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Journal of Nuclear Materials 449 (2014) 168–172

Contents lists available at ScienceDirect

Journal of Nuclear Materials

journal homepage: www.elsevier.com/locate/jnucmat

The durability of iodide sodalite

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HIGHLIGHTS

- Dense iodide sodalite prepared by HIP of hydrothermally synthesised powders.
- Sodalite was free from leachable secondary phases.
- Leach tests indicate self-arresting congruent dissolution.

ARTICLE INFO

Article history:
Received 10 January 2014
Accepted 10 March 2014
Available online 17 March 2014

ABSTRACT

An iodide sodalite wasteform has been prepared by Hot Isostatic Pressing of powder produced by hydrothermal synthesis. The wasteform was free of leachable secondary phases which can mask leaching mechanisms. Leaching is by congruent dissolution and leach rates decrease as Si and Al accumulate in the leachate. Differential normalised leach rates are 0.005–0.01 g m^{-2} d^{-1} during the 7–14 day period. This indicates that sodalite dissolution in natural groundwater, already saturated in these elements, will be very low.
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1. Introduction

The current best practice for the management of fission product iodine (both the stable I-127 and the long-lived I-129 with a 15.7 million year half-life) is by discharge to sea. This approach is known as dilute and disperse – dilution into a much larger reservoir of iodine and dispersal by marine currents. With the anticipated global renaissance of nuclear power and a realisation that once through fuel cycles may be unattractive, it will become necessary to review this strategy. Social and political attitudes will have evolved and future spent fuel processing plants may not always have access to suitable discharge routes. This may lead to a requirement for the immobilisation of fission product iodine in a durable wasteform. Iodine is highly mobile in the geosphere such that, on the timescales of the half-life of I-129, if released from any geological disposal facility it will return to the biosphere and then the sea rapidly. Hence it is necessary for the wasteform and other engineered barriers to retain iodine for a time scale on the order of a half-life. Accordingly, good leaching data for any candidate wasteform is essential in assessing its suitability for long term disposal. It is recognised that a wasteform must also be practical to fabricate and this aspect will be referred to throughout this paper. It is noted here that silver iodide, whilst insoluble in pure water, is unstable under reducing conditions and in halide containing groundwater and therefore unsuitable as a wasteform under those conditions. Sodalite has been studied previously as a suitable wasteform phase [1–4] but its leaching behaviour has remained undefined. The work reported here constitutes a brief, but to our knowledge unparalleled, study on the durability of sodalite as a wasteform for the immobilisation of iodine.

For reference, the sodalite structure can be described based around a covalent structural unit called a beta cage, shown in Fig. 1. The vertices of this cage are occupied alternately by aluminium and silicon atoms joined by bridging oxygens sitting approximately at the midpoint of each edge. Prototypically, within each cage sits an Na_4X tetrahedron with each sodium ion oriented towards one of the 6-rings of the beta cage and the anion, X, at the body-centre of the cage. The cages can then be stacked in a simple cubic array by sharing of the 4-rings. In so doing, eight beta cages, with their centres at the vertices of a cube, define a further beta cage with its centre at the body centre of that cube. The standard formula of sodalite is commonly given as $Na_8(AlSiO_4)_6X_2$, this being the composition of a unit cell, rather than reduction to $Na_4(AlSiO_4)_3X$. This is a simple description of the sodalite structure and incorporation of higher charge anions and cations is widely documented in the mineral archive. Anion free cages within the aluminosilicate framework are another mechanism by which charge balance is maintained.

