Release of uranium from candidate wasteforms

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ABSTRACT

Large volumes of depleted natural and low-enriched uranium exist in the UK waste inventory. This work reports on initial investigations of the leaching performance of candidate glass and cement encapsulation matrices containing UO_3 powder as well as that of uranium oxide powders. The surface areas of UO_3 powder and the monolith samples of UO_3 conditioned in the glass and cement matrices were very different making leaching comparisons difficult. The results showed that for both types of monolith conditioned samples a steady increase of uranium concentration in solution with time was generally not observed. The wt.% of uranium leached from UO_3 conditioned in the lead borosilicate glass wasteform was approximately five orders of magnitude less than that leached from UO_3 powder. Similarly, the quantities of uranium leached from UO_3 conditioned in composite cement made with ordinary Portland cement, and from magnesium phosphate cement, were approximately four and three orders of magnitude, respectively, less than that leached from UO_3 powder. The performance of a mixed oxide borosilicate glass wasteform was only slightly better than that of UO_3 powder. This work shows that wasteforms based on encapsulation in lead borosilicate glass and cement matrices have the greatest potential for further development.

Introduction

THE large volumes of depleted natural and low-enriched uranium (DNLEU) in the UK waste inventory make the evolution of uranium wasteforms a high priority area of research for the Nuclear Decommissioning Authority (NDA) Radioactive Waste Management Directorate (RWMD) (Nuclear Decommissioning Authority *et al.*, 2008). To address this issue, the NDA has started an integrated programme of work on uranics of which the information detailed here is part. Having previously identified gaps in the knowledge associated with the performance of candidate wasteforms in a repository environment, the leaching performance of selected glass and cement matrices containing UO_3 has been assessed. This has allowed identification of the

binding matrices that exhibit the most potential for further development as encapsulants for current uranium waste streams. Due to the low radioactivity of the uranium wastes in question, glass and cement matrices are being considered as waste encapsulants. The use of cementitious matrices for encapsulation of these uranium wastes may produce durable wasteforms in which the mobility of the radionuclides is low, and is likely to offer processing advantages such as ease of wasteform production in comparison to glass binding matrices.

Samples and experimental

The majority of the uranic material used in the test wasteforms was UO_3, which was made by fluidized bed thermal denitration of uranyl nitrate liquor. Two glass encapsulation matrices were tested; a mixed alkali borosilicate glass referred to here as MWAZ-glass, and a lead borosilicate glass referred to here as Pb-glass. It should be

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noted that the term encapsulation refers to physically surrounding the waste in a glass matrix rather than using the conventional high level waste (HLW) vitrification process where radionuclides are dissolved into the glass and are chemically immobilized by substitution into the glass structure. Although very low leach rates have been observed from uranium dissolved in borosilicate matrices (Peeler *et al.*, 2011), the waste loading is limited by the solubility in the glass, and high melting temperatures are required (>1000ºC). Hence, by using encapsulation it was hoped that higher waste loadings and easier processing conditions could be achieved. The composition of the two glass encapsulants used were (1) MWAZ glass,(57.2 wt.% SiO_2, 20.3 wt.% B_2O_3, 10.1 wt.% Na_2O, 4.6 wt.% Li_2O, 3.5 wt.% Al_2O_3 and 4.3 wt.% ZnO); and (2) Pb-glass, (10.4 wt.% SiO_2, 10.2 wt.% B_2O_3, 0.7 wt.% Al_2O_3 and 78.7 wt.% PbO). The UO_3 content of the glass wasteforms was varied to investigate waste loadings and in some cases UO_3 was pre-converted to U_3O_8 to attempt to prevent the formation of large voids in the hardened glass matrix due to the release of oxygen from the decomposition of UO_3 at the temperatures required for glass melting. The effect of the pre-conversion to U_3O_8 was assessed by leaching glass samples made with the converted U_3O_8 and comparing the results. The glass samples were fabricated by weighing out the required amounts of UO_3 and glass powder and mixing them using a Retsch Mixer-Mill MM301. The resultant glass powder mixtures were then loaded into small ($22 \times 12 \times 12$ mm) alumina boats, placed in a furnace, heated up to the required temperature (varying between 750 and 1050ºC), sintered/melted for approximately 3 to 4 hours, and cooled to room temperature.

