Viser Technology Pte. Ltd.
Research and Application of Materials Science
DOI: 10.33142/rams.v4i1.8457

Research Article Open Access

Unsaturated transport properties of water molecules and ions in graphene oxide / hydrated calcium silicate nanochannels: from basic principles to complex environmental performance effects

Zhuye HUANG, Yong FENG, Hongwei WANG, Lei FAN*

School of Civil Engineering and Architecture, Zhejiang University of Science & Technology, Hangzhou, China

***Corresponding Author:** *Lei FAN, E-mail: fanleigl@foxmail.com*

Abstract:
The problems of traditional concrete such as brittleness, poor toughness and short service life of concrete engineering under acid rain or marine environment need to be solved urgently. Hydrated calcium silicate (C-S-H) is a key component to improve the mechanical properties and durability of concrete. However, the traditional method of concrete material design based on empirical models or comparative tests has become a bottleneck restricting the sustainable development of concrete. The synthesis method, molecular structure and properties of C-S-H were systematically described in this paper; The interface structure and interaction of graphene oxide / calcium silicate hydrate (C-S-H / GO) were discussed. On this basis, the saturated and unsaturated transport characteristics of ions and water molecules in C-S-H / GO nanochannels under the environment of ocean and acid rain were introduced. The contents of this review provide the basis for improving the multi-scale transmission theory and microstructure design of concrete. It has important guiding significance for analyzing and improving the service life of concrete in complex environment.

Keywords: *acid rain environment ; marine environment ; Service life of concrete ; Graphene oxide / calcium silicate hydrate ; molecular dynamics ; Unsaturated transport of ions and water molecules.*

Abbreviations: C-S-H , Hydrated calcium silicate; GO, Graphene oxide ; C-S-H / GO, Hydrated calcium silicate / Graphene oxide ; MD, molecular dynamics; SFCB, Steel continuous fiber composite reinforcement; SEM, scanning electron microscope; LK , Lerf-Klinowski ; DSM , Dynamic structural model.

1 Introduction

With the continuous development of science and technology, concrete materials are extensive used in various buildings. It is a kind of composite heterogeneous material, which has the distinguishing features of high compressive strength and good compatibility with the surrounding environment. At the same time, it has low production cost and easy access to raw materials. Therefore, its strength and durability have been studied by many researchers [1-6]. The effect of surroundings on the durability of concrete is one of the most common factors. Among them, acid rain and ocean are the two most common environments that influence the endurance of concrete.

With the development of industrialization, the impact of acid rain on all parts of the world has become more and more serious in the past ten years. And the erosion of acid rain causes huge economic losses every year. It is estimated that China's annual economic loss in building materials due to acid rain exceeds 2.5 billion dollars [7-8]. At the same time, due to the superposition of multiple and complex factors (such as salinity, climate and biology), the corrosion of marine engineering structures has also become a worldwide problem. The corrosion of marine buildings in the world has caused serious economic losses. According to statistics, the cost of highway bridges in the United States due to concrete corrosion reached 27.6 billion dollars in 1998; 75% of concrete bridges in England and Wales are corroded by seawater, and the maintenance cost is twice as high as the construction cost; The corrosion of marine engineering in China is also serious, and the loss of marine corrosion accounts for about 1 / 3 of the total corrosion loss, as high as 700 billion RMB. Therefore, strengthening the durability and strength of concrete structures in these environments and extending the service life are essential research directions.

In view of these factors, adding admixture to cement-based materials is a major means to prepare high-performance concrete materials. Admixture is an

Received on April 10, 2022; Accepted on May 11, 2022

indispensable part of concrete, which is the consensus of all civil workers now. High performance concrete mainly improves the workability and durability of concrete by adding additives. In particular, high-efficient water reducing agent can fully disperse cement particles and improve the pore structure and interface microstructure on the basis of reducing water consumption. Therefore, the concrete is more dense and the mechanical properties are greatly improved. Whether impermeability or chloride ion diffusion, sulfate corrosion resistance and wear resistance are better than concrete without admixture. It not only improves the workability of concrete, but also improves its durability and strength. So, it is possible to prepare high performance concrete with high strength and high durability only by mixing high efficiency water reducing agent.

And admixtures can be divided into inorganic admixtures, organic admixtures and composite admixtures according to chemical composition. Among them, organic admixtures account for the vast majority of concrete admixtures, such as high-performance water reducer, retarder and so on[9].

Z.C. Lu [10]studied the role of organic admixtures with different functional groups in cement hydration. He summarized that the addition of organic admixtures can improve the plasticity of concrete materials and prevent the occurrence or increase of cracks. Besides, it can also effectively improve the service strength and service life of concrete. On the other hand, he found the difference between the functional groups and molecular structures contained in the small organic molecules in the organic admixtures will affect the cement hydration. The carboxyl groups on the polymer surface can prolong the cement hydration time, which is conducive to ensuring the workability of concrete.

C-S-H is the main cementation phase of concrete materials, accounting for over half of cement hydration products. Therefore, research on materials based on hydrated calcium silicate has been paid more and more attention. In addition, graphene oxide as a derivative of graphene has excellent mechanical properties and has gradually become a popular cement-based modified material.

Meanwhile, in order to simulate and analyze more intuitively, molecular simulation of materials was led into the research field of new concrete materials at the beginning of the 21st century, especially in the study of microstructure and performance of hydration products of cement.

The environment such as acid rain and ocean has a great impact on the service life of concrete. They circulate dry and wet in the concrete. So, the water and ions in concrete belong to unsaturated transport. At the same time, M. Devasena et al.[11] employed GO to study its influence on the mechanical properties and durability of concrete. Their results showed that when the addition amount of GO was 0.1%, the strength of concrete increased by the highest extent. The compressive strength of concrete with 0.1% GO was 11% higher than that without GO when the flexural strength was 4% higher. Therefore, the demand for unsaturated transport of water and ions in C-S-H / GO is increasing every year. However, due to the relatively complex structure of C-S-H and other reasons, the research on micro mechanism is limited.