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http://dx.doi.org/10.1016/j.jnucmat.2014.03.016
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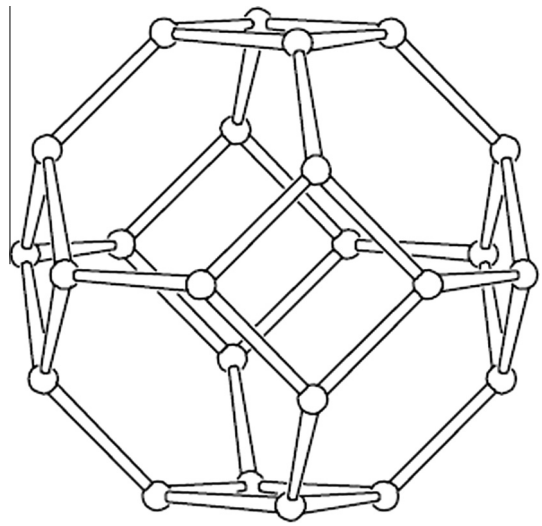

Fig. 1. Schematic representation of a beta cage. The vertices are occupied by aluminium or silicon atoms with bridging oxygens at the midpoint of each edge.

2. Materials and methods

2.1. Fabrication of iodide sodalite

In the preparatory work to a wider study of candidate iodine wasteforms, we became aware of the generic sodalite synthesis method reported by Stein [5], and applicable to a range of anions. It was recognised that this was not going to be a practical iodine capture method but would be valuable if it led to a good quality sodalite sample. Stein's hydrothermal synthesis method was modified slightly by doubling the amounts of $Al(OH)_3$ and colloidal SiO_2 used to increase the sodalite yield. The product of hydrothermal synthesis, hereinafter referred to as the "product", was retrieved and washed as recommended by Stein. The dried product was then Hot Isostatically Pressed (HIP) at 900 and 1100 °C in copper and nickel HIP cans respectively to consolidate it into a monolith, hereinafter referred to as the "wasteform". HIP dwell periods were for 2 h at 200 MPa. Copper and nickel were chosen as HIP can materials because other samples in the wider study contained AgI and these metals would eliminate the risk of reactions with AgI within the HIP can. In parallel with the work reported here, a wider range of samples were produced, typically by solid state synthesis reactions. These are not described in detail but included three useful comparators which will be referred to during the results and discussion:

(a) Iodide sodalite synthesised by solid state reaction of NaI and an excess of nepheline – $NaAlSiO_4$.

$$3\ NaAlSiO_4 + NaI \rightarrow Na_4(AlSiO_4)_3I$$

(b) Silver iodide sodalite synthesised by solid state reaction of AgI and an excess of nepheline.

$$3\ NaAlSiO_4 + AgI \rightarrow AgNa_3(AlSiO_4)_3I$$

(c) Iodide vanadinite – $Pb_{10}(VO_4)_6I_2$ – synthesised by solid state reaction of PbI_2 with an excess of $Pb_3(VO4)_2$ [6].

$$3\ Pb_3(VO_4)_2 + PbI_2 \rightarrow Pb_{10}(VO_4)_6I_2$$

2.2. Characterisation and leach testing

The phase content of the product and wasteform was confirmed by X-ray diffraction (XRD) using Cu Kα radiation.

The sodalite wasteforms were retrieved mechanically from the HIP cans. For leach testing the wasteforms were size reduced and the 75–150 μm fraction separated by sieving, with fines removed by washing in non-polar toluene. The fines were then used for XRD.

A JEOL 3010 transmission electron microscope (TEM) operating at 300 keV in bright field mode was used to study the product and the wasteform. For analysis by TEM, the product was suspended on a holey-carbon-film covered copper grid. The wasteform was prepared by conventional mechanical thinning followed by ion milling using a Gatan Precision Ion Polishing System to achieve electron transparency. The product was also imaged using an FEI Inspect F50 field emission gun scanning electron microscope (FEGSEM).

Leach tests on the defined particle size fractions of wasteform were conducted at 90 °C in a 0.025 M $KHCO_3$ + 0.015 M KOH solution which buffered to pH 11. This was deemed appropriate to simulate the alkaline environment of many proposed geological disposal facilities and also to stabilise leached iodine as iodide ions. The required wasteform mass was calculated from geometric considerations to give a surface area of 50 cm^2, and the leachant volume was 50 cm^3 giving a surface area to volume ratio of 1 cm^{-1}. Three leach tests were prepared for each wasteform, to be terminated at each of 3, 7 and 14 days. The alkaline leachate was used to determine the amount of leached iodine. Aliquots of acidified leachate were analysed for cations. Analysis was by ICP-AES.

