Silica-based waste form for immobilization of iodine from reprocessing plant off-gas streams

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Abstract

A high selectivity and sorption capacity for iodine and a feasible consolidation to a durable SiO₂-based waste form makes silver-functionalized silica aerogel (Ag⁰-aerogel) an attractive choice for the removal and sequestration of iodine compounds from the off-gas of a nuclear fuel reprocessing plant. Hot uniaxial pressing of iodine-loaded Ag⁰-aerogel (20.2 mass% iodine) at 1200°C for 30 min under 29 MPa pressure provided a partially sintered product with residual open porosity of 16.9% that retained ~93% of sorbed iodine. Highly iodine-loaded Ag⁰-aerogel was successfully consolidated by hot isostatic pressing at 1200°C with a 30-min hold and under 207 MPa. The fully densified waste form had a bulk density of 3.3 × 10³ kg/m³ and contained ~39 mass% iodine. The iodine was retained in the form of nano- and micro-particles of AgI that were uniformly distributed inside and along boundaries of fused silica grains.

Keywords: Immobilization; Iodine; Silver-functionalized silica aerogel; Hot uniaxial pressing; Hot isostatic pressing; Silica-based waste form

1. Introduction

The aqueous reprocessing of used nuclear fuel results in the release of various radionuclides into the off-gas system with radioiodine (¹²⁹I) being of a particular concern because of its long half-life (1.6 × 10⁷ years) and high mobility in the environment. Under current U.S. regulations [1-3], ¹²⁹I must be captured and immobilized into a durable waste form for long-term storage in a geological disposal facility. These stringent regulations require an overall plant decontamination factor around 2000, which means that only one iodine atom out of 2000 is not captured by the sorbent [4,5]. It is, therefore, essential to develop

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highly efficient sorbents for capture of iodine and waste forms for its safe disposal on a scale of geological time. A number of waste forms have been considered and are being developed worldwide for iodine conditioning such as low-melting glasses [6,7], sodalites [8,9], and apatite-like minerals [10-13]. However, none of these potential waste forms can be used as both a sorbent and a viable waste form. They can either encapsulate iodine loaded sorbent or sequester iodine that was removed from it. In the United States, the current benchmark material for radioiodine capture is reduced silver mordenite (Ag^0Z) and that for the waste form is Ag^0Z immobilized in a low-temperature glass composite material [14]. However, the primary alternative option for the removal and sequestration of iodine compounds from the off-gas of a nuclear fuel reprocessing plant is silver-functionalized silica aerogel (Ag^0 -aerogel). This advanced material, which is synthesized in the form of granules bigger than 0.85 mm with a surface area $\sim 150 \text{ m}^2/\text{g}$, pore volume $\sim 0.5 \text{ mL/g}$, and bulk density $\sim 500 \text{ kg/m}^3$, exhibits excellent sorption properties for iodine. Iodine capacities up to 480 mg/g were demonstrated with decontamination factors over 10,000 in laboratory tests with simulated dissolver off-gas streams [15,16]. In addition, in contrast to Ag^0Z , Ag^0 -aerogel retained high selectivity and sorption capacity for iodine even after a long-term exposure to dry/humid air [17,18], dry air containing 2% NO_2 [19] and dry air containing 1% NO [20]. This is important considering the possibility of the reprocessing plant idling, which would result in exposure of sorbent to heated air containing water vapor and possibly NO and NO_2 gases.

A potentially simple conversion to a highly durable and leach-resistant SiO_2 -based waste form by simultaneous application of fast heating rates to temperatures above 1000°C and pressures up to 210 MPa makes Ag^0 -aerogel an attractive choice for long-term immobilization of radioiodine. Previously, iodine retention of $>92\%$ has been demonstrated in a hot uniaxially pressed sample [21]. Also, the preliminary investigation of the feasibility of hot isostatic pressing (HIP) for consolidating powders of Ag^0 -aerogel clearly showed that this method can be effectively used to produce material of near-theoretical density [22]. Promising preliminary results were also obtained for samples consolidated with spark plasma sintering (SPS), which offers the advantage of high densification rates at a lower processing temperature.

