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Solubility and Stability of Nesquehonite ($MgCO_3 \cdot 3H_2O$) in NaCl, KCl, $MgCl_2$, and NH_4Cl Solutions

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This work reports the stability and solubility of nesquehonite in several salts (NaCl, NH_4Cl, $MgCl_2$, and KCl) over the temperature range of (15 to 35) °C. The needle-like nesquehonite used in this work was prepared by the reaction of analytical pure $MgCl_2$ with Na_2CO_3. The concentration investigated for all salts was up to 4 $mol \cdot dm^{-3}$ NaCl, 3.5 $mol \cdot dm^{-3}$ NH_4Cl, 4 $mol \cdot dm^{-3}$ $MgCl_2$, and 1.0 $mol \cdot dm^{-3}$ KCl at ambient temperature. The solubility of nesquehonite in pure water was found to decrease with temperature within the temperature range in which nesquehonite is the stable phase. In NaCl solutions, the solubility of nesquehonite initially increases to a maximum value and then decreases gradually with an increase of the common salt concentration. It was further found that the addition of $MgCl_2$, NH_4Cl, or KCl causes the solubility of nesquehonite to increase due apparently to complexation. XRD and SEM examination of the equilibrated solids showed that nesquehonite is stable in pure water up to 50 °C, but its stability region becomes smaller in concentrated brines.

Introduction

Nowadays, numerous chemicals, such as NaCl, KCl, LiCl, $MgCl_2$, and boric acid (H_3BO_3) are extracted from salt lake brines.[1,2] Qarham salt lake is well-known for its huge reserves of potassium representing more than 90 % of all potassium deposits in China. However, the brines in Qarham salt lake also contain extremely high Mg content with a Mg/K ratio up to 30 and Mg/Li ratio up to 1000. Approximately 20 million tonnes annually of magnesium chloride are generated as a byproduct or waste of the potassium fertilizer industry in Qinghai, China. After the exploitation of potash salts, the waste brine is almost a pure solution of magnesium chloride containing a minor amount of lithium, boron, and other minor constituents.[3] Magnesium chloride cannot be utilized effectively and is discarded back into the lakes. This has caused not only the wasting of valuable magnesium resources but also a serious environmental problem. Therefore, extraction and application of magnesium, lithium, and boron resources existing in the saline lakes in China is becoming more and more important from economic, environmental, and technological points of view.

Magnesium chloride (or bischofite) has potentially a huge variety of applications in industry. Most importantly, it is a raw material for production of magnesium oxide, magnesium hydroxide, and magnesium metal. About 107 kg of magnesium metal can be produced from 1 m^3 of bischofite-saturated brine. For the purpose of realizing the comprehensive usage of all resources of Qinghai lakes, the use of magnesium chloride to a practical end should be investigated. Hence, a novel process was proposed by Wang et al.[4] to exploit the extraction and utilization of magnesium resources existing in discarded brine. In this process, magnesium is recovered by precipitation of nesquehonite. This magnesium mineral compound[5] was selected as a target precipitate due to its good filtration properties. Nesquehonite upon calcination yields high-quality magnesium oxide (MgO).

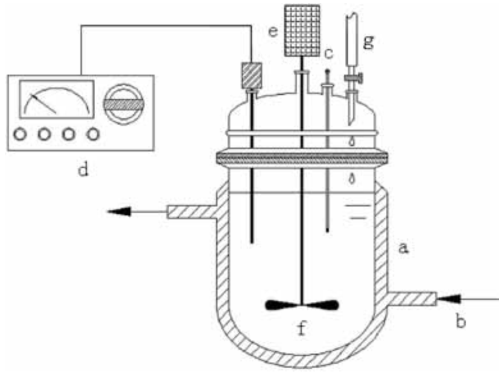

Figure 1. Experimental setup used in the $MgCO_3 \cdot 3H_2O$ synthesis process.

The solubility and phase equilibrium of salts in electrolyte aqueous solutions play a significant role in the development, design, optimization, and operation of precipitation processes. Solubility is essential to determine phase relationships in a system that includes unstable or metastable solid phases.[6,7] The magnesium carbonate solids in equilibrium with solution can be transformed to other phases depending on the concentration and nature of the electrolyte as well as its temperature.[8] For example, $MgCO_3 \cdot 3H_2O$ is unstable when the pH of the solution is above 11. For this reason, the solubility and stability of $MgCO_3 \cdot 3H_2O$ are essential properties relevant the precipitation process in which nesquehonite is precipitated by the reaction of $MgCl_2$ with Na_2CO_3 or $(NH_4)_2CO_3$.

To date, there are several reports about the stability and solubility of $MgCO_3 \cdot 3H_2O$ in pure water and salt solutions.

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Table 1. Chemical Reagents Employed

compound name	formula	purpose	provider	purity
magnesium chloride	$MgCl_2 \cdot 6H_2O$	solubility and synthesis	Sinopharm Chemical Reagent Co. Ltd.	⩾ 98.0 %
sodium carbonate	Na_2CO_3	synthesis	Chemical Company of Beijing	⩾ 99.8 %
ammonium chloride	NH_4Cl	solubility	Chemical Company of Beijing	⩾ 99.5 %
sodium chloride	NaCl	solubility	Chemical Company of Beijing	⩾ 99.5 %
potassium chloride	KCl	solubility	Chemical Company of Beijing	⩾ 99.5 %

As early as 1915, Wells[9] determined the solubility of magnesium carbonate in natural waters. Walter[10] measured the solubility of nesquehonite ($MgCO_3 \cdot 3H_2O$) in water, and it is known that the solubility increases with further increasing pressures of carbon dioxide and decreases with increasing pH of the solution and temperature. Cameron and Seidell[11] reported the solubility of magnesium carbonate in several aqueous electrolytes. The previous studies show that there are very limited investigations in determining the solubility and stability of $MgCO_3 \cdot 3H_2O$ in geologically relevant brines containing NaCl, KCl, and $MgCl_2$.

In this study, needle-shaped $MgCO_3 \cdot 3H_2O$ was carefully prepared first by a novel precipitation technology at a relatively low temperature by the reaction of $MgCl_2$ with Na_2CO_3 in supersaturated solutions without using any organic additives. Subsequently, the solubility and stability of $MgCO_3 \cdot 3H_2O$ in pure water within the temperature range of (25 to 70) °C and in the Na−Mg−K−NH$_4$−Cl brines of different concentrations at (15, 25, and 35) °C were measured systematically at atmospheric pressure.

Experimental

Chemicals. All chemical reagents used in the experiments were analytical grade without further purification. The water used in all experimental work for solution preparation, dilution, crystal washing, etc. was double-distilled water (conductivity $< 0.1\ \mu S \cdot cm^{-1}$) unless otherwise specified (Table 1).

