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## **Alkali silica reaction: a view from the nanoscale**

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# Abstract

Understanding the formation of Alkali-silica reaction gel (ASR gel) and its behavior in cement pore network solutions is the key to mitigate one of the main causes of the strength retrogression of concrete. We herein propose a scenario to explain how ASR formation in cement pores can damage the cement paste structure that is supported by state-of-the-art atomistic simulations. We show the formation of an ASR gel at the atomic scale and how the drying or calcification affects its structure and strength. Moreover, we demonstrate that the alkali ions that are released during calcification are attracted by the gel and remain in its vicinity. The high concentration of ions in the solution modifies the interaction of the ASR gel with the cement pore walls and can lead to concrete damage.

## I. INTRODUCTION

Cement is widely used as a construction material. It is a highly connected porous structure [1] mainly composed of calcium silicate hydrate gel (C-S-H gel). After hardening, an important cause of cement loss of durability is the formation of alkali-silica reaction gels (ASR gel) in the pore network. The ASR gel formation is initiated by the dissolution of aggregates in mature cement pore solution but the reason why it creates cracks and damage in the cement matrix is not completely understood because of the complexity of the mechanisms. Over the recent decades, this phenomenon has motivated many studies [2–4] showing the general need for improving the lifetime of cement and to reduce environmental costs [5, 6]. It is generally well accepted that ASR gel forms in the pore network due to the presence of a high concentration of alkali in a solution that stems from the dissolution of metastable minerals at high-pH. Nonetheless, there is no consensus on how this gel will create cracks in cement-based materials.

On one hand, studies of the ASR has lead to the general idea that ASR gel does not flow in the cement pore network due to its viscosity or its hardness [7–15]. In order to build up pressure that can damage the cement structure, the ASR gel must have to withstand more pressure than the cement pore walls. On the other hand, other studies suggested that ASR gel is a soft and compressible material, which can expand in the pore network of cement and which displays yield stress of 10 kPa [16, 17] and a bulk modulus as low as 0.1 MPa [18]. It has been shown by electron spectroscopy measurements that the ASR gel is found in all the

microporous structures of the cement matrix, which indicates that it can flow in the pore network[16].

The disagreement between these different hypotheses stems from the variety and complexity of the systems as well as the difficulty in characterizing them. Moreover, ASR gel formation is followed by other mechanisms, such as alkali recycling due to the leaching of alkali ions from the ASR gel itself to the pore network solution. This could refuel the reaction of the ASR gel formation and a high concentration of alkali could also create dis-joining pressure if the ions remain in the vicinity of the gel[19].

A complete understanding of the atomistic structure is essential to predict how chemical conditions will influence the formation of ASR gel and its structure. So far, no atomistic models have been proposed to explain the formation and hardening of this gel, which is the key to understand the damage process. Herein, we propose an approach based on brief-parallel tempering [20] (a method to accelerate the reaction of atoms) to observe the formation of the ASR gel in solution. We show that is a soft gel that can flow in the pore network. In that framework, we then simulate the several mechanisms that could transform the ASR gel: the gel drying over time due to water evaporation that will reinforce its mechanical properties; the calcification of the gel that will increase its viscosity and clog the pore network leading to damage due to the formation and growth of the ASR gel; and, the high concentration of ions in the pore solution at the interface between the ASR gel and the cement pore walls that will modify the interaction between the ASR and the C-S-H gels. Although these ions could play an important role in the pore network clogging and in building up pressure on the C-S-H pore walls, their localization at the atomic scale has not been thoughtfully studied yet.

## II. SIMULATION METHODS

In order to determine the structure of ASR gels, we have first simulated the formation of such systems starting from a solution containing only silicate monomers, water and alkali cations ( $K^+$  and  $Na^+$ ). In Figure 1, a possible scenario of damage due to ASR gel formation is proposed. The gel formation corresponds to stage (ii) shown in figure 1, the gel starts to form in a solution containing highly dispersed silicates and alkali ions.

