Anion capture with calcium, aluminium and iron containing layered double hydroxides

J. D. Phillips, L.J. Vandeperre

Department of Materials and Centre for Advanced Structural Ceramics

Imperial College London, South Kensington Campus, SW7 2AZ London, UK

j.phillips@imperial.ac.uk, l.vandeperre@imperial.ac.uk

Corresponding author:

L.J. Vandeperre,

Department of Materials and Centre for Advanced Structural Ceramics,

Imperial College London, South Kensington Campus, SW7 2AZ London, UK,

l.vandeperre@imperial.ac.uk,

Tel: +44 (0)2075946766

Anion capture with calcium, aluminium and iron containing layered double hydroxides

J. D. Phillips, L.J. Vandeperre

Department of Materials and Centre for Advanced Structural Ceramics

Imperial College London, South Kensington Campus, SW7 2AZ London, UK

Abstract

The competitive adsorption of nitrate, chloride and carbonate in layered double hydroxides (LDH) with the general formula $\text{Ca}^{2+}_{(1-x)}(\text{Al}^{3+}_{(1-y)}, \text{Fe}^{3+}_{(y)})_x (\text{OH})_2 \cdot x\text{NO}_3^- \cdot n\text{H}_2\text{O}$ was investigated. Both normal ion exchange by exposure to a solution containing different anions, as well as addition of calcined material to solution thereby exploiting the memory effect of LDHs was studied. Changes in the interlayer anion changed the interlayer spacing of the LDH. The order of preference of intercalation was $\text{Cl}^- \approx \text{CO}_3^{2-} > \text{NO}_3^-$. When multiple anions were present in the exchange solution, LDHs with several distinct interlayer spacing were produced indicating that LDHs with different anions in the interlayer existed at the same time. However for extended exchange times (14 days) where high concentrations of carbonate anion were present, the layered structure was destroyed resulting in the formation of calcite, CaCO_3 .

Keywords: layered double hydroxides, ion exchange, waste management

1. Introduction

Graphite has been used extensively in the nuclear industry. In the UK for example, graphite was used as a moderator in Magnox and advanced gas cooled reactors [1].

Such graphite was normally treated prior to usage to remove boron impurities by exposing it to gaseous chlorine or chlorine-containing compounds at temperatures up to 2775 K. Some residual chlorine remained in the graphite after this treatment and direct activation of the natural isotope ^{35}Cl during in-service irradiation lead to formation of ^{36}Cl , an isotope with a half life of 3×10^5 years [2]. To date, no decision has been made in the UK with regards to the treatment and/or storage of graphite wastes. One option is deep geological disposal after encapsulation in cementitious materials, but (thermal) treatment options are also still being considered as it is hoped that the substantial volume of the graphitic wastes, which could amount up to 33% of the volume of the storage facility, could be reduced [3].

Irrespective of the solution that eventually is pursued, the mobility of the $^{36}\text{Cl}^-$ anion is of concern. It is known that the $^{36}\text{Cl}^-$ can leach out of the graphite [4] so any contact of the graphite with water during safe-storage prior to decommissioning would have to be avoided, and water flow through a deep geological disposal facility could potentially release the $^{36}\text{Cl}^-$ to the environment. In addition, such leaching can also release ^{14}C from the graphite in the form of the carbonate anion through water-catalyzed oxidation of the graphite [4]. If the thermal treatment options are pursued, then the chlorine will be released from the graphite as a volatile species and gas scrubbers will have to remove the chlorine from the gas stream, so that again $^{36}\text{Cl}^-$ anions in water are obtained.

To address the need for a storage solution for chloride anions, the use of a new type of layered double hydroxides, compatible with cement for final storage, is being investigated. The materials could be used to capture the $^{36}\text{Cl}^-$ from the gas scrubber solutions, to passively capture any $^{36}\text{Cl}^-$ being released from the graphite by incorporation of these materials into the encapsulating cement matrix or to capture $^{36}\text{Cl}^-$ from intentional leach treatments of the graphite prior to disposal.

