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R. Pénélope, L. Campayo, M. Fournier, A. Gossard, A. Grandjean. Solid sorbents for gaseous iodine capture and their conversion into stable waste forms. *Journal of Nuclear Materials*, 2022, 563, pp.153635. 10.1016/j.jnucmat.2022.153635 . cea-04711739

**HAL Id: cea-04711739**

**<https://cea.hal.science/cea-04711739v1>**

Submitted on 13 Nov 2024

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# 1 Solid sorbents for gaseous iodine capture and their conversion into 2 stable waste forms

3

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12

## 13 **Abstract**

14 The reprocessing of nuclear fuel generates gaseous radionuclides including various isotopes  
15 of xenon, krypton and iodine. Iodine, mainly present as long-lived <sup>129</sup>I (half-life,  $1.57 \times 10^7$   
16 years) and short-lived <sup>131</sup>I (half-life, 8.02 days) is a particular concern because of its high  
17 volatility and mobility in the environment. Deep geological disposal is therefore favored over  
18 release into the marine environment or the atmosphere. To this end, gaseous iodine must first  
19 be captured in solid sorbents and then immobilized in a stable waste form. While the literature  
20 on iodine sorbents (also called filters) and iodine immobilization materials is extensive, the  
21 conversion of the sorbents into stable waste forms has not received as much attention. The  
22 aim of this review is to examine the links between these two research fields: iodine trapping  
23 on solid sorbents and iodine conditioning matrices described in the literature.

24

25 *Keywords:* adsorption, disposal, environment, filter, immobilization, nuclear, matrix

26

27 **1.**

## 28 **2. Introduction**

29 Nuclear fuel reprocessing generates various types of waste, notably minor actinides and  
30 fission products. These are managed using different treatment processes depending on their  
31 level of activity and half-life. High-level waste is more often vitrified for deep geological  
32 disposal [1–4]. One of the main isotopes of iodine in fission products is iodine-131, whose  
33 short half-life (8.02 days) and high radioactivity ( $4.6 \times 10^{15}$  Bq·g<sup>-1</sup>) make it particular  
34 dangerous if released into the environment [5–7]. The other main iodine isotope produced by  
35 fission, iodine-129 ( $6.7 \times 10^6$  Bq·g<sup>-1</sup>) poses a long-term risk because of its long radioactive  
36 half-life (15.7 million years) [5–7]. As well as being highly volatile and propagating readily in  
37 air and groundwater, iodine is absorbed by the thyroid gland in mammals, and exposure to  
38 high doses therefore has severe toxic effects [8,9].

39 This means that specific processes are required to manage radioactive iodine. Vitrification in  
40 borosilicate glass, as used for high-level waste, is not a viable option since iodine volatilizes  
41 rapidly at the high temperatures involved ( $> 1000^\circ\text{C}$ ) [10–12]. As a result, iodine is managed  
42 in some countries such as France and the UK by isotopic dilution in marine environments  
43 limited by reject regulations.

44 Other management approaches that avoid release into the environment are under study.  
45 Transmutation, which involves transforming long-life radionuclides into shorter-lived  
46 radioisotopes or stable elements, is an attractive solution [13–16]. However, deep geological  
47 disposal is currently seen as the most feasible alternative.

48 This approach rests on the immobilization of iodine in a durable matrix material guaranteed to  
49 remain stable over millions of years in the chosen geological environment. Different materials  
50 have been studied for this application with most of the studies focused on ceramics and  
51 glasses [17]. For instance, in the French context, for ceramics, apatites with several  
52 compositions (lead-vanadate, calcium-phosphate ...) have received much attention [18–20]  
53 because of their irradiation stability and high iodine content [21]. This interest comes from  
54 geological investigations of the natural nuclear reactors in the Franceville basin (Gabon) that  
55 have shown that they have good long-term durability [22,23]. For glasses, low temperature  
56 forming glasses are often required to overcome volatility issues coming from the poor thermal  
57 stability of iodine-containing materials. This feature can be illustrated by the case of silver  
58 phosphate-based glasses [24–26] that have low melting temperature and can incorporate high  
59 iodine amount [27].

60 Before immobilization however, the gaseous iodine produced in nuclear fuel reprocessing  
61 plants needs to be captured efficiently. This can be done using various wet processes (caustic  
62 scrubbing, the Iodox or Mercurex processes [28–32]) or by dry scrubbing, using solid  
63 sorbents. The main advantage of dry systems is that non-dispersible solid waste is obtained  
64 directly compared to wet processes where several steps are required. Selective solid sorbents  
65 for iodine capture have been reviewed extensively [17,33–35], but the question of  
66 transforming these materials into a stable waste form is rarely discussed. When it is discussed,  
67 several steps are often necessary to get a suitable wastefrom from a solid sorbent designed for  
68 the trapping of gaseous iodine and this requires most of the time the use of chemical processes  
69 [17]. Actually, very few solid sorbents were seen “versatile” enough to be directly converted  
70 in a minimum of steps into a dense monolith that could be further disposed of in a deep  
71 geological repository. However, new insights have been obtained in this field in the recent

72 years and it was thought that it could be a good opportunity to make a freeze on the current  
73 state of the art in this field.

74 Hence, the aim of this review is to investigate the possible links between the selective iodine  
75 sorbents described in the literature and the immobilization matrices (monolithisation  
76 processes) that have been developed from these sorbents.

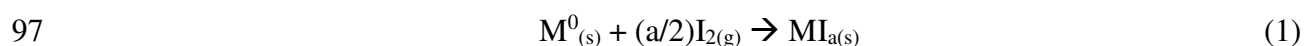
77 The first part of the review focuses on the various mechanisms available to capture molecular  
78 ( $I_2$ ) and organic ( $CH_3I$ ) iodine. Then, the iodine trapping properties of sorbents from literature  
79 is presented according to their composition. Their direct transformation (processes in which  
80 sorbents are used directly as a primary material without prior transformation) into waste forms  
81 after iodine capture is also discussed. The physicochemical properties (microstructure,  
82 chemical durability etc.) of the resulting waste forms are discussed in detail. Sorbents whose  
83 conversion into waste forms has not been studied or involves wet processing and potential  
84 secondary iodine effluents are not considered.

### 85 **3. Iodine capture mechanisms**

86 Various sorbents can be used to capture molecular or organic gaseous iodine through  
87 several mechanisms. In physisorption, iodine is captured on the surface of the sorbent via  
88 weak and readily reversible Van der Waals-type interactions. This is the phenomenon  
89 typically exploited in metal-organic frameworks (MOFs) [36–38] and activated carbon [39–  
90 41]. In other sorbents, the reactivity of certain metals and cations for iodine is exploited to  
91 capture the latter by chemisorption in what are known as the active sites of the sorbent. On  
92 interaction with these active sites, gaseous iodine forms salts, mainly iodide ( $I^-$ ) compounds.  
93 Iodine is then captured irreversibly through the formation of strong chemical bonds with high  
94 dissociation energies. Different chemical reactions can occur depending on the nature of

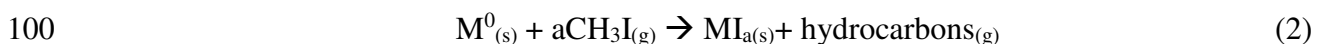
95 active site (metallic, cationic) and the type of iodine (molecular or organic) involved.

96 Molecular iodine reacts with metallic active sites (a metallic element, M) as follows:



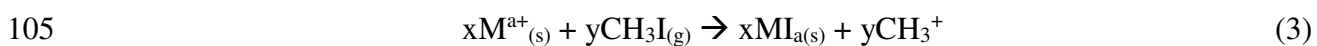
98 (a is an integer greater than 0).

99 The reaction with organic iodine is similar, but with hydrocarbons as secondary products:



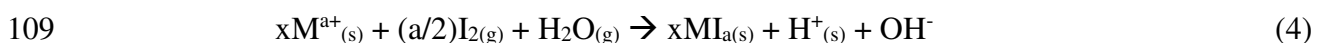
101 When the active site is cationic ( $M^{a+}$ ) and integrated in the sorbent's structure (rather than  
102 forming a separate phase), this means it contributes to the electrical neutrality of the material.

103 Reactions with iodine thereby lead to a charge deficit. With organic iodine, the reaction can  
104 be charge balanced by positively charged methyl groups:

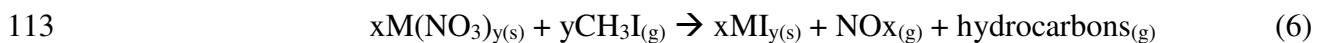
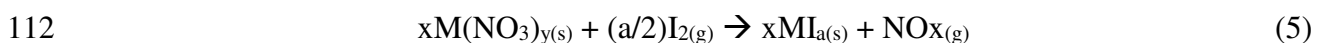


106 (with integers  $x \geq y > 0$ ).

