Cs retention and diffusion in C-S-H at different Ca/Si ratios

Eduardo Duque-Redondo^{†,*}, Kazuo Yamada[‡], Iñigo López-Arbeloa[†] and Hegoi Manzano[§]

[†]Molecular Spectroscopy Laboratory, Department of Physical Chemistry, University of the Basque Country UPV/EHU, Aptdo. 664, 48080, Bilbao, Spain.

[‡]Fukushima Branch, National Institute for Environmental Studies, Miharu, Tamura, Fukushima, 963-7700, Japan.

[§]Department of Condensed Matter Physics, University of the Basque Country UPV/EHU, Aptdo. 664, Bilbao, Spain.

Cement and concrete have been widely used as a barrier to isolate many types of contaminants, including radioactive waste, in repository sites. Nevertheless, the intrusion of groundwater in those nuclear repositories may release those contaminants by leaching mechanisms. Because of this, the retention and diffusion processes in cement matrix require to be analyzed in depth. The adsorption in cement and C-S-H gel, its main hydration product, is influenced by factors as the pH, the composition or the alkali and alkaline earth content. In this work, molecular dynamics simulations were employed to study the role of Ca/Si ratio of the C-S-H in the capacity to retain Cs and diffusivity of these ions in gel pores. For that purpose, we built four different C-S-H models with Ca/Si ratios from 1.1 to 2.0. The results indicate better cationic retention at low Ca/Si ratios due to the interaction of the cations with the bridging silicate tetrahedrons. However, the average diffusion coefficients of the cations decrease at higher Ca/Si ratios because the high ionic constraint in the nanopore that induces a long-range ordering of the water molecules.

Introduction

Nuclear power supplies the 11.5% of global electricity consumption in 2017, according to the World Nuclear Association. Nuclear energy has advantages such as low polluting emissions, the reliability or the low cost of the electricity production in comparison with other energy sources. However, nuclear power also has drawbacks; the main one is the management and final disposal of spent nuclear fuel. Not all the fission products produced in nuclear reactors are radioactive, but a significant number of them are dangerous and long-lived radioisotopes. ¹³⁷Cs is one of the main fission products present in spent nuclear fuel. Radiocesium is extremely harmful for humans¹, highly volatile² and constitutes the main source of radiation in the zones of alienation in Chernobyl and Fukushima³.

Cementation is a process that involves the solidification of low- and intermediate-level radioactive waste, suitable for medium- and long-term storage. Cement-based materials act as diffusion barrier, immobilizing the contaminants by adsorption and precipitation^{4,5}. Ordinary Portland cement (OPC) is the most employed cement-type in radioactive waste cementation⁶, and its main hydration product, calcium silicate hydrate (C-S-H) gel, has successfully isolated the radionuclides in specific sorption and reaction sites of their surface^{4,7}. Even though C-S-H has an inherently low solubility and diffusibility⁸, there can be leaching mechanisms that may induce the potential migration of the contaminants and their release^{9,10}. This reflects the importance of achieving a better understanding of the parameters that control the retention mechanisms in C-S-H and cement.

Many experimental studies have been done on Cs uptake in cement^{11–13}. These studies highlight the impact of the experimental

conditions in Cs retention. For instance, the sorption in Cs can be enhanced at pH ~ 11, since at higher pH values the sorption sites of C-S-H might be saturated by the presence of a great amount of calcium hydroxide. These studies also indicate that the retention is better at low Ca/Si ratios and when aluminum is incorporated to the C-S-H structure^{14–16}.

In spite of there being many experimental reports about retention and dynamics of Cs in C-S-H, the molecular scale mechanism that governs those processes has not been fully determined and quantified. Molecular dynamics (MD) simulations allow to gain insight into adsorption and desorption processes at atomic level. Many researchers took 14Å-tobermorite as a model due to the structural resemblance to C-S-H^{17–19}, in order to simplify the study of Cs retention in C-S-H, both from an experimental and simulation point of view^{20–24}. From these studies, it can be drawn that the retention mechanism is based on electrostatic sorption on the surface defects and that the interlaminar Ca is not exchangeable²¹.

