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Citation: MAHON, D., CLAUDIO, G. and EAMES, P.C., 2017. An experimental investigation to assess the potential of using MgSO₄ impregnation and Mg²⁺ ion exchange to enhance the performance of 13X molecular sieves for interseasonal domestic thermochemical energy storage. Energy Conversion and Management, 150, pp.870-877.

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Metadata Record: https://dspace.lboro.ac.uk/2134/24715

Version: Published

Publisher: © The Author(s). Published by Elsevier Ltd.
An experimental investigation to assess the potential of using MgSO₄ impregnation and Mg²⁺ ion exchange to enhance the performance of 13X molecular sieves for interseasonal domestic thermochemical energy storage

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1. Introduction

Approximately 26% of the UK’s primary energy consumption is used specifically for domestic space heating (DSH) and domestic hot water (DHW) production [1]. The majority of this, 88%, comes directly from gas and oil with only 2% coming from renewable energy sources [1]. Decarbonising DSH and DHW represents a huge challenge for the UK government which is targeting a reduction of CO₂ emissions of 20% by 2020 and 80% by 2050 [2].

The amount of energy utilised from renewable sources can be increased by effective Thermal Energy Storage (TES). In a domestic environment thermal energy is typically required when the energy supplied from renewable sources is low (i.e. thermal energy demand is high in the winter and low in the summer). TES can be used to bridge the gap between supply and demand [3–5].

The three main forms of thermal energy storage are Sensible Thermal Energy Storage (STES), Latent Thermal Energy Storage (LTES) and Thermochemical Energy Storage (TCES) [6–8]. In STES a material is heated and then the material is subsequently stored (i.e. water, rock, concrete [6,7]) at an elevated temperature by an insulated container. In LTES the storage material is heated or cooled above or below its phase change temperature taking advantage of the energy absorbed or released during the phase transition.

Thermochemical Energy Storage (TCES) offers the potential to store thermal energy almost loss free for an indefinite amount of time [9] (i.e. allowing storage of solar energy during summer peri-
The energy density offered by thermochemical materials can be three times larger than phase change materials (PCM) at temperatures below 150 °C [10,11]. A thermochemical Energy Storage Materials (TCESM) when heated will separate into a working pair of materials, until the thermal energy is required, and they can be recombined to release heat on demand. LTES and TCES can be used to improve utilisation of solar energy gains from a solar thermal collector by allowing heat captured at periods of low or no demand, to be stored and subsequently used when needed. A conventional Flat plate, Vacuum Tube solar thermal Collector (VTC) or a Vacuum Flat Plate solar thermal Collector (VFPC) could be utilised to provide heat to a thermal energy store. Vacuum solar thermal collectors can reach temperatures up to 150 °C [12] making them viable for use with many promising thermochemical working pairs. Research has been conducted into assessing the performance of solar thermal collectors with LTES materials [13–15].

Absorbent materials such as zeolites can be used to store thermal energy by adsorption [5,16–19]. Zeolites typically have very large surface areas and high porosity [20], but their energy density for heat storage is typically less if compared to salt hydrates used for heat storage [5]. Moreover, zeolites typically do not suffer from many issues which salt hydrates, particularly MgSO4·7H2O and MgCl2·6H2O, suffer from (i.e. agglomeration) [21]. Therefore, zeolites have shown promising results when used in large scale systems [17,22,23].

Magnesium Sulfate heptahydrate (MgSO4·7H2O), a salt hydrate, is a promising material for TCES. This material has a high theoretical energy density (2.8 GJ/m³) [10], is non toxic, is cost effective (£61/ton) and can be dehydrated at temperatures below 150 °C. When MgSO4·7H2O is dehydrated it yields MgSO4 + H2O which are both non-toxic materials. The major drawback of MgSO4·7H2O is represented in its utilisation at large scales due to the agglomeration phenomena, which occurs when the material is rehydrated (discharged), resulting in both low power output and low total energy output [24,25]. In an attempt to address these problems, a range of composite materials utilising LiCl [24], MgCl2 [25] and MgSO4 [26] have been the object of several studies by the scientific community around the world.

