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Short communication

Indicator of carbonation front in concrete as substitute to phenolphthalein

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ABSTRACT

A method to substitute the recognized toxic phenolphthalein in mortars and concretes is proposed. It comprises putting a portland cement sample in contact with an innocuous solution, curcumin-based, which acts as an indicator yielding a red color in areas where there is alkaline reserve (pH ~12) and yellow in carbonate zones (pH ≤9).
Solutions containing curcumin extracted from commercial turmeric powder and from the rhizomes of the turmeric plant were prepared by using ethanol as a solvent. Subsequently it has been experienced with solutions in which curcumin has been used with a purity of over 95%.
The dissolution of curcumin can be used with the same reliability as phenolphthalein in the carbonation process with the advantage that it is safe and presents no health risks.

1. Introduction

Reinforced concrete is a mixed structural element of concrete and steel [1]. The steel reinforcement remains passivated due to the high alkalinity produced by the hydration of the cement phases but can be corroded if the pH drops as a result of carbonation.

The cement hydration products portlandite ($Ca(OH)_2$) and sodium and potassium hydroxides provide a pH of about 12.5. However the influence of different factors, mainly atmospheric CO_2 and SO_2 may cause the disappearance by reaction of these hydroxides and therefore a decrease in pH. The scientific community believes that below a pH of 9.5 armor may be affected by corrosion processes.

Due to that the concentration of CO_2 in the atmosphere with respect to SO_2 is much higher, the term of *carbonation* is usually generalized as the sole process of lowering the pH in mortars and concretes due to such reactions. Specifically, the carbonation is the reaction not only of calcium compounds in the hydrated cement [2], mainly $Ca(OH)_2$ [3,4] but also of C–S–H [5] according to the following reactions:

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O.$$

$$C\text{–}S\text{–}H + 3CO_2 \rightarrow 3CaCO_3 \cdot 2SiO_2 \cdot 3H_2O.$$

Although it has been described that the non-hydrated calcium silicates may also be affected and carbonated [6]:

$$C_3S + 3CO_2 + xH_2O \rightarrow SiO_2 \cdot xH_2O + 3CaCO_3.$$

$$C_2S + 2CO_2 + xH_2O \rightarrow SiO_2 \cdot xH_2O + 2CaCO_3.$$

Carbonation affects the concrete microstructure by reducing the porosity [7,8] but also, as already described, it greatly influences the pH drop of the pore solution and thus depassivates the steel reinforcing.

To check for carbonation in the concrete, or the depth at which it reaches, phenolphthalein solution [1,9–11] is generally used. The said solution is usually 1% phenolphthalein in ethanol or in a mixture of 70% ethanol and 30% water.

Phenolphthalein is an organic compound of formula $C_20H_{14}O_4$ widely used as a pH indicator. A pH indicator is a substance that changes color depending on the pH of the solution in which it is located. In the case of phenolphthalein, it is colorless at lower pH values, of approximately 9, while values exceeding 10,5 present a characteristic purple or magenta. Since a mortar or concrete that has not been carbonated has a pH of 12,5 or higher, whereas if carbonated the pH drops to values of <9, the use of the phenolphthalein is well suited for visually checking this process.

The use of this solution is widespread, but in the descriptions of product safety, there are certain peculiarities that suggest or even require its replacement with less hazardous compounds:

According to the classification done by the Regulation (EC) No 1272/2008 [12]) phenolphthalein is suspected of causing genetic defects

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(H341) and can cause cancer (H350). This regulation replaces Directive 67/548/EEC [13] or Directive 1999/45/EC [14], which already considered this substance as:

- T: toxic.
- R45: may cause cancer.
- Xn: harmful.
- R68: possible risk of irreversible effects.

As mentioned above, we have experimented in our laboratories to obtain a safe indicator that has the same benefits as phenolphthalein and can replace this compound in concrete carbonation tests without risk to human health.

2. Experimental

Both mortar prisms and concrete cores have been used for the testing. While mortar samples were 4 × 4 × 16 cm OPC (ordinary portland cement) with carbonate aggregates, concrete samples were of 5 cm diameter made of OPC and granitic aggregates extracted from a Spanish dam. All samples had been stored in our laboratory for 3 years and were therefore partly carbonated. Mortar specimens were cut with a diamond saw and concretes were split with a hammer in order to have undisturbed sections for staining. Having decided on the most appropriate solution, different samples have been dyed by using phenolphthalein in half of the sample and the new indicator in the other half.

