Vitreous–Ceramic Bonding Enamel: The Key to Strengthening Reinforced Concrete by CO2 Sequestration

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ABSTRACT

Carbonation or carbon sequestration in concrete has been recognized as a method for strengthening concrete by converting the non-strength producing phases (formed during cement hydration) into calcite and producing improvement in the structure of the calcium silicate hydrate gels. This technique for making dense, strong concrete cannot be used in conventional steel-reinforced concrete because the lower pH fails to provide adequate protection against corrosion of the steel reinforcement. A chemically-resistant vitreous coating that contains a reactive calcium silicate was developed to protect the reinforcing steel and to increase the bond strength to approximately three to four times the bond strength that normally develops on the bare steel surface. Carbonated test cubes containing uncoated steel fibers showed corrosion, while coated steel fibers showed no corrosion. By protecting the steel the enamel coating will provide a large volume of reinforced concrete available for carbon sequestration and thereby improve both the concrete and the environment.

INTRODUCTION

Carbonation of Concrete

Calcium hydroxide compounds formed during the hydration of portland cement in concretes and mortars can react with carbon dioxide in the atmosphere. The chemical reaction that produces the alkali and alkali earth hydroxides is usually written in cement chemistry notation as follows:

$$CS + H \longrightarrow CSH + \text{Calcium Hydroxide,}$$

where C=CaO, H=H_2O, and S=SiO_2.

This reaction produces the alkalinity (pH of the fresh concrete to 12.5 to 13) that is typical of fresh concrete and mortar. The higher pH's are associated with concrete that contains higher levels of sodium and/or potassium. After exposure to air the pH starts to

drop as the hydroxides react with carbon dioxide in the surrounding air and are converted to carbonates. The reaction us usually written as follows:

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O$$
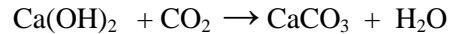
The carbonation reaction is associated with an increase in strength and density in the hydrated product. The crystallization of carbonates adds to the cementation produced by the calcium silicate hydrate gels and also fills in the pore spaces [Thomas and Skalny, 2006; Cizer et al., 2008]. Although the conversion of calcium hydroxide to calcium carbonate produces an increase in volume; the new carbonate phases form in the pore space and the overall effect is the for the concrete mass to shrink [Neville, 1995]. The rate of the reaction in cemented products exposed to the air is typically slow due to the low partial pressure of CO_2 in the atmosphere (0.03-0.06% v/v) and the slow rate of diffusion of the gas into the pores in the concrete. The rate at which the carbonation reaction proceeds depends on the availability of the reactants, the amount of pore space, and the pore connectivity of the concrete.

Artificial Carbonation of Concrete

When hydrating concretes and mortars are exposed to high levels of CO_2, carbonation occurs at the surface of the fresh cementitious material. The initial reaction is the formation of calcium carbonate from calcium hydroxide and the acceleration of the formation of calcium silicate hydrate-like gels. Three minutes of carbonation can accelerate the hydration of C_3S and produce hydration equivalent to what would form during 12 hours of normal hydration [Bertos et al., 2004]. Experiments with cement pastes have shown that strengths approaching 1000 kg/cm^2 (98 MPa) could be obtained in 15 minutes [Young, Berger, and Breese, 1974]. Carbonation can potentially be very useful in rapidly hardening thin-walled concrete or mortar materials [Verbeck, 1958; Saetta and Vitaliani, 2005].

Carbon Sequestration through Carbonation of Concrete

Artificial carbonation of concrete can have beneficial effects by increasing the surface hardness of concrete and the strength of thin concrete items as well as shorten the curing time for fresh concrete. Since capturing carbon dioxide by artificial concrete carbonation can add value to a concrete product; artificial carbonation of concrete has been proposed as a system for reducing the levels of man-made carbon dioxide in the atmosphere [Bukowski, and Berger, 1979; Harrison, 2005; Yixin, Mirza, and Wu, 2006; Haselbach, 2009]. Yixin, Mirza, and Wu [2006] report that carbonation for 2 hours with 100% CO_2 can sequester up to 16% of the CO_2 (measured by direct gain in mass) and gain the strength equivalent of two months of conventional curing. The carbonation is sufficient to produce an all-solid section of concrete that is 14 mm in thickness. Hasselback, and Ma [2008] have shown that carbon adsorption on the surfaces of the carbonation products in concrete results in an uptake of CO_2 that is greater than would be accounted for by carbonation. Surface complexation on pure calcite may produce an uptake of 30% in excess of the CO_2 needed to form the calcite. Precast concrete items are a major segment of the concrete market and they can be processed (and possibly improved) by artificial carbonation. One potential processor indicates that 60 tons of carbon dioxide could be sequestered as solid calcium carbonate for every 1000 tons of concrete produced [Hamilton, 2008]. Yixin, Zhou, and Monkman [2006] suggest that carbonation could replace steam curing of concrete contributing directly to the reduction of greenhouse gas emissions.

