Metal Ammonium Phosphates Ion Exchangers for the Remediation of Low-Level Nuclear Wastes

Alistair F. Holdsworth,[1,2]* Harry Eccles,[1]* and Gary Bond[1]

1) Research Centre for Smart Materials, Faculty of Science & Technology, University of Central Lancashire, Fylde Road, Preston, United Kingdom, PR1 2HE.
2) Now at the School of Chemical Engineering & Analytical Science, University of Manchester, Oxford Road, Manchester, United Kingdom, UK, M13 9PL.
* Corresponding Authors: Alistair.Holdsworth@manchester.ac.uk; HEccles@uclan.ac.uk

Abstract: The nuclear industry generates large volumes of liquid wastes during decommissioning and decontamination activities which require extensive clean-up for recycle and/or disposal. The disposal of spent ion exchange materials used to clean these decontamination liquors is challenging and costly for the nuclear industry due to problematic end-of-life handling and low capacities of these materials for most radionuclides. Certain mixed-metal phosphates could be advantageous in this role due to their inherent vitrification properties and potentially high capacities for cationic and/or anionic radionuclides. Similar ammonium-based ion exchangers like the caesium-selective ammonium phosphomolybdate (AMP) are well known in the nuclear industry, but outside of this, such materials remain largely unexplored for this purpose. In this publication, we assess several metal ammonium phosphates (MAPs) and related compounds prepared using a continuous flow technique for their ability to act as ion exchangers for the remediation of surrogate radionuclides from a model decontamination solution, and discuss their possible implementation for the cleanup of low-level nuclear wastes.

Keywords: ion exchange, nuclear waste, remediation, decontamination, decommissioning, ammonium phosphates, metal phosphates, metal ammonium phosphates, ammonium metal phosphates, surrogate radionuclides.

1: Introduction

Decommissioning and decontamination are integral to the nuclear fuel cycle. Over the next few decades, these will increase significantly as many reactors and associated facilities reach the end of their useful lives.[1] Decontamination processes during decommissioning operations serves as a means of re-categorising nuclear wastes to lower levels, reducing disposal costs.[2,3] Surfaces are typically decontaminated with large volumes of various aqueous solutions which are become contaminated with radionuclides,[2,3] amongst other reagents.[4] Concentration of the dilute radioactive species in these liquid wastes onto a much smaller volume of solid adsorbent allows for recycling. Regardless of nature, these adsorbents then require disposal, a factor which remains a challenge to this day.[2,3] In this publication, we undertake an initial assessment of several inorganic mixed-metal phosphate adsorbents with potentially high capacities for radionuclides in the remediation of such decontamination solutions and with a promising end-of-life disposal strategy to address these challenges.

Struvite-K ($KMgPO_4.6H_2O$) and some calcium phosphates can sequester Cs^+ from aqueous solutions,[5,6] forming stable, insoluble ceramics upon calcination,[7] though to our knowledge this has never been extended to other target ions. Compounds of the form $AMPO_4$ are readily prepared at scale from low-cost reagents,[8-11] have very high theoretical capacities (856 mg/g Cs^+ uptake on MgAP, summarised in **Table 1**) and similar systems have demonstrable vitrification properties for disposal.[2,12-14] This facile preparation contrasts with zirconium, titanium and titanyl phosphates ($M(HPO_4)_2$ or NH_4TiOPO_4), well-known layered adsorbents normally prepared using inefficient batch hydrothermal methods.[15,16] The well-characterised ammonium phosphomolybdate (AMP), a highly-selective adsorber of Cs^+ ions from acidic solutions, is believed to function by ion exchange using NH_4^+ ions, though H^+ exchange has been reported for other phosphate adsorbents.[15] Several of our previous publications have explored the use of AMP for, heterogeneous isolation of Cs^+ in reprocessing flowsheets, granting a direct recovery and disposal route to this energetic fission product, which could mitigate many of the challenges within the recycling of spent fuel.[17-20] For decontamination purposes however, selectivity is unnecessary, rather an ability to absorb a wide range of radionuclide contaminants is often preferred.[21]

We previously demonstrated[22] an efficient, scalable continuous flow synthesis method[23] for the quantitative preparation of metal ammonium phosphates (MAPs) and related compounds with a small particle sizes (< 24 μm), narrow size distributions, and high surface areas (up to 50 m^2/g, see **Table 1**). This publication presents a cursory investigation into the potential of six MAPs (MgAP, MnAP, FeAP, CoAP, NiAP, ZnAP) and one hydrogen phosphate (SnHP) in adsorbing five ions from a model spent decontamination liquor: Cs^+, Sr^{2+}, Zr^{4+}, Ce^{4+} and MoO_4^{2-}. Here, Ce is present as a surrogate for U and other polyvalent ions that may be present in such liquors.[21]