Three cement formulations were tested. These were a 3:1 composite of blast furnace slag (BFS):ordinary Portland cement (OPC) and a 3:1 composite of pulverized fuel ash (PFA):OPC, with these samples made at water:cement solids ratios of 0.35 and 0.45, respectively. The OPC, BFS and PFA powders were all produced to a Sellafield Ltd (SL) specification and were all provided by SL. A magnesium phosphate cement, referred to as MPC, was also tested. This MPC paste was made with a water:solids ratio of 0.3 and the composition and mix ratios were (1) 1.5:1 (molar ratio) $MgO:KH_2PO_4$; (2) 50 wt.% PFA of $MgO + KH_2PO_4 +$ water; and (3) 1.8 wt.% boric acid (H_3BO_3) of MgO +

KH_2PO_4 + water. The MgO, KH_2PO_4 and boric acid were all commercially available products. The UO_3 loadings used for the BFS:OPC, PFA:OPC and MPC systems were 28.85±0.95, 24.70±2.30 and 29.65±0.85 wt.% of the hardened cement paste, respectively. The cement samples were prepared by adding the required quantity of U directly to the required quantity of cement paste that had been pre-mixed in a modified small-scale mixer, and mixing the final product until a homogenous paste was produced. All cement samples contained no additives (such as superplasticizers). Samples of UO_3, U_3O_8 and UO_2 powders were also tested.

The leach test used was the Materials Characterization Centre Test 1 (MCC-1, Test Matrix B) (ASTM, 1998) carried out over 28 days at 90ºC but modified to additionally test the cement samples at 40ºC. All samples were leached in deionized water held in perfluoroalkoxy-polymer screw-lidded jars. All 90ºC samples were held in a heating oven in air whereas the cement samples tested at 40ºC were held in a water bath. All 28 day samples were tested in triplicate. The leachate solutions obtained were analysed for U concentration using inductively coupled plasma mass spectroscopy (ICP-MS).

Some of the unleached samples and samples leached for 28 days were analysed using scanning electron microscopy/energy-dispersive spectroscopy (SEM/EDX) to investigate homogeneity, microstructural characteristics and to investigate any surface alteration layers formed on the leached samples. A large quantity of SEM/EDX data was obtained, but only those representative of the principal results are reported here.

Results and discussion

In this study, the range of different sample types, different sample preparation techniques and the presence of significantly different amounts of porosity in the samples analysed meant that any analysis of leach test data that used the geometrical surface area would be highly questionable. Due to these problems with surface area, the monolith samples are referred to herein as being 'conditioned' samples of UO_x contained within the glass and cement matrices. Assessment of the quantity of U leached from the samples under similar test conditions (wt.%) has been used to enable a comparison to be made across the sample range.

TABLE 1. Data for UO_x powder samples (after 28 days leaching).

Oxide type	Quantity of U leached (wt.%)
UO_3	1.47−0.55
UO_2	0.0888−0.0927
U_3O_8	0.0621−0.066

Oxide powders

The majority of UO_2 and U_3O_8 particles were in the range 0.3−20 µm, whereas the UO_3 had the majority of particles in the 20−300 µm range. The leaching data for the oxide powders is shown in Table 1. The results for UO_2 and U_3O_8 were very similar with the quantity of U leached ranging from approximately 0.062 to 0.093 wt.%. However, the wt.% leached after 28 days from the sample of UO_3 was approximately an order of magnitude higher than for UO_2 and U_3O_8.

UO_x conditioned in glass matrices

The SEM/EDX analysis of the unleached glass samples showed that, despite there being a significant number of spherical voids caused by bubbles of air trapped in the samples during the consolidation process and/or as a result of decomposition of the uranium trioxide, the Pb-glass matrix appeared to wet the surface of the UO_x particles better than the MWAZ-glass. This analysis also showed that a separate phase containing U, Pb, Si and O formed on the surface of the uranium oxide particles during fabrication, when heated with the Pb-glass. This has potentially important implications for the durability of the wasteform as it is this phase that will first come into contact with the leachate when the encapsulant glass dissolves away.