Composite materials have been studied for their property to increase the energy density of porous absorbent materials with the addition of salt hydrates [26–28]. The methodology used for adding the salt hydrates into the porous hosts is typically the wetness impregnation method [26–28].

Another method used to improve the energy density of absorbent materials is through the ion exchange process. Absorbent materials, particular zeolites can be put through an ion exchange process to replace the current ions with other ions having higher selectivity to the material. The hydration energy of zeolites depends on the amount of cations which are accessible to the adsorbed material which, for TES, is commonly water [29]. Water absorbed by zeolites is bonded in two main ways: firstly the weakly bound water on the surface and within the voids of the zeolite and secondly through strong interactions with the ions within the zeolite material [30]. The amount of ions within a zeolite type material and the amount of ion’s which can be exchanged is a function of the Si/Al ratio of the material [30] due to the cations balancing the net negative charge of the alumina silicate structure [29]. A lower Si/Al ratio also results in a more hydrophilic zeolite [31]. Molecular sieves adsorption properties, crystal cage and hydration can be altered by ion exchange [32]. Research has shown that ion exchange changes the water uptake of zeolites [33].

The objective of this research is to understand the performance of 13X molecular sieves for domestic thermochemical energy storage. This work investigates the impregnation of 13X molecular sieves with MgSO4 and also putting 13X molecular sieves through an ion exchange process to assess the improvements in the energy output of the materials for domestic TCES. The research presented in this paper investigates MgSO4 which has been impregnated within two different absorbent materials (13X molecular sieve and zeolite-Y). Both materials have regular alumina silicate cage structures which can be impregnated with MgSO4. Both of the materials can be used as sorption thermochemical energy storage materials. When impregnated with MgSO4 the energy storage density should increase. The effect of Mg2+ ion exchange with Na+ ions within the 13X crystal lattice has also been investigated. The ion exchange enhancement is shown to provide an improvement to the energy output of the 13X molecular sieves. This paper reports the methods used to create the composite materials and the effect that it has on the thermochemical properties of the materials.

2. Methodology

2.1. Wetness impregnation

The 13X material was sourced in both a fine powder (3–5 μm) and in pellets of approximately 3.2 mm diameter from Sigma-Aldrich. A commonly used method to impregnate a salt hydrate within a porous absorbent is wetness impregnation [26–28]. The 13X pellets were baked at 150 °C in an oven to remove any water from the pores. This temperature was selected since this is the maximum temperature the material will be exposed to when employed in a domestic environment with heat supplied from a VFPC. An aqueous solution, of MgSO4, was then applied to the 13X pellets. Due to capillary forces the aqueous solution is drawn into the cage structure of the material. The impregnated wet pellets were then dried within an oven at 150 °C to remove any water and to allow the MgSO4 to re-crystallise within the cage structure.

In an attempt to obtain good dispersion and absorption of MgSO4 within the 13X pellets different strengths of aqueous MgSO4 solutions were trialled. Each trial used the maximum volume of solution which can be absorbed by the dry 13X pellets. It was found that after 1 impregnation ~12.9 wt% of MgSO4 was
2.2. Pellet preparation method

Many absorbent materials are difficult to source in pellet form because they are more commonly available as a fine powder. A method has been developed to create composite pellets from powder. In the developed method the 13X powder and the binder were initially dried at 150°C in an oven for 3 h. Subsequently the dried powder and binder were mixed with a saturated solution made from MgSO₄·7H₂O dissolved in deionised water at 20°C. The binder material used was attapulgite ground into a fine powder. The resulting slurry was dried within an oven at 150°C for 3 h to remove excess water. Once dried, the material was ground down into a fine powder and deionised water was added and mixed until the solution thickened into a soft clay consistency. This mixture was then put through a pellet press to form the pellets. The formed pellets were then placed back into the oven and dried at 150°C for 3 h. The pellets formed using this methodology are referred to as 13XMK. This methodology was also used to create the zeolite pellets from powder and this material is referred to as ZMK in this paper.

