

含水 鹽化마그네슘의 脫水 特性 考察†

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Dehydration characteristics of Magnesium Chloride Hydrate†

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요 약

마그네슘 용융염전해의 원료물질로 무수염화마그네슘이 일반적으로 사용된다. 그러나 함수염화마그네슘으로부터 무수염화마그네슘을 제조하기 위한 탈수과정은 가수분해가 동반되어 마그네슘 산화물들이 생성되므로, 공기 중에서 탈수를 통한 무수염화마그네슘 제조는 어렵다. 본 연구에서는 공기중에서와 염화수소 분위기 하에서 탈수 온도(200~600°C)에 따른 탈수특성을 비교하였다. 공기중에서는 탈수온도가 증가함에 따라 MgOHCl과 MgO가 생성되었지만, 염화수소 분위기하에서는 300°C 이상에서 무수염화마그네슘이 생성되었다. 염화수소 분위기에서 무수염화마그네슘은 약 300°C에서 생성되기 시작하여 500°C에서 결정화가 완전히 이루어 지는 것을 확인하였다. 탈수실험에 사용된 염화수소는 모두 물에 용해시켜 염산으로 회수되었으며, 수용액 온도 20°C에서 최대 41%의 염산을 회수할 수 있었다.

주제어 : 함수염화마그네슘, 탈수, 무수염화마그네슘, 염화수소, 염산

Abstract

Anhydrous magnesium chloride, dehydration product from magnesium chloride hydrate is a general raw material to prepare electrolytic magnesium. However, the dehydration is not trivial and can be accompanied by hydrolysis leading to the production of undesirable hydroxy chloride compounds of magnesium. Therefore, dehydration process is actually the most complicated and hardest in the electrolysis methods for the production of magnesium. In this work, the influence of dehydrating temperature has been studied at the temperature range from 200°C to 600°C in air and HCl gas atmosphere individually to compare the results. With increasing of dehydration temperature MgOHCl and MgO were obtained in air. On the other hand, when the temperature was increased above 300°C anhydrous magnesium chlorides were prepared in HCl gas atmosphere. Anhydrous magnesium chloride was formed at near 300°C and completely crystallized at about 500°C. All of the HCl used as atmosphere gas in the dehydration was recovered as hydrochloric acid solution at a water vessel up to 41% by weight at 20°C.

Key words : magnesium chloride hydrate, dehydration, anhydrous magnesium chloride, hydrogen chloride, hydrochloric acid

1. Introduction

There are two general processes for the commercial production of magnesium which is the lightest structural metal. In the first process, magnesium

chloride is recovered from the raw materials and converted to metal by molten salt electrolysis. The second process involves the reduction of magnesium oxide with silicon or aluminum under vacuum at high temperature.

The electrolytic production of magnesium requires high-purity, anhydrous magnesium chloride which has a high affinity for water and is found in nature as a

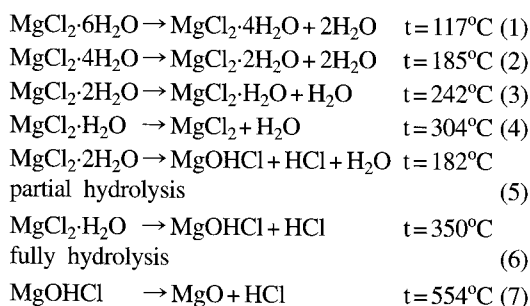
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plurality of hydrates ($MgCl_2 \cdot nH_2O$, $n=1, 2, 4, 6, 12$). The presence of oxygen species in the electrolyte of electrolytic magnesium production processes is severely detrimental and significantly lowers the efficiency of electrolytic cells. Therefore, the dehydration of magnesium chloride hydrates to produce anhydrous magnesium chloride is of great importance to electrolytic magnesium production process^{1,2,3}.

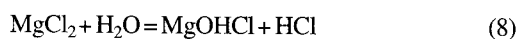
Magnesium chloride hydrate usually exists as $MgCl_2 \cdot 6H_2O$ at room temperature. It can be dehydrated stepwise through $MgCl_2 \cdot nH_2O$ ($n=4, 2, 1, 0$) and hydrolyzed to $MgOHCl$, and eventually $MgCl_2$ and $MgOHCl$ transform to MgO at high temperature when O_2 is present within atmosphere gas⁴.

The followings are the decomposition and hydrolysis of magnesium chloride hydrates at some temperatures⁵:



During dehydration in ambient atmosphere, magnesium chloride hydrates tend to decompose in the hydrolysis reaction to magnesium hydroxy chloride at the temperature range from 182 to 350 according to the reaction (5) and (6), and magnesium hydroxy chloride converted entirely to magnesium oxide and hydrogen chloride gas at 554 according to reaction (7). Hence, the preparation of anhydrous magnesium chloride from the magnesium chloride hydrates in air is very difficult.

