

Cambridge University Press & Assessment

978-1-605-11721-8 — Scientific Basis for Nuclear Waste Management XXXVIII

Edited by Josef Matyáš , Stéphane Gin , Robert Jubin , Eric Vance

Excerpt

[More Information](#)

Capture and Immobilization of Radionuclides

Mater. Res. Soc. Symp. Proc. Vol. 1744 © 2015 Materials Research Society
 DOI: 10.1557/opl.2015.297

Current Status of Immobilization Techniques for Geological Disposal of Radioactive Iodine in Japan

Kazuya Idemitsu¹, Tomofumi Sakuragi²

¹ Department of Applied Quantum Physics and Nuclear Engineering, Kyushu University, Fukuoka, Japan

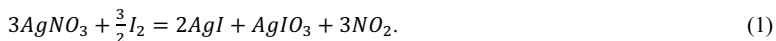
² Radioactive Waste Management Funding and Research Center, Tokyo, Japan

ABSTRACT

Nuclear reprocessing plants in Japan produce radioactive iodine-bearing materials such as spent silver adsorbents. Japanese disposal plans classify radioactive waste containing a given quantity of iodine-129 as Transuranic Waste Group 1 for spent silver adsorbent or as Group 3 for bitumen-solidified waste, and stipulate that such waste must be disposed of by burial deep underground. Given the long half-life of iodine-129 of 15.7 million years, it is difficult to prevent release of iodine-129 from the waste into the surrounding environment in the long term. Moreover, because ionic iodine is soluble and not readily adsorbed, its migration is not significantly retarded by engineered or natural barriers. The release of iodine-129 from nuclear waste therefore must be restricted to permit reliable safety assessment; this technique is called “controlled release”. It is desirable that the release period for iodine be longer than 100,000 years. To this end, several techniques for immobilization of iodine have been developed; three leading techniques are the use of synthetic rock (alumina matrix solidification), BPI (BiPbO₂I) glass, and high-performance cement. Iodine is fixed as AgI in the grain boundary of corundum or quartz through hot isostatic pressing in synthetic rock, as BPI in boron/lead-based glass, or as cement minerals such as ettringite in high-performance alumina cement. These techniques are assessed by three models: the corrosion model, the leaching model, and the solubility-equilibrium model. This paper describes the current status of these three techniques.

INTRODUCTION

In Japanese nuclear reprocessing plants, radioactive iodine in the off-gas pretreatment process is collected using silver adsorbent. This spent silver adsorbent includes ¹²⁹I and is categorized as Transuranic (TRU) Waste Group 1 for geological disposal [1]. In the case of the Rokkasho Reprocessing plant in northern Japan, which has a maximum reprocessing capacity of 800 tU/year, 40 years of operation is estimated to produce 51 TBq of ¹²⁹I. The silver-sorbent used for iodine filters is an alumina-based material loaded with silver nitrate (AgNO₃). Iodine reacts with AgNO₃ and is fixed as silver iodide (AgI), or silver iodate (AgIO₃) like in other silver-doped sorbents used for iodine [2, 3]. Trapping of iodine by silver-loaded sorbents is expected to follow the reaction



Because the half-life of ¹²⁹I is 15.7 million years, it is difficult to prevent the release of ¹²⁹I from waste into the surrounding environment in the long term. Moreover, as ¹²⁹I exists in

groundwater in anionic form, it is not expected that ^{129}I dispersal will be retarded by sorption onto most of the barrier materials used in the geological disposal environment. Thus, the peak exposure dose is easily affected by geological environmental conditions such as groundwater flow rate. To lower the peak ^{129}I exposure dose, it is more effective to decrease the rate of dissolution of waste or to elongate the release period, rather than to delay the start of dissolution. This approach is called “controlled release”. To obtain the desired iodine release-delaying capability for waste, the relationship between the maximum ^{129}I exposure dose and the iodine release period has been assessed through calculations [4]. Results show that the peak exposure dose from ^{129}I in each hydrologic condition assessed could be made lower than $10\ \mu\text{Sv/year}$ when the iodine release period was longer than 10^5 years, which has led to the goal of developing waste forms that can suppress release for at least this duration.

