

## Designing wasteforms for technetium: anion capture with layered double hydroxides

J.D. Phillips and L.J. Vandeperre  
 Department of Materials, Imperial College London  
 (correspondence: l.vandeperre@imperial.ac.uk)

### ABSTRACT

Technetium, Tc, is a long-lived radionuclide, Tc-99 has a half life of  $2.1 \times 10^5$  years and is produced with a yield of approximately 6% during nuclear fission. Currently the pertechnetate anion,  $\text{TcO}_4^-$ , is captured from a spent fuel reprocessing waste stream by the addition of Tetraphenylphosphonium Bromide, TPPB, with an efficiency of 95%. It has been shown that exposure to an alkaline environment, such as that found in the pores of cement, can result in the degradation of TPPB and subsequent release of  $\text{TcO}_4^-$  to the environment. It is proposed that an integrated capture and disposal solution could be developed employing layered double hydroxides, LDHs, as the capture medium and thermally converting these LDHs to stable ceramic phases. To this end layered double hydroxides with the general formula  $\text{Ca}_{(1-x)}(\text{Al}_{(1-y)}, \text{Fe}_y)_x(\text{OH})_2 \cdot x(\text{NO}_3) \cdot n\text{H}_2\text{O}$ , a composition suitable for conversion to Brownmillerite  $\text{Ca}_2(\text{Al}, \text{Fe})_2\text{O}_5$ , a hydration phase found in cements have been produced. The ability of these materials to capture anions from solution were investigated. Anions with a greater charge density were found to preferentially intercalate into the LDH phases in the order  $\text{Cl}^- > \text{CO}_3^{2-} > \text{NO}_3^- > \text{ReO}_4^-$ . In addition during competitive-multi anion trials, several anions were incorporated into the LDH structure.

### INTRODUCTION

Tc-99, produced within nuclear fission reactions with a yield of 6% has a half life of  $2.1 \times 10^5$  years. This isotope is of great environmental concern as it found as the pertechnetate anion,  $\text{TcO}_4^-$ , which is highly mobile in groundwater as it does not bind well to soils. Currently, in the UK, a technetium containing waste stream from the reprocessing of spent nuclear fuel is treated with a process employing Tetraphenylphosphonium Bromide, TPPB, to capture the  $\text{TcO}_4^-$  anion with an efficiency of 95% [1]. The solids produced during this process are then incorporated into a cementitious wasteform for long term disposal.

It has been shown by Aldridge et al [2] that in an alkaline environment, such as the conditions encountered in the pore water of cements, TPPB can degrade and the  $\text{TcO}_4^-$  anion can become mobile again. It is highly desirable to immobilize this anion to prevent migration in the biosphere and so an alternative class of materials has been investigated.

Layered double hydroxides are a novel class of materials which exhibit excellent anion capture properties [3]. They are structurally related to the naturally occurring mineral Brucite,  $\text{Mg}(\text{OH})_2$ , in which a fraction of the divalent cations, x, has been

substituted for trivalent cations. LDHs consist of positively charged metal hydroxide sheets with the general formula  $[\text{M}^{\text{II}}_{(1-x)}\text{M}^{\text{III}}_x(\text{OH})_2]^{x+}$  in which  $\text{M}^{\text{II}}$  and  $\text{M}^{\text{III}}$  represent a divalent and trivalent cation respectively. Located between these sheets are hydrated anions which are present to balance the charge on the surface of the sheets which can be considered to have the general formula  $[x \cdot \text{A}^{z-} \cdot n\text{H}_2\text{O}]$ , where  $\text{A}^{z-}$  is an anion of charge z. The composition of both the cation sheet and the interlayer anion is highly variable.

In order to determine how effective these compositions are at capturing the pertechnetate anion from solution a non-active surrogate was employed during this study. Previous studies by Kang et al [4] employed the perrhenate,  $\text{ReO}_4^-$  anion as a surrogate for pertechnetate due to its similar physical and chemical properties. In their work the absorption of  $\text{ReO}_4^-$  and subsequently  $\text{TcO}_4^-$  within a MgAl LDH structure was found to be dependent on the pH of the solution and the initial concentration of the anion in the capture solution.

Two models have been proposed for the mechanism of anion exchange in LDHs, the first is direct exchange of one anion for a preferred one in solution. The second is a dissolution reprecipitation mechanism in which the LDH

dissolves and increases the pH of the solution resulting in reprecipitation of a new LDH phase containing the anions present in the solution. The latter effect can be enhanced by first calcining the LDH material to drive off the interlayer anions, and subsequently adding the calcined powder to the solution containing the anions to be captured. This is known as the 'memory effect' in which an LDH can reform its layered structure from a calcined state.