The formation of oligomers is a slow process compared to times reachable by Molecular

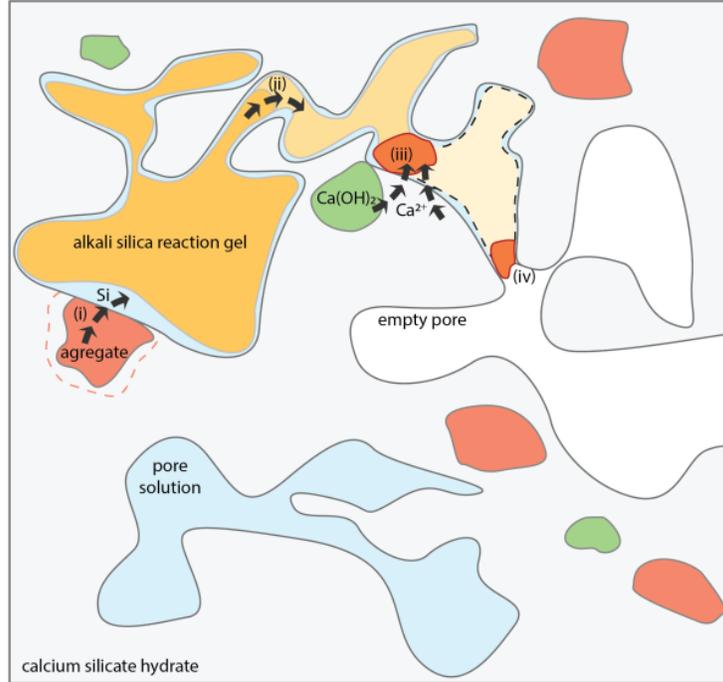


FIG. 1. Process of Alkali silica reaction gel formation leading to damage with ASR flow in the pore network. The C-S-H matrix is in grey, the water is in blue, the empty pore is in white, the ASR gel is in orange, the aggregates are in red and portlandite is in green. (i) Due to high pH, the formation of ASR gel is preceded by the dissolution of aggregates in the pore solution. ASR gel is formed in the solution in presence of an high concentration of silicates and ions. The ASR gel structure has to be determined from atomistic calculations. (ii) The soft gel grows in the highly-connected pore network due to the production of ASR gel. (iii) Calcification will harden the ASR gel and release ions into the pore network solution that will strengthen the ASR/C-S-H gel interaction. The pore network will be clogged and the gel hardness is increased at the surface. The process of calcification is investigated herein. (iv) As shown hereafter, drying of the gel will participate to clogging the pore network if the pore network is not entirely saturated with water. Drying, which is still misunderstood at the atomic scale, can affect measurements of the mechanical properties.

Dynamics (MD) simulations due to the energy barrier of 0.2-0.6 eV to form Si-O bonds [21, 22]. We have used a recent accelerated simulation method, which is based on the parallel tempering method (PT), also called replica exchange [23]. In PT, the system of interest is replicated several times and each replica runs at different temperatures – high-temperature replica having a higher probability of crossing high-energy barriers. After a given time, two

configurations can be exchanged. In the case of brief-PT, the PT is regularly interrupted leading to low-temperature states periodically repopulating the ensemble of simulations [20]. The aim of such a method is to overcome large energy barriers that are limiting the range of times that can be reached by classical MD simulations. This enables us to observe the formation and dissociation of high-energy barriers and thus accelerate the dynamics by several orders of magnitude[20, 24].

As described hereinafter, the gel that has been formed in those conditions is a non-viscous gel with relatively low connectivity. Therefore, we investigated a scenario in which the gel can flow in the pore network and can be transformed due to changes in the local chemical composition (drying or calcification).

The second stage of simulations consists in drying the system, which corresponds to stage (*iv*) shown in Fig. 1. To dry the system, we simply remove water molecules from the gel that has been previously formed and we monitor the temporal evolution of its microstructure.