Several techniques for immobilization of iodine have been developed for this purpose [5-12]. These have been narrowed down to three techniques: synthetic rock (alumina matrix solidification), BPI (BiPbO_2I) glass, and high-performance cement. These techniques were classified into three types according to the model used for their assessment, namely, the leaching model, the distribution equilibrium model, and the solubility-equilibrium model. In this paper, the current status of these techniques is described.

SYNTHETIC ROCK (ALUMINA MATRIX SOLIDIFICATION) BY THE HOT ISOSTATIC PRESS PROCESS

In synthetic rock, iodine in the form of silver iodide is sealed within the grain boundaries of densely solidified corundum through hot isostatic pressing (HIP). Because natural hard rock provides long-term durability with a matrix that is difficult to dissolve and that does not easily allow water to penetrate, the contained chemical elements are not easily released. Therefore, it is assumed that rocks converted to a crystalline material by HIP are stable and capable of immobilizing iodine over long periods.

In HIP process, the waste silver adsorbent is pulverized and packed into a capsule, which is pre-heated at $450\ ^\circ\text{C}$ in vacuum for 2 h, then heated at $1200\ ^\circ\text{C}$ and $175\ \text{MPa}$ for 3 h as shown in Fig. 1. This procedure generates very little secondary waste.

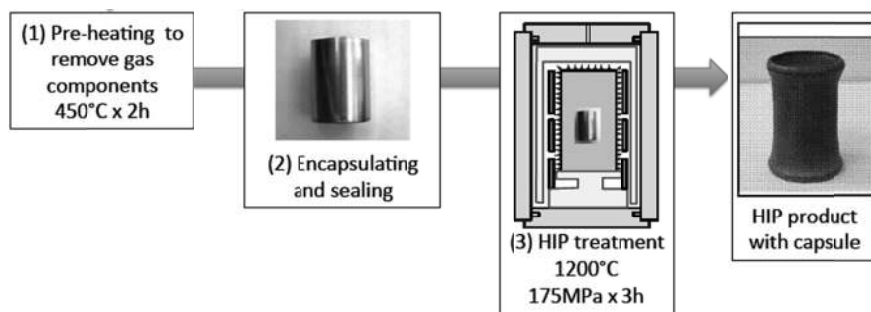
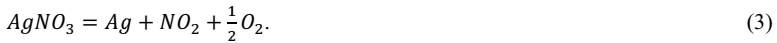


Fig. 1 HIP process for immobilization of iodine fixed in Ag-alumina filter

During pre-heating, silver iodate and silver nitrate are decomposed to silver iodide and silver as shown by the following reactions



Iodine is not released as a gas [13]. The microstructure of the HIP product is shown in Fig. 2. Silver iodide is surrounded by alumina. The concentration of AgI in the waste form was approximately 20wt%. A certain amount of void (black parts in Fig. 2) was observed. The void ratio could be reduced to less than 5% by HIP after pre-heating at 450 °C for 3 h in vacuum below 7×10^{-2} Pa, whereas around 15% porosity remained with no pre-heating, as shown in Fig. 3. Uniaxial compressive strength observed for the HIP product was as high as 1.1 GPa.

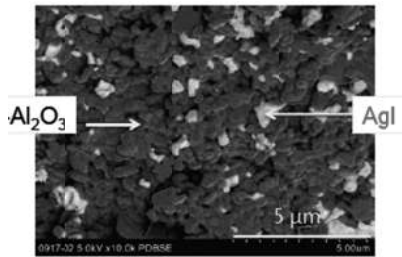


Fig. 2 Microstructure of HIP product

As recieved	Degassing	
	1200°C	1300°C
Porosity 15%	5%	4%

Fig. 3 Porosity reduction by degassing at 450 °C for 3 h in vacuum before HIP

Silver iodide is among the most stable iodides and has an extremely low solubility product, as low as 10^{-16} at 25 °C [14]. Although silver might be reduced to metallic silver, which could lead to a release of iodine under reducing conditions, a metallic silver layer could form and protect against the transport of reactants, which could subsequently suppress the release of iodine [15]. However, hydrosulfide concentrations as high as 1 mM could increase the discharge of iodine. X-ray diffraction patterns of HIP products are shown in Fig. 4 before and after contact

with leachant containing 1 mM of Na₂S at 25 and 60 °C. After contact with leachant, silver sulfide was observed in the HIP product, as shown in Fig. 5. It is assumed that the following reaction occurs