Synthesis of Nesquehonite ($MgCO_3 \cdot 3H_2O$). The experiments were performed in a 1 L double-jacket glass reactor heated by a water circulator as shown in Figure 1. A standard volume (400 mL) of $MgCl_2$ solution of 0.5 M located in the reactor (a) was heated to 40 °C with the aid of the circulation of hot water (b). Solution temperature was monitored with a thermometer (c). pH was monitored with a pH meter (d). Upon attainment of the desired temperature, addition of Na_2CO_3 solution (400 mL) of 0.5 M (according to the molar ratio $Mg^{2+}:CO_3^{2-} = 1:1$) was started simultaneously with the initiation of stirring at 300 rpm. Stirring was provided by a motor drive (e), and a 2-blade radial impeller (f) was used. The location of the impeller and four baffles attached to the lid provided uniform mixing. During the $MgCl_2$−Na_2CO_3 reaction, Na_2CO_3 addition by titration was done using a standardized burette (g), while the addition speed was $3.3\ mL \cdot min^{-1}$. When the addition procedure was completed, stirring continued for 2 h. Then, the white precipitate was collected, filtered off, and washed with distilled water three times (to remove any possible ionic remnants), and finally dried in an oven at 50 °C for 10 h.

Characterization. The structure and morphology of the synthesized samples were examined using X-ray powder diffraction and scanning electron microscopy. X-ray powder diffraction (XRD, X'Pert PRO MPD, PANalytical, Netherlands) patterns were recorded on a diffractometer (using Cu Kα radiation) operating at 40 kV/30 mA. A scanning rate of $0.02° \cdot s^{-1}$ was applied to record the patterns in the 2θ angle range from 5° to 90°. The morphology and particle size of the as-synthesized samples were examined by a scanning electron microscope (SEM, JEOL-JSM-6700F).

Table 2. Solubility of $MgCO_3 \cdot 3H_2O$ (1) in H_2O (2)

stirring time	solubility as $MgCO_3$ in different units		
h	C_1/g·L^{-1}	M_1/mol·L^{-1}	m_1/mol·kg^{-1}
	$T = 25$ °C		
1.0	0.7466	0.008855	0.008913
2.0	0.7488	0.008898	0.008941
3.0	0.7488	0.008898	0.009152
4.0	0.7701	0.009152	0.009176
20.0	0.7906	0.009395	0.009448
24.0	0.8057	0.009575	0.009612
	$T = 30$ °C		
0.5	0.7179	0.008361	0.008422
1.0	0.7088	0.008361	0.008401
1.5	0.7357	0.008537	0.008577
2.0	0.7376	0.008609	0.008645
2.5	0.7414	0.008619	0.008686
3.0	0.7323	0.008686	0.008712
24.0	0.7364	0.008734	0.008782
	$T = 40$ °C		
0.5	0.6811	0.008094	0.008162
1.0	0.6766	0.008041	0.008130
2.0	0.6998	0.008316	0.008623
3.0	0.7220	0.008580	0.008654
4.0	0.7301	0.008676	0.008745
5.0	0.7314	0.008692	0.008757
6.0	0.7212	0.008570	0.008893
	$T = 50$ °C		
0.5	0.6544	0.007776	0.007865
1.0	0.6722	0.007988	0.008107
2.0	0.7568	0.008993	0.009101
3.0	1.7865	0.02123	0.02158
4.0	2.4042	0.02857	0.02892
5.0	0.9879	0.01174	0.01188
6.0	1.0106	0.01201	0.01217
	$T = 60$ °C		
0.033	0.5965	0.007089	0.007207
0.5	0.6668	0.007924	0.008075
1.0	1.1066	0.01315	0.01336
1.5	1.7293	0.02055	0.02086
2.5	1.6477	0.01958	0.01987
3.5	1.5980	0.01899	0.01930
4.5	1.5164	0.01802	0.01831
6.0	1.4129	0.01679	0.01707
	$T = 70$ °C		
0.033	0.6188	0.007353	0.007524
0.167	0.6677	0.007935	0.008126
0.5	1.8521	0.02201	0.02251
1.0	1.1310	0.01344	0.01374
2.0	1.1200	0.01331	0.01360
3.0	1.0594	0.01259	0.01286
4.0	0.9963	0.01184	0.01213
5.0	0.8191	0.009734	0.009944

Dissolution of Nesquehonite ($MgCO_3 \cdot 3H_2O$). The approaches that determine the solubility of salts in solutions can be categorized as either the dissolution or precipitation method.[12] The dissolution method is considered to be more reliable and feasible since it avoids the complication of formation of intermediate phases that is commonly encountered in precipitation. In this work, the dissolution method was employed.

Procedure. A typical experimental procedure can be described as follows. The 200 mL of salt solution of known composition was introduced to Erlenmeyer flasks, 250 mL volume, which

Table 3. Solubility of $MgCO_3 \cdot 3H_2O$ (1) in NaCl (2) + H_2O (3)[a]

solution parameters		solubility as $MgCO_3$ in different units		
M_2/mol·L^{-1}	ρ_s/g·mL^{-1}	C_1/g·L^{-1}	M_1/mol·L^{-1}	m_1/mol·kg^{-1}
		$T = 15$ °C		
0.1	1.0037	1.1289	0.01339	0.01343
0.3	1.0101	1.5437	0.01831	0.01848
0.5	1.0165	1.8093	0.02146	0.02172
0.7	1.0270	1.9611	0.02326	0.02363
0.9	1.0361	2.1137	0.02507	0.02555
1.0	1.0364	2.1929	0.02601	0.02658
1.5	1.0562	2.3430	0.02779	0.02868
2.0	1.0758	2.4273	0.02879	0.02999
2.5	1.0932	2.4399	0.02894	0.03053
3.0	1.1113	2.3152	0.02746	0.02925
3.5	1.1306	2.2300	0.02645	0.02853
4.0	1.1455	2.1035	0.02495	0.02560
		$T = 25$ °C		
0.1	1.0012	1.0665	0.01265	0.01272
0.3	1.0090	1.3700	0.01625	0.01641
0.5	1.0165	1.6415	0.01947	0.01973
0.7	1.0241	1.7722	0.02102	0.02142
0.9	1.0320	1.9071	0.02262	0.02314
1.0	1.0364	1.9189	0.02276	0.02282
1.5	1.0563	2.1255	0.02521	0.02604
2.0	1.0758	2.1752	0.02580	0.02650
2.5	1.0932	2.2165	0.02629	0.02726
3.0	1.1113	2.1541	0.02555	0.02732
3.5	1.1306	2.0470	0.02428	0.02623
4.0	1.1455	1.9366	0.02297	0.02521
		$T = 35$ °C		
0.1	1.0012	0.9982	0.01184	0.01191
0.3	1.0052	1.3119	0.01556	0.01578
0.5	1.0148	1.4948	0.01773	0.01802
0.7	1.0202	1.6609	0.01970	0.02015
0.9	1.0289	1.7798	0.02111	0.02166
1.0	1.0333	1.8093	0.02146	0.02205
1.5	1.0526	1.9560	0.02320	0.02409
2.0	1.0720	2.0310	0.02409	0.02528
2.5	1.0897	2.0470	0.02428	0.02589
3.0	1.1078	2.0420	0.02422	0.02603
3.5	1.1253	1.9501	0.02313	0.02517
4.0	1.1432	1.8304	0.02171	0.02392

[a] Equilibration time: 6 h.

