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Comparison of the fluoride, arsenate and nitrate anions water depollution potential of a calcined quintinite, a layered double hydroxide compound

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Abstract The potential for removing anionic pollutants such as F^-, $HAsO_4^{2-}$, and NO_3^- from water by mixed oxides issued from the moderate thermal treatment of quintinite (Mg_4Al_2 LDH) has been studied. This compound shows good trapping properties for F^- and $HAsO_4^{2-}$, and a low potential for NO_3^-, due to the competition with OH^-. The competition between these three anions and CO_3^{2-} has been envisaged and shows that CO_3^{2-} is able to easily replace F^- and NO_3^-, making the mixed oxides issued from MgAl LDH an inappropriate trap for F^- and NO_3^-. However, only small amounts of arsenic are released after the CO_3^{2-} introduction in water. Moreover, arsenates are able to replace carbonates even at lower concentrations. This means that $HAsO_4^{2-}$ anions present a stronger affinity than CO_3^{2-} for the LDH structure. This makes mixed oxides issued from MgAl LDH very promising materials for the removal of arsenic in polluted waters.

Introduction

Quintinite ($Mg_4Al_2(OH)_{12}CO_3 \cdot 3H_2O$) is a member of the large family of compounds known as layered double hydroxides (LDHs). They are composed of brucite-like layers positively charged owing to the substitution of a part of the M^{2+} cations by M^{3+} cations [1]. In order to neutralise these positive charges, anions, associated with variable amounts of water, are inserted between the layers [2]. Their general formula is $[M(II)_{1-x}M(III)_x(OH)_2]\ [A^{n-}]_{x/n} \cdot mH_2O$, where usually, M(II) is a divalent cation such as Mg^{2+}, Mn^{2+}, Zn^{2+}, Co^{2+}, Cd^{2+}, Cu^{2+}, Ni^{2+}, ..., M(III) a trivalent cation such as Al^{3+}, Fe^{3+}, Cr^{3+}, Ga^{3+}, ... [1] and A^{n-} is an anion that can be as simple as inorganic anions such as Cl^-, F^-, Br^-, OH^-, SO_4^{2-} or CO_3^{2-} [3], to complex as DNA [4]. Due to their layered structure and as the A^{n-} anions can be exchanged [3], these compounds are also known as anionic clays. Their remarkable properties make that LDHs have found numerous applications, as catalysts or catalyst precursors [5, 6], as ion exchangers [3, 7, 8], in separation science [9] or as part of new heterostructured nanohybrids such as inorganic/inorganic, organic/inorganic or bio/inorganic materials [4, 10, 11]. As conventional clays can be used for heavy metal depollution, anionic clays can be planned to be used for anionic depollution [12–19].

Moreover, these compounds also present a singular property of reconstruction: indeed, after a moderate thermal treatment, they lead to amorphous mixed oxides with high specific surface areas, that give back the LDH structure in presence of OH^- and anions solutions [1]. This property can be of great importance for environmental applications as it could lead to recyclability and sustainable development.

Even if anionic pollutions have been less studied than heavy metals pollutions, they can be of major importance in some areas, due to geological aspects and/or human activities. The utmost critical and studied anionic pollution, which is a major public health problem, is certainly the presence of arsenic in drinking waters of Bangladesh. In-

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deed, the average As concentration in water in Bangladesh is 0.06 mg L^{-1}, with values as high as 16 mg L^{-1} [20]. These values are far beyond the 0.01 mg L^{-1} threshold fixed by the World Health Organization [21].

Important concentrations of fluoride can be found in water due to human activities. Tanzania is one of the most affected country: indeed, concentrations in piped waters as high as 8 mg L^{-1} during the rain season and 12.7 mg L^{-1} during the dry season are observed [22]. The threshold value fixed by the World Health Organization values is only 1.5 mg L^{-1}, far below the concentrations observed in Tanzania [21].

Nitrates water pollutions are usually due to intensive agricultural activities. This is the case of Brittany, the western part of France, where nitrates concentrations up to 250 mg L^{-1} can be observed [23]. These values are far beyond the 50 mg L^{-1} WHO threshold [21].

