Research Article

Cs$_3$Bi$_2$I$_9$–hydroxyapatite composite waste forms for cesium and iodine immobilization

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Abstract: Perovskite-based ceramic composites were developed as potential waste form materials for immobilizing cesium (Cs) and iodine (I) with high waste loadings and chemical durability. The perovskite Cs$_3$Bi$_2$I$_9$ has high Cs (22 wt%) and I (58 wt%) content, and thus can be used as a potential host phase to immobilize these critical radionuclides. In this work, the perovskite Cs$_3$Bi$_2$I$_9$ phase was synthesized by a cost effective solution-based approach, and was embedded into a highly durable hydroxyapatite matrix by spark plasma sintering to form dense ceramic composite waste forms. The chemical durabilities of the monolithic Cs$_3$Bi$_2$I$_9$ and Cs$_3$Bi$_2$I$_9$–hydroxyapatite composite pellets were investigated by static and semi-dynamic leaching tests, respectively. Cs and I are incongruently released from the matrix for both pure Cs$_3$Bi$_2$I$_9$ and composite structures. The normalized Cs release rate is faster than that of I, which can be explained by the difference in the strengths between Cs–I and Bi–I bonds as well as the formation of insoluble micrometer-sized BiOI precipitates. The activation energies of elemental releases based on dissolution and diffusion-controlled mechanisms are determined with significantly higher energy barriers for dissolution from the composite versus that of the monolithic Cs$_3$Bi$_2$I$_9$. The ceramic-based composite waste forms exhibit excellent chemical durabilities and waste loadings, commensurate with the state-of-the-art glass-bonded perovskite composites for I and Cs immobilization.

Keywords: cesium (Cs); iodine (I); perovskite; nuclear waste; hydroxyapatite

1 Introduction

Cesium (Cs) and iodine (I) are two of the most problematic radioactive fission products associated with the complex waste streams of the high level liquid wastes of 600,000 to 750,000 gallons in total at the Savannah River Site [1]. Short-lived $^{137}$Cs ($t_{1/2} = 30.17$ y) is one of the major heat generators for initial storage, and long-lived $^{135}$Cs ($t_{1/2} = 2.3 \times 10^6$ y) is a dose contributor for long-term geological disposition of nuclear wastes. The removal of Cs salt containing both $^{135}$Cs and $^{137}$Cs from radioactive liquid wastes requires
a large-sized and complicated industrial design of filters, ion exchange columns, and unique resins [2]. The safe disposal of radioactive iodine-129 ($^{129}$I) is of particular importance and challenge for effective nuclear waste management [3–5] as a result of its long half-life ($t_{1/2} = 15.7 \times 10^6$ y), high volatility during processing, high water solubility, and environmental mobility. Both Cs and I are highly volatile for nuclear waste immobilization, and therefore require special considerations to manage [6–8]. Waste form materials based on ceramic or glass were developed for Cs immobilization. Particularly, hollandite with a general formula of $\text{AB}_2$($\text{X}_3$)$\text{O}_{16}$, such as ($\text{Ba},\text{Cs})(\text{Al},\text{Ti})_2\text{Ti}_6\text{O}_{16}$ [9,10], $\text{Ba}_{1.5-\text{x}}\text{Cs}_x\text{Cr}_2\text{Ti}_5\text{O}_{16}$ [11], and $\text{Cs}_0.1\text{Ba}_{1.0}(\text{Ti}_{0.6}\text{Al}_{1.5})_3\text{Ti}_5\text{O}_{16}$ [12,13] have been recognized as a promising host phase for the immobilization of Cs.

Similarly, various types of waste materials have been developed for long-term storage and disposal of $^{129}$I, including Ag-based sorbents, such as Ag-zeolite [14,15] and Ag-functionalized silica aerogel [16] to capture off-gas iodine from chemical reprocessing of spent nuclear fuels and glass-based waste matrices for encapsulating iodine [17]. The Ag-based waste forms rely on the stronger chemical affinity between Ag and I. However, the application of Ag-based large-scale deployment for the reprocessing of I in spent nuclear fuels is economically and environmentally challenging [18]. The Ag-based absorbers, such as Ag-mordenite, display a relatively low iodine mass loading at around 10 wt%, and a large volume of waste form matrix is required to confine radioactive iodine [14]. Chalcogen-based aerogels, or chalcogels, have displayed exceptional iodine mass loadings up to 68 wt%; however, the adsorbed Cs and I on the aerogels or chalcogels are thermodynamically unstable, which tend to dissociate at elevated temperatures [19].

A chemical process integrating AgI with lead iodoapatites was proposed as a potential option for the disposal of $^{129}$I [20]. In addition to Ag-based absorbents, Bi-based sorbents have also been investigated for $^{129}$I remediation [21] to form BiI$_3$ and BiOI upon capture of iodine from off-gases, offering a promising route for developing Bi-based $^{129}$I waste forms [22]. Borosilicate glass is the baseline waste forms for liquid wastes; however, very limited iodine (typically less than 1 wt%) can be incorporated into borosilicate glass because of its low solubility in the glass matrix and high volatility during the high temperature vitrification process [23,24]. Other types of waste forms including apatite structure-type (with a general chemical formula of $\text{M}_{10}(\text{XO}_4)\text{Y}_2$ with M = Pb, Ca; X = P, V; Y = I) were proposed as promising waste form phases for iodine incorporation. Iodoapatite (e.g., Pb$_5$(VO$_4$)$_3$I) has shown promise in confining iodine during consolidation and leaching processes, and iodoapatite can be embedded into a lead orthovanadophosphate (Pb$_{10}$(VO$_4$)$_{13}$(PO$_4$)$_2$I$_2$) to form a core–shell composite showing high durability and minimized iodine release [25]. Iodate–hydroxyapatite with a 7 wt% iodine loading and dense lead–vanadate iodoapatite Pb$_5$(VO$_4$)$_3$I$_{1-x}$ (x = 0–0.15) (in general 5–7 wt% iodine) have also been synthesized [26,27].