The leach test results for the glass samples showed that a steady increase in U-concentration in solution with time was generally not observed for most of the samples. The leachate analysis results did not show any definite saturation effects and the data obtained were very irregular with lots of 'excursions' or outlying data points making it impossible to fit a straight line or report any trends. However, using the values of wt.% leached after 28 days (Table 2) shows that the principle of using a glass encapsulant as a conditioning matrix for UO_x powder to reduce the exposed surface area is a feasible process. Note that for some samples, outlying points were not included in the ranges shown in Table 2. The quantity of U released from the conditioned glass samples is generally several orders of magnitude lower than that leached from the unconditioned UO_x powder. The study clearly showed that the choice of glass binder material is key to producing a wasteform with the required properties, with the Pb-glass having significantly lower releases than the MWAZ-glass. This may be due to the

TABLE 2. Data for UO_x glass samples (after 28 days leaching).

UO_x:Glass ratio	Glass type	UO_x type	Glass melt temp. (ºC)	Quantity of U leached (wt.%)
50:50	MWAZ-glass	UO_3	550	0.090−0.097
60:40	MWAZ-glass	UO_3	550	0.17−0.23
75:25	MWAZ-glass	UO_3	850	0.42−0.50
40:60	MWAZ-glass	UO_3	550	0.28−0.32
50:50	MWAZ-glass	U_3O_8	550	$0.0163-0.0164^{\dagger}$
50:50	Pb-glass	U_3O_8	550	$5.0-9.0 \times 10^{-6\ddagger}$
40:60	Pb-glass	UO_3	500	$3.4-12.0 \times 10^{-5}$
25:75	Pb-glass	UO_3	500	$1.5-8.5 \times 10^{-5\S}$
100:0*	n/a	UO_3	n/a	1.1−1.6

* A test to establish leach rates for unencapsulated UO_3 powder.
[†] Not including the outlying point of 0.484 wt.%.
[‡] Not including the outlying point of 3.52×10^{-4} wt.%.
[§] Not including the outlying point of 1.5×10^{-3} wt.%.
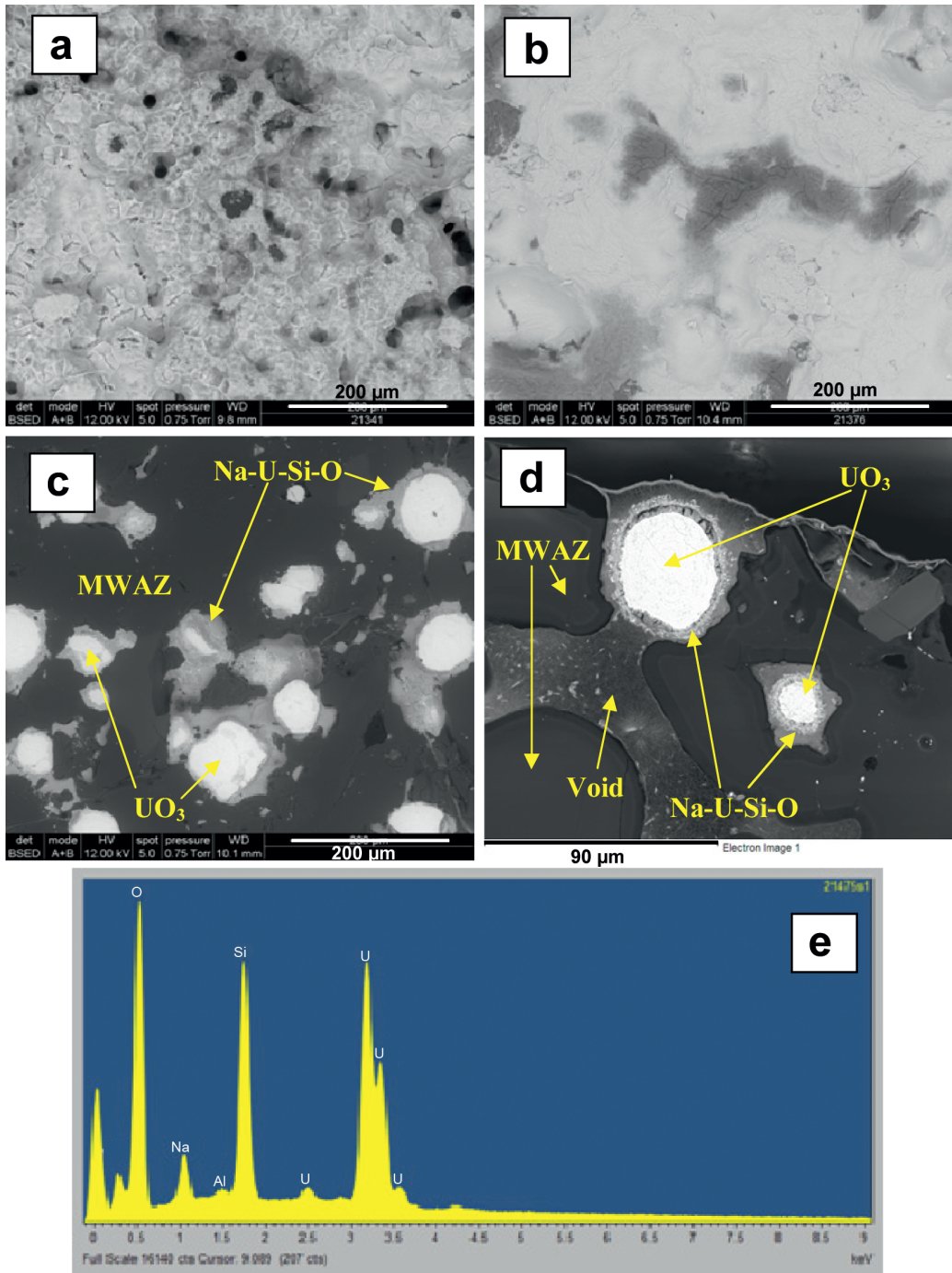
FIG. 1. Scanning electron microscopy (SEM) backscattered-electron images of the 28 day leached 50:50 UO_3:MWAZ (550ºC glass melting temperature) glass; (*a*) top surface, (*b*) cut surface, (*c*) mounted cross-section, (*d*) mounted cross-section at edge of sample and (*e*) energy-dispersive spectroscopy (EDS) trace representative of the white phase on the sample surface and of the alteration phase surrounding the UO_3 particles.

