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研究課題名（和文）A study on water tightness and chloride penetration of hydrophobic concrete

研究課題名（英文）A study on water tightness and chloride penetration of hydrophobic concrete

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研究成果の概要（和文）：本研究では，撥水材を混合したモルタルを対象として，構造物の耐久性と密接に関連する水分浸透特性，塩化物イオンの侵入抵抗性，および鉄筋腐食について実験的検討を行った。撥水モルタルは，シリコンオイルを主成分とする撥水材を使用し，撥水材を直接混入する方法と，撥水材を噴霧した細骨材を練り混ぜる方法の2種類の方法で作製した。その結果，普通モルタルと比べて，撥水モルタルは，ひび割れが発生した場合でも高い撥水性と遮塩性を発揮し，鉄筋の腐食を抑制する効果が明らかになった。それに加え，圧縮強度，収縮などの基本特性の測定を行い，圧縮強度は低下するものの，普通モルタルと比べて収縮が減ることが明らかとなった。

研究成果の学術的意義や社会的意義
撥水性をコンクリートの表層に付与する表面含浸工法が多く使われているが，ひび割れが撥水層より深く進行した場合，ひび割れを通じてコンクリート内部に水分が浸透する可能性が指摘されている。本研究では，撥水材を混和材としてモルタルとコンクリートに混入し，表層のみならず内部にも撥水性を付与する。こういった内部撥水性により，ひび割れが発生してもコンクリートの水分浸透と塩化物イオン侵入に対する抵抗性が低下せず，長期耐久性の向上に期待が寄せられている。

研究成果の概要（英文）：In this study, cement mortars that have bulk hydrophobicity were made, and their properties, for example, water absorption and chloride resistance, were studied experimentally. First, two types of hydrophobic mortars were made by directly adding a hydrophobic agent in mixing or spraying the agent on sand before mixing. Hydrophobicity was confirmed by measuring contact angle. Then, water absorption test was performed under uncracked and cracked conditions. It was found that, because of the bulk hydrophobicity, the surfaces of cracks were water repellent, leading to less water absorption for the hydrophobic mortars. After that, experiments of chloride penetration and corrosion were carried out. The results indicated that the hydrophobic mortars showed less chloride diffusion, resulting to a less corrosion for the rebars inside the mortars. Finally, strength and shrinkage behaviors were measured. The hydrophobic mortars were found to have a lower strength but less shrinkage.

研究分野：コンクリート材料

キーワード：コンクリート　水分浸透　撥水　塩化物イオン　鉄筋腐食　ひび割れ　強度　収縮

１．研究開始当初の背景

Deteriorations of concrete are closely related to water ingression. For example, chloride ions diffuse into concrete with water, causing corrosion of steel bars. From the viewpoint of durability, water tightness of concrete is very important. This is usually achieved by optimizing the mix proportion to decrease diffusivity. Another common way is to coat the surface using hydrophobic agent, making concrete become water repellent.

In spite of low diffusivity or surface coating, concrete loses its water tightness significantly if crack occurs. Crack becomes a convenient channel for water and ions, so accelerates deterioration. Repairing cracks spends a lot of cost, time and labors. An idea way, from maintenance viewpoint, is that cracked concrete could keep its water tightness even without repairs. Towards this direction, recently a concept of hydrophobic concrete is attracting the attentions of researchers. Manufactured by mixing hydrophobic agent (HPA) as admixtures, not only the surface but also the bulk concrete tends to be water repellent. Compared with surface coating, hydrophobic concrete saves the labor and time of treatment. More importantly, it shows a potential that, even if the crack occurs, the overall water tightness of concrete can be preserved, because the crack surface is also water repellent. Therefore, it is advantageous in both reducing maintenance cost and increasing the durability of concrete, having a broad perspective of practical use.

２．研究の目的

This study focuses on a type of hydrophobic cementitious materials. In this study, with different agent dosages and manufacturing processes, the water tightness of hydrophobic mortar and hardened cement paste, especially under cracked condition, are systematically studied. Furthermore, its resistance to chloride ion penetration and corrosion are studied experimentally. It is expected that this research will improve the understanding of durability of hydrophobic concrete, promoting its practical use. In details, the study includes below:

1). Quantitative evaluation on water tightness of hydrophobic mortar and hardened cement paste under cracked condition.

2). Study on the chloride ion penetration and steel corrosion in hydrophobic cementitious materials.

3). Study on the properties of hydrophobic cementitious materials, for example, strength and shrinkage.

