

Anion exchange materials for radiochemical applications

A.D. Butterworth, S.E. Dann and C.A. Kirk
Department of Chemistry, Loughborough University
(correspondence: s.e.dann@lboro.ac.uk)

ABSTRACT

The synthesis, stability and anion exchange properties of layered hydroxyl salts (LHS) containing Cu, La, Ni and Zn as storage materials for ^{129}I and ^{99}Tc have been investigated. Single phase materials of the formula $\text{M}_2(\text{OH})_3\text{X}\cdot\text{YH}_2\text{O}$ where $\text{M} = \text{Ni, Cu, Zn}$ and $\text{X} = \text{NO}_3$ and OAc were prepared hydrothermally and via titration using solutions of the appropriate metal salts with sodium hydroxide. The structures consist of layers of edge-sharing metal hydroxide octahedra together with an interlayer space containing the anion and in some cases water molecules. Experiments showed that copper-based LHS gave the greater reliability in exchange reactions with specifically the acetate analogue showing the greater efficiency. The full exchange capability of copper hydroxyacetate was then explored using a variety of anions (I^- , IO_3^- , IO_4^- , $\text{Cr}_2\text{O}_7^{2-}$, SbO_3^- and ReO_4^-) and reaction parameters (time and redox conditions) to examine the stability of the phase and the efficacy of the exchange

INTRODUCTION

A long term solution for the immobilisation and storage of iodine-129 and technetium-99 produced as a by-product of nuclear fission is urgently required. Containment of both species is difficult due to their anionic nature and mobility in the environment. Iodine-129 (half life 1.29 million years) has a considerable risk associated with it due to a number of physical properties such as volatility, ability to form corrosive salts and ease of displacement of iodide-129 by other anionic species in ground waters. In addition, iodide-129 has the potential to accumulate in the thyroid of humans and animals as it is assimilated in the functioning of the gland. Technetium-99 is relatively immobile in its elemental form, however technetium-99 is readily oxidised to the anion $^{99}\text{TcO}_4^-$. The pertechnetate anion is extremely mobile in the environment and if ingested, like iodine-129, can be considered a biohazard. At present, the common route for disposal of long lived volatile anionic species is via discharge into the ocean. This dilution and dispersion approach is used to ensure minimal exposure to humans. However, this method of disposal is no longer deemed acceptable and ever-tighter regulations to reduce the amount of nuclear waste discharged into the marine environment are certain to be passed. Therefore, a new inexpensive approach for the sustainable and safe long-term immobilisation of iodine-129 and technetium-99 is needed.

In this paper, layered materials capable of intercalating interlayer inorganic and organic guest molecules are being explored as a potential solution for the immobilization of iodine-129 (as I^- , IO_3^- and IO_4^-) and technetium-99 (as TcO_4^-) as well as other anionic species such as $\text{Cr}_2\text{O}_7^{2-}$, NO_3^- , SbO_3^- and Cl^- which are either other radioactive species or competitor anions present in nuclear waste. These layered hydroxyl salts are cheap, insoluble and are closely related to natural materials which are stable in high pH conditions. The properties of cationic exchange materials such as clays, metal phosphates and zeolites are well known and have been used within the nuclear industry for many years. However, anionic exchange materials have achieved much less attention. Layered Double Hydroxides (LDH) are a group of anion exchange materials which have received much interest due to their ability to catalyse reactions and provide a starting point for inorganic-organic hybrids¹. The structure consists of positively charged metal-hydroxide layers with an interlayer spacing that is occupied by a charge balancing anion. LDH's have a brucite like structure, which consists of M^{2+} cations co-ordinated octahedrally by hydroxide ions. A fraction of the divalent cations can be replaced with trivalent cations and generate a positive charge on the layers and so necessitate the need for charge balancing anions². A difference of 0.5Å in ionic radius between the two metal cations can be tolerated leading to a compositionally diverse group of materials³. The anion exchange

capabilities of LDHs are well known and have been extensively studied though the resulting products have variable stability depending on pH/temperature. Layered hydroxyl salts (LHS) are structurally related to LDHs and may also be classified as anionic clays. Typically, while the structure is similar to the LDH's the interactions between the anions and the layers are much stronger leading to much better physical and chemical stability e.g. $\text{Cu}_2(\text{OH})_3\text{NO}_3$ is both stable at pH 11-12 and has good thermal stability to 200°C. In the following studies, LHS are investigated for ion exchange capability and stability⁴.