Layered double hydroxides are structurally related to the mineral Brucite ($\text{Mg}(\text{OH})_2$) and Portlandite ($\text{Ca}(\text{OH})_2$). A fraction, x , of the divalent sites (Mg^{2+} , Ca^{2+}) within the biplanar octahedral sheets are substituted isomorphously for trivalent cations (Al^{3+} , Fe^{3+}). The result of this substitution is the formation of a net positive charge on the surface of the sheet, and can be thought of as anionic equivalents of typical cationic clays. Hydrated anions in the interlayer galleries between the sheets, balance the positive charge and this provides the typical layered double hydroxide structure.

While the most common and extensively studied layered double hydroxides are those based on the naturally occurring mineral Hydrotalcite, $\text{Mg}_6\text{Al}_2(\text{CO}_3)(\text{OH})_{16} \cdot 4(\text{H}_2\text{O})$ [5], there is a calcium based layered double hydroxide known as Friedel's Salt or Hydrocalumite with the general formula $\text{Ca}_2\text{Al}(\text{OH})_6[\text{Cl}_{1-x}(\text{OH})_x] \cdot 3(\text{H}_2\text{O})$ [6]. The focus of the work presented here was to investigate the ability of these materials to exchange anions and initial work was carried out comparing the relative stability of possible competing anions present either in the waste stream or in the storage environment: nitrate (NO_3^-), chlorine (Cl^-) and carbonate (CO_3^{2-}) anions.

It is well known that the anion capture efficiency of LDHs can be increased by first thermally treating the layered double hydroxide powder to drive off the existing interlayer anions[7]. The calcination results in the gradual loss of the regular layered structure. Upon addition of this calcined material to an anionic solution the layered structure is reformed, incorporating anions from the solution in the vicinity of the powder. This is known as the memory effect. Therefore experiments were conducted to establish both the normal ion exchange ability of the materials as well as the exchange via the memory effect.

2. Experimental

The reagents employed in this study were all $\geq 98\%$ pure and were not purified further prior to use. Layered double hydroxides with the general formula

were produced via a co-precipitation method. Calcium nitrate tetrahydrate ($\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, Sigma Aldrich), aluminium nitrate nonahydrate ($\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, Fluka) and iron nitrate nonahydrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, Sigma Aldrich) were dissolved in distilled water in the desired stoichiometric ratio to give a 2 M solution. This solution was added dropwise to a solution containing sodium nitrate (NaNO_3 , Fisher Scientific), whilst being stirred vigorously. The precipitating solution was maintained at pH 12 by the simultaneous addition of a 1 M sodium hydroxide (NaOH , Riedel de Haen) solution. The precipitate formed was separated from the solution by vacuum enhanced filtration (0.65 μm pore size, Millipore). This filter cake was resuspended in distilled water and filtered once more to remove any unwanted nitrate salt residue; the solids were then dried at 353 K in an oven overnight.

For experiments investigating direct exchange 1 g of $\text{Ca}_4\text{Al}_2(\text{OH})_{12}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ was placed into a vial containing 50 ml of NaOH solution at pH 14, in addition the solution contained the desired interlayer anion as a solution of their sodium salt, 0.1M sodium chloride (NaCl , VWR International, Analar) or 1M sodium carbonate (Na_2CO_3 , Sigma Aldrich, Fluka). The exchange was allowed to occur for one hour and for an extended period of 14 days, before the solids were filtered by the same method as during production. The period of 14 days was selected to obtain a first indication whether these materials could store the chloride over an extended period of time or not.

For experiments investigating the ‘memory effect’, samples of $\text{Ca}_{(1-x)}(\text{Al}_{(1-y)},\text{Fe}_{(y)})_x(\text{OH})_2 \cdot x\text{NO}_3 \cdot n\text{H}_2\text{O}$ produced via the co-precipitation method were calcined in a tube furnace for 1 hour at 853-873 K in an air atmosphere. This temperature was chosen as it is known that $\text{Ca}_4\text{Al}_2(\text{OH})_{12}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ decomposes in a number of distinct steps. Initially dehydration occurs in two steps, the first at 343 K and then the remaining water is lost at 383 K. This is followed by the reduction of the nitrate anion, NO_3^- , to nitrite, NO_2^- , and simultaneous partial dehydroxylation of the layers in the range of 433 – 700 K. At 823 K all the interlayer nitrate anions have been lost and above this temperature further dehydroxylation occurs until $\text{Ca}_4\text{Al}_2\text{O}_7$ remains at 1573 K [8]. 0.5 g of calcined powder was placed into a vial containing distilled water and the desired anion or anions for exchange (NO_3^- , Cl^- , CO_3^{2-}) present as the sodium salts described above. The pH of this solution was increased to pH 14 by the addition of NaOH solution to a total volume of 50 ml. The vials were sealed and exchange was allowed to occur for 1 hour and for an extended period of 14 days. The precipitate was again separated from the the exchange solution by filtration.

