

Hydrophobicity Mechanism of Cementitious Material Containing Carboxylic Acid Ammonium

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Abstract. *Hydrophobic treatment of cement pastes is most effective way to resist the penetration of water with aggressive ions to improve durability of cement-based materials. In this paper, the mechanism of carboxylic acid ammonium salt integral addition on hydrophobicity of cement-based materials is analyzed. The effects of carboxylic acid ammonium salt on hydrophobicity, moisture diffusion and hydration products are investigated by experimental methods. The results of water vaporsorption isotherm show that the addition of carboxylic acid ammonium salt increases the pore volume. The simplified analytical hydrodynamic model of cone type pore and Young's relationship is proposed to analyze the relation between characteristic parameters of pore and the permeability of cementitious materials. It can be concluded that the hydrophobicity results from the change of pore structure and the hydrophobic surface of cone region. These results provide the guidance to design the durability and develop the new hydrophobic agent used in cementitious material.*

Key words: *Hydrophobicity, Permeability, Pore Structure, Hydrodynamic Effects.*

1. Introduction

Concrete composites are basic materials for infrastructure in corrosive environments containing seawater and saline soil[1]. It is known that concrete consisting of cement shows the porous characteristics and hydrophobicity meaning that water can efficiently transport through the pore system. When water sources with various aggressive ions such as chloride and sulfate ion penetrate into concrete interior, concrete matrix and the reinforcement is eroded causing the deterioration of materials and structure. In view of this, concrete modified by hydrophobic agent attracts extensive attention in reducing the permeability of concrete and improving the durability of concrete structure. [2-8]. The hydrophobic modification of concrete can be achieved by two methods including surface and integral hydrophobic method[9-12]. Due to the fact that the newly exposed surface is also the hydrophobicity and the permeability of concrete is not affected after surface peels or cracks occur, it can be noticed that the integral hydrophobic modification of concrete materials presents better water resistance and durability. A new type hydrophobic agent has been invented to improve the permeability of concrete by integral method [13] but the modification mechanism of hydrophobic admixtures has not been clearly understood.

Some mechanisms focused on the surface of pores are proposed to reveal the hydrophobic phenomenon, it is believed that the surfaces of the pores show coated with a later of molecules in the presence of stearic acid type or a layer of coalesced or separate particles in the presence

of wax emulsions or lattices[14]. When the hydrophobic agent is utilized in integral method, the hydrophobic agent will interact with hydration products[15] and influence the pore system which is the passing channel of water, the characteristics of pore system also play a key role in hydrophobic phenomenon. In previous study, it has been shown that irregular flaky crystals were generated among the C-S-H gel[16]. In this point of view, the theory of hydrophobic surface of pore cannot be utilized to explain the hydrophobicity mechanism. Some studies have shown that water is resisted in the pore to achieve the selective function, the pore morphology plays an most critical role in water penetration[17,18].

To further elucidate the mechanism hydrophobicity of cementitious materials added by hydrophobic agent, in this research, the effects of carboxylic acid ammonium salt on hydrophobicity, moisture diffusion and hydration products are investigated by experimental methods. The simplified analytical hydrodynamic model of cone type pore and Young's relationship are applied to explain the mechanism.

2. Materials and Methods

2.1 Material

The ordinary Portland cement is provide by China United Cement Co., LTD and the the chemical and mineral compositions are shown in Table 1. The mineral phases were measured by X-ray diffraction and Rietveld analysis. The carboxylic acid salt type water-resistant agent used in research is provided by Jiangsu Sobute New Materials Co., Ltd.

Table 1 Chemical and mineral compositions of ordinary Portland cement by XRF and XRD measurement

Chemical composition (wt.%)				Phase composition (wt.%)	
Oxides	XRF]	Oxides	XRF		
CaO	62.714	TiO ₂	0.329	C ₃ S	56.7
SiO ₂	19.191	Na ₂ O	0.183	C ₂ S	14.3
Al ₂ O ₃	4.446			C ₃ A	3.2
SO ₂	2.362			C ₄ AF	12
Fe ₂ O ₃	3.16			CaSO ₄ ·2H ₂ O	2.4
MgO	1.941			CaSO ₄ ·0.5H ₂ O	0.7
K ₂ O	0.453			Ca(OH) ₂	3.5
				amorphous	6.3

2.2 Experimental Techniques

2.2.1 Hydrophobicity and surface wettability

According to the Chinese standard JC 474-2008, the hydrophobicities of mortar added by different amounts of carboxylic acid ammonium salt were tested. The water to cement ratio and

sand to cement ratio of mortars were 0.5 and 1.0, in addition, the cement pastes are prepared with at water to cement ration of 0.35 which minimizes the bleeding effect. The mortar samples were dried at 40°C for two day sand then polished with alcohol, water contact angle was tested using an optical contact angle measurement(Drop Shape Analyzer-DSA25). Deionized water was applied as test liquid and the droplet volume was set at 8 μ l.

