A-2-5 CO₂ surface treatment for permeability improvement of cementbased materials

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ABSTRACT: The beneficial effect of carbonate precipitation as surface treatment to enhance concrete properties has been gradually disclosed in the last decade. This research was carried out with the intention to study the changed properties of cement mortar with w/c ratios of 0.4 after CO₂ treatment and further water curing. CO₂ treatment was used to enhance the quality of surface layer of the mortars 24 h after casting. The CO₂-treated specimens were tested for water absorption and water vapor transmission, and results were compared with the untreated mortar specimens. Chloride permeability of mortar discs was assessed by the rapid chloride migration test (RCM). In addition, thermogravimetric analysis (TGA) were employed to investigate the changes in chemical compositions of the surface layer after CO₂ treatment. Experimental result on cement mortar revealed that CO₂ surface treatment was successfully executed to leading a 0.8-1.6 mm CaCO₃ protective layer. The impermeability of cement mortar increased significantly by CO₂ surface treatment and the water curing.

KEY-WORDS: Water penetration, cement-based materials, surface treatment, permeability, carbon dioxide.

INTRODUCTION

Surface treatment is one of the effective protection methods to improve the durability of concrete[1]. It has been widely used for marine structures and bridge decks. The most common commercial surface treatment techniques include polymer coatings and hydrophobic impregnation.

Calcium carbonate precipitation has been adopted recently for concrete surface treatment due to its good stability. Calcium carbonate precipitation on concrete surface can introduced through two methods[2,3]. The first one is bacterial-induced mineralization, in which calcium carbonate forms from microbial cells and biochemical activities. Many studies indicated that durability of the mortar was affected by bacterial carbonate precipitation. The surface deposition of calcium carbonate decreased the water absorption, gas permeability, and chloride permeability by 20-80%, 17-33% and 39-51%, respectively, depending on the initial porosity of the specimens and bacteria. However, the cultivation of bacteria on concrete surface requires careful control, and the nutrient solutions for the bacteria development are expensive. The second method uses dimethyl carbonate (DMC) solution which hydrolyzes slowly and forms carbonate and methanol (CH₃OH) at room temperature and pressure. DMC has high biodegradability and low toxicity, but the treatment process should follow specific procedure and cannot show good protection without multiple treatments. Hence, it is important to identify an effective and quick method for producing a calcium carbonate protective layer without these drawbacks.

 CO_2 can react with harden cement paste directly and generates calcium carbonate, which may engender important changes of microstructure, like porosity, pore size distribution, connectivity, etc, and hence significant changes of transport properties of harden cement-based materials [4]. Carbonation of harden concrete, also referred as weathering carbonation, primarily results from long term exposure of concrete to atmospheric CO_2 . This behavior has been extensively studied. The carbonation of harden concrete cannot be used for providing protection based on three aspects[5]. Firstly, studies indicated that the carbonation products and pore structures of carbonated layer are noticeably influenced by the composition of cementitious materials, CO_2 concentration and degree of carbonation. Besides, it is generally accepted that the natural carbonation associates with reduction in pH of the

pore solution, which can lead to the initiation of reinforcement corrosion. Therefore, it is considered as a major detrimental issue to long term performance of concrete. Thirdly, the natural carbonation of harden concrete is a slow process. Steffens et al. showed it took about five years to get concrete fully carbonated.

Anhydrate cement clinker is also very reactive with CO_2 . Concrete blocks after 2-4 h of CO_2 curing achieved similar strength to those after 24 h of steam curing. In addition, CO_2 cured blocks also possessed lower porosity, water absorption and shrinkage[6]. They demonstrated that the early carbonation leaded to a reduction in calcium hydroxide near the surface while maintaining a pH above the corrosion threshold value at the core. Whereas, carbonation curing is generally used for dry plain concrete because the diffusion rate of CO_2 in saturated capillary pores is about 10,000 times slower than that in unsaturated capillary pores[7].

Current researches of concrete treatment have been focused on the effects of advanced coating systems and bacterial carbonate precipitation, but limited work has been done on exploring to apply CO_2 to concrete treatment. The presented work is the first part of a series study seeking to develop the CO_2 surface treatment of precast concrete products which might have strengthens in both economic and environmental aspects. Here, we investigated how the CO_2 surface treatment affected the strength and permeability of the concrete at one-day age.

EXPERIMENTAL

A P. I. 42.5 Portland cement with a specific surface area of 336 m²/kg was used. Natural river sand with a density of 2610 kg/m³ was used as fine aggregate. The grading of the sand is shown in Table.2. An industrial grade CO_2 with a purity of >99% was used.

All the mortars were prepared with a constant water -to -cement ratio of 0.4 and sand-to-cement ratio of 1.5. The cement mortars were mixed in a rotary mixer for 3 min, then cast in different moulds, and consolidated using a vibration table. Cubic specimens of $40 \times 40 \times 40$ mm were cast for compressive strength and water absorption testing; cylinder specimens of $\Phi75 \times 100$ mm and $\Phi110 \times 100$ mm were made in PVC molds for water vapor transmission and rapid chloride migration (RCM) testing respectively. All freshly cast specimens were covered with a plastic sheet and cured in a room at T= 20 ± 1 °C and RH $\geq 98\%$ for 24 h.

All cubic specimens were demolded 24 hours after casting. All these specimens were then placed in a pressurized CO_2 chamber. The chamber was first vacuumed before the CO_2 gas injection. The CO_2 treatment time was 3 h. The CO_2 pressure in the chamber was kept at 0.2 MPa during the treatment. A RH of 70% in the chamber was maintained using saturated calcium nitrate solution. All faces of the cubic samples, but only one or two ends of cylinders were in contact with CO_2 gas.



