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Development and characterization of a new $MgSO_4$-zeolite composite for long-term thermal energy storage

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Abstract

A seasonal chemical heat store, based on the hydration/dehydration cycle of a magnesium sulphate ($MgSO_4$) composite material, has been developed. During the summer, the material stores heat by an endothermic dehydration reaction and heat used for space heating is released in winter by rehydrating the material. For that specific purpose, a new thermal energy storage composite material has been developed, which is the subject of the present paper.

The active material needs to be dispersed to optimise the gas-solid reaction kinetics and the thermal power released/absorbed. Zeolites have proved to be a favourable porous expanded structure for $MgSO_4$, with energy densities of 150-400 $kWh.m^{-3}$ at a storage temperature compatible with solar thermal collectors. Characterisation by thermogravimetric analysis (TGA) and differential scanning calorimeter (DSC) on 10 mg samples show that almost 80% of the total energy density can be stored at 150°C although the material is not fully dehydrated. At a bigger scale, during hydration tests on 200g sample, an energy density of 0.18Wh/g is

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achieved, i.e. 45% of the theoretical energy density of the form-stable zeolite-$MgSO_4$ composite sorbent. Microcalorimetry measurements have confirmed that this energy density value remains at this level over 3 charge/discharge cycles.

Keywords: thermal energy storage; thermochemical process; long-term storage; zeolites; magnesium sulphate; seasonal storage; building application

1. Introduction

Thermal energy storage systems could make an important contribution in reducing our dependency on fossil fuels, but also in contributing to a more efficient and environmentally benign energy use [1], [2]. As demand in thermal comfort of buildings rises, the energy consumption correspondingly increases. For example, in France, the energy consumption of buildings has increased by 30% in the last 30 years. Housing and tertiary buildings are responsible for the consumption of approximately 46% of all energies and approximately 19% of the total CO_2 emissions [3].

The annual solar energy incident on building surfaces is far greater than the building needs for space heating and hot water, especially during the summer season. It is obvious that a long-term thermal energy storage system is a means to rationalize the use of this renewable energy. Thermal energy storage can be accomplished either by using sensible heat storage, latent heat storage, physical sorption heat storage or chemical heat storage. Chemical heat storage has the highest potential for seasonal heat storage (figure 1): the storage density is high and there is no heat loss to the environment during storage.

Potential candidates for chemical heat storage are numerous but some of them have been identified in [4]:

- $MgSO_4$ & H_2O with an energy storage density of 2.8GJ/m^3,

- Si & O_2 with an energy storage density of 37.9GJ/m^3,

- FeO & CO_2 with an energy storage density of 2.6GJ/m^3,

- FeO & H_2O with energy storage density of 2.2GJ/m^3,

- $CaSO_4$ & H_2O with energy storage density of 1.4GJ/m^3.

Among the potential candidates, magnesium sulphate is the most appropriate because of its high energy density, its storage temperature compatible with solar collectors, the availability of the chemical reaction compounds and its non-toxicity. The subject of this study is to develop and characterize a magnesium sulphate based composite material for long-term thermal energy storage.

[Fig. 1 about here]

2. Presentation of the thermal energy storage concept

The main principle of the storage system is based on an open system that uses the moisture of the ventilation exhaust air from the building as a source of water for the exothermal hydration reaction. The heat generated by the reaction is used to heat incoming fresh air via a mechanical heat recovery heat exchanger (balanced ventilation system with heat recovery) that provides heating to the building. A schematic of the heat release process, typically in winter, is shown in figure 2.

The storage of heat in the material, typically in summer, requires hot air between 80°C and 150°C. The higher the temperature, the greater is the amount of heat stored. Air solar collectors with evacuated tubes are used in order to reach higher temperatures and to obtain an optimised operation time with a good performance. The hot air from the collectors is used to

transfer heat and recharge the thermal energy storage system. The material developed for the storage system must be compatible with this specific feature.

[Fig. 2 about here]

3. Composite material development

3.1 Heuristic arguments

The thermochemical storage working pair is magnesium sulphate ($MgSO_4$) / water vapour (H_2O). Heat is released/stored by the hydration/dehydration of magnesium sulphate by the following reaction:

$$MgSO_4.7H_2O \Leftrightarrow MgSO_4 + 7H_2O$$

Magnesium sulphate used as a fine powder is difficult to use in a storage reactor because it rapidly forms a skin of the hydrated salt on the surface of the bulk powder when it reacts with humid air. This skin then forms a barrier to further solid/gas reaction between the moist air and the surface of the solid, which considerably slows down the reaction and limits its power. A composite material was therefore developed, using a microporous matrix to offer a high specific surface for reaction and a high magnesium sulphate impregnation. A zeolite based matrix in the form of pellets was used to take advantage of the additional storage capability of the host matrix by sorption of water.

The temperature lift obtained for two composites tested, zeolite+$MgSO_4$ and silica gel+$MgSO_4$, is shown in figure 3. The objective of a storage system for use in buildings is to have a temperature lift of at least 20°C during the heat release process. The selected candidate for our studies is a mesoporous zeolite matrix with magnesium sulphate.

[Fig. 3 about here]

3.2. Preparation of the composite material

The composite material is prepared by impregnation of magnesium sulphate in a zeolite matrix using an aqueous solution of $MgSO_4$. A 13X zeolite molecular sieve from MERCK is used. This material is pelletized in beads of 2 mm diameter. The aqueous solution of $MgSO_4$ is gradually concentrated by successive additions of appropriate quantities salt, until full incorporation of magnesium sulphate into the zeolite matrix, or the solution is filtered after a period of at least 2h to obtain the desired level of salt.

The impregnated zeolite is then dried in a furnace at 150°C in air. At this temperature, the material is only partially dehydrated, since the zeolite complete dehydration occurs above 200°C. However, this is sufficient for the release of 6 moles of water from $MgSO_4.7H_2O$. The set point of 150°C is chosen as a temperature, which can easily be reached with evacuated tube solar-thermal collectors. The dehydration step is allowed to continue in the oven until the sample mass become stable. By this method, 50 mg samples of zeolite-$MgSO_4$ composite materials have been prepared, with $MgSO_4$ content ranging from 10 to 25%$_{wt}$.

4. Characterization of the storage composite material

4.1. SEM characterization of the zeolite/$MgSO_4$ composite material

Scanning Electron Microscopy (SEM) pictures of zeolite, zeolite-15%$_{wt}$ $MgSO_4$ (ZM15), and zeolite-25%$_{wt}$ $MgSO_4$ composite (ZM25) are shown in figure 4. When observing both images from (a) to (c), it can be clearly seen that the microporosity of the zeolite pellet is gradually occupied by the $MgSO_4$ salt as the mass fraction of $MgSO_4$ increases.

[Fig. 4 about here]

4.2. Thermogravimetric analysis of form-stable zeolite/$MgSO_4$

Thermogravimetric analyses (TGA) were performed on the samples to determine loss of water with increasing temperature. The TGA of 10 mg of pure magnesium sulphate is shown in figure 5. There are three stages of dehydration depending on the temperature: 22°C, 71°C and 261°C. When comparing the TGA curve with the temperatures available from evacuated tube collectors, it appears that the optimum temperature of dehydration is about 150°C which correspond to a dehydration level of about 89%.