Perovskite structural types, in a general chemical formula of AMO$_3$, is also a major phase (around 20 vol%) in the leading multiphase waste form assemblage SYNROC [28]. In addition, metal–halide perovskites and their derivatives such as $\text{A}_2\text{MX}_6$ or $\text{A}_3\text{M}_2\text{X}_9$ display diverse crystal chemistry and structural flexibility, and possess exciting optoelectronics and photovoltaic properties [29–31]. Large amounts of Cs, Sr, Co, and I can be incorporated into the A-site and X-site of the metal–halide perovskite, and the metal–halide perovskite derivatives possess large capacity for halogen incorporation (Cl and I), making them an attractive host phase for problematic halogen radionuclides from the reprocessing of spent nuclear fuels and off-gas. However, metal–halide perovskites for waste form applications are limited by low thermal stability and high water solubility, intrinsic to many host phases containing iodine or chlorine salts. For example, our previous studies indicated that a Sn-based perovskite $\text{Cs}_3\text{SnI}_6$ for Cs and I incorporation was very sensitive to water corrosion, and can be easily dissociate into to CsI and SnO$_2$ upon water attack [32]. Using atomic-layer deposition to form a nano-scale TiO$_2$ behaving as a potentially passivation film, the chemical durability of the perovskite can be enhanced as evidenced by short-term leaching test. Glass-bonded metal–halide perovskite waste forms were also designed by incorporating the Bi-based metal–halide perovskite $\text{Cs}_3\text{Bi}_2\text{I}_6$ into silica to form either composite or core–shell structures, displaying superior chemical durability as compared with the state-of-the-art iodine waste form materials and meanwhile very high waste loadings [33]. These results highlight immense potentials of metal–halide perovskites as advanced waste form materials for challenging radionuclides such as Cs and I and the importance of optimizing materials/structural design to achieve improved performance.
In this work, we report the concept of metal–halide perovskite–ceramic composite waste forms by embedding Bi-based metal–halide perovskite Cs$_3$Bi$_2$I$_9$ into a highly durable hydroxyl-apatite matrix for Cs and I immobilization, and evaluate the chemical durabilities and kinetics of elemental release. Dense metal–halide Cs$_3$Bi$_2$I$_9$ perovskites and nano-sized hydroxyapatite (HA) composites were consolidated by a low-temperature and high-pressure spark plasma sintering (SPS) process. The densified Cs$_3$Bi$_2$I$_9$ pellet and composite structure pellets (Cs$_3$Bi$_2$I$_9$ + HA) were subjected to laboratory-scale aqueous durability tests, and elemental leaching behaviors were measured by inductively coupled plasma mass spectrometry (ICP-MS). The microstructure alteration and passivation behavior were also studied in order to achieve the mechanistic understandings of short-term chemical durability, providing scientific insights into the design, selection, and development of ceramic waste forms.

2 Experimental procedure

2.1 Cs$_3$Bi$_2$I$_9$ and HA powder synthesis

The Cs$_3$Bi$_2$I$_9$ powders were synthesized through a solution-based approach following Reaction (1) [34]:

$$3\text{CsI} + 2\text{BiI}_3 \rightarrow \text{Cs}_3\text{Bi}_2\text{I}_9$$

The mixture of CsI (390 mg, Alfa Aesar) solution in 20 mL deionized water and BiI$_3$ solution (590 mg, Alfa Aesar) in 20 mL methanol was vigorously stirred by magnetic bars for 1 h at room temperature (RT). A color change and powder precipitation were immediately visible upon mixing the precursor solution. The solution was centrifuged at 2000 r·min$^{-1}$ for 5 min, after which the supernatant was poured off, and the remaining precipitates were dried in a centrifuge tube at 80°C in a vacuum oven overnight.

The HA powders were first synthesized through a wet chemical deposition between Ca(OH)$_2$ and H$_3$PO$_4$ following Reaction (2):

$$10\text{Ca(OH)}_2 + 6\text{H}_3\text{PO}_4 \rightarrow \text{Ca}_{10}$$

$$\text{(PO}_4)_6$$

$$\text{(OH)}_2 + 18\text{H}_2\text{O}$$

The HA powders were first synthesized through a wet chemical deposition between Ca(OH)$_2$ and H$_3$PO$_4$ following Reaction (2):

$$10\text{Ca(OH)}_2 + 6\text{H}_3\text{PO}_4 \rightarrow \text{Ca}_{10}\text{(PO}_4)_6$$

$$\text{(OH)}_2 + 18\text{H}_2\text{O}$$

2.2 SPS consolidation of the Cs$_3$Bi$_2$I$_9$ and Cs$_3$Bi$_2$I$_9$ + HA composite pellets

Pellet densification was conducted by SPS using a Model 10-3 SPS system (Thermal Tech. LLC.). For each sintering, starting powders (~1 g) were loaded into a graphite die with an inner diameter of 6 mm and the inner surface wrapped by a graphite foil (0.20 mm thick) to facilitate the sample removal after sintering. Sintering was carried out in an Ar environment at a current pattern of 25 ms on and 3 ms off. Sample temperatures were measured with a K-type thermocouple inserted into the bottom punch at a depth roughly 2 mm below the sample. The graphite between the thermocouple and the bottom of the sample resulted in a difference in the temperature measured by the thermocouple and actual temperature within the sample.