2.2.2 X-ray diffraction analyses

The hydration products were analyzed by X-ray diffraction analysis (Bruker D8) with a scanning range from 5 to 70°, the scanning rate is set at 0.02 °/s. To cease hydration, all cement pastes samples were soaked in isopropanol for 48 hours. Samples were crushed in a ball mill and manually through 80 μ m square-mesh sieve after being placed in a vacuum drying oven for 48 hours at 20 °C, 10wt.% corundum was added to the sample powder as standard reference. TOPAS 4.0 was utilized for Rietveld analysis to quantify the crystal phases.

2.2.3 Water vapor sorption isotherm

Water vapor sorption measurement was conducted using a dynamic water vapor sorption analyzer (Hydrosorb 1000, Quantachrome). A vacuum dried paste of about 30 mg was used for each measurement at 20 °C. The humidity p/p₀ of adsorption and desorption branches were from 5% to 98% with 10% intervals.

3. Experimental Results

3.1 Effect of Carboxylic Acid Ammonium Salt on Water Adsorption

Carboxylic acid ammonium salt addition aims at reducing the the rate of water adsorption in cement-based materials. The previous study [13] has presented the synthesis method and chemical properties of water-resistant admixture used in this research. It has been shown in Fig.1 (a) that water resistance ability of mortar added with water-resistant admixture is significantly higher than pure mortar. Furthermore, the pure mortar presents water adsorption rate of 0.029%/min while that of mortar with 0.6% water-resistant admixture is decreased to 0.0082%/min. When the hydrophobic agent amount increases to 0.9% and 1.2%, the adsorption rate is slightly reduced to 0.0062 %/min. The water adsorption ability change trend of mortars with different amounts of carboxylic acid ammonium salt is shown in Fig.1 (b). It is exhibited that when 0.6% carboxylic acid ammonium salt are mixed into the mortar, the water adsorption ability is reduced by more than 70% while the degree of decrease in water absorption of cement pastes with 0.9% and 1.2% hydrophobic agent is not changed significantly. It is indicated that the mortar containing small amount of carboxylic acid ammonium salt behaves excellent water resistance, indicating that permeability and the corrosion rate of cement-based materials caused by aggressive ion are reduced.

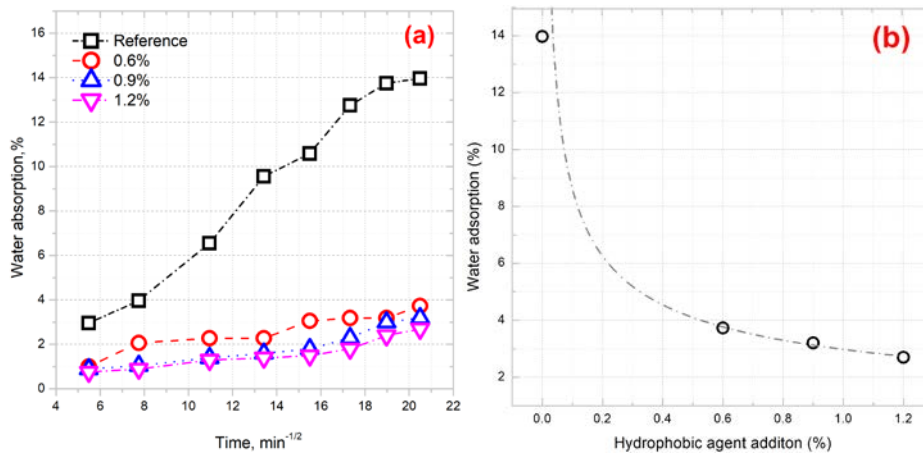


Fig.1. (a) Hydrophobicity properties [16] and (b) change trend of mortars containing various amounts of hydrophobic agents.

3.2 Effect of Carboxylic Acid Ammonium Salt on Water Sorption Isotherm of Cement Pastes

Moisture diffusion can be characterized by dynamic vapor sorption, the humidity test cycle and the weight change response of cement pastes containing different amount of carboxylic acid ammonium salt are shown in Fig.2. It has been shown that adsorption water content is lower in 5% - 60% humidity but increased sharply after 60% humidity. The adsorption and desorption isotherms acquired from the kinetics of drying and wetting of cement paste in Fig.2 are exhibited in Fig.3.