107 With molecular iodine however, charge balancing from the environment is required. This can  
108 for instance involve a hydrogen ion from the decomposition of a water molecule:



110 Sorbents can also have salts as active sites, most commonly nitrates. Reactions with molecular  
111 and organic iodine generate nitrogen oxides ( $NO_x$ ) as follows:

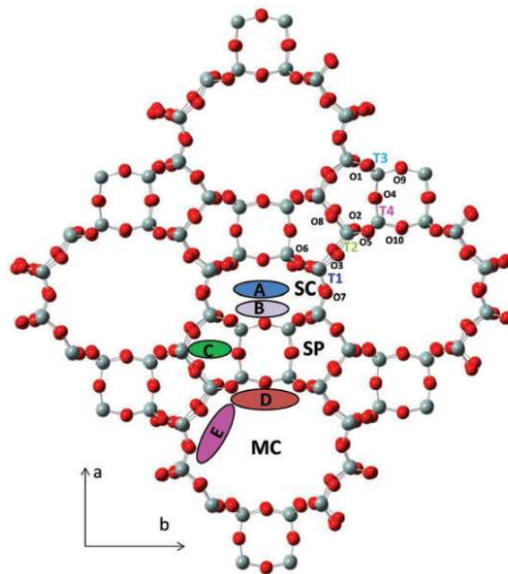


#### 114 **4. Silver mordenites**

115 Mordenites (MORs) are porous aluminosilicate zeolites with the chemical formula  
116  $(Ca,Na,K_2)Al_2Si_{10}O_{24} \cdot 7H_2O$  and an orthorhombic structure (Cmcm space group) [42]. After  
117 cationic exchange with silver ions,  $Ag^+$ -MORs can be used as iodine sorbents, while after  $H_2$   
118 treatment, the metallic silver in  $Ag^0$ -MORs behaves as an active site.

119 4.1. Location and insertion of silver into mordenites

120 Structurally, mordenite (Figure 1) consists of several cages occupied by cations ( $\text{Na}^+$ ,  $\text{Ca}^{2+}$ ,  
121  $\text{K}^+$ ). Mordenites are the most studied zeolites for iodine adsorption because they are stable in  
122 acid gases (radioactive iodine is generated in a nitric acid environment) and because they are  
123 one of the rare zeolites that can be synthesized with a wide range of Si/Al ratios [43,44]. This  
124 ratio is important because it allows the cation content of the structure to be adjusted without  
125 modifying the crystal structure or lattice parameters [45]. The cation content of the structure,  
126 and thus its  $\text{Ag}^+$  content, is inversely proportional to the Si/Al ratio. As shown in Figure 1,  
127 silver ions can occupy several different sites in the structure.



128  
129 **Figure 1.** Crystal structure of mordenite with the main channel (MC), side channel (SD) and side  
130 pocket (SP).  $\text{Ag}^+$  cations can occupy the sites indicated by capital letters (A-E) and Al atoms occupy  
131 the tetrahedral sites T1–T4. (Si atoms in grey, O in red) [45].

132  
133  $\text{Ag}^+$ -MOR is usually transformed into  $\text{Ag}^0$ -MOR by heating in flowing  $\text{H}_2$ . This leads to the  
134 substitution of  $\text{Ag}^+$  by  $\text{H}^+$  and the migration of the former to the surface of the material where  
135 it forms silver metal nanoparticles [46–48].

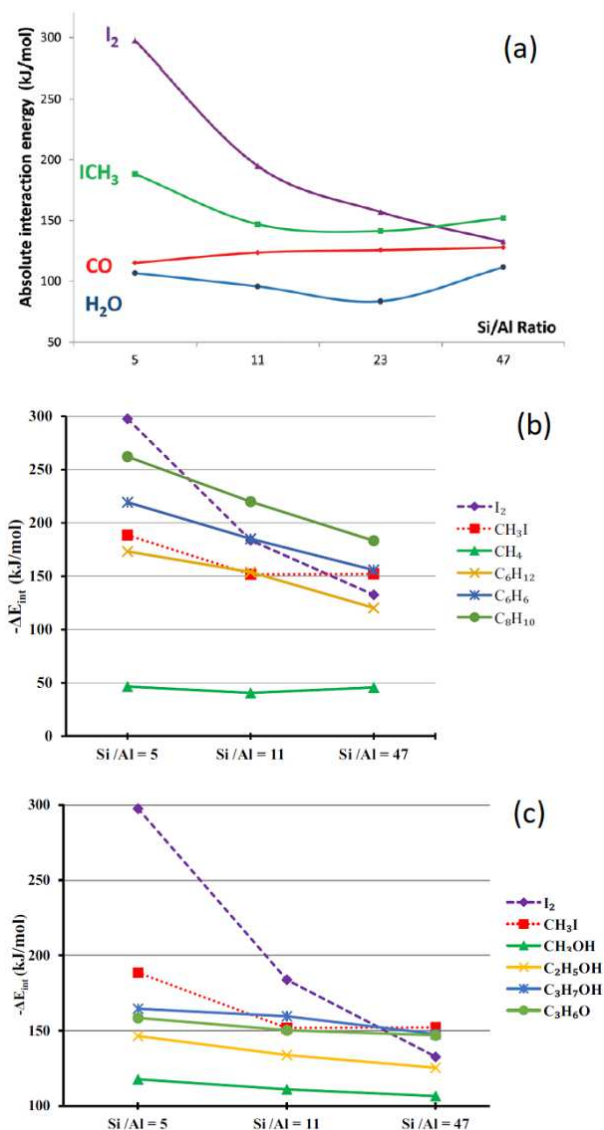
#### 136 4.2. Iodine capture performance of Ag<sup>+</sup>-MORs

137 The iodine capture properties of Ag<sup>+</sup>-MORs in the presence of contaminants have been  
138 studied by DFT modelling. Chibani et al. calculated the mean interaction energies between  
139 Ag<sup>+</sup>-MORs and different compounds (I<sub>2</sub>, CH<sub>3</sub>I, CO et H<sub>2</sub>O) as a function of the Si/Al ratio  
140 (and thus the Ag<sup>+</sup> content; Figure 2a) [45]. Their results show that at low Ag<sup>+</sup> contents (Si/Al  
141 ratios of 47 and 23), the interaction energies of iodine species are slightly lower than those of  
142 water molecules and of CO, suggesting a competition effect, in particular with CO, as  
143 described for faujasite by Chebbi et al. [49]. Reducing the Si/Al ratio (down to 11 or 5), leads  
144 to a substantial decrease in the interaction energies with iodine species, while those for CO  
145 and H<sub>2</sub>O remain almost unchanged. This implies that increasing the Ag<sup>+</sup> content of  
146 mordenites favours interactions with iodine species over those with CO and H<sub>2</sub>O.

147 The results of a similar study [50] involving different organic contaminants such as methane  
148 (CH<sub>4</sub>), cyclohexane (C<sub>6</sub>H<sub>12</sub>) and methanol (CH<sub>3</sub>OH), shown in Figure 2b,c, indicate that  
149 iodine can only be selectively captured in the presence of these organic compounds at the very  
150 lowest Si/Al ratios (here, 5). These studies show that contaminants (H<sub>2</sub>O, CO, hydrocarbons  
151 etc.) typically have a negative effect on the performances of Ag<sup>+</sup>-MORs.

152 The capture properties of Ag<sup>+</sup>-MORs for CH<sub>3</sub>I were studied under dynamic conditions using  
153 breakthrough experiments at 100°C [51]. Sorbents containing 5.9 and 7.3 wt.% silver were  
154 found to capture 82 and 120 mg·g<sup>-1</sup> of iodine respectively (28 and 34% of which was  
155 physisorbed), indicating that the amount of iodine captured is proportional to the silver  
156 content of the sorbent, although a considerable proportion is physisorbed.





157

158 **Figure 2.** (a) Average interaction energy in absolute value between Ag<sup>+</sup>-mordenites with several Si/Al  
 159 ratios and different gaseous compounds [45]. (b,c) Evolution of the interaction energies of Ag<sup>+</sup>-  
 160 mordenites with (b) iodine compounds and hydrocarbons or (c) oxygenated compounds, as a function  
 161 of the Si/Al ratio [50].

### 162 4.3. Iodine capture performance of Ag<sup>0</sup>-MORs

163 Scheele et al. used a specific fixed bed capture setup with a mixture of CH<sub>3</sub>I and air  
 164 percolating through a column filled with sorbent to study the iodine capture efficiency of Ag<sup>0</sup>-  
 165 MORs [48]. Several parameters were varied, such as the temperature (from 86 to 200°C), the  
 166 gas flow rate (3.75 to 15 m·min<sup>-1</sup>) and the presence or not of NO and NO<sub>2</sub>. The maximum

167 capacity of the sorbents was found to be proportional to temperature and inversely  
168 proportional to the gas flow rate and the amount of NO<sub>x</sub> present. A reasonable explanation for  
169 these results is that NO<sub>x</sub> reacts with active sites thereby reducing the sorbent's capacity for  
170 iodine. Meanwhile, increasing the flow rate reduces the contact time of iodine with the active  
171 sites, and thus presumably also the capture rate. The variation with temperature is harder to  
172 explain. Under optimal conditions (200°C, 3.75 m·min<sup>-1</sup> flow rate, no NO<sub>x</sub>), the iodine  
173 sorption capacity was 217 mg·g<sup>-1</sup>. In the presence of contaminants (NO<sub>x</sub> and H<sub>2</sub>O) and at  
174 150°C, the sorption capacity was found to be 52 mg·g<sup>-1</sup>[52].

175 In another study focussing on I<sub>2</sub> capture under dynamic conditions (without NO<sub>x</sub>) [47], Ag<sup>0</sup>-  
176 MORs were found to capture 115, 135, and 100 mg·g<sup>-1</sup> on average at 100, 150 and 200°C,  
177 respectively. The authors state that the loading capacity should decrease as the temperature  
178 increases, but between 100 and 150°C the opposite was observed. The proposed explanation  
179 is that the water initially present in Ag<sup>0</sup>-MOR hinders I<sub>2</sub> capture by reacting with Ag<sup>0</sup>. Since  
180 there is more water in the structure at lower temperatures, this explains why more iodine is  
181 captured at 150°C than at 100°C. Another interesting result of this study is that the proportion  
182 of chemisorbed iodine decreases from 97 to 91% between 100 and 200°C.

