

# X-RAY DIFFRACTION ANALYSIS on POST TREATMENT of Ca-Mg-Al-LAYERED DOUBLE HYDROXIDE SLURRY

**E Heraldy<sup>1,2</sup>, K D Nugrahaningtyas<sup>1,2</sup> and Heriyanto<sup>1</sup>**

<sup>1</sup>Department of Chemistry, Mathematics and Natural Sciences Faculty, Sebelas Maret University, Jl.Ir. Sutami 36 A Kentingan, Surakarta, Indonesia 57126

<sup>2</sup>Solid State Chemistry & Catalysis Research Group, Chemistry Department, Sebelas Maret University, Jl.Ir. Sutami 36 A Kentingan, Surakarta, Indonesia 57126

E-mail: eheraldy@mipa.uns.ac.id

**Abstract.** This research objectives to study post treatment on Ca-Mg-Al-Layered Double Hydroxide (Ca-Mg-Al-LDH) slurry which was prepared from brine water by cooling treatment. The cooling rate was varied from 1 to 3 °C/min by using stirring and without stirring, and the cooling time was done at 0, 30 minutes and 24 hours. The quantitative X-ray diffraction (QXRD) was employed on Ca-Mg-Al-LDH using Le Bail refinement method. The refinement results found another Mg-Al-LDH and Ca-Al-LDH phases, such as Mg(OH)<sub>2</sub>, Al(OH)<sub>3</sub> and CaCO<sub>3</sub>. The highest phase composition on material Ca-Mg-Al-LDH using Le Bail refinement was showed by Al(OH)<sub>3</sub>.

## 1. Introduction

Layered double hydroxides (LDHs), known as hydrotalcite-like (HT) compounds or anionic clays, consist of positively charged metal hydroxide sheets, interlayer anions, and water [1]. Commonly, LDH is expressed in the general formula,  $[M^{2+}_{1-x}M^{3+}_x(OH)_2]^{x+}(A^{n-})_{x/n} \cdot yH_2O$ , where  $M^{2+}$  is divalent cation,  $M^{3+}$  is trivalent metal cation, and  $A^{n-}$  is the exchangeable anion (usually carbonate, chloride or nitrate) and  $0.2 < x < 0.33$ ; y is the amount of interlayer H<sub>2</sub>O [2-7]. LDH is known have a high surface area, basicity properties, stable to thermal treatments and have a memory effect [5]. With such properties, LDHs is widely used as catalysts [6], adsorbents [7], anion exchange [8], corrosion resistance [9] pharmaceutical [10] and photocatalysis [11].

Some researchers have developed LDHs from artificial seawater as source metal ion magnesium [12] and also from seawater [13]. Zhang et al. [14], prepared LDHs using both calcium and magnesium as source divalent metal ion and aluminum as source trivalent metal ion. In addition, Herald et al. [15] synthesized LDHs with calcium and magnesium from brine water. Therefore, brine water which are contains magnesium, calcium [16] have great potential as the metallic source for LDHs synthesis. Moreover, Rives et al. [2] was showed that some experimental parameters can influence the LDH crystallized, such as temperature in the reactor, pH, concentration metallic salts and alkaline solution, the flow rate of reactants and aging time of the precipitate. Previous research has been demonstrated that the aging time of the precipitate [17] and cooling time treatment [18] on LDHs slurry are the main important parameters in the formation and crystallization of LDHs.

Besides that, to determine the metallic concentration in precipitates, several analytical methods were commonly used. However, these methods may not suitable for quantifying the relative



phase abundances in precipitates due to the precipitates usually contain crystal and amorphous phases with similar elemental compositions [19]. Hence, quantitative phase analysis using XRD data could be further by approached with Rietveld refinement [19,20] and Le Bail method [20,21]. The aim of this paper is to discuss the crystal structure with Le Bail method on the post-treatment of Ca-Mg-Al-LDH slurry from brine water.

