Solid-state speciation of interlayer anions in layered double hydroxides

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Abstract

Layered double hydroxides (LDH) have been proposed for phosphate (PO_4) recovery and recycling from waste streams due to their high anion exchange capacity, good stability and high affinity towards PO_4 . The high affinity towards PO_4 strongly relates to the electrostatic interaction with PO_4 , and thus the charge of PO_4 . However, the anion speciation of intercalated PO_4 , i.e. either H_2PO_4^- , HPO_4^{2-} or PO_4^{3-} is often overlooked. This study was set up to measure solid phase PO_4 speciation through ion exchange stoichiometry, x-ray diffraction (XRD), attenuated total reflection Fourier-transform infrared spectroscopy (ATR-FTIR) and modelling. Six phase pure Mg/Al LDH materials were synthesized using co-precipitation of metal nitrate (NO_3^-) solutions with varying $\text{M}^{2+}/\text{M}^{3+}$ ratio at pH 12 and pH 10. The LDHs synthesized at pH 12 contained larger equivalent fractions of intercalated OH^- , smaller fractions of NO_3^- and smaller interlayer distance than those prepared at pH 10, likely because of the higher OH^- concentration in the more alkaline synthesis solutions. Two high charge LDHs prepared at pH 12 or 10 were selected, exchanged with PO_4 (0-20 mM initial PO_4 , 24h) at one starting pH (7.20); desorption was subsequently performed with carbonate (3 mM, initial pH 8.4) during 480 h. The resulting solution concentrations of NO_3^- , PO_4 and CO_3 and the pH allowed the identification of the anion exchange stoichiometry. The LDH synthesized at pH 12, which had a large fraction of exchangeable OH^- , adsorbed PO_4 as $\text{HPO}_4^{2-}/\text{PO}_4^{3-}$, in exchange for both NO_3^- and OH^- anions. The material synthesized at pH 10 containing a lower fraction of exchangeable OH^- , therefore, adsorbed mainly HPO_4^{2-} in exchange for NO_3^- anions. The carbonate exchange was consistent with adsorption of divalent CO_3^{2-} . The pH dependent speciation modelling showed that the exchanged PO_4 ions have higher charge compared to those in the contacting solution. This study suggests that the highest P content of LDH is obtained in high charge materials holding divalent PO_4 anions, i.e. materials synthesized at lower pH and/or exchanged in solutions with low alkalinity.

Introduction

Layered double hydroxides (LDHs) are a class of inorganic materials, consisting of stacked metal hydroxide layers alternated by exchangeable anions in the interlayer gallery. These materials are often represented by the general formula $[M^{2+}_{1-x} M^{3+}_x (OH)_2]^{x+} [A^{m-}_{x/m} \cdot nH_2O]^{x-}$, with x equal to the molar ratio $M^{3+}/(M^{2+} + M^{3+})$ and A^{m-} the intercalated anion. As derived from this formula, the presence of trivalent metal cations in the hydroxide layers induces a positive charge excess in the layers, which is counterbalanced by an anion population in the interlayer gallery and on the outer surface.

Hydrotalcite is a naturally occurring Mg-Al LDH, with CO_3^{2-} anions on the exchange complex. These CO_3^{2-} anions are strongly bound through electrostatic interaction in the interlayer gallery due to a high anion charge, a small molecular size and energetically favorable positioning between the LDH layers. Following the development of synthetic LDH production [1], numerous other anions have been introduced into the interlayer of LDH materials for various applications (medical [2], catalytic [3], environmental [4], agronomical [5]). Recently, LDHs have also been proposed as adsorbents for orthophosphate (PO_4) [6,7] bringing forward a new technique to isolate and recycle PO_4 from wastewater [8–10]. Especially LDHs with a high anion exchange capacity (AEC) (e.g. $M^{2+}/M^{3+} \approx 2$) have shown high affinity towards PO_4 [11]. Many recent PO_4 -LDH studies describe the anion exchange process by quantification of the PO_4 removal from an aqueous solution, thereby assuming that i) initially bound anions (e.g. NO_3^- or Cl^-) are released according to the charge balance on the solid phase, and ii) the initial anion population on the exchange complex is well-defined [12–14]. However, a more detailed description of the anion exchange, substantiated by measurements of anion exchange stoichiometry or by spectroscopic observations of anion speciation on the exchange complex, is often lacking. Evaluating the anion charge balance can provide proof for the removal of PO_4 from solution via reversible electrostatic interactions on the LDH, rather than via precipitation. Precipitation is often observed, but results in a limited PO_4 desorption or recovery and is, therefore, a major disadvantage for PO_4 reuse [6,15,16].

The determination of anion speciation of phosphates (i.e. relevant species of PO_4 : H_2PO_4^- , HPO_4^{2-} , PO_4^{3-}) and carbonates (relevant species of CO_3 : HCO_3^- , CO_3^{2-}) plays an important role in the LDH recycling application for PO_4 . This is because of the pH dependent charge (Figure 1) [11,17,18] which affects the uptake by LDHs in two ways: i) with a higher negative charge, less anions are required to compensate the AEC of the LDH, and ii) the anion charge determines the affinity of a specific LDH for the anion. Anion speciation can thus have far-ranging consequences for the PO_4 recovery by LDHs, yet the material characteristics and chemical conditions favoring the uptake of one specific anion species remain unclear. In previous LDH studies, the issue of the multivalence of PO_4 is often ignored [13,19], or the anion speciation in the original contacting solution is assumed to mirror the speciation in the interlayer gallery, without further proof [20]. Woo et al. introduced different PO_4 anion species in a Ca-Fe LDH by varying the pH of the exchange solution, but whether the solution PO_4 forms were also introduced in the LDH interlayer is unclear [21]. Several studies observed that increasing the solution pH decreased the molar PO_4 uptake by the LDH [7,22]. This can be related to the presence of increasingly higher charged PO_4 anions in solution and in the LDH at higher pH. Alternatively, this might also be attributed to an increasing competition between OH^- and one and the same PO_4 species (e.g. the divalent HPO_4^{2-}) at increasing pH. Using Raman spectroscopy, Frost et al. showed that the speciation of PO_4 in Zn-Al LDHs depends on the initial pH of alkaline PO_4 solutions [23]. However, more insight is required on the parameters determining the uptake of PO_4 from pH neutral solutions.

The goal of this study was to determine the anion exchange stoichiometry on Mg-Al LDHs during i) the uptake of PO_4 by as-synthesized LDHs, and during ii) the long-term incubation of the obtained materials in CO_3 solution. The charge balance of interacting anions was investigated by the anion concentrations and speciations in the exchange solutions (OH^- , NO_3^- , PO_4 , CO_3), while the obtained LDH materials were characterized with XRD and ATR-FTIR. Finally, anion exchange modelling was included to calculate the pH dependent speciation in solution and on the solid phase.

