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Synthesis of Magnesium Carbonate Polymorphs from Indonesia Traditional Salt Production Wastewater

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Abstract

Magnesium carbonate nesquehonite crystals were synthesized by mixing of the salt manufacture wastewater (bittern) and Na_2CO_3 with molar ratio 1:1 at room temperature. The effect of pH range (8-10) and initial magnesium concentration range (10,000-40,000 ppm) were investigated. Crystal morphology was observed using scanning electron microscopy and energy dispersive X-ray spectroscopy confirmed with X-ray diffraction. Large changes in morphology were observed in the increasing of initial concentration, which strongly depend on the pH. With an increase of pH, magnesium carbonate nesquehonite crystals change to hydromagnesite. However, reaction crystallization with initial magnesium concentration 40,000 ppm is found do not produce magnesium carbonate hydrated. Crystallization of magnesium carbonate nesquehonite is favored in the pH 8-9 with initial concentration in 10,000-20,000 ppm.

Keywords: Bittern; Magnesium; Magnesium carbonate hydrate; Morphology; Nesquehonite

Introduction

Salt production from seawater resulted bittern as a concentrated wastewater after salt crystallization that has high magnesium (Ayoub *et al.*, 2000; Lychnos *et al.*, 2010). Replace to Some traditional salt farmer discard bittern back into sea It can be as a pollutant in sea ecosystem because mineral concentration of bittern can be 10 times larger than sea (Danoun, 2007). Bittern has potential to influence mangrove growth and can cause deforestation until its mortality (Tewari *et al.*, 2003). In order to preserve sea environment, bittern should have treated before discharge back into sea. The availability of inexpensive mineral sources and the high magnesium of bittern make magnesium recovery is worth and significant process.

Magnesium carbonate widely needed in industrial process of paints, ceramics, cosmetics, pharmaceuticals, preparation of paper and other magnesium based chemicals. Magnesium carbonate include hydromagnesite, nesquehonite, magnesite, etc (Lou *et al.,* 2004). Magnesium recovery was reported in some studies such as magnesium oxalate (Tran *et al.,* 2013) and magnesium carbonate (Tran *et al.,* 2016) from Uyuni Salar brine, precipitation magnesium carbonate using polyacrylamide (Guo *et al.,* 2010), magnesium carbonate from reaction between magnesium hydroxide and carbon dioxide (Han *et al.,* 2014), need spacing between coma and magnesium magnesium carbonate by mixing magnesium chloride and carbon dioxide (Hao and Al-Tabbaa, 2014).

Although there have been some studies on the recovery of magnesium, to our knowledge, there are no studies on the recovery of magnesium under the influence of sodium carbonate at room temperature. In this study, the recovery magnesium carbonate was investigated by considering the effect of pH and initial concentration of natural bittern sample comprehensively.

2. Materials and Methods

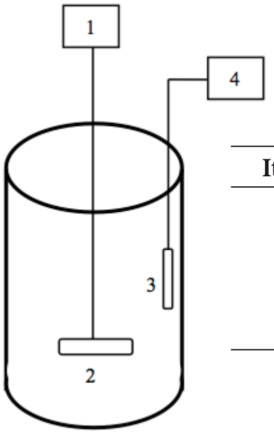
2.1 *Traditional salt production waste water*

The natural wastewater (bittern) was sourced from the crystallization plot of the traditional salt manufacture in Sampang, East Java, Indonesia. The bittern sample was collected by grab sampling and contained 10,000-40,000 ppm of Mg^{2+}.

2.2 *Batch reactor and operation*

The process used in this study to recover magnesium as magnesium carbonate conducted at pH 8-10 (Tran *et al.,* 2016). This experiment was carried at room temperature (25 °C). The magnesium recovery tests were conducted in 1-L beaker as a batch reactor. Schematic of experimental apparatus can be illustrated in Figure 1.

