Structural effects of calcination on Cs-exchanged copper hexacyanoferrate (Cs,K)₂CuFe(CN)₆ loaded on mesoporous silica particles

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HIGHLIGHTS
- No Cs loss at 1000°C from Cs-exchanged copper hexacyanoferrate on mesoporous silica.
- No Cs-retaining additives were used.
- Cs retention attributed to the in-situ formation of an alkali silicate glass.
- Calcination leads to cyanoferrate decomposition, pore closure and crystallization.

GRAPHICAL ABSTRACT

ABSTRACT

Porous silica particles functionalized by potassium copper hexacyanoferrate (KCu-HCF@silica) are investigated as selective sorbents to remove radioactive cesium from contaminated effluents. This article reports the thermal behavior of Cs:KCu-HCF@silica particles at the laboratory scale, in view of developing hot isostatic pressing processes to compact the Cs-loaded particles into dense waste forms. The data show that the spent particles cannot be hot-pressed directly because the release of volatile compounds does prevent compaction. Preliminary calcination in air leads to (i) the decomposition of Cs:KCu-HCF, (ii) the closure of the mesopores of silica and a reduction in the particles' specific surface area, (iii) the crystallization of silica into cristobalite, all without significant Cs loss. This retention of Cs is due to the in-situ formation of a Cs based silicate glass with the siliceous particles.

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1. Introduction

The large variety of nuclear waste, legacy waste in particular, has driven the development of new waste architectures based on the latest progress in nanochemistry to immobilize nuclear waste as effectively as possible [1]. Some of the most promising hierarchical
structures currently being investigated are multi-scale porous silica materials that entrap radionuclides. Cesium (\(^{137}\text{Cs}\)) is one of the most abundant radionuclides in liquid effluents and one of the most toxic for humans and the environment. Sorbents designed to capture Cs from a liquid and confine it in a solid phase have been widely researched, but the future of the final waste form has rarely if ever been considered [2]. We have recently developed a granular material composed of potassium-copper hexacyanoferrate (KCu-HCF) particles loaded onto larger silica particles for the continuous selective removal of Cs [3,4]. This sorbent is inherently hierarchical with a structural motif (KCu-HCF) sitting on a larger support (mesoporous silica). A major fraction of the potassium in the material exchanges with Cs in the solution, thereby capturing the radionuclide in a solid phase [5].

After exchange, the Cs is, in theory, trapped within the KCu-HCF located in the porous network of the submillimeter silica particles. A final waste form should ideally be monolithic and chemically inert; therefore, to condition the spent sorbent for storage, its specific surface area (\(\approx 100–200 \text{m}^2 \text{g}^{-1}\)) has to be minimized and the silica particles need to be immobilized. Spent sorbents can be conditioned by mixing them with cement. However, the waste load is usually limited and HCF is unstable in basic environments [6,7]. Low-pH cements would have to be used but these were not considered here. It is possible to increase the waste loading and durability of the material by using a low temperature glass that melts and binds the particles [8]. However, the simplest approach is to calcine the sorbent, usually with an additive to ensure the Cs remains in the annealed sample. Wu et al. have shown that Cs is retained during the solidification of silica and ammonium molybdophosphate with added allophane (33 wt%) when heated to 1000 °C [10]. Bartos et al. have investigated the possibility of immobilizing Cs via the ceramation of titanium ferrocyanide into lithium titanate [11]. An interesting approach reported by Yin et al. involves solidifying Ni-HCF onto silica [12]. While the calcination of the Cs sorbent without an additive at 1000 °C might lead to ca. 50% Cs loss, adding allophane (one of nine additives tested) was found to reduce Cs loss during annealing [11]. However, this was achieved with an additive ratio of about 20–50 wt%, substantially increasing the volume of the waste [11]. Finally, Ikarashi et al. found that 99% of the Cs in a natural zeolite functionalized with Ni-HCF was retained during calcination and explained this by the formation of a CsAlSiO\(_4\) phase [13].

The goal of our project is to immobilize the spent sorbent by hot isostatic pressing (HIP). This typically involves heating the particles to 750 °C under 200 MPa in a sealed metallic container. The sample densifies as the container is compressed. This technique is currently being investigated for the conditioning of iodine-129 and other radionuclides [13–15]. However, HIP requires that any volatile products be removed prior to thermal treatment as these would act against the compaction of the container. As mentioned above, the literature shows that Cs is volatilized in the absence of additives. In this paper, we report the thermal behavior and structural evolution of Cs:KCu-HCF loaded onto mesoporous silica grains.

