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Encapsulation of caesium-loaded Ionsiv in cement

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ABSTRACT

The microporous material Ionsiv is used for ^{137}Cs removal from aqueous nuclear waste streams. In the UK, Cs-loaded Ionsiv is classed as an intermediate-level waste; no sentencing and disposal route is yet defined for this material and it is currently held in safe interim storage on several nuclear sites. In this study, the suitability of fly ash and blast furnace slag blended cements for encapsulation of Cs-Ionsiv in a monolithic wasteform was investigated. No evidence of reaction or dissolution of the Cs-Ionsiv in the cementitious environment was found by scanning electron microscopy and X-ray diffraction. However, a small fraction ($\leq$1.6 wt.%) of the Cs inventory was released from the encapsulated Ionsiv during leaching experiments carried out on hydrated samples. Furthermore, it was evident that K and Na present in the cementitious pore water exchanged with Cs and H in the Ionsiv. Therefore, cement systems lower in K and Na, such as slag based cements, showed lower Cs release than the fly ash based cements.

1. Introduction

Caesium is the least abundant of the stable alkali metals and not typically found in the biosphere. Its major radioactive isotopes, ^{134}Cs and ^{137}Cs, were released to the environment by nuclear weapons detonation or accidents in nuclear power plants. Uranium fission generates ^{137}Cs as a by-product, which decays with a half-life of 30 years; this radionuclide is biologically active and mobile, requiring sequestration and immobilisation. Of key concern is the release of Cs radio-isotopes by corrosion of spent nuclear fuel elements in cooling ponds and orphan fuels in legacy waste silos. Consequently, the aqueous effluent from such fuel storage facilities requires remediation to recover Cs (and other) radio-isotopes before discharge to the environment.

Several microporous materials are known for their capability to selectively incorporate Cs. The natural zeolite clinoptilolite is currently used successfully for Cs removal from aqueous nuclear waste streams, such as that arising from legacy waste ponds at the Sellafield site. Alternatively, the commercial product Ionsiv (IONSIV® IE-911, UOP LLC, Des Plaines, Illinois, USA) has been developed, and is used for Cs sequestration in fuel storage ponds. The principal phase in Ionsiv is a crystalline silicotitanate (CST), formulated $HNa_3Ti_4Si_2O_{14}\cdot4H_2O$ [1], which incorporates Cs more selectively than clinoptilolite [2,3].

The sodium present in CST can be fully exchanged for hydrogen by ion exchange in dilute HCl yielding $H_2Ti_2SiO_7\cdot1.5H_2O$, which has a higher Cs selectivity than its Na form [4,5]. This exchange occurs essentially on two sites, one situated in the framework coordinated by silicate oxygen atoms (4 of 6 coordination sites) and water molecules (2 of 6 coordination sites); the other site is situated in channels formed in (001) direction (also containing H_2O). Detailed descriptions appear in [4,6]. Under appropriate conditions, Cs exchanges for H partially on the channel sites, but not within the framework. The Cs ion diameter suits the channel diameter, which is considered one reason for the Cs selectivity of CST. Due to space limitation, not all channel sites can be exchanged, resulting in the maximum exchanged composition of $Cs_{0.4}H_{1.6}Ti_2SiO_7\cdot H_2O$ [6], or $Cs_{0.5}H_{1.5}Ti_2SiO_7\cdot H_2O$ according to [4]. It should be noted that in the commercial product, utilised in this study, amorphous $Zr(OH)_4$ served as a binder, and Ti was substituted with 30 mol% of Nb for enhanced selectivity. The Nb-form has a slightly larger unit cell, and therefore, Cs can be accommodated in the channels involving less framework expansion than in case of pure CST [1].

As discussed above, Cs-exchanged Ionsiv is considered an intermediate-level waste (ILW) and requires a sentencing and disposal route. Cementitious materials have proven to be suitable encapsulants for many nuclear waste applications. However, the use of cement based matrices for encapsulation of Ionsiv (and related ion exchange materials) may have several potential drawbacks:

- Reaction or decomposition of CST in the high pH cementitious pore solution and release of Cs, as reported in case of clinoptilolite in [7]. The Cs retention by ordinary Portland cement (OPC) was shown to be too low to allow for safe disposal [8].
- Further ion exchange of Cs with competing ions from the cement and subsequent Cs release into the cement.
- Desorption of Cs from Ionsiv due to elevated temperatures [3], which can occur during the exothermic cement hydration.

