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The Kinetics of Magnesium Carbonate Crystallization for Traditional Salt Production Wastewater Recovery

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Abstract. The kinetics of crystallization of magnesium carbonate (nesquehonite) at room temperature (27°C) has been examined using an electrical conductivity method during process of nucleation. Magnesium carbonate hydrate from a reaction of magnesium chloride (MgCl₂) and sodium carbonate (Na₂CO₃) in supersaturated condition was analyzed. Variations of batch reactor experimental are magnesium chloride initial concentration (500-3.000 mg/L) and operating pH (8-14). In this paper, we studied the crystallization kinetics of magnesium carbonate via an electrical conductivity method, a concentration monitoring method. By monitoring electrical conductivity during the solution reaction process, changes in [Mg²⁺] can be measured and an induction period of nucleation could be determined. Crystal has been formed was confirmed with powder X-ray Diffractometer (XRD) analyses. The results show that magnesium carbonate is formed during operating condition pH 10 with magnesium chloride initial concentration 3.000 mg/L. The nucleation process of magnesium carbonate crystallization can be represented by second-order reaction equation with R² is 0.8. The induction period of magnesium carbonate crystallization is 50 second.

Introduction

Magnesium carbonate is used in many industries. For example, MgCO₃ can be used for preparation of papers, ceramics, cosmetics, paints, pigment, rubber, pharmaceuticals and as precursors to prepare magnesium based chemical [1]. Magnesium carbonate can be produced in various carbonates such as magnesite, nesquehonite, lansfordite, and hydromagnesite. This formation based on the temperature, pH, and concentration of reactant during operation [1], [2]. Study on crystallization of MgCO₃ can provide important technological parameters for production in industry.

When the solubility ion product of MgCO₃ is greater than its solubility product constant (K_{sp}) in solution, it is possible to precipitate MgCO₃ crystals. However, crystal growth in a saturated solution is a delicate process and the crystallization kinetics is determined by several complex factors [3]. Crystallization includes four processes: formation of supersaturated solution, emergence of a new phase, nucleation, and crystal growth. In a solution system, ionic or molecular do not exist individually but interact with each other to form small molecular clusters. The molecular clusters reach a dynamic equilibrium, and the whole system is thermodynamically stable. When the solution system reaches supersaturated condition, the dynamic equilibrium between the clusters will change and simultaneously form a large number of molecular clusters with varying sizes [4]. The research methods to study crystallization kinetics used concentration monitoring method measures ion concentrations during the process. In this paper, we studied the nucleation crystallization kinetics of magnesium carbonate in supersaturated solution via an electrical conductivity method. The changes of magnesium concentration were monitored by electrical conductivity during nucleation process.

Materials and Methods

The starting chemicals were reagent grade $MgCl_2 \cdot 6H_2O$, Na_2CO_3 , sodium hydroxide and chloride acid (>99%). The magnesium salt ($MgCl_2 \cdot 6H_2O$) as synthetic wastewater and Na_2CO_3 were first dissolved in distilled water, separately. Then the two solutions were mixed together by constant mechanical stirring (235 rpm) and monitored for an electrical conductivity change. Sodium hydroxide and chloride acid were used to stabilize solution at pH operation needed. The changes in pH during crystallization process were monitored by pH sensor. Fig. 1 shows the diagram for a typical experimental apparatus.

Color visual observation of solution during process determines whether the solution can resulting solid represent $MgCO_3$ crystal. The relationship between ion concentration and electrical conductivity in the supersaturated solution can be determined by measuring the variation of electrical conductivity versus time. Reaction order of $MgCO_3$ and the nucleation rate constant are determined via curve fitting by plotting magnesium concentration versus time.