The sintering of the monolithic Cs$_3$Bi$_2$I$_9$ pellets followed a similar routine as a prior study on Cs$_2$SnCl$_6$ [33], and featured the heat rate of 100 °C·min$^{-1}$, and a low-temperature SPS sintering was conducted with the peak temperatures ranging from 200 to 300 °C. It is also notable that the SPS has been successfully applied to prepare iodine-bearing apatite ceramics for the immobilization of radioactive iodine [35,36]. A uniaxial pressure was applied with the preloading pressure of 10–40 MPa maximum at a steady rate to match the increase of temperature. The Cs$_3$Bi$_2$I$_9$ + HA composite pellets were synthesized by first mixing equal masses of Cs$_3$Bi$_2$I$_9$ with HA in a mortar and pestle followed by SPS consolidation. A similar consolidation procedure was applied with a peak consolidation temperature of 500 °C and a maximum pressure of 400 MPa. Instead of using a graphite die, a tungsten carbide die was used to hold the mixing powders.

Temperature was increased gradually from 25 to 500 °C with a heating rate of 100 °C·min$^{-1}$. The uniaxial pressure was increased from 10 to 400 MPa maximum at a steady rate to match the increase of temperature. The peak temperature and pressure were held for 5 min followed by air cool in Ar atmosphere. After sintering and removing the sample from the graphite die, the sintered pellets were mechanically polished in anhydrous ethanol with a 1200 grit sandpaper, and then stored in a vacuum desiccator before characterization and chemical durability measurements. The density of the as-sintered pellets show an average particle size of 50 nm.

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sample pellets was determined via the Archimedes’ method using a balance with anhydrous ethanol acted as the suspension agent. The theoretical density of the composite pellets was determined based on the rule of mixture [37].

2.3 Microstructure characterization

The purity and crystallinity of the synthesized Cs$_3$Bi$_2$I$_9$ powders and sintered pellets before and after leaching experiments were examined using X-ray diffraction (XRD) with a Panalytical X’Pert Pro system (Westborough, USA) using a copper target ($K_a = 0.15406$ nm) at a step size of 0.026° and 100 ms per step. Sample morphologies were examined in a Carl Zeiss Supra (Jena, Germany) field emission scanning electron microscopy (SEM) system under a 10 keV acceleration voltage. Raman spectra of bulk samples were collected in a micro-Raman system (Renishaw Invia) using a 514 nm (green) laser. A typical spectrum was acquired with an exposure time of 10 s with 3 times accumulation at an operation power of 20 mW. SEM observations and analyses of fractured surfaces were conducted by using a Carl Zeiss Supra after leaching tests. Scanning transmission electron microscopy (STEM) characterization was carried out using a Thermo Fisher Scientific Titan 80-300 TEM. Semi-quantitative elemental analysis based on energy dispersive spectroscopy (EDS) spectra was performed using a Super-X EDS tool associated with the STEM. A focused ion beam (Versa 830, FEI, USA) was applied to machine a thin slice of sample lamella from the top surface towards inner matrix in order to investigate the surface alteration and degradation mechanisms of Cs$_3$Bi$_2$I$_9$ + HA composites upon leaching.

2.4 Chemical durability measurement

The densified Cs$_3$Bi$_2$I$_9$ pellets and composite pellets were hand polished, rinsed with anhydrous ethanol, and dried in air. Sample geometries were examined under an optical microscopy. Static chemical durability tests were conducted for ~10 d at 25, 58, and 90 °C for pure Cs$_3$Bi$_2$I$_9$ pellets following ASTM C1220 [38], a standardized test method for static leaching of monolithic waste forms for disposal of radioactive wastes. The solid sample was loaded into a PTFE capped (closed) system with a leachate of 18 MΩ deionized water and a sample-surface-area-to-solution-volume ($S/V$) ratio of 5 m$^{-1}$. The pellet sample was fully immersed in the leachate, which was retrieved with an interval of 1 d. In each interval, 0.1 mL solution was sampled, diluted by 100 times using 10 mL deionized water acidified by 8% pure HNO$_3$, and analyzed by a Varian 820 quadrupole ICP-MS.

More vigorous semi-dynamic leaching tests were carried out for the Cs$_3$Bi$_2$I$_9$ + HA composite structure pellets to accelerate leaching following the ASTM C1308 standard test [39]. Similar $S/V$ ratios were used, and the leachate was exchanged every day. Three temperatures range from 25, 58, and 90 °C were also applied to the semi-dynamic leaching test. The concentration of species $i$, $m(i)$ in g·m$^{-2}$, leached out from the solid sample into the leachate was calculated as shown in Eq. (3):

$$m(i) = \frac{C(i) \times \text{Dilution factor}}{S/V}$$

where $C(i)$ is the concentration of ion species measured by ICP-MS, and the dilution factor was 100. The value of $S/V$ was assumed to be a constant during the sampling duration, and $m(i)$ was further converted to mol·m$^{-2}$·d$^{-1}$ for Cs/I molar ratio calculations.

The normalized elemental release rates ($L_N$) were further determined through the following Eq. (4) in order to make comparison of the chemical durability between sample pellets and the data from previous literature:

$$L_N = \frac{L}{\text{Weight percent}}$$

The kinetics of Cs$_3$Bi$_2$I$_9$ leaching behavior in aqueous solutions was attempted by fitting the quantified cumulative mass of leachable species including Cs and I concentrations as a function of time based on the Cote model until reaching the optimized fitting parameters with minimum $R^2$ (see Eq. (5)) [40]:

$$m(t) = k_1t + k_2t^{1/2} + k_3(1 - e^{-k_4t})$$

This semi-empirical mathematical model considers three simple leaching mechanisms: the first term, $k_1t$, representing a linear dissolution behavior; the second and third terms corresponding to the mass transport controlled by diffusion and species exchange between the matrix surface and solution, respectively. The long-term release rates of Cs and I can be derived based on the rate constant of $k_1$ from the Cote model evaluated at infinity time.
3 Results and discussion