The present study investigates the interactions between Cs-Ionsiv cement formulations used for encapsulation of ILW in the UK. The

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blended cement systems including fine pozzolans were chosen due to their low pH pore solutions, expected reduced reaction with the Ionsiv, and their low heat of hydration. Leach tests were undertaken to evaluate the overall suitability of the cement formulations as encapsulation matrices for Cs-Ionsiv.

2. Experimental

2.1. Ion exchange

The Na present in Ionsiv was fully exchanged with hydrogen according to [4]. Subsequent H–Cs exchange was achieved by agitating 180 g of H-Ionsiv in 0.75 l of 1 M ^{133}CsCl solution, for 24 h at room temperature, on a roller mixer. The milky dispersion was separated using a 38 μm sieve and sufficient amounts of distilled water; the CsCl solution was renewed, followed by another 24 h of mixing and subsequent separation of the exchange solution. The resulting Cs-Ionsiv was agitated in 0.75 l of water for 3 min, recovered by filtration and washed with distilled water. This process was repeated 8 times, followed by drying at 60 °C for 24 h.

This procedure provided 3.8 times the amount of Cs required for maximum Cs-loading, as reported in [6]. Electron microprobe analysis (EMPA, CAMECA SX-51) on the exchanged Cs-Ionsiv determined a Cs content of 13.56 wt.%, compared to 12.98 wt.% stated in [6].

2.2. Cement sample preparation

Ordinary Portland cement (OPC) blended with blast furnace slag (BFS) or pulverised fly ash (FA) was used to prepare the encapsulation matrices for the Cs-Ionsiv. The raw materials were provided by the National Nuclear Laboratory (NNL, UK) and comply with their specifications. Producers of these materials were Castle Cement Ltd. (OPC), and Civil and Marine and Ash Resources Ltd. (BFS, FA), chemical compositions, as specified by the provider, are given in Table 1.

200 g batches of 3:1 BFS:OPC, 9:1 BFS:OPC, and 3:1 FA:OPC were dry mixed with and without 20 wt.% of Cs-Ionsiv. Water was added to achieve a water/reactant ratio of 0.35; the OPC, BFS, and FA were considered as reactants. After 3 min of hand mixing, the pastes were poured into 50 ml polypropylene tubes (diameter 2.7 cm), closed airtight and cured at 20 °C.

2.3. X-ray diffraction and electron microscopy

After curing for different time spans, up to 113 d, the samples were removed from the moulds, stored in acetone for one week and then dried in a desiccator under low vacuum. Discs were cut from the middle of the cylindrical samples, and the resulting surfaces were analysed by X-ray diffraction (XRD) in a Siemens D500 diffractometer (Cu Kα radiation, graphite diffracted beam monochromator) operating in reflection mode.

The cut specimens were impregnated under vacuum, ground and polished down to 1 μm diamond paste. Ionsiv beads were embedded in resin and prepared in the same fashion in order to expose their cross-sections. After carbon coating, the surfaces were examined by scanning electron microscopy (SEM) in a JEOL JSM 6400 equipped with a semi-quantitative energy dispersive spectroscopy system (EDS). Selected spots on these surfaces were quantitatively analysed by wavelength dispersive spectroscopy (WDS) on an EMPA CAMECA SX-51.

Table 1
Chemical compositions of raw materials.

	OPC [wt.%]	PFA [wt.%]	BFS [wt.%]
CaO	64.58	1.44	42.10
SiO_2	20.96	48.64	34.50
Al_2O_3	5.24	25.88	13.74
Fe_2O_3	2.61	7.57	0.97
MgO	2.09	1.42	7.29
SO_3	2.46	1.20	
K_2O	0.59	2.83	0.49
Na_2O	0.28	1.91	0.22
TiO_2		0.92	
Chloride	0.05		0.02
Insoluble residue	0.27		
Loss on ignition		4.16	

2.4. Leach test experiments

Samples cured for 113 d were removed from the moulds and cut on a diamond saw into cubes, of side 15 mm, using deionised water as cooling fluid. The cubes were cut from the centre of the sample so that all cube surfaces were fresh cuts as distant as possible from the original sample surface. After rinsing, the cubes were cleaned in an ultrasonic deionised water bath for 20 s, rinsed again and put into 500 ml of water (ACS reagent grade), resulting in a sample surface area to leachate volume ratio (SA/V) of 2.7 m^{-1}. Teflon baskets were used to prevent contact of the sample with the polypropylene bottle and sealing of a cube surface. Specimen preparation from demoulding to the start of the leach test was done individually for each sample within less than 8 min.

