Study on crystal transformation process of magnesium carbonate hydrate based on salt lake magnesium resource utilization

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Abstract: The crystal transformation process of magnesium carbonate hydrate by the reaction of magnesium sulfate (MgSO₄) with ammonium carbonate [(NH₄)₂CO₃] was investigated. MgSO₄ is one of the main magnesium resources of the Lop Nur salt lake in the Xinjiang Autonomous Region of China. Magnesium carbonate hydrates with different chemical compositions were prepared. The transformation process of the 2 crystals, MgSO₄ and (NH₄)₂CO₃, was analyzed by Raman spectroscopy, and the associated changes in crystal morphology were observed by scanning electron microscopy. The needle-like MgCO₃·3H₂O transformed into sheet-like 4MgCO₃·Mg(OH)₂·4H₂O when the temperature was increased from 323 K to 333 K. The changes in the relative contents of these 2 crystals during the transformation process were analyzed by thermoanalysis. The crystal transformation process is discussed from the viewpoint of the crystal plane and growth unit changes.

Key words: Crystal morphology, growth units, magnesium carbonate hydrates, crystal transformation

1. Introduction

The Lop Nur salt lake in Xinjiang Autonomous Region, China, is the largest brine deposit subtype salt lake in the world. The lake is of the Na⁺, K⁺, Mg²⁺/Cl⁻, SO₄²⁻·H₂O 5-element water–salt system and contains abundant Mg resources, mainly MgCl₂ and MgSO₄ (>1.1 × 10¹⁰ t). The comprehensive utilization of Mg resources has significant economic and socioenvironmental benefits and has thus gained increasing attention.

MgCO₃·3H₂O and 4MgCO₃·Mg(OH)₂·4H₂O (hereafter referred to as 414) are 2 important inorganic chemical products and intermediates mostly produced with the Mg resources of salt lakes as the raw material. Due to its excellent mechanical properties, MgCO₃·3H₂O whisker has widely been used in plastic, rubber, ceramic, and printing ink for strengthening and modification.¹² In contrast, 414³⁻⁶ is not only an intermediate for the preparation of highly pure magnesia and magnesium salt series products, but is also an important inorganic functional material.⁷⁻⁸ Previous research has shown that MgCO₃·3H₂O can be converted into 414 under certain conditions. This crystal transformation can be used to develop flexible technology for Mg resource utilization. The same raw materials and equipment can be used to obtain different products by simply adjusting different process parameters, thereby ensuring quick adjustment according to the application.

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The crystal transformation of MgCO$_3$·3H$_2$O into 414 has been studied previously, with the main raw materials being MgCl$_2$ and Mg(NO$_3$)$_2$. Mitsuhashi et al. developed a method for generating needle-like MgCO$_3$·3H$_2$O and microtubular 414 via the carbonation of aqueous Mg(OH)$_2$ suspension with CO$_2$ at 308–343 K. Hopkinson et al. reported the transformation of nesquehonite to hydromagnesite in the system CaO-MgO-H$_2$O-CO$_2$ through an experimental FT-Raman spectroscopic study. Davies and Bubela found that nesquehonite can be readily altered to hydromagnesite via an intermediate phase. Hopkinson et al. reported that the transformation of nesquehonite to hydromagnesite displays mixed diffusion and reaction-limited control and proceeds through the production of metastable intermediates. Using MgCl$_2$ and NH$_4$HCO$_3$ as raw materials, Yan et al. found a transition temperature range of 323–338 K, indicating the effect of different precipitants on the transition temperature of crystals. Zhang et al. reported a transition temperature range from 328 K to 338 K for the reaction between Mg(NO$_3$)$_2$ and K$_2$CO$_3$, which positively increases with the temperature and pH. Hao et al. found a transition temperature range of 313–353 K for these 2 crystals. They described the transformation as a nucleation–dissolution–recrystallization mechanism. These findings indicate that Mg sources and reaction conditions affect the transition process of the 2 crystals.

