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Preliminary investigation of chlorine speciation in zirconolite glass-ceramics for plutonium residues by analysis of Cl K-edge XANES

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ABSTRACT

A zirconolite glass-ceramic material is a candidate wasteform for immobilisation of chlorine contaminated plutonium residues, in which plutonium and chlorine are partitioned to the zirconolite and aluminosilicate glass phase, respectively. A preliminary investigation of chlorine speciation was undertaken by analysis of Cl K-edge X-ray Absorption Near Edge Spectroscopy (XANES), to understand the incorporation mechanism. Cl was found to be speciated as the Cl⁻ anion within the glass phase, according to the characteristic chemical shift of the X-ray absorption edge. By comparison with Cl K-edge XANES data acquired from reference compounds, the local environment of the Cl⁻ anion is most closely approximated by the mineral marialite, in which Cl is co-ordinate to 4 x Na and/or Ca atoms.

INTRODUCTION

A significant fraction of the UK plutonium stockpile, predicted to reach 140 tons at the end of nuclear fuel reprocessing, is known to be unsuitable for reuse as (U,Pu)O₂ mixed oxide (MOX) nuclear fuel.¹⁻³ A zirconolite glass-ceramic wasteform is under development for the immobilisation and disposal of contaminated plutonium and plutonium residues as a waste.^{1,4-7} In this wasteform, the plutonium is targeted for immobilisation by solid solution in the zirconolite phase, for which there is high confidence in long term performance, given the evidence available from natural analogues and investigation of prototype and surrogate materials. The contaminants and impurities

are targeted for immobilisation within the accessory aluminosilicate glass phase, which should therefore have a high solubility for these elements. Some of the waste plutonium inventory is contaminated by chlorine resulting from degradation of the polyvinyl chloride (PVC) liner used within the can-in-can storage package.⁸ It is thought that thermal and radiation induced degradation of PVC resulted in the release of HCl which was subsequently adsorbed onto the surface of the PuO₂. Chlorine is known to have a low solubility in silicate glasses, typically < 3 wt%,⁹⁻¹¹ above which phase separation of a chloride salt (such as NaCl) is observed. Incorporation of Pu within such a salt, would afford a highly soluble instant release fraction, which would be a challenge to wasteform disposability. To address this issue, one approach is heat treatment of the plutonium waste prior to immobilisation, in order to volatilise the chloride contaminant. Alternatively, if there is confidence that the chlorine can be accommodated within the solubility limit of the glass phase, with sufficient head room, for the highest expected chlorine content, then heat treatment prior to immobilisation will not be required. The aim of this work, therefore, was to make a preliminary investigation of chlorine solubility and speciation in a baseline zirconolite glass-ceramic, comprising 30 wt% CaZrTi₂O₇-ceramic and 70wt% NaAlSi₃O₈-glass. Cl K-edge X-ray Absorption Spectroscopy was exploited to directly probe the speciation and local environment of Cl atoms, by analysis of the X-ray Absorption Near Edge Structure (XANES) and comparison with data from well characterised reference compounds. More generally, understanding the speciation and solubility of Cl in silicate glasses is an important consideration, since the incorporation of hydrosaline liquids in silicate melts at subduction zones is known to be of importance for the global chlorine cycle.¹⁰

EXPERIMENTAL

Zirconolite glass-ceramics were fabricated by hot isostatic pressing. Reagents (CaTiO₃, TiO₂, ZrO₂, Na₂SiO₃, Al₂O₃, SiO₂, NaCl) were batched to a target stoichiometry of 70 wt% CaZrTi₂O₇ ceramic and 30 wt% NaAlSi₃O₈ glass. The Cl concentration in the glass phase was targeted to be 0.3 – 2.5 wt% Cl, with replacement of 2 NaCl for Na₂O on a molar basis, such that the overall Na concentration remained constant. Reagent powders were milled at 500 rpm for 30 min in a planetary mill with heptane as the milling medium (in which NaCl is insoluble). Milled powders were calcined overnight at 600 °C and packed into stainless steel canisters (approximately 50 ml initial capacity). The canisters were evacuated at room temperature and baked-out at 300 °C before being welded closed. The HIP (Hot Isostatic Pressing) cycle applied a process temperature of 1250 °C for 4 h under 103 MPa of argon gas pressure, as previously described.⁵⁻⁷ The HIPped glass ceramics were characterised for phase assemblage, in particular for phase separation of chloride compounds, by powder X-ray diffraction (XRD: Bruker D2 Phaser, Ni filtered Cu K α radiation, and Lynxeye detector) and Scanning Electron Microscopy with Energy Dispersive X-ray analysis (SEM/EDX: Hitachi TM3030, Bruker Quantax 30 EDX system).

