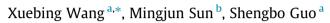
Construction and Building Materials 220 (2019) 607-614

Contents lists available at ScienceDirect

Construction and Building Materials

journal homepage: www.elsevier.com/locate/conbuildmat

Water absorption characteristics of cement-based materials based on the chemical reaction $\overset{\scriptscriptstyle \, \times}{}$



^a School of Civil Engineering and Architecture, Hubei University of Arts and Science, Xiangyang 441053, China
^b School of Materials and Metallurgy, Wuhan University of Science and Technology, Wuhan 430081, China

HIGHLIGHTS

• Capillary permeation was the main force in the early stage of water absorption of cement-based materials.

• Absorption mass fraction was increased with the water absorption time and finally reached to a certain content.

• Hydrolysis was not merely occurred in the process of water absorption.

ARTICLE INFO

Article history: Received 16 February 2019 Received in revised form 2 June 2019 Accepted 6 June 2019 Available online 24 June 2019

Keywords: Cement-based materials Underground water Absorption Mathematical model Cement hydrolysis

ABSTRACT

With the development of urban infrastructure, subway and other underground projects are gradually being constructed in various cities. The influence of water absorption on surface of cement-based materials has therefore become more and more important. A mathematical model and the relative experiment of water absorption in cement mortar were investigated. The results showed that the change of radius of pore was decreased and absorption mass fraction was increased with the increased of absorption time. The possibility and direction of reaction during this process were studied, and the result showed that hydrolysis was not merely occurred in this process.

© 2019 Elsevier Ltd. All rights reserved.

1. Introduction

Cement-based material is one of the most useful materials in civil engineering. Based on the characteristic of porous of cement-based material, its service performance change accordingly. When they are built in the underground environment, water tends to penetrate cement-based materials as capillary force. Because of existence of other ions in groundwater, it penetrated into the materials and lead to be affected of durability of materials. Therefore, the research of absorption of underground water on surface of cement-based materials is important.

The recent research of absorption behavior was mainly focused on the fitting equation. the fitting method was adopted in the research of Martys et al. [1] to study the transport law of moisture in cement-based materials, and the fitted equation was as follows:

* Corresponding author.

E-mail address: wangxuebing@hbuas.edu.cn (X. Wang).

 $\frac{W}{A} = St^{\frac{1}{2}} + S_0 \tag{1}$

In this equation, *W* represented the total amount of water; *A* was the contact surface area of the sample; *t* was the test time; *S* was the water absorption coefficient and represented the sorptivity of a material, and S_0 was the correction coefficient. This equation was widely used to evaluate the permeation performance in service life of concrete structures, water absorption coefficient *S* was therefore an important parameter [2–5]. Sorptivity was obtained empirically from the slope of the cumulative volume of absorbed water per unit of area of inflow surface versus the square root of time [6].

Based on the basic Eq. (1), many other equations were used to study the process of water absorption. Tegguer [7] summarized and corrected the equation and proposed a new Eq. (2).

$$W = C_1 + S_1 t^{\frac{1}{2}} - C_2 t \tag{2}$$

Among them, C_1 , S_1 , C_2 was the constant respectively.

Chunhua Shen and others [8] considered the effect of diffusion on this basis and the result was:







^{*} Foundation by Hubei Provincial Natural Science Foundation of China (2018CFC872), the foundation for fostering of HBUAS(2018kypygp007)

$$\frac{W}{A} = B \left[1 - \exp\left(-S_2 t^{\frac{1}{2}} / B \right) \right] + d \tag{3}$$

Among them, S_2 was 17.2 kg/m³ and *B* was 0.38 mm when the sample was mortar; *d* was the water content by diffusion and it can be calculated by:

$$\frac{\partial d}{\partial t} = D \frac{\partial^2 d}{\partial x^2} \tag{4}$$

Among them, *x* was the depth of diffusion.

But in some situation, the sorptivity and square root of time were not quit fitted to a line, therefore it was fitted by the power function [9].

However, these equations were all based on the method of fitting, and the parameters obtained had no physical meaning.

In order to study the change of porosity of cement-based materials, Mercury intrusion porosimetry (MIP) and small angle X-ray scattering methods were used. However, the preprocessing of these methods were all characterized by drying the sample firstly and then measuring the pore size indirectly. Both methods had their own disadvantages. Firstly, these methods cannot directly determine the changes in the pore size of cement-based materials in a humid environment. Secondly, both of them were all the damage analysis and the measured samples were handled to small block or powder, so the experiments cannot be carried out continuously. The measurement principle of low field nuclear magnetic resonance technique was based on the relaxation time of hydrogen atom, it can transform to determination of the pore size of cement based materials [10]. Because the absorption behavior of cement based materials resulted in the change of water in the pores, the low field nuclear magnetic resonance technique was an effective method to measure the process of water absorption of cement based materials.