In this paper, we have employed molecular dynamics simulations to study how the capability of C-S-H to retain Cs and the diffusivity of these ions are influenced by the Ca/Si ratio. For that purpose, we built four C-S-H systems with an increasing Ca/Si ratio, from 1.1 up to 2.0, which contains 0.26 Cs ions per C-S-H mol. This Cs concentration is equivalent to a Cs/Ca ratio of 0.85, maximum value found experimentally in 14Å-tobermorite²³. The number of defects or sorption sites rises as the Ca/Si ratio is increased, but this also implies higher content of Ca that can saturate those high-affinity sites. We have evaluated the competition between both mechanisms, quantifying the number and types of sorption sites, as well as the amount of Ca and Cs retained. The dynamics of these cations are also studied by means of their diffusion coefficients, exploring the impact of Ca/Si ratio on their behavior.

Simulation details

In order to build realistic C-S-H models we have followed the procedures reported in previous works^{16,25,26}. The initial unit cell of 14Å-tobermorite²⁷ was replicated to obtain a simulation box with dimensions of 2.6 x 3.1 x 3.3 nm³, corresponding to the x, y and z axis. The random deletion of bridging silicate groups, combined with the addition Ca in the interlaminar space to maintain the electroneutrality of the system, results in the increase of the Ca/Si ratio. In this way, we were able to build C-S-H models with Ca/Si ratios of 1.1, 1.3, 1.67 and 2.0.

We run energy minimization, followed by equilibration in the isobaric-isothermal ensemble (NPT) for 5 ns at 300K using the ReaxFF force field^{28–30}. This force field enables the structural, volumetric and chemical relaxation of our C-S-H models, making possible the dissociation of water molecules in dangling oxygen atoms from the new Q¹ sites of the silicate chains. After creating the bulk models with different Ca/Si ratios, we expanded the interlaminar space to create a pore of 1 nm and filled it with Cs ions and water until reaching bulk water density. ReaxFF has not yet implemented parameters for Cs ions, so our models were transferred to traditional force fields. We employed CSHFF force field³¹ for the C-S-H substrate and Åqvist³² for the Cs ions. We run molecular dynamics using LAMMPS³³, using the Ewald summation method³⁴ and the Verlet algorithm³⁵ to compute the long-range Coulombic interactions and to integrate the motion equations, respectively. We first performed our simulations in the canonical ensemble (NVT) at 300K with thermostat coupling constant of 0.1 ps during 0.5 ns and using a time step of 0.5 fs. The systems were further relaxed for extra 0.5 ns in the isobaric-isothermal ensemble (NPT) at room conditions (300K and 1 atm) with a barostat coupling of 1 ps. The final pore widths are given in Table 1. A final molecular dynamics simulation is carried out in the canonical ensemble for 0.1 μs at 300K, long enough to capture the diffusion properly.

Results

CSH models structure. The final properties of the C-S-H models at the studied Ca/Si ratios before expanding the interlaminar space to create a 1 nm pore are given in Table 1, along with the final pore widths after the expansion. The values of our systems are compared with experimental and computational models reported in literature, showing good agreement. On the one hand, the agreement in the mean chain length (MCL) and C-S-H composition (H/Ca and H/Si parameters) is because we have selected those values in order to replicate the experimental C-S-H systems reported in the literature. On the other hand, in our simulation the Ca-OH/Ca and Si-OH/Si parameters are given by chemical relaxation provided by ReaxFF force field. It can be seen that there is a good agreement between the values from the literature and the ones obtained in our simulations.

Table 1. Final properties for C-S-H models at Ca/Si ratios from 1.1 to 2.0 of our simulations and from literature (values in parentheses).

Ca/Si	1.1	1.3	1.67	2.0
MCL ^{25,36}	5.67 (5.8-6.2)	3.0 (2.9-3.3)	2.4 (2.3-2.6)	2.2 (2.1)
H/Ca ^{37,38}	1.7 (1.7)	2.3 (2.2)	2.5 (2.4)	2.8 (2.7)
Ca-OH/Ca ^{39,40}	0.23 (0.13-0.19)	0.29 (0.25-0.23)	0.37 (0.44-0.29)	0.47 (0.62-0.36)
Si-OH/Si ⁴²	0.32 (0.34)	0.25 (0.29)	0.15 (0.20)	0.10 (0.13)
d ₀₀₁ (Å)	12.21	12.39	12.23	13.38
Pore width (Å)	14.44	15.00	15.46	15.69

Density profiles. We have computed the density profiles of our systems in order to study the distribution of the species contained in the nanopores of C-S-H. The density profiles of Cs, Ca and water molecules in C-S-H models shown in Figure 1 were obtained using a simulation trajectory of 20 ns, averaging and normalizing the atomic positions. We have considered the Guggenheim interface convention⁴² in the analysis of these density profiles. Thus, it is possible to distinguish three different regions: the bulk solid region of C-S-H below the lower interfacial limit ($z = -2.5$ Å), the bulk liquid region of the nanopore above the upper interfacial limit ($z = 0$ Å) and the extended interfacial region enclosed by the previous regions. In addition to the density profiles, we have also included a snapshot of the C-S-H nanopores of each analyzed system, facilitating the interpretation and comprehension.