The ram travel data for SPS indicated that rapid consolidation of powders can be performed at temperatures below 950°C due to enhanced sintering kinetics [22]. However, the high heating seems to occur preferentially at the grain boundaries and this local melting resulted in the particles and inclusions of Ag to be predominantly distributed at points of grain contacts. A small concentration of additives such as colloidal silica was needed to prevent accumulation of a large fraction of silver nanoparticles at the grain boundaries. Since HIP is a more mature technology than SPS and is now the baseline process for the high-level calcine waste at the Idaho National Laboratory Site [23] and for the intermediate-level waste byproducts of molybdenum-99 production in Australia [24], HIP processing was selected for further investigation.

The main purpose of the study reported here was to investigate HIP consolidation of Ag⁰-aerogel containing low and high concentration of non-radioactive iodine and determine whether a fully dense waste form can be produced and 100% retention of iodine achieved without using any additives. The study also investigated the effect of more material to prepare samples (1.5 vs. 0.5 g) and the effect of prepressed pellets which were isostatically pressed at 345 MPa before processing to achieve more intimate contact between particles, on consolidation with HIP. The consolidated samples were analyzed with a helium gas pycnometer for apparent density; with the Archimedes method for open porosity and apparent density; with scanning electron microscopy and energy dispersive spectroscopy (SEM-EDS) for the extent of densification, macro- and microstructural changes, and distribution of individual elements; and with X-ray diffraction (XRD) for crystalline phases.

2. Experimental procedure

2.1 Materials

Powders of Ag⁰-aerogel with or without iodine were prepared for processing with hot uniaxial pressing (HUP) and HIP. A batch of Ag⁰-aerogel granules with a particle size of less than 0.85 mm was synthesized using a previously developed procedure [15]. Briefly, the silver nanoparticles were produced on the propylthiol-modified pore surfaces of silica aerogel by reducing the silver thiolate adduct ions at

165°C for 2 h under flowing 2.7% H₂ in Ar. The granules were black in color with yellow spots and had a bulk density of $\sim 0.6 \times 10^3$ kg/m³. Iodine-loaded Ag⁰-aerogel granules were prepared in a Teflon assembly shown in Figure 1. The bottom vessel contained ~ 0.5 or 3 g of solid non-radioactive iodine (the amount required to produce a low- or high- iodine-loaded material, respectively) and the top vessel contained four vials; each vial contained either ~ 0.4 or 1.2 g of Ag⁰-aerogel, depending on the amount of the material required for consolidation experiments. The assembly was kept in an oven at 150°C for 24 h. Subsequently, the vials were removed from the assembly and left in the oven at 150°C for 1 h before being transferred into a desiccator for 1 h (kept under 10 kPa in-house vacuum) to remove any physically adsorbed or condensed iodine. The mass gains, i.e., iodine loadings for the low-iodine-loaded samples ranged from 19.7 to 21.9 mass% and for the high-iodine-loaded samples from 34.8 to 35.5 mass% as determined with an analytical balance of 0.1 mg sensitivity. The prepared samples were hand ground with a mortar and pestle before consolidation with HUP and HIP.

2.2 Methods of densification

Two methods, HUP and HIP, were investigated to effectively consolidate Ag⁰-aerogel containing or lacking iodine into a fully dense silica-based waste form.

2.2.1 Hot uniaxial pressing

Two powdery samples of Ag⁰-aerogel were consolidated with HUP, one with and one without iodine but both containing ~ 8 mass% organic moiety (installed on the surface of the pores during the synthesis of Ag⁰-aerogel). The iodine-loaded sample contained 20.2 mass% iodine (removal of organic moiety increases concentration of iodine to 22.0 mass%). Approximately 0.2-g samples were loaded into alumina crucibles (9.55 mm OD $\times$ 6.42 mm ID $\times$ 19.10 mm tall), covered with an alumina lid, and compressed with a 6 kg weight on the plunger rod. Each of these crucibles, one at a time, was secured with a Pt wire spring to the alumina push rod, which was mounted to the Duramaster rod cylinder (Greenco Mfg. Corporation, Tampa, FL) outside of the furnace. The rod cylinder was pressurized with air, extending the push rod and compressing the sample in the crucible with 29 MPa pressure against a

mullite block inside the furnace that was preheated to 1200°C. After 30 min, the rod was retracted from the furnace and the crucible was removed and transferred into a desiccator for an hour before being weighed on a four-digit balance to determine mass loss (used to calculate iodine retention in the product).