This research focused on the utilization of MgSO$_4$ sources in the Lop Nur salt lake because only a few studies have reported on the crystal transition process with MgSO$_4$ as the raw material. The process was investigated by the controlled dropwise addition of (NH$_4$)$_2$CO$_3$ to MgSO$_4$ solution. The changes in the crystal plane and growth units were examined.

2. Experimental

All starting materials were of analytical reagent grade and were used as received without further purification. Solutions of 1 mol/L MgSO$_4$ and (NH$_4$)$_2$CO$_3$ were prepared by dissolving stoichiometric amounts of MgSO$_4$ and (NH$_4$)$_2$CO$_3$ in deionized water (dH$_2$O). The experimental conditions were as follows: temperature range, 323–333 K (323, 325, 327, 329, 331, and 333 K); stirring speed, 300 rpm; and (NH$_4$)$_2$CO$_3$ dropping rate, 2 mL/min. The initial solutions were 300 mL of 1 M MgSO$_4$ and 300 mL of 1.2 M in (NH$_4$)$_2$CO$_3$ solution. The MgSO$_4$ solution was transferred to mold at the high stirring speed of 300 rpm. The (NH$_4$)$_2$CO$_3$ solution was added dropwise to the vigorously stirred MgSO$_4$ solution at a speed of 2 mL/min. The solution was stored at a certain temperature during the process of dropping. The white precipitate that formed was collected, filtered, washed several times using dH$_2$O and ethanol, and dried at 80 °C for 8 h.

An RM2000 confocal microprobe Raman spectroscope (Renishaw Company, UK) was used for phase analysis. A Quanta 200F scanning electron microscope (SEM; 200 V to 30 kV accelerating voltage; 25–200× magnification; FEI Quanta Company, USA) and a JEM-2100LaB$_6$ high-resolution transmission electron microscope (200 kV accelerating voltage; 50–1500× magnification; Japan Electronics Co., Ltd.) were used for morphological and structural analyses. An SDTQ600 simultaneous thermal analyzer (TA Company, USA) was used for thermal analysis. The heating rate was 10 °C/min. The change in pH was detected by a pH meter. CO$_3^{2−}$ was detected based on the methods of a previous study.

3. Results and discussion

3.1. Phase analysis of magnesium carbonate hydrate

Figure 1 shows the Raman spectra of 6 samples prepared at different temperatures. It seems from Figure 1 that there are only 2 characteristic peaks for all of the samples made from the reaction of MgSO$_4$ and (NH$_4$)$_2$CO$_3$.
solutions. The wavenumber at 1100 cm\(^{-1}\) is a characteristic peak of MgCO\(_3\cdot3\)H\(_2\)O, and the wavenumber at 1119 cm\(^{-1}\) is a characteristic peak of 414.\(^{18}\) Hopkinson et al.\(^{10}\) reported that a high-intensity band at 1099 cm\(^{-1}\) indicated the presence of nesquehonite and a high-intensity band at 1121 cm\(^{-1}\) was assigned to hydromagnesite. This coincides with the results of the present experiment. The characteristic peak attributed to MgCO\(_3\cdot3\)H\(_2\)O was gradually weakened, whereas that attributed to 414 was enhanced for all samples between 323 and 333 K. These results indicate the gradual transition from MgCO\(_3\cdot3\)H\(_2\)O to 414 with increased temperature.

