Chemical Evolution of Pore Solution in Metakaolin Concrete During Water Evaporation

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Metakaolin concrete is a kind of porous material, which contains a variety of chemical ions in the pores. Solutions in these pores are exposed to the atmosphere and exist evaporation and condensation processes, therefore, the pore solution volume of concrete changes all the time. When the ion concentration in the pore solution changes, it has an important impact on the strength development and durability of concrete. However, the real-time monitoring of the concentration of pore solution was difficult. To study the chemical evolution of pore solution in concrete, the variation of saturated vapor pressure on the surface of metakaolin concrete was studied based on the Cisternas-Lam rule. The evaporation rate of solvent in the pore solution of concrete under the corresponding saturated vapor pressure in this paper was studied by the Stefan diffusion method. The dynamic equilibrium process equation of ions in pore solution was then established based on the thermodynamic equilibrium equation. Based on the above model, the change process of the pore solution of metakaolin concrete was studied, and it was verified by the results of the literature.

Keywords: concrete, solution chemistry, humidity, chemical properties.

1. INTRODUCTION

Concrete is widely used in various kinds of buildings because of its high compressive strength and low price [1–3]. It is a composite material that consists essentially of a binding medium within which are embedded particles of aggregate [4]. Cement concrete is a composite cementitious material composed of coarse aggregate, fine aggregate, cement hydration products, unhayed cement particles, liquid such as free water and crystal water, as well as gas in pores and cracks [5]. Cement concrete materials are often used as structural materials and often face severe service environment. When evaluating the long-term durability of cement concrete, mathematical modeling needs to be used for research. However, the cement in concrete is hydrated for a long time, and the chemical reaction leads to the fact that this process cannot be calculated simply by evaporation model, but by mathematical model combined with chemical reaction effect.

Among the hydration of cement concrete products, the change of pore can affect chloride diffusion, carbonation and hydroxide leaching and other durability performances [6, 7]. The factors affecting the pore structure of cement concrete can include water cement ratio and supplementary cementitious materials. Firstly, the pore structure of concrete can be changed by the addition of water. The ratio of water to cement (w/c) is an important index that affects the performance of concrete, and the pore structure and strength of concrete [8]; Secondly, supplementary cementitious materials (SCM), as the main component of concrete, also have a profound impact on the performance of concrete [9]. SCM mainly refers to the artificial or natural mineral materials and industrial wastes directly added together with other components of concrete in the process of concrete mixing. Its purpose is to improve the performance of concrete, adjust the strength grade of concrete and save the amount of cement [10]. SCM can be divided into active and inactive mineral admixtures. Among them, active mineral admixtures can react with Ca(OH)2 to form cementitious materials. It mainly includes fly ash, slag and metakaolin, etc. [11]. In addition, there are also some inactive mineral admixtures. Compared with cement, the hydration rate of SCM is relatively low. Therefore, in the early stage of cement hydration, metakaolin can be used as micro aggregates to fill the pore structure of concrete. Because the particle size of metakaolin is small, it can improve the particle gradations of sand and gravel [12]. Besides, the form of mineral admixture itself also affects the workability of concrete [13].

When the cement in concrete is hydrated, the pore structure of concrete changes. In this process, the pore solution fills the whole pore of cement concrete curing in water or Ca(OH)2 saturated solution. When the humidity of the external atmosphere decreases, the solvent in the pore solution gradually diffuses to the atmosphere in a gaseous state. In terms of macro proformas, the influence of free water content in pore solution on concrete performance is multi lower deviatoric strength capacity, higher volumetric stiffness, and more strain rate sensitivity [14].

At present, the means used to study the loss of moisture in concrete are usually measured by mass change or humidity change [15, 16]. Zachary C. Grassley et al. established the distribution model of dry shrinkage stress of
constant of the ideal gas, 8.314 J

water is gradually diffused into the atmosphere.

evaporated into gaseous water, and then the gaseous

the moisture in the concretes can gradually evaporate to

atmosphere. The vapor pressure on the surface of pore

solution in concrete is greater than that of air, therefore,

increase, while Ca2+ and OH- gradually combine and precipitate [19, 20]. How to simulate the evolution of ions in the pore solution of concrete during water evaporation is a prerequisite for the subsequent evaluation of the durability of concrete materials. However, in the current research, the changes of the model caused by the concentration of ions in concrete were ignored, so they cannot explain the changes of micro ions in the evaporation process of concrete materials from the chemical mechanism.

