 fractions of powder in the range of 45–900 microns. The grain size distribution of each of these fractions was found to be ideal in comparison with that of the tuff. Fig. 1 shows the size distribution of the fraction between 45–90 microns.

Table 1

The mineral composition of the studied samples

Sample number	1	2	3	4	5	6	7	8	9	10
Calcite	9.33	11.93	9.73	10.77	13.23	2.40	7.60	6.60	6.40	6.47
Analcime	7.93	7.00	5.27	5.37	8.37	6.47	11.40	7.14	8.87	8.77
Philipsite	21.15	22.10	21.77	22.67	20.63	23.90	35.30	28.70	26.77	25.90
Chabazite	25.63	23.07	21.13	20.90	15.57	—	—	—	—	—
Olivine	20.03	22.33	19.20	26.63	23.00	8.77	10.31	9.93	8.83	10.03
Epidote	—	—	—	—	—	9.33	—	12.10	10.40	9.93
Clay	—	—	—	—	—	38.47	35.37	25.60	31.40	34.20
Amorphous phase	13.87	13.57	22.87	13.63	19.17	10.66	—	9.93	7.33	4.70

Each of the fractions was washed several times with deionized waters in order to get rid of potential soluble salts. We measured the conductivity of the washing water after each washing to monitor the presence of eventual soluble salt. We stopped washing when the conductivity became close to the conductivity of deionized water. The obtained result was verified on the example of non-fractioned sample, after the extraction of iron impurities magnetically and that of minimal size fraction (less than 45 microns). Then the powder was dried in an oven at 400°C for 4 hours.

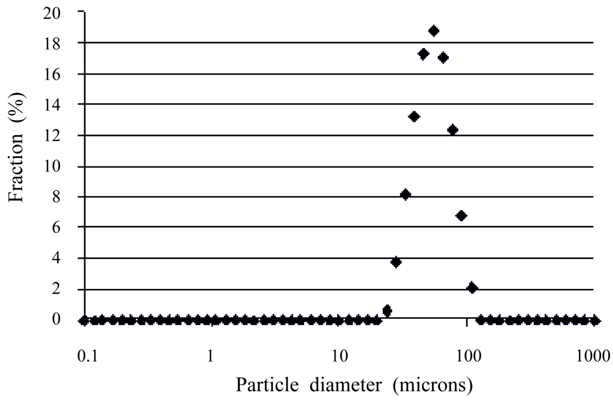

Figure 1. **The grain size distribution of particles of the first sample in the 45–90 microns fraction.**

2. Experimental procedure

The experimental procedure was chosen in order to quantify the results of desorbing and absorbing water as well as the results of heat absorption and release. The experimental process is as follows:

- A fixed quantity from each fraction (for studying the grain sizes effect) was taken;
- The fixed quantities were put into metal boxes which they were marked and weighted after weighing the metal boxes separately;
- The marked boxes were put into the thermostat to heat for one hour at each fixed temperature in the interval 40–200°C starting from 40°C and getting up rise to 150°C by a step of 5°C and after that directly to 200°C;
- The boxes were weighted after each heating step. This was done in order to measure the water loss of each box;
- After each heating step the samples were rapidly mixed with water of fixed quantity separately, until they are cooled down to the ambient temperature with stirring the mixture and measuring the temperature variation which is the difference of the temperature after the sample is mixed with water and ambient temperature changes. This was done in order to measure the energy release.

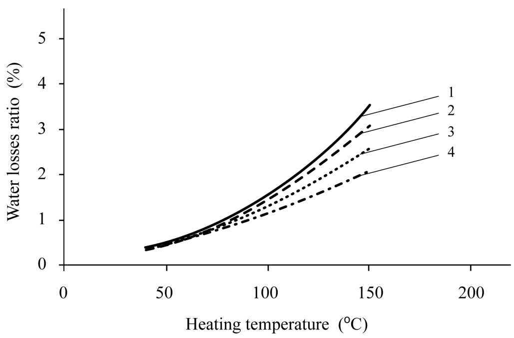

Figure 2. **The dependence of ratio of water losses mass (in %) to initial fraction mass on the heating temperature in the case of sample 1. Here it should be noted that: 1 stands for fraction of dimensions less than 20 microns, 2 stands for fraction of dimensions (125–180 microns), 3 stands for fraction of dimensions (355–500 microns) and 4 stands for fraction of dimensions (710–1000 microns).**

3. Experimental results and discussion

During the process of heating it was found (see Fig, 2 related to the sample 1) that:

– The water loss from each fraction increases with increasing the heating temperature. The water losses are sufficiently high when the temperature is more than 100°C. This means that the stored energy is also big and vice versa;
– At the same temperature, the water loss increases with decreasing the grain size of natural zeolitic tuff fraction. This can be easily explained by noting that the total specific surface area becomes larger when the particle's size becomes smaller;
– A similar picture is obtained when treating any of the studied samples mentioned in Table 1.

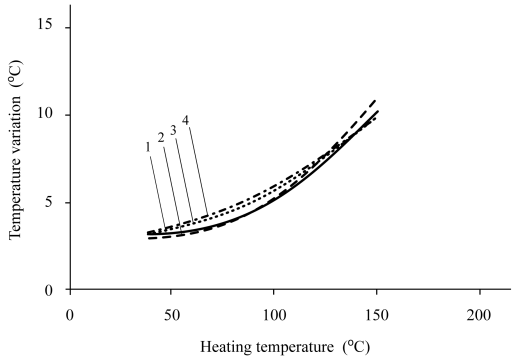

Figure 3. **The dependence of temperature variation on the heating temperature in the case of sample 1. Here it should be noted that 1 stands for fraction of dimensions less than 20 microns, 2 stands for fraction of dimensions (125–180 microns), 3 stands for fraction of dimensions (355–500 microns) and 4 stands for fraction of dimensions (710–1000 microns).**

On the other hand, during the process of heat release it was found (see Fig. 3 related to the sample 1) that the temperature variation of each fraction rises with increasing temperature. This means that the released energy increases with increasing heating temperature and vice versa. A similar result was obtained with other samples.

Conclusions

On the basis of obtained results we can conclude that:

– When the heating temperature is below 100°C, the effect of powder dimensions in storing energy is roughly the same. So we can recommend the Syrian natural zeolitic tuff as the storing materials below 100°C. As the operating temperature of the conventional flat-plate solar collectors generally is below 100°C we can mention that this aforementioned conclusion has important significance;
– When the heating temperature is in the range 100–200°C, the grain sizes of the zeolitic tuff have a clear influence. The small grain size of natural zeolitic tuff fraction has obvious advantages.

The tentative idea of utilizing natural zeolites to store solar heat energy is feasible.

Finally we mention here, that our attention will be paid, in the near future, to the forming method, and the storing energy device structure.

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Использование сирийских природных цеолических туф в солнечных тепловых применениях

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В данной работе с экспериментальной точки зрения рассматривается вопрос применимости сирийских природных цеолических туф в солнечных тепловых применениях. Для исследования были взяты несколько образцов цеолических туф с разных высот пробуренной скважины. Было обнаружено, что при температуре ниже 100°C сирийские цеолические туфы обладают хорошей способностью запасать тепловую энергию. Полученные результаты позволяют сделают вывод о возможности использования природных цеолитов для запасания тепловой энергии. Основными факторами, влияющими на способность цеолитов запасать энергию, являются их состав и размеры зёрен. Поскольку в обычных плоских солнечных коллекторах температура обычно не достигает 100°C, полученные результаты имеют важное значение.