2. Experimental

2.1. Sample preparation

Samples of Cs:KCu-HCF@silica, mesoporous silica particles loaded with potassium copper hexacyanoferrate partially exchanged with Cs (\(\sim 1\) wt% Cs), were prepared by precipitation as described previously [3]. Briefly, the silica particles (10 g; CTI; diameter, 250–500 \(\mu\)m) were put in pure water at 20 °C and droplets of a KOH solution (\(10^{-1}\) M) were added until the pH stabilized to 9. After drying, the solid was placed in a copper nitrate solution (\(5.10^{-2}\) mol/L) for 2 h at 20 °C, washed in ultrapure water and then placed for 2 h in a second solution enriched in potassium hexacyanoferrate (\(10^{-1}\) mol/L) and potassium nitrate (\(10^{-1}\) mol/L). The solid residue was washed in ultrapure water and dried before the K–Cs ion-exchange step. The KCu-HCF content in the silica was measured by dissolution and inductively coupled plasma atomic emission spectrometry (ICP-AES) analysis with a Thermo-Fisher Scientific iCAP 7400DV equipment, after dissolution into nitric acid.

The solid sample (350 g) was placed in 1 L of ultrapure water enriched with Cs (60 mg/L) for 24 h at 20 °C. The suspension was filtered and the Cs-enriched solid was dried at 60 °C for 2 days. After Cs exchange, cesium sample’s uptake was measured from the cesium concentration drop in the bath.

2.2. Thermal analysis

The thermal behavior and structural evolution of Cs:KCu-HCF@silica particles was characterized by differential thermogravimetric analysis in air and argon (DTGA), differential scanning calorimetry in air (DSC) and high-temperature X-ray diffraction in air (HT-XRD). The DTGA measurements were performed using a Setaram Evo 16 instrument; the DSC experiments were carried out on a Setaram Multi HTC96 system, and the HT-XRD data were recorded using a D8 Bruker Advance diffractometer (Cu Kα radiation) equipped with an HTK1200 Antton Paar furnace, an incident-beam Goebel mirror, and a Lynxeye position sensitive detector. The temperature was varied in 100 °C increments from 100 °C to 1000 °C during the heating and cooling stages. At each temperature, the XRD patterns were recorded over a 10–90° 20 range for approximately 5 h per XRD pattern.

Batches of Cs:KCu-HCF@silica and non-functionalized silica particles were characterized (specific surface area, chemical composition, microstructure) before and after annealing in air at 100–1000 °C. Chemical compositions were measured by inductively coupled mass spectrometry (for Cs) or atomic emission spectroscopy (for Cu, Fe, K, Si) after dissolution. The specific surface area and pore size distributions were determined by nitrogen adsorption isotherms using a Quantachrome Instruments NovaTough LX\(^3\) device. The dehydration process before these measurements was critical because HCF is known to be heat-sensitive. Based on prior experience, the samples were heated at 90 °C for 18 h under 1 mmHg vacuum to avoid under- or over-drying. This was done directly in the glass tubes placed on the adsorption measuring station to avoid having to move the samples and prevent air entering the tubes. The microstructure of the samples was investigated by scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDS) using a Zeiss Supra 55 device equipped with a Bruker AXS X-Flash Detector 4010 system.

The different phases in the sample annealed at 1000 °C were quantified by XRD using an internal alumina standard [16]. Micro absorption was accounted for using the Brindley correction (see supplementary data). This sample density was also measured by helium pycnometry with a Micromeretics ASAP 2010.

Cesium retention was investigated by performing DSC experiments on the silica support alone, Cs:KCu-HCF alone, and a mixture of both. The mixed sample was also observed by SEM.

3. Results

3.1. Thermal analysis and in-situ XRD

The DTGA signals of a Cs:KCu-HCF@silica sample heated in air are shown in Fig. 1. The mass loss was about 8.5% but no Cs or Cs-based fragments were detected. The first thermal event, at

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233 ± 3 °C is attributed to the decomposition of HCF [11]. There were also two unexpected exothermic events: at 954 ± 3 °C during heating and at 133 ± 3 °C during cooling. These were subsequently assigned using in-situ XRD data.

This experiment was repeated under argon to simulate a typical HIP experiment (data not shown). As expected from Yin et al.’s measurements [11], there was weight loss between 300 and 800 °C, which can be attributed to the decomposition of HCF and the release of hydrogen cyanide. These results show that the spent sorbent cannot be treated directly by HIP under argon because this volatilization will oppose the desired compaction of the container. We therefore focused on the thermal behavior of the material in air. The results of in-situ high-temperature XRD experiments are shown in Fig. 2.