Reaction (4) and (6) can be combined to express the hydrolysis of $MgCl_2$ as reaction (8).



Hydrolysis can be prevented by use of HCl. If the partial pressure of HCl exceeds that of the equilibrium state, anhydrous magnesium chloride can be obtained via its back reaction.

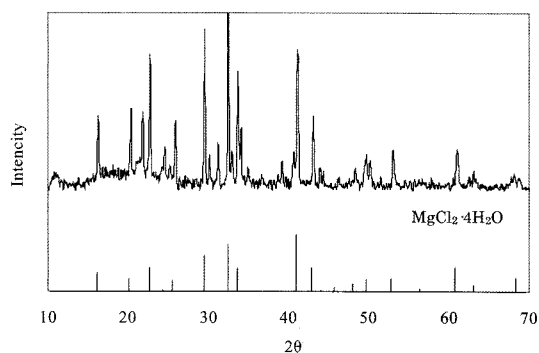


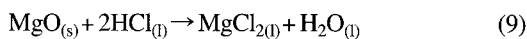
Fig. 1. XRD pattern of the dried magnesium chloride hydrate (100°C, 24hr).

In this work, the influence of dehydrating temperature has been studied at the temperature range from 200 to 600 both in air and HCl gas atmospheres, and the optimal condition for dehydration was investigated. All of the used HCl gas in the dehydration experiments was recovered in a water vessel to recycle it as hydrochloric acid solution.

2. Experiments

2.1. Materials

Magnesium oxide(JUNSEI, 98%) and hydrochloric acid(DC chemical, 35%, s.g. 1.18) were used to prepare aqueous magnesium chloride solution. Following is the reaction of magnesium oxide with hydrochloric acid.



The aqueous magnesium chloride solution obtained by the above reaction was condensed and crystallized using a rotary evaporator with conditions of 80°C, 90 rpm, 0.05 atm. Thereafter, the crystallized sample was dried at 100°C, for 24 hours prior to dehydration.

Fig. 1 shows XRD spectrum of the dried sample which was confirmed as $MgCl_2 \cdot 4H_2O$, and it was used as raw material for the dehydration experiments.

2.2. Dehydration

In each experiment, a 5 g of the raw material charged in a quartz boat was placed in a tube furnace, then it was heated with 10°C/minute up to the desired temperature level (200-600°C). After holding for 30 minutes at each temperature, the samples were rapidly

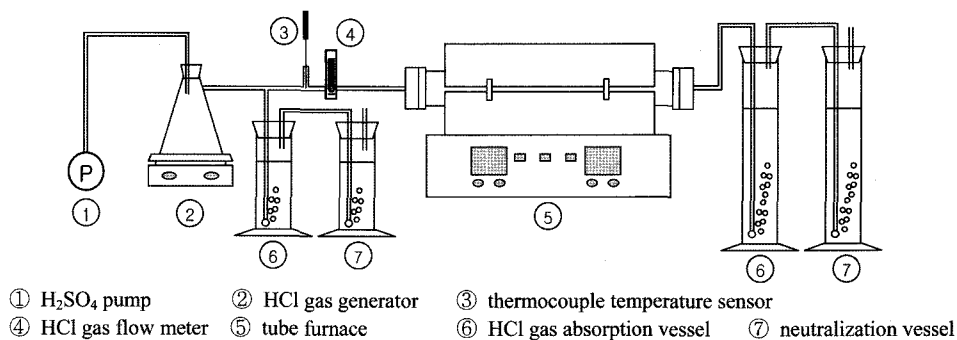
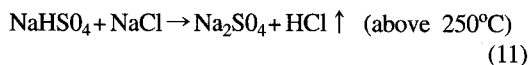
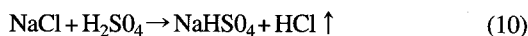


Fig. 2. Schematic diagram of the dehydrating equipment.

cooled to the room temperature with argon gas purging, and canned immediately after weight measurement. Thereafter, the samples were analyzed by XRD (X-ray Diffraction, RIGAKU, RU-200, Cu K α) method.

The dehydration experiments were done both in air and HCl gas atmospheres to compare the results. The HCl gas used for dehydration in HCl gas atmosphere was prepared by following reactions.



