Thermal Dehydration of Magnesium Chloride 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℃-468℃[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.

2. Methods and Results

2.1 Materials

$MgCl_2$ (Anhydrous, 99%) was purchased from Thermo scientific. $MgCl_2$ was stored and prepared in an Ar atmosphere glove box ([O_2], [H_2O] < 5ppm). Carbon crucibles were used as experimental cells.

2.2 Experimental setup

Dehydration experiments were conducted in a high-temperature furnace connected to glove box. $MgCl_2$ was placed in a carbon crucible and heated at temperature of 170℃, 200℃, 300℃, 400℃, 500℃, and 600℃ under vacuum conditions. (Fig. 1) At each temperature condition, the $MgCl_2$ was maintained for 24 hours prior to sampling, and then the process is repeated by heating to the next temperature condition. The water content of each sample was then measured. The $MgCl_2$ samples were finely ground for Karl-Fischer titration. All operations were carried out in a glove box filled with Ar ([O_2], [H_2O] < 5ppm).

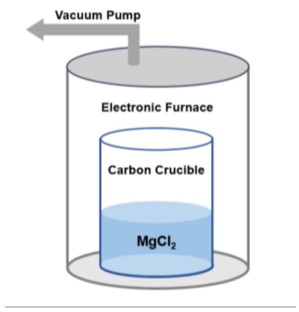

Fig. 1. Diagram of Equipment for Thermal Dehydration

2.3 Analytical Method

The following analyses were conducted to characterize the reagent. X-ray diffraction (XRD) analysis was utilized to assess crystallinity, using an air-tight holder to prevent exposure to air. Scanning electron microscopy-energy dispersive spectroscopy (SEM-EDS) analysis was conducted after vacuum filtration to identify impurities. The reagent, upon dissolution in ultrapure water, and the resultant solid from vacuum filtration through a 0.45 μm filter, were analyzed using SEM-EDS. The hygroscopicity of the $MgCl_2$ sample was determined by monitoring its weight change in air.

The water content of the reagent and dehydrated samples was measured via the Karl-Fischer titration. Due to the hygroscopic nature of $MgCl_2$, sample analysis was conducted in a glove box to maintain inert atmosphere.

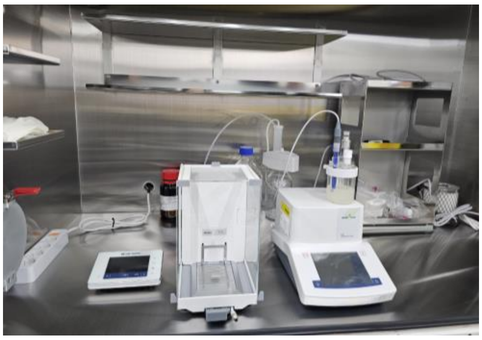

Fig. 2. The equipment setup for Karl-Fischer moisture analyzer inside the glove box

2.4 Results

XRD analysis of the reagent (Fig. 3) displayed peaks for $MgCl_2$ and MgO, with no hydrate forms detected. SEM-EDS analysis of the solid of the reagent (Fig. 4) revealed impurities such as Fe and Zr. After exposing the reagent to air, the weight change was monitored and a weight gain of 0.9 %/h was observed. (Fig. 5)

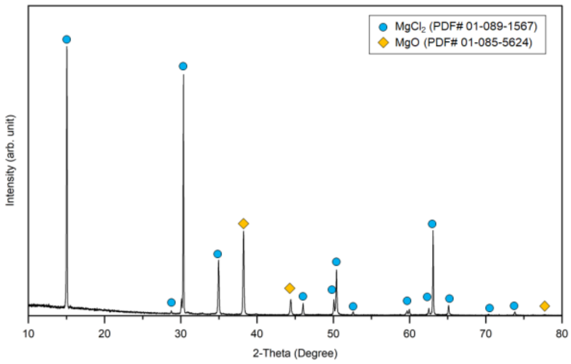

Fig. 3. XRD result of anhydrous $MgCl_2$ reagent

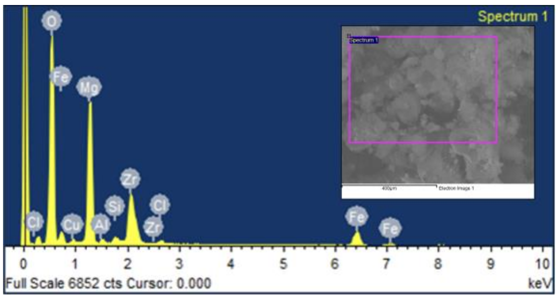

Fig. 4. SEM-EDS analysis result after vacuum filtration of anhydrous magnesium chloride reagent

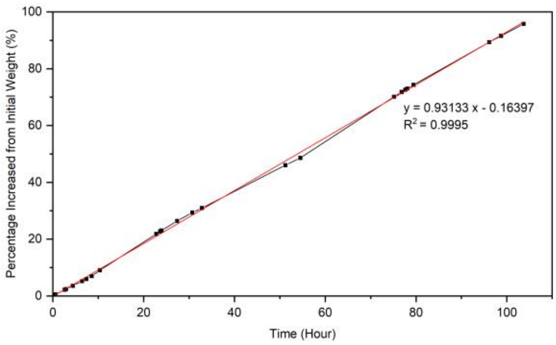

Fig. 5. The percentage increased from initial weight (%) of anhydrous $MgCl_2$ reagent stored in air

After dehydration at 170℃, the sample contains a water content of 20 % relative to the original reagent, which means that 80 % of the water was removed. The percentage of dehydration increased as the dehydration temperature increased. At 600℃ the water content was 51 ppm, meaning about 99 % of the water was removed. (Fig. 6)

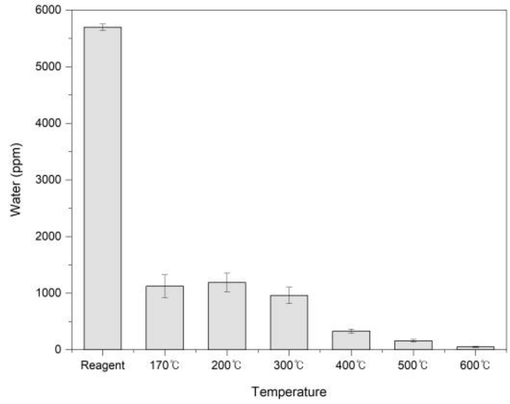

Fig. 6. Water content of $MgCl_2$ reagent and samples after thermal dehydration at each temperature

3. Conclusions

The anhydrous $MgCl_2$ reagent contained impurities such as MgO, Fe, and Zr. The anhydrous $MgCl_2$ reagent exhibited a higher water content before thermal dehydration, yet XRD analysis did not identify any hydrate formations. It was shown that $MgCl_2$ absorbs almost constantly 0.9 %/h of water for at least 100 hours. When $MgCl_2$ is dehydrated at 600℃ without any additives or strong acid gas, the reagent with a high water content can be dehydrated to 51 ppm.

Given the highly hygroscopic nature of $MgCl_2$, achieving low water content is challenging. However, considering that commercially available ultradry reagents typically guarantee approximately 50 ppm of water, we can conclude that thermal dehydration, without any additives, is an effective method for dehydrating $MgCl_2$ prior to its application in MSR.

REFERENCES

[1] Q. Huang, G. Lu, J. Wang, J. Yu, Thermal decomposition mechanisms of $MgCl_2 \cdot 6H_2O$ and $MgCl_2 \cdot H_2O$, 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