A-1-4 Preparation and properties of permeable fluorocarbon-silane composite material used as concrete protecting coating

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ABSTRACT: This paper prepared a permeable fluorocarbon-silane composite material (FC-S) that was used as concrete protecting coatings. Different fluorocarbon and silane were firstly selected, and various fluorocarbon to silane ratios were also tried. The intermiscibility, as well as water absorptions and penetration depths was used to achieve the optimized mix proportions. The FC-Ss with the optimized materials and fluorocarbon to silane ratios were then utilized as concrete protecting coatings. The water absorption, resistance to chloride attack and freeze-thaw cycles, and gas permeability of the coated concrete samples were analyzed. Further comparisons were also made between the properties of FC-S and those of the polyacrylic emulsion protecting materials. The results demonstrate that the oil-borne fluorocarbon works well with silane, and that the best fluorocarbon to silane ratios are 1:5 for the M20 mortars, and 5:1 for the M50 mortars, respectively. Compared to the unprotected concrete samples, a lower water absorption, as well as a higher resistance to the chloride attack and freeze-thaw cycles can be expected by using the FC-S. The concrete that is protected by the FC-S also shows a good gas permeability. Therefore, the FC-S material is believed to have good resistance to both water and aggressive conditions, and allow the gas to exchange in and outside the concrete.

KEY-WORDS: Fluorocarbon, silane, coating materials, gas permeability.

INTRODUCTION

Reinforced concrete is the most widely used building material. Usually, it has good durability and long term properties when used in unaggressive or less aggressive conditions. However, the properties of reinforced concrete would suffer sharp deteriorations, when subjected to some aggressive conditions, e.g. flowing water, sea water, and freeze-thaw circle. As a result, it is quite meaningful to protect the concrete structures with coating materials, which may prevent the concrete from the aggressive conditions, thus expending the service life.

Surface coating aims to wipe out sources of the aggressive substance, which performs quite good protecting properties. The most widely used coating materials can be divided into several types, including epoxy resin paints [1], polyurea coatings [2.3], polyacrylic emulsions [4], etc. In recent years, fluorocarbon coating materials have drawn great attention of the public, and been studied widely. It has good resistance properties to ultraviolet light, abrasion, impact, and weathering. Besides, the fluorocarbon materials also have some self-cleaning ability. These brilliance properties have made it widely utilized in the surface protecting of mental and composite materials [5, 6].

Organosilicon impregnated materials, e.g. silane and siloxane, usually has good hydrophobicity and chemical stability. When applied onto the surface of concrete, it can form a protective layer both on the surface and on the pore walls. This layer can stop the transmission of water effectively, and protect the concrete from corrosion. As a result, the service life can be prolonged [7-9].

Due to the brilliant performance of fluorocarbon and silane on the surface protecting [10, 11], this study aims to prepare a fluorocarbon-silane composite material (FC-S). Based on the intermiscibility and properties on mortar samples, an optimized mix proportions is achieved. The optimized FC-S is applied to concrete, so the resistance properties can be investigated.

EXPERIMENTAL

Preparation of FC-S

The FC-S was prepared by mixing specific types of fluorocarbon materials and silane materials.
In Section 3, two different types of fluorocarbon materials were tried. One was the oil-borne fluorocarbon, which consisted fluorocarbon resin, fatty polyisocyanate, and diluting agent. The other was water-borne fluorocarbon, which consisted fluorocarbon emulsion and film-forming additive. Two different types of silane were also attempted: type WRL-810 liquid silane, and type WRL-908 creamed silane. The compositions of FC-S materials were listed in Table 1.

Table 1. Composition of FC-S used in mortar samples

Serious number	Fluorocarbon	Silane
OL	oil-borne fluorocarbon	liquid silane
OC	oil-borne fluorocarbon	creamed silane
WL	water-borne fluorocarbon	liquid silane
WC	water-borne fluorocarbon	creamed silane

In Section 4, two different types of liquid silane: Z-6403 and Z-6341 were also tried. As a comparison, the polyacrylic emulsion was also utilized. The coating materials used here were listed in Table 2.

