

THERMOCHEMICAL STORAGE USING COMPOSITE MATERIALS: FROM THE MATERIAL TO THE SYSTEM

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Abstract

A seasonal chemical heat store, based on the hydration/dehydration cycle of a magnesium sulphate (MgSO_4) composite material, is under development. 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 is developed.

The active material needs to be dispersed to optimise the gas-solid reaction kinetics and the thermal power released/absorbed. Zeolite has proved to be a favourable porous expanded structure for MgSO_4 , with energy densities of 150-400 kWh/m³ at a storage temperature compatible with solar thermal collectors. Characterisation by Thermo Gravimetric Analysis (TGA) and Differential Scanning Calorimetry (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 greater scale, during hydration tests on 200g samples, an energy density of 0.18Wh/g is achieved, i.e. 45% of the theoretical energy density of the form-stable zeolite- MgSO_4 composite sorbent.

Keywords: thermal energy storage, thermochemical storage, magnesium sulphate, zeolite, composite sorbent.

1. Introduction

Nowadays, thermal energy storage systems are essential for reducing dependency on fossil fuels and then contributing to a more efficient environmentally benign energy use [1]. As demand in thermal comfort of buildings rise increasingly, the energy consumption is correspondingly increasing. For example, in France, the energy consumption of buildings has increased by 30% 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 CO₂ emissions [2].

The annual solar energy incident on building surfaces is far more important than the building needs, i.e. space heating and hot water, especially during the summer season. It is obvious that a long-term thermal energy storage system is necessary 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 a seasonal heat storage (fig 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 [3] :

- MgSO_4 & H_2O with an energy storage density of 2.8 GJ/m^3 ,
- Si & O_2 with an energy storage density of 37.9 GJ/m^3 ,
- FeO & CO_2 with an energy storage density of 2.6 GJ/m^3 ,
- FeO & H_2O with an energy storage density of 2.2 GJ/m^3 ,
- CaSO_4 & H_2O with an energy storage density of 1.4 GJ/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 and the availability of the chemical reaction components. The subject of this study is to develop a magnesium sulphate based composite material for long term thermal energy storage.

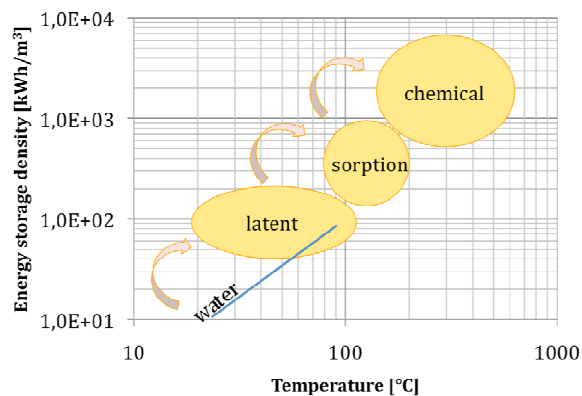


Fig. 1. Storage density versus physical phenomena

2. Presentation of the thermal energy storage concept

The main idea 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 hydration exothermal reaction into a reactor. 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 composite material, typically in summer, requires hot air between 80°C and 150°C . The higher is 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.

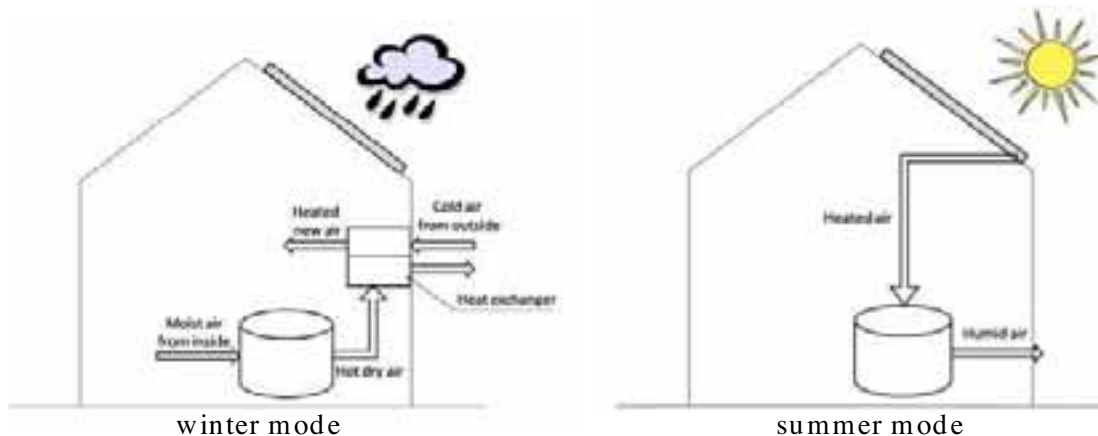
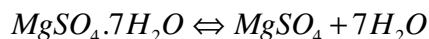