#### 183 4.4. Differences between Ag<sup>+</sup>- and Ag<sup>0</sup>-MORs

184 The oxidation state of Ag in these sorbents has a direct effect on the iodine adsorption  
185 capacity and the types of AgI crystals formed. Nan et al. demonstrated this behavior by  
186 modulating the H<sub>2</sub> reduction treatment (170 up to 500 °C during 24 up to 336 h) of the  
187 sorbents and therefore the Ag<sup>0</sup> content to the detriment of Ag<sup>+</sup> [47]. After 24 h reduction at  
188 230°C, the iodine adsorption capacity measured in a continuous flow setup (temperature not  
189 specified) was 65 mg·g<sup>-1</sup>, whereas after 24 h at 400°C (complete reduction) the adsorption  
190 capacity was 105 mg·g<sup>-1</sup>. There is therefore an increase of iodine loading capacity when the

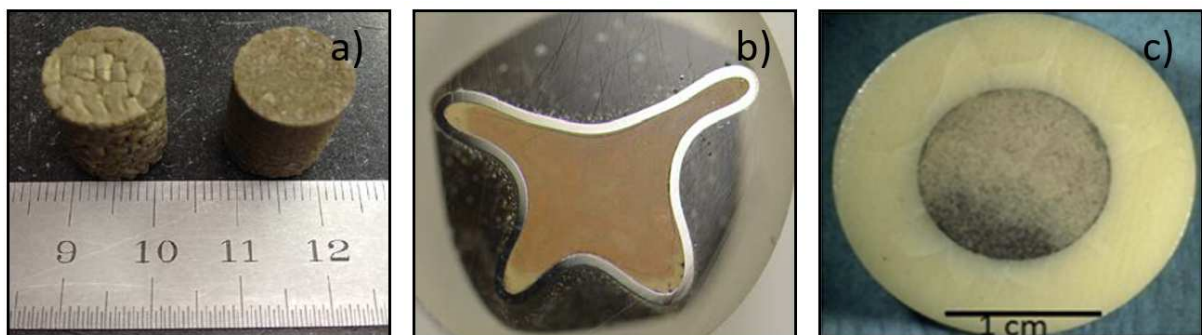
191 quantity of  $\text{Ag}^0$  increases explained by a better accessibility of iodine with active sites  
192 principally localized on the surface [46–48].  
193 Regarding the crystal structure of the silver iodide produced, Chapman et al. [53] found that  
194 below  $147^\circ\text{C}$ , a single  $\beta$ -AgI phase (with wurtzite structure) forms regardless of the oxidation  
195 state of the silver ( $\text{Ag}^0$  or  $\text{Ag}^+$ ). However, this is not the case at higher temperatures. In the  
196 presence of  $\text{Ag}^0$ , two phases form:  $\alpha$ -AgI (body-centered cubic structure) and a metastable  $\gamma$   
197 phase. The crystallites of the  $\alpha$ -phase are sub-nanometer in size and found on the inside of the  
198 pores in the  $\text{Ag}^0$ -MOR while the crystallites of  $\gamma$ -AgI are micrometer scale and found on the  
199 surface. In the presence of  $\text{Ag}^+$ , only the  $\alpha$ -phase forms and is found exclusively in the pores.  
200 Thus, while  $\text{Ag}^+$ -MORs capture less iodine than  $\text{Ag}^0$ -MORs, the AgI crystallites that form in  
201 the former are all nanoconfined inside the structure.

#### 202 4.5. *Conversion of iodine-loaded $\text{Ag}^0$ -MORs into stable waste forms*

203 The conversion of iodine-loaded  $\text{Ag}^0$ -MOR into waste forms by hot pressing has been  
204 studied at Oak Ridge National Laboratory [54]. Preliminary tests using hot uniaxial pressing  
205 (HUP, at  $750^\circ\text{C}$  at 27.5 MPa) on sorbents without iodine showed that the pressure with this  
206 technique was insufficient to collapse the mordenite pores and that the resulting materials  
207 were too friable (Figure 3a). However, thanks to the higher pressures achievable by hot  
208 isostatic pressing (HIP) (175 MPa at  $525^\circ\text{C}$ ), the materials obtained (in galvanized steel  
209 containers) were monolithic, compact and non-friable, and consisted of a mixture of  
210 crystalline (AgI and  $\text{Ag}(\text{IO}_4)$ ) and amorphous regions. Furthermore, no iodine volatilization  
211 was detected. HIP at  $700^\circ\text{C}$  produced the same results (Figure 3b). However, the chemical  
212 durability of this waste form was not studied. It is also possible to convert these sorbents (and  
213 more generally temperature sensitive sorbents) by densification at ambient temperature [55].  
214 By mixing them with ductile metallic powder (Sn, Au, Cu ...), a compacted metallic matrix

215 which encapsulates the iodine-loaded sorbents can be obtained after uniaxial pressing at  
216 172 MPa.

217 Another method that has been studied to transform these sorbents into stable waste forms is to  
218 mix them with a low sintering temperature glass. Garino et al. mixed AgI-MOR with Bi<sub>2</sub>O<sub>3</sub>-  
219 SiO<sub>2</sub>-ZnO glass powder at 20/80 wt.% [56]. Metallic silver was added in excess (5 wt.%) to  
220 capture any iodine (most likely the physisorbed portion) released during the treatment. The  
221 mixture was uniaxially pressed at 70 MPa to form pellets that were then heated at 550°C for  
222 1 h. Cohesive multiphase materials were obtained, consisting of amorphous, Bi<sub>4</sub>(SiO<sub>4</sub>)<sub>3</sub>,  
223 mordenite and AgI phases, in the form of a composite AgI-MOR core, glass shell matrix, as  
224 shown in Figure 3c. The thermal treatment led to partial crystallization of the glass into  
225 Bi<sub>4</sub>(SiO<sub>4</sub>)<sub>3</sub>, and transformation of metallic silver into AgI. Chemical durability tests performed  
226 for 7 days in deionized water (15 mL for 1.5 g of sample) at 90°C indicates that the element  
227 detected at the highest concentration in solution was boron, at 8.6 ppm.



228  
229 **Figure 3 .** (a) Photograph of AgI-mordenite matrices obtained from (left) pellets and (right) powder  
230 after hot uniaxial pressing at 750°C and 27.5 MPa [54,57]. (b) Photograph of a AgI-mordenite matrix  
231 obtained after hot isostatic pressing at 700°C and 175 MPa [54,57]. (c) Photograph of a sintered  
232 core/shell matrix with a 100% glass shell and glass/AgI-mordenite/Ag core [56].

233

234 The different techniques presented above and more specifically the densification at ambient  
235 temperature [55] can potentially be used on faujasites, another kind of porous aluminosilicate

236 belonging to zeolite family. Several works have demonstrated the performances of silver-  
237 faujasites both for I<sub>2</sub> and CH<sub>3</sub>I trapping [51,58–61].

## 238 **5. Silver-silica aerogels**

239 Aerogels are extremely porous semi-rigid materials with very high specific surface area  
240 (sometimes greater than 1000 m<sup>2</sup> g<sup>-1</sup>) and containing more than 90 wt.% air [62,63]. They are  
241 composed mainly of carbon materials, silicon and metal oxides and are good candidate  
242 materials for the capture and immobilization of gaseous iodine.

### 243 *5.1. Iodine capture performance and aging of silver-silica aerogels with thiol* 244 *functions*

245 In this context, silver-silica aerogels have been functionalized with thiol functions by  
246 reaction with silane-thiol (Si-SH) groups [64]. When the sorbent is impregnated with an  
247 AgNO<sub>3</sub>-containing solution, these thiol functions lead to the formation of silver complexes (S-  
248 Ag bonds) in the structure, such that the silver is covalently bonded to the silicon network.  
249 Ag<sup>0</sup>-based sorbents are finally obtained after thermal treatment under argon/H<sub>2</sub>. In dynamic I<sub>2</sub>  
250 adsorption experiments in humid air at 150°C, these sorbents captured 480 mg·g<sup>-1</sup> iodine in  
251 11 days, with very little physisorption (less than 10 mg·g<sup>-1</sup>) [64]. In iodine release  
252 experiments performed after 2 months' storage in the laboratory (at ambient temperature and  
253 pressure), the sorbents released 15% of the captured iodine under static conditions (at 150°C  
254 in air containing 2 vol.% NO<sub>2</sub>) [65] and 43% under dynamic conditions (flowing air + 1 vol.%  
255 NO) [66]. Over 6 months' storage in humid air, without NO<sub>x</sub>, around 22 wt.% of the iodine  
256 was released [66].

257 Thus, although these sorbents capture iodine by chemisorption, the iodine seems to be  
258 released as they age under the effect of different gaseous species. The stability of the sorbents  
259 over time is therefore an important consideration to limit iodine release.

260 Matyas et al. studied the ageing process in these aerogels (in the absence of iodine) in  
261 different gases (air, H<sub>2</sub>O and NO) at 150°C [67]. In the presence of NO, the surface thiol  
262 groups are oxidized, leading to the formation of R-SO<sub>4</sub> sulphate groups. In air (dry or humid),  
263 some of the thiol groups become oxidized to sulphate and silver sulphate is produced. This is  
264 the proposed mechanism through which AgI becomes destabilized and the material is thought  
265 to age.

### 266 *5.2. Iodine capture performance of silver-silica aerogels without thiol* 267 *functions*

268 Riley et al. prepared Al-Si-O and Na-Al-Si-O aluminosilicate aerogels impregnated with  
269 AgNO<sub>3</sub> for I<sub>2</sub> capture [68]. While the Ag loading efficiency of the Al-Si-O aerogels was low,  
270 with few silver active sites on the surface, limiting the iodine adsorption capacity, the  
271 impregnation of the Na-Al-Si-O gels was much more efficient, with Ag<sup>+</sup> replacing Na<sup>+</sup> ions in  
272 the structure by cationic exchange (as in mordenites). In iodine loading tests performed in an  
273 iodine-saturated chamber at 150°C, the iodine sorption capacity of the Na-Al-Si-O aerogels  
274 was measured at 517 mg·g<sup>-1</sup> and at 555 mg·g<sup>-1</sup> after reduction of the Ag<sup>+</sup> to Ag<sup>0</sup> by heat  
275 treatment under argon/H<sub>2</sub>. The ageing behaviour of these sorbents was not studied however.

