

Technical Note

An argument for using alizarine yellow R and indigo carmine to determine in situ the degree of alkalinity in reinforced concrete

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ABSTRACT

The commonest way of determining the passivation of steel in reinforced concrete is to spray a pH indicator onto the surface of a reinforced concrete specimen. To do so, the traditional indicator used has been phenolphthalein in ethanol, which shifts from colourless to purple in the pH range of 8.5–10.0. If the concrete encasing the rebar turns purple, it indicates it is passivated; that is, it has a film of iron oxide impermeable to oxygen that protects it from oxidation. However, the reduction in the pH of the concrete due to carbonation (between 11.4 and 8.5) indicates, despite the reddish-purple colour, the disappearance of the passive layer of the steel. Consequently, we propose a novel in situ technique for determining with a high degree of reliability, the passive state (pH over 11.7) and the active state (pH under 11.4) using two reactants: alizarine yellow R and indigo carmine.

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1. Introduction

Carbonation of concrete involves a chemical reaction that takes place between portlandite generated in cement hydration with carbon dioxide [1–3]. Carbonation reduces pH value of concrete pore solution (about 12.5–13.5 [4]), making factible the active state of the embedded reinforcement steel bars [5]. It is known that concrete is a protective cover of reinforcements in highly alkaline environment: a passive film of iron oxide exists on the reinforcement surface and oxidation of reinforcement is inhibited [4].

The zones of carbonation can be identified as completely carbonated, partly carbonated and uncarbonated. The completely carbonated zone is defined by the colourless depth of the phenolphthalein indicator. In this zone, the degree of carbonation is over 50%, and the pH of the pore solution is 9.0 or less. In the partly carbonated zone, pH of the pore solution ranges from 9.0 to 11.4, the degree of carbonation varies from 0% to 50%. For the uncarbonated zone, the pH of the pore solution is higher than 11.4, and no signs of carbonation are observed [6].

Phenolphthalein indicator method has usually been used to monitor the boundary marking the carbonation front [7–9], where concrete is alkaline. The indicator used is a phenolphthalein 1% ethanol solution with 1 g phenolphthalein and 90 ml 95 v/v% ethanol diluted in water to 100 ml [10]. The phenolphthalein turns from uncoloured to purple in a pH-range from 8.5 to 10.0, as de-

scribed in EN 14630:2006 [11]. If the concrete encasing the rebar turns purple, it indicates it is passivated; that is, it has a film of iron oxide impermeable to oxygen that protects it from oxidation. In contrast, if the colour does not change, then the steel framework has lost its passivating film. Since it is active, corrosion is possible if conditions favour it.

However, there exists a partially carbonated zone where the pH value is not easily detected using a phenolphthalein indicator [2,12]. Additionally, it has been reported that concrete at the pH of 10.5 or less will not be able to passivate the steel reinforcement [13]. It has also been shown that carbon dioxide could react at depths greater than those indicated by a phenolphthalein indicator [2]. Many research findings [3,4] have indicated that phenolphthalein indicator measures the degree of carbonation at a pH of 9.0; hence, areas of partial carbonation where the pH ranges from 9.0 to 11.4 could not be tested. Consequently, the depths of carbonation in concrete and the subsequent corrosion risks have often been underestimated [4]. So they suggest that is necessary a more reliable pH indicator than the phenolphthalein solution in detecting the carbonation hazard. Other alternative pH test procedures previously reported in the literature [14–16] do not work efficiently in the whole pH range from 9 to 11.4 either. The aim of this communication is suggest a novel technique to evaluate through pH indicators the carbonation depth for a reinforced concrete. The experiments reveal that two more reliable pH indicators, with ability to distinguish pH value from 9 to 11.4, can be developed to not to underestimate the corrosion risks.