(a) Specimen Cutting and Surface Treatment for Water Vapor Transmission Testing



(b) Specimen Cutting and Surface Treatment for RCM Testing Fig.1 Illustration of sample preparation



Fig.2. Schematic drawing of CO₂ surface treatment setup

RESULTS AND DISCUSSION

Water absorption

The initial water absorption rates of surface treatment cement mortars are shown in Fig. 3. In general, the CO_2 surface treatment reduced the water absorption rate of cement mortars. the water absorption rate of the control mortar after 90 min of soaking was 380 sqrt (time/s), while average reductions of 20.8 % after the 3 h of CO_2 treatment were observed. The decrease in water absorption of the carbonated cement mortars could result from the formation of CaCO₃, which can effectively reduce the porosity and capillary pore structure inside the surface layer.



Fig.3. Effect of CO₂ surface treatment on the water absorption ratio of cement mortars

Water-vapor transmission

The water-vapor transmission results of cement mortars without and with CO₂ surface treatment are shown in Fig. 4. It illustrates that the mass loss increased linearly with time. the CO₂ treated samples exhibited lower water-vapor transmission than the corresponding control mortars. After 576 h of exposure, the mass loss of the control sample was 6.4 g, and reduced by 16.9% and 32.8% for the 3 h and 6 h CO₂ treated samples, respectively. The slopes of scatter lines in the steady state shown in Fig. 6 are depicted in Fig. 7. The CO₂ surface treatment reduced the water vapor permeability coefficients from 3.3×10^{-6} g/mm²·h to 2.7×10^{-6} and 2.1×10^{-6} g/mm²·h after 3 h and 6 h hours of CO₂ treatment. Variations in the reduction of these coefficients reflect the pore-refining characteristics of CO₂ surface treatment.



Fig.4. Effects of CO₂ surface treatment the water vapor transmission of cement mortars

RCM testing

Fig. 5 presents the results of RCM coefficient of mortars without and with surface treatment cement. The RCM coefficient for Series 0.4 control sample was 17.6×10^{-12} m²/s, and reduced to 14.9×10^{-12} m²/s and 13.1×10^{-12} m²/s after 3 h and 6 h of CO₂ treatment respectively. As previously discussed, this improvement might be attributed to the reduce in the total porosity of the surface layer upon carbonation. Weathering carbonation and related corrosion problems in harden cement-based materials have been widely studied. It is a slow reaction that reduces the hydroxide concentration in the pore solution, destroys the passivity of the embedded reinforcement bars, increases the diffusion of chloride ions, and thus greatly reduces the service life of reinforced concrete structures [8,9]. However, the CO₂ surface treatment only affected very limited surface layer, but greatly reduced the diffusion of chloride ions.



Fig.5. Effects of CO2 surface treatment on the chloride migration coefficient of cement mortars

Thermogravimetric analyses

Fig. 6 shows the TG/DTG results of powders taken from the 0.2 mm outer surface layer of mortar samples. The decomposition of $CaCO_3$ at a lower temperature (500-680 °C) is related to the amorphous calcium carbonate.

However, the mass loss between intermediary (680-780 °C) and high (780-990 °C) temperature is likely associated with poorly crystallized phase (vaterite and aragonite) and well-crystallized calcite [10,11]. The peaks of decarbonation in samples after 3h and 6h CO₂ treatment were both not higher than 680 °C, which meant that the amorphous calcium carbonate was the main carbonation product. Additionally, the sample with 6 h CO₂ treatment was slightly shifted to lower temperature compared with that with 3 h CO₂ treatment, implying a slight decrease in crystallization degree. The possible reason was that more C-S-H participated in the carbonation reaction when the duration of treatment extended to 6 hour.

To understand how the CO₂ treatment influences the early-age cement mortars, the amount of CaCO₃ in the outer layer ranged from 0 to 2.0 mm was measured by an interval of 0.2 mm as shown in Fig. 10. As expected, the control sample without carbonation treatment contained less than 5% CaCO₃ along the depth (0-2.0 mm). The product was most likely formed by atmospheric carbonation of the Ca(OH)₂ from cement hydration. As high as 43.2 % CaCO₃ contents for carbonated samples were found in 0.2 mm surface layer after 6 h of CO₂ treatment.



Fig.6. Effect of CO₂ treatment of on TG and DTG curves of 0.2 mm surface layer in the mortars

CONCLUSIONS

The following conclusions can be drawn from this study:

- 1 The reacted depth of CO_2 surface treatment increased with the prolongation of treatment time period and w/c ratio. The influence depth of 3 h and 6 h CO_2 surface treatment on cement mortar with w/c = 0.4 were 1.0 mm and 1.6 mm respectively.
- 2 The CO₂ surface treatment could improve impermeability of cementitious materials. It demonstrates significant effect on reducing the water absorption by 15-30%, depending on treatment duration and w/c. CO₂ surface treatment showed similar effect on water-vapor transmission. Meanwhile, it could also reduce the diffusion of Cl⁻ which might increase after carbonation of harden cement.
- 3 The anhydrate cement clinker, Ca(OH)₂ and C-S-H would react with CO₂ during the treatment, result in a protective layer of calcium carbonate, C-S-H with lower Ca/Si ratio, and silica gel. The content of CaCO₃ would increase with the treatment duration, but its degree of crystallization was higher after 3h treatment than that after 6h treatment.

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