THE STRUCTURE OF LAYERED HYDROXY SALTS

Copper hydroxynitrate, $\text{Cu}_2(\text{OH})_3\text{NO}_3$ is a LHS found naturally that exists as two structurally related dimorphs; either a synthetic monoclinic phase or a natural orthorhombic phase. There has been considerable research on the exact structure of these two dimorphs and the relationship between the two phases. Other layered hydroxyl salts containing divalent and trivalent metal cations including Ni, Ln (La-Lu), Co, Mn, Cr, Ca, Mg, Y, Fe, and Zr have also been reported. LHS can be broadly separated into two groups, based on either a zinc hydroxynitrate ($\text{Zn}_5(\text{OH})_8(\text{NO}_3)_2 \cdot \text{YH}_2\text{O}$) type structure or a copper hydroxynitrate ($\text{Cu}_2(\text{OH})_3(\text{NO}_3) \cdot \text{YH}_2\text{O}$) type structure. In $\text{Zn}_5(\text{OH})_8(\text{NO}_3)_2 \cdot \text{YH}_2\text{O}$, one quarter of the octahedral sites within the brucite layers are vacant with two Zn^{2+} cations occupying tetrahedral sites located on either side of the vacant octahedral sites. This creates a positive charge within the layers with the composition $(\text{Zn}_3\text{Zn}_2(\text{OH})_8)^{2+}$, where Zn is occupying an octahedral site and Zn is occupying a tetrahedral site⁵. The positive charge on the layer is then compensated by a charge balancing anion held either electrostatically or chemically bonded to the metal cation within the interlayer spacing. Water molecules are also sometimes incorporated into the interlayer spacing. In the $\text{Cu}_2(\text{OH})_3(\text{NO}_3) \cdot \text{YH}_2\text{O}$ system, one quarter of the hydroxide anions are replaced by nitrate anions coordinated directly to the copper cation (Figure 1)⁶.

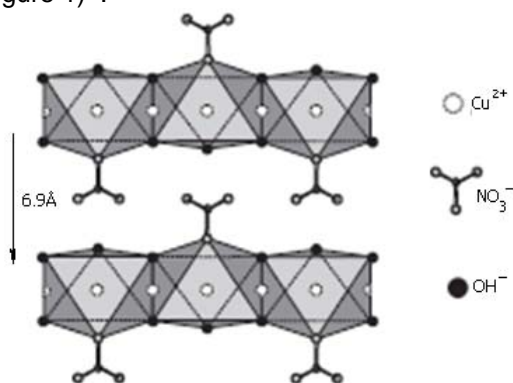


Figure 1 The structure of copper hydroxynitrate

ANION EXCHANGE CAPABILITIES

LHSs have been shown to undergo exchange reactions with a variety of anions ranging from large organic molecules to smaller inorganic species of varying shapes and sizes. One of the most interesting aspects of these materials is the varying degree of reversibility of these exchange processes (Figure 2)⁷. Halides are practically irreversibly exchanged with the hydroxyfluoride being the most stable product. The theoretical anion-exchange capacities (assuming complete exchange of the interlayer nitrate anions) of the Zn, Cu, Ni, and La hydroxy nitrates are 3.2, 4.2, 4.3 and 4.0 meq/g respectively⁸.

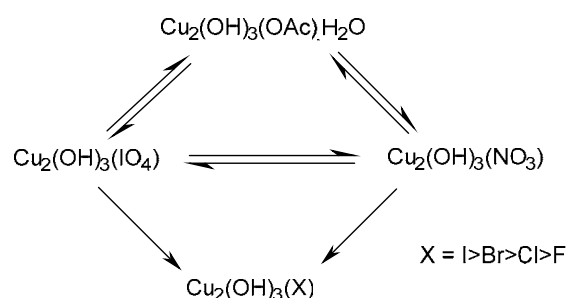


Figure 2 A schematic to show the exchange potential of several anions.