### 276 *5.3. Conversion of iodine-loaded silver-silica aerogels into stable waste forms*

277 Matyas et al. have studied the effects of densification on silver-silica aerogels with thiol  
278 functions as a means to immobilize captured molecular iodine [69]. After HUP (1200°C, 29  
279 MPa), the measured residual open porosity was 17% with 7% iodine loss. After HIP (1200°C,  
280 207 MPa), with the sorbent encased in a metal canister, 100% densification was obtained and

281 no iodine release was detected. HIP therefore seems to be the best option to densify iodine-  
282 loaded aerogels. Scanning electron microscopy (SEM) analysis of these material's  
283 microstructure after sintering revealed four separate phases, identified by X-ray diffraction  
284 (XRD) as an amorphous silica-based phase, metallic silver, Ag<sub>2</sub>S, and AgI. The chemical  
285 durability of this waste form was not studied.

## 286 **6. Silver silica and silver alumina**

287 Solid supports based on mesoporous alumina (Al<sub>2</sub>O<sub>3</sub>) or silica (SiO<sub>2</sub>) impregnated with  
288 silver nitrate are some of the earliest-studied materials for gaseous iodine capture [28,70].  
289 These sorbents are now widely used in nuclear reprocessing plants.

### 290 *6.1. Iodine capture performance of silver silica*

291 Solid sorbents based on silica impregnated with silver nitrate were developed in Germany  
292 in the 1970s for the Kalshruhe pilot reprocessing plant (WAK, shut down in 1992) to comply  
293 with regulations on iodine release into the atmosphere [71]. These sorbents, sold under the  
294 name AC-6120, are prepared as small beads, 1–2 mm in diameter and have a specific surface  
295 area of 65–110 m<sup>2</sup> g<sup>-1</sup>, a pore size distribution of 20–40 nm and a maximum Ag<sup>+</sup> content of  
296 12 wt.% [28]. Decontamination factors (DFs, the ratio of the concentration or activity of the  
297 gaseous iodine before and after passing through the sorbent) greater than 99% have been  
298 measured in laboratory-scale fixed bed adsorption experiments for I<sub>2</sub> in air containing 1–5  
299 vol.% NO<sub>2</sub> [72]. The removal efficiency is substantially lower at high levels of humidity  
300 however, dropping from 99% at 70% relative humidity to 27% at 100% relative humidity.  
301 These sorbents were successfully used in the WAK plant to remove at least 90% of the iodine  
302 from the off-gas [71].

## 303 6.2. *Conversion of iodine-loaded silver silica into stable waste forms*

304 Wada et al. used HIP (750°C, 100 MPa) to densify 13.2 wt.% iodine-loaded silver silica,  
305 achieving a volume reduction of 48% [73]. No iodine release was detected during the  
306 treatment. The waste form obtained (Figure 4) consisted of SiO<sub>2</sub>, Ag, and AgI phases,  
307 indicating that the iodine was retained as silver iodate and did not enter the silica matrix. The  
308 chemical durability of this waste form was not investigated however.



309  
310 **Figure 4.** Photograph of an iodine-loaded silver-silica waste form obtained by hot isostatic pressing at  
311 750°C and 100 MPa [73].

## 312 6.3. *Iodine capture performance of silver alumina*

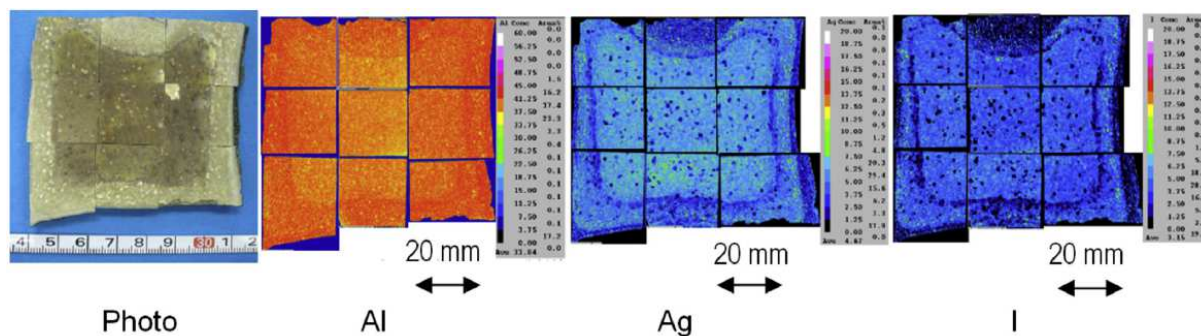
313 Silver-loaded alumina sorbents were developed in Japan in the 1980s for the Tokai  
314 reprocessing plant (shut down in 2014) [28]. These sorbents in the form of beads roughly 2  
315 mm in diameter can carry up to 24 wt.% silver and their physical properties are similar to  
316 those of the silver-silica beads described in the preceding paragraph. In laboratory-scale  
317 experiments at 150°C under dynamic conditions with flowing air containing CH<sub>3</sub>I, the iodine  
318 sorption capacities of materials with 10 and 24 wt.% Ag were measured at 100 and 230 mg  
319 g<sup>-1</sup> [74]. Experiments performed under the same conditions but this time with I<sub>2</sub> yielded  
320 similar results, with a sorption capacity of 220 mg g<sup>-1</sup> for the material loaded with 24 wt.%  
321 Ag [75]. The extraction performance seems therefore to depend little on the form of the  
322 iodine. It was also shown that 78% of the silver in the material reacted with iodine to form



323 AgI and the DF was found to be proportional to temperature over the range 25–150°C. The  
324 authors suggest that this is because iodine and silver are less likely to interact at lower  
325 temperatures [75]. In another study however, the performance of these sorbents for I<sub>2</sub> under  
326 dynamic conditions was found to vary little with temperature over 100–650°C except for a  
327 drop at the highest temperature [76]. This is likely because the silver had melted (above  
328 558°C), leading to volatilization of the iodine. This is in keeping with iodine release tests  
329 performed on AgI-loaded sorbents, which showed weight loss starting from about 530°C [75].  
330 Studies have also shown that when the pores inside the material are too small, the DF of these  
331 sorbents tends to decrease as the relative humidity of the environment increases, [77,78].  
332 Indeed, capillary condensation leads to pores smaller than 50 nm becoming filled with water  
333 molecules, preventing any contact between the gaseous iodine and the silver active sites and  
334 reducing the sorption efficiency. This effect does not occur in pores larger than 50 nm,  
335 explaining why the efficiency of sorbents with pores mainly 40–70 nm in diameter was  
336 maintained at more than 95% at a relative humidity of 95% [77].

#### 337 *6.4. Conversion of iodine-loaded silver-alumina into stable waste forms*

338 These sorbents can be stabilized by HIP treatment. Figure 5 from Masuda et al. [79] shows  
339 that after thermal pretreatment at 480°C (to remove contaminants), and HIP at 175 MPa and  
340 1200°C, the concentration of silver (aluminium) is much higher (lower) in the core of the  
341 sample than on the outside. This is consistent with the presence of two phases, namely AgI  
342 mainly in the center and Al<sub>2</sub>O<sub>3</sub> mainly on the outside.



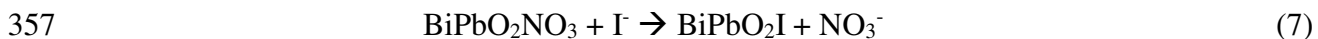
343 Photo Al Ag I  
 344 **Figure 5.** Cross-sectional photograph of an iodine-loaded silver-alumina sorbent after hot isostatic  
 345 pressing (1200°C, 175 MPa) and the corresponding elemental distributions measured by electron  
 346 probe microanalysis [79].

347  
 348 By adding a second pretreatment step, in a vacuum ( $< 7 \times 10^{-2}$  Pa) at between 400 and 500°C,  
 349 Matsuda et al. were able to reduce the void volume inside the densified waste from 15 vol.%  
 350 to less than 5 vol.% [79].

## 351 7. Lead-bismuth

### 352 7.1. Mechanism of iodine capture

353 Lead bismuth-based sorbents have been developed by Mukunoki et al. [80] to regenerate  
 354 primary sorbents. This process involves treating loaded gaseous iodine sorbents (for example,  
 355 Ag-based sorbents) **under** H<sub>2</sub> flow to reduce and desorb the iodine. The released gaseous  
 356 iodine is then captured in a BiPb<sub>2</sub>O<sub>2</sub>NO<sub>3</sub> sorbent by ion exchange via the following reaction:



### 358 7.2. Conversion of iodine-loaded lead-bismuth

359 Once loaded with iodine, the second sorbent is mixed with ZnO and vitrified at 540°C (low  
 360 enough to ensure no iodine is released) producing a homogenous glass with 2 wt.% iodine  
 361 [80]. In chemical durability tests performed at ambient temperature in a reducing

362 environment, the formation of an alteration layer on the surface of the glasses was observed,  
363 which should favour iodine retention, particularly in basic environments. These results are  
364 difficult to interpret however.