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inhibition of aqueous dissolution by the U-Pb-silicate phase that forms on the surface of the UO_x powder during fabrication.

Analysis of the leached samples by SEM/EDX showed that both the MWAZ-glass and Pb-glass samples contained significant void space. However, although the Pb-glass samples contained these voids and/or bubbles, it was apparent from the SEM images that these were not connected and hence would not allow significant liquid percolation through the samples. The MWAZ-glass samples, on the other hand, had voids surrounding the UO_3 particles, which appeared to be linked. The leached MWAZ-glass samples contained extensive U-bearing alteration phases on the sample surface and within the voids surrounding the UO_3 particles. These are illustrated in Fig. 1. Figure 1a,b clearly shows the presence of a significant amount of alteration phase on the surface of the MWAZ-glass as fibrous white material. Analysis by EDX (Fig. 1e) showed that the white material contained mainly U, Si, Na and O, indicating that a sodium-uranium silicate phase had formed at the surface. The cross-section image in Fig. 1c showed that water had penetrated into the sample through the voids surrounding the UO_3 particles resulting in the formation of an alteration phase within the voids. The EDX analysis showed that this phase contained mainly U, Si, Na and O, and was therefore likely to be the same phase as observed on the surface of the sample. The image in Fig. 1d shows a cross-section of a UO_3 particle at the leached surface of the sample. Four distinct areas are present: the MWAZ glass matrix, the UO_3 particles, a Na-U-Si-O alteration layer surrounding the UO_3 particles, and a series of connected 'voids' where the encapsulation is incomplete.

The SEM analysis of the Pb-glass leached wasteforms is shown in Fig. 2, which shows SEM backscattered-electron images of the 28-day leached as-cut surface of the 50:50 U_3O_8:Pb glass sample fabricated at 550ºC at various magnifications, plus a cross-section image of the edge of the sample. At low magnifications, the surface of the Pb-glass sample shown in Fig. 2 appears to be relatively unaltered by leaching, but at higher magnification there is evidence of some alteration, with the presence of some platelet-like material on the glass surface. The SEM image of the sample edge (bottom right image in Fig. 2) clearly shows an alteration layer ~1 μm thick that has a slightly lower backscatter contrast than the bulk. The EDX traces in Fig. 2 suggest that this may be caused by a Pb deficiency and slight enrichment in Si compared to the surrounding glass. This fine platelet material appears to be associated with the glass rather than the U_3O_8 phase and was found on the surface all of the UO_x-Pb glass samples.