Table 2. Coating materials used in concrete samples

Serious number	Coating materials
Reference	None
1#	FC-S: oil-borne fluorocarbon and WRL-808 creamed silane
2#	FC-S: oil-borne fluorocarbon and Z-6403 liquid silane
3#	FC-S: oil-borne fluorocarbon and Z-6341 liquid silane
4#	Polyacrylic emulsion

Coating methodology

The FC-S was applied to the sample surfaces by brush, before which the surfaces were totally cleared and dried. Every surface was applied for three to seven times, and the samples were weighted in order to make the FC-S on every surfaces was almost equal in weight.

Mortar and concrete samples

Mortar and concrete samples were prepared in order to test the properties of the FC-S. Cement was type 42.5R ordinary Portland cement, whose water requirement for normal consistency was 28.4%. Fine aggregate was nature river sand, the apparent density was 2592kg/m^3, the modulus of fineness was 3.02. Coarse aggregate was crushed limestone ranging from 5mm to 20mm. The super plasticizer was naphthalene.
The mortar samples were prepared in 70.7mm cubic molds, while the concrete samples were in 100mm cubic molds. The mix proportions were shown in Table 3 and Table 4.

Table 3. Mix proportion of mortar samples (kg)

Strength grade	Cement	Sand	Water	Super plasticizer
M20	1	2	0.6	-
M50	1	2	0.35	0.02

Table 4. Mix proportion of concrete samples (kg/m^3 concrete)

Strength grade	Cement	Sand	Limestone	Water	Super plasticizer
C20	312.09	911.31	989.34	187.26	-
C50	459.77	850.57	924.14	160.92	4.6

Test methodology.

Water absorption

The test method for water absorption was based on the Chinese standard JTJ 275-2000, Corrosion Prevention Technical Specifications for Concrete Structures of Marian Harbour Engineering.

Penetration depth

The penetration depth was tested by indicator dye method, described in JTJ 275-2000. The specimens were firstly dried at 40 °C for 24h. Then, they were split by a loading machine. A water-borne dye was then sprayed onto the split surface, so the penetration depth can be directly measured.

Freeze-thaw resistance

Before the freeze-thaw tests, all the specimens were placed in 15 to 20 °C water for four days. The freeze-thaw process was based on the slow-freezing method described in GB/T 80082, Standard for test methods of long-term performance and durability of ordinary concrete. 25 freeze-thaw circles were applied, and the relative dynamic modulus of elasticity was tested by a type CTS-25, in order to measure the freeze-thaw resistance.

Chloride resistance

To measure the chloride resistance of the samples, the coated specimens were firstly immersed in wt 3% NaCl solution for 28 days. Then the concrete were taken out and crushed. The outmost layer (0 to 10mm) of the concrete was smashed into powders. 20g powders were placed into 20mL deionized water and stirred for 24 hours. Afterwards, the turbid solution was filtered, and the chloride content was tested. Finally, the chloride content in the concrete was calculated to measure the chloride resistance.

Gas permeability

The concrete was firstly cut into pieces whose thickness was 25mm, and dried at 40 °C for four days. Then the concrete specimen was placed into a device shown in Fig. 1, before which methanol was added into the inner container. The concrete specimen was sealed to the inner container by silicon sealants in case of any possible air leakage. Then, the concrete specimen and the inner container were weighted, and put into a water bath. The methanol losses (in g/min) were recorded with the time going by, until the weight of the specimen and the inner container became constant.

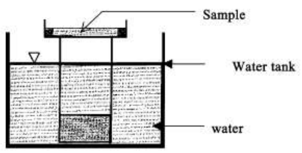


Fig. 1. Test device for gas permeability

OPTOMIZED MIX PROPORTIONS

To Fig. out the optimized mix proportions of the FC-S, different fluorocarbon and silane were firstly selected, and verified fluorocarbon to silane ratios were also tried.