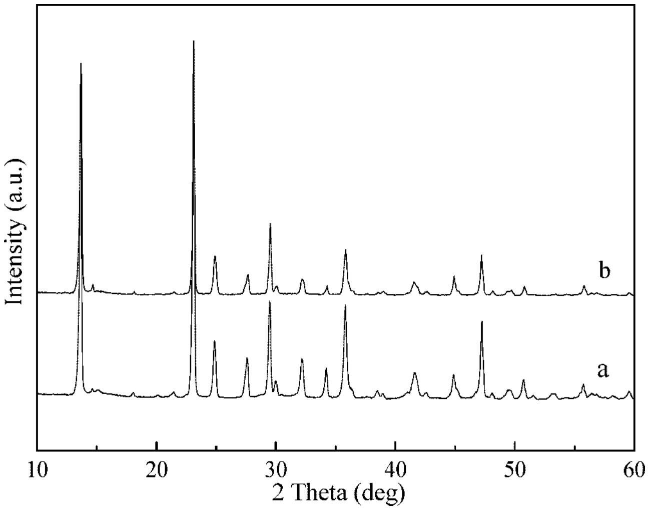

Figure 2. XRD pattern of synthesized $MgCO_3 \cdot 3H_2O$ material compared with the literature data. (a) Literature value. (b) Experimental value.

Table 4. Solubility of $MgCO_3 \cdot 3H_2O$ (1) in NH_4Cl (2) + H_2O (3)[a]

solution parameters		solubility as $MgCO_3$ in different units		
M_2/mol·L^{-1}	ρ_s/g·mL^{-1}	C_1/g·L^{-1}	M_1/mol·L^{-1}	m_1/mol·kg^{-1}
		$T = 15$ °C		
0.1	1.0011	2.6768	0.03175	0.03197
0.3	1.0046	4.5738	0.05425	0.05513
0.5	1.0105	5.5999	0.06642	0.06790
0.7	1.0144	6.7962	0.08061	0.08309
0.9	1.0184	7.2633	0.08615	0.08983
1.0	1.0179	7.4724	0.08863	0.09262
1.5	1.0273	8.6165	0.1022	0.1089
2.0	1.0355	9.4849	0.1125	0.1224
2.5	1.0446	10.539	0.1250	0.1388
3.0	1.0495	11.045	0.1310	0.1492
3.5	1.0563	11.171	0.1325	0.1544
		$T = 25$ °C		
0.1	1.0013	2.7848	0.03303	0.03330
0.3	1.0028	4.6278	0.05489	0.05589
0.5	1.0092	5.8553	0.06945	0.07081
0.7	1.0120	6.7591	0.08017	0.08284
0.9	1.0160	7.5959	0.09009	0.09382
1.0	1.0190	7.9875	0.09474	0.09836
1.5	1.0259	9.3972	0.11146	0.11821
2.0	1.0347	10.361	0.12289	0.13290
2.5	1.0400	11.175	0.13254	0.14676
3.0	1.0479	11.626	0.13790	0.15598
3.5	1.0517	11.904	0.14119	0.16397
		$T = 35$ °C		
0.1	1.0003	2.9702	0.03523	0.03562
0.3	1.0010	4.8799	0.05788	0.05916
0.5	1.0057	5.9093	0.07009	0.07172
0.7	1.0084	7.2566	0.08607	0.08931
0.9	1.0129	7.9951	0.09483	0.09911
1.0	1.0154	8.2531	0.09789	0.10201
1.5	1.0227	9.8794	0.11718	0.12471
2.0	1.0305	10.958	0.12997	0.14122
2.5	1.0396	11.747	0.13933	0.15439
3.0	1.0459	12.530	0.14862	0.16854
3.5	1.0523	12.753	0.15126	0.17560

[a] Equilibration time: 6 h.

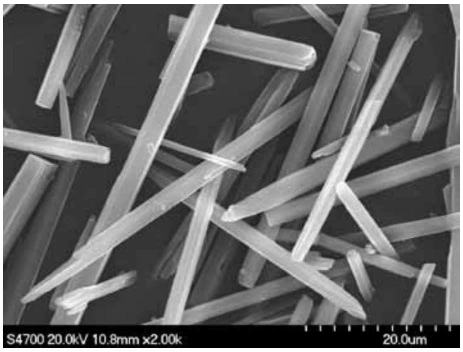

Figure 3. SEM morphology for the synthesized $MgCO_3 \cdot 3H_2O$ material.

were equipped with a magnetic stirrer and capped with glass stoppers. The flasks were then immersed in a temperature-controlled water bath, allowing the solution to stir continuously for about 0.5 h to establish the temperature equilibrium. The temperature was kept constant within 0.1 °C. Then, excess solid (3 g of nesquehonite) was quickly added to the solutions in flasks, which were tightly capped again by using glass stoppers to avoid the absorption of CO_2. The standard equilibration time used was 6 h, and the determination of equilibration time is explained in the next section. After the solid−liquid equilibrium was attained, stirring was stopped to allow solids to settle. The supernatant solution was then withdrawn and immediately filtered by using 0.22 μm Whatman Puradisc syringe filters. The clear filtrate was added into a 25 mL volumetric flask which was kept in the water bath and then heated to bath temperature for measuring the density of nesquehonite saturated solution. The contents of Mg and C were determined by titration of EDTA or the TOC method. The solubility (*s*) of nesquehonite, expressed as moles per kilogram of H_2O^{1-}, was obtained from the Mg or C analysis. The solid phase was filtered and washed

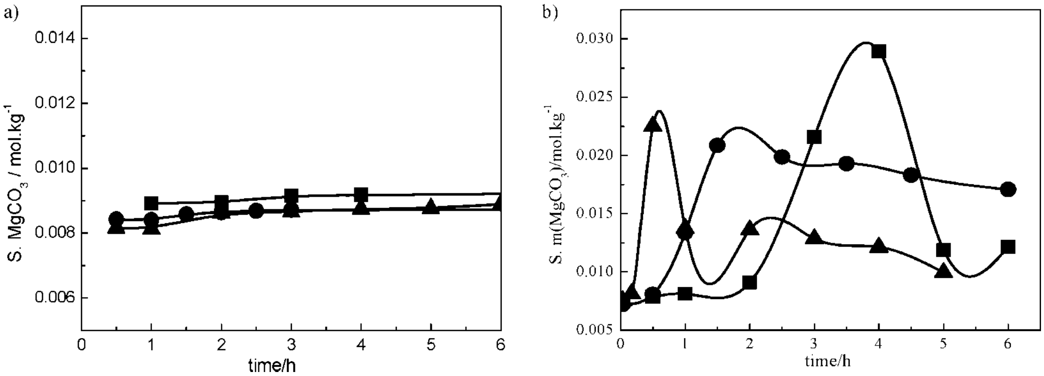

Figure 4. Solubility of $MgCO_3\cdot 3H_2O$ in pure water at different temperatures. (a) (25 to 40) °C: ■, 25 °C; ●, 30 °C; ▲, 40 °C. (b) (50 to 70) °C: ■, 50 °C; ●, 60 °C; ▲, 70 °C.

