Effective Media* for Immobilising and Isolating Radionuclides from Aqueous Nuclear Wastes: Reaction Products of Bone Char and Uranyl Ions

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ABSTRACT

The reaction of uranyl ions with bone char under a variety of laboratory conditions leads to products (e.g. uranium modified bone char) that are effective in incorporating and retaining radionuclides. The products are highly insoluble and are compositionally analogous to natural uranium-bearing minerals found in the supergene environment. A calcium uranium oxyhydroxide, similar to becquerelite is produced when bone char reacts with uranyl ions at elevated temperatures and pressures under mildly acidic conditions (pH~4). Under more acidic conditions (pH~3), a compound similar to phosphuranylite forms whilst in the presence of excess phosphate, a compound similar to chernikovite is produced. Radiotracer studies show the various products incorporate a wide range of elements including Am, Cd, Ce, Co, Cs, Eu, Mn, Pd, Pu, Ru, Sm, Sn, Tc, Y, Zn and Zr. Four uptake mechanisms are inferred to occur and vary according to the element. These are ionic substitution into the uranyl compound or hydroxyapatite and surface adsorption onto hydroxyapaptite or carbon. This makes the modified bone char materials generally applicable for the adsorption of a wide range of diverse species. Once incorporated/adsorbed, the radionuclides are not readily leached under neutral or mildly acidic conditions thereby providing a stable solid phase. The wide range of elemental species adsorbed / incorporated into the UMBC, the relative ease of producing these compounds and their stability indicates that there is considerable potential for the application of this material in the isolation of radionuclides from aqueous nuclear waste streams and the stabilisation of these wastes during storage and disposal. Possible long-term storage options could include packaging of the dried phosphatic powders, grouting with cement, or incorporation into phosphatic or borosilicate glass.

INTRODUCTION

Bone char is a long established product generated by the carbonisation of sun-dried animal bones at 500 - 700°C in the absence of oxygen. The material consists primarily of apatite (probably a

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* *Patent Applied For*

hydroxyapatite) and approximately 10% elemental carbon with some carbonate arising from the formation of CaO during the ashing process and subsequent reaction with atmospheric CO_2. The material has found applications in the sugar and water purification industries as a cost effective and efficient means of decolourising sugar liquors and in removing trace impurities. The material has been shown to have a high adsorption capacity for a wide range of inorganic and organic contaminants including heavy metals such as Cd, Cu and Zn (Wilson *et al*, 2003; Choy *et al*, 2004; Choy & McKay 2005a, 2005b) where maximum sorption capacities of up to 0.477, 0.709 and 0.505 mmol/g respectively have been reported. Bone char has also been investigated for the removal of Sb and Eu radioisotopes from radioactive wastes (Abdel Raouf & Daifullah, 1997). Hydroxyapatite is known to react with uranyl ions to produce stable uranium phosphates. Natural phosphates such as apatite and monazite are stable over geological timescales and studies of the durability of such phosphates have been used to assess their potential value as long term radionuclide immobilisation media (Ewing, 2001). Synthetic phosphates have been extensively investigated for immobilisation of nuclear wastes prior to disposal in deep geological repositories due to the stability of many of their compounds.

In this study, the reaction of uranyl ions with bone char under a range of conditions was investigated as well as the identification of the uranium products and potential mechanisms for their formation. Also assessed was the incorporation of other radionuclides typical of nuclear wastes into the uranium compounds, the adsorption of these radionuclides directly onto bone char and the stability of the resulting materials. The formation of the uranium compounds via reaction with bone char immobilises many other radionuclides present in the reaction mixture through incorporation within the U phosphate. Such a process, coupled with the ability for bone char to adsorb a wide range of contaminants, would provide a cost effective approach for the isolation of both uranium and associated radionuclides from aqueous nuclear waste streams as well as effectively immobilising the radionuclides prior to long term storage / disposal.

METHODOLOGY

The bone char (fines) used in all experiments was supplied by Brimac Services Ltd. The starting material consisted of the fine black powder with >90% of the powder <400 μm which comprises 70–76% hydroxyapatite, 7–9% $CaCO_3$ and 9–11% carbon. Seven tests were carried out using a range of treatments to study the interaction of radionuclide or stable elements solutions with bone char.

