

# A DFT based equilibrium study of a chemical mixture Tachyhydrite and their lower hydrates for long term heat storage

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**Abstract.** Chloride based salt hydrates are promising materials for seasonal heat storage. However, hydrolysis, a side reaction, deteriorates, their cycle stability. To improve the kinetics and durability, we have investigated the optimum operating conditions of a chemical mixture of  $\text{CaCl}_2$  and  $\text{MgCl}_2$  hydrates. In this study, we apply a GGA-DFT to gain insight into the various hydrates of  $\text{CaMg}_2\text{Cl}_6$ . We have obtained the structural properties, atomic charges and vibrational frequencies of  $\text{CaMg}_2\text{Cl}_6$  hydrates. The entropic contribution and the enthalpy change are quantified from ground state energy and harmonic frequencies. Subsequently, the change in the Gibbs free energy of thermolysis was obtained under a wide range of temperature and pressure. The equilibrium product concentration of thermolysis can be used to design the seasonal heat storage system under different operating conditions.

## 1. Introduction

The variation of solar radiation with geographical basis, daily and seasonal basis is the major concern in its large scale utilizations. The solution of this intermittency is the solar energy storage. Solar energy can be stored in the form of chemical energy (in batteries) or in the form of thermal energy. Thermal energy can be stored by sensible heat, latent heat or thermochemical form. Thermochemical form has highest energy density compared to other thermal forms, therefore suitable for compact heat storage. Salt hydrate, carbonates and hydroxide are major class of promising thermochemical materials (TCMs) for seasonal heat storage [1, 2, 3]. Salt hydrates store energy via a reversible physico-chemical reaction in which it undergo dehydration-hydration reaction for charging and discharging cycle respectively. Chloride based salt hydrates are one class of TCMs having good storage capacity and fast kinetics. Hydrolysis is an irreversible side reaction, which appears in chloride based hydrates (usually in  $\text{MgCl}_2$  hydrates). It produces corrosive  $\text{HCl}$  gas and affects the durability of chloride based salt hydrates.

Mixture of salt hydrates is used to improve the kinetics and hinder undesired side reactions. Hydrolysis can be hindered by mixing with other halides [4]. To decrease the dehydration temperature of  $\text{Mg}(\text{OH})_2$  and  $\text{Ca}(\text{OH})_2$ , various salts like chlorides, acetates, sulphates, and nitrates have been doped and nitrates was found to be effective in decreasing the dehydration temperature [6]. The chemical dopant has been chosen based on either scientific approach or trial and error approach. In the scientific approach, the dopant is chosen as similar structure as the base material while in the second method it is based on a chemical intuition [7]. Posern



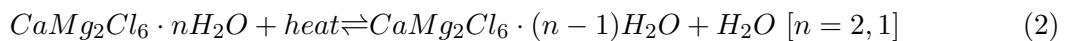
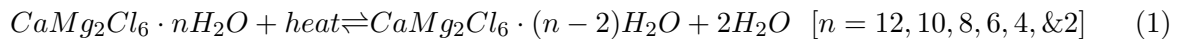
and Kaps have been observed that 20 % of  $\text{MgSO}_4$  hydrate and 85 %  $\text{MgCl}_2$  hydrate mixture has better hydration rate and higher temperature lift [5]. Rammelberg et al. [20] have examined many salt hydrate mixtures to overcome the operational challenges of TCMs like agglomeration, slow kinetics and durability. They observed that the mixture of  $\text{CaCl}_2$  and  $\text{MgCl}_2$  hydrates has faster kinetics and better durability than their ingredient salt hydrates.