3.1 Characterization of the as-sintered Cs$_3$Bi$_2$I$_9$ and composite structure pellets

The high density of sintered pellets with a theoretical density higher than 90% was affirmed by the absence of porosity in the SEM images (Figs. 1(a) and 1(b)). The measured sample pellet physical density (4.44 and 3.88 g·cm$^{-3}$) and the relative density can be seen in Fig. 1(d). Such an absence of pores also signifies the advantage of SPS to successfully retain gaseous species inside the crystalline matrix due to short sintering durations and low sintering temperatures, which is not possible using conventional consolidation approaches because of the phase decomposition and high volatility of Cs and I. The dual-phase crystalline structure for the composite is demonstrated in Fig. 1(b) as the phase with light contrast represents the HA phase, and the dark phase represents the Cs$_3$Bi$_2$I$_9$ crystals, which are encapsulated by the HA particles. The thermal stability of the pure Cs$_3$Bi$_2$I$_9$ and composite structures were characterized by a dual thermogravimetric analysis–differential scanning calorimetry (TGA–DSC) thermal analyzer, and the results are shown in Fig. 1(c). The onset decomposition temperatures for both composites and pure Cs$_3$Bi$_2$I$_9$ are close to 525 °C, and severe phase decomposition occurs after 600 °C where nearly all of the Cs$_3$Bi$_2$I$_9$ is lost at 1000 °C as demonstrated in the TGA curves. Furthermore, the red dash curve for the Cs$_3$Bi$_2$I$_9$ + HA composite structure clearly confirms that 50 wt% of Cs$_3$Bi$_2$I$_9$ is successfully incorporated into the composite, suggesting a high retention of Cs and I without any decomposition and elemental loss during the SPS consolidation (Fig. 1(c)).

XRD spectra provide the most decisive evidence for the phase distributions and crystallinity within the samples. The obtained XRD spectra in Fig. 2(a) are consistent with a previous study [41], showing a single phase Cs$_3$Bi$_2$I$_9$ in the as-synthesized powders and pellets sintered at 300 °C by SPS. All diffraction peaks match the theoretical ones although only major peaks are indexed in the figure, and no impurities or secondary phases are observed. Similarly, the XRD pattern (the top pattern in Fig. 2(c)) of the Cs$_3$Bi$_2$I$_9$ + HA composite structure confirms dual phases of Cs$_3$Bi$_2$I$_9$ and HA major peaks, consistent with the SEM observation (Fig. 1(b)), and no impurities can be

![Fig. 1](image-url)
observed. The Raman spectrum (Fig. 2(d)) of the as-synthesized Cs$_3$Bi$_2$I$_9$ pellet shows two broad peaks at 80 and 146 cm$^{-1}$.

### 3.2 Surface alteration of Cs$_3$Bi$_2$I$_9$ and composite pellets upon leaching

The crystalline nature of the surface alteration product of Cs$_3$Bi$_2$I$_9$ leached at 25 °C under static conditions for 10 d was determined by the XRD and Raman spectra (Figs. 2(b) and 2(d)). The XRD profile denoted by the red pattern in Fig. 2(b) shows the formation of a secondary crystalline phase BiOI post leaching, which is also evidenced by the SEM images in Figs. 3(a) and 3(c) [42,43]. A loosely-packed BiOI nanosheet layer (in several hundreds of micrometers thick) fully covers the matrix surface, and the strong diffraction peaks for the BiOI suggest a significant surface alteration, consistent with the microstructural observation to be discussed later. The BiOI phases observed by the XRD can also be confirmed by the Raman spectra (Fig. 2(d)) showing two strong Raman peaks at 85 and 150 cm$^{-1}$, which can be attributed to the A$_{1g}$ and E$_g$ internal Bi–I stretching modes of BiOI, respectively [44,45]. There is also one relatively weak peak at 106 cm$^{-1}$ in the Raman spectrum, which can be attributed to the A$_g$ mode of BiI$_3$ [46], as an intermediate phase during water degradation. This finding indicates that BiOI is probably the hydrolysis product of BiI$_3$ as shown in Reactions (6) and (7) [44]:

$$\text{Cs}_3\text{Bi}_2\text{I}_9 \rightarrow 3\text{CsI} + 2\text{BiI}_3 \quad (6)$$

$$\text{BiI}_3 + \text{H}_2\text{O} \rightarrow \text{BiOI} + 2\text{HI} \quad (7)$$

Similar to the pure Cs$_3$Bi$_2$I$_9$, the water interaction between the Cs$_3$Bi$_2$I$_9$ + HA composite structure under 90 °C for 11 d also results in the formation of the secondary crystalline phase of BiOI along with the dissolution of the Cs$_3$Bi$_2$I$_9$ grains at the surface of the composites. Figure 2(c) also shows the XRD pattern of the composite after leaching test (the red spectrum) with the existence of multi-phases. Specifically, the formation of BiOI can be evidenced by the appearance of the diffraction peaks of (012) ($2\theta = 29.645^\circ$) and (110) ($2\theta = 31.7^\circ$). Note that these diffraction peaks
from BiOI also overlap the diffraction from HA and Cs₃Bi₂I₉, and the formation of the BiOI nanosheets are further evidenced by the microstructure characterization and microanalysis to be discussed in Figs. 4 and 5. As compared with monolithic perovskites with significant surface alteration, only limited Cs₃Bi₂I₉ grains located at the surface of the polished pellets experience surface alteration. Therefore, the Cs₃Bi₂I₉ phase is still evident in the XRD pattern from the embedded perovskites without alteration. In addition, the crystalline peaks from the HA remain high intensity after the water interaction, which indicates that the HA is highly water stable without obvious degradation, consistent with its highly durable nature.