- **Raw Bone Char only**

- **Carbon-free bone char only:** Carbon-free bone char was prepared by igniting the original bone char at 600°C for two days in an air atmosphere to produce a white solid. During ignition, the material lost approximately 14 wt% through the loss of carbon

- **Uranium modified bone char (UMBC$_s$)** was prepared by mixing uranyl acetate solution with the raw fine bone char powder. During the initial characterisation stages, the mass ratio of U : Bone char was varied from 0.2 to 1.5 to determine the optimum U loading on the bone char. Subsequently the U : Bone char mass ratio was fixed at 0.35. The pH of the reaction mixture was typically 4-5.

- **Uranium modified bone char (P-UMBC)** Preparation of uranium modified bone char was also performed in the presence of excess phosphate to produce (0.24 g of Na_2HPO_4 (0.0017 moles PO_4) were added to a mixture of bone char and uranyl acetate prior to heating).

- **Acid washed bone char + U acetate (UMBC$_{H+}$);** This material was prepared after removal of the carbonate fraction from the bone char.

- **Carbon-free uranium modified bone char (UMBC$_{ig}$)** was prepared using the above procedure but replacing bone char with ignited bone char in the reaction mixture.

- **Uranium modified bone char (H-UMBC$_s$)** was prepared by reacting raw bone char + U acetate under acidic conditions.

In element uptake experiments, trace concentrations of stable elements and / or radionuclides were added to the reaction mixture prior to heating with the total concentration not exceeding 0.007mmol / g bone char. The pH of the reaction mixture was adjusted to 4.5 using sodium hydroxide and an acetate buffer. Unless otherwise stated, the mixture was heated under pressure in a sealed high pressure microwave digestion vessel (CEM MDS 2000 oven and UDV vessels) to the desired temperature / pressure for a specified time. In one experiment, the mixture was heated in a PTFE beaker in a water bath to 90°C at atmospheric pressure to investigate the rate of reaction at lower temperatures and atmospheric pressures. On completion of the test preparation, the mixture was allowed to cool and the solution carefully decanted off the solid and filtered through a Whatman 40 filter paper. The solid was rinsed and dried overnight under an IR-lamp and then weighed to determine the quantity of material produced. Uranium loadings were determined by measuring the proportion of uranium that remained in the filtrate using high resolution gamma spectrometric measurement of the ^{235}U 186 keV gamma line. Identification of the compounds present in the solid phase was performed using X-ray powder diffraction analysis. The solid phase was ground and loaded into a holder. X-ray diffraction analysis of the ground solid was performed using a Panalytical X'pert Pro system using Fe-filtered Co K_α line and operating at 35 kV and 35mA.

In initial trials, a mixture of gamma emitting radionuclides containing ^{241}Am, ^{109}Cd, ^{57}Co, ^{60}Co, ^{137}Cs, ^{54}Mn, ^{88}Y and ^{65}Zn along with the alpha emitting radionuclide ^{239}Pu was added to the reaction mixture prior to heating. After heating, the mixture was filtered and the quantity of gamma emitting radionuclides present in the filtrate determined by HPGe gamma spectrometry. The ^{239}Pu content of the filtrate was then determined following ion exchange purification using alpha spectrometry. In later trials, a mixture of gamma emitting radionuclides and stable elements were included with the reaction mixture. The range of species were chosen to reflect the radionuclides (including activation products, fission products and actinides produced via neutron capture by ^{235}U or ^{238}U) typically present in nuclear wastes and which contribute significantly to the radiological impact of the wastes during long term repository disposal. After heating and filtration, the proportion of the species remaining in solution was determined using gamma spectrometry, alpha spectrometry or ICPMS. During the leaching tests the labelled UMBC and P-UMBC were leached using 0.1M HCl, 0.25M NaOH or deionised water. In addition, labelled bone char, UMBC$_{ig}$, H-UMBC and ignited UMBC were leached with water. Approximately 0.2g of sample was leached with 20ml of leachate for 4 days at 70°C in a water

bath. The mixture was then filtered through a 0.45µm membrane filter and the quantity of species leached was determined using either gamma spectrometry or ICPMS.