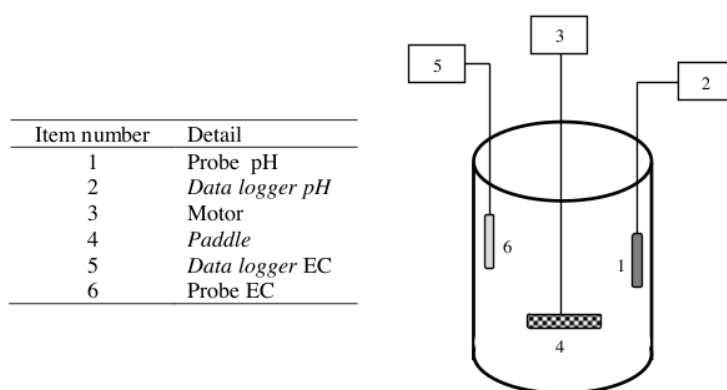


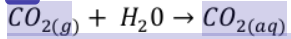
Figure 1 Typical experimental apparatus

Results and Discussion

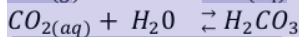
The key for crystallization kinetics is the control of $MgCO_3$ precipitation is a nucleation and growth process related to its critical particle size. Interaction of Mg^{2+} and CO_3^{2-} in solution to form $MgCO_3$ nucleation need controlling of formation supersaturated solution. Table 1 shows the experimental conditions used at different pH, various initial concentrations, supersaturation value and color visual observation of the mixture of $MgCl_2$ and Na_2CO_3 solutions. The color of mixed solution between $MgCl_2$ and Na_2CO_3 at operation observed into two groups clear and clear white. The clear color indicates no solid formed from the pH operation 8-10 and initial magnesium 500-2,500 mg/L, otherwise the clear white color indicates solid formed from the process. Considering the color of mixed solution is important because for further analysis needed solution must be able to precipitate indicating magnesium carbonate formed [4]. To confirm solid form is magnesium carbonate crystal, XRD analysis was conducted to observe white solid formed. XRD analysis conducted to observe the solid formed in Fig. 3 to 7 (initial magnesium concentration 3,000 mg/L with operating pH 10 to 14). Comparing with magnesium carbonate reference graph as reported in Fig.8, Fig. 3 has a similarity of the peak curve shown magnesium carbonate nesquehonite. For further analysis of kinetics was conducted using the data resulted from pH 10 operation.

The carbonate balance in water is influenced by pH, at low pH (<4.5) water containing dissolved CO_2 will react with H_2O to form H_2CO_3 (Eq.1 and Eq.2). The increasing pH causing H_2CO_3 dissociate to HCO_3^- at pH between 4.5 to 8.3 (Eq.3). At pH 8.3 above, HCO_3^- will change to CO_3^{2-} (Eq.4). The balance of the carbonate system can be seen in Fig. 2. The equilibrium reaction equation for the carbonate system in water is as follows [5,6]:

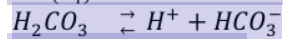
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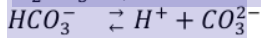
(Eq.1)



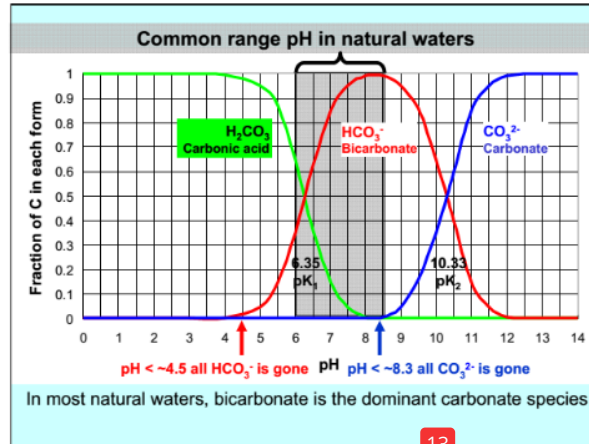
(Eq.2)



(Eq.3)



(Eq.4)



13

Figure 2 Carbonate balance [5,6]