The crystalline peaks in Fig. 2A that disappear between 200 and 300 °C can be assigned to K₂CuFe(CN)₆ (ICDD PDF No. 01-075-0023), which is similar to the (K,Cs)₂CuFe(CN)₆ phase of the crystalline HCF component of the material. The disappearance of these peaks confirms that the sorbent decomposes at ~200–300 °C. Fig. 2B shows that the sample remains amorphous between 300 and 800 °C, crystallizes into β-cristobalite (#00-027-0605) between 800 and 1000 °C and seems to be fully crystallized at 1000 °C. The DTA peak at 954 ± 3 °C (Fig. 1) must therefore correspond to this crystallization process. The β-to α-cristobalite (#00-039-1425) transformation that occurs between 200 and 100 °C during cooling (Fig. 2C) corresponds to the DTA peak at 133 °C (Fig. 1) [17]. The extra peaks in Fig. 2C are due to cristobalite twinning, as confirmed by DIFFaX simulations (Supplementary Fig. S1) [18]. Note also that pure silica crystallizes into cristobalite at 1120 °C under the same conditions (Supplementary Fig. S3).

3.2. Effect of temperature on sorbent composition and porosity

The temperature evolutions of the chemical composition and of the specific surface area of Cs:KCu-HCF@silica particles are presented in Fig. 3.
The concentrations of the different elements vary little between the samples calcined at different temperatures, indicating that their overall composition does not change during calcination at temperatures up to 1000 °C. This is consistent with the fact that no Cs was detected by DTGA mass spectrometry (data not shown), even if cesium compounds can easily condense on surfaces which could have prevented their detection. The presence of HCN was detected as reported in a previous work [12]. Before calcination, the samples are red, which is typical of KCu-HCF, but become umber-colored, camel brown and light blue after heat treatment at 200–600, 700 and 800–1000 °C, respectively (Fig. 3). The particles treated at 1000 °C tend to agglomerate, but are easily separated by manual shaking. Heat treatments up to 600 °C have little effect on the specific surface area of the samples, which remains at ~160 m²/g but higher temperatures lead to a sharp decrease, down to 20 m²/g in the sample calcined at 1000 °C.

The nitrogen isotherms measured for samples kept at 25 °C and treated at 600–1000 °C are shown in Fig. 4A and values extracted from isotherms are shown in Table 1. The corresponding dependence of the pore volume on the calcination temperature is compared with data for pristine silica in Fig. 4B and the corresponding pore size distributions are shown in Fig. 4C and D, respectively. Before annealing, the sample is mesoporous, with four peaks in the pore size distribution centered at 3, 4.5, 6.5 and 8 nm. These values are typical for mesoporous silica [19]. Heat-treating the sample at 600 °C does not significantly alter the pore size distribution but the component centered at 4.5 nm is weaker in the data from the samples calcined at 700 and 800 °C and the micropores disappear (Fig. 4C). The pore size distributions of the samples heated to between 800 and 1000 °C are increasingly broader, indicating that higher temperatures lead to a closing of the mesopores, which is complete at 1000 °C. Micropores appear once more in the samples calcined at 900 and 1000 °C (Fig. 4C inset). Despite this, the total pore volume of the sample decreases from 0.67 cm³/g in the powder treated at 700 °C down to 0.53 cm³/g, 0.19 cm³/g and 0.02 cm³/g in those treated at 800, 900 and 1000 °C, respectively (Fig. 4B).

However, the facts that the pore size distribution for pristine silica (Fig. 4D) and for Cs:KCu-HCF@silica particles (Fig. 4C) evolve with the calcination temperature in the same way show that the decrease in specific surface area is not caused by the additional phase or phases in the functionalized silica. The difference between the cristobalite crystallization temperatures (Fig. 4C) has no measurable effect on the pore volume of the powders.

