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Assessing carbonation depth using pH indicators: A comparison between phenolphthalein and thymolphthalein indicator

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A B S T R A C T

Carbonation in concrete reduces alkalinity and increases the risk of steel reinforcement corrosion in the presence of moisture. Carbonation depth measurement using pH indicator is a widely used and standardised approach for assessing the carbonation-affected region in concrete for concrete durability evaluation. This study compares the carbonation depth obtained using phenolphthalein and thymolphthalein indicators in cement mortars and concretes subjected to natural and accelerated carbonation in a widely used and standardised approach of assessing the carbonation-affected range in cement combinations with varying clinker contents. Results demonstrate that the use of 1% thymolphthalein indicator provides similar carbonation depth to 1% phenolphthalein solution, confirming its usage for carbonation depth measurement in laboratory evaluation and for condition assessment in the field structures subjected to ambient carbonation.

Keywords : *Carbonation; pH indicators; Carbonation front; Phenolphthalein indicator*

1. Introduction

Concrete carbonation is a key durability concern for reinforced concrete structures, known to modify the alkalinity [1,2], phase assemblage [3,4], and dimensional stability [5–8] in the CO_2-affected region and eventually cause reinforcement corrosion in reinforced concrete structures [9,10]. Atmospheric CO_2 diffuses into the pore networks of cementitious materials to react with all hydration products, including calcium hydroxide, C-S-H, ettringite, etc., to form calcium carbonate. This reaction is accompanied by a reduction in the alkalinity of the pore solution, which can be easily obtained using a pH indicator to measure the carbonation affected depth [11]. Such measurement is a standard approach to assess concrete durability performance [12]. Since the reduction of the pH drops below ~9 increases the corrosion risk of reinforcement steel, measurement of carbonation depth can be related to the durability performance of reinforced concrete structures. Carbonation rate (in, mm/d$^{0.5}$ or mm/year$^{0.5}$) estimated based on carbonation depth over time is used as a predictor for corrosion initiation [13,14] and service life modelling [15,16] with the assumption that steel will corrode when the carbonation-affected depth, as per pH indicator measurement, is greater than the cover depth. Although mere measurement of a single point carbonation depth using pH indicator as carbonation affected region is a simplification of complex cement-CO_2 interaction process [17,18], specifically in alternative low carbon cements [19], carbonation depth is still used widely for assessment of concrete durability and to engineer the performance of concrete mixture based on carbonation rates to ensure carbonation depth can be limited below the steel surface during the intended design service life.

Traditionally, phenolphthalein, which changes from pink to colourless as the pH drops below ~9, has been used to identify the carbonation front as a single point transition for engineering assessment. However, carbonation is a gradual reactive transport process, and pH can vary across the carbonated region and the carbonation-affected region may even extend beyond the pH indicator measurement depth as a partially carbonation region or carbonation transition zone [20,21]. There are growing concerns over the use of phenolphthalein, as it is regarded to be possibly carcinogenic (IARC Group 2B) to humans. There is an increasing shift towards different indicators, such as thymolphthalein with a close-by pH transition range, which may also be used to assess carbonation depth. While phenolphthalein (pH transition ~8.2–10.0) is widely used to identify carbonation depth, thymolphthalein (pH transition ~9.3–10.5) may detect a marginally different carbonation depth due to the difference in its alkaline sensitivity. Thus, it is not clear whether carbonation depth using both indicators would be comparable between different studies or in comparison with previously established data and models in the literature based on phenolphthalein carbonation depth. This study compares the measured carbonation depths obtained using both these indicators on a wide range of cement combinations in cement mortars and concrete specimens exposed to both natural and accelerated CO_2 exposure.

2. Experimental program

2.1 Specimens and carbonation exposure details

EN 196-1 [22] standard cement mortar prisms (40 × 40 × 160 mm) were prepared at a water–cement ratio of 0.5 with 10 combinations of cement blends, previously reported in [23], were exposed to accelerated carbonation at 1% CO_2 and 57% RH. Concrete specimens of 100 mm x 100 mm x 500 mm were prepared with 7 cement combination, discussed in detail elsewhere [24]. Specimens were exposed to accelerated carbonation at 3% CO_2 and 57% RH. All specimens were cured for 28 days in a moist room and then preconditioned at 57% RH for 14 days before accelerated carbonation exposure. Natural carbonation was carried out in indoor sheltered conditions at 20°C and 57% relative humidity (RH) in controlled conditions for the entire duration of the exposure. More detailed descriptions of cement blends, concrete mixture and exposure duration can be found in [23,24].