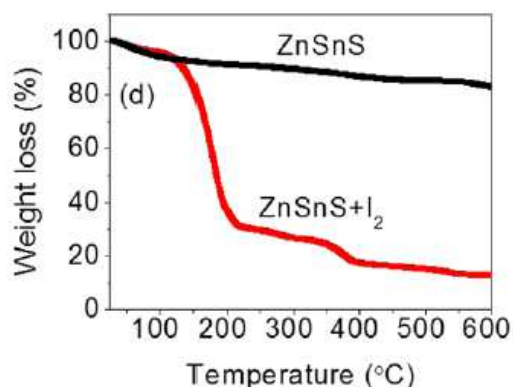
## 365 **8. Chalcogels**

### 366 *8.1. Iodine capture performance*

367 Chalcogenide-based aerogels (chalcogels) with chemical formula  $\text{Sn}_2\text{S}_3$  (SnS) and  
368  $\text{Sb}_{13.5}\text{Sn}_5\text{S}_{20}$  (SbSnS) are another type of material that has been developed to trap and  
369 immobilized iodine [81]. In static  $\text{I}_2$  capture tests performed under vacuum in desiccators  
370 (temperature not specified), the loading capacity of the SnS sorbent reached  $680 \text{ mg}\cdot\text{g}^{-1}$ . In  
371 powder form, the sorbents became saturated after about 5 days and in the form of granules,  
372 after about 20 days. This is because the pores are much more accessible in the powder. With  
373 the SbSnS sorbent, the sorption capacity was measured at  $540 \text{ mg}\cdot\text{g}^{-1}$ , and the conclusions  
374 regarding the physical form of the sorbent (powder or granular) were the same. X-ray  
375 diffraction data showed the presence of several iodine-containing phases,  $\text{SnI}_4$  and  $\text{SnI}_4(\text{S}_8)_2$  in  
376 the SnS sorbent, and  $\text{SbI}_3$  and  $\text{SbI}_3(\text{S}_8)_3$  in the SbSnS sorbent.

377 Subrahmanyam et al. have also investigated chalcogels for iodine capture [82]. They notably  
378 developed a  $\text{Zn}_2\text{Sn}_2\text{S}_6$  sorbent with a specific surface area of  $400 \text{ m}^2\cdot\text{g}^{-1}$ , a wide range of pore  
379 sizes (from micro to macroscale) and tin active sites that react with iodine by chemisorption to  
380 form  $\text{SnI}_4$ . The sorption capacity of this material for  $\text{I}_2$  was measured at  $2250 \text{ mg}\cdot\text{g}^{-1}$  in a  
381 sealed nitrogen environment at  $60^\circ\text{C}$ , and  $1970 \text{ mg}\cdot\text{g}^{-1}$  in static conditions under vacuum at  
382  $22^\circ\text{C}$ . The authors explain the lower performance in the second test by surface oxidation due  
383 to prolonged exposure to air during preparations, which reduced the number of tin active sites.  
384 Subsequent thermogravimetric analysis of sorbents with and without iodine (Figure 6) showed  
385 weight loss of about 70% between  $150$  and  $200^\circ\text{C}$ , indicating iodine release from the melting

386 of  $\text{SnI}_4$  at  $143^\circ\text{C}$ . A further 10% of the initial weight was lost between 200 and  $400^\circ\text{C}$ ,  
387 corresponding to the volatilization of  $\text{SnI}_4$  at  $348^\circ\text{C}$ .



388

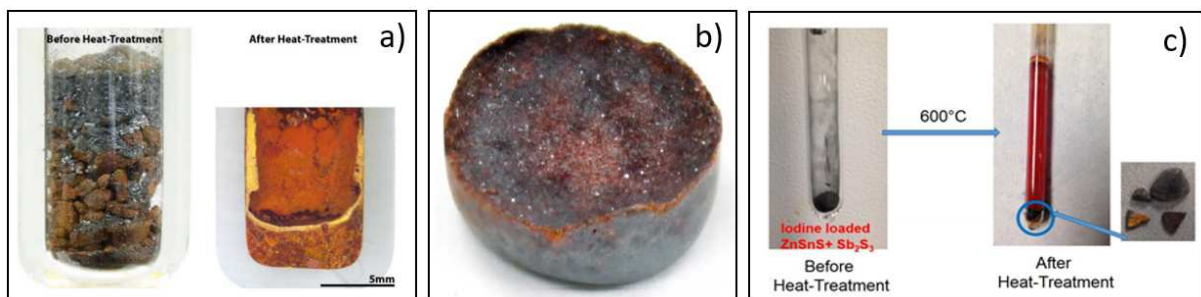
389 **Figure 6.** Thermogravimetric analysis of  $\text{Zn}_2\text{Sn}_2\text{S}_6$  before and after iodine capture [82].

## 390 8.2. Conversion of iodine-loaded chalcogen into stable waste forms

391 Since SnS does not form a glass by itself [83,84], Riley et al. investigated the possibility of  
392 vitrifying their SnS sorbents after adding germanium [81]. The precursors were sealed inside a  
393 quartz tube and heated for 10 min at 400, 500 and  $600^\circ\text{C}$ , leading to the release of black  
394 fumes inside the tube. Figure 7a shows the samples before and after heat treatment. X-ray  
395 diffraction analysis revealed the presence of an amorphous phase,  $\text{SnI}_4$  (corresponding to the  
396 yellow areas in Figure 7a),  $\text{SiO}_2$  (from the quartz tube) and  $\text{GeS}_4$ . Energy dispersive X-ray  
397 spectroscopy (EDS) showed that 24 at% of the iodine was in the amorphous phase. The  
398 chemical durability of this potential waste form was not studied.

399 The SbSnS sorbent was consolidated directly in a sealed quartz tube with the sample placed  
400 inside a glassy carbon crucible to avoid any  $\text{SiO}_2$  entering the final waste form [81]. No  
401 germanium was required in this case because the Sb-Sn-S-I system forms a homogeneous  
402 glass at  $600^\circ\text{C}$ . Red fumes were observed in the tube when the sample was taken out of the  
403 oven after 3 h at  $600^\circ\text{C}$ . The material obtained after a second heat treatment at  $500^\circ\text{C}$  is  
404 shown in Figure 7b. X-ray diffraction and EDS showed the presence of several crystalline  
405 phases such as SbSI,  $\text{SbI}_3$  and  $\text{SiO}_2$  as well as heterogeneities linked with the porous nature of

406 the material. The vitrification conditions tested here do not therefore produce a dense and  
407 homogeneous immobilization matrix.  
408 Similar tests were performed on iodine loaded  $Zn_2Sn_2S_6$  sorbents with the aim of transforming  
409 them into solidified waste [82].  $Sb_2S_3$  was added to promote the formation of a homogeneous  
410 glass. The precursors were heated at  $600^\circ C$  and then water quenched. The contents of the  
411 quartz tube before and after heat treatment are shown in Figure 7c. The presence of orange  
412 deposits on the side of the tube after heat treatment is a sign of volatilisation. The final glassy  
413 material was found to consist mainly of antimony and sulfur, with 25 wt.% iodine and small  
414 amounts of zinc and tin, indicating a type of ternary Sb-S-I glass [85]. The residues on the  
415 side of the tube were found to contain  $SbI_3$  and  $SbSI$ . The chemical durability of this potential  
416 waste form has not been studied.



417  
418 **Figure 7.** (a) Photographs of iodine-loaded SnS filters mixed with  $GeS_2$  (left) before heat treatment  
419 and (right) a polished cross-section after heat treatment [81]. (b) Photograph of iodine-loaded SbSnS  
420 filters after vitrification at  $600^\circ C$  [81]. (c) Photograph of iodine-loaded  $Zn_2Sn_2S_6$  filters after  
421 vitrification at  $600^\circ C$  [82].

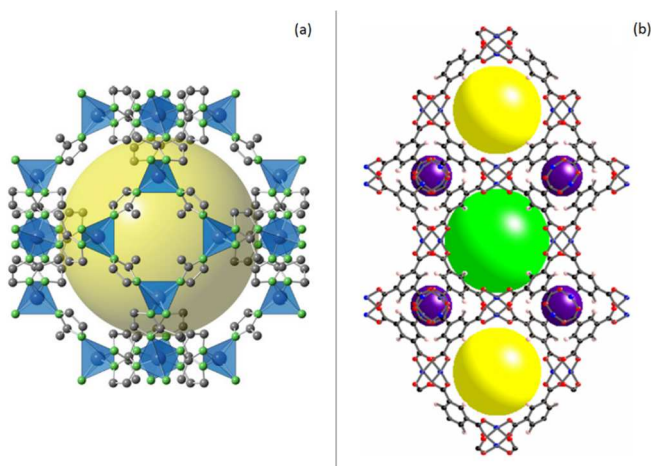
## 422 9. Metal organic frameworks (MOFs)

423 Metal–organic frameworks (MOFs) are hybrid organic-inorganic crystalline materials  
424 consisting of metal ions or clusters coordinated by organic ligands and forming organized 1D,  
425 2D, or 3D structures with specific surface areas that can be as high as  $10^4 m^2 \cdot g^{-1}$ . Their high

426 porosity and the large quantities of different structures make them often considered for iodine  
427 trapping [35].

### 428 9.1. Iodine capture performance of ZIF-8 and HKUST-1

429 The MOFs that have been studied the most for iodine gas capture are the ZIF-8 and  
430 HKUST-1 (also known as Cu-BTC) classes, whose crystal structures are shown in Figure 8.  
431 Zeolite imidazolate frameworks (ZIFs) consist of zinc tetrahedra connected by imidazolate  
432 linkers and HKUST-1 (Hong Kong University of Science and Technology) is made up of  
433 copper dimers connected by trimesic acid linkers.



434  
435 **Figure 8.** Crystal structures of (a) ZIF-8 ( $\text{Zn}^{2+}$  in blue, N in green, C in grey ; the yellow sphere is a  
436 pore) and (b) HKUST-1 ( $\text{Cu}^{2+}$  in blue, O in red, C in black and H in pink ; the yellow, green and  
437 purple spheres are pores of different sizes) metal-organic frameworks [86,87].