Materials and methods

LDH synthesis and characterization

Six Mg-Al LDHs were synthesized using the co-precipitation method, by varying the synthesis pH and the Mg/Al ratio in the precursor solution. For this, $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Acros Organics, USA) and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (Fluka, USA) were dissolved in MilliQ™ water to obtain a 50 mL mixed solution with varying molar Mg/Al ratio (2, 3 or 4) and total metal concentration of 3 M. Using a B. Braun perfusor pump, this solution was added at a rate of 10 mL h^{-1} to a 600 mL solution with either pH 10 or 12 (adjusted with NaOH) under vigorous stirring. A constant pH was maintained with the help of a Metrohm Titrino 702 by the dropwise addition of a 3 M NaOH solution. The synthesis was performed at room temperature and in a nitrogen atmosphere to prevent CO_2 from dissolving in the reaction solution. The material was ripened in the synthesis mixture for 0.5 h, while continuing vigorous stirring. Afterwards, the remaining suspension was recovered by centrifugation (20 minutes, 15000 g) and decantation. The material was washed three times with MilliQ™ water and subsequently dried at 60°C . The LDH materials were termed based on their synthesis pH and Mg/Al ratio, e.g. LDH12(2) prepared at pH 12 with molar Mg/Al ratio of 2. The obtained solid samples were dissolved in HCl, to determine the metal content of the materials with inductively coupled plasma optical emission spectrometry (ICP-OES, PerkinElmer Optima 3300 DV) and the nitrate content with a sulfonamide colorimetric method (SKALAR). The molar mass of the as-synthesized materials, as well as their expected anion exchange capacity (AEC), were calculated from the measured Mg/Al ratio, the water content and the expected anion population. The water content was determined with thermogravimetric analysis (TGA, see below). The anion population was based on the measured NO_3^- content, the remainder attributed to OH^- anions to equal the LDH's AEC.

Crystallographic and morphological characteristics of the as-synthesized LDHs were investigated by x-ray diffraction (XRD) and scanning electron microscopy (SEM). Powder XRD analysis was performed with a STOE STADI P Combi instrument in the Debye-Scherrer geometry ($\text{CuK}\alpha_1$) using an image plate

detector ($2\theta=0-62^\circ$; $\Delta 2\theta=0.03^\circ$). The SEM micrographs were obtained using a PHILIPS XL 30 FG microscope on Pt coated samples. The ATR-FTIR spectra were obtained with a Varian 620-IR. The as-synthesized LDHs were characterized with TGA using a TGA Q500 V6.7 Build 203 (TA instruments) with Pt pan. The TGA measurement was performed with a 5°C min^{-1} heating ramp to 500°C in a N_2 atmosphere. Nitrogen adsorption isotherms at 77 K were measured using a Micromeritics 3Flex 3500 gas physisorption instrument. The samples were degassed before measurement at 413 K under vacuum (10^{-2} mbar) for 6 h. The charge density of the hydroxide layers (C_d , in $e\text{ nm}^{-2}$) is calculated using the formula: $C_d = xe/(a^2 \sin 60^\circ)$, with $a = 2d_{010} = 0.309\text{ nm}$, $x = \text{M}^{3+}/(\text{M}^{2+} + \text{M}^{3+})$, and e the elementary charge ($e = 1.602 \cdot 10^{-19}\text{ C}$) [24].

LDH exchange with PO_4

Anion exchange experiments were performed with LDH12(2) and LDH10(2) materials. The uptake of PO_4 was determined by equilibrating 40 mg of the as-synthesized materials in 10 mL solutions containing different initial concentrations of KH_2PO_4 , i.e. 0, 1, 3, 6, 9 or 20 mM, starting from MilliQ™ water. The largest concentration is equivalent to 140 % of the highest AEC at the solid-liquid ratio used (PO_4 as H_2PO_4^-). The inorganic C (CO_3) concentration of the starting solution was $< 0.02\text{ mM}$ (Total Carbon analyser, TC: Shimadzu TOC-L). The pH of the initial KH_2PO_4 solutions was adjusted to 7.20 with a dilute NaOH solution. Each treatment was carried out in triplicate. The suspensions were shaken end-over-end for 24 h at 20°C , and afterwards centrifuged (3000 g, 20 min). The P concentration in the supernatant was determined by ICP-OES. Also the pH was recorded and the NO_3^- concentration determined using ion chromatography (IC: Dionex ICS-2000 with a AS15 IC column). The obtained materials were separated by centrifugation, washed (adding 2 mL of MilliQ™) to remove unadsorbed PO_4 , and dried at 60°C after recovery. The total P content of the dried LDH materials after reaction was determined by ICP-OES after digestion in boiling aqua regia, and the obtained materials were characterized with XRD and ATR-FTIR. Reference ATR-FTIR samples for the identification of the

different anion species were: NaNO_3 , KNO_3 , NaH_2PO_4 , KH_2PO_4 , Na_2HPO_4 , K_2HPO_4 , Na_3PO_4 , K_3PO_4 , NaHCO_3 and Na_2CO_3 (Figure S1).

LDH exchange with CO_3

The stoichiometry upon CO_3 exchange was determined in the $\text{NO}_3^-/\text{OH}^-$ LDHs (as-synthesized LDH12(2) and LDH10(2)) and the materials obtained after exchange with PO_4 at various degrees, i.e. materials after exchange in 0, 1, 3, 6, 9 or 20 mM PO_4 . First, triplicate 25 mg samples of each LDH were shaken end-over-end in 51.2 mL Milli-Q at 20 °C during 4 h, which allowed unsorbed PO_4 to dissolve before starting the anion exchange. Before and after this incubation step, the NO_3^- , PO_4 and CO_3 concentration in the solution was determined. After sampling, 200 μL of a 0.75 M NaHCO_3 stock solution was added to the 50 mL suspensions to obtain a 3 mM CO_3 concentration. Two of the three replicates were also spiked with carrier free ^{14}C -labeled Na_2CO_3 at a dose of 280 Bq per sample, while one of the replicates remained ^{14}C -isotope free. Blank solutions (without LDH material) with the same volume as the samples were included by adding the ^{14}C or non- ^{14}C CO_3 spike to MilliQ™ solutions. The initial CO_3 concentration of 3.0 mM was confirmed with the TC analyses, and an initial pH of the blanks of 8.45 was recorded. The initial CO_3 concentration (3 mM) was selected as a tradeoff between sufficiently large to saturate the AEC and sufficiently small to quantify the CO_3 sorbed from concentration differences between initial and final solution. The ^{14}C activity in the solution was measured with the liquid scintillation counter (LSC) Tricarb 3110 TR, by adding 0.5 mL of a 0.02 M NaOH solution and 2 mL of a scintillation cocktail (Ultima Gold AB) to a 1 mL supernatant sample. The LSC was adopted for more accurate determination of CO_3 concentration differences than with the TC to avoid errors by CO_2 gas exchange between liquid samples and the atmosphere. At the same time, comparing TC and LSC allows identification of potential atmospheric CO_2 uptake in the alkaline solutions during the ion exchange reactions. This suggests to be negligible: the CO_3 in blank solutions (no LDH) was measured with TC before, during and after the incubation experiment, and remained

stable at 3.0 mM. Hence, the decrease of the ^{14}C activity in the liquid subsamples from LDH suspensions, relative to the blank samples, was used to quantify the CO_3 uptake in the LDH.