After capture of the anions within the interlayer of the LDH, the solid material is filtered from solution and allowed to dry. In order to produce a durable waste form, the LDH powder will be thermally converted to stable ceramic phases. For the compositions employed in this study, these phases will be Brownmillerite,  $\text{Ca}_2(\text{Al}, \text{Fe})_2\text{O}_5$ , and calcium oxide,  $\text{CaO}$ . These phases occur in cements, and as such are expected to be more stable when disposed of in a cementitious waste form for final disposal. One of the main challenges with the thermal conversion of LDHs phases which are intended to store  $\text{TcO}_4^-$  is the volatility of Tc at relatively low temperatures.  $\text{Tc}_2\text{O}_7$  has the lowest boiling point,  $311^\circ\text{C}$  [5], of the oxides of technetium. It is desirable therefore, to convert the LDH phases to stable ceramic phases below this temperature if possible.

## EXPERIMENTAL

### Sample Production

LDHs with the general formula  $\text{Ca}_{(1-x)}(\text{Al}_{(1-y)}, \text{Fe}_y)_x(\text{OH})_{2-x}(\text{NO}_3)_n \cdot n\text{H}_2\text{O}$  were produced via a co-precipitation method in which the nitrate salts of the metal cations were dissolved in the desired stoichiometric ratio. This solution was added dropwise to a solution containing the desired interlayer anion, maintained at pH14 by the simultaneous addition of 1M NaOH solution. The resulting precipitate was separated from the solution by vacuum enhanced filtration, before re-suspension in distilled water and further filtration to remove any undesired excess nitrate salts from the product. Further details on the experimental conditions employed can be found in the literature [6].

For experiments requiring calcined material  $\text{Ca}_{(0.67)}(\text{Al}_{0.5}, \text{Fe}_{0.5})_{0.33}(\text{OH})_{2.0.33}(\text{NO}_3)_n \cdot n\text{H}_2\text{O}$  was heat treated to  $550\text{--}600^\circ\text{C}$  in tube furnace under an air atmosphere for 1 hour. In this temperature range the interlayer anions have volatilized, and the hydroxide sheets have dehydroxylated to leave a mixed oxide powder [6].

### Exchange procedure

In order to determine whether one anion could be exchanged for another within the interlayer of the LDH a series of tests were conducted. Either 1g of uncalcined material or 0.5g of calcined material

was placed into a 50ml centrifuge tube containing 50ml of NaOH solution at pH 14. In addition each tube contained a stoichiometric excess (for full exchange of the existing anion in the interlayer) of a  $\text{Na}_2(\text{A}^{z-})$  salt, where  $\text{A}^{z-}$  was  $\text{Cl}^-$ ,  $\text{NO}_3^-$  or  $\text{CO}_3^{2-}$ .

To determine whether there was competition between anions during capture, a series of experiments was conducted in which a 1g sample of  $\text{Ca}_{(0.67)}(\text{Al}_{0.5}, \text{Fe}_{0.5})_{0.33}(\text{OH})_{2.0.33}(\text{NO}_3)_n \cdot n\text{H}_2\text{O}$  was placed into a solution containing two anions. The pairs of anions used were,  $\text{Cl}^-$  and  $\text{CO}_3^{2-}$ ,  $\text{Cl}^-$  and  $\text{NO}_3^-$  and  $\text{NO}_3^-$  and  $\text{CO}_3^{2-}$ . The exchange reaction was allowed to occur for 1 hour; in addition another batch with an extended reaction time of 4 weeks was produced which ensured equilibrium was attained.

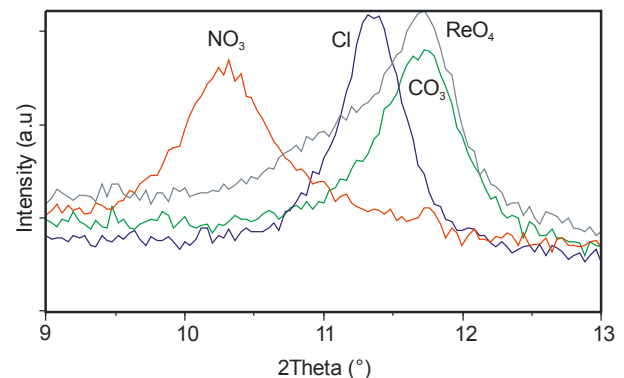
### Characterisation

The solid powders produced in this experiment were analysed using a Phillips PW1720 powder x-ray diffractometer or a PW3050/60 Goniometer with PW3373/00 x-ray tube using  $\text{Cu K}_\alpha$  radiation in each case. Chemical analyses of the composition of the LDHs produced and the extent of  $\text{ReO}_4^-$  capture were confirmed by inductively coupled plasma optical emission spectroscopy (ICP-OES, Perkin Elmer). The solids were digested in 5%  $\text{HNO}_3$ , and the concentration of Re in solution before and after exchange were measured.