An intermediate leaching sample of the pure Cs₃Bi₂I₉ pellet was also analyzed in detail to reveal the leaching mechanism. The samples after leaching at 25 °C in deionized water for 42 h are shown in Figs. 3(a)–3(d). After leaching, the sample was fractured deliberately into two pieces to expose the cross-section of the altered sample to reveal the microstructure evolution of the pellet. Figure 3(a) clearly shows a distinct altered structure with the loose BiOI flake layer of a thickness around 200 μm on the altered matrix underneath. The lateral sizes of the BiOI flakes range from 500 nm to several micrometers as shown in the high-resolution SEM image in Fig. 3(b). The BiOI sheets vertically aligned on the top of the altered matrix. Few amounts of BiOI flakes can be observed along with the original micro-sized Cs₃Bi₂I₉ grains on the altered matrix (Fig. 3(d)). Figure 3(c) demonstrates the top view of the surface alteration layer of Cs₃Bi₂I₉ after 42 h of static leaching at 25 °C, clearly showing a uniformly distribution of loosely-packed BiOI flakes with different morphologies horizontally aligned on the top surface. The unique microstructure and morphology of the horizontally-aligned BiOI nanosheets can be attributed to the surface re-precipitation of the BiOI flakes once the concentration of Bi and I in bulk solutions is above their solubility. The surface re-precipitation of BiOI will further be discussed later in Fig. 7.

For composite pellets, as the Cs₃Bi₂I₉ phase is encapsulated into the HA matrix, only Cs₃Bi₂I₉ grains located at the pellet surface are directly exposed to water attached. Thus, the chemical durability of the composite can be greatly improved with reduced release of Cs and I. For the Cs₃Bi₂I₉ + HA composite after 90 °C water interactions (11 d), the leached

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**Fig. 3** (a) Cross-section view SEM image of the Cs₃Bi₂I₉ pellet surface exposed to water for 42 h, showing the surface morphological transition from the sheet-like passivation layer to altered Cs₃Bi₂I₉; (b) high-magnification view of the flask-structure in the passivation layer; (c) top-view SEM image showing surface alteration and accumulation of the BiOI flakes for the Cs₃Bi₂I₉ pellet (the inset: high-magnification SEM image of the surface flask structure); and (d) SEM image showing the interfacial morphology between the alteration layer and the perovskite matrix.

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surface was partially covered by the BiOI flakes only on the top surface of Cs$_3$Bi$_2$I$_9$ exposed to water, as shown in the SEM image in Fig. 4(a). The corresponding EDS mappings show Bi and I enriched in the area covered by the BiOI flakes, and no Cs is detected indicating that majority Cs in the Cs$_3$Bi$_2$I$_9$ located on the pellet surface is leached out. The area without BiOI is enriched in Ca and P, which denote calcium hydroxyapatite, clearly confirming the dual crystalline phase structure as shown in the previous XRD profile.

In order to further understand the degradation behavior and the formation of the BiOI alteration layer on the composite structure, STEM–EDS analysis was carried out on the FIB cutting lamella, which exposes the cross-section of the composite structure sample as shown in Figs. 5 and 6. The elemental mappings in Fig. 5 demonstrate the vertically aligned flake enriched with Bi, I, and O on the top of the altered matrix, confirming the formation of a BiOI. A distinct interface between the BiOI flakes and matrix underneath is observed, indicating that the BiOI alteration layer mainly grows from the matrix via interaction between the Cs$_3$Bi$_2$I$_9$ matrix and water molecule. Similar to the SEM observation, the lateral size of the BiOI flake is ~500 nm. The size of the HA grains in the matrix is less than 100 nm, as shown in Fig. 5(a). The bright-field (BF) STEM image in Fig. 6 represents the scanning area of the unaltered matrix, where the black particles represent nano-sized Cs$_3$Bi$_2$I$_9$ particles fully encapsulated into the highly densified HA matrix. As shown by the elemental mapping, no element deficiency is observed indicating no release of Cs and I from the perovskite grains embedded into the HA matrix. Particularly, for the grains of Cs$_3$Bi$_2$I$_9$ encapsulated by the HA matrix, the release of elements will only occur through the transport of water molecules and elements along the grain boundaries of the HA matrix. The highly densified HA matrix acts as a physical barrier to slow down water molecule and element transport, and the highly durable nature of the HA against water corrosion will greatly improve the chemical durability and slow down the elemental release, which will be discussed in Section 3.3.

3.3 Chemical durability of the monolithic Cs$_3$Bi$_2$I$_9$ and Cs$_3$Bi$_2$I$_9$ + HA composites

3.3.1 Static leaching results for the pure Cs$_3$Bi$_2$I$_9$ pellets

To further understand the leaching behavior and mechanism, static leaching experiments were conducted on pure Cs$_3$Bi$_2$I$_9$ pellets at three temperatures ranging from 25, 58, and 90 °C for 256 h (~10 d) in deionized water. Solution analysis was performed using ICP-MS providing insights on the elemental releasing behavior. The cumulative mass of Cs and I as a function of time is plotted in Figs. 7(a) and 7(b), and the corresponding atomic ratio (I/Cs) is shown in Fig. 7(c). The mass accumulation curves of Cs and I with respect to time are composed of two distinct stages, a build-up stage (about 6–7 d) for Cs followed by a re-precipitation stage with decreased concentrations for both Cs and I in the leachate. This can be attributed to the solution feedback of both I and Cs from the over-saturated leachate during the static leaching test according to the transition state theory (TST) model [47].
build-up of the dissolved molecules in bulk solutions and thus reduced under-saturation, the dissolution rate reduces accordingly. Once the elements in the solution exceed their solubility, precipitation can occur, ultimately controlling the dissolution kinetics and thus elemental concentration in bulk solution. Leaching at higher temperature (90 °C) leads to enhanced release of both Cs and I, and thus leads to less duration to reach over-saturating in bulk leachates and re-precipitation, particularly for iodine (~4 d for re-precipitation as shown in Fig. 7(b)).