All samples were incubated at 20 °C and shaken end-over-end. At specific moments (after 4 h, 1 d, 3 d, 7 d, 20 d incubation) the suspensions were centrifuged (3000 g, 20 min) to determine the PO_4 concentration (ICP-OES), the NO_3^- concentration (IC), the CO_3 concentration (LSC) and the pH (only at day 20) in liquid subsamples of the supernatant. The decrease of the ^{14}C activity in the liquid subsamples from LDH suspensions, relative to the small changes in the blank samples, was used to quantify the CO_3 uptake in the LDH. After 20 d incubation, the suspensions were centrifuged and the non- ^{14}C -labeled LDH samples were recovered, dried at 60 °C, and characterized with XRD and ATR-FTIR spectroscopy.

Modeling LDH incubation in PO_4 and in CO_3 solutions

The incubation of the LDHs in PO_4 solutions with varying concentration, as well as the desorption of the obtained materials in a CO_3 solution, were modelled using the Gaines and Thomas model for ion exchange reactions:

in which X and Y are the exchanging anions; the subscript s indicates the sorbed anion.

The Gaines and Thomas model defines the equilibrium constant as:

$$K_c(Y^{n-} - X^{m-}) = \frac{(N_Y)^m (X^{m-})^n}{(N_X)^n (Y^{n-})^m} \quad (2.2)$$

in which $K_c(Y^{n-} - X^{m-})$ is the Gaines and Thomas selectivity coefficient of the reaction in which Y replaces X_s . The N_Y or N_X are equivalent fractions on the AEC of the exchanger phase, i.e. the fraction of the charge occupied defined as:

$$N_i = \frac{z_i [i_s]}{[S_T]} \quad \text{with} \quad \sum_i N_i = 1 \quad (2.3)$$

in which z_i the charge of ion and ST the site capacity, i.e. the AEC.

This approach assumed a non-specific and pure electrostatic binding of the different anions in the interlayer gallery, i.e. among all species involved here (PO_4^{3-} , NO_3^- , CO_3^{2-}) the K_c values are all 1. As a result, the Gaines and Thomas notation reduces to a Donnan model approach, in which selectivity among ions is merely related to the ion charge, e.g. trivalent anions are highly preferred over divalent anions according to this model. One exception is made: The K_c (OH^- – NO_3^-) is set to 100. This was calculated from the observed large fraction of OH^- in the LDH12(2): that fraction equals $N_{\text{OH}^-} = 0.7$ at the synthesis pH = 12 (10^{-2} M OH^-) while the NO_3^- concentrations in the synthesis solution was 0.48 M. This yields a K_c (OH^- – NO_3^-) ≈ 100 . The larger selectivity of the OH^- ion logically relates to its high charge density of this small anion.

The modelling allowed to calculate the extent of adsorption and desorption of PO_4 and predicting the equilibrium pH as OH^- anions are exchanged with PO_4 ions and change the solution pH by reacting with remaining PO_4 in solution. Furthermore, the anion speciation on the solid phase was modelled. The modelling used VMinteq 3.1 to solve the mass and charge balance equations with the Davies equation for ionic strength corrections, 25°C, no solution-gas exchanges of CO_2 and using the adapted standard thermodynamic database in that model, with the exception of the K_c (OH^- – NO_3^-) ≈ 100 as described above.

Results and discussion

The charge properties of the LDHs

The co-precipitation procedure yielded six phase-pure LDH materials by varying the synthesis pH and the Mg/Al ratio, as confirmed by XRD. The synthesis at different pH affects the actual Mg/Al ratio in the obtained material (Table 1). At a higher precipitation pH, a material with a slightly higher Mg/Al ratio is obtained. This is likely a result of the increasing Al(III) solubility when changing the pH from 10

to 12. The TGA curves of the materials are presented in Figure S2. The weight loss before reaching 200 °C is attributed to the release of physically adsorbed water [25]. An accurate calculation of the AEC of all materials is presented in Table 1. From the abundance of NO_3^- anions in the synthesis mixture (about 0.48 M), a single NO_3^- anion population may be expected on the exchange complex of the LDHs. However, the comparison of the NO_3^- content with the expected AEC suggests that this is not the case (Table 1). This is especially pronounced for the co-precipitation synthesis using the molar 2/1 metal for precipitation pH 12. The remaining anion population is very likely made up by OH^- anions, adsorbed during synthesis in alkaline conditions, or, possibly, traces of CO_3 anions. The $\text{OH}^-/\text{NO}_3^-$ selectivity explains the equivalent fractions on the exchange complex. A relatively lower NO_3^- content is found in the materials with an increasing layer charge density (Table 1). This is the result of the higher charge density of OH^- compared to NO_3^- . Therefore, OH^- anions are more suitable to compensate the positive layer charge in LDHs with a low $\text{M}^{2+}/\text{M}^{3+}$ ratio. This trend is also reflected in the interlayer spacing of the LDHs, calculated from the position of the (003) reflection in the XRD pattern (Bragg's Law) (Table 1). This spacing indicates the presence and orientation of intercalated anions. The orientation of planar anions, such as NO_3^- , thereby responds to the layer charge density of the hydroxide layers. Generally, a more vertical positioning of intercalated NO_3^- anions is required to compensate the charge as the structural positive layer charge increases [26]. Here, the LDHs prepared at pH 12 have a significantly smaller interlayer spacing compared to the LDHs prepared at pH 10. An OH^- anion bears the same charge as a NO_3^- anion, but is significantly smaller and, therefore, has a higher charge density. The layer charge of pH 12 LDHs is compensated by OH^- anions to a large extent, which allows horizontal positioning of interlayer NO_3^- anions and thus a closer packing of the hydroxide layers. In contrast, in the pH 10 LDHs, the fraction of intercalated OH^- anions is limited and the exchange complex is dominated by the larger NO_3^- anions. This results in a densely packed, more vertically oriented NO_3^- interlayer anion population, and thus significantly higher interlayer spacing.