RESULTS AND DISCUSSION

Uranium Loading Capacities, Effect of Temperature/Pressure/Time, Effect of Degassing
In all cases where the reaction was performed in water the solid produced via the reaction of uranyl acetate with bone char settled at the bottom of the reaction vessel and was readily separated from the aqueous phase. The product appeared blue-grey in colour but turned black on grinding. SEM imaging showed that the uranium was present as a surface covering on the bone char. On ignition, the sample turned yellow brown with a loss in mass of 14% (dry / ignited ratio = 1.16). Increasing the mass of uranyl acetate relative to the bone char in the reaction mixture resulted in a lighter material although again, the colour reverted to the black of the original bone char on grinding. The efficiency of uranium incorporation into the solid phase was dependent on the pressure/ temperature conditions for the preparation. At 90°C and atmospheric pressure the % U incorporated was only 58% but this increased to 96% when the reaction was performed at 170°C. The reaction time at this temperature appeared relatively fast with 94% incorporation of U being achieved after only 20 minutes. Although U incorporation appeared to be inefficient at atmospheric pressures (with only 58% of the uranium incorporated into the solid phase after 60 minutes at 90°C), increasing the pressure led to a 97% uptake of U after 7 days. The use of sealed vessels at elevated temperatures clearly accelerates the reactions. Quantitative incorporation of uranium in the solid phase was observed for uranium loadings between 0.2 and 0.9 gU/g bone char. Above this concentration, the uranium loading in the solid phase remained constant giving a maximum U loading of *ca* 1.2g U/g bone char equivalent to 5 mmol/g bone char. U loading capacities were improved by degassing the bone char prior to performing the reaction (Table 4). Loading capacity was significantly reduced to 63% on using ignited bone char (using a 0.35g U /g bone char ratio) suggesting that either the carbon plays an important role in the reaction or that those other components within the bone char had been altered during the heating process. The introduction of additional phosphate resulted in 100% uptake of U at the same U / bone char loading.

Composition of Product
X-ray diffraction of the product showed that the main uranium compound in UMBC produced under the standard conditions was equivalent to a uranium oxyhydroxide called becquerelite, $Ca(UO_2)_6O_4(OH)_6 \cdot 8H_2O$. There appeared to be no significant difference between the compounds produced at atmospheric and elevated pressures. Ignition of the UMBC (containing becquerelite) resulted in the formation of a uranium oxide $UO_{2.5}$. When the preparation was performed under acidic conditions, a fine material was formed which remained suspended in the aqueous phase. XRD analysis of the bulk H-UMBC and the fine material gave similar reflectance spectra consistent with phosphuranylite, $Ca(UO_2)_3(PO_4)_2(OH)_2 \cdot 6H_2O$ along with a low intensity reflection at 10.3Å possibly indicating low levels of autunite. The lack of fluorescence under long wave UV light confirmed that autunite was not a significant component of the product. In the presence of phosphate (P-UMBC), the uranium phosphate, chernikovite $(UO_2HPO_4)(H_2O)_4$, was produced. Fluorescence of the product under long wave UV light was consistent with chernikovite (Van Haverbeke *et al*, 1996).

Incorporation of Trace Elements

Uptake of radionuclides on untreated bone char was generally high with > 95% Am, Cd, Co, Mn, rare earth elements, Sn, Th, Y Zn and Zr being adsorbed by the bone char. Uptake of Tc and Ru were lower at 71% and 79% respectively whilst only 29% of ^{137}Cs was adsorbed. Uptake of ^{99}Tc and ^{137}Cs was even lower on ignited bone char. Incorporation of radionuclides in the UMBC tended to be comparable with adsorption onto bone char alone with the exception of ^{99m}Tc and ^{137}Cs (see Table I). For ^{137}Cs the uptake efficiency increased to 88% when bone char was replaced with UMBC. Technetium-99m uptake appeared to decline slightly to 62%. Plutonium-239 was also efficiently incorporated into the UMBC with >99% of Pu being removed from solution. Acid-washing the bone char prior to preparing the UMBC$_{H+}$ did not affect the uptake efficiency of any elements studied. When the reaction was performed under acidic conditions, the uptake efficiency for both ^{99m}Tc and ^{137}Cs increased to > 90% although the uptake of ^{54}Mn and ^{109}Cd fell slightly to *ca* 80%. When phosphate was added to the reaction mixture, the uptake of all radionuclides was >90%. For UMBC$_{ig}$, a reduction in uptake efficiencies for ^{54}Mn, ^{60}Co and ^{65}Zn was observed, with efficiencies declining to 71, 56 and 85% respectively. However, the lowest uptake efficiency of 7% was observed for ^{99m}Tc. The enhanced uptake of Cs on UMBC (containing becquerelite), H-UMBC (containing phosphuranylite) and P-UMBC (containing chernikovite) compared with bone char alone suggests that incorporation of Cs in the becquerelite, phosphuranylite and chernikovite is the dominant uptake mechanism. The lack of enhanced uptake of Tc as Tc(VII) on UMBC suggests that incorporation of the pertechnetate anion into becquerelite is not significant and is in agreement with Chen *et al* (2000) who concluded that substitution of TcO$_4^-$ into such compounds would result in underbonding at the U^{6+} site and destabilise the crystal structure. However, given this observation, the enhanced uptake of TcO$_4^-$ in the presence of chernikovite is unexpected and warrants further investigation.

