MOLECULAR DYNAMICS AND REACTION KINETICS ANALYSES OF GAMMA RADIATION IMPACT ON CONCRETE HYDRATION

by

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MOPAC and LAMMPS molecular dynamics codes and reaction kinetics code based on multi-ionic continuum-based model are used to analyze the impact of gamma radiation on concrete hydration. The experimental studies showed that while cured with the low gamma dose concrete shows a statistically significant increase in its strength compared to conventionally cured concrete. The potential reason is the interactions of gamma rays with water causing concrete faster hydration. The question then to ask is would the higher gamma dose enhance the concrete curing further producing its higher strength. This paper provides in-depth numerical analyses of the high-dose gamma radiation effect on concrete based on molecular dynamics and reaction kinetics models. Under these conditions, it is assumed that gamma radiation interacting with water within the concrete induces water radiolysis. These numerical simulations show that the reactivity is generally increased in the presence of electrophiles. However, the early hydration models of tricalcium silicate (alite) and dicalcium silicate (belite) with H^+, OH^-, and H_3O^+ show that the hydration process is slowed down leading to a lower concrete strength. Additionally, the reaction kinetics model used to estimate the effect of $[OH^-]$ on tricalcium silicate hydration shows that an increase or decrease of $[OH^-]$ during tricalcium silicate hydration can respectively slow down or enhance its rate of hydration. The dose necessary to produce the water radiolysis resulting in varying $[OH^-]$ during tricalcium silicate hydration is required to be extremely high and therefore, will damage the concrete structure itself. This leads to the conclusion that increasing the gamma dose to concrete above that used in the experimental studies in order to induce water radiolysis will not improve concrete strength, therefore water radiolysis is not the required condition for improving concrete strength when cured under gamma radiation.

Key words: LAMMPS, MOPAC, early concrete hydration, multi-ionic continuum-based model, alite, belite, water radiolysis, gamma radiation

INTRODUCTION

Studies about cement, adjuvants, and concrete over the last three decades have identified their intrinsic characteristics that influence the concrete strength development and have shown that ultra-high performance concrete with a compressive strength of 150 MPa and even up to 800 MPa can be created [1]. Some of these studies also led to concrete with faster strength development at its early stage of curing in thus providing stronger concrete earlier [2]. The development of new methods to enhance concrete strength and the development of methods to increase the overall strength of concrete are the two areas of research that the concrete industry continuously pursues. As described in [3-5] and shown in fig. 1, the low gamma dose applied to curing concrete leads to an increased concrete strength (in all cases the source is ^{137}Cs). The complexity of concrete structure and variations in the experiments such as but not limited to concrete composition, the process of mixing concrete ingredients and environmental conditions (temperature, humidity) affect the final concrete strength measurements, thus explaining the differences in the values obtained in these experiments.

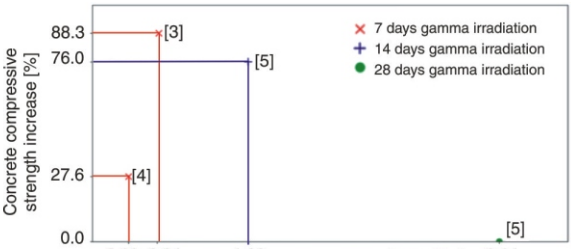

Figure 1. Experimental percent increase of concrete compressive strength as a function of gamma dose and exposure time [3-5]

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The existing and on-going studies on the effects of gamma radiation on concrete refer to matured concrete and high doses in the range of MGy or higher [6-9]. The exposure to high gamma dose has a negative impact on concrete compressive strength as well as its durability. Phenomena that are identified to lead to decreased concrete strength are but not limited to boosted alkali-silica reactions and an increase in concrete temperature. At these high doses, water radiolysis becomes also a significant phenomenon leading to an increase of internal pressure and production and buildup of $H_{2(g)}$ (explosive gas) [6]. Figure 2 describes the water radiolysis process in concrete pores [9, 10]. The interaction of ionizing radiation, such as gamma radiation, with a water molecule, results in water ionization ($H_2O^+ + e^-$) or water excitation (H^2O^*). About 10^{-12} s after the interaction, the e^- thermalizes to become e^-_{aq}. During the same time, the excited water molecules and ionized water molecules undergo different processes in creating new radicals and molecules that interact with themselves and water itself. Between 10^{-12} and 10^{-6} s, these radicals and molecules continue to interact between themselves and water but also diffuse within the water. At 10^{-6} s, the new species are created, the four different radicals (H, OH, HO_2, and e^-_{aq}.) and four different molecules (H_2, H_2O_2, OH^-, and H_3O^+), also called the primary products. H_3O^+ is also sometimes replaced in the primary products by H^+ [11]. Their production yields are expressed in molecules per 100 eV deposited in water. These yields are dependent on pH and the linear energy transfer (LET). The presence of some of the primary products of water radiolysis (H^+, H_3O^+, and OH^-) in small quantity improves the reactivity of tricalcium silicate and dicalcium silicate with water [5] and therefore the reason to investigate further their potential effect on early concrete hydration.

Tricalcium silicate and dicaldium silicate, also called alite and belite, respectively, are the two compounds of cement (representing one of the main components of concrete) that contribute the most to concrete strength when mixed with water [12]. An improvement of the reactivity of alite/belite with water could mean that alite and belite might react faster with water leading to increased concrete strength. The OH and e^-_{aq}. have the highest production yields at the pH of concrete and are very close to molecules/ions involved during alite and belite hydration (OH^- and H_2O) [9]. Therefore, they could potentially influence their hydration. Knowing that the alite and belite hydration are extremely complex processes [12] and not fully understood, numerical simulations are then used to analyze the conditions of concrete hydration assuming water radiolysis takes place.

In this paper, we present in-depth numerical analyses of concrete strength development in the presence of high dose gamma radiation using molecular orbital PACkage (MOPAC) and large-scale atomic/molecular massively parallel simulator (LAMMPS) molecular dynamics codes and reaction kinetics code based on multi-ionic continuum-based model (MI-CBM) to understand if the high gamma dose will boost concrete strength. These numerical simulations show that the reactivity of alite with water and belite with water is generally increased in the presence of electrophiles. However, the early hydration models of alite and belite with water containing H^+, OH^-, and H_3O^+ show that the hydration process is slowed down leading to its lower strength. Additionally, the reaction kinetics model used to estimate the effect of $[OH^-]$ alite hydration shows that an increase or decrease of $[OH^-]$ during alite hydration can respectively slow down or enhance its rate of hydration. However, the dose necessary to induce $[OH^-]$ variation (due to water radiolysis) during alite hydration is very high so that it will damage the concrete itself. This leads to the conclusion that using high gamma source intensity and dose to concrete above the one used in the experiment in [4] to induce water radiolysis, will not improve concrete strength.

MOLECULAR DYNAMICS STUDY ASSESSING GAMMA RADIATION IMPACT ON CEMENT HYDRATION

The MOPAC models of alite and belite hydration

The MOPAC model is developed based on the frontier molecular orbital (FMO) theory [13-15]. The

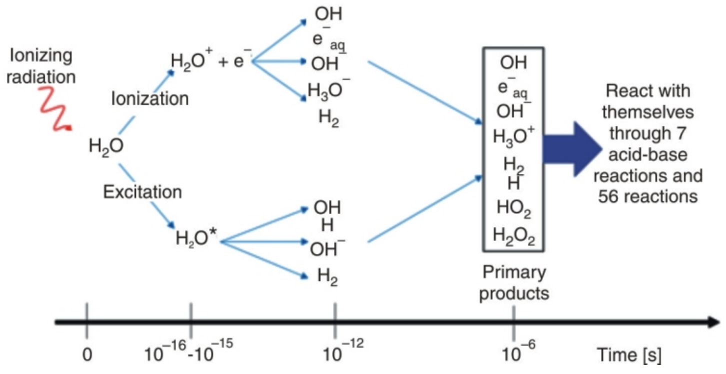


Figure 2. Water radiolysis process in concrete pore [9, 10]

FMO theory can be used to determine how likely a certain reaction is to occur (*i. e.*, reactivity). The theory is based on the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), where HOMO is the orbital with the less energetically bonded electrons, and LUMO is the orbital level that new electrons occupy. Therefore, the HOMO and LUMO of two molecules are analyzed to determine the HOMO-LUMO gap such as HOMO molecule 1 – LUMO molecule 2 or HOMO molecule 2 – LUMO molecule 1. The smaller the gap is, the more likely the reaction is to occur.

