B-2-2 In-situ synthesized calcium oxalate film on the surface of cement based materials

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ABSTRACT: A calcium oxalate mineralized film was synthesizedin-situ on the surface of acement-based material to protect against water penetration. X-ray diffractometry (XRD) and scanning electron microscope (SEM)results showed that the film was homogeneous and denseand was highly compatible with the cement paste. The film thickness increased with increasing concentrations of oxalic acid from 0.5mol/L to 1.5mol/L. Based on the analysis of the contact angle and surface free energy data, the calcium oxalate mineralized film can resis twater penetration effectively and can improve the hydrophobicity of the cement-based materials.

KEY-WORDS: Mineralized film, in-situ synthesized, cement, surface protection, porous materials, x-ray techniques

INTRODUCTION

Concrete durability means minimizing the possibility of aggressive elements to enter the concrete under certain environmental conditions[1]. Surface coatings have a significant role to play in concrete protection by controlling the ingress of aggressive agents[2].Currently used protective agentsare mainly divided into organic, inorganic, and hybrid (both organic and inorganic) compounds based on the chemical composition of the adhesives. Examples include organic polymer film systems like silane[3], low-polymerization siloxane, and epoxy resin[4].Organic products possess excellent hydrophobicity, stain-resistance, breathability, and other characteristics. In spite of this, the products have poor temperature resistance and undesigned for specific crack widths. Inorganic protective coatings like silicate materials can lead to complex physical and chemical reactions with cement hydration of alkaline substances, resulting in an enhanced and dense concrete surface with increased wear resistance. Even though this kindof material is difficult to meet the requirements of high durability and harsh service environments.

A new class of advanced organic-inorganic material, polymer-nanoclay composites, has emerged with excellent mechanical properties and barrier characteristics with only a few percent of well-dispersed clay reinforcements[5-6]. Ricky,etal[7] evaluated the barrier performance of silane/clay nanocomposites and they found that boththe neat silane and nanocomposite coatings significantly reduced the moisture permeability of concrete. With the progress of the industry, the protective film technology will be more environmentally friendly and easier to use in the future. Zhang, et al [8]detected a natural film (calcium oxalate) which had

protected the stone tower from atmospheric erosionmore than one thousand years. The authors obtained good protective performance results with regard to hydrophobicity, stain-resistance, and acid resistance via synthesized calcium oxalate in the laboratory at room temperature and conducted a preliminary investigation [9-10]. The objective of this study is to use in-situ chemical combinations to produce the mineralized film on the surface of cement based materials. The micro interface between the mineralized film and the cement based material, and the free energies of the mineralized film were analyzed.

EXPERIMENTAL

The cement and water used in the experiments were P.O 42.5 Portland cement (ShenZhen Haixing Onoda Cement Co. Ltd., Guangdong, China) and deionized water (Shenzhen Benno Industrial Co., Ltd.). The other chemicals data used in the experimentwas accorded to the paper that our partner wrote [11]. The cement paste samples were prepared with a water-to-cement ratio(w/c ratio) of 0.4. The cement was mixed with water uniformly, cast in a mold (20 mm×20 mm×20 mm) and cured at a temperature of 23 ± 0.5 °Cand a relative humidity of $95 \pm 5\%$ for 28 days. Oxalic acid solutions with different concentrations (0.5 mol/L, 1.0 mol/L, 1.5 mol/L, 2.0 mol/L) were prepared using oxalic acid dihydrate. Subsequently, the oxalic acid solutions were applied to the surfaces of the specimen and dried naturally in the lab.

Analysis of the mineralized filmwas performed by X-ray diffractometry(XRD) with Cu K α radiation (λ =0.154 nm) and a scanning range from 5 °to 80 °(2 θ). A scanning electron microscope (SEM)(Quanta TM 250) analysis was conducted for the test under the condition of 15kv to characterize the microstructure of the test block profile and the mineralized film thickness. The contact angle (CA) was measured with anOCA 20 measuring device(DataPhysics Instruments, Germany). Based on thecaptive bubble method[11], the CA was identified using the OCA's SCA 20 software. For obtaining reliable experimental results, measurements were took two times at different points on the polished surface of the specimen. The surface free energy was calculated based on the CA results.

Immersion test was used for proving water resistance of samples. The cement were cast into 30mm *30mm*30 mmmolds, after cured at a temperature of 23 ± 0.5 °C and a relative humidity of $95 \pm 5\%$ for 28 days and then brush 2 layers and 5 layers of oxalic acid solution respectively on the samples surface. And then dried at 50 °C to constant weight. Making the samples soaked in water, weighed every 24h and record.

RESULTS AND DISCUSSION

XRD spectra of Fig.1indicated that the main component of the mineralized film was calcium oxalate monohydrate. It also can be seen that there were also some characteristic peaks of calcium carbonate and calcium hydroxide which formed the background of the mineralized film in the XRD spectra. Calcium hydroxide is the hydrate product of cement and calcium carbonate is the carbonation result of the cement paste exposed to the air. Besides, XRD results further showed that the characteristic peaks of the mineralization film increased with the increase in oxalic acid concentration from 0.5 mol/L to 1.5 mol/ L. This indicated that calcium oxalate monohydrate hada higher crystallinity as the concentration increased. Calcium oxalate monohydrate does not dissolvein water orin acidic solutions. Compared with calcium carbonate, the solubility of calcium oxalate monohydrate is lower by nearly an order of magnitude [12]. Due to this characteristic, it was deduced that the mineralized filmw ould improve the concrete's resistance to erosion by various media in the environment, especially the resistance to acids.