３．研究の方法

(1) Materials and HPA blending

Ordinary Portland cement and river sand were used to make mortar and cement paste. A type of non-reactive alkyl denatured silicone oil, which is a commercial product of surface hydrophobic agent, was used as HPA. It has a molecular structure of siloxane with a replaced side chain by long chain alkyl (Fig. 1). Two methods were employed to blend the HPA into the mortar: (1) direct mixing, which was to disperse the HPA into water evenly, and poured it into the mixer with cement and sand to mix; (2) sand spraying, which was to spray an amount of HPA on the surface of dry sand, and stir the sand repeatedly to hydrophobize it evenly, followed by that the sprayed sand was dried, and mixed with cement and water for mortar. For comparison, normal mortar without blending of HPA was prepared as a reference group.

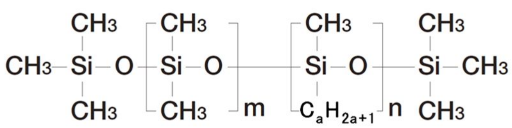


Fig. 1 Molecular structure of the HPA

Fig. 2 Cracked specimens for absorption

(2) Water absorption

- Uncracked mortar

40×40×160 mm prism specimens were casted. At 7-day age, two types of drying were applied prior to the absorption procedure. One was to dry the specimen at 20°C and RH 60%, and the other was that at 40 ˚C and RH 40% in an oven. After the drying, the specimens were placed into water, with the water level 1 cm above the upper surface. Absorption ratio was calculated by dividing the weight gain to the original weight at the point of absorption.

- Cracked mortar

40×40×75 mm prism specimens were prepared. An artificial crack penetrating the specimens was made at the top surface (Fig. 2). The width of induced crack was about 0.3 mm. Similar with the uncracked mortar, two types of pre-dry conditions were applied, 20°C & RH 60% and 40 ˚C & RH 40%. After that, each specimen was coated with epoxy resin on the side and bottom surfaces, remaining the top surface open in air. A sink was set on the top surface for absorption.

(3) Contact angle

The upper and bottom surfaces of mortar specimens were polished. A droplet of water was dripped on with a pipet on each surface for several times. The shape of the droplet was observed using a digital microscope. Drawing a tangent line along the droplet from its contact point with the mortar surface, contact angle was measured (Fig. 3).

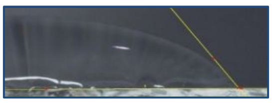


Fig. 3 Measurement of the contact angle

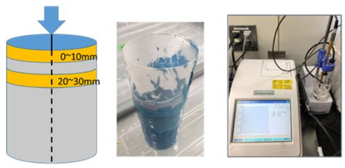


Fig. 4 Chloride diffusion test

(4) Chloride diffusion

The specimens for chloride absorption were cylinder with 50 mm in diameter and a 70 mm height (Fig. 4). The specimens were dried at 20°C & RH 60%. Similar with water absorption of cracked specimens, side and bottom surfaces were coated with epoxy resin. A sink was set on the top surface. The diffusion experiment was conducted by filling the sink with 10% salt solution. The specimens were cut by saw to obtain slices, at the depth of 0 ~ 10 mm and 20 ~ 30 mm from diffusion surface. The slices were crushed and grinded into powder, and sieved through 149μm mesh. The fine powder was vacuum dried. The total chloride content in the powder was analyzed. 5 g powder was mixed with 80 ml nitrate acid solution with a concentration 1.0 mol/L. Heated to boiling and standing for 5 min, the suspension was kept stirring. Then, the suspension was filtered. Potentiometric titration against silver nitrate was implemented for the filtered solution, to determine the content of chloride ions in the solution. The total content of chloride in the mortar was calculated.

(5) Corrosion

60×60×150mm prismatic specimens were prepared with a D10 steel rebar pre-embedded in each specimens before mixing. Two artificial cracks with the width of 0.2mm were prepared at the top surfaces. The specimens were coated using epoxy resin for all of the surfaces except the cracked top surfaces (Fig. 5). A cycle of 8-hour immersion in 10% NaCl solution and 40-hour drying at 20°C & 60% was repeated until different times, for example, 14 days, 28 days, and 60 days. Then, the specimens were broken and the surfaces of the steel bars were observed for corrosion degree.