The MOPAC semi-empirical molecular dynamics (MD) simulation code, the HOMO and LUMO are calculated for alite ($3CaO \cdot SiO_2$) belite ($2CaO \cdot SiO_2$), jennite [$Ca_9Si_6O_{18}(OH)_6 \cdot 8H_2O$], tobermorite [$Ca_5Si_6O_{16}(OH)_2 \cdot 4H_2O$], water ($H_2O$), and silicate (representing the fine aggregate, (SiO_2) [16, 17]. The reactivity values for the aforementioned six molecule combinations shown in tab. 1 are calculated according to

$$\text{Reactivity} \\ \text{minimum}(\left|\text{HOMO}_1 \quad \text{LUMO}_2\right|, \left|\text{HOMO}_2 \quad \text{LUMO}_1\right|) \tag{1}$$

where 1 refers to Molecule 1 in tab. 1 and 2 refers to Molecule 2 in tab. 1

The H_3O^+, OH^-, H^+, OH, and e^-_{aq}. ions/radicals are added around the alite, belite, jennite, and tobermorite molecules as follow:

– addition of 1 to 10 (increment of 1) H_3O^+ ions,
– addition of 15 to 100 (increment of 5) H_3O^+ ions

Table 1. Molecule combinations used for the reactivity calculations with MOPAC

Molecule 1	Molecule 2
Alite	Water
Belite	Water
Jennite	Water
	Tobermorite
Silicate	Water
	Silicate

For each of these combinations, the HOMO and LUMO are calculated and the reactivity with water or silicate is determined. In each simulation, 18 molecules of alite and 16 molecules of belite are used [18]. Figures 3 and 4 show the reactivity of alite and belite with water in the presence of H_3O^+, OH^-, H^+, OH, and e^-_{aq}., respectively. The reactivity of alite with water is 8.22 eV. As shown in fig. 3, with the addition of few H_3O^+, OH^-, H^+, OH, and e^-_{aq}. ions/radicals, the reactivity decreases, showing a higher chance of interactions between the two molecules. The reactivity decreases to 5.7 eV with the introduction of two H_3O^+ ions *i*. e. to 6.3 eV due to the introduction of four OH^- ions. However, as the number of H_3O^+ and OH^- ions introduced increases, the reactivity increases, approaching its initial value of 8.22 eV. For H^+, OH, and e^-_{aq}., the reactivity value generally decreases and then for H^+ and e^-_{aq}., levels off with the addition of more radicals or ions. Alite is known to be the main compound of concrete that affects its strength at the early stage of curing. Therefore, the early development of concrete strength (between zero and seven days) could

Figure 3. The MOPAC simulated reactivity of alite with water in the presence of H_3O^+, OH^-, H^+, OH, or e^-_{aq}. (initial reactivity represents reactivity of alite with water only)

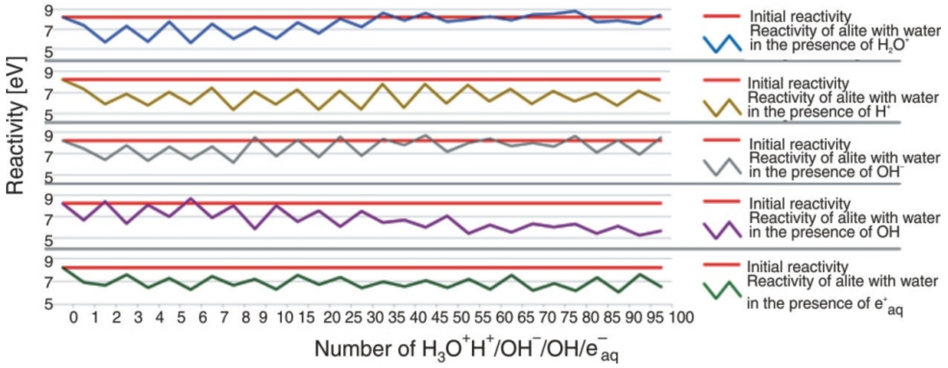
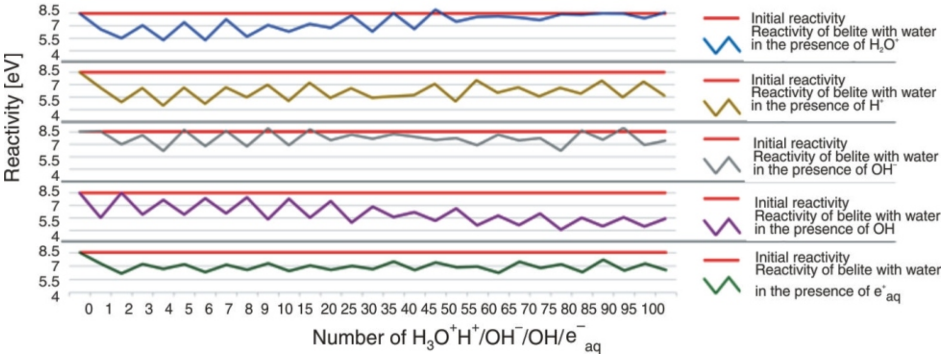


Figure 4. The MOPAC simulated reactivity of belite with water in the presence of H_3O^+, OH^-, H^+, OH, or e^-_{aq}. (initial reactivity represents reactivity of belite with water only)



be faster when cured in the presence of gamma radiation due to increased reactivity of alite with water. However, these reactivity calculations are not time-dependent and therefore can only be seen as predictions [19]. The so-called dynamics models are necessary to further study the effect of high gamma dose on alite hydration and are presented in the next section.

The reactivity of belite with water is 8.53 eV. As shown in fig. 4, the introduction of OH^- ions makes the reactivity oscillate between lower and slightly higher reactivity values, to 6.2 eV with the introduction of four OH^- ions and to 9.0 eV with the introduction of 90 OH^- ions. The reactivity decreases to 5.3 eV with the introduction of four H_3O^+ ions and slowly increases back to the reactivity value of belite with water alone, 8.5 eV, 8.5 eV, 7.9 eV, and 8.6 eV with the introduction of 85, 90, 95, and 100 H_3O^+ ions, respectively. The additions of H^+, OH, or e^-_{aq}. decrease the reactivity value; for example, the addition of 75 OH molecules decreases the reactivity to 4.1 eV. Belite is responsible for the concrete strength development at the late stage of curing (after 7 days). Therefore, the early development of concrete strength (between zero and seven days) could be faster in the presence of products of water radiolysis due to belite reacting faster with water. The dynamics models are necessary to further study the effect of high gamma dose on belite hydration and are presented in the next section.

Alite with water is more reactive than belite with water. An explanation of the higher reactivity of alite with water is that some oxygen atoms in the alite are loosely bound compared to the oxygen atoms in belite and thus react more easily with an electrophile [20]. Hence, it is possible that an electrophile created due to water radiolysis such as H^+, H_3O^+, and OH, will directly react with the alite loosely bound oxygen atoms in thus boosting the alite hydration. This hypothesis is further investigated in the dynamics model presented in the next section.