To solve this problem, combined with the Cisternas-Lam model of saturated vapor pressure in seawater, this paper analyzes the concentration of volume and the change of ion concentration of the system caused by the evaporation of water in concrete pore solution, the influence of salt effect in Na+, K+, Ca2+ and OH- ions and the precipitation of slightly soluble products. The chemical process of the system under this process is studied and verified by the change of pore solution of metakaolin concrete.

2. THEORETICAL RESEARCH

Many concrete constructions are often directly exposed to the air which experiences humidity changed atmosphere. The vapor pressure on the surface of pore solution in concrete is greater than that of air, therefore, the moisture in the concretes can gradually evaporate to the outside atmosphere.

2.1. Vapor pressure of the surface of materials

When the concrete lose water, liquid water mainly evaporated into gaseous water, and then the gaseous water is gradually diffused into the atmosphere. Generally, the diffusion motions of matter need the existence of a corresponding driving force. As an ideal gas, it followed the law of ideal gas:

\[ P_i = \frac{n_iRT}{V_g} \]

where \( P_i \) is the pressure of \( i \); \( V_g \) is the volume, \( n_i \) was the mole of gas; \( T \) is the thermodynamic temperature; \( R \) is the constant of the ideal gas, 8.314 J·mol\(^{-1}\)·K\(^{-1}\).

The content of gaseous water in the atmosphere is expressed by humidity and it is expressed by the ratio of vapor pressure (\( P_0 \)) to saturated vapor pressure (\( P \)):

\[ RH = \frac{P_0}{P} \]

According to the literature [21], the saturated vapor pressure of water vapor in the air is related to temperature:

\[ P(T) = 611.2 \exp \left[ \frac{-1045.8511577–21394.6662629}{T} + 1.09690447–1.3003741 \times 10^{3} T^{-1} + 7.7472984 \times 10^{-3} T^{-2} – 2.1649005 \times 10^{-12} T^{-4} \right] \]

On the surface of an aqueous solution, liquid water is converted to gaseous water by evaporation. At this interface, the gaseous water produced vapor pressure on the surface of the aqueous solution. For non-disintegrated compounds, when the compound is dissolved in solution, the relationship between the vapor pressure on the surface of the aqueous solution and the concentration of the solvent obeys Raoult's law, that is, the vapor pressure on the surface of the aqueous solution is proportional to the concentration of the solute in the solution [22]. However, for dissociable inorganic chemical ions, Raoult's law is not obeyed. Cisternas proposed the corresponding Cisternas–Lam rules to explain the vapor pressure law of ionic compounds in an aqueous solution. This rule was used to calculate the vapor pressure of seawater. Because there were many ions in the aqueous solution of concretes, this method was also adopted in this paper. The Cisternas–Lam rules are as follows [23]:

\[ \log P_A = K I \left[ A - \frac{B}{T-E_0} \right] + \left[ C - \frac{D}{T-E_0} \right] \]

where:

\[ A = A_S + 3.60591 \times 10^{-4} I + M_S/2303 \]

\[ B = B_S + 1.3829821 - 0.0311851^2 \]

\[ C = C_S - 3.99334 \times 10^{-4} I - 1.11164 \times 10^{-4} I^2 + \frac{M_S(1-\chi)}{2303} \]

\[ D = D_S - 0.1384811 + 0.0751511^2 - 1.79277 \times 10^{-3} I^3 \]

\[ \chi = \frac{2(u_+u_-)}{u_+^2+u_-^2} \]

where \( P_A \) is the vapor pressure; \( I \) is the ionic strength; \( M \) is the molecular weight of the solvent; \( K \) is an electrolyte parameter; \( A_S, B_S, C_S, D_S \), and \( E_0 \) are solvent parameter respectively; \( u_+ \) is the number of moles of cations; \( u_- \) is the number of moles of anions; \( Z \) is the valence of the cation; \( Z_\text{c} \) is the valence of the anion, the water constants are as follows: \( A_S=0.021302, \ B_S=-5.390915, \ C_S=7.192959, \ D_S=1730.2857, \) and \( E_0=39.53 \). The \( K \) values of 0.03664 and 0.04702 were obtained.