[Fig. 5 about here]

The same TG analysis performed on 10 mg of the zeolite-$MgSO_4$ composite materials show a less resolved curve, with a more continuous dehydration phase. The tested materials are zeolite-$MgSO_4$ with $10\%_{wt}$, $15\%_{wt}$, and $20\%_{wt}$ of $MgSO_4$ (respectively ZM10, ZM15, and ZM20). The successive dehydration steps are no longer discernable (figure 6). In terms of mass percent of water desorbed, the behaviours of the composites compared to the zeolite are difficult to separate.

[Fig. 6 about here]

The similarity between the zeolite-$MgSO_4$ materials and the pure zeolite TGA curves seems to show that $MgSO_4$ does not behave like a salt hydrate anymore when it is in the zeolite pores. Many hypotheses are under investigation, such as a replacement of the charge balancing cations of the 13X zeolite skeleton (mainly Na^+ in the 13X type) by Mg^{2+} ions from

magnesium sulphate. This assumption needs to be confirmed or refuted by complementary analyses.

A second series of tests with isothermal steps at 150°C have been performed to simulate the (re)charge dehydration phase at a constant temperature, as it takes place in the storage system. We thus assume the ideal case of a summer day, when the inlet air temperature, which corresponds to the outlet air collector temperature, rapidly increases to the level required for the material dehydration. These dehydration tests at the mg scale with an isothermal step at 150°C coroborates the TGA results in Fig 5: a large part of total the energy density can be used even if the material is not fully dehydrated, which requires higher temperatures (~ 270°C). Indeed, 90% of the initial water content of hydrated $MgSO_4$ and 80% of the initial water content of the hydrated zeolite-$MgSO_4$ materials is lost at T≤150°C, after 2 hours.

4.3. Differential scanning calorimeter analysis of form-stable zeolite/$MgSO_4$

The apparatus is a heat flow calorimeter (figure 7). The principle is based on the difference of specific heat capacities between a reference material and the sample, which creates a temperature difference. The heat flux difference is then calculated using this temperature difference [5].

[Fig. 7 about here]

The study of the material (re)charge dehydration phase has been pursued with Differential Scanning Calorimetry (DSC) tests with an isothermal step at 150°C. These measures were performed on zeolite, $MgSO_4$ and zeolite-$MgSO_4$ materials ZM10, ZM15 and ZM20 to make a comparative study. The deepest endothermic peak corresponds to the zeolite-15%wt$MgSO_4$ dehydration, but the results show low differences between the samples. A quantitative study

has then been launched with micro-calorimetry experiments to actually measure the amount of energy released. The study has focused on the form-stable composite zeolite-15%$_{wt}$$MgSO_4$ (see part 4.6).

[Fig. 8 about here]

4.4. Porosity measurements

Porosity measurements have been carried out on pure zeolite 13X pellets as well as zeolite - 25% $MgSO_4$, by analyzing the adsorption isotherms of two different gases within the pores of the materials:

- adsorption of nitrogen N_2 at 77K, in order to study the whole porosity of the samples
- adsorption of carbon dioxide CO_2 at 293K, in order to specifically study the microporosity of the material.

The composite with 25% $MgSO_4$ was chosen because tests showed that this concentration is not optimal and the material is overload with the salt hydrate. Both tests have been carried out after a preparation at 200C° during 13 hours under vacuum. The N_2 adsorption isotherms belong to type I according to BET classification, which accounts for a mainly microporous material, i.e. with pore diameter < 2 nm (figure 9) [6].

[Fig. 9 about here]

Because of the great affinity of CO_2 vs N_2 for these materials under these experimental conditions, and its higher diffusivity at a temperature level of 293K, the adsorbed CO_2 quantities can be determined with an excellent precision at low relative pressure.

[Fig. 10 about here]

The analysis of the N_2 and CO_2 isotherms can be used to evaluate the specific area, the pore volume and the pore size distribution. Total specific area S_t and pore volume V_t is given by the Langmuir model, whereas the Dubinin-Asthakov model only accounts for the microporous specific area S_μ and pore volume V_μ (table 1). The porosity measurements comparison between zeolite and ZM25 is relative to the same zeolite mass, since zeolite is the host material. The analysis of N_2 isotherms based on the Langmuir method shows that the impregnation of zeolite by magnesium sulphate causes a decrease of the pore volume of about 46%. This could be caused either by penetration of $MgSO_4$ into the micropores, excess $MgSO_4$ blocking the surface of some of the pores, or by a breakdown/enlargement of part of the micropores induced by the impregnation of the salt. The latter could explain why larger pores appear in the magnesium sulphate treated sample. In addition, 96-97% of the zeolite total specific area is obtained from micropores in both the pure zeolite and the composite material, but this area has been reduced to a half in the composite material.

The Dubinin-Asthakhov analysis of the CO_2 isotherm leads to S_μ and V_μ values superior to S_t and V_t values evaluated by the Langmuir method, because CO_2 is a far more appropriate probe than N_2 for microposrosity, specifically if the porosity is not homogeneous. The porosity measurements can still be compared with the same evaluation method. As seen with N_2 isotherms, the results of CO_2 adsorption show a dramatic decrease of the microporous specific area and porous volume (≈ 33%). Since part of the microporosity cannot be reached by the N_2 molecule, the porosity measurements relative to CO_2 adsorption prove more reliable.

[Table 1 about here]

The pore size distribution measured with the DFT technique confirmed that the samples are essentially microporous with an average pore diameter is between 0.8 and 0.9 nm (figure 11). For more accuracy, the results comparison referred to the pore volume at constant zeolite mass. The insertion of $MgSO_4$ within the zeolite pores give rise to a light mesoporosity with a large distribution, within the range of 4-40 nm. However, this phenomenon is minor in comparison with the predominance of the microporosity.

[Fig. 11 about here]

4.5. Macro-reactor experiment of form-stable zeolite/$MgSO_4$

Sorption tests have been carried out in a macro-reactor described in the figure 12. This reactor is not perfectly insulated which means that the temperature rise measured is lower than what could be reached in a system with better insulation. It is divided in two zones: the first contains the sample (200g of zeolite-$MgSO_4$) whereas the second is dedicated to humidity measurements.

[Fig. 12 about here]

The influence of two main controlling parameters was studied: the air mass flow and air relative humidity (at fixed temperature of 25°C). At the building scale, the storage system will be integrated by using the humidity in the house as a water vapour source for the hydration (discharge) reaction. The temperature lifts and the corresponding release of thermal power as a function of time are represented in the figures 13 and 14 respectively.

[Fig. 13 about here]

[Fig. 14 about here]

The maximum temperature lifts and power values are measured for the highest airflow rate available with this setup (8L/min) and the highest relative humidity (80%). During these tests, the energy density achieves the maximum value of 0.18Wh/g with an airflow rate of 8L/min and an inlet air at 50%RH. This value corresponds to 45% of the theoretical energy density of zeolite-$MgSO_4$. The results reveal that the system is highly sensitive to the humidity of the inlet air. Indeed, the hydration curve of ZM15 with humid air at 20% RH and a flow rate of 8L/min, shows a flat pattern. This behaviour tends to indicate that the inlet air relative humidity must reach a threshold value of about 50% in order to get $\Delta T=15°C$ in the reactor.