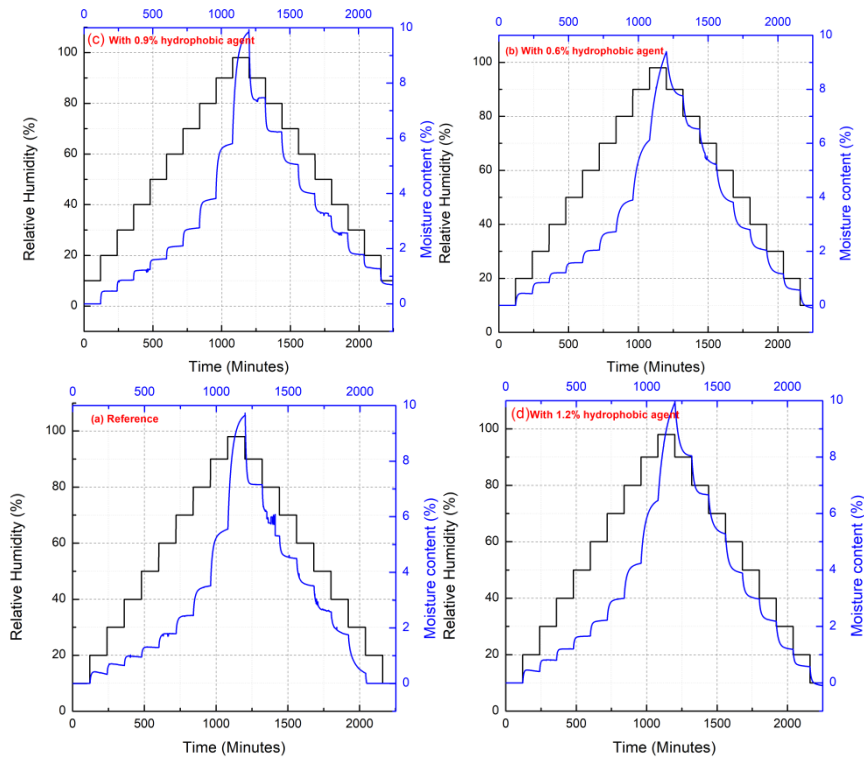


Fig.2. The kinetics of drying and wetting of cement paste for w/c 0.35 containing (a) 0%, (b)0.6%, (c) 0.9% and (d)1.2% hydrophobic agent. The black and blue lines represent relative humidity and moisture content shown on the primary and secondary y-axis.

It can be seen in Fig.3 that there is an obvious hysteresis loop between the adsorption and desorption isotherm, some similar conclusions about the adsorption isotherm can be draw for sample with and without carboxylic acid ammonium salt. The water adsorption content increases with humidity and the water adsorption amount in pastes with hydrophobic agent is obviously higher than reference sample, in addition, the water adsorption amount in 98% humidity is almost similar for all samples. However, desorption isotherm shows obvious difference between cement paste containing hydrophobic agent and reference sample. From 98% to 70%, the loss of water content in paste with hydrophobic agent is higher than that in reference sample. When the environment humidity decreases from 70% to 20%, the loss of the water content in paste with hydrophobic agent is obviously lower than that in reference sample—desorption isotherm difference between representative pastes with 1.2 wt. % hydrophobic agent and reference sample is marked by arrow shown in Fig. 3 (b).

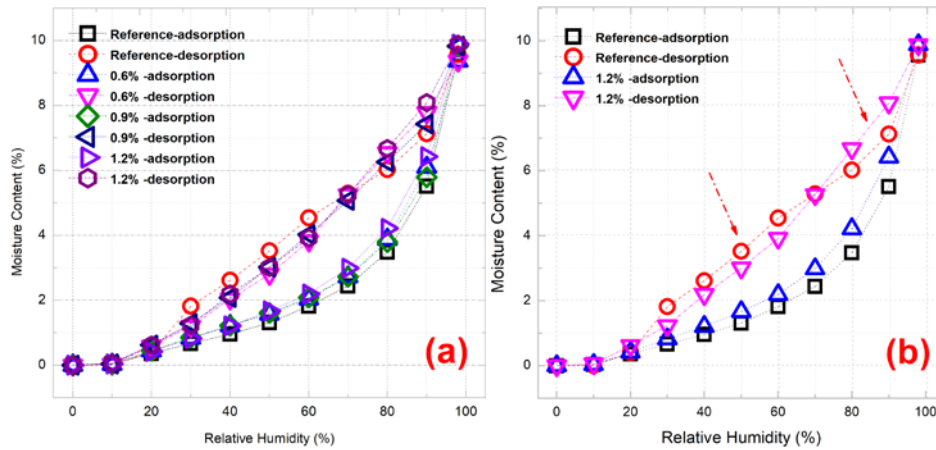


Fig.3. Moisture sorption isotherms for cement pastes containing different amount of carboxylic acid ammonium salt acquired across a range of relative humidity: (a) different amount and (b) the reference sample and sample with 1.2% hydrophobic agent. The adsorption and desorption are fitted by the dashed lines.