Fig. 2. Presentation of the storage concept: heat release from the store (left) and heat storage (right)

3. Composite material development : heuristic arguments

The chemical reaction concerning the sulphate magnesium is:



Magnesium sulphate is a fine powder which is difficult to use in a storage reactor. A composite material was therefore developed, using a mesoporous matrix to offer a high specific surface allowing 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. These pellets form a bidispersed porous structure: whereas the zeolite crystals are microporous (pore diameter 1nm), the zeolite pellets are mesoporous (pore diameter > 2nm).

The temperature lift obtained for the two composites tested, zeolite+MgSO₄ and silica gel+MgSO₄, is shown in figure 3. The objective of a storage system for building use is to have a temperature lift of at least 20°C during the heat release process. The selected candidate for our studies is then a mesoporous zeolite matrix with magnesium sulphate.

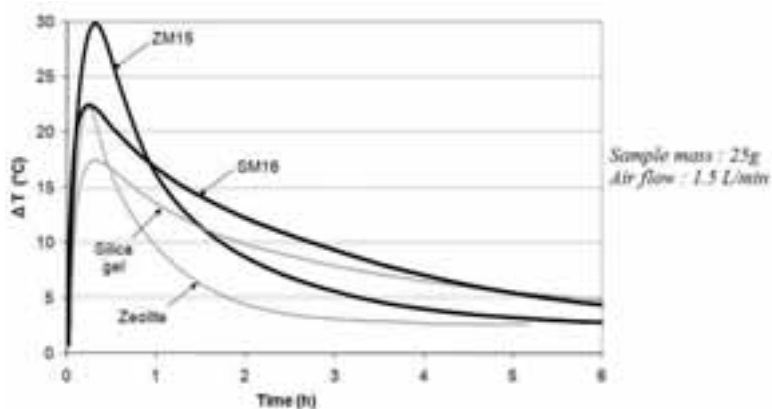


Fig. 3. Temperature lift versus composite material – Hydration

4. Characterisation of the storage composite material

4.1. SEM characterisation of the zeolite/MgSO₄ composite material

The Scanning Electron Microscope (SEM) pictures of zeolite, zeolite-15%_wtMgSO₄ (ZM15), and zeolite-25%_wtMgSO₄ composite (ZM25) are shown in fig. 4. When observing both images from (a) to (c), it can be clearly seen that the mesoporosity of the zeolite pellet is gradually occupied by the MgSO₄ salt as the mass fraction of MgSO₄ increase.

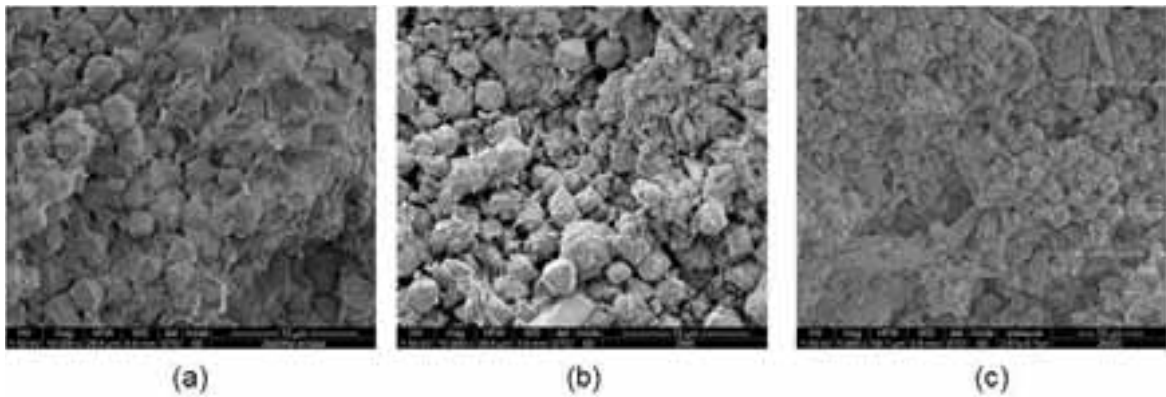


Fig. 4. SEM pictures of (a) zeolite, (b) form-stable zeolite/15%_wtMgSO₄ composite, (c) zeolite-20%_wtMgSO₄ composite

4.2. Thermogravimetric analysis of form-stable zeolite/MgSO₄

Thermogravimetric analysis or thermal gravimetric analysis (TGA) was performed on the samples to determine changes in weight in relation to change in temperature. The TGA of 10 mg of pure magnesium sulphate is shown in fig 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%.