The aim of this paper is to evaluate the potential of mixed oxides issued from the moderate thermal treatment of a $Mg_4Al_2(OH)_{12}CO_3 \cdot 3H_2O$ LDH for anionic (fluoride, arsenate or nitrate anions) water depollution. Indeed, many studies have been reported for hydrotalcite but none specifically to quintinite, whereas Sato et al. [24] have shown that the anionic selectivity is different for $Mg_{0.61}Al_{0.26}$ and $Mg_{0.77}Al_{0.15}$ compounds. In order to be consistent with the field data presented above, concentrations of 10 mg L^{-1} for fluorides, 16 mg L^{-1} for arsenic and 100 mg L^{-1} for nitrates have been chosen.

Material and methods

The starting MgAl mixed oxides issued from the moderate thermal treatment of a $Mg_4Al_2(OH)_{12}CO_3 \cdot 3H_2O$ LDH are a commercially available material (Süd Chemie Syntal HSAC 701). The Mg/Al ratio is equal to 2.12.

Deionised water has been systematically decarbonated by N_2 bubbling overnight in order to avoid the presence of carbonates. Indeed, carbonates are known to be the anions with the highest affinity for the LDH structure [3]. Consequently, all the experiments have been realised at 25 °C in closed reactors under flowing N_2 in order to avoid carbonate pollution, and vigorous stirring.

pH values have been recorded by a Mettler Toledo Seven Multi pH-meter.

Anionic solutions (10 mg L^{-1} for fluorides, 16 mg L^{-1} for arsenic and 100 mg L^{-1} for nitrates) are composed by 400 mL of deionised water and 4 mL of a solution containing the fluoride, arsenate or nitrate anions. The solution containing the fluoride anions has been prepared from NaF (Certipur solution, Merck). The solution containing the arsenic has been prepared from $NaHAsO_4 \cdot 7H_2O$ (Merck, 98.5% purity) and the solution containing the nitrate anions has been prepared from $NaNO_3$ (Prolabo, 99.5% purity).

Two hundred milligrams of the mixed oxides issued from the moderate thermal treatment of a $Mg_4Al_2(OH)_{12}CO_3 \cdot 3H_2O$ LDH have been put in each 404 mL solution. It should be noted that the anion exchange capacity of the mixed oxides is higher than the amount of anions present in the solution, whatever the anions. Consequently, the whole amount of the anionic pollutants could be trapped by the mixed oxides present in the solution.

Five millilitre of regular samplings have been realised from 5 min to 168 h. The samples are filtered at 0.2 µm and the concentrations of anions have been measured by atomic absorption (Varian SpectrAA 220 FS) or ICP/AES (Jobin Yvon Horiba Ultima 2) for arsenic, and by ionic chromatography (Dionex) for fluoride and nitrate anions. After 71 h of contact between mixed oxides and nitrates, arsenates and fluorides solutions, 2.25 mL of a sodium carbonate solution, in order to reach a concentration of 10^{-3} mol L^{-1} of carbonate, are added, to investigate the competition between carbonate anions and nitrate, arsenate, and fluoride anions. Indeed, carbonate anions are known to present the highest known affinity for the MgAl LDHs [3].

Powder X-ray diffraction (XRD) patterns have been performed on a Siemens D 500 diffractometer using CoK_α radiation ($\lambda = 0.17889$ nm) and operating at 40 kV and 30 mA at room temperature. The scans have been recorded from 4° to 84° (2θ) with a step of 00.2° and a counting time of 1 s per step.

The specific surface area of the commercially available heat treated $Mg_4Al_2(OH)_{12}CO_3 \cdot 3H_2O$ compound has been determined from the nitrogen adsorption isotherm at 77 K treated according to the BET method. Prior to the measurements, the sample has been outgassed at 110 °C for 72 h. At the end of the outgassing process, the residual pressure is below 0.05 mbar. The measurement has been realised in a multipoint adsorptometer Micromeritics Tristar 3000.