3. Results and discussion

3.1. Material characterisation

3.1.1. Hydrothermal product

The XRD trace of the product, Fig. 2, showed it to be essentially a single phase sodalite structure. It is clear that the lattice parameter of the product, 8.96 Å, is somewhat smaller than that reported in the PDF2 database for iodide sodalite, 9.0109 Å [PDF2 standard 32-1031]; and our own material made by solid state synthesis was in excellent agreement with this standard. The decrease in lattice parameter was initially attributed to two mechanisms, and XRD from the wasteform indicated that both operate. The two mechanisms are the formation of anion free cages and cages in which the anion is the smaller hydroxide rather than the intended iodide.

From peak broadening the particle size can be estimated using the Scherrer equation as 25–30 nm. This value is caveated for two reasons: firstly the XRD system used was not accurately calibrated for such measurements; and secondly the OH^- occupied and

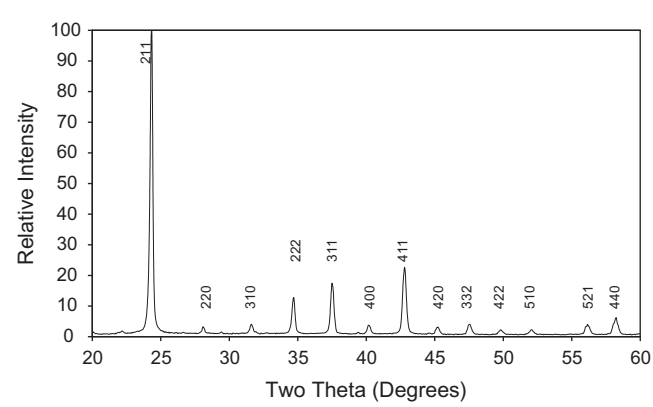

Fig. 2. X-ray diffraction trace from hydrothermally synthesised iodide sodalite product.

anion-free beta cages may not be homogeneously distributed and this may also contribute to peak broadening.

A TEM image of the product is shown in Fig. 3. This indicates a particle size around 50 nm, in good agreement with that estimated by XRD. Imaging of the product by FEGSEM, Fig. 4, confirms its polycrystalline character. This suggests that the product forms by a process of repeated nucleation and growth, with new crystallites nucleating on the surface of existing ones.

3.1.2. HIPped wasteform

Visual examination of the wasteform revealed it to be translucent, which is consistent with a grain size significantly less than the wavelength of visible light. Fragments of wasteform from near to the HIP can wall were also slightly coloured – brown in the case of copper cans, grey for nickel. This indicates some diffusion of the HIP can material into the wasteform.

The XRD trace from the wasteform is shown in Fig. 5 and differs from the hydrothermal product in two ways: there is an ingrowth of nepheline as a second phase; and the lattice parameter of the sodalite phase has increased to 9.00 Å. The former is attributed to the coalescence of anion-free beta cages which then collapse to form nepheline – note that an anion-free sodalite would have the composition $Na_3\,\square^+(AlSiO_4)_3\,\square^-$ where $\square^+$ and $\square^-$ represent vacancies on the Na and anion sites in the prototype. This then clearly reduces to nepheline as the stable phase during HIP. Assuming all anion-free beta cages are eliminated in this way, linear interpolation between the lattice parameters of the hydroxyl and iodide sodalite end members suggests that the anion occupancy of the beta cages is 90–95% iodide and 5–10% hydroxide. By assigning a lattice parameter to a hypothetical anion-free sodalite this approach could be extended to estimate the fraction of anion free cages, but we do not believe this exercise adds any significant value to the main crux of this paper. There were no noticeable differences between the XRD traces for the wasteforms HIPped at 900 and 1100 °C. From peak broadening it is estimated that the grain size has increased slightly from the product to around 40 nm.