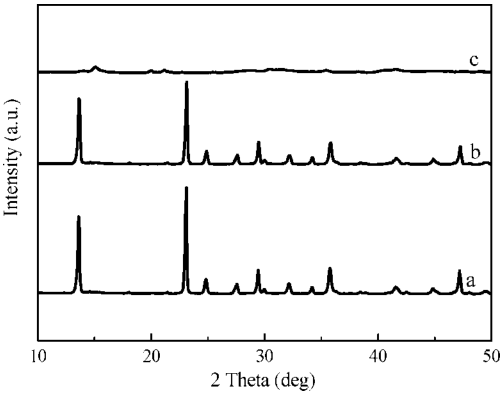

Figure 5. XRD pattern of $MgCO_3\cdot 3H_2O$ in water. (a) 25 °C, (b) 40 °C, (c) 50 °C.

three times with water. The washed solids were dried at 50 °C for 12 h and then analyzed by X-ray powder diffraction to determine whether the solid phase had been altered by phase transformation. Additionally, scanning electron microscope (SEM) image techniques were also used for examination of the solid phases.

Determination of Equilibration Time. The equilibration time in solubility measurements normally varies from several hours to several days depending on the dissolution rate of the solid phase and the applied conditions.[13] Power et al.[14] reported that the equilibrium of gypsum dissolution in pure water is reached within 1 min. Li and Demopoulos[6] reported that the equilibration time of solid and liquid can be reached within 0.5 h in determining the solubility of calcium sulfate dihydrate in HCl solution. The experimental results showed that the solubility equilibrium between nesquehonite and solution can be obtained within 3 h. The dissolution of $MgCO_3\cdot 3H_2O$ in NaCl solutions can reach equilibrium within 0.5 h. However, a longer time of 6 h was selected to ensure solubility equilibrium.

Reproducibility. The solubility of nesquehonite in pure water has been investigated by Walter.[10] Similar experiments were carried out by the authors to verify the reproducibility and accuracy of the adopted procedure in this work. The solubility value of nesquehonite in pure water at 25 °C from the literature[10] with the partial pressure (0.0345 Pa)[15] of carbon dioxide in the atmosphere is 0.01187 $\text{mol}\cdot\text{kg}\cdot\text{H}_2\text{O}^{1-}$ by using an interpolation method, while the experimental data in this study are 0.00961 $\text{mol}\cdot\text{kg}\cdot\text{H}_2\text{O}^{1-}$. The uncertainty of the determined solubility values was within ± 0.00226 $\text{mol}\cdot\text{kg}\cdot\text{H}_2\text{O}^{1-}$ with a relative deviation of 0.5 %.

Table 5. Solubility of $MgCO_3\cdot 3H_2O$ (1) in $MgCl_2$ (2) + H_2O (3)[a]

solution parameters		solubility as $MgCO_3$ in different units		
$M_2/\text{mol}\cdot\text{L}^{-1}$	$\rho_s/\text{g}\cdot\text{mL}^{-1}$	$C_1/\text{g}\cdot\text{L}^{-1}$	$M_1/\text{mol}\cdot\text{L}^{-1}$	$m_1/\text{mol}\cdot\text{kg}^{-1}$
		T = 15 °C		
0.1	1.0057	0.7953	0.009433	0.009477
0.3	1.0206	0.9763	0.01158	0.01168
0.5	1.0375	1.1736	0.01392	0.01407
0.7	1.0510	1.2680	0.01504	0.01530
0.9	1.0661	1.4577	0.01729	0.01766
1.0	1.0725	1.5395	0.01826	0.01871
1.5	1.1065	1.9088	0.02264	0.02353
2.0	1.1415	2.2182	0.02631	0.02771
2.5	1.1767	2.8809	0.03417	0.03649
3.0	1.2106	3.2544	0.03860	0.04185
3.5	1.2438	3.6473	0.04326	0.04766
4.0	1.2752	4.5831	0.05436	0.06103
		T = 25 °C		
0.1	1.0035	1.3047	0.01548	0.01559
0.3	1.0184	1.3757	0.01632	0.01651
0.5	1.0323	1.5120	0.01793	0.01824
0.7	1.0471	1.6384	0.01943	0.01985
0.9	1.0643	1.7649	0.02093	0.02143
1.0	1.0703	1.8527	0.02198	0.02258
1.5	1.1065	2.1998	0.02609	0.02713
2.0	1.1417	2.6010	0.03085	0.03251
2.5	1.1730	3.0246	0.03588	0.03848
3.0	1.2052	3.7363	0.04432	0.04836
3.5	1.2397	4.0876	0.04848	0.05369
4.0	1.2714	4.3637	0.05176	0.05835
		T = 35 °C		
0.1	1.0021	1.7225	0.02043	0.02062
0.3	1.0160	1.7655	0.02094	0.02124
0.5	1.0321	1.8278	0.02168	0.02206
0.7	1.0474	1.8970	0.02250	0.02298
0.9	1.0614	1.8700	0.02218	0.02277
1.0	1.0680	2.1187	0.02513	0.02588
1.5	1.1018	2.2469	0.02665	0.02785
2.0	1.1334	2.3818	0.02825	0.03002
2.5	1.1716	2.6372	0.03128	0.03358
3.0	1.2024	2.7493	0.03261	0.03565
3.5	1.2354	2.9281	0.03473	0.03859
4.0	1.2609	3.0478	0.03615	0.04118

[a] Equilibration time: 6 h.

Results and Discussion

Purity and Morphology of $MgCO_3\cdot 3H_2O$. Figure 2 displays the XRD pattern of the synthesized material compared with literature data.[5] All peaks in the XRD pattern were in good agreement with the $MgCO_3\cdot 3H_2O$ reference data.[5] The sharp diffraction peaks implied a good crystallinity of our target compound, $MgCO_3\cdot 3H_2O$.

Figure 3 provides an SEM image of the synthesized $MgCO_3\cdot 3H_2O$ material. As can be observed, the needle-like particles

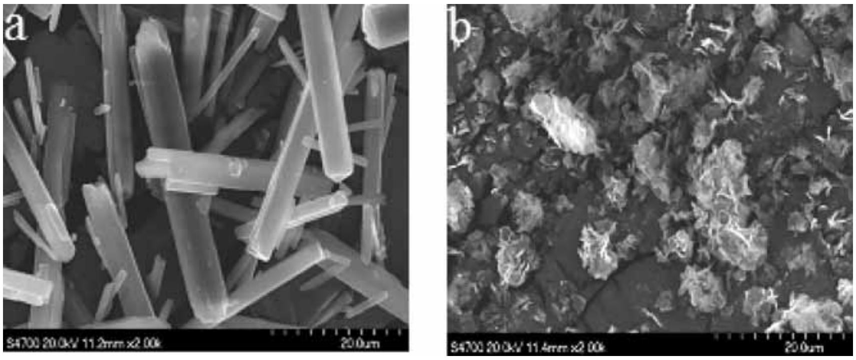

Figure 6. SEM morphologies of $MgCO_3 \cdot 3H_2O$ in water after 6 h. (a) 25 °C, (b) 60 °C.