Results and discussion

First of all, the structure of the commercially available heat treated $Mg_4Al_2(OH)_{12}CO_3 \cdot 3H_2O$ compound has been checked by XRD. The thermal treated LDH exhibit an XRD pattern of a poorly crystalline compound (Fig. 1). This compound as a structure similar to that of MgO, but with the strong lines of MgO shifted to higher 2θ. This indicates smaller lattice parameters due to the partial substitution of Mg by Al, 0.720 Å and 0.535 Å, respectively [25]. This result is in agreement with the

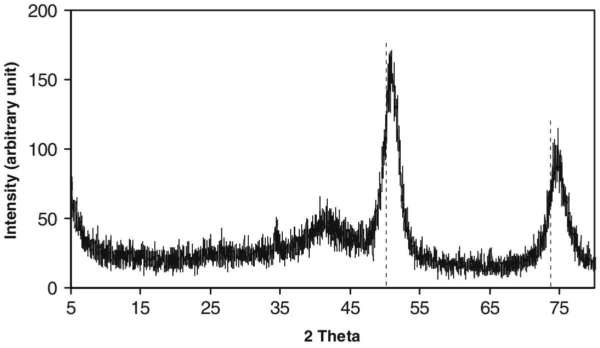

Fig. 1 XRD pattern of the oxides issued from the thermal treatment of $Mg_4Al_2(OH)_{12}CO_3 \cdot 3H_2O$ (dotted lines indicate the position of the strong lines of MgO)

mixed oxides usually obtained after a moderate heat treatment of MgAl LDHs compounds [1]. This material presents an important specific surface area of 191 $m^2\ g^{-1}$.

pH measurements have been realised in-situ. Figure 2 presents the evolution of pH values of the solutions for the three different anions studied. pH values before the addition of the mixed oxides issued from the moderate thermal treatment of the LDH are 8.50, 7.78 and 8.31 for nitrates, fluorides and arsenates solutions, respectively. Figure 2 shows that the behaviour of the three curves is very similar. Indeed, they all present a pH increase when time of contact is increasing to a constant value near 10.4–10.5. For arsenic, between these pH values, the dominant species will be $HAsO_4^{2-}$ (p*K*a = 11.5).

If the pH curves are similar, the trapping behaviour of the quintinite regarding to fluorides, nitrates and arsenates are very different.

Solutions containing fluorides

Figure 3 exhibits the concentration of fluoride in the solution as a function of time. It clearly shows that the quantity of fluorides in water is first decreasing when increasing the time of contact with the mixed oxides issued from the moderate thermal treatment of the LDH, and then reaches a constant value of about 20% of fluorides remaining in the solution, from 5 h to 70 h.

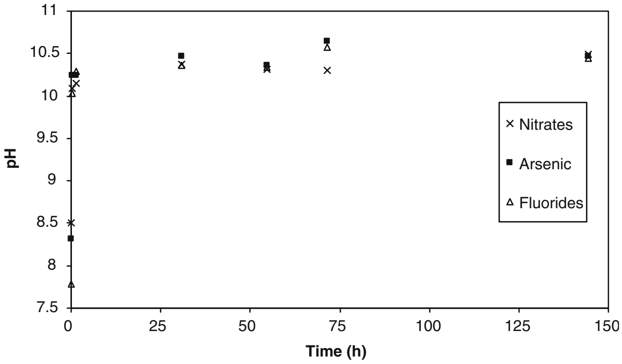

Fig. 2 pH value of the nitrates, fluorides and arsenates solutions as a function of time (200 mg of solid in 404 mL solutions containing 10 mg L^{-1} of fluorides, 16 mg L^{-1} of arsenic and 100 mg L^{-1} of nitrates, respectively)

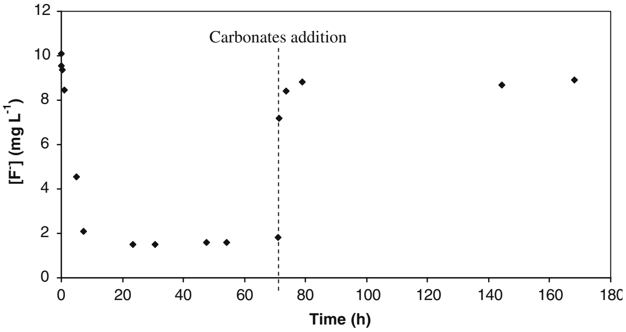

Fig. 3 Concentration of fluorides in the solution as a function of time (200 mg of solid in 404 mL solution containing 10 mg L^{-1} of fluorides)

The first decrease of the fluorides concentration is what is expected if reconstruction of the LDH takes place. Indeed, to equilibrate the positive charge of the brucite-like layers, the compound will need to incorporate anions. Moreover, recent studies related to the reconstruction of LDHs [26–28], mainly in carbonated solutions, have shown that the reconstruction is a fast process (from 5 h to less than 5 min, respectively). These results suggest that the reconstruction is surely already completed after 7 h when the concentration in fluorides remaining in the solution reaches a constant value of about 20%. This implies that the LDH has surely been reconstructed with fluoride as intercalated anions.