The experimental procedures are outlined below: (a) 800 mL bittern sample were placed in 1 L beaker; (b) the weighed sodium carbonate was added into beaker; (c) mixing used one



Item number	Detail
1	Motor
2	Paddle
3	pH probe
4	Data logger

Figure 1. Schematic of experimental apparatus.

paddle with 235 rpm; d) each reaction lasted was monitored by pH sensor connected to data logger; (e) pH operation adjusted to a desired level by dropping 3N NaOH and 1N HCl solution into beaker while stirring; (f) samples was taken from supernatant to measure the required parameters and solid formed was also taken for determining its characters.

2.3 Analytical methods

Analytical methods were based on the standardized procedures given by American Water Works Association. The cation Mg^{2+} concentration in the bittern was measured by the titration of ethylenediaminetetraacetic acid (EDTA) standard solution. pH was monitored using analog pH meter connected to data logger. The micrographic investigation of the crystal samples was identified by Scanning Electron Microscopy (SEM) (Phenom ProX) technique. The crystal composition analyses were evaluated with Energy Dispersive X-ray Spectroscopy (EDS), with an accelerating voltage of 15.0 kV (Phenom ProX) and further confirmed with powder X-ray Diffractometer (XRD) analyses (using a Siemens D5000 XRD with a copper Ka radiation (k= 1.5406 Å) operating at a voltage and current power of 40 kV and 30 mA).

3. Results and Discussion

3.1 Effect of initial magnesium concentration

The effect of initial magnesium concentration on the crystal morphology is shown in Figure 2A and 2B. It was found that the increasing of magnesium concentration influenced the morphology crystal formed. Figure 2 (A-1, A-2, A-3, B-1, B-2 and B-3) show that at concentrations of 10,000 and 20,000 ppm resulted magnesium carbonate crystal with plate-block shaped. The morphology of magnesium carbonate resulted from this work confirmed with previous study that reported the morphology of magnesium carbonate crystal appeared plate-block shaped and small rod shaped in special reaction (Guo *et al.,* 2010; Han *et al.,* 2014; Tran *et al.,* 2016). While, at concentration of 40,000 ppm was resulting cubic crystals shaped shown in Figure 2C. Figure 2 (C-1, C-2 and C-3) illustrates the effect of magnesium concentration caused unformed magnesium carbonate crystal. It was found that the initial magnesium concentration influenced the dispersibility of sodium carbonate in the liquid (Wang *et al.,* 2011). The highest initial magnesium concentration indicates a high degree Baume (BE). The greater value of BE means the more viscous the solution (Lychnos *et al.,* 2012). Viscosity can affect the formation of magnesium carbonate hydrate crystals. Crystallization process is the formation of solid through diffusion process from solution. Crystal grows from supersaturated solution, solute leaves the solution through a solid-liquid interface and forms part of crystal. The growth of crystal started from single solute molecule, ions or atoms until formed crystal lattice. After the solute diffused from the liquid phase to interface area, it will be adsorbed on the solid surface to form crystal. An initial magnesium concentration of 40,000 ppm is a viscous solution that becomes a barrier in the mixing of dissolved magnesium and sodium carbonate. So, the interface becomes closed which caused the diffusion of solute magnesium transport to solid-liquid interface could not be conducted (Wang *et al.,* 2011)

Table 1. EDS analysis of crystal formed

pH	**Atomic concentration (%)**														
	10,000 ppm					**20,000 ppm**					**40,000 ppm**				
	Mg	C	O	Na	Cl	Mg	C	O	Na	Cl	Mg	C	O	Na	Cl
8	19.4	4.28	75.6	0.61	0.07	19.3	4.17	75.5	0.87	0.11	23.1	2.9	72.5	1.00	0.50
9	12.2	13.3	74.0	0.38	0.01	13.8	12.4	73.3	0.47	0.03	11.4	30.3	55.6	2.00	0.70
10	18.0	17.5	62,5	1.50	0.42	19.5	3.18	75.9	1.36	0.05	9.46	14.2	55.6	15.8	4.85

