

Experimental Investigation of a Solid / Moist Air Thermo chemical Storage Process for Waste Heat Recovery

Mr. Jeffy Scaria
Dept. of Mechanical Engineering
LBS College of Engineering
Kasaragod, India

Prof. Swaraj Kumar B
Dept. of Mechanical Engineering
LBS College of Engineering
Kasaragod, India

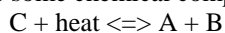
Abstract— Thermal energy storage (TES) is regarded as an enabling technology with a variety of applications, especially regarding energy efficiency and usage of renewable and waste heat. TES materials, in this aspect, provide much higher storage capacities per mass or volume compared to sensible or latent heat storage, often by a factor of 10 or more compared to water storage, which is the most often used storage type. Moreover, thermo chemical storage materials can store the heat for infinite time without insulation and are regarded as a key technology for heat transport and long term storage. TES is based on two reactions, one endothermic and one exothermic which are reversible. In this work our aim was to design a thermo chemical heat storage system that can store waste heat from a stationary IC engine exhaust for long durations and which should be able to heat water for household purposes when required. In this study we reviewed various thermo chemical materials based on its characteristics and our requirements, $MgCl_2 \cdot 6H_2O$ or magnesium chloride hex hydrate was chosen. Dehydration of $MgCl_2 \cdot 6H_2O$ at about $120^\circ C$ into $MgCl_2 \cdot H_2O$ stored heat energy (charging), and hydration of this mono hydrate released the stored heat (discharging). A reactor for the reversible reaction and heat transfers from the chemical to water and from exhaust to chemical was designed and fabricated. In this work the TES capability of the reactor is investigated. Making of an efficient, compact and practical reactor was the core idea of the work. Promising results were obtained from the magnesium chloride hex hydrate filled thermo chemical reactor. Upto 65.35% of the stored thermal energy were recovered from the reactor after one day of storing. And 37.72% of the stored thermal energy were recovered after one month of storage.

Keywords—Thermal Energy Storage, Thermochemical Heat, Magnesium Chloride.

I. INTRODUCTION

The main principle of thermo chemical TES is based on a reaction that can be reversed:

Let A,B and C be some chemical compounds.



In this reaction, a thermo chemical material (C) absorbs energy and is converted chemically into two components (A and B), which can be stored separately. The reverse reaction occurs when materials A and B are combined together and C is formed. Energy is released during this reaction and constitutes the recovered thermal energy from the TES. The storage capacity of this system is the heat of reaction when

material C is formed. When energy is released, the reaction is exothermic.

Thermo chemical TES systems have several advantages over other types of TES:

- Components (A and B) can usually be stored separately at ambient temperature, after cooling to ambient conditions subsequent to their formation. Therefore there is little or no heat loss during the storing period and, as a consequence, insulation is not needed.
- As a result of the low heat losses, thermo chemical TES systems are especially suitable for long-term energy storage (e.g., seasonal storage).
- Thermo chemical materials have higher energy densities relative to PCMs and sensible storage media. Because of higher energy density, thermo chemical TES systems can provide more compact energy storage relative to latent and sensible TES. This attribute is particularly beneficial where space for the TES is limited or valuable.

The main objective of this work is to study the feasibility of thermo chemical energy storage system. Compared to sensible and latent thermal energy storage systems, chemical thermal energy storage system has very high energy storage density. Also in the process, thermal energy is stored as chemical energy. Hence thermal energy can be stored in room temperatures, which means there will be no loss due to convection or radiation.

In this work, first objective is to select the source of heat used for storing. Even though the first idea was to use solar heat, due to difficulties in obtaining high temperatures and maintaining that temperature it was discarded. Then the waste heat from the exhaust of diesel engine was selected. The next main objective is to select a suitable thermo chemical compound. Chemical compound is selected according to the temperature availability from the source. Chemical compound selection is through a wide literature survey.

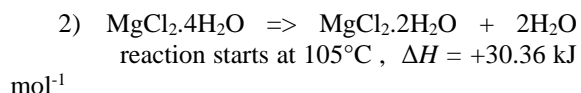
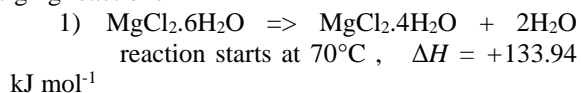
After selecting the thermo chemical compound, its reactions and enthalpy changes during the reactions are to be studied. Then a reactor for the charging and discharging reactions is to be designed and fabricated. After fabrication, the reactor is to be tested for its thermal storage capabilities under various conditions.