2.3. Ion exchange methodology

13X molecular sieve pellets were put through an ion exchange process to replace Na⁺ ions with Mg²⁺ ions. First, a saturated solution of MgSO₄ was created using 71 g of MgSO₄·7H₂O for every 100 g of deionised water used. The 13X pellets were then added to the solution. For every 10 g of 13X pellets 171 g of solution was used. The solution containing the 13X pellets was stirred for 5 min to ensure all of the pellets sunk in the solution. The pellets were left in the solution for the desired ion exchange time period. Once the chosen time period was over the pellets were filtered out of the solution and washed with deionised water. For every 10 g of 13X pellets 100 ml of deionised water was used to wash the pellets. The washing was performed to remove any excess salt solution which was on the pellets to avoid salt recrystallisation within the pores or on the surface of the 13X pellets which cause pore blocking and ultimately reduce their performance. The 13X pellets which were prepared using this methodology are referred to as 13X Mg Ionz h, where z is the ion exchange time period length in hours.

2.4. Thermal analysis

To determine the dehydration enthalpy of each TCESM a Differential Scanning Calorimeter (DSC) was used. Before commencing the dehydration experiments each sample, of ~10 mg, was hydrated in air at 20°C with ~56% Relative Humidity (RH) for a minimum of 18 h. This hydration condition was selected because it is easily achievable during winter time in the UK [34]. Prior to testing in the DSC all pellets were crushed into a fine powder.

To determine the sensible heat component of each TCESM sample the DSC was programmed to ramp temperature from 20 to 150°C at a rate of 5°C/min and then hold the samples isothermally for 1 h allowing dehydration of the samples. After the isothermal period the samples were cooled down to 20°C. This heating cycle was then repeated again afterwards. Due to the samples being dehydrated the measured heat flow, from the second ramp up cycle, is due to the samples heat capacity. The measured endothermic heat flow from each ramp up cycle was integrated using a sigmoidal integration. By subtracting the second “sensible” heat flow from the first sensible and dehydration heat flow, the heat flow due to dehydration of the TCESM was finally quantified. To assess the mass loss from the TCESM during heating, H₂O in this case, a TGA was used. Each TGA sample, of ~4 mg, was hydrated at ~56%RH at 20°C for a minimum of 18 h. The samples were then dehydrated within the TGA by heating from 20 to 150°C with a temperature ramp rate of 5°C/min followed by an isothermal period of 1 h held at 150°C.

The 1 h isothermal period at 150°C was a sufficient period for dehydration to occur evidenced by the measured heat flow in the DSC which became constant and from the mass loss of the samples within the TGA which ceased during the 1 h period.

2.5. 200 g dehydration hydration cycle test apparatus

To test the hydration of materials on a more realistic scale a system using 200 g of TCESM material was constructed. The system consisted of a 75 mm diameter stainless steel chamber 155 mm long in which the TCESM was stored. The chamber was covered with a 25 mm thick layer of glass wool insulation. At the base of the chamber there is a 12.7 mm diameter pipe through which a flow of hot or humid air can be introduced. The hot air flow from a temperature controlled hot air gun was used to dehydrate the TCESM. A humid air stream was created by bubbling air through a 9 litre water tank. This air stream was then mixed with an air supply with low humidity. The required RH percentage was maintained by controlling the flow rate of both air streams. Air with the required humidity, was then introduced into the TCESM chamber, at a rate of 10 L/min, to rehydrate the TCESM material.

Temperature (thermocouples) and humidity sensors were utilised to measure the characteristics of the input air flow. Thermocouples at the entrance and exit of the TCESM chamber were used to measure air temperatures during the duration of the tests.

2.6. SEM and EDX analysis

SEM and EDX analysis was performed to assess the ion exchange process in the 13X pellets. The samples were mounted on a carbon stub prior to being examined using a table top Hitachi TM3030 SEM.

3. Results and discussion

3.1. Comparison of 13X powder, 13X pellets and zeolite-Y powder absorbents

Initial experimental tests assessed the dehydration heat flow and energy storage characteristics of the 13X powders, 13X pellets and zeolite-Y powder with the DSC plots presented in Fig. 1. The endothermic heat flow is due to the enthalpy required for dehydration from the first sensible and dehydration heat flow, the heat flow due to dehydration of the TCESM was finally quantified. To assess the mass loss from the TCESM during heating, H₂O in this case, a TGA was used. Each TGA sample, of ~4 mg, was hydrated at ~56%RH at 20°C for a minimum of 18 h. The samples were then dehydrated within the TGA by heating from 20 to 150°C with a temperature ramp rate of 5°C/min followed by an isothermal period of 1 h held at 150°C.