Tachyhydrite ( $\text{CaMg}_2\text{Cl}_6 \cdot 12\text{H}_2\text{O}$ ) is a chemical mixture of  $\text{CaCl}_2$  and  $\text{MgCl}_2$  hydrates. It is a naturally occurring hygroscopic material, present in evaporite deposits and cretaceous potash formation [9, 10]. It has been shown a potential application in chemical conversion from  $\alpha$  to  $\beta$  form of spodumene [11]. The salt hydrates of  $\text{CaCl}_2$ ,  $\text{MgCl}_2$ ,  $\text{MgSO}_4$  have been explored using DFT-GGA [16, 17, 18]. In this present study, we will obtain the thermolysis of various hydrates of  $\text{CaMg}_2\text{Cl}_6$  under a wide range of temperature and pressure. The relative stability of their hydrate is analyzed by means of DFT calculations. We obtain the Bader charges and vibrational frequencies for the stable configurations. Subsequently, the equilibrium product concentrations of dehydration and hydrolysis reaction are obtained under various temperature and pressure regimes. These equilibrium curves can be used to predict the operating range and the onset temperature of  $\text{HCl}$  formation (hydrolysis) of various hydrates of  $\text{CaMg}_2\text{Cl}_6$ . These equilibrium curves can be used to design the seasonal heat storage system.

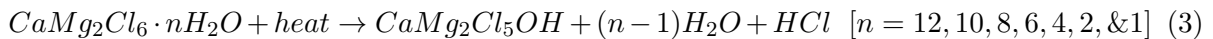
## 2. Methodology

In the present study, all the gaseous molecule of  $\text{CaMg}_2\text{Cl}_6$  hydrates are optimized in DFT using Perdew-Wang exchange and correlation functional (PW91) [15] under generalized gradient approximation (GGA) [13] implemented in Amsterdam Density Functional (ADF) program [12]. A spin restricted Kohn-Sham method is used with double-polarized triple- $\zeta$  basis set by keeping the maximum integration accuracy.

$\text{CaMg}_2\text{Cl}_6$  hydrates can undergo a cycle of hydration/dehydration reactions. The plausible dehydration reaction of  $\text{CaMg}_2\text{Cl}_6$  hydrates can be described similar to the  $\text{CaCl}_2$  and  $\text{MgCl}_2$  hydrates as:



Hydrolysis, an irreversible undesirable side reaction may compete with dehydration in the thermolysis of tachyhydrite. Hydrolysis can be described as;



To investigate the equilibrium condition of above reactions, it is essential to obtain the Gibbs free energy ( $G$ ) of each components at given pressure ( $p$ ) and temperature ( $T$ ). The Gibbs free energy of molecule is defined as:

$$G(T, p) = E^{\text{tot}} - TS^{\text{tot}} + pV \quad (4)$$

The partial contributions in the above equation include total energy ( $E^{\text{tot}}$ ), configurational entropic contribution ( $TS^{\text{tot}}$ ), and  $pV$  term. These partial terms can be further partitioned as:

$$E^{\text{tot}} = E^{\text{rot}} + E^{\text{trans}} + E^{\text{vib}} + E^{\text{ZPE}} + E^{\text{gr}} \quad (5)$$

and

$$S^{\text{tot}} = S^{\text{trans}} + S^{\text{rot}} + S^{\text{vib}} \quad (6)$$

Where in  $E^{rot}$ ,  $E^{trans}$ ,  $E^{vib}$ ,  $E^{ZPE}$ , and  $E^{gr}$  are rotational, translational, vibrational, zero point energy and electronic ground state energy respectively. A  $S^{trans}$ ,  $S^{rot}$ , and  $S^{vib}$  are translational, rotational, and vibrational contribution of the entropy. The optimized geometry, harmonic frequencies, and electronic ground state energy are required to obtained the Gibbs free energy of a molecule under ideal polyatomic gas assumption [21].

The  $\Delta G$  of a chemical reactions can be expressed as:

