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Consolidation of iodine-loaded Ag^0-functionalized silica aerogel with HUP, HIP, and SPS

Fuel Cycle Research & Development

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SUMMARY

The U.S. Department of Energy Office of Nuclear Energy is currently investigating alternative sorbents for the removal and immobilization of radioiodine from the gas streams in a nuclear fuel reprocessing plant. One of these alternative sorbents, silver-functionalized silica aerogel (Ag^0-aerogel), shows promise as a potential replacement for silver mordenite because of its high selectivity and sorption capacity for iodine. Moreover, a feasible consolidation of iodine-loaded Ag^0-aerogel to a durable SiO_2-based waste form makes this aerogel an attractive choice for sequestering radioiodine.

The main purpose of the study reported here was to investigate consolidation options for Ag^0-aerogel powders with or without iodine and with or without sintering additives using hot uniaxial pressing (HUP), hot isostatic pressing (HIP), and spark-plasma sintering (SPS). The selected densified 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.

To convert the iodine-loaded Ag^0-silica aerogel into a waste form, rapid consolidation with HUP, HIP, and SPS at moderate temperatures and pressures yielded a final waste form consisting of AgI particles encapsulated in fused silica. Processing (1200°C for 30 min under 29 MPa pressure) of Ag^0-aerogel loaded with 20.2 mass% of iodine using HUP provided a product with residual open porosity of 16.9%. However, ~93% of sorbed iodine was retained in the sintered material. Densification with HIP at 1200°C for 30 min under 207 MPa pressure resulted in a fully dense silica-based waste form of 3.3×10^3 kg/m^3 bulk density containing ~22 mass% of iodine. Iodine was retained in the form of nano- and micro-inclusions of AgI dispersed in the silica matrix. Additives were not needed to enhance the sintering process as evidenced by the lack of open porosity and 100% retention of iodine in the consolidated product. Future tests will tell whether additives such as raw silica aerogel or Ag^0-aerogel are required for HIP to produce a fully dense waste form from iodine-loaded Ag^0-aerogel containing higher concentrations of captured iodine. Processing of samples using SPS with or without iodine revealed the benefit of additive-enhanced sintering. The samples containing additives (raw silica aerogel, colloidal silica, and Ag^0-aerogel) shrank faster and at lower temperatures (<900°C). In addition, additives significantly improved the distribution of silver compounds in the fully densified products, thereby considerably decreasing the number of micrometer-sized inclusions of AgI, Ag, and Ag_2S at the grain boundaries.

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ABBREVIATIONS

Ag^0-aerogel	silver-functionalized silica aerogel
DIW	deionized water
HIP	hot isostatic pressing
HUP	hot uniaxial pressing
ID	internal diameter
OD	outer diameter
Pt	platinum
SEM-EDS	scanning electron microscopy and energy dispersive spectroscopy
SPS	spark-plasma sintering

1 INTRODUCTION

During the aqueous reprocessing of used nuclear fuel, volatile iodine-129 is released into the off-gas treatment system, which is required to control the emissions within safe and regulatory compliance limits. The current benchmark material for radioiodine capture is silver mordenite (AgZ) and the reference waste form is AgZ immobilized in a low-temperature glass composite material (Nenoff et al. 2008). 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 exhibits excellent sorption properties for iodine. Iodine capacities up to 480 mg/g were demonstrated with decontamination factors over 10,000 for laboratory tests with simulated dissolver off-gas gas streams (Matyáš et al. 2011; Soelberg and Watson 2012). In addition, Ag^0-aerogel retained high selectivity and sorption capacity for iodine even after a long-term exposure to dry/humid air (Bruffey et al. 2012, 2013) and dry air containing 2% NO_2 (Jubin et al. 2014). Furthermore, 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 this new sorbent an attractive choice for long-term immobilization of radioiodine.

Previously, iodine retention of >92% has been demonstrated in a hot uniaxially pressed sample (Matyáš et al. 2011). Also, the preliminary investigation of the feasibility of hot isostatic pressing (HIP) and spark-plasma sintering (SPS) for consolidating powders of Ag^0-aerogel clearly showed that these methods can be effectively used to produce material of near-theoretical density (Matyáš et al. 2013). In addition, the ram travel data for SPS indicated that rapid consolidation of Ag^0-aerogel can be performed at temperatures below 950°C.

The main purpose of the study reported here was to investigate consolidation options for Ag^0-aerogel powders with or without iodine and with or without sintering additives using HUP, HIP, and SPS. The selected densified 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 MATERIAL

Powders of Ag^0-aerogel, with or without iodine and with or without sintering additives, were prepared for processing with HUP, HIP, and SPS.

2.1 Ag^0-aerogel

A batch of Ag^0-aerogel granules was synthesized using a previously developed procedure (Matyáš et al. 2011), before being sieved into two size fractions: <0.85 mm and 0.85−2 mm. A fraction with a particle size of less than 0.85 mm was used to generate iodine-loaded material. The granules of this size were black in color with a few yellow spots and had a bulk density of ~0.6×10^3 kg/m^3. Brunauer, Emmett, Teller characterization revealed a surface area of 113.8 m^2/g, pore volume of 0.41×10^{-6} m^3/g, and an adsorption/desorption pore size of 20/13 nm, respectively. A small amount of granules were also hand-ground to powder with a mortar and pestle, and the resulting powder was used alone or mixed with sintering additives or as a sintering additive to prepare samples for HIP and SPS.

2.2 Iodine-loaded Ag^0-functionalized silica aerogel

Samples of iodine-loaded Ag^0-aerogel were prepared in an assembly made of Teflon®, shown in Figure 1. Bottom and top vessels contained ~0.5 g of solid I_2 (amount required to produce a partially iodine-loaded material) and four vials, respectively. Each vial contained ~0.4 g of Ag^0-aerogel granules with a particle

size <0.85 mm. 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 (kept under vacuum of 10 kPa) for 1 h and weighed with an analytical balance with 0.1 mg sensitivity to determine mass gain, i.e., iodine loadings. Table 1 shows concentrations of iodine from 18.1 to 21.9 mass% for iodine-loaded samples. These samples were then hand-ground with a mortar and pestle, and used to prepare samples for HIP (HIP 4−7) and SPS (SPS 4−7).