Generally, the adsorption/desorption curve of cement-based materials conforms to the IUPAC-recommended type IV adsorption curve and H3 type hysteresis curve whose adsorption characteristic curve of porous materials contains micro pores and mesopores[19]. It should be noted that the addition of carboxylic acid ammonium salt changes the morphology of the desorption isotherm. In order to analyze the pore structure change, the vapor isotherm hysteresis is defined as the difference between the pore water content in desorption process and that in the adsorption process. The results of hysteric curve with respect to pastes mass acquired across moisture sorption isotherms for cement pastes containing different amount of carboxylic acid ammonium salt are presented in Fig.4. As for pastes with or without hydrophobic agent, the hysteric difference between adsorption and desorption process is not obvious. The adsorption/desorption hysteresis exists in the entire relative humidity range, in addition, the maximum hysteric content of reference sample exists in 70% while that of paste containing different amount of hydrophobic agent at 80% [20]. It should be noted that the hysteresis value of pastes containing different amount of hydrophobic agent is obviously lower than reference sample.

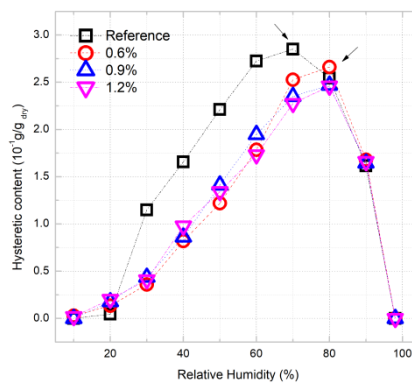


Fig.4. The hysteric curve with respect to pastes mass acquired across moisture sorption isotherms for cement pastes containing different amount of carboxylic acid ammonium salt. The dash lines show the fit to the hysteric curve.

3.3 Effect of Carboxylic Acid Ammonium Salt on Pore Structure of Cement Pastes

On the basis of the assumption of cylindrical pore shape in equilibrium state, the relationship between pore size (d_k) and relative vapor pressure (p/p_0) can be expressed by the Kelvin equation [21]:

$$d_k = \frac{4\gamma V}{RT \ln(p/p_0)} \quad (1)$$

Where d_k is the Kelvin diameter of pores, γ is surface tension of water with $7.28 \times 10^{-2} \text{ Nm}^{-1}$, V is the molar volume of water with $18 \times 10^{-6} \text{ m}^3/\text{mol}$, R is the ideal gas constant at value of $8.314 \text{ J}\cdot\text{mol}^{-1}/\text{K}$, T is the ambient temperature at value of 298.15 K .

However, the Kelvin diameter cannot represent the true diameter of material pores due to the fact that there is a certain thickness of adsorption layer on the pore walls. Assuming that the thickness of the adsorption layer is t , the true pore diameter d can be expressed as:

$$d = d_k + 2t \quad (2)$$

In addition, the thickness t of the adsorption layer is a function of the relative vapor pressure p/p_0 . According to the experimental results on tricalcium silicate and dicalcium silicate, the relationship between the thickness of the adsorption layer and the relative vapor pressure is obtained as follows [22]:

$$t = 3.85 - 1.89 \ln[1 - \ln(p/p_0)] \quad (3)$$

Based on the vapor isotherm results, the water vapor adsorption amount of the pore under relative vapor pressure can be obtained. Suppose it is further considered that the density of adsorbed water and capillary water is the same as that of normal water ($\rho = 1 \text{ g/mL}$). In that case, the pore volume and pore distribution can be calculated and shown in Fig.5.