$$\Delta G = \sum G_{prod} - \sum G_{reac} \quad (7)$$

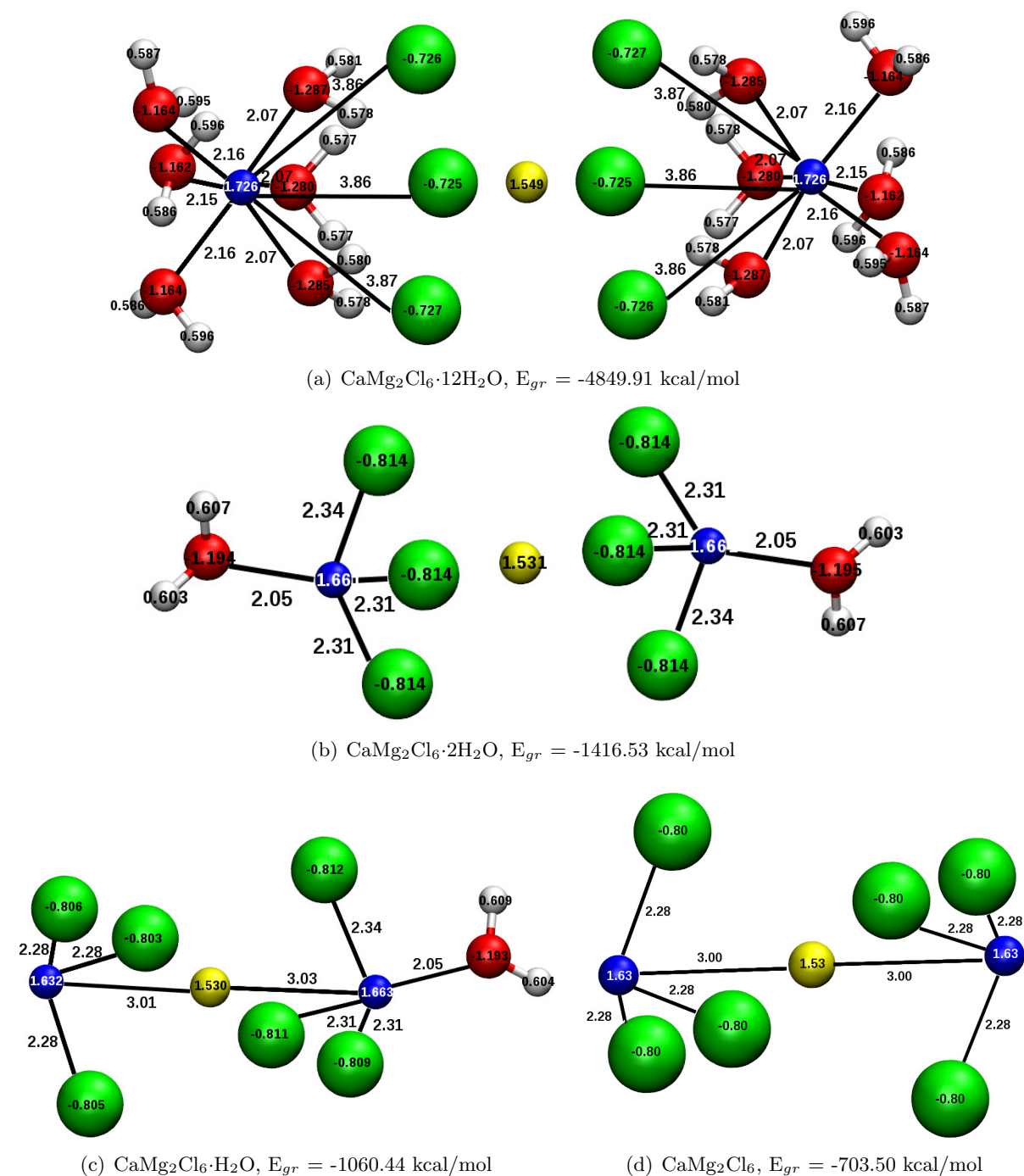
Where  $G_{prod}$  and  $G_{reac}$  is Gibbs free energy of product and reactant respectively. The equilibrium concentration of products and reactants can be obtained by equating  $\Delta G$  to zero. The physical state of reactants and products are essential to calculate the  $\Delta G$  of a reaction. Experimentally,  $\text{CaMg}_2\text{Cl}_6 \cdot 12\text{H}_2\text{O}$  remains in solid phase and  $\text{H}_2\text{O}$ ,  $\text{HCl}$  exist in the gaseous phase. The physical states of lower hydrates are remain unknown and computationally challenging for solid phase.

The Gibbs free energy of crystalline phase of  $\text{MgCl}_2$  hydrates were lower than the gas phase energy of the  $\text{MgCl}_2$  hydrates [16, 19]. Although, these calculations were carried out for another solid salt hydrates, this should hold true for  $\text{CaMg}_2\text{Cl}_6 \cdot 12\text{H}_2\text{O}$  also. Hydrolysis reaction usually happen in the liquid phase salt hydrates mixture [16]. As the solid phase of lower hydrates of  $\text{CaMg}_2\text{Cl}_6$  are unexplored experimentally, the  $\Delta G$  can be estimated by Gibbs free energy of gaseous phase ( $G_{gas}$ ). The equilibrium thermodynamic study of thermolysis of  $\text{CaMg}_2\text{Cl}_6$  hydrates under gas assumption will be considered as the safety limits of these reactions in seasonal heat storage systems.