4.6. Micro-calorimetry experiments

Micro-calorimetry analyses were performed using a Calvet apparatus (figure 15). The calorimeter is made up of two vessels: an internal vessel, where the sample is placed, located inside an external vessel, the calorimetric block, maintained at constant temperature. These two vessels are linked by multiple thermocouples, interconnected in series, which guarantee a good thermal contact and a high precision. When the adsorption occurs in the experimental cell, the heat released is quickly transferred to via the thermocouples to the calorimetric block. The internal vessel temperature is not affected by this heat transfer due to the high thermal conductivity and the large size of the calorimetric block. Therefore, the reaction takes place in isothermal conditions [7].

[Fig. 15 about here]

Water vapour adsorption on a 100 mg sample of form-stable composite pellets (ZM15) was studied by micro calorimetry at 30°C. This sample had previously undergone 3

sorption/desorption cycles. The sorption occurs in a macro reactor as presented in figure 12, whereas desorption is made in an oven at 150°C.The experimental adsorption isotherm as a function of the equilibrium vapour pressure is shown in figure 16. The curve is typical of the adsorption in a microporous material (type I isotherm in the BET classification). The adsorbed mass fraction at equilibrium is close de 0.15 g/g.

[Fig. 16 about here]

Other characteristics can be determined by micro calorimetry, such as differential and integral adsorption heat. An isothermal (30°C) adsorption integral heat of 4532 J/g of water vapour is achieved, which is nearly twice as high as the latent heat of vaporisation of water. The resultant energy density reaches 0.18 Wh/g of ZM15. This value is very close to the thermal energy released during the first hydration at the macro scale (see part 4.5.). This result is particularly interesting, since it proves that the heat storage material ZM15 is able to keep high energy density after at least 3 charge/discharge cycles.

The volumetric energy density of material is a key characteristic for the design of a compact thermal energy storage system. The energy density of the composite material ZM15 was measured by micro-calorimetry at 166 $kWh.m^{-3}$, which indicates an increase of 27% in comparison with the theoretical energy density of pure zeolite 13X (figure 17).

[Fig. 17 about here]

5. Conclusion

The development and characterisation of a novel zeolite/$MgSO_4$ form-stable composite for low temperature heat storage applications in buildings is presented in this paper. The $MgSO_4$

component was confined in the microporous structure of the zeolite pellets with an optimum percentage of 15%$_{wt}$. With an airflow rate of 8L/min and an inlet air at 50%RH, an energy density of 0.18Wh/g (166 kWh.m^{-3}) is obtained, i.e. 45% of the theoretical energy density of ZM. Micro calorimetry experiments reveal that this energy density level is maintained over three charge/discharge cycles. Compared to a water-based storage with a temperature lift of 50°C, which has an energy density of 55 kWh.m^{-3}, a ZM15-based system would thus lead to a 3 times more compact storage tank. Based on all these results, the form-stable composite proves to be a promising thermal energy storage material suitable for long term storage purposes, thanks to its good thermal properties, thermal and chemical reliability. Further research will focus on the optimisation of the host material properties and the evaluation of the storage system energy density in real operating conditions in large-scale experiments.

Acknowledgements

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Isotherm type	N_2 isotherm 77K				CO_2 isotherm 293K	
Model	Langmuir		Dubinin-Asthakhov		Dubinin-Asthakhov	
Characteristics	S_t (m^2/g)	V_t (cm^3/g)*	S_μ (m^2/g)	V_μ (cm^3/g)*	S_μ (m^2/g)	V_μ (cm^3/g)*
Zeolite (reference: sample mass)	957	0.389	921	0.374	934	0.374
ZM25 (reference: sample mass)	413	0.182	400	0.142	546	0.219
ZM25 (reference: zeolite mass)	475	0.209	460	0.163	627	0.252

* at P/P_0=0.98

Table 1. Porosity characteristics of zeolite and ZM25

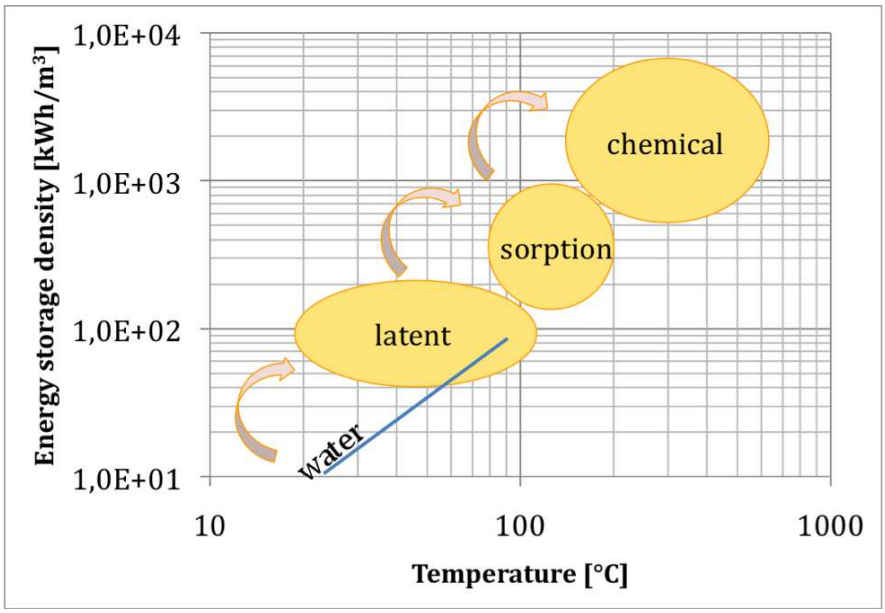


Figure 1. Storage density versus physical phenomena involved

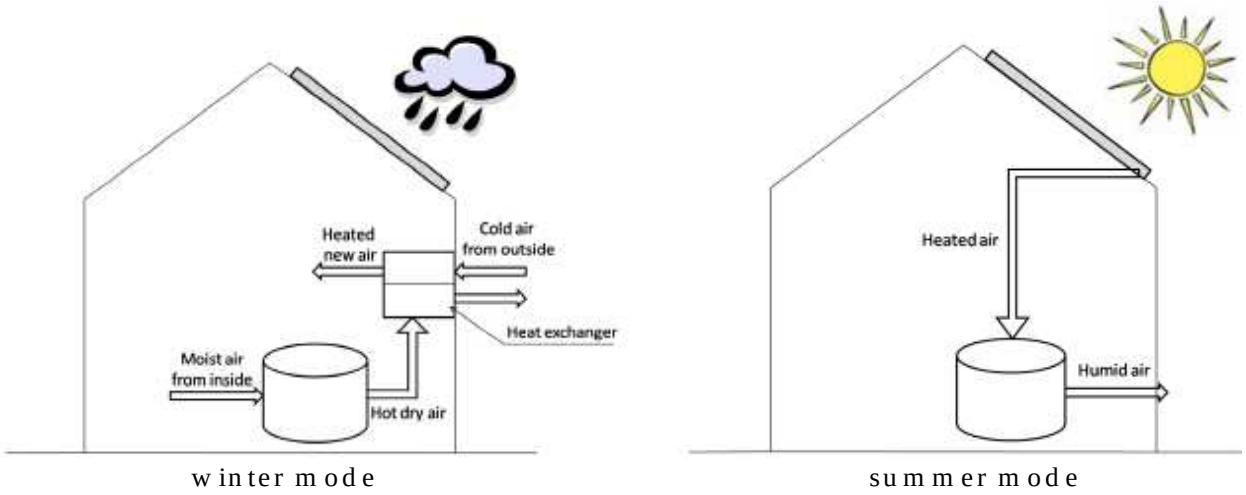


Figure 2. Presentation of the storage concept: heat release from the store (left) and heat storage (right)