Characterisation of the materials consisted of x-ray diffraction. X-ray diffraction was carried out with either a Phillips PW1720 powder x-ray diffractometer or a PW3050/60 Goniometer with PW3373/00 x-ray tube using Cu K_α radiation.

Quantitative phase analysis was performed on the LDH phases to determine the affinity for different anions. Crystallographic data for CaAl LDHs containing NO_3^- , Cl^- , and CO_3^{2-} were obtained from the ICSD Inorganic Crystal Structure Database [9-11]. These were modified with the assumption that Fe^{3+} would simply substitute for Al^{3+} in the structure. The data files were then refined against data for CaAlFe LDHs with a single anion produced in this work. The refined data files were then employed to carry out a Rietveld analysis of the data obtained in test with multiple anions. All refinements were done using Highscore Plus (PANalytical, The Netherlands).

3. Results and Discussion

3.1 Characterisation of the as-produced LDH

$\text{Ca}_4(\text{Al,Fe})_2(\text{OH})_{12} 2\text{NO}_3 \cdot n\text{H}_2\text{O}$ produced via the co precipitation method was ground to a free-flowing white powder. The X-ray diffraction pattern of the as-produced sample is presented in Figure 1. Most peaks observed are consistent with typical X-ray diffraction patterns of similar layered double hydroxides. Minor carbonate contamination is also evident from the characteristic peak of calcite at $29.4^\circ 2\theta$ and, as will be discussed below, from the shoulder in the low angle reflection near $11^\circ 2\theta$. The presence of sodium nitrate, NaNO_3 and portlandite, $\text{Ca}(\text{OH})_2$, was also detected. The former was a slight residue remaining after rinsing and the latter due to the simultaneous precipitation of $\text{Ca}(\text{OH})_2$ when the CaAlFe LDH phase was precipitated.

3.2 Direct exchange

Upon exposure of a $\text{Ca}_4(\text{Al,Fe})_2(\text{OH})_{12} 2\text{NO}_3 \cdot n\text{H}_2\text{O}$ LDH to single anion solutions of NaCl (1M) and Na_2CO_3 (0.1M) the x-ray diffraction patterns presented in Figure 2 were obtained. For clarity only the low angle, (003), peak is shown to highlight the variation in interlayer spacing for different anions.

It is apparent from Figure 2 that exposure of the NO_3^- intercalated LDH to Cl^- and CO_3^{2-} containing solutions has led to the formation of an LDH phase with a smaller d-spacing which is consistent with a decrease in thermochemical radius in the case of Cl^- , ($\text{Cl}^- = 0.168 \text{ nm}$, $\text{NO}_3^- = 0.200 \text{ nm}$ [12]) and an increase of anion charge in the case of NO_3^- exchanging with CO_3^{2-} (0.189 nm). This is in agreement with the literature which states that anions with a higher charge density will preferentially exchange with those of lower charge density [13]. As mentioned previously, the presence of a shoulder at a higher angle than either the Cl^- , or NO_3^- , as in Figure 1,

is typically indicative of the formation of a CO_3^{2-} intercalated LDH as a minor additional phase.

When $\text{Ca}_4(\text{Al,Fe})_2(\text{OH})_{12} \cdot 2\text{NO}_3 \cdot n\text{H}_2\text{O}$ LDH was exposed to solutions containing two anions, either NO_3^- and Cl^- (Figure 3), CO_3^{2-} and NO_3^- (Figure 4), or CO_3^{2-} and Cl^- (Figure 5), the LDHs which formed within 1 hour contained multiple interlayer spacings. Figure 3a illustrates again that intercalation of Cl^- is favoured over NO_3^- : even when these anions are present in equal amounts, only a Cl^- intercalated LDH appears to form. Figure 4a illustrates that the same is true for carbonate anions. The x-ray diffraction patterns obtained for CO_3^{2-} and Cl^- at different relative concentration are presented in Figure 5 and show that there is a somewhat stronger affinity for Cl^- ions than for CO_3^{2-} ions although the effect is much less strong than when the competition is with nitrate ions.

