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Letter to the Editor

Immobilisation of ^{129}I by encapsulation in tin by hot-pressing at 200 °C

E.R. Vance *, D.S. Perera, S. Moricca, Z. Aly, B.D. Begg

Materials and Engineering Science, ANSTO, Menai, NSW 2234, Australia

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Abstract

The volatility of iodine-129 and its soluble nature in anionic form makes it very difficult to incorporate in ceramic or glassy solids for the purpose of long-term immobilisation. Thus encapsulation in a low-melting metal such as tin is an attractive option, and we describe experiments in which we have hot-pressed AgI-bearing alumina beads surrounded by tin powder at 200 °C.

1. Introduction

^{129}I is a beta-emitting radioactive waste product that is normally very soluble in water as iodide or iodate and it features prominently in long-term performance assessments of immobilised high-level waste from nuclear fuel reprocessing because of its long half life of 1.6×10^7 years. To negate this effect on the performance assessments the iodine would need to be immobilised for times comparable to its half life, that is, millions of years. Most attempts to immobilise it have employed the same methods as those successfully used for other high-level waste radionuclides, viz. incorporation in the lattice of a synthetic mineral (such as sodalite [1]). Cement has also been investigated for this purpose [2,3]. However, the aqueous solubility of I and its general volatility at elevated temperatures (>500 °C) make these approaches difficult. The problem in general of immobilising ^{129}I has been reviewed several times up until 1990 [4–6], but little further work appears to have been done in recent times.

One method of capturing ^{129}I is to adsorb it from a gas stream heated at ~200 °C onto a $AgNO_3$-impregnated ceramic to form Ag^{129}I. A range of commercial porous $AgNO_3$-impregnated porous alumina and silica sorbents is commercially available for this purpose. They are in the form of >50% porous beads which are ~2 mm in diameter. Ag-mordenite is also commercially available for this purpose (unexchanged mordenite has a composition of $(Ca, Na_2, K_2)Al_2Si_{10}O_{24} \cdot 7H_2O$). In principle these materials are candidates for geological immobilisation and indeed consolidation by hot isostatic pressing (HIPing) at 750 °C/98 MPa has been tried [7]. However TCLP [8] limits on Ag release are only 5 mg/L and while AgI is normally seen to be highly insoluble in water, it is actually quite soluble in reducing conditions [6].

Transmutation to stable ^{130}Xe by neutron capture in high fast neutron fluxes has also been suggested [9] but the long irradiation times and potential difficulties

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* Corresponding author.
E-mail address: erv@ansto.gov.au (E.R. Vance).

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with target design (especially since the daughter product is gaseous) make this method problematic, to say the least.

Here we report a different approach, viz. immobilisation via encapsulation in a low-melting durable metal (focussing mainly on Sn, melting point 232 °C) using powder metallurgy and high pressures (tens of MPa) and modest temperatures (~200 °C) to produce consolidation. Stable ^{127}I was used in the experiments reported.

2. Experimental

Elemental I (Ajax Fine Chemicals, Australia, 99.8% purity) was reacted with commercial $AgNO_3$ impregnated porous alumina sorbents to form AgI by heating in a sealed vessel at 150 °C for 12 h. Details of the sorbents and the method are given elsewhere [10]. AgI was distributed homogeneously throughout the sorbents as observed by scanning electron microscopy (SEM) and ~10 wt% of I was taken up by the sorbents [10].

In previous work [11,12] carried out using ceramic and glass matrices, the AgI-containing sorbents were contained near the centre of a pellet formed from the glass or ceramic matrix. It was difficult to keep the sorbent particles together. To overcome this problem an open Al can of diameter 15 mm and 15 mm height was filled with several grams of AgI containing sorbents. A 25 mm diameter die with the bottom plunger in place was filled to about 10 mm with Sn powder (−44 μm, typically <10 μm, average 9.4 μm) and the Al can was placed in the centre of the die on the powder bed. The die was filled with more Sn powder to surround and cover the can to a depth of ~20 mm. The assembly was compacted via a top plunger to a pressure of 20 MPa. Such pellets were ejected for subsequent HIPing.

For HIPing, the ejected compact was placed in a cylindrical Cu can of almost the exact diameter (25 mm) and 5 mm higher than the compact. A tube containing a filter was welded on to the Cu can and the can evacuated. Then the tube was crimped and welded. The can was HIPed using an AIP 6-30H HIP (American Isostatic Presses Inc., USA) at 200 °C in 100 MPa of argon gas for 1 h. The can was cooled and then cut open to remove the compact. A similar experiment was carried out using Cu powder (ACL Bearing, Tasmania; <10 μm) instead of Sn powder; this was HIPed however at 400 °C for 1 h at 100 MPa of Ar pressure.

