

CURRENT RESEARCH ON I-129 IMMOBILIZATION

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ABSTRACT

Radioactive ^{129}I has a half-life of 1.57×10^7 years and is produced in the nuclear fuel cycle. One method of conditioning ^{129}I is to adsorb it from a gas stream heated at $\sim 200^\circ\text{C}$ onto a AgNO_3 -impregnated ceramic to form Ag^{129}I . A range of commercial porous AgNO_3 -impregnated porous alumina and silica sorbents are available for this purpose. Once ^{129}I is incorporated as Ag^{129}I then the long term immobilization is a challenging problem because of the long half-life of ^{129}I and its volatility during processing. In this paper we review the work carried out by various investigators in attempting to contain this Ag^{129}I and our current program. It covers the immobilization of AgI in glasses, ceramics and other matrices by sintering, hot pressing or hot isostatically pressing (HIPing). The volatilization of AgI above its melting point of $\sim 552^\circ\text{C}$ entails that HIPing in a can is a very good option to produce a dense material. The matrix selected has to densify at low temperatures to prevent the AgI volatilization. The selection of the matrix, the HIPing temperature and the aqueous durability of the matrix will determine the best solution for the immobilization of ^{129}I via AgNO_3 -impregnated sorbents.

INTRODUCTION

Radioactive ^{129}I is a beta-emitter with a half-life of 1.57×10^7 years and is produced in the nuclear fuel cycle. There are several ways of capturing ^{129}I as reported by the IAEA [1]. One method of conditioning ^{129}I is to adsorb it from a gas stream heated at $\sim 200^\circ\text{C}$ onto a AgNO_3 -impregnated ceramic to form Ag^{129}I [1]. This is the only method we are considering in this paper. A range of commercial porous AgNO_3 -impregnated porous alumina and silica sorbents is commercially available for this purpose. The sorbents are in the form of beads ~ 2 mm in diameter and $>50\%$ porous. The long term immobilization is a challenging problem because of the long half-life of ^{129}I and its volatility during processing. The melting point of AgI is $\sim 552^\circ\text{C}$ and it volatilizes rapidly above this temperature and also some volatilization takes place $>410^\circ\text{C}$ [2]. In this paper we review some of the methods adopted in immobilizing the Ag^{129}I in the literature and the work we have carried out.

SILVER IODIDE IMMOBILIZATION

Use of Glass Matrices

Noshita et al. [2] mixed AgI with Ag_2O and P_2O_5 to form a glass at $\sim 400^\circ\text{C}$ containing ~ 50 mol% AgI . The MCC-1 leach test was carried out at 35°C in reducing conditions and the leach rate for I for the first 10 days was 6×10^{-8} g/cm²/d. They concluded there was no volatilization of AgI because the melting temperature of the glass was below the melting point of AgI .

AgI has also been solidified in borosilicate glass processed at 900°C and sustained a 10% weight loss due to I volatilization [3]. The work concentrated only on studying the evaporation of AgI and leaching studies were not carried out.

We investigated a lead-iron phosphate glass claimed to be suitable for immobilization of high-level nuclear waste [4]. The glass composition $\text{Pb}_{0.20}\text{Fe}_{0.11}\text{P}_{0.65}\text{O}_2$ was made by shear mixing $\text{Pb}(\text{NO}_3)_2$, H_3PO_4 and $\text{Fe}(\text{NO}_3)_3$ in water. The resultant slurry was poured into a Pt crucible and dried in an oven for 18 h at 105°C. The dried product was melted at 800°C for 1 h in a Pt crucible. The resultant glass was ground to a fine powder using a WC-lined percussion mill. AgI-containing sorbents were mixed in different ratios, uniaxially pressed and HIPed in a mild steel can at 500°C for 1 h at 100 MPa. The XRD analysis of the HIPed glass matrix showed the major crystalline phases present as AgI, Al_2O_3 , $\beta\text{-Ca}(\text{PO}_3)_2$ and $\text{Fe}_3(\text{PO}_4)_2$. The phosphate phases derived from devitrification of the glass on cooling. No-Pb containing crystalline phase was detected, which indicates most of the Pb was probably still in the glassy phase. It is seen (Fig. 1) that the AgI is mostly within the sorbent, but there was some AgI in the matrix. On opening the cans no I was detected on the inside surfaces of the cans or on the compacts. Although some AgI migrates from the sorbent to the matrix within the time of heating and under pressure it has not migrated widely, 400 μm at most. Therefore at near ambient temperatures it is correspondingly less likely to migrate. However because of this migration we wanted to explore whether ceramic matrices were better for this purpose.