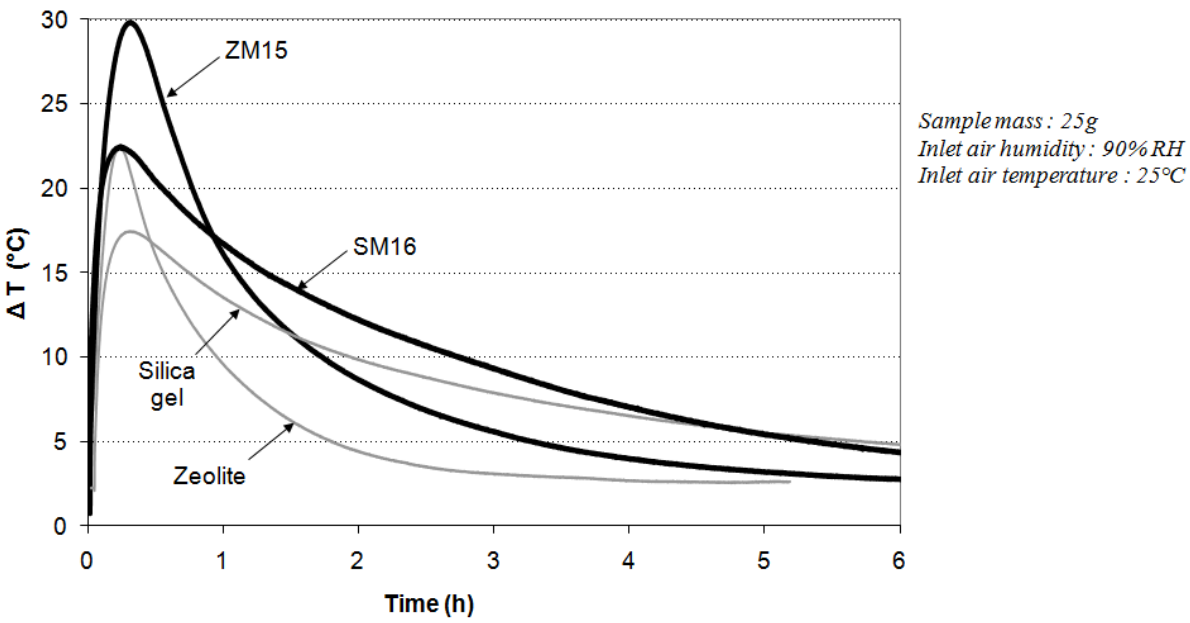


Figure 3. Temperature lift versus composite material – hydration (SM16 is a Silica gel/$MgSO_4$ composite material and ZM15 a zeolite/$MgSO_4$ composite material)

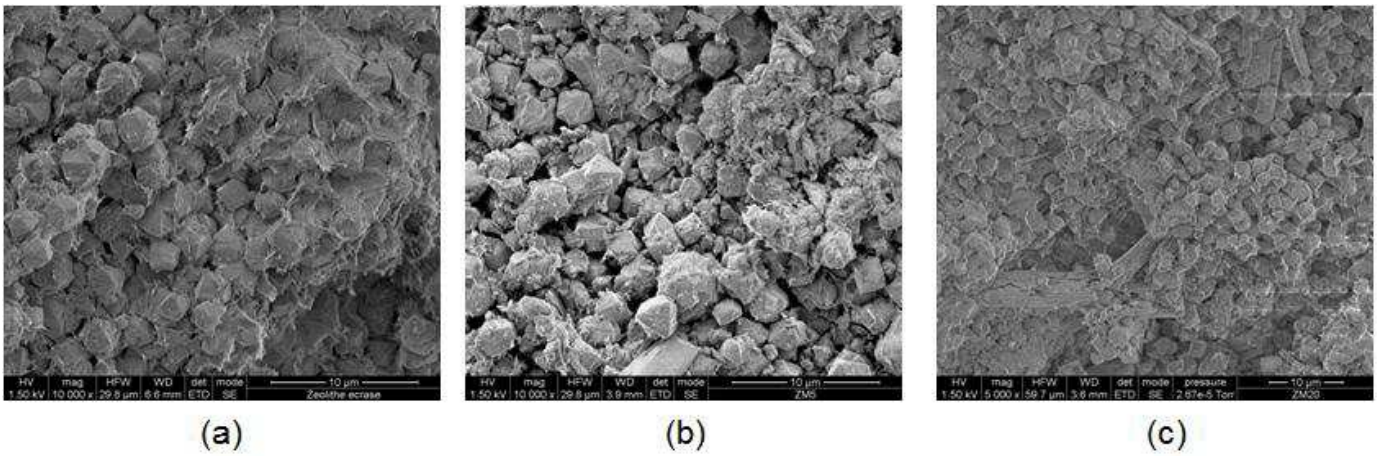


Figure 4. Pictures of (a) zeolite, (b) form-stable zeolite/15%$_{wt}$$MgSO_4$ composite, (c) zeolite-20%$_{wt}$$MgSO_4$ composite