Cl K-edge XANES data from glass ceramics, and reference compounds, were acquired on Beamline 8 of the DELTA storage ring, Germany.¹² The configuration utilised a Si (111) double crystal monochromator and harmonic rejection mirror; the incident intensity ($I_0(E)$) was determined by electron yield utilising a gold grid electrode, the fluorescence yield ($I_f(E)$) was measured using a Canberra large area Passivated Implanted Planar Silicon (PIPS) detector. Measurements were performed in vacuum, using powdered samples and reference compounds ground to a fine powder, mixed with polyethylene glycol, and pressed into 10 mm diameter pellets. Reference compounds included: synthetic NaCl, CaCl₂, and CaCl₂·2H₂O; and the minerals marialite (Na₄Al₃Si₉O₂₄Cl),

sodalite ($\text{Na}_8\text{Al}_6\text{Si}_6\text{O}_{24}\text{Cl}_2$), and variant hackmanite. Specimens of sodalite (BM.1985,79) and marialite (BM.1971,216) were provided by the Natural History Museum, London, UK. All XANES data were dead time corrected and processed using the ATHENA software¹³ with standard background subtraction and normalisation procedures.

RESULTS AND DISCUSSION

Zirconolite glass-ceramics were initially characterized by powder XRD and SEM/EDX analysis.¹⁴ The phase assemblage was found to comprise zirconolite as the major phase, plus a minor glass phase, as demonstrated by the example microstructure presented in Fig. 1. Additionally, sphene (CaTiSiO_5), rutile (TiO_2), baddelyite (ZrO_2), and zircon (ZrSiO_4), were identified as trace accessory phases, as shown in Fig. 1. The phase assemblage did not change with chlorine content up to 0.9 wt% Cl, whereas for 1.7 wt% and 2.5 wt% Cl content, NaCl was apparent as an additional trace impurity phase in both XRD and SEM/EDX data. EDX analysis demonstrated Cl to be partitioned exclusively to the glass phase below a solubility limit of 0.9 ± 0.1 wt% Cl, well above the maximum envisaged chlorine incorporation rate of 0.4 wt. %. The determined solubility limit for Cl is within the range of 0.5 – 3.0 wt% reported for natural and synthetic silicate glasses, depending on composition and conditions of formation⁹⁻¹¹.

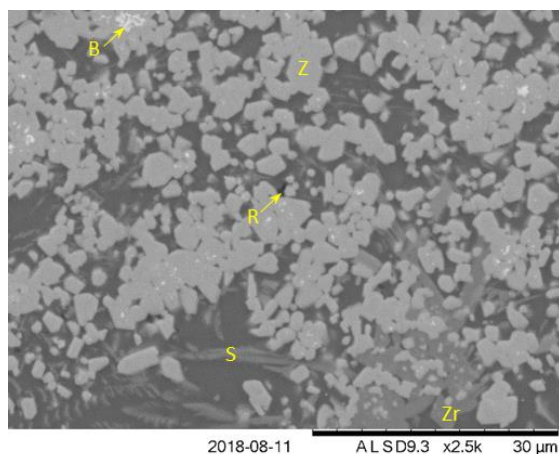


Figure 1: Microstructure (back scattered electron image) of zirconolite glass-ceramic (0.9 wt% Cl), comprising zirconolite (light grey; Z), ZrO_2 (white; B), TiO_2 (black; R), and CaTiSiO_5 and ZrSiO_4 (mid grey; S and Zr respectively).

Cl K-edge XANES data were acquired, in fluorescence mode, from the chloride reference compounds (Figures 2 and 3) and glass-ceramic materials (Figure 4), to understand the incorporation mechanism within the glass phase of the glass-ceramics. Figure 2 shows Cl K-edge XANES data for Na salts incorporating Cl in formal oxidation states Cl^{7+} (NaClO_4), Cl^{5+} (NaClO_3), Cl^{3+} (NaClO_2) and Cl^- (NaCl). In these compounds Cl is co-ordinated, respectively, to: 4 x oxygens in ClO_4^- tetrahedra; 3 x oxygens in ClO_3^- pyramids; 2 x oxygens in bent ClO_2^- units; and 6 x Na in an octahedral arrangement in NaCl .¹⁵ These Cl K-edge XANES data show increasing chemical shift of E_0 with oxidation state, relative to NaCl, of approximately +4 eV for NaClO_3 and +8 eV for NaClO_4 . In contrast, the E_0 of NaClO_2 is shifted approximately -1 eV relative to that of NaCl. Overall, these data and chemical shifts are in good agreement with those reported for the same compounds by McKeown *et al.*,¹¹ bearing in mind the different methodologies between the studies (note that McKeown *et al.* report their chemical shifts relative to $E_0 = 2823.5$

eV for CF_3Cl). Further comparison of the data of the reference compounds shown in Figure 2 with those previously reported, identified additional features in our data not reported by McKeown *et al.*¹¹ – highlighted by an asterisk. From comparison of the XANES data of the reference compounds it was inferred that the NaClO_4 sample was slightly contaminated by NaClO_3 and NaClO_2 , and NaClO_3 by NaClO_2 . It is believed that material was transferred between the samples as the vertical sample stack was translated between analyses.