2.2. Analysis of the process of water diffusion from materials to atmosphere

There is a corresponding driving force when the vapor pressure is different between the surface of the aqueous solution and the external atmosphere, so the gaseous water gradually diffuses from the interior of the concrete to the atmosphere or from the opposite direction. The vapor pressure in the atmosphere is less than that on the surface of pore water of concrete because the ambient humidity was less than 100 % under daily conditions. As a result, the gaseous water inside the concrete gradually diffuses to the external atmosphere. From the macroscopic properties of the material, the mass of concretes began to decline. As gaseous water diffuses from the concrete to the outside atmosphere, the atmosphere can be regarded as a stagnant component. The diffusion can be regarded as the diffusion of gaseous water, and the diffusion process follows Stefan diffusion [24]:

\[ \bar{N}_{AB} = -D_{AB} \bar{V}_A + C_A \bar{u}_M \]

where \( N_{AB} \) is the net molar flux; \( C_T \) is the overall concentration; \( C_A \) is the concentration of component \( A \); \( D_{AB} \) is the diffusion coefficient of component \( A \) in component \( B \).

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is the molecular diffusion coefficient; \( y_A \) is the proportion of component \( A \), which can be expressed as:

\[
y_A = \frac{c_A}{c_T},
\]

(6)

where \( n_M \) is the average molar velocity:

\[
u_M = \frac{\sum_{i=1}^{\infty} c_i v_i}{c_T},
\]

(7)

If gaseous water and stagnant air are regarded as ideal gases respectively, they follow Dalton's law of partial pressure. Since the gaseous water in the pores of concretes only diffused in one-dimensional direction (z), Eq. 5 can be calculated as follows [25]:

\[
N_A = \frac{D_{ABp}}{R_T(z-z_1)} \ln \frac{P-p_{A1}}{P-p_{A1}}, \quad \text{and} \quad S = \pi r^2.
\]

(8)

The variation trend of gaseous water diffusion coefficient at different pressure and temperature is as follows [27]:

\[
D_{AB} = D_0 \frac{P_s}{P} \left( \frac{T}{T_0} \right)^{1.75}.
\]

(11)

Among them, \( D_0 \) is diffusion coefficient, 0.22 cm²/s; \( P_0 \) and \( T_0 \) is the standard pressure and temperature, respectively. \( D \), \( P \), \( T \) were diffusion coefficient, pressure, and temperature under non-standard state, respectively.

For the diffusion coefficient of porous materials, the diffusion coefficient is [24]:

\[
D_{AB'} = D_{AB} \cdot \frac{\varphi}{\tau},
\]

(12)

where \( \varphi \) is the porosity of porous materials, which can be expressed as:

\[
\varphi = \frac{V_p}{V},
\]

(13)

where \( V \) and \( V_p \) are the volume of concrete and the pores volume of material respectively; \( \tau \) is the tortuosity of porous materials, and it can be expressed as [28]:

\[
\tau = \frac{L_e}{L} = 1 + f \ln \left( \frac{1}{\varphi} \right),
\]

(14)

where \( L_e \) is the zigzag distance; \( L \) is the linear distance; \( f \) is a constant, and the value was 0.63.

2.3. Effect of water evaporation on pore solution volume of cementitious materials

The pressure difference between the saturated vapor pressure of the solution and the partial pressure of gaseous water in the atmosphere is the driving force for the diffusion.

When the concretes are in a completely humid atmosphere, the pores of the materials are full of water, so the pore size is equal to the size of the pore solution (\( V_{50} \)). However, when the water in the pores of concretes diffuses outward by the form of gaseous water, and the volume of solution in the concretes is gradually decreased:

\[
V_s = V_{50} - N_u \pi r^2 z = V_{50} - \frac{V_p}{L} z,
\]

(15)

where \( N_u \) is the number of pores; \( r \) is the average radius of pores.