The 1 h isothermal period at 150°C was a sufficient period for dehydration to occur evidenced by the measured heat flow in the DSC which became constant and from the mass loss of the samples within the TGA which ceased during the 1 h period.
tion (water loss) and the sensible heat required for heating the samples up to 150 °C. Sigmoidal integration of the DSC measurements was used to estimate the average total enthalpies reported in Table 1. It is clear that zeolite-Y has the highest dehydration enthalpy (not including the sensible heat enthalpy).

The lower endothermic heat flow and dehydration enthalpy measured for the 13X pellets compared to the 13X powder is due to the binding material used to bind and hold the powder in pellet form. The binding material reduces the total amount of 13X material per unit weight, available for water sorption.

3.2. Comparison of 13X materials with different absorbed quantities of MgSO4 prepared using the wetness impregnation method

The wt% of MgSO4 absorbed by 13X pellets can be varied using the wetness impregnation method, leading to different dehydration enthalpies. The DSC calculated dehydration enthalpy (first cycle enthalpy minus second cycle enthalpy) measurements and TGA determined mass loss for 13X samples with varying wt% of MgSO4 are shown in Fig. 2. It is evident that increasing wt% of MgSO4 leads to a decrease in dehydration enthalpy. This is corroborated by the TGA mass loss data which also decreases with increasing wt% of MgSO4.

The predicted enthalpy for each sample is indicated by the green bars in Fig. 2. The predicted values were calculated based on the DSC determined dehydration enthalpies for both pure MgSO4·7H2O and 13X pellets. MgSO4·7H2O has a dehydration enthalpy of 1118 J/g when dehydrated with the same temperature program used for the 13X pellets (ramp rate 5 °C/min and maximum temperature of 150 °C). The dehydration enthalpy of the 13X pellets was determined to be 479 J/g. Due to the significantly higher dehydration enthalpy of MgSO4·7H2O it was expected that the dehydration enthalpy of the impregnated pellets would increase with increasing wt% of MgSO4, leading to a more energy dense material with higher dehydration enthalpy. The mass loss (water loss) of the samples with impregnated MgSO4 did not increase with increasing MgSO4 content. However, the MgSO4 and the 13X materials do not hydrate (discharge) and dehydrate (charge) as anticipated when combined in a composite form, as explained in Section 3.3 of this paper. Similar research has also reported lower heats of sorption from MgSO4 impregnated zeolites than expected. [26].

3.3. Analysis of DSC plots for composite 13x + MgSO4 materials to determine cause of lower dehydration enthalpies than expected

Fig. 3 shows the DSC dehydration plots for each of the composite materials tested after the hydration process. Fig. 3 shows that the DSC dehydration heat flow plot is significantly different for the ZMK composite material (a composite material consisting of zeolite, MgSO4 and a binder) when compared to the 13X materials tested and 13xMK (composite material consisting of 13X, MgSO4 and a binder). Both ZMK and 13xMK are pellets produced in the laboratory, using the method described previously in Section 2.2, and were both crushed into a powder for the DSC and TGA tests.

From Fig. 3 at 73 °C the MgSO4 sample exhibits a strong endothermic peak correlated to a loss of 6 water molecules, which was established from analysis of the DSC and TGA results of MgSO4·7H2O dehydration. The dehydration peak is also present (green plot) for the ZMK material. This is the only composite material tested in which the MgSO4 dehydration is seen. This peak is the reason the ZMK material exhibits an average DSC dehydration enthalpy of (715 J/g) and it indicates that the MgSO4 is rehydrating and subsequently dehydrating within the zeolite material.