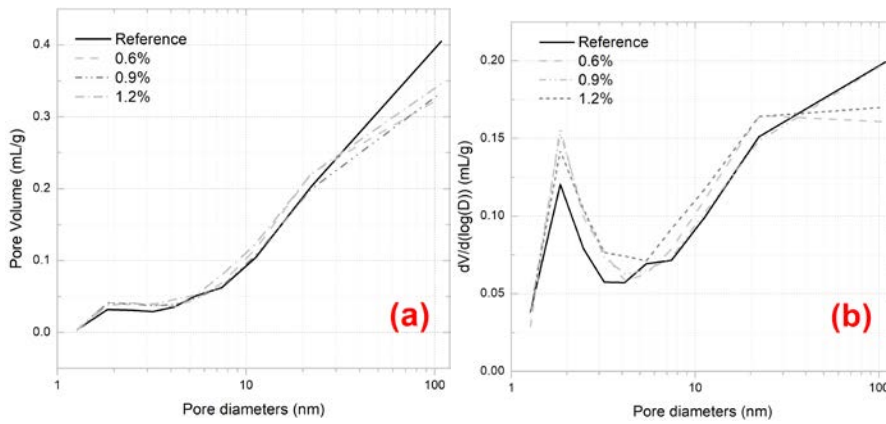


Fig.5. (a) The cumulative pore volume and (b) distribution plots of pore volume evaluated from water vapor sorption isotherm of cement pastes containing different amount of hydrophobic agent. Pore distribution of pure cement pastes and the samples containing different amount

hydrophobic agent exhibit significant differences. It is general that the pore volume of the cement pastes containing different amounts of hydrophobic agent is larger volume than that of reference sample and the distribution trend is similar. However, it is noted that the pore volume around 100 nm of samples with hydrophobic agent is obviously lower than cement paste sample, which can be attributed that the water adsorption amount of cement paste containing hydrophobic agent between 98% and 80% is lower than that of reference sample in same measurement time rather than the smaller meso pore volume. The results of pore volume measurement are based on the water adsorption amount, the addition of hydrophobic agent shows significant influence on water adsorption in higher humidity (80%-100%) which is closely related to the pore structure, therefore pore volume calculation shows obvious difference.

3.4 Effect of Carboxylic Acid Ammonium Salt on Hydration Products

To reveal the mechanism of hydrophobicity caused by carboxylic acid ammonium salt, the impact of water-resistant admixture on hydration products due to the fact that the amount of hydration products occupied in space between two particles. XRD patterns of cement samples containing carboxylic acid ammonium salt after 28d hydration period are shown in Fig.6 (a). Fig.6 (b) presents the content of hydration products analyzed couple with Rietveld analysis. It can be seen from Fig. (a) that the intensity of diffraction shows little difference between the sample incorporated with carboxylic acid ammonium salt and the pure cement pastes but the intensity of Ca(OH)_2 and calcium carboxylate slightly increases. From the Fig.6(b), the results can be found that the crystal products like CH and Aft+AFm presents little change and the amount of C-S-H increases slightly, in conclusion, there is no obvious difference between the sample with carboxylic acid ammonium salt and the pure cement pastes.

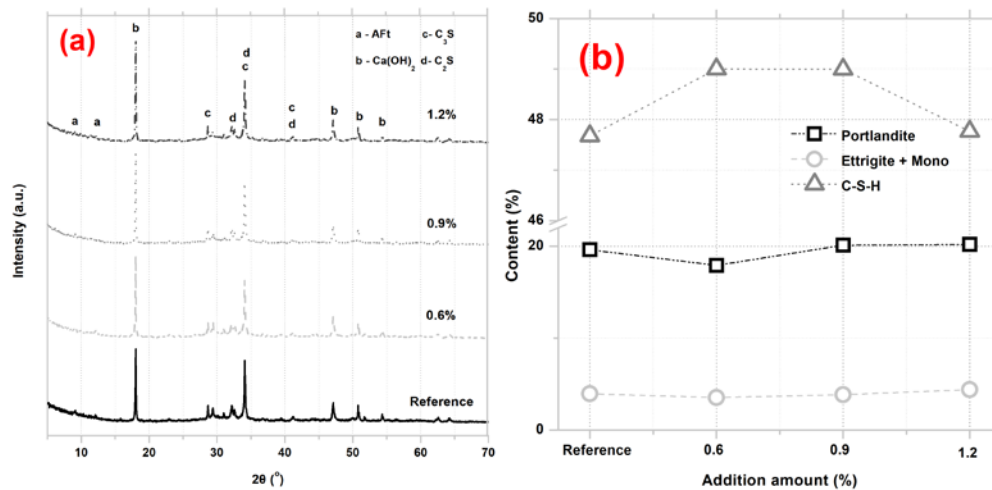


Fig.6. (a) XRD patterns and (b) content of Portlandite, Ettringite and C-S-H after 28 days of hydration time of cement pastes with different hydrophobic agents.