### 3. Structure of various hydrates

The initial geometry of tachyhydrite is taken from known experimental structure [9]. The geometry optimization is carried in DFT formalism under the GGA approximation on the gaseous molecule of  $\text{CaMg}_2\text{Cl}_6 \cdot 12\text{H}_2\text{O}$ . The optimized structure of  $\text{CaMg}_2\text{Cl}_6 \cdot 12\text{H}_2\text{O}$  is symmetric as shown in Figure 1(a). The Mg atoms became hydrated with six  $\text{H}_2\text{O}$  molecules and form a distorted octahedral structure. These two distorted octahedron structures are connected via a bridge octahedral structure made of  $\text{CaCl}_6$ . The optimized structure is similar to the experimental crystal [9]. The Bader atomic charge on the O atoms of hydrated water facing towards the bridge layer of  $\text{CaCl}_6$  are 0.12 more electronegative and 0.09 Å shorter than non-facing O atoms (extreme left and right  $\text{H}_2\text{O}$  atoms). The Mg-Cl coordination length and atomic charges on Ca, Mg and Cl are symmetric in both of these distorted octahedron. The Mg-O coordination lengths are 2.07 and 2.15 Å. The experimental crystalline phase Mg-O coordination lengths are 2.10 and 2.01 Å, shows a good agreement between the experimental crystal structure and the DFT optimized structure

The structure of the lower hydrates are obtained by successive removal of the two  $\text{H}_2\text{O}$  atoms and re-optimization of structure in GGA-DFT. The Mg-Cl coordination length is continuously decreasing with the hydration number and it became 2.3 Å for  $\text{CaMg}_2\text{Cl}_6 \cdot 2\text{H}_2\text{O}$  as shown in Figure 1(b). The hydration strength of Mg atom progressively increases with decrease in the hydration number. The electro-positive atomic charge on Ca and Mg atom is decreases from 1.726 to 1.63 and 1.549 to 1.530 as the hydration number varies from 12 to 1. The average electronegative charge on Cl atoms is keeps on decreasing from (-0.75 to -0.80) with the decrease in the hydration number from 12 to 2. The atomic charge distribution suggests that electrostatic interactions play a major role in stability and hydration of these hydrates.



**Figure 1.** The optimized structures of  $\text{CaMg}_2\text{Cl}_6 \cdot 12\text{H}_2\text{O}$ ,  $\text{CaMg}_2\text{Cl}_6 \cdot 2\text{H}_2\text{O}$ ,  $\text{CaMg}_2\text{Cl}_6 \cdot \text{H}_2\text{O}$  and  $\text{CaMg}_2\text{Cl}_6$ . Bader charges and coordination lengths (in Å) are shown. Color scheme: Ca = yellow, Cl = green, Mg = blue, O = red and H = white.

#### 4. Enthalpy change in thermolysis

We have obtained the binding enthalpy ( $E_{bind}$ ) of various salt hydrates as:

$$E_{bind} = E_{CaMg_2Cl_6 \cdot nH_2O} - (E_{CaMg_2Cl_6} + nE_{H_2O}) \quad [n = 12, 10, 8, 6, 4, 2, \&1] \quad (8)$$

The enthalpy change in dehydration of salt hydrate per mole of water ( $E_{dehyd}$ ) is defined as:

$$\Delta E_{dehyd} = \begin{cases} 0.5 \times [E_{CaMg_2Cl_6 \cdot (n-2)H_2O} + 2E_{H_2O} - E_{CaMg_2Cl_6 \cdot nH_2O}], & (n = 4, 6, 8, 10, 12) \\ E_{CaMg_2Cl_6 \cdot (n-1)H_2O} + E_{H_2O} - E_{CaMg_2Cl_6 \cdot nH_2O}, & (n = 1, 2) \end{cases} \quad (9)$$