In the process at pH greater than 8.3 provides a greater chance of the availability of bicarbonate so that it can support the formation of magnesium carbonate (Eq.3). But in this study magnesium carbonate actually formed at pH 10. Probably, at pH 8 and 9, the solubility of magnesium carbonate and supersaturated condition has not been reached. Precipitation of ions in solution to form precipitates consists of several steps. Beginning to determine which anions/cations will be deposited in the form of carbonate or hydroxide, determine the appropriate stirring to contact between the anion and cation. Precipitates are formed and then the precipitation process continues. To determine whether the hydroxide precipitates or carbonate precipitates formed can precipitate or not, it is determined from the value of the precipitate solubility product compared to the value of the constants of solubility (K_{sp}). If the value of the solubility product is greater than K_{sp} value, precipitation occurs [7]. Crystallization can occur in solutions with supersaturated conditions as a driving force for the formation of crystals [8,9]. Whereas at pH above 10, this condition more carbonate ions will be available but more alkaline pH the amount of hydroxide ion (OH^-) in solution will be greater. According to [10] if there is (OH^-) in the solution, it will play a role in forming $Mg(OH)_2$.

2

Table 1 Experimental solution conditions and value of supersaturation at different pH and initial magnesium concentration

serial number	initial Mg^{2+} (mg/L)	initial CO_3^{2-} (mg/L)	super saturation	visual colour of mixed solution						
				pH						
				8	9	10	11	12	13	14
A1-A7	500	2.21	42.4	clear	clear	clear	clear white	clear white	clear white	clear white
B1-B7	1,000	4.42	172.61	clear	clear	clear	clear white	clear white	clear white	clear white
C1-C7	1,500	6.63	389.63	clear	clear	clear	clear white	clear white	clear white	clear white
D1-D7	2,000	8.83	693.44	clear	clear	clear	clear white	clear white	clear white	clear white
E1-E7	2,500	11.04	1084.07	clear	clear	clear	clear white	clear white	clear white	clear white
F1-F7	3,000	13.25	1561.5	clear	clear	clear white	clear white	clear white	clear white	clear white