All Cl K-edge XANES data acquired from reference compounds incorporating anionic Cl^- , and the glass-ceramic materials, shown in Figures 3 and 4 showed E_0 within a narrow range of $2827.4 - 2827.8 \pm 0.5$ eV, determined as the first peak in the first-derivative of the spectra, as summarized in Table 1. The common E_0 for the reference compounds and glass-ceramics implies a common chlorine speciation in all materials as the Cl^- anion, and the presence of oxidized Cl species can be confidently ruled out.

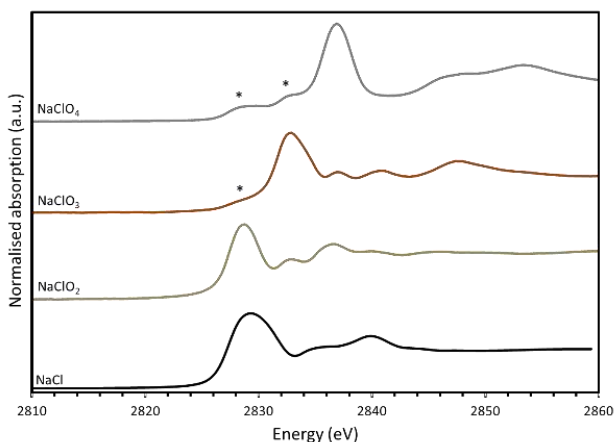


Figure 2: Cl K-edge XANES data of NaCl , NaClO_2 , NaClO_3 and NaClO_4 , incorporating Cl^- , Cl^{3+} , Cl^{5+} and Cl^{7+} species respectively.

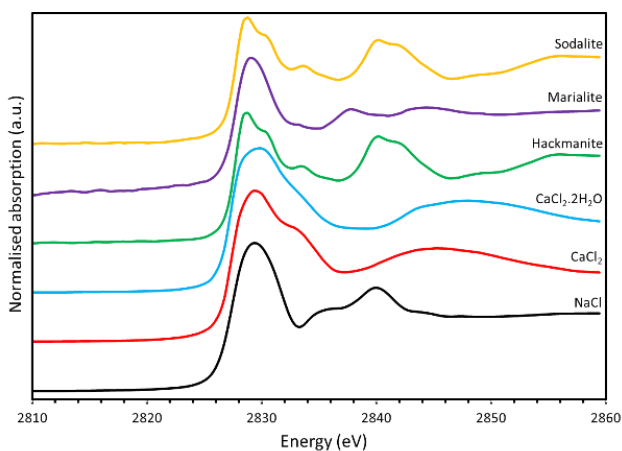


Figure 3: Cl K-edge XANES data from reference compounds NaCl , CaCl_2 , $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$, hackmanite, marialite and sodalite

Comparison between the XANES features of the glass-ceramic and reference compounds in Figures 2 and 3 provided some further insight into the local environment of the Cl^- anion within the glass phase. A weak feature at 2840 eV was just observable in the

XANES of the glass-ceramic composition with 0.9 wt% Cl; this increased in relative magnitude with increased Cl content in the compositions with 1.7 and 2.5 wt% Cl, together with a feature at 2836 eV. Concomitantly, a subtle change in the profile of the white line was observed, with two distinctive components apparent at lower Cl content merging to give a single component at a Cl content of 1.7 wt% and greater. The features observed at 2835 eV and 2840eV in the spectra of the glass-ceramics, and white line profile comprising a single component, are characteristic of the XANES of NaCl and are therefore interpreted as arising from exsolution of NaCl from the glass phase above 0.9 wt% Cl incorporation, consistent with SEM/EDX and XRD data.

