Review

Methods for measuring pH in concrete: A review

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ABSTRACT

pH is an important parameter to indicate the alkalinity level of concrete. The most severe concrete damages are caused or accompanied by dropping of the alkalinity level and consequently, decrease of the pH value of concrete. Therefore, it is crucial to measure the pH of concrete by an accurate and reliable method. This paper critically reviews the methods that have been developed for measuring the pH of fresh and hardened concrete. These methods are categorized in two broad divisions including destructive and non-destructive methods. The expression, ex-situ and in-situ methods are explained in detail as destructive methods, while the use of embedded potentiometric electrodes (mainly metal/metal oxide electrodes) and fibre optic sensors are evaluated as non-destructive methods. Also, advantages and drawbacks of each method are investigated and they are compared based on different technical and practical aspects. Despite the broad range of used methods for measuring the pH of concrete, there is no standardized test procedure. Because of the important role of pH with regard to durability of concrete structures, it is highly recommended that the required measures are taken to develop a specific standard test method for measuring the pH of concrete with a high level of accuracy, repeatability and reproducibility.

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Contents

1. Introduction

In general, pH is one of the most important parameters which has to be measured in many works of analytical chemistry research. Therefore, many researchers have worked to develop different electrochemical and non-electrochemical measurement techniques. Vonau and Guth summarized experimental methods for measuring pH values as shown in Fig. 1 [1]. The

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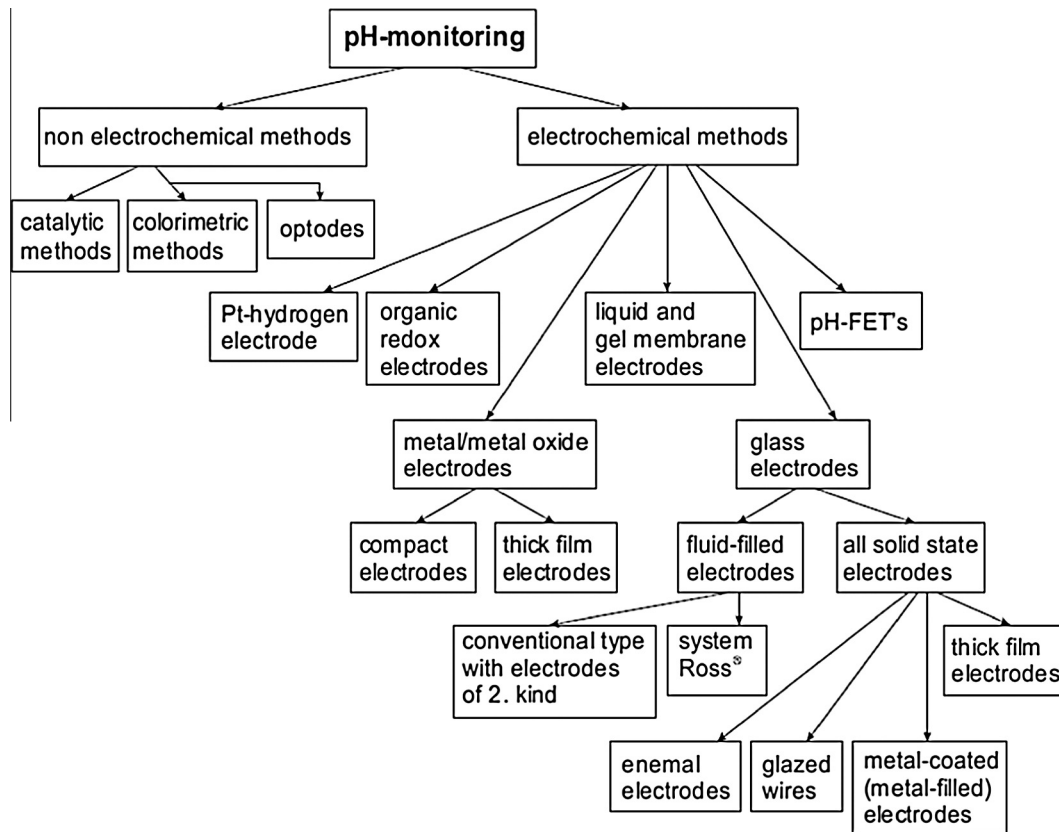 E-mail address: Nele.DeBelie@UGent.be (N. De Belie).