The transition from MgCO\(_3\cdot3\)H\(_2\)O to 414 in MgSO\(_4\) and (NH\(_4\))\(_2\)CO\(_3\) solution systems can also be interpreted from the triangular plot of compositional characteristics of common magnesium hydrates and hydroxyl carbonates. The whole process can be regarded as a solvent-mediated transition process and MgCO\(_3\cdot3\)H\(_2\)O gradually dissolving with 414 gradually generating, which follows the dissolution recrystallization steps. In a study by Hopkinson et al.,\(^{12}\) the transition processes in the MgO-H\(_2\)O-CO\(_2\) system were investigated in detail; the process displayed mixed diffusion and reaction-limited control and proceeded through the production of metastable intermediates, which contain the peaks not presented by 414. However, it seems that the metastable intermediates are not obviously illustrated in Figure 1 for the samples made by MgSO\(_4\) and (NH\(_4\))\(_2\)CO\(_3\) solution systems. This may be attributed to the effects of SO\(_4^{2-}\) and NH\(_4^+\) ions in solutions on the triangular plot of compositional characteristics of common magnesium hydrates and hydroxyl carbonates.

![Figure 1. Raman spectra of the samples at different temperatures: a) 323 K, b) 325 K, c) 327 K, d) 329 K, e) 331 K, f) 333 K.](image)

3.2. Morphological analysis of magnesium carbonate hydrate

The SEM images of the samples prepared at different temperatures are shown in Figures 2a–2f. The crystals in Figure 2a were acicular and well-dispersed, with a smooth surface. The crystals synthesized at 323 K were 13.5–46.8 \(\mu\)m long and 3.19–9.50 \(\mu\)m in diameter. Figures 2b and 2c show that the crystal surface was rough and contained small particles. At 325 K, the crystals had diameters of 2.00–6.84 \(\mu\)m. At 327 K, the diameter ranged from 1.99 to 4.07 \(\mu\)m. Figure 2d shows that at 329 K, some small particles became flaky on the crystal surface, and the crystal diameters were 3.95–7.73 \(\mu\)m. Figure 2e shows that at 331 K, the flaky particles enlarged and maintained the acicular morphology, and the crystal diameters were 4.28–6.82 \(\mu\)m. At 333 K, the flaky particles further enlarged and formed agglomerates, which appeared as spherical crystals with diameters of 4.53–7.50 \(\mu\)m. The crystal diameters then gradually decreased until the crystals completely disappeared. Flaky particles were further produced and enlarged.
3.3. Thermogravimetric analysis of magnesium carbonate hydrate

Raman analysis revealed that the product at 323–333 K was a mixture of MgCO$_3$·3H$_2$O and 414 crystals. To determine the relative content of these 2 crystals accurately, thermogravimetric (TG) analysis was performed on the 6 samples and the results are shown in Figures 3a–3f.

![Figure 3. TG-T and derivative TG-T curves at different temperatures: a) 323 K, b) 325 K, c) 327 K, d) 329 K, e) 331 K, f) 333 K.](image)
Figure 3. Continued.

Figure 3a indicates that the total weight loss reaches 68.76% at 323 K. Davies and Bubela\textsuperscript{11} reported that the total weight loss of nesquehonite (MgO·CO\textsubscript{2}·3H\textsubscript{2}O) equaled 71.3%, which is very close to the product at 323 K. In contrast to their findings, it can be concluded that the approximate majority of the product at 323 K is MgCO\textsubscript{3}·3H\textsubscript{2}O. Figures 3e and 3f indicate that the total weight loss of the product reaches 61.64% at 331 K and 58.58% at 333 K. Davies and Bubela also reported that the total weight loss of protohydromagnesite equals 60.8%. Hao et al.\textsuperscript{15} reported the DTA curve’s 3 endothermic peaks with maxima located at 179.4 °C, 271.3 °C, and 421.1 °C, and this is consistent with the thermal behavior of Figure 3e at 333 K in the present paper. The product between 331 K and 333 K is thus likely to be an intermediate in the process of the transformation of nesquehonite into hydromagnesite. This is consistent with the results in this paper.