The effects of layer charge (Mg/Al ratio) on the interlayer spacing differs between the pH 10 and pH 12 samples. At a decreasing layer charge (increasing Mg/Al) in the pH 10 LDHs, the interlayer spacing

of the LDHs strongly decreased. A lower charge density allows a more horizontal NO_3^- anion positioning. In contrast, at a decreasing layer charge density in the pH 12 LDHs, the interlayer spacing slightly increased. This is associated with the increased fraction of NO_3^- in the exchange complex, in turn attributed to a lower $\text{OH}^-/\text{NO}_3^-$ selectivity in materials with a lower charge density (see above). Consequently, the NO_3^- anions occupy a larger fraction of the AEC, and compensate for the layer charge with a more vertical interlayer positioning.

Out of the six as-synthesized LDHs, LDH12(2) and LDH10(2) were selected for stoichiometric exchange experiments. The clear difference in the fraction of OH^- content on their exchange complex, combined with the need of a high layer charge density for a performant PO_4 uptake makes the comparison of LDH12(2) and LDH10(2) of interest. A more detailed material characterization was performed for these two LDHs. A layered morphology can be derived from the SEM micrographs (Figure S3), yet the typical hexagonal crystals are not readily recognized. The BET surface area of both LDHs is similar: $14.7 \text{ m}^2 \text{ g}^{-1}$ for LDH12(2) and $18.1 \text{ m}^2 \text{ g}^{-1}$ for LDH10(2) (Table 1), with LDH12(2) having slightly more mesopores compared to LDH10(2) (Figure S4). The ATR-FTIR spectroscopy can provide insight in the identity, and possibly also the speciation, of the anions on the exchange complex of LDHs. From the spectra of LDH12(2) and LDH10(2), the presence of NO_3^- in the interlayer of both LDHs is suggested by the clear vibration mode of NO_3^- shown by the band at 1345 cm^{-1} (Figure 2a) [13,26,27]. This band, attributed to NO_3^- , is also clearly present in the spectra of reference salts NaNO_3 and KNO_3 (Figure S1). However, on the exchange complex of LDH10(2), likely also a minor amount of CO_3^{2-} is present, as shown by the band at 1413 cm^{-1} [28]. This band, attributed to CO_3^{2-} , is also present in the spectra of reference salts Na_2CO_3 (Figure S1). The broad band in the $3600\text{-}3000 \text{ cm}^{-1}$ region is attributed to the OH stretching of structural hydroxyl groups, interlayer H_2O molecules and possibly interlayer OH^- anions, while the band at 1645 cm^{-1} relates to the bending mode of H_2O molecules (not shown in Figure 2a) [17].

The adsorption isotherms of LDH12(2) and LDH10(2) are presented in Figure 3a and 3b. The high AEC of LDH10(2) results in a PO_4 uptake up to 1.76 mmol g^{-1} , whereas the PO_4 uptake by LDH12(2) is slightly lower with a maximum of 1.28 mmol g^{-1} . These PO_4 uptake capacities are comparable to values from previous studies [11]. During PO_4 uptake, LDH stability is maintained, as suggested by XRD (Figure 2b).

In the analysis given below, the reactions of LDH12(2) and LDH10(2) are treated as complete anion exchange. Therefore, it is assumed that specific bonding sites on the crystal fringes account only for a small fraction of the total exchangeable surface. This distinction is important because the crystal fringes of LDH materials, as opposed to a basal LDH surface, exhibit a pH dependent charge, comparable to that of oxide phases.

Using ATR-FTIR, the speciation of PO_4 on LDH12(2) and LDH10(2) was spectroscopically determined after incubation in 20 mM PO_4 solutions (Figure 2a). In the spectrum from the recovered LDH10(2), bands at 977 and 1049 cm^{-1} reveal that HPO_4^{2-} is the dominant PO_4 species in the sample [29]. The spectrum of the recovered LDH12(2) shows a band at 1024 cm^{-1} , proving PO_4^{3-} to be present [29]. Also a minor band at 970 cm^{-1} , which could relate to HPO_4^{2-} , is shown. The fingerprint of the H_2PO_4^- anion species is absent in both samples, and the band at 1345 cm^{-1} is less pronounced compared to that in the spectra from the as-synthesized LDHs, which aligns with the release of NO_3^- . At the initial pH of 7.2, the speciation of PO_4 in the exchange solutions is 50 % H_2PO_4^- and 50 % HPO_4^{2-} . The spectroscopically observed PO_4 speciation on the LDH after equilibration significantly deviates from the speciation initially present in solution, with much less H_2PO_4^- , more HPO_4^{2-} and even more PO_4^{3-} being observed, for the LDH12(2). It can be noted that the fingerprint of the PO_4^{3-} anions in the LDH is in good agreement with that of the reference salts with PO_4^{3-} (K_3PO_4 , Na_3PO_4), while this is less the case for the comparison of the HPO_4^{2-} and H_2PO_4^- fingerprint (Figure S1).

The XRD results of the PO_4 exchanged LDHs provide insights on the intercalation of the PO_4 anions in both LDHs. Comparing the patterns of the as-synthesized LDH10(2) material with the PO_4 exchanged

material (Figure 2b), a nearly complete shift of the (003) reflection is observed relating to a decreased interlayer spacing of 4.13 Å to 3.80 Å. This suggests the almost complete replacement of interlayer NO_3^- by PO_4 (HPO_4^{2-}) [11]. In contrast to the symmetrical (003) reflection of the as-synthesized LDH12(2), the (003) reflection of the incubated LDH12(2) material is asymmetrical, as a result of the convolution of the NO_3^- exchanged (003) reflection at $11.37^\circ 2\theta$ and an additional less pronounced reflection at $\sim 10.70^\circ 2\theta$. This suggests that not all interlayer galleries in this material are occupied by PO_4 anions. This could be a result of the relative high selectivity of the initially present anion population (mixture of NO_3^- and OH^-) relative to PO_4 anions.