Fig. 1. A summary of experimental methods to measure pH values in analytical chemistry [1].

non-electrochemical methods were introduced earlier so that for example, Arrhenius developed his method based on the catalytic measurements in 1889 [1]. Furthermore, colorimetric methods which were broadly used previously are based on the colour change of an organic acid-system and are currently used in the optodes for measuring pH values [1].

On the other hand, the most crucial deterioration mechanisms of reinforced concrete structures including corrosion, carbonation and acid attack are related to the level of alkalinity of concrete. The pH, which is defined as the negative logarithm of the concentration of active hydrogen ions, shows the level of alkalinity of concrete under different conditions. The pH of ordinary Portland cement concrete is usually between 12.5 and 13 [2], but it can decrease due to deterioration mechanisms such as chloride ingress, carbonation or acid attack [3]. Chloride ingress into concrete can result in a pH reduction due to the formation of hydrochloric acid. Furthermore, the carbonation process, in which calcium hydroxide in concrete is transformed into calcium carbonate, can reduce the pH of concrete to values less than 9 [4]. The initiation of corrosion of embedded rebars in concrete can occur for lower threshold chloride concentrations when the pH of the concrete decreases as shown in Fig. 2 [5]. This process can accelerate destabilization of the protective passivation layer on the rebars and initiate corrosion in reinforced concrete elements [3]. Fig. 2 shows that a pH drop of concrete to values less than 11 in the vicinity of the rebars can result in initiation of active corrosion in the presence of nearly zero ppm of chloride ions [5].

Therefore, it is very important to measure the pH of concrete and many researchers have developed different methods for this purpose in concrete engineering. This paper critically reviews available methods for studying pH of concrete at different stages.
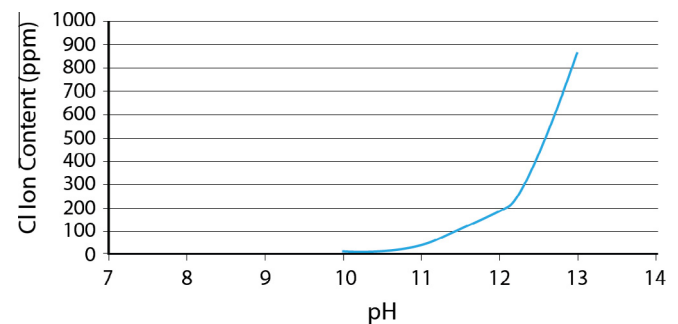

Fig. 2. Relation between the threshold chloride concentration and the pH of concrete for initiation of corrosion [5].

2. pH measurement methods for fresh concrete

Although most research has focused on the pH of hardened concrete, some researchers have evaluated pH variation of fresh concrete within the first hours after mixing which is usually around 13 and more for normal concrete with ordinary Portland cement (OPC) [2,6]. This can imply less importance of pH fluctuations of fresh concrete which has normally more predictable and almost constant behaviour compared to pH variations of the hardened concrete particularly under long-term deteriorations during the service life of the concrete structures. The pH of the fresh concrete can be estimated by direct applying the pH strips into the fresh mixture. However, this method is not reliable enough and might be useful only for rough estimation of the pH value of fresh concrete. Another method consists of directly inserting a low-alkali-error glass pH electrode which is the most common pH sensor on the market. However, this is not recommended due to the fragility

Table 1
Measured ion concentration and pH of pore solution of fresh paste and mortar acquired with the vacuum filtration method.

Time (h)	pH and ion concentration of cement paste (mmol/l) [6]						
	Na	K	Ca	Si	S	OH (free)	pH
1	76	395	21	0.11	168	170	13.2
2	77	404	21	0.13	175	160	13.2
4	78	401	21	0.13	176	160	13.2
6	83	408	19	0.17	180	160	13.2
Ion concentration of cement paste (mmol/l) after 2 h of hydration at 60 °C [12]							
Paste	47	296	29.4	0.05	185	160	–
Mortar	30	234	25.5	0.07	142	140	–