The final stage of simulations corresponds to calcification [i.e., stage (*iii*) in Fig. 1]. The goal of this method is to study the replacement of  $\text{Na}^+$  and  $\text{K}^+$  in ASR gels by  $\text{Ca}^{2+}$  and keep an interface between the gel and the surrounding solution. A standard molecular dynamics would not diffuse fast enough the cations to do the exchange since this process happens at longer time scales (i.e., in general months). For this, a new simulation cell is built. On the right side, it contains the hydrated gel that has been previously formed. On the left side it contains a solution containing  $\text{Ca}^{2+}$  [ Fig. 4(a)]. The two parts are separated by a reflective wall that can not be crossed by ions. During the dynamics, we have made grand canonical Monte Carlo steps in order to substitute  $\text{Ca}^{2+}$  with 2  $\text{Na}^+$  (or 1  $\text{K}^+$  and 1  $\text{Na}^+$ , or 2  $\text{K}^+$ ) in the solution. In this simulation, the ions from one side or the other of the wall are in interaction as if there was no wall. The purpose of this wall is to separate clearly the solution from the gel and avoid mixing both parts so as to study in detail the interface between the solution and the gel.

All the simulations were carried out with LAMMPS [25]. The system contains 100 Si atoms, 100  $\text{Na}^+$  and 10  $\text{K}^+$  (and 55  $\text{Ca}^{2+}$  ions for the calcification simulation). The whole simulation box contains 1100 water molecules and has the following dimensions  $33 \times 33 \times 44 \text{ \AA}^3$ . Note that ASR gels composition in cement can vary from sample to sample[26, 27] and the alkali composition affects the gel's structure[28]. Herein, considering the computational cost of the method, we have simulated the gelation of a single alkali-silica gel with a model

composition of Na/Si=1, Ca/Si=0.1, K/Si=0.1, and 40% water content. This configuration corresponds to experimental studies on ASR gel formation under controlled humidity[27]. The gels were synthesized under 95% relative humidity and contain approximately of 40% water for the gel composition that has been simulated herein.

The time step is 0.25 fs, in order to ensure that water molecule dynamics are correctly reproduced. Reactive potentials of the type ReaxFF [29] have been employed, with the widely used parameter set of Forgaty et al. [30]. Those parameters have been calibrated to study silicate materials and reproduce the correct energy barrier for the formation of Si-O bonds compared to DFT calculations [20], which is essential to study the formation of the ASR gels. It has shown good performances to reproduce the silicate gel formation [20]. For the brief-PT method, we have used 16 replicas with temperatures ranging from 300K to 800K. The PT exchanges have been intended every 50 steps. ASR gel formation happens on a long time scale that is inaccessible with classical MD at room temperature, this method allows to quickly observe Si-O bond formation or dissociation that is necessary for the formation of the ASR gel, thus enhancing the dynamics.

### A. Gelation

Nuclear magnetic resonance of  $^{29}\text{Si}$  has long been used to study the structure of silicates. By simulations, we can evaluate the quantity of Si in each site from  $Q^0$  to  $Q^4$  during the ASR gel formation. To catch the evolution of the speciation, we report in Fig. 2 the quantity  $Q^n$  that reflects the connectivity of the silicate species in solution, where n is the number of Si-O-Si bonds associated to one Si (e.g.  $Q^0$  is a silicate monomer). Since the simulation starts in a solution containing only silicate monomers, initially, all Si are in a  $Q^0$  site. At the beginning of the simulation, the number of  $Q^1$  rises from zero, while the first dimers are formed in solution. The quantity  $Q^1$  quickly reaches a maximum of 50% of the total number of silicon atoms and we observe the increase of  $Q^2$ , which indicates the formation of long linear chains of silicates. After convergence of the  $Q^n$  distribution, almost half of the silicon atoms are in a  $Q^2$  position. Moreover, the sum of  $Q^3$  and  $Q^4$  is about 45% leaving the remaining 5-10% for the  $Q^1$ . This indicates that all the monomers have reacted and that the silicate chains that have been formed are long (as shown by the large quantity of  $Q^2$ ) and contain rings, which is indicated by the presence of  $Q^3$  and  $Q^4$ .