The ICP-MS results suggest that the release of Cs is higher than that of I as evidenced by the fact that the atomic ratio of I/Cs is significantly below the stoichiometric value (3:1) during the static leaching period (Fig. 7(c)). A concentration of I lower than its stoichiometric ratio in the leachate is consistent with the formation of protective BiOI flakes on the surface, reducing the concentration of iodine in the solution. The observed non-congruency at the early stage could be explained by the intrinsic structure feature and the chemical bonding of Cs and I in the crystal. Cs$_3$Bi$_2$I$_9$ crystal features a highly anisotropy bonding environment, specifically, the close-packed [Bi$_2$I$_9$]$^{3-}$ octahedron has strong ionic–covalent Bi–I atomic interactions, and the structural unit [Bi$_2$I$_9$]$^{3-}$ bind one to another by bridging
Cs$^+$ between the octahedron without strong covalent bonding. Only weak van der Waals interactions occur between each of the [Bi$_2$I$_9$]$^-$ octahedron, which are more likely to become the starting point to initiate dissolution. The relatively weak Cs–I interactions make Cs more easily detached from the matrix than iodine ions as a result of the strong ionic-covalent Bi–I bonding. The weakly-bonded Cs ions are dissolved into bulk solution relatively quickly, while iodine ions, bonded by strong ionic-covalence with Bi, dissolve relatively slow. This is also consistent with the formation of water insoluble BiOI nanosheets with a preferential release of Cs from the perovskite crystals. The difference in the bonding strength has been used to explain the incongruent dissolution of some glass waste forms [47].

The in-situ formation of BiOI flakes on the surface of Cs$_3$Bi$_2$I$_9$ is of particular significance as BiOI itself is water insoluble [48]. Surprisingly, no accountable concentration for Bi ion above the instrument detection limit can be measured due to the formation of relatively-insoluble BiOI. The absence of Bi ion concentration in the leachate indicates that Bi is not released out from the matrix instead of forming water insoluble BiOI flakes during leaching. The formation of such an alteration layer has slowed down though not being able to completely stop the release of Cs and I. One of the possibilities could be the loose-packed morphology of BiOI flakes, which is still permeable to water molecular transport. Therefore, further developments of Cs$_3$Bi$_2$I$_9$-based ceramic for hosting radioactive iodine waste could focus on the fabrication of the assemblage with compositions known to be less leachable with a continuous, dense alteration layer that protects the matrix. In addition, both the Cs and I release rates are significantly higher for elevated temperatures, suggesting that the elemental transport and dissolution of Cs$_3$Bi$_2$I$_9$ is thermodynamically driven. In order to further reveal the thermodynamic behavior, the activation energy of both Cs and I can be calculated via the Arrhenius equation (8) as below:

$$\ln k = \ln A - \frac{E_a}{RT}$$  (8)

where $k$ stands for the rate constants (based on the different mechanisms) that can be derived from the linear dissolution mechanism (initial rapid dissolution typically occurred in ceramic dissolution) at the early stage of the leaching test, $lnA$ is a constant, $E_a$ is the activation energy, $T$ is the temperature, and $R$ stands...
for the universal gas constant. By building the correlation between lnk and 1/T linearly, the $E_a$ values can be determined. Figure 7(d) demonstrates the fitting curves for both Cs and I for the sample pellet post static leaching test. The fitting parameters derived from the linear dissolution behavior are summarized in Table 1 and used to calculate the activation energy. The activation energies, $E_a$, for direct dissolution of Cs and I are 27.8 and 33.8 kJ·mol$^{-1}$, respectively. The initial rapid dissolution of ceramics is typically controlled by the dominant mechanism of direct dissolution due to the bond breaking from crystal structures. The $E_a$ determined could be the energy barrier required to overcome to break Cs–I and Bi–I bonds from the Cs$_3$Bi$_2$I$_9$. This result implies that a higher energy barrier is required for breaking Bi–I bonds in the <BiI$_9$> polyhedron with a higher activation energy for iodine release. In contrast, the weak bond of Cs in bridging two-dimensional layers of interconnected <BiI$_9$> leads to a lower $E_a$ required for Cs dissolution, thus leading to a faster dissolution of Cs relative to iodine release than their stoichiometric ratio.

### 3.3.2 Semi-dynamic leaching results of Cs$_3$Bi$_2$I$_9$ + HA composite structure

The chemical durability of the Cs$_3$Bi$_2$I$_9$ + HA composite pellets was also tested by the semi-dynamic protocol, which is an accelerated and aggressive testing compared with static leaching, as a result of much improved durability of the composites. As compared with static leaching conducted in static leaching for monolithic pellets, no solution feedback effects are expected with periodic replacement of the leachate. Therefore, semi-dynamic leaching test leads to higher elemental release rates than static leaching test for the same materials. Our testing results indicate much lower elemental release rates for the composite pellets under the more aggressive semi-dynamic testing protocol than the rates determined for the monolithic pellets tested by static leaching. These results highlight greatly improved chemical durability of the Cs$_3$Bi$_2$I$_9$ + HA composite than these of monolithic compositions, which will be discussed in details below.