The speciation of PO_4 in the LDHs is elaborated with respect to the exchange capacity of both LDHs. The positive structural charge of LDHs is derived from the presence of Al cations in the octahedral sites of the hydroxide layers. This means that, from a theoretical point of view, each Al cation introduces one positive charge, which is compensated by one negative charge of an interlayer anion. The total Al content can therefore be interpreted as proportional to the AEC of an LDH material. The molar NO_3^- content in the as-synthesized LDH12(2) and LDH10(2) and the molar PO_4 content of those LDHs after incubation in PO_4 , were plotted relative to the molar Al content of the material (Figure 4). The molar NO_3^- content relative to the molar Al content of LDH12(2) and LDH10(2) again suggests that, next to NO_3^- anions, also OH^- anions are present on the exchange complex of the as-synthesized LDHs. Additional proof of the speciation of PO_4 in the two LDHs can be provided by the position of the molar Al/ PO_4 ratio (Figure 4). The molar Al/ PO_4 ratio of the PO_4 -exchanged LDH10(2) equals 2.3, which allows HPO_4^{2-} to be present since the XRD and PO_4 uptake suggests the LDH to be well-exchanged with PO_4 . The molar Al/ PO_4 ratio of the PO_4 -exchanged LDH12(2) is close to 3, which would theoretically allow the presence of solely PO_4^{3-} anions. The XRD (Figure 2b), however, shows a double peak at the 003 reflection, suggesting that the interlayer gallery of LDH12(2) is not completely occupied by PO_4 anions and that some residual OH^- remains, i.e. not all charges are compensated by the trivalent PO_4^{3-} . Therefore, a PO_4 population of PO_4^{3-} with traces of HPO_4^{2-} is suggested for LDH12(2), which is in line with the results from ATR-FTIR.

313 The presence of HPO_4^{2-} on LDH10(2) and of PO_4^{3-} on LDH12(2) is the result of the anion exchange
 314 reaction with the anion population present in the as-synthesized materials. Different exchange
 315 reactions can characterize the uptake of PO_4 in exchange with NO_3^- and/or OH^- , to obtain the solid-
 316 state PO_4 species identified with ATR-FTIR:

321 in which the subscript s indicates the sorbed anions. The relative contribution of each of these
 322 reactions to the overall PO_4 uptake by an LDH conceptually depends on the ratio of the sorbed species
 323 (NO_3^- and OH^-) to those in solution (PO_4), i.e. on the mass and type of LDH relative to the solution
 324 volume and its initial PO_4 concentration. As a consequence, the predominant reactions occurring in
 325 specific PO_4 uptake conditions also determine the equilibrium conditions, including the solution NO_3^-
 326 concentration and solution pH. The $\text{NO}_3^-/\text{PO}_4$ exchange stoichiometry is different between the
 327 LDH12(2) and LDH10(2) materials (Figure 3a and 3b). After determining the amount of poorly sorbed
 328 NO_3^- in the materials from the results with the 0 mM PO_4 solutions, the molar ratios of NO_3^- release
 329 over PO_4 uptake in the actual anion exchange reaction range for all LDH12(2) suspensions between
 330 0.87 and 0.96 (Figure 3a) depending on the extent of exchange; for the LDH10(2) suspensions these
 331 values range between 1.91 and 2.07 (Figure 3b). Also clear differences are shown between the final
 332 pH of the exchange solutions from LDH12(2) and LDH10(2) (Figure 5a). For the LDH12(2) material, the
 333 final pH of the suspension strongly increases with increasing initial PO_4 concentration, yielding pH
 334 values up to 10.3. With initial PO_4 concentrations exceeding 6 mM, LDH12(2) becomes saturated with
 335 PO_4 . There, the buffering effect of excess PO_4 in solution allows the solution pH to return to more
 336 neutral values. This trend in solution pH over initial PO_4 concentration suggests that the OH^- release is

linked to the uptake of PO_4 . The same trend is present in LDH10(2) suspensions, yet much less pronounced. This evidences the limited presence of OH^- anions on the exchange complex of as-synthesized LDH10(2). The observed effects of PO_4 uptake on the pH of the exchange solution contradict the literature assumption that the anion speciation of PO_4 in the interlayer can be derived from the final solution pH [30], i.e. the final pH of the exchange solution is rather a consequence than a cause of the speciation during ion exchange.

The equilibrium conditions of the exchange reactions occurring during the incubation of as-synthesized LDH12(2) and LDH10(2) in solutions with different initial PO_4 concentration are modelled, using the initial anion exchange population (Table 1) and the initial solution composition (PO_4 concentration, K concentration, pH). Using the anion selectivity as dictated by the Gaines and Thomas model, combined with a measured selectivity of $K_c (\text{OH}^- - \text{NO}_3^-)$ equal to 100, the speciation of anions on the exchange complex at equilibrium was modelled (Table 2). The results show comparable trends between the modelled and the measured PO_4 uptake and NO_3^- release (Figure 3), yet differences in the exact exchange stoichiometry are present. The trend of the solution pH in response to the initial solution PO_4 concentration is in very good agreement with the measured pH trend. Here, also modelled pH values up to 10.4 are obtained at intermediate initial PO_4 concentration, and a further increase of the PO_4 concentration results in a strong decrease of the modelled pH. A comparable trend is shown for the modelled pH trend of the LDH10(2) material. The modelled pH trend is clearly more pronounced than the measured pH trend. According to the model, the HPO_4^{2-} anion is the pronounced PO_4 anion present in both LDHs, yet the fraction of H_2PO_4^- , HPO_4^{2-} and PO_4^{3-} anions on the exchange complex slightly changes with a varying initial PO_4 concentration. For example, the PO_4^{3-} anion is present in the samples exposed to intermediate initial PO_4 concentration (3-6-9 mM), whereas at high initial PO_4 concentration the fraction of the PO_4^{3-} species on the exchange complex is minimized as result of a more pronounced pH buffering effect. With the modelled results, underlying mechanisms during PO_4 uptake, e.g. release of initially present alkalinity, or the buffering effect at high PO_4 concentration, are confirmed. Yet, there are also some clear and important differences between the

modelled and the measured results. For example, the presence of the PO_4^{3-} species in LDH12(2) is very pronounced in the ATR-FTIR spectrum of that material, whereas the model predicts a predominant HPO_4^{2-} speciation in LDH12(2).

The same model was used to calculate the pH dependent PO_4 speciation on the solid phase. Here, the solution pH at values between pH 6 to 11 and the equilibrium anion population on LDH12(2) and LDH10(2) is calculated for different initial PO_4 concentrations (Figure 6). The AEC used in these calculations was 14.4 mmol L^{-1} for LDH12(2) and 15.5 mmol L^{-1} for LDH10(2), which is derived from the measured AEC of the as-synthesized LDHs and the L:S ratio used in the PO_4 uptake experiments. In the modelled solution pH range of 6 to 11, the HPO_4^{2-} anion is always the dominant PO_4 species on both LDHs. Generally, this shows that the PO_4 speciation on the solid phase (Figure 6) does not mirror the PO_4 speciation in solution (Figure 1), as result of the selectivity of LDHs to stronger bind the PO_4 species with higher charge. At an increasing initial PO_4 concentration, the fraction of OH^- anions on the LDHs decreases, to the benefit of PO_4 anions. This allows the presence of minor fractions of H_2PO_4^- (low pH values) and of PO_4^{3-} (high pH values). These fraction of H_2PO_4^- and PO_4^{3-} remain, however, small relative to the AEC. Increasing the solution pH decreases the fraction NO_3^- on the exchange complex as result of the uptake of OH^- anions (at low PO_4 concentration) or the uptake of HPO_4^{2-} and OH^- anions (at intermediate and high PO_4 concentrations).