A TEM image of the wasteform is shown in Fig. 6 and the apparent grain structure is consistent with that measured from XRD. Electron diffraction from an area containing multiple crystallites indicated that they shared a common orientation, hence the demarcation between crystallites may be more akin to stacking faults than grain boundaries.

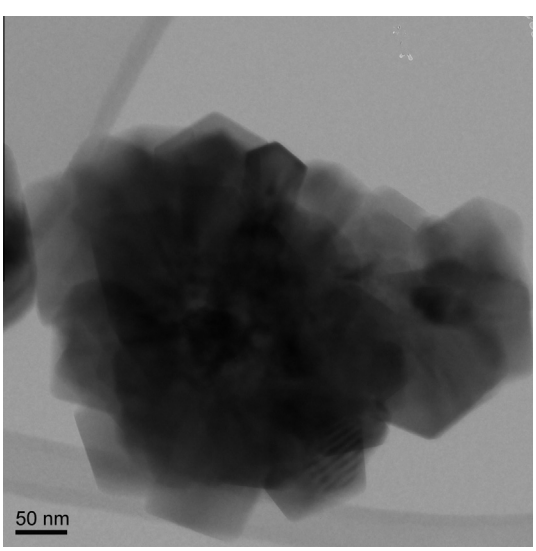

Fig. 3. TEM image of hydrothermally synthesised iodide sodalite product.

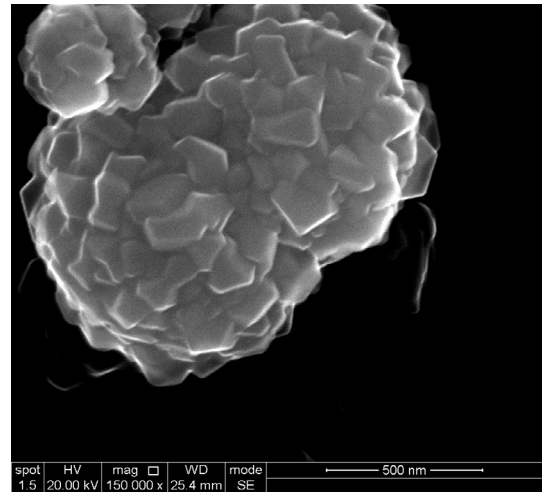

Fig. 4. FEGSEM image of hydrothermally synthesised iodide sodalite product.

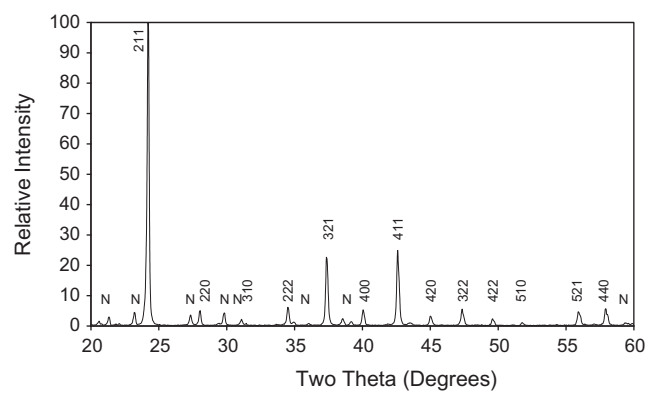

Fig. 5. X-ray diffraction trace from HIPped iodide sodalite wasteform. N indicates ingrown nepheline phase – some N annotations cover two peaks.