2: Experimental

2.1 Materials

The adsorbents (MgAP, MnAP, FeAP, CoAP, NiAP, ZnAP, and SnHP) were synthesised and characterised as described previously.[22] All powders were dried overnight at 80 °C before testing. Analar grade caesium nitrate, strontium nitrate, ceric ammonium nitrate, zirconyl nitrate, sodium molybdate, and nitric acid were acquired from Fisher Scientific or Sigma-Aldrich and used as procured. Deionised water (> 18 MΩ/cm) was used for all experiments. The model decontamination liquor was made from 1000 ppm stock solutions of Cs^+, Sr^{2+}, Zr^4, Ce^{4+} and MoO_4^{2-}. The molybdate stock solution was acidified to pH 6 with nitric acid before use to convert to the protonated form. The model solution contained 4 ppm Cs^+ and Zr^{4+}, 2.7 ppm Sr^{2+} and Mo (as MoO_4^{2-}, 2.7 ppm Mo) and 49 ppm Ce^{4+}, with a recorded pH of 3.3.

2.2 Batch and Time-Dependent Adsorption Studies

Batch adsorption studies were conducted using 50 ml of the model liquor and 0.25 g of adsorbent. Samples were agitated at 180 rpm (Julabo SW ZZ) at 25 °C with an aliquot taken after 24 h. These were diluted with 1% nitric acid and analysed using ICP-OES (Thermo-Scientific iCAP 7000) and ICP-MS (Thermo-Electron X-Series) for
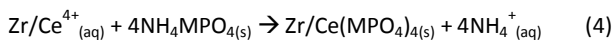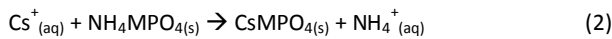
metals content to determine uptake, with appropriate multi-standard calibrations performed before analysis. The pH of the test solution was measured pre- and post-equilibration. Duplicate results were within experimental error (+/- 2%). Time-dependent adsorptions to determine rates of uptake were analysed in the same manner with aliquots taken after 0.5, 1, and 2 h. Distribution coefficients (k_d values, in ml/g) were calculated according to **Equation 1**, where C_0 and C_e are the initial and equilibrium liquor concentrations respectively, V is the volume of liquor (ml), and m is the mass of adsorbent (g) utilised in the experiment.

$$k_d = (C_0 - C_e)/C_e.V/m \qquad (1)$$

MAP	Formula	MW	Theoretical capacity (mg/g)					BET	PSD
		g/mol	Sr^{2+}	Zr^{4+}	Mo^{VI}	Cs^+	Ce^{4+}	(m^2/g)	(μm)
MgAP	$MgNH_4PO_4.H_2O$	155.33	282	147	309	856	226	15.7	13.6
MnAP	$MnNH_4PO_4.H_2O$	185.96	236	123	258	715	188	4.6	22.8
FeAP	$FeNH_4PO_4.H_2O$	186.87	234	122	257	711	187	49.8	9.5
CoAP	$CoNH_4PO_4.H_2O$	189.96	231	120	253	700	184	6.5	23.5
NiAP	$NiNH_4PO_4.6H_2O$	279.79	157	82	171	475	125	9.5	7.7
ZnAP	$ZnNH_4PO_4$	178.41	246	128	269	745	196	3.6	9.7
SnHP	$SnHPO_4$	214.69	204	106	223	619	163	4.7	6.5

Table 1: Theoretical capacities of the candidate adsorbents (accounting for MW and the above stoichiometry), alongside BET surface areas and particle sizes previously reported.[22]

The adsorption of the cations from the model liquor onto the tested adsorbents are believed to occur via exchange with ammonium ions as for AMP,[17-20] with the exception of SnHP, where H^+ ions are exchanged instead. The behaviour of molybdate (MoO_4^{2-}) may lie more in adsorption rather than true ion exchange,[25] but the chemical nature of these interactions is beyond the scope of this initial study. The exchange of the higher valence ions is, in theory, more favourable entropically (**Equations 2-4**)[26] as driven by the displacement of greater numbers of ammonium ions and both inner and outer sphere waters of hydration, and likely energetically via binding of oxophilic ions such as Zr^{4+} with phosphate. Additionally, the theoretical capacities for the polyvalent ions are lower,[26] although hydrolysis reduces the effective charge which can affect otherwise unlikely adsorption process.[21,27-29] **Table 1** summarises the theoretical capacities of the seven candidate adsorbents alongside some previously recorded physiochemical properties.[22]

$$Cs^+_{(aq)} + NH_4MPO_{4(s)} \rightarrow CsMPO_{4(s)} + NH_4^+_{(aq)} \qquad (2)$$

$$Sr^{2+}_{(aq)} + 2NH_4MPO_{4(s)} \rightarrow Sr(MPO_4)_{2(s)} + 2NH_4^+_{(aq)} \qquad (3)$$

$$Zr/Ce^{4+}_{(aq)} + 4NH_4MPO_{4(s)} \rightarrow Zr/Ce(MPO_4)_{4(s)} + 4NH_4^+_{(aq)} \qquad (4)$$