Properties of various thermo chemical compounds were reviewed on various research papers and review papers. $MgCl_2 \cdot 6H_2O$ and $CaCl_2 \cdot 6H_2O$ had temperature levels useful for space and water heating and $Mg(OH)_2$ and $Ca(OH)_2$ were good for higher temperature levels ($> 500 K$). While $Ca(OH)_2$ showed good reactivity and overall behavior, but only relevant for high-temperature heat storage. $Mg(OH)_2$ and the hydrated sulphates showed less sufficient reactivity in the hydration process. The calcium sulphate can be used only for low temperature applications. The chloride salt hydrates on the other hand showed good reactivity under all circumstances. But they are known to be quite corrosive and show a certain tendency to over-hydrate, developing a gel-like consistency which significantly hinders the ability to store and release heat. Moreover, when using $MgCl_2 \cdot 6H_2O$, care is to be taken, as the material shows thermal decomposition releasing HCl above certain temperatures. Whereas reviewed papers state that thermal decomposition of $MgCl_2 \cdot 6H_2O$ starts at temperatures above $100-130^\circ C$, in their experiments at low pressures. Hence comparing all factors observed from other research papers, it is concluded that magnesium chloride is the best material to be used for thermo chemical application in the charging temperature range of $100^\circ C$ to $130^\circ C$.

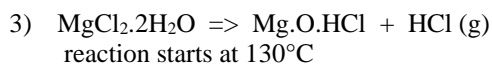
II. CHEMICAL REACTIONS INVOLVED

Enthalpy data for the reactions were obtained from *national institute of standards and technology (NIST), chemistry web book*.

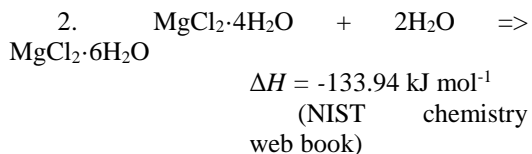
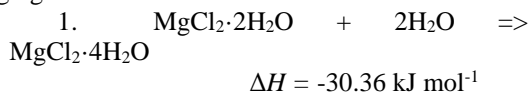
Charging reactions



Above two are the required reactions. Further dehydration of $MgCl_2 \cdot 2H_2O$ is not possible by heating. Further heating starts following reaction, which is irreversible and must be avoided.



Discharging reactions



Where, ΔH is the enthalpy change during reaction.

Molar mass of $MgCl_2 \cdot 6H_2O$ is 203.3 g/mol

Molar mass of $MgCl_2 \cdot 2H_2O$ is 131.1 g/mol

Total enthalpy change

$$-133.94 \text{ kJ mol}^{-1} + -30.36 \text{ kJ mol}^{-1} = -164.24 \text{ kJ mol}^{-1}$$

Mass of $MgCl_2 \cdot 2H_2O$ to test in the reactor is 600 g , which is 4.57 moles. Hence total hydration enthalpy is $4.57 \text{ mol} \times -164.24 \text{ kJ mol}^{-1} = \mathbf{751.6 \text{ kJ}}$. Hence 600 g of $MgCl_2 \cdot 2H_2O$ can store 751.6 kJ of thermal energy.

III. EXPERIMENTAL SETUP AND PROCEDURE

The thermo chemical reaction requires sufficient quantity of moisture to come in contact with the chemical compound. The heat released during the reaction should be transferred to the flowing water. Both these requirements are made possible in thermo chemical reactor system. The reactor fabricated for the experiment is shown in Fig 1. The thermo chemical reactor was made with stainless steel material. Water inlet is supplied through the centre pipe, from which water travels through 6 branches in radial direction, which individually branches into double pipes. The double pipes are enclosed in rectangular trays, which carries the thermo chemical compound. The branched out water joins into the outer circular pipe, and hot water is taken out from a single outlet. The moisture needed for the thermo chemical reaction is supplied from the top directly to the trays.