of these electrodes, which are usually expensive, and due to the negative influence of residual cement paste on the long-term functionality of the electrode. According to the published literature, a common method for determining the pH of fresh concrete is extracting the concrete pore solution and then measuring the pH value of the solution by using a pH electrode or by hydroxide titration against acids [6–12]. The most practised method of extracting pore solution of fresh concrete is pressure filtration [7,8]. Furthermore, Larbi et al. extracted pore solution of fresh concrete for further chemical analysis, including pH measurements, by filtration under vacuum [9,10]. They measured hydroxide concentration by titration with HNO₃. The vacuum filtration method was also used by other researchers for obtaining concrete pore solution at early ages up to 6 h [6,11,12]. Table 1 summarizes some of their results of ion concentration analysis. The first section of Table 1 shows no significant changes in concentrations of different ions as well as the pH of the Portland cement (type I) paste with water to cement ratio of 0.4. Moreover, it can be seen that the extracted concrete pore solution is dominated by hydroxide, potassium, sodium, calcium and sulphur during the first hour due to the fast dissolution of the alkali sulphates of the cement and the presence of the calcium sulphate phases [11]. After that, these concentrations remain almost constant due to the consumption of calcium sulphate phases and the formation of portlandite on them [6]. Furthermore, Leemann et al. showed that there is no remarkable difference between concentrations of hydroxide and other ions of cement paste and mortar after two hours of hydration at 60 °C, as can be seen in the second section of Table 1 [12]. However, the ion concentration of the paste is slightly higher compared to the mortar which can be attributed to a lower water to cement ratio of the cement paste (0.31) in comparison with the mortar (0.47).

Furthermore, Oertel et al. acquired pore solution of ultra-high performance concrete by a two-step centrifugation (5 min at 5000 rpm and 90 min at 200 rpm) and measured the pH value of the concrete pore solution with an electrode [13].

3. pH measurement methods for hardened concrete

Available methods for measuring the pH of hardened concrete have been categorized in different ways. However, the authors prefer to divide them into two main categories of destructive and non-destructive methods. The three most widely used destructive methods including the expression method, the in-situ leaching and the ex-situ leaching technique as well as two more developed non-destructive methods including embedded potentiometric electrodes and optic fibre sensors are explained in detail in the following sections.

3.1. Destructive methods

3.1.1. Expression method

There is a general agreement in concrete engineering that the extraction of the pore solution of small pieces of hardened concrete

under hydraulic pressure is the most common technique for acquiring pore solution for further analysis including pH measurements. According to Taylor [14], Longuet reported the first results of using this method for extracting pore solution from Portland and slag cement pastes with water to cement ratio of 0.5 after a curing period of maximum two years [15]. He used 343 MPa as the maximum pressure for extracting the pore solution. However, Barneyback and Diamond developed this technique for acquiring pore solution from mortar by applying pressures up to 550 MPa [16]. Fig. 3 shows the isometric half-section of a pore fluid expression die according to Barneyback and Diamond.

In principal, the pore fluid expression device consists of a hollow steel cylinder in which concrete samples are located, a steel piston which is located on the top of the concrete sample inside the hollow steel cylinder and a steel base plate which has few drainage channels for collecting the extracted concrete pore solution. In terms of pH measurement after extracting the concrete pore solution, researchers reported pH values using a commercial pH electrode or determining hydroxide ion concentrations which can be used for calculating the pH.

Furthermore, although different researchers have used devices with almost similar geometry for extracting the concrete pore solution, other test conditions such as maximum load, loading regime, preconditioning of the samples were different. Table 2 presents different conditions which were used by researchers for performing the expression method. It can be seen that there is no standardized test procedure for measuring the pH by using the expression method and different conditions were applied in these works so that it is sometimes hard to compare different reported results. To clarify the influence of these parameters, some of the most dominant ones are discussed thoroughly in this section.

Different loading regimes have been applied for extracting the concrete pore solution since the development of this method. Duchesne and Berube compared three different pressure intervals (0–560, 0–200 and 200–560 MPa) and reported that the alkali concentrations of cement pastes (w/c: 0.5) at 7 and 28 days are not affected by the applied pressure [22]. This is consistent with the results which were reported by Cyr et al. [18]. Fig. 4 shows their results including concentrations of K, Na, Ca and Si ions for mortars (w/c: 0.5) at the age of 28 days.

Although three different maximum pressure loads (500, 750 and 1000 MPa) were applied on the samples, there is no
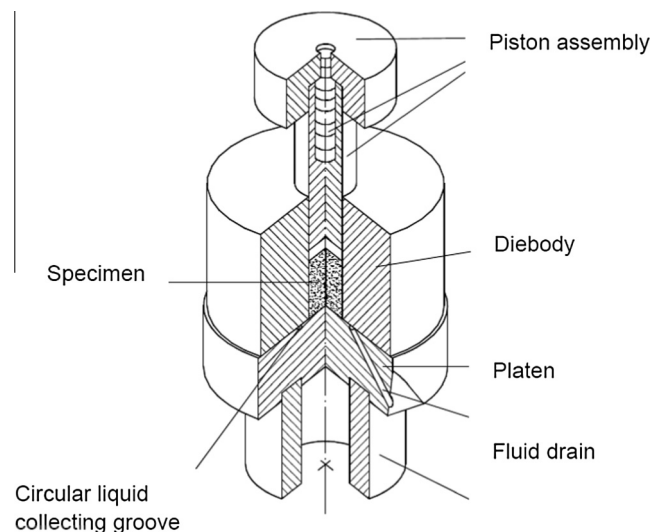

Fig. 3. Isometric half-section of pore fluid expression die according to Barneyback and Diamond [16].