The Problem with Carbon Sequestration in Concrete Products

Both artificial and natural carbonation remove one of the major sources of alkalinity in concrete, calcium hydroxide. Normally the pH of inter-pore fluids in concrete is 12.5 due to the presence of calcium hydroxide. The pH may be even higher (up to 13.5) if sodium and/or potassium are present. The pH of the concrete stabilizes a coating of iron oxide on the surface of mild steel that is typically used in concrete reinforcement. When the pH drops below 8.5, the iron oxide coating is no longer stable and can oxidize to form alternate products such as $Fe(OH)_3 \cdot 3H_2O$. These hydrated oxides have a volume that is over six times the volume of the original steel. The expansion usually puts the surrounding concrete in tension, and as corrosion progresses, the concrete cracks and the steel reinforcement is debonds from the concrete [Locke, 1986; Borgard et al., 1990]. If mild steel reinforcement cannot be used then the reinforcement has to be non-metallic or a metal less prone to corrosion, such as stainless steel. This adds to the cost of the precast item and may not provide the strong reinforcement typical of mild steel. Other alternatives are polymer-coated mild steel, or galvanized steel; but these materials typically have lower concrete-to-reinforcement bond strengths.

USE OF REACTIVE CERAMIC-VITREOUS ENAMELED STEEL

Bonding Enamel-coated Steel in Concrete or Mortar

A new coating for steel that consists of a vitreous enamel with and outer coating of hydraulically reactive cement offers a useful alternative that protects the reinforcing steel even in aggressive (salty) environments and improves the concrete-to-reinforcement bond (Fig. 1). This coating allows the precast steel-reinforced material to be carbonated while still protecting the steel from corrosion and providing a high-strength bond between the coated steel and the surrounding concrete. Lynch et al. [2007] presented the methods used to produce the porcelain enamel coating on the surface of the steel as well as reporting that the composite vitreous enamel coating made with alkali-resistant glass and hydrating calcium silicates (basically the hydraulically setting compounds in Portland cement) could produce a bond strength that was three or four types that obtained with bare steel or with enamelled steel. Table 1 shows comparative data on mortar-to-steel bond strengths.

Fig. 1. Examples of Steel Test Rods Coated with Vitreous Enamel with an Outer Layer of Fused Cement. One in. = 2.54 cm.

Table 1. Comparisons of Steel-to-Mortar Bond Strengths

Treatment	Average Peak Force (N)	Std. Deviation (N)	Average Bond Strength (MPa)	Source
Steel rod, smooth			2.5	Fernandes, Varum, and Costa, 2007
Steel fiber			2.04-2.72	Maage, 1978
Steel cylinder end			2.9-3.4	Page, Al Khafaf, and Richie, 1978
Steel decking, trapezoidal			0.077	Chaklos, Yulismana, and Earl, 2004
Uncoated steel rods	2618.2	466.2	2.06	Lynch et al., 2007
Enamelled steel rods without Portland cement	3497.9	540.8	2.70	Lynch et al., 2007
Rods with enamel containing Portland cement	11124.6	236.3	8.79	Lynch et al., 2007

The ability of the coated rods to produce a strong bond with surrounding mortar or concrete and provide a vitreous coating is important because other coating techniques, plating or polymer coating, typically will not improve the bond strength and in some cases decrease the bond strength [Chang, and Yeih, 2001; Cheng et al., 2005].