Vessels containing the leachate and sample, as well as a blank leachate containing no sample, were stored at 40 °C. After 1, 3, 7, 28, and 91 d, 5.7 ml were removed from each leachate, syringe filtered (0.2 μm, polypropylene media and housing), and acidified with 0.1 ml of 69% nitric acid (ACS reagent grade). Leachate chemistry was analysed by inductively coupled plasma atomic emission spectroscopy (ICP-AES). The chemical concentrations measured were corrected to the aliquot volume without nitric acid and, in case of the 3–91 d samples, to the initial leachate volume of 500 ml (assuming the ion concentration was always considerably below the solid–liquid equilibrium). The concentrations of all elements measured in the blanks were at all times below the detection limit, except Ca being always lower than 1 wt.% of the smallest measurement of a non-blank leachate.

A second experiment was undertaken to simulate the chemical environment of the Cs-Ionsiv in the cement matrix during cement hydration. 10 g Cs-Ionsiv was placed in 14 ml of artificial cementitious pore water with pH = 12.7 (composition given in Table 2, after measurements of pore solutions from mature BFS and FA modified cements [9], and solutions of fresh cements [10]) and stored at 40 °C for 3 d, followed by 25 d at 20 °C. The same conditions were applied to a blank containing the same pore water, but no Ionsiv. The leachate and blank were then removed, filtered, acidified, and analysed as described above.

3. Results and discussion

3.1. Ionsiv structure and morphology

The crystal structure of H-CST changes during exchange of hydrogen with caesium from $P4_2/mbc$ to $P4_2/mcm$ [6]. With further increasing Cs-loading, the relative peak heights of certain XRD reflections change. But after Ionsiv leaching in the artificial cementitious pore water, relative and absolute XRD peak intensities and positions were unchanged (Fig. 1). This implies that the crystallinity of the sample was maintained and further ion exchange, e.g. Cs with

Table 2
Leachate compositions measured by ICP-AES before and after leaching of Cs-Ionsiv; the concentrations of SO_4 and Cl were known from the leachate preparation and were not measured.

	Nb [ppb]	Cs [ppm]	K [ppm]	Na [ppm]	Ca [ppm]	SO_4 [ppm]	Cl [ppm]
Before leaching	<0.1	0.00	4330.05	1460.37	245.10	4200	50
After leaching	<0.1	1327.28	2705.62	293.02	240.95		

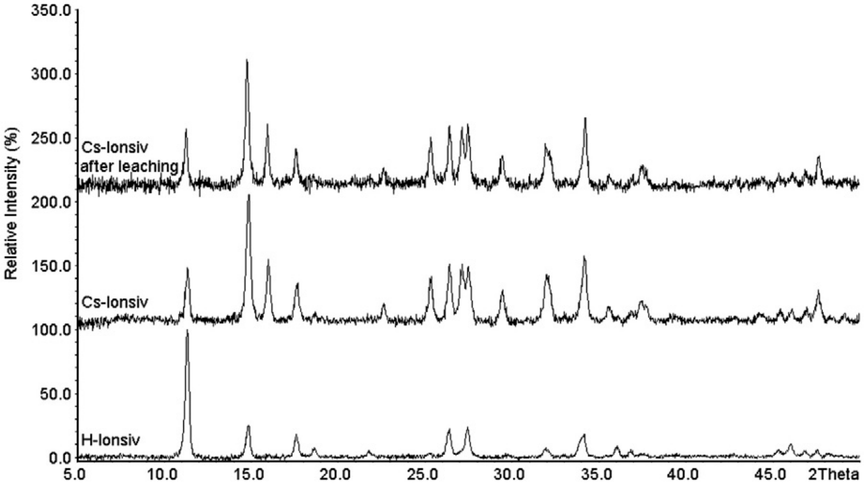


Fig. 1. XRD traces of H-Ionsiv, Cs-Ionsiv, and Cs-Ionsiv after leaching in artificial cementitious pore water.