The size of the interlayer spacing can dramatically change depending on the occupying anion. Most LDHs and LHSs reported contain nitrate as the exchangeable anion however examples of acetate, benzoate, sulfate and chloride containing materials have also been reported⁵. In copper hydroxynitrate, the gallery spacing is $\sim 6.9\text{\AA}$ however when nitrate is replaced by a smaller chloride anion, the gallery spacing is reduced to $\sim 5.7\text{\AA}$. The reduction of the interlayer spacing inhibits the ability of anions to enter the gallery spacing and access the exchangeable sites, which explains why halide exchange is irreversible. Similarly, LHS synthesized using large exchangeable anions such acetate, are less stable and prone to anion exchange with smaller species. Copper hydroxyacetate is similar to its nitrate equivalent however the acetate anion is held electrostatically within the layers and a water molecule is bonded directly to the copper cation (Figure 3). This results in a much larger gallery spacing of $\sim 9.3\text{\AA}$ that in theory will be more susceptible to exchange with smaller anions.

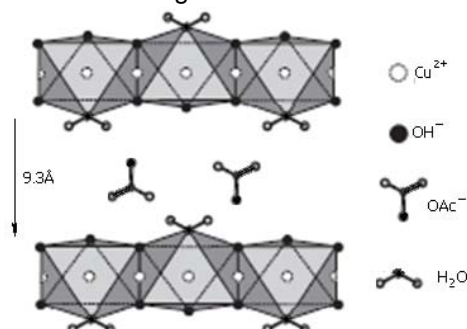


Figure 3 The structure of copper hydroxyacetate

SYNTHESIS OF LAYERED HYDROXY SALTS

A standard method of digestion of a metal oxide or metal dust in a concentrated solution of a metal (M=Zn, Ni, La, Co, Cu and Mn) nitrate salt at high temperatures, contained within a Teflon-lined autoclave, was used to synthesis all layered nitrate materials. Due to the instability of layered acetate materials above 100°C, this method could not be used for synthesis of metal acetate materials. Single phase metal hydroxyacetate samples were therefore prepared by a different method using titration of dilute metal (M= M=Zn, Ni, Co and Cu) acetate with NaOH (Cu:OH = 1:1).

SUITABILITY AND RELIABILITY OF METAL HYDROXY ANALOGUES

Both metal hydroxyacetate and hydroxynitrate materials undergo exchange reactions and a variety of different metals have been in their synthesis. Previous work in the study has shown that although all layered Zn, Ni, La, Co, Cu and Mn hydroxyl materials exhibit anion exchange capabilities, only copper base analogues gave reliable and reproducible results in respect to both nitrate and acetate analogues. The rate of exchange of both copper hydroxynitrate and copper hydroxyacetate was therefore explored using iodide as the target anion as a standard.

$\text{Cu}_2(\text{OH})_3(\text{X}) \cdot \text{YH}_2\text{O}$ ($\text{Y}=\text{NO}_3^-, \text{OAc}^-$) (0.1M) was added to a solution of sodium iodide (20 ml) in a molar ratio of 1:1. The solution was then stirred for 1 day at room temperature and the resulting solid product filtered and recovered (Figure 4).

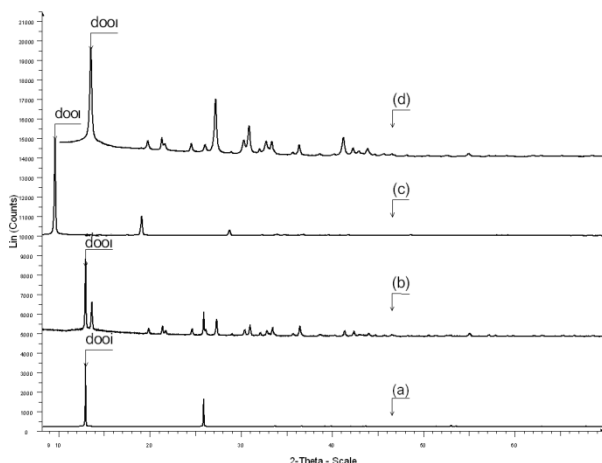


Figure 4 Powder XRD pattern of copper hydroxynitrate (a) exchanged with sodium iodide after (b) 1 day and copper hydroxyacetate (c) exchange with sodium iodide after (d) 1 day