The density profiles shown in Figure 1 reveal that water and cationic species can be located both in the extended interphase and in the bulk liquid region. The peaks under the upper interfacial limit correspond to deep-rooted species, accommodated in the cavities and structural defects of the C-S-H surface. These profiles also show strong peaks just above the upper interfacial limit for the cations due to electrostatic interactions established with the surface. Likewise, it is also possible to see strong peaks for water molecules at short distances from the upper limit, especially intense at higher Ca/Si ratios. This may indicate an ascending hydrophilicity of the C-S-H surface as the Ca/Si ratio increases. Besides that, there is an increasing amount of non-adsorbed Cs and Ca ions in the bulk liquid region as the Ca/Si grows. This trend is particularly marked for Ca ions, since they are completely adsorbed in the C-S-H surface at low Ca/Si ratios, but the amount of non-adsorbed Ca in the pore increases gradually as the Ca/Si ratio is higher. This clearly indicates that the cation retention is worsened as the Ca/Si ratio is increased, which can be seen in the snapshots with the naked eye. This is in the line of the findings reported by Glasser and Hong, who indicated that the retention is enhanced in C-S-H at lower Ca/Si ratio^{43,44}. In the following section, we quantify and discuss the cationic sorption.

Figure 1. Density profiles and their corresponding snapshots of the atomistic simulations of C-S-H at Ca/Si ratios of (a) 1.1, (b) 1.3, (c) 1.67 and (d) 2.0 with a constant Cs concentration of 0.26 Cs/mol of C-S-H. In the density profiles, the black dashed line represents the upper interfacial boundary, while the profiles of Cs, Ca and water molecules are plotted in light blue, yellow and dark blue, respectively. The garnet tetrahedrons of the snapshots correspond to silicate chains, whereas the light blue and yellow balls are the Cs and Ca ions. Water and hydroxyl groups are illustrated as double and simple blue sticks.

Types of adsorption sites. The partitioning resulting of the Guggenheim convention facilitates the classification of the cations according to their adsorption configurations: inner-sphere and outer-sphere adsorption. These adsorption configurations have already been reported for C-S-H²⁶ and exhibit structural differences that affect to their retention capacity (See Figure 2). On the one hand, the inner-sphere sorption sites are located in the extended interfacial region, where the cations are generally trapped in cavities

formed by pair and bridging silicate tetrahedrons. The interactions established between the C-S-H surface and cations adsorbed in inner-sphere sites are very strong and stable. On the other hand, the outer-sphere sorption sites are located just above the upper interfacial limit. In this configuration, the retention depends mainly on bridging silicates, so the interaction between surface and cations is not as strong as in inner-sphere sorption. Thus, the peaks of the cations in the density profiles below and above the upper interfacial limit are related to inner-sphere and outer-sphere adsorbed species, respectively. Additionally, there are other ions solvated in the C-S-H pore. Hereinafter, we will refer to the non-adsorbed cations as pore species.

Figure 2. Snapshots of the MD simulations corresponding to the local structure of Cs ions adsorbed in inner-sphere sorption sites (left) and in outer-sphere sorption sites (right) in C-S-H with Ca/Si of (a) 1.1 and (b) 2.0. The yellow and light blue balls represent intrinsic Ca and Cs ions, respectively, the garnet tetrahedrons correspond to the silicate chains and hydroxyl groups and water molecules are illustrated as simple and double blue sticks.

Since the sorption configuration may affect not only to the retention of the cations, but also to other properties such as the diffusivity, it is necessary the characterization of the type of sorption that takes place for Cs and Ca. The relative amount of Cs and Ca adsorbed in inner-sphere and outer-sphere sorption sites is given in Table 2, as well as the number of cations solvated in the nanopore of C-S-H, called pore cations.