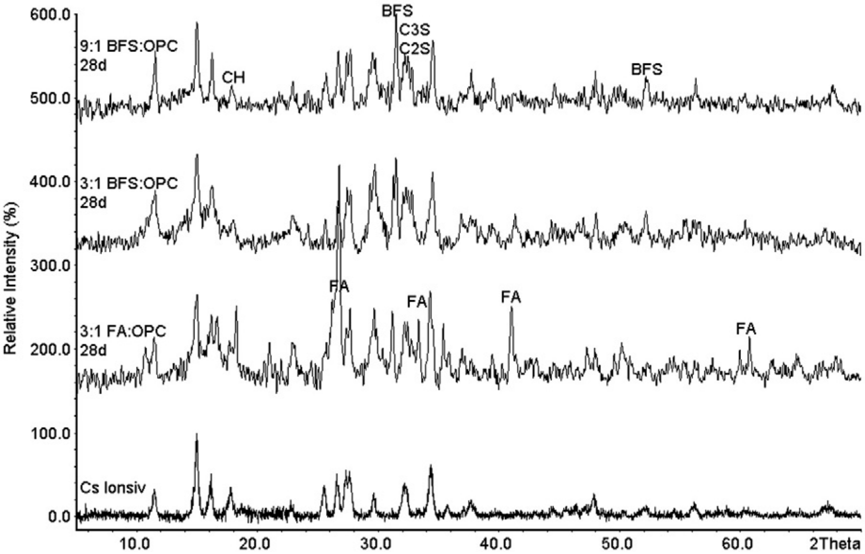


Fig. 2. XRD traces of Cs-Ionsiv, and Cs-Ionsiv encapsulated in 3 different cementitious systems, hydrated for 28 d.

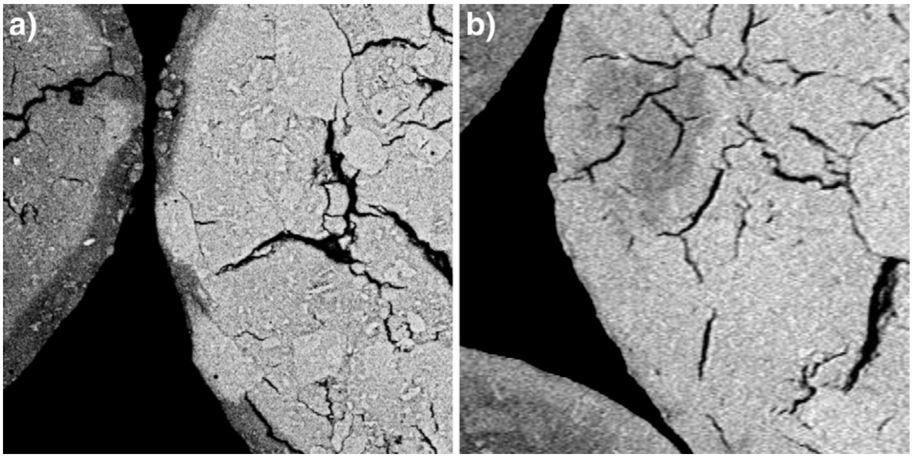
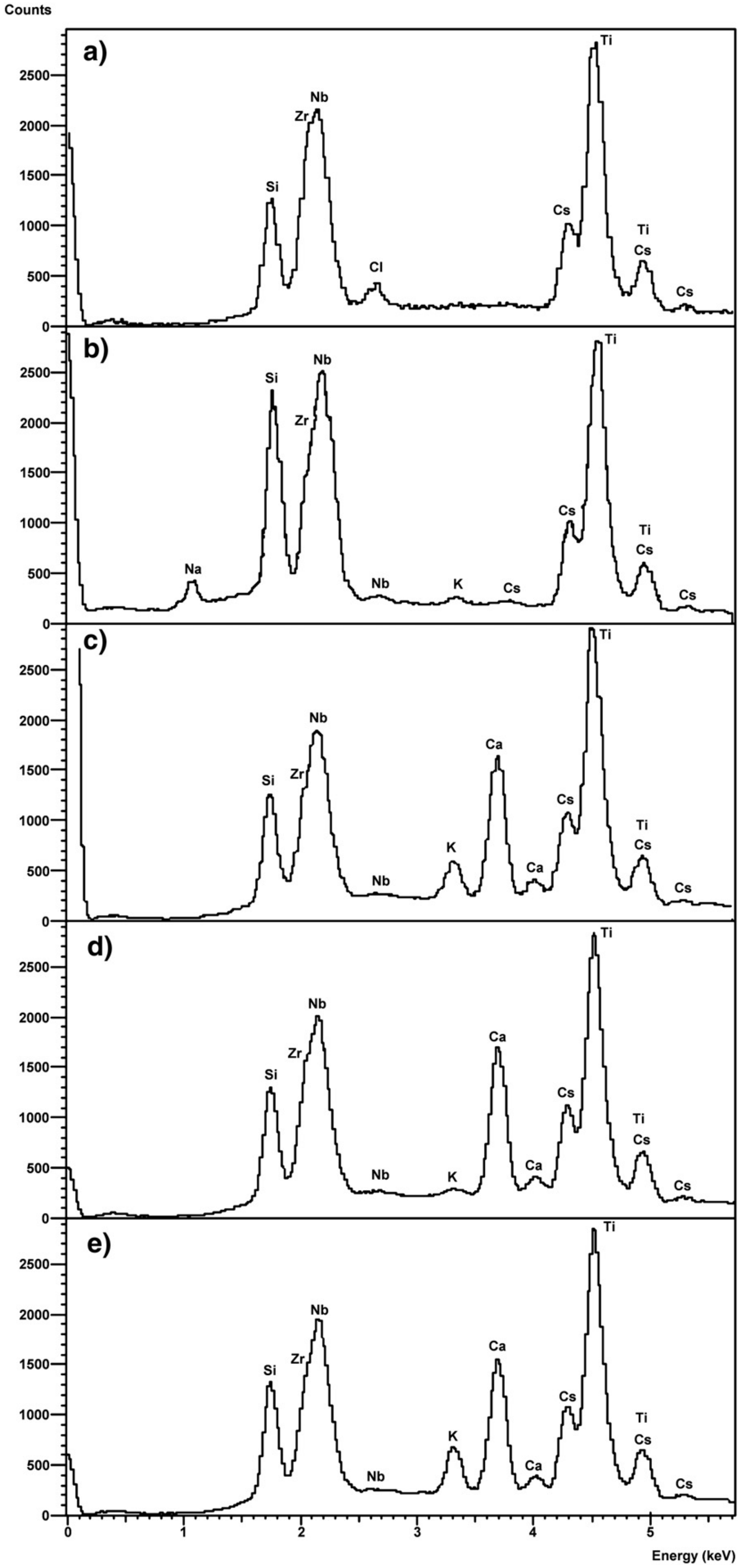