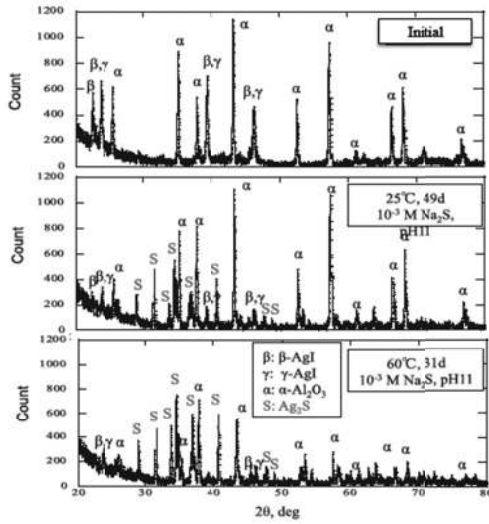


Fig. 4 XRD patterns of HIP product before and after contact with leachant containing 1 mM Na₂S at 25 and 60 °C

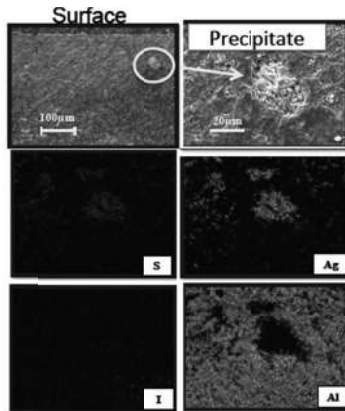


Fig. 5 Silver sulfide precipitation by contact with leachant containing 1 mM Na₂S

Because silver sulfide was precipitated in the HIP product, hydrosulfides could diffuse into the HIP product through pores or grain boundaries. Therefore, it is necessary to avoid exposure to hydrosulfide to suppress discharge of iodine from the HIP product.

BPI GLASS

An inorganic anion exchanger, BiPbO₂NO₃, was developed to remove and immobilize various kinds of industrial waste liquids and anions, in particular, halogens generated as a result of nuclear power generation [16, 17]. The vitrification process of BPI glass is shown in Fig. 6. Initially, H₂ gas is used as a reductant to release iodine from a spent iodine filter. Then, the iodide ion is included in the BPI through a reaction with an inorganic anion exchanger, BiPbO₂NO₃. The ion exchange reaction is as follows,



The BPI was mixed with a glass frit, the composition of which is also shown in Fig. 6, and was heated to 540 °C for vitrification. A low melting temperature of 540 °C is used to avoid iodine volatilization during vitrification. The target composition of the BPI vitrified waste form is shown in Table I. The BPI glass is formed by mixing BPI with B₂O₃/PbO-based glass, a type of lead-containing glass used for radiation shielding. The crystal structure of BPI (BiPbO₂I) is chemically stable and is similar to that of the natural mineral perite (BiPbO₂Cl), as is shown in Fig. 6.