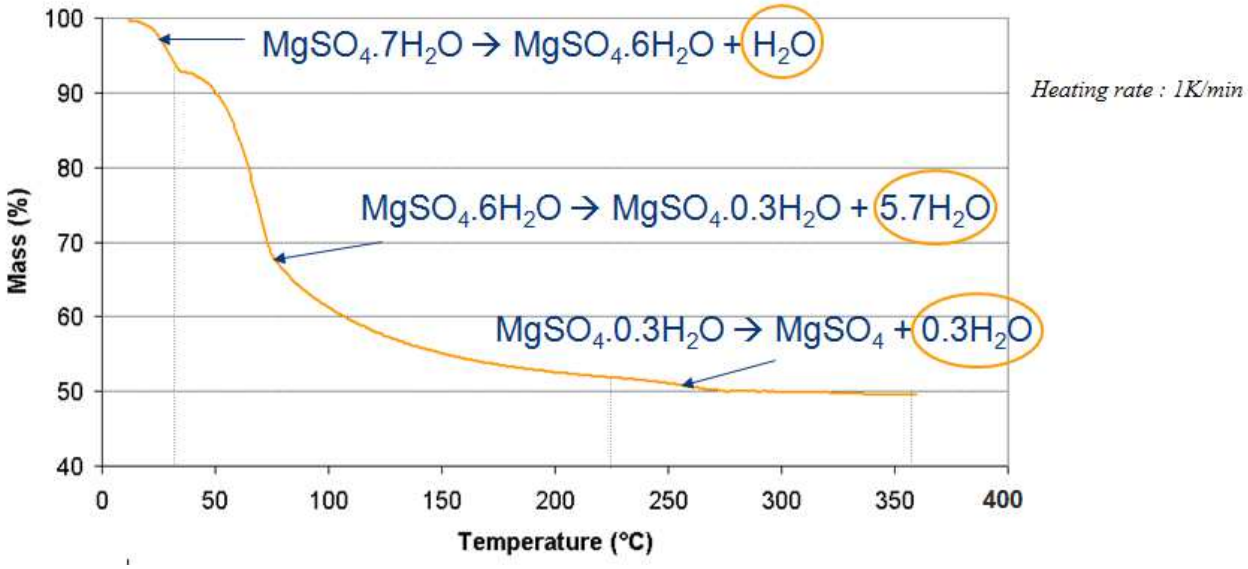


Figure 5. Thermogravimetric analysis of pure $MgSO_4$

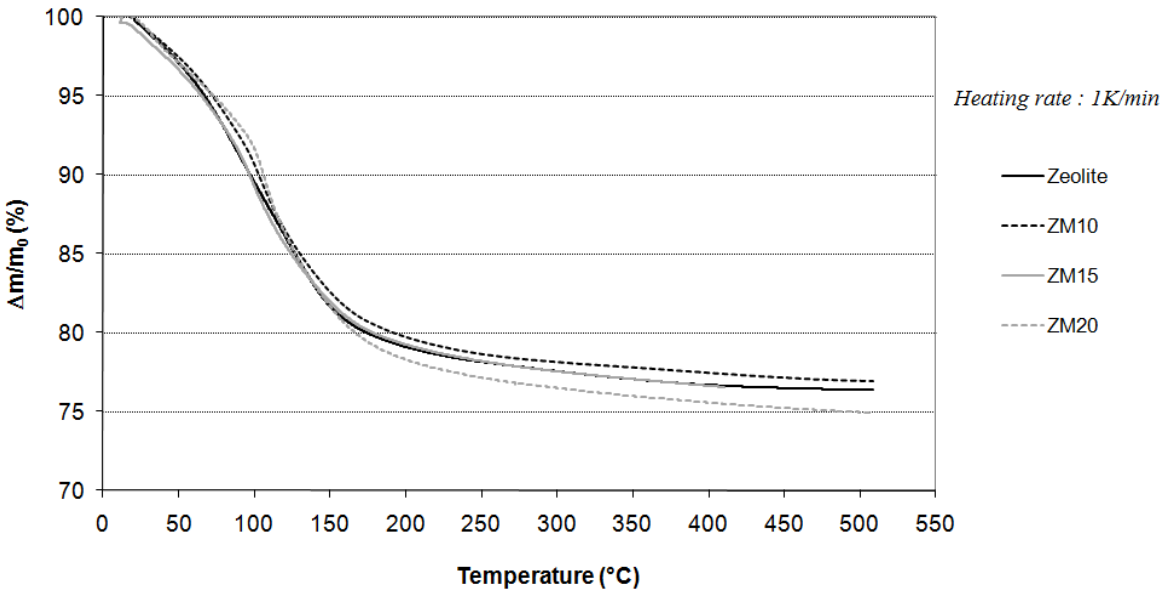


Figure 6. Thermogravimetric analysis of the zeolite/$MgSO_4$ composites

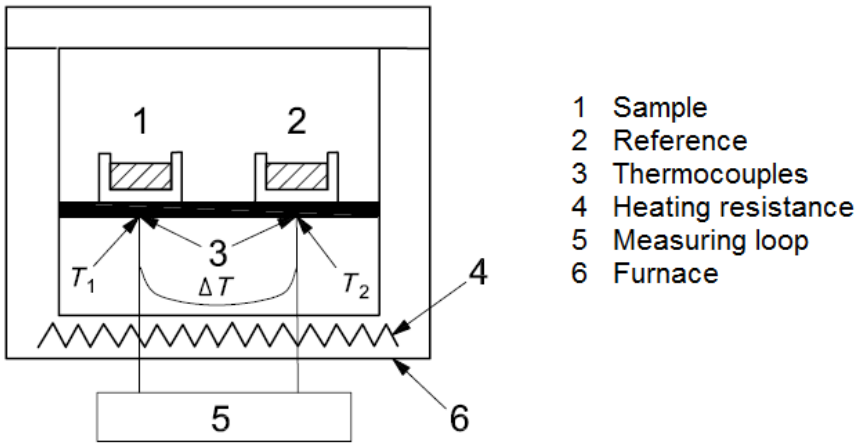


Figure 7. Principle of the heat flow calorimetry

