

Dehydration of Magnesium Chloride at Pre- and Post-Melting Point Temperatures for Molten Salt Reactor Application

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1. Introduction

Magnesium chloride (MgCl_2) is utilized as a component within molten salts systems due to its thermophysical properties such as lowering the melting point in eutectic salts systems. It is studied not only in Molten Salt Reactors (MSR) but also in Concentrating Solar Power (CSP) plants. However, it is notably hygroscopic, reacting with water to generate corrosive hydrochloric acid gas at 167°C - 468°C [1,2]. Furthermore, the reaction of MgCl_2 with water yields magnesium oxide, a solid byproduct that may accumulate in reactors, potentially causing mechanical failures.

Consequently, the dehydration process of the salt is critical to inhibit its reaction with water prior to its application in MSR. Prior research has employed highly acidic compounds, such as HF and HCl gas, for the removal of water from MgCl_2 [3,4]. This study investigated the optimized conditions for dehydration using only thermal dehydration without additives. Through thermal dehydration, we have successfully removed 99% of the water content. However, during the course of this study, we observed that after the melting point of MgCl_2 , the salt exhibits a tendency to reabsorb water, leading to rehydration. We observed same tendency from commonly used molten salts such as KCl, and CaCl_2 . To address this issue, we are currently exploring the mitigation method

2. Methods and Results

2.1 Materials

MgCl_2 (Anhydrous, 99%) were purchased from Thermo scientific. MgCl_2 (Ultra dry, 99.99%) were purchased from Alfa Aesar. MgCl_2 were stored and prepared in an Ar atmosphere glove box ($[\text{O}_2]$, $[\text{H}_2\text{O}] < 5$ ppm). Carbon crucibles were used as experimental cells.

2.2 Experimental setup

Dehydration test were carried out in a high-temperature furnace connected to glove box. MgCl_2 was put into a carbon crucible. The experiments were conducted at temperatures both below and above the

melting point of MgCl_2 . The pre-melting temperatures tested were 170°C , 200°C , 300°C , 400°C , 500°C , and 600°C under vacuum conditions, while the post-melting temperatures were 700°C and 800°C . (Fig. 1) Each temperature was maintained for 24 h to achieve dehydration, followed by sampling. Subsequently, the same sample was subjected to successive experiments at the next temperature level. Water content of each sample was then measured.

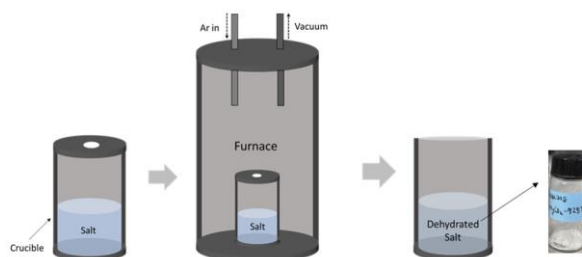


Fig. 1. Schematic diagram of thermal dehydration

To compare to the stepwise temperature in the pre-melting temperatures tests, we conducted an experiment where the temperature was raised to 600°C all at once for 23 h and held for 1 h.

The water content was measured by the Karl-Fischer titration. It is widely used method for analyzing water content in salts. For comparison, the water content of the ultra dry reagent in the glass ampoule was also analyzed. The MgCl_2 samples were finely ground before Karl-Fischer titration. All operations were carried out in a glove box filled with Ar ($[\text{O}_2]$, $[\text{H}_2\text{O}] < 5$ ppm).

2.2 Dehydration results at pre-melting points

The water content of the sample dehydrated at 170°C (24 h) was analyzed to be 20% relative to the original reagent, indicating that 80% of the water was removed at this temperature. Except for the 200°C (48 h) sample, the results show that higher dehydration temperatures lead to an increased rate of water removal. Interestingly, the 200°C (48 h) sample exhibited a higher water content compared to the 170°C (24 h) sample. This is likely due to the non-uniform removal of water at lower temperatures, which results in a larger standard

deviation. As shown in Fig. 2, the standard deviation of water content decreases with increasing dehydration temperature (or extended dehydration time). The sample dehydrated at 600°C showed a water removal efficiency of 99%, resulting in a water content of 51 ppm. This is even lower than that of commercially available ultra-dry reagents.