Water was an important carrier of chemical ions for the durability of the material in the groundwater. Various ions in the groundwater were transported into the cement based materials with the transport of water which were chemically reacted with the hydrated products in the material and eventually formed a variety of corrosion products [11,12]. These corrosion products included ettringite and gypsum and other products which lead to change the original pore structure of the materials, thus change the durability of materials [13]. Chen, et al. [14] found that the structure of C-S-H was changed with NH⁴₄ solution participated and Q³ of SiO⁴₄ was formed in this structure; We had following study the detail change process of structure of C-S-H and found that it was changed from chain structure to net structure [12]. Therefore, it was important to study the change of pore structure caused by the presence of water in the pores of cement-based materials.

2. Theoretical process of absorption model

2.1. Theoretical calculation of absorption

The transmission of chemical ions in water was mainly based on the Fick's second law, it was generally believed that the driving force of diffusion was due to the concentration difference between two sides of the material [15,16]. However, cement-based materials at service environment was often faced the condition of both pressure water and capillary force for the water existed environment. For example, the depth of underground traffic system was usually above 10 m, sometimes even more than 30 m, pressure head was therefore increased; meanwhile, cement-based material was a kind of porous material, capillary force was existed in water of pores. According to these analysis, two kinds of forces were both existed in cement-based material. Therefore, the transmission of the cement-based materials was different with the general transmission. When water was initially absorbed into cementbased materials, total content of water (Q) entering the cementbased materials through pores was mainly included:

$$\mathbf{Q} = \mathbf{Q}_c + \mathbf{Q}_d \tag{5}$$

Among them, Q_c represented the water content caused by capillary absorption, Q_d was the water content caused by diffusion. The diffusion caused by concentration difference was relatively small. According to Fick's second law, the diffusion coefficient of water in cement-based materials was about $D = 10^{-12} \text{ m/s}[17]$, so the diffusion rate was very slow. In this paper, the mechanism of early moisture transfer was discussed. Driving force of capillary and pressure head were far greater than that of concentration difference, so the diffusion factor was neglected. On the flow of capillary absorption, water can be regarded as an incompressible Newton fluid which was followed Hagen-Poiseuille law (Eq. (6)) [18], it was applicable to the calculation of steady seepage process of water and good results had been obtained. Bo Yang et al. [19] considered it suitable to investigate the through-thickness permeability of woven fabrics. Pouya et al. [20] analyzed the permeability of an infinite matrix containing disc-shaped cracks based on this formula.

$$\frac{dV}{dt} = \frac{\pi \sum P}{8\eta l} r^4 \tag{6}$$

Among them: *V* represented volume; *P* was driving pressure; *r* was the average radius of pores in cement-based material; *l* was the average depth of pores; η was the viscosity of water, and it value was about 1.0050×10^{-3} N·s·m⁻² [21] when the temperature was 20 °C.

When water was permeated in cement-based materials, this process can be regarded as the effect of multiple force. Both of forces were mainly consisted of the capillary force and the gravity of external water. The direction of this force was based on the sum direction of capillary force and pressure difference of water between the inside and outside of materials. According to the calculation method of different forces, the capillary force, the pressure of underground water and the gravity of the inner water are calculated by Eq. (7) [22,23]:

$$G = \rho gh, \ p_c = \frac{2\gamma}{r'} \cos\theta, \ p_l = \rho gl \tag{7}$$

Among them: *G* represented the pressure of underground water; ρ was the density of water, and its value was 1000 kg/m³; g was the gravity acceleration; *h* was the depth of materials under the earth. p_c was the pressure intensity caused by surface tension; the surface tension of water was expressed by γ and its value was about 0.0728 N·m⁻¹ at the temperature of 20 °C [21]. p_l was the gravity caused by the water that had permeated into the material. *l* was the height of the external water, *r*' was the radius of the capillary pore, and θ was the contact angle.

The pores in cement-based material can be considered the same, therefore they can be simplified as a capillary pore which was showed in Fig. 1.

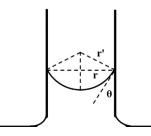


Fig. 1. Schematic diagram of pore in cement-based materials.

The relation between radius of pores in cement-based material and radius of curvature of liquid surface of solution in pores was therefore calculated by Eq. (8) [24].

$$r = r'\cos\theta \tag{8}$$

When the contact angel was equal to 0, r = r'.

In actual civil engineering structures, the depth of ground water was generally being much larger than its thickness. For example, the thickness of prefabricated reinforced concrete segment was generally 300–600 mm (China National Standard: GB/T 22082-2008 "reinforced concrete segment"), but the depth of general underground rail traffic engineering was more than 10 m. Therefore, the influence of gravity in Eq. (7) was ignores.