There were 2 possible decomposition reactions:

\[ MgCO_3 \cdot 3H_2O \rightarrow MgO + CO_2 \uparrow + 3H_2O \uparrow \quad (1) \]
\[ 4MgCO_3 \cdot Mg(OH)_2 \cdot 4H_2O \rightarrow 5MgO + 4CO_2 \uparrow + 5H_2O \uparrow \]
To prove that the solid powder added was MgCO$_3$·3H$_2$O or 414, the respective theoretical weightlessness values were calculated according to Eqs. (1) and (2). The molar ratio and quality percentage of MgCO$_3$·3H$_2$O and 414 (Table 1) were further obtained by the cross-method.

Table 1. The molar ratio and mass percent ratio of the precursor mixture at different temperatures.

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>323</th>
<th>325</th>
<th>327</th>
<th>329</th>
<th>331</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molar ratio of A/B</td>
<td>26</td>
<td>11</td>
<td>7</td>
<td>3</td>
<td>1</td>
</tr>
<tr>
<td>Mass percent ratio of A/B</td>
<td>8.1</td>
<td>3.2</td>
<td>2.2</td>
<td>0.9</td>
<td>0.4</td>
</tr>
</tbody>
</table>

Legend: A, MgCO$_3$·3H$_2$O; B, 414.

Table 1 presents the calculated quantitative information of MgCO$_3$·3H$_2$O and 414 at different temperatures.

Figure 4. Quantitative analysis of magnesium carbonate hydrates (■ quality percentage of MgCO$_3$·3H$_2$O; ● quality percentage of 414).

Figure 4 shows that all crystals were MgCO$_3$·3H$_2$O at a reaction temperature of 298–318 K, and all crystals were 414 at 333–363 K. The quality percentage of MgCO$_3$·3H$_2$O gradually decreased whereas that of 414 increased from 323 K to 333 K, thereby confirming the Raman analysis results.

The results of TG indicate that the total weight loss of the product at 333 K is 58.58%. The theoretical weight loss of 414 is 57.08%, while that of MgCO$_3$·3H$_2$O is 71.01%. It is apparent that the content of MgCO$_3$·3H$_2$O is very low. The results of TG indicate that the total weight loss of the product at 323 K is 62.11%. Therefore, it can be seen that all MgCO$_3$·3H$_2$O can be converted into 414.

Table 2 shows that the conversion of Mg$^{2+}$ before and after reaction is more than 99% between 323 and 333 K. Therefore, all of the Mg$^{2+}$ transforms into MgCO$_3$·3H$_2$O, intermediate, or 414. The total amount of the crystal is 1 mol under the experimental conditions.

3.4. Crystal plane analysis of magnesium carbonate hydrate during the transformation process

The electron diffraction and transmission electron microscope (TEM) images of the 3 samples at 323 K, 331 K, and 333 K are shown in Figures 5a–5d. The calibration of electron diffraction images is shown in Table 3.
Table 2. The conversion of Mg²⁺ before and after reaction.

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>The concentration of Mg²⁺ before reaction (g/L)</th>
<th>The concentration of Mg²⁺ after reaction (g/L)</th>
<th>Conversion of Mg²⁺ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>323</td>
<td>25.02</td>
<td>0.2010</td>
<td>99.20</td>
</tr>
<tr>
<td>325</td>
<td>25.02</td>
<td>0.2112</td>
<td>99.16</td>
</tr>
<tr>
<td>327</td>
<td>25.02</td>
<td>0.2001</td>
<td>99.20</td>
</tr>
<tr>
<td>329</td>
<td>25.02</td>
<td>0.1996</td>
<td>99.20</td>
</tr>
<tr>
<td>331</td>
<td>25.02</td>
<td>0.1991</td>
<td>99.21</td>
</tr>
<tr>
<td>333</td>
<td>25.02</td>
<td>0.2452</td>
<td>99.02</td>
</tr>
</tbody>
</table>

Figure 5. a) Electron diffraction pattern at 323 K; transmission images of crystals at b) 323 K, c) 331 K, and d) 333 K.

Table 3. Calibration results of TEM images at different temperatures.