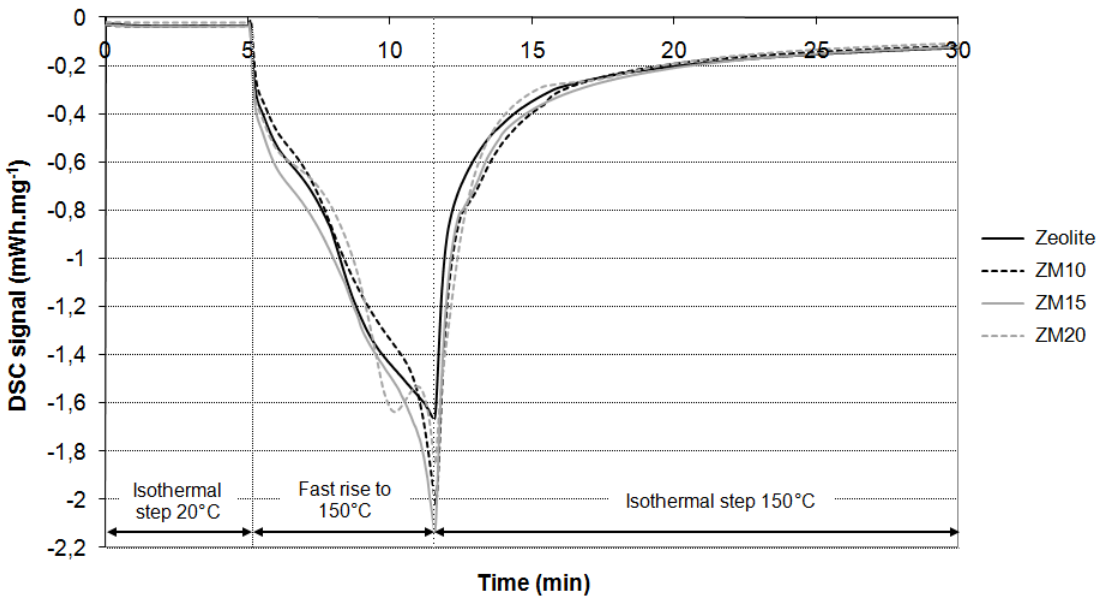


Figure 8. DSC analysis of the zeolite/$MgSO_4$ composites

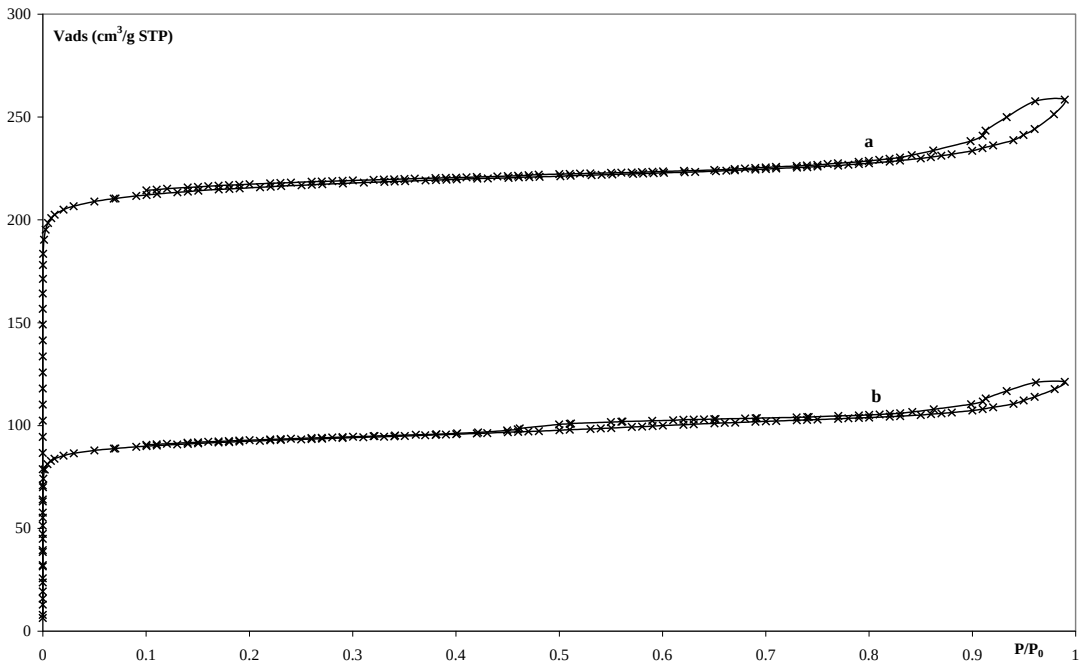


Figure 9. N_2 adsorption isotherm on pure zeolite (a) and ZM25 (b) at 77K

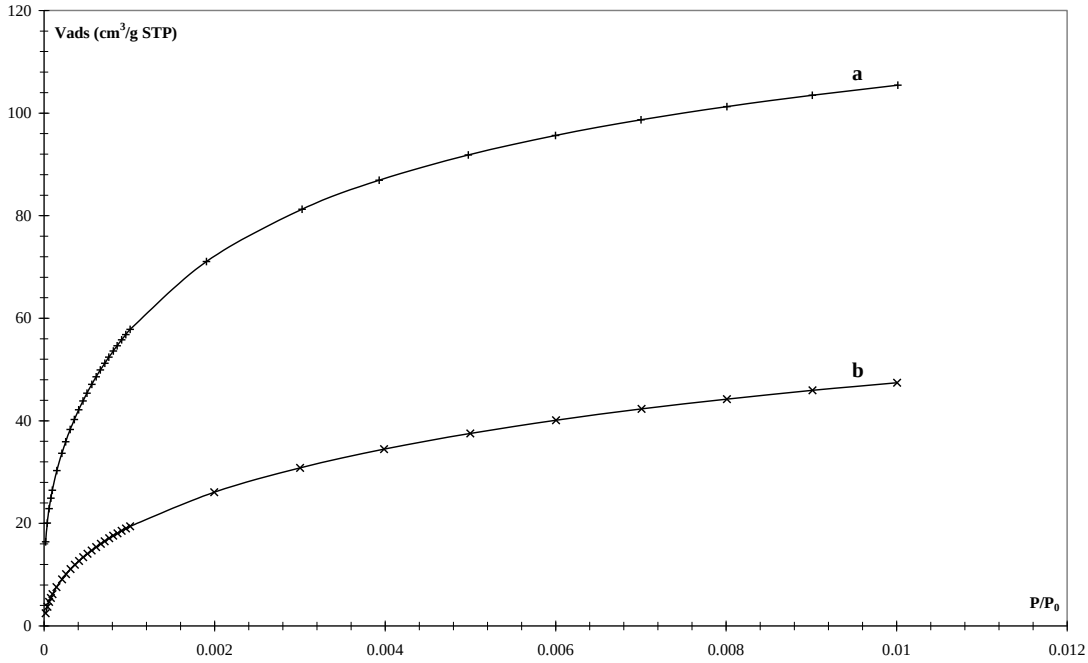
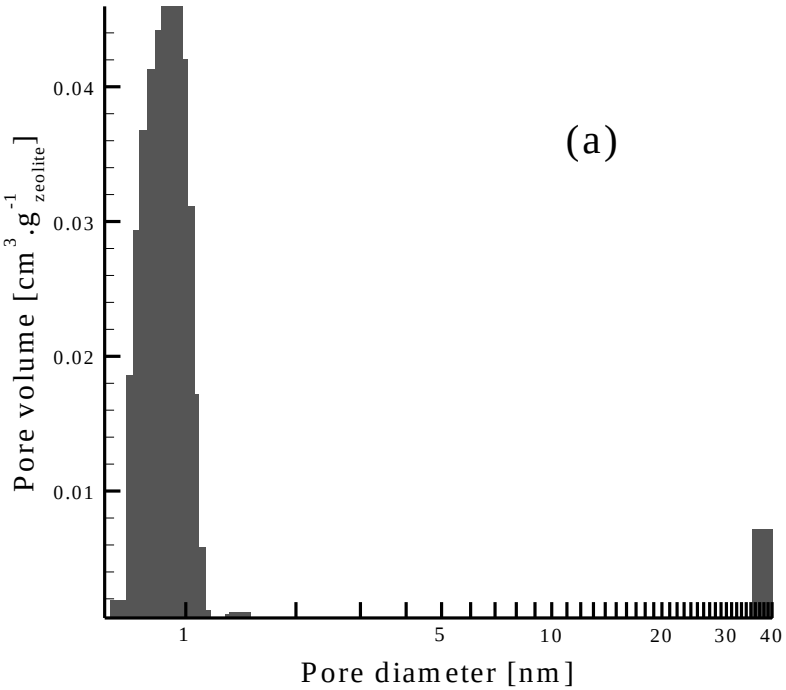