## RESULTS AND DISCUSSION

### Single Anion – Direct Exchange

The magnitude of the interlayer spacing for calcium based layered double hydroxides is highly sensitive to the thermochemical radius and charge of the interlayer anion. In each of this sequence of experiments it was observed that when exchange had occurred, the position of the (003) peak, as shown in Figure 1. The peak position after exchange was in good agreement with the position obtained for phases produced by direct coprecipitation with a different counter-anion in the precipitating solution (Table 1).

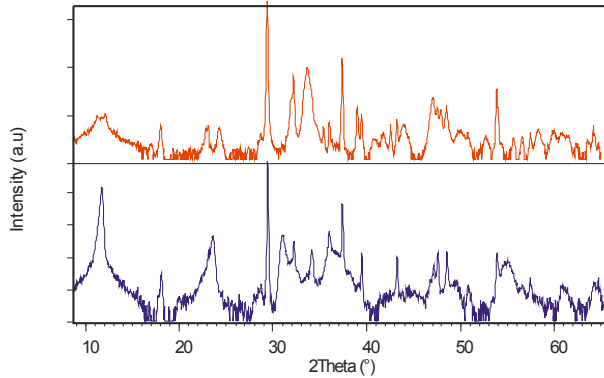


**Figure 1** (003) peak present in the XRD patterns obtained for an  $\text{NO}_3^-$  intercalated LDH in the as produced condition and exchanged with  $\text{Cl}^-$ ,  $\text{CO}_3^{2-}$  and  $\text{ReO}_4^-$  (as labelled in Figure)

In the case of  $\text{ReO}_4^-$  exchange the (003) peak is at the same d-spacing as the  $\text{CO}_3^{2-}$  exchanged sample. It is thought that in this instance  $\text{ReO}_4^-$  has not been incorporated into the LDH structure, in fact, the LDH has captured  $\text{CO}_3^{2-}$  anions which were present in the solution in equilibrium with the atmosphere. Subsequent analysis by ICP-OES to measure the rhenium content of this sample confirmed this hypothesis

**Single Anion – Reformation**

The x-ray diffraction pattern obtained for the calcined LDH powder is presented in Figure 2.



**Figure 2** The characteristic peaks of calcite dominate the pattern in the calcined state, due to carbonate contamination within the furnace (top), despite this contamination an LDH structure reformed upon addition to a  $\text{ReO}_4^-$  solution (bottom).

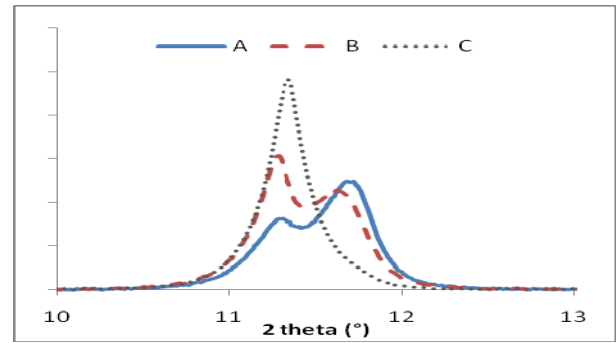
After addition of the calcined material to a solution containing  $\text{ReO}_4^-$  anions the LDH structure reformed, however this conversion was not fully reversible and so some calcite remains in the sample. A similar result was observed as for the uncalcined material, in which the (003) peak for the LDH coincided with the one attributed to  $\text{CO}_3^{2-}$  LDH. Analysis of the solids by ICP-OES confirmed that the level of uptake of  $\text{ReO}_4^-$  anions were much lower than theoretically attainable.

**Multiple Anions – Direct Exchange**

When multiple anions were present in the exchange solution, exchange occurred for both ions present in the solution. The x-ray diffraction patterns obtained for a series of  $\text{NO}_3^-$  LDHs exposed to  $\text{Cl}^-$  and  $\text{CO}_3^{2-}$  containing exchange solution in which the ratios of  $\text{Cl}:\text{CO}_3$  was varied are presented in Figure 3. It is apparent that as the mole fraction of  $\text{Cl}^-$  is increased from 0.1 to 0.9 the peak at  $11.63^\circ 2\theta$  increased in intensity accordingly, whilst the peak at  $11.66^\circ 2\theta$  attributed to  $\text{CO}_3^{2-}$  decreases. A similar effect was observed for exchange of  $\text{NO}_3^-$  LDH with solutions containing  $\text{NO}_3^-$  and  $\text{Cl}^-$  and  $\text{NO}_3^-$  and  $\text{CO}_3^{2-}$ .