Figure 2C-2 and 2C-3 represent the crystals formed as a cubic shape, as the magnesium concentration was 40,000 ppm. It may possible crystal formed contains sodium and chloride. As reported (Radenović *et al.,* 2005; Wang *et al.,* 2015), the crystal shape of natural salt sodium chloride is cubic form. This can be confirmed from EDS analysis result of the crystals formed in Table 1. Table 1 reported that crystal formed from high magnesium concentration contains sodium 2% and 15.8% with operation condition pH 9 and 10, respectively. Cubic crystal with operation condition pH 9 and 10 contains chloride 0.7% and 4.85%. The highest amount of sodium and chloride were found in the crystal formed in operating condition pH 10. Sodium is the largest mineral in bittern and could be an impurities in magnesium extraction (Jiang *et al.,* 2009; Sulistiyono, 2017).

3.2 The effect of pH

The effect of pH on the morphology of magnesium carbonate crystal formed from natural bittern is shown in Figure 2. With the increase in pH, the products changed from "plate-block shaped" in aggregation to independent crystal. It is found out that lower pH was likely to produce finer aggregated particles (Figure 2A-1, 2A-2, 2B-1 and 2B-2) compared with higher one, which acquired more dispersive crystals (Figure 2A-3 and 2B-3). The reason of it is attributed to the lower pH value restriction on the nucleation rate of hydrated magnesium carbonate formation, due to the dominance of bicarbonates; so the nuclei tend to aggregate together. However, with the ascended pH value, the nucleation rate gradually increases, thus to be able to crystallize into particles independently (Hao and Al-Tabbaa, 2014).

Recovery magnesium carbonate can be represented following reactions:

$$Mg^{2+} + CO_3^{2-} + 3H_2\,O \rightarrow MgCO_3.\,3H_2\,O \quad (a)$$

$$CO_3^{2-} + H_2\,O \leftrightarrow OH^- + HCO_2^- \quad (b)$$

$$5Mg^{2+} + 4CO_2^{3-} + 2OH^- + 4H_2\,O \rightarrow (MgCO_3)\ 4.\ Mg(OH)_2.\ 4H_2\,O \quad (c)$$

$$5Mg^{2+} + 4CO_2^{3-} + 2OH^- + 5H_2\,O \rightarrow (MgCO_3)\ _4.\ Mg(OH)_2.\ 5H_2\,O \quad (d)$$

$$5Mg^{2+} + 4CO_2^{3-} + 2OH^- + 8H_2\,O \rightarrow (MgCO_3)_4.\ Mg(OH)_2.\ 8H_2\,O \quad (e)$$

Based on the chemical reaction of magnesium carbonate hydrated, pH affected to magnesium carbonate hydrated formed. In operation condition pH is alkaline, the solution contains more OH^-. The equilibrium of the solution following the reaction (b), while OH^- addition can react with Mg^{2+} to form $Mg(OH)_2$. This condition is illustrated by Equation (c) for hydromagnesite and Equation (d) and (e) for dypingite (Tran *et al.,* 2016).