Fig 1. Thermo chemical reactor

In first test, reactor trays were filled with $MgCl_2 \cdot 6H_2O$. Engine exhaust was connected to the reactor inlet. Engine was started and temperature started building up. In 5 minutes the double pipe wall temperature reached $118^\circ C$ and dehydration started. After 20 minutes chemical compound around the double pipe were completely dehydrated, but heat was not reaching the bulk in whole tray. The engine was turned off. After a cooling off time of 20 minutes, the discharging performance was tested, Water inlet at 2 lpm (liters per min) was supplied at inlet and water sprayed on top of dome to start the reaction. hot water temperature was measured at outlet and results were plotted. In the second test, $MgCl_2 \cdot 6H_2O$ was dehydrated by heating it on a gas burner. So that the whole compound could be dehydrated evenly to test the compounds storing capability. In this test 1 kg of $MgCl_2 \cdot 6H_2O$ was heated to obtain 600 g of $MgCl_2 \cdot 2H_2O$. Each tray filled with 100 g of $MgCl_2 \cdot 2H_2O$. Water inlet at 2 lpm was supplied at inlet and water sprayed on top of dome to start the reaction. hot water temperature was measured at outlet.



Fig 2. Tray half filled with $MgCl_2 \cdot 6H_2O$, double pipe passing through tray visible

In third test, the dehydrated $MgCl_2 \cdot 2H_2O$ was stored for 1 month in an air tight jar, so as to test the storing potential of the compound. The performance was tested for same quantity and method as in second test. And the results were noted down and plotted.

By the inferences from second and third tests, fourth test was conducted with an additive mixed with the thermo chemical compound. $Mg_3Si_4O_{10}(OH)_2$, hydrated magnesium silicate or also called as talc was added as anti caking agent to improve the heat discharge during hydration. Same quantity of 600 g and same water flow rate of 2lpm were used in the experiment to compare it with previous performances

IV. EXPERIMENT RESULTS

In first test, $MgCl_2 \cdot 6H_2O$ in the tray was heated with the exhaust heat from the engine for 20 minutes. But the whole compound in the tray could not be dehydrated, as the contact area was not sufficient. The compound which was in contact with the double pipe inside the tray was dehydrated to $MgCl_2 \cdot 2H_2O$. Total energy required to dehydrate 930.43g of $MgCl_2 \cdot 6H_2O$ into 600g of $MgCl_2 \cdot 2H_2O$ is **751.6 kJ**.

As we could not obtain required dehydration, the percentage of recovered energy was not calculated.