Fig. 3. SEM BSE images with a width of 200 μm of (a) Cs-Ionsiv, and (b) Cs-Ionsiv after leaching in artificial cementitious pore water.


Counts
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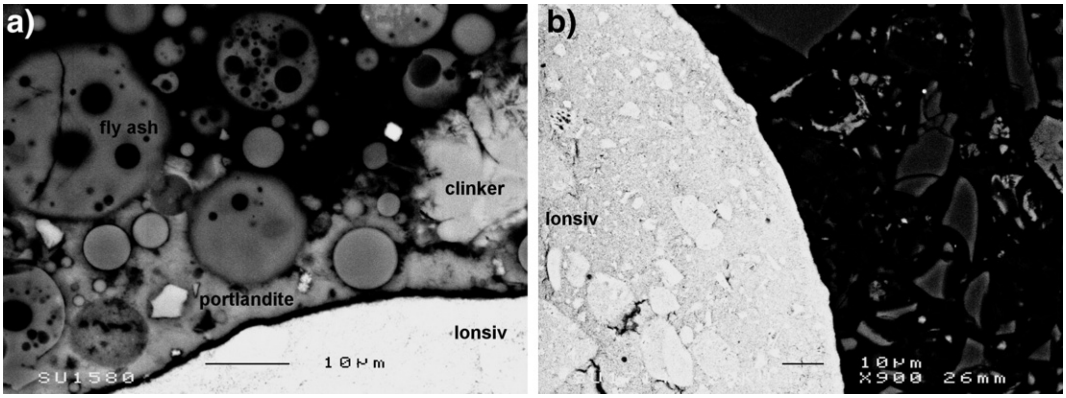

Fig. 5. SEM BSE images of (a) sample 3:1 FA:OPC with 20% Cs-Ionsiv hydrated for 3 d, and (b) 3:1 BFS:OPC with 20% Cs-Ionsiv hydrated for 28 d.

competing ions present in the artificial cementitious pore water, was too small to influence XRD reflections within the sensitivity of the method.

The cement samples including the Cs-Ionsiv hydrated for 28 d showed XRD patterns consistent with the findings from leaching of Cs-Ionsiv without cement in cementitious pore water: the Cs-Ionsiv reflections were still present, superimposed by the cement, fly ash, and slag reflections (Fig. 2). The hydration characteristics of the blended cement systems were described elsewhere [11].