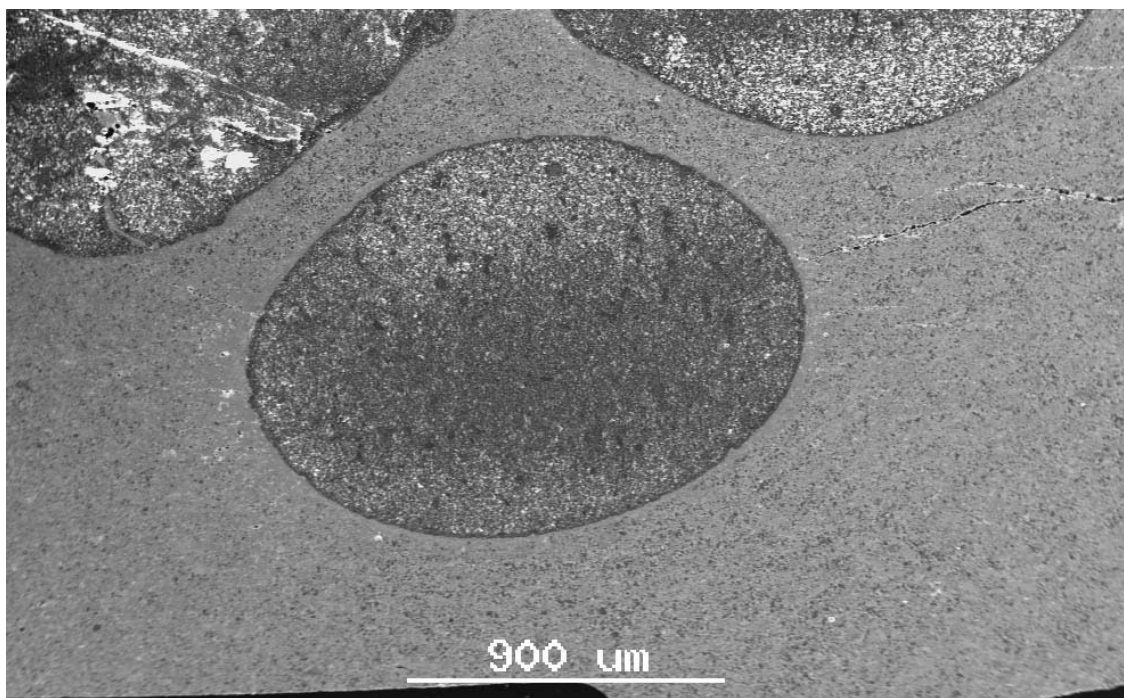


Fig. 1 The AgI (shiny white areas) is concentrated mostly in the round alumina sorbents but some AgI is seen in the glass matrix close to sorbents.

Use of Ceramic Matrices

Kato et al. [5] mention the mixing of an AgI containing filter from a processing plant with apatite followed by hot pressing. However, none of the details have been given regarding the temperature or the composition of apatite.

It was claimed in a patent [6] that by surrounding AgI with an apatite of formula $M_{10}(XO_4)_{2-2x}(PO_4)_{2x}$, $M = Cd$ or Pb , $X = V$ or As , such that $0 < x < 1$, and hot pressing between $500-800^\circ C$ for 1-3 h, a barrier to confine the AgI will be formed. If I were to volatilize then it would form the iodoapatite, $M_{10}(XO_4)_{6-6x}(PO_4)_{6x}I_2$.

Fujihara et al. [7] packed AgI-containing porous silica sorbents into a stainless steel capsule and carried out hot isostatic pressing (HIPing) at $750^\circ C$ for 3 h at 98 MPa. They showed that the iodine was contained within the silica sorbent. However, the stainless steel was the only barrier to the intrusion of ground water if the HIPed material was placed in a geological nuclear waste repository.