The radius of cement-based materials was not unchanged in every process during the permeation of water. According to chemical reactions of this process, water can participate to react with the hydration product of cement which mainly included C–S–H, C–A(F)–H [25], free water can finally transform to bound water in this process. Take the 9.3 Å tobermorite (C_5S_6H) for instance, based on the chemical reaction, this processes can be expressed as Eqs. (9) and (10).

$$C_5 S_6 H + 4 H \rightleftharpoons C_5 S_6 H_5 \tag{9}$$

$$C_5 S_6 H_5 + 4 H \rightleftharpoons C_5 S_6 H_9 \tag{10}$$

These three chemical reaction products were all called as tobermorite and their physical performances were showed in Table 1 [26,27].

According to Table 1, the molar volume of three types of tobermorite were increased with content of bound water. In the process of absorption of water into the cement-based materials, water firstly penetrated the pores of cement-based material and then reacted with C—S—H, the volume was increased and induced the radius of pores decreased [28]. In the process of making materials, the cement as one of raw materials was evenly distributed in the material. With the hydration of the cement in the material, the hydrated product C-S-H was therefore formed in the material evenly.

Based on the solid phase reaction kinetics, according to the mechanism of first order reaction, kinetic equation of this process can be expressed as Eq. (11) [29].

$$\frac{dG'}{dt} = KF(1 - G')G' \approx KFt \tag{11}$$

where: K was the reaction rate constant; F was the reaction surface area, it can be assumed that it was not changed in every process; G'was the reaction percent, because the hydration products that reacted with water in materials can be considered to be evenly distributed in the material, so the reaction percent of the material can be expressed as Eq. (12).

$$G' = \frac{x'}{l'} \tag{12}$$

Among them: x' was the reaction depth; l' was the theoretical thickness.

The hydration products caused the volume expansion of cement-based materials and resulted in the change of radius of cement-based materials. In a relatively dry environment, the

Table 1Physical performance of three types of tobermorite [21,26].

formula	C_5S_6H	$C_5S_6H_5$	$C_5S_6H_9$
Density (g/cm ³)	2.7	2.44	2.2
Molar volume (cm ³ /mol)	243.7	299.2	364.5
d (Å)	9.3	11.3	14

bound water content of C—S—H can be gradually lost. According to the data in Table 1, when the bound water of C—S—H gradually lost, the volume of the C—S—H was gradually shrinking [28,30]. Conversely, when water penetrated gradually to the material, the related chemical reaction was carried on. During this process, water content of C—S—H was therefore increased, and its molar volume was increased gradually. In this process, water was penetrated from the pores gradually to the interior of material. When water entered the cement-based material, the expansion part of C—S—H after absorbing water caused the radius of the pore decreased gradually. Therefore, the radius of pores can be changed by the Eq. (13).

$$r = R - x'(s - 1) \tag{13}$$

where: *R* was the initial radius of pores; *s* was the expansion ration per unit reaction depth.

Because the pores in cement-based materials could be approximated as cylinders [28,30], the volume of them was:

$$V = \pi r^2 l \tag{14}$$

Based on the above analysis and calculation, the Eq. (6) can be converted into a first order linear differential equation [26] and it can be solved to calculate the relation of absorption trend of underground water.

Because absorption mass of cement-based material can be monitored in real time, it can be converted as:

$$Q_c = \frac{\Delta m}{m_d} = \frac{n\pi r^2 \rho l}{m_d} \tag{15}$$

Among them, Δm and m_d were the mass of absorbed water and dried test sample; n was the number of pores of the test sample.

3. Materials and methods

3.1. Raw material

The cement used in the experiment was the commercial P.O 42.5N Portland cement. Physical properties and oxide compositions of cement was showed in Tables 2 and 3 respectively.

After hydration of cement, hydration products mainly contained C-S-H, C-A(Fe)-F, ettringite, CH and calcium, these hydration products were evenly distributed in cementitious materials.

Standard sand was used in this experiment, which was according to China national standards GB178-1997. It was natural round silica sand with content of SiO_2 not less than 98%.

3.2. Preparation of cement mortar

Test mortars were prepared according to the China national standard GB/T 17671-1999 "method of testing cementsdetermination of strength", water cement ratio was 0.5 and 0.45 respectively, and cement sand ratio was 1:3. Each mortar was mechanically stirred by a mixer and then loaded into the mould which the size was 40 mm \times 40 mm \times 160 mm. The samples were and compacted and then cured for 28 days under the condition of temperature 20 °C and RH > 90%. Then the specimens were dried in an oven at 105 °C, measured its mass at intervals until it reached a constant mass. The test samples were following cooled in the dryer. One surface of mortar which size was $40 \text{ mm} \times 160 \text{ mm}$ was then left behind for follow-up experiments and other five surfaces were sealed with paraffin wax mixed with a little amount of rosin. Samples were finally supported by two glass rods and placed in a container, and then added water slowly to the container until the absorbed surface of sample was soaked in over $1 \sim 2 \text{ mm}$ depth.