For the samples which were allowed to exchange for an extended period a similar trend was observed for the  $\text{NO}_3^-$  and  $\text{Cl}^-$  samples. However in each of the samples which contained  $\text{CO}_3^{2-}$  at higher concentrations, the samples had nearly

completely decomposed, and lost their layered structure which is undesirable.



**Figure 3** X-ray diffraction pattern of the (003) peak for: Sample A [ $\text{Cl}$  0.1  $\text{CO}_3$  0.45], Sample B [ $\text{Cl}$  0.5  $\text{CO}_3$  0.25] and Sample C [ $\text{Cl}$  0.9  $\text{CO}_3$  0.05]. Where the compositions described are in mole fraction.

**Table 1** Details of the thermochemical radius and observed d-spacings for as produced LDHs with the desired counter-anion in the precipitation solution, and the d-spacing observed after exposure of a  $\text{NO}_3^-$  LDH to different anion solutions.

Anion	Thermo-chemical Radius (nm)	D-Spacing (003) as produced (nm)	D-Spacing (003) post Exchange (1hour) (nm)
$\text{NO}_3^-$	0.200	0.8593	N/A
$\text{CO}_3^{2-}$	0.189	0.7551	0.7549
$\text{Cl}^-$	0.168	0.7917	0.7796
$\text{ReO}_4^-$	0.227	N/A	0.7563

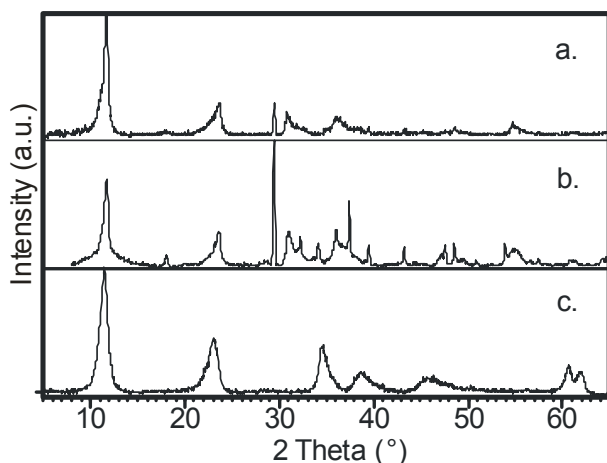
**Capture of Perrhenate**

The uptake of the perrhenate anion into the LDH structure was quantified by ICP-OES the results of these analyses are presented in Table 2 in which the uptake of the perrhenate anion into the LDH structure is expressed as a percentage of the theoretical maximum for full charge balance of the LDH structure by  $\text{ReO}_4^-$  anions. The x-ray diffraction patterns obtained for these samples exposed to a  $\text{ReO}_4^-$  solution are presented in Figure 4.

**Table 2** Summary of the uptake of the  $\text{ReO}_4^-$  anion expressed as a percentage of the theoretical maximum for complete charge balance of the LDH by  $\text{ReO}_4^-$ .

Sample	$\text{ReO}_4^-$ Uptake
CaAlFe LDH	2.94%
Calcined CaAlFe LDH	2.32%
MgAl LDH	1.82%

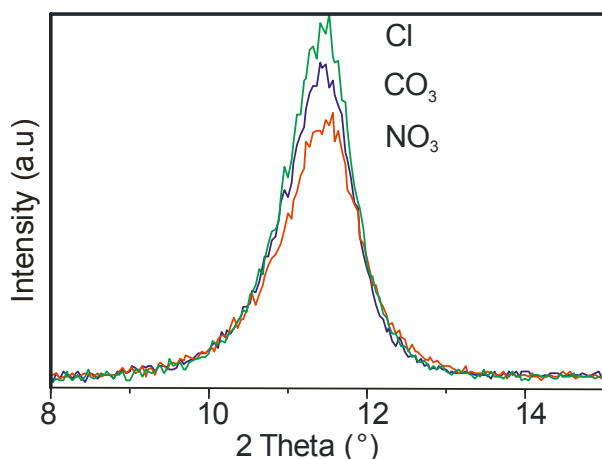
Work by Kang and co-workers [8] has demonstrated that it is possible to capture both  $\text{ReO}_4^-$  and  $\text{TcO}_4^-$  within a MgAl LDH structure by first calcining the material and subsequently reforming the LDH structure in solution. Currently the cause of the low uptake of  $\text{ReO}_4^-$  into Ca based LDHs is unknown however work is ongoing to rule out several hypotheses.