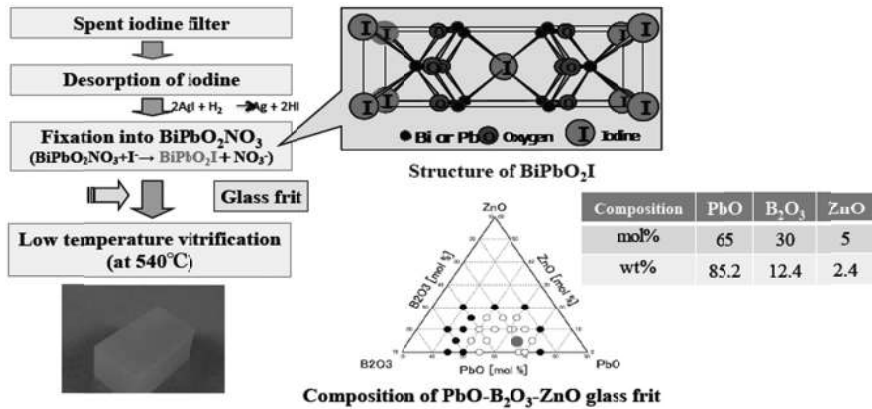


Fig. 6 Vitrification process and structure of BPI glass

Table I. Target composition of the BPI glass

Elements	I	B	Pb	Zn	Bi	O
mol%	1.0	19.8	22.1	1.6	1.0	54.5

Leaching examinations were conducted by using the leachants shown in Table II. The result of the leaching examinations is shown in Fig. 7, where normalized mass loss of iodine is plotted as a function of normalized mass loss of boron. As shown in Fig. 7, iodine and boron dissolved congruently and the amount of dissolution increased with increasing concentration of bicarbonate. Solids were observed at the end of leaching experiments and altered layers and precipitates were found (see Fig. 8). The thicknesses of altered layers in the experiments using synthetic seawater and equilibrated with bentonite were plotted as a function of leaching period. The precipitates were found to be $Pb_3(CO_3)_2(OH)_2$, hydrocerussite, $NaPb_2(CO_3)_2OH$, $CaCO_3$, and aragonite. It is therefore necessary to avoid carbonates to suppress discharge of iodine from BPI glass.

Table II Conditions of leaching experiments running for up to 800 days

Leachant	Reducing agent	S/V (cm ⁻¹)
NaCl 0.0055, 0.055, 0.55 M	Electrolytic iron	0.1
Synthetic sea water NaCl 0.55 M + NaHCO ₃ 0.05 M	Electrolytic iron	0.1
Equilibrated water with bentonite (Kunigel-V1)	Electrolytic iron	0.1 - 9.0
Equilibrated water with cement (OPC, HFSC)	Electrolytic iron	0.1

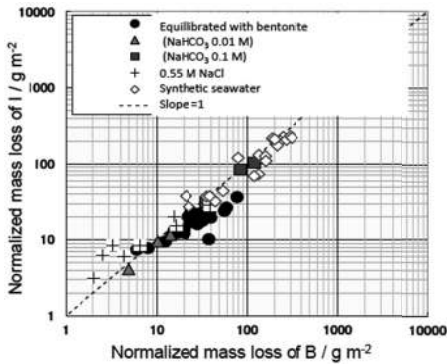


Fig. 7 Relation between normalized mass loss of iodine and boron

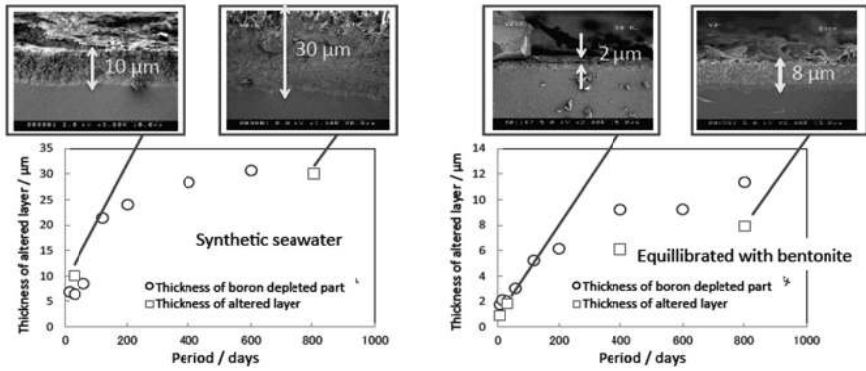


Fig. 8 The thickness of altered layers observed on BPI glass contact with synthetic seawater and equilibrated with bentonite as a function of the leaching period

HIGH-PERFORMANCE CEMENT

Generally, iodine weakly adsorbs onto ordinary cementitious materials. However, some cement hydrates such as ettringite (AFt: $\text{Ca}_6[\text{Al}(\text{OH})_6]_2(\text{SO}_4)_3 \cdot 26\text{H}_2\text{O}$) and monosulfate (AFm: $[\text{Ca}_2\text{Al}(\text{OH})_6]_2(\text{SO}_4) \cdot 6\text{H}_2\text{O}$) easily adsorb anions. The high-performance cement technique uses sulfate-added calcium aluminate cement. Iodine is fixed as IO_3^- due to its high affinity for AFt and AFm [12]. The process for the immobilization of iodine in cement is shown in Fig. 9. Iodine is separated from spent silver filters in alkaline solution by treatment with Na_2S and is then converted into iodate ions via treatment with ozone. The iodate ions are immobilized through kneading and solidification with alumina cement and gypsum in a weight ratio of 100:15.5.