438  
439 Sava et al. have shown that ZIF-8 can capture up to  $1250 \text{ mg}\cdot\text{g}^{-1} \text{ I}_2$  when placed inside a  
440 hermetically adsorption chamber at  $77^\circ\text{C}$  and ambient pressure [88]. Under the same  
441 experimental conditions, Chapman et al. measured an iodine loading of  $1200 \text{ mg}\cdot\text{g}^{-1}$  [89].  
442 These results are in keeping with the maximum loading level of  $1487 \text{ mg}\cdot\text{g}^{-1}$  calculated using  
443 Monte-Carlo simulations [90]. The temperature in these simulations was  $25^\circ\text{C}$  and dynamic  
444 effects were ignored. In a more recent combined experimental and modelling study [91], the

445 two approaches yielded similar results for I<sub>2</sub> capture at 75°C and 1.17 bar, with loading  
446 capacities of 1100 mg·g<sup>-1</sup> (calculated) and 1170 mg·g<sup>-1</sup> (measured under static conditions).  
447 MOFs are usually used in a powdery form. This is why Tang et al. worked on a way to  
448 transform them into easily usable sorbents [92]. They made a mixed membrane sorbents by  
449 mixing ZIF-8 with polyethersulfone. In their initial form, ZIF-8 can trap iodine with a  
450 capacity of 876 mg·g<sup>-1</sup> (temperature not specified) whereas after transformation, they can  
451 reach 1387 mg·g<sup>-1</sup>. This modification has the double beneficial effect of increasing the  
452 capacity (supposed to be related with the increase of void volume) and making these sorbents  
453 easily usable which is important at industrial scale.

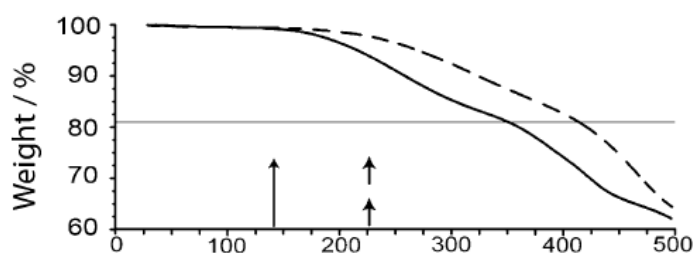
454 For HKUST-1, the combined experimental and modelling study was also carried out [91]. The  
455 loading level predicted by simulations was much higher than the experimental measurements  
456 under static conditions (1450 vs 760 mg·g<sup>-1</sup>) [91]. The authors suggest that this discrepancy  
457 may be due to differences in pore sizes. Indeed, while in HKUST-1 the large cavities and pore  
458 apertures are respectively 14 and 10 Å in diameter, the pores in ZIF-8 are much smaller  
459 (respectively 11.6 and 3.4 Å across) [88,93]. This means that physisorbed iodine is more  
460 likely to desorb in HKUST-1 than in ZIF-8. Furthermore, I<sub>2</sub>-framework interactions were  
461 estimated to be weaker in HKUST-1 than in ZIF-8. Under the same experimental conditions  
462 but with a relative humidity of 3.5%, Sava Gallis et al. measured an iodine sorption capacity  
463 of 1750 mg·g<sup>-1</sup> [36], indicating that at low concentrations, water vapor promotes iodine  
464 capture but does not alter the selectivity of HKUST-1.

465 The iodine sorption performance of HKUST-1 and ZIF-8 have also been studied under  
466 dynamic conditions. Chebbi et al. measured sorption capacities of 1425 and 7 mg·g<sup>-1</sup> for  
467 HKUST-1 and ZIF-8, respectively, in CH<sub>3</sub>I sorption tests performed at 35°C until saturation  
468 (for up to 130 min) [94]. For HKUST-1, the results are similar to those measured in static  
469 experiments [36]. For ZIF-8 however, the authors explain the very low iodine loading

470 capacity by the large CH<sub>3</sub>I molecules (5–6 Å) being unable to pass through the narrow pore  
471 apertures (3.4 Å) in the structure. This drastic drop in efficiency is therefore due to the use of  
472 CH<sub>3</sub>I (instead of I<sub>2</sub> for the static experiments) rather than the dynamic nature of the  
473 experiments. These results show that while ZIF-8 is only well suited to trap I<sub>2</sub>, HKUST-1 can  
474 be used to trap iodine in both molecular and organic form.

## 475 9.2. *Temperature dependence of iodine retention*

476 Transforming sorbents into stable waste forms often requires heating to eliminate pores in  
477 the structure. Understanding the temperature behaviour of iodine-loaded sorbents is therefore  
478 important because there are no active functions involved. Using thermogravimetric analysis,  
479 Sava et al. [88] observed that weight loss in their iodine-loaded sorbents began at 120°C  
480 regardless of the iodine content. Indeed, I<sub>2</sub> trapped by physisorption is much more thermally  
481 unstable than chemisorbed iodine. Thereafter, the thermal decomposition of ZIF-8, which  
482 begins at around 302°C inevitably leads to the release of the remaining iodine, even the  
483 portion trapped in the smallest pores [95,96]. Bennett et al. [97] have nevertheless shown that  
484 the thermal stability of these materials can be increased, and iodine release reduced, by ball  
485 milling for 30 min at 25 Hz, which collapses the porous network. Thermogravimetric analysis  
486 of the sorbents before and after ball milling (Figure 9) showed that mass loss in the  
487 (amorphous) treated sorbents only began above 200°C and that iodine was only completely  
488 released at about 425°C, compared with about 350°C in the (crystalline) untreated material.  
489 These results highlight how pore closure acts as a physical barrier against iodine release.



490



491 **Figure 9.** Thermogravimetric analysis of iodine-loaded ZIF-8 before (solid line) and after (dashed  
492 lined) ball milling [97].

493

494 Similar results have been described for HKUST-1, with iodine release beginning at  
495 temperatures as low as 150°C [36] and completed at about 250°C with the thermal  
496 decomposition of the network.

497 Despite this physisorption phenomenon, MOFs look promising as reversible sensors to detect  
498 gaseous iodine, even at very low concentration, for nuclear site monitoring [98–100].

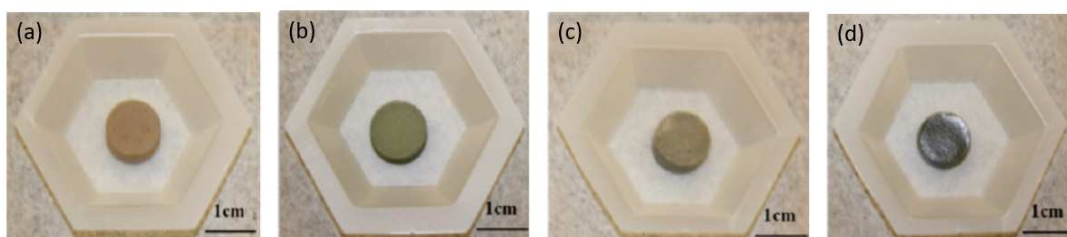
### 499 9.3. Conversion of MOF-glass composites into stable waste forms

500 Sava et al. investigated coating with Bi<sub>2</sub>O<sub>3</sub>-ZnO-B<sub>2</sub>O<sub>3</sub> and Bi<sub>2</sub>O<sub>3</sub>-ZnO-SiO<sub>2</sub> glass powders  
501 as a means to transform these MOFs into durable glass-composite waste forms [101]. The  
502 MOFs (10 wt.%) were mixed in a mortar and pestle with glass powder (80 wt.%) and metallic  
503 silver (10 wt.%), included to capture (as AgI) any iodine released during the treatment  
504 process. The pellets were then heat treated at 500°C, forming dense, cohesive monoliths  
505 (Table 1, Figure 10).

506 **Table 1.** Characteristics of iodine-loaded sintered glass composite materials [101]

Sample	Precursors	Phases
Glass composite 1	Bi <sub>2</sub> O <sub>3</sub> -ZnO-B <sub>2</sub> O <sub>3</sub> + ZIF-8	BiOI + BiI <sub>3</sub> + Ag <sup>0</sup> + AgI
Glass composite 2	Bi <sub>2</sub> O <sub>3</sub> -ZnO-B <sub>2</sub> O <sub>3</sub> + HKUST-1	BiOI + Bi <sub>12</sub> SiO <sub>20</sub> + Ag <sup>0</sup> + AgI
Glass composite 3	Bi <sub>2</sub> O <sub>3</sub> -ZnO-SiO <sub>2</sub> + ZIF-8	Amorphous area + Ag <sup>0</sup> + AgI
Glass composite 4	Bi <sub>2</sub> O <sub>3</sub> -ZnO-SiO <sub>2</sub> + HKUST-1	Amorphous area + Ag <sup>0</sup> + AgI

507



508

509 **Figure 10.** Photographs of iodine-loaded sintered glass composite materials [101], produced from (a)  
510  $\text{Bi}_2\text{O}_3\text{-ZnO-B}_2\text{O}_3 + \text{ZIF-8}$ , (b)  $\text{Bi}_2\text{O}_3\text{-ZnO-B}_2\text{O}_3 + \text{HKUST-1}$ , (c)  $\text{Bi}_2\text{O}_3\text{-ZnO-SiO}_2 + \text{ZIF-8}$  and (d)  
511  $\text{Bi}_2\text{O}_3\text{-ZnO-SiO}_2 + \text{HKUST-1}$  precursors.