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2. Materials and methods

This new technique is based on two reactants: alizarine yellow R and indigo carmine, and a colour chart to determine, with complete reliability, the passive state or active state of rebar in concrete. A description of the colour chart provided with the technique is given in Fig. 1, that shows two bands with the colour transition that occurs during the colour shift of each of the reactants, allowing the determination of a passivation state with alizarine yellow R (red colour, pH over 11.7) and of depassivation with indigo carmine (blue colour, pH under 11.4).

The proposed reactants are solutions of the indicators alizarine yellow R and indigo carmine. Alizarin yellow R (Panreac Company, Barcelona, Spain), one of azo dyes with a structure combining nitrobenzene and salicylic acid (pK_a of 11.0), has been previously used as a pH indicator [17] and supplied without further purification. Sulphonated indigo (indigo carmine, IC, indigo-5,50-disulphonic acid di-sodium salt, pK_a of 12.2, C.I. Acid Blue 74, C.I. Natural Blue 2) was used as supplied by Panreac Company, Spain.

Alizarine yellow R is a 0.5 v/v% solution of this indicator in a mixture of acetone and ethanol. This solution changes from yellow to reddish at a pH range of 10.1 to 12.0, unequivocally indicating a passivating film on the steel when the reddish colour is fully developed. Indigo carmine is a 0.5 v/v% solution of this indicator in a mixture of acetone and water. It shifts from blue to yellow at a pH range of 10.0–11.4, definitively indicating the active state of the rebar in the concrete.

Both the average phenolphthalein colourless depth (X_p) and the mean carbonation depth (X_n) using this novel technique were measured according to the method used in a previous work [7].

3. Results

Several samples of 19 year old reinforced concrete were taken by wet core drilling from interior pillars (in non-aggressive conditions). Concrete was made with a type II Portland cement 35, the aggregate used was crushed limestone with fineness modulus 2.376 and nominal grain size of 20 mm. Table 1 shows the mixture proportions for a water–cement ratio of 0.66. Compressive strength values average 20 MPa.

Previously to perform the pH tests, a cylindrical core sample was cut using dry-cutting segmented diamond blade and was

Table 1
Concrete mixture proportions.

Mixture proportions (W/C = 0.66)			
Cement (kg/m ³)	Water (kg/m ³)	Coarse aggregate (kg/m ³)	Fine aggregate (kg/m ³)
300	200	1290	645

brushed clean, then immediately sprayed on the freshly surface with phenolphthalein and the two novel reactants (Fig. 2a). After compressive strength measurements, a second core sample was sprayed on the freshly fracture surface; later, this sample was examined to determine whether the rebar lies within the zone turning reddish. If so, it is supposed to be covered by a passivating film. However, if the colour remains orangish-yellow, then coat an adjacent area (not overlapping) with indigo carmine. After about another minute, examine the sample to see whether the rebar lies within the zone that has turned blue. If so, the rebar has an active state and may be undergoing corrosion (Fig. 2b). Study of the colours and their interpretation is made easy by the colour chart of Fig. 1.

Both this novel technique for determining carbonation depth and the phenolphthalein method can produce an accuracy of 0.5 mm. As shown in Fig. 3, the discrepancy in results between the two analytical methods leads to state that the mean carbonation depth (X_n) using this novel technique, compared to the phenolphthalein colourless depth (X_p) on average, has a greater value. Relative standard deviations were below 2%. In fact, the depth of the carbonation front (known as X_c) can be assumed about two times greater than that observed from a phenolphthalein test [6]. It should be also noted that X_n and X_c parameters show similar values.