UO_3 conditioned in cement matrices

As with the samples of UO_x conditioned in glass matrices, a steady increase in U-concentration with duration was not generally observed for the samples conditioned in cement and it was not therefore possible to calculate the release rate of uranium. However, the quantity of uranium leached from the cement conditioned samples after 28 days (Table 3) varied by up to two orders of magnitude across the three cement systems. The highest quantity of uranium was leached from the MPC and didn't appear to be temperature or time dependant. The data obtained also suggested that there were no trends associated with leaching temperature. Although not considered here, when interpreting the results obtained in further detail, the effect of the conditions of encapsulation (such as paste pH and Eh) on uranium solubility should be assessed.

TABLE 3. Data for UO_3 cement samples (after 28 days leaching).

Cement system	Leaching temperature (ºC)	Quantity of U leached (wt.%)
BFS:OPC	40	$3.20-3.73 \times 10^{-4}$
BFS:OPC	90	$1.78-4.15 \times 10^{-4}$
PFA:OPC	40	$1.80-2.08 \times 10^{-4}$
PFA:OPC	90	$2.74-4.24 \times 10^{-5}$
MPC	40	$1.11-1.19 \times 10^{-3}$
MPC	90	$1.24-1.40 \times 10^{-3}$

There was little difference in the general distribution and appearance of the uranium-bearing phases in the cement conditioned samples leached at either 40 or 90ºC when analysed by SEM/EDX, and there were no visual indications that the leached samples had started to soften or disintegrate at the leaching temperatures used.

The microstructural appearance and distribution of uranium in each type of sample was similar and there appeared to be no significant difference in distribution specific to any of the three types of systems studied or specific to whether each sample had been subject to leaching. No observable movement of uranium was seen in these samples suggesting that the release of uranium into solution was from the external faces of the monoliths. The areas of uranium were generally no larger than approximately 200 μm, and the appearance of these areas was similar for each type of hardened cement paste studied and for both the unleached and leached samples.

Many SEM images were obtained for each cement system, and those presented in Figs 3−5 have been chosen as being most representative.

The compositional information obtained from studying the EDX traces suggested the phase composition of each type of sample, as described in the following text.

(1) The BFS:OPC samples appeared to be primarily composed of a main matrix of calcium silicate hydrate (CSH) with embedded particles of unreacted BFS and areas of uranium-rich material.

(2) The samples of PFA:OPC appeared to be composed of a main matrix of CSH with embedded spheroidal particles of PFA and areas of uranium-rich material similar to those seen in the BFS:OPC samples.

(3) The MPC samples were mainly composed of a main matrix of magnesium potassium phosphate hydrate with embedded spheroidal particles of PFA and areas of uranium-rich material.

(4) For each type of cement conditioned sample the EDX traces obtained were very similar for both the unleached and leached samples.

Although high waste loadings of up to 75 wt.% UO_3 were incorporated into MWAZ-glass conditioned samples, the leaching performance of these samples was very poor in comparison to that of both the Pb-glass and cement conditioned wasteforms, with a difference of up to approximately five orders of magnitude. The quantity of uranium leached from UO_x conditioned in the MWAZ-glass was more comparable with that of the unencapsulated UO_3 powder than with the quantity leached from the Pb-glass and cement conditioned wasteforms, which could be due to the leachant having more access to the uranium in these samples. The quantity of uranium leached from the glass conditioned wasteforms containing U_3O_8 was approximately one order of magnitude less than that leached from the same samples containing UO_3 which indicates the effect that uranium oxidation state has on leachability. The quantity of uranium leached from the cement conditioned UO_3 was between approximately two to three orders of magnitude more than that leached from the Pb-glass conditioned samples but was still between three to four orders of magnitude less than that leached from the unencapsulated UO_3 powder. The quantity of uranium leached from the two samples of unencapsulated UO_3 powder tested at the same time as the glass and cement conditioned wasteforms were very similar showing consistency in the experimental procedure employed.