## 2. Experimental

### 2.1 Material

Brine Water was taken from Tanjung Jati B CFPP, Jepara, Indonesia. The reagents  $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ ;  $\text{Na}_2\text{CO}_3$ ;  $\text{AgNO}_3$ ;  $\text{HCl}$  37%,  $\text{LaCl}_3$  and aquadest were analytical grade and used without further purification.

### 2.2 Synthesis of Ca-MgAl-LDHs

LDHs compounds with the molar ratio  $(\text{Ca}+\text{Mg})/\text{Al}$  is 0.5 was prepared by coprecipitation method. Into brine water as calcium and magnesium source was added  $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$  solution and the alkaline solution  $\text{Na}_2\text{CO}_3$  0,1 M until pH was adjusted  $\approx 10$ . The suspension was stirred 1 h at 65 °C, and then the slurry was washed with distilled water until free ion  $\text{Cl}^-$  ( $\text{AgNO}_3$  test). The slurry was separated by centrifugation at a speed of 2000 rpm for 15 min and then dried overnight at 105 °C.

Powder X-ray Diffraction (XRD) patterns of Ca-Mg-Al-LDHs material were conducted using Brucker AXS D8 Advance diffractometer at 40 kV and 35 mA with Cu  $\text{K}\alpha$  radiatio ( $\lambda=0.1540$  nm). The diffraction intensity was measured between 10° and 80°. The crystallite size of LDHs was calculated from the main reflection (11°) using the Scherrer formula:  $D = \frac{0.9 \cdot \lambda}{\beta \cdot \cos \theta}$ , where  $D$  is

the crystallite size (nm); 0.9 is the shape factor;  $\lambda$  is the wavelength of the Cu  $\text{K}\alpha$  radiation (0.1540 nm),  $\beta$  is the full width at half maximum (FWHM) and  $\theta$  is the Bragg diffraction angle. In addition, the XRD could be utilized to evaluate the peak broadening with the crystallite size and the lattice strain due to the presence of dislocations in LDHs using the Williamson-Hall (W-H) analysis [22] :

$$\beta \cdot \cos \theta_{hkl} = \frac{0.9 \cdot \lambda}{D} + 4\varepsilon \sin \theta_{hkl} \quad (1)$$

where  $\varepsilon$  is strain present in LDHs crystal. The lattice parameters  $c$  and  $a$  were calculated from the diffraction plane positions of  $d_{003}$ ;  $d_{006}$ ;  $d_{009}$  and  $d_{110}$  [17], with lattice parameters formula  $c = d_{003} + 2d_{006} + 3d_{009}$  and  $a = 2d_{110}$ . The product was confirmed by powder X-ray diffraction (JCPDS #890460 for MgAl-LDHs and JCPDS #870493 for CaAl-LDHs). Rietveld refinement and Le Bail refinement were performed using the refinement program, RIETICA. Peak profiles were modelled using a pseudo-voigt peak shape. The other experimental parameters refined were the instrument zero, scale factor, the lattice parameters and the peak shape parameters  $u$ ,  $v$ ,  $w$ ,  $\gamma_0$  and  $\gamma_1$  [20].