Another HIP run was performed using a dumbbell-shaped Cu can, ~60 mm maximum diameter and ~50 mm high. This was half-filled with Sn powder, an Al can with I-loaded sorbent was placed in the centre and then the can filled with more Sn powder, vibrating to maximise the filling. After evacuation and sealing as described above the can was HIPed at 200 °C for 1 h at 100 MPa. After HIPing the can was sectioned and the beads can be seen inside the open Al can which in turn is surrounded by dense tin (see Fig. 1).

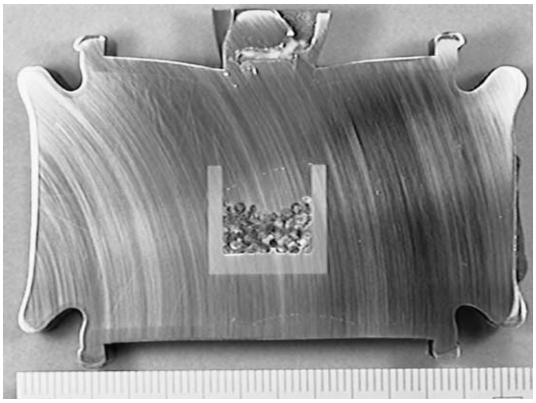

Fig. 1. AgI-containing sorbents in an Al can inside (sectioned) Sn-filled HIPed Cu can. HIPing carried out at 200 °C for 1 h at 100 MPa Ar gas pressure (small divisions on graduated scale = 1 mm).

All compacts were sectioned and examined under an optical microscope and their open porosity was determined according to Australian Standard [13] procedure. The HIPed compact was diamond polished to <0.1 μm finish and etched for 5 min in a solution of alcohol/perchlorate and examined by optical microscopy. Also a similar section was examined by SEM.

To study the aqueous durability of the compacts two types of tests were carried out. The TCLP test [7] was carried out on the 2 mm sized I-impregnated alumina sorbents prior to immobilisation. For these tests the only relevant element was Ag, however we analysed for both I and Al also. To demonstrate the aqueous durability of Sn, the MCC-1 leaching test [14] was performed on a Sn monolith which was HIPed at 200 °C, cut with a diamond saw and polished to a 1 μm diamond finish, avoiding the use of polar liquids. These leaching solutions were analysed by inductively-coupled mass spectrometry for Ag and Al and by an ion-selective electrode for I.

3. Results and discussion

The TCLP test results on the unconsolidated beads showed that there was no detectable (<0.01% of inventory) I released but the Ag release was about 140 ppm. This value was well above the acceptable limit of 5 mg/L for USA landfills [7], showing that more protection was necessary for the materials to be suitable for disposal. Washing of the sorbent before conducting the TCLP test reduced the TCLP value to 35 ppm, still above the limit. The lowering of the value is attributed to the existence of unreacted $AgNO_3$ being present in the sorbent.

For the HIPed compact no pores in the tin were observed under an optical microscope (Fig. 2) and there were only a few pores visible in the SEM micrographs (Fig. 3). These pores may be due to polishing damage and pull-out. The measured density of the Sn section of the HIPed compact was 7.27 g/cm^3 and this value is very close to the theoretical density of Sn (7.28 g/cm^3).

Both Sn and Cu are highly corrosion resistant, and Sn-coated metals are used for food storage and containment. Cu has been studied extensively as an encapsulant for spent fuel in Sweden [15]. The MCC-1 leach test on the Sn monolith yielded leach rates $<6 \times 10^{-5}$ g/m^2/day for 0–21 days. This value is extremely low by MCC-1 test standards, and corresponds to the removal of only a few nm/year in the short term (or a few mm per million years). Sn is not on the TCLP list of hazardous metals and the known high durability of metallic tin is consistent with these extremely low leach rates.

We are currently looking at means other than HIPing of encapsulating the iodine-bearing sorbents in powdered metals, notably by sintering, hot-forging and uniaxial hot-pressing.