**Figure 4** X-ray diffraction patterns obtained for a sample of a.)  $\text{Ca}_{0.67}(\text{Al}, \text{Fe})_{0.33}(\text{OH})_2(\text{NO}_3)_{0.33} \cdot n\text{H}_2\text{O}$ , b.) sample of 'a' calcined at  $575^\circ\text{C}$  for 1 hour, c.)  $\text{Mg}_{0.7}\text{Al}_{0.3}(\text{OH})_2 \cdot (\text{NO}_3)_x \cdot n\text{H}_2\text{O}$  each rehydrated in a  $\text{NaReO}_4$  solution.

### MgAl LDHs

To investigate whether the sensitivity of the interlayer spacing to the thermochemical radius of the anion occurred in other LDH compositions, MgAl LDHs were produced by a similar method to that employed for Ca based LDHs. It was observed that the interlayer spacing changed very little for samples produced with different anions in the precipitating solution or for MgAl- $\text{NO}_3^-$  LDH material exposed to different anion solutions. It is thought that the large variation in d-spacing observed for the Ca based LDHs is due to the fact that the Ca cation is seven coordinated whereas Mg is six coordinated. The large size of the calcium cation means that it distorts the aluminium octahedra and bonds with a water molecule or anion in the interlayer.



**Figure 5** XRD patterns of the (003) peak obtained for a  $\text{NO}_3^-$  intercalated MgAl LDH (bottom) which had been exchanged with,  $\text{CO}_3^{2-}$  (middle) and  $\text{Cl}^-$  (top).

### CONCLUSIONS

Layered double hydroxides based on calcium, aluminium and iron have been produced with the formula  $\text{Ca}_{(0.67)}(\text{Al}_{0.5}, \text{Fe}_{0.5})_{0.33}(\text{OH})_2 \cdot 0.33(\text{NO}_3)_x \cdot n\text{H}_2\text{O}$  for the capture of anions from solution. It was observed that it is possible to exchange one anion

for another when starting from the composition above. The order of preference for intercalation was found to be  $\text{Cl}^- \approx \text{CO}_3^{2-} >> \text{NO}_3^- > \text{ReO}_4^-$

When the LDH powder is exposed to a solution containing multiple competing anions, a LDH with multiple interlayer spacing will form. This demonstrates that the LDH structure can accommodate different anions simultaneously. The uptake of  $\text{ReO}_4^-$  anions into the interlayer of Ca based LDH materials was lower than expected and the cause of this is currently unknown, however several hypotheses are being investigated.

### FUTURE WORK

The mechanism of absorption of the CaAlFe LDH system will be investigated in an effort to increase the capture efficiency of the material. Further work on this system will investigate the durability of the final ceramic waste forms in the conditions expected during final disposal and storage. In addition the ability of these compositions to capture the antimonate anion from solution will also be investigated.

### REFERENCES

- [1] J. Reed, Technetium to go, Nuclear Engineering International, 49 (2004) 14-17.
- [2] S. Aldridge, P. Warwick, N. Evans, S. Vines, Degradation of tetraphenylphosphonium bromide at high pH and its effect on radionuclide solubility, Chemosphere, 66 (2007) 672-676.
- [3] K.-H. Goh, T.-T. Lim, Z. Dong, Application of layered double hydroxides for removal of oxyanions: A review, Water Research, 42 (2008) 1343-1368.
- [4] M.J. Kang, K.S. Chun, S.W. Rhee, Y. Do, Comparison of Sorption Behavior of  $\text{I}^-$  and  $\text{TcO}^-$  on Mg/Al Layered Double Hydroxide, Radiochimica Acta, 85 (1999) 57-63.
- [5] M.J.d. Exter, S. Neumann, T. Tomasberge, Immobilization and Behavior of Technetium in a Magnesium Titanate Matrix for Final Disposal, Materials Research Society Symposium Proceedings, 932 (2006).
- [6] J.D. Phillips, L.J. Vandepierre, Designing Wasteforms for Technetium, in: DIAMOND '09 Conference, York, 2009.
- [7] Roobottom, Thermochemical Radii of Complex Ions, Journal of Chemical Education, 76 (1999) 1570.
- [8] M.J. Kang, S.W. Rhee, H. Moon, Sorption of  $\text{MO}_4^-$  ( $\text{M} = \text{Tc}, \text{Re}$ ) an Mg/Al Layered Double Hydroxide by Anion Exchange, Radiochimica Acta, 75 (1996) 169-173.