Figure 10. CO_2 adsorption isotherm on pure zeolite (a) and ZM25 (b) at 293K



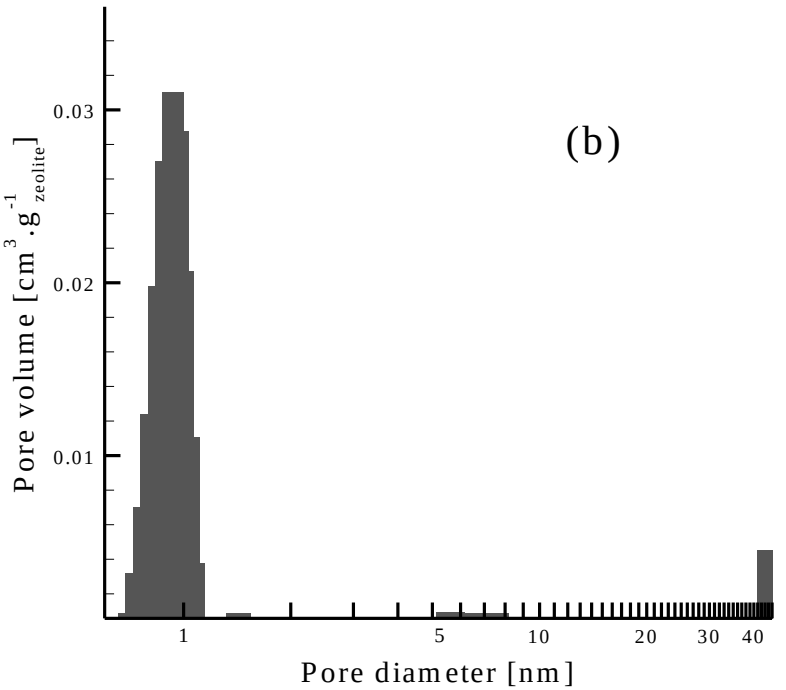


Figure 11. Pore size distribution of zeolite (a) and ZM25 (b)

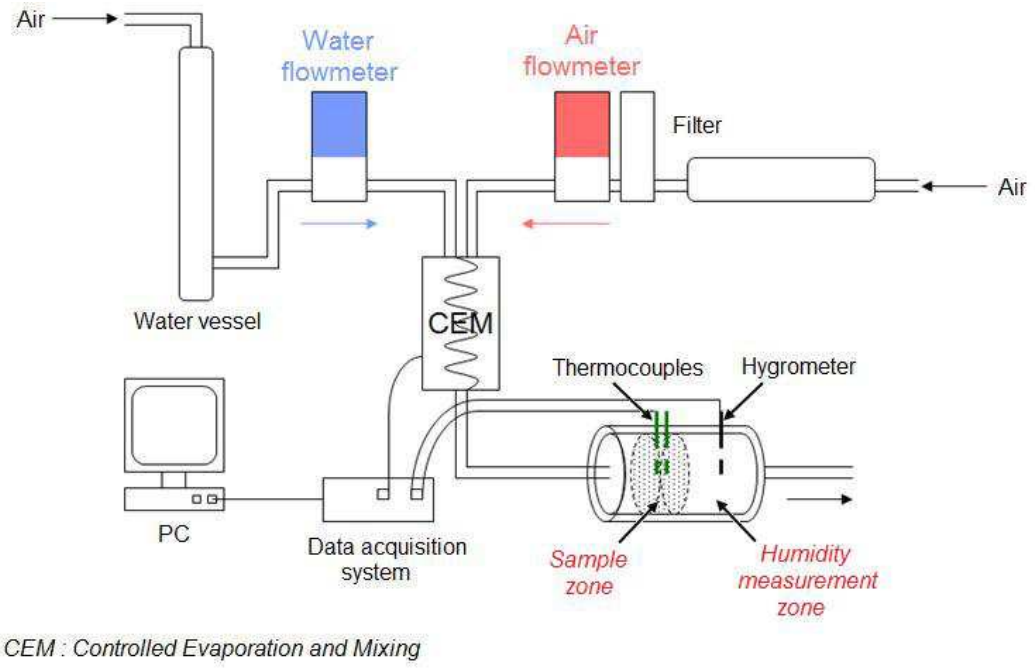


Figure 12. Experimental set-up for hydration tests

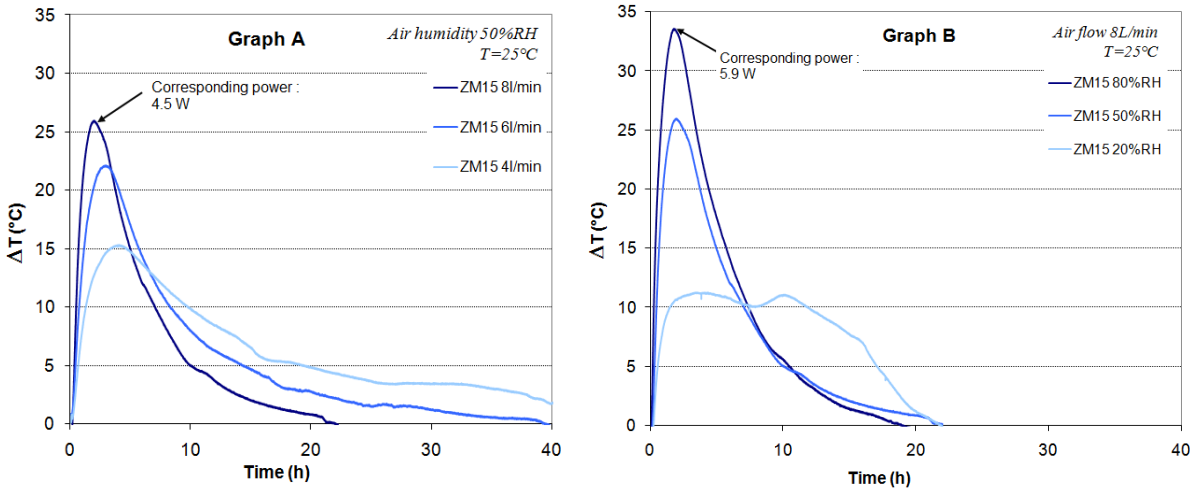


Figure 13. Temperature lifts in the macro-reactor - Influence of the air flow (graph A) and humidity (graph B)

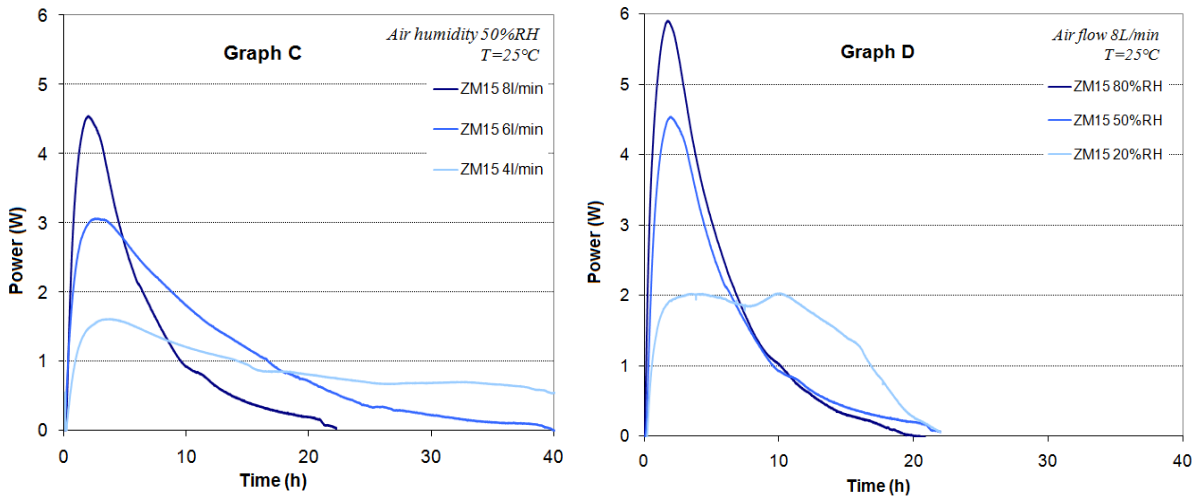


Figure 14. Power released in the macro-reactor - Influence of the air flow (graph C) and humidity (graph D)

