Carbonation as an Indicator of Crack Age

Information on carbonation products, means for detecting carbonation, and carbonation as a concrete chronometer

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Determination of carbonation of concrete is usually made during the course of petrographic examinations and is an important step taken during investigations of mechanisms contributing to deterioration. It's been suggested that the depth of carbonation at a crack can also be used to determine the age of a crack—an important issue considered during many investigations.[1,2]

CARBONATION PRODUCTS

All portland cement hydration products carbonate to form the products shown in Table 1. Although calcium hydroxide is sometimes said to be the first (or only) component that carbonates, this is not always the case. Based on unpublished studies by Erlin and Greening at the Research and Development Laboratories of the Portland Cement Association, some of the calcium hydroxide in samples from the extensive carbonation studies by Verbeck[3] remained uncarbonated in an ocean of other carbonated portland cement hydrates.

Further studies revealed calcium hydroxide crystals carbonate along prism faces rather than basal faces (Fig. 1). The basal face is usually predominant; thus, carbonation proceeds very slowly when calcium hydroxide crystals are squat or platy. These uncarbonated crystals can persist long after other hydration phases with greater surface areas, such as calcium silicate hydrates, have carbonated.

DETECTING CARBONATION

The most common method for a petrographer to detect carbonation is to spray a cut or broken concrete section with a phenolphthalein alcoholic solution. As

TABLE 1:

PRODUCTS FORMED WHEN PORTLAND CEMENT HYDRATION PRODUCTS CARBONATE

Portland cement hydration product	Carbonation products
Calcium hydroxide	Calcite and water
Calcium silicate hydrate	Calcite, silica gel, and water
Calcium aluminate hydrate	Calcite, alumina gel, and water
Hydrated ferrite phases	Calcite, ferric oxide, alumina gel, and water
Ettringite and calcium monosulfoaluminate	Gypsum, alumina gel, and water

shown in Fig. 2, the solution remains clear on carbonated concrete, but turns pink at noncarbonated areas. The test is actually an indicator of pH of concrete surfaces, but because carbonation reduces pH, the test also provides an indirect indication of carbonation.

Some less frequently used methods include:
- Spraying a proprietary "rainbow indicator" on concrete surfaces that results in a range of colors representing different pH values;
- Pressing pH-indicating strips onto moistened surfaces and observing the resulting color corresponding to different pH values; and
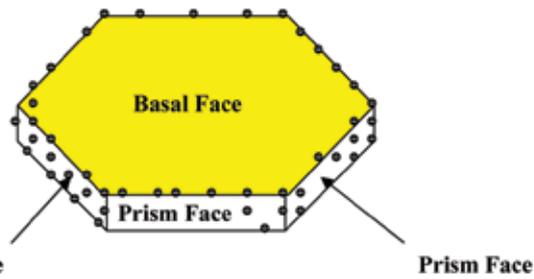- Using a pH probe and digital meter to measure the pH of crushed concrete-water slurries.

Fig. 1: Carbonation occurs preferentially on prism faces of calcium hydroxide crystals

Fig. 2: Depth of carbonation of a freshly fractured surface determined by spraying with a phenolphthalein solution that turns pink at noncarbonated areas
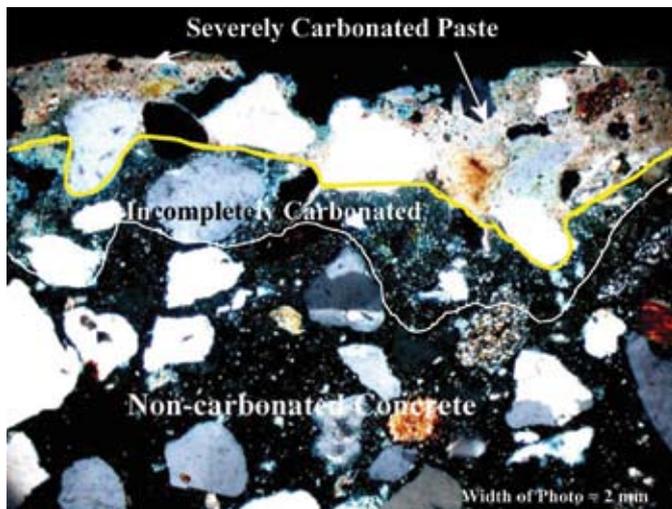

Fig. 3: Depth of carbonation observed on a thin section using a petrographic microscope

Two very accurate microscopical methods are also commonly used by petrographers to determine depths of carbonation and are described in ASTM C 856, "Standard Practice for Petrographic Examination of Hardened Concrete":[4]