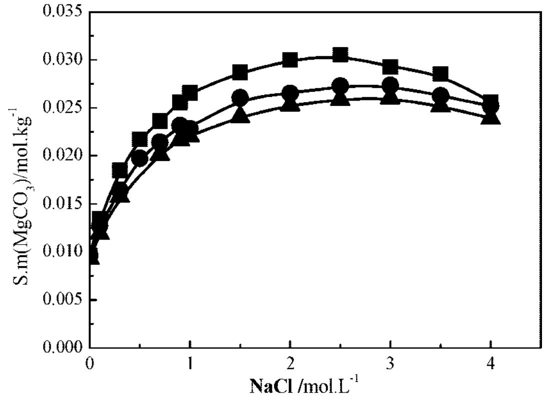

Figure 7. Solubility of $MgCO_3 \cdot 3H_2O$ in NaCl solutions at different temperatures. ■, 15 °C; ●, 25 °C; ▲, 35 °C.

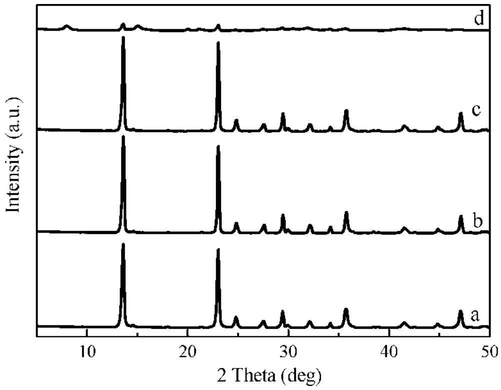

Figure 8. XRD pattern of $MgCO_3 \cdot 3H_2O$ in NaCl solutions after 6 h. (a) 15 °C, (b) 25 °C, (c) 35 °C, (d) 40 °C.

exhibit a smooth surface, and the crystals consisted of large straight whiskers with fairly uniform width and length.

A certain amount of $MgCO_3 \cdot 3H_2O$ was dissolved in excessive solution of hydrochloric acid with low concentration. The concentration of magnesium ion in the solution was determined by a titration method using standard EDTA solution with the error below 0.5 %. The results showed that the purity of the $MgCO_3 \cdot 3H_2O$ sample synthesized in this study was 99.4 %, which satisfies the requirement of solubility measurements.

Solubility of $MgCO_3 \cdot 3H_2O$ in Pure Water with Time. $MgCO_3 \cdot 3H_2O$ solubility in pure water was measured at (25, 30, 40, 50, 60, and 70) °C. The dissolution time varied from (0.0 to 24) h at different temperatures to determine the equilibration time. The results of experimentally determined solubility are summarized in Table 2 and demonstrated graphically in Figure 4. In Table 2, the solubility of $MgCO_3 \cdot 3H_2O$ was expressed both in molarity ($M/\text{mol} \cdot \text{dm}^{-3}$) and molality ($m/\text{mol} \cdot \text{kg}^{-1}$) for convenient practical and thermodynamic reference.

Figure 4a shows that at (25 to 40) °C the solubility of $MgCO_3 \cdot 3H_2O$ increases slowly within 3 h and then stabilizes. In reference to temperature, the solubility decreases systematically as the temperature increases from (25 to 40) °C. The solubility data of $MgCO_3 \cdot 3H_2O$ as shown in Figure 4b demonstrate that nesquehonite experienced complicated phase transformation at (50 to 70) °C.

The XRD analysis of equilibrated solid phases showed $MgCO_3 \cdot 3H_2O$ in pure water to be stable at the temperature range of (25 to 40) °C, while the transformation of the solid phase was observed above 50 °C. The results of XRD analysis are presented in Figure 5. Typical SEM images are presented in Figure 6. It can be clearly seen that nesquehonite is a needle-shaped phase and stable for 6 h at 25 °C while it was transformed to amorphous phases of magnesium carbonate after equilibrium exposure to a solution at 60 °C.

Solubility of $MgCO_3 \cdot 3H_2O$ in Sodium Chloride Solution. The solubility of $MgCO_3 \cdot 3H_2O$ in sodium chloride solution was determined by the same method at (15, 25, and 35) °C. The investigated concentration of sodium chloride solution is from (0.1 to 4.0) $\text{mol} \cdot \text{L}^{-1}$. The determined solubility of $MgCO_3 \cdot 3H_2O$ is summarized in Table 3 and Figure 7. The general behavior observed shows a decrease in solubility of $MgCO_3 \cdot 3H_2O$ with increasing temperature. It increases reaching a maximal value and then decreases with the increasing concentration of NaCl. XRD analysis (Figure 8) showed the solid phase to be stable within the temperature range of (15 to 35) °C. However, $MgCO_3 \cdot 3H_2O$ can be transformed to amorphous phases of $MgCO_3$ above 40 °C. The equilibrated solids were examined by SEM. Typical SEM images are presented in Figure 9. It can be clearly seen that the solid phase of $MgCO_3 \cdot 3H_2O$ is needle-shaped at (15 to 35) °C, while the surface of the solid is covered by sheetlike particles at 40 °C.

Solubility of $MgCO_3 \cdot 3H_2O$ in Ammonium Chloride Solution. The same approach was used to obtain the solubility of $MgCO_3 \cdot 3H_2O$ in NH_4Cl [(0.1 to 4.0) $\text{mol} \cdot \text{L}^{-1}$] solutions at (15, 25, and 35) °C. The results determined in this study are given in Table 4 and graphically in Figure 10. The solubility of $MgCO_3 \cdot 3H_2O$ sharply increases with increasing solution concentration and increases with increasing temperature. Hydrolysis of NH_4^+ is responsible for this elevation of solubility. The detailed explanation will be presented in another section. XRD patterns (Figure 11) show that $MgCO_3 \cdot 3H_2O$ is stable within the temperature range of (15 to 35) °C in NH_4Cl solutions.

Solubility of $MgCO_3 \cdot 3H_2O$ in Magnesium Chloride Solutions. The solubility of $MgCO_3 \cdot 3H_2O$ at (15, 25, and 35) °C in magnesium chloride solutions with concentrations up to 4 $\text{mol} \cdot \text{dm}^{-3}$ was determined by using the same procedure. It is very difficult to obtain the solubility of nesquehonite by

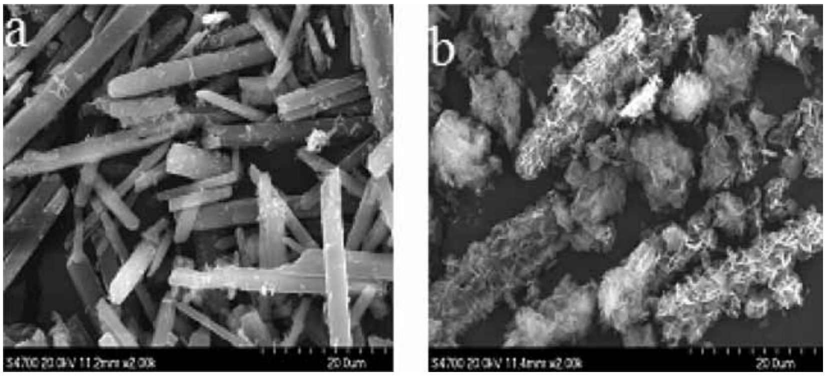

Figure 9. SEM images of $MgCO_3 \cdot 3H_2O$ after 6 h. (a) 35 °C, (b) 40 °C.