We have shown that it was possible using stable I to immobilize the AgI captured on alumina sorbents in a ceramic matrix by HIPing at $700^\circ C$ for 1 h at 150 MPa in a stainless steel can without any loss of AgI [8]. The composition of the ceramic matrix selected in that work was $Ca_5(PO_4)_3$ such that if any iodine were to volatilize it might form $Ca_5(PO_4)_3I$, an iodoapatite similar to fluorapatite ($Ca_5(PO_4)_3F$), which occurs naturally. However, it was not possible even with HIPing at $700^\circ C$ to replace F^- with I^- . The AgI was contained mostly within the porous sorbents (see Fig. 2).

To overcome this porosity we selected a composition in the $PbO-V_2O_5$ system where the lowest eutectic was $\sim 480^\circ C$, where we would expect a material in this system to be dense when HIPed at $700^\circ C$ [8]. We selected the nominal composition $Pb_5(VO_4)_3$ by mixing 80.4 wt.% $Pb(NO_3)_2$ and 19.6 wt.% V_2O_5 . The aim was that if any I were to volatilize from included sorbents it would react to form $Pb_5(VO_4)_3I$. This material was HIPed in a stainless steel can at $700^\circ C$ for 1 h at 100 MPa. The X-ray diffraction analysis showed $Pb_3(VO_4)_2$ (major) and PbO (minor) as the phases present in the HIPed material and a small amount of corundum from the sorbent. The energy dispersive spectroscopic analysis of the matrix showed only $Pb_3(VO_4)_2$ (based on the ratio of Pb to V), indicating that no iodine had volatilized to form $Pb_5(VO_4)_3I$. The AgI was located within the sorbent, and not in the matrix. Although the maximum HIP temperature was $700^\circ C$, well above the volatilization temperature range of AgI, there was no evidence for volatilization or migration of elemental I (Fig. 3). The lead vanadate matrix therefore appears to be a suitable matrix for containing the sorbents by HIPing where the I can be immobilized as AgI within these sorbents. However while an initial TCLP test carried out to determine the aqueous durability showed only < 0.01 ppm of iodine released, the releases of Pb and Ag were ~ 3500 and 700 ppm respectively, thus exceeding the 5 ppm limit requirements of the US environmental regulations for hazardous land fills, for Pb and Ag. Hence we are investigating other matrices for immobilization of ^{129}I .

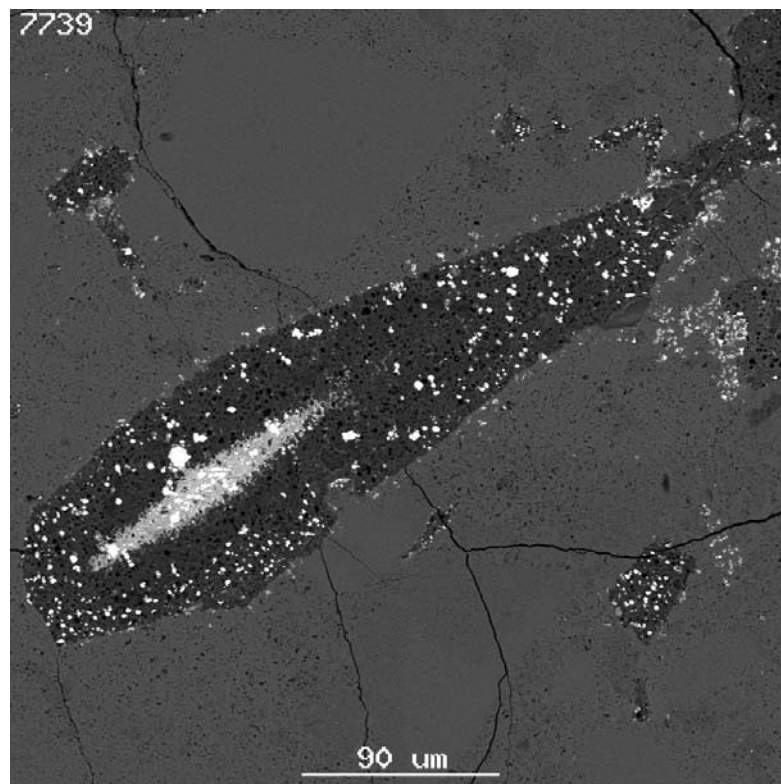


Fig. 2 The AgI (Shiny White Areas) is concentrated mostly in the crushed alumina sorbents but some AgI is seen in the calcium phosphate matrix close to sorbents. The porosity of the matrix is also seen.