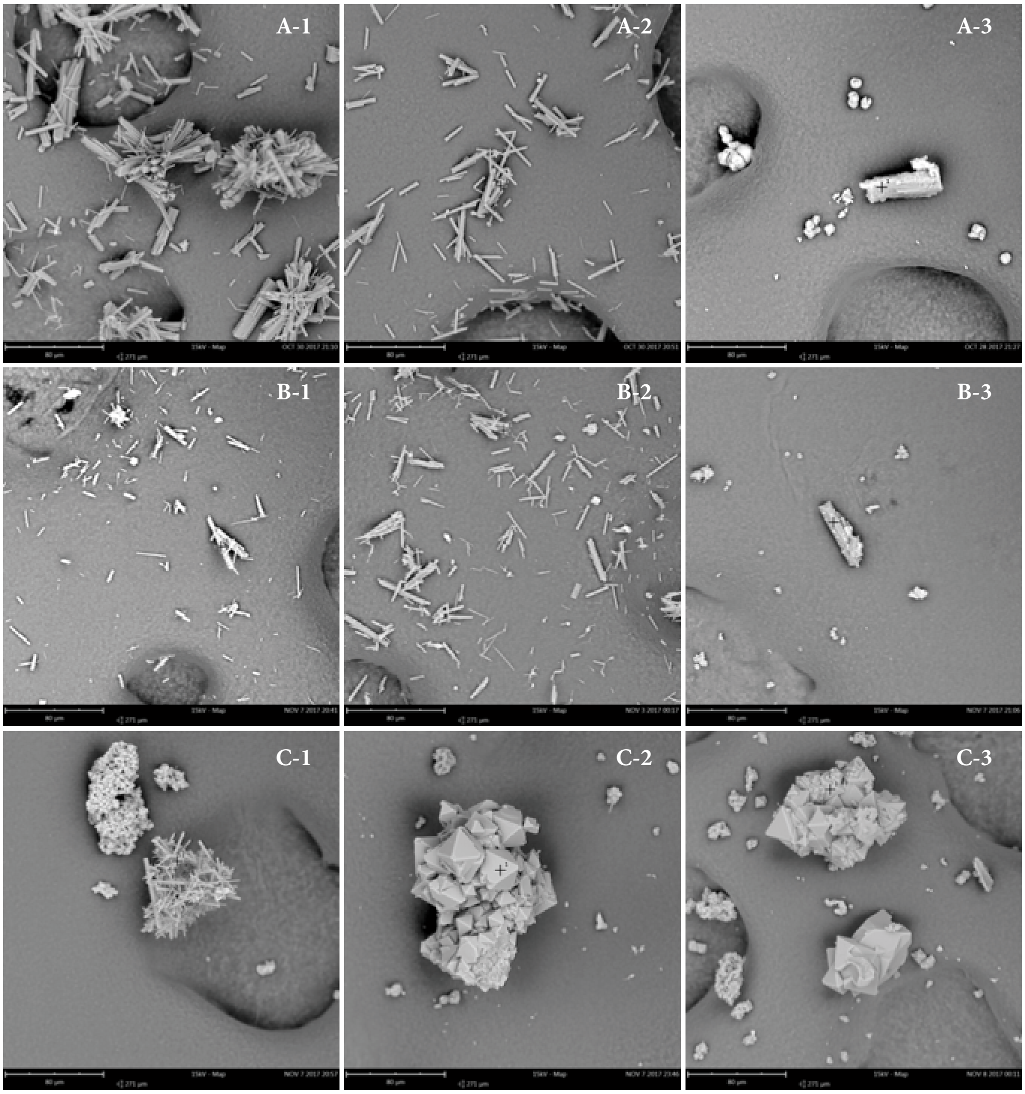
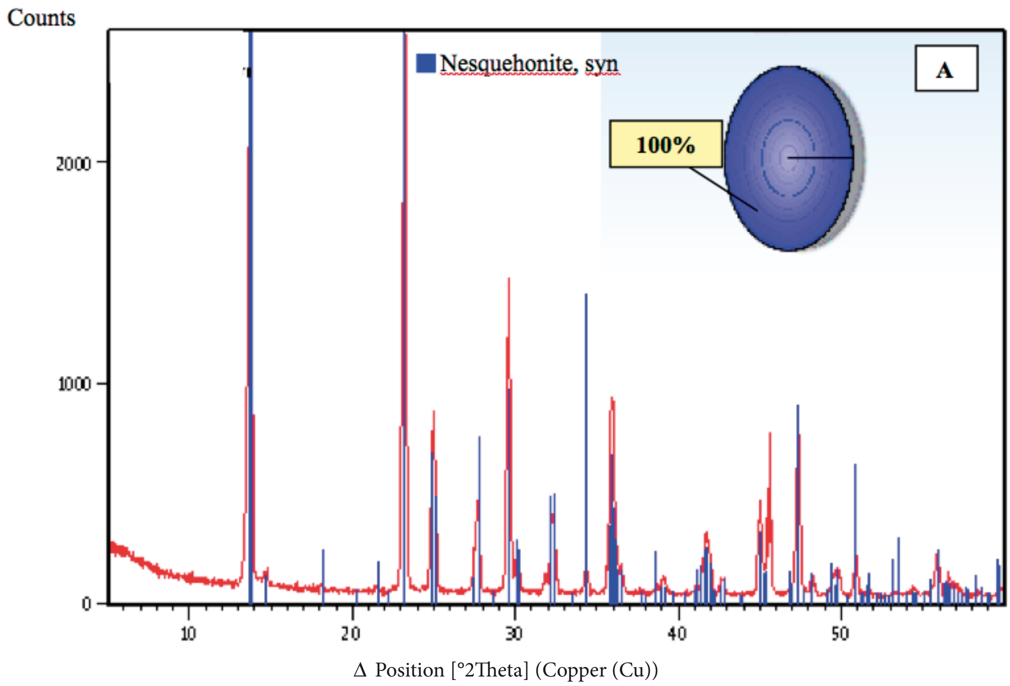


