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Moderately alkaline pore solutions migrating through carbonated portland cement paste in contact with embedded steel can destabilize the protective passive film on the surface of steel and initiate corrosion.

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Concrete Carbonation: Significance and Proper Testing

What Is Carbonation and Why Do We Care?

Pore solutions in portland cement paste are naturally highly alkaline, with pH typically between 12 and 13. Highly alkaline pore solutions in concrete, mortars, and grouts are predominantly maintained by dissolution of calcium hydroxide—Ca(OH)₂ which is commonly referred to as portlandite—in hydrated portland cement paste. These solutions promote the formation of a passive and protective film on the surface of embedded steel.

However, the calcium hydroxide in hydrated portland cement can convert to more stable calcium carbonate (CaCO₃), which is primarily the mineral calcite, when exposed to carbon dioxide (CO₂) dissolved in pore solutions. It is generally accepted that calcium hydroxide carbonates most readily when reacted with CO_2 dissolved in pore solutions to form calcium carbonate and water through the following reaction:

Ca(OH) _{2 (calcium hydroxide)}	+	CO _{2 (aqueous)}	-
CaCO _{3 (calcium carbonate)}	+	$H_2O_{(liquid)}$	

Carbonation of portland cement paste significantly decreases the concentration of calcium hydroxide in the paste, reducing the pH of pore solutions in equilibrium with carbonated paste to values much lower than the depassivation threshold of embedded steel (pH around 9.5). Moderately alkaline pore solutions migrating through carbonated portland cement paste in contact with embedded steel can destabilize the protective passive film on the surface of steel and initiate corrosion. Thus, measuring the depth of carbonation relative to the depth of reinforcing steel can be important when assessing cause and/or future potential of corrosion-induced concrete deterioration.

Although it increases the risk of reinforcing steel corrosion, carbonation can have some beneficial effects on concrete. Carbonation reduces micro-porosity and increases concrete strength in portland cement concrete and can also be considered to "capture" or "sequester" CO₂ from the atmosphere.

The rate of carbonation depends on many factors but is most rapid when the internal relative humidity (RH) of the concrete element is in the range of 50 to 70 percent. Carbonation of cement paste at very dry conditions or when the concrete is immersed in water is slow or essentially stops. The depth of carbonation is approximately proportional to the square root of the concrete age. Porous, poor-quality concrete may exhibit significant carbonation during the period from sample extraction to laboratory examinations, and depth of carbonation from core cylindrical surfaces can also serve as an indicator of the

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Concrete Carbonation (CONTINUED)

relative quality of the concrete. In contrast, dense, well-designed concrete carbonates very slowly and takes decades or even over a hundred years to carbonate to the depth of the reinforcement.

Measuring Carbonation

To detect carbonation, a phenolphthalein solution is typically used in the field or in the laboratory to indicate the depth of the carbonation front in concrete, mortars, and grouts. Phenolphthalein changes from clear to a pink color on freshly saw-cut or fractured surfaces in areas where the pH is above approximately 8 to 9.5 (Figure 1). This pH level can be taken as a conservative indicator of the depth of carbonation for corrosion assessment since the risk of carbonation-related corrosion increases when pH of the concrete drops below approximately 9.5.

It is worth noting that phenolphthalein is an organic staining indicator of pH, not direct carbonation, and can also change color due to the presence of a surface hardener or other chemicals that may raise pH. Petrographers can see and differentiate carbonation and other products directly using thin section examinations. Therefore, thin section examination is considered the most accurate method to evaluate carbonation when in doubt, particularly if carbonation depth is small or partial carbonation exists. Carbonated portland cement paste exhibits much different optical characteristics (golden bright color) when viewed under cross-polarized light in thin section relative to mainly black, non-carbonated portland cement paste (Figure 2). In addition, carbonation often causes a beige discoloration in the paste fraction of concrete that is visible from visual inspection.



Figure 1. Photo of a fractured concrete surface showing the depth of carbonation from the exposed surface of the concrete (areas of the surface that did not stain pink) after applying a phenolphthalein solution. Note that the carbonation depth is deeper along a crack. The carbonation pattern indicates that the crack is not new or recent. Photo provided by Derek Cong.

Things to Consider

Phenolphthalein solutions can be sprayed on fractured surfaces, sawcut surfaces, cores, or core holes to assess depth of carbonation. Regardless of the type of surface, the surface to be tested needs to be roughly perpendicular to the exposed surface of the structure, and it needs to be fresh (i.e., within 15 minutes of cutting or extracting). It is also recommended to dry the surface using a hair dryer or fan to remove any bleed water (to avoid stain migration) before applying the phenolphthalein solution. Multiple, light sprays are recommended. Closely watch the color change during spraying and wait for a couple of minutes to allow the staining reactions to occur before photographing or measuring the depth of carbonation. Re-wetting the sprayed surface with a mild water mist or wiping using a moist paper towel (wiping from the exterior to the interior) may improve the color contrast between carbonated and non-carbonated concrete. Caution should be taken to avoid performing phenolphthalein testing on

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Concrete Carbonation (CONTINUED)



Figure 2. Thin section photomicrograph imaged in cross-polarized light showing near-surface carbonated paste (above dashed yellow line) that is golden bright due to a higher birefringence relative to non-carbonated paste (below dashed yellow line).

fractured surfaces that tend to occur along pre-existing cracks, which may be carbonated, leading to results that are not representative of the concrete as a whole. Testing a sawcut or fractured surface perpendicular to a crack may provide relative age information of the crack (Figure 1).

Old, historic concrete (pre-1940s) typically contains large unhydrated or partially hydrated portland cement particles in the bulk carbonated zone. These cement particles may or may not be carbonated. When the cement particles see water from cutting or sample extraction, hydration of the cement raises the local pH level higher than 9.5 and may lead to ambiguous carbonation assessment. In such a situation, thin section examinations would provide more definitive assessment of carbonation.

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