2.2.2 Hot isostatic pressing

Table 1 shows two sets of two samples of Ag⁰-aerogel that were consolidated with HIP, each set containing samples with and without iodine. The organic moiety was removed from all samples without iodine loss (the samples were heated from 25 to 350°C at a rate of 5°C/min, held at 350°C for 10 min, and air quenched) because gases evolved from its decomposition can prevent densification of the powder inside the metal fixture [22]. The first set of samples was prepared from powders of Ag⁰-aerogel that already had the organic moiety removed. Approximately 0.4-0.5 g was pressed into 14.9 mm pellets (~1 mm thick) with a benchtop Carver press (Carver, Inc., Wabash, IN) at 62 MPa before being transferred into an ~15 mm dimple (~1 mm deep) in the circular 0.016 mm thick tantalum sheet (38 mm in diameter) and covered by a circular flat sheet, also 38 mm in diameter. The second set of samples was prepared using a three-step process: 1) ~1–1.5 g of powdery samples were prepressed under 9 MPa pressure with a benchtop Carver press, 2) the prepressed pellets were isostatically pressed under 345 MPa with a research-scale isostatic press (CIP32260, Avure Technologies, Columbus, OH), and 3) isostatically pressed pellets were heat treated to remove the organic moiety. Each pellet was then transferred into a tantalum fixture made of two circular 0.016-mm-thick tantalum sheets (38 mm in diameter), each with a ~15-mm-diameter dimple (~1.5 mm deep). These two sheets were placed opposite each other so that the pair of dimples formed a volume to hold the pellets. The inside surfaces of the circular sheets were coated with carbon for easier removal of the samples. The fixtures with samples were then degassed at approximately 0.01 Pa, sealed by electron-beam welding, and processed with HIP at American Isostatic Pressing (Columbus, OH) in a research-scale HIP instrument, which had carbon heating elements and used argon gas to pressurize the chamber. All four fixtures were processed at the same time and were heated at 20°C/min from room temperature to 1200°C with a 30-min hold and consolidated under

207 MPa. Figure 2 shows the temperature and pressure profiles for the samples during processing with HIP.

2.3 Sample characterization

The consolidated samples were analyzed with a helium gas pycnometer for apparent density; with the Archimedes method for open porosity and apparent density; with SEM-EDS for the extent of densification, macro- and microstructural changes, and distribution of individual elements; and with XRD for crystalline phases.

2.3.1 Density – Archimedes method

The samples were weighed on an analytical balance (Sartorius model A200S, Brinkmann Instruments Co., Westbury, New York) to an accuracy of 0.1 mg (m_{dry}) before being suspended in ethanol (EtOH) for 2 h under in-house vacuum (10 kPa) to allow the EtOH to penetrate any open and surface-connected porosity. The samples were then weighed both suspended in EtOH (m_{sus}) and in air saturated with EtOH (m_{sat}). The apparent densities of the samples were calculated according to Eq. (1):

$$\rho_{sample} = \frac{m_{dry} \rho_{EtOH}}{(m_{sat} - m_{sus})} \quad (1)$$

where m_i is the mass in the i -th configuration (i = dry, saturated and suspended, respectively), and ρ_{EtOH} is the density of EtOH at the temperature of the test (0.79029×10^3 kg/m³ at 19°C) [25]. The open porosity of the samples was calculated according to Eq. (2):

$$\%OpenPorosity = \frac{(m_{sat} - m_{dry})}{(m_{sat} - m_{sus})} \times 100 \quad (2)$$

A sample of aluminum with a density 2.7000×10^3 kg/m³ and zero open porosity was run in duplicate with the samples to validate the obtained densities and open porosities. The measured densities, 2.6950 and 2.6899×10^3 kg/m³, and open porosities, 0.07 and 0.43%, were in good agreement with values for aluminum metal.