- In the first method, small paste specimens are picked from freshly fractured surfaces using a needle probe. To determine if calcium carbonate is present, these specimens are immersion-mounted on slides so they
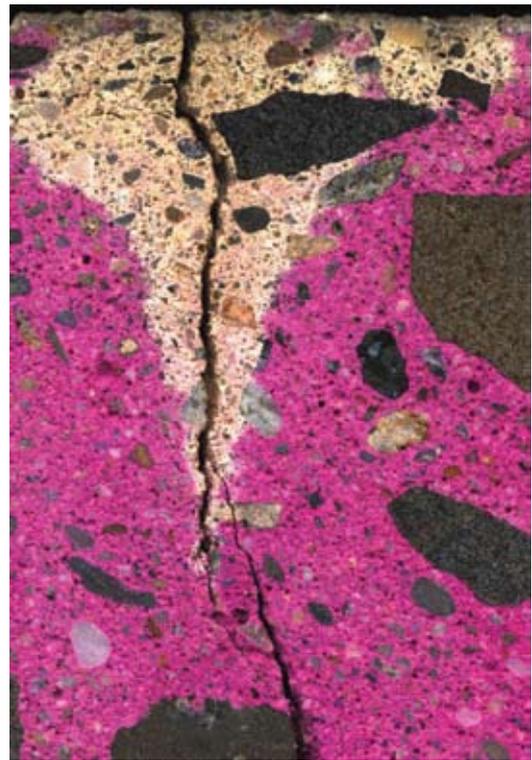

Fig. 4: Lapped cross section of concrete showing carbonation flanking a 2.5 in. (65 mm) deep vertical crack. The V-shaped carbonation zone does not extend to the end of the crack

can be observed using a petrographic microscope. The depth of carbonation is determined by viewing specimens taken at various distances from the original exposed surface; and

- In the second method, a thin section is prepared, and a petrographic microscope is used to identify the carbonated concrete, as shown in Fig. 3.

Unlike methods that measure surface pH, microscopical methods are not affected by alkali migration to surfaces due to wetting of the sample while it is being prepared.[2] Additionally, when concrete is attacked by acidic solutions, an amorphous zone leached of lime usually overlies a zone of carbonation. This zoning is easily observed using microscopical methods but is not observable when the acid-affected surface is sprayed with phenolphthalein or rainbow indicators or tested as a slurry.

CARBONATION AS A POSSIBLE CHRONOMETER

Depth of carbonation (D) is related to the concrete exposure time to CO_2 (t) by the equation $D = K\sqrt{t}$, where K is the carbonation coefficient. This relationship has been used by many as a possible concrete chronometer and even suggested as a method of determining the age of cracks.[1,2] This equation is valid only under steady-state environmental conditions (steady supply of CO_2) and

uniform paste properties (allowing steady diffusion of CO_2). These conditions, however, are usually not attained in field exposures. Field environments vary as temperature, relative humidity, and CO_2 concentration fluctuate, and diffusion properties vary with variations in paste properties caused by finishing, consolidation, bleeding, and curing.

Also contributing to the variations are surface-applied materials, some of which remain on surfaces, while others penetrate to various depths. These materials also usually degrade with time. Each of these factors affects the accuracy of crack-age predictions based on this equation.

When asked to determine the age of cracks in terms of years, we sometimes use carbonation depths in two similar concretes or carbonation distances in two adjacent cracks in similar exposures to determine their relative ages. During our investigations, we've observed that the zones of carbonation associated with cracks usually taper with depth and are usually V-shaped, as shown in Fig. 4, where the point of the V either extends to the end of the crack or is slightly short of the end. Also shown in Fig. 4 is another crack near the bottom of the vertical crack that does not show carbonation. It would appear that this bottom crack is younger. The distance of carbonation flanking the major crack decreases with increasing distance from the surface, so the carbonation depth-distance relationship from a crack wall needs to be carefully evaluated. Preferably, it should be measured in the region where the crack intersects the surface. At the surface, however, carbonation associated with the crack coincides with normal carbonation of paste at the surface. For cracks that extend completely through a section of concrete, such as deep drying shrinkage cracks in a slab, the zones of carbonation flanking crack walls may terminate short of the end of cracks (Fig. 4) or be symmetrical and extend the full depth of cracks (Fig. 5).

We've also observed that the distance of carbonation from a crack wall:

- Usually increases with crack width;
- Increases with continued exposure to CO_2;
- Decreases with depth in a tapered crack;
- Decreases as a crack fills with dirt, fills with secondary deposits, or experiences autogenous healing;
- Increases with increased CO_2 concentration inside a crack; and
- Increases with increased water-cement ratio.