The MOPAC models for jennite and tobermorite

Calcium silicate hydrate (C-S-H) that is formed as a result of alite and belite hydration, is the main compound of the cement paste responsible for concrete strength [21]. The two most common C-S-H structures are extremely close to the jennite and tobermorite crystal structures, therefore jennite and tobermorite are analyzed [12]. Figures 5 and 6 show the reactivity of jennite and tobermorite with water in the presence of H_3O^+, OH^-, H^+, OH, and e^-_{aq}., respectively. The reactivity of jennite with water is 7.38 eV. By adding H_3O^+ ions, the reactivity is improved for few ions added but as more and more ions are added, the reactivity value increases and goes above the reactivity value of jennite and water only. For OH^- ions, the reactivity value oscillates around the reactivity value of jennite and water only. However, the presence of H^+, OH, or e^-_{aq}, decreases the reactivity; for example, the addition of 95 OH radicals reduces the reactivity to 3.09 eV. The same trends are obtained for

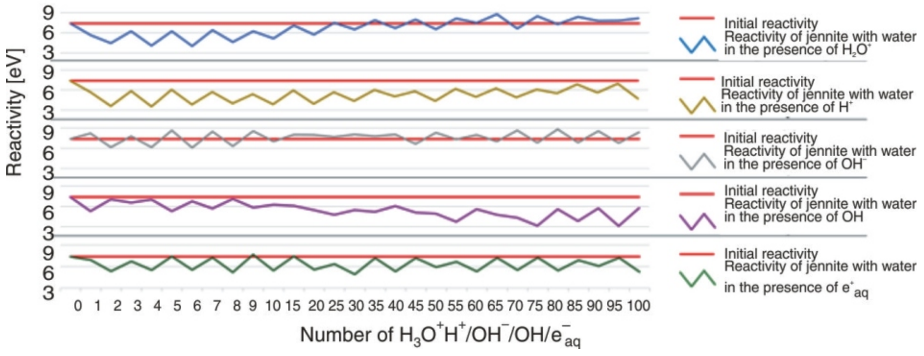


Figure 5. The MOPAC simulated reactivity of jennite with water in the presence of H_3O^+, OH^-, H^+, OH, or e^-_{aq}. (initial reactivity represents reactivity of jennite with the water only)

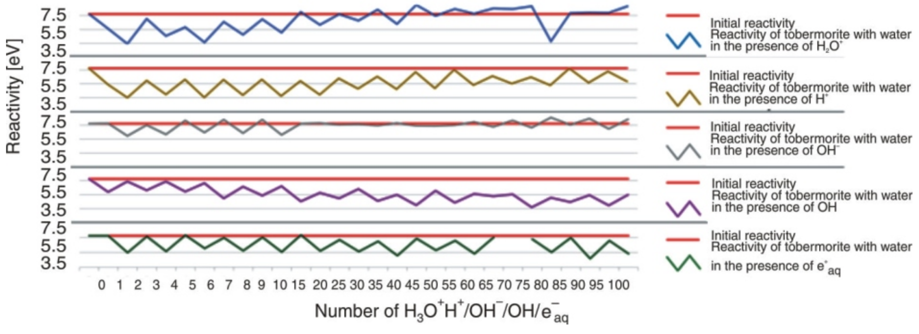


Figure 6. The MOPAC simulated reactivity of tobermorite with water in the presence of H_3O^+, OH^-, H^+, OH, or e^-_{aq}. (initial reactivity represents reactivity of tobermorite with the water only)

tobermorite. With the general improvement of reactivity higher production of H^+, OH, and e^-_{aq}. than H_3O^+, OH^- the hydration process might continue, resulting in different C-S-H molecules of higher strength.

Figures 7 and 8 show the reactivity of jennite and tobermorite with silicate in the presence of H_3O^+, OH^-, H^+, OH, and e^-_{aq}., respectively. As can be seen in fig. 7, there is a general improvement in the reactivity of jennite with water. The reactivity of tobermorite with water shows no general trend but it can be observed from fig. 8 that the reactivity oscillates around its initial value in the presence of H_3O^+, OH^-, H^+, OH, and e^-_{aq}. The bonding between C-S-H molecules and the aggregates can be one source of failure of concrete [21]. Improving the reaction between the C-S-H molecules and the aggregates could increase the durability and improve concrete strength. Therefore, the presence of H_3O^+, OH^-, H^+, OH, and e^-_{aq}. might improve the bonding between jennite type C-S-H and aggregate in thus improving concrete strength. Because the reactivity of tobermorite with silicate oscillates around its initial value, no general conclusion can be made on the bonding of tobermorite and silicate.

With a possible improvement in the reactivity of jennite and tobermorite with water and jennite with silicate, the concrete strength might be improved to some extent. However, as it will be shown in the following sections, dynamics and reaction kinetics models show that at a very high gamma dose, water radiolysis has a negative impact on concrete strength development that is not compensated by a potential better bonding of C-S-H with aggregates or a more hydrated C-S-H.

The LAMMPS models of alite and belite hydration

The LAMMPS molecular dynamics models of alite/belite early hydration are developed to verify the MOPAC results. The LAMMPS is a molecular dynamics code used to study material properties or interactions between various materials [22]. Among the multiple force fields within LAMMPS, the ReaxFF force field is selected in order to simulate the early hydration of alite and belite [23]. The parameters of the force field are obtained from [19] that are initially created by merging the ReaxFF parameters for Si-O-H from Ref [24] and Ca-O-H from [25] and then used to study C-S-H [26, 27], alite [19], and belite [28].

Three different simulation models are developed to study the alite early hydration, and they are as follows:

- *First alite early hydration model*: monoclinic alite crystal structure is built based on [29] for which the unit cell parameters of the crystal structure are a = 12.235 Å, b = 7.073 Å, c = 9.298 Å, and β =116.31° (a, b, and c are the lengths on the x-axis, y-axis, and z-axis of the crystal structure and β is the angle between the x-axis and z-axis of the crystal structure). A superstructure of alite is built in LAMMPS containing three alite crystal structures in all three directions of the crystal reaching at least 2 nm length per direction. Water (density = 1 gcm^{-3}) is added surrounding the alite superstructure. Energy minimization is conducted using the Polak-Ribière version of the conjugate gradient

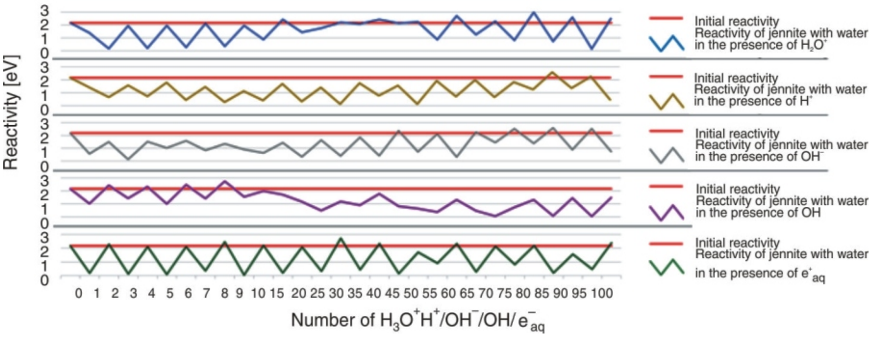


Figure 7. The MOPAC simulated reactivity of jennite with silicate in the presence of H_3O^+, OH^-, H^+, OH, or e^-_{aq}. (initial reactivity represents reactivity of jennite with silicate only)

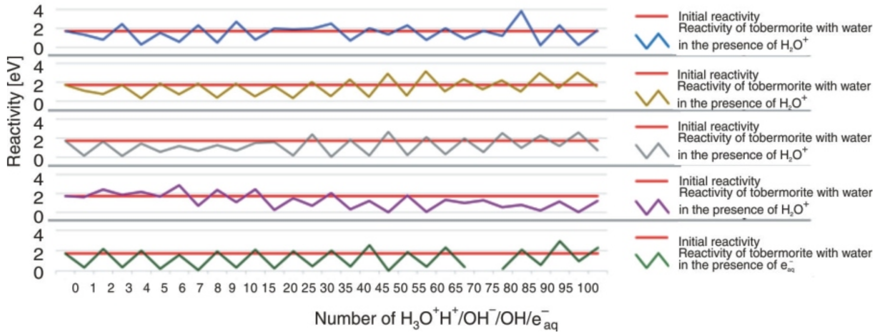


Figure 8. The MOPAC simulated reactivity of tobermorite with silicate in the presence of H_3O^+, OH^-, H^+, OH, or e^-_{aq}. (initial reactivity represents reactivity between of tobermorite with silicate only)

algorithm implemented in LAMMPS with 10^{-5} kcal mol^{-1} and 10^{-6} kcal mol^{-1} Å^{-1} for the cut-off tolerance of energy and force, respectively. To replicate the basic condition of an environment where alite and water are mixed, a Nose-Hoover thermostat of 298 K (damping parameter of 20 fs) and pressure of 1 atm (damping parameter of 200 fs) are applied in the model. The velocity Verlet integrator, a method used to integrate the equation of motion, is used with a time-step of 0.2 fs. The simulation is run over a period of 2 ns for a total of 10 000 000 time steps.