Figure 1. Assembly to produce iodine-loaded Ag^0-aerogel; iodine vapors at 150°C for 24 h.

Table 1. Concentration of iodine in mass % for iodine-loaded Ag^0-aerogel.

Method	Sample[(a)]	Iodine loading, mass %
HIP	4	20.2
	5	21.9
	6	19.7
	7	20.1
SPS	4	18.3
	5	18.1
	6	18.1
	7	18.7

(a) Used for preparation of iodine-loaded samples: HIP 4−7 and SPS 4−7.

2.3 Sintering additives

Three types of additives were investigated in this study to enhance the sintering and retention of iodine: 1) heat-treated silica aerogel, 2) colloidal silica (Ludox® CL-X colloidal silica, 45 mass% suspension in H_2O, Sigma Aldrich), and 3) heat-treated and non-heat-treated Ag^0-aerogel. Heat-treated silica aerogel was produced from as-received silica aerogel (United Nuclear Scientific, MI) by ramp-heating ~100 mL of granules on a Pt-plate at 5°C/min from room temperature to 700°C, holding at 700°C for 12 min, and air quenching. This process removed trimethyl silyl groups (installed by the manufacturer to make the aerogel hydrophobic) from the surface of the pores. The colloidal silica was used as received from the vendor. Heat-treated Ag^0-aerogel was produced from synthesized Ag^0-aerogel by ramp-heating ~1 g of granules in a Pt-box at 5°C/min from room temperature to 350°C, holding at 350°C for 10 min, and air quenching (Matyáš et al. 2013). This process removed organic moiety installed on the surface of the pores during the functionalization process (Matyáš et al. 2011). Heat-treated granules of silica aerogel

and heat-treated and non-heat-treated granules of Ag^0-aerogel were then hand-ground using a mortar and pestle to fine powders before being added to selected samples.

3 EXPERIMENTAL METHODS OF INVESTIGATION

3.1 Density − Archimedes method

The selected samples of Ag^0-functionalized silica aerogel that were consolidated with HUP and SPS were weighed on an analytical balance (Sartorius model A200S, Brinkmann Instruments Co., Westbury, New York) to an accuracy of 0.1 mg (m_{dry}) and then suspended in deionized water (DIW) for 2 h under in-house vacuum (10 kPa) to allow the DIW to penetrate any open and surface-connected porosity. Next, the samples were weighed both suspended in DIW (m_{sus}) and in air saturated with DIW (m_{sat}). The apparent densities of the samples were calculated according to Equation (1):

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

where m_i is the mass in the i-th configuration (i = dry, saturated and suspended, respectively), and ρ_{DIW} is the density of DIW at the temperature of the test (0.9978×10^3 kg/m^3 at 22°C) (ASTM C693-93). The open porosity of samples was calculated according to Equation (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/m^3 and zero open porosity was run with the samples to validate obtained densities and open porosities. The measured density, 2.6899×10^3 kg/m^3, and open porosity, 0.43 %, were in good agreement with values for aluminum metal.

3.2 Density – Helium pycnometry

A helium pycnometer (AccuPyc II 1340, Micromeritics Inc., Norcross, GA) was used to determine the apparent volume (the volume of the solid material excluding surface-connected porosity, but including closed pores) of selected samples by measuring the pressure change of helium (99.995%) in a calibrated volume. The apparent density was calculated from the known sample masses. 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, 2.7000×10^3 kg/m^3, at 20°C. The measured density of $2.6192 \pm 0.0172 \times 10^3$ kg/m^3 was ~3% lower than that of the standard, but still in good agreement with the known value.

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.

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 energy dispersive spectroscopy (EDS; Apollo XL, AMETEK, Berwyn, PA) for elemental spot analysis and dot mapping, which revealed the distribution of individual elements in densified samples.

3.4 X-ray diffraction

Selected samples were hand-ground to a fine powder with an agate mortar and pestle. This powder was dispersed in a couple of drops of ethanol before being collected with a pipette and deposited on a surface of the 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 Kα target (λ = 1.5406 Å) set to a power level of 40 kV and 40 mA, goniometer radius of 250 mm, 0.3° fixed divergence slit, and position-sensitive detector LynxEye™ with a collection window of 3° 2θ. The scan parameters were 0.03° 2 θ step size, 4 s dwell time, and 5 to 70° 2-θ scan range. A Bruker AXS DIFFRAC*plus* EVA was used to identify crystalline phases.

3.5 Methods of densification

Three methods of consolidation were used in this study: 1) HUP, 2) HIP, and 3) SPS. HUP was used to consolidate powdery samples of Ag^0-aerogel with or without iodine. HIP and SPS were used to consolidate pellets (HIP) and powders (SPS) of Ag^0-aerogel with or without iodine and with or without sintering additives.

3.5.1 Hot uniaxial pressing

Table 2 provides details about two Ag^0-aerogel samples with or without iodine with organic moiety present, which were processed using HUP (Matyáš et al. 2011, 2012). Approximately 0.2 g powdery samples were loaded into alumina crucibles (9.55 mm OD × 6.42 mm ID × 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 a 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, the crucible was removed, and the sample was air quenched on an alumina plate. The crucibles with samples were then put in a desiccator for an hour before being weighed on 4-digit balance to determine mass losses, which were used to calculate iodine retention in the product.

Table 2. Powders of Ag^0-aerogel with or without iodine processed with HUP.

Sample ID	Organic moiety	Iodine (mass%)
HUP-1	present	NA
HUP-2		20.2[(a)]

(a) Removal of organic moiety (~8 mass%) from iodine-loaded sample increased concentration of iodine to 22 mass%.
NA = iodine not present

3.5.2 Hot isostatic pressing

Table 3 provides a summary of the powders and powder mixtures of Ag^0-aerogel needed to prepare 0.4−0.5 g pellets for HIP. A total of seven samples were prepared: 1) Ag^0-aerogel, 2) Ag^0-aerogel containing 10 mass% of silica aerogel, 3) Ag^0-aerogel containing 10.5 mass% of colloidal silica, 4) iodine-loaded Ag^0-aerogel, 5) iodine-loaded Ag^0-aerogel containing 10.7 mass% of silica aerogel, 6) iodine-loaded Ag^0-aerogel containing 10.6 mass% of colloidal silica, and 7) iodine-loaded Ag^0-aerogel containing 9.5 mass% of Ag^0-aerogel.