However, 20% of fluoride anions remain in solution. This result is surprising as, as previously mentioned, the amount of anions present in the solution is not high enough to lead to the full reconstruction of the 200 mg of mixed oxides. This apparent discrepancy between these results can easily be explained if fluorides are not the only anions involved in the reconstruction. Indeed the presence of another anion species would explain why all the fluoride anions have not been used during the reconstruction of the LDH. As the experiments have been realised under flowing N_2, the only anions present in the solution except fluorides are hydroxyl. Moreover, with solutions exhibiting basic pH (from 8.5 to 10.5), OH^- anions are present in great quantities in the solution. So a competition between fluorides and hydroxyls for the reconstruction of the LDH phase takes place. This competition is ruled by the differences in affinity for the LDH structure of the two anions and by their relative concentrations. Miyata [3] has shown that the hydroxyl anion has a slightly stronger affinity for the MgAl LDH structure than the fluoride anion. This explains why only 80% of the available fluoride anions are trapped during the LDH reconstruction.

Thus, mixed oxides issued from the moderate thermal treatment of MgAl LDH exhibit a good potential for trapping fluoride anions.

However, when carbonates are added to the solution, near 90% of the trapped F$^-$ anions are released in the solution in less than 8 h, by ion exchange between carbonate and fluoride anions, as carbonate present the highest known affinity for the MgAl LDHs [3].

These results are consistent with those obtained by Das et al. [17] on ZnAl-LDH (Zn/Al = 2). These authors have observed that the adsorption of fluorides is never complete but limited to 85.5% of the fluorides concentration in the solution. Moreover, these authors have investigated the competition between sulphate or phosphate and fluoride anions and shown that the adsorption of fluorides is decreasing when increasing the concentrations of sulphate or phosphate. These results are in good agreement with those obtained with carbonates in this study.

However, the competition with carbonates represents a bigger problem than the competition with sulphate or phosphate. Indeed, these three compounds can be found in water and thus limit the trapping of fluorides but the dissolution of CO$_2$ in water from atmosphere represent a quite infinite reservoir of carbonate and so, makes that calcined quintinite present finally a poor potential for trapping fluoride anions.

Solutions containing nitrates

Figure 4 exhibits the concentration of nitrates in the solution as a function of time. The nitrates behaviour seems very similar to the fluorides one. Figure 4 clearly shows that the quantity of nitrates in water is first decreasing when increasing the time of contact with the mixed oxides issued from the moderate thermal treatment of the LDH, down to a value of about 84% of nitrates remaining in the solution. The main difference between fluorides and nitrates is that the plateau observed after 7 h for fluorides is not really a plateau for the nitrates. Indeed, between 7 h and 70 h, there is a slight increase of the concentration of nitrates in the solution from 84 g L^{-1} to 87 g L^{-1}.

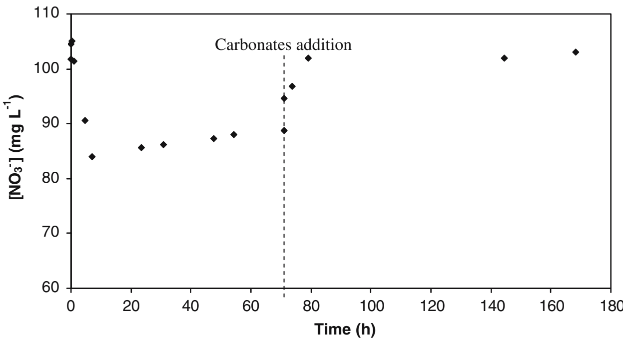

Fig. 4 Concentration of nitrates in the solution as a function of time (200 mg of solid in 404 mL solution containing 100 mg L^{-1} of nitrates)

The similar behaviour for nitrates and fluorides seems to indicate that the same process is occurring. The reconstruction is finished after 7 h. As for the fluorides, the nitrates are in competition with hydroxyl for the reconstruction of the LDH phase. However, only 15% of the nitrates were trapped, compared to 80% for the fluorides. As the nitrates and fluorides quantities in solution are quite similar, 6.45×10^{-4} mol and 2.11×10^{-4} mol, respectively, this indicates that the nitrates should have a lower affinity for the MgAl LDH structure than fluorides. This is consistent with the results of Miyata [3], that shown that the affinity for the MgAl LDH structure of hydroxyl anion is slightly stronger than the affinity of fluoride and far stronger than the affinity of nitrates.