The enthalpy change in hydrolysis of salt hydrate ( $\Delta E_{hydro}$ ) is defined as:

$$E_{hydro} = [E_{CaMg_2Cl_5OHCl} + (n-1)E_{H_2O} + E_{HCl} - E_{CaMg_2Cl_6 \cdot nH_2O}] \quad (n = 1, 2, 4, 6, 8, 10, \& 12) \quad (10)$$

**Table 1.** Enthalpy change in binding, dehydration and hydrolysis reactions. The parentheses represents di to anhydrous dehydration enthalpy

Molecule	$E_{bind}$ kcal/mol	$E_{dehyd}$ kcal/mol	$E_{hydro}$ kcal/mol
CaMg <sub>2</sub> Cl <sub>6</sub> ·12H <sub>2</sub> O	-187.85	7.41	198.52
CaMg <sub>2</sub> Cl <sub>6</sub> ·10H <sub>2</sub> O	-173.04	15.30	183.71
CaMg <sub>2</sub> Cl <sub>6</sub> ·8H <sub>2</sub> O	-142.44	7.26	153.11
CaMg <sub>2</sub> Cl <sub>6</sub> ·6H <sub>2</sub> O	-127.92	17.37	138.59
CaMg <sub>2</sub> Cl <sub>6</sub> ·4H <sub>2</sub> O	-93.18	19.95	103.85
CaMg <sub>2</sub> Cl <sub>6</sub> ·2H <sub>2</sub> O	-53.27	26.21 (26.63)	63.94
CaMg <sub>2</sub> Cl <sub>6</sub> ·H <sub>2</sub> O	-27.06	27.06	37.73

The binding enthalpy of the salt hydrates monotonically increases with hydration number as shown in Table 1. It indicates that hydration process becomes energetically favorable with increase in hydration number. The change in enthalpy of dehydration per mole of released water molecule is maximum for mono-hydrate and keeps on decreasing till octa-hydrate. It has a sudden peak for deca-hydrate bringing it to the level of the hexa, and it decreases again for dodeca being almost equal to the octahydrate. The intramolecular hydrogen bonding may be a plausible reason for the exceptional stability of the deca-hydrates. Another observation is that the enthalpy change in hydrolysis continuously increasing with hydration number. This employs, hydrolysis is relative difficult for higher hydrates.

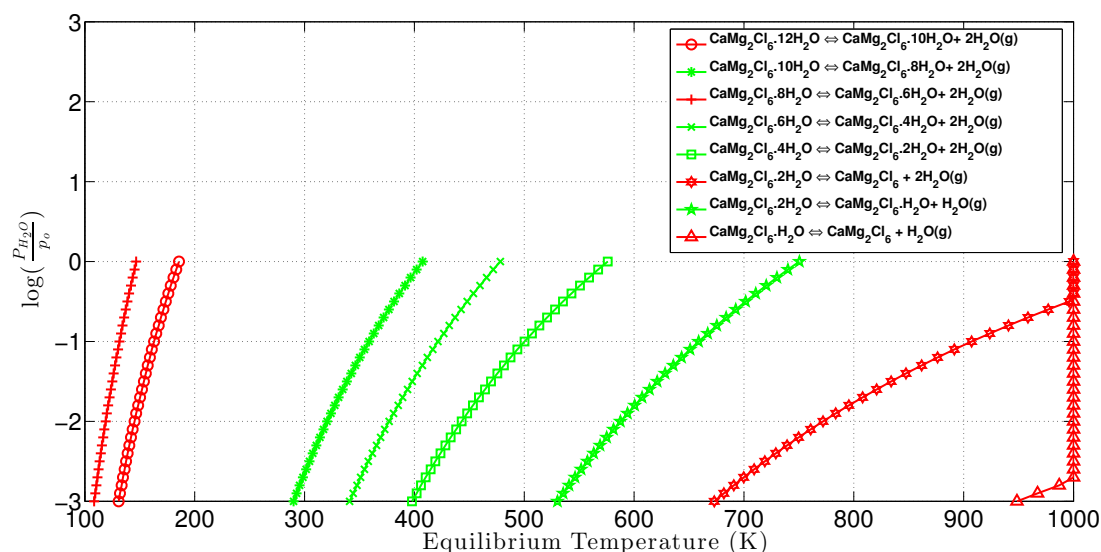
#### 5. Atomistic thermodynamic equilibrium study