Table 3. Powders and powder mixtures of Ag^0-aerogel for preparation of pellets for HIP.

Sample ID	Organic moiety	Iodine[(d)] (mass%)	Additives[(a)]		
			Colloidal silica (mass%)	Silica Aerogel[(b)] (mass%)	Ag^0-aerogel[(c)] (mass%)
HIP-1	Removed[(c)]	NA	–	–	–
HIP-2		NA	–	10	–
HIP-3		NA	10.5	–	–
HIP-4		22.1	–	–	–
HIP-5		21.3	–	10.7	–
HIP-6		19.1	10.6	–	–
HIP-7		19.6	–	–	9.5

(a) Concentrations of additives in mass% in the samples of Ag0-aerogel with removed organic moiety and with or without iodine.
(b) Ramp-heated at 5°C/min from room temperature to 700°C, held at 700°C for 12 min, and air quenched to remove trimethyl silyl groups.
(c) Heat-treated from room temperature to 350 °C at a rate of 5 °C/min, held at 350 °C for 10 min, and air quenched to remove organic moiety from functionalization.
(d) Concentrations of iodine in the samples with additives and organic moiety removed.
NA = iodine not present; – = not added.

The organic moiety was removed from all samples before processing with HIP because gases evolved from its decomposition can prevent densification of the powder inside the metal fixture (Matyáš et al. 2013). The additives were homogenously mixed with Ag^0-aerogel with or without iodine using a mortar and pestle. Target amounts of colloidal silica were added to selected samples with pipettes. To remove water, the samples with colloidal silica were left in an oven at 105°C overnight. Each powdery sample 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) of the circular 0.016 mm thick tantalum sheet (38 mm in diameter) and covered by a circular flat sheet of the same diameter. 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 with 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 seven 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.

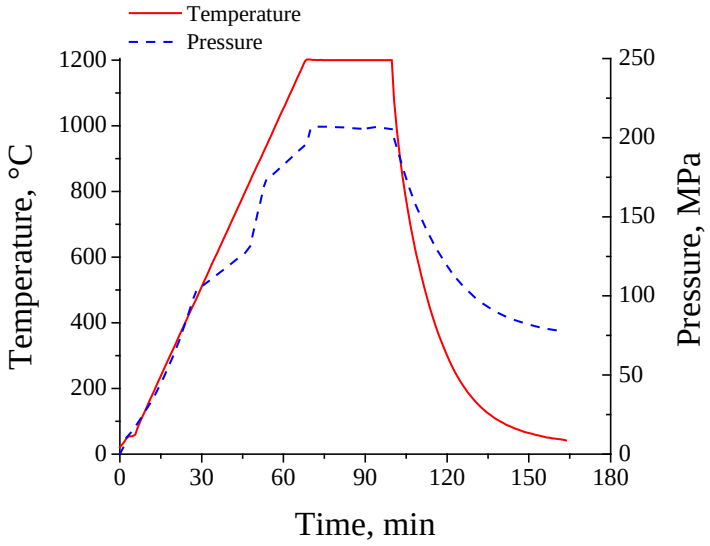

Figure 2. Temperature and pressure as a function of time for samples processed with HIP.

3.5.3 Spark-plasma sintering

A total of seven 0.4−0.5 g powdery samples were processed at California Nanotech Corporation (Cerritos, California) with a laboratory-scale SPS instrument, Fuji Electronic Dr. Sinter Lab Series SPS-515S (Syntex Inc., Kanagawa, Japan). Table 4 provides a summary of the powders and powder mixtures of Ag^0-aerogel for SPS: 1) Ag^0-aerogel, 2) Ag^0-aerogel containing 10.1 mass% of silica aerogel, 3) Ag^0-aerogel containing 9.9 mass% of colloidal silica, 4) iodine-loaded Ag^0-aerogel, 5) iodine-loaded Ag^0-aerogel containing 8.4 mass% of silica aerogel, 6) iodine-loaded Ag^0-aerogel containing 8.5 mass% of colloidal silica, and 7) iodine-loaded Ag^0-aerogel containing 8.5 mass% of Ag^0-aerogel. The organic moiety was not removed from the samples. The powders of heat-treated silica aerogel and non-heat-treated Ag^0-aerogel, and a colloidal solution of silica were added to samples to improve the sintering process. Each sample was loaded into a 10 mm diameter, high-strength, graphite die and rapidly step-wise heated to 1100°C. Powders were heated under argon and 42 MPa pressure from room temperature to 500°C at 158°C/min, from 500 to 1000°C at 300°C/min, from 1000 to 1100°C at 100°C/min, and finally held at 1100°C for 30 min under 74 MPa pressure. Then, the SPS instrument was turned off and samples rapidly cooled to temperatures below 400°C under flowing argon. Figure 3 shows the temperature and pressure histories for the samples processed with SPS.

Table 4. Powders and powder mixtures of Ag^0-aerogel for preparation of samples for SPS.

Sample ID	Organic moiety	Iodine[(d)] (mass%)	Additives[(a)]		
			Colloidal silica (mass%)	Silica Aerogel[(b)] (mass%)	Ag^0-aerogel[(c)] (mass%)
SPS-1	present	NA	–	–	–
SPS-2		NA	–	10.1	–
SPS-3		NA	9.9	–	–
SPS-4		20.4	–	–	–
SPS-5		18.6	–	8.4	–
SPS-6		18.6	8.5	–	–
SPS-7		18.6	–	–	8.5

(a) Concentrations of additives in mass% in the samples with or without iodine.
(b) Heat-treated to remove trimethyl silyl groups,
(c) Non-heat-treated powder.
(d) Concentrations of iodine in the samples with additives and organic moiety removed.
NA = iodine not present; – = not added.