- *Second alite early hydration model*: consists of the alite superstructure surrounded by water and is performed with the same parameters and conditions as in the first alite early hydration model, but 10 % of water molecules are replaced with H^+ and OH^- (90 % water, 10 % H^+ and OH^-).
- *Third alite early hydration model*: consists of the alite superstructure surrounded by water and is performed with the same parameters and conditions as in the first alite early hydration model, but 20 % of water molecules are replaced with H_3O^+ and OH^- (80 % water, 10 % H_3O^+, and 10 % OH^-).

The ReaxFF force field computes the charge of each ion/molecules at each time step by using the conventional charge of each atom, so free radicals such as OH are automatically viewed by LAMMPS as OH^-. For this reason, no simulations are performed with the addition of free radicals.

In order to study the belite early hydration, the three following different models are developed:

- *First belite early hydration model*: consists of a monoclinic belite crystal structure that is built based on ref. [30] (β-C2S) in which the unit cell parameters of the crystal structure are $a = 5.502$ Å, $b = 6.745$ Å, $c = 9.297$ Å, and $\beta = 94.59^{\circ}$ (these parameters have the same meaning as in the alite crystal structure). A superstructure of at least 2 nm in length per direction is then created and surrounded by water. The parameters, simulation conditions, and simulation time are the same as used in the alite model.
- *Second belite early hydration model*: consists of belite superstructure surrounded by water and the parameters and simulation conditions are the same as in the first belite early hydration model, but 10 % of water molecules are replaced with H+ and OH^- (90 % water, 10 % H^+ and 10 % OH^-).
- *Third belite early hydration model*: consists of belite superstructure surrounded by water and the parameters and simulation conditions are the same as in the first belite early hydration model, but 20 % of water molecules are replaced with H_3O^+ and OH^- (80 % water, 10 % H_3O^+, and 10 % OH^-).

Based on [19, 28], the total simulation time is 2 ns. This simulation time allows to visualize the early hydration of alite and belite, as well as the effects of H^+, H_3O^+, and OH^- on alite and belite early hydration, showing how the presence of H^+, H_3O^+, and OH^- influences the early hydration of alite and belite with water.

Early hydration of alite

The density profile of hydrogen atoms, calcium atoms, and silicon atoms for all three alite models are presented in fig. 9 for one of the surfaces perpendicular to the *y*-axis, $(0\bar{1}0)$ surface (Miller indices notation[1]). In the simulation model with alite and water, there is no dissolution zone, which is a zone where the alite atoms and water species coexist. In the models with H_3O^+ and OH^-, a very thin dissolution zone of 0.6 Å is formed after 2 ns. However, this does not represent a start of hydration since the dissolution zone is very thin and does not increase during 2 ns. The non-hydration of the $(0\bar{1}0)$ surface can be explained by water tessellation [19]. The water at the interface of alite organizes itself in a stable configuration hindering the hydration. For the (001) surface, the density profile of calcium, hydrogen, and silicon atoms in all three alite early hydration models are very different, as can be seen in fig. 10, where a clear dissolution zone is observed. The thickness of the dissolution zone is 2.25 Å for the alite and water model, 2 Å for the alite, water, OH^-, and H^+ model, and 1.5 Å for the alite, water, OH^-, and H^+ model. For the other interface surfaces of the alite and water, the density profiles are between the density profiles of the $(0\bar{1}0)$ surface and the (001) surface. Alite has loosely bonded oxygen atoms [20] allowing them to create bonds easily with hydrogen atoms migrating inside the alite, therefore explaining the fast migration of hydrogen atoms inside the alite.

The hydration process of alite is based on hydrogen hopping [19] similar to the Grotthuss mechanism [31] that consists of the migration of hydrogen atoms through material by creating bonds with oxygen atoms and moving from one oxygen atom to another deeper in the material. In all three simulation models, water molecules dissociate at the surface of alite. The hydrogen atoms that are no longer bonded to oxygen atoms will create new bonds with an oxygen inside the alite. Then, they create new bonds with other oxygens atoms deeper inside the alite, allowing their migration into the alite. Figure 11 shows an example of a hydrogen hopping. One of the hydrogen atoms from the water molecule creates a new bond with an oxygen atom from SiO^{4-}. The hydroxide ion reorients itself with the hydrogen pointing towards the outside of the alite. The hydroxide ion then maintains this orientation. It is also observed that the hydrogen hopping process is much slower when it reaches a layer with orthosilicate. In the

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[1] In the Miller indices notation, the surface (*hkl*) is the surface with normal vector $h\vec{a} \quad k\vec{b} \quad l\vec{c}$ where $\vec{a}$,$\vec{b}$, and $\vec{c}$ being the vector of the reciprocal lattice. The *h*, *k*, and *l* are fractioned to crystal structure parameters. Negative indices are denoted with a bar (–*h* is written as $\bar{h}$)

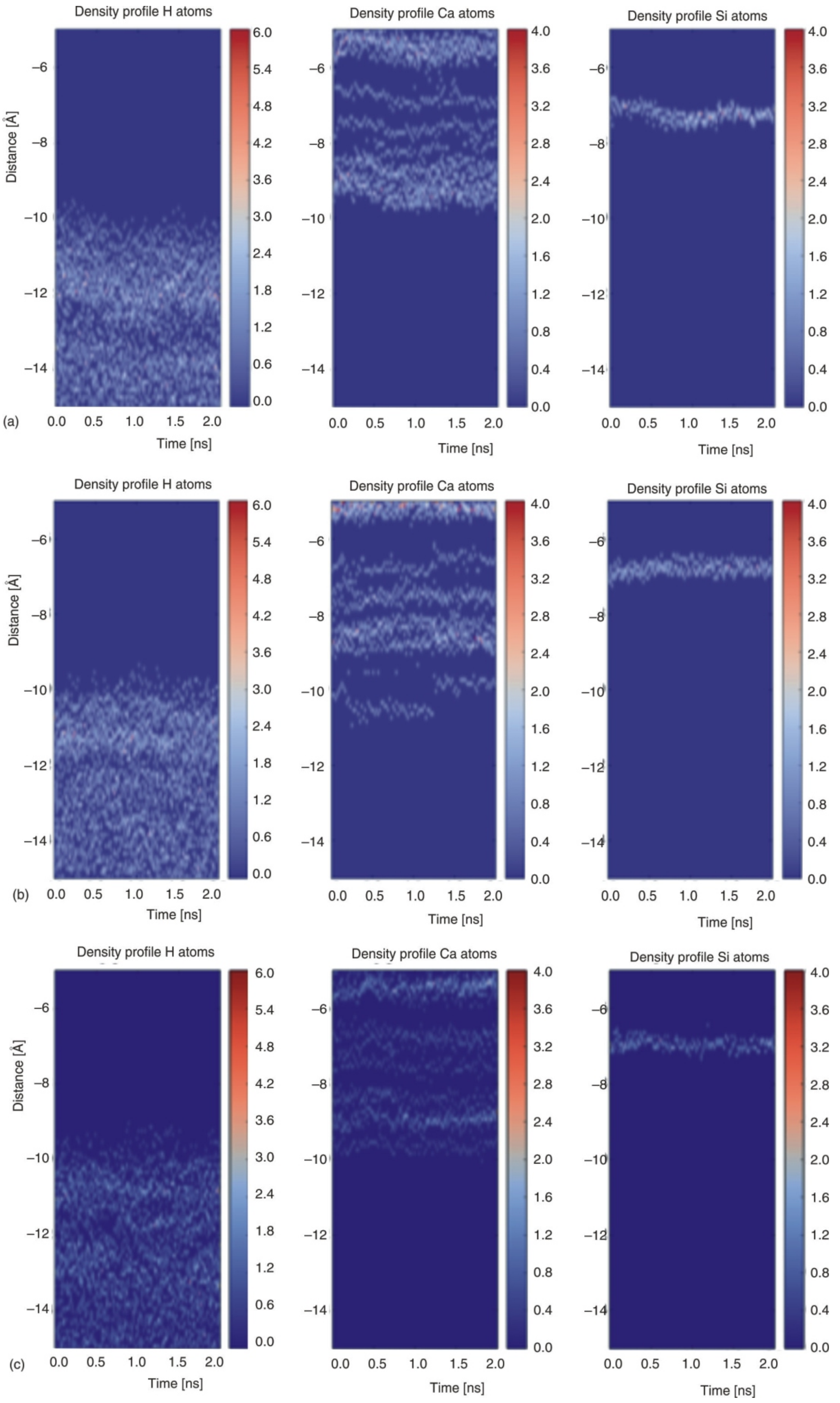

Figure 9. Density profiles along *y*-axis between –15 Å and –5 Å of hydrogen (left), calcium (middle), and silicon (right) atoms for the $(0\bar{1}0)$ surface: (a) alite and water, (b) alite, water, H^+, and OH^-, and (c) alite, water, H_3O^+, and OH^-. [Interface between water and alite is located at –10 Å; densities are expressed in a number of atoms; 1 Å = 10^{-10} m]