LDH exchange with CO_3

The anion exchange reactions occurring during the reaction of the as-synthesized and PO_4 -exchanged LDHs in a 3 mM CO_3 solution (chiefly HCO_3^-), reach equilibrium after 168 h (Figure 7). The XRD patterns of the materials obtained after 480 h incubation suggest a generally good LDH stability during the reaction. Therefore, it can be assumed that the interplay of anions mainly occurs on the LDH phase.

The reaction of the as-synthesized LDHs with CO_3 leads to increasing NO_3^- concentrations and decreasing CO_3 concentrations in solution, a result of $\text{NO}_3^-/\text{CO}_3$ anion exchange; the PO_4 anion is absent in this exchange. At different stages of this anion exchange reaction, the molar ratio of CO_3

taken up over the NO_3^- being released varies between 1.03-1.18 for LDH12(2) (Figure 7a), while for LDH10(2) this ratio varies between 0.41-0.58 (Figure 7b). This is in line with the concept that this material contains large fractions of OH^- in the interlayer spacing. The interlayer spacing of the LDH12(2) after incubation in CO_3 is very comparable to the spacing of the as-synthesized material (from 2.98 Å to 2.92 Å) (Figure 2b). The orientation of the NO_3^- in the as-synthesized LDH12(2) and CO_3^{2-} in the incubated LDH12(2) is almost the same. The NO_3^- and the CO_3^{2-} anions have a similar size [11], but a similar positioning of both anions in the interlayer is only possible due to the presence of intercalated OH^- anions in the as-synthesized material. For LDH10(2), the observed CO_3/NO_3 exchange ratio varies between 0.47-0.58. The interlayer spacing of as-synthesized LDH10(2) significantly decreases during incubation in CO_3 (from 4.13 Å to 2.88 Å). This interlayer spacing of 2.88 Å relates to a CO_3 anion orientation with an angle of $\sim 32^\circ$ relative to the basal plane. A more horizontal orientation of the intercalated planar anion is only possible with an increase in the anion charge density, in order to compensate for the loss in the vertically projected charge density due to the change in orientation. This suggests a CO_3 uptake in the form of the CO_3^{2-} anion for LDH10(2). Also, the reflection derived from intercalated NO_3^- is absent in the pattern from LDH recovered from incubation, which suggests a nearly complete $\text{NO}_3^-/\text{CO}_3^{2-}$ exchange. The solution pH of the LDH12(2) suspensions increases from 8.45 to 9.09, while the final pH of the LDH10(2) suspensions is only 8.63 (Figure 5b). The final pH of the blanks is 8.57. It must be noted that the effective changes in the solution pH will be rather limited compared to the observed pH changes in the PO_4 uptake reactions (Figure 5a) because of the stronger buffering effect of the 3 mM CO_3 solution and the much lower solid:liquid ratio in the CO_3 uptake reaction than in the PO_4 uptake reaction. The ATR-FTIR spectrum of the recovered LDH12(2) shows the presence of CO_3^{2-} , while this is less clear for LDH10(2).

The incubation of PO_4 -exchanged LDHs, obtained from previous incubation in 20 mM PO_4 , is characterized by a PO_4 release of up to 0.57 mmol g⁻¹ for LDH12(2) (Figure 7e) and up to 0.55 mmol g⁻¹ for LDH10(2) (Figure 7f), which is respectively 54 % and 33 % of the initial P content in the materials. Comparable values were obtained in a previous study [31]. The release of NO_3^- is absent during this

incubation, because most of the NO_3^- has been removed from these samples during the PO_4 uptake reaction. The reaction taking place can therefore be described as a PO_4/CO_3 anion exchange. At different stages of the anion exchange reaction, the molar ratio of CO_3 taken up over the PO_4 being released varies between 0.95-1.12 for LDH12(2), while for LDH10(2) this ratio varies between 0.73-0.84. It is expected that the $\text{HPO}_4^{2-}/\text{PO}_4^{3-}$ anions in LDH12(2) are replaced by CO_3^{2-} ; the HPO_4^{2-} anions in LDH10(2) are also replaced by CO_3^{2-} .

The maximum value of the (003) reflection in the pattern from the PO_4 -exchanged LDH12(2) material recovered after CO_3 exchange is very comparable to that from the freshly PO_4 -exchanged LDH12(2) (from 2.98 Å to 2.94 Å). This means that, also in these samples, the positioning of the CO_3^{2-} anions in the interlayer gallery is comparable to that of the initially bound NO_3^- anions. Notice, however, that the symmetry of the (003) reflection is much more pronounced in the pattern from the material recovered after CO_3 exchange than in that of the freshly PO_4 -exchanged LDH12(2), which is the result of a significant release of intercalated $\text{HPO}_4^{2-}/\text{PO}_4^{3-}$ in the former. For LDH10(2), the interlayer spacing significantly decreases from 3.80 Å to 3.21 Å, related to the intercalation of CO_3^{2-} . However, an asymmetric (003) reflection is shown for the recovered material, proving that not all interlayer HPO_4^{2-} is desorbed. Finally, both patterns of the recovered LDHs show the formation of a minor boehmite phase (16.3 2 θ) during the 480 h incubation period. This phase is probably negligible in terms of its effect on the anion exchange stoichiometry measurement on the LDH phase, yet it illustrates the loss of LDH crystallinity during long-term incubation. The final solution pH is higher for the LDH12(2) suspension compared to the LDH10(2) suspension (Figure 5b). This could be attributed to the initial presence of PO_4^{3-} in the LDH12(2) material after incubation in PO_4 with the PO_4^{3-} reacting as a strong base in these solution. Additionally, some OH^- anions could still remain on the exchange complex of the PO_4 -exchanged LDH12(2), thereby also causing the alkalinization of the CO_3 exchange solution. The ATR-FTIR spectra of the obtained materials show that the PO_4 release is more pronounced for LDH12(2) than for LDH10(2), which aligns with the observed relative desorption. The presence of CO_3^{2-}

anions can be confirmed in the spectrum from recovered LDH10(2), but this is less clear for the spectrum of recovered LDH12(2).