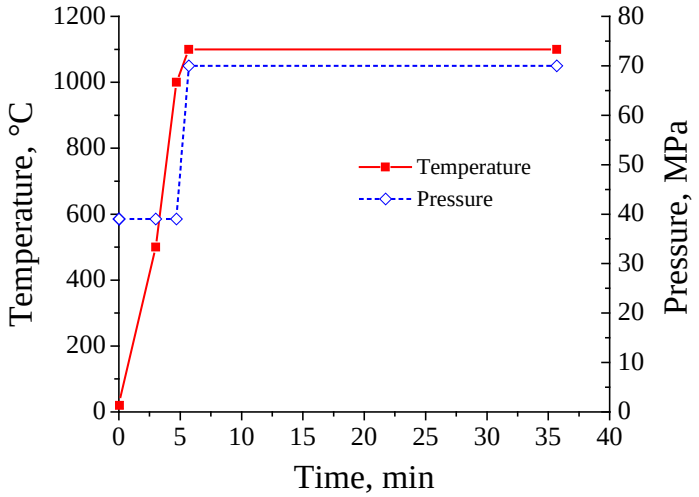

Figure 3. Temperature and pressure as a function of time for samples processed with SPS.

4 RESULTS AND DISCUSSION

Figure 4 shows a SEM backscattered electron image of iodine-loaded Ag^0-aerogel sample (HUP-2) after processing with HUP. The different shades of gray for silica grains correspond to different concentrations of uniformly dispersed nanoparticles of Ag, Ag_2S, and AgI. Also, micrometer-sized nodules of Ag, Ag_2S, and AgI formed at grain boundaries. In addition, the sample was not fully sintered (contained ~16.9% of open porosity), as evidenced by the presence of small cavities. The initial mass of iodine-loaded Ag^0-aerogel sample (HUP-2) was 239.5 mg, of which 48.4 mg (20.2 mass% of total) was iodine and the remaining 191.1 mg was Ag^0-aerogel. If only Ag^0-aerogel (HUP-1) was processed with HUP the sample lost 16.3 mass%. This means a loss of 31.2 mg for 191.1 mg of Ag^0-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 the iodine retention of 92.2%, which was observed for a sample initially containing 15.4 mass% of iodine and which was heat-treated under the same conditions (1200°C for 30 min) but at a lower pressure of 0.1 MPa (Matyáš et al. 2011).

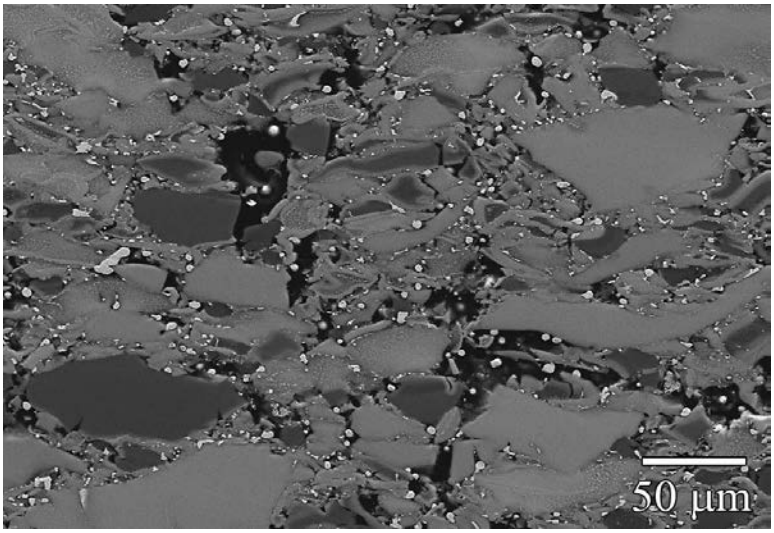

Figure 4. SEM backscattered electron image of HUP-processed iodine-loaded Ag^0-aerogel (HUP-2). White and light gray spots are nanoparticles and micrometer-sized nodules of Ag, Ag_2S, and AgI.

Figure 5 shows a SEM backscattered electron image of Ag^0-aerogel (HIP-1) after processing with HIP. The sample was fully densified and had an apparent density of 3.0918 ± 0.0256 g/cm^3. Table 5 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 followed 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 Ag_2S were distributed throughout the grains and along grain boundaries of consolidated product. The presence of Ag and Ag_2S was confirmed by XRD analysis as shown in the Figure 6.

Figure 7 shows the distribution of individual elements (Ag, I, and Si) and the morphology of particles in the HIP-processed iodine-loaded Ag^0-aerogel (HIP-4). The fully densified sample had an apparent density of 3.2852 ± 0.0245 g/cm^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. XRD analysis, shown in the Figure 8, also identified other crystalline phases in the sample such as Ag and Ag_2S. 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 to add additives to enhance the sintering process. Figure 9 shows SEM backscattered images of HIP-processed iodine-loaded Ag^0-aerogel with added raw silica aerogel (HIP-5) or Ag^0-aerogel (HIP-7). Processing using HIP

produced fully dense samples with nicely distributed particles and micrometer-sized inclusions of Ag, Ag_2S, and AgI. In contrast, for iodine-loaded Ag^0-aerogel with added colloidal silica, which is shown in the Figure 10, these particles and inclusions were predominantly distributed at the grain boundaries and even formed "small lakes" there. It remains to be determined if this excessive accumulation of AgI at the interface will result in the faster release of iodine from the densified product. Future tests will reveal whether additives such as raw silica aerogel or Ag^0-aerogel are needed to produce a fully dense waste form from iodine-loaded Ag^0-aerogel containing higher concentrations (~40 mass%) of captured iodine.