Therefore, this paper summarizes the construction of multi-scale C-S-H/GO variable model using molecular dynamics method to study the unsaturated transport of water molecules and ions. It can provide a basis for improving the multi-scale transport theory and microstructure design of concrete, which can also have important guiding significance for analyzing and improving the service life of concrete in complex environments

2 Environment and concrete structure

2.1 Influence of environment on durability of concrete structure

Environment is an important factor influencing the ruggedness of concrete. Freezing thawing, sulfate and other different environments will have various adverse effects on the mechanical properties and ruggedness of concrete materials. Acid rain and ocean are the two most common environments that affect the durability of concrete.

When the concrete construction is eroded by acid rain, cement hydration products will react with acid rain to form ettringite or gypsum, which will dilate its volume by 1.5-2.2 times and generate tensile stress inside, resulting in cracks and spalling in the concrete. Its mechanical properties, interface bonding and composition will change accordingly [12-19], and finally the strength and durability of the concrete structure will gradually decrease [20-21].

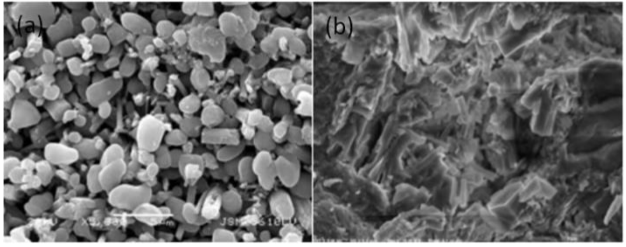

Figure 1 SEM of concrete before (a) and after (b) acid rain erosion [22]

In the marine environment, concrete structures bear static and hydrodynamic loads due to water pressure and have complex stress states [23-24]. In addition, water is easy to penetrate into concrete under high pressure, which will result in the decline of its internal mechanical performance. Although some scholars have fully considered the quiescent condition and fatigue behavior of concrete structures in epeiric sea [25-30], it is still difficult to analyze the impact of high water pressure in deep sea [31-32]. At the same time, the concrete construction in the district where the water level drops is most vulnerable to corrosion. In this district, the concrete is repeated to dry and wet cycles, which leads to complex chemical reactions of chloride ions, sulfate ions and magnesium ions in seawater to cement concrete [33-36]. There is also physical erosion caused by crystallization pressure of sea salt and wave action in this area [37]. When the concentration of chloride ion in reinforced concrete attains a certain range, the chloride ion will be adsorbed on the superficial layer of reinforcement, thus accelerating the corrosion rate. Under the condition of sufficient chloride ion and water, the corrosion rate of reinforcement will be accelerated with the large amount of chloride ion [38]. With the increase of corrosion, the volume will gradually increase to 2-6 times of the original reinforcement volume, thus generating expansion pressure on the boundary between cement and reinforcement. After that, the tensile stress loss will lead to concrete cracking and delamination. It also will reduce the cross-sectional area of reinforcement, and finally damage the durability of concrete structure [39-40].

Figure 2 marne corrosion surface[41]

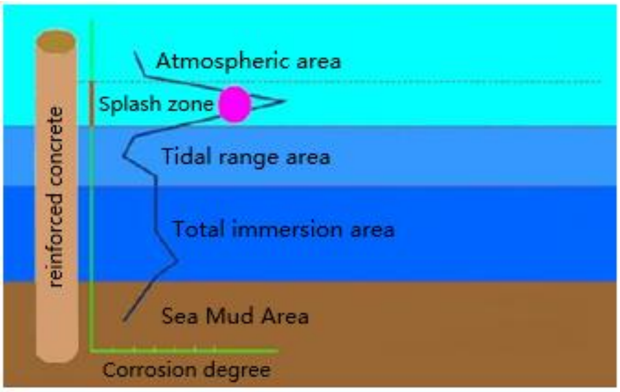

Figure 3 characteristics of marine corrosion zoning[42]

Because these environments have an important influence on the durability and strength of concrete, it is particularly important to research these factors.

2.2 Research status in various countries

According to the environment of acid rain, H.F. Yuan et al. [43] examined the degradation model of concrete corroded by sulphuric acid and built a simplified damage model to describe the deterioration of concrete induced by gypsum expansion in accordance with the acid rain environment. The resistance of glass powder content in cement materials to sulfuric acid was researched by H. Siad et al. [44]. They discovered that adding more glass powder to mortar will boost its resistance to sulfuric acid. F. Girardi and R.D. Maggio [45] studied the resistance of concrete mixtures to periodic sulfuric acid and sulfate solutions, and the results showed that the deterioration of concrete mixtures was particularly serious when the samples contained ordinary aggregates and were regularly exposed to sulfuric acid and mixed sulfate solutions. M. Mahdikhani et al. [46] found when exposed to sulfuric acid rain, silica-containing concrete samples' mechanical properties and durability were examined. They discovered that as the acidity of the solution increases, the concrete's quality degrades, its resistance and adsorption coefficient rise, but its compressive strength falls. In their study of the dry-to-wet cycle test for concrete under sulfate-accelerated corrosion, J.J. Guo et al. [47] investigated the effect of dry-to-wet duration ratio on sulfate corrosion of concrete. According to the test results, there are three stages to the sulfate change during dry-wet cycle erosion: the increasing period, the fluctuating period, and the quick decreasing period.H. Siad et al. [48] also recommended a new treatment procedure to accelerate the degradation process of concrete sulfate erosion, and found that the use of supplementary pretreatment in the dryer is an important acceleration of the degradation process. After studying the damage process of concrete subjected to sulfate attack under bending force and dry wet cycle, J.M. Gao [49] found that both bending load and dry wet cycle can hasten concrete degradation.

For the marine environment, H. Fazli et al. [50] investigated the effects of the marine environment on the bonding and exposed surface of concrete slabs. They discovered that a 12-month marine exposure had little effect on the performance of the epoxy resin between the carbon fiber reinforced polymer composite and concrete. W.H. Hu et al. [51] conducted an experimental study on the uniaxial compressive strength of concrete under natural and saturated conditions, and found that the concrete sample showed greater strength under water saturated conditions. C. Poinard et al. [52] reported that in the cyclic hydrostatic test, the most serious damage of cement matrix was observed between 60 and 150 MPa, and the linear elastic behavior was observed when the confining pressure was less than 60 MPa.