Figure 8 shows the cumulative concentrations of Cs and I for the composite structure, in which the elemental concentrations of each elements measured by the semi-dynamic leaching test summed up with the previous cumulative concentration are used to construct the concentration–time curves. As shown in Figs. 8(a) and 8(b), after initial rapid dissolution in the first two days, the increment in the subsequent testing is minimal and almost saturates after day 2, indicating very low elemental dissolution rates. Detailed dissolution mechanisms and kinetics for the composite pellets are also revealed by the solution analysis results shown in Fig. 8. Similar to the pure Cs$_3$Bi$_2$I$_9$, the elemental release is also thermodynamically controlled though with different dominated mechanisms. Both I and Cs release rates are the highest for 90 °C, following by 58 °C, and the lowest release rates are observed for 25 °C. Compared to pure Cs$_3$Bi$_2$I$_9$, the atomic ratio of I/Cs is above the stoichiometric ratio of 3.0 during the semi-dynamic leaching test (Fig. 8(c)). Unlike the static leaching test, the leachate is always under-saturated during the semi-dynamic leaching period without solution feedback due to the periodic leachate exchange. Therefore, the approximately constant Cs and I release rates following by the initial rapid dissolution from perovskite grains at the surface can be mainly attributed to the physical barrier of the HA matrix and the possible formation of the BiOI alteration layer.

The time evolution of the elemental release rates is fitted by the Cote model, and the dominant mechanisms of controlling elemental release are revealed at different stages (Fig. 9). The corresponding rate constants for different mechanisms (direct dissolution: $k_1$, diffusion: $k_2$, and surface effect: $k_3$ and $k_4$) are summarized in Table 2. Overall, all of the three mechanisms together control the leaching behavior of Cs and I. The fitting parameters demonstrating both long-term I and Cs release rates are dominated by diffusion-controlled mechanism. Figures 9(c) and 9(d) show the fitting profiles of the dissolution rates for both Cs and I for the composite tested at 58 °C as an example. The initial fast dissolution rates in day 1 and 2 are mainly controlled by the surface effects, e.g., the surface defects from sample preparation and mechanical polishing leading to

| Table 1 | Rate constants ($k_i$) based on dissolution mechanism of the pure Cs$_3$Bi$_2$I$_9$ pellet evaluated by static leaching |
|----------|------------------|
| Element | Temperature | $k_1$ | $b$ | $R^2$ |
| I       | 25 °C     | 0.190 | 0.510 | 0.870 |
|         | 58 °C     | 1.049 | 0.504 | 0.960 |
|         | 90 °C     | 2.130 | 7.600 | 0.930 |
| Cs      | 25 °C     | 0.150 | 0.165 | 0.950 |
|         | 58 °C     | 0.590 | 0.285 | 0.940 |
|         | 90 °C     | 1.100 | 34.000 | 0.960 |
Fig. 8  Semi-dynamic leaching of the Cs₃Bi₂I₉ + HA (50 wt%) composite pellets: (a, b) cumulative concentrations of I and Cs (the right axis represents the cumulative release concentrations related to the leaching test at 25 °C), (c) atomic ratios of I/Cs, and (d) calculated activation energies derived based on the long-term diffusion dominated mechanism.

Fig. 9  Elemental release rates of (a) Cs and (b) I of the Cs₃Bi₂I₉ + HA (50 wt%) composites subjected to semi-dynamic leaching test at different temperatures (fitting by Cote model are shown as the broken line), (c, d) kinetic analysis of the elemental release rates by Cote model reveals dominant mechanisms for the composite tested at 58 °C as an example.

higher elemental release rates. After 3 d water exposure, the dissolution is mainly dominated by a diffusion controlled process, in which the water molecules and released elements need to transport through the dense apatite matrix or grain boundaries across the bulk solution to the inner composite matrix. The activation
energies, \( E_a \), for the long-term dissolution behavior are also determined for the composite based on the long-term diffusion mechanism. The activation energies for Cs and I are 58 and 60 kJ·mol\(^{-1}\), respectively, significantly higher than the \( E_a \) for the corresponding elements in pure Cs\(_3\)Bi\(_2\)I\(_9\). The higher activation energies determined for the composite structure compared to the monolithic Cs\(_3\)Bi\(_2\)I\(_9\) are closely related to their dominant mechanisms—long-term diffusion controlled mechanism for the composites and direct dissolution for monolithic composites.

As compared to the pure Cs\(_3\)Bi\(_2\)I\(_9\), the cumulative release rate of the composite structure is an order of magnitude lower than that of pure Cs\(_3\)Bi\(_2\)I\(_9\) after normalizing to its corresponding Cs and I loadings (normalization via the following Eq. (4): \( L_N = \frac{L}{\text{Weight percent}} \)). Figure 10 shows the comparison in the long-term normalized release rates for the composite pellets subjected to the semi-dynamic leaching test and the pure monolithic Cs\(_3\)Bi\(_2\)I\(_9\) subjected to the static leaching test. During the leaching tests, the water molecules need first to bypass the HA matrix to reach out the Cs\(_3\)Bi\(_2\)I\(_9\) grains. Therefore, the dense HA matrix can act as a physical barrier to slow down the transport of water molecules and elemental release. The order-magnitude lower elemental release rates for the composite pellets subjected to a more aggressive semi-dynamic leaching than those of monolithic pellets by static leaching clearly demonstrate the feasibility of using the Cs\(_3\)Bi\(_2\)I\(_9\) + HA ceramic-based composite in enhancing waste form’s chemical durability.

The chemical durability of the designed perovskite–HA ceramic composite is evaluated within the context of current state-of-the-art waste form materials [49–62] for Cs and I immobilization including the glass-bonded metal–halide perovskite composites proposed by our group [34]. Figure 10 summarizes the comparison with respect to the key performance indicators of waste loadings and chemical durability. As compared to the Cs\(_3\)Bi\(_2\)I\(_9\)–silica composite structure (Figs. 10(a) and 10(b)), the Cs\(_3\)Bi\(_2\)I\(_9\) + HA composites demonstrate comparable performance for immobilizing both I and Cs at RT, but slightly higher elemental release rates than the Cs\(_3\)Bi\(_2\)I\(_9\) + silica at 90 \(^\circ\)C. The difference can be attributed to the microstructure of the ceramic composite in which the HA matrix displays a nano-sized grain structure with the average grain size of less than 100 nm. Microstructure of the composite design profoundly impacts the transport behavior and subsequent surface alteration. Microstructure control, e.g., using micro-sized HA as the encapsulated matrix, is expected to further improve the chemical durability of the HA composites in future material design and waste form development.