4. Discussion

Concrete is a physical barrier separating steel from the atmosphere. The steel–concrete interface forms a passivating, self-regenerating film [18] due to a basically electrochemical process [19] that depends on the high alkalinity of the concrete (pH of 12.5–13.5) caused by the calcium, sodium, and potassium hydroxides dissolved in the aqueous solution of its pore network [20] and on the existence of a suitable electrochemical potential in

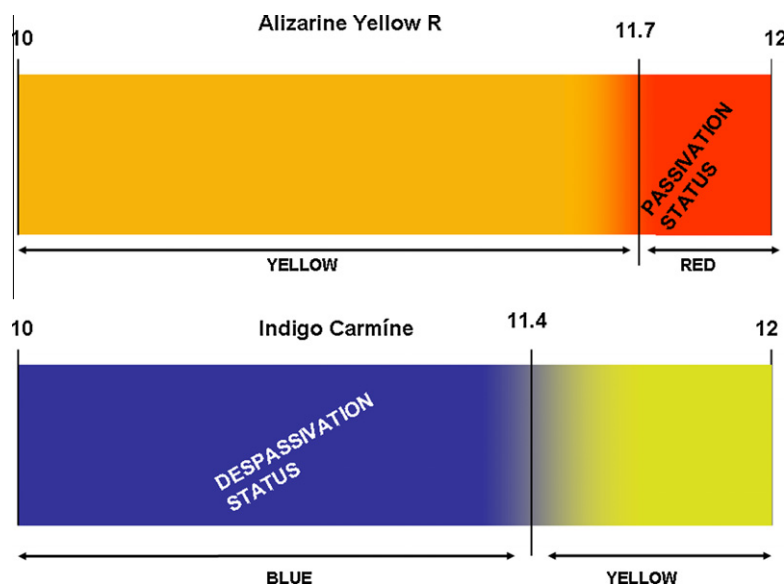


Fig. 1. Colour chart.

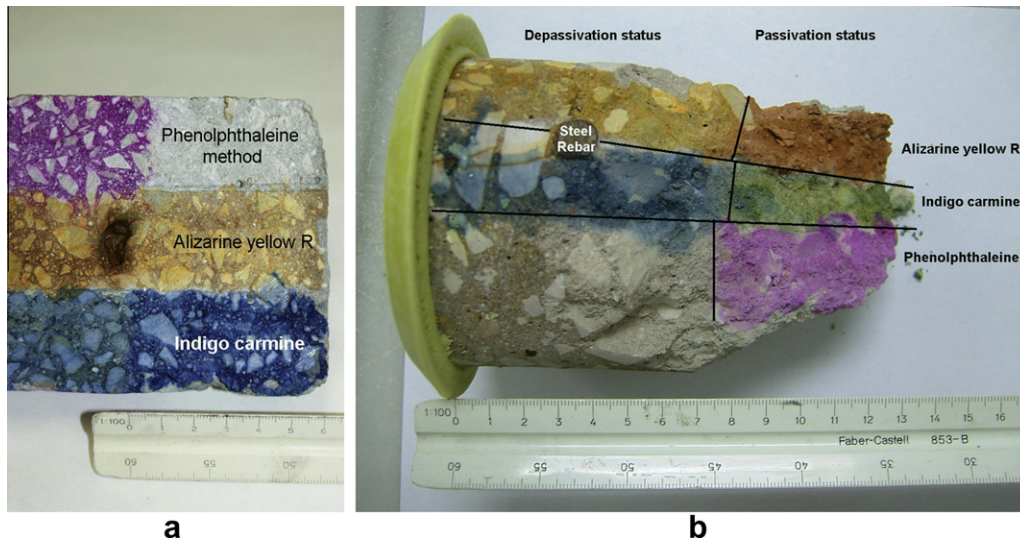


Fig. 2. Comparative of the new technique and phenolphthalein method in: (a) cutted surface concrete core and (b) concrete core after compressive strength test.