The CO_3 exchange of partially PO_4 -exchanged LDHs, e.g. those incubated in 3 mM PO_4 , is characterized by a release of both NO_3^- and PO_4 anions (Figure 7c and 7d). For LDH12(2), the molar amount of desorbed PO_4 is larger than the molar amount of desorbed NO_3 , while the reverse is true for LDH10(2). Incubation of the as-synthesized LDHs and the PO_4 -exchanged (20 mM) LDHs revealed a CO_3 uptake as CO_3^{2-} by both LDHs. Assuming a trivalent PO_4^{3-} and NO_3^- to be desorbed in exchange for a divalent CO_3^{2-} on LDH12(2), the measured charge balance of $\text{CO}_3/(\text{NO}_3+\text{PO}_4)$ ranges from 0.95-1.08. The contribution of OH^- initially bound on the exchange complex of the PO_4 -exchanged LDH12(2) in this reaction is unknown. With HPO_4^{2-} and NO_3^- exchanging with CO_3^{2-} on LDH10(2), the measured charge balance of $\text{CO}_3/(\text{NO}_3+\text{PO}_4)$ ranges from 1.01-1.21. Also here, the final pH remains higher for the suspensions with LDH12(2) compared to those with LDH10(2).

The modelled results of the NO_3^- and PO_4 release and CO_3 uptake generally deviate from the measured results (Figure 7). This could be attributed to the fact that this modelling was performed starting from the modelled anion exchange population after PO_4 uptake, rather than from an experimentally determined anion population. The latter option is, naturally, beyond the capabilities to determine this accurately. The modelled pH shows for both LDH materials a decrease in the pH of the CO_3 solutions with an increasing initial PO_4 adsorption concentration (Figure 5d). This effect is linked to (i) the fact that with increasing exposure to PO_4 , the obtained materials contain increasingly less OH^- anions that can affect pH during incubation in CO_3 , and to (ii) the fact that a higher PO_4 uptake can result in a higher PO_4 release during incubation in CO_3 , and thus stronger buffering. This same trend is present in the measured pH results, yet much less pronounced. In line with the measured pH results, higher modelled pH values were obtained for the LDH12(2) suspensions compared to the LDH10(2) suspensions. The modelled anion population shows that CO_3 is predominantly present as CO_3^{2-} in the LDHs pretreated in solutions with a relative low initial PO_4 concentration (Table 3). For the LDHs

pretreated in higher PO_4 concentrations, however, also the fraction of HCO_3^- becomes very significant on the exchange complex. Again, this is due to the fact that less alkalinity is present in the LDHs pretreated in high PO_4 concentrations. The fraction of CO_3 on the exchange complex strongly decreases with increasing initial presence of PO_4 anions, which is in alignment with the measured results on CO_3 uptake. This is likely caused by the high selectivity of the predominant PO_4 species (HPO_4^{2-}) and the predominant CO_3 species (HCO_3^-), both in the model as in the actual exchange. This also results in a limited modelled PO_4 release, 22 % of the total PO_4 for LDH12(2) and 31 % for LDH10(2). Also the measured PO_4 desorption yield shows that selectivity for specific PO_4 and CO_3 species can have far-reaching consequences for the potential of PO_4 -LDH recovery applications. After 168 h incubation in 3 mM CO_3 , 54 % of PO_4 is desorbed from LDH12(2) treated in 20 mM PO_4 , while only 33 % of PO_4 is desorbed from PO_4 exchanged LDH10(2). This could be a result of a more pronounced PO_4 intercalation in LDH10(2) compared to LDH12(2), as the counter diffusion of PO_4 and CO_3 is known to be a limiting factor for PO_4 desorption [31].

Conclusion

Taken together, this study revealed that a large fraction of the AEC in as-synthesized Mg-Al LDH can be occupied by OH^- . This affects the speciation of oxyanions with pH dependent charge. The relative NO_3^- content of LDHs synthesized from NO_3^- salts was lower for the LDHs prepared at pH 12 compared to those prepared at pH 10. The presence of OH^- anions on the exchange complex of the LDHs, which is more pronounced for a synthesis in more alkaline conditions, explained this trend. At both pH values, the NO_3^- content of the materials increased with increasing $\text{M}^{2+}/\text{M}^{3+}$ ratio, suggesting a lower $\text{OH}^-/\text{NO}_3^-$ selectivity as the layer charge density decreases. The speciation of PO_4 anions taken up by LDH12(2) and LDH10(2) was determined from the exchange stoichiometry during LDH incubation in PO_4 solutions. The high OH^- bearing LDH synthesized at pH 12 adsorbed PO_4 as PO_4^{3-} and minor amounts of HPO_4^{2-} , in exchange with a mixture of both NO_3^- and OH^- anions, whereas the low OH^-

bearing material synthesized at pH 10 adsorbed HPO_4^{2-} in exchange with mainly NO_3^- . This is corroborated by the charge balance in the materials, XRD and ATR-FTIR measurements, the latter confirmed the presence of $\text{HPO}_4^{2-}/\text{PO}_4^{3-}$ anions in LDH12(2) and HPO_4^{2-} anions in LDH10(2). The as-synthesized and PO_4 -exchanged LDH12(2) and LDH10(2) were incubated in CO_3 solutions to determine anion exchange stoichiometry. For all materials, likely divalent CO_3^{2-} is exchanged with adsorbed PO_4 . The observed exchange stoichiometry's were in line, but not identical, to the proposed reactions. Analytical precision should be enhanced, e.g. by using pH stat exchanges to record the net OH^- exchange. In addition, the observed exchange reactions might be modelled to infer the selectivity coefficient for the different species and for better quantifying the underlying reactions and suggested solid state speciations. This research highlighted the importance of synthesis conditions on the speciation of PO_4 in LDHs, and therefore also the capacity of LDHs for polyvalent anions such as PO_4 . This study suggests that highest P content of LDH is obtained in high charge materials holding divalent PO_4 anions, i.e. materials synthesized at lower pH and/or exchanged in solutions with low alkalinity.

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601 **Tables**

602

603 **Table 1** Properties of the as-synthesized LDH materials, with x the fraction of metals present as Al.

Material	Synthesis	Solution molar	Molar	x	Layer	NO ₃ ⁻	Estimated	Water	Material	Anion	Interlayer	BET
	pH	Mg/Al ratio	Mg/Al ratio		charge	content	sorbed OH ⁻	content	molar mass ^a	exchange	spacing	surface
					density		content			capacity		area
		(-)	(-)	(-)	(e nm ⁻²)	(mmol g ⁻¹)	(mmol g ⁻¹)	(%)	(g mol ⁻¹)	(mmol _c g ⁻¹)	(Å)	(m ² g ⁻¹)
LDH12(2)	12	2	2.6	0.28	3.4	1.09	2.50	14.6	77.4	3.59	2.98	14.7
LDH12(3)	12	3	3.4	0.23	2.8	1.13	1.88	11.0	75.3	3.01	3.06	-
LDH12(4)	12	4	4.3	0.19	2.3	1.92	0.51	11.5	77.7	2.43	3.23	-
LDH10(2)	10	2	2.1	0.32	3.9	2.66	1.21	11.8	85.0	3.87	4.13	18.1
LDH10(3)	10	3	3.3	0.23	2.8	3.11	<0.1	9.6	84.5	2.78	3.62	-
LDH10(4)	10	4	4.2	0.19	2.3	3.11	<0.1	11.2	83.3	2.30	3.30	-

604 ^a Molar formula of the material: Mg_{1-x}Al_x(OH)₂(NO₃)_y(OH)_z (H₂O)_n, with y + z = x.