3.2: Batch Adsorptions

The 24 h distribution coefficients of the five ions in the model liquor onto our seven adsorbent compounds are presented graphically in **Figure 1**. The highest k_d values after 24 h were observed for Ce^{4+} and Zr^{4+}, followed by Sr^{2+}, and finally Cs^+. This demonstrates a decreasing

3: Results and Discussion

3.1: General Observations and Proposed Mechanisms of Action

The seven adsorbents were exposed to the model liquor containing the five metals for 24 h with aliquots taken after this period to determine adsorption and/or ion exchange performance. The initial, slightly acidic pH of the model liquor (3.3), results from the partial hydrolysis of the small, highly charged ions present.[24] The pH of the model liquor increases to a neutral equilibrium value of between 7 and 8 within 5 minutes of the addition of the MAP adsorbents and maintains this throughout the duration of exposure, though the slightly acidic conditions are maintained with SnHP.

trend in the affinity of each target ion for our adsorbents with decreasing charge density. The behaviour of Mo^{VI} is intermediate, likely due to the variable and different chemistry between this species and the other metals tested.

FeAP shows poor adsorption of Zr, Mo and Cs from the model liquor. This corresponded with a colour change from the initial dark green of the starting material to off-white after 24 h. This likely results from the oxidation of Fe^{2+} to Fe^{3+}, forming ferric phosphate. The observed adsorption of Sr^{2+} and Cs^+ possibly arise from formation of mixed-metal phosphates,[6] though further analysis would be required to confirm this. The performance of FeAP before oxidation remains unquantified.

Both MgAP and NiAP can interconvert between mono- and hexahydrated derivatives via hydrolysis and dehydration respectively, as per **Equation 5**, with speciation of these two compounds dependent on temperature, concentration, and a multitude of other factors.[30,31] The 24 h adsorptions of Sr^{2+}, Zr^{4+} and Mo^{VI} onto MgAP and NiAP are similar, although the MgAP affinities for Cs^+ and Ce^{4+} are higher.

$$MgNH_4PO_4.H_2O_{(s)} + 5H_2O_{(l)} \longleftrightarrow MgNH_4PO_4.6H_2O_{(s)} \qquad (5)$$
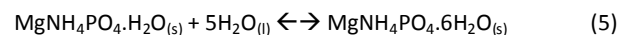
As previously stated, we believe SnHP functions via exchange of H^+ ions instead of NH_4^+ as for the MAPs, meaning the lower pH of the model liquor is maintained after 24 h. This likely explains the observed increase in Mo^{VI} absorption after 24 h, alongside the increased Zr^{4+} affinity.
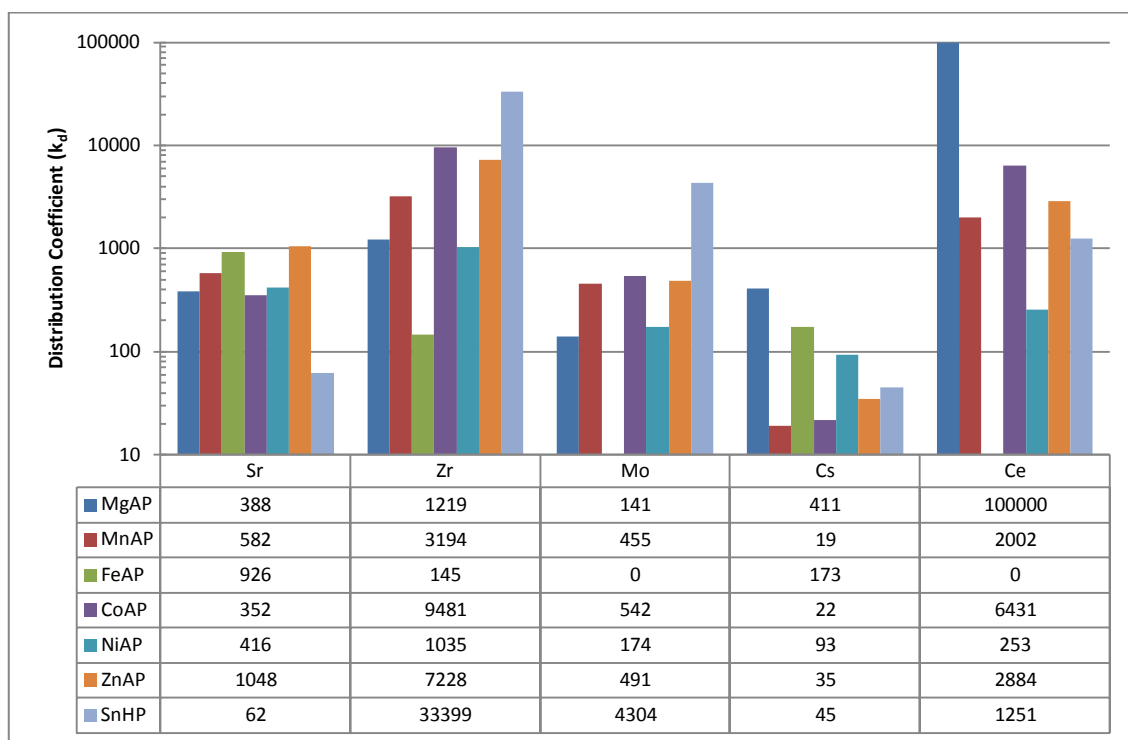
Figure 1: Distribution coefficients of the five elements in the model liquor on the seven tested adsorbents after 24 h. The MgAP uptake of Ce (100%) was given an arbitrary value of 100 000 for graphical purposes.