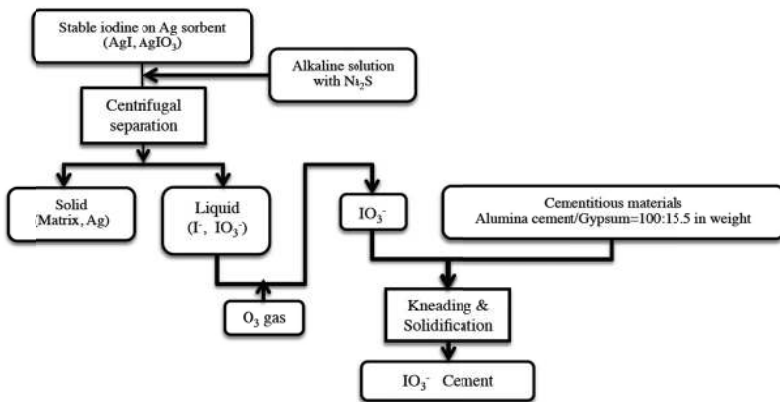


Fig. 9 Process for immobilization of iodine from silver sorbent into cementitious material

Because of the pretreatment in alkaline solutions, phase transition of iodine into a gas is rare, and the iodine recovery rate is extremely high at over 99.96%. The iodine content in the cement form was estimated to be about 2%.

Immersion experiments have been conducted by using simulated ground water and seawater to investigate the iodine release behavior from the iodine-immobilized cement under geological disposal conditions [18]. Iodine-immobilized cement for immersion experiment was prepared by mixing 0.4 M of NaIO_3 solution and calcium aluminate cement including gypsum. The cement was ground and grains 250 to 355 μm in diameter were collected as the sample. Fresh groundwater (FGW) and saline groundwater (SGW) were prepared for the simulated groundwater used as immersion solution. Powdered sample and immersion solution were placed into a container at a given liquid-solid ratio and kept in a glove box under inert atmosphere. The iodine release fraction as a function of the liquid-solid ratio is plotted in Fig. 10. Higher salinity enhanced the release of iodine. Iodine release could also be caused by dissolution of minerals in cement waste. Mineral composition and iodine distribution on the minerals is shown in Fig. 11 and Fig. 12, respectively. Initially, iodine existed in AFt, AFm, and hydrogarnet (HG). The result of mineral composition analysis indicated that AFt and AFm decreased with the increase in the liquid-solid ratio, whereas calcite increased. Most iodine existed in the AFt phase, was released mainly with the dissolution of AFt. Monosulfate dissolved out at a lower liquid-solid ratio than did AFt. In SGW conditions, almost all iodine was released at liquid-solid ratios between 50 and 150 cm^3/g and in FGW conditions at liquid-solid ratios between 600 and 900 cm^3/g . Calculation of the iodine release fraction was conducted using the thermodynamic data in Table III [19] and is also shown in Fig. 10. Carbonate in the immersion solution could also affect the dissolution of iodine-bearing minerals such as AFt, since calcium would be consumed with carbonate.