3.5 Effect of Hydrophobic Agent on Contact Angle

The results of measured contact angle affected by the different amounts of hydrophobic agent were shown in Fig.7. It can be seen that the contact angle of the surface of cement pastes

obviously increases with the increase of the carboxylic acid ammonium salt amount from 0.6 wt.% to 1.02 wt.%. Moreover, with the increase of carboxylic acid ammonium salt addition from 0.6% to 1.2%, the contact angle show 78.4°, 83.5° and 102.4° when the contact angle of reference sample occurs at 17.84°. The addition of carboxylic acid ammonium salt shows obvious influence on the water contact angle which represents the water adsorption resistance of cement pastes indicating that the addition of hydrophobic agent can decrease the water adsorption.

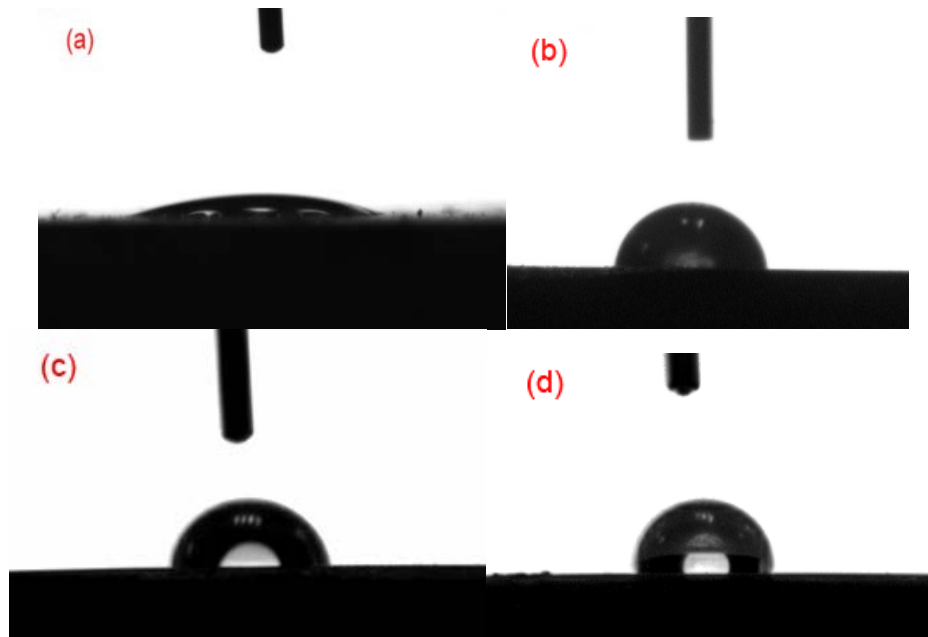


Fig.7. Contact angle of cement pastes mixed with various amounts of carboxylic acid ammonium salt at the moment of water drop application.

4 Discussions

4.1 The Effect of Carboxylic Acid Ammonium Salt on Moisture Diffusion

An important phenomenon observed from the water vapor adsorption isotherm shown in Fig.3 and Fig.4 is that the water vapor more easily penetrates into the cement pastes with hydrophobic agent than reference sample from 20% to 80% humidity while the rate of moisture penetration of sample with hydrophobic agent obviously is reduced from 80% to 98% humidity compared to the pure cement pastes. Similarly, it is shown in desorption isotherm that the diffusion rate of water in cement pastes with hydrophobic agent is lower than reference sample from 98% to 70% humidity while the moisture loss rate of cement pastes with hydrophobic agent is higher than pure Portland cement paste. The difference between moisture adsorption and desorption rates causes the change in the hysteric curve. It can be concluded that water vapor easily penetrates into the cement pastes added by hydrophobic agent in low humidity but difficultly penetrate and escape in high humidity, compared to the pure cement pastes.

The moisture diffusion in cement materials is related to the porosity, the pore structure and the surface of the pores. Based on the result of pore characteristics and the hydration products

affected by hydrophobic, it has been shown that the addition of carboxylic acid ammonium salt increases the porosity of cement pastes, the hydration degree and the hydration products show little difference between the pastes with and without hydrophobic agent. In previous study [16], it has been confirmed that the addition of hydrophobic agent causes that irregular flaky crystals has generated among the hydration products of cement pastes. From this point of view, the porosity and the surface of pores are not the main reason for the limitation of moisture diffusion. It can be inferred that the generation of the flaky crystals results in the change of pore structure when hydrophobic agent is added into the cement pastes.

As shown in Fig.4, the maximum hysteric value of sample with and without hydrophobic agent occurs at 80% and 70% humidity corresponding to the 7.41nm and 11.21nm pore. In this humidity, there is no smaller empty pore over the range between 80% and 98%, the pores larger than 11.21nm show the large resistance when the smaller pores are filled with moisture.