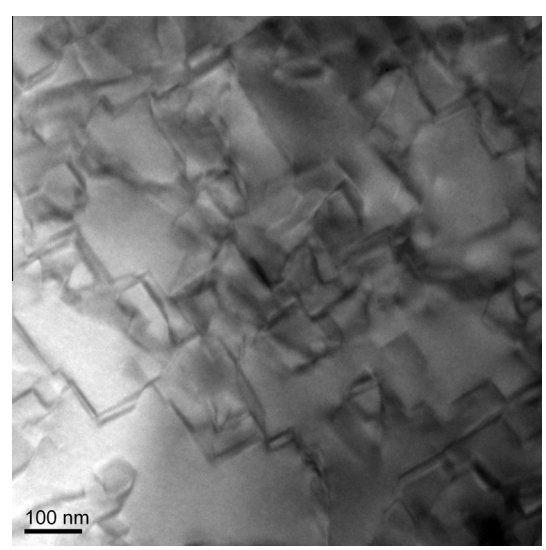

Fig. 6. TEM image of HIPped wasteform.

3.2. Leach testing

Initially the leach data for iodine alone are considered. The normalised iodine mass losses as a function of leach test duration for

wasteforms HIPped at 900 and 1100 °C are shown in Fig. 7. Given that the six data points are from six different leach tests their agreement is considered to be excellent. By contrast, the iodine losses from the iodide sodalite prepared by solid state synthesis were an order of magnitude higher, indicative of unreacted NaI even though the sample had been formulated to contain an excess of nepheline, and did so as shown by XRD. Incomplete reaction was more clearly demonstrated in the solid state synthesis between AgI and nepheline, in which XRD showed a sodalite phase together with both reactants.

It is trivial to calculate normalised iodine leach rates over the duration of each test, but what is more informative is the inferred incremental leach rate over the 7–14 day period. This can be calculated from the difference between the 7 and 14 day normalised mass losses and gives a differential leach rate of 0.005–0.01 g m^{-2} d^{-1}. This is equivalent to the removal of 2–4 nm of wasteform per day.

We now turn to the leach rates of the other constituents of the wasteform. The molarities of Na, Al, Si and I in leachates after each test duration for wasteforms HIPped at 900 and 1100 °C are shown in Fig. 8a and b respectively. The molarities normalised by the stoichiometry of the wasteform are shown in Fig. 9a and b. Presenting the data in this way shows the conformity of leaching to the stoichiometry of the wasteform, although why the values for Si are consistently somewhat higher than the other three components is not clear – the sodalite product as synthesised may be more Si rich than the ideal stoichiometry of the phase. The data suggest that the wasteform is leaching by congruent dissolution; in effect, to release the iodine, the aluminosilicate framework that surrounds each anion in its beta cage needs to be dissolved. More importantly, given that these are static leach tests, the data imply that the wasteform retards its own dissolution. And most probably this is due to the increasing concentration of the dissolved Al and Si. In any geological disposal environment it is reasonable to expect that the groundwater a wasteform comes into contact with will be close to saturation in both Al and Si, and hence the 7–14 day differential leach rates reported here are no worse than a pessimistic representation of the performance of this wasteform in the disposal environment. This may explain the slight divergence of the iodine losses for the 900 and 1100 °C HIPped wasteforms seen in Fig. 7; the quantity of the 900 °C wasteform leach tested had a slightly higher surface area and hence would approach saturation sooner.

By contrast, identical leach tests on the iodide vanadinite suggested an incongruent leaching mechanism in which iodine release was approximately an order of magnitude higher than matrix dissolution, and the actual iodine loss from iodide vanadinite was also an order of magnitude higher than from iodide sodalite after 14 days. Spectroscopic studies have suggested that an ion exchange mechanism may operate for this wasteform [7]. We also subjected a portion of the iodide vanadinite to a 3 day leach test in a KCl based leachant. At the end of this period the previously colourless leachate was demonstrably yellow, consistent with massive iodine loss. Further, energy dispersive spectroscopy of the leach grains suggested surface enrichment of chlorine. Note, this was a qualitative observation and is convoluted by the overlap of the Pb Mβ and Cl Kα lines. Our funding for this work was limited and we welcome independent verification of these findings.