In the present study, we have obtained the equilibrium compositions (partial pressure) of products formed during the thermolysis (dehydration / hydrolysis) of various hydrates of CaMg<sub>2</sub>Cl<sub>6</sub>. We obtained the Gibbs free energy of each reactant and product from atomistic DFT calculations and equilibrium compositions are obtained by equating  $\Delta G$  to zero. In the heat storage systems, the partial pressure of water ( $p_{H_2O}$ ), partial pressure of HCl ( $p_{HCl}$ ) and temperature (T) are controlling variables while partial pressure of salt hydrates are kept constant (1 atm). Thus, partial pressure of salt hydrate is kept constant in all the calculations.

### 5.1. Dehydration reaction of salt hydrates

Dehydration is an endothermic reaction in which hydrate molecules absorb thermal energy and disintegrate into lower hydrate or anhydrous form. To understand the effect of temperature on the dehydration reaction of  $\text{CaMg}_2\text{Cl}_6$  hydrates, the equilibrium products of dehydration reaction is investigated in the temperature range of 100 to 1000 K. The equilibrium temperature-vapor pressure obtained from dehydration reactions of  $\text{CaMg}_2\text{Cl}_6$  hydrates is shown in Figure 2. For seasonal heat storage, the typical operating temperatures are about 273 - 500 K. We have represented the dehydration reaction falling in this range with green color, and outside of this range with red color. The dodeca and octa hydrates of  $\text{CaMg}_2\text{Cl}_6$  dehydrates at very low temperature (<200 K). This behavior is consistent with their low dehydration enthalpy change as given in Table 1.

The dehydration of deca, hexa, tetra and di (from di to mono conversion) descends in 273 to 500 K temperature range. These reactions have dehydration enthalpy ranging from 15.0 to 26.21 kcal/mol. The partial water pressure of 0.001 atm is obtained at 130.7, 290, 108.5, 341, 397.7, 673 K (530.3 for di to mono dehydration) and 948.5 K for dodeca, deca, octa, hexa, tetra, di and mono hydrate of  $\text{CaMg}_2\text{Cl}_6$  respectively. The deca, hexa, tetra and di (from di to mono conversion) achieved 1 atm vapor pressure at 407.5, 478.2, 576 and 750.5 K respectively. Therefore  $\text{CaMg}_2\text{Cl}_6 \cdot n\text{H}_2\text{O}$  [ $n=10,6,4$  and 2] can be screened as potential candidate for heat storage from the dehydration point of view.

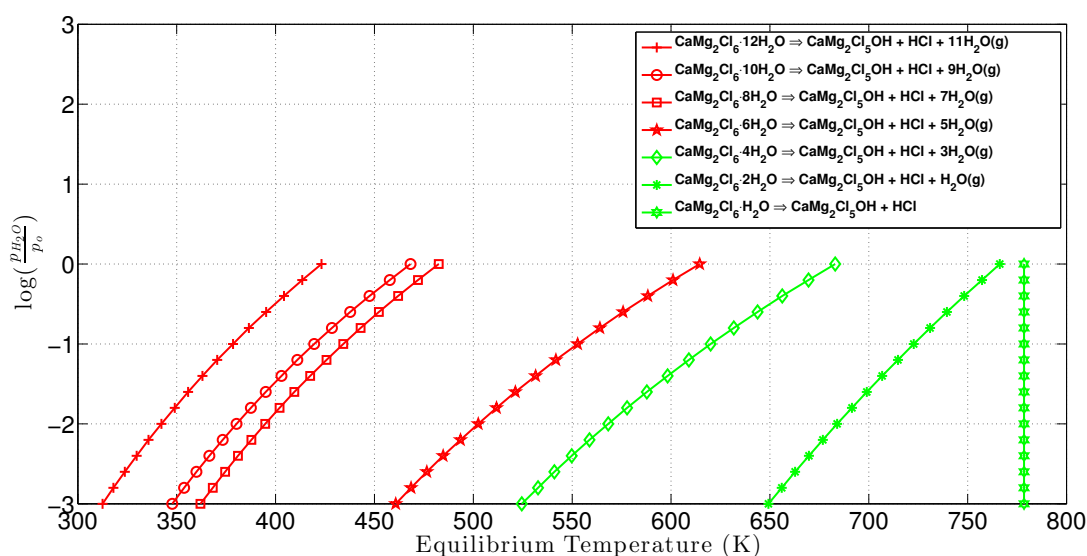


**Figure 2.** Equilibrium product concentrations for the dehydration reactions of  $\text{CaMg}_2\text{Cl}_6$  hydrates at various temperatures and constant partial pressure of hydrate,  $p_o = 1$  atm