Measurements on synthetic ASR gels [28, 31] or extracted from concrete samples [32] show that most of the structures are dominated by  $Q^2$  and  $Q^3$ , which is what we observe in the simulation. In particular for  $Na/Si = 1$ ,  $Q^2$  are prominent in NMR and Raman spectroscopy measurements [28]. In recent studies, it has been shown that pure silicate gels have lower silicate connectivity than alkali-rich silicates [20, 24]. In this work, we observe that ASR gels are more connected than pure silica gels simulated using the same method [20, 33]. At the same water/Si ratio, the simulated ASR gel has  $Q^0=0\%$ ,  $Q^1=10\%$ ,  $Q^2=40\%$ ,  $Q^3=40\%$ ,  $Q^4=10\%$ , whereas the pure silica gel has  $Q^0=10\%$ ,  $Q^1=25\%$ ,  $Q^2=40\%$ ,  $Q^3=20\%$ ,  $Q^4=5\%$ . This result indicates the role of ions in the structuration of silicate chains, i.e., the increase of crosslinks is solely due to the presence of ions in the initial solution. In the gel, ions have a dual role: they act as a charge compensator near a  $Si-O^-$  groups that are more reactive than  $Si-OH$  groups, or they are solvated. Solvated ions will impede water molecules from hydrolyzing silicate chains and therefore help the formation of structures with more crosslinks [34]. Note that  $Na^+$  ions are also bond-makers in silica glass.

In order to compute the bulk modulus, we have used the elastic bath method [35, 36] developed for soft materials. In this technique, we couple the simulation cell to an elastic bath (here we have used a bath with a strength of 5 GPa). The calculated bulk modulus for the ASR gel is 0.1 MPa, which is in agreement with mechanical tests showing weak mechanical properties in humid ASR gels [37]. This is one order of magnitude less than the C-S-H tensile strength of about 3 MPa [38] and two to three orders of magnitude less than the bulk modulus calculated for C-S-H gel structures using ReaxFF [39]. This value at 40% water content is in the order of magnitude of experimental values measured for the swelling pressure caused by ASR formation [18]. The simulation results show that the ASR gel, which is formed at high relative humidity in the cement pore network, is a non-viscous gel with low mechanical properties compared to the C-S-H gel. In order to create cracks in the cement structure, this gel has to overcome physical transformation in order to strengthen itself or to clog the pore network. Hereinafter, we investigate the role of drying and calcification on the structure of the ASR gel.