Table 2. Percentage of cations adsorbed in inner-sphere and outer-sphere configurations and the pore ions in C-S-H for Cs and Ca ions. The total number of Cs is constant and equivalent to 0.26 Cs per mol of C-S-H for any Ca/Si ratio. The total number of Ca grows with the Ca/Si ratio from 0.34 to 0.71 Ca per mol of C-S-H.

Ca/Si ratio	Cs			Ca		
	Inner	Outer	Pore	Inner	Outer	Pore
1.1	16%	49%	35%	36%	64%	0%
1.3	21%	41%	38%	31%	33%	36%
1.67	27%	19%	54%	32%	26%	42%
2.0	31%	4%	65%	33%	7%	60%

The data from Table 2 show that the number of cations adsorbed in the two types of sorption sites decreases. This results from the reduction of the number of the high affinity sites of the surface due to the decrease of bridging silicates at higher Ca/Si ratios. Therefore, those values indicate that the retention is enhanced at lower Ca/Si ratios. In fact, at Ca/Si ratio of 1.1, there is no Ca dissolved in the nanopore, all Ca ions are adsorbed in the C-S-H surfaces. Nevertheless, the interpretation of the percentage of adsorbed and non-adsorbed Ca is not so easy since the amount of Ca in C-S-H nanopores is not constant, increases as the Ca/Si ratio grows. For that reason, we have calculated the number of inner-sphere and outer-sphere sorption sites per area of C-S-H surface for Cs and Ca, which is independent of the ionic concentration (see Table 3).

Table 3. Number of inner/outer-sphere adsorption sites per nm² of C-S-H and the sum of them for Cs and Ca. The total number of Cs ions is constant and equivalent to 1.66 Cs per nm² of C-S-H surface for any Ca/Si ratio. The total number of Ca ions increases from 2.07 Ca per nm² of C-S-H surface for Ca/Si of 1.1 to 4.55 for a ratio of 2.0.

Ca/Si ratio	Cs			Ca		
	Inner	Outer	Sum	Inner	Outer	Sum
1.1	0.30	0.79	1.09	0.75	1.32	2.07
1.3	0.36	0.70	1.06	0.99	1.06	2.05
1.67	0.46	0.32	0.78	0.98	0.81	1.79
2.0	0.52	0.07	0.59	1.50	0.32	1.82

It can be seen that the total number of sorption sites decreases as the Ca/Si ratio rises for both Cs and Ca ions. However, it is remarkable that number of inner-sphere and outer-sphere sites follow opposite directions: as the Ca/Si ratio grows, the number of inner-sphere adsorption sites increases, while the number of outer-sphere sorption sites is substantially reduced. This is due to decrease of the bridging silicate groups, the main responsible of retention in the outer-sphere configurations, facilitating the interaction of the cations with the pairing silicates.

It is also interesting that the total number of sorption sites for Ca remains almost constant, with a slight deviation for Ca/Si ratio of 1.3. For Ca, the decrease of outer-sphere sorption sites is compensated by the increase of the inner-sphere sites. This is due to the high charge density of Ca, a divalent cation with relatively small size. In this way, Ca ions are able to approach closer to the surface, to inner-sphere sorption sites. In contrast, the moderate increase of inner-sphere sorption sites for Cs cannot compensate the loss of outer-sphere sites, since Cs has much higher size than Ca and lower charge, hindering its approach to inner-sphere sorption sites.

Diffusion coefficients. In order to avoid leaching processes of the retained cations in C-S-H it is indispensable low diffusion coefficients, aside from a good retention capacity. For that purpose, we have

computed the mean square displacement (MSD)⁴⁵, and through the Einstein relationship⁴⁶ we obtained the diffusion coefficient (D):

$$D = \frac{1}{2d} \lim_{t \rightarrow \infty} \frac{MSD}{t}$$

where d is the dimensionality of the system.

Figure 3 shows the average diffusion coefficients of water molecules and Cs ions as a function of the distance from the C-S-H surface. It can be seen for all the systems that the diffusion coefficients of deep-rooted water are relatively low, but increase progressively until reaching the nanopore. It should be noted that the diffusion coefficient of water molecules confined in C-S-H nanopores is considerably reduced at any Ca/Si ratio in comparison with the experimental⁴⁷ ($\sim 2.3 \cdot 10^{-9} \text{ m}^2 \text{ s}^{-1}$) and simulated⁴⁸ ($\sim 2.5 \cdot 10^{-9} \text{ m}^2 \text{ s}^{-1}$) values measured for bulk water. This is due to the structural and electrostatic confinement effect^{49–52}, which provokes a reduction of the diffusion coefficients in comparison with the value in bulk water. Moreover, there is a drastic decrease of the diffusivity as the Ca/Si ratio increases. The reasons of this decrease will be discussed in the following section.