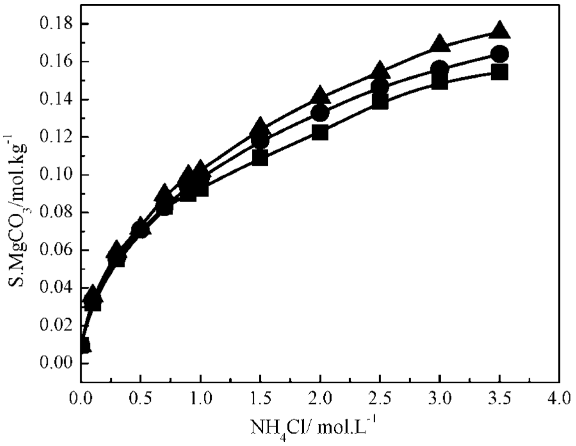

Figure 10. Solubility of $MgCO_3 \cdot 3H_2O$ in NH_4Cl solutions at different temperatures. ■, 15 °C; ●, 25 °C; ▲, 35 °C.

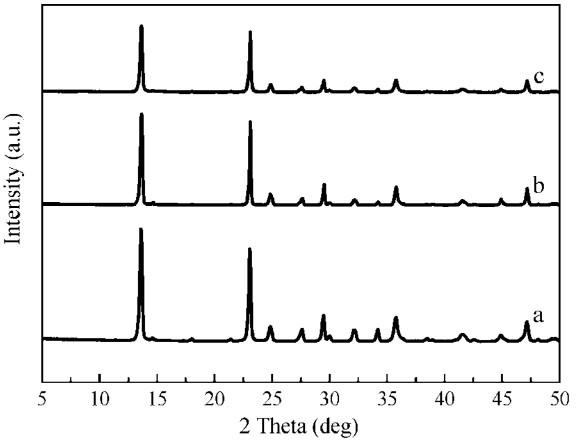

Figure 11. XRD pattern of $MgCO_3 \cdot 3H_2O$ in NH_4Cl solutions after 6 h. (a) 15 °C, (b) 25 °C, (c) 35 °C.

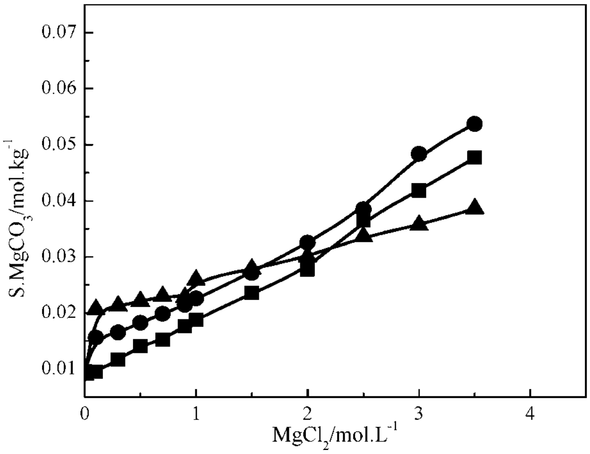

Figure 12. Solubility of $MgCO_3 \cdot 3H_2O$ in $MgCl_2$ solutions at different temperatures. ■, 15 °C; ●, 25 °C; ▲, 35 °C.

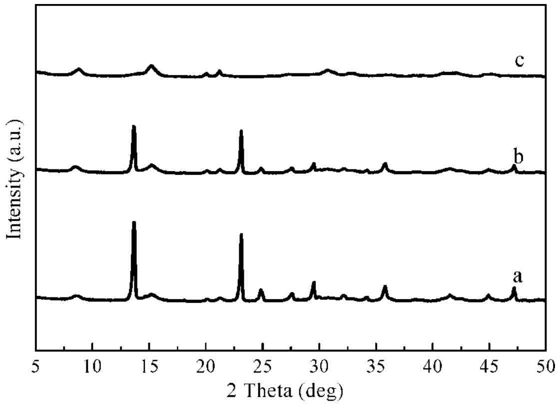

Figure 13. XRD pattern of $MgCO_3 \cdot 3H_2O$ in $MgCl_2$ solutions after 6 h. (a) 15 °C, (b) 25 °C, (c) 35 °C.

determining the Mg content in concentrated magnesium chloride solution. So we decided to use the TOC method to analyze the C content to obtain the solubility. TOC is often used to determine C of organic and inorganic substances in environmental applications. The obtained experimental solubility data is shown in Table 5 and Figure 12. Figure 12 illustrates that the solubility of $MgCO_3 \cdot 3H_2O$ increases with the concentration of $MgCl_2$ and temperatures up to 25 °C. However, XRD patterns as shown in Figure 13 demonstrated that nesquehonite in more than 1.0 $mol \cdot L^{-1}$ $MgCl_2$ at 35 °C was transformed into an amorphous phase of $MgCO_3$.

Solubility of $MgCO_3 \cdot 3H_2O$ in Potassium Chloride Solutions. The solubility of $MgCO_3 \cdot 3H_2O$ in potassium chloride solutions with concentrations up to 1 $mol \cdot dm^{-3}$ at 25 °C was determined by using the same procedure. The obtained experimental solubility data is shown in Table 6 and Figure 14. Figure 14 illustrates that the solubility of $MgCO_3 \cdot 3H_2O$ increases with the concentration of KCl. XRD patterns as shown in Figure 15 demonstrated the solid phase to be stable at 25 °C up to 1 $mol \cdot dm^{-3}$ KCl.