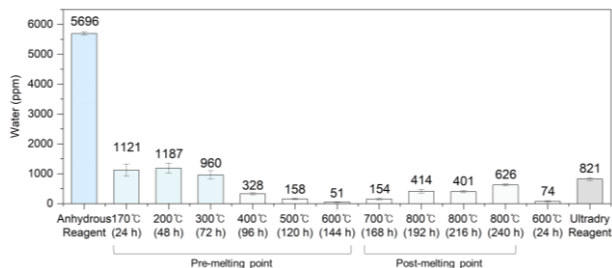


Fig. 2. Water content of magnesium chloride reagent and samples after thermal dehydration at Pre- and post-melting points

Fig. 3 shows the results of water content analysis from samples collected from the upper and lower parts of the crucible after dehydration. Except for 170°C (24 h) and 600°C (144 h), the water content in the samples collected from the lower part of the crucible was higher than that in the samples collected from the upper part. For 170°C (24 h) to 300°C (72 h), the relatively low dehydration temperatures and short durations resulted in large standard deviations in water content. Consequently, there is a significant difference in water content between the upper and lower parts of these samples. However, in the 400°C (96 h) to 600°C (144 h) samples, the difference in water content between the upper and lower parts of the crucible is smaller, and the standard deviations are also reduced.

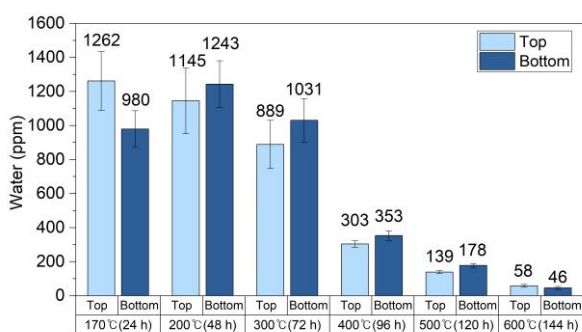


Fig. 3. Water content of magnesium chloride reagent and samples at the top and bottom of the sample crucible.

2.3 Dehydration at post-melting points

To investigate the effects of dehydration above the melting point, the water content of samples heated to 700°C and 800°C was analyzed and presented in Fig. 2.

The samples at 700°C and 800°C showed higher water content compared to those dehydrated at 600°C, with the sample at 800°C exhibiting higher water content than the one at 700°C. To further explore this phenomenon of rehydration as the salt melts, similar experiments were conducted with other salts to see if this behavior occurs with them as well.

Commonly used molten salts such as LiCl-KCl, LiCl, KCl, and CaCl₂ were placed in a carbon crucible and heated in an electric furnace, similar to the MgCl₂ experiments, to analyze the water content before and after melting. The results in Fig. 4 shows that, like MgCl₂, KCl and CaCl₂ also exhibited an increase in water content after melting. LiCl also shows a slight increase in water content near the melting point and an increase in standard deviation values. Comparing the melting points of these salts, it can be suggested that the rehydration phenomenon occurs in salts with relatively higher melting points.

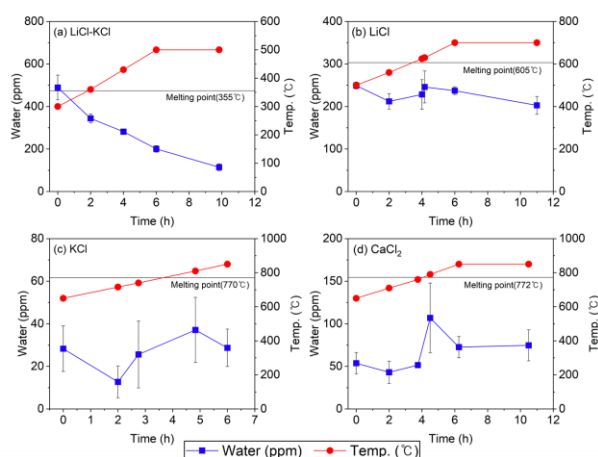


Fig. 4. Water content of LiCl-KCl, LiCl, KCl, CaCl₂ at pre- and post-melting points

3. Conclusions

When MgCl₂ is dehydrated at 600°C without any additives or strong acid gas, the reagent with a high water content can be dehydrated to 51 ppm.

At temperatures above the melting point, the salt tends to reabsorb water that was previously removed. Therefore, a method to mitigate this rehydration is necessary. Further research is required to investigate methods for mitigating rehydration.

REFERENCES

- [1] Q. Huang, G. Lu, J. Wang, J. Yu, Thermal decomposition mechanisms of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ and $\text{MgCl}_2 \cdot \text{H}_2\text{O}$, *Journal of Analytical and Applied Pyrolysis*, Vol.90, p.159-164, 2011
- [2] Y. Zhao, J. Vidal, Potential scalability of a cost-effective purification method for MgCl_2 -Containing salts for next-generation concentrating solar power technologies, *Solar Energy Materials & Solar Cells*, Vol.215, 110663, 2020
- [3] Y. Zuo, Y. Song, R. Tang, Y. Qian, A novel purification method for fluoride or chloride molten salts based on the redox of hydrogen on a nickel electrode, *RSC Advances*, Vol.56, 2021
- [4] D.M. Smith, M.P. Neu, E. Garcia, L.A. Morales, Hydration of plutonium oxide and process salts, NaCl, KCl, CaCl_2 , MgCl_2 : effect of calcination on residual water and rehydration, *Waste Management*, Vol.20, p.479-490, 2000