Figure 3. Evolution of the average diffusion coefficient as a function of the distance from the C-S-H surface of (a) water molecules and (b) Cs ions at the studied Ca/Si ratios. The black dashed line at $z = 0 \text{ Å}$ represents the upper interfacial limit, while the red, blue, yellow and green lines represent the coefficients at Ca/Si ratios of 1.1, 1.3, 1.67 and 2.0.

The diffusion coefficients of Cs ions are also plotted (Figure 3b) as a function of the distance from the C-S-H surface. This enables the evaluation of the diffusivity of the Cs ions adsorbed in the inner and outer-sphere configurations, as well as the non-adsorbed ones. It can be seen that the diffusion coefficients of the adsorbed Cs are almost negligible in comparison with the values of non-adsorbed Cs ions. In fact, there is a difference of two orders of magnitude in the diffusion coefficients of adsorbed and non-adsorbed Cs. Likewise, Cs ions in inner-sphere sorption sites exhibit diffusion coefficients one order of magnitude lower than in outer-sphere sites. As with water, the Cs diffusivity is strongly affected by the Ca/Si ratio, decreasing dramatically as this ratio increases. This sharp reduction is related with the decrease of the water diffusivity. In any case, the diffusion of confined Cs is much lower than bulk water⁵³: $2.1 \cdot 10^{-9} \text{ m}^2 \text{ s}^{-1}$, up to three orders of magnitude higher than the diffusion of Cs in C-S-H with Ca/Si ratio of 2.0.

Hydrophilic character. So far, we have found that as the Ca/Si ratio is increased, the retention is worsened, but also the diffusion coefficients are reduced. In order to explain this apparent contradiction, it should be considered how the structural defects on the silicate chains and the cationic content affect to the dynamic of the species confined in the nanopore.

Ockwig et al.⁵⁴ reported that the dynamics of confined water in the channel of clays are strongly influenced by the presence of structural defects in their silicate chains. These defects are related with the hydrophobic/hydrophilic character of clays, and can be extrapolated to C-S-H⁵⁵: a higher Ca/Si ratio implies more defects in the silicate chains, increasing the number of dangling oxygen atoms and in turn increases the charge of C-S-H surfaces. This increase of acceptor groups facilitates the formation of hydrogen bonds between the surface and the water molecules, increasing the hydrophilicity of the C-S-H. In fact, this phenomenon has already been observed in the density profiles (Figure 1), which exhibit stronger peaks of water in the proximities of C-S-H surface as the Ca/Si grows. The increase of the hydrophilicity results in constrained motion of the water molecules in the vicinities of the hydrophilic surface⁵⁵. Moreover, this may induce a long-range ordering of the water molecules, reflected in stronger polarization of the water molecules in comparison with the self-polarization in bulk water⁵⁶. The polarization of the pore water may contribute to create an organized hydrogen bonds network, decreasing the motion of the water molecules. In addition, it should be noted that the cations located in the nanopore, and particularly the Ca, also facilitates the order in the interlaminal space due to their contribution to increase the ionic force that polarizes the water molecules. At higher Ca/Si ratios there are more Ca ions in the nanopore, so the polarization of the water molecules increases as the Ca/Si ratio rises. This polarization improves the ordering and decreases the diffusivity of the water molecules. In turn, the order and diffusivity of water provokes the decrease of the diffusion coefficients of the cations in the nanopore.

To check this hypothesis, we have evaluated the residence time of water molecules in the C-S-H surface (Figure 4a), the water dipolar moment (Figure 4b) and the lifetime of hydrogen bond network (Figure 4c) in the nanopore at the Ca/Si ratios under study.