This far stronger affinity of hydroxyl compared to nitrates also explains the slight increase of the concentration of nitrates in the solution observed between 7 h and 70 h. Indeed, due to this important difference of affinity, some nitrates used for reconstruction can be exchanged with hydroxyl, leading to a slight increase of the nitrates concentration in solution.

Thus, mixed oxides issued from the moderate thermal treatment of quintinite exhibit a low potential for trapping nitrate anions. Moreover the exchange between nitrates and hydroxyl after reconstruction, due to the important difference of affinity makes that MgAl mixed oxides issued from LDH cannot be planned to be used as traps for nitrates in water, whatever their concentration.

Finally, when carbonates, the anions with the strongest affinity for the MgAl LDH structure, are added to the solution, NO$_3^-$ anions are fully released in the solution in less than 8 h, by ion exchange between carbonate and nitrate anions.

Solutions containing arsenates

Figure 5 exhibits the concentration of arsenic in the solution as a function of time. It clearly shows that the quantity of arsenic in water is first decreasing when increasing the time of contact with the mixed oxides issued from the moderate thermal treatment of the LDH, and becomes null after about 7 h and remains equal to 0 up to 70 h.

Contrary to the results obtained for nitrates or fluorides, arsenic depollution is total. This means that the reconstruction of the LDH has used all the available HAsO$_4^{2-}$ anions, preferentially to OH$^-$ anions. This is consistent with the results of Miyata [3] that has found that SO$_4^{2-}$ and CO$_3^{2-}$

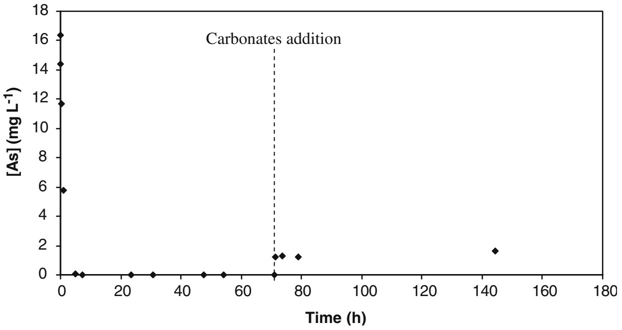

Fig. 5 Concentration of arsenic in the solution as a function of time (200 mg of solid in 404 mL solution containing 16 mg L^{-1} of arsenic)

are preferentially trapped in the structure rather than OH^-, F^-, Cl^-, Br^-, I^- or NO_3^-, and has concluded that divalent anions are preferentially used to reconstruct the LDH structure rather than the monovalent anions.

So, mixed oxides issued from the moderate thermal treatment of quintinite appear as a very promising trapping agent for arsenic in aqueous solutions.

Moreover, when carbonates are added to the solution, only a small amount of arsenates is released in the solution, near 8% after 8 h and near 10% after 73 h. As the carbonate concentration is slightly higher than that of arsenic, the small amount of arsenic released in the solution after the carbonate addition seems to indicate that $HAsO_4^{2-}$ anions present a similar or stronger affinity than CO_3^{2-} for the MgAl LDH structure.

In order to check this affinity, 357.2 mg of a fully reconstructed LDH with CO_3^{2-} (5 days in 0.1 M Na_2CO_3) [28] had been put in 404 mL of a solution containing 16 mg L^{-1} of arsenic (357.2 mg of a fully reconstructed LDH with CO_3^{2-} do represent the same mole value than 200 mg of mixed oxides). Figure 6 exhibits the concentration of arsenic in the solution as a function of time. It shows that the concentration of arsenic in solution is decreasing very fast. Indeed, after only 30 min, half of the arsenic has been removed from the solution. Then the concentration of arsenic in solution remains constant, near 8 mg L^{-1}, at least up to 47 h. This experiment clearly shows that a part of the arsenate anions in the solution have been exchanged with some of the carbonate anions of the LDH. So the arsenate anions are able to replace the carbonate anions. The affinity for the MgAl LDH structure of the $HAsO_4^{2-}$ anions is stronger than the CO_3^{2-} one, as even at lower concentrations (indeed, as previously mentioned, the quantity of As added in the solution, does not allow to fully occupied the anion sites of the LDH), 50% of the As in solution is exchanged with the CO_3^{2-} of the reconstructed LDH.