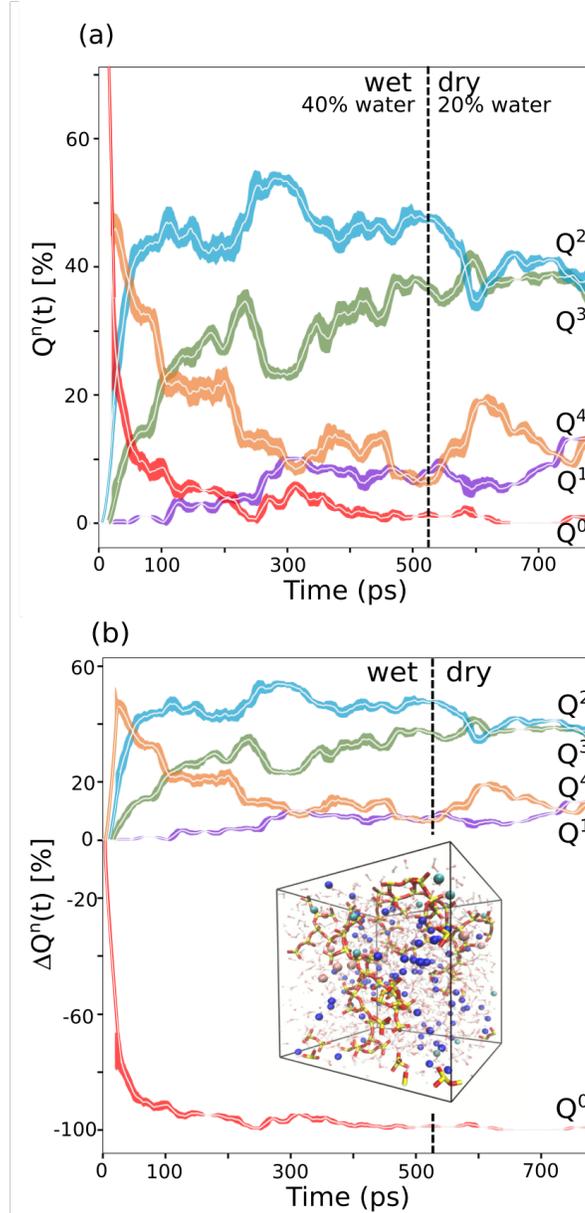


FIG. 2. (a) Evolution of  $Q^n$  during the simulated formation of the gel and drying. The shadow corresponds to the standard error calculated over the 500 previous steps. (b) variations  $\Delta Q^n$  during the formation of the gel and drying. The inset is a snapshot of the ASR gel at 40% water content after formation. It shows the highly connected silicate structure of the silicate chains.

## B. Drying

Drying has been identified as a possible cause of atomistic rearrangement in silica gels[16, 40]. One of the reasons is that dry gels could have a composition close to hydrated glasses and

form siloxane bridges at low temperatures. This is likely to affect the results of experiments obtained in non-controlled humidity environments to measure the structural and mechanical properties of ASR gels [20]. In order to investigate the effect of drying on the structural properties of ASR gels, we have removed half of the water molecule from the system (the water content is 20% of the mass in order to simulate water retention from the gel). The evolution of  $Q^n$ , as shown in figure 2, is quick towards densification.

In Fig. 2(a and b), we observe on the right side that the drying also has an effect on the connectivity of the ASR gel. In particular, there is an increase in the number of  $Q^4$  and a decrease in the number of  $Q^2$ . However, the evolution of the connectivity is not as marked as it is for pure silica gels[20]. This can be explained by the fact that ASR gel already contains 40%  $Q^3$  and 5%  $Q^4$  at 40% water content. Nonetheless, it is important to note that after drying, the silicate chains are percolating in two points (species that are connected all across the simulation cell). This is due to the densification of the gel at 20% water content (see Figure 4(b and d)). The percolation of gels at the atomic scale can be seen as the limit between a gel structure and a colloidal structure. This is reflected in an increase in the mechanical properties as we calculated that the dried gel has a bulk modulus of 10 GPa. This is consistent with the percolation which is observed in the system and it indicates the strength of silica gels is mostly due to the silica chains and the loss of durability of silicate structures is linked to the reverse oligomerization process [41, 42]. This value is lower but in the same order of magnitude as the values reported for C-S-H gels in the literature (50-70GPa)[39, 43, 44]. Those values, calculated for the C-S-H gels, have been calculated on well-ordered atomic arrangements so the calculated values correspond to the highest expected values. More realistic values have been calculated recently using density functional theory calculations on amorphous C-S-H gel structures with defects. The reported values for Young's modulus range from 18 to 25 GPa [45], which is close to the value we have obtained for the dried ASR gel. Our results indicate that the bulk and Young's modulus of silica-based gels (e.g. N-A-S-H, C-A-S-H [46]) is strongly related to the connectivity in the gels and to the degree of percolation of the silicate chains. Ions, being in the solution, affect the mechanical properties indirectly by playing a bond-builder or bond-breaker role. Therefore, determining the atomistic structure of these gels and their connectivity is essential. In agreement with the experiments, we observe that the loss of water has a drastic effect on the structural properties of ASR gel[40]. Such a drying could

occur in different regions of the porous network and in particular in micro-cracks in which more crystalline ASR structures has been measured[16]. Note that in our simulations, the effect of drying is reversible if we increase the water content from 20% to 40%.