Fig. 4. (A) Nitrogen isotherms of Cs:KCu-HCF@silica samples before and after calcination at different temperatures. (B) Pore volume in the samples and pristine silica as a function of the calcination temperature. The stars indicate the temperatures of cristobalite crystallization for Cs:KCu-HCF@silica (at 850 °C) and pristine silica (1120 °C). (C,D) Pore size distribution for (C) Cs:KCu-HCF@silica particles and (D) pristine silica calcined at different temperatures. The inset in part (C) is an expanded view of the region between 1.25 and 3.25 nm.
3.3. Sorbent microstructure after 1000 °C heat treatment

Fig. 5A shows that after heat treatment, the Cs:KCu-HCF@silica particles are not homogeneous. They are composed of two phases (i) grains of 10 μm maximum (ii) a surrounding “white phase” with backscattered electrons (Fig. 5B). The detailed image reveals a structure where the grains have radial cracks, filled with the same “white phase” located between the grains (Fig. 5C). Another image in the near zone is shown in Fig. 5D. The EDS map of Fig. 5D shows that Cs (Fig. 5E), K (Fig. 5F) and Cu (Fig. 5G) are present in the surrounding “white phase”. Silicon is detected in this phase and in the grains (Fig. 5H).

However, the fact that a “white phase” is still detected by SEM after having been heat treated at 1000 °C while no other crystalline phase than cristobalite was observed by XRD indicates that this “white phase” is amorphous. Therefore, the “white phase” is different in nature from the raw material. The approximate composition of the “white phase” evaluated by EDS is SiO2 87 wt%, Cs2O 7 wt%, K2O 3 wt%, Cu0 2 wt%, Fe2O3 <1 wt%. Quantitative XRD measurements on the sample heat treated at 1000 °C indicate that its amorphous content is 19 ± 6 wt% (see supplementary material). The measured density of the sample by pycnometry was 2.4243 g cm−3.

A 1000 °C heat treated sample was let for three days in a NaOH solution (pH = 10). The resulting sample was observed by SEM without polishing and reported in Fig. 6. The surrounding “white phase” was partially removed but this is enough to highlight the grain microstructure. The grain rounded shape and size are confirmed in Fig. 6A. In Fig. 6B, the radial crystallites geometry is confirmed.

On the basis of the DTGA, in-situ XRD results reported in section 3.1 and the X-ray map in Fig. 5H, it can be reasonably supposed that the rounded grains seen in Fig. 5B–D and Fig. 6 are cristobalite.

3.4. Nature of the cesium host phase

Additional thermal analyses were performed to investigate the effects of the silica environment on Cs:KCu-HCF decomposition. The DSC curves of pure Cs:KCu-HCF powder and a 30 wt% mixture with pristine silica grains are compared in Fig. 7A. In the absence of silica, the decomposition of Cs:Cu-HCF extends from 175 to 575 °C with three major thermal events at roughly 175, 225 and 575 °C and a minimum in the signal at about 600 °C. When mixed with silica, there are still three thermal events but the first two are weaker and the signal minimum at higher temperatures occurs at 425 °C rather than 600 °C. After cooling, the mixture sample consisted of silica particles and dense millimeter-sized black flakes. Fig. 7B shows the black flakes encased in epoxy resin after removing the silica residues and Fig. 7C is a SEM image of a flake. The same elements (plus Fe) are detected by EDS (Fig. 7D, Si, K, Cs, Fe, Cu and O) as for the “white phase” observed in Cs:KCu-HCF@silica (Fig. 5E–H).

4. Discussion

4.1. Global mass loss

The overall mass loss of 8.5 wt% can be correlated to the sample composition. The concentration of K–Cu–HFC particles into the silica sample was found to be 7 ± 1 wt%, with a chemical formula K1.6Cu1.2Fe(CN)6. After Cs exchange, the Cs uptake was calculated by difference between Cs concentration before/after exchange and gives a Cs:KCu-HCF formula of K0.6Cs1.0Cu1.2Fe(CN)6. The water content of the samples can be estimated to 5 wt% according to the first mass loss below 200 °C of the DTGA, as shown on Fig. 1. So the missing 3.5% mass loss to reach the 8.5% overall mass loss can be attributed to Cs:KCu-HCF decomposition. If we consider that all C and N atoms are lost, a 39% theoretical mass loss can be calculated. For the whole sample (silica and KCu-HCF), a global mass loss of 2.7 ± 0.4 wt% can be expected. This is close to the 3.5% value estimated from the DTGA measurement.

4.2. Cesium retention

The retention of cesium by the Cs:KCu-HCF@silica particles during heating at up to 1000 °C can be explained by the in-situ formation of a cesium silicate glass above 233 °C formed from the siliceous matrix and the decomposition products of Cs:KCu-HCF. SiO2 and Fe2O3 are glass network formers and Cs and K, network modifiers.