Table	2
-------	---

Physical properties of cement.

Specific surface area/m ² kg ⁻¹	Standard consistency water consumption/%	Setting time/min		Flexural strength/MPa		Compressive strength/MPa	
		Initial	Final	3d	28d	3d	28d
379	27.5	190	245	5.8	9.2	28.4	50.0

Table 3

Oxide compositions of cement/wt%.

CaO	SiO ₂	Al_2O_3	Fe ₂ O ₃	MgO	SO ₃	K ₂ O	TiO ₂	Total	Total
65.03	18.50	4.22	2.90	0.67	3.71	0.76	0.29	98.33	3.42

After the experiment started, the mortars were taking out regularly to determinate the relative data.

3.3. Measurement method

During the test, the changes of sample were monitored mainly by the pore size distribution and the absorption mass fraction changes of the material. Before monitoring, liquid water of surface of cement mortar was absorbed through a towel to ensure that the liquid water on the surface was absorbed completely. a towel was used to wipe the test mortar to dry the surface moisture. Then the related test was carried out. The pore size distribution of the material was detected by the low field nuclear magnetic resonance technique (MesoMR23-060H-I (Suzhou), pore size above 0.001μ m); Determination of mass changes were used by the electronic balance(operation range being 0–1000 g, precision being 0.01 g) and the absorption mass fraction was therefore calculated by Eq. (15).

4. Results and discussion

4.1. Changes of pore structure of sample at different soaking time

The pore structure of sample at different absorption time were determined by low field nuclear magnetic resonance technique, and the result was showed in Fig. 2.

Because of the change of water in C-S-H and pore structure, the radius of pores in the cement mortar were also changed. According to Fig. 2, the radius of pores was decreased with the increased of absorption time. When the pore size of cement mortar was reducing, the capillary tension was gradually increased according to Eq. (7). Due to existence of C-S-H in the cement mortar, its volume in these specimens was increased with the humidity [28,30], which lead to decrease of the radius of the cement mortar according to Tab.1. As the decreasing of the radius of cement mortar, the capillary tension was therefore increased. To analyze the change of pore size of cement mortar, the most probable radius of cement mortar at different absorption time was compared. The result was showed in Fig. 3.

It can be found that the pore size of mortar was gradually decreased with the change of the absorption time. From the above study, the change of pore size of cement mortar with different water cement ratio was also different. With the decrease of water cement ratio, the initial pore size of cement mortar was decreased. When the water absorption reached a certain time, the pore size of cement mortar decreased to a fixed value. In cement based materials, the relation between porosity and water cement ratio was [27]:

$$\varepsilon_0 = 1 - \frac{\left(1 + \frac{W_0^n}{C'}\right) V_{hc}}{V_c' + V_w(\frac{W'}{C'})}$$
(16)

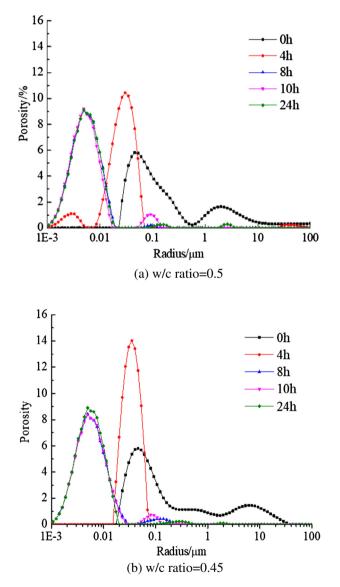


Fig. 2. Pore structure change of hardened cement with different water cement ratio.

where: ε_0 was the porosity of material; W_n^0 , V_{hc} , $V_{c'}$ and V_w were constants when raw cement material was unchanged, so porosities of cement-based materials were increased with water cement ratio (W'/C'). As the water cement ratio of cement mortar decreased, the porosity of cement mortar was therefore decreased due to the decreased of mixing water during the hydration process. With the

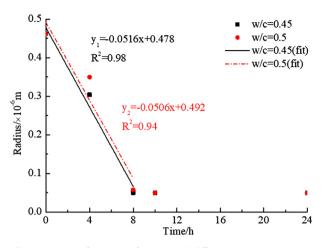


Fig. 3. Variation of pore size of mortar with different water cement ratio.

water entering into cement mortar, the hydration products of cement mortar caused the volume expansion after water absorption [31]. However, even if the expansion of hydration products can make the pores of cement mortar decreased, the porosity of cement mortar cannot disappear completely, but only to a certain extent.