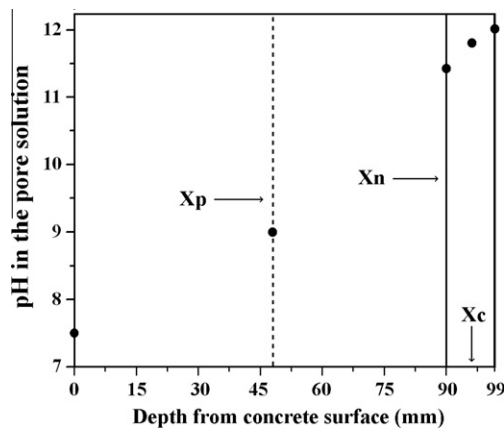


Fig. 3. Relationship between carbonation depth and pH in the pore solution for concrete. Notes: X_p = phenolphthalein colourless depth; X_n = carbonation depth using the novel technique; and X_c = depth of the carbonation front.

accordance with the iron Pourbaix diagram. In this way, the steel will remain passive indefinitely unless there is a decrease in pH, which would trigger the destruction of the passive state.

The stripping away of the protection of the concrete framework is basically due to the presence of depassivating ions, especially chlorides, and to carbonation which rate depends mainly on the relative humidity, the availability of CO_2 , grade of concrete and the environmental temperature where the concrete element is placed [21]. In any case, the carbonation process allows a local or general occurrence of a pH below a critical value in the concrete.

As soon as the hardened concrete begins to undergo carbonation, even at atmospheric carbon dioxide concentrations of 0.03% by volume [22] or similar, the concrete will have two zones with different pH, an inner pH over 12 and an outer pH near 7. When the framework lies within the zone undergoing carbonation, at a pH of under 11, the passive film of the steel disappears [23]. Other authors report that the concrete needs an even higher pH of over 11.4 and even 11.7 in some cases for the steel to be completely protected against corrosion [24–26].

However, the reduction in the pH 9–11.4 of the concrete due to carbonation suggests, despite the reddish-purple colour, the disappearance of the passive layer of the steel. These values are evi-

dently significantly different from those indicated by the phenolphthalein test [3,4]. In short, phenolphthalein is completely reliable in establishing the active state of the steel in reinforced concrete (at pH under 8.5 it is colourless and the steel is depassivated). Nevertheless, phenolphthalein is inconclusive in determining the passive state (at pH between 9.0 and 11.4, the phenolphthalein turns purple but the steel is depassivated). It is only above a pH of 11.7 that this test is once again reliable.

Finally, it should be considered that the risk of reinforcing steel corrosion does not only depend on the pH threshold, but it is also induced by some additional factors: the presence of ions such as chlorides, availability of O_2 , concrete resistivity, moisture content, among others. As a consequence, methods based on pH indicators can be only used as preliminary tests. Alternatively, rebar corrosion on existing structures may be assessed by different methods such as open circuit and surface potential measurements, linear polarization resistance measurements, embeddable corrosion monitoring sensor and cover thickness measurements [27].

5. Conclusions

The aforementioned technique proves to be technically feasible because of its simplicity, as is currently the phenolphthalein test and it is also applicable to the inspection of structural elements embedded in reinforced concrete to control them more thoroughly. These new indicators permit us to determine with higher reliability and accuracy the degree of alkalinity as an indication of partial carbonation or risk of corrosion of the steel used for the construction of reinforced and prestressed concrete.

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References

- [1] Atis CD. Accelerated carbonation and testing of concrete made with fly ash. *Constr Build Mater* 2003;17:147–52.
- [2] Parrott LJ. A review of carbonation in reinforced concrete. Wexham Springs (UK): Cement and Concrete Association; 1987.