When combined with Eq. 13 and Eq. 14 and substituted into Eq. 16, it can be changed into:

\[
N_u = \frac{V_p}{S_L}, \quad V_s = \frac{V_p}{L} (Lr - z).
\]

(16)

The mass of evaporation is:

\[
ms = \rho_w \frac{V_p}{L} z.
\]

(17)

In the hydration process of concretes, the porosity is gradually changed with the hydration rate. In general, the porosity in cementitious concrete can be calculated by the Eq. 18 [29]:

\[
\varphi = \left\{ \begin{array}{ll}
\varphi_c & \text{if } w/c > 0.39 \\
0, w/c \leq 0.39 & \text{otherwise}
\end{array} \right.
\]

(18)

\[
f_c = \left[ 1 + \frac{Pc}{\rho_c} \left( \frac{w}{c} \right) - \frac{P_c}{\rho_c} \left( \frac{w}{c} \right)^2 \right]^{-1}.
\]

(19)

Among them, \( P_c \), \( \rho_c \), \( \rho_w \), and \( \rho_h \) are the density of cement, sand, water, and air respectively; \( s/c \) is sand binder ratio and \( a/c \) is the ratio of gas content to cement. \( s, c, w \) respectively represents the mass of sand, cement, and water. \( \alpha_c \) is the hydration degree and its value can be expressed as [29]:

\[
\alpha_c = 1 - 0.5 \left[ (1 + 1.67t)^{-0.6} + (1 + 0.29t)^{-0.48} \right],
\]

(20)

where \( t \) is the hydration time. For different types of cement hydration rate, the hydration rate is modified on this basis.

2.4. Effect of reducing pore solution of concrete on the concentration of each ion

The main components of cement were 3CaO·SiO₂(C₃S), 2CaO·SiO₂(C₂S), 3CaO·Al₂O₃(C₃A), 4CaO·Al₂O₃·Fe₂O₃(C₄AF) and dihydrate gypsum, which began to react after adding water. In the chemical reaction process, Ca(OH)₂, CaO·SiO₂·H₂O, ettringite and other reaction products can be formed, and Ca²⁺, OH⁻, AlO₂⁻, SO₄²⁻ and other ions also existed in the solution. Because the solubility product constant of Ca(OH)₂ was much larger than that of CaO·SiO₂·H₂O and ettringite, the two chemical ions which accounted for the largest part of these ions were Ca²⁺ ion and OH⁻ anion. The two chemical ions had the following chemical equilibria:

\[
Ca^{2+}(aq) + 2OH^-(aq) = Ca(OH)_2(s).
\]

(21)

The thermodynamic equilibrium was as follows:

\[
K_{Sr(OH)} = a_{Ca^{2+}}(a_{OH^-})^2.
\]

(22)

When the cement component contained high K₂O and Na₂O, the solubility of K₂O and Na₂O was 792 g/L and 770 g/L respectively, so these two kinds of alkali metal
oxides can dissolve and exist in the solution. After adding water to cement, these alkali metal oxides were also rapidly dissolved in the hydration process, which lead to the increase of pH in concretes and the corresponding ionic strength. If the content of K2O and Na2O in cement were litter, the Ca2+ and OH- ions can be considered as hydration of C3S and C2S, so the ratio can be considered as 1:2. However, if the contents of K2O and Na2O are high, the concentrations of OH- anion in the solution are too high, which changes the concentration of Ca2+ in the solution accordingly.

When the pore solution of the concrete was evaporated or dried, its volume was decreased, which lead to the increase of ion concentration in the material. Currently, the concentration of each ion was as follows:

\[ C_x(t+1) = \frac{C_x(t)\gamma(t)}{V(t+1)}, \]  

(23)

where \( x \) is Ca2+, OH-, K+, Na+ respectively.

When the pore solution was concentrated, the concentration of each ion was increased, so that the chemical equilibrium of Ca2+ and OH- ions reacted again, and further precipitation of CH occurred. The chemical reaction is expressed as Eq. (22). If \( \beta \) is the content of which reacted in the reaction, Eq. (23) can be converted as:

\[ \gamma_{Ca}(\gamma_{Ca} - \beta)\gamma_{OH}(\gamma_{OH} - 2\beta)^2 = K_{sp(CH)}, \]  

(24)

\[ I = \frac{1}{\gamma} \sum_i M_i \bar{x}_i^2; \quad lgy_i = -\frac{\gamma_{Ca}x_i}{\gamma_{OH}^{1/2}} \]  

(25)

where \( K_{sp(CH)} \) is the solubility product constant of Ca(OH)2, and its value is \( 5.5 \times 10^{-6} \); \( \gamma_{Ca} \) and \( \gamma_{OH} \) are the activity coefficients of Ca2+ ion and OH- ion respectively.