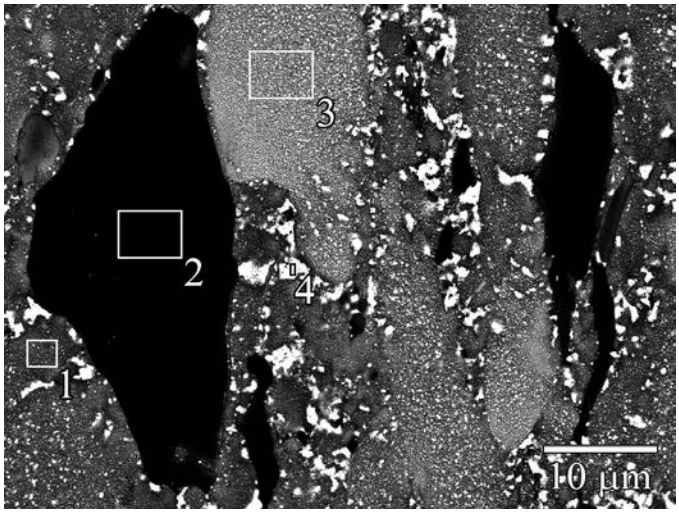

Figure 5. SEM backscattered electron image of HIP-processed Ag^0-aerogel (HIP-1). White spots are nanoparticles and micrometer-sized nodules of Ag and Ag_2S.

Table 5. Concentrations of Ag, S, Si, and O in mass% for areas from Figure 5 (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

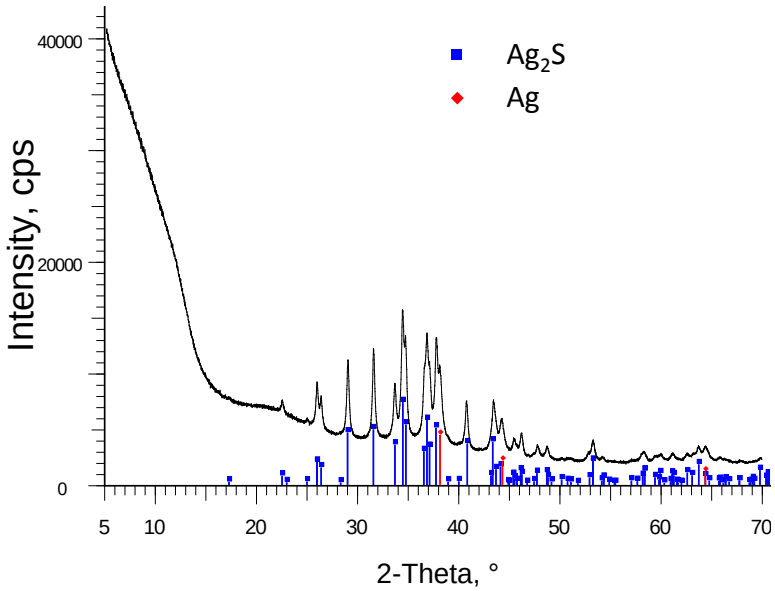

Figure 6. XRD pattern and identified phases for HIP-processed Ag^0-aerogel (HIP-1).

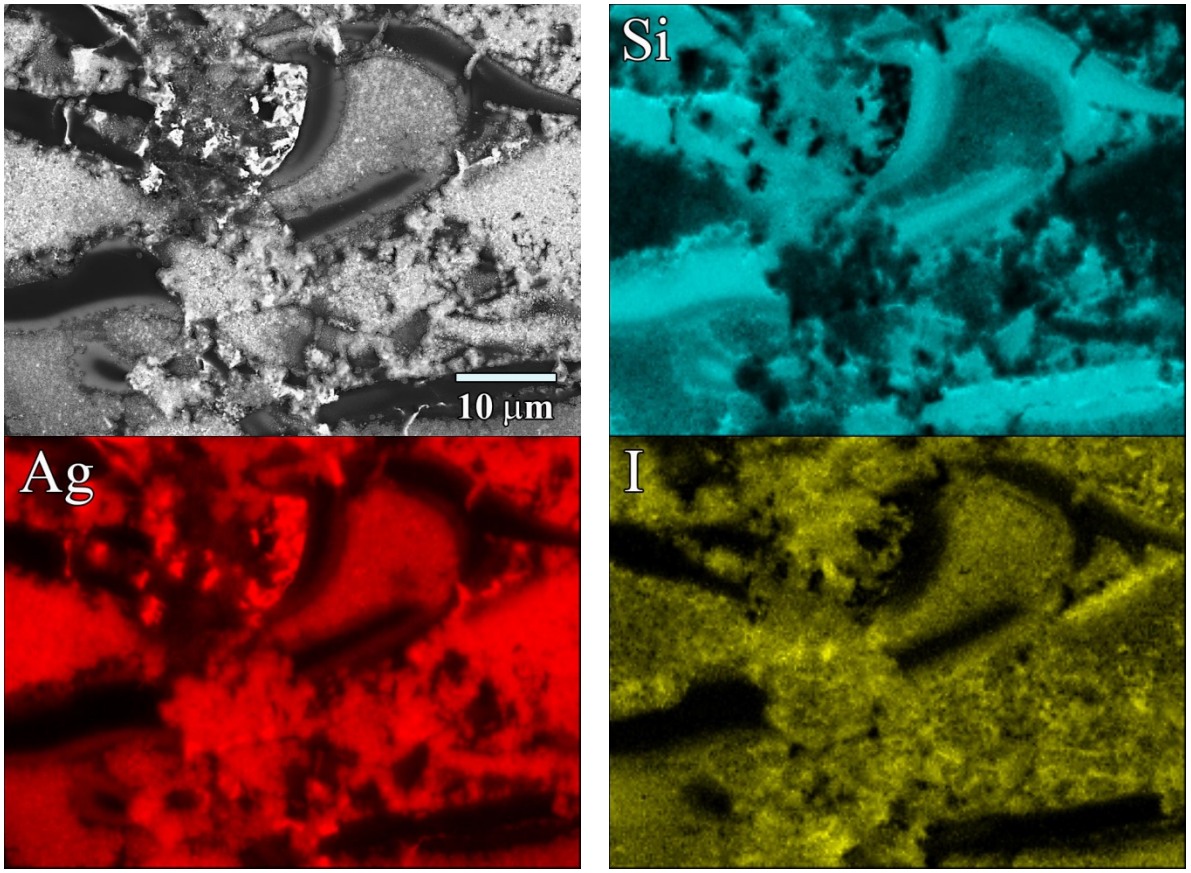

Figure 7. Elemental dot map of the small area for HIP-processed iodine-loaded Ag^0-aerogel (HIP-4).