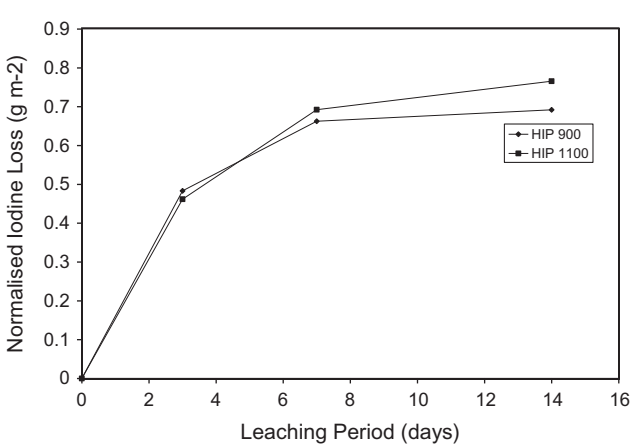

Fig. 7. Normalised iodine losses for wasteforms HIPped at 900 and 1100 °C.

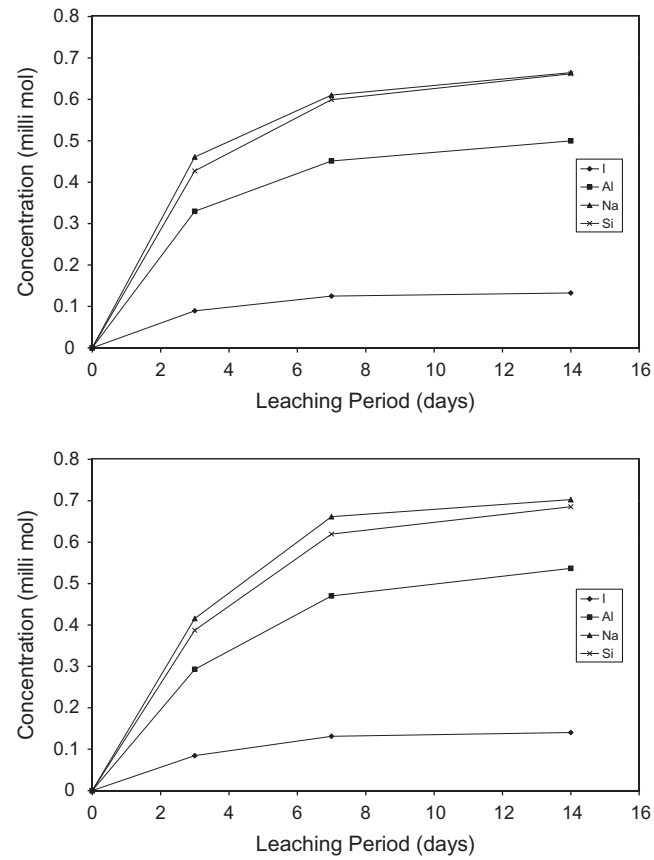

Fig. 8. Leachate molarities for all wasteform components for 900 °C HIP (top) and 1100 °C HIP (bottom).

3.3. General comments

The results reported explicitly here indicate that an iodide sodalite phase would constitute a highly leach resistant wasteform, as expected from the existence of many natural analogues. The key challenge lies in producing a wasteform in which all of the iodine has been incorporated into the sodalite phase. This requires mixing of the iodide and precursor on a more intimate scale than was achieved for the solid state syntheses reported here – and such methods are impractical for wasteform manufacture anyway.