Figure 2. Crystal products SEM profile (magnification 1000x) obtained from initial magnesium of (A) 10,000, (B) 20,000 and (C) 40,000 ppm under different conditions of pH (1) 8, (2) 9 and (3) 10.

3.3 Characterization of $MgCO_3$ hydrate product

Powder X-ray diffraction was performed to verify the product from the reaction of natural bittern with sodium carbonate at room temperature. The XRD identification was conducted on the sample product with plate-block shaped that indicated magnesium carbonate hydrate crystal (Guo *et al.*, 2010; Han *et al.*, 2014). Operation condition resulted plate-block shaped crystal were conducted by mixing magnesium concentration (10,000-20,000) ppm and sodium carbonate on pH (8-9).

Figure 3 presents typical XRD patterns compared with references database of the representative sample product in a plate-block



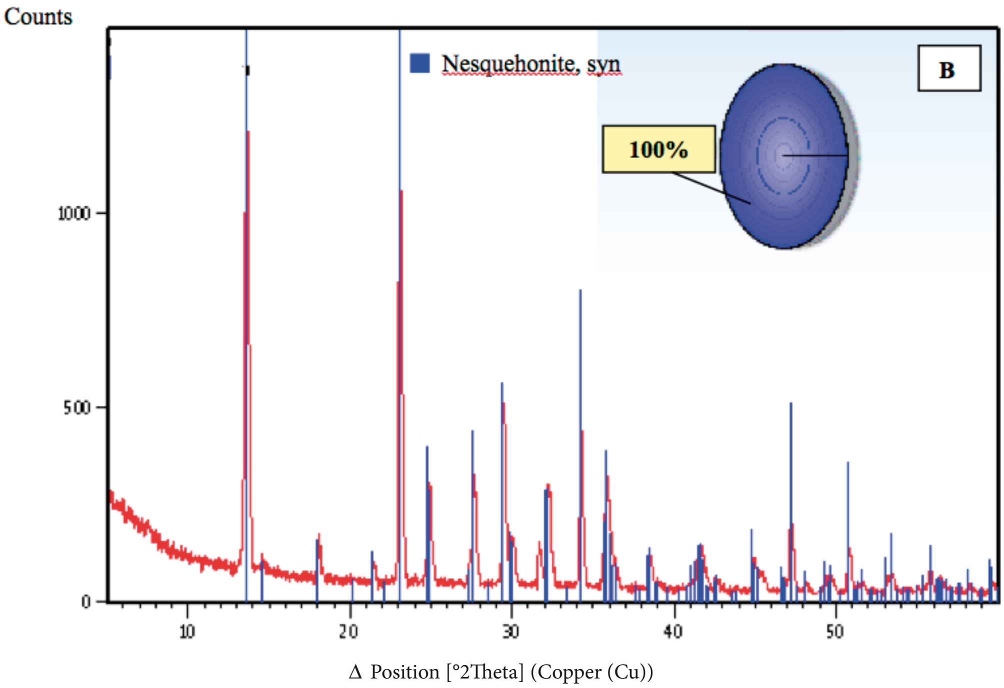


Figure 3. Typical XRD pattern of crystal product compared with reference data: (A) pH 8 (from Figure 2A-1) and (B) pH 9 (from Figure 2A-2).