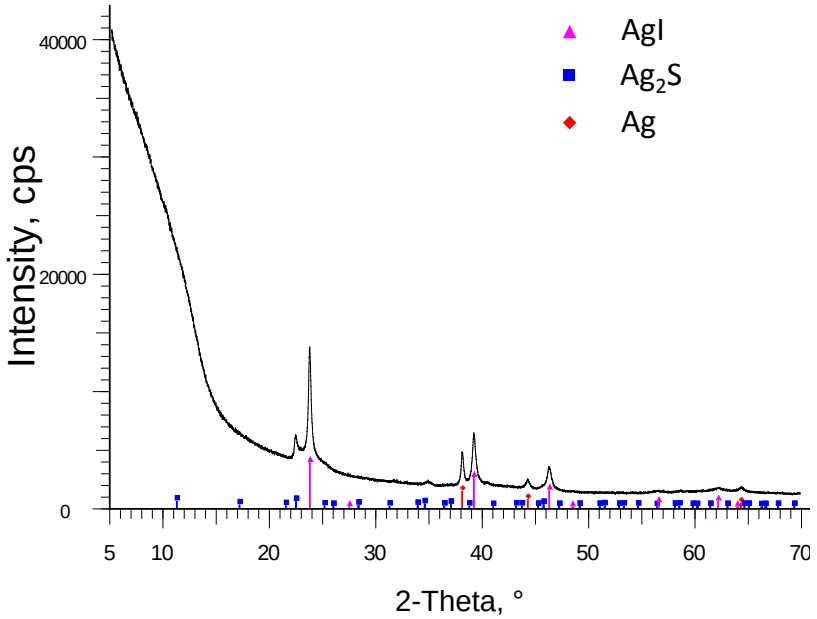

Figure 8. XRD pattern and identified phases for HIP-processed iodine-loaded Ag^0-aerogel (HIP-4).

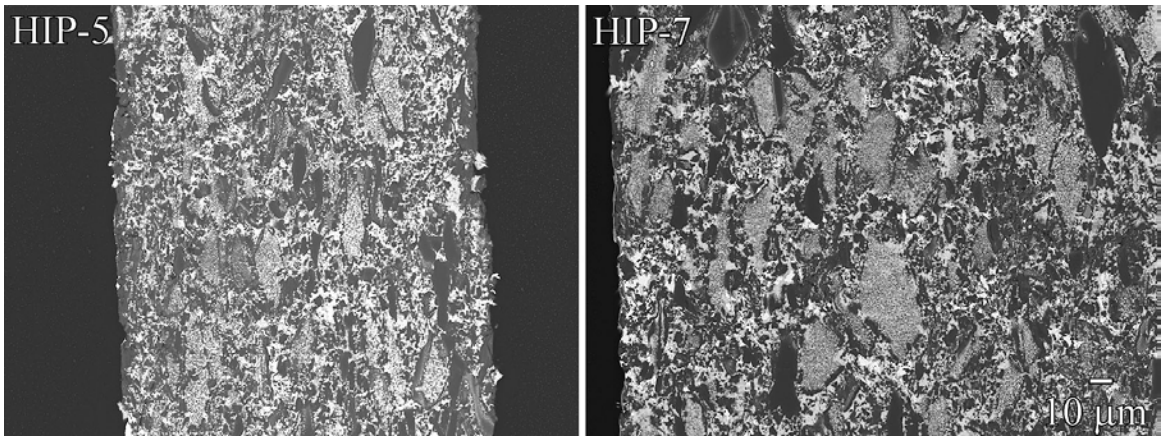

Figure 9. SEM backscattered electron images of HIP-processed iodine-loaded Ag^0-aerogel with added raw silica aerogel (HIP-5) or with added Ag^0-aerogel (HIP-7). White spots are nanoparticles and micrometer-sized nodules of AgI, Ag, and Ag_2S.

Figure 11 shows pressure and ram displacement as functions of temperature for SPS-processed samples: SPS-1 (Ag^0-aerogel), SPS-2 (Ag^0-aerogel with added raw silica aerogel), and SPS-3 (Ag^0-aerogel with added colloidal silica). While SPS-2 and 3 samples gradually shrank (with a rate of ~0.7 µm/°C) during heating from 600 to 1025°C under constant pressure of 42 MPa, the SPS-1 sample shrank only a little (a total of 47 µm) and its thickness remained constant from 800 to 1075°C. The fast shrinkage observed for SPS-2 and 3 samples provides direct evidence of additive-enhanced sintering. A benefit of using additives when processing a sample with SPS is shown in Figure 12, which includes SEM micrographs of SPS-1 and -2 samples. Addition of 10 mass% of raw silica aerogel significantly decreased the number of micrometer-sized inclusions of Ag and Ag_2S at the grain boundaries. Most of the Ag and Ag_2S remained entrapped in the silica grains.

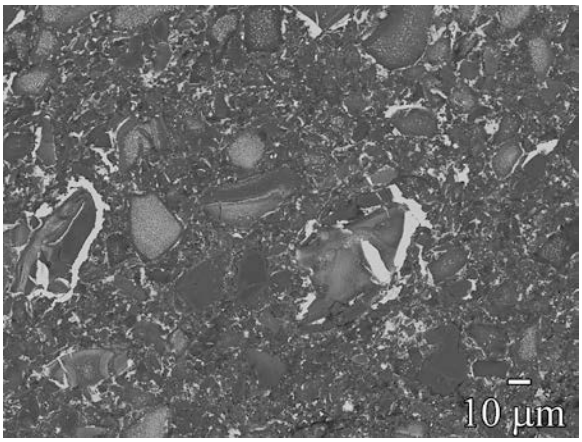

Figure 10. SEM backscattered electron image of HIP-processed iodine-loaded Ag^0-aerogel with added colloidal silica (HIP-6). White spots are nanoparticles and micrometer-sized nodules of AgI, Ag, and Ag_2S.