Conclusions

The quantity of uranium leached over 28 days from UO_x conditioned in glass and cement wasteforms, and from UO_3, UO_2 and U_3O_8 powders, has been measured experimentally. The main conclusions are as follows:
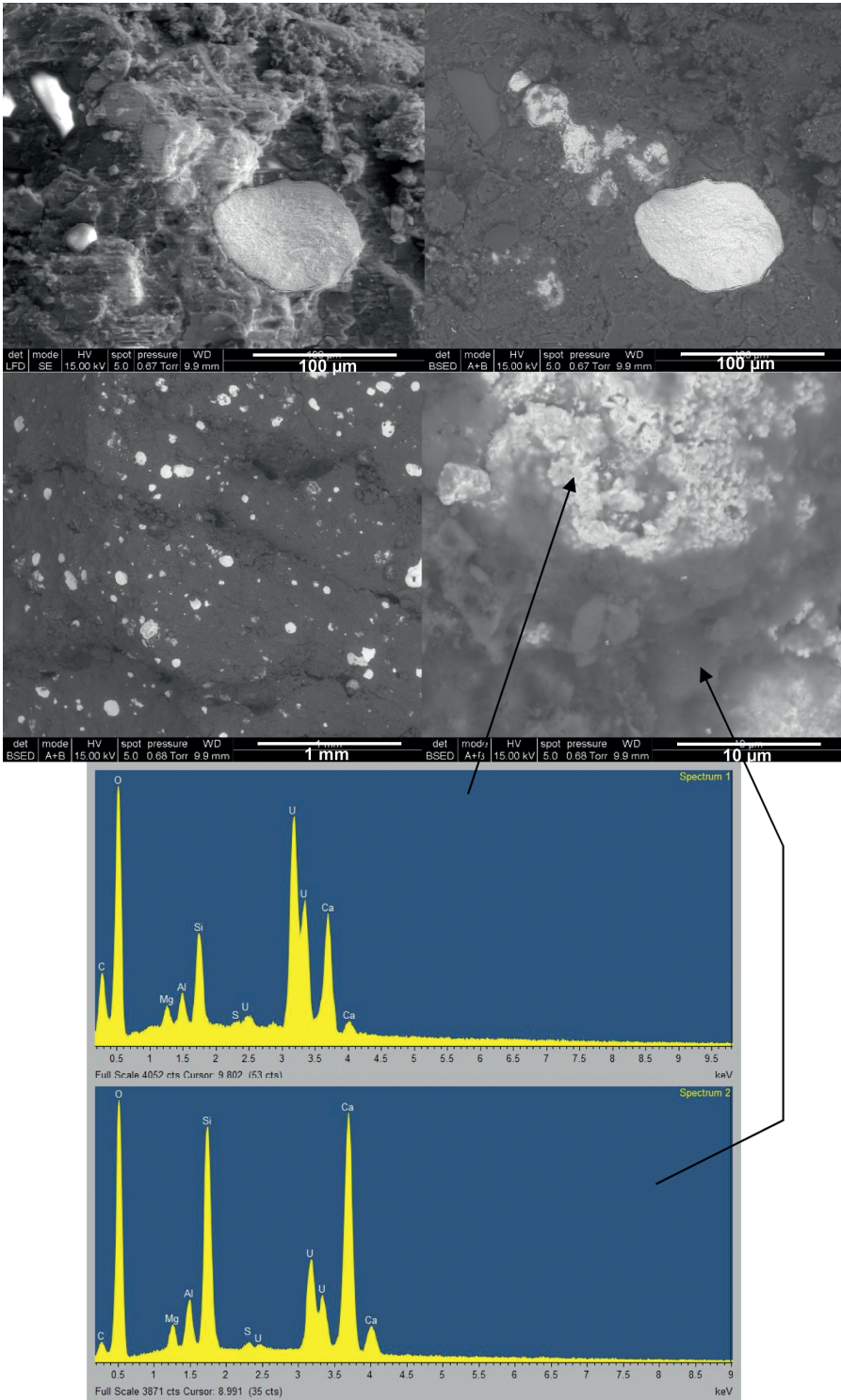
(1) The quantity leached from the UO_3 conditioned in lead borosilicate glass was approximately five orders of magnitude less than that leached from UO_3 powder.

(2) The quantity leached from UO_3 conditioned in wasteforms based on ordinary Portland cement was approximately four orders of magnitude less than that leached from UO_3 powder.