After 1 day exposure to sodium iodide solution, the XRD patterns indicate that iodide exchange for nitrate is incomplete with the d_{001} reflection for both the anion analogues present. The relative intensities of the two d_{001} reflections indicate that nitrate is still the majority anion occupying the interlayer spacing and complete exchange was only observed after 10 days. This reaction was much slower than anticipated, the reason for this may be that due to a large particle size of the

copper hydroxynitrate as a result of the high temperature needed for synthesis. The increased particle size decreases the surface area for an exchange reaction to occur. In the case of copper hydroxyacetate, complete exchange occurs within 1 day with only the d_{001} reflection for copper hydroxyiodide present. This confirms that the larger gallery spacing of the acetate analogue plays a large role in the efficiency of an exchange reaction. The next step is to determine the amount of time needed for a complete exchange of iodide for acetate. Copper hydroxyacetate is added to a sodium iodide solution as explained above and the reaction observed. It was noted that within 30 seconds of addition of the exchange material, a colour change from blue to yellow-green was observed indicating a reaction had already taken place. After just 10 mins exposure to the sodium iodide solution, the XRD pattern indicated a complete exchange (Figure 5).

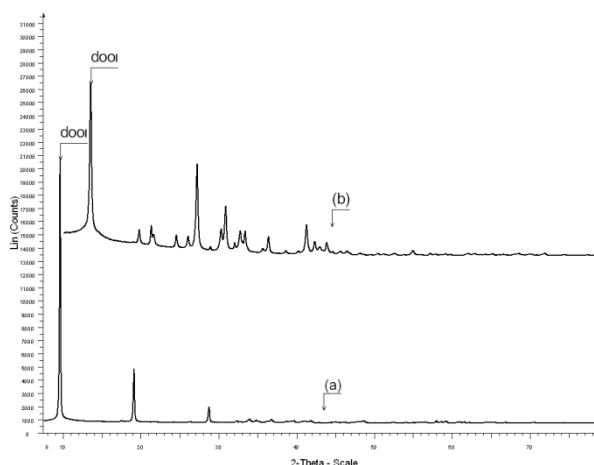


Figure 5 Powder XRD pattern of copper hydroxyacetate (a) exchanged with sodium iodide after (b) 10 mins

The stability of copper hydroxyacetate in a high anionic strength solution and an oxidizing solution was then explored. Copper hydroxyacetate was added to a solution of sodium iodide as described previously, however the molar ratio was increased to 10:1 (iodide:acetate). Copper hydroxyacetate was also added in a molar ratio of 1:1 to a solution containing sodium chlorate as described above to create a highly oxidizing environment (Figure 6).

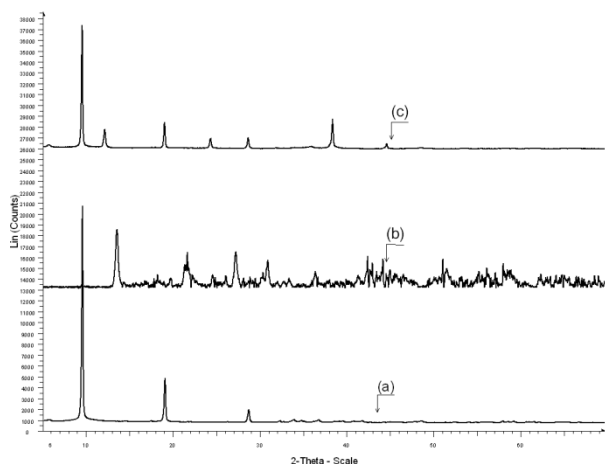


Figure 6 Powder XRD patterns of copper hydroxyacetate (a) exchanged with sodium iodide in a ratio of 1:10 (b) and exchanged with sodium chlorate in a ratio of 1:1

From the XRD pattern it can be seen that in a highly concentrated iodide solution, some loss of crystallinity is observed. An exchange does take place and the copper hydroxyiodide formed is stable past a 10:1 (anion:exchange material) molar ratio with no elemental iodine formed. The acetate layered material is also stable in high oxidizing conditions of the chlorate solution with a small amount of exchange taking place.