Figure 13 shows SEM high magnification image for SPS-3 sample including areas used for EDS elemental analysis. As shown in the Table 6, these areas contained different concentrations of Ag (0.8 - 73.9 mas%), S (0.9 - 5.9 mass%), and Si (5.2 - 48.9 mass%). The brighter the area the higher was the concentration of Ag and S. The detected low concentrations of sodium come from colloidal silica where it was being used as a solution-stabilizing counter ion. Two sources of carbon impurities are possible: 1) carbon from colloidal silica (contains 7% of ethylene glycol), and 2) carbon from graphite foil (separates the powder from the graphite die and punch).

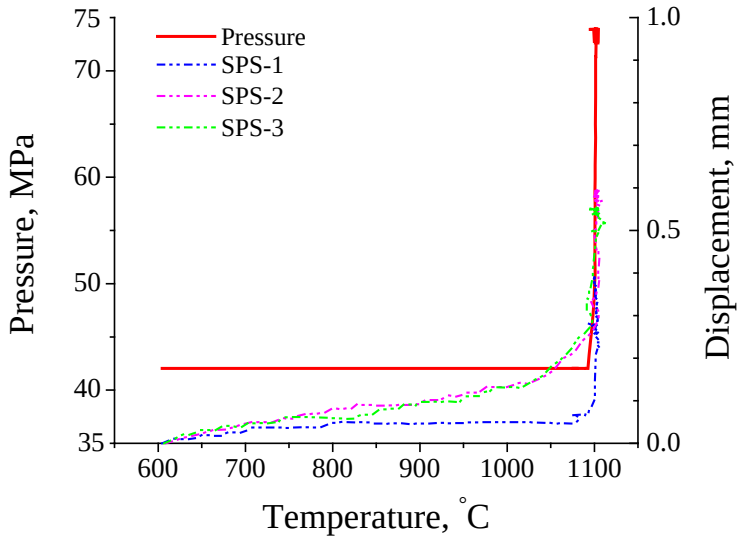

Figure 11. Pressure and ram displacement (broken lines) as functions of temperature for SPS samples (SPS-1 to 3) free of iodine.

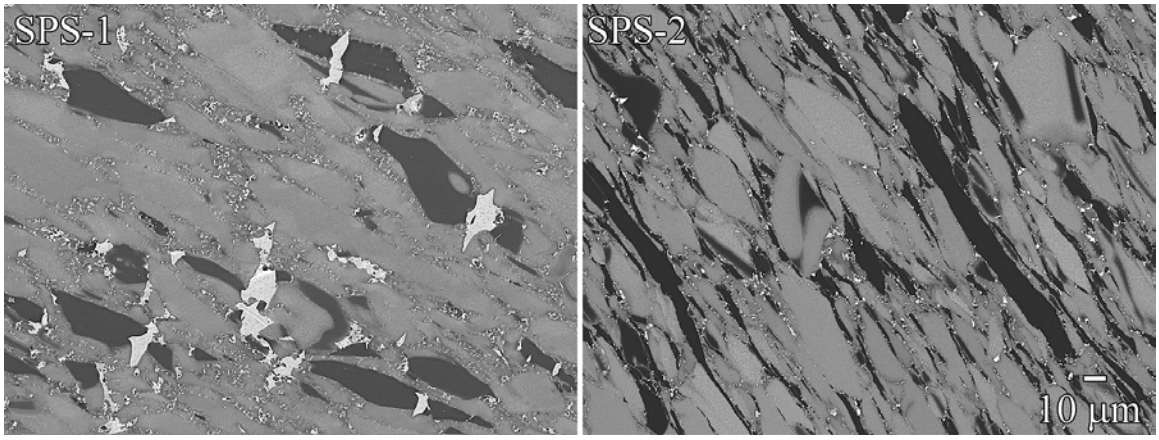

Figure 12. SEM backscattered electron images of SPS-processed Ag^0-aerogel (SPS-1) and Ag^0-aerogel with added raw silica aerogel (SPS-2). White spots are nanoparticles and micrometer-sized nodules of Ag and Ag_2S.

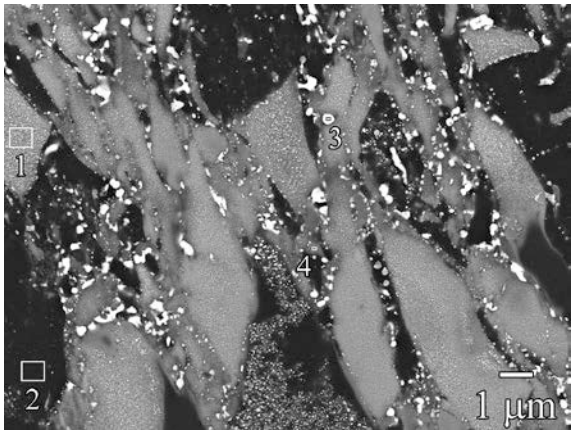

Figure 13. SEM backscattered electron image of SPS-processed Ag^0-aerogel with added colloidal silica (SPS-3) and areas for EDS measurement. White spots are nanoparticles and micrometer-sized nodules of Ag and Ag_2S.

Table 6. Concentrations of Ag, S, Si, O, Na, and C in mass% for areas from Figure 13 (SPS-3, area 1–4).

Area	Si	O	Ag	S	Na	C
1	22.33	21.71	44.94	5.89	0.72	4.40
2	48.87	44.70	0.77	0.87	0.18	4.60
3	5.19	14.92	73.85	1.77	0.46	3.80
4	30.95	31.46	28.83	4.16	0.28	4.32

Figure 14 shows detailed backscattered electron micrographs of small areas for SPS-processed iodine-loaded samples (SPS-4 to 7) with or without additives. As for non-iodine-loaded Ag^0-aerogel, addition of raw silica aerogel, colloidal silica, and Ag^0-aerogel significantly improved distribution of silver compounds in the sintered samples. Iodine was retained in the form of nanoparticles and micrometer-sized inclusions of AgI. A fully densified iodine-loaded sample SPS-4 had a density 2.4781 ± 0.0080 g/cm^3. Addition of Ag^0-aerogel increased the density to 2.8934 ± 0.0080 g/cm^3. These densities were lower than expected (compared to samples processed with HIP) and are due to significant contamination with graphite from graphite foil (used as a liner for the inner wall of the graphite die and a spacer on top of the punch). This cross-contamination, which varied from sample to sample, prevented determination of iodine retention through mass balance measurements. Figure 15 shows pressure and ram displacement as a function of temperature. The ram displacement curves suggest that SPS temperatures can be substantially reduced (<900°C) with small amounts of additives. The sintering shrinkage was enhanced the most by adding Ag^0-aerogel to the iodine-loaded sample, followed by colloidal silica, and raw silica aerogel.