4.2 Pore Structure and Pore Resistance

The hysteric curve occurring in reference cement pastes is attributed to the narrow necks which relate to the unidirectional moisture desorption, however, the addition of hydrophobic agent also influence the moisture adsorption process. The pore channel connected to the cone type pore can be used to explain the double-sided moisture diffusion, the schematic diagram and characteristic parameter of the proposed channel are shown in Fig.8. It is considered that the cone consists of hydrophobic products and normal hydration products.

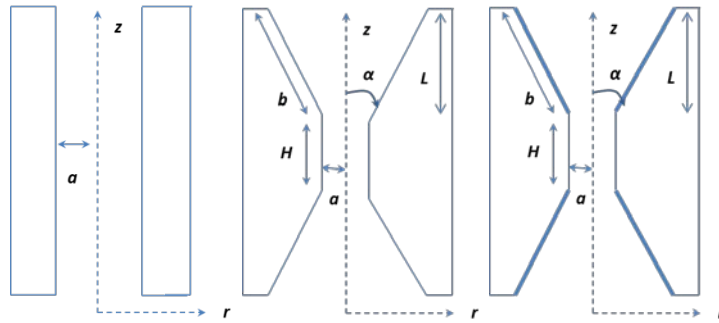


Fig.8. An illustration of pore structure of cement paste in presence and in absence of hydrophobic agent including cylinder type pore and cone type pore, the thick solid line represents the hydrophobic surface.

From the analysis of the moisture diffusion and the microstructure, the water entrance should be analyzed by the hydrodynamics. Based on the exact solution for the Stokes flow through a circular aperture in an infinitely thin membrane, the total hydrodynamic resistance R of the pore can be expressed as follows:

$$R = K^{-1} = \frac{\Delta P}{Q} = \frac{C\eta}{a^3} \quad (4)$$

Where K is permeability, ΔP is pressure drop, C is the numerical prefactor, Q is flow rate through the aperture and a is the aperture radius.

The total hydrodynamic resistance of pore consists of the resistance in cone entrance pressure, cone region and the cylinder entrance, it is expressed as:

$$R = R^{con,ent} + R^{con} + R^{cyl,ent} \quad (5)$$

Due to the fact that the Stoke flow is radial with a velocity that decreases with reciprocal radius square, in the situation that the b/a is obviously large, the resistance in cone region is vanished. Collecting formula (4)-(5), the total resistance of the pore with cone region can be expressed:

$$R = \frac{C\eta}{a^3} \left[\left(1 + \frac{L}{a} \tan \alpha\right)^{-3} + \sin \alpha \right] \quad (6)$$

Based on the derivation of total resistance of the pore, the characteristic parameter L/a is selected as 1, 5, 10, 20, the total pore resistance and permeability various with cone angle for perfect slip in the cones is shown in Fig.9. It is shown that there is a minimum resistance existing in the different channels. The pore resistance is very low around 10° while it increases with the opening angle. The L/a is another factor that influences pore resistance, the pore with $L/a=1$ show the higher pore resistance indicating that slender pore with cone region presents the higher pore resistance. Accordingly, the results of permeability are consistent with the pore resistance as shown in Fig.9 (b). It can be referred that the addition of hydrophobic agent can change the L/a and the opening angle which increases the pore resistance the

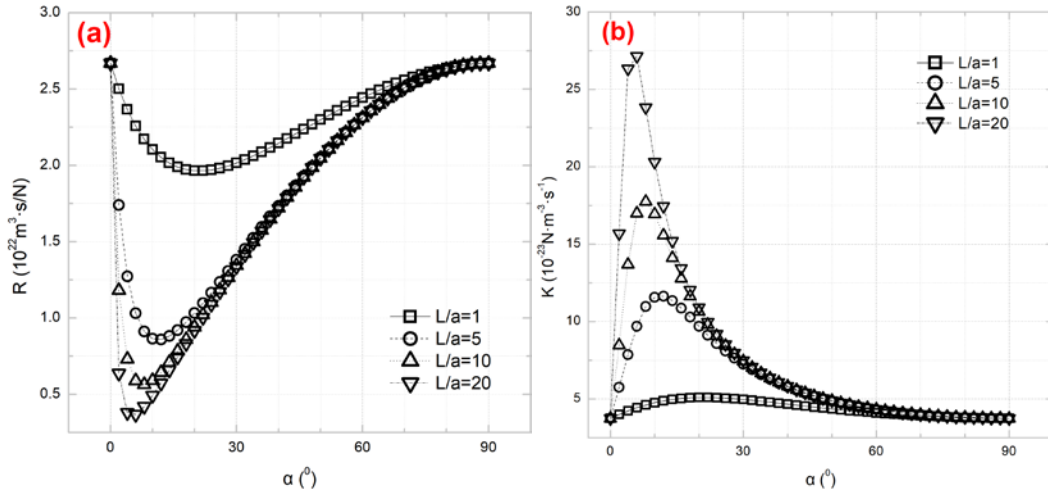


Fig.9.(a) Pore resistance and (b) permeability calculated based on the variation of cone angle for perfect slip in the cones. The pore length is set.