FIG. 2 (*facing page*). Scanning electron microscopy (SEM) backscattered-electron images and associated energy dispersive spectroscopy (EDS) traces of the 28-day leached as-cut surface of 50:50 U_3O_8:Pb (550ºC glass melting temperature) glass at various magnifications.
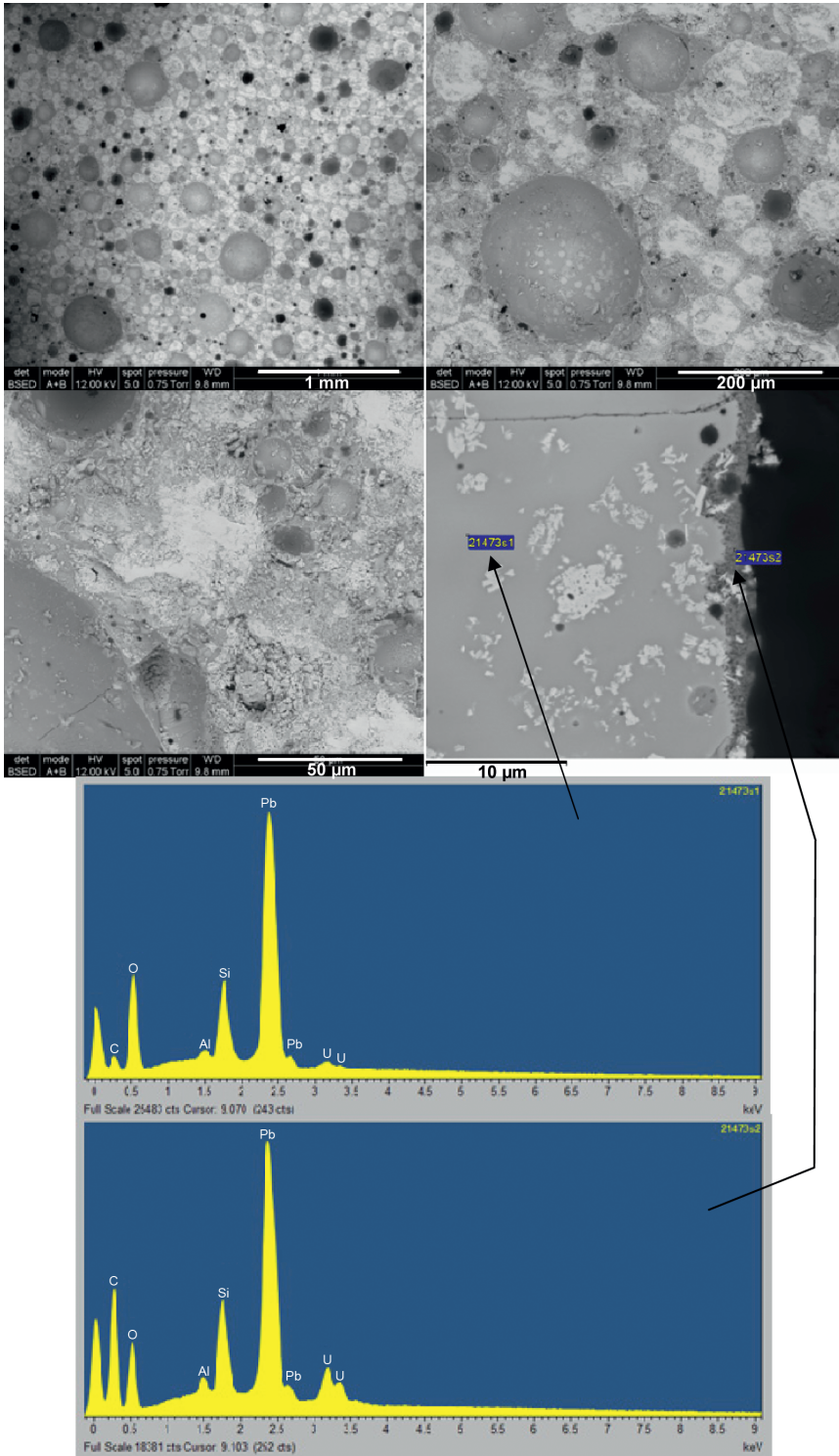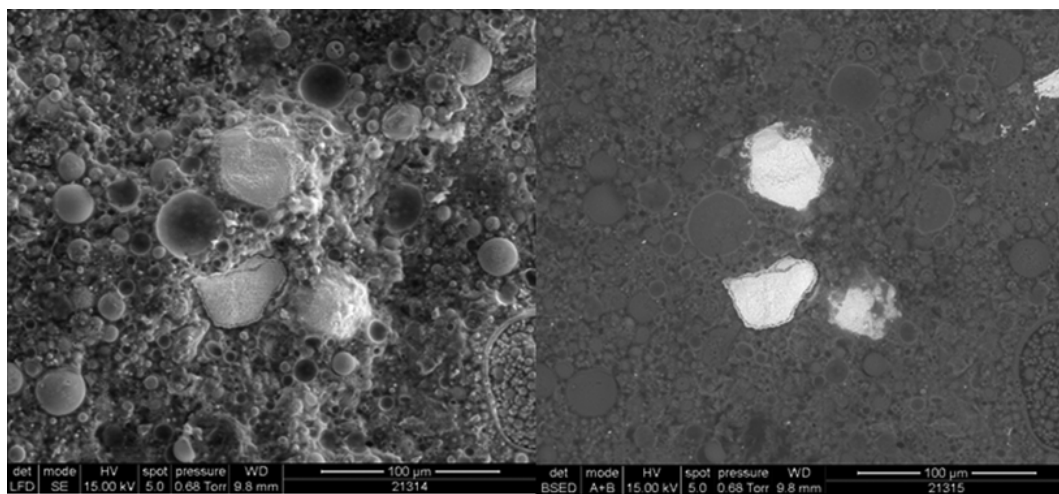
FIG. 4. Scanning electron microscopy (SEM) secondary-electron (left) and backscattered-electron (right) images of fractured surface of pulverized fuel ash:ordinary Portland cement paste (PFA:OPC) leached at 90ºC.
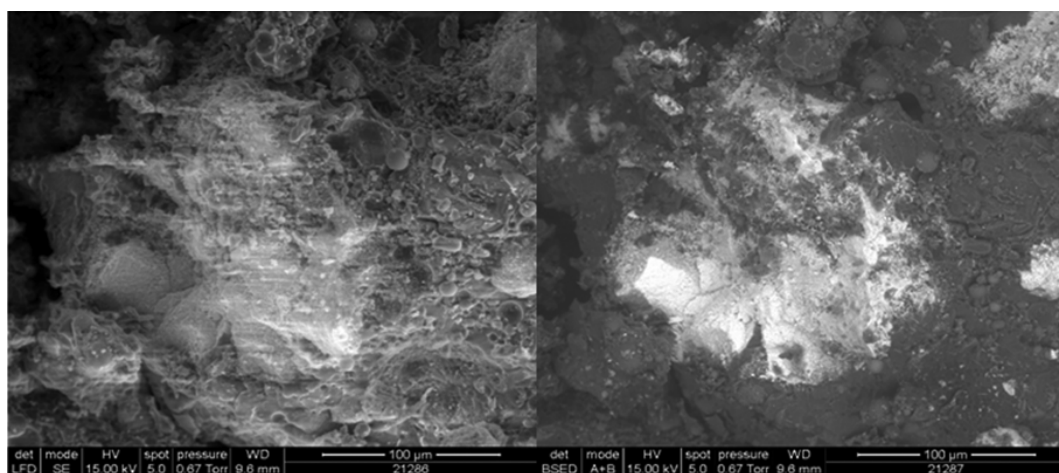