3.3: Rate of Adsorption

In order to assess the rate of metal ion adsorption from the model liquor onto our adsorbents, ZnAP was selected for further study, with aliquots taken after 30 mins, 1 hour, and 2 hours of exposure and analysed in the same manner as the batch experiments above. This data is presented in **Figure 2** below, expressed as percentage of each metal ion adsorbed, demonstrating that adsorption is rapid, attaining high levels within 30 minutes of exposure, though some equilibration occurs beyond this time.[21,32] This suggests that the kinetics of adsorption or exchange for this class of compound are rapid for most of the cations in the model liquor, with the exception of Cs^+ and Sr^{2+}.
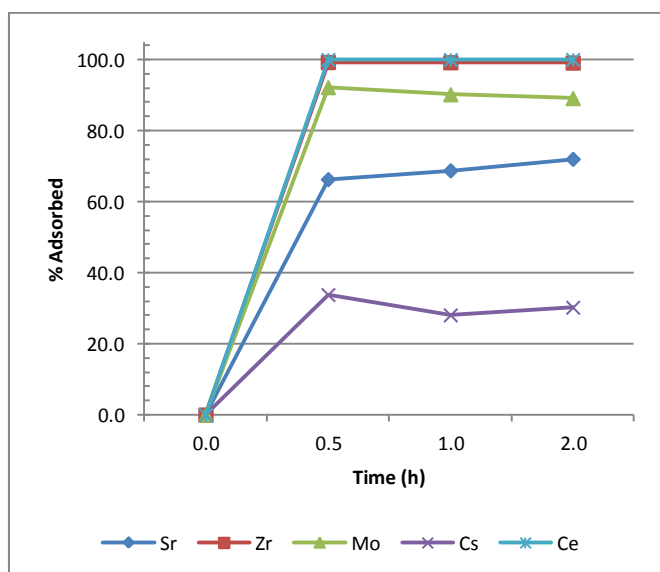

Figure 2: Variation in adsorption (as % of total metal ion on solid) from model liquor onto ZnAP with time.

4: Discussion and Conclusion

The results presented have demonstrated the efficacy of some MAPs and related compounds to chemically adsorb several problematic species from a model decontamination liquor containing five such elements in varying concentrations. This work was conducted as an initial screening study to identify the most promising candidate(s) for further study, and as such only the multi-element solution was analysed, rather than separate single-ion uptake measurements.

As stated in the introduction, these materials are of interest as a potential immobilisation matrix for adsorbed radionuclides with the addition of an appropriate flux; MAPs decompose upon heating to form ceramic pyrophosphates, as per **Equation 6**,[31] which allows for formation of an insoluble glassy wasteform.[13,14]

$$2NH_4MPO_4.nH_2O_{(s)} \rightarrow M_2P_2O_{7(s)} + 2NH_{3(g)} + (n+1)H_2O_{(g)} \qquad (6)$$
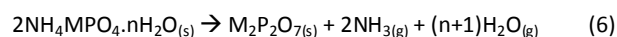
We have presented promising uptakes of Zr, Mo, and Ce from our model liquor by the majority of the candidate adsorbents tested, along with demonstrable rapid kinetics of adsorption as initial observations in the presented scoping study. Several variations in adsorbent chemistry can be attributed to several chemical factors[21,30-32] which will be explored further in subsequent publications.

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