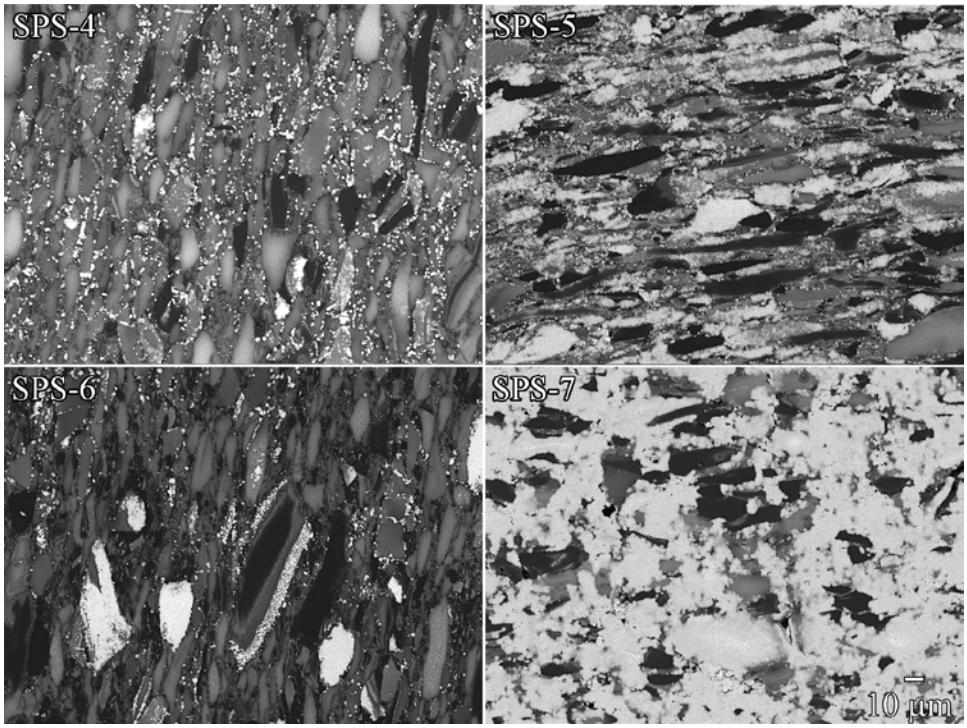

Figure 14. SEM backscattered electron images of SPS-processed iodine-loaded Ag^0-aerogel (SPS-4), iodine-loaded Ag^0-aerogel with added raw aerogel (SPS-5), colloidal silica (SPS-6), and Ag^0-aerogel (SPS-7). White spots are nanoparticles and micrometer-sized nodules of AgI, Ag, and Ag_2S.

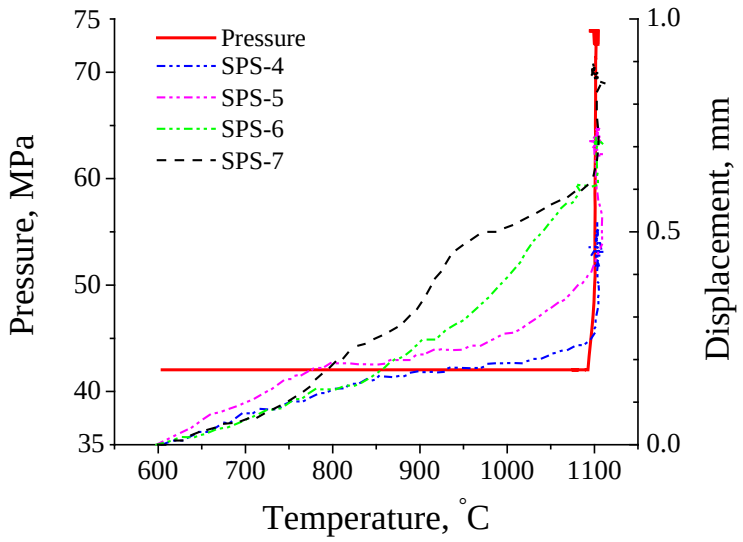

Figure 15. Pressure and ram displacement (broken lines) as functions of temperature for SPS samples (SPS-4 to 7) containing iodine.

5 CONCLUSIONS

To convert the iodine-loaded Ag^0-silica aerogel into a waste form, rapid consolidation with HUP, HIP, and SPS at moderate temperatures and pressures yielded a final waste form consisting of AgI particles encapsulated in fused silica. HUP-processing (1200°C for 30 min under 29 MPa pressure) of Ag^0-aerogel loaded with 20.2 mass% of iodine provided a product with a residual open porosity of 16.9%. However, ~93% of sorbed iodine was retained in the sintered material. Densification with HIP at 1200°C for 30 min under 207 MPa pressure resulted in a fully dense silica-based waste form of 3.3×10^3 kg/m^3 bulk density containing ~22 mass% of iodine. Iodine was retained in the form of nano- and micro-inclusions of AgI dispersed in the silica matrix. Additives were not needed to enhance the sintering process as evidenced by the lack of open porosity and 100% retention of iodine in the consolidated product. Future tests will tell whether additives such as raw silica aerogel or Ag^0-aerogel are required for HIP to produce a fully dense waste form from iodine-loaded Ag^0-aerogel containing higher concentrations of captured iodine. Processing of samples using SPS with or without iodine revealed a benefit of additive-enhanced sintering. The samples containing additives (raw silica aerogel, colloidal silica, and Ag^0-aerogel) shrank faster and at lower temperatures (<900°C). In addition, additives significantly improved the distribution of silver compounds in the fully densified products, thereby considerably decreasing the number of micrometer-sized inclusions of AgI, Ag, and Ag_2S at the grain boundaries.

6 ACKNOWLEDGEMENTS

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