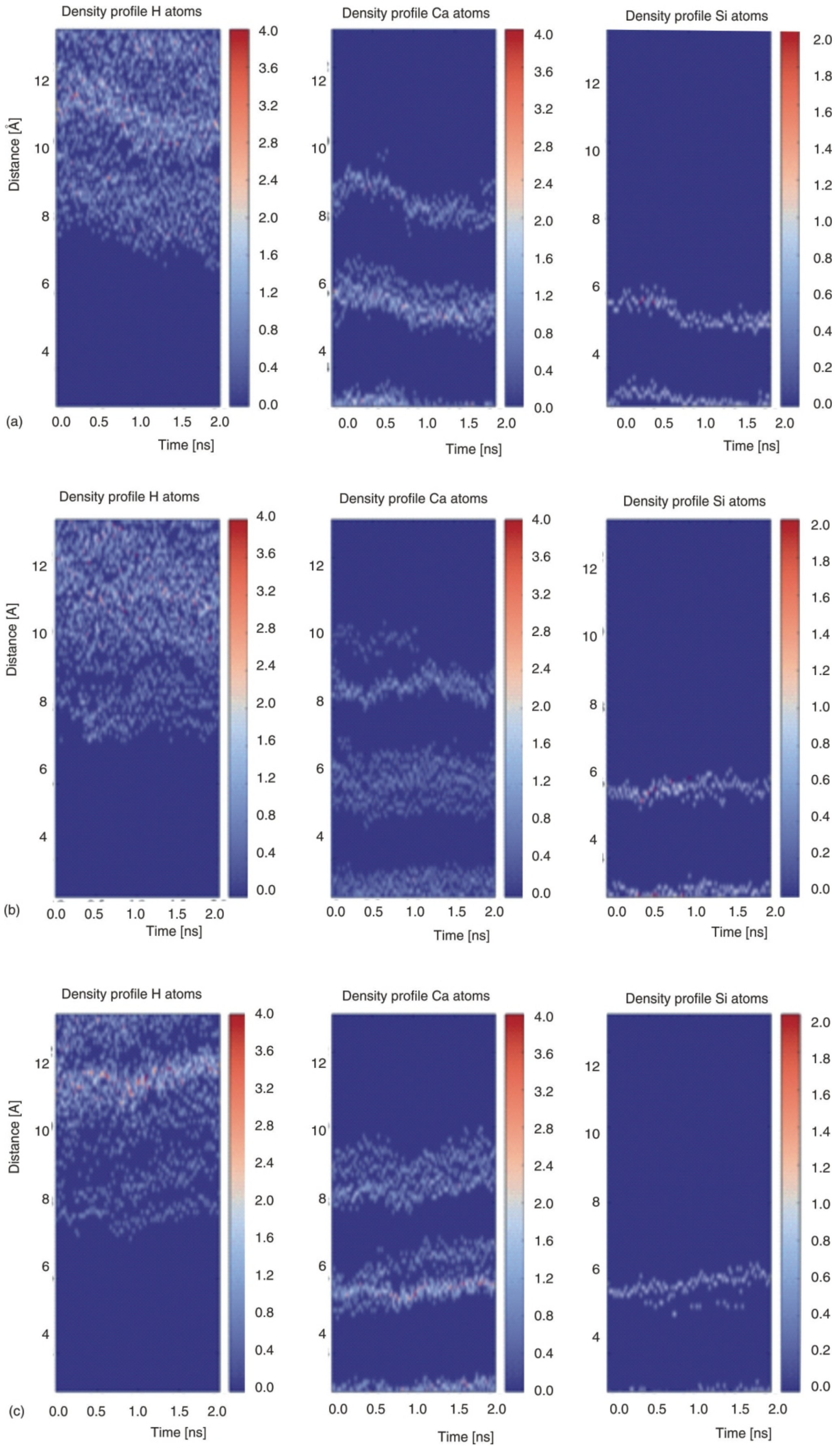

Figure 10. Density profiles along z-axis between 3 Å and 13 Å of hydrogen (left), calcium (middle), and silicon (right) atoms for the (001) surface: (a) alite and water, (b) alite, water, H^+, and $OH^–$, and (c) alite, water, H_3O^+, and $OH^–$. [Interface between water and alite is located at 9 Å; densities are expressed in a number of atoms; 1 Å = $10^{–10}$ m]

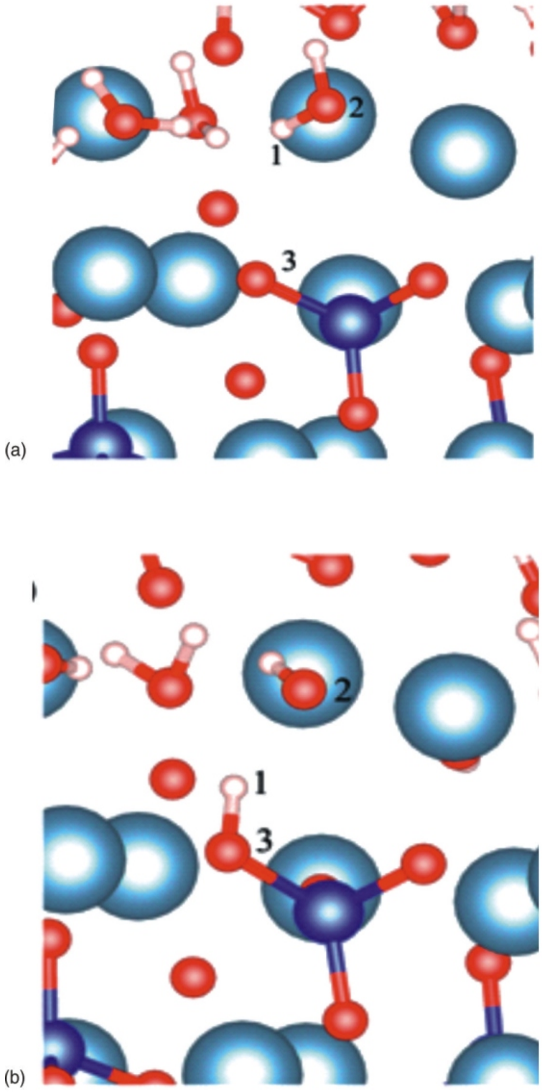

Figure 11. Example of hydrogen hopping obtained from the simulation model with alite and water only: (a) at 1.82 ns, hydrogen atom is bonded with oxygen atom, (b) at 1.84 ns, hydrogen atom is no longer bonded with the same oxygen atom but with another oxygen atom [1: hydrogen atom, 2: oxygen atom, 3: oxygen atom]

hydrogen hopping process, hydrogen atoms can create new bonds with oxygen atoms from an orthosilicate. However, it is observed that hydrogen atoms can then create new bonds with oxygen atoms in the same plane that is not in an orthosilicate rather than going deeper in the alite, slowing down the hydration process.