In summary, the drying does not have a large influence on the connectivity of the system but it drastically changes the shape of the silica chains and we observe percolation at HR=20%. These results indicate the importance of considering the humidity in the systems when doing measurements of the atomistic structure and mechanical properties of ASR gels. Moreover, the drying could increase the viscosity and clog the pore network in the case of the formation of ASR gel in an unsaturated pore network [Fig. 1(iv)]. This could be one cause of the irreversible damages observed in cement structures. Other effects can also modify the atomistic structure and increase the mechanical strength, in particular calcification of the ASR gel.

### C. Calcification

Calcification could reduce the flowability of the gel and add up with other mechanisms such as swelling (in particular due to water intake), clogging of the pore network, production of additional ASR gel, and lead to damage. It is important to understand the difference between divalent and monovalent ions in the structuration of the gels. The process of calcification has been simulated using the method described in section II and Fig. 1(iii). Herein, we investigate the evolution of the silicate connectivity, the behavior of ions released in the solution.

Swelling of the ASR gel after calcification is often suggested as a cause of the cement damage because it could induce pressure on the cement pore walls[47]. As observed on Fig. 4(d,e), the calcification of the ASR gel shrinks the gel and increases its density. This suggests that in-situ, the swelling could be due to an intake of water. Experimentally, it has been observed that calcium in ASR gels modifies its swelling properties[27] and that some gels don't swell. In the simulations, the swelling can not explain pressure build-up on cement but the calcification will affect the atomistic structure in several different ways. Therefore, it is necessary to investigate other effects than swelling that could be caused by calcification.

To separate the effects of drying and calcification, the calcification has been performed on

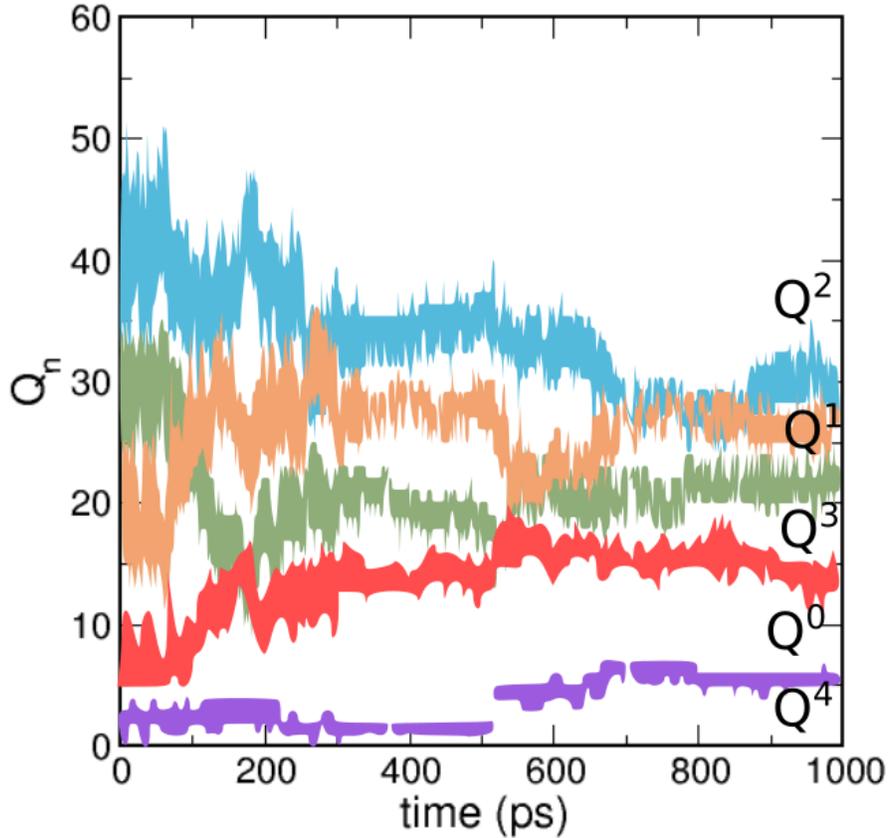


FIG. 3. Evolution of  $Q^n$  during a simulation of the calcification. Ions are being exchanged during the first 100 ps of the simulation until all ions has been exchanged. During the last 900 ps of the simulation, ions are not exchanged.