In recent years, scholars from various countries have done lots of research in this district, which provides a variety of new ideas for enhancing the ruggedness of concrete. However, due to the relatively complex construction of C-S-H in concrete, the liquid-solid interface interaction, the saturation model established by the experiment is not applicable to the unsaturated state and so on, which limits the research on the micro mechanism, especially the research on the molecular scale. Therefore, it is particularly important to build a multi-scale model by MD to research the unsaturated transport of water molecules and ions in C-S-H, which provides a theoretical basis for the microstructure design of concrete.

3 MD theory and Application

The main characteristic spatial scales of concrete cementitious materials are divided into macro scale, meso scale, micro scale and nano scale. In the first three scales, scholars in various countries have many relevant test methods and theories, and a set of mature research systems. A example multi-scale complicated material is cement, especially the complex structure of C-S-H in the nano scale limits the study of its micro and nano mechanism. Therefore, using molecular simulation as an auxiliary means of experiments can model multi-scale and effectively solve the limitations of experiments.

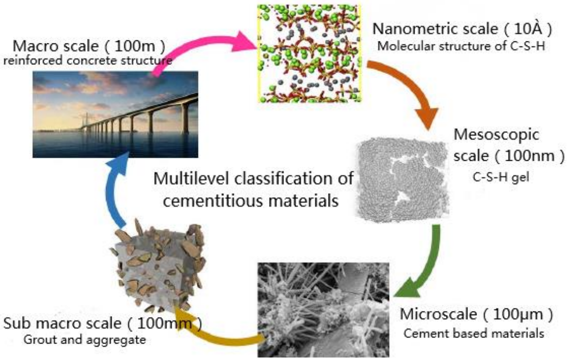

Figure 4 multi-scale representation of cement materials [53]

Molecular simulation is a method to simulate the structure and movement of molecules by using a computer molecular model in the unit of atoms, so as to simulate various chemical and physical attributes of molecular systems. It is based on experiment, through the basic principle to build the corresponding model and algorithm, so as to deduce the reasonable molecular structure and molecular motion. It can simulate static molecular structure and dynamic molecular motion. There are two main simulation methods: molecular Monte Carlo method and MD method.

In the molecular simulation of new concrete materials, the molecular kinematics method is generally used. This method primarily uses Newtonian mechanics to simulate the motion of the molecular system. Samples are taken from systems made up of various molecular states in order to calculate the configuration integral of the molecular system, which is then used to determine the molecular system's thermodynamic behavior and other pertinent information.

Its advantage is that the force between atoms is equivalent to the motion between particle coordinates by using appropriate simplified conditions, thus avoiding complex quantum calculation equations. While ensuring the accuracy, it greatly improves the applicable scope of atomic simulation, and can reach the operation of millions of atoms.

Because of the ocean, the environment such as acid rain is in an unsaturated state. However, most of the experimental studies of various researchers are based on the saturation model. However, the saturated model is not suitable for the unsaturated state, so there is a certain error between the experimental results and the reality. Therefore, studying the unsaturated transport of C-S-H / GO by MD can not only solve the limitations of experiments, but also solve the difficulties of finite element method or linear elastic fracture mechanics in continuum theory. It can observe and model multi-scale and simulate complex chemical reactions, so as to increase the longevity of cement-based materials even more.

4 Molecular structure and properties of multi-scale cement-based materials

4.1 Molecular structure and properties of C-S-H

C-S-H has the characteristics of strong surface activity, light weight, hydrophilicity and poor compatibility with organic aggregates. It is the primary product of hydration of cement-based cementitious materials. It can absorb some alkali metal ions and inhibit alkali aggregate reaction to some extent, so as to enhance the compressive strength of concrete in all aspects, effectively improve the cracking resistance and impermeability of concrete. At the same time, it is a mesoporous medium with pores that range in size from 0.5 nm to 10 nm [54-57], which can be used as a crucial conduit for ion transport.

In addition, C-S-H is a layered and arranged construction with complex chemical bonds. At the same time, other added polymers further increase the complexity of its structure. So far, it is generally believed that C-S-H and Tobermorite crystals have similar crystal structures, with short layer ordered and long layer disordered gel properties. The morphology of C-S-H is in an amorphous state, and the accumulated particles form relatively loose flakes. Defective silicon chains grow on the calcium layer of its crystal structure, which form a silicon calcium framework. Water molecules, calcium hydroxyl groups and silicon hydroxyl groups are distributed in the adjacent interlayer regions, which are characterized by high silicon calcium ratio, low silicon chain polymerization degree and low crystallinity.

P.A. Bonnaud et al. [58] researched the properties of confined water in C-S-H under different relative humidity through giant regular Monte Carlo simulation, and found that the influence of confined water on C-S-H condensation depends on the inter particle spacing between C-S-H particles. N. Giovambattista et al. [59] investigated the impact of surface polarity on the composition, dynamics, and mechanical characteristics of silicate interlayer water. The findings demonstrate that the hydrophilicity and hydrophobicity of silicate chains influence the structure of water molecules on the surface, and that the ice-like water layer of silicate crystals is responsible for the low rate of water molecule diffusion near the hydrophobic surface. M.J.A. Qomi et al. [60] ran MD simulations on 150 models with various Ca/Si ratios,. It was discovered that the matrix's composition affects the physical and chemical characteristics of water. According to M. Youssef et al. [61], the radial interaction between non-bridged oxygen atoms (O-NB) and hydrogen atoms in the interfacial water molecules is what gives C-S-H nanopore surfaces their hydrophilicity. D.S. Hou et al. [62] improved the solid-liquid interface model of calcium hydroxysilicate and discovered that the silicate chain deflects chloride ions under extensive simulation over a long period of time. In addition, they also showed that calcium ions adsorbed on the solid-liquid interface can enhance the adsorption of chloride on the surface.