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>R_m (cm)</th>
<th>R_c (nm)</th>
<th>d (nm)</th>
<th>d* (nm)</th>
<th>{hkl}</th>
</tr>
</thead>
<tbody>
<tr>
<td>323.0</td>
<td>6.550</td>
<td>13.70</td>
<td>0.1460</td>
<td>0.1457</td>
<td>(810)</td>
</tr>
<tr>
<td></td>
<td>6.300</td>
<td>6.632</td>
<td>0.3016</td>
<td>0.3030</td>
<td>(100)</td>
</tr>
<tr>
<td>331.0</td>
<td>13.00</td>
<td>13.68</td>
<td>0.1462</td>
<td>0.1457</td>
<td>(810)</td>
</tr>
<tr>
<td></td>
<td>4.800</td>
<td>6.621</td>
<td>0.3021</td>
<td>0.3030</td>
<td>(100)</td>
</tr>
<tr>
<td></td>
<td>3.850</td>
<td>5.310</td>
<td>0.3766</td>
<td>0.3850</td>
<td>(001)</td>
</tr>
<tr>
<td>333.0</td>
<td>4.200</td>
<td>8.750</td>
<td>0.2286</td>
<td>0.2298</td>
<td>(100)</td>
</tr>
<tr>
<td></td>
<td>7.000</td>
<td>5.858</td>
<td>0.3414</td>
<td>0.3812</td>
<td>(001)</td>
</tr>
</tbody>
</table>

Legend: \( R \) is the diameter of the ring or distance between 2 symmetric spots and \( d \) is the interplanar spacing. \( R_m \), measured value; \( R_c \), calculated value; \( d^* \), value of standard card.
As shown in Figures 5a–5d and Table 3, MgCO$_3$·3H$_2$O crystals grew along the $<810>$ direction and formed 1-dimensional morphology at 323 K. On the other hand, the 414 crystal grew along the $<001>$ and $<100>$ directions to form 2-dimensional morphology at 333 K. At 331 K, the crystal-reserved (810) plane related to MgCO$_3$·3H$_2$O crystal was observed with the production of a new (001) plane. Given that the newly produced crystal plane belonged to the 414 crystal, the crystal at 331 K was considered as a transition state during the transformation process. According to the crystal diffraction intensity data (Table 3), the intensity of the (810) plane gradually weakened and eventually disappeared. By contrast, the intensities of the (100) and (001) planes gradually strengthened, suggesting the enforcement of (100) and (001) planes.

According to the TEM calibration (Table 3) and previously simulated results, the ideal morphological images of the MgCO$_3$·3H$_2$O and 414 crystals should be like those in Figures 6a and 6b. MgCO$_3$·3H$_2$O crystallized in the monoclinic space group $P2_1/n(14)$, with lattice parameters $a = 1.2112$ nm, $b = 0.5365$ nm, and $c = 0.7697$ nm. The octahedron showed the chain distribution along the $<810>$ direction. On the other hand, 414 crystallized in the monoclinic space group $P2_1/c(14)$, with lattice parameters $a = 1.011$ nm, $b = 0.894$ nm, and $c = 0.838$ nm. The crystal grew into a 2-dimensional sheet structure along the $<100>$ and $<001>$ directions.

3.5. Growth unit analysis of magnesium carbonate hydrate during the transformation process

Previously simulated results$^{19}$ have shown that MgCO$_3$·3H$_2$O crystal formation is caused by the [Mg-O$_6$]$^{10-}$ octahedral, the growth unit of MgCO$_3$·3H$_2$O crystal. Mg is coordinated by 4 oxygen atoms in the CO$_3$ group and 2 H$_2$O molecules. The formation of the 414 crystal is caused by the $[4+1+1]$-coordination (Mg coordinated by 4 oxygen atoms of the CO$_3$ group, 1 H$_2$O ligand, and 1 OH group) and $[4+2]$-coordination (Mg coordinated by 4 oxygen atoms of the CO$_3$ group and 2 OH groups). These 2 forms of coordination are the growth units of 414 crystal.