3. RESULTS AND DISCUSSION

3.1. Influence of mineral admixtures on water loss of cement concrete

In order to improve the performance and durability of cement concrete materials, many supplementary cementitious materials are often added into cement concrete, which can improve the pore structure of concrete.

3.1.1. Pozzolanic effect of metakaolin

Metakaolin, as supplementary cementitious material, is the product of kaolin calcined at high temperatures [30]. It is mainly composed of Al2O3·2SiO2, which can react with Ca(OH)2 during cement hydration [31]. The hydration types of products are similar to hydration products of cement. Therefore, the addition of metakaolin can promote the hydration of cement in concrete [32]. Zhang y et al. studied the effect of mineral admixtures (fly ash) on the hydration rate of cement [33], in combination with the above discussion, Eq. 20 can be transformed into:

\[ \alpha_m = 1 - e^{-Bm\gamma}; \]  

(26)

\[ \alpha = \frac{\lambda x_c + \alpha_m m}{c + m}, \]  

(27)

where \( B_m \) is a constant, 0.0216d-1; \( \alpha_m \) is the hydration rate of metakaolin; \( M \) is the content of metakaolin; \( \lambda \) is the correction factor.

3.1.2. Micro aggregate effect of metakaolin

Metakaolin, as a kind of SCM, plays the role of micro aggregate in cement concrete. These mineral admixtures and other aggregates together form the skeleton of concrete, which changes the strength and pore structure of concrete. This effect is called the "micro aggregate effect". To study this effect, Eq. 19 can be rewritten as follows:

\[ f_c = \frac{V}{V_p} = \frac{c + m}{c_p m_p} \]  

(28)

Based on the above research, the model was validated by the data in the literature. Erhan Gu¨neyisi et al. Have studied various properties of concrete mixed with metakaolin, including strength, water absorption, mass loss, etc., and accumulated abundant data [34].

The model designed in this paper was used for calculation, and the data in the literature were used for comparison, and the results were shown in Fig. 1.

![Fig. 1. Weight loss vs. drying time graphs MK concretes](image)

According to the comparison between the model and the experimental results, the experimental results were in good agreement with the model calculation results. According to the model results, the water loss in concrete was increased with the increase of drying time. According to Eq. 18, with the hydration of cement, the porosity of concrete was gradually decreased, and the corresponding pore size was also gradually decreased. With the increase of metakaolin content, the pore structure of concrete was improved due to its micro aggregate effect and pozzolanic effect. In this process, the pore size of concrete decreased gradually, which lead to the decrease of the evaporation rate of water in the pores, and increased the ability of concrete to retain water.

3.2. Variation of concentration of ions in concrete with water evaporation

Pore solution of concrete contained a lot of Ca2+, OH-, K+, Na+ ions, there were also AlO2-, SiO4^+ plasma, but its concentration was low. When the pore solution in concrete evaporated gradually, the volume of the pore solution decreased. According to Eq. 23, the concentration of each
ion in the pore solution was changed. Based on the above model, the results were shown in Fig. 2 and Fig. 3.

Fig. 2. Changes of concentration of Ca\(^{2+}\) and OH\(^{-}\) vs. drying time graphs of MK concretes

Fig. 3. Changes of concentration of K\(^{+}\) and Na\(^{+}\) vs. drying time graphs of MK concretes