The phase diagrams of the Cs2O–SiO2 and K2O–SiO2 binary systems indicate that the presence of alkali species drastically reduces the melting temperature of silica (1713 °C for pure silica), with eutectic points at 875–910 °C and 772–785 °C in the presence of 9–16 at.% Cs and 9–29 at.% K, respectively [20,21]. The role of copper is not clear but it probably acts as a network modifier [22]. However, there is no clear indication of a glass transition in the DTA data, with no event occurring between 233 °C and the crystallization of silica at 954 °C. This may be because the formation of the glass coincides with the decomposition of HCF and the thermal signals overlap. This would explain why no well crystallized products of the decomposition of Cs:KCu-HCF were detected by XRD, assuming that nanocrystallized or minor products would have also been not detected. As a confirmation, the DSC data in Fig. 7A show that the presence of silica has a strong effect on the decomposition of Cs:KCu-HCF. So, the formation of a glass is a plausible explanation for the fact that the Cs:KCu-HCF decomposition process ends at 425 °C when mixed with silica instead of 600 °C alone. The black scraps seen in section 3.4 are believed to be an equivalent glass of the alkali silicate glass seen in the 1000 °C sample.

The Cs retention is not coherent with of Yin et al.’s work where silica gels matrices were also used but Cs retention was obtained only with additives [11]. It is not obvious why our samples show a better Cs retention than silica gels used by Yin et al. However, the functionalization processes of silica are rather comparable except the fact that our process starts with a first KOH treatment which is

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Specific surface area (m²g⁻¹)</th>
<th>Porous volume (cm³g⁻¹)</th>
<th>Average pore radius (nm)</th>
</tr>
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<tbody>
<tr>
<td>20</td>
<td>158.8</td>
<td>0.68</td>
<td>6.24</td>
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<tr>
<td>600</td>
<td>153.6</td>
<td>0.69</td>
<td>6.24</td>
</tr>
<tr>
<td>700</td>
<td>138.2</td>
<td>0.67</td>
<td>7.63</td>
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<tr>
<td>800</td>
<td>92</td>
<td>0.53</td>
<td>9.84</td>
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<tr>
<td>900</td>
<td>42.1</td>
<td>0.20</td>
<td>7.66</td>
</tr>
<tr>
<td>1000</td>
<td>18.8</td>
<td>0.02</td>
<td>1.59</td>
</tr>
</tbody>
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Table 1: Specific surfaces, porous volume and average pore radiuses as extracted from nitrogen isotherms presented in Fig. 4A.
not made by Yin et al. This patented treatment allows a modification of the silica surface charge and strongly enhances the copper and hexacyanoferrate precipitation [23]. It is possible that this treatment could give an advantage in terms of reactivity of Cs: KCu-HCF and silica. However, a glass was obtained without the KOH treatment as reported in section 3.4. It is shown that a simple mixture has already an impact on the decomposition of Cs: KCu-HCF by shifting the last thermal event at 425 °C instead of 600 °C (Fig. 7). It is believed that the KOH treatment gives another beneficial impact because only one peak is seen in Fig. 1. However, no further investigation was done to understand more deeply the KOH effect because we were focusing on the structural evolution.

4.3. Structural sample’s evolution with temperature

The decomposition temperature of Cs: KCu-HCF detected by DTGA (ca. 230 °C) is in agreement with the literature [11,12]. At this temperature, the elements Cs, K, Fe, Cu from Cs: KCu-HCF should in theory be present as oxides. However, ferrocyanides are supposed to decompose into volatile nitrogen and carbon oxides by

![Figure 5](image-url)

**Fig. 5.** (A–D) Scanning electron micrographs (backscattered electron imaging) of Cs:KCu-HCF@silica after heat treatment at 1000 °C. (E–H) Energy-dispersive X-ray map with Cs, K, Cu and Si localizations in part (D).
consuming oxygen [11]. This would drastically reduce the fugacity of oxygen during heat treatment locally in the porous network. The amount of oxygen required to oxidize Cs:KCu-HCF can be estimated as follows. Given a 7 ± 1 wt% of Cs:KCu-HCF content in the silica phase with a pore volume of 0.75 cm³/g filled with air (20% O₂) and a Cs:KCu-HCF stoichiometry of K₀.₆Cs₁.₀Cu₁.₂Fe(CN)₆, the formation of CO₂ and NO₂ alone requires around 34 times more air than is present in the pores and in the crucible. Oxidizing all the elements in HCF would consume ~60 times the volume of air initially present, indicating that fresh oxygen is required to maintain a stable oxygen fugacity. The samples were heated in air so there was a constant supply of atmospheric oxygen. So it is supposed that all elements forming HCF were oxidized. It is supposed that the first glass clusters were formed where the HCF crystals were.