Stability of $MgCO_3 \cdot 3H_2O$ in Na−Mg−NH_4−K−Cl Brines. The stability of $MgCO_3 \cdot 3H_2O$ in Na−Mg−NH_4−K−Cl brines was also determined along with solubility measurements. The results are summarized in Table 7. It can be observed that $MgCO_3 \cdot 3H_2O$ is stable in pure water at temperatures to 50 °C. In NaCl solutions, it becomes unstable at above 40 °C, while in NH_4Cl solutions it is stable at (15 to 35) °C. $MgCO_3 \cdot 3H_2O$ was found to be stable in $MgCl_2$ solutions below 35 °C in

Table 6. Solubility of $MgCO_3 \cdot 3H_2O$ (1) in KCl (2) + H_2O (3)[a]

solution parameters		solubility as $MgCO_3$ in different units		
M_2/mol·L^{-1}	ρ_s/g·mL^{-1}	C_1/g·L^{-1}	M_1/mol·L^{-1}	m_1/mol·kg^{-1}
		T = 25 °C		
0.1	1.0016	1.0699	0.01269	0.01278
0.2	1.0066	1.2554	0.01489	0.01503
0.3	1.0114	1.4198	0.01684	0.01705
0.35	1.0123	1.4611	0.01733	0.01760
0..4	1.0149	1.5699	0.01862	0.01893
0.5	1.0206	1.6137	0.01914	0.01950
0.55	1.0214	1.6204	0.01922	0.01964
0.6	1.02552	1.6769	0.01989	0.02032
0.7	1.0290	1.7275	0.02049	0.02101
0.8	1.0336	1.7832	0.02115	0.02175
0.9	1.0394	1.8118	0.02149	0.02214
1.0	1.0434	1.8573	0.02203	0.02278

[a] Equilibration time: 6 h.

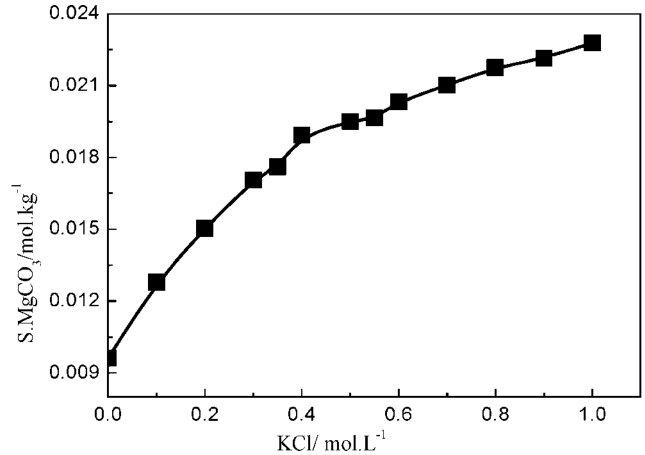

Figure 14. Solubility of $MgCO_3 \cdot 3H_2O$ in KCl solutions at 25 °C.

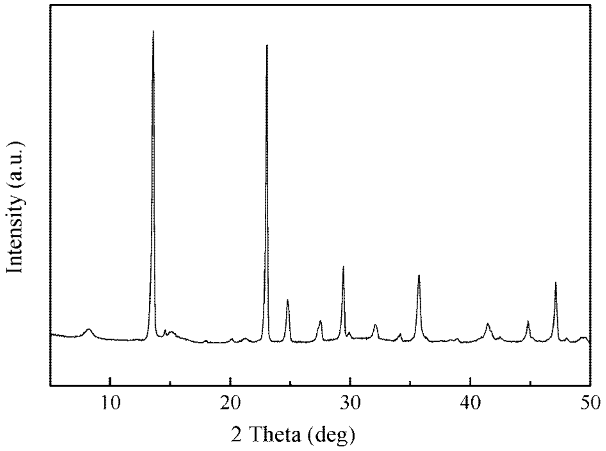

Figure 15. XRD pattern of $MgCO_3 \cdot 3H_2O$ in KCl solutions after 6 h at 25 °C.

concentrations up to 4.0 mol·dm^{-3} but to be unstable above 1.0 mol·dm^{-3} $MgCl_2$ at 35 °C. Finally, it is stable in KCl solutions (< 1 M) at 25 °C.

Thermodynamic Interpretation. The observed behavior of $MgCO_3 \cdot 3H_2O$ solubility in the current study may be explained by considering various equilibria, both solid−liquid and chemical solution (speciation), involved in the system. The solubility equilibrium for $MgCO_3 \cdot 3H_2O$ solids in aqueous electrolytes is expressed as follows

$$MgCO_3 \cdot 3H_2O(s) \leftrightarrow Mg^{2+} + CO_3^{2-} + 3H_2O \tag{1}$$

The equilibrium constant of nesquehonite in the solution is given by

$$K_{sp} = a^{2+}_{Mg} a_{CO_3^{2-}} a^3_{H_2O} = (m_{Mg^{2+}}\gamma_{Mg^{2+}})(m_{CO_3^{2-}}\gamma_{CO_3^{2-}})a^3_{H_2O} \tag{2}$$

where $m_{Mg^{2+}}$ and $m_{CO_3^{2-}}$ are the molal concentrations of cation Mg^{2+} and anion CO_3^{2-} in solution. $\gamma_{Mg^{2+}}$ and $\gamma_{CO_3^{2-}}$ are the ion activity coefficients, and a_{H_2}O is the activity of water in solution. The solubility of $MgCO_3 \cdot 3H_2O$ is complicated in electrolyte solutions due to the formation of the bicarbonate (HCO_3^-) ion. Its dissociation equilibrium is expressed as

$$HCO_3^- \leftrightarrow H^+ + CO_3^{2-} \tag{3}$$

The thermodynamic equilibrium constant of reaction 3 is described as

$$K_1 = \frac{(m_{H^+}\gamma_{H^+})(m_{CO_3^{2-}}\gamma_{CO_3^{2-}})}{(m_{HCO_3^-}\gamma_{HCO_3^-})} \tag{4}$$

The solubility of $MgCO_3 \cdot 3\ H_2O$ is also related to the pressure of carbon dioxide.

$$CO_2 + H_2O \leftrightarrow H^+ + HCO_3^- \tag{5}$$

The thermodynamic equilibrium constant of reaction 5 is described as

$$K_2 = \frac{(m_{H^+}\gamma_{H^+})(m_{HCO_3^-}\gamma_{HCO_3^-})}{a_{H_2O}P_{CO_2}} \tag{6}$$

Substituting eq 6 into 4 yields the following relationship

$$K_1 = \frac{(m_{H^+}\gamma_{H^+})^2(m_{CO_3^{2-}}\gamma_{CO_3^{2-}})}{a_{H_2O}P_{CO_2}K_2} \tag{7}$$

In the system $MgCO_3 \cdot 3H_2O(s)$ + H_2O, the solubility of $MgCO_3 \cdot 3H_2O$ (*s*) is expressed by the molal concentration of the Mg^{2+} ion or the summation of all the carbon-bearing species

$$s = m_{Mg^{2+}} = m_{CO_3^{2-}} + m_{HCO_3^-} \tag{8}$$

Substituting eqs 6 and 7 into eq 8 yields the following relationship

$$s = \frac{K_2 a_{H_2O}P_{CO_2}}{m_{H^+}\gamma_{H^+}}\left[\frac{1}{\gamma_{HCO_3^-}} + \frac{K_1}{m_{H^+}\gamma_{H^+}\gamma_{CO_3^{2-}}}\right] \tag{9}$$

Equation 9 indicates qualitatively that the solubility of nesquehonite increases with increasing pressures of carbon dioxide in water as described in the literature.