It is expected that the hydrogen hopping occurs faster in the simulation model with OH^- and H^+ since water molecules have already been dissociated, but as shown in fig. 10, the hydrogen hopping is slower (fewer hydrogen atoms have migrated inside the alite crystal superstructure) in the simulation model of the alite, water, H^+, and OH^- compared to the simulation model with alite and water only. Therefore, the presence of H^+, and OH^- slow down the early hydration of alite. This indicates that during the hydration of alite, the quantity of H^+ and OH^- present in water, and therefore their concentrations, plays an important role in the reaction of alite with water. An excess of H^+ and OH^- hinders the natural dissociation of water into H^+ and OH^- slowing the early hydration process. The reaction kinetics model presented in the following section explains more this aspect in more detail. In the simulation model with H_3O^+ and OH^-, the hydrogen hopping is even slower since there are fewer hydrogen atoms present in the dissolution layer and so is the early hydration of alite. This significant slowdown of the hydration process of alite with water is explained by the excess of H_3O^+ and OH^- in water hindering the hydration, similarly with OH^- and H^+. Also, it is noted that H_3O^+ dissociates slower at the interface of alite than water, leading to less hydrogen being available to migrate inside the alite, and therefore contributing to further slowing down of hydration process.

The presence of H^+, OH^-, and H_3O^+ could improve the early hydration of alite with water in two ways: improvement of reactivity of alite with water (the water molecules react faster with alite and therefore the process of dissociation into H^+ and OH^- happening during the hydration of alite is faster) and, by having water molecules already split into H^+ and OH^- (part of hydration mechanism). In both cases, if the early hydration is improved, then more hydrogen atoms migrate into the alite crystal superstructure. However, the LAMMPS models show the opposite, it shows a slower hydration.

The hydration of alite can be divided into multiple periods as sketched in fig. 12 [32]. The first period of hydration represents the initial phase in which the reaction rate drastically slows down when alite starts to be in contact with water. When reaction rate stops decreasing, the second period called the induction period or dormant phase, starts with the reaction rate showing its lowest value. The third period, called the acceleration phase, is where the alite reaction rate significantly increases until reaching its maximum. After reaching its maximum, the reaction rate starts to decrease, this is the so-called deceleration period. Many theories have been developed to explain the decrease of a reaction rate right after the beginning of hydration and why it stays at a low value during the induction period. The most accepted theory explains that there is the creation of a protective layer

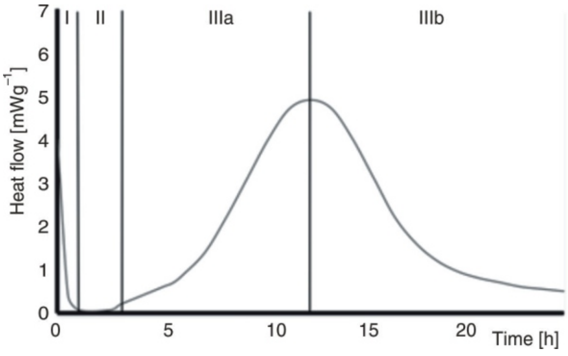

Figure 12. Heat flow curve of alite [33]

between water and anhydrous alite [32]. This layer of hydrates stops water to migrate through it to reach the anhydrous alite. As shown in fig. 9(a), some surfaces of alite do not hydrate while fig. 10(a) shows that the hydration can be slowed down once reaching an orthosilicate layer. Both phenomena explain why the alite rate of hydration drastically decreases after contacting with water. The second case as shown in fig. 10(a) shows an important decrease in reaction rate of alite after contact with water is established. The hydration process (hydrogen migration) is very fast between orthosilicate layers but very slow in crossing the layers. Therefore, the reaction rate of alite is decreasing as the orthosilicate layers are crossed while the outer alite layer continues to hydrate. Such a theory has not yet been proven.

Early hydration of belite

Figure 13 shows density profile of hydrogen, calcium and silicon atoms along the *y*-axis near one of the surfaces of the belite superstructure, (010) surface, for the three belite simulation models. A dissolution zone is created for the belite and water with a thickness of only 0.7 Å compared to 2.25 Å in the alite and water case. As expected, the belite layer is much thinner than the alite since belite is less reactive than alite. The dissolution zone thickness for belite, water, H^+, and OH^- is 1.1 Å. In both cases, only a few hydrogen atoms are in this zone but in the model with H^+ and OH^-, there are even fewer hydrogen atoms. The dissolution zone tends to be formed at the beginning of the simulation (process) for the belite and water model but later for belite, water, H^+, and OH^- where the first hydrogen atoms at the level of calcium atoms are formed at 80 ps. The model of belite with water, H_3O^+, and OH^- shows no formation of the dissolution zone. The same conclusion can be derived for the alite: the presence of H^+, OH^-, and H_3O^+ slow down the early hydration process (less hydrogen migrating inside the belite). The hydration process during 2 ns of simulation is barely observed. Dissociation of water into hydroxide ions and hydrogen atoms as well as hydrogen atoms bonded to the oxygen of an orthosilicate are observed.

Table 2 summarizes the results of discussed reactivity calculations and early hydration models of alite and belite with water in the presence of products of water radiolysis. Alite and belite are responsible for concrete strength development before and after seven days, respectively, because of their reactions with water being different. Due to the improvement of reactivity of alite with water in the presence of products of water radiolysis, alite might reacts faster with water, leading to alite dissolving quicker, thus more C-S-H be created, and therefore, leading to a higher concrete strength. In the case of belite, the reactivity calculations show that the presence of products of water radiolysis improves its reactivity with water. Therefore, belite might also react faster with water, and hence, it might contribute to concrete strength development during its first seven days of curing. To analyze these (static) reactivity calculation models, the dynamics models of early hydration of alite with water and belite with water in the presence H^+, OH^-, and H_3O^+ are developed. The presence of H+ and OH- slows down the early hydration (hydrogen hopping) because of the excess quantity of H^+ and OH^- present in the water influences the water dissociation. The presence of H_3O^+ and OH^- slows down the early hydration for the same reason. The H_3O^+ reacts slower with alite/belite than water in thus leading to less hydrogen being available to migrate inside the alite and belite, thus slowing down the early hydration further. Therefore, the presence of H^+, OH^-, and H_3O^+ has a negative impact on concrete strength development; this is in contrary to reactivity calculations influences by other phenomena happening during the hydration that were captured in these models.

REACTION KINETICS STUDY ASSESSING IMPACTS OF GAMMA RADIATION ON CONCRETE HYDRATION

Very few studies exist on alite hydration reaction kinetics and multi-ionics [33, 34]. For this study, the multi-ionic continuum-based model (MI-CBM) described in [34], a 1-D model based on physics, chemistry, reaction kinetics, and multi-ionic transport, is selected. A sphere of radius 0.00025 cm surrounded by water represents Alite. In the time-dependent model, the alite radius decreases and a C-S-H layer outside of the alite develops. The model parameters were obtained from experimental data or other simulation models as described in [34]. The alite rate of hydration curve obtained using MI-CBM has a similar trend to one shown in fig. 12, [34]. In MI-CBM, only OH^- is considered. The other products of water radiolysis were not implemented because the calculation of their concentrations is not important or is not part of the alite hydration. Therefore, to explore the effect of OH^- on alite hydration, the MI-CBM is applied.

Adding a constant addition rate or constant removal rate in the model modifies the concentration of OH^-. Figure 14 shows the MI-CBM dimensionless rate of alite hydration and the C-S-H inner and outer radii. The inner radius and outer radius correspond to the inner radius and outer radius of the C-S-H layer divided by the initial radius of the alite sphere. The constant removal rate and the constant addition rate were selected to be -15 mmolL^{-1} and 15 mmolL^{-1} (the equilibrium concentration of OH^- reached in the model is 60 mmolL^{-1}).