Where a carbonated crack intersects one that is not carbonated or has a thinner zone of carbonation, the carbonated crack is usually, but not necessarily, older. Relative ages of cracks in the same concrete can be determined from carbonation distances flanking cracks if they are of similar widths and exposed to similar environments. To determine absolute age, the age of at least one crack having the same width in the same
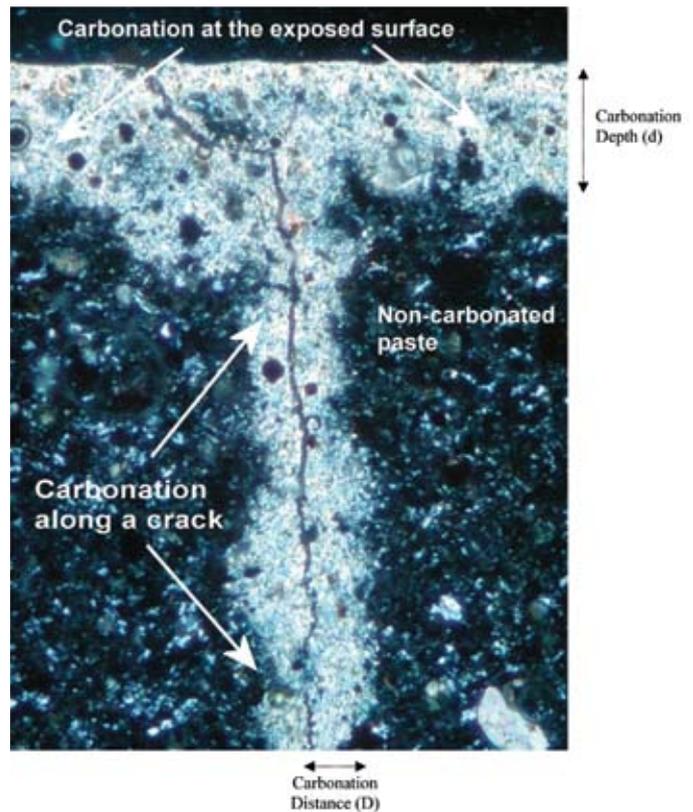
Fig. 5: Photomicrograph showing carbonation zones near an exposed surface and flanking a crack
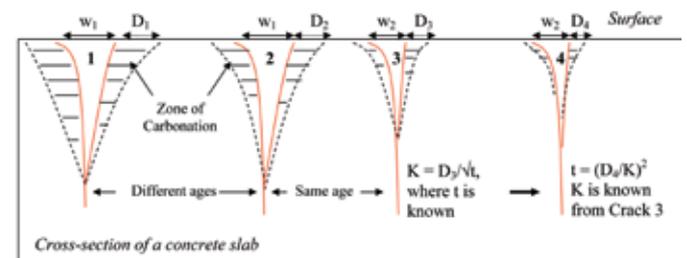
Fig. 6: Schematic cross sections of four cracks in a concrete slab. Each crack and the zone of carbonation flanking it taper with depth. Crack 1 is the oldest. Cracks 2 and 3 are the same age. The age of Crack 4 can be determined relative to the age of Crack 3 using the carbonation coefficient K determined from Crack 3

concrete and exposed to a similar environment as the unknown crack must be known. In this case, K can be determined from the crack with a known age. Examples are shown in Fig. 6.

There are many limitations to using carbonation as a reliable chronometer of crack age. Even in situations where the age of one crack is known and the crack with

an unknown age is of similar width, age determination is based on the assumption that K is the same for both cracks, which means that all factors affecting K are the same. The closer the two cracks are, the more valid this assumption becomes. Comparing cracks from different locations in a structure, however, decreases the accuracy of the age determination. Also, attempting to determine the age of a crack by comparing the carbonation distance from the crack walls with the depth of carbonation from an exposed surface is invalid due to unknown differences in the K values.

ALTERNATIVE CRACK AGE INDICATORS

In addition to carbonation, several other approaches are helpful in determining the age of cracks. For example, cracks spanned by bridges of paste indicate they were formed when the concrete was semi-plastic. Crack surfaces that are smooth indicate they were formed before concrete had attained much strength. Cracks that intersect air voids and pass *through* secondary deposits indicate formation after the deposit precipitated.

Coatings on crack surfaces or spanning cracks obviously demonstrate that the cracks are older than the coating. Finally, where two cracks intersect and one contains secondary deposits, the crack containing secondary deposits is usually older.

Because of the numerous limitations we've presented, we believe carbonation can, at best, be used as a qualitative measure of crack age. In most cases, however, determining the age of a crack by measuring the depth of carbonation along its walls is highly unreliable—the equation depends on conditions that are rarely met in the field.

References

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