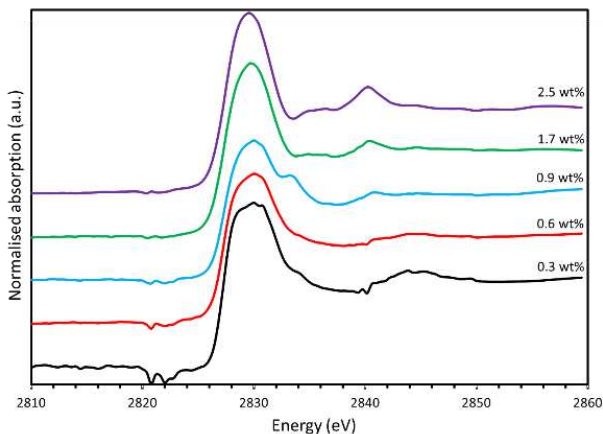


Figure 4 Cl K-edge XANES data glass ceramic compositions with 0.3 wt%, 0.6 wt%, 0.9 wt%, 1.7 wt% and 2.5 wt% Cl.

Table 1: Determined edge positions from Cl K-edge XANES data of reference compounds and glass-ceramic materials.

Sample	Edge Position - E_0 (eV)
NaCl	2827.4
CaCl ₂	2827.5
CaCl ₂ ·2H ₂ O	2827.5
Hackmanite	2827.8
Marialite	2827.8
Sodalite	2827.8
Glass-Ceramic: 0.3 wt% Cl	2827.4
Glass-Ceramic: 0.6 wt% Cl	2827.2
Glass-Ceramic: 0.9 wt% Cl	2827.4
Glass-Ceramic: 1.7 wt% Cl	2827.4
Glass-Ceramic: 2.5 wt% Cl	2827.4

The Cl K-edge XANES data of the 0.3 and 0.6 wt% glass-ceramic compositions (in which SEM/EDX and XRD confirm Cl partitioning exclusively to the glass phase) most closely resemble those of the mineral marialite based on comparison of the profile of the white line and post-edge XANES features. Marialite, prototypically, Na₄Al₃Si₉O₂₄Cl, is characterized by Cl co-ordinated to 4 x Na atoms, within an aluminosilicate cage formed by corner sharing AlO₄ and SiO₄ tetrahedra.¹⁶ Incorporation of Ca and K within marialite is known, and quantitative EDX analysis of our marialite specimen afforded a composition of Na_{3.18}K_{0.13}Ca_{0.54}Si_{8.49}Si_{3.54}O₂₄Cl_{0.95} normalized to the expected oxygen stoichiometry. Additionally, qualitative EDX analysis of the glass phase in the glass-ceramic materials, determined a detectable minor content of CaO. Thus marialite provides a plausible model

for Cl incorporation within the aluminosilicate glass phase of the glass ceramic materials with Cl co-ordinated to 4 x Na / Ca atoms.

The Cl K-edge XANES of sodalite and hackmanite present a white line composed of two features, whilst the white line of CaCl₂ and CaCl₂.2H₂O have a distinctive shoulder; these features are not observed in the XANES spectra of the glass-ceramic materials. Cl is co-ordinated to 3 x Ca cations in a trigonal arrangement in CaCl₂, and 4 x Na cations in a tetrahedral arrangement in sodalite and its photochromic variant hackmanite.^{17,18} Thus, the chemical environment of Cl in these reference compounds are less plausible models for the Cl environment in the glass ceramic materials.

In their analysis of chloride bearing borosilicate glasses developed for immobilization of Hanford low activity wastes, McKeown *et al.* propose an incorporation mechanism whereby Cl is incorporated within linear CaCl₂ species, similar to that in the mineral davynite, based on their analysis of Cl K-edge XANES data and modelling of EXAFS data¹³. Likewise, ³⁵Cl MAS-NMR studies of simple Na₂O-Al₂O₃-SiO₂ and Na₂O-CaO-Al₂O₃-SiO₂ glasses have provided evidence for Cl co-ordination by both Na and Ca.¹⁹ Our Cl K-edge XANES data, and inferred Cl speciation as Cl⁻ co-ordinated to 4 x Na / Ca atoms, are consistent with these studies on related glass compositions.

CONCLUSION

Preliminary investigation of the microstructure of Cl solubility in glass-ceramics for Pu immobilisation, established a solubility limit of 0.9 wt% Cl. Below the solubility limit, Cl is incorporated within the glass matrix, with exsolution of NaCl above the solubility limit. Cl K-edge XANES analysis of zirconolite glass-ceramic materials and reference compounds points to a local environment in the aluminosilicate glass phase similar to that in the mineral marialite, in which Cl is coordinated to 4 x Na / Ca atoms. Above the Cl solubility limit in the aluminosilicate glass phase, the XANES data show features characteristic of NaCl, consistent with observation of this phase in both XRD and SEM/EDX data. Our findings are consistent with the available but limited studies of Cl speciation and local environment in silicate glasses.

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