The transport of water and molecules in C-S-H nano channels is a major factor affecting the durability of concrete. Therefore, it is essential to study the C-S-H through MD, so as to regulate the ion transport in the C-S-H microstructure in order to obtain good durability.

4.2 Molecular structure of GO and its application in concrete

Graphene oxide, a graphene derivative, has gained popularity as a cement-based modified material because of its excellent mechanical properties. Graphene is the material with the highest strength known to human beings. However, because of its hydrophobic surface, it is difficult to dissolve and diffuse in water. Therefore, graphene oxide with high hydrophilicity is used as a new material for concrete research. Although the strength of GO is marginally inferior to that of graphene, it still retains the advantages of graphene's superior mechanical properties and super high specific surface area. It also has hydroxyl, carboxyl, epoxy and other active functional groups. These functional groups make it have excellent reaction activity, reduce the van der Waals force between graphene layers to avoid the two layers from converging, and can easily composite with other materials.

After oxidation treatment, GO still has the layered structure of graphite, but each layer's graphene monolayer has had several oxygen functional groups added to it, making the single graphene structure exceedingly complicated. Although computer simulation, nuclear magnetic resonance and other methods have been used for analysis, the precise structure of GO cannot be determined. At present, several structural models have been put out regarding the structure of GO , including LK model, dynamic structural model (DSM), two-component structural model and so on. The most widely accepted crystal structure model is the LK model, which randomly distributes hydroxyl and epoxy groups on the GO monolith and introduces carboxyl and carbonyl groups near the monolith's edge.

Compared with other carbon based nanomaterials (such as carbon nanotubes, carbon nanofibers, etc.), the attached oxygen-containing function makes GO a highly dispersed reinforcing agent in cement matrix, and these materials are easy to agglomerate in cement-based composites [66-67]. According to A. Mohammed et al. [68], GO inclusions increase the porosity of GO reinforced cement-based composites. Therefore, with the increase of GO percentage, the chloride ion permeability increases and the adsorption value decreases.

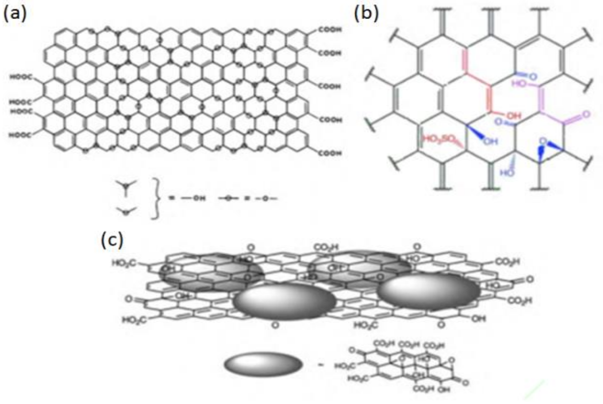

Figure 5 (a) LK model [63] , (b) DSM [64] and(c) two component structure model [65]

C.D. Sanglakpam [69] and others found that adding GO to concrete improved the ability of resisting sulfate attack, and with the increase of the percentage concentration of GO and gobm, the carbonation depth decreased. R.R. Bellum [70] and others found that the dense microstructure of the geopolymerized concrete sample made with graphene is beneficial for enhancing the geopolymer reaction. The GO with high specific surface area has the advantage of filling the gap and improving the strength performance of geopolymer concrete. S. Lv et al. [71] found that the oxygen-containing functional groups on the GO surface can offer adsorption sites for cement and promote the crystallization of cement hydration products through testing methods.

Although there is no unified theory about the chemical structure of GO at present, its tensile strength and compressive strength are enhanced by 53% and 91% respectively contrasted with those of the composites without graphene oxide, and the amount of 0.5% - 1% of other nano admixtures is reduced by nearly 20 times, which effectively reduces the carbon footprint in the cement production process, Therefore, it is necessary to study the unsaturated transport of GO in C-S-H by MD.

4.3 Synthesis and properties of C-S-H/GO

4.3.1 Synthesis of C-S-H / GO

C-S-H can be synthesized by hydrothermal synthesis, single ore hydration, solution synthesis and so on. Among them, the solution synthesis method is to dissolve calcium salt and silicon salt with deionized water, add 1-2ml sodium hydroxide solution to the mixed solution to keep the solution under alkaline conditions, and then add the two to the dispersant separately to obtain a mixed solution of C-S-H, which is relatively stable. Then, wash the sample with deionized water and absolute ethanol repeatedly, filter and wash at least three times, and then place the filtered C-S-H in the vacuum drying oven for drying for 1-2 days to obtain C-S-H.

The synthetic methods of GO mainly include Brodie method, staudmaier method and Hummers method. They all use strong protonic acid to deal with the original graphite to form a first-order graphite interlayer compound, and then add strong oxidant to oxidize it. Among them, Hummers method is the most widely used method with the best effect and the highest safety. It is to add natural graphite powder to sulfuric acid placed in the ice bath, add potassium permanganate and sodium nitrate under strong stirring, reduce excess manganese dioxide and potassium permanganate with 30% hydrogen peroxide and 1mol / L hydrochloric acid after three reaction stages, and after the black suspension turns bright yellow under the treatment of hydrogen peroxide, centrifuge the suspension until neutral, and dry at 60 ℃ to obtain graphite oxide. Finally, put the graphite oxide sheet into a beaker, add ultrapure water, and sonicate it to completely disperse it, so as to obtain GO solution.

4.3.2 Microstructure and property evolution of C-S-H/GO under complex environment

Under the erosion of acid rain environment, ions will invade along the C-S-H pore channel, and then react with it to form ettringite or gypsum, which will expand the original volume by 1.5-2.2 times, thus reducing the durability and strength of concrete. When GO with high surface area and good dispersion is added, the defect region of C-S-H can be repaired by forming an interlocking layered structure, improving its pore size distribution, reducing the total porosity and blocking its nanochannel connectivity, thus effectively preventing ion erosion and effectively alleviating the influence of acid rain environment on the strength and ruggedness of C-S-H.