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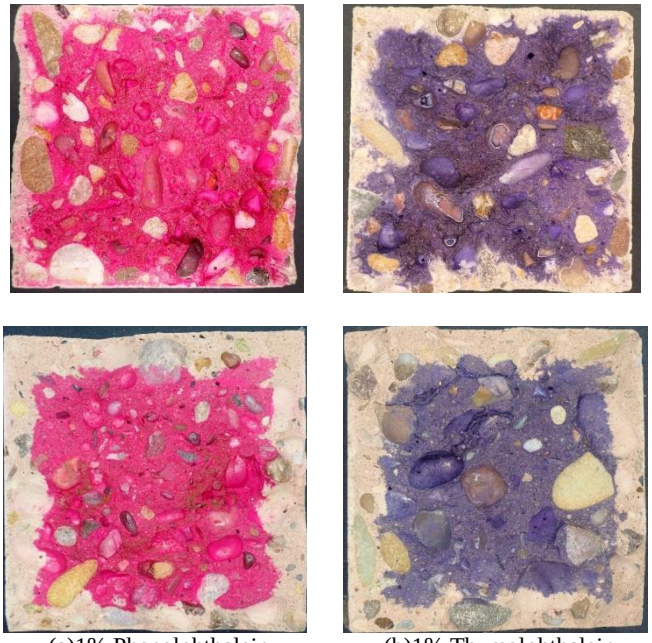
2.2 Carbonation depth testing procedure

After carbonation exposure, the specimen was split using a mechanical splitter and the freshly broken surfaces were sprayed with a fresh mist of 1% phenolphthalein indicator (prepared in 100 ml isopropyl alcohol) or 1% thymolphthalein (prepared in 100 ml isopropyl alcohol). Phenolphthalein appears colourless at lower pH and fuchsia at higher pH with a pH transition range of 8.2-10 and thymolphthalein appears colourless at lower pH and blue at higher pH with a pH transition range of 9.3-10.5 which is moderately above phenolphthalein pH transition range. The carbonation depth measurement was carried out after 30 min and within 2 hours in all instances as colour might fade over time specifically in the pH transition zone.

Figure 1 shows the carbonation depth obtained for concrete specimens after 28 days of accelerated carbonation exposure. Carbonation depth was measured at 4 points across each side of the specimen surface, i.e., an average of 16 data points at each exposure age. Although standards recommend the use of 1% phenolphthalein indicator prepared in 70% alcohol + 30% water. The presence of water was found to modify the carbonation depth observed due to leaching, etc, as stated in [18,24]. Hence, both indicator solutions were prepared 1% in 100 ml of isopropyl alcohol. Figure 1 presents the carbonation depth measured using both indicators in two concrete mixes with a difference in observed carbonation depth.



(a)1% Phenolphthalein indicator

(b)1% Thymolphthalein indicator

Figure 1 Carbonation depth obtained using two indicators on an OPC concrete (top) and low carbon concrete with 45% clinker replacement (bottom)

3. Results and discussion

Figure 2A and 2B present a comparison of measured carbonation depths in cement mortar and concrete obtained using phenolphthalein and thymolphthalein indicator, respectively. In Figure 2A, carbonation depth in cement mortar was assessed using both indicators after natural and accelerated carbonation exposure to assess the difference based on carbonation exposure condition between the indicators. There is a limited difference in the carbonation depth measured using both indicators, highlighting that both phenolphthalein and thymolphthalein offer a similar measurement of the carbonation-affected region in cement mortar and concrete. The carbonation depth obtained from both accelerated and natural carbonation is compared in Fig. 2A, so any difference in reaction mechanism in environmental exposure is also shown not to produce a significant shift in the measured carbonation depth, as the carbonation depth from two indicators remains closely aligned to the line of equality. This affirms the robustness of thymolphthalein as a potential alternative to the widely used phenolphthalein, similar to the previous observation in [25].