There were Ca\(^{2+}\), OH\(^{-}\), K\(^{+}\) and Na\(^{+}\) ions in the pore solution of concrete, and there were chemical equilibria of Ca(OH)\(_2\) and Ca\(^{2+}\), OH\(^{-}\) in this system. When the volume of the pore solution decreased, the concentration of these ions was increased. When the concentration of Ca\(^{2+}\) ions and OH\(^{-}\) anions increases to the reactive concentration, the chemical reaction can be carried out according to Eq. 21 to form Ca(OH)\(_2\). However, in this process, the ionic strength of the pore solution of concrete increased gradually, and the ionic atmosphere thickness also increased. Based on Debye-Huckel law, the ionic activities of various ions were also decreased, which affected the chemical reaction of Ca\(^{2+}\) and OH\(^{-}\) anions. Based on the model calculation that with the increase of drying time, the calcium ion in the pore solution of concrete decreased, while the OH\(^{-}\), K\(^{+}\), Na\(^{+}\) ions gradually increase. This was consistent with the results of Lothenbach et al. [20].

3.3. Variation of the surface vapor pressure of pore solution in concrete during drying

At a certain temperature, the molecules with higher energy on the surface of water escaped from the surface to become vapor molecules by overcoming the attraction between liquid molecules. Some of the evaporated molecules may hit the liquid surface and be absorbed into the liquid phase, and this process was called condensation. In the beginning, the evaporation process is dominant, and the condensation rate increased with the increase of steam density. When the evaporation rate of a liquid equalled the condensation rate, the liquid and its vapor were in equilibrium. At this time, the pressure of steam was called the saturated vapor pressure at this temperature. When there was a non-volatile solute in water, the surface of the solution was occupied by solvated solute molecules, so that the number of solvent molecules evaporated from the surface of the solution in unit time was less than that from the pure solvent, and the vapor pressure of the solution was lower than that of the pure solvent at equilibrium. The concentration of various ions in the pore solution of concrete changed during the concentration process. Based on the Cisternas–Lam rules, the vapor pressure on the surface of the solution can be calculated. The results are shown in Fig. 4.

Fig. 4. Vapor pressure vs. drying time graphs of MK concretes

In the process of evaporation of pore solution of concrete, the ion concentration of pore solution gradually increased, the ionic strength of pore solution also increased, the part of the solution surface occupied by solute molecules was more, so that the number of solvent molecules evaporated from the solution surface in unit time was less. Therefore, the corresponding vapor pressure gradually decreased.

3.4. Chemical reaction mechanism of metakaolin concrete during evaporation

In the hydration process of cement, Ca(OH)\(_2\), xCaO·SiO\(_2\)·yH\(_2\)O, ettringite and other reaction products can be formed. Al\(_2\)O\(_3\)·2SiO\(_2\), as the main component of metakaolin, can react with Ca(OH)\(_2\) after cement hydration and is called secondary hydration reaction[30, 31]. The main reaction products are C\(_5\)A\(_5\)S\(_2\)H\(_{10}\), Ca\(_2\)AH\(_{13}\), CSH, C\(_3\)AH\(_6\), C\(_2\)ASH\(_8\). The precipitation-equilibrium between hydration
products and pore solution is therefore existed, and Ca$^{2+}$, \( \text{OH}^- \), \( \text{AlO}_2^- \), \( \text{SO}_4^{2-} \) and other ions are existed in the solution. However, concrete is often in direct contact with the environment, and the changes of humidity and steam pressure in the environment will change with the change of climate.

According to the colligative property of the solution, part of the surface of pore solution of metakaolin concrete is occupied by the solvated solute molecules when non-volatile solute is dissolved in the solvent, so that the number of solvent molecules evaporated from the solution surface per unit time is less than that evaporated from the pure solvent. At equilibrium, the vapor pressure of the solution is lower than that of the pure solvent. Therefore, with the increase of ion concentration in pore solution, the vapor pressure will decrease, which is consistent with the results in the model.

4. CONCLUSIONS

The model of the evaporation process of pore solution of concrete was established and the change process of pore solution of metakaolin concrete was used to verify.
1. The relationship between the concentration of pore solution and the vapor pressure of the external environment was established by studying the changes of ions in pore solution.
2. Based on the mathematical model, the concentration of pore solution caused by evaporation, and the change of saturated vapor pressure of pore solution surface and its influence on evaporation rate were considered.
3. Considering the pozzolanic effect and micro aggregate effect caused by the addition of metakaolin, the changes of ions and saturated vapor pressure of metakaolin concrete in the process of pore solution evaporation were calculated by using the model.

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