In the case of freezing and thawing, the water in the channel of C-S-H will be frozen by cold, and the volume will start to increase, thus expanding the pores and forming water pressure, which will lead to concrete cracking and damage. When GO is added, due to the benefits of its large specific surface area, it can condense each phase, make it closely arranged, reduce the interface effect, improve the mechanical properties and reduce the influence of freezing and thawing environment on the physical properties of C-S-H.

Scholars from various countries have also conducted corresponding research on relevant aspects. W.L. Yang [72] et al. Studied that when the content of GO is 0.08%, the compressive strength of slag cement at 28d is increased by 10%, and the compressive strength of concrete at 28d is raised by 5.8%, and the fluidity of concrete, the corrosion coefficient of hydrogen and sulfate resistance are significantly improved. A. Mohammed et al. [68] studied the effect of GO on the transport performance of cement-based materials. The outcomes demonstrated that after adding GO, the anti chloride ion corrosion performance and water permeability of the test pieces were improved. GO crosslinked the hydrated crystals to form a relatively dense structure, decreased the invasion of chloride ions, and helped the concrete materials to be used in the marine environment for a longer time.

5 Study on structure and properties of C-S-H / GO based on MD theory

According to the structural similarity performance, the C-S-H model is usually replaced by Tobermorite 11 Å model for relevant simulation analysis. Its cell size is the a = 22.32 Å, b= 22.17 Å, c= 22.77 Å (α= 90°, β= 90°,γ= 90°)。 After that, the silicon tetrahedron partially bridged in the silicon chain was deleted, and the calcium silicon ratio of the model was adjusted to 1:4. Finally, a micro crack was generated in the z-axis direction along the middle of the cutting model.

The GO model uses graphite crystal instead of simulation analysis. Its cell size is the a = 2.46 Å, b= 4.26 Å, c= 3.4 Å (α= 90°,β= 90°,γ= 90°)。 Then, each unit cell was copied 15 times, 7 times and 1 times along the X, Y and Z directions, respectively. Then, on the basis of this graphene model, three functional groups of hydroxyl, epoxy and carboxyl were added to obtain the final GO structure. The number of three functional groups was 24, 24 and 12 respectively.

After the two models are constructed respectively, the GO model can be inserted into the nano-cracks of the C-S-H model for corresponding analysis. [70]

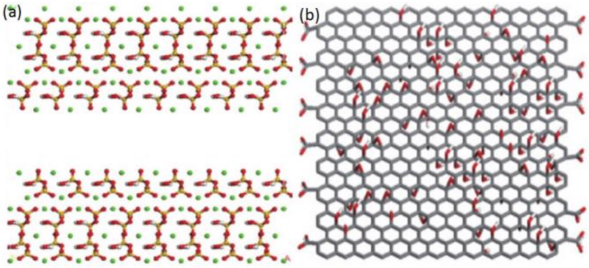

Figure 6 (a) Tobermorite 11Å model and (b) GO model [73]

5.1 Structural analysis of C-S-H / GO

The local structure of calcium ion in C-S-H determines the interface strength between it and GO. It acts as a bridge connecting adjacent silicon layers and can enhance the mechanical strength of multilayer graphene oxide sheets. However, calcium ions are present close to silicates, and silicate tetrahedron provides more oxygen sites for them, making calcium ions preferentially connected to them, which further results in the non-connection of more than half of the interlayer calcium ions to GO. Meanwhile, in water molecules, the hydrogen network formed between hydroxyl groups and functional groups also plays a key part in bridging calcium silicate sheets and GO. But due to the fracture of C-S bond, there are very few hydrogen bonds directly connected between C-S-H and GO. In addition, because of the weak interaction between the epoxy and oxygen atoms in the silicate chain, the hydrogen bond between the epoxy group in GO and the calcium silicate sheet is the weakest.

S. Sharma et al. [74] prepared two kinds of GO with thickness of 14nm, sheet diameter of 900nm, and thickness of 3nm, sheet diameter of 100nm by different methods, and studied the influence of the two GO on cement hydration crystals. The results showed that the large-size GO had more obvious regulating effect on hydration crystals, and the growth of hydration crystals was more dispersed; While the small diameter GO is more favorable to reduce the porosity and pore volume. The addition of GO can refine the microstructure of hydration products and efficiently enhance the macro bending strength and compressive strength. Q. Wan et al. [75] also studied the influence of different mixing amounts of GO on the microstructure, and found that the formation speed of hydrated crystals was accelerated, the arrangement tended to be regular, the acicular crystal clusters were significantly increased in the early stage, the number and volume of pores in the microstructure were significantly decreased, and the strength and toughness of the specimen were improved.

5.2 Mechanical properties of C-S-H / GO nanostructures

The GO reinforced C-S-H has superior mechanical characteristics when receiving tensile load because of the robust Ca-O bond and hydrogen bond. The interface region between two dissimilar materials often has weak load resistance, and fracture always happens there. However, the GO-reinforced C-S-H composite initially fails in the base material's matrix before breaking at the interface. This failure mechanism is very favorable for the devise of cement composite materials. It can simultaneously deform the C-S-H and GO composite materials to resist the load.

The chemical bonding between the functional groups of C-S-H and GO can effectively enhance the brittleness of materials. In addition, the carboxyl and hydroxyl groups in GO can maintain good stability and high interfacial strength in C-S-H, thus ensuring and improving the stability and durability of materials.

B. Fakhim et al. [76] researched the mechanical properties of GO cement-based composite. GO sol was prepared by oxidation-reduction and ultrasonic method and added to cement mortar to prepare GO cement-based composite. The results reflected that the best content of GO was 1.5wt%, which could improve the tensile strength of the material by 48%. Through FE-SEM, XRD and other tests, it is found that GO can slow down the development of cracks and promote, nucleate and template the formation of C-S-H gel. S. Lv et al. [77] Studied the influence of GO on the microstructure and performance of cement paste and its mechanism by preparing naphthalene water reducer / GO composite solution and adding it into cement mortar. Through comparison, the compressive strength and flexural strength of the sample can reach 65.4 MPa and 10.6 MPa when 0.06 g GO is added into 100 g of cement, respectively, increasing by 29.3% and 41.4%. SEM observation shows that GO can promote cement hydration reaction to form dense lamellar structure.