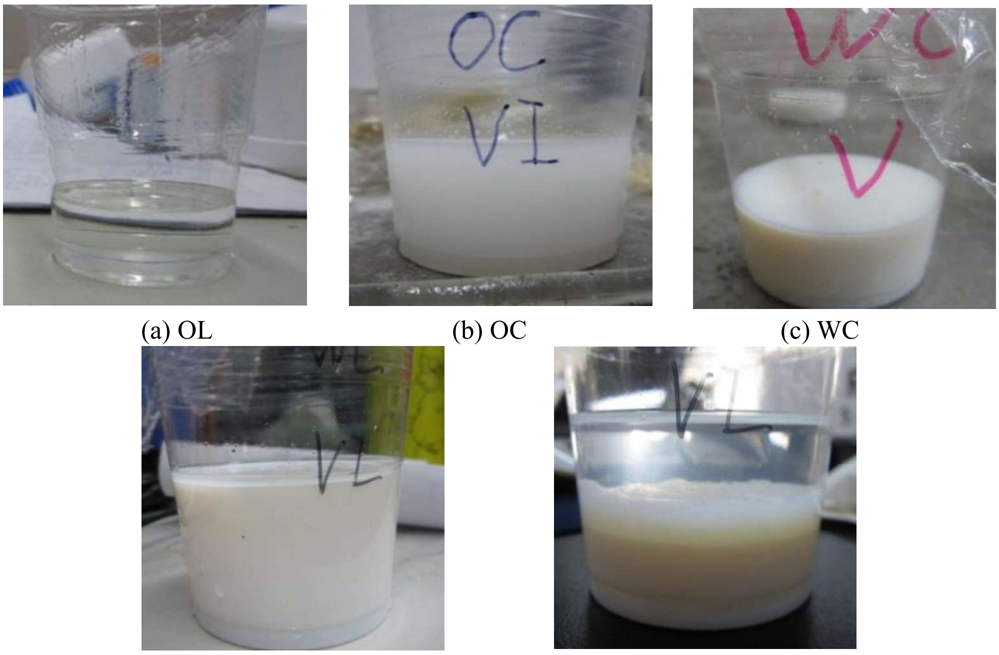
Intermiscibility

To make a general judgment of the intermiscibility between different fluorocarbons and silanes, a dissolution test was firstly conducted by mixing them directly. The results are illustrated in Fig. 2.

It is quite clear that the intermiscibility of serious OL, OC and WC were quite good. Although the mixtures looked in different colors, they were uniform and well-distributed. Oppositely, the mixture of serious WL was layered. The liquid silane floated on the top, which looked transparent, while the water-borne fluorocarbon lied on the downside, which looked milky. When this sample was mixed by an ultrasonic mixer, the fluorocarbon and silane could also dissolve in each other. However, it is denying that the intermiscibility of water-borne fluorocarbon and liquid silane are much worse than those of other mixtures.

Water absorption

The water absorption of FC-S coated mortar samples is shown in Fig. 3. Compared to the uncoated samples, whose water absorption were 0.17565mm/min1/2 and 0.00729 mm/min1/2 for M20 and M50 samples, respectively, the coated samples had a reduced water absorption. Although FC-S takes water-proof effect whatever mix proportion is utilized, the specific water absorption values differed among samples. Since the cross-linking reactions between the creamed silane and fluorocarbon are easier than those between the liquid silane and fluorocarbon, the hydrolysis reaction is more sufficient, leading to a higher conversion. Therefore, the coatings on the surface of the mortar samples tend to be better distributed. So the samples with creamed silane usually had lower water absorption than those with liquid silane, whether used in M20 mortars, or in M50 ones.