The residence times of the water molecules in the C-S-H surface increases progressively as the Ca/Si ratio becomes higher, from 0.6 ns for the lowest ratio studied to 4.7 ns for Ca/Si ratio of 2.0, as it can be seen in Figure 4a. This indicates that the motion of those molecules is more restrained in the vicinities of the C-S-H surface as the Ca/Si ratio grows. On the other hand, the deletion of bridging silicates at higher Ca/Si provokes the growth of the electrostatic field in the nanopore. This originates a polarization of the water molecules, upshifting the dipole moment to larger values than the self-polarization in bulk water, as it is shown in Figure 4b. The dipole moment for bulk water is 2.44 D, was computed using the SPC flexible model⁵⁷, but in C-S-H the dipole moment is upshift up to 2.48 D and 2.52 D for Ca/Si ratios of 1.1 and 2.0, respectively. This also confirms the intensification of the hydrophilicity of the C-S-H as Ca/Si

ratio grows. Finally, we have computed the hydrogen bond lifetime in order to prove if the polarization of the water molecules creates a stronger hydrogen bond network that causes the decrease of the diffusivity of the species in the nanopore. As can be seen in Figure 4c, the lifetime of the hydrogen bonds of water molecules confined in C-S-H is higher than in bulk water, but in turn is higher as the Ca/Si ratio rises. Thus, the half-life of the hydrogen bonds in bulk water is 40 ps. This value increases up to 44 ps for hydrogen bonds in C-S-H with a Ca/Si ratio of 1.1, and reaches 60 ps at Ca/Si ratios of 2.0. This enhanced hydrogen bond network restrains the motion of the water molecules, and also reduces the diffusivity of the cations dissolved in the nanopore.

Figure 4. (a) Autocorrelation functions of water-surface oxygen atoms for the C-S-H at the studied Ca/Si ratios. (b) Water dipole moment in bulk water, C-S-H with Ca/Si ratio of 1.1 and 2.0. (c) Hydrogen bond lifetimes for bulk water and water confined in C-S-H at the studied Ca/Si ratios. Red, blue, yellow and green lines correspond to the C-S-H systems with Ca/Si ratios of 1.1, 1.3, 1.67 and 2.0, respectively, whereas the black line is referred to bulk water.

Conclusions

In this work, we have explored the role of the Ca/Si ratio in the retention and diffusivity of Cs confined in a C-S-H nanopore of 1 nm at constant Cs concentration, 0.26 Cs/mol of C-S-H. For that reason, we have developed four C-S-H models with Ca/Si ratios ranging from 1.1 to 2.0. We have studied the distribution of the Cs and intrinsic Ca in the pore, the type of adsorption for both cations, the number of high affinity sites in the C-S-H surface and diffusivity of those cations under different Ca/Si ratios.

The analysis of the arrangement of the species located in the nanopore shows that as the Ca/Si is increased, there are more cations dissolved in the C-S-H nanopores. In fact, the number of Cs desorbed at Ca/Si ratio of 2.0 is almost twice than at a ratio of 1.1. The type of adsorption is also modified at different Ca/Si ratios. As the Ca/Si ratio is increased, the silicate chains are shortened by deletion of bridging silicate groups, making the pairing silicate groups more accessible to the cations. Thus, the number of outer-sphere adsorption sites, which involve preferably bridging silicates, decreases, while it is increased the number of inner-sphere adsorption sites, based basically on the pairing silicates. Nevertheless, the increase of inner-sphere adsorption sites does not compensate the loss of outer-sphere ones, so the total number of high affinity sites in the C-S-H surface is reduced at almost half of the total at low Ca/Si ratios.

The study of dynamics of the species located in the nanopore shows that their diffusivity is progressively reduced as the Ca/Si ratio rises. For Cs ions, the reduction of its diffusion coefficient is over 90% for the C-S-H with the highest Ca/Si ratio studied with respect to the one with the lowest ratio. The increase of the hydrophilicity of the C-S-H nanopore as the Ca/Si ratio grows is the main responsible of the decrease of water diffusivity. The higher number of dangling oxygen atoms in the C-S-H surface at higher Ca/Si ratios, facilitates the formation of hydrogen bonds between the surface and the pore water. This reduces the mobility of the water molecules in the vicinities and induces a long-range ordering, polarizing the water molecules and reducing the global diffusion coefficients. Likewise, the cations, especially Ca ions, whose content grows at higher Ca/Si ratios, also contribute to increase the electrostatic field that polarizes the water molecules and enhances the hydrogen bond network. Thus, the motion of the water molecules is hindered, and consequently it hinders the motion of the cations solvated in the pore. Therefore, despite having much worse retention at high Ca/Si ratios, the diffusion coefficients of Cs ions in the nanopore decrease. Nevertheless, in order to prevent the released of Cs confined in C-S-H nanopores, is essential strong retention in the sorption sites rather than low diffusivity in the pore.