5.3 Analysis of interfacial atomic dynamics of C-S-H / GO

The hydrogen bonding of C-S-H and the coordination between Ca-O make the graphene oxide sheet stably confined in the nano gap of C-S-H, and the connection between the two is very stable. At the same time, the carboxylate functional group on GO has strong polarity and hydrophilicity, which can limit the adjacent water molecules through hydrogen bonding and play a role in stabilizing the interlayer water. Because the interlayer water can travel quickly and create a strong separation pressure, which decreases the stability of the chemical bonds in C-S-H and lowers the silicate materials' characteristics. Hydrophilic functional groups can efficiently stop water from moving, increasing the tensile strength of materials.

As mentioned above, the chemical bond between calcium ion and oxygen in functional groups and the hydrogen bond at the interface play a key role in bridging GO and C-S-H. The high strength Ca-Oc bond ensures the stability of GO and C-S-H binding. Calcium ions combine with adjacent water and hydroxyl groups to form a stable hydrated structure, while it is strongly restricted in the cage constructed by Si-O-Ca bonds. The bond strength of calcium ions between different functional groups should be GO-COOH > GO-OH > GO-Oo. Because carboxylate groups have high binding energy to calcium ions on the surface, GO-COOH can remain on the surface of C-S-H for a relatively long time.

The stability of the hydrogen bond depends on the polarity of the functional oxygen atom. Therefore, the carboxyl group model with high degree of protonation in GO can closely attract adjacent hydrogen atoms and improve bonding stability. On the contrary, epoxy groups with low polarity and weak hydrophilicity have weak restrictions on the movement of hydrogen atoms.

5.4 Chemical reaction of C-S-H / GO model

The closed environment of C-S-H will affect the stability of functional groups on GO, leading to its bond breaking and reforming. The calcium ions in the C-S-H layer move to the vicinity of the Oc of the epoxy group, stretching the broken C-O bond and generating the C = O bond. However, because the electronegativity of the epoxy group is low, the attraction between GO and C-S-H is very weak, so only a very small part will be destroyed to form the C = O bond.

Additional interactions between functional groups and C-S-H will take place. As time goes on, water molecules and C-OH groups will continue to decrease, when Si-OH and Ca-OH molecules will increase (eq.1).

This suggests that the hydrolysis reaction will not be prevented by the reaction of C-OH groups, but rather will be further promoted in the latter stages. But at the same time, carboxyl group can also inhibit the dissociation reaction of water to a certain extent, and affect the diffusion degree of GO in water according to the pH value (eq.2).

$$CaO\cdot SiO\cdot mH_2O+GO\text{-}OH+H_2O\rightarrow Ca(OH)_2+SiO_2(H_2O)_m+CO_2 \quad (1)$$

$$GO\text{-}COOH\rightarrow GO\text{-}COO^-+H^+ \quad (2)$$

Therefore, it can be shown that the non bridged sites and equilibrium ions provided by the C-S-H surface contribute to the deprotonation of the functional groups in the graphene oxide sheet, and the degree of reaction depends largely on the activity of the functional groups. On the other hand, the deprotonation reaction affects the hydrolysis reaction of water molecules in C-S-H, and the hydrolysis dissociation and deprotonation of GO will disturb the flatness of graphene bottom structure.

6 Unsaturated transport of water molecules and ions in C-S-H / GO

Ion transport affects the physical and chemical properties of cement-based materials in concrete, including ion diffusion and salt solution capillary adsorption. As the main product of hydration of cement-based cementitious materials, C-S-H, the change of water content makes its internal structure partially irreversible, which inevitably affects the permeability. In addition, C-S-H becomes the dominant factor controlling water permeability at very low saturation [78-79]. In the past decade, most of the research in the laboratory has focused on the ion transport in saturated cement-based materials. However, the on-site concrete structure is rarely saturated in the actual use environment, so the ion transport is a water dependent process. Therefore, it is very important for us to study the ion transport in unsaturated cement-based materials.

6.1 Experimental research status of unsaturated transport of water molecules and ions in C-S-H / GO

For the ion migration mechanism of saturated cementitious materials, scholars have almost studied it on the basis of Fick's second law. However, these assumptions are not tenable in reality. Therefore, more and more scholars propose amendments to these assumptions and multi-scale experimental and simulation studies. L. Homan et al.[80] analyzed the influence of water transport on chloride ion penetration in partially saturated and fully saturated concrete. The results confirm the coupling effect between water transport and chloride penetration in concrete. Z. Liu et al.[81] studied the transport characteristics of multi-component ions in the pores of C-S-H in saturated state through molecular dynamics simulation. They found that the calcium silicon ratio had a significant impact on the adsorption of chloride ions on the surface of C-S-H. And the adsorption was strongest when the calcium silicon ratio was 1.2.

For the ion migration mechanism of unsaturated cementitious materials, some scholars still use Fick's second law to study. But some scholars considered diffusion and convection separately. They believed that chloride ions were transported by convection at a certain depth of the concrete surface when they were transported in the form of diffusion beyond this depth[82]. E.P. Nielsen [83] analyzed the transport process of chloride ions according to the Fick's law. He attributed all the effects caused by convection effects to the chloride diffusion coefficient. A. Ayman [84] deduced the chloride ion transport equation considering convection effect. However, the convection term ignores the chloride concentration gradient. So the governing equation does not strictly satisfy the law of conservation of matter. Y. Zhang [85] obtained the multi-component partial differential equation of chloride ion transport process under the dry wet cycle. It uses saturation as the driving force of water diffusion which is complicated to determine the boundary conditions, so it is not conducive to practical application.

And many experiments have focused on ion diffusion or capillary adsorption of saline solutions in C-S-H pore channels. They use nuclear magnetic resonance technology or quasi elastic neutron scattering technology to study the water in the pore channel, analyze its mobility, and divide it into chemically bound water, physically adsorbed water and capillary water according to the results. P. Yu and R.J. Kirkpatrick [86] studied the kinetic characteristics of chloride binding on C-S-H mineral analogues in contact with chloride aqueous solution using NMR relaxation method, thus proving the weak chloride ion binding ability of C-S-H surface. D.S. Hou et al. [87] also concluded that the adsorption capacity of chloride ions on C-S-H channels is weak, and found that chloride ions can be indirectly adsorbed through the adsorbed cations.