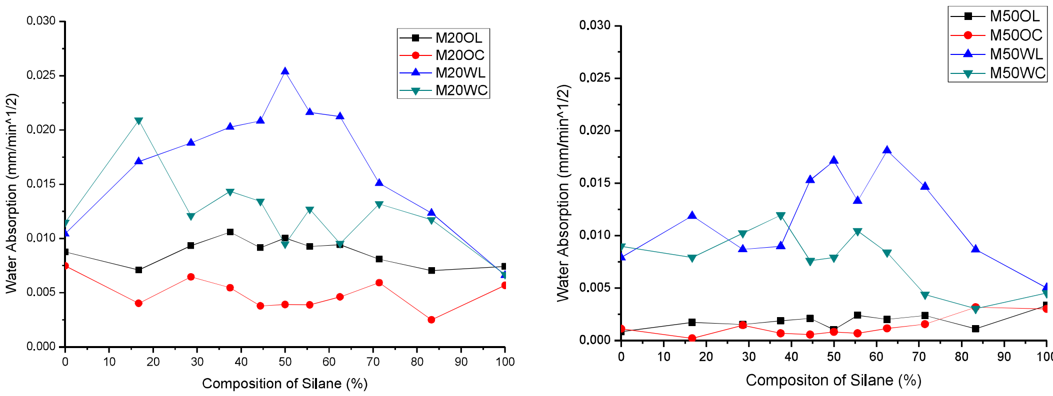


(a) OL (b) OC (c) WC

(d) WL (before ultrasonic mixing) (e) WL (after ultrasonic mixing)

Fig. 2. Intermiscibility of different mixtures

To the samples with oil-borne fluorocarbon, the lowest water absorption appeared when the fluorocarbon to silane ratios were 1:5 for the M20 mortars, and 5:1 for the M50 mortars, respectively. In fact, the dosing of silane can improve the hydrophobicity of fluorocarbon, while the dosing of fluorocarbon can prevent the silane from over-quick volatilization. However, when these two materials are used in similar amounts, the cross-linking reactions between them happen fiercely, so the hydrophobic group may be destroyed. What is worse, the cross-linking reactions in between the oil-borne fluorocarbon will also be restrained.



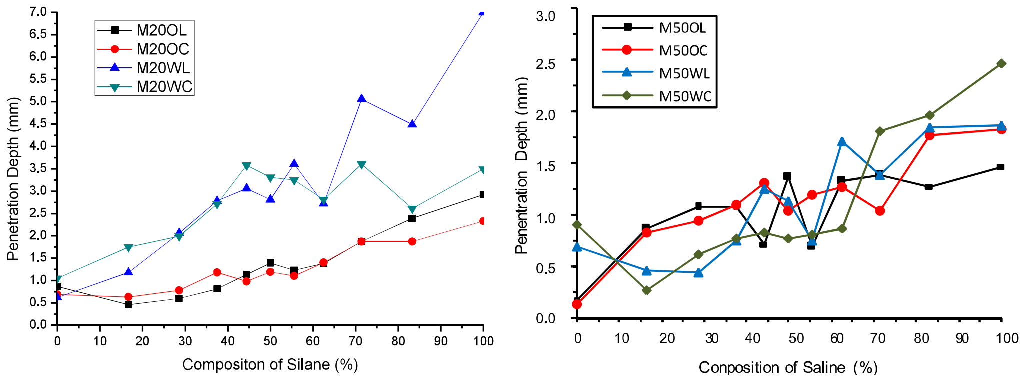
(a) M20 mortars (b) M50 mortars

Fig. 3. Water absorption tested in mortar samples

To the samples with water-borne fluorocarbon, the lowest water absorption appeared when the silane proportion was 100%, which may be caused by the bad intermiscibility between the water-borne fluorocarbon and silane, as was mentioned in Section 3.1.

Penetration depth

Fig. 4 shows the penetration depth of the FC-S at different mix proportions. Generally speaking, a bigger penetration depth can be expected at higher silane dosage rates.When the FC-S was used in the M20 mortars, the penetration depths of the samples with water-borne fluorocarbon were far deeper than those with oil-borne fluorocarbon. Since the cement matrix is mainly made up of portlandite, CSH gel, and other hydrophilic composites, water-borne fluorocarbon tends to penetrate easier, so the penetration depth of FC-S which consists water-borne fluorocarbon is deeper.When the FC-S was applied to the M50 mortars, the penetration depth became much lower than those in M20 mortars. Additionally, the differences between samples that were made up of different types of fluorocarbon and silane were not as big. These phenomena are believed to be caused by the low porosity of the M50 mortars.