2.3.2 Density – helium pycnometry

A helium pycnometer (AccuPyc II 1340, Micromeritics Inc., Norcross, GA) was used to validate apparent densities obtained with the Archimedes method. The apparent density was calculated using the known sample mass and an apparent volume (the volume of the solid material excluding surface-connected porosity, but including closed pores) that was determined by measuring the pressure change of helium (99.995%) in a calibrated volume. The pycnometer was operated with a 1 mL sample cup. The volume of the cup was calibrated with a 0.7182 ± 0.0001 mL tungsten cylinder. The calibration was checked with a sample of aluminum of known density, $2.7000 \times 10^3 \text{ kg/m}^3$, at 20°C. The measured density of $2.6860 \pm 0.0056 \times 10^3 \text{ kg/m}^3$ was in good agreement with the density of the standard.

The samples were weighed on an analytical balance to the nearest 0.1 mg. The cup with samples was purged (cell filling/expulsion of helium) 10 times to remove air and moisture from the sample and the inside of the chamber. This was followed by 10 measurement cycles of the sample volume for density determination, the results of which were averaged.

2.3.3 Scanning electron microscopy and energy dispersive spectroscopy

A JEOL JSM-7001F/TTLS scanning electron microscope (JEOL USA, Inc., Peabody, MA) equipped with a field emission gun was used to examine polished thin sections of selected samples in low vacuum mode at an accelerating voltage of 15 kV to minimize beam penetration. Polished cross sections were analyzed for the extent of densification, the amount of open porosity, and the character of grain boundaries. An EDAX Si-drift detector was used to conduct EDS (Apollo XL, AMETEK, Berwyn, PA) for elemental spot analysis and dot mapping, which revealed the distribution of individual elements in densified samples.

2.3.4 X-ray diffraction

The samples were hand-ground to a fine powder with an agate mortar and pestle. This powder was dispersed in a couple of drops of EtOH before being collected with a pipette and deposited on the surfaces of zero-background XRD sample holders. The samples were scanned with an X-ray diffractometer (Bruker D8 Advanced; Bruker AXS Inc., Madison, WI) configured with a Cu K α target ($\lambda = 1.5406 \text{ \AA}$)

set to a power level of 40 kV and 40 mA, goniometer radius of 250 mm, 0.3° fixed divergence slit, and LynxEyeTM position-sensitive detector with a collection window of 3° 2 θ . The scan parameters were 0.03° 2 θ step size, 4 s dwell time, and 5 to 70° 2 θ scan range. Bruker AXS DIFFRACplus EVA software was used to identify crystalline phases.

3. Results and discussion

3.1 Hot uniaxial pressing

Figure 3 shows an SEM backscattered electron image of iodine-loaded Ag⁰-aerogel after processing with HUP. The different shades of gray for silica grains correspond to different concentrations of uniformly dispersed nanoparticles of Ag, Ag₂S, and AgI. In addition, micrometer-sized nodules of Ag, Ag₂S, and AgI formed at grain boundaries. It was hypothesized that grinding of Ag⁰-aerogel granules with a mortar and pestle produced particles with fractured surfaces covered by Ag and AgI nanoparticles. Since the melting temperatures of Ag and AgI are 961°C and 558°, respectively, these nanoparticles would coalesce at the grain boundaries and form micrometer-sized nodules by capillary forces and viscous flow during sintering at 1200°C. The Ag₂S was produced during the processing by a reaction of silver with thiols which were anchored onto the pores surfaces of silica aerogel during preparation of Ag⁰-aerogel. The sample was not fully sintered as evidenced by the presence of small cavities. This agreed well with the open porosity of ~16.9% measured by the Archimedes method. The initial mass of iodine-loaded Ag⁰-aerogel sample was 239.5 mg, of which 48.4 mg (20.2 mass% of total) was iodine and the remaining 191.1 mg was Ag⁰-aerogel. If only Ag⁰-aerogel was processed with HUP, the sample lost 16.3 mass%. This converts to a loss of 31.2 mg for 191.1 mg of Ag⁰-aerogel. However, the actual mass loss was 34.8 mg. The extra loss of 3.6 mg is related to iodine and resulted in the retention of 92.6% of sorbed iodine in the sintered product. This value is similar to an iodine retention of 92.2% that was observed for a sample that initially contained 15.4 mass% of iodine and that was heat-treated under the same conditions (1200°C for 30 min) but at a lower pressure of 0.1 MPa [10].