Author information

*E-mail: eduardo.duque@ehu.eus

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References

- 1 A. T. Ramalho and A. C. H. Nascimento, *Health Phys.*, 1991, **60**, 67–70.
- 2 M. Jantunen, A. Reponen, P. Kauranen and M. Vartiainen, *Health Phys.*, 1991, **60**, 427–434.
- 3 A. Real, S. Sundell-Bergman, J. F. Knowles, D. S. Woodhead and I. Zinger, *J. Radiol. Prot.*, 2004, **24**, A123–A137.
- 4 J. Real, F. Persin and C. Camarasa-Claret, *J. Environ. Radioact.*, 2002, **62**, 1–15.
- 5 F. Macáček, in *Natural Microporous Materials in Environmental Technology*, Springer, 1999, pp. 109–135.
- 6 F. P. Glasser and M. Atkins, *MRS Bull.*, 1994, **19**, 33–38.
- 7 K. Volchek, M. Y. Miah, W. Kuang, Z. DeMaleki and F. H. Tezel, *J. Hazard. Mater.*, 2011, **194**, 331–337.
- 8 P. Hewlett, *Lea's chemistry of cement and concrete*, Butterworth-Heinemann, 2003.
- 9 T. M. Krishnamoorthy, S. N. Joshi, G. R. Doshi and R. N. Nair, *Nucl. Technol.*, 1993, **104**, 351–357.
- 10 K. G. Papadokostaki and A. Savidou, *J. Hazard. Mater.*, 2009, **171**, 1024–1031.
- 11 C. Shi and A. Fernandez-Jimenez, *J. Hazard. Mater.*, 2006, **137**, 1656–1663.
- 12 N. D. M. Evans, *Cem. Concr. Res.*, 2008, **38**, 543–553.
- 13 R. W. Crawford, C. McCulloch, M. Angus, F. P. Glasser and A. A. Rahman, *Cem. Concr. Res.*, 1984, **14**, 595–599.
- 14 M. Ochs, D. Mallants and L. Wang, *Radionuclide and Metal Sorption on Cement and Concrete*, Springer International Publishing, 2015.
- 15 S. Bagosi and L. J. Csetényi, *Cem. Concr. Res.*, 1998, **28**, 1753–1759.
- 16 E. Duque-Redondo, K. Yamada, I. L. Arbeloa and H. Manzano, 2018.
- 17 H. F. W. Taylor, *J. Am. Ceram. Soc.*, 1986, **69**, 464–467.
- 18 I. G. Richardson, *Cem. Concr. Compos.*, 2000, **22**, 97–113.
- 19 L. B. Skinner, S. R. Chae, C. J. Benmore, H. R. Wenk and P. J. M. Monteiro, *Phys. Rev. Lett.*, 2010, **104**, 195502_1–195502_4.
- 20 M. Tsuji, S. Komarneni and P. Malla, *J. Am. Ceram. Soc.*, 1991, **74**, 274–279.
- 21 S. Komarneni, D. Roy, C. Fyfe and G. Kennedy, *Cem. Concr. Res.*, 1987, **17**, 891–895.
- 22 S. Komarneni and M. Tsuji, *J. Am. Ceram. Soc.*, 1989, **72**, 1668–1674.
- 23 M. Miyake, S. Komarneni and R. Roy, *Mater. Res. Bull.*, 1989, **24**, 311–320.
- 24 J. Jiang, P. Wang and D. Hou, *Phys. Chem. Chem. Phys.*, 2017, 27974–27986.
- 25 M. J. Abdolhosseini Qomi, K. J. Krakowiak, M. Bauchy, K. L. Stewart, R. Shahsavari, D. Jagannathan, D. B. Brommer, A. Baronnet, M. J. Buehler, S. Yip, F.-J. Ulm, K. J. Van Vliet and R. J. M. Pellenq, *Nat Commun*, 2014, **5**, 1–10.
- 26 E. Duque-Redondo, K. Yamada, I. López-Arbeloa, H. Manzano, E. D. REDONDO, Y. Kazuo, I. López-Arbeloa and H. Manzano, *Phys. Chem. Chem. Phys.*, 2018, (In press).
- 27 E. Bonaccorsi, S. Merlino and A. R. Kampf, *J. Am. Ceram. Soc.*, 2005, **88**, 505–512.
- 28 K. Chenoweth, A. C. T. van Duin and W. A. Goddard, *J. Phys. Chem. A*, 2008, **112**, 1040–1053.
- 29 J. C. Fogarty, H. M. Aktulga, A. Y. Grama, A. C. T. van Duin and S. A. Pandit, *J. Chem. Phys.*, 2010, **132**, 174704_1–174704_10.
- 30 H. Manzano, R. J. M. Pellenq, F.-J. Ulm, M. J. Buehler and A. C. T. van Duin, *Langmuir*, 2012, **28**, 4187–4197.
- 31 R. Shahsavari, R. J.-M. Pellenq and F.-J. Ulm, *Phys. Chem. Chem. Phys.*, 2011, **13**, 1002–1011.
- 32 J. Åqvist, *J. Phys. Chem.*, 1990, **94**, 8021–8024.
- 33 S. Plimpton, *J. Comput. Phys.*, 1995, **117**, 1–19.
- 34 P. P. Ewald, *Ann. Phys.*, 1921, **369**, 253–287.
- 35 L. Verlet, *Phys. Rev.*, 1967, **159**, 98–103.
- 36 J. J. Chen, J. J. Thomas, H. F. W. Taylor and H. M. Jennings, *Cem. Concr. Res.*, 2004, **34**, 1499–1519.
- 37 K. Fujii and W. Kondo, *J. Chem. Soc. Dalt. Trans.*, 1981, 645–651.
- 38 X. D. Cong and R. J. Kirkpatrick, *J. Am. Ceram. Soc.*, 1996, **79**, 1585–1592.
- 39 J. J. Thomas, J. J. Chen, H. M. Jennings and D. A. Neumann, *Chem. Mater.*, 2003, **15**, 3813–3817.
- 40 J. S. Dolado, M. Griebel and J. Hamaekers, *J. Am. Ceram. Soc.*, 2007, **90**, 3938–3942.
- 41 X. Cong and R. J. Kirkpatrick, *Adv. Cem. Based Mater.*, 1996,