Table 1 compares the uptake of anions as determined using the Rietveld analysis with their abundance in the starting solution. Because CO_3^{2-} has twice the charge compared to the other ions, the mole fraction LDH present was recalculated to a “site occupancy” in which one site is associated with a unit charge to be balanced. The quantitative results confirm that Cl^- and CO_3^{2-} uptake is significantly greater than NO_3^- and that Cl^- is somewhat preferred over CO_3^{2-} . Hence, the relative affinity for these three anions is:

It is interesting to note that a high affinity for chlorine noted in these experiments is consistent with the natural occurrence of Friedel’s salt which contains Cl^- in the interlayer, whereas for magnesium based layered double hydroxide the mineral containing carbonate, hydrotalcite, is more common.

Extended exposure (14 days) did not affect the uptake ratio in the Cl^- - NO_3^- system. However in samples, which contained a higher concentration of carbonate anion, the majority of the LDH structure was destroyed, see Fig. 4b and 5b, with calcite forming instead. In both cases the remaining LDH could be attributed to a Cl^- or NO_3^- loaded LDH, but this obviously does not indicate a strong preference for intercalation.

3.3 Memory effect capture

Calcination of the LDH at 823 K lead to the formation of multiple phases: brownmillerite, $\text{Ca}_2(\text{Al,Fe})_2\text{O}_5$, calcium oxide, CaO , and some calcium carbonate, CaCO_3 , as determined from the x-ray diffraction presented in Figure 6.

Upon addition of the calcined material to solutions containing nitrate, chloride or carbonate ions, an LDH structure was reformed with an interlayer spacing which was attributable to capture of each of these anions. In addition some carbonate LDH was detected in the X-ray diffraction pattern; Figure 7 shows one example for the exposure of calcined material to a 0.1M Cl^- solution. Calcite, CaCO_3 had also formed due to exposure to an air atmosphere during rehydration of the calcined powder.

3.4 Discussion

The affinity for Cl^- and CO_3^{2-} of the layered double hydroxides investigated here shows that these materials could potentially be used to delay any release of $^{36}\text{Cl}^-$ or $^{14}\text{CO}_3^{2-}$ from graphitic wastes or could be used to capture and store $^{36}\text{Cl}^-$ or $^{14}\text{CO}_3^{2-}$ from intentional leaching treatments of graphite as well as for the treatment of scrubber solutions containing $^{36}\text{Cl}^-$ after thermal treatment of the graphitic wastes. The affinity for CO_3^{2-} is in line with observations for many layered double hydroxides. For example in layered double hydroxides made by substitution of Al^{3+} ions in magnesium hydroxide sheets, CO_3^{2-} is the most favoured anion[7]. The fact that Ca-based layered double hydroxides show such a strong affinity for Cl^- makes these materials more useful for Cl^- capture.

One issue of concern for long term storage, is that these materials are prone to decomposition by carbonation. However, it should be pointed out that the concentration of carbonate ion, which cause conversion into carbonate in 14 days was much higher than the expected carbonate ion concentrations in water percolating a geological storage site. For example, if the water percolates through bentonite, the carbonate concentration is only expected to be of the order of tens of millimoles per liter [14] whereas decomposition was observed for CO_3^{2-} concentrations in excess of 0.125 M only. Moreover, such decomposition would not be as problematic for any ^{14}C captured, as it would in all probability be incorporated in the calcium carbonate that forms during decomposition of the layered double hydroxides. It will nevertheless be important to study the limits of the stability further in future work.

4. Conclusions

Layered double hydroxides based on compositions containing calcium, aluminium and iron were produced with NO_3^- as the charge balancing anion. Upon exposure to solutions containing a different anion or anions the NO_3^- anion was exchanged in the order of $\text{Cl}^- \approx \text{CO}_3^{2-} > \text{NO}_3^-$. The capture of Cl^- preferentially is of interest for the capture of Cl^{36} a radionuclide of concern during the decommissioning of sites where graphite has been extensively used.