The comparison of the Cs and I release rates for the perovskite–HA composites with waste form materials reported in the literature is shown in Figs. 10(c) and 10(d). In general, the Cs\(_3\)Bi\(_2\)I\(_9\) + HA (50 wt%) composites reported in this study display simultaneously high waste loadings and chemical durability. In the case of 50 wt% Cs\(_3\)Bi\(_2\)I\(_9\)–HA composite, the elemental loadings of Cs and I are 10.8 and 30.3 wt%, respectively. The waste loadings of the Cs\(_3\)Bi\(_2\)I\(_9\) + HA (50 wt%) composite are higher than those of hollandite (Ba,Cs)(Al,Ti)\(_2\)Ti\(_6\)O\(_{16}\) (Cs) [9] and lead vanadate iodoapatite [27] but with high waste loadings (e.g., only 9 wt% iodine waste loading in iodoapatite). Note that materials are tested by different testing protocols (e.g., MCC-1, ASTM C1308, ASTM C1220, PCT testing, etc.) and at different testing conditions (with various solvents, temperature, pH values, and sample geometry (pellets vs. powders)) and different \( S/V \), making a direct comparison challenging. Detail testing protocols and conditions can be found in Tables S1 and S2 in the Electronic Supplementary Material (ESM). In this study,

### Table 2: Rate constants (\( k_a \)) of Cs\(_3\)Bi\(_2\)I\(_9\) + HA samples as evaluated by semi-dynamic leaching test

| Element | Temperature | \( k_1 \) (mol/(m\(^2\)·d)) | \( k_2 \) (mol/(m\(^2\)·d\(^{0.5}\))) | \( k_3 \) | \( k_4 \) | \( R^2 \) |
|---------|-------------|-----------------|-----------------|------|------|-------|
| Cs      | 25 °C       | 0.002           | 0.11            | 1    | 0.016 | 0.996 |
|         | 58 °C       | 0.008           | 3.98            | 1    | 1.288 | 0.850 |
|         | 90 °C       | 0.013           | 7.537           | 1    | 5.64  | 0.960 |
| I       | 25 °C       | 1.00E-04        | 0.08            | 1    | 5.00E-03  | 0.998 |
|         | 58 °C       | 1.60E-04        | 2.73            | 1    | 0.009 | 0.960 |
|         | 90 °C       | 0.002           | 4.92            | 1    | 5.98  | 0.980 |

The values of \( k_a \) were determined by the long-term rates shown in Figs. 10(c) and 10(d). The Cs and I release rates for the ceramic composites are lower than those of hollandite (Ba,Cs)(Al,Ti)\(_2\)Ti\(_6\)O\(_{16}\) (Cs) [9] and lead vanadate iodoapatite [27] but with high waste loadings (e.g., only 9 wt% iodine waste loading in iodoapatite).
Fig. 10  Normalized long-term rates of (a, c) I and (b, d) Cs in the Cs$_3$Bi$_2$I$_9$ + HA (50 wt%) composite as compared with the state-of-the-art silica bond composite (50 wt%) and waste forms from literature research at RT and 90 °C. Note that the rates for the silica and HA composites are determined by semi-dynamic leaching test. The normalized rates for pure Cs$_3$Bi$_2$I$_9$ were determined from linear fitting of the cumulative concentration–time curve by static leaching before re-precipitation occurred. The leaching protocols and conditions in the literature can be found in Table S1 in the ESM, and the detailed waste loadings and normalized rates are summarized in Table S2 in the ESM.

the semi-dynamic leaching protocol was chosen to evaluate the chemical durability of Cs$_3$Bi$_2$I$_9$–HA, avoiding the solution feedback occurred for the static leaching protocol (PCT, MCC-1) for the majority of the state-of-the-art nuclear waste forms ever reported. The semi-dynamic leaching protocol also allows to evaluate the waste form performance close to a near-field environment with a dynamic water flow. Therefore, the Cs$_3$Bi$_2$I$_9$–HA composite design in this study offers a new approach to develop durable waste form materials with greatly-improved waste loadings, which are of significance for effective nuclear waste management.

4 Conclusions

In summary, a new strategy of designing advanced waste form materials based on waste-loaded phases embedded in a high durable matrix in the ceramic–ceramic form is reported with the goal of significantly improving materials’ chemical durability and waste loadings. Particularly, the ceramic-based composites are developed by incorporating 50 wt% Cs$_3$Bi$_2$I$_9$ into a high durable HA matrix by low-temperature and high-pressure SPS consolidation. The chemical durability and leaching mechanisms are assessed by accelerated leaching test and compared with the monolithic Cs$_3$Bi$_2$I$_9$. For both pure Cs$_3$Bi$_2$I$_9$ and composite structure, Cs and I are incongruently released from the matrix with the formation of a less soluble secondary product of BiOI flakes resulting from the hydrolysis product of the intermediate phase BiI$_3$ during water interaction. The highly densified HA matrix acts as a very effective physical barrier to slow down the transport behavior and the release of Cs and I, as evidenced by much higher activation energy for elemental release and transition of the mechanisms from dissolution-controlled to diffusion-controlled behaviors. The design of the waste-loaded host phase in a durable ceramic matrix leads to significantly improved chemical durability meanwhile high loadings, of significance for effective managements of problematic of Cs and I.
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Electronic Supplementary Material

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