Fig.1. XRD Analysis of the products on the cement mortar surface

Because there are free Ca^{2+} in the cement paste, the following reaction can occur when the oxalic acid solution is applied to the cement surface of the specimen:

$$C_2O_4^{2-} + Ca^{2+} = CaC_2O_4 \downarrow (sediment).$$

The thicknesses of the mineralized film formed by the reaction of 0.5 mol/L, 1.0 mol/L, 1.5 mol/L, and 2.0 mol/L oxalic acid withthe specimen was $17.27 \mu m$, $25.20 \mu m$, $27.61 \mu m$, and $14.18 \mu m$ respectively .With the increase of oxalic acid concentration, the mineralized film thickness increased, the voids inside the filmwere filled, the porosity was reduced, and the connectivity between the cement paste and the environment was diminished. It could be inferred that the impermeability of the cement-based materials was improved. By reason of the concentration appeared to be too high, the thickness of the mineralized film decreased when the oxalic acid concentration reached 2.0 mol/L. On the whole, the interface between the mineralized film and the cement paste was continuous and dense, and there was no apparent physical interface between the film and thecement paste. This mineralized film was highly compatible with the cement paste and bonded strongly with a solid interface.



Fig.2. SEM images of the mineralized film formed in-situ with (a) 0.5, (b) 1.0, (c) 1.5 and (d) 2.0 mol/L of oxalic acid

The results of the CAs are presented in Table 1.The total surface free energy of the untreated sampleis 62.31 mJ /m and the adhesion work is 134.71mJ/m showed in Table 2.Compared with treated samples, the adhesion work was lower than the untreated.This also indicated that calcium oxalate formed both on the surface of the cement paste and inside of the specimen.The smaller the adhesion power, the less was the surface affinity for water, in other words, calcium oxalate inside the specimen and on the surface, improving the water repellency, preventing the intrusion of other media, and decreasing the potential deterioration of concrete structures. The change of calcium oxalate concentration significantly affected both the dispersion component and the polarity component, resulting in a variation in the total surface free energy. The sespecimens treated with oxalic acid exhibited lower energy than the untreated specimens, indicating the amount of calcium oxalate generated on the surface and proving surface hydrophobicity. In future studies, we plan to test the use of the mineralized film on the surface of the cement-based material with regard to resistance to chemicals.

Fig. 3 shows the water resistance of calcium oxalate coatings with different concentrations. The curves of water absorption decreases with the increase of oxalic acid concentration. When the concentration of oxalic acid is 1.5 mol / L, the water absorption is the smallest, which is consistent with the result of surface energy, that fully proves the waterproof property of calcium oxalate coating. When the concentration of oxalic acid reaches 2.0mol / L, the water resistance of the coating decreases, because the concentration of oxalic acid is not conducive to the formation of calcium oxalate. In addition, compared with the sample of brushed 2 layers of oxalic acid solution,

the samples with 5 layers showed a much lower water absorption which indicates a better water resistance. As the number of layers was increased, the solution further penetrated into the sample so that more calcium oxalate forme to fill the pores, preventinge infiltration of water and improve the water resistance of the sample.

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Droplet/bubble	Average of CAs (°)						
	0.5	1.0	1.5	2.0	0		
Hexane	31.43	32.13	35.98	27.18	28.13		
Heptane	31.63	34.18	34.25	33.68	26.95		
Octane	29.40	34.30	34.83	34.95	33.53		
Nonane	35.48	35.93	40.13	27.85	32.03		
Decane	32.98	36.43	35.78	33.60	32.23		
Air	34 38	33.20	37.25	33.18	32.13		

Table1. Contact angles(CAs) determined for different samples

Table 2. Measurements of surface	e free energy at 23 ± 0.5 °	C(mN/m)
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Sample	Polar	Dispersion	Total surface adhesion	Polar
	component	component	free energy work	component
0.5	43.47	17.33	60.80	133.04
1.0	42.40	18.82	61.22	133.51
1.5	41.64	17.20	58.84	130.89
2.0	43.74	17.84	61.58	133.90
0	44.12	18.19	62.31	134.71



Fig.3. Water absorption of tsamples coated with calcium oxalate coatings in different concentrations.

CONCLUSIONS

Mieralized film coducted by a simple method. The analytical results indicated that this film was highly compatible with the cement paste and the thickness increased from 0.5mol/L to 1.5mol/L with the increase of the oxalic acid concentration. The in-situ calcium oxalate mineralized film can resist the permeation of water effectively while maintaining its hydrophilicity. This avoided or reduced stress failures of the protective material on the surface, and due to the in-situ growth, no peeling was observed.

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