(a) M20 mortars (b) M50 mortars

Fig. 4. Penetration depth

Based on the results and analysis above, it can be found that the oil-borne fluorocarbon works well with both liquid silane and creamed silane, and that the optimized fluorocarbon to silane ratios are 1:5 for the M20 mortars, and 5:1 for the M50 mortars, respectively.

PROPERTIES OF CONCRETE SAMPLES

In this section, the oil-borne fluorocarbon was firstly utilized in company with different silane at the optimized fluorocarbon to silane ratios, so the properties on concrete samples are tested.

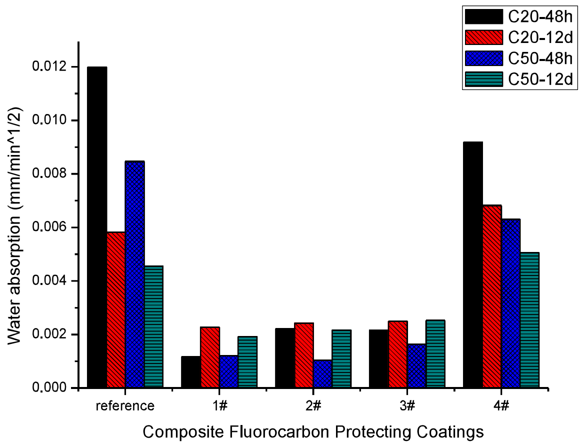


Fig.5. Water absorption tested in concrete samples

Water absorption

The water absorptions on concrete samples are illustrated in Fig. 5. It can be seen that the water absorptions of the FC-S coated samples (Sample 1, 2, and 3) were much lower than the unprotected samples, as well as the polyacrylic emulsion coated samples. To the unprotected samples and the polyacrylic emulsion coated samples, the concrete becomes fully filled with water soon after being immersed, so the capacity of the concrete to absorb water weakens as time going by. As a result, their water absorptions at 12d were lower than those at 48h. However, when the concrete is protected by the FC-S, the water fills into the concrete at quite a low speed, and the samples will not become water-saturated as easy. Therefore, to the FC-S coated samples, the 12d water absorptions were a little higher than the 48h ones. It is also clear that the water absorptions tested in C50 samples were lower than those in C20 samples, simply because the C50 concrete is more compact than the C20 one.

Freeze-thaw resistance of concrete.

Fig. 6 shows the relative dynamic modulus of elasticity of C50 concrete samples after 25 freeze-thaw circles. The relative dynamic modulus of elasticity of the FC-S coated samples (sample 1, 2, and 3) ranged from 95% to 97%, demonstrating a better freeze-thaw resistance than the uncoated concrete and the polyacrylic emulsion coated concrete.

The effect that the freeze-thaw circles take on the concrete depends mostly on the existing of water: when the water fills the pores inside concrete, it may cause volume expansions on freeze-thaw circles so to damage the concrete matrix. When the concrete is coated by the FC-S, the capillary pores will be blocked, so the pores will not be easily filled with water. This phenomenon also demonstrates that the FC-S will protect the concrete from the damages of the aggressive conditions.