4.2. The relationship between absorption mass fraction and time

Absorption mass fraction of the sample was measured at different absorption time. Generally, the initial flow rate changes quickly, and with prolonging of absorption time, the flow rate change was gradually slowed down. Thus, when the absorption mass fraction was measured, the initial interval time was smaller, and the time interval was gradually relaxed. Fig. 4 was the relation between absorption mass fraction change of mortar and time. The surface tension of water was about 73 mN/m; the viscosity of water was about 1.0050×10^{-3} N·s·m⁻² when the temperature was 20 °C. Thus, the mathematic model was calculated and the curves were showed in Fig. 4.

As was showed in Fig. 4, when the mortars were soaked upon the water, the mass of mortar was increased with time. At the initial stage of absorption, the change of water absorption mass fraction of mortar was very fast. However, with the increased of time, absorption mass fraction was gradually decreased. After reaching a certain time, the absorption mass fraction of mortar was gradually attained stability. With the increase of time, the radius of pore in cement-based materials gradually became small, so that the water absorption quality of cement-based materials gradually decreased. With the decreased of water cement ratio, the absorption mass fraction of cement mortar with high w/c was lower than that of mortar with low w/c at the same water absorption time. The absorption mass fraction of cement mortar was decreased with water cement ratio when balance of water absorption was reached. However, pores in the cement mortar and other cement based materials were not cylindrical and they were random existed, so it increased the path of water flow and slowed down the speed of water transformation. Based on this reason, the experimental data was slightly smaller than the model in Fig. 4.

In order to predict the penetration depth of water, the theoretical penetration depth of water was calculated by the known parameters. The result was showed in Fig. 5.

The penetration depth of water was increased with time according to Fig. 5, it was firstly increased slowly and then changed fast. the change trend of mortar in this experiment was opposite to the trend of relationship of mass change. As can be seen in Fig. 3, lower the w/c, lower size of the pores that had higher presence and higher was the depth and capillary force. However, even if the capillary force was increased, according to Eq. (15), as the radius of cement mortar was decreased gradually, the trend of penetration depth of cement and absorption mass fraction was not the same Fig. 6.

4.3. Chemical model of absorption process

Drying and absorption process of cement-based materials were the relatively opposite processes. Based on the former researches, these two processes of cement-based materials were proposed by some mathematics models which mainly based on the fitting method. In recent year, depend on the chemical reaction of drying and water absorption processes, some microstructure models were proposed. Among them, during the drying process, water in interlayer of C-S-H chains was lost and was evaporated through the pores of cement-based material. In this process, the volume of cement-based material was also decreased. When water was absorbed in this system, the volume of material was gradually expanding. In Jennings' model [13], the process of drying and wetting circle of material was a physical process and just involved in the content of evaporation and absorption of water in the pores of cement-based materials, and the chemical reaction between chains of C-S-H was not happened in this process Fig. 7.

However, Ippei Maruyama et al. [33] found that the chemical reaction was happened in layer of C-S-H chains of cement-based

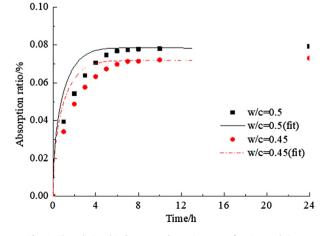


Fig. 4. The relationship between absorption mass fraction and time.

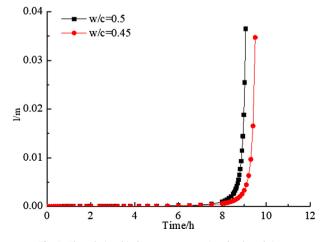


Fig. 5. The relationship between penetration depth and time.

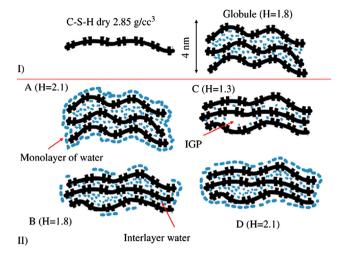
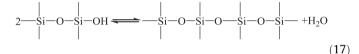


Fig. 6. The model of drying process of C—S—H proposed by H.M. Jennings [32]

materials (Fig. 8) and Q^3 of silicon oxygen tetrahedron structure was formed in two chains of C-S-H.

The former our research was also found that this phenomenon was happened in the stability of C-S-H in the NH⁴₄ solution which participated in the reaction[12]. But in the absorption process water was absorbed in the materials and weather Q³ of silicon oxygen tetrahedron structure which polymerized in the drying process was hydrolyzed again? To calculate the stability of Q³ of silicon oxygen tetrahedron structure in this process, the quantum mechanics calculation method was used. Firstly, the reaction of polymerization and hydrolyzation during the process of drying and wetting respectively can be described by Eq. (17) [14].