To determine if the loss of the MgSO4 dehydration peak was due to the wetness impregnation method used to create the 13x + MgSO4(Xwt%) pellets, a sample of 13xMK material was created with the same MgSO4 content as the 13x + MgSO4(12.9 wt%) sample. The DSC heat flow plot for this material is presented in Fig. 3 and appears similar to all of the 13X samples which do not exhibit the MgSO4 dehydration peak. The average dehydration enthalpy of the 13xMK sample was 487 J/g, a similar value to the pure 13X pellet sample, which was 479 J/g. This value is significantly higher than the 13x + MgSO4(12.9 wt%) sample (433 J/g) due to the amount of binder within the pellets. The amount of binder in the 13xMK pellets can be controlled where as the sourced 13X pellets have a set amount of binder from the manufacturer. The laboratory developed preparation method (see Section 2.2) leads to higher dehydration enthalpy (J/g) than the standard wetness impregnation method. Other characteristics such as hydration enthalpy or hydration rate (power output) could be improved if different preparation methods are utilised.

The absence of the MgSO4 dehydration peak in the 13X based materials is due to the MgSO4 which does not hydrate in these samples. Both preparation methods used 13X molecular sieves as a host material and both have an absence of the MgSO4 dehydration peak. The MgSO4 dehydration peak is present for the ZMK

<table>
<thead>
<tr>
<th>Table 1</th>
<th>DSC determined averaged enthalpies of absorbent zeolite materials over the temperature range of 20–150 °C.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>13X pellets</td>
</tr>
<tr>
<td>Dehydration enthalpy + sensible enthalpy (J/g)</td>
<td>626</td>
</tr>
<tr>
<td>Dehydration enthalpy only (J/g)</td>
<td>479</td>
</tr>
</tbody>
</table>
material suggesting the lack of MgSO₄ dehydration peak is due to the 13X material and to a pore blocking effect which has also been suggested in other work [26]. If MgSO₄ blocks pores in the 13X material it will reduce the available surface area for water adsorption within the 13X material.

When creating the pellets from the powder absorbent material ion exchange can take place between the Mg²⁺ ions in the MgSO₄ solution and the Na⁺ ions in the 13X powder. The slurry formed when creating the pellets contains all ions both Mg²⁺ and Na⁺, neither of which are removed during the process and so will be present in the final produced pellets. This should not prevent the MgSO₄ from recrystallising within the formed pellets, either within the cage structure or on the surface of the 13X material. The ion exchange that occurs is not detrimental to the thermal energy storage potential even if a higher wt% of MgSO₄ is used to create the pellets. Measurements confirm that the ion exchange of Na⁺ ions with Mg²⁺ ions actually leads to an increased dehydration enthalpy (see Section 3.7).

3.4. 200 g dehydration/hydration cycle testing results

The materials tested on a more practical 200 g scale were 13X pellets, 13x + MgSO₄(12.9 wt%), ZMK and 13xMK. Fig. 4 presents the hydration results for each 200 g experiment. Each material was hydrated and dehydrated for at least 3 times with Fig. 4 showing the average for each sample. Fig. 4 shows also the variation of Delta T (between the air inlet and outlet) achieved when hydrating each material with an air flow rate of 10 L/min of ~5%RH at 20 °C after being dehydrated to 150 °C using air heated by a hot air gun. The results show that the 13X pellets and the ZMK have the highest hydration enthalpies of 496 J/g and 490 J/g, respectively. The 13x + MgSO₄(12.9 wt%) and the 13xMK enthalpies are 407 J/g and 385 J/g, respectively.

The 13x + MgSO₄(12.9 wt%) material achieves a higher value of Delta T (i.e. higher peak power output) for the same hydration conditions as the 13X pellets. The DSC data presented in Fig. 3 shows no sign of the MgSO₄ 6H₂O dehydration suggesting the MgSO₄ does not produce any heat, indicating that all heat derives from the hydration of the 13X material. The reason for the increased power output of this material relative to the pure 13X pellets will require further investigation. A possible explanation is the dehydration of the 13x + MgSO₄(12.9 wt%) pellets (formed by immersing 13X pellets in a MgSO₄ solution) within the oven, which drives off all excess water from the solution, results in the recrystallisation of MgSO₄. This is responsible for cracks and larger vapour channels through the impregnated 13x + MgSO₄(12.9 wt%) pellets. The larger vapour channels would allow for faster hydration of the 13X material resulting in higher power outputs.