3.2 Hot isostatic pressing

Figure 4 shows a SEM backscattered electron image of Ag⁰-aerogel (HIP-1) after processing with HIP.

The sample was fully densified and had an apparent density of $3.0918 \pm 0.0256 \times 10^3 \text{ kg/m}^3$. Table 2 shows EDS analysis of four different areas for this sample. Concentrations of Ag varied from ~3 mass% in black areas to ~37 mass% in dark gray areas, ~49 mass% in light gray areas, and ~80 mass% in white micrometer-sized inclusions. An increased concentration of Ag was accompanied by increased concentration of sulfur, which varied from <1 mass% in black areas to >10 mass% in white spots.

Similar to the samples processed with HUP, nanoparticles and micrometer-sized inclusions of Ag and Ag₂S were distributed throughout the grains and along grain boundaries of the consolidated product.

Figure 5 shows the distribution of individual elements (Ag, I, and Si) and the morphology of particles in the HIP-processed iodine-loaded Ag⁰-aerogel (HIP-2). The fully densified sample had an apparent density of $3.2852 \pm 0.0245 \times 10^3 \text{ kg/m}^3$ and contained ~22 mass% of iodine. Iodine was retained in the form of nano- and micro-particles of AgI, which were uniformly dispersed in the silica-based matrix.

Some micrometer-sized inclusions of AgI were also located along grain boundaries. It remains to be determined whether the presence of AgI inclusions at the interface will result in faster release of iodine from the densified product. However, it is expected that the release of iodine will be limited by the physical barrier provided by the encapsulating silica matrix. The dissolution rates of AgI in the interior are expected to be much lower owing to the limiting effects of mass transport. The presence of other crystalline phases such as Ag and Ag₂S was confirmed by XRD analysis as shown in Figure 6. The lack of open porosity and 100% retention of iodine in the consolidated product indicated that for iodine loadings (concentrations of captured iodine) ~20 mass% there will be no need for additives to enhance the sintering process.

Figure 7 details the distribution and morphology of AgI and Ag₂S inclusions in the HIP-consolidated iodine-loaded Ag⁰-aerogel (HIP-4). The fully densified sample had an apparent density of $3.246 \times 10^3 \text{ kg/m}^3$ as measured with the Archimedes method. The density was in good agreement with the $3.2618 \pm 0.0082 \times 10^3 \text{ kg/m}^3$ obtained with a gas pycnometer measurement. The sample contained ~39 mass%

iodine which was retained in the form of nano- and micro-particles of AgI. These particles were uniformly dispersed in the silica-based matrix. The presence of crystalline phases such as AgI and Ag₂S was confirmed by XRD analysis, the results of which are shown in Figure 8. The lack of open porosity and 100% retention of iodine in the consolidated product indicated that, even for iodine loadings (concentrations of captured iodine) close to 40 mass%, there will be no need to include additives to enhance the sintering process and produce a fully consolidated waste form. Figure 9 shows a high magnification image of sample HIP-4 that indicates areas used to determine elemental composition with EDS measurement. The EDS data, shown in Table 3, shows that the concentrations of Ag and I ranged from 5.5 to 26.4 mass% and from 2.9 to 7 mass%, respectively. The concentration of sulfur remained nearly constant, ~0.3–0.4 mass%.

These results show excellent consolidation of the iodine-loaded Ag⁰-aerogel with HIP, considering the limited number of samples run to date.