Based on the quantum mechanics method, the software Guassion 09 was used to calculated the bond length and Gibbs free energy of Eq. (17) [11]. To calculate this process simplicity, the end of the chain in Eq. (17) was connected by OH⁻ anions. The calculation type of this process was FREQ and calculation method was RB3LYP. The bond length of reactant and formation products were finally calculated and the results were showed in Fig. 8, the number in this figure represents the length of bond. To show the figure clearly, H atoms were not displayed.

As can be seen from the Fig. 8, since the whole molecule of reactant was completely symmetric with middle O atom, the bond lengths of each Si—O and O—H bonds were nearly equal respectively. After the chemical reaction, as the molecules becoming larger, the interactions between the atoms in the molecules were resulting in uneven Si—O bond length distribution in structure of product (Fig. 8(b)) caused by factors such as steric hindrance.

Eq. (18) was used to calculated the standard Gibbs free energy of formation for the reaction (17). According to the result of quantum mechanics method, the value of free energy of reactant of this reaction and production and water was -1109.9097 hartree and -2142.6189 hartree and -76.4160 hartree respectively, and the value of the standard state Gibbs free energy of reaction was therefore -40.9 kJ/mol.

$$\Delta_r G_m^{\Theta} = \Delta_p G^{\Theta} - \Delta_r G^{\Theta} = -40.9 \text{KJ/mol}$$
(18)

where: $\Delta_r G^{\Theta}_m$ was the standard state Gibbs free energy of reaction; $\Delta_r G^{\Theta}$ and $\Delta_p G^{\Theta}$ was the standard Gibbs free energy of formation for each reactant and products respectively.

To estimate the reaction direction of Eq. (17), the concentration of reactant and formation products must be considered. Therefore, the Gibbs free energy of reaction ($\Delta_r G_m$) in real reaction was calculated by Eqs. (19) and (20) [22].

$$\Delta_r G_m = \Delta_r G_m^{\Theta} + RT \ln Q_f \tag{19}$$

$$Q_f = \frac{\left(\frac{a_P}{d\Theta}\right)\left(\frac{a_W}{d\Theta}\right)}{\left(\frac{a_R}{d\Theta}\right)^2} \tag{20}$$

where: Q_f was equilibrium constant of Eq. (17); R was standard state mole gas constant; T was Kelvin temperature. a_R , a_p and a_w , a^{Θ} were the activity of reactant, product, water and standard concentration respectively.

According to fundamental of thermodynamics, a reaction can happen spontaneous only if $\Delta_r G_m < 0$. According to Eq. (18) [22], the value of standard Gibbs free energy of Eq. (17) was negative, so this reaction can happen spontaneous through the direction of positive reaction. Cement-based materials were always cured in the standard or real environment, therefore water was presented in the pores of materials, according to Eq. (17), water was participated in the reaction and it was the role of formation products. Due to the large content of water, according to Eqs. (19)-(20), it can induce the increased of Q_f and $\Delta_r G_m$. When the value of $\Delta_r G_m$ was greater than 0 and this reaction cannot react spontaneous. When drying process of cement based material was continuously proceeding and the content of water was gradually decreased. When the content of water was below a critical value which $\Delta_r G_m$ was equal to 0, the reaction (17) can gradually happen. The result of Ippei Maruyama et al.'s research showed that the it was happened during the drying process when RH was less than 11% [34].

When the wetting process was happened, was there a corresponding chemical reaction going on according to inverse reaction of Eq. (17)? Firstly, as can be seen from the quantum mechanical calculations, the reaction cannot possibly happen during the initial process because $\Delta_r G^{\Theta} > 0$. Since the content of Q^3 state of silicon tetrahedron formed in the drying process was far less than that of Q^2 , it was not easy to carry out the reaction even if a large content of water was involved in the reaction process. For example,

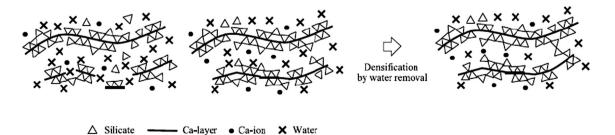
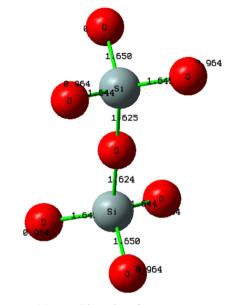
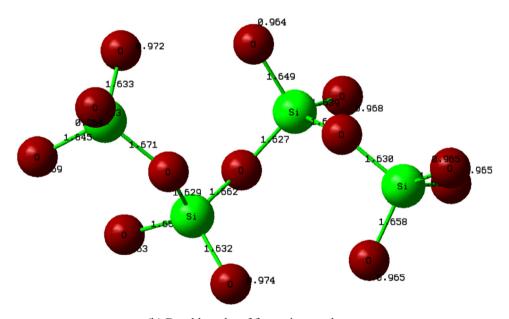


Fig. 7. The model of drying process of C-S-H proposed by Ippei Maruyama et al. [34].