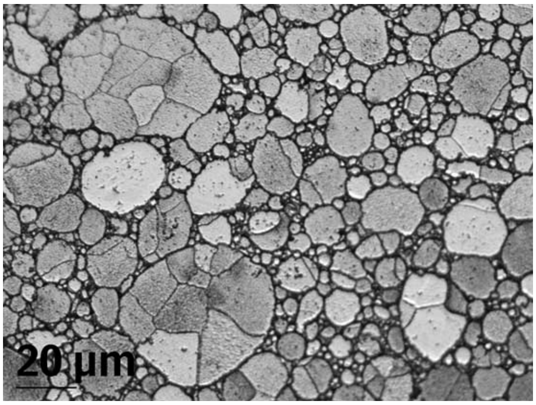

Fig. 2. Optical micrograph of HIPed Sn showing the microstucture. Etch pits are seen but not any porosity.

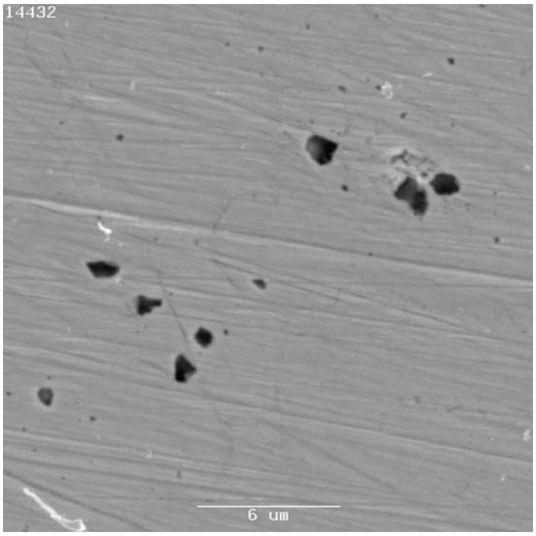

Fig. 3. Secondary SEM image of polished Sn showing occasional pores, which may have been produced due to surface damage.

4. Conclusion

HIPing at 200 °C enables the incorporation of I-bearing alumina beads in a dense tin encapsulant and it is proposed that the iodine would likely be immobilised for millions of years in a geological repository.

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References

[1] D.M. Strachan, H. Babad, in: Ceramics in Nuclear Waste Management, CONF-790420, US Department of Energy, 1979.

[2] M. Toyohara, M. Kaneko, N. Mitsutsaka, H. Fujihara, N. Saito, T. Murase, J. Nucl. Sci. Technol. 39 (2002) 950.

[3] M.T. Morgan, J.G. Moore, H.E. Devaney, G.C. Rogers, C. Williams, E. Newman, in: G.J. McCarthy (Ed.), Scientific Basis for Nuclear Waste Management, 1, Plenum, New York and London, 1979, p. 453.

[4] E.R. Vance, D.K. Agrawal, B.E. Scheetz, J.G. Pepin, S.D. Atkinson, W.B. White, Report DOE/ET/41900-9, US Department of Energy, 1981.

[5] Treatment, conditioning and disposal of iodine-129, Technical report Series No. 276, International Atomic Energy Agency, Vienna, 1987.

[6] P. Taylor, Atomic Energy of Canada Limited Report, AECL-10163, 1990.

[7] H. Fujihara, T. Murase, R. Wada, T. Nishimura, T. Imakia, Y. Sugimura, Y. Kurimoto, Radioactive Waste Management and Environmental Remediation-ASME 1999.

[8] Toxicity Characteristic Leaching Procedure (TCLP), EPA method 1311, EPA SW-846, 1999.

[9] Accelerator-driven Systems (ADS) and Fast Reactors (FR) in Advanced Nuclear Fuel Cycles, A Comparative Study, OECD report, 2002.

[10] D.S. Perera, B.D. Begg, D.J. Cassidy, R.L. Trautman, E.R. Vance, J. Austral. Ceram. Soc. 39 (2004) 81.

[11] D.S. Perera, E.R. Vance, R.L. Trautman, B.D. Begg, WM '04, Tucson, AZ, USA, 29 Feb–1 Mar 2004 (CD-ROM, Paper No. 4089), 2004.

[12] D.S. Perera, B.D. Begg, R.L. Trautman, D.J. Cassidy, E.R. Vance, R.A. Day, in: Proceedings of International HIP Conference, HIP '02, Moscow, Russia, All-Russia Institute of Light Alloys, Moscow, 2003, p. 162.

[13] Australian Standard AS 1774.5-2001, Standards Australia, 2001.

[14] MCC-1 Static Test, Nuclear Waste Materials Handbook, US Report No. DOE/TIC-11400, Material Characterisation Centre, Hanford, 1984.

[15] B. Iversson, J. Osterberg, R. Sandstrom, L. Werme, in: W. Lutze, R.C. Ewing (Eds.), Scientific Basis for Nuclear Waste Management XII, Materials Research Society, Pittsburgh, PA, USA, 1989, p. 397.