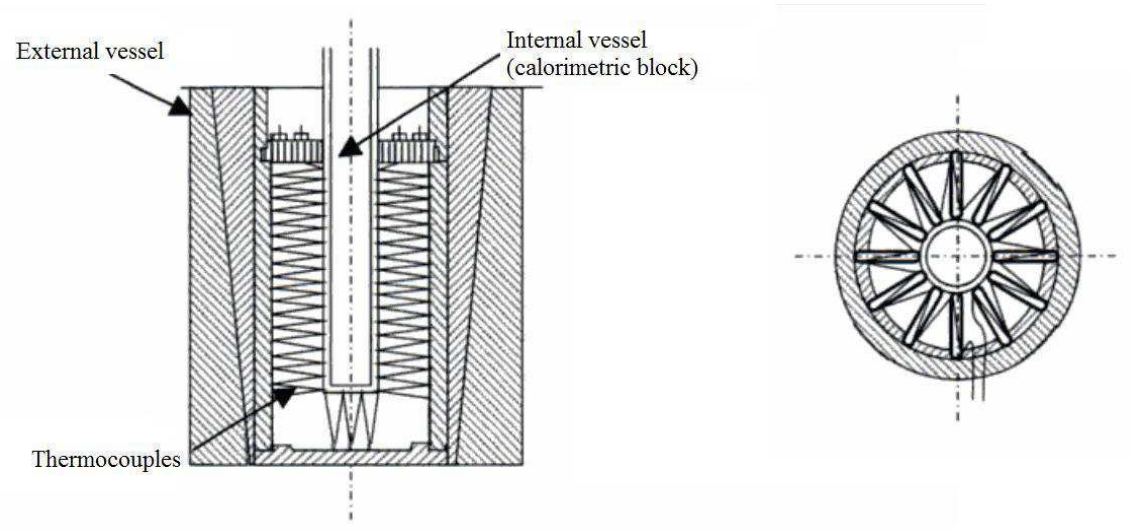


Figure 15. The Calvet calorimetric cell (cross-section and top view)

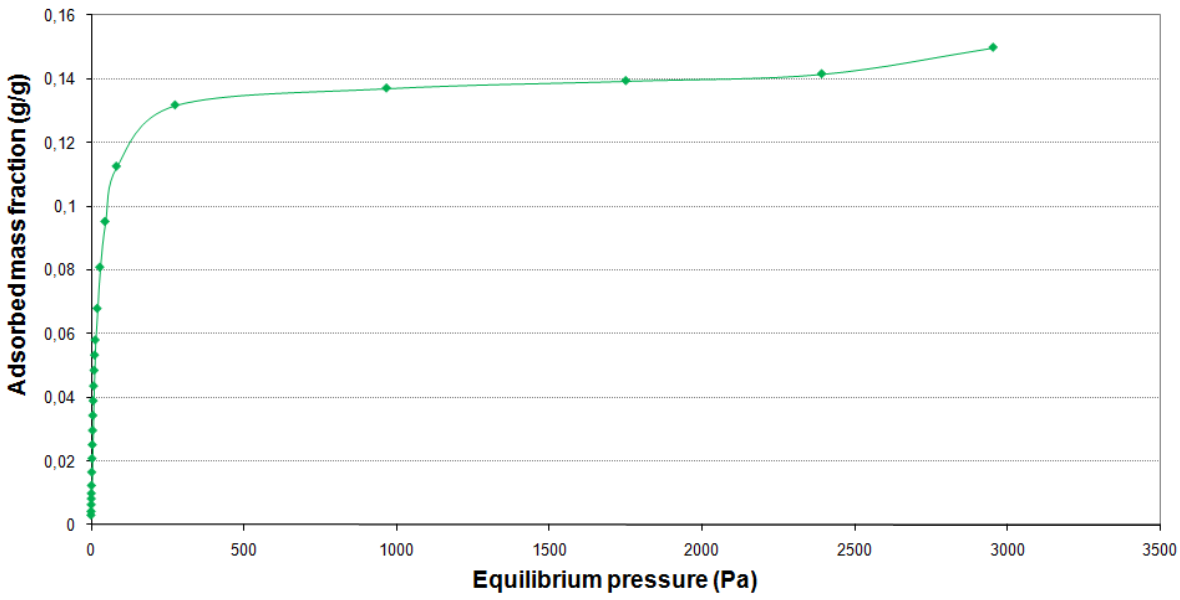


Figure 16. Water vapour isotherm on ZM15 composite material at 30°C

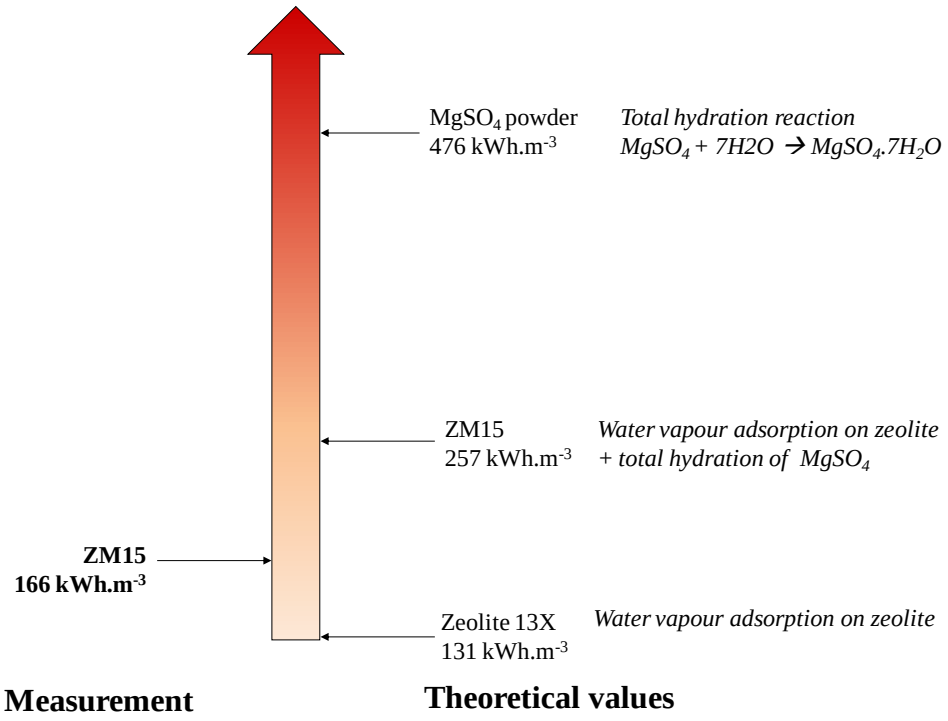


Figure 17. Energy densities comparison