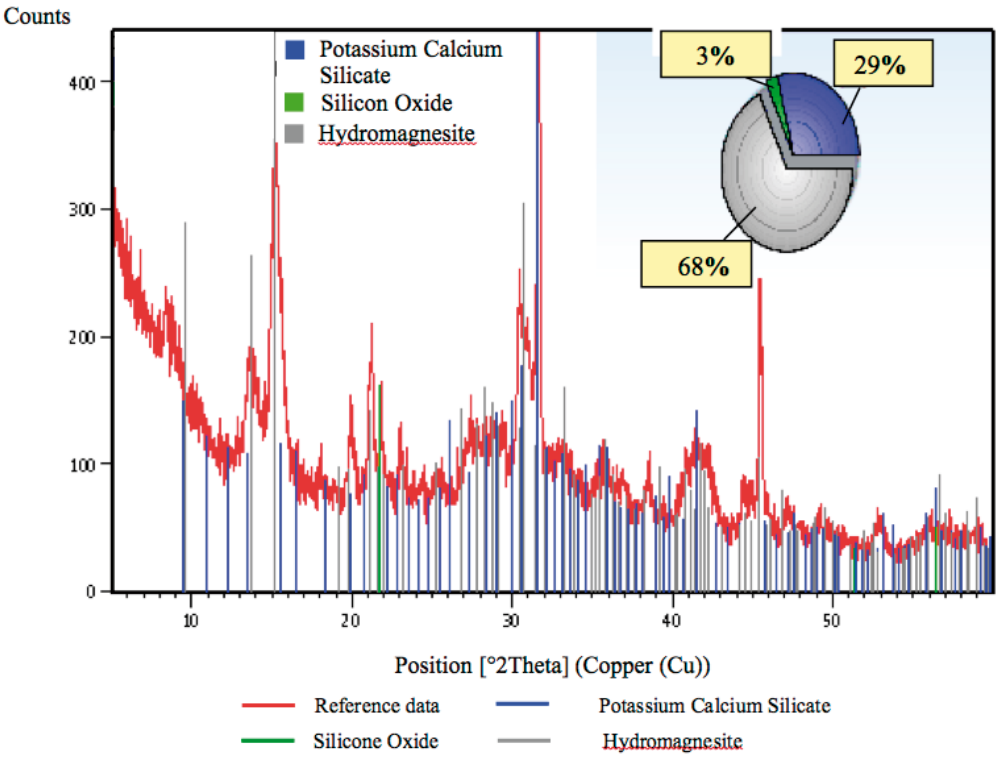


Figure 4. Typical XRD stick pattern of crystal product (from Figure 2A-3) compared with reference data.

shape (from Figure 2A-1 and 2A-2). It can be seen from Figure 3A and 3B that the XRD results agree quite well with reference code 01-070-1433 calculated from ICSD using POWD-12++, which means that nesquehonite $MgCO_3{\cdot}3H2O$ was synthesized in this study. The shape of the peak indicates that the $MgCO_3$ trihydrates are well crystallized. The XRD results show crystals formed comprised 100% nesquehonite.

Such identification is confirmed by previous study that reported the basic carbonate mineral $MgCO_3{\cdot}3H_2O$ is formed at room temperature (25 °C) (Guo *et al.*, 2010; Xiong and Lord, 2008).

