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The durability of iodide sodalite

Ewan Maddrell [a,*], Amy Gandy [b], Martin Stennett [b]

[a] National Nuclear Laboratory, Sellafield, Seascale, Cumbria CA20 1PG, UK
[b] Department of Materials Science and Engineering, The University of Sheffield, Mappin Street, Sheffield S1 3JD, UK

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.

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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.

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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[*] Corresponding author. Tel.: +44 (0)1946 788903.
E-mail address: ewan.r.maddrell@nnl.co.uk (E. Maddrell).

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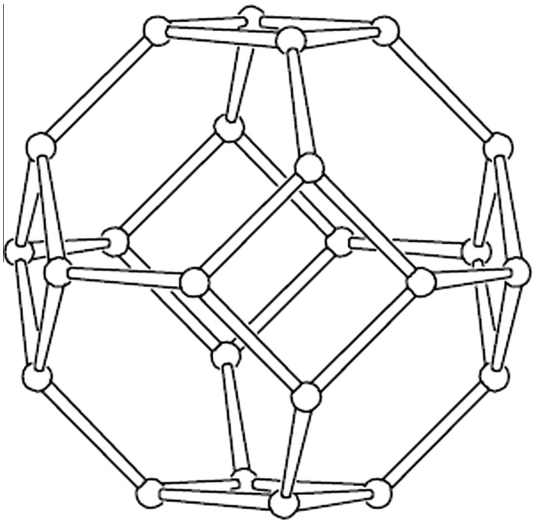

Fig. 1. Schematic representation of a beta cage. The vertices are occupied by aluminium or silicon atoms with bridging oxygens at the midpoint of each edge.

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

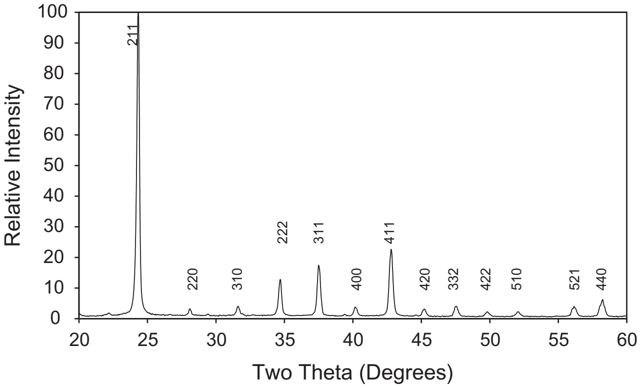

Fig. 2. X-ray diffraction trace from hydrothermally synthesised iodide sodalite product.