EXCHANGE CAPABILITIES OF $\text{Cu}_2(\text{OH})_3(\text{OAc})\cdot\text{H}_2\text{O}$

It has been shown that copper hydroxyacetate is a suitable material when immobilizing iodide however other anionic species likely need attention include IO_3^- , IO_4^- , TcO_4^- , Cl^- , SbO_3^- and $\text{Cr}_2\text{O}_7^{2-}$. Exchange reactions involving the relevant sodium salts (ReO_4^- used as a surrogate for TcO_4^-) and copper hydroxyacetate were carried out as previously described (Figure 7).

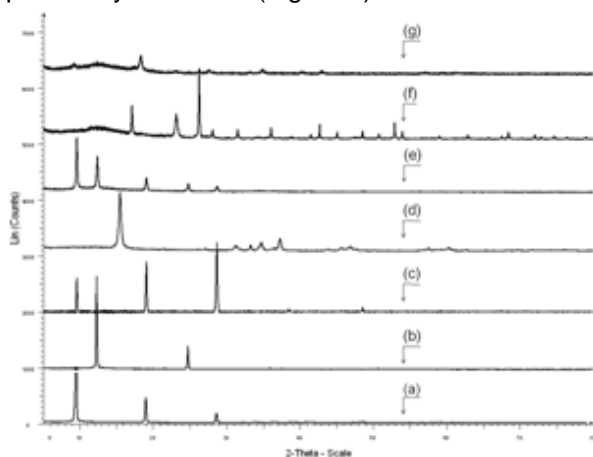


Figure 7 Powder XRD pattern of copper hydroxyacetate (a) exchanged with sodium periodate (b), sodium iodate (c) sodium chloride (d), sodium antimonite (e), potassium perrhenate (f) and sodium dichromate (g)

After 1 hour exposure to the various sodium salts, from the XRD patterns it can be seen that a shift in the d_{001} reflection occurs in reactions with IO_4^- , Cl^- , SbO_3^- and ReO_4^- indicating an exchange has taken place. The shift of the d_{001} reflection to a higher 2θ

angle in all exchanged products represents a reduction in the interlayer spacing and interestingly the positions of the d_{001} reflection for periodate and antimonite are at similar 2θ angles indicating both anions are of similar size. Remnants of the starting material are present in exchange with SbO_3^- , however this is expected due to the poor solubility of sodium antimonate. Despite the occurrence of $\text{Cu}_2(\text{OH})_3(\text{IO}_3)$ in nature, exchanges with iodate have proved unsuccessful. A possible reason for this inhibited migration of the iodate anion into the gallery spacing is the stereoactive lone pair of electrons present in the pyramidal shape. This electron rich lone pair may inhibit the ability of the iodate anion to enter the negatively charged interlayer spacing. Exchange reactions with $\text{Cr}_2\text{O}_7^{2-}$ degraded the starting acetate material. The divalent dichromate anion causes decomposition of the structure and the formation of copper(II) oxide. It should be noted however that in the presence of other monovalent anions, no degradation takes place and the dichromate anion takes no part in a reaction.

POLYMORPHIC PROPERTIES OF $\text{Cu}_2(\text{OH})_3(\text{Cl})$

The exchange reaction with chloride formed a layered material named botallackite that is also found in nature. Botallackite is polymorphous with two other minerals named clinoatacamite and atacamite⁹. Previous synthetic attempts to form botallackite have shown it to be unstable and readily converts to clinoatacamite¹⁰. In this study however, botallackite formed via an exchange reaction is stable in a variety of conditions. Conversion to clinoatacamite can be achieved via treatment in a sonicating bath at 30°C for 30 mins (Figure 8).