The morphology and microstructure of Cs-Ionsiv and Cs-Ionsiv exposed to artificial cementitious pore water, were compared by SEM (examples given in Fig. 3). The sections of the beads appeared very heterogeneous in backscattered electron (BSE) imaging in case of all Ionsiv types. Grey values changed from bead to bead, within regions of one bead, and occasionally showed concentric structures parallel to the bead surface. The darker rim ~10 µm thick along the surface was an artefact due to low density resin intrusion.

The different grey value regions in Cs-Ionsiv, and Cs-Ionsiv exposed to the artificial cementitious pore water, were analysed by EDS (Fig. 4a and b). The different grey values can be explained by small variations in amounts of binder $Zr(OH)_4$ present as well as by slight differences in the amount of Ti exchanged with Nb. The spectrum of Fig. 4b was acquired with a different EDS detector which impedes direct comparison of the signal intensities. Inhomogeneities in porosity or surface roughness are also expected to increase the heterogeneous appearance of Ionsiv in the BSE images.

Of greater importance was the presence of sodium and potassium in the Cs-Ionsiv exposed to the artificial cementitious pore water (Fig. 4b), which can be explained by ion exchange of H or Cs in the Cs-Ionsiv with Na and K in the pore water solution. This is discussed further in Section 3.2. The presence of Cl in the Cs-Ionsiv is due to the Cs-exchange procedure, in which H-Ionsiv is exposed to CsCl solution. Cl can be exchanged on certain sites in zeolite-type structures, whereas vacancies are expected to maintain charge balance in the Ionsiv. However, Ionsiv seems to be more selective for K, Na, or Ca, because Cl mostly leaves the structure in the presence of those cations.

The outermost zones of the Ionsiv bead sections were carefully examined and compared. Especially in case of the Cs-Ionsiv exposed to artificial cementitious pore water, no reaction product or sign of dissolution could be found (Fig. 3).

The microstructure of the encapsulated beads, their interfaces and the different cementitious matrices hydrated for 1 to 28 d were investigated by SEM/EDS. Compared to an unblended OPC cement, the overall hydration was low and resulted in high porosity of all samples, in line with the findings in [11]. The slow reacting BFS and FA grains show no or only very small reaction rims.

No decomposition or reaction of the Ionsiv could be observed in any of the Cs-Ionsiv/ blended cement samples (Fig. 5). Fig. 5a shows portlandite coexisting with Cs-Ionsiv, without evidence of the formation of a reaction product. The gap at the interface is a preparation artefact. Older samples also showed no evidence of Ionsiv reaction.

EDS spot measurements and line scans revealed that Cs remained homogenously distributed within the Ionsiv. Small Cs variations reflected the compositional variations of the Ionsiv, e.g. different amounts of binder, which does not incorporate Cs. Compared with the Cs-Ionsiv exposed to artificial cementitious pore water, the Cs-Ionsiv in the different blended cements adsorbed K and Ca, but less or even no Na (Fig. 4b–e, sodium content in c–e is underestimated due to less sensitive EDS detector). This applied to all samples at all ages, whereas in general, K and Na contents increased with age and were often slightly higher closer to the Ionsiv interface. EDS spot measurements of numerous hydrates (portlandite and CSH) showed that they do not contain Cs at any hydration time within the sensitivity of EDS.

Ca is present in Ionsiv encapsulated in cement (Fig. 4c–e), but absent in Ionsiv leached in the artificial cementitious pore water. A possible explanation is given below, taking leaching data into account.

3.2. Leaching

The Cs-Ionsiv was exposed to artificial cementitious pore water, whose composition was compared before and after 28 d leaching (Table 2). The absence of Nb in the leachate implied that the CST framework did not significantly decompose, in agreement with XRD and SEM/EDS data. In contrast, a considerable fraction of Cs was leached out of the Cs-Ionsiv, corresponding to 1.46 wt.% of the Cs present before leaching. The decrease of K and Na in the artificial cementitious pore water during leaching (Table 2), together with the presence of K and Na in the leached Cs-Ionsiv (Fig. 4c), suggested that Cs in the Ionsiv exchanged with K and Na from the artificial cementitious pore water. Converting these results into fractions of Ionsiv sites suitable for H, Cs, Na, or K occupancy (100% equals the total number of H sites in H-Ionsiv, or the sum of H and Cs sites in Cs-Ionsiv), approximately 2.6% of the total possible sites in the Ionsiv were occupied by K and Na after leaching, whereof 0.3% had been occupied by Cs before leaching (Table 3). These low numbers were expected, as Ionsiv is designed for very selective exchange with Cs, where maximal site occupancy is approximately 20%. It is known that K and Na can occupy H/Cs sites in the channels of the CST as well as H sites close to the framework [4,12].