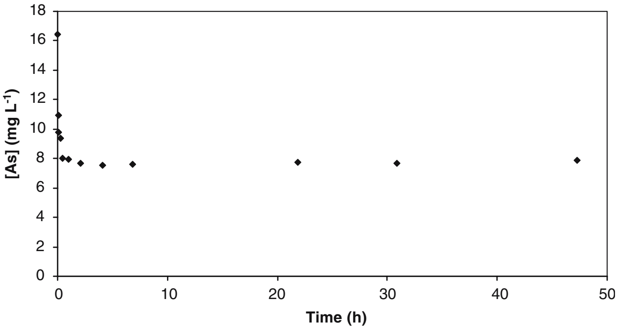

Fig. 6 Concentration of arsenic in the solution as a function of time (357.2 mg of LDH-CO_3 in 404 mL solution containing 16 mg L^{-1} of arsenic)

Figure 7 shows the XRD patterns of the fully CO_3^{2-} reconstructed LDH and of the same sample after 47 h in the As solution. The XRD patterns confirm that the LDH structure has been maintained, and that no new compound has crystallised, especially no As containing compound.

A full study of the LDH reconstruction by arsenic species that will allow to finely characterise the trapping properties of LDH and LDH-issued materials is in progress.

Conclusion

The potential of mixed oxides issued from the moderate thermal treatment of quintinite ($Mg_4Al_2(OH)_{12}CO_3 \cdot 3H_2O$) for anionic (fluoride, arsenate or nitrate anions) water depollution has been evaluated.

The mixed oxides issued from the moderate thermal treatment of the quintinite have shown a low potential for

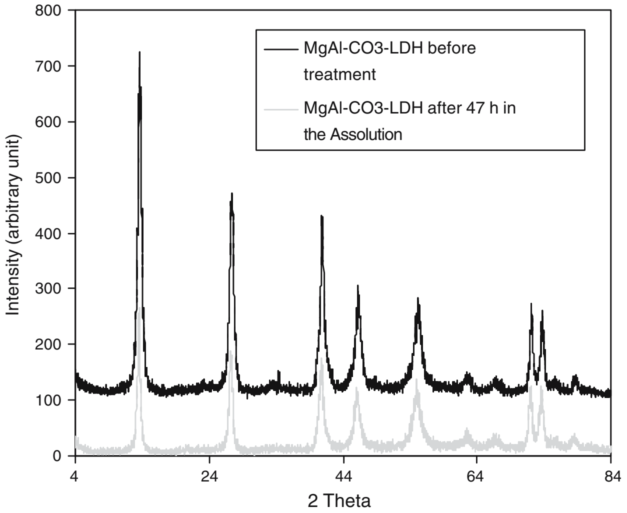

Fig. 7 XRD patterns of the fully CO_3^{2-} reconstructed LDH and of the same sample after 47 h in the As solution

trapping nitrate anions. Indeed, only 15% of the nitrates present in the solution have been trapped, due to the competition with OH^-. Moreover, when CO_3^{2-} is added, NO_3^- anions are fully released in the solution.

Regarded to the fluoride anions, the mixed oxides issued from the moderate thermal treatment of the quintinite exhibit a good potential for trapping these anions, as 80% of the fluorides present in the solution have been trapped. However, when CO_3^{2-} is added, 90% of the trapped F^- anions are released in the solution. So in presence of carbonates, the potential for trapping F^- anions of the mixed oxides issued from the moderate thermal treatment of the MgAl LDH becomes poor.

Finally, the potential for trapping As with the mixed oxides issued from the moderate thermal treatment of the quintinite appears very promising: 100% of the As in the solution has been trapped by the LDH and CO_3^{2-} addition only leads to the release of 20% of the trapped As. This suggests that the $HAsO_4^{2-}$ anions are showing a higher affinity for the MgAl LDH structure than the CO_3^{2-} anions.

This allows to complete the Miyata's scale: $HAsO_4^{2-} \geq CO_3^{2-} > SO_4^{2-} > OH^- > F^- > Cl^- > Br^- > NO_3^- > I^-$.

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