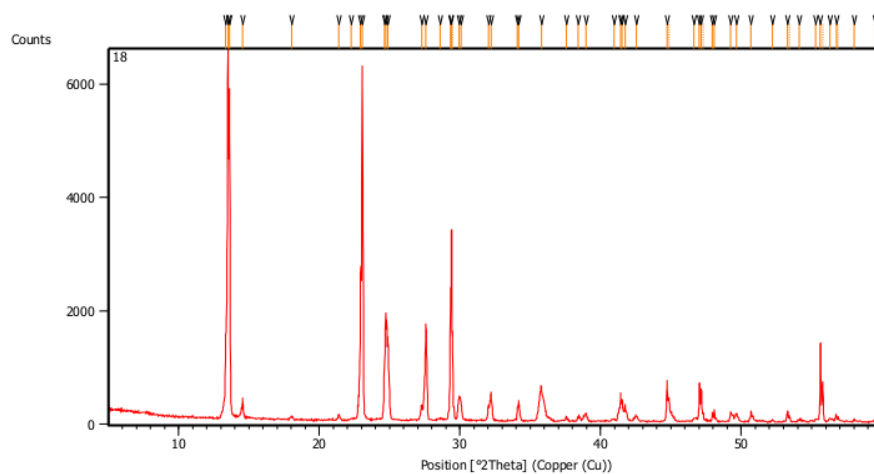


Figure 3 XRD result at operating pH 10

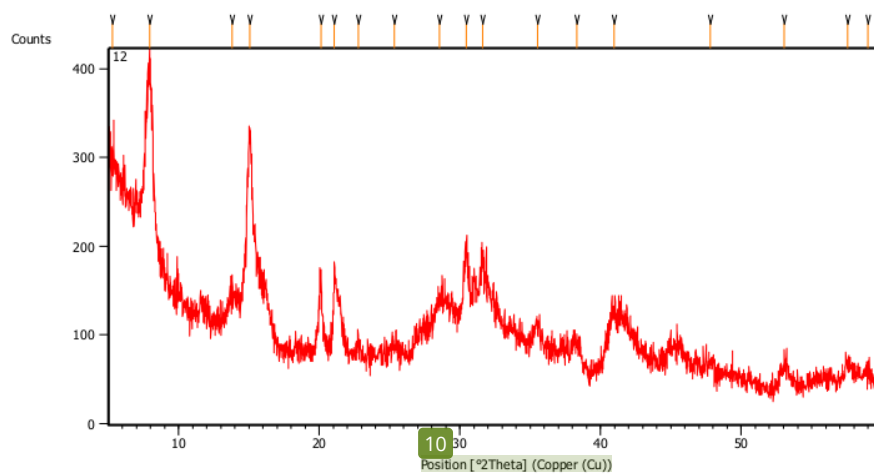


Figure 4 XRD result at operating pH 11

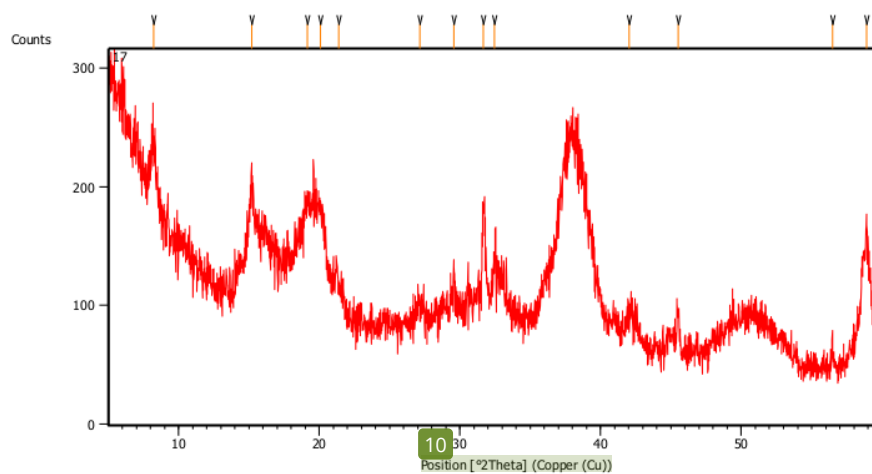


Figure 5 XRD result at operating pH 12

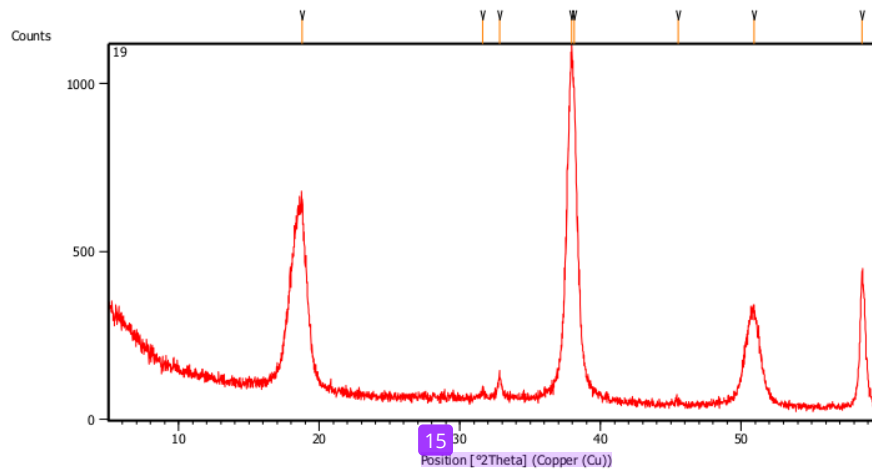


Figure 6 XRD result at operating pH 13

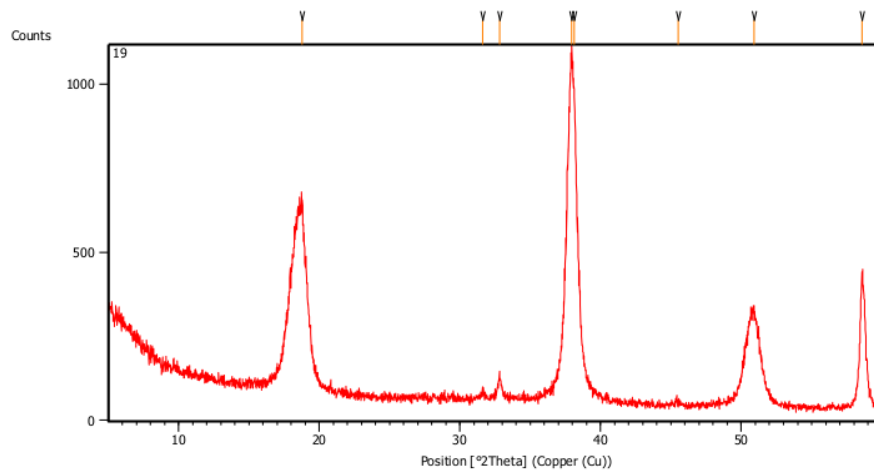


Figure 7 XRD result at operating pH 14

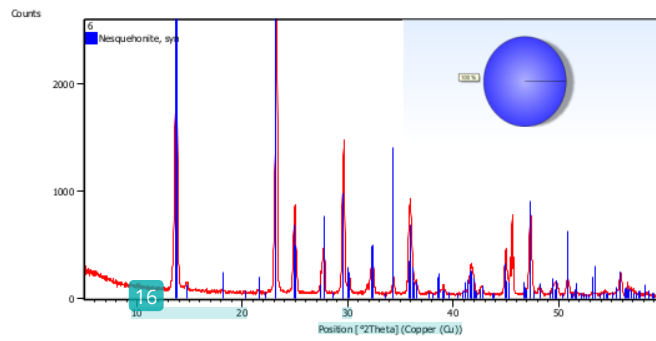


Figure 8 Comparison with reference graph of magnesium carbonate hydrate

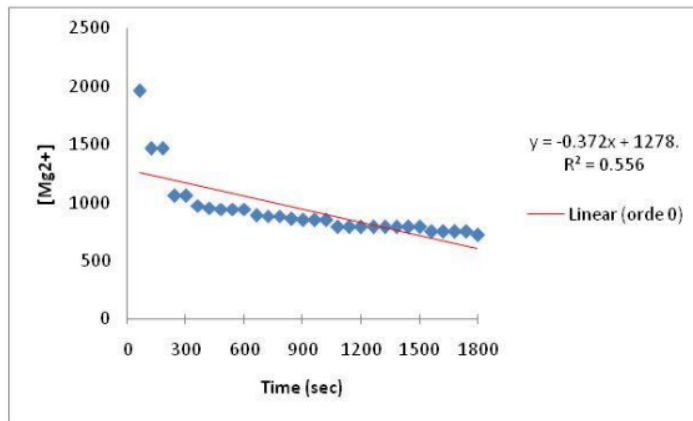


Figure 9 Linear order 0 graphs for crystallization of magnesium carbonate

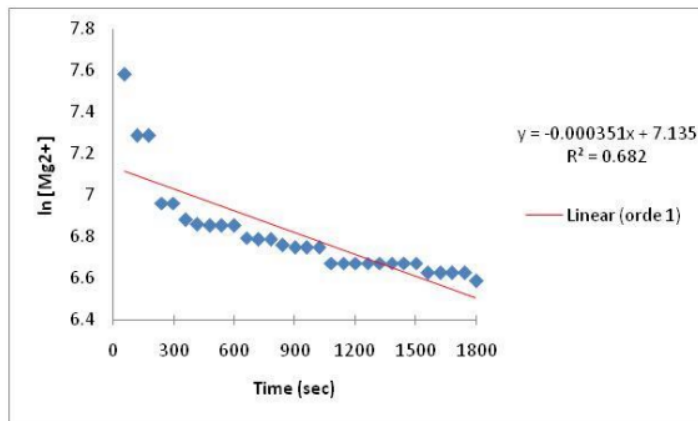


Figure 10 Linear order 1 graphs for crystallization of magnesium carbonate

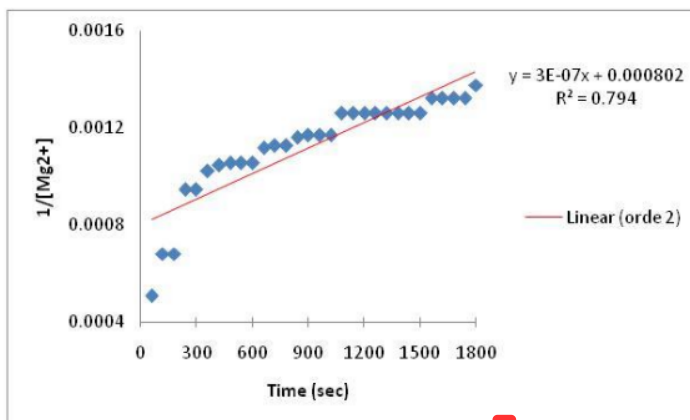


Figure 11 Linear order 2 graphs for crystallization of magnesium carbonate