3.5. Comparison of dehydration/hydration cycle results from theory, DSC measurements and 200 g sample tests

The predicted dehydration enthalpies and the enthalpies measured by DSC and the 200 g test equipment are presented in Fig. 5. The theoretical values are the expected enthalpies for each material, which are calculated using the DSC determined values of each component and their weighted average value. There are two losses in performance calculated: first the percentage of loss between the theoretical values and the measured DSC results and secondly the percentage of loss between the measured DSC and the measured 200 g results.

The 13X pellets loss in performance, from the DSC measurements to the 200 g results, is negative resulting in negligible performance losses when scaled up to 200 g. The two composite materials containing 13X (13x + MgSO₄(12 wt%) and 13xMK) suffer reductions in performance from their theoretical values to the DSC measurements. The 13x + MgSO₄(12 wt%) suffers a reduction of 6% from the DSC to the 200 g measurements, with the 13xMK suffering a reduction of 21%. The laboratory preparation method suffers from a greater loss in performance from DSC to 200 g scale compared to the wetness impregnation method.

The ZMK material exhibits no loss in performance from the theoretical to the DSC measurements, from the DSC to 200 g measurements the reduction is 31%. The wetness impregnation method suffers from minimal performance losses. The reason for the performance losses for the wetness impregnation sample (13x + MgSO₄(12.9 wt%)) is due to no MgSO₄ hydration in this sample.

The choice of preparation method to achieve the best performance will depend on the amount of binder in the commercially created pellets. The two best candidate materials for testing at a larger scale would be the 13X pellets or the ZMK material as they produce the highest hydration enthalpy. If the laboratory preparation method could be optimised to reduce scaling losses the ZMK material has the potential to achieve much higher hydration heat output increasing by 46%, up to 715 J/g, as achieved in the DSC testing of ZMK.

3.6. Theoretical dehydration enthalpy, excluding MgSO₄·xH₂O enthalpy, compared to DSC and 200 g sample measured tests

The theoretical dehydration enthalpy for each of the samples tested without the dehydration enthalpy from the MgSO₄·xH₂O has been calculated. Table 2 shows the calculated and the experimentally measured values. The calculated theoretical values in Table 2 are shown to be within 2% of the measured DSC values for the 13X samples prepared using the wetness impregnation method, suggesting that the dehydration enthalpy from the MgSO₄·xH₂O is not present and the measured dehydration enthalpy is due to the 13X material only. The 13xMK materials
The percentage difference from the theoretical to the measured DSC value is –10%, which is higher than expected. This is because the 13X MK are produced using the laboratory pellet preparation method which allows the MgSO₄ to recrystallise within the pellets outside of the 13X lattice. The percentage difference for the ZMK material from theoretical to the measured DSC is –129%, due to the hydration of MgSO₄ within the zeolite which has a significant dehydration enthalpy within the ZMK material.

When comparing the theoretical dehydration enthalpy to the 200 g sample results we have noticed the same trend in percentage difference. The percentage difference between the theoretical values and the 200 g hydration results are 4%, 13% and –56% for 13X + MgSO₄ (12.9 wt%), 13XMK and ZMK, respectively.

### 3.7. 13X Mg ion exchange pellet testing results

To improve the energy output of the 13X pellets, they were exposed to an ion exchange process where each Mg²⁺ ion replaced two Na⁺ ions. Fig. 6 shows the DSC dehydration enthalpy and TGA mass loss of the 13X Mg ion exchanged pellets and for 13X pellets which have not been put through an ion exchange process. The ion exchanged pellets have a higher dehydration enthalpy and a greater mass loss.

The reason for the increased dehydration enthalpy and the mass loss of the 13X ion exchanged samples is due to the bonding of H₂O to the Mg²⁺ ions within the 13X pellets. Due to the high hydration energy of Mg²⁺ ions the modified 13X pellets have more bonded H₂O around the Mg²⁺ ion sites and a higher hydration energy [30, 35]. Contrastingly the Na⁺ ion sites have a lower hydration energy [35]. Other studies have also reported an increase in hydration heat from zeolites after a Mg ion exchange [35, 36].