1 ml/min of sulfuric acid (Matsuno Chemicals Ltd., 98%, s.g. 1.84) was fed into the HCl gas generation reactor where 100g of NaCl (DC chemical, 99.5%) was previously charged. HCl gas generated by the reactions flew into the tube furnace (mean flow rate of 0.2 L/min.) through a line.

The experimental apparatus consisted of HCl gas generator, electric tube furnace, water vessel for absorbing outlet gas and neutralization vessel filled with 0.1N NaOH solution. All the lines and equipment were HCl compatible. Fig. 2 is a schematic diagram of the experimental apparatus.

HCl gas from the outlet of the reaction tube was dissolved in its absorption vessel, and then concentration of saturated hydrochloric acid was analyzed by titration with NaOH solution.

3. Results and Discussion

3.1. Dehydration in air

Fig. 3 shows the XRD spectra of the dehydration

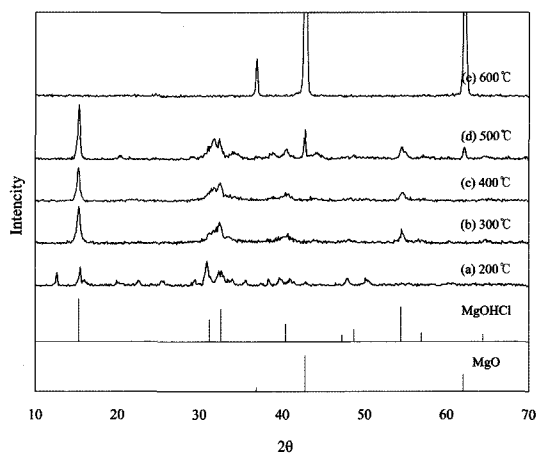


Fig. 3. XRD patterns of products with dehydrating temperature in air atmosphere.

products. Fig. 3 (a) is the XRD pattern of the product at 200. The product was a mixture of magnesium chloride monohydrate and dihydrate followed by reaction (2) and (3), and also a small quantity of MgOHCl by the partial hydrolysis reaction was observed.

With increasing of dehydration temperature poorly crystalline MgOHCl were identified in the XRD spectra in Fig. 3 (b), (c), (d). It was thought that dehydration of magnesium chloride monohydrate or dihydrate followed according to the reaction (5) and (6) instead of the reaction (2), (3), (4) under the ambient atmosphere. Also, when the holding temperature was increased to 500°C, a mixture of MgO and MgOHCl was produced as shown in Fig. 3 (d). It seemed that MgOHCl decomposed to MgO at this temperature.

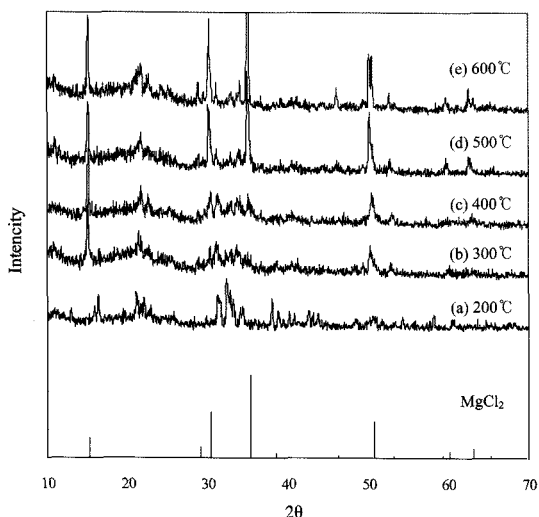


Fig. 4. XRD patterns of products with dehydrating temperature in HCl gas atmosphere.

The final product of the dehydration was found out MgO as shown in Fig. 3 (e).

These results confirmed that the dehydration under air atmosphere could not produce an anhydrous magnesium chloride.

3.2. Dehydration in HCl gas atmosphere

The dehydrations were carried out in HCl gas atmosphere with the same experimental conditions. Fig. 4 presents the XRD spectra for the products of dehydration.

The product at 200°C was a mixture of magnesium chloride monohydrate and dihydrate followed by reaction (2) and (3). Since the dehydration temperature was not sufficient to remove all water in the samples, no anhydrous magnesium chloride was found.

When the dehydrating temperature was increased above 300°C, anhydrous magnesium chlorides began to form. No MgOHCl or MgO peaks were observed in any XRD spectra even at temperature higher than the equilibrium decomposition temperature of MgOHCl. It was thought that the dehydration went on according to equation (2), (3) and (4) stepwise, and high HCl partial pressure prevented the magnesium chloride monohydrate or dihydrate from forming MgOHCl.