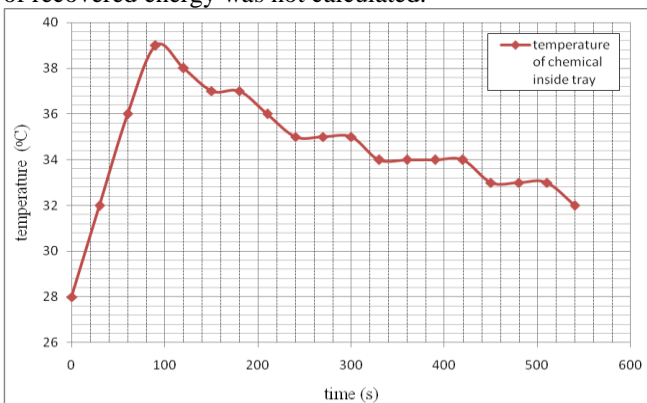


Fig 3. Temperature of chemical compound inside reactor tray, test 1

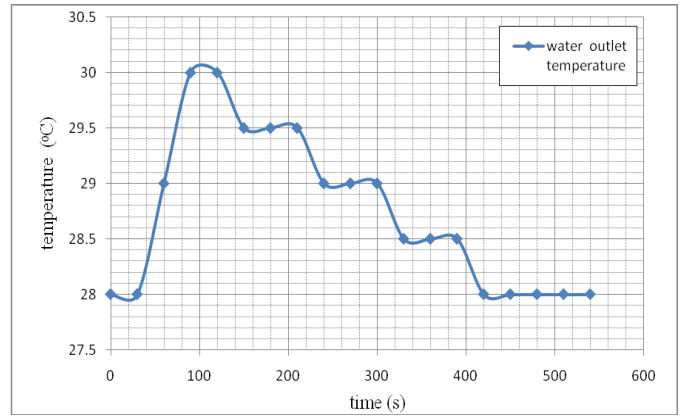


Fig 4. Temperature of water outlet from the reactor, test 1

In test 2, $MgCl_2 \cdot 6H_2O$ was heated on a gas burner to completely dehydrate it. Dehydration started at 100°C. Above 120°C pungent smell was observed, which was the emission of HCl gas. So temperature was maintained between 100°C and 120°C. After dehydration the compound was stored in an air tight jar. After 24 hrs the stored compound was taken out and 600 g of $MgCl_2 \cdot 2H_2O$ was filled into 6 trays 100g each. Water at initial temperature 28°C was supplied to the inlet at 2lpm. Moist air for reaction was supplied from top with water sprayer.

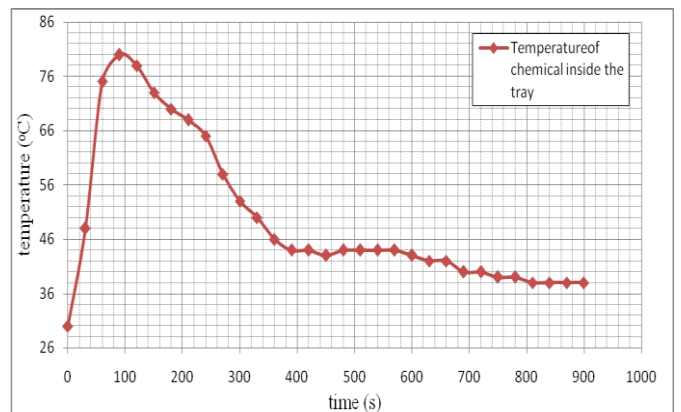


Fig 5. Temperature of chemical compound inside reactor tray, test 2

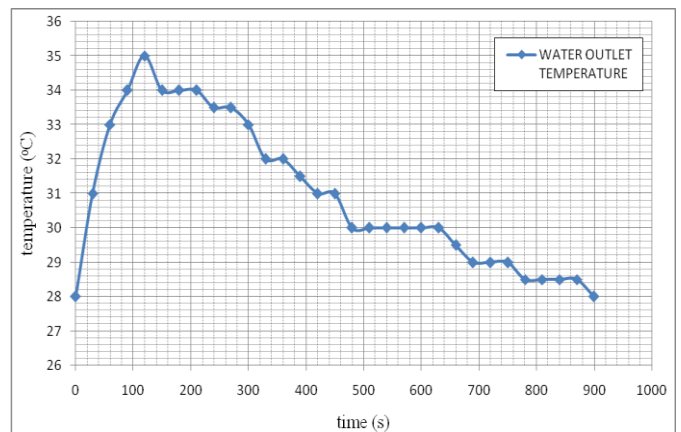


Fig 6. Temperature of water outlet from the reactor, test 2

A maximum temperature of 80°C was observed inside the tray. For water outlet maximum temperature rise of 7°C was observed after 120s. temperature difference became 0 after 900s.

To calculate the heat recovered following method of integration was used.

$$\text{Total heat recovered, } Q = \rho \cdot V \cdot C_p \int \Delta T \cdot dt$$

The function of temperature difference to integrate for this test estimated from MS EXCEL is

$$t = 0.2829 + 0.103T - 5.73 \times 10^{-4} T^2 + 1.24 \times 10^{-6} T^3 - 1.23 \times 10^{-9} T^4 + 4.53 \times 10^{-13} T^5$$

$$Q = 0.1385 \int_0^{900} t \cdot dt$$

$$= 0.1385 \times 2728.29$$

$$= \mathbf{377.93 \text{ kJ}}$$

The total heat of hydration being 751.6 kJ, **50.28 %** was recovered from the thermo chemical compound

In test 3, the long term thermal storage capability of the thermo chemical compound was tested. The dehydrated MgCl₂.2H₂O 600 g was stored in a closed air tight glass jar for 1 month. Being rainy season, atmosphere relative humidity was 90 – 95 %. After 1 month the compound seemed same but was clogged into small lumps. The compound was filled in reactor for test. Water initial temperature was 29 °C, and flow rate was 2 lpm.