Leachability of Trace Elements and U

The leachability of a range of elements from bone char, UMBC (prepared from untreated, acid-washed and ignited bone char), P-UMBC and ignited UMBC using 1% HCl, 1% NaOH and water was investigated (see Table II). The final pH of the solutions varied depending on the solid being leached and the leaching agent. Leaching of both UMBC and P-UMBC with 0.1M HCl resulted in a leachate with a final pH of 1.6. Leaching of the same materials with either water or 0.25M NaOH resulted in a leachate pH between 6 and 7. Similar pHs were observed in leachates of UMBC prepared from acid-washed bone char (UMBC$_{H+}$) and ignited bone char (UMBC$_{ig}$). However, higher pHs of 8–9 were observed for water leachates of bone char and ignited UMBC. No significant leaching of elements was observed from bone char or UMBC variants at neutral to alkaline pHs for all elements with the exception of Tc. At pH 8.8, 21% of Tc was leached from ignited UMBC whilst 8% of the Tc was leached from bone char at similar pHs. Leaching of Tc from ignited UMBC suggests that the loss of carbon reduces the ability of the material to retain Tc and is consistent with the proposed role that carbon plays in the initial uptake of Tc. The low leachability of Cs in the presence of Na is unexpected given the proposed uptake mechanism of ion exchange into the interlayers of the uranium minerals. Burns (1999) suggested that such uptake mechanisms would be reversible and would lead to the release of incorporated Cs with time. Such a release is not apparent in this work and may suggest that the Cs is more irreversibly retained in the UMBC. At pH 1.6, significant leaching (40 – 92%) of Cs, Mn, Co, Zn, Cd, Ce, Sm, Eu and Am was observed. Zr was also leached but to a lesser extent, with only 1% and 8%

of the Zr being leached from the UMBC and P-UMBC respectively. Leaching of U was lower even under acidic conditions with 5 – 7% being dissolved.

Table I. Percentage Incorporation of Elements into Various Products

Test	Description	pH	Alkali Metal	Transition metals									p-block	Lanthanides			Actinides		
			Cs	Mn	Co	Zn	Y	Zr	Tc	Ru	Pd	Cd	Sn	Ce	Sm	Eu	Th	Pu	Am
31	Bone char only	9.1	29	100	100	100	100	100	71	79	96	100	100	100	100	100	100	n.m.	100
36	Ignited bone char only	7.1	7	100	100	100	100	100	30	100	100	100	100	100	100	100	100	n.m.	99
27	Bone char + U acetate (UMBC)	4.7	88	95	98	99	100	100	73	98	100	100	100	100	100	100	100	> 99	100
28	Bone char + U acetate + phosphate (P-UMBC)	4.9	95	97	99	100	100	100	94	92	100	100	100	100	100	100	100	n.m.	100
29	Acid washed bone char + U acetate (UMBC$_{H+}$)	4.2	91	90	96	97	100	100	70	100	100	100	100	100	100	100	100	n.m.	99
30	Ignited bone char + U acetate (UMBC$_{ig}$)	4.6	91	71	56	85	100	100	31	92	97	100	100	100	100	100	100	n.m.	100
32	Bone char + U acetate under acidic conditions (H-UMBC)	4.0	99	82	94	91	100	100	46	100	100	77	100	100	100	100	100	n.m.	99

All results are expressed as % of element removed from original solution onto the solid phase
pH refers to the final pH of the solution after reaction;   n.m.   not measured