FIG. 5. Scanning electron microscopy (SEM) secondary-electron (left) and backscattered-electron (right) images of fractured surface of magnesium phosphate cement (MPC) paste leached at 40ºC.

(3) The quantity leached from UO_3 conditioned in the magnesium phosphate cement was approximately three orders of magnitude less than that leached from UO_3 powder.

(4) The quantity leached from UO_3 conditioned in the mixed oxide borosilicate glass was approximately one order of magnitude less than that leached from UO_3 powder.

(5) The quantity leached from UO_2 and U_3O_8 powders was approximately one and a half orders of magnitude less than that leached from UO_3 powder.

FIG. 3 (*facing page*). Scanning electron microscopy (SEM) secondary-electron (top left) and backscattered-electron (top right, bottom left and right) images and associated energy-dispersive spectroscopy (EDS) traces of fractured surfaces of blast furnace slag:ordinary Portland cement (BFS:OPC) paste leached at 90ºC.

(6) The quantity of uranium leached from the UO_3 conditioned in the cement matrices did not appear to be temperature dependant at 40 and 90°C over 28 days leaching. The distribution/appearance of uranium-rich areas was similar for all cement systems studied and leaching temperature appeared to have no effect on distribution.

(7) Differences in surface area characteristics and the presence of high porosity/voidage introduced a high degree of variability in the leach test results.

Acknowledgements

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