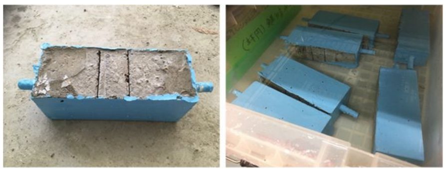


Fig. 5 Corrosion test

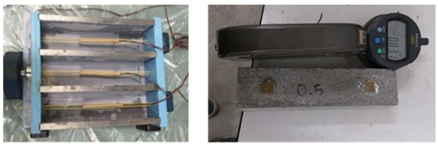


Fig. 6 Shrinkage test

(6) Strength and shrinkage

Cylindrical specimens of diameter 50 mm and height 100 mm were prepared for compressive strength. Those specimens were kept sealed under 21±1°C, and the measurement was carried out at the ages of 7 days and 28 days, respectively.

For shrinkage test (Fig. 6), 40×40×160 mm prisms were prepared. A type of embedded strain gauge was fixed in the center of the mold by thread. Each surface of the mold was surfaced with Teflon sheet to eliminate friction. After casting, the top surface was sealed. Measurement of deformation began immediately, and data was recorded by a data logger. The measurement of autogenous shrinkage was continued until the 7-day age. During the process, the specimens were stored at 21±1°C.

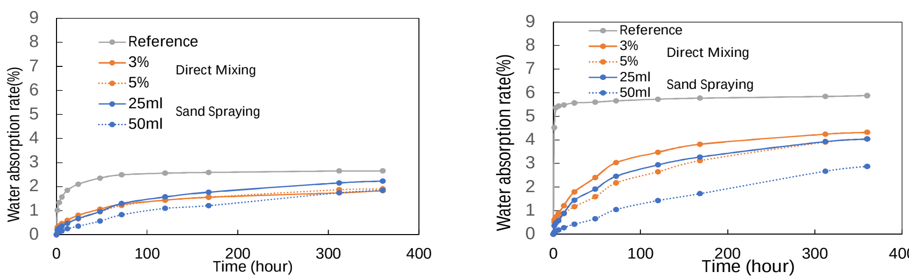
At the age of 7 days, sealing was removed, exposing the specimens at 21±1°C and RH 60%. Drying shrinkage was kept measuring for two weeks. As a comparison, another method was implemented according to JIS A 1129-2. Specimens with the same size and sealing until 7 days, sticking two metal pins on the surface in the longitudinal direction. Their distance, during the drying, was measured using a portable lengthmeter.

4．研究成果

(1) Water absorption

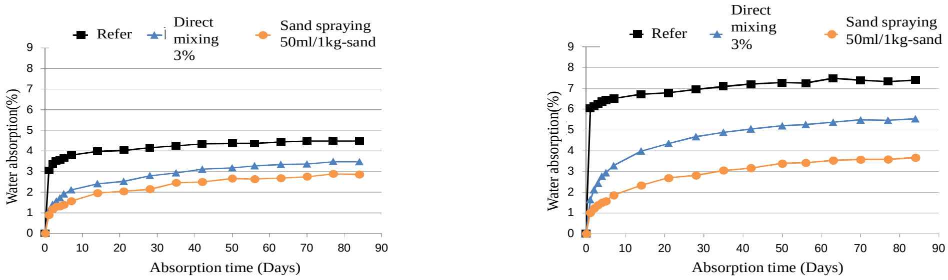
For uncracked specimens (Fig. 7), it can be found that the hydrophobic mortars, either made by direct mixing or sand spraying, show much lower water absorption than the normal mortars. In addition, the mortars made by sand spraying show less water absorption than those by direct mixing. This effect is higher when more HPA was sprayed to the sand (50ml HPA/1kg-sand> 25ml HPA/1kg-sand). Moreover, for direct mixing, higher addition ratio of HPA causes lower water absorption. Also, when the specimens were pre-dried under more severe condition (40°C & RH 40%), high water tightness (low water absorption) can be preserved in the case of the hydrophobic mortars.

For cracked specimens (Fig. 8), it can be found that the hydrophobic mortars have much less water absorption than the normal ones. Similar with the un-cracked specimens, water tightness is better for the sand-spraying specimens (50ml HPA/1kg-sand) than the direct-mixing specimens. This indicates that, even cracks occur, the hydrophobic mortars still preserve a good water tightness because of the water repellency at crack surfaces.



(a) Uncracked specimens (20°C & RH 60%)　(b) Uncracked specimens (40°C & RH 40%)

Fig. 7 Water absorption of uncracked specimens



(a) Cracked specimens (20°C & RH 60%) (b) Cracked specimens (40°C & RH 40%)

Fig. 8 Water absorption of cracked specimens

(2) Contact angle

The result of contact angle is shown in Fig. 9. It can be seen that the contact angles of the hydrophobic mortars are much higher than the normal ones, especially those made by sand spraying. The sand-spraying specimens have contact angles above 90º. For direct mixing, after 28 days, the contact angles increase significantly compared to those at 7-day age. The whole results are consistent with the water absorption test. A higher contact angle leads to less water absorption.

