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

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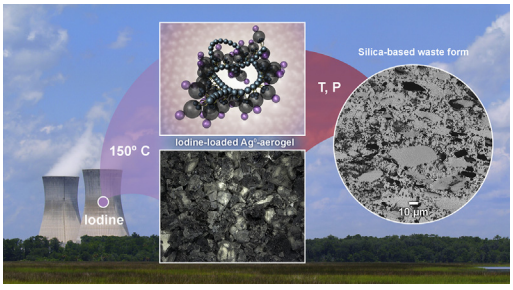
## HIGHLIGHTS

- Silver-functionalized silica aerogel is an effective sorbent and a viable waste form for iodine.
- Simultaneous application of fast heating rates and high pressures produced a fully dense product.
- HIPing produced a fully consolidated waste form with a bulk density of 3.3 × $10^3$ kg/$m^3$ and containing ~39 mass % of iodine.

## GRAPHICAL ABSTRACT

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## ABSTRACT

A high selectivity and sorption capacity for iodine and a feasible consolidation to a durable $SiO_2$-based waste form makes silver-functionalized silica aerogel ($Ag^0$-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 $Ag^0$-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 $Ag^0$-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 × $10^3$ kg/$m^3$ 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.


## 1. Introduction

The aqueous reprocessing of used nuclear fuel results in the release of various radionuclides into the off-gas system with radioiodine ($^{129}$I) being of a particular concern because of its long half-life (1.6 × $10^7$ years) and high mobility in the environment. Under current U.S. regulations [1–3], $^{129}$I 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 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

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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 ~150 $m^2$/g, pore volume ~0.5 mL/g, and bulk density ~500 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 $Ag^0$-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 $Ag^0$-aerogel with or without iodine were prepared for processing with hot uniaxial pressing (HUP) and HIP. A batch of $Ag^0$-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% $H_2$ in Ar. The granules were black in color with yellow spots and had a bulk density of ~0.6 × $10^3$ kg/$m^3$. Iodine-loaded $Ag^0$-aerogel granules were prepared in a Teflon assembly shown in Fig. 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 $Ag^0$-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 $Ag^0$-aerogel containing or lacking iodine into a fully dense silica-based waste form.

#### 2.2.1. Hot uniaxial pressing

Two powdery samples of $Ag^0$-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 $Ag^0$-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


**Fig. 1.** Assembly to produce iodine-loaded $Ag^0$-aerogel; samples were exposed to iodine vapors at 150 °C for 24 h.