When multiple anions were present in solution, an LDH structure formed which contained multiple interlayer spacing, each characteristic of LDHs with a distinct interlayer anion. It was noted that the NO_3^- anion was easily displaced by both Cl^- and CO_3^{2-} . Prolonged exposure (14 days) to exchange solutions which contained a high concentration of the CO_3^{2-} anion resulted in a loss of the layered double hydroxide structure and the formation of calcite. This warrants further attention if these materials are to be used for long term storage of $^{36}\text{Cl}^-$ but is expected to be less important for any ^{14}C captured.

Acknowledgements

This work was funded by the Engineering and Physical Sciences Research Council of the UK under grant EP/F066523/1 Decommissioning, Immobilisation and Management of Nuclear Wastes for Disposal.

References

- [1] C.W.E. Addison, S. Barlow, M.A. Bassett, J. Buffery, R. Burcl, A.G. Davies, M. Dubourgh, F. V., G. Holt, B.J. Marsden, P.C. Minshall, A. Morales, M. E., E. Mulyanto, G.B. Neighbour, F. Pineau, P. Poskas, A. Romenkov, M. Shirakawa, A. Suvorov, Y.A. Verzilov, A.J. Wickham, S.J. Wisbey, M. Wise, Characterization, treatment and conditioning of radioactive graphite from decommissioning of nuclear reactors, in: IAEA-TECDOC-1521, IAEA, 2004, pp. 82.
- [2] F.J. Brown, J.D. Palmer, P. Wood, Derivation of a radionuclide inventory for irradiated graphite-chlorine-36 inventory determination, in: Proceedings of IAEA Technical Committee Meeting held in Manchester, UK, IAEA, Vienna, 1999, pp. 143-152.
- [3] Draft Strategy, Nuclear Decommissioning Authority, Moor Row, UK, 2010.
- [4] W.J. Gray, W.C. Morgan, Leaching of ^{14}C and ^{36}Cl from Hanford reactor graphite, in: Pacific Northwest Laboratory - report 6769, 1988, pp. 93.
- [5] S. Miyata, Synthesis of new Hydrotalcite-like Compounds and and their Physico Chemical Properties, Chemistry Letters, (1973) 843-848.
- [6] L. Vieille, I. Rousselot, F. Leroux, J.-P. Besse, C. Taviot-Gueho, Hydrocalumite and Its Polymer Derivatives. 1. Reversible Thermal Behavior of Friedel's Salt: A Direct Observation by Means of High-Temperature in Situ Powder X-ray Diffraction, Chemistry of materials, 15 (2003) 4361-4368.
- [7] X. Duan, D.G. Evans, Layered double hydroxides, in: D.M.P. Mingos (Ed.) Structure and Bonding, Springer-Verlag, Berlin, 2005.
- [8] G. Renaudin, J.P. Rapin, B. Humbert, M. François, Thermal behaviour of the nitrated AFm phase $\text{Ca}_4\text{Al}_2(\text{OH})_{12}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and structure determination of the intermediate hydrate $\text{Ca}_4\text{Al}_2(\text{OH})_{12}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$, Cement and Concrete Research, 30 (2000) 307-314.
- [9] G. Renaudin, F. Kubel, J.P. Rivera, M. Francois, Structural phase transition and high temperature phase structure of Friedel's salt $3(\text{CaO})(\text{Al}_2\text{O}_3)(\text{CaCl}_2) \cdot 10(\text{H}_2\text{O})$, Cem. Concr. Res., 29 (1999) 1937-1942.
- [10] M. Francois, A cementitious compound with composition $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CaCO}_3 \cdot 11\text{H}_2\text{O}$, Acta Cryst. C. Crystal structure communications, 54 (1998) 1214.
- [11] G. Renaudin, M. Francois, The lamellar double-hydroxide (LDH) compound with composition $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Ca}(\text{NO}_3)_2 \cdot 10\text{H}_2\text{O}$, Acta Cryst. C. Crystal structure communications, 55 (1999) 835-838.