### 5.2. Hydrolysis reaction of salt hydrates

Hydrolysis is a side reaction reaction which produces HCl and  $\text{H}_2\text{O}$ . To understand the effect of temperature on hydrolysis, we have varied the concentrations of each of the reaction products while keeping the concentration of other product fixed. Firstly, the equilibrium temperature is varied from 300-800 K at constant HCl pressure (0.0001 atm). The fixed low HCl pressure ( $p_{\text{HCl}} = 0.0001$  atm) has low pressure gradient and represents slows hydrolysis rate. Such low concentrations of HCl can be used as safety limits for heat storage system. The onset of HCl formation temperature ( $p_{\text{H}_2\text{O}} = 0.001$  atm) is shown in Figure 3. Hydrolysis is an undesirable

reaction in typical operating range (273 - 500 K) of seasonal heat storage application. We have represented the hydrolysis curve with green color for those hydrates whose hydrolysis starts above 500 K, and rest with red color. The difference between Figure 2 and Figure 3 is that in the later case hydrolysis is considered. Hydrolysis starts at higher temperature than dehydration as enthalpy change in hydrolysis is much higher than enthalpy change in dehydration (see Table 1). The onset of HCl formation is 312.5, 347.7, 362.0, 460.75, 524.5, 649.2, and 778.5 K for dodeca hydrate to mono hydrate respectively. To prevent the hydrolysis below 500 K, tetra and lower hydrates seem to be an ideal candidate. Hexa hydrate can also be a suitable candidate when operating temperature is below 450 K.



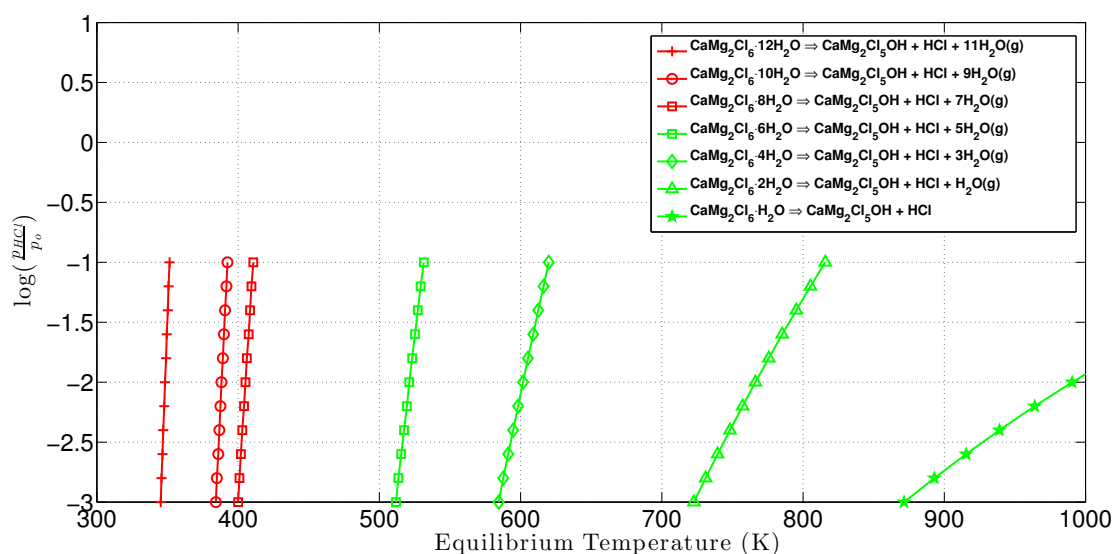
**Figure 3.** Equilibrium product concentration for the hydrolysis reactions of  $\text{CaMg}_2\text{Cl}_6$  at various temperatures and fixed HCl pressure  $p_{\text{HCl}} = 0.0001$  atm and  $p_o = 1$  atm.