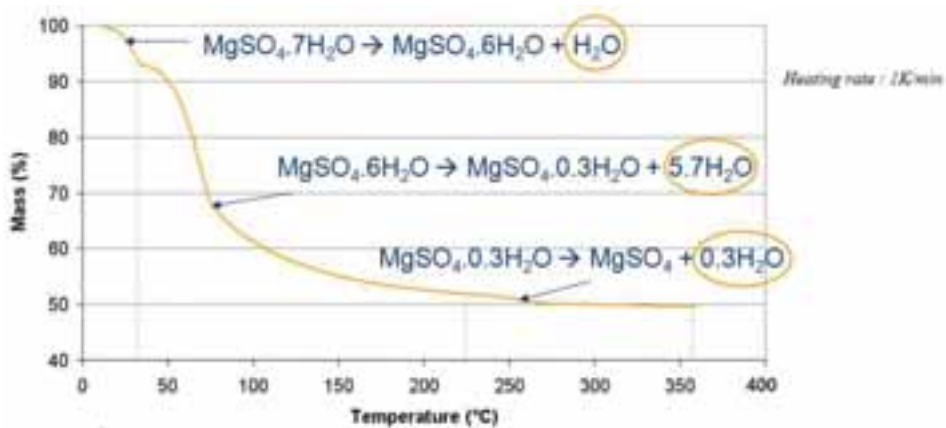


Fig. 5. Thermogravimetric analysis of pure MgSO₄

The same TG analysis performed on 10 mg of the zeolite-MgSO₄ composite materials show a less resolved curve, with a more continuous dehydration phase. The tested materials are zeolite-MgSO₄ with 10%_{wt}, 15%_{wt}, and 20%_{wt} of MgSO₄ (respectively ZM10, ZM15 and ZM20). The successive dehydration steps are no longer discernable (fig. 6). In terms of mass percent of water desorbed, the behaviours of the composites compared to the zeolite are difficult to separate.

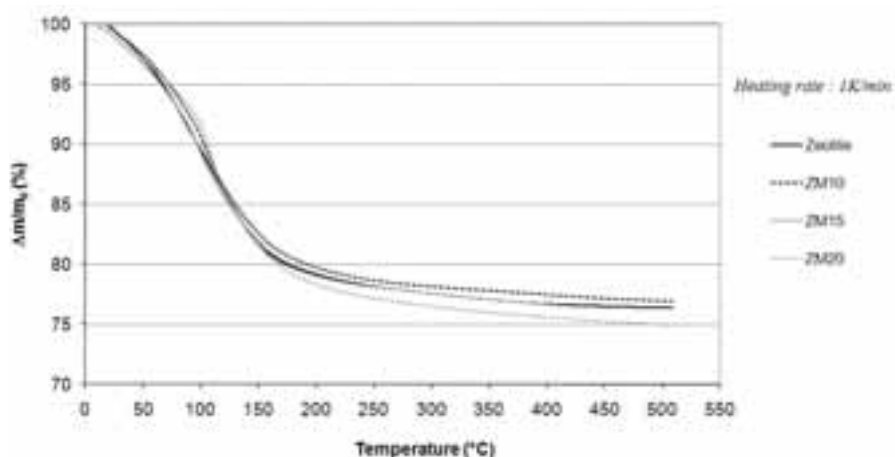


Fig. 6. Thermogravimetric analysis of the zeolite/MgSO₄ composites

Other dehydration tests at the mg scale with an isothermal step at 150°C give relevant information : a large part of the total 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 MgSO₄ and 80% of the initial water content of the hydrated zeolite-MgSO₄ materials is lost at T ≤ 150°C, after 2 hours.

4.3. Differential scanning calorimetry analysis of form-stable zeolite/MgSO₄

The apparatus is a heat flow calorimeter (fig. 7). The principle is based the difference of specific heat capacities between a reference material and the sample, which create a temperature difference. The heat flux difference is then calculated using this temperature difference [4].