The determination of reaction kinetics of magnesium carbonate crystallization process was conducted by kinetic calculation based on the reaction order. Figure 9-11 shows the behavior of changes in magnesium concentration is depicted in linear graphs to determine the appropriate reaction order. The graph that has the tendency of a straight line or the value of R^2 closest to 1 represented in Fig. 11 (0.8) as order 2. The slope value of the 2nd order linear equation is 3×10^{-7} . The kinetics reaction equation of magnesium carbonate nucleation crystallization at pH 10 is $\frac{1}{c} = \frac{1}{c_0} + (3 \times 10^{-7}) \cdot t$.

The induction time can be determined from duration time during the first concentration decrease [11]. Table 2 shows that magnesium concentrations decreased for the first time at 50 seconds. Concentration at the 50th reached 1,465 mg/L with initial concentration of 1,961 mg/L.

Table 2 Magnesium concentration during 52 second

Second	[Mg ²⁺]	Second	[Mg ²⁺]	Second	[Mg ²⁺]	Second	[Mg ²⁺]
1	1961,87	14	1961,87	27	1961,87	40	1961,87
2	1961,87	15	1961,87	28	1961,87	41	1961,87
3	1961,87	16	1961,87	29	1961,87	42	1961,87
4	1961,87	17	1961,87	30	1961,87	43	1961,87
5	1961,87	18	1961,87	31	1961,87	44	1961,87
6	1961,87	19	1961,87	32	1961,87	45	1961,87
7	1961,87	20	1961,87	33	1961,87	46	1961,87
8	1961,87	21	1961,87	34	1961,87	47	1961,87
9	1961,87	22	1961,87	35	1961,87	48	1961,87
10	1961,87	23	1961,87	36	1961,87	49	1961,87
11	1961,87	24	1961,87	37	1961,87	50	1465,25
12	1961,87	25	1961,87	38	1961,87	51	1465,25
13	1961,87	26	1961,87	39	1961,87	52	1465,25

Summary

Magnesium carbonate crystal was produced by the operating condition at pH 10, with induction time was 50 seconds. Nucleation of magnesium carbonate crystallization following the second-order with the slope is 3×10^{-7} .

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