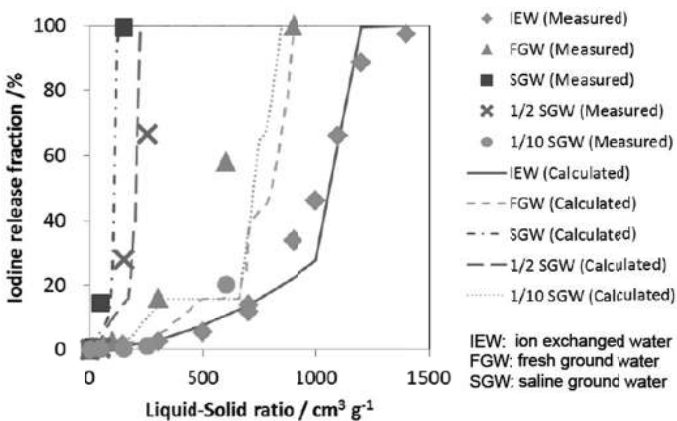


Fig. 10 Iodine release fraction as a function of liquid/solid ratio

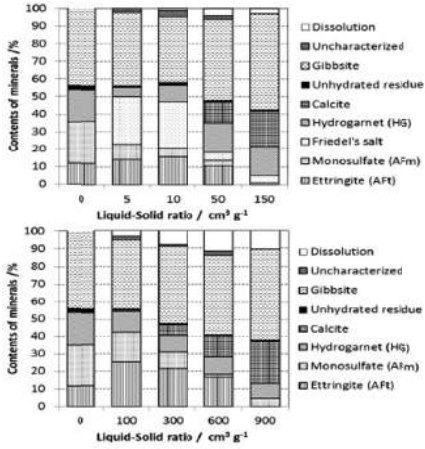


Fig. 11 Relationship between mineral composition and liquid/solid ratio (top, SGW; bottom, FGW)

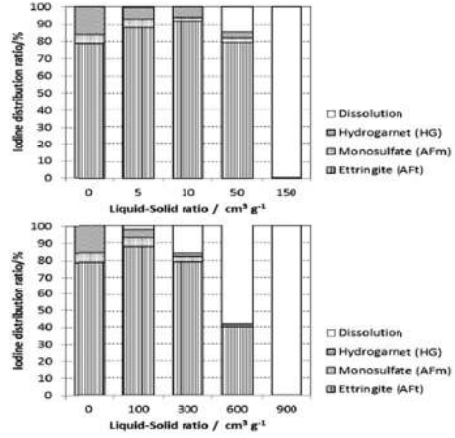


Fig. 12 Relationship between iodine distribution on minerals and liquid/solid ratio (top, SGW; bottom, FGW)

Table III Thermodynamic data of iodine-bearing minerals at 25 °C [19]

Minerals	Chemical reaction	log K
IS-AFt	$\text{Ca}_6(\text{Al}(\text{OH})_6)_2 \cdot 3((\text{IO}_3)_{0.5}(\text{SO}_4)_{0.5}) \cdot 24.5(\text{H}_2\text{O}) \cdot (\text{OH})_{1.5}$ $= 6\text{Ca}^{2+} + 2\text{Al}(\text{OH})_4^- + 1.5\text{IO}_3^- + 1.5\text{SO}_4^{2-} + 5.5\text{OH}^- + 24.5\text{H}_2\text{O}$	-51.29
AFt	$\text{Ca}_6\text{Al}_2\text{O}_6 \cdot (\text{SO}_4)_3 \cdot 32\text{H}_2\text{O}$ $= 6\text{Ca}^{2+} + 2\text{Al}(\text{OH})_4^- + 3\text{SO}_4^{2-} + 4\text{OH}^- + 26\text{H}_2\text{O}$	-43.94
IO ₃ ⁻ AFm	$(\text{CaO})_3 \cdot \text{Al}_2\text{O}_3 \cdot \text{Ca}(\text{IO}_3)_2 \cdot 12\text{H}_2\text{O}$ $= 4\text{Ca}^{2+} + 2\text{Al}(\text{OH})_4^- + 2\text{IO}_3^- + 4\text{OH}^- + 6\text{H}_2\text{O}$	-36.8
I-HG	$\text{Ca}_3\text{Al}_2(\text{OH})_8(\text{IO}_3)_4 = 3\text{Ca}^{2+} + 2\text{Al}(\text{OH})_4^- + 4\text{IO}_3^-$	- 33.20

SUMMARY

The peak exposure dose from ¹²⁹I in each geologic condition observed could be reduced to lower than 10 μSv/year when the iodine release period was longer than 10⁵ years. Consequently, the goal is to develop waste forms that can suppress release for at least 100,000 years. Three techniques have been developed for this purpose, synthetic rock (alumina matrix solidification) by HIP, BPI glass, and high-performance alumina cement.

For synthetic rock, hydrosulfide as high as 1 mM could affect iodine release due to silver sulfide precipitation. Hydrosulfide could diffuse through pores or the grain boundary of the corundum matrix. Pre-heating for degassing before HIP is effective in reducing porosity. For