Substituting eqs 2 and 7 into eq 8 yields the following relationship

Table 7. Stability of $MgCO_3 \cdot 3H_2O$ in Na−Mg−NH_4−K−Cl Brines

T/°C	M/mol·L^{-1}	t/h	equilibrated solid phase(s)
25 to 40	pure water	6	$MgCO_3 \cdot 3H_2O$
50 to 70	pure water	6	other phases
15	0.1 to 4.0 mol·L^{-1} (NaCl)	6	$MgCO_3 \cdot 3H_2O$
25	0.1 to 4.0 mol·L^{-1} (NaCl)	6	$MgCO_3 \cdot 3H_2O$
35	0.1 to 4.0 mol·L^{-1} (NaCl)	6	$MgCO_3 \cdot 3H_2O$
40	0.1 to 4.0 mol·L^{-1} (NaCl)	6	other phases
15	0.1 to 4.0 mol·L^{-1} (NH_4Cl)	6	$MgCO_3 \cdot 3H_2O$
25	0.1 to 4.0 mol·L^{-1} (NH_4Cl)	6	$MgCO_3 \cdot 3H_2O$
35	0.1 to 4.0 mol·L^{-1} (NH_4Cl)	6	$MgCO_3 \cdot 3H_2O$
15	0.1 to 4.0 mol·L^{-1} ($MgCl_2$)	6	$MgCO_3 \cdot 3H_2O$
25	0.1 to 4.0 mol·L^{-1} ($MgCl_2$)	6	$MgCO_3 \cdot 3H_2O$
35	0.1 to 1.0 mol·L^{-1} ($MgCl_2$)	6	$MgCO_3 \cdot 3H_2O$
35	1.5 to 4.0 mol·L^{-1} ($MgCl_2$)	6	other phases
25	0.1 to 1.0 mol·L^{-1} (KCl)	6	$MgCO_3 \cdot 3H_2O$

$$s = \frac{K_{sp}(m_{H^+}\gamma_{H^+})^2}{K_1 K_2 a_{H_2O}^4 P_{CO_2}\gamma_{Mg^{2+}}} \qquad (10)$$

Equation 10 shows that if the pressure of CO_2 is kept constant the solubility of $MgCO_3 \cdot 3H_2O$ increases with increasing concentration of H^+. One example is the solubility of $MgCO_3 \cdot 3H_2O$ in ammonium chloride solutions. The pH of solution decreases with the increasing concentration of ammonium chloride because of the hydrolysis of ${NH_4}^+$. The hydrolysis reaction is expressed as follows

$$NH_4^+ + H_2O \leftrightarrow NH_4OH + H^+ \qquad (11)$$

This is the reason by which the solubility of $MgCO_3 \cdot 3H_2O$ in ammonium chloride media consistently increases with increasing concentration of ammonium chloride.

Conclusions

The solubility of $MgCO_3 \cdot 3H_2O$ in pure water, NaCl, NH_4Cl, $MgCl_2$, and KCl for a range of conditions was investigated. The solubility of $MgCO_3 \cdot 3H_2O$ in water decreases with increasing temperature. In NaCl solutions, it increases reaching a maximum and then decreases gradually with further increasing salt concentration. It decreases with temperature. The solubility of $MgCO_3 \cdot 3H_2O$ in NH_4Cl increases with increasing concentration and temperature. The solubility of $MgCO_3 \cdot 3H_2O$ in $MgCl_2$ also increases with increasing salt concentration at (15 to 25) °C. However, the transformation of the solid phase was observed when the concentration of $MgCl_2$ exceeded 1 $mol \cdot L^{-1}$ at 35 °C. The solubility of $MgCO_3 \cdot 3H_2O$ in KCl also increases with increasing salt concentration up to 1.0 $mol \cdot L^{-1}$ KCl at 25 °C. The behavior of solubility of $MgCO_3 \cdot 3H_2O$ was partially explained by thermodynamic interpretation considering the various equilibria in solution. XRD results and SEM micrographs indicate that the nesquehonite crystals are unstable at elevated temperatures converting to other phases.

Literature Cited

(1) Zhang, B.; Tang, Y.; Yang, C.; Huang, S.; Wu, J. *Exploitation of the saline in China*; Science Publication: Beijing, 1999; pp 99−107.

(2) Hu, Q. *The production and application of magnesium compounds*; Chemical Industry Publication: Beijing, 2004; pp 11−31.

(3) Hsu, K. J. Process and apparatus for recovery of Lithium in a helminthoid evaporator. United States Patent, 2001, No.6, 197, 152 B1.

(4) Wang, Y.; Li, Z.; Demopoulos, G. P. Controlled precipitation of nesquehonite by the reaction of $MgCl_2$ with $(NH_4)\,_2CO_3$ at 303K. *J. Cryst. Growth.* **2007**, *310*, 1220–1227.

(5) Giester, G.; Lengauer, C. L.; Rieck, B. The crystal structure of nesquehonite, $MgCO_3 \cdot 3H_2O$, from Lavrion, Greece. *Miner. Petrol.* **2000**, *70*, 153–163.

(6) Li, Z.; Demopoulos, G. P. Solubility of $CaSO_4$ phases in aqueous HCl + $CaCl_2$ solutions from 283 to 353 K. *J. Chem. Eng. Data* **2005**, *50*, 1971–1982.

(7) Dutrizac, J. E. Calcium sulphate solubilities in simulated zinc processing solutions. *Hydrometallurgy* **2002**, *65*, 109–135.

(8) Li, Z.; Demopoulos, G. P. Model-based construction of Calcium sulfate phase-transition diagrams in the HCl-$CaCl_2$-H_2O system between 0 and 100 °C. *Ind. Eng. Chem. Res.* **2006**, *45*, 4517–4524.

(9) Wells, R. C. The solubility of magnesium carbonate in nature waters. *J. Chem. Soc.* **1915**, *37*, 1704–1707.

(10) Walter, D. K. The solubility of magnesium carbonate (nesquehonite) in water at 25°C and pressures of carbon dioxide up to one atmosphere. *J. Chem. Soc.* **1929**, *51*, 2093–2097.

(11) Cameron, F. K.; Seidell, A. The solubility of magnesium carbonate in aqueous solutions of certain electrolytes. *J. Phys. Chem.* **1903**, *7*, 578–590.

(12) Hefter, G. T.; Tomkins, R. P. T. *The experimental determination of solubilities*; John Wiley & Sons, Ltd: U.K., 2003; pp 259−264.

(13) Lucas, A.; Rodriguez, L.; Sanchez, P.; Carmona, M.; Romero, P.; Lobato, J. Comparative study of the solubility of the crystalline layered silicates α-$Na_2Si_2O_5$ and δ-$Na_2Si_2O_5$ and the amorphous silicate $Na_2Si_2O_5$. *Ind. Eng. Chem. Res.* **2004**, *43*, 1472–1477.

(14) Power, W. H.; Fabuss, B. M.; Satterfield, C. N. Transient solubilities in the calcium sulfate-water system. *J. Chem. Eng. Data* **1964**, *9*, 437–442.

(15) Stratton, R.; Stepanian, M.; Brooks, C. L. *Chemistry*; Houghton Mifflin Company: USA, 1997; p 224.

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