Once the glass was formed, its viscosity diminishes above the glass transition (Tg). The glass transition temperatures of SiO₂-

Fig. 6. (A) Scanning electron micrographs (backscattered electron imaging) of Cs:KCu-HCF@silica after heat treatment at 1000 °C and put in basic media to remove the white phase. (B) is an enlargement of (A).

![Fig. 6](image)

Fig. 7. (A) Differential scanning calorimetry curves of pure Cs:Cu-HCF and a mixture of pure Cs:Cu-HCF (30 wt%) and mesoporous silica grains (70 wt%) heated at 10 °C/min in air. (B) Photograph of the black flakes obtained at the end of the calorimetry experiment, set in epoxy resin. (C) Scanning electron micrograph (backscattered electron imaging) of a typical black flake and (D) the corresponding energy-dispersive x-ray spectrum.

![Fig. 7](image)
alkali glasses are typically between 300 and 500 °C [24,25]. We have considered this range for the glass of this study. The viscosity of a lithium cesium silicate glass decreases by about three orders of magnitude between 500 and 700 °C to reach 10^3 dPa s [23]. A glass can be considered as a melt at this viscosity [26]. For the cesium potassium silicate glass of this study, a similar viscosity evolution with the temperature was supposed. It can be supposed that the glass wets the surface of the silica particles above 700 °C and forms large domains of glass as shown in Fig. 5A–D. In agreement with the literature [27,28], the glass does not enter the pores, because the same decrease in pore volume is observed for pristine and functionalized silica. So the glass should stay at the sample surface.

At 954 ± 3 °C, silica crystallizes into cristobalite and forms the rounded grains (max. 10 μm) seen in Figs. 5 and 6. It is believed that crystallites grow with a radial geometry partly drowned in the alkali silicate glass. This explains the presence of the glass in the inner part of the cristobalite grain in Fig. 5C. Higuchi at al. have shown that silica mixed with K2O and Cs2O crystallizes to cristobalite between 800 and 1200 °C, depending on the concentration of alkali species [29]. First, this may explain why cristobalite is detected either at 900–1000 °C by DTA or at 800–900 °C by HT-XRD. This difference may be also a kinetic effect because XRD heating rate is slower than the DTA one. Second, Higuchi et al.’s DTA exothermic events at between 300 and 450 °C, assigned to silica–alkali reactions, whereas no such events were detected in our study. This supports the hypothesis that in our material, the alkali species react with silica at lower temperatures, maybe as soon as they are released during the decomposition of HCF. About the emergence of new micropores in the material when cristobalite crystallizes (Fig. 4A inset), it may be explained by a decrease in wettability compared with silicate glass. It is supported by the work of Aneziris et al. [30] who have studied the wetting behavior of amorphous and crystalline silicon dioxide in contact with a silicate slag at 1130 °C (in the low viscosity region), which adheres more strongly to amorphous silica than cristobalite. About the effect cristobalite twinning on glass wettability, it was found in the literature that surface roughness influences the microscopic wettability of silica glass by water [31]. The fact that the silica support crystallizes at a higher temperature in the absence of the functional group indicates that the presence of the silicate glass favors the early crystallization of cristobalite. This observation is in agreement with Shinohara and Kohyama’s results [32].

The glass content as evaluated by XRD quantification (19 ± 6 wt %) was refined by the measured density of 2.4243 g cm⁻³. If we consider a cristobalite theoretical density of 2.33 g cm⁻³ [33], a glass density between 2.9 and 3 [34] on the basis of the glass approximate composition by EDS, a glass content between 17.4 and 19.8 wt% can be evaluated. A revised value of 18.5 ± 1.5 wt% glass is then proposed.

5. Conclusions

This study shows that cesium sorbents based on copper hexacyanoferrate cannot be hot isostatic pressed without pretreatment because mass loss would prevent densification. However, a first heat treatment in air without any additives leads to the decomposition of copper hexacyanoferrate and reduces the pore volume from 0.67 cm³/g to 0.02 cm³/g with no Cs loss. Our data indicate that cesium is retained in the calcined sample in the form of a cesium potassium silicate glass. After calcination, the powder consists of cristobalite (81.5 ± 1.5 wt%) and the cesium potassium silicate glass (18.5 ± 1.5 wt%), which can readily be hot pressed. The presence of the glass phase will presumably affect the degree of densification that can be achieved.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jnucmat.2019.151887.

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