the structure with 40% of water content. Figure 3 shows the evolution of the connectivity in the gel during and after calcification. The first result is that the number of crosslinks, indicated by  $Q^3$  and  $Q^4$ , has changed during the calcification. The number of  $Q^3$  is reduced by about 10 and the number of  $Q^4$  is increased by about 4. This is in agreement with experimental data[28] showing that gels with calcium have more  $Q^4$  than gels with only alkali. The mean-chain length has increased and the longest silicate chain has percolated through the whole simulation cell (more than  $33\text{\AA}$ ). The final structure is mostly composed of  $Q^2$  (50%) that corresponds to the bonding often observed in calcium silicate hydrate gels [48]. When the simulated gel calcifies, the bulk modulus of the gel increases by 2 orders of magnitude (from 0.1 GPa to 10 Gpa).

In the initial stage [Fig. 4(a) and (b)], the density of silicates is almost constant across

the simulation cell – in the gel side of the simulation box. After exchanging calcium ions, we can observe a densification of the silicates towards the edge in contact with the solution [Fig. 4(d)]. The density distribution of  $\text{Ca}^{2+}$  follows a similar trend since most of those ions have been exchanged with the solution. Meanwhile, the density of  $\text{Na}^+$  near the reflective wall surface is higher than far from the surface.

#### D. Role of alkali ions during calcification

The released alkali ions remain in the vicinity of the ASR gel and do not diffuse freely in the gel’s pore solution because they are interacting with the negatively charged ASR gel surface. Note that this effect is not observed with  $\text{Ca}^{2+}$  ions before ionic exchange. This can be explained by the fact that in the gel,  $\text{Na}^+$  and  $\text{K}^+$ , being monovalent, will compensate the charge locally near the  $\text{Si-O}^-$  sites whereas  $\text{Ca}^{2+}$ , being divalent, will compensate the charge for two  $\text{Si-O}^-$  sites. As a result, after calcification, the charges on the silicate chains are partially but not completely screened by  $\text{Ca}^{2+}$  ions in the gel.

It is often suggested that alkali ions are ”recycled” after calcification to dissolve aggregates and pursue the alkali-silicate reaction[49]. Herein we show that alkali ions that remain attracted by the ASR gel after leaching will not fully be reused to dissolve more aggregates as often suggested in the models. In our model, only 20% of the alkali ions are localized at a distance larger than  $5\text{\AA}$  from the ASR gel surface. Note that these ions could diffuse at longer time scales in the solution and reused to form ASR gel.

The presence of alkali ions near the ASR gel surface will drastically change how the ASR gel interacts with the cement pore walls that are negatively charged at the surface due to the presence of anionic groups. For instance, the interaction between C-S-H nanoparticles in cement is mostly due to the presence of ions in the solution in-between the nanoparticles [50]. In line with primitive model results[19], the disjoining ASR-CSH osmotic pressure that develops could be due to this alkali layer at the interface between the rigid-CSH wall and the rigid Ca-ASR gel. Hence our results support that the origin of cement paste degradation due to ASR results from the Ca to Na exchange over time, which can happen over years. This paves the way to reconstruct the interaction potential between two ASR gel aggregates using a fully atomistic approach. Moreover, a study of the potential mean force acting on the C-S-H and on the ASR gel (using the microstructures) for different alkali concentrations