(a) Bond lengths of reactant



(b) Bond lengths of formation product

Fig. 8. Bond length of reactant and formation product.

the reaction mechanism such as slag and fly ash was hydrolyzed of Q^3 and Q^4 of silicon tetrahedron structure, but the reaction rate was very slow, so the means such as acid excitation and alkali excitation were used to accelerate the chemical reaction. Therefore, hydrolysis was not merely occurred in the process of water absorption.

5. Conclusions

Based on the Hagen-Poiseuille law and quantum mechanics method, a mathematical model of water absorption of cementbased material was established by analyzing the chemical reaction during the process of water absorption.

- (1) In the early stage of water absorption, capillary permeation was the main force in water absorption of cement-based materials. The pore size of cement mortar was decreased with the decrease of w/c and finally reduced to a fixed value.
- (2) Absorption mass fraction was increased with time, it was increased rapidly and finally reached to a certain content. The depth of penetration was also increased with the water absorption time, but the trend was not same with change of flow quality, it was increased slowly and finally change to rapidly.
- (3) According to quantum mechanics method, the wetting process of cement based material was happened spontaneous, but hydrolysis was not merely occurred in the process of water absorption.

Declaration of Competing Interest

None.

References

- Nicos S. Martys, Chiara F. Ferraris, Capillary transport in mortars and concrete, Cem. Concr. Res. 27 (1997) 747–760, https://doi.org/10.1016/S0008-8846(97) 00052-5.
- [2] Xuemei Liu, Kok Seng Chia, Min-Hong Zhang, Water absorption, permeability, and resistance to chloride-ion penetration of lightweight aggregate concrete, Constr. Build. Mater. 25 (2011) 335–343. 10.1016/j.conbuildmat.2010.06.020.
- [3] Marcos Lanzón, P.A. García-Ruiz, Evaluation of capillary water absorption in rendering mortars made with powdered waterproofing additives, Constr. Build. Mater. 23 (2009) 3287–3291, https://doi.org/10.1016/ j.conbuildmat.2009.05.002.
- [4] B. Belleghem, R. Montoya, J. Dewanckele, et al., Capillary water absorption in cracked and uncracked mortar-A comparison between experimental study and finite element analysis, Constr. Build. Mater. 110 (2016) 154–162, https://doi. org/10.1016/j.conbuildmat.2016.02.027.
- [5] Aiguo Wang, Peng Liu, Kaiwei Liu, et al., Application of air-cooled blast furnace slag aggregates as replacement of natural aggregates in cement-based materials: a study on water absorption property, J. Wuhan Univ. Tech.-Mater. Sci. Ed. 33 (2018) 445–451, https://doi.org/10.1007/s11595-018-1843-6
- [6] M.H.F. Medeiros, P. Helene, Surface treatment of reinforced concrete in marine environment: influence on chloride diffusion coefficient and capillary water absorption, Constr. Build. Mater. 23 (2009) 1476–1484, https://doi.org/ 10.1016/j.conbuildmat.2008.06.013.
- [7] A. Djerbi Tegguer, Determining the water absorption of recycled aggregates utilizing hydrostatic weighing approach, Constr. Build. Mater. 27 (2012) 112– 116, https://doi.org/10.1016/j.conbuildmat. 2011.08.018.
- [8] Chun-hua Shen, Zhong-he Shui, Zi-chen Zhou, Research on water transport and kinetics in cement-based materials, J. Wuhan Univ. Tech.-Mater. Sci. Ed. 29 (2007) 84–87, https://doi.org/10.1016/ s1672-6529(07)60007-9.
- [9] G.D. Ransinchung, Brind Kumar, Veerendra Kumar, Assessment of water absorption and chloride ion penetration of pavement quality concrete admixed with wollastonite and microsilica, Constr. Build. Mater. 23 (2) (2009) 1168– 1177, https://doi.org/10.1016/j.conbuildmat.2008.06.011.
- [10] M. Fourmentin, P. Faure, P. Pelupessy, V. Sarou-Kanian, U. Peter, D. Lesueur, S. Rodts, D. Daviller, P. Coussot, NMR and MRI observation of water absorption/ uptake in hemp shives used for hemp concrete, Constr. Build. Mater. 124 (2016) 405-413, https://doi.org/10.1016/j.conbuildmat.2016.07.100.
- [11] Xuebing Wang, Zhihua Pan, Xiaodong Shen, et al., Stability and decomposition mechanism of ettringite in presence of ammonium sulfate solution, Constr. Build. Mater. 124 (2016) 786–793, https://doi.org/10.1016/j.conbuildmat. 2016.07.135.
- [12] Xuebing Wang, Zhihua Pan, Chemical changes and reaction mechanism of hardened cement paste-(NH4)2SO4-H2O system, Constr. Build. Mater. 152 (2017) 434–443, https://doi.org/10.1016/j.conbuildmat.2017.07.018.
- [13] Xuebing Wang, Xu. Kangning, Yexue Li, et al., Dissolution and leaching mechanisms of calcium ions in cement based materials, Constr. Build. Mater. 180 (2018) 103–108, https://doi.org/10.1016/j.conbuildmat.2018.05.225.