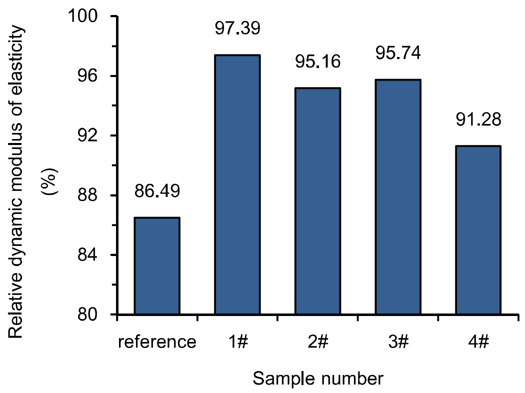


Fig. 6. Relative dynamic modulus of elasticity

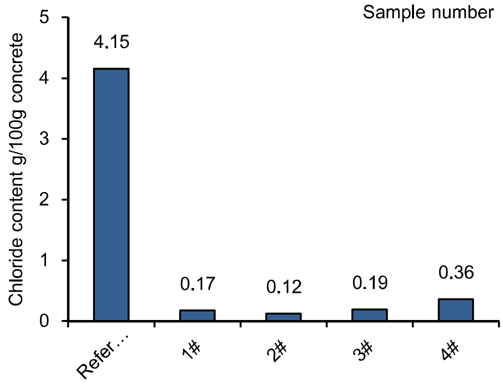


Fig. 7. Chloride content

Chloride transmission

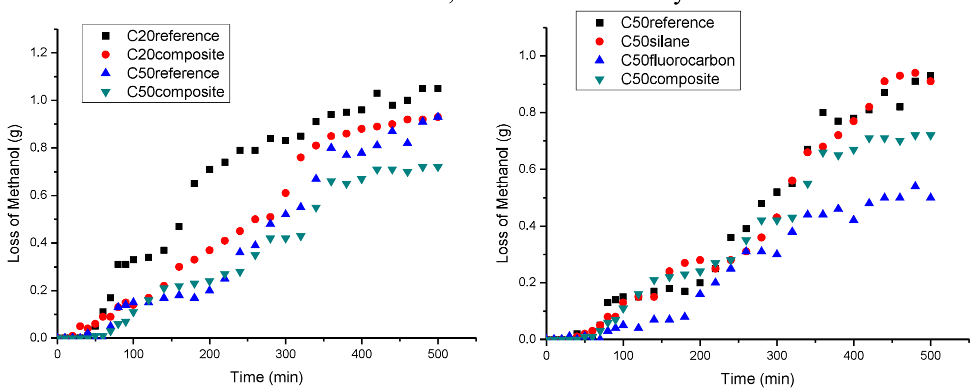
Fig. 7 illustrates the chloride content of the concrete after immersion test. These samples come from the outmost layer (0 to 10mm) of the samples. It can be seen that the chloride contents of both the FC-S coated sample and the polyacrylic emulsion coated ones were lower by more than an order of magnitude. Additionally, the FC-S shows a better protecting effect for chloride attack than the polyacrylic emulsion, which indicates that the FC-S can stop both water and chloride from getting into concrete samples. This also demonstrates that the FC-S can be potentially used in preventing the corrosion of steel bars.

Gas permeability

The results of gas permeability tests are shown in Fig. 8. Generally speaking, the loss of methanol increased with time going by. Since the compactness of C50 concrete is better than those of C20 concrete, it is more difficult for the methanol vapor to pass through the concrete. Therefore, without FS-C coatings, the losses of methanol of C50 concrete were simply smaller than those of C20 concrete.

When the concrete samples are protected by the FS-C, the FS-C fills some of the pores inside the concrete, so it becomes harder for the methanol to pass through the concrete. As a result, the loss of methanol of FS-C coated samples was smaller than those uncoated samples, both for the C20 concrete and for the C50 concrete.

Fig. 8(b) compares the gas permeability among the uncoated samples (series reference), the fluorocarbon coated samples, the silane coated samples, and the FS-C coated samples (series composite). As a matter of fact, silane did not have big influences on the loss of methanol, while fluorocarbon reduced the loss of methanol evidently. FC-S composite material also reduced the loss of methanol, but not so effectively as the fluorocarbon does.



(a) C20 and C50 samples coated by FS-C (b) C50 samples coated by different materials

Fig.8. Gas permeability

Table 5 lists the loss of methanol and the gas permeability of these samples. It is simple that the uncoated C20 sample had the best gas permeability, because of the low compactness and the unfilled capillary pores. When the C20 sample is coated by the FC-S, FC-S forms a thin layer on the surface of the concrete. The capillary pores are mostly filled, so the gas permeability reduced by around 7%. The C50 sample coated with silane had similar gas permeability to the reference samples, indicating that the silane does not form any protective layer to prevent the passing of methanol vapor. The sample coated with fluorocarbon enjoyed a 39% reduction of the gas permeability, due to the perfect film formation effect of fluorocarbon. The gas permeability of FC-S coated sample decreased by about 18%. Since the FC-S consists partly of silane, which is not useful in reducing gas permeability, the film formation effect of FC-S is weaker than that of the fluorocarbon.