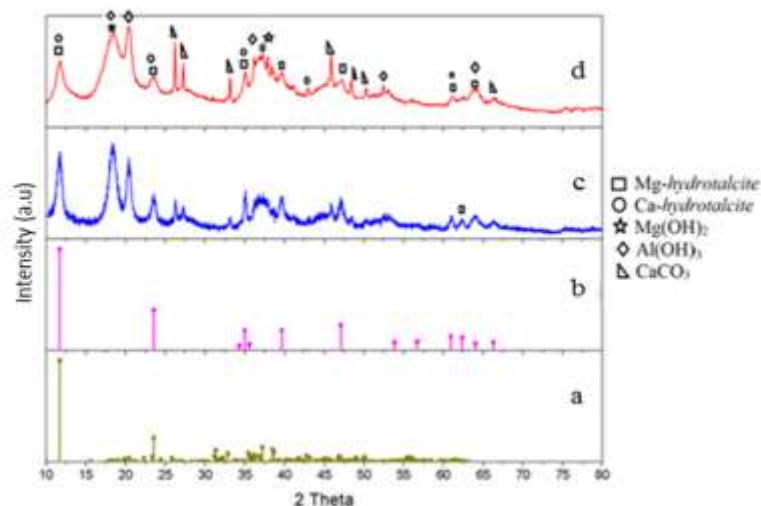
## 3. Result and discussion

Fig. 1 showed that the XRD patterns of Ca-MgAl LDHs with different treatment, without (HT-1) and with stirring (HT-2) treatment. As shown in Fig 1, the diffraction pattern of HT-1 and HT-2 have sharp and symmetric peaks at  $2\theta = 11^\circ$  (003);  $23^\circ$  (006);  $33^\circ$  (009) [16] and  $61^\circ$  (110) [22], which are the characteristics of LDH compounds. When XRD patterns were compared with JCPDS Mg-LDHs (JCPDS #890460) and Ca-LDHs (JCPDS #870493), another phase has found such as  $\text{Mg}(\text{OH})_2$  (JCPDS #070239),  $\text{Al}(\text{OH})_3$  (JCPDS #070324) and  $\text{CaCO}_3$  (JCPDS #862334). This was due to the radius size of  $\text{Ca}^{2+}$  ion was larger than that of  $\text{Mg}^{2+}$  ion [2,17] and because of the synthesis method could not ensure the Ca, Mg and Al cations mixed uniformly, then some Ca, Mg and Al cation agglomerated and formed the  $\text{CaCO}_3$ ,  $\text{Mg}(\text{OH})_2$  and  $\text{Al}(\text{OH})_3$ , respectively [6]. Fig. 2 showed that the  $2\theta$  (11°) has low intensity when cooling down very rapidly, so this causes a LDHs content decreased. When Thermal decreased rapidly, crystal structure organized unstable and not good. Treatment with variation cooling time 0, 30 min and 24 h in Fig. 3 shows diffraction degree 11°, 23° and 37° is a LDH

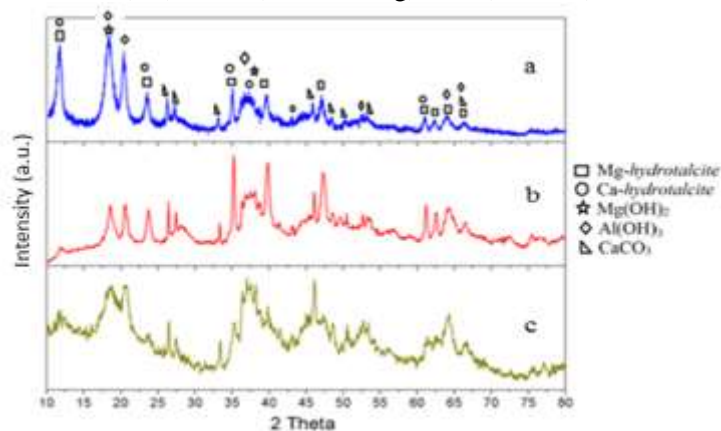
phase. Peak disposed wider with increasing cooling time, so this makes a form LDHs like as amorf. Cooling time with stirring could make a collision particle one another particle perfectly, but very longer stirring could make crystal structure broken or collapse.