- [14] Jeffrey J. Chen, Jeffrey J. Thomas, Hamlin M. Jennings, Decalcification shrinkage of cement paste, Cem. Concr. Res. 36 (2006) 801–809, https://doi.org/10.1016/ j.cemconres.2005.11.003.
- [15] Xuebing Wang, Zhihua Pan, Xiaodong Shen, et al., Diffusion characteristic of sulfate anion in surface region of cement mortar at early stage, J. Wuhan Univ. Tech.-Mater. Sci. Ed. 32 (2017) 358–364. 10.1007/s11595-017-1603-0.
- [16] C. Desmettre, J.P. Charron, Water permeability of reinforced concrete with and without fiber subjected to static and constant tensile loading, Cem. Concr. Res. 42 (2012) 945–952, https://doi.org/10.1016/j.cemconres.2012.03.014.
- [17] Xiao-Bao Zuo, Cheng Yu WeiSun, Numerical investigation on expansive volume strain in concrete subjected to sulfate attack, Constr. Build. Mater. 36 (2012) 404–410, https://doi.org/10.1016/ j.conbuildmat.2012.05.020.
- [18] Babak Mohammadi, Michelle Nokken, Sajjad Mirvalad, Development of in situ water absorption method: laboratory study and field validation, J. Mater. Civil. Eng. 29 (2017), https://doi.org/10.1061/(ASCE)MT.1943-5533.0002045.
- [19] Bo Yang, Shilong Wang, Yankai Wang, Effect of Nesting in Laminates on the Through-Thickness Permeability of Woven Fabrics, Appl. Compos. Mater. 25 (2018) 1237–1253, https://doi.org/10.1007/s10443-018-9699-8.
- [20] Ahmad Pouya, Minh-NgocVu, Fluid flow and effective permeability of an infinite matrix containing disc-shaped cracks, Adv. Water. Resour. 42 (2012) 37–46, https://doi.org/10.1016/j.advwatres. 2012.03.005.
- [21] Speight G. James, Lange's Handbook of 2004 Chemistry, McGraw-Hill Professional Publishing, New York, 2004.
- [22] Fu. Xiancai, Physical Chemistry, 5th Edition., High Education Press, Beijing, 2005.
- [23] Shiqiao Gao, Capillary Mechanics, Science Press, Beijing, 2009.
- [24] P. Atkins, J. De Paula, Physical Chemistry, 9th Edition., W. H. Freeman and Company, New York, 2010.
- [25] H.F.W. Taylor, Cement Chemistry, Lightning Source Inc, La Vergne, 1997.
- [26] Peter C. Hewlett, Lea's Chemistry of Cement and Concrete, 4rd Ed., Butterworth-Heinemann, Oxford, 2003.
- [27] Lu. Ping, Introduction to Cement Material Science, Tongji University Press, Shanghai, 1991.
- [28] Weiguo Shen, Gejin Gan, Chunmin Lian, et al., Progresses on the Nano Scale Structure Model of C-S-H and the Shrinkage Mechanism, Mater. Sci. 2 (2012) 1–11, https://doi.org/10.12677/ ms.2012.21001.
- [29] Qitu Zhang, Fundamental of inorganic materials science, East China University of Technology Press, Shanghai, 2007.
- [30] Qiao Zheng, Zheng He, Simulation of force between calcium silicate hydrate nanoparticles, Eng. J. Wuhan Univ. 46 (05) (2013) 583–587. 1671-8844(2013) 05-0583-05.
- [31] David Benavente, M. Peter Lock, Ángeles García Del Cura, et al., Predicting the Capillary Imbibition of Porous Rocks from Microstructure, Transport. Porous Med. 49 (2002) 59–76, https://doi.org/10.1023/A:1016047122877.
- [32] Hamlin M. Jennings, Refinements to colloid model of C-S-H in cement: CM-II, Cem. Concr. Res. 38 (2008) 275–289, https://doi.org/10.1016/j. cemconres.2007.10.006.
- [33] Ippei Maruyama, Hiroshi Sasano, Strain and crack distribution in concrete during drying, Mater. Str. 2014 (47) (2014) 517–532, https://doi.org/10.1617/ s11527-013-0076-7.
- [34] Ippei Maruyama, Yukiko Nishioka, Go Igarashi, et al., Microstructural and bulk property changes in hardened cement paste during the first drying process, Cem. Concr. Res. 58 (2014) 20–34, https://doi.org/10.1016/j. cemconres.2014.01.007.