A starting point, demonstrated by Hyatt et al. [8], is the thermal occlusion of the iodide salt into a zeolite. This occurs by heating the physical mixture to 500 °C and results in the iodide diffusing into the pores of the zeolite. Subsequent work by Sheppard et al. demonstrated that an occluded iodide zeolite mixture could be converted to sodalite by HIP [9]. The ultimate aspiration is to combine these findings into a means by which the capture and immobilisation of iodine can be integrated into the dissolver off-gas system of a spent nuclear fuel processing plant. The capture

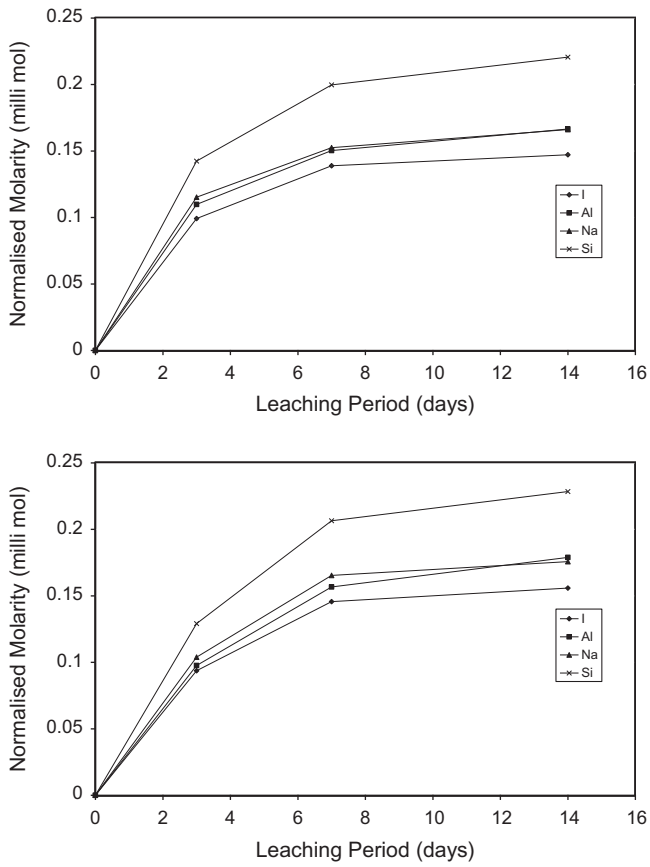

Fig. 9. Normalised leachate molarities for all wasteform components for 900 °C HIP (top) and 1100 °C HIP (bottom).

of iodine from the gaseous phase onto solid substrates is well demonstrated, and commercial sorbents are available. The principle behind these is simply the dispersal of fine silver metal or nitrate particles within a high surface area substrate. The requirement is then to design the substrate such that it converts to the intended wasteform during HIP. Serendipitously this has been achieved with commercially available silver substituted zeolite A [9], however, this substrate would be unstable in the highly acidic environment of a conventional dissolver off-gas system. A conceptual rethink would be required to include an acid recombination stage from which the off-gas would emerge dry and suitable for the capture of iodine, and any other volatile nuclides, on solid substrates.

4. Conclusions and future work

The principal objective of this paper has been to present what we believe to be baseline leaching data for the sodalite phase – that is, leach rates that any sodalite based wasteform should match. Further leach tests are required to establish whether the mechanisms conjectured here are valid. Most simply this will involve varying the surface area to leachant volume and simulated ground waters, but a more sophisticated approach should involve single pass flow through testing.

The long term stability of sodalite wasteforms must also be investigated in respect of the decay of I-129 to Xe-129. This involves a change in charge for which, in the standard sodalite formulation of $Na_4(AlSiO_4)_3X$ there is no clear compensation mechanism. By contrast, if the sodalite phase is formed from AgI its composition will be $AgNa_3(AlSiO_4)_3X$. The silver ion is significantly less resistant to reduction than sodium and may readily be reduced to a silver atom. This would provide a mechanism by which charge neutrality is maintained, but the stability of such a cluster within a beta cage would need to be investigated.

Acknowledgment

A.G. and M.S. gratefully acknowledge support from the Engineering and Physical Sciences Research Council, United Kingdom under Grant Numbers EP/I012214/1, EP/G037140/1, and EP/L014041/1.

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