- [12] Roobottom, Thermochemical Radii of Complex Ions, Journal of Chemical Education, 76 (1999) 1570.
- [13] J. He, M. Wei, B. Li, Y. Kang, D.G. Evans, X. Duan, Preparation of Layered Double Hydroxides, Structure and Bonding, 119 (2006) 89-119.
- [14] D. Arcos, F. Grandia, C. Domenech, A.M. Fernandez, M.V. Villar, A. Muurinen, T. Carlsson, P. Selling, P. Hernan, Long-term geochemical evolution of the near field repository: Insights from reactive transport modelling and experimental evidences, Journal of contaminant hydrology, 102 (2008) 196-209.

Anion Solution (Mole Fraction)		LDH Composition (Mole Fraction)		Site Occupancy	
Cl ⁻	NO ₃ ⁻	Cl ⁻	NO ₃ ⁻	Cl ⁻	NO ₃ ⁻
0.1	0.9	0.88	0.12	0.88	0.12
0.5	0.5	0.97	0.03	0.97	0.03
0.9	0.1	0.98	0.02	0.98	0.02
CO ₃ ²⁻	NO ₃ ⁻	CO ₃ ²⁻	NO ₃ ⁻	CO ₃ ²⁻	NO ₃ ⁻
0.9	0.1	0.70	0.30	0.83	0.17
0.5	0.5	0.73	0.27	0.84	0.16
0.1	0.9	0.36	0.64	0.53	0.47
Cl ⁻	CO ₃ ²⁻	Cl ⁻	CO ₃ ²⁻	Cl ⁻	CO ₃ ²⁻
0.1	0.9	0.65	0.35	0.48	0.52
0.5	0.5	0.74	0.26	0.59	0.41
0.9	0.1	0.98	0.02	0.97	0.03

Table 1: Details of the compositions of multiple anion solutions used in mole fraction, and the mole fraction of the two LDH phases formed after exposure to the anion solution. The final columns indicate the fraction of the charged sites balanced by a given anion, calculated from the measured mole fraction of the LDH phases present.

Figures

Figure 1 X-ray diffraction pattern obtained from a sample of $\text{Ca}_4(\text{Al,Fe})_2(\text{OH})_{12} 2\text{NO}_3 \cdot n\text{H}_2\text{O}$ produced via the co precipitation method. The presence of calcite and the shoulder on the first peak are indicative that minor carbonate contamination occurred during production.

Figure 2 (003) peak present in the XRD patterns obtained for an NO_3^- intercalated LDH in the as produced condition and exchanged with Cl^- and CO_3^{2-} (as labelled in Figure)

(a)

(b)

Figure 3 X-ray diffraction pattern of the (003) peak after exchange with solutions containing Cl⁻ and NO₃²⁻ ions for an exchange time of (a) 1 h and (b) 14 days. The legend gives the relative presence of anions in mole fraction of 0.5M equivalent mole total.

(a)

(b)

Figure 4 X-ray diffraction pattern of the (003) peak after exchange with solutions contain CO₃²⁻ and NO₃⁻ ions for an exchange time of (a) 1 h and (b) 14 days. The legend gives the relative presence of anions in mole fraction of 0.5M equivalent mole total.

(a)

(b)

Figure 5 X-ray diffraction pattern of the (003) peak after exchange with solutions contain CO₃²⁻ and Cl⁻ ions for an exchange time of (a) 1 h and (b) 14 days. The legend gives the relative presence of anions in mole fraction of 0.5M equivalent mole total.

Figure 6 X-ray diffraction pattern obtained for a sample of $\text{Ca}_4(\text{Al,Fe})_2(\text{OH})_{12} 2\text{NO}_3 \cdot n\text{H}_2\text{O}$ which was calcined at 823 K in air.

Figure 7 X-ray diffraction pattern obtained for a sample of calcined $\text{Ca}_4(\text{Al,Fe})_2(\text{OH})_{12} 2\text{NO}_3 \cdot n\text{H}_2\text{O}$ which was allowed to exchange with a 0.1M Cl^- solution for 1hr. The peaks for the LDH phase are attributable to LDHs phases containing both Cl^- and CO_3^{2-} as the interlayer anions, which can be seen most clearly from in the (003) peak shown in the inset.