Table 3 shows the values of the inner radius, outer radius, and rate of hydration after at 7.5 hours and 24 hours, the precent of alite that reacted with water and the precent of C-S-H created compared to the model with no modification of OH^- at 24 hours. In the case of constant removal of OH^-, the rate of hydration

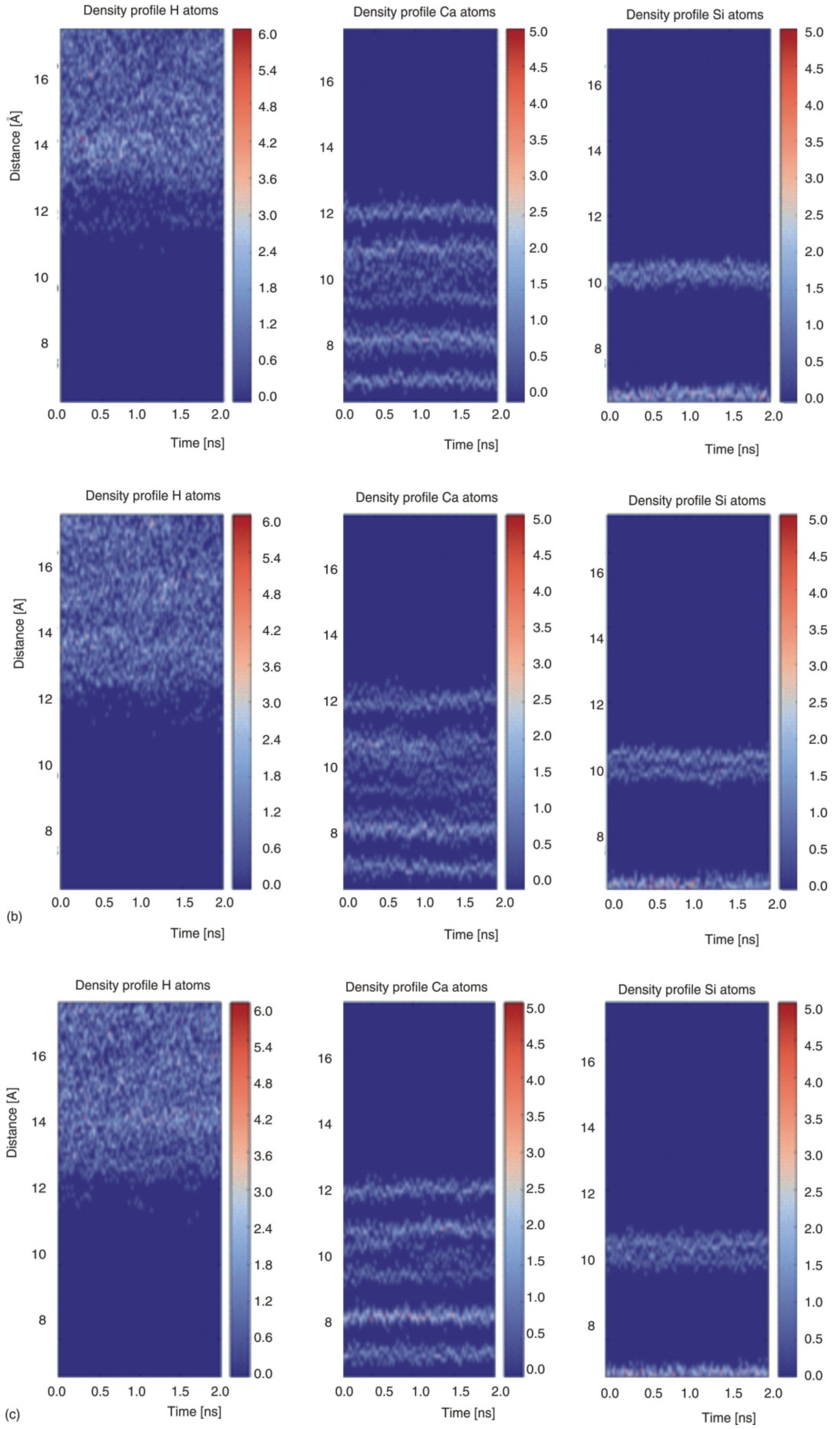

Figure 13. Density profiles along *y*-axis between 7 Å and 17 Å of hydrogen (left), calcium (middle), and silicon (right) atoms for the (010) surface: (a) belite and water, (b) belite, water, H^+, and OH^-, and (c) belite, water, H_3O^+, and OH^-. [Interface between water and belite is located at 12 Å; densities are expressed in a number of atoms; 1 Å = 10^{-10} m]

Table 2. Summary of the MOPAC reactivity models and LAMMPS early hydration models of alite and belite with water in the presence of products of water radiolysis

Models	Effects of the presence of products of water radiolysis	Effects on cement hydration	Concrete strength development after seven days of curing
MOPAC reactivity model of alite with water	Reactivity with water is generally improved	Faster – leading to more alite reacting with water and therefore more C-S-H precipitating	Faster
MOPAC reactivity model of belite with water		Faster – possibility of belite hydration to contribute to early strength (seven days) development	
LAMMPS model of early hydration of alite with water	Less hydrogen migrating into alite/belite due to the excess of H^+, $OH^–$, and H_3O^+ that hinders the dissociation of water and therefore the early hydration;	Slower	Slower
LAMMPS model of early hydration of belite with water	H_3O^+ reacts slower than water with alite and belite, reducing the number of hydrogen atoms available to migrate inside alite/belite		No impact (belite does not contribute)

of alite is higher in all the phases of alite hydration (initial, dormant, acceleration, and deceleration phases) leading to more C-S-H precipitating, as shown in fig. 14(b) and 14(c). The outer radius has a higher value and the inner radius has a lower value than the initial model. In the case of the constant addition of $OH^–$, the effects are the opposite showing a slower hydration of alite. After 24 h, the constant removal of $OH^–$ leads to ~8 % more alite reacting with water and an increase of 56 % of C-S-H volume compared to the original MI-CBM (no modification of $OH^–$ concentration). The constant removal of $OH^–$ disrupts the solution equilibria created by alite dissolution. More alite tends to react with water to compensate for the removal of $OH^–$, leading to more C-S-H precipitating to maintain the solution equilibria regarding the other ions (Ca^{2+}, …). The constant addition of $OH^–$ leads to 6.5 % less alite reacting with water and a decrease of 28 % of C-S-H volume compared to the original MI-CBM (no modification of $OH^–$ concentration). The disruption of the solution equilibria in this case by having a higher OH- concentration than at equilibria, leads to less alite reacting with water. Therefore, less C-S-H precipitate to maintain the solution equilibria regarding the other ions (Ca^{2+}, …). In the early hydration models of alite with the presence of $OH^–$, the simulations models are in the latter case: the $OH^–$ concentration is above the OH- equilibria concentration, therefore less alite react with water as seen in fig. 10. As can be seen in fig. 13, less belite reacts with water because the $OH^–$ concentration is above the $OH^–$ equilibria concentration. From the results obtained in LAMMPS and MI-CBM models, it can be concluded that water radiolysis may only impact alite and belite hydration by disturbing the solution equilibria during hydration.

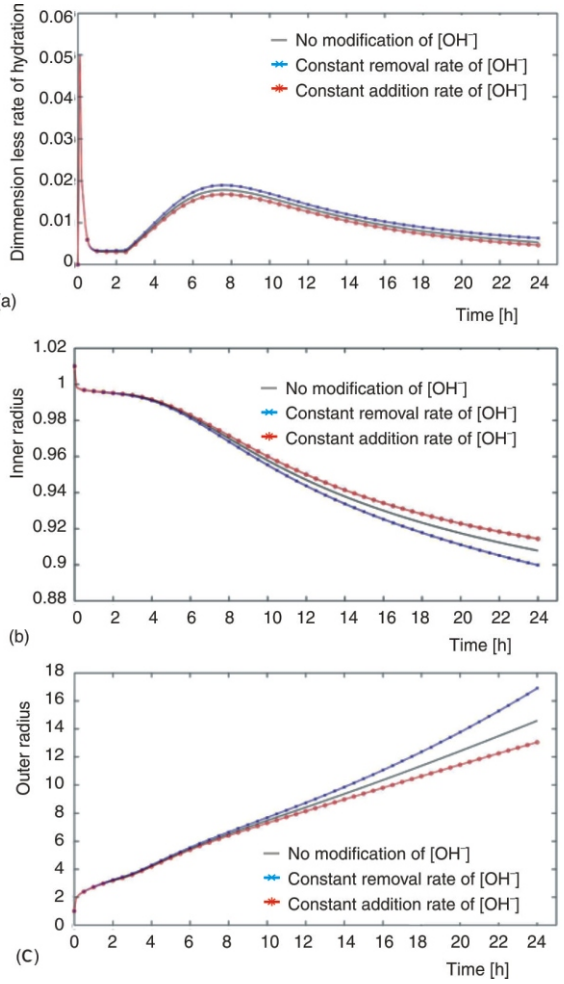

Figure 14. (a) the MI-CBM dimensionless rate of alite hydration, (b) the MI-CBM C-S-H inner radius, (c) the MI-CBM C-S-H outer radius