Figure 4 shows typical XRD stick patterns compared with references database (code 01-070-1177) represent that the crystal formed is hydromagnesite $Mg_5(CO_3)_4(OH)_2(H_2O)_4$ and other compounds. Crystal product resulted by initial magnesium concentration 10,000 ppm with operating pH 10 resulting hydromagnesite (68%), potassium calcium silicate (29%) and silicon oxide (3%).

Operation condition with pH 10 of initial magnesium concentration 40,000 ppm was resulting cubic crystal shaped. The product confirmed with XRD analysis as shown in Figure 5. The result was confirmed by reference code 01-071-4461 from ICSD calculation that product contains halite/sodium chloride and other compounds. Figure 5 shows that the crystal comprised halite (27%), sodium nickel silicate (59%) and potassium nickel fluoride (14%).

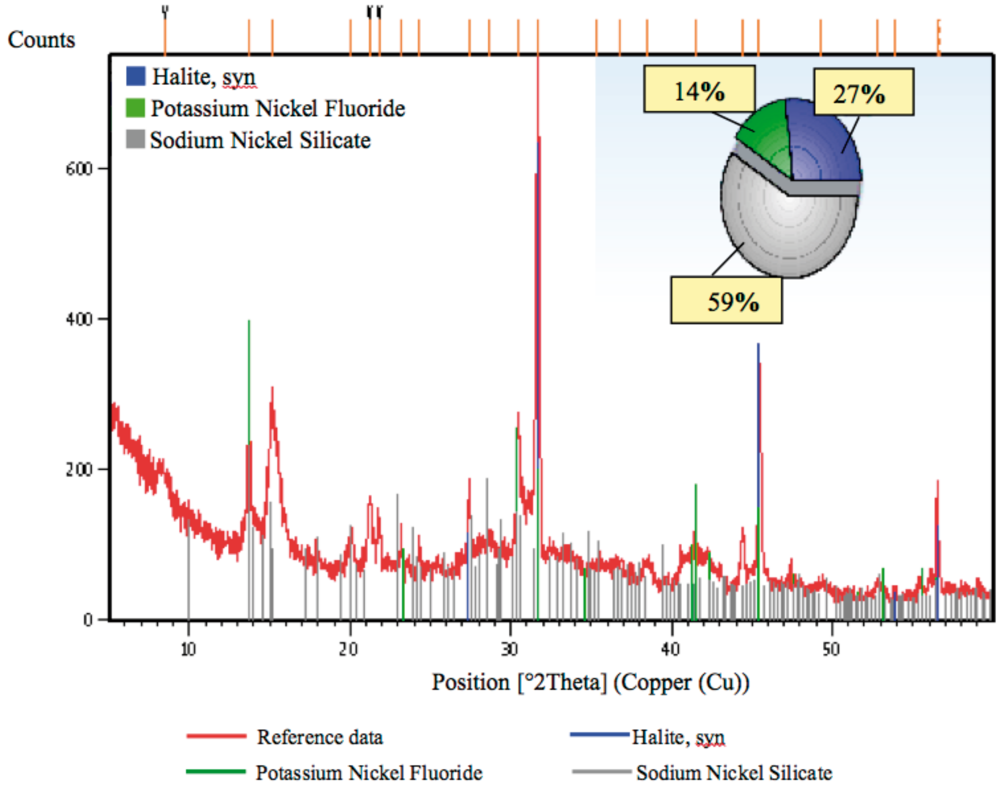


Figure 5. Typical XRD stick pattern of crystal product (from Figure 2C-3) compared with reference data.

4. Conclusions

Magnesium carbonate was synthesized using natural bittern and sodium carbonate at the room temperatures (25 °C). Magnesium carbonate nesquehonite crystals were found to be synthesized at the reaction pH of 8-9 and magnesium initial concentration 10,000-20,000 ppm. Magnesium carbonate hydromagnesite crystal was formed by mixing magnesium concentration 10,200-20,000 ppm and sodium carbonate at pH operation 10. Our results indicate that enhanced of pH and magnesium initial concentration strongly influenced the morphology and chemical contains of crystal.

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