- 3**, 144–156.
- 42 E. A. Guggenheim, *Thermodynamics-an advanced treatment for chemists and physicists*, 1985.
- 43 F. P. Glasser, in *MRS Proceedings*, Cambridge Univ Press, 2002, vol. 713, pp. 721–732.
- 44 S.-Y. Hong and F. P. Glasser, *Cem. Concr. Res.*, 1999, **29**, 1893–1903.
- 45 M. Brehm and B. Kirchner, *J. Chem. Inf. Model.*, 2011, **51**, 2007–2023.
- 46 A. Einstein, *Ann. Phys.*, 1905, **322**, 549–560.
- 47 K. Krynicki, C. D. Green and D. W. Sawyer, *Faraday Discuss. Chem. Soc.*, 1978, **66**, 199–208.
- 48 M. W. Mahoney and W. L. Jorgensen, *J. Chem. Phys.*, 2001, **114**, 363–366.
- 49 A. G. Kalinichev, J. W. Wang and R. J. Kirkpatrick, *Cem. Concr. Res.*, 2007, **37**, 337–347.
- 50 H. Manzano, S. Moeini, F. Marinelli, A. C. T. van Duin, F.-J. Ulm and R. J. M. Pellenq, *J. Am. Chem. Soc.*, 2012, **134**, 2208–2215.
- 51 M. J. A. Qomi, M. Bauchy, F.-J. Ulm and R. J.-M. Pellenq, *J. Chem. Phys.*, 2014, **140**, 054515_1–054515_11.
- 52 P. A. Bonnaud, H. Manzano, R. Miura, A. Suzuki, N. Miyamoto, N. Hatakeyama and A. Miyamoto, *J. Phys. Chem. C*, 2016, **120**, 11465–11480.
- 53 L. Yuan-Hui and S. Gregory, *Geochim. Cosmochim. Acta*, 1974, **38**, 703–714.
- 54 N. W. Ockwig, J. A. Greathouse, J. S. Durkin, R. T. Cygan, L. L. Daemen and T. M. Nenoff, *J. Am. Chem. Soc.*, 2009, **131**, 8155–8162.
- 55 M. Youssef, R. J. M. Pellenq and B. Yildiz, *J. Am. Chem. Soc.*, 2011, **133**, 2499–2510.
- 56 F. Coudert, R. Vuilleumier and A. Boutin, *ChemPhysChem*, 2006, **7**, 2464–2467.
- 57 H. J. C. Berendsen, J. P. M. Postma, W. F. van Gunsteren and J. Hermans, in *Intermolecular forces*, Springer, 1981, pp. 331–342.