However, most of the studies on the unsaturated transport of water molecules and ions are based on macroscopic experiments or theoretical formulas, so it is difficult to find the microscopic mechanism of the transport characteristics of water molecules and ions. Therefore, it is very necessary to establish the C-S-H / GO model with MD to study the unsaturated transport of water molecules and ions, which provides a considerable basis for the durability design of concrete.

6.2 MD theory and model of C-S-H / GO

At present, the experimental and theoretical research on water and ion transport at the macro level has been relatively mature, and the research on the micro mechanism is relatively small. However, to explore the reaction and characteristics between material atoms from the microscopic scale will help us to understand the essence of things more deeply, and then better guide the development of concrete. Therefore, research on the microscopic mechanisms of concrete has received increasing attention in recent years [88].

X.Y. Wang et al. [89] established theoretical diffusion equations in saturated, unsaturated and dry states by using Fick's theorem and mass balance equation; J.Y. Sun [90] studied the transmission law of water in unsaturated concrete, and carried out numerical analysis and calculation on the transmission law of water when the concrete is capillary water absorption. The transport properties of water molecules and erosion ions in C-S-H using MD were investigated by D.S. Hou et al. [91]. The findings demonstrate that water molecules move at a faster pace than ions do, and the penetration depth of ions is positively related to the pore size of C-S-H nanoparticles.

With the rapid development of high-performance computing equipment, it is feasible to simulate the amorphous C-S-H on the molecular scale by MD, which can not only determine the performance change mechanism of cement concrete subjected to ion and water molecule erosion and destruction at the same scale, but also make it possible to design the material structure and predict the performance at the molecular scale, So as to realize the multi-scale modeling of GO / C-S-H and the integrated research of microstructure / ion control / performance in complex environment.

M. Wang et al. [92] proposed a three-dimensional mechanism model of GO functional group structure regulating hydration products and microstructure. The model believes that GO is connected into a three-dimensional network structure from the vertical and horizontal directions, and then - COOH at the edge of GO and Ca $^{2+}$ of hydration product $Ca(OH)_2$ form COO-CA-OOC to connect the three-dimensional network structure. At the same time, the hydration product is further inserted into the three-dimensional structure to compact the microstructure, Realize the regulation of GO functional groups on the interface of cement-based composites. In another work, D.S. Hou [93] et al found through reaction force field MD that the hydroxyl and carboxyl groups of GO provided a large number of oxygen sites to accept hydrogen bonds and bind with adjacent sodium ions, thereby fixing water molecules and ions on the GO surface. GO-COOH is deeply rooted in C-S-H, further blocking the connectivity of transport channels and "cage" water and ions in the entrance region of gel pores. In addition, W.L. Jin et al. [94] established a theoretical model of chloride ion transport in partially saturated concrete by considering the time of dry wet cycle, the initial saturation of pores and the saturation of surface layer during drying, and verified the reliability of the model through experiments.

Therefore, it is of great theoretical significance and engineering application value to deeply study the dynamic evolution of ions and water molecules in GO / C-S-H nanochannels. It is also significant to investigate the influence of interface bonding strength, structural stability, surface / interface chemical state and mechanical properties through configuration design and MD theroy.

6.3 Unsaturated transport mechanism of ions and water molecules in nanopores

C-S-H has micro/nano pores, including small gel pores (5 ～ 100 Å) and capillary pores (＞ 100 Å). Some water molecules are changed during the cement hydration step into chemically bonded water, which is then closely associated with the C-S-H layer through the development of Ca-OH and Si-OH connections. The remaining water molecules are used to fill the gel pores and pores. A significant number of sodium, potassium, calcium, and hydroxide ions are released from the cement as the chemical reaction progresses and are intensely concentrated in the nanopores. Meanwhile, due to the strong interaction between water and silicate oxygen atoms, the water molecules adsorbed on the C-S-H surface have higher bulk density, orientation preference and lower diffusivity. In addition, the transport of water and ions in the channels is also affected by slip effect, dynamic contact angle and effective viscosity.

Y. T. Jia et al.[95] employed MS to study the water and ions in the unsaturated and saturated C-S-H channels. Their results show that the transport of water molecules in saturated state is mainly an interactive transport process formed by the mutual diffusion of upper and lower water molecules, which slows down the diffusion speed of water molecules in solution along the channel. So the invasion speed of ions carried is slower than that in unsaturated state. Because of the large number of water molecules, the restriction effect of other water molecules filled in the pores makes the hydration film at the interface more compact and stable, which also increases the retention time of ions at the interface. This strong interaction makes chloride ions firmly adsorbed on the pore surface. At the same time, it can further attract sodium ions and grow into large ion clusters. Because the width of the pore is limited, this kind of ion clusters formed on the surface combine with the ion clusters in the solution to prevent subsequent water molecules and ions from entering. Thus, the transport speed of water molecules and ions is too slow and the number of ions entering the channel is too small.

Besides, their results also prove that the transport of water molecules and ions in the unsaturated state is mainly driven by capillarity. Water molecules are transmitted in the form of meniscus along the C-S-H channel interface, which is consistent with the actually observed capillary absorption phenomenon. At the same time, the transmission speed of water molecules and ions is faster than that in the saturated state.

In terms of dynamics, due to the adsorption of ions at the pore interface and the formation of ion clusters, the movement speed of water molecules in the unsaturated state is stronger than that of ions. Silicate links on the surface of C-S-H can provide non bridged oxygen sites to connect with sodium ions, and calcium ions on the surface of C-S-H can capture chloride ions to form ion pairs. The strong interaction between sodium ions and the interface makes the long-term retention of sodium ions lead to the surface shedding of calcium ions to form ion clusters in the solution. If the ion cluster is too large, it can block the nanochannel and prevent the invasion of water molecules and ions.