512

513 No iodine release was detected during heat treatment, which usually is the main limitation of  
514 this process. Table 1 shows that all four glass composites contained  $\text{Ag}^0$  and  $\text{AgI}$ . However,  
515 whereas the composites prepared using  $\text{Bi}_2\text{O}_3\text{-ZnO-SiO}_2$  powder had amorphous areas, those  
516 prepared with  $\text{Bi}_2\text{O}_3\text{-ZnO-B}_2\text{O}_3$  contained several crystalline phases. The presence of iodine  
517 in the amorphous regions was not studied. Thermogravimetric analysis showed that they  
518 remained stable up to  $500^\circ\text{C}$ , with less than 1% weight loss. After chemical durability tests  
519 performed in 10 mL deionised water at  $90^\circ\text{C}$  for 7 days, inductively coupled plasma–mass  
520 spectrometry analysis of the supernatant revealed detectable concentrations of iodine only for  
521 glass composite 1 (97 ppm, Table 1). This is because crystalline  $\text{BiI}_3$  is partially soluble in  
522 water [102]. Longer tests performed under reducing conditions would be interesting to  
523 establish whether these glass composites can be used for deep geological disposal.

#### 524 9.4. *Conversion of other MOFs designed for iodine trapping*

525 The previous paragraph demonstrates the possibility of transforming iodine-loaded MOFs  
526 ( $\text{HKUST-1}$  and  $\text{ZIF-8}$ ) into glass composite conditioning matrices. In that case, metallic silver  
527 is used to chemisorb iodine that had been initially trapped in the MOFs (by formation of  $\text{AgI}$ )  
528 and glass powder precursors act as a physical and chemical barrier to prevent iodine release  
529 (encapsulation). Thereby, even if the different phases formed in the final matrices can be  
530 linked to the intrinsic nature of the MOF (metals, organic linkers ...), this process seems to be  
531 transposable to other types of existing MOFs. A recent review on the different MOFs  
532 designed for gaseous iodine trapping (and in solution) has been published by Xie et al. [35].

533 Hereafter, other works (published after the review of Xie et al.) dealing with the trapping of  
534 gaseous iodine are also discussed.

535 Chen et al. focused their work on Zr-based MOFs because of their versatility to be synthesized  
536 with various organic linkers [103]. Their iodine capture tests in static conditions at 80 °C  
537 reveal a capacity of 2180 mg·g<sup>-1</sup> for MOF-808 and 1450 mg·g<sup>-1</sup> for NU-1000. These high  
538 capacities are directly linked to high specific surface areas (1930 and 2126 m<sup>2</sup>·g<sup>-1</sup>  
539 respectively) and are due to high connectivity between pores and rigid organic linkers. On the  
540 other hand, UiO-67 and MOF-867, which have higher specific surface areas (2638 and 2403  
541 m<sup>2</sup>·g<sup>-1</sup> respectively), are less efficient for iodine trapping in the same conditions (530 and 880  
542 mg·g<sup>-1</sup> respectively). Their lower connectivity and the nature of the flexible organic linkers  
543 can explain these results. Other tests with relative humidity of 18 % showed a sharp decrease  
544 of around 70 % of the maximum loading for all previous MOFs. Among Zr-based MOFs,  
545 UiO-66 also demonstrated a capacity of 660 mg·g<sup>-1</sup> in static conditions at 80 °C [103]. To  
546 improve the efficiency of UiO-66, some works focused on their chemical modification by  
547 adding organic linkers to increase electro-donating properties [104,105]. These modifications  
548 made it possible to reach a capacity of 1330 mg·g<sup>-1</sup> in static conditions at 75 °C. However,  
549 the highest capacity obtained for UiO-66 sorbents was finally obtained thanks to the presence  
550 of defects in the structure [106]. In that case, iodine capture tests in static conditions at 80 °C  
551 reveal a capacity of 2250 mg·g<sup>-1</sup>. Leloire et al. also demonstrated the interest of using UiO-  
552 66-NH<sub>2</sub> sorbents (UiO-66 functionalized with NH<sub>2</sub> groupements) in severe nuclear conditions  
553 [107]. Their millimetric spherical sorbents (size range of 0.5-1.4 mm) made with a binderless  
554 method were irradiated under doses of 2 MGy of gamma irradiation. The results indicated the  
555 conservation of their size and structure. Moreover, others irradiation tests were carried out on  
556 the same sorbents but loaded with radioactive iodine. After 30 h of exposure under a flow of  
557 irradiated air (1.9 kGy·h<sup>-1</sup>) at 120 °C, 3.5 bar and 20 % of relative humidity, no radioiodine

558 was released which proves the stability of these materials under simulated nuclear accidental  
559 conditions.

560 A new kind of MIL-101 was studied in the presence (or not) of Cu nanoparticles encapsulated  
561 inside them to improve their chemical affinity with I<sub>2</sub> [108]. The different tests done in static  
562 conditions at 77 °C (up to 12 h) showed a capacity of 3000 mg·g<sup>-1</sup> for MIL-101 without Cu  
563 against 3420 mg·g<sup>-1</sup> with Cu nanoparticles. Results obtained for MIL-101 without Cu are not  
564 so far from the computational study done by Salles and Zajac where a capacity of around  
565 2200 mg·g<sup>-1</sup> was estimated under the same conditions [109]. Studies on organic iodide  
566 trapping were also carried out with MIL-101 [110]. The dynamic test in presence of CH<sub>3</sub>I/N<sub>2</sub>  
567 gas (done at 150 °C) indicated a capacity of around 240 mg·g<sup>-1</sup>. This result (rather low) could  
568 be explained by the high temperature condition of the test or the larger volume of CH<sub>3</sub>I  
569 (compared to I<sub>2</sub>). However, like for UiO-66, by modifying organic linkers, it is possible to  
570 increase the capacity. With triethylenediamine and hexamethylenetetramine, capacities of 710  
571 mg·g<sup>-1</sup> and 620 mg·g<sup>-1</sup> can be reached respectively. The authors explained this improvement  
572 by a better stability of the modified MIL-100 against temperature.

573 MOF-808 was studied by Wang et al. in order to obtain bead-shaped sorbents of around 2 mm  
574 of diameter [111]. This type of study is of interest in the perspective of an industrial use of  
575 MOFs for iodine trapping where easy to handle materials are targeted. Their sorbents  
576 (obtained through a wet synthesis by addition of poly(vinylidene fluoride) at 30 wt.%) can trap  
577 1420 mg·g<sup>-1</sup> of iodine in static conditions at 80 °C during 24 h. However, it is lower than the  
578 powdery form of MOF-808 for which 2010 mg·g<sup>-1</sup> was obtained. In dynamic conditions, the  
579 same capacity was obtained (1360 mg·g<sup>-1</sup>) and the authors demonstrated that the time to reach  
580 saturation was shorter when temperature and iodine concentration increased. On the other  
581 hand, the presence of water makes these sorbents less efficient due to the hydrophilic property  
582 of Zr metal in the structure.

583 Some unusual MOFs have also been studied for gaseous iodine trapping like NUC-5 with In  
584 as metallic cluster [112]. I<sub>2</sub> capture test in static conditions at 77 °C indicated a capacity of  
585 780 mg·g<sup>-1</sup>. However, thermogravimetric analysis highlighted an iodine release from 30 °C up  
586 to 200 °C, temperature for which no more iodine was present. Modified MIF-53 with fumaric  
587 acid demonstrated good iodine capture properties [113]. Tests performed under static  
588 conditions at different temperatures (room temperature up to 70 °C) revealed a capacity of  
589 around 1120 mg·g<sup>-1</sup> for the test carried out at 70 °C. Gogia et al. synthesized a nitrogen-rich  
590 3D MOF which has the particularity of trapping I<sub>2</sub> in static conditions at 70 °C with a capacity  
591 of 2130 mg·g<sup>-1</sup>.

592 New types of MOFs allowing the trapping of iodine by chemisorption are also under  
593 investigation. The aim is to obtain sorbents that can retain iodine at high temperature which  
594 could be particularly useful in the case of a nuclear accident or if a heat-treatment is necessary  
595 to obtain a conditioning matrix. Jung et al. developed a bismuth-based MOF (Bi-mna) which  
596 can trap around 700 mg·g<sup>-1</sup> of iodine in static conditions from 77 up to 300 °C [114]. Even if  
597 its capacity is lower than that of other MOFs, none iodine release was measured out below  
598 300 °C because of the formation of BiI<sub>3</sub> and Bi-O-I bonds.

## 599 **10. Conclusion and future prospects**

600 This review has focused on the characteristics of solid sorbents for gaseous radioactive  
601 iodine capture (I<sub>2</sub> or CH<sub>3</sub>I), listed in Table 2, whose conversion into stable waste has been  
602 described in the literature. The development of these materials has been guided by the  
603 objective of producing a waste form suitable for deep geological storage to minimize their  
604 radiological impact.

605 The sorbents can trap iodine by two different mechanisms. One is associated to physisorption  
606 where iodine is weakly and reversible trapped on the surface thanks to Van der Waals-type

607 interactions. The other one using chemisorption insure an irreversible trapping of iodine  
608 through the formation of strong chemical bonds between the active sites (metals, cations or  
609 salts) and iodine. The active sites are often made of silver ( $\text{Ag}^0$ ,  $\text{Ag}^+$  or  $\text{AgNO}_3$ ) because it has  
610 an extremely strong thermodynamic affinity for iodine with correspondingly strong  
611 interaction energies (less than  $-100 \text{ kJ}\cdot\text{mol}^{-1}$ ). The reaction product of these reagents is  $\text{AgI}$ .  
612 In some cases (minority report by comparison with silver), other metals like Bi or Cu are  
613 considered.