(3) Chloride diffusion and corrosion

The chloride diffusion of cracked specimens is shown in Fig. 10. It can be found that, because of the higher water tightness for the hydrophobic mortars, especially under cracked conditions, the chloride diffusion is reduced compared with the normal mortar. This indicates a higher resistance to the corrosion of steel rebar because of the higher resistance to chloride ingress. For the corrosion test, indeed corrosion rust was found at the surface of steel rebars in normal mortar, while steel rebars in the hydrophobic mortar were still intact (Fig. 11). Therefore, the results are consistent with each other.

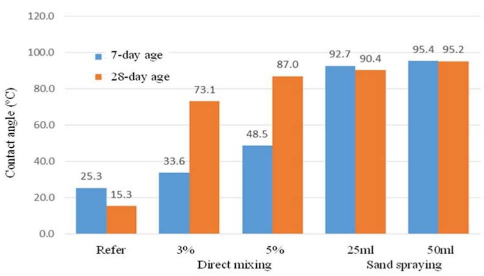


Fig. 9 Contact angle

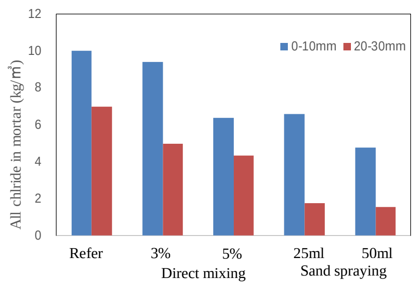


Fig. 10 Chloride diffusion

(a) normal mortar (b) hydrophobic mortar

Fig. 11 Corrosion

(4) Strength and shrinkage

The strength of the mortars is shown in Fig. 12. It can be seen that the strength shows opposite trend compared to the water absorption. The hydrophobic mortars have lower strength than the normal ones, especially for those made by sand spraying. In addition, the higher addition ratio or spraying ratio of HPA causes the lower strength. This trend is mainly caused by weakened transition zone between cement paste and sand, coarsened pore structure of hardened cement paste due to the addition of HPA. Therefore, if hydrophobic mortar or concrete is used for structural members, the strength needs to be carefully considered. For example, lower water-to-cement ratio can be adopted to compensate the strength reduction.

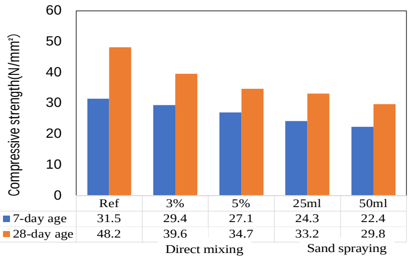


Fig. 12 Compressive strength

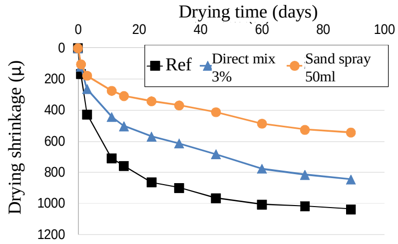


Fig. 13 drying shrinkage

The drying shrinkage is shown in Fig. 13. The hydrophobic mortars show much less shrinkage then the normal mortar. This trend is more significant for the case of sand-spraying specimen. The shrinkage was almost reduced by 50% compared to the normal one. Therefore, it can be concluded that, in addition to a high water tightness, the hydrophobic mortar also shows less shrinkage, which is beneficial to the durability of structures.

５．主な発表論文等

〔雑誌論文〕（計 3 件）

① **浅本晋吾，古田悠佳，欒堯，米田大樹：撥水材を混入したセメント系材料の内部撥水性と材料特性の検討，コンクリート工学論文集**, Vol.29, No.1, pp. 11-19, 2018（**査読有**）

② Y Luan, S Asamoto, T Yoneda：An Experimental Study of Shrinkage Behavior of Bulk Hydrophobic Mortar, **コンクリート工学年次論文集，** Vol.39， pp. 409-414, 2017（**査読有**）

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〔学会発表〕（計 1 件）

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〔図書〕（計 0 件）

〔産業財産権〕

○出願状況（計 0 件）

○取得状況（計 0 件）

〔その他〕

ホームページ等

６．研究組織

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