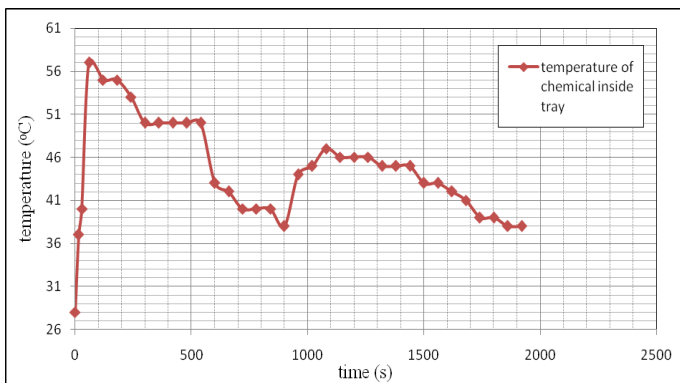


Fig 7. Temperature of chemical compound inside reactor tray, test 3

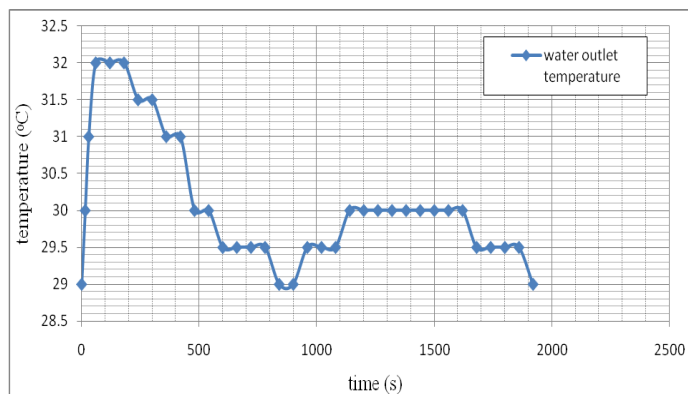


Fig 8. Temperature of water outlet from the reactor , test 3

The maximum tray temperature was only 57 °C, and maximum temperature difference obtained for water flow was 3 °C. 14 minutes (840 s) after start ΔT became 0. On stirring the chemical compound inside the tray, small lumps

of compound were crushed. Again a rise in chemical temperature was observed. There was a corresponding rise in water outlet temperature. After 32 minutes (1920s) from the start of the test water ΔT again was 0. This time hydration of the chemical seemed complete. The function of temperature difference to integrate for this test estimated from MS EXCEL is

$$t = 0.933 + 0.023T - 0.84 \times 10^{-5} T^2 + 1.12 \times 10^{-7} T^3 - 5.94 \times 10^{-11} T^4 + 1.115 \times 10^{-14} T^5$$

$$Q = 0.1385 \int_0^{1920} t \cdot dt$$

$$= 0.1385 \times 2047.37$$

$$= \mathbf{283.56 \text{ kJ}}$$

The total heat of hydration being 751.6 kJ, **37.72 %** was recovered from the thermo chemical compound even after 1 month storage .

From test 3 it was observed that , MgCl₂.2H₂O attracts moisture from atmosphere very fast . It tends to form lumps of crystals. Which during hydration process, prevents the MgCl₂.2H₂O in the inner part of the lump to be in contact with moisture. Hence prevents or slows down heat release from the chemical compound.

Use of anti caking agents can prevent lump formation in powdered substances. One of the most common anti caking agent is hydrated magnesium silicate also called as talc (Mg₃Si₄O₁₀(OH)₂).

In test 4 after dehydrating MgCl₂.6H₂O on gas burner, 600g of MgCl₂.2H₂O was mixed with 50g of talc and was stored in a glass jar. After 24 hrs the mixture was taken for the test. 108 g on each tray, water initial temperature was 28°C. water flow rate was kept same as other tests, 2 lpm.