- [3] Lo Y, Lee HM. Curing effects on carbonation of concrete using a phenolphthalein indicator and Fourier-transform infrared spectroscopy. *Build Environ* 2002;37:507–14.
- [4] Chang JJ, Yeih W, Huang R, Chen ChT. Suitability of several current used concrete durability indices on evaluating the corrosion hazard for carbonated concrete. *Mater Chem Phys* 2004;84:71–8.
- [5] Papadakis VG, Vayenas CG, Fardis MN. Fundamental modeling and experimental investigation of concrete carbonation. *ACI Mater J* 1991;88:363–73.
- [6] Chang ChF, Chen JW. The experimental investigation of concrete carbonation depth. *Cement Concr Res* 2006;36:1760–7.
- [7] Ramezani-pour AA. Properties and durability of pozzolanic cement mortars and concretes. PhD thesis. UK: Civil Engineering Department, The University of Leeds; 1987.
- [8] Claisse PA. The properties and performance of high strength silica fume concrete. PhD Thesis. UK: The University of Leeds; 1988.
- [9] Paillere AM, Raverdy M, Grimaldi G. Carbonation of concrete with low-calcium fly ash and granulated blast furnace slag: influence of air-entraining agents and freezing and thawing cycles. In: Proceedings of ACI canmet second international conference on fly ash, silica fume, slag and natural pozzolans in concrete, SP-91, Madrid; 1986. p. 541–62.
- [10] Fukushima T, Yoshizaki Y, Tomosawa F, Takahashi K. Relationship between neutralization depth and concentration distribution of CaCO_3 - $\text{Ca}(\text{OH})_2$ in carbonated concrete. In: Malhotra VM, editor. *Advances in concrete technology*. ACI SP-179, Tokushima; 1998. p. 347–63.
- [11] UNE-EN 14630. Products and systems for the protection and repair of concrete structure – test methods – determination of carbonation depth in hardened concrete by the phenolphthalein method. Madrid: AENOR; 2006.
- [12] RILEM Committee CPC-18. Measurement of hardened concrete carbonation depth. *Mater Struct* 1988;18:453–5.
- [13] Bentur A, Diamond S, Berke NS. *Steel corrosion in concrete: fundamentals and civil engineering practice*. London: Edmundsbury press; 1997.
- [14] Jung WY, Yoon YS, Sohn YM. Predicting the remaining service life of land concrete by steel corrosion. *Cement Concr Res* 2003;33:663–77.
- [15] Yu MY, Lee JY, Chung Ch. The application of various indicators for the estimation of carbonation and pH of cement based materials. *J Test Eval* 2010;38 [Paper JTE102382].
- [16] Lee HJ, Kim DG, Cho MS. A study for carbonation degree on concrete using a phenolphthalein indicator and Fourier-transform infrared spectroscopy. *WASET J* 2012;62:184–90.
- [17] Williams TR, Lautenschleger M. Titration of weak acids with tetramethylguanidine as solvent. *Talanta* 1963;10:804–8.
- [18] Gancedo JR, Alonso C, Andrade C, Gracia M. AES study of the passive layer formed on iron in saturated hydralime solutions. *Corrosion* 1989;45:976–7.
- [19] Sagoe-Crentsil KK, Glasser FP. Steel in concrete. Part I. A review of the electrochemical and thermodynamic aspects. *Glusser Mag Concr Res* 1989;41:205–12.
- [20] Committee Euro-International du Beton. Bulletin no. 152. Corrosion of reinforcement. Lausanne; 1984. p. 73–93.
- [21] Neville AM. *Properties of concrete*. 4th ed. London: Longman Group UK Ltd.; 1995.
- [22] Sirvent I. *Technology and therapy of concrete*. 1st ed. vol. 1. Valencia: Red Abogacia Libros; 1997.
- [23] Committee Euro-International du Beton. Bulletin no. 243. Strategies for testing and assessment of concrete structures. Lausanne; 1998. p. 76–92.
- [24] Gjorv OE. Steel corrosion in reinforced and prestresses concrete structures. *Nordisk Betong* 1982;2-4:147–51.
- [25] Saeki N, Takada N, Fujita Y. Influence of carbonation and sea water on corrosion of steel in concrete, vol. 6. Tokyo: Transport Japanese Concrete Institute; 1984. p. 155–62.
- [26] Krajci L, Janotka I. Measurement techniques for rapid assessment of carbonation in concrete. *ACI Mater J* 2000;97:168–71.
- [27] Song H-W, Saraswathy V. Corrosion monitoring of reinforced concrete structures – a review. *Int J Electrochem Sci* 2007;2:1–28.