Use of Other Matrices

There are many other work [eg. 9]] where sodalite has been used directly to immobilize I but not via AgI. Nakazawa et al. [10] have described the synthesis of I-containing sodalite ($\text{Na}_8(\text{AlSiO}_4)_6\text{I}_2$) by reacting NaI (formed from the AgI), SiO_2 and NaAlO_2 at 800°C . About 50% of the I was lost during heating. Leaching of the sodalite in deionised water after 70 days showed an I concentration of 2×10^{-4} g/mol at a pH of 8.8.

Finally an AgI-containing filter from a processing plant was embedded in metallic copper powder and hot pressed at 700°C at a pressure of 25 MPa for 3 h [11]. The filter with the AgI was contained within the copper matrix. The corrosion rate of copper matrix in anaerobic conditions was reported as $\sim 4 \mu\text{m}/\text{y}$.

We are at present investigating other matrices and the initial results are highly promising.

CONCLUSIONS

We have reviewed the immobilization of AgI containing sorbents using various matrices such as glass, ceramics and metals. The volatilization of AgI above its melting point of $\sim 564^\circ\text{C}$ indicates

that HIPing in a can is a very good option to produce a dense material. The matrix selected has to densify at low temperatures to prevent AgI volatilization and prevent aqueous attack. The selection of the matrix, the HIPing temperature and the aqueous durability of the matrix will determine the best solution for the immobilization of ^{129}I via AgNO_3 -impregnated sorbents.

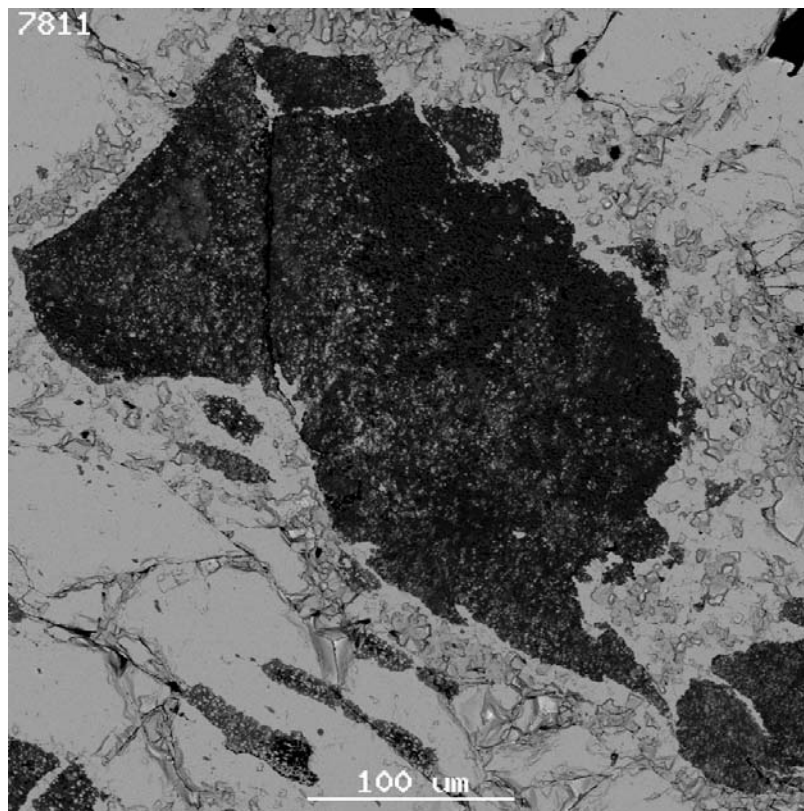


Fig. 3. The AgI (shiny white areas) is concentrated in the crushed alumina sorbents. None seen in the lead vanadate matrix. Dense areas of the matrix are also seen. The cracks are due to mechanical stresses attendant upon opening the can.

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