Table 5. Methanol loss and gas permeability

	C20		C50			
	uncoated	FC-S	uncoated	silane	fluorocarbon	FS-C
Loss of methanol (mg/min)	2.34	2.17	2.06	2.06	1.25	1.69
Gas permeability ($mm^2/min \times 10^{-21}$)	1.305	1.210	1.149	1.149	0.697	0.943

As a comparison to the gas permeability, Fig. 9 provides the water absorbing mass of uncoated samples, and the samples coated with fluorocarbon, silane, and FC-S. As time going by, the uncoated sample absorbs the most amount of water. The samples coated with different materials all have reduced water absorbing masses. However, the FC-S has the best ability to prevent the concrete from absorbing water.

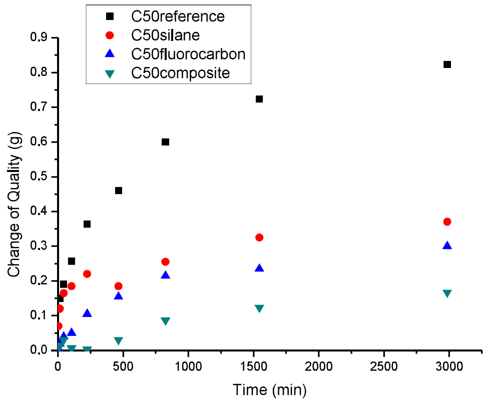


Fig.9. Water absorbing mass of fluorocarbon, silane, and FC-S coated samples

Table 6 shows the water absorption of the samples in Fig. 9. Similar to the results in Fig. 9, the water absorption of the uncoated sample was the largest. When the concrete is coated with silane, the water absorption became smaller, but the gas permeability kept almost unchanged, as was shown above. Usually, the silane helps to form a hydrophobic layer on the surface of the concrete, which helps to prevent the water from entering the concrete. However, this hydrophobic layer does not affect the gas permeability. So the silane may not protect the concrete from some aggressive gas or vapor. The fluorocarbon reduces the water absorption, but strongly affects the gas permeability of concrete, which may stop the potential exchange of substance between concrete and the air. The FC-S composite material has the lowest water absorption, as well as proper gas permeability. It not only helps to protect the concrete from the aggressive water, but also produces some routes for the exchange of substance.

Table 6. Water absorptions of fluorocarbon, silane, and FC-S coated C50 samples

	uncoated	silane	fluorocarbon	FS-C
Water absorption ($mm/min^{1/2}$)	0.00846	0.00302	0.00347	0.00121

CONCLUSIONS

When different type of fluorocarbon and silane are used to prepare the FC-S, water-borne fluorocarbon and liquid silane do not show good intermiscibility, while other composites dissolve easily in each others. Whatever mix proportion is, FC-S can effectively reduce the water absorption of samples, but the FC-S that consists oil-borne fluorocarbon generally has lower water absorption. Although the penetration depths of FC-S that consists water-borne fluorocarbon seem to be a little bigger in M20 mortars, the penetration depths in M50 mortar are nearly unchanged. Therefore, oil-borne fluorocarbon is preferred to prepare the FC-S, and the optimized fluorocarbon to silane ratios are 1:5 and 5:1 for the M20 and M50 mortars, respectively.

When the optimized FC-S is used to coat the concrete samples, it works quite well to prevent both water and aggressive solutions to enter the concrete. The test results show that the FC-S can not only reduce the water absorption, it can also improve the resistances of freeze-thaw circles and chloride attack. Despite the fact that FC-S composite material can stop the transmission of water, its gas permeability is better than both the fluorocarbon and the silane.

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