Corrosion Resistance of Bond Enamel-coated Steel

Weiss et al. [2009] reported on a corrosion study conducted by placing bare and bonding-enamel coated mild steel rods in NaCl-saturated quartz sand. This exposure represented the conditions that would occur in fully carbonated concrete or mortar when all of the alkalinity of the concrete was removed, salt had infiltrated the concrete and oxygen was able to diffuse into the pore space in the concrete. After 40 days the bare rods had corroded to the point that iron oxide built up and cemented the sand to the rod. The only effect observed on the bonding enamel coated rod was the hydration of the portland cement that was embedded in the outer surface of the vitreous enamel (Fig. 2). The hydration of the cement raised the pH of the glassy surface. Vitreous or porcelain enamel is one of the most durable, chemically resistant coatings that can be put on steel and can protect the reinforcement from corrosion even in aggressive environments.

Fig. 2. Corrosion Observed on Uncoated Rod (Left) Compared to Uncorroded Vitreous-Ceramic Coated Test Rods (Right) After 40-Days Exposure to Sand Saturated with 3.5% Nacl Solution. The Dull Surface on the Uncorroded Rod was Formed when the Exterior Layer of Portland Cement Hydrated

Investigation of the Effects of Carbonation on Bonding Enamel-coated and Uncoated Steel

In order to examine the effects of carbonation in concrete or mortar, samples of a standard ASTM C109 mortar were prepared using a Type I-II Portland cement [ASTM, 2007]. Standard 50-mm cubes were prepared with no fibers, bare metal fibers, and fibers coated with the bond enamel. The cubes with fibers were cast with 75 g of 15-mm long mild steel fibers as reinforcement. The samples were cured at 23 °C for three days in 100% humidity cabinet. After curing, the samples were demolded, and placed in a container with a small amount of dry ice so that the cubes were in a 100% carbon dioxide atmosphere. Examination of the cubes after three days showed that the pH of exposed surface had dropped to about 8. The carbonated samples were then removed from the CO_2-exposure container and immersed in a tank containing 55-mm depth of 3.5% NaCl solution. After six days of exposure the ends of the uncoated fibers began to rust on the surface of the uncoated test cubes. No rust was observed on the control cubes or those containing coated steel reinforcement (Fig.3).
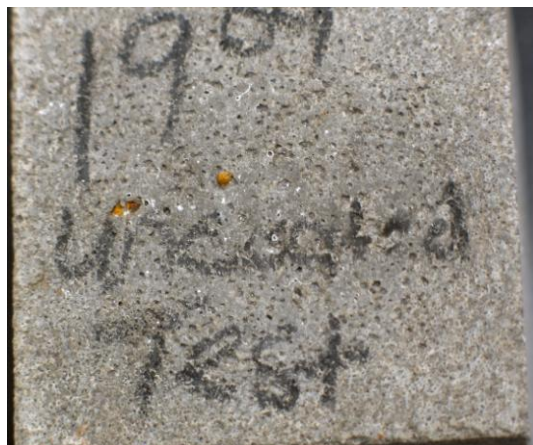
Fig. 3. Photo of Carbonated Mortar Cubes After 6 Days Exposure in a 3.5% NaCl Solution (Left). Note the Rust Spots on the Cubes Containing Uncoated Fibers Indicating Corrosion (Right).

Concretes containing randomly-oriented steel fibers have improved tensile and brittle properties; but this type of reinforcement is the hardest to protect from corrosion [Rider and Heidersbach, 1980]. Because the fibers are found at the surface there is minimal to no protection provided by the covering concrete. Normally only stainless steel fibers can be used in aggressive environments. These test results indicate the bonding enamel-coated fibers can survive in a severe environment even when the concrete is carbonated. The success with this type of reinforcement suggests that in general, bonding enamel-coated steel can survive in carbonated concrete in situations such as a marine environment without using any other type of protection.

CONCLUSIONS

A review of the literature and experimental work indicates that:

1. Steel reinforcement coated with a composite of vitreous enamel and a hydraulically-reactive glassy ceramic (like portland cement) will not cause a loss of bond strength with surrounding concrete
2. Bonding enamel-coated steel can survive in carbonated concrete even in a severely corrosive environment such as salt water.
3. If coated with a vitreous-ceramic bonding enamel, the common types of concrete reinforcement steel (rebar, wire mesh, and steel fiber) can all be used in artificially carbonated concretes where uncoated steel would be at risk of corrosion. The bonding-enamel coating makes it practical to consider sequestering carbon dioxide in reinforced concrete.

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