614 The various silver-functionalized sorbents reviewed here, namely silver mordenites, silver-  
615 silica aerogels and silver alumina can trap iodine efficiently at up to  $200 \text{ mg}\cdot\text{g}^{-1}$ . In  
616 chalcogels, other active sites such as Sb and Sn can be used, whereas in MOFs, the absence of  
617 active sites means that iodine is exclusively trapped by physisorption in the pores of the  
618 material. In this case, the pore size distribution can make the materials selective for certain  
619 forms of iodine. Although physisorption is reversible, very high iodine loading capacities can  
620 be achieved ( $> 1000 \text{ mg}\cdot\text{g}^{-1}$ ). Note however that comparing the loading capacities in terms of  
621 milligrams per gram of sorbent is difficult because the sorbents have different specific  
622 masses. It would be more informative to express results in millimoles of iodine per mole of  
623 sorbent, or as milligrams of iodine per  $\text{cm}^3$  of sorbent.

624 To transform these sorbents into stable waste forms after iodine capture, the open porous  
625 network has to be collapsed or blocked to limit the release of iodine in contact with a  
626 propagation medium. This is achieved by heat treatment, in some cases at high pressure. HUP  
627 and HIP have thereby been used to transform silver-functionalised sorbents directly, without  
628 adjuvants. Results show that the waste forms obtained with HIP are less porous, with no  
629 iodine release during the process. After both HUP and HIP, the solidified waste contains  
630 multiple phases, with iodine present as  $\text{AgI}$ . Other types of sorbents can be vitrified. This  
631 process is effective for lead bismuth sorbents, producing a homogeneous glass with no iodine

632 volatilisation. For chalcogels however, the release of vapours means the sorbents have to be  
633 vitrified in sealed quartz tubes. A multiphase material is obtained with iodine retained at the  
634 active sites. With MOFs finally, multiphase glass-composite waste forms with iodine trapped  
635 as AgI have been obtained by mixing the sorbent with glass powder and  $\text{Ag}^0$ , and then heat-  
636 treating pressed pellets of the mixture. Even though the iodine was initially physisorbed, none  
637 was released during the process, mainly thanks to the addition of  $\text{Ag}^0$ . Studies show that the  
638 volatility of iodine can be managed, but requires either a sealed environment, often with  
639 pressure treatment (such as in HIP), or low temperature vitrification, often with additional  $\text{Ag}^0$   
640 (to produce a homogenous glass or a composite in which the amorphous phase acts as a seal  
641 and diffusion barrier for the sorbent). The best choice of conversion process depends on the  
642 type of sorbent but also on technico-economic factors.

643 Very little data is available on the chemical durability of the waste forms produced, despite  
644 this being a crucial point in evaluating the radiological impact of these materials, since water  
645 is the main contact medium in geological storage. The data that are available were obtained  
646 under a variety of alteration conditions ( $\text{H}_2\text{O}$  or reducing environments, temperatures ranging  
647 from 25 to 90°C) and are difficult to extrapolate to the actual conditions in storage sites,  
648 which depend on the local geology, pH, groundwater composition, redox potential etc.  
649 Nevertheless, under anoxic conditions, thermodynamic data show that phases such as AgI are  
650 not stable and iodine trapped in this form is likely to be released [115,116]. It is therefore  
651 crucial to perform chemical durability tests in conditions that are representative of those in  
652 actual geological repositories.

653 Regarding immobilization matrices developed specifically for iodine with potentially high  
654 chemical durability [117–119], these are not compatible with current dry filtration systems for  
655 iodine capture. They may however serve as starting materials to synthesize new sorbents and  
656 provide a source of new solutions for effective iodine management.

**Table 2.** Summary of reviewed results.

	Silver-mordenite	Silver-silica aerogels	Silver alumina	Lead bismuth	Chalcogels	ZIF-8 and HKUST-1
<b>Active sites</b>	Ag <sup>+</sup> or Ag <sup>0</sup>	Ag <sup>+</sup> or Ag <sup>0</sup>	AgNO <sub>3</sub>	BiPbO <sub>2</sub> NO <sub>3</sub>	1) S 2) Sb 3) Sn	None
<b>Measured iodine sorption capacity</b>	120 mg·g <sup>-1</sup> with Ag <sup>+</sup> (dynamic test with CH <sub>3</sub> I)  217 mg·g <sup>-1</sup> with Ag <sup>0</sup> (dynamic test with CH <sub>3</sub> I)	480 mg·g <sup>-1</sup> (thiolated Ag <sup>+</sup> , dynamic test with I <sub>2</sub> )  517 mg·g <sup>-1</sup> (unthiolated-Ag <sup>+</sup> , static test with I <sub>2</sub> )  555 mg·g <sup>-1</sup> (unthiolated-Ag <sup>0</sup> , static test with I <sub>2</sub> )	- 230 mg·g <sup>-1</sup> (dynamic test with CH <sub>3</sub> I)  - 220 mg·g <sup>-1</sup> (dynamic test with I <sub>2</sub> )	Not reported	1) 680 mg·g <sup>-1</sup> (static test with I <sub>2</sub> )  2) 540 mg·g <sup>-1</sup> (static test with I <sub>2</sub> )  3) 2250 mg·g <sup>-1</sup> (static test with I <sub>2</sub> )	- ZIF-8: 1250 mg·g <sup>-1</sup> (static test with I <sub>2</sub> )  - ZIF-8: 7 mg·g <sup>-1</sup> (dynamic test with CH <sub>3</sub> I)  - HKUST-1: 1750 mg·g <sup>-1</sup> (static test with I <sub>2</sub> )  - HKUST-1: 1425 mg·g <sup>-1</sup> (dynamic test with CH <sub>3</sub> I)
<b>Iodine capture mechanism</b>	Chemisorption	Chemisorption	Chemisorption	Chemisorption	Chemisorption	Physisorption
<b>Contaminants and sensitivities</b>	- Hydrocarbons and CO for low Ag <sup>+</sup> content  - NO <sub>x</sub> and H <sub>2</sub> O for Ag <sup>0</sup>	NO and H <sub>2</sub> O for thiolated Ag <sup>+</sup> gel  No information for unthiolated gels	H <sub>2</sub> O for pores < 50 nm	Not reported	Not available	Not available
<b>Conversion into stable waste forms</b>	Starting from Ag <sup>0</sup> material: 1) HUP (750 °C, 27.5 MPa)  2) HIP (700 °C, 175 MPa)  3) HUP with addition of glass and Ag <sup>0</sup> flakes (550 °C, 70 MPa)	Starting from thiolated-Ag <sup>+</sup> gel:  1) HUP (1200 °C, 29 MPa)  2) HIP (1200 °C, 207 MPa)	HIP (1200 °C, 175 MPa)	Vitrification with ZnO (540 °C)	1) Vitrification in quartz tube with GeS <sub>2</sub> (600 °C)  2) Vitrification in quartz tube (600 °C)  3) Vitrification in quartz tube with Sb <sub>2</sub> S <sub>3</sub> (600 °C)	Pressing followed by thermal treatment (500 °C):  with Bi <sub>2</sub> O <sub>3</sub> -ZnO-B <sub>2</sub> O <sub>3</sub> and Ag <sup>0</sup> 1) I <sub>2</sub> -loaded ZIF-8 2) I <sub>2</sub> -loaded HKUST-1  with Bi <sub>2</sub> O <sub>3</sub> -ZnO-SiO <sub>2</sub> and Ag <sup>0</sup> 3) I <sub>2</sub> -loaded ZIF-8 4) I <sub>2</sub> -loaded HKUST-1



	Only for Ag <sup>0</sup> material:						
<b>Waste form microstructure</b>	1) Not reported	Only for thiolated-Ag <sup>+</sup> gel:				1) Glass + SnI <sub>4</sub> + SiO <sub>2</sub> + GeS <sub>4</sub>	1) BiOI + BiI <sub>3</sub> + Ag <sup>0</sup> + AgI
	2) Glass + AgI + AgI(IO <sub>4</sub> )	1) Not reported	AgI + Al <sub>2</sub> O <sub>3</sub>	Homogeneous glass		2) SbSI, SbI <sub>3</sub> , SiO <sub>2</sub>	2) BiOI + Bi <sub>12</sub> SiO <sub>20</sub> + Ag <sup>0</sup> + AgI
	3) Glass + AgI + Bi <sub>4</sub> (SiO <sub>4</sub> ) <sub>2</sub> + mordenite	2) Glass + AgI + Ag <sup>0</sup> + Ag <sub>2</sub> S				3) Glass + SbI <sub>3</sub> + SbSI	3) Glass + Ag <sup>0</sup> + AgI
<b>Chemical durability</b>	Only for Ag <sup>0</sup> material:						
	1) Not studied				Reducing environment at 25 °C for 7 d.		For all waste forms:
	2) Not studied	Not studied	Not studied	Not studied	Formation of alteration layer limiting iodine release	Not studied	Deionized water at 90 °C for 7 d. Negligible iodine release except for 1)
	3) Deionized water at 90 °C for 7 d. Low release of glass elements						

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# Solid sorbents for gaseous iodine capture and their conversion into stable waste forms

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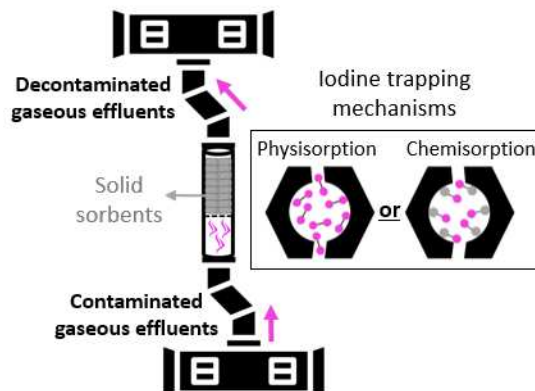
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## Graphical abstract

### Iodine trapping on solid sorbents



### Transformation of iodine-loaded sorbents