**Table 1.** Treatment at slurry Ca-MgAl-LDHs during formation LDH crystal and lattice parameter.

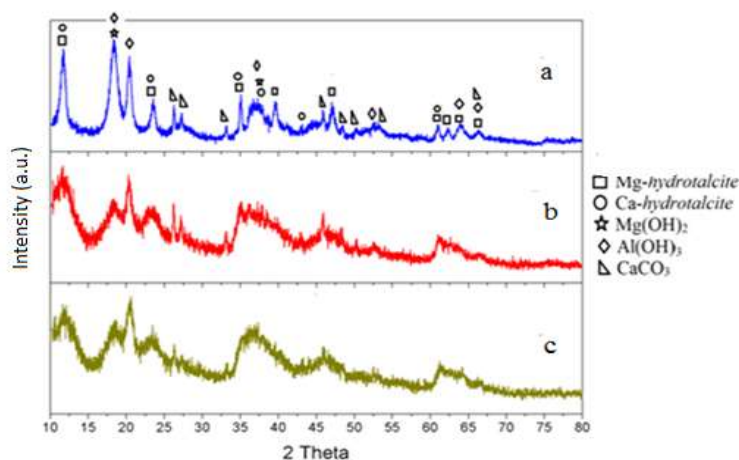
Material	Treatment			Lattice	
	Stirring	Cooling rate	Cooling time	<i>a</i> (nm)	<i>c</i> (nm)
HT-1	Without	1 °C/min	0 h	0.2907	2.2756
HT-2	With	1 °C/min	0 h	0.3046	2.2820
HT-3	With	2 °C/min	0 h	0.3028	2.2582
HT-4	With	3 °C/min	0 h	0.3055	2.2559
HT-5	With	1 °C/min	30 min	0.3044	2.2845
HT-6	With	1 °C/min	24 h	0.3053	2.2827
Commercial Mg-LDH	-	-	-	0.3045	2.2851



**Figure 1.** XRD pattern synthesized LDHs with a) Ca-Al LDHs (JCPDS #870493), b) Mg-Al LDHs (JCPDS #35096), c) HT-2 (with stirring) dan d) HT-1 (without stirring).



**Figure 2.** XRD pattern synthesis Ca-Mg-Al-LDHs with variation cooling rate a) 1 °C/min (HT-2), b) 2 °C/min (HT-3) dan c) 3 °C/min (HT-4).



**Figure 3.** XRD pattern synthesis Ca-Mg-Al-LDHs with variation cooling time, a) 0 min (HT-2), b) 30 min (HT-5) dan c) 24 hour (HT-6).

Lattice parameter  $a$  refers distance of octahedral O-O in layer and lattice parameter  $c$  is the distance of interlayer [25]. This showed that HT-1 experience decreasing distance interlayer due to uneven distribution in balancing anion with the commercial Mg-LDH as the standard of comparison. Table 2 showed the lattice parameter at LDH treatment between HT-1 and HT-2 was different. HT-2 has higher lattice than HT-1, but HT-2 with other treatment has similar lattice parameter value  $a$  and  $c$ .

Table 2 showed that the LDH treatment between HT-1 and HT-2 have different crystallite size ( $D$ ) on Scherer and Williamson-Hall Method, which HT-2 has higher crystallite size than HT-1. The crystallite size increased over the course of the experiment, suggesting that crystal growth occurred concurrently with the nucleation as the early formed LDHs slowly increased in crystallinity [24]. The decreased in crystallite size with the rising of cooling rate treatment at 1, 2 and 3°C/min might be explained that a LDHs structure lead to form small piece. In addition, the decreased in crystallite size with the rising of cooling time could be explained by partial dissolution of early formed amorphous LDHs as shown in Fig 3, which contributing to the aggregation and growth of larger crystal [17].