605

606 **Table 2** The modelled equilibrium conditions of LDH incubation in PO₄ solutions with varying concentration. The speciation of the anions on the LDH phase is presented as a fraction of the AEC.

Material	Initial PO ₄ concentration	PO ₄ concentration	% PO ₄ sorbed	NO ₃ ⁻ concentration	pH	Exchange complex population (% of AEC)				
	(mM)	(mM)		(mM)		PO ₄ ³⁻	HPO ₄ ²⁻	H ₂ PO ₄ ⁻	OH ⁻	NO ₃ ⁻
LDH12(2)	0 (AS)	0.00	0	0.00	6.2	0	0	0	70	30
	1	0.01	100	1.40	9.6	3	12	0	65	11
	3	0.64	79	3.20	10.3	7	30	0	55	8
	6	2.52	58	3.60	10.4	8	43	0	44	5
	9	4.77	47	3.70	10.3	8	54	0	33	5
	20	13.20	34	3.74	8.9	0	95	0	1	4
LDH10(2)	0 (AS)	0.00	0	0.00	5.8	0	0	0	30	70
	1	0.00	100	1.60	8.8	1	12	0	27	60
	3	0.06	98	4.50	9.3	3	36	0	20	41
	6	0.84	86	7.30	9.4	3	65	0	10	23
	9	2.70	70	8.20	8.7	0	81	0	1	17
	20	12.80	36	9.00	7.2	0	83	5	0	11

609 **Table 3** The modelled equilibrium conditions of LDH incubation in a CO₃ solution. The incubated LDH material was preincubated in solutions with varying PO₄ concentrations followed by
 610 desorption with a CO₃ solution. The speciation of the anions on the LDH phase is presented as a fraction of the AEC.

Material	Initial PO ₄ concentration (mM)	PO ₄ concentration (mM)	NO ₃ ⁻ concentration (mM)	CO ₃ concentration (mM)	pH	Exchange complex population (% of AEC)					
						PO ₄ ³⁻	HPO ₄ ²⁻	CO ₃ ²⁻	HCO ₃ ⁻	OH ⁻	NO ₃ ⁻
LDH12(2)	0 (AS)	0.00	0.50	2.20	9.5	0	0	71	9	18	2
	1	0.05	0.20	2.30	9.6	1	8	65	8	17	1
	3	0.10	0.10	2.30	9.4	1	21	55	10	12	1
	6	0.10	0.00	2.30	9.3	1	31	47	11	10	0
	9	0.20	0.00	2.40	9.1	1	40	39	12	7	0
	20	0.20	0.00	2.50	8.0	0	74	7	17	1	0
LDH10(2)	0 (AS)	0.00	1.00	1.90	8.4	0	0	51	29	4	16
	1	0.01	0.90	2.00	8.4	0	12	46	27	4	12
	3	0.04	0.70	2.40	8.5	0	34	33	22	3	7
	6	0.09	0.40	2.40	7.3	0	57	17	21	2	3
	9	0.10	0.30	2.50	8.0	0	68	8	21	1	2
	20	0.10	0.20	2.50	8.2	0	67	11	19	1	1

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615 **Figure 1** The speciation of carbonic acid (above) and phosphoric acid (under) derived anions as a function of the pH of a
 616 solution.

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Figure 2 ATR-FTIR spectra (Figure a) and XRD patterns (Figure b) of the as-synthesized LDHs, of the LDHs obtained after incubation in a 20 mM PO_4 , and of the as-synthesized and PO_4 exchanged LDHs (20 mM) after incubation in 3 mM CO_3 . The interlayer spacing, calculated from the position of the (003) reflection in the XRD patterns, is given for each material.

Figure 3 Figure a and b: The PO₄ adsorption isotherms of LDH10(2) and LDH12(2), combined with the NO₃⁻ release from each sample, obtained after 24 h incubation at 20°C. Error bars denote standard deviation (N=3) but are sometimes smaller than the symbol size and not visible. Figure c and d: The modelled equilibrium conditions are based on the initial PO₄ solution concentration and the initial anion exchange complex population of LDH10(2) and LDH12(2).

Figure 4 The molar NO₃⁻ content in the as-synthesized LDH12(2) and LDH10(2), and the molar PO₄ content of those LDHs after incubation in 20 mM PO₄, relative to the molar Al content of the material. The different lines indicate the maximal content for anions with formal valence of 1, 2 or 3 assuming that each Al³⁺ confers one equivalent charge per g of LDH.

Figure 5 Figure a: The final pH of the PO_4 solutions (after 24h incubation) as a function of the initial PO_4 concentration; error bars denote standard deviation (N=3) but are sometimes smaller than the symbol size and not visible. Figure b: The final pH of the CO_3 solutions (after 480 h incubation) given for each incubated materials. error bars represent the standard deviation (N=2). The modelled equilibrium pH of both the PO_4 uptake reaction (Figure c) and the PO_4 release reaction (Figure d), based on the initial anion solution concentrations and the initial anion exchange complex population of LDH10(2) and LDH12(2).

Figure 6 The modelled anion population on the AEC of as-synthesized LDH12(2) (top) and LDH10(2) (bottom) after equilibration in PO₄ solutions (1, 6, 20 mM), relative to a constant solution pH. The AEC used in these calculations was 14.4 mmol L⁻¹ for LDH12(2) and 15.5 mmol L⁻¹ for LDH10(2), which is derived from the measured AEC of the as-synthesized LDHs and the L:S ratio used in the P uptake experiments.

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648 **Figure 7** The uptake of CO₃ and the release of PO₄ and NO₃ by the as-synthesized (AS) LDH10(2) and LDH12(2) materials
 649 (Figure a and b), and the materials obtained after treatment in 3 mM (Figure c and d) and 20 mM (Figure e and f) PO₄
 650 solutions, presented as a function of the incubation time. Error bars denote standard deviation (N=2) but are sometimes
 651 smaller than the symbol size and not visible. The modelled anion uptake and release at equilibrium are presented by the
 652 white data points.