The enthalpy and mass loss for samples prepared for 24, 48 and 72 h overlaps, with no apparent advantage gained using a 72 h period for ion exchange compared to a 24 h period. The 13X pellets have reached their ion exchange capacity, under the exchange conditions used, within 24 h. The capacity could be increased if the temperature used for the ion exchange process was increased [37]. The increase in mass loss and dehydration enthalpy for the 1 h ion exchange samples is significantly lower than that of samples prepared with exchange periods of 24, 48 and 72 h.

Fig. 7 shows the average sensible enthalpy (J/g) and the performance for each ion exchanged sample. The performance percentage is calculated as the (dehydration enthalpy divided by total enthalpy). The sensible enthalpy is the energy lost prior to the discharge which is due to charging of the material throughout the summer months when there is a small heat load in a domestic environment [3]. The sensible enthalpy for each of the ion exchange samples is 118 J/g (±2 J/g) and 148 J/g for the 13X pellets which have not been put through an ion exchange process.

The performance of each ion exchange sample, neglecting the 1 h sample, is 81.8% (±0.13%), 5.5% higher than the 13X pellets which have not been put through an ion exchange process. The ion exchanged samples also have a higher performance than the 13X powder sample. A higher performance is beneficial for materials and will result in higher efficiency if used in a seasonal heat storage system. The increase in performance of the ion exchanged pellets is firstly due to the increased dehydration enthalpy (explained in Section 3.7) and also due to a decreased sensible enthalpy.

The more sensible enthalpy for the samples prepared for 24 h, 48 h and 72 h are within 0.13% and 2 J/g, respectively which means that the ion exchange reaches its maximum percentage between 1 h and 24 h. The quantification of the optimum ion exchange time period will require further investigation.

### 3.8. SEM and EDX analysis of 13X ion exchanged pellets

13X pellets and each ion exchanged sample were analysed using SEM and EDX. To collect the data for the EDX and SEM results presented (Figs. 8–10) several different samples of each pellet were tested and also data was collected for several locations within each pellet. The EDX composition values obtained were then averaged and normalised for Mg and Na content to determine the changing composition of the pellets. Fig. 8 shows the EDX determined changing composition of the interior of the 13X pellets before and after different periods of the ion exchange process. After the 24 h ion exchange process 60% (±4%) of the sodium had been

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**Table 2**

Calculated theoretical dehydration enthalpies for samples, not accounting for the MgSO₄·H₂O dehydration enthalpy, compared to the measured DSC and 200 g enthalpy results over the temperature range 20–150 °C.

<table>
<thead>
<tr>
<th>Sample name</th>
<th>13X pellets</th>
<th>13X + MgSO₄ (4.4 wt%)</th>
<th>13X + MgSO₄ (7.3 wt%)</th>
<th>13X + MgSO₄ (9.2 wt%)</th>
<th>13X + MgSO₄ (12.9 wt%) wetness impregnation</th>
<th>13XMK</th>
<th>ZMK</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dehydration enthalpy theory (excluding MgSO₄) (J/g)</td>
<td>479</td>
<td>464</td>
<td>450</td>
<td>441</td>
<td>423</td>
<td>442</td>
<td>314</td>
</tr>
<tr>
<td>DSC Dehydration enthalpy (J/g)</td>
<td>479</td>
<td>466</td>
<td>445</td>
<td>437</td>
<td>433</td>
<td>487</td>
<td>715</td>
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<tr>
<td>% difference</td>
<td>0%</td>
<td>0%</td>
<td>1%</td>
<td>1%</td>
<td>–2%</td>
<td>–10%</td>
<td>–129%</td>
</tr>
<tr>
<td>200 g hydration enthalpy (J/g)</td>
<td>496</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>407</td>
<td>385</td>
<td>490</td>
</tr>
<tr>
<td>% difference</td>
<td>–4%</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>4%</td>
<td>13%</td>
<td>–56%</td>
</tr>
</tbody>
</table>

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**Fig. 6.** DSC dehydration enthalpy and TGA dehydration mass loss results of 13X ion exchanged pellets.