The effect of temperature on hydrolysis under constant water vapor pressure ( $p_{\text{H}_2\text{O}} = 0.01$  atm) is shown in Figure 4. The slope of hydrolysis curve decrease from dodeca hydrate to mono hydrate as shown in Figure 4. The molar ratio between the HCl to  $\text{H}_2\text{O}$  decreases from mono to dodeca hydrate, therefore for a particular change in temperature affect maximum to mono-hydrate.

## 6. Conclusions

We have carried out a GGA-DFT calculations to obtain the optimized structures, Bader atomic charges and frequencies of various  $\text{CaMg}_2\text{Cl}_6$  hydrates. The atomic charge distribution reveals that the stability and hydration strength of  $\text{CaMg}_2\text{Cl}_6$  hydrates are dominated by electrostatic interactions. The structural property, ground state energy and harmonic frequencies are used to quantify the Gibbs free energy of each reactant for given  $T$ ,  $P$ . The atomistic thermodynamic approach is used to quantify the equilibrium product concentration of thermolysis at various temperature and pressure conditions for various hydrates of  $\text{CaMg}_2\text{Cl}_6$ .

The effect of temperature on the dehydration of tachyhydrite is similar to the experimental dehydration of the  $\text{CaCl}_2$  and  $\text{MgCl}_2$  hydrates. The dehydration of  $\text{CaMg}_2\text{Cl}_6 \cdot 12\text{H}_2\text{O}$  and  $\text{CaMg}_2\text{Cl}_6 \cdot 8\text{H}_2\text{O}$  starts at sub-zero temperature thus indicates that they are not stable at room temperature. The dehydration of  $\text{CaMg}_2\text{Cl}_6 \cdot 10\text{H}_2\text{O}$ ,  $\text{CaMg}_2\text{Cl}_6 \cdot 6\text{H}_2\text{O}$ ,  $\text{CaMg}_2\text{Cl}_6 \cdot 4\text{H}_2\text{O}$ , and  $\text{CaMg}_2\text{Cl}_6 \cdot 2\text{H}_2\text{O}$  starts below 500 K. The hydrolysis reactions of  $\text{CaMg}_2\text{Cl}_6$  hydrates



**Figure 4.** Equilibrium product concentration for the hydrolysis reactions of  $\text{CaMg}_2\text{Cl}_6$  at various temperatures and fixed  $\text{H}_2\text{O}$  pressure  $p_{\text{H}_2\text{O}} = 0.01$  atm and  $p_o = 1$  atm.

are investigated under constant  $p_{\text{HCl}}$  and  $p_{\text{H}_2\text{O}}$ . The onset of HCl formation (hydrolysis) temperature are obtained for a safety limit of  $p_{\text{HCl}}$  (0.0001 atm) under different temperature and pressure conditions. Hydrolysis of tetra, di and mono hydrates start above 500 K at the safety limit. Hydrolysis of these hydrates under constant vapor pressure ( $p_{\text{H}_2\text{O}} = 0.01$ ) also begins above 500 K. In the lack of experimental studies, it can be concluded from the present studies that  $\text{CaMg}_2\text{Cl}_6 \cdot 10\text{H}_2\text{O}$ ,  $\text{CaMg}_2\text{Cl}_6 \cdot 6\text{H}_2\text{O}$ ,  $\text{CaMg}_2\text{Cl}_6 \cdot 4\text{H}_2\text{O}$ , and  $\text{CaMg}_2\text{Cl}_6 \cdot 2\text{H}_2\text{O}$  are potential candidate for long term seasonal heat storage. It is expected that these hydrates can improve the hydrolysis resistance compared to  $\text{MgCl}_2$  hydrates. Therefore can enhance the durability of the system.

### 6.1. Acknowledgments

This work is part of the Industrial Partnership Programme (IPP) 'Computational sciences for energy research' of the Foundation for Fundamental Research on Matter (FOM), which is part of the Netherlands Organisation for Scientific Research (NWO). This research programme is co-financed by Shell Global Solutions International B.V.

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