4. Conclusion

The results from consolidation tests clearly showed that rapid consolidation of iodine-loaded Ag^0 -aerogel with HUP and HIP yields a final waste form consisting of AgI particles encapsulated in a silica-based matrix. HUP-processing (1200°C for 30 min under 29 MPa pressure) of Ag^0 -aerogel loaded with 20.2 mass% of iodine did not produce a fully dense product but a sintered product with a residual open porosity of 16.9%. Interestingly, ~93% of sorbed iodine was still retained in the sintered material. In contrast, densification of iodine-loaded Ag^0 -aerogel containing 20.2 mass% iodine with HIP at 1200°C for 30 min under 207 MPa pressure resulted in a fully dense silica-based waste form of $3.3 \times 10^3 \text{ kg/m}^3$ bulk density containing ~22 mass% iodine. Iodine was retained in the form of nano- and micro-inclusions of AgI dispersed in the silica matrix. The lack of open porosity and 100% retention of iodine in the consolidated product indicated that additives were not needed to enhance the sintering process. This was confirmed even for higher iodine loadings close to 40 mass%. Highly iodine-loaded Ag^0 -aerogel was successfully consolidated using HIP under the same conditions as the low-iodine-loaded sample. The fully densified product had a bulk density of $3.3 \times 10^3 \text{ kg/m}^3$ and contained ~39 mass% of iodine which was also retained in the form of nano- and micro-particles of AgI. However, the chemical durability testing of densified products will tell whether additives such as raw silica aerogel are required to enhance the long-term performance of the high-iodine-loaded waste form. It is expected that for a fully densified waste form with uniformly distributed inclusions of AgI the release of iodine will be limited by the physical barrier provided by the encapsulating silica matrix. In addition, scale-up of the consolidation with HIP is needed to demonstrate the effectiveness of this method. This should not be difficult considering that HIP is well established at commercial scales. However, HIP-processing requires material to be encapsulated in a container, such as Ta, which needs to be designed to generate a product of reliable shape and dimensions.

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6. References

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Tables and Figures

Table 1. Samples of Ag⁰-aerogel processed with HIP. ^(a) Organic moiety from functionalization was removed by ramp-heating at 5°C/min from room temperature to 350°C, holding at 350°C for 10 min, and air quenching. ^(b) Iodine loading after removal of organic moiety (HIP-2 and HIP-4 contained ~ 8 and 10 mass% organic moiety, respectively).

Sample ID	Organic Moiety ^(a)	Iodine ^(b) (mass%)
HIP-1	removed	0
HIP-2		22.1
HIP-3		0
HIP-4		38.8

Table 2. Concentrations of Ag, S, Si, and O in mass% for areas from Figure 4 (HIP-1, area 1–4).

Area	Si	O	Ag	S
1	29.39	28.70	37.43	4.48
2	49.75	46.72	2.78	0.75
3	22.36	22.34	49.29	6.01
4	4.04	6.35	79.53	10.08

Table 3. Concentrations of Si, O, Ag, and S in mass% for areas from Figure 9 (HIP-4, areas 1–4).

Area	Si	O	Ag	S	I
1	30.95	43.42	19.87	0.44	5.32
2	34.81	55.94	5.55	0.23	3.47
3	19.32	46.79	26.40	0.45	7.04
4	29.51	56.35	10.86	0.34	2.94

Figure 1. Assembly to produce iodine-loaded Ag⁰-aerogel; samples were exposed to iodine vapors at 150°C for 24 h.

Figure 2. Temperature and pressure as a function of time for samples processed with HIP.

Figure 3. SEM backscattered electron image of HUP-processed iodine-loaded Ag⁰-aerogel. White and light gray spots are nanoparticles and micrometer-sized nodules of Ag, Ag₂S, and AgI distributed along or inside of silica grains.

Figure 4. SEM backscattered electron image of HIP-processed Ag^0 -aerogel (HIP-1). White spots are nanoparticles and micrometer-sized nodules of Ag and Ag_2S distributed inside silica grains or along grain boundaries.

Figure 5. Elemental dot map of a small area of HIP-processed iodine-loaded Ag^0 -aerogel (HIP-2). Iodine loading 22.1 mass%.

Figure 6. XRD pattern and identified phases for HIP-processed iodine-loaded Ag⁰-aerogel (HIP-2).

Figure 7. SEM backscattered electron image of HIP-processed iodine-loaded Ag⁰-aerogel (HIP-4). White and light gray inclusions are nanoparticles and micrometer-sized nodules of AgI and Ag₂S dispersed in a silica-based matrix.

Figure 8. XRD pattern and identified phases for HIP-processed iodine-loaded Ag⁰-aerogel (HIP-4).

Figure 9. High magnification SEM backscattered electron image of HIP-processed iodine-loaded Ag^0 -aerogel (HIP-4). White and light gray inclusions are nanoparticles and micrometer-sized nodules of AgI and Ag_2S dispersed in a silica-based matrix. Elemental composition of highlighted areas 1–4 is summarized in Table 3.