When GO is added to C-S-H, the flow velocity of the fluid in the C-S-H nanochannel largely depends on the type of functional groups embedded in the coated plate on the inner surface of C-S-H. The hydroxyl and carboxyl groups in the graphene oxide sheet provide enough oxygen sites to accept hydrogen bonds and bind to the adjacent sodium ions, thus effectively resisting the entry of water molecules and ions. In particular, the surface calcium atoms in the C-S-H play a dominant role in connecting the non bridged oxygen sites and oxygen functional groups in the silicate chain in the graphene oxide sheet, which enhances the chemical bond at the interface. The carboxyl groups on the GO further blocks the connectivity of the transport channel and condenses the water and ions in the inlet area of the gel hole.

Graphene oxide sheets separate from the surface of C-S-H as a result of the van der Waals interaction between GO and C-S-H being greatly weakened by the entry of ions and water molecules. Water and ions are barely repelled by the divided graphene oxide sheets.

In addition, the graphene oxide sheet slows down the intrusion of ions and water in C-S-H pore through the cage effect. With the increase of gel pore size, the effect will gradually weaken, and the fixation effect caused by the attraction of GO plays a major role in resisting the invasion of water molecules and ions.

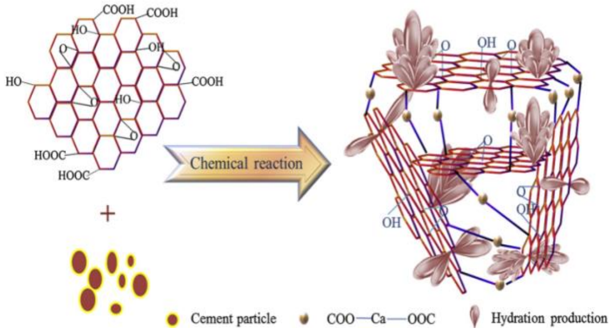

Figure 7 model of GO regulating hydration products and microstructure [92]

Due to the coupling and fixation between the two interfaces of C-S-H nanopore, a transition zone with slow migration speed is formed at the entrance of the pore. The existence of the transition zone can well inhibit the intrusion of ions with large hydration layer. Therefore, the pore diameter of C-S-H can be less than 2nm, which has a certain filtering effect on water molecules and ions. At the same time, harmless ions can also be added to C-S-H to make it grow into larger ion water clusters, preventing the invasion of other water molecules and ions. In this way, the transport of ions can be regulated from the microstructure so that C-S-H can obtain good strength and durability.

7 Conclusion and future prospects

This paper mainly introduces the influence of the environment on the durability of concrete and the two new concrete materials, C-S-H and GO, and also introduces the relevant characteristics of studying the unsaturated transport of water molecules and ions in C-S-H / GO from the nano and micro scale by MD.

GO has strong universality, but its output is low. So GO is expensive and cannot be widely used in practice now. Many researchers have proposed some improved methods. E. Siegfried et al.[96] reduced the production of CO_2 by keeping the reaction temperature at 0~10℃ and prolonging the oxidation time. In this way, GO with fewer defects is obtained. L. Peng et al.[97] used strong oxidant K_2FeO_4 instead of $KMnO_4$ to prepare GO, which can avoid the introduction of polluting heavy metals and the generation of toxic gases in the preparation process. This method can also recover sulfuric acid, which is a safe, efficient and low-cost environmental protection method. Therefore, high-quality and more GO products can be prepared at the same cost with the continuous optimization of GO preparation technology in the future. And the price of GO will gradually decrease, which can be widely used in actual projects.

In the past, the research on water and ion transport of C-S-H/GO in unsaturated environment mainly used micro scale or macro scale single scale. Moreover, the research mainly focuses on the influence of a single erosive ion on unsaturated transport. So the research still needs to be improved in many aspects. The following aspects can be considered:

(1) The MD simulation of C-S-H / GO model still has some limitations and does not fully reflect the uncertainty of C-S-H and GO structure. If we can build mesoscopic and even macroscopic models, we can better realize the confirmation and connection between simulation and experiment.

(2) The dispersion of cement-based materials strengthened by nano materials has always been one of the core issues. When the mixing amount of GO is faced with a large number of concrete materials, the mechanism efficiency may be too low and it is difficult to effectively disperse GO. Therefore, it is necessary to study and formulate large-scale GO dispersion technology to ensure that GO can be fully improved.

(3) In real life, natural electric fields exist in the ocean and other environments. Under the action of electric fields, water molecules and ions will be affected accordingly. Therefore, it is necessary to further study the unsaturated transport of water molecules and ions in C-S-H / GO under the action of electric field.

(4) The varied interface structure, complex solid-solid and liquid-solid interface interactions in C-S-H/GO limit the microscopic study. So it is necessary to study the local interface of C-S-H/GO to analyze the role of GO in C-S-H.

(5) Since there are many kinds of ions invading into

C-S-H, and there may be certain mutual reactions between them, it is necessary to consider the invasion depth and influence of different ions in unsaturated transport.

(6) There are actually three zones (saturated zone, transition zone and unsaturated zone) in unsaturated cementitious materials, which also affect the unsaturated transport of water molecules and ions. Therefore, it is necessary to consider the interaction between saturated zone, transition zone and unsaturated zone.

Supplementary notes:

Figure 3:

Atmospheric area: This area is affected by sea salt particles and land atmosphere.

Splash area: In this area, the dry and wet environment caused by seawater splash and the temperature rise caused by sunlight form the most serious corrosion environment.

Tidal range area: This area is affected by sea tide.

Total immersion area: In this area, the corrosiveness of seawater is mainly affected by dissolved oxygen, flow rate, temperature, salinity, pH value, pollution factors and biological factors.

Sea Mud Area: In this area, dissolved oxygen, temperature and the role of anaerobic organisms are the main factors affecting corrosivity.

Declaration of competing interest

No potential conflict of interest was reported by the authors.

Acknowledgments

This work was supported by a Doctoral program of Zhejiang University of science and technology (F701104L08).

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