**Table 2.** The crystallite size ( $D$ ) slurry Ca-MgAl-LDHs with Debye-Scherrer and Williamson-Hall method.

Material	Scherer method (nm)	Williamson-Hall method (nm)
HT-1	4.64036	1.85614
HT-2	26.56207	0.17229
HT-3	192.58	-0.71324
HT-4	59.25385	2.30629
HT-5	256.7667	0.40821
HT-6	0.00203	0.26905
Commercial Mg-LDH	0.05538	2.46102

Le Bail refinement method was performed for both samples using as initial values the lattice parameters from standard JCPDS. The refinement had the following order: change the cell parameter value, histogram parameter, lattice parameter and instrumental peak shape. For each step were used 30 cycles. Table 3 shows the detail about result of refinement for Ca-MgAl LDHs with various treatment. The reliability index parameters i.e. the pattern factor ( $R_p$ ), the weighted pattern factor ( $R_{wp}$ ), and the goodness of fit ( $\chi^2$ ), which is indicated the quality of refinement work in this study, are presented in Table 3. The ideal value for  $\chi^2$  is 1,0 [26] or 3,0 [19], and all of the refinement was observed to be of

acceptable quality [26]. In Table 3, it was demonstrated that LDHs containing a single phase shows the  $\chi^2$  value is larger than many phases. It was indicated that LDHs have contained many phases such as Mg-Al-LDH, Ca-Al LDH, Mg(OH)<sub>2</sub>, Al(OH)<sub>3</sub> and CaCO<sub>3</sub> whereas Al(OH)<sub>3</sub> phase shows > 60%.

**Table 3.** Result Le Bail refinement with various phase.

Material	Phase Composition					Value		
	Mg-LDH	Ca-LDH	CaCO <sub>3</sub>	Al(OH) <sub>3</sub>	Mg(OH) <sub>2</sub>	<i>R<sub>p</sub></i>	<i>R<sub>wp</sub></i>	$\chi^2$
HT-1						25.38	33.92	279
	56.00	44.00				3.63	4.85	5.85
	28.86	22.97	48.07			2.47	3.3	1.99
	10.38	8.13	17.15	64.34		1.91	2.71	1.91
	10.30	8.21	16.99	63.73	0.77	1.87	2.59	1.76
HT-2						24.61	37.99	6.05
	55.95	44.05				7.16	7.45	0.23
	28.96	22.97	48.07			7.2	7.4	0.23
	10.42	8.09	17.28	64.2		7.14	7.71	0.25
	none	none	none	none	none	none	none	none
HT-3						20.35	28.5	5.67
	55.87	44.13				3.88	9.17	2.687
	29.03	22.95	48.03			3.17	5.79	1.089
	10.39	8.15	17.14	64.33		1.50	4.28	0.61
	10.30	8.12	16.98	63.83	0.77	1.95	4.81	0.78
HT-4						19.49	19.42	4.32
	55.99	44.01				3.18	5.35	4.26
	28.91	23.01	48.02			2.56	4.13	0.96
	10.38	8.19	17.13	64.31		1.81	3.88	0.86
	10.26	8.12	17.00	63.83	0.77	1.82	3.55	0.73
HT-5						12.52	12.12	0.58
	56.76	43.24				7.34	8.54	0.29
	45.57	36.17	19.07			6.44	8.1	0.26
	10.37	8.20	17.06	64.37		8.74	12.52	0.67
	none	none	none	none	none	none	none	none
HT-6						12.06	17.11	1.24
	56.17	43.83				7.51	8.42	0.30
	44.76	36.17	19.07			8.11	12.51	0.67
	10.37	8.18	17.12	64.32		5.49	7.85	0.27
	none	none	none	none	none	none	none	none

#### 4. Conclusion

The result from this study confirmed that treatment with stirring provided higher crystallite size and lattice parameter compared the treatment without stirring. Meanwhile the cooling rate treatment lead to decrease crystallite size and the cooling time treatment has increase crystallite size. It is indicated by crystal growth occurred in nucleation and slow formation. On X-ray diffraction analysis has found another phase Mg-Al LDH and Ca-Al LDH, such as  $\text{Mg}(\text{OH})_2$ ,  $\text{Al}(\text{OH})_3$  and  $\text{CaCO}_3$ , which is supported by result analysis of refinement Le Bail, whereas  $\text{Al}(\text{OH})_3$  phases shown the highest phase.

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