Mass loss rates of the dehydrated products at each temperature were measured. Assuming a total conversion of $MgCl_2 \cdot 4H_2O$ to $MgCl_2$, the calculated total mass loss

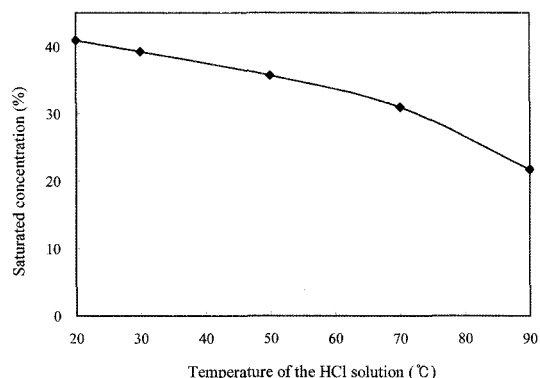


Fig. 5. Saturated concentration of hydrochloric acid with solution temperature.

is 43.1% (molecular weight of $MgCl_2 \cdot 4H_2O$ and $MgCl_2$ are 167.2 and 95.2 respectively), which is fairly close to that measured (44%) in the temperature range 300 to 600°C. So it concluded that the samples were almost dehydrated to anhydrous magnesium chloride.

But well-crystalline $MgCl_2$ was not identified until 400°C. Peak intensity increased with increasing temperature as shown in the figure 4. It can be seen that the degree of crystallinity of the $MgCl_2$ increased with increasing temperature. From the results it was considered that anhydrous magnesium chloride was formed at near 300°C and completely crystallized at about 500°C.

3.3. Recycling of HCl gas

The outlet HCl gas was absorbed into a water vessel to recycle it as hydrochloric acid solution which could be re-used at the chlorination of MgO.

In this experiment, as mentioned before, HCl gas was generated by the reaction of sulfuric acid with sodium chloride. The outlet gas from the reaction tube flew into a water vessel and then HCl gas was absorbed in water. Highly concentrated hydrochloric acid could be produced due to its high solubility. However, as the absorption carried on continuously, temperature of hydrochloric acid solution increased up to 90°C due to the exothermic reaction between HCl gas and water. Since solubility of HCl gas decreases with increasing of temperature, the temperature in the absorption vessel has an essential effect on the absorption. To increase the concentration of hydrochloric acid a

better cooling is recommended.

Fig. 5 shows the saturated concentration of hydrochloric acid with solution temperature. Theoretically hydrochloric acid can be obtained about 57% from absorption of HCl gas at room temperature⁶⁾, but in this experiment concentrated hydrochloric acid was produced through water-cooling up to 41% by weight at 20°C.

The recycled hydrochloric acid could be used in chlorination of MgO to make a magnesium chloride hydrate which could be used as raw material to prepare anhydrous magnesium chloride.

4. Conclusions

This study was carried out to prepare anhydrous magnesium chloride from magnesium chloride hydrate ($MgCl_2 \cdot 4H_2O$). Magnesium chloride hydrate should be dehydrated under HCl gas atmosphere to form an anhydrous magnesium chloride because hydrolysis reaction producing MgOHCl or MgO occur in air atmosphere.

It was found that dehydration at any temperature higher than 300°C could make anhydrous magnesium chloride in HCl gas atmosphere, and no MgOHCl or MgO formed. It was also confirmed that anhydrous magnesium chloride was formed at near 300°C and

completely crystallized at about 500°C.

All of the HCl used as atmosphere gas in the dehydration could be recovered as hydrochloric acid solution in water vessel up to 41% by weight at 20°C, and it could be recycled at the chlorination step.

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References

1. S. Kashani-Nejad and R. Harris, 2006: Oxides formed during the dehydration of magnesium chloride hexahydrate, *Magnesium Technology in the Global Age*, pp. 81-92.
2. Georges J. Kipouros and Donald R. Sadoway, 2001: A thermochemical analysis of the production of anhydrous $MgCl_2$, *Journal of Light Metals* 1, pp. 111-117.
3. Horst, E. Friedrich and Barry. L. Mordike, 2006: *Magnesium Technology*, p. 35.
4. Long Guangming and Ma Peihua, 2003: The reaction of $MgCl_2 \cdot 4H_2O$ with CCl_2F_2 , *Thermochimica Acta* 403, pp. 231-235.
5. S. Kashani-Nejad, K-W. Ng and R. Harris, 2004: Characterization of MgOHCl/MgO mixtures with infrared spectroscopy, *Magnesium Technology, TMS*, pp. 161-165.
6. The Merck Index, 1983: RAHWAY. N. J., U.S.A., Merck & CO., Inc, p. 696.

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