Figure 7 shows that the pH of the filtered solution increased with increased temperature. Figure 8 shows that the concentration of CO$_3^{2-}$ decreased in the solution. Therefore, the proportion of CO$_3^{2-}$ around Mg$^{2+}$ can decrease in the form of an anionic coordination polyhedron, and the proportion of OH$^-$ around Mg$^{2+}$ can increase in the form of an anionic coordination polyhedron. The formation of an anionic coordination polyhedron with OH$^-$ with increased temperature is probably beneficial. Previous simulated results$^{19}$ indicated that the beneficial formation of 2 coordinations constituted 414.
The thermodynamic parameters of magnesium carbonate hydrate in the \( \text{MgO-CO}_2\cdot\text{H}_2\text{O} \) system reveal that the value of \( \Delta G^0_f \) for the produced \( \text{MgCO}_3\cdot3\text{H}_2\text{O} \) crystal is \(-1723.95 \text{ kJ/mol}\), and that for the produced 414 crystal is \(-5864.66 \text{ kJ/mol}\). The values of \( \Delta G^0_f \) for both crystals are less than 0, indicating that they can be produced spontaneously. High temperatures benefit the transformation from \( \text{MgCO}_3\cdot3\text{H}_2\text{O} \) to 414 crystal because the reaction is endothermic.

![Figure 7. Changes in the solution pH with temperature.](image)

![Figure 8. Changes in \( \text{CO}_3^{2-} \) concentration in the solution with temperature.](image)

The changes in crystal morphology during the transformation are shown in Figures 9a–9d, which demonstrate the transformation of the crystal morphology of magnesium carbonate hydrate within the specified temperature range. Figure 9a shows that at 325 K, the crystal was acicular-shaped, and stepwise screw dislocation was found on top of the crystal. When the temperature was increased to 327 K, screw dislocations along the crystal side and top became more significant, and flake particles were observed along these steps. When the temperature was increased further to 331 K, numerous flaky crystals were produced and finally aggregated to form petal shapes.

According to the screw dislocation theory proposed by Frank,\(^{20}\) whiskers are essentially the result of the extension along the dislocation direction. The whisker side should be a low-energy surface, where the supersaturation must be sufficiently low. These exposed steps provide preferential energy areas for crystal growth. Therefore, crystals can grow along a certain crystal plane under very low supersaturation because the combination of atoms becomes more firm in the positions of steps or distortions as the preferential areas for atoms or ions are obtained. Thus, whiskers are produced as shown in Figure 9a. The composition of growth units changed with increased temperature. The flaky materials produced at the crystal top and side were 414 crystal composed of 2 ligands, destroying the chain structure composed of the \([\text{Mg-O}_6]^{10-}\)-octahedron. With increased temperature, such transformation became more significant and more 414 crystals comprising 2 ligands appeared. Consequently, the final form of 414 crystal was entirely composed of flaky structures.
Figure 9. SEM images of crystal morphology during the transformation process at a) 325 K, b) 327 K, c) 329 K, and d) 331 K.

4. Conclusion
MgCO$_3$·3H$_2$O crystal can be obtained at 298–323 K, the 414 crystal at 333–363 K, and the mixture of MgCO$_3$·3H$_2$O and 414 at 323 and 333 K. The quality percentage of MgCO$_3$·3H$_2$O gradually decreased and that of 414 gradually increased at 323–333 K. At 331 K, the crystal-reserved (810) plane related to the MgCO$_3$·3H$_2$O crystal formed and produced a new (001) plane. This finding suggested that the crystal was in a transition state from MgCO$_3$·3H$_2$O to 414. Growth unit analysis revealed the benefit of forming the 2 coordinations composed of 414. The transformation process of the crystals was discussed from the viewpoint of the changes in the crystal plane and growth units.

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References