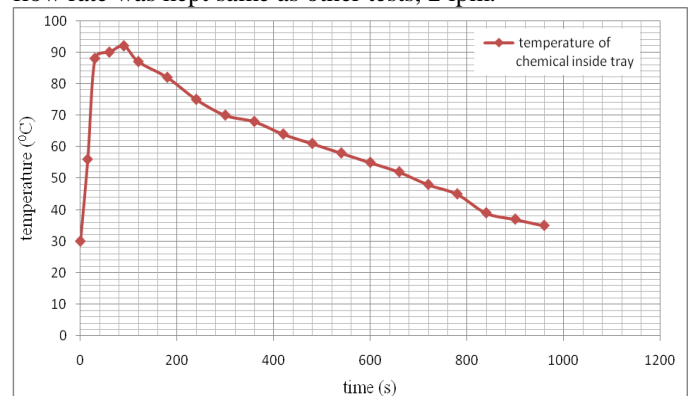


Fig 9. Temperature of chemical compound inside reactor tray, test 4

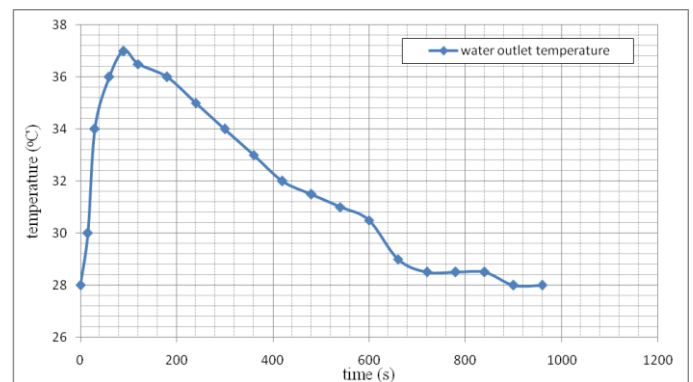


Fig 10. Temperature of water outlet from the reactor , test 4

The function of temperature difference to integrate for this test estimated from MS EXCEL is

$$t = 0.92 + 0.143T - 8.25 \times 10^{-4}T^2 + 1.84 \times 10^{-6}T^3 - 1.83 \times 10^{-9}T^4 + 6.79 \times 10^{-13}T^5$$

$$\begin{aligned} Q &= 0.1385 \int_0^{960} t \cdot dt \\ &= 0.1385 \times 3546.4 \\ &= 491.17 \text{ kJ} \end{aligned}$$

The total heat of hydration being 751.6 kJ, 65.35 % was recovered from the thermo chemical compound. So addition of talc improved the heat recovery efficiency by avoiding lump formation.

V. CONCLUSIONS

Thermo chemical heat storage materials (TCM) have been subject of research for quite a long time. From the data obtained from various research papers and considering the heat source and requirements, a thermo chemical heat storage system was designed and fabricated.

Magnesium chloride gave a storage density of 0.717 GJ/m³. Which is very high compared to ordinary sensible and latent heat storage systems. In first test it was found that the heat exchange from the exhaust to chemical was not efficient, because of smaller contact area. But for the given engines back pressure limitation, adding the number of pipes was not safe. Tests were conducted in the period of April to June of the year 2015. Relative humidity during tests were in the range 90%-94%. Still in long storage period test 37.72% heat was recovered after 1 month storage. As the wall temperature were highly fluctuating and partially filled pipe flows, conduction/convection heat losses were not calculated separately.

Efficiency of the system in various tests were calculated by comparing the heat recovered from system to the total enthalpy of the reaction, that is the total energy stored in the chemical. Heat recovered from system was calculated by integration method, as the water outlet temperatures were varying continuously with time. Test 2 gave an efficiency of 50.28%. From test 2 and 3, the problem of lump formation was observed. Hence talc was mixed as anti caking agent. It reduced lump formation, and improved the efficiency drastically. Test 4 with talc additive gave an efficiency of 65.35%.

REFERENCES

- [1] Ali H. Abedin and Marc A. Rosen "A Critical Review of Thermochemical Energy Storage Systems" Faculty of Engineering and Applied Science, University of Ontario Institute of Technology, Oshawa, Ontario, 2011.
- [2] H.A. Zondag, V.M. van Essen, L.P.J. Bleijendaal, B.W.J. Kikkert, M. Bakker "Application of MgCl₂·6H₂O for thermochemical seasonal solar heat storage" 5th International Renewable Energy Storage Conference IRES November 2010, Berlin, Germany
- [3] a) N.B. Singh, b) B. Middendorf. "Calcium sulphate hemihydrate hydration leading to gypsum crystallization" a) DDU Gorakhpur University, Chemistry Department, Gorakhpur, India, b) University of Dortmund, Department of Building Materials, Dortmund, Germany, 2007
- [4] National Institute of Standards and Technology (NIST), chemistry web book