Fig. 4. Representative EDS spot measurements of (a) Cs-Ionsiv, (b) Cs-Ionsiv after leaching in artificial cementitious pore water, (c) Cs-Ionsiv in 3:1 BFS:OPC, (d) Cs-Ionsiv in 9:1 BFS: OPC, and (e) Cs-Ionsiv in 3:1 FA:OPC, cements hydrated for 28 d.

Table 3
Site occupancies of cations in Cs-Ionsiv after different treatments; 100% equal the sum of possible exchange sites in the Ionsiv.

	Cs-Ionsiv	Cs-Ionsiv after leaching in artificial cem. pore water	Cs-Ionsiv encapsulated in 3:1 BFS: OPC after leaching in H_20	Cs-Ionsiv encapsulated in 9:1 BFS: OPC after leaching in H_20	Cs-Ionsiv encapsulated in 3:1 FA:OPC after leaching in H_20
H	80.00	77.64	77.76	79.02	76.09
Na		1.46	0.96	0.46	2.27
K		1.19	1.40	0.63	1.92
Cs	20.00	19.71	19.88	19.89	19.72
	100.00	100.00	100.00	100.00	100.00

Calculated from ion concentrations in the leachates.

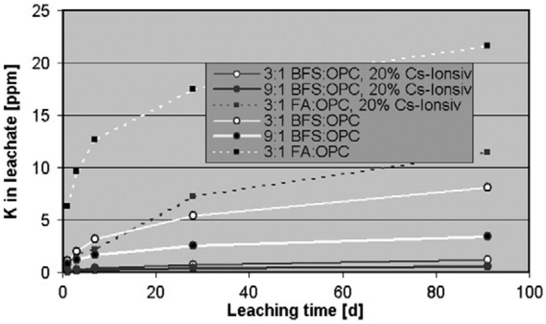

Fig. 7. ICP-AES measurements of K in the leachates from cement samples with and without Cs-Ionsiv. Lines are shown for better readability only.

From the data in Tables 2 and 3, the selectivity coefficient (K_c) can be calculated after [13], assuming the reverse exchange of M in Ionsiv with Cs in solution ($M = \mathrm{Na} + \mathrm{K}$). The calculated log K_c of 2.7 is higher than reported by [13] (log $K_c = -1.8$, $M = \mathrm{Na}$). This discrepancy can be explained by the fact that the ion exchange is not fully reversible [5], and by the partial Nb substitution in the Ionsiv used in this study. In addition, experimental parameters like initial ion concentrations and solid–liquid ratio differ significantly.

The three blended cements with/ without Cs-Ionsiv were exposed to deionised water. After 91 d, 1.4 wt.% of the Cs adsorbed in Ionsiv encapsulated in FA blended cement was found in the leachate, whereas the slag blended cements showed a significantly smaller release of approximately 0.6 wt.% (dots in Fig. 6). Due to the high Cs solubility and the large leachate volume relative to the sample, parabolic leaching kinetics describing a diffusion controlled process [14] fitted the data very well ($R^2 > 0.99$, lines in Fig. 6).

The higher Cs release from the Ionsiv-containing FA blended cement can be explained by the higher availability of cations suitable for exchange of Cs in the Ionsiv. K and Na concentrations were significantly higher in the leachate from FA blended cement than in the leachates from BFS samples (Figs. 7 and 8). Furthermore, all leachates from Cs-Ionsiv-containing samples showed much lower K and Na concentrations than leachates from samples without Ionsiv. Assuming that the differences in amount of K and Na in the leachates from samples with and without Cs-Ionsiv did exchange Cs and H in the Cs-Ionsiv encapsulated in the cements, the site occupancy in Ionsiv at 91 d was estimated (Table 3). 100% equals the total number of H sites in H-Ionsiv, or the sum of H and Cs sites in Cs-Ionsiv. In Ionsiv encapsulated in BFS blended cements, approximately 1–2.5% of the possible sites were taken by K and Na, whereof 0.1% had been occupied by Cs before encapsulation. In Ionsiv encapsulated in FA blended cement, approximately 4% of the possible sites were taken by K and Na, whereof 0.3% had been occupied by Cs before encapsulation. These numbers were in the same range as the exchange expected during leaching of the Cs-Ionsiv in artificial cementitious pore water. However, the ion exchange during leaching has to be added to the exchange expected already during hydration.