The effect of water radiolysis on $OH^–$ concentration during alite hydration is estimated based on [9]. The concentration of new species created by water radiolysis during the first 24 hours of irradiation at the dose rate of 0.1 $Gys^{–1}$ are very low compared to $OH^–$ concentration. Therefore, the variation of $OH^–$ concentration due to water radiolysis (some of the new species react with themselves creating $OH^–$ or react with $OH^–$ consuming it) is expecting to be very low. As

Table 3. Rate of hydration at 7.5 hours (highest rate of hydration rate) and at 24 hours, C-S-H inner radius at 24 hours, and C-S-H outer radius at 24 hours, percent of alite that has reacted with water and the percent of C-S-H created compared to the model with no modification of OH^- at 24 hours. [The inner radius and outer radius are divided by the initial alite radius making them dimensionless, the rate of hydration is also dimensionless]

	Rate of hydration at 7.5 hours	Rate of hydration at 24 hours	Percent of alite that has reacted compared to the initial MI-CBM at 24 hours	Inner radius at 24 hours	Outer radius at 24 hours	Percent of C-S-H created compared to the initial MI-CBM at 24 hours
Initial MI-CBM: No modification of $[OH^-]$	$1.78\ 10^{-2}$	$5.33\ 10^{-3}$	100	$9.08\ 10^{-1}$	$1.46\ 10^{1}$	100
MI-CBM with constant removal rate of $[OH^-]$	$1.89\ 10^{-2}$	$6.33\ 10^{-3}$	1.08	$9.15\ 10^{-1}$	$1.69\ 10^{1}$	156
MI-CBM with constant addition rate of $[OH^-]$	$1.67\ 10^{-2}$	$4.66\ 10^{-3}$	0.94	$9.00\ 10^{-1}$	$1.31\ 10^{1}$	0.72

Table 4. Summary of the effects of water radiolysis on alite and belite hydration and concrete strength

Model		Effects on hydration	Effects on C-S-H	Dose rate effects	Concrete strength
LAMMPS models of early hydration of alite and belite in the presence of H^+, OH^-, and H_3O^+		Slower hydration due to the excess of H^+, OH^-, and H_3O^+	Less C-S-H precipitates	High dose rate	Lower
MI-CBM	Removal of OH^-	Solution equilibria changed (lower $[OH^-]$); therefore, more alite reacts with water	More C-S-H precipitates in order to maintain the solution equilibria regarding the other ions (Ca^{2+}, …)	Extremely high dose rate is necessary to see a noticeable variation of OH^-. This dose rate will result in damaging concrete	Lower
	Addition of OH^-	Solution equilibria changed (higher $[OH^-]$); therefore, less alite reacts with water	Less C-S-H precipitates to maintain the solution equilibria regarding the other ions (Ca^{2+}, …)		

the MI-CBM shows, only a significant variation of OH^- concentration can affect alite hydration positively or negatively. Therefore, a dose rate of the order of magnitude higher than 0.1 Gys^{-1} is required to produce a significant variation of OH^- concentration during alite hydration. At such a high dose rate, the production of $H_{2(g)}$ is significant, hugely increasing the concrete internal pore pressure. Such significant increase in internal pore pressure during concrete curing will certainly lead to concrete damage. Additionally, such a high dose rate will induce high production of free radicals and ions in water due to water radiolysis. As seen in the molecular dynamics models of alite/belite, water, OH^-, and H_3O^+, the presence of species not naturally involved in alite and belite hydration slow down the hydration process. Finally, other detrimental phenomena might also appear because the dose will reach the MGy range or higher [6-8]. Therefore, using gamma radiation to cure concrete inducing water radiolysis does not increase the concrete strength.

Table 4 compares the molecular dynamics and reaction kinetics models. The reaction kinetics analyses confirm the molecular dynamics conclusion: the water radiolysis impacts alite and belite hydration by changing the solution equilibria which means that the dose rate needed is extremely high (many order of magnitude higher than 0.1 Gys^{-1}). At such a high dose rate, the concrete will be damaged resulting in its lower strength.

CONCLUSIONS

Molecular dynamics models and reaction kinetics models are developed to numerically assess the effects of water radiolysis on concrete hydration.

When concrete is exposed to low dose gamma radiation during its early curing phase (first seven days) its compressive strength is increased [4]. At a significantly higher dose, it is expected that water radiolysis will develop within the concrete – the question would be if water radiolysis will further enhance the concrete strength development and what gamma dose would be the threshold value? Therefore this paper describes a numerical assessment of the effects of water radiolysis on concrete strength development (in other words, the gamma dose delivered to concrete during its early stage of curing) based on reactivity calculation and modeling of the early hydration of alite/belite with water in the presence of products of water radiolysis. These analyses show that the reactivity value, representing the likeliness of a reaction to occur (the lower the value the more likely for reaction to take place), of alite with water and belite with water is decreased (*i. e.* higher likelihood of reacting) depending on water radiolysis products and its quantity. Dynamics model of early hydration of alite with water and belite with water in the presence of H^+, OH^-, and H_3O^+ shows that the presence of H^+, OH^-, and H_3O^+ slows down the hydration of alite and belite. The excess of H^+, OH^-, and H_3O^+ in water hinders the water dissociation leading to the slower hydration and therefore a lower concrete strength. Additionally, an increase or decrease of [OH$^-$] during alite hydration shows that it can slow down or enhance its rate of hydration, respectively. To achieve such OH$^-$ variation due to water radiolysis, the dose rate must be that high that will damage the concrete (high internal pressure and detrimental phenomena [6-8] are expected), therefore decreasing its strength. This leads to the conclusion that water radiolysis induced within the concrete in its early stage of curing will not increase its strength.

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AUTHORS' CONTRIBUTIONS

All modeling and analyses are developed and written by Q. Faure. T. Jevremovic provided supervision on the overall paper content and through the entire study. The manuscript was written by Q. Faure with the review and supervision by T. Jevremovic.

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ПРИМЕНА МОДЕЛА МОЛЕКУЛАРНЕ ДИНАМИКЕ И РЕАКЦИОНЕ КИНЕТИКЕ У АНАЛИЗИ УТИЦАЈА ГАМА ЗРАЧЕЊА НА ХИДРАТАЦИЈУ БЕТОНА

MOPAC и LAMMPS, рачунарски кодови молекуларне динамике и програмски код реакционе кинетике заснован на вишејонском континуум моделу, искоришћени су за анализу утицаја гама зрачења на хидратацију бетона. Експерименталне студије показале су да при третирању ниским дозама гама зрачења бетон показује статистички значајно повећање чврстине у поређењу са конвенционалним третирањем. Могући разлог за то је интеракција гама зрачења са водом што води бржој хидратацији. Поставља се питање да ли би третирање бетона вишим дозама зрачења довело до даљег повећања његове снаге. Овај рад даје детаљне нумеричке анализе ефеката високе дозе гама зрачења на бетон, засноване на моделима молекуларне динамике и реакционе кинетике. Под овим условима, претпостављено је да гама зрачење у интеракцији са водом у бетону индукује радиолизу воде. Ове нумеричке симулације показују да је реактивност обично увећана у присуству електрофила. Међутим, модели ране хидратације трикалцијум силиката (алит) и дикалцијум силиката (белит) са H^+, OH^- и $H3O^+$, укузују да је процес хидратације успорен што води мањој чврстини бетона. Додатно, модел реакционе кинетике коришћен за процену утицаја $[OH^-]$ на хидратацију трикалцијум силиката показује да повећање или смањење $[OH^-]$ током хидратације трикалцијум силиката може респективно смањити или повећати брзину хидратације. Доза потребна да произведе радиолизу воде, која следи у варијацији $[OH^-]$ током хидратације трикалцијума силиката, мора бити екстремно висока што доводи до оштећења структуре самог бетона. Може се закључити да повећање дозе бетона изнад вредности коришћене у експерименту ради индуковања радиолизе воде неће повећати снагу бетона, те радиолиза воде није потребан услов за повећање снаге бетона при третирању гама зрачењем.

Кључне речи: MOPAC, LAMMPS, хидрашација свежеī бешона, вишејонски коншинуумски модел, алиш, белиш, радиолииза воде, īама зрачење