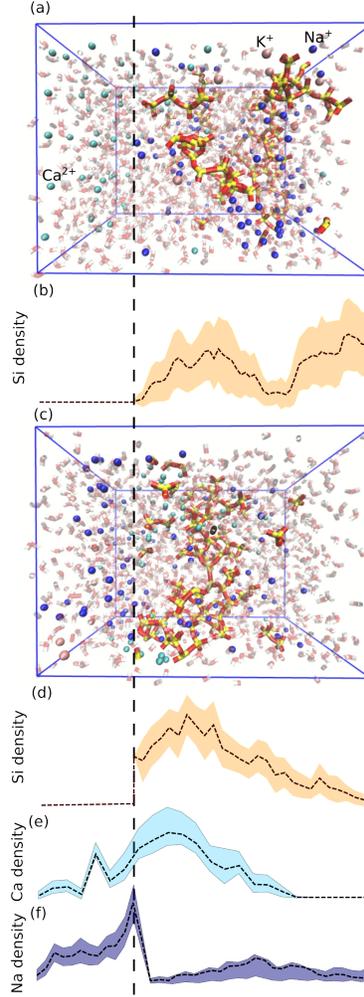


FIG. 4. During the initial steps (a) the solution contains only calcium and the gel has a composition of  $\text{Na}/\text{Si} = 1$ ,  $\text{Ca}/\text{Si}=\text{K}/\text{Si}=0.1$ . The density of silicates (b) is well distributed in the box and several species has been formed. During calcification (c), the alkali ions in the solution has been replaced by  $\text{Ca}^{2+}$ . The final density profile of silicates (d) shows that silicates are attracted by the ions in the solution. In the final state, (e) the gel is filled with  $\text{Ca}^{2+}$  and (f) the solution is filled with  $\text{Na}^+$ .

could give interesting insights on the poremechanical properties of this system [51, 52] and in particular on the influence of the ionic concentration and the type of ions (monovalent or divalent).

The fact that ions remain close to the ASR gel opens new areas of research to try to mitigate ASR damage at a low cost. To understand mitigation, the investigation of the role of ions appears to be key since they play a role at all stages of the ASR gel transformation

(during the dissolution of aggregates, during the formation of ASR gel in the pore network, and during calcification). Since the ASR gel is mostly material with low mechanical properties compared to the C-S-H gel, understanding the diffusion of ions during calcification by atomistic simulation is essential. In order to mitigate ASR damage, one option would be to remove the alkali from the solution in the interlayer between the C-S-H and the ASR gels. For this, the models that we propose can be deployed to study the competition between different ions and their affinity to the C-S-H and the ASR gel surfaces. For instance, lithium salts are used in ASR gel mitigation[53] but it is still unclear how it can mitigate damage. Little is known on the role of lithium as it has primarily been considered as a mitigator of the aggregate dissolution, this could be assessed with the method developed herein.

More recently, studies have shown that it is possible to mitigate the freeze-thaw damage by rendering the C-S-H surface hydrophobic, for instance by using carbon particles [54]. A similar approach could be designed for the mitigation of ASR damages since the presence of ions near the gel is herein identified as a factor of risks. Depleting the interlayer of water and alkali could be done similarly by rendering the surface hydrophobic.

### III. CONCLUSION

The atomistic structure of ASR gels has been obtained for the first time from a solution in which silicates are all in a monomeric form. For this, the brief-PT method, which is an accelerated molecular dynamics method, has been performed. The structure that has been formed for wet ASR gel indicates that it is a soft material with low mechanical strength, which contradicts the common scenario in which the ASR gel is growing and pressures the cement pore walls leading to irreversible damages.

We have analyzed other mechanisms that can harden the ASR gel or clog the cement pore network and we have shown that both drying and calcification effects lead to a strengthening of the ASR gel that can be one of the causes of the formation of cracks in cement. These results are in agreement with mechanical tests and structure analysis experiments.

Finally, we have revealed that when the calcification occurs, alkali ions are released in the pore solution but they remain near the ASR gel. Therefore, the interactions between the ASR gel and the C-S-H gel are modified. This is another cause that can lead to the appearance of irreversible damages in cement concrete by pressuring the cement pore wall

by the intermediate of an ionic-rich solution. This indicates that the ASR damage could be mitigated by removing the ions that can accumulate in between the ASR gel and the cement pore walls.

#### IV. ACKNOWLEDGEMENTS

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