4.3 The Hydrophobic Cone Pore Surface

In pore resistance derivation process, it is assumed that the water can perfectly slip at the wall. However, on the basis of results of microstructure affected by hydrophobic agent, the cone region results from the generation of the flaky crystals[16], it should be stated that the surface of cone region is hydrophobic. The Young's relation can be utilized to calculate the equilibrium of a meniscus inside a channel at nano scale in the following:

$$P = \frac{-4\gamma_{LV}}{d} \cos(\theta - \alpha) \quad (7)$$

Where γ_{LV} is interfacial free energy, θ is the contact angle, α is the opening angle in cone channel. When $\theta - \alpha > 90^\circ$, the pressure in the pore is positive, and the $\theta - \alpha \leq 90^\circ$, spontaneous infiltration occurs.

If the pore diameter is set at 10 nm, the infiltration pressure changes with the opening angles as shown in Fig.10. On the other hand, the relation between diameter and the pressure is shown in Fig.10 (b). It is shown that the pressure decreases with the diameter, hydrophobic surface of cone shows large infiltration resistance when moisture diffuses from the entrance of the cone region to the entrance of the cylinder pore. It can be concluded that the hydrophobicity results from the change of pore structure and the hydrophobic surface of cone region.

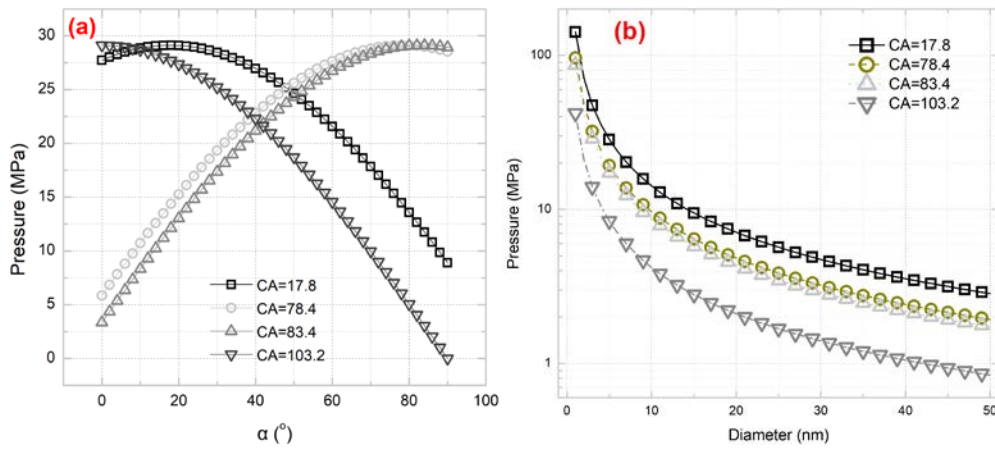


Fig.10.(a) Opening angle and (b) pore size effects on infiltration pressure in cone space with hydrophobic surface, calculated based on the Young's relation.

5. Conclusions

The carboxylic acid ammonium salt is mixed into the cement-based materials to resist moisture penetration with aggressive ions which benefits improvement of concrete durability. The effects of carboxylic acid ammonium salt on hydrophobicity of mortar, moisture diffusion of cement pastes and amount of hydration products is investigated by experimental methods. The results present that cement-based materials with carboxylic acid ammonium salt perform excellent water repellence. Furthermore, the pore structure is calculated from the water adsorption content which shows that the addition of hydrophobic agent increases pore volume. Based on the simplified analytical hydrodynamic model of cone type pore and Young's relationship, the relation between characteristic parameters of pore and the permeability of cementitious materials is analyzed. It can be concluded that the generated cone type pores and the hydrophobic surface of cone caused by hydrophobic agent addition play an important role in permeability, resulting from that irregular flaky crystals generate among C-S-H and produce opening cone type pores when the carboxylic acid ammonium salt is added into the cement-based materials.

Acknowledgements

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