**Fig. 7.** Sensible enthalpy and performance (dehydration enthalpy/total enthalpy) of 13X ion exchanged pellets.
replaced by magnesium. The results show that the ion exchange methodology has successfully replaced Na$^+$ ions with Mg$^{2+}$ ions within the 13X pellets. Fig. 8 shows that the Mg$^{2+}$ and Na$^+$ ion contents of the 24, 48, and 72 h samples are all within 10% of each other, demonstrating that the ion exchange process is completed in the first 24 h.

Fig. 9 shows the EDX determined composition values for the external surfaces of the 13X ion exchanged samples. The composition on the external surface is significantly different if compared to the interior of the pellets (presented in Fig. 8) in terms of Mg versus Na content. The external surfaces of the pellets have a much higher Mg content (average 84%) after the ion exchange process (24 h, 48 h and 72 h samples) compared to the interior (average 57%). The 13X pellets have a much higher ion exchange percentage at the external surface compared to the interior. The internal ion exchange can reach the same percentage as the external surface if a higher temperature is utilised in the ion exchange process (discussed in Section 3.7). A higher ion exchange percentage in the interior would result in increased hydration heat and performance of the 13X pellets.

A higher ion exchange percentage takes place at the external surface of the pellets because the Mg$^{2+}$ ions can easily exchange with the Na$^+$ ions. It is more difficult for the Mg$^{2+}$ ions to exchange with the interior Na$^+$ ions of the pellets.

EDX data and SEM images of the interior and external surface structure of the pellets were taken. Fig. 10 shows SEM images of the 13X pellets after a 24 h ion exchange process. Image 1 shows an image of a pellet fragment, images 2–4 show enlargements of image 1 and images 5 and 6 compare the different structures of the internal and the external surfaces of the pellet. The images show that the external surface of the 13X pellets, after a 24 h ion exchange process, is very different from the internal surface. The internal surface consists of regular sphere shaped objects (zeolite structures) connected with voids in-between creating a porous structure where as the external surface is less regular and less porous. There is a reduction in the ion exchange percentage within the interior of the pellets especially if compared with the external surface; this is due to the external surface of the pellets being less porous than the interior. A less porous external surface will reduce the ability of the Mg$^{2+}$ ions to ion exchange with the Na$^+$ ions in the interior core of the pellets.

The pellet samples were broken into fragments to perform EDX and SEM analysis, to allow the interior structure as well as the surface of the pellets to be analysed.

4. Conclusions

Two different absorbents, 13X and zeolite-Y, have been shown to exhibit similar dehydration properties through thermal analysis. The 13x material was shown to be a poor host for MgSO$_4$ as there are no signs of MgSO$_4$·6H$_2$O dehydration in DSC and 200 g tests for any of the 13X materials impregnated with MgSO$_4$. Two materials with the same MgSO$_4$ wt% (13xMK and 13x + MgSO$_4$(12.9 wt%)) were created and tested using different pellet preparation methods. Both of them did not show signs of MgSO$_4$ hydration.

The 200 g dehydration cycle experiments show that the 13X pellets and the ZMK pellets have the best properties for use in thermochemical heat storage systems from the materials tested. Zeolite-Y is shown to be a suitable host material for MgSO$_4$ because of the high energy density reported in our experiments. The pellet preparation method, used to create pellets from absorbent powders, suffers performance losses when moving from DSC measurements to 200 g scale system measurements. If this method is optimised the hydration heat of the ZMK could be increased by 46%.

After Mg$^{2+}$ ion exchange with the 13X pellets the properties for heat storage improve. The pellets, after a 24 h ion exchange period, have a higher DSC dehydration enthalpy and a lower sensible enthalpy component. This results in an improved performance by 5.5%.

Further research is required to test the ion exchanged pellets at a larger volume to assess their potential for heat storage on an industrial scale. Further investigation into the optimisation of the ion exchange process should also be performed to determine the highest percentage of ion exchange possible in the 13X pellets.
Acknowledgements

This work was supported in full by the UK Engineering and Physical Sciences Research Council (EPSRC) [grant number: EP/K011847/1], i-STUTE and a Loughborough University PhD studentship.

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