The results presented in Figure 2B on concrete specimens show a moderately higher scatter in measured carbonation depth compared to cement mortar, which is expected due to large aggregate fractions in concrete specimens, which inherently increase the scatter in the carbonation depth measurement at the near-surface region and also due to the presence of interfacial transition zones that are a weak link for carbonation to progress. However, trends are still aligned to confirm that both phenolphthalein and thymolphthalein offer comparable and reliable measurements of carbonation depth in concrete mixes with a wide range of clinker content from portland cement to 50% clinker replacement binder that was used here, from as reported in [24]. Although it should be noted that thymolphthalein showed a clearer carbonation-affected region in OPC than phenolphthalein due to slightly higher pH sensitivity at 10.5 pH, as shown in Figure 1. However, this difference is still within the scatter obtained in the measurement, which is typically based on 16 depth measurements at clearly visible maximum depth points parallel to the surface, except the instance of an isolated deeper point, indicating distortion due to air voids or microcracking [11,26]. Also, the similarity between the carbonation depth obtained using phenolphthalein and thymolphthalein indicates a narrower pH shift zone between the measurement pH ranges of these two indicators. Other indicators, such as Alizarin yellow R (pH transition ~10.1-12), may be preferred to trace carbonation with a completely different pH threshold to obtain multi-step pH-affected region assessment, if that is desired.

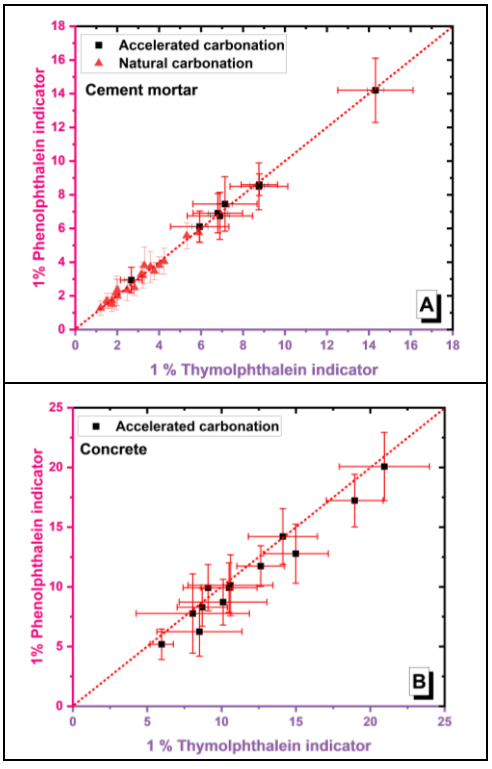


Figure 2 Comparison between phenolphthalein and thymolphthalein indicators in cement mortar (A) and concrete (B) specimens

Carbonation of cementitious materials is accompanied by a gradual reduction of pore solution alkalinity, and once the pH drops below a threshold (~9.0), the passivation of the embedded steel reinforcement becomes unstable, increasing corrosion risk. Therefore, using an indicator with a transition range marginally above this critical alkalinity level is essential to provide a conservative assessment of the carbonation front. The close similarity in pH sensitivity (max. pH transition range of 10-10.5) ensures that both phenolphthalein and thymolphthalein indicators would provide a conservative estimate of the carbonation front, thereby supporting safer assessments of reinforcement protection during durability assessment between various

concrete mixtures and also in condition assessment of concrete structures as per IS 516 [27,28].

4. Conclusion

This study highlights the influence of indicator choice on the measured carbonation depth of cement-based materials. A solution of 1% phenolphthalein and 1% thymolphthalein in 100 ml alcohol was found to provide similar carbonation depth and indicates a narrower alkaline zone between the measurement range of these two indicators. Measured carbonation depths were nearly similar across a range of cement blends with varying clinker content, exposure conditions and duration. This close agreement suggests that either indicator is suitable for routine field and laboratory assessments of carbonation-affected depth. Thymolphthalein indicator can be used as a suitable alternative for the estimation of carbonation depth for concrete carbonation evaluation due to the IARC Group 2B 'possibly carcinogenic' categorisation of phenolphthalein.

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