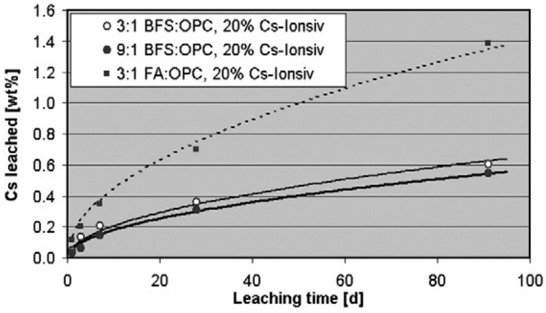

Fig. 6. Dots: ICP-AES measurements of Cs released from the cement samples containing Cs-Ionsiv, converted to wt.% of total Cs present in sample. Lines: best fit of diffusion controlled parabolic curves.

The role of Ca in this study is not yet fully understood. Its presence in Cs-Ionsiv encapsulated in blended cements (Fig. 4c–e) suggests that Ca exchanges into CST, as measured in case of the amorphous CST analogue [5]. But the Ca concentration in the cementitious pore water did not decrease significantly during leaching of Cs-Ionsiv (Table 2), and Ca concentrations in leachates of cements with and without Ionsiv were equivalent. These results suggest no Ca exchange into CST. A possible explanation of this contradiction is the approximately four times higher Ca concentration in fresh cements (up to 7 h) compared to the used artificial pore water [15]. Furthermore, Ca exchanged into Ionsiv can be replaced by the cement. As ion exchange is not fully reversible [5], the amount of Ca measured by EDS (Fig. 4c–e) stayed in the Ionsiv after Ca concentration in the pore water dropped. However, carbonation has to be considered as possible error source, because all experiments were conducted under air atmosphere.

4. Conclusions

This investigation has demonstrated that the Ionsiv framework is stable within the cementitious environments investigated. The pozzolanic reaction described in case of Cs-loaded clinoptilolite [7], encapsulated in the same blended cements as used in this study, was not observed.

Several data strongly suggest that the observed release of Cs from Ionsiv into artificial cementitious pore water is due to Cs exchange with K and Na from the pore water. But within the three cementitious matrices studied, the release of Cs from the Ionsiv into the matrices during hydration could not be confirmed. Considering the Cs fraction released into the artificial cementitious pore water incorporated into the hydrates of the cement encapsulating the Cs-Ionsiv, the Cs content in the hydrates would be around 1–1.5 wt.% (degree of hydration 0.5, homogenous distribution assumed). This is just around the sensitivity limit of EDS. The amount of artificial cementitious pore water in the

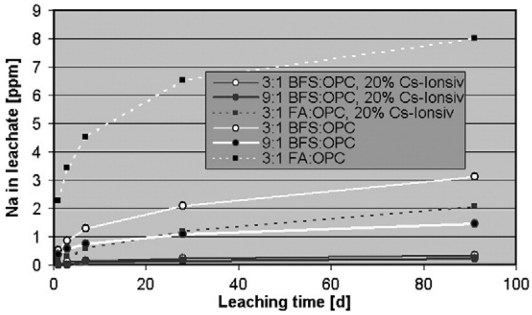

Fig. 8. ICP-AES measurements of Na in the leachates from cement samples with and without Cs-Ionsiv. Lines are shown for better readability only.

analogue experiment, where Cs release occurred, stays constant, whereas the amount of pore water in the real sample decreases rapidly during hydration. The latter increases K and Na concentration, which should lead to further exchange of K and Na with Cs from the Ionsiv. Therefore, the presence of Cs in the cement hydrates is strongly suspected, but could not been shown. We cannot exclude Cs loss from the cement matrix during SEM specimen preparation.

Cement sample leaching experiments resulted in a 1.4 wt.% release of total Cs after 91 d in case of FA blended cement. Only approx. 0.6% was released from slag cement systems. Again, it is very likely that K and Na leached out of the cement matrices exchange with Cs and H in the Ionsiv. Therefore, the Cs release from BFS blended cements is lower than from FA blended cements because of their smaller release of K and Na.

Lower Na and K concentrations in the cementitious environment, and a more realistic, lower Cs-loading of the Ionsiv, may decrease the Cs release during leaching.

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