The quality of the products, used to prepare the solutions, was verified by X-ray diffraction (XRD). The samples were analyzed by X-ray diffractometer model 2002 JSO-DEBYEFLEX Seifert, provided with a copper anode and nickel filter. A sweep from 4° to 60° 2θ at a speed of 1°/min was performed.

A hot plate with magnetic stirring and an ultrasonic bath were used to maximize the curcumin extracted from commercial turmeric.

3. Results and discussion

In the search for alternative solutions to phenolphthalein, the first experiments were performed with 5×10^{-3} M potassium hexacyanoferrate (II) solution, to which HNO_3 has been added to acidify and obtain a pH value slightly below 1. This solution was used to selectively stain the cement paste, leaving unchanged the aggregate in studies to calculate the amount of cement in hardened concrete [15,16]. The staining with hexacyanoferrate works only in carbonated concrete, by staining intensely blue areas that would be colorless if phenolphthalein was used (Fig. 1).

Unlike phenolphthalein the potassium hexacyanoferrate (II) presents no health risks. However, to prepare the solution with a pH value slightly below 1 it is necessary to add an acid, and certain cyanide vapors in the process may appear. For that reason, the research focused on obtaining an absolutely harmless indicator.

Different natural pH indicators were investigated with the result that curcumin was the best suited because its pH range is more like phenolphthalein [17]. Curcumin is a natural dye with molecular formula $C_{21}H_{20}O_6$ coming from turmeric. In the European Union, it is authorized with the E-100 product code used in various food additives.

The extraction processes of curcumin from turmeric, described in the literature, are characterized by solid–liquid extraction using alkaline solvent at moderate temperature. After this stage curcumin is acidified to acquire the acidic crystalline structure which has a characteristic of yellow, and ultimately is dried to obtain the dye powder [18,19].

3.1. First studies

For an optimal solution, containing enough curcumin to display distinctly different areas of concrete that are either carbonated or not, tests were conducted with different turmeric commercial products and also directly with the rhizomes of the plant with similar results. As suggested by recent research, an ultrasonic extraction process was applied to improve the yield and purity of the extracted curcumin [20,21] in addition to using a temperature of 60 °C.

Fig. 2 shows the XRD spectra of the two samples of commercial turmeric from major Spanish supermarkets. No differences were found between samples, and peaks corresponding to curcumin are not clearly seen.

The solution with 1 g of commercial turmeric in 100 ml of ethanol acquires a certain tone that is more pronounced when the amount of turmeric is 2 g and, being 4 g the maximum coloration obtained (Fig. 2). In any case the amount of turmeric may be higher until saturated as it is finally filtered before used.

3.2. Second studies

The low concentration of curcumin in commercial turmeric (amounts below 2%) and the fact that different products may have different contents, make it impossible to propose a solution containing an exact percentage of curcumin, so further tests were conducted in a second stage with pure curcumin.

Pure curcumin from food additive suppliers was obtained. The samples were analyzed by XRD to check their purity. Fig. 3 shows a diffractogram of curcumin that is marketed as "turmeric dietary supplement containing more than 95% curcumin". The spectrum clearly identifies just the reflections corresponding to the curcumin. The following tests were conducted with this compound.

Solutions were prepared with concentrations of 0,25%, 0,50%, 0,75% and 1% of curcumin in ethanol. Fig. 4 shows the result of the

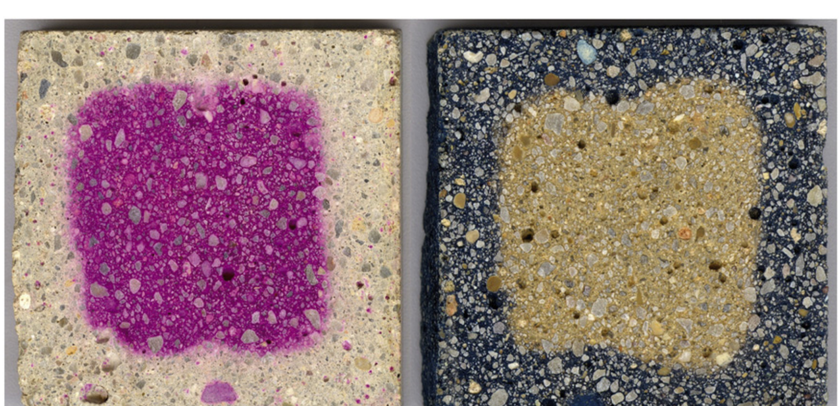

Fig. 1. 4 × 4 cm mortar sections stained with phenolphthalein (left) and 5×10^{-3} M potassium hexacyanoferrate (II) (right).