Table II. Leaching of Elements from Various Products under a Range of Conditions

Test	Description	Leachate	pH	Alkali metal	Transition metals								p-block	Lanthanides			Actinides		
				Cs	Mn	Co	Zn	Zr	Tc	Ru	Pd	Cd	Sn	Ce	Sm	Eu	Th	U	Am
27	Bone char + U acetate (UMBC)	water	6.4	2	< 5	< 1	< 5	< 5	< 2	< 10	< 2	< 5	< 10	< 1	< 1	< 1	< 5	< 1	< 1
		1% HCl	1.6	73	87	53	73	1	< 2	< 10	< 2	92	< 10	76	49	63	< 5	7	57
		1% NaOH	5.9	2	5	2	7	< 5	< 2	< 10	< 2	4	< 10	< 1	< 1	< 1	< 5	< 1	< 1
27 ig	ignited UMBC	water	8.8	< 1	< 5	< 1	< 5	< 5	21	< 10	< 2	< 5	< 10	< 1	< 1	< 1	< 5	< 1	< 1
28	Bone char + U acetate + phosphate (P-UMBC)	water	7.4	1	< 5	< 1	< 5	< 5	3	< 10	< 2	< 5	< 10	< 1	< 1	< 1	< 5	< 1	< 1
		1% HCl	1.6	75	81	53	81	8	< 2	< 10	< 2	90	< 10	56	27	45	< 5	5	48
		1% NaOH	6.1	4	< 5	< 1	< 5	< 5	4	< 10	< 2	< 5	< 10	< 1	< 1	< 1	< 5	< 1	< 1
29	Acid washed bone char + U acetate (UMBC$_{H+}$)	water	6.5	< 1	< 5	< 1	< 5	< 5	< 2	< 10	< 2	< 5	< 10	< 1	< 1	< 1	< 5	< 1	< 1
30	Ignited bone char + U acetate (UMBC$_{ig}$)	water	6.2	< 1	< 5	< 1	< 5	< 5	< 2	< 10	< 2	< 5	< 10	< 1	< 1	< 1	< 5	< 1	< 1
31	Bone char only	water	8.3	< 1	< 5	< 1	< 5	< 5	8	< 10	< 2	< 5	< 10	< 1	< 1	< 1	< 5	N/A	< 1
32	Bone char + U acetate prepared under acidic conditions (H-UMBC)	water	5.9	< 1	< 5	< 1	< 5	< 5	< 2	< 10	< 2	< 5	< 10	< 1	< 1	< 1	< 5	< 1	< 1

N/A – not applicable; All results refer to the percentage of element leached relative to the amount loaded onto the solid

CONCLUSIONS

Reaction of uranyl ions with fine bone char at pH 4-5 and elevated temperatures and pressures results in the formation of a compound analogous to the natural mineral becquerelite. Under more acidic conditions, leaching of phosphate from the hydroxyapatite results in the formation of phosphuranylite whilst the addition of excess phosphate produces chernikovite. The U loading capacity of the bone char was high with up to 0.9gU/g bone char.

Quantitative uptake of elements on both raw and ignited bone char was found for Mn, Co, Zn, Y, Zr, Pd, Cd, rare earths, Th and Am indicating that these elements will adsorb to the hydroxyapatite component of the char. Tc was adsorbed quantitatively to bone char but not to ignited bone char showing that carbon is important in the uptake of this element. Cs was not adsorbed efficiently to either bone char or ignited bone char but was quantitatively retained in the UMBC variants indicating incorporation of this element into the uranium compound. For most elements, there was no significant difference between the uptake observed for UMBC or P-UMBC although for Tc, the uptake efficiency was higher on P-UMBC. It is therefore apparent that a range of mechanisms control the uptake of elements onto UMBC and are responsible for the wide range of species that may be extracted. The results also demonstrate the superiority of UMBC over raw bone char or hydroxyapatite in the non-selective retention of waste radionuclides.

The leachability of U and other elements was low from bone char and UMBC variants at pH 5–8. Leaching of Cs, Mn, Co, Zn, Cd, rare earths and Am was observed under more acidic conditions with little difference being observed between the UMBC and P-UMBC implying that the presence of phosphates did not reduce the leachability at this pH. However, even under acidic conditions, the proportion of U leached was low (~7%).

The wide range of species adsorbed / incorporated into the UMBC, the relative ease of producing these compounds and their stability indicates that there is considerable potential for the application of this material in the isolation of radionuclides from aqueous nuclear waste streams and the stabilisation of these wastes during storage and disposal. Possible long-term storage options could include packaging of the dried phosphatic powders, grouting with cement, or incorporation into phosphatic or borosilicate glass.

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