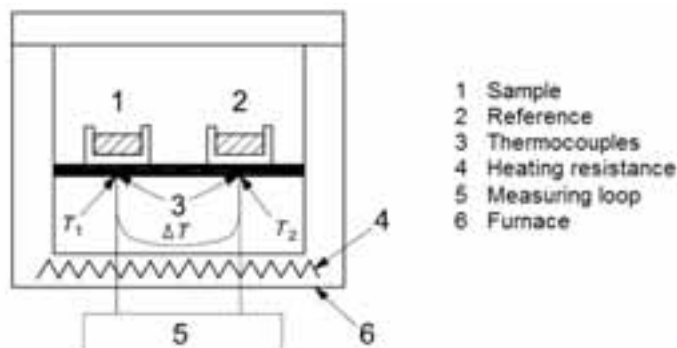


Fig. 7. Principle of the heat flow calorimetry

Differential Scanning Calorimetry (DSC) measures have been performed on zeolite, MgSO_4 and zeolite- MgSO_4 materials ZM10, ZM15 and ZM20. The deepest endothermic peak corresponds to the zeolite-15%_wt MgSO_4 dehydration. 15%_wt seems to be close to the optimal proportion of magnesium sulphate.

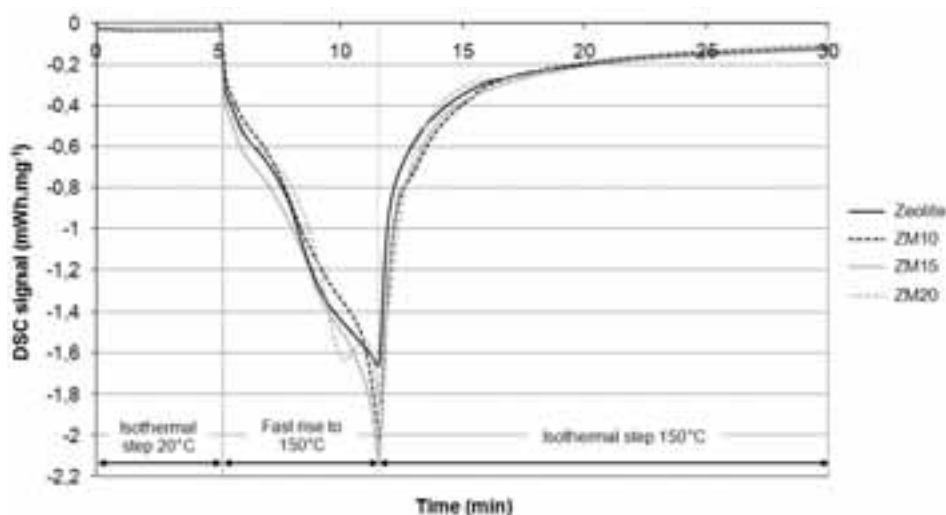


Fig. 8. DSC analysis of the zeolite/ MgSO_4 composites

4.4. Macro-reactor experiment of form-stable zeolite/ MgSO_4

Hydration tests have been carried out in a macro-reactor described in the figure 9. This reactor is divided in two zones : the first contains the sample (200g of zeolite- MgSO_4) whereas the second is dedicated to humidity measurements.

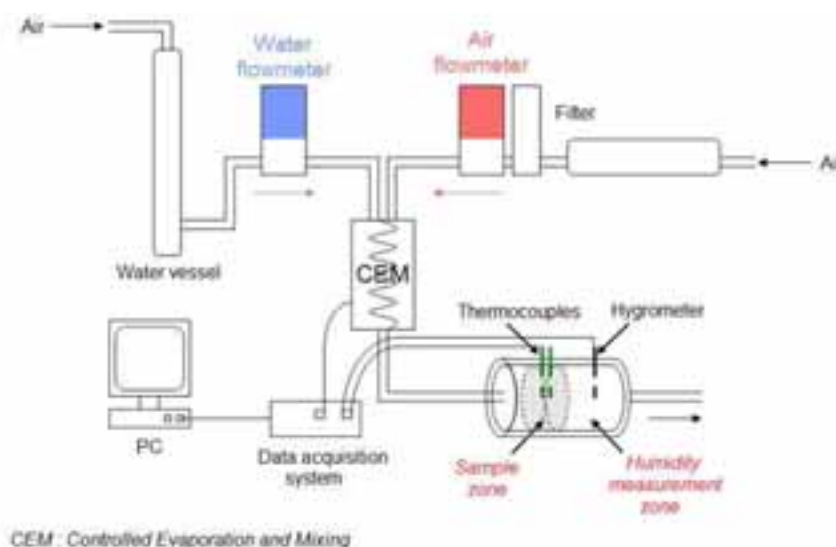


Fig. 9. Experimental set-up for hydration tests

The influence of two main controlling parameters has been studied : the air mass flux 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 released thermal powers as a function of time are respectively represented in the figures 10 and 11.