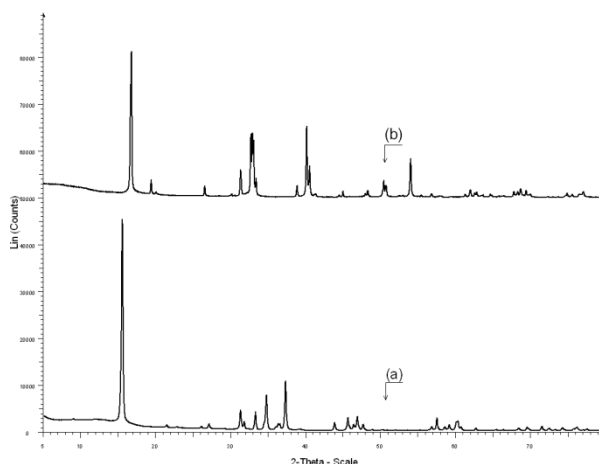


Figure 8 Powder XRD pattern of botallackite (a) and clinoatacamite (b) after treatment in a sonicating bath

Clinoatacamite is the most stable polymorph of the $\text{Cu}_2(\text{OH})_3\text{Cl}$ series and is not prone to anion exchange due to a non-layered structure. This polymorphism has only been observed in copper hydroxychlorides however conversions to a non-layered more stable material may be possible in other exchange products such as $\text{Cu}_2(\text{OH})_3\text{I}$, $\text{Cu}_2(\text{OH})_3\text{IO}_4$, $\text{Cu}_2(\text{OH})_3\text{SbO}_3$ and $\text{Cu}_2(\text{OH})\text{TcO}_4$.

CONCLUSION

Layered hydroxysalts have potential as ion exchangers for anions containing radioactive species such as iodine. This study has shown that using large exchangeable anions such as acetate allows reactions with iodide to occur in less than 10 mins and results are reproducible. The exchange material is not stable past 100°C as previous studies have shown however this study indicates that copper hydroxyacetate and its exchanged analogues are stable in solutions of high anionic strength and oxidizing conditions. Exchanges with other anions likely to be of interest to the radiochemical industry include periodate, chloride, antimonite and perrhenate (Rh used as a surrogate for Tc) have been successful. Using XRD to analyze the products formed give a qualitative result to whether an exchange has occurred however quantitative analysis is also need. Several methods may be used including an ion specific probe, radioactive tracing and ICP analysis. A stable sample of layered copper hydroxychloride (botallackite) has been formed despite previously being described as unstable. Conversion of botallackite into a more stable and un-layered polymorph named clinoatacamite has been achieved via treatment in a sonicating bath. This method may be applicable to other layered exchanged materials.

REFERENCES

- 1 D. W. Bruce and D. O'Hare, *Inorganic Materials*, Wiley Chichester, 1997
- 2 E. Kandare and J. M. Hossenlopp, *Inorg. Chem.*, **45**, 3766 (2006)
- 3 S. P. Newman and W. Jones, *J. Solid State Chem.*, **148**, 26 (1999)
- 4 S. Miyata, *Clays Clay Miner.*, **31**, 305 (1983)
- 5 D. C. Pereira, D. L. A. de Faria and V. R. L. Constantino, *J. Braz. Chem. Soc.*, **17**, 1651 (2006)
- 6 M. Meyn, K. Beneke and C. Lagaly, *Inorg. Chem.*, **32**, 1209 (1993)
- 7 J. T. Rajamathi, S. Britto and M. Rajamathi, *J. Chem. Sci.*, **117**, 629 (2005)
- 8 S. P. Newman and W. Jones, *J. Solid State Chem.*, **148**, 26 (1999)
- 9 R. L. Frost, W. Martens, J. T. Kloprogge and P. A. Williams, *J. RAMAN Spec.*, **33**, 801 (2002)
- 10 F. C. Hawthorne, *Mineralo. Magazine*, **49**, 87 (1985)