

Designing Wasteforms for Technetium

Anion sorption with precursors for ceramic phases

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Introduction

The aim of this project is to develop materials for the capture and immobilisation of water soluble anionic radionuclides. The materials produced should be suitable precursors for stable ceramic phases in which to store the waste after it has been captured. Pertechnetate is highly mobile in groundwater and it is therefore highly desirable to capture and immobilise this anion within a solid. The anion sorption capability of layered double hydroxides (LDH) is excellent. This is due to their structure which consists of ordered positively charged sheets intercalated with interchangeable hydrated anions. The composition of LDH materials can be tailored to produce suitable ceramic precursors.

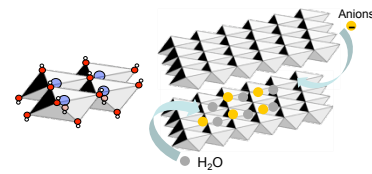


Fig 1. Schematic structure of layered double hydroxides.

Material Production

Layered Double Hydroxides containing Ca, Al and Fe were produced via a co-precipitation method. The samples were allowed to age at room temperature for 24-48 h in order to improve the crystallinity of the product.

The general formula for CaAlFe(NO₃) LDHs is Ca_{1-x}(Al_yFe_{1-y})_x(OH)₂(NO₃)_x. A pure LDH was obtained for x=0.3 which is close to the reported limit of x=1/3.

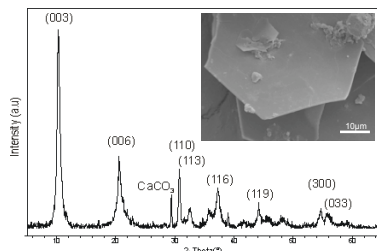


Fig 2. X-ray diffraction pattern of Ca₂Al_{0.5}Fe_{0.5}(OH)₂NO₃ and SEM image of platelet structure (inset).

Activation of Adsorption

The ability of LDHs to capture/exchange ions can be greatly enhanced by calcining the powder to drive off the interlayer anions.

The so called 'memory effect' enables the LDH structure to be reformed after calcination simply by addition to a solution.

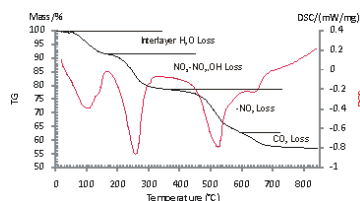


Fig 3. TGA and DSC trace for a sample of Ca₂Al_{0.5}Fe_{0.5}(OH)₂NO₃

Anion Capture

If the sample is rehydrated in a solution the layered structure is reformed as the calcined material absorbs anions from the solution.

A sample of LDH (Fig 4a) was calcined to 600°C (Fig 4b) and then rehydrated in deionised water reforming a layered structure (Fig 4c).

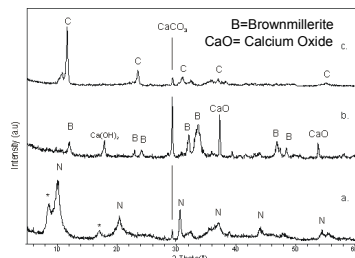


Fig 4. XRD patterns obtained for a) NO₃-CaAlFe LDH (N), b) sample of 'a' heat treated to 600°C, c) rehydrated in H₂O CO₃-CaAlFe LDH (C).

Thermal Conversion

The ultimate aim of this project is to produce stable wasteforms. It is hoped that ⁹⁹Tc will remain captured within the collapsed LDH structure as it is converted from LDH to Brownmillerite Ca₂AlFeO₅ for example. The LDHs produced can be thermally converted to ceramic phases by calcination.

XRD patterns of samples calcined to different temperatures revealed that Brownmillerite-like compounds were produced at temperatures as low as 400°C, see Figure 5. Below this temperature some of the original LDH structure remained. This suggests that dissolution of Tc into a ceramic structure might be possible at low temperatures and hence that volatilisation of Tc (B.P. Tc₂O₇: 310°C [3]) might be avoided.

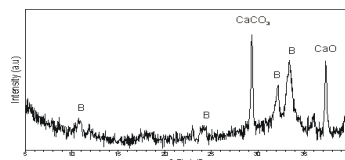


Fig 5. XRD pattern obtained from CaAlFe-NO₃ heat treated to 400°C, B=Brownmillerite, CaCO₃=calcium carbonate, CaO = Calcium Oxide.

Nitrate salts of Ca, Fe and Al were dissolved in deionised water in the desired stoichiometric ratio. This solution was then added dropwise, with vigorous stirring, to a flask containing NaNO₃ solution kept at pH greater than 12 by the simultaneous addition of NaOH solution. The precipitate was separated from the solution by vacuum filtration and rinsed with water to remove residual salts from the product.

Aging at elevated temperatures (50-60°C) improved the crystallinity (Figure 2, inset) of the samples however for very long aging times Ca₂Al_{1.54}Fe_{0.46}[(OH)₂]₃ was formed. An XRD pattern obtained from Ca₂Al_{0.5}Fe_{0.5}(OH)₂NO₃ is shown in Figure 2 it exhibits features typical of an LDH structure.

The thermogravimetric (TGA) and differential scanning calorimetry (DSC) curves are presented in Figure 3 for a CaAlFe-LDH with x=0.3. The multi-stage weight loss is common for LDHs and in good agreement with literature [1].

The processes labeled in Figure 3 are likely to occur across the temperature range and not at set points. The mass loss at 650°C is thought to be due to the decomposition of calcite in the structure, present due to carbonate contamination (~12 wt%). The memory effect occurred fully for calcinations up to 600°C and partially up to 950°C.

The adsorption efficiency of these compositions of LDH will be determined using ICP-OES.

The location of the (003) peak has shifted to a higher angle (10.08-11.68°2θ), Figure 4c. This is indicative of a reduction of interlayer spacing (8.76-7.57Å) and hence the presence of a smaller anion. It is suggested that this would be the carbonate anion (CO₃²⁻), from equilibration of the water with the atmosphere, as it is the only anion available in the system.

The mechanism of adsorption [2] will be investigated employing ReO₄⁻ as a surrogate for TcO₄⁻.

Conclusions

- For Ca based LDHs, the ratio of trivalent to divalent ions for pure LDH formation is limited to 0.3-0.33. The relative content of Al and Fe can be varied freely.
- Limited stability range in terms of pH and temperature. Ca₂Al_{1.54}Fe_{0.46}[(OH)₂]₃ formed above 50°C after 20 h.
- Carbonate contamination was limited to 12 wt%.
- The memory effect exists in CaAlFe LDHs up to 600°C and is only partially lost to temperatures as high as 950°C.
- Thermal conversion to Brownmillerite possible at temperatures as low as 400°C.

References:

- Renaudin, G., et al. Cement and Concrete Research, 2000, 30(2): p. 307-314.
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