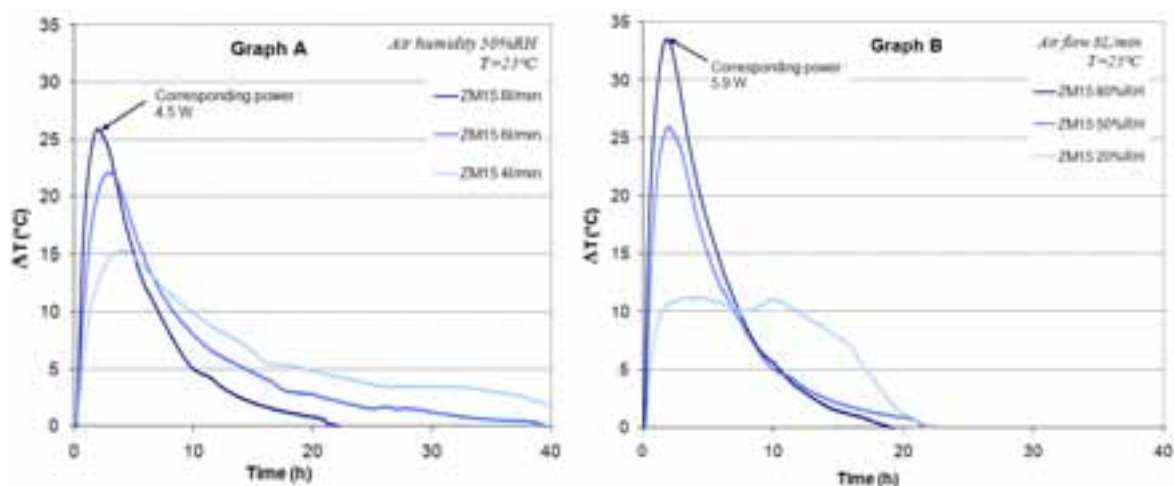


Fig. 10. Temperature lifts in the macro-reactor - Influence of the air flow (graph A) and humidity (graph B)

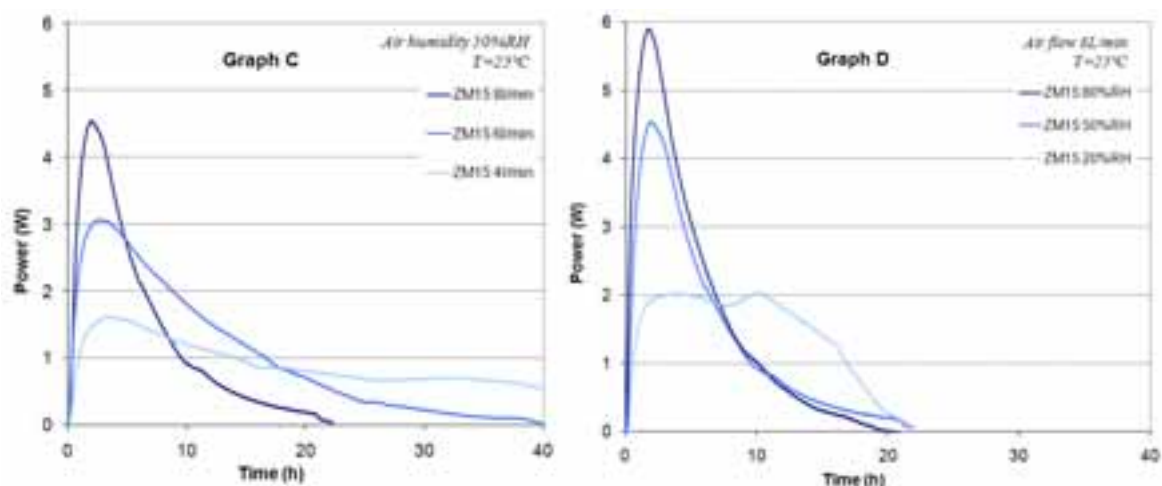


Fig. 11. Power released in the macro-reactor - Influence of the air flow (graph C) and humidity (graph D)

The maximum temperature lifts and power values are measured for the highest airflow rate (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-MgSO₄. The results show that the system is highly sensitive to the humidity of the inlet air. Indeed, the inlet air relative humidity must be at least at 50% in order to get a usable heat with a $\Delta T=15^{\circ}\text{C}$.

5. Conclusion

The development and characterisation of a novel zeolite/MgSO₄ form-stable composite for low temperature heat storage applications in buildings is presented in this paper. The MgSO₄ component was confined in the mesoporous 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 is obtained, i.e. 45% of the theoretical energy density of ZM. 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.

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