Table 2
Details of procedures used by different researchers to extract concrete pore solution.

Maximum pressure (MPa)	pH or OH titration	Material[a]	Ref.
530	Electrode	P/M	Leemann et al. [12]
250	Electrode	P	Deschner et al. [2,17]
1000	Electrode	M	Cyr et al. [18]
550	OH titration against 0.01 N HCl	C	Haque and Kayyali [19]
343	OH titration and electrode	P	Tritthart [20]
375	Electrode	C[b]	Sagues et al. [21]
560	N.A.[a]	P/M	Duchesne and Berube [22]
500	Electrode	C/M	Räsänen and Penttala [23]
530	Electrode	P	Lothenbach et al. [6,11]
550	OH titration	P/M	Barneyback and Diamond [16]
650	Electrode	M	Li et al. [24]
550	OH titration against H$_2$SO$_4$ (0.05 N)	P	Shehata et al. [25]
550	OH titration against 0.01 N HCl	P	Kayyali and Haque [26]
375	Titration	P	Page and Vennesland [27]
200	Electrode	C	Li et al. [28]
343	OH titration	P	Longuet [15]

[a] N.A.: not available, P: Paste, M: Mortar, C: Concrete.
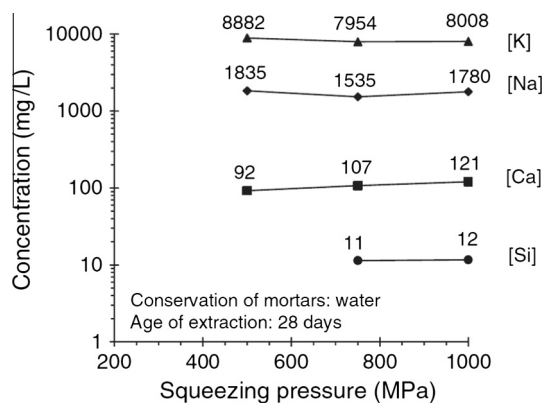[b] After removing coarse aggregates.

Fig. 4. Effect of maximum applied pressure on ion concentration in extracted pore solution of mortars (w/c: 0.5) at age of 28 days [18].

remarkable variation in the measured concentrations of ions. However, the maximum applied pressure can affect the amount of the extracted pore solution. Cyr et al. reported 1.4, 4.9 and 7.3 g extracted pore solution after applying 500, 750 and 1000 MPa, respectively [18]. Moreover, they concluded that the minimum applied pressure should be more than 300 MPa for extracting the pore solution.

It can be seen from Table 2 that many researchers have used the expression method for paste and mortar. According to Duchesne and Berube [22], the alkali concentration and pH of extracted pore solutions were not affected significantly by the presence of aggregates which is consistent with what was reported by Leemann et al. [12]. However, this statement cannot be extended to all types of aggregates including reactive aggregates which may change alkali concentration of the pore solution due to alkali-aggregate reactions (AAR).

In general, pH values of hardened concrete increase gradually over time [6,12,29]. Many researchers investigated the ion concentration and pH values of neat ordinary Portland cement (OPC) samples [16,17,29,30]. Fig. 5 shows the evolution of the alkali and hydroxide ions of OPC samples with water to cement ratio of 0.5 [2]. It should be noted that the hydroxide concentration was calculated based on the measured pH values by using a pH electrode which was calibrated against KOH solutions with known concentrations.

Evolution of the ion concentrations and pH of fresh OPC samples were discussed earlier in Table 1. After hardening and in the time frame between 8 h and one day, it can be seen that ion concentrations changed remarkably due to depletion of the calcium sulphates so that the pH value was increased from 13.1 at 8 h to 13.7 at one day [2]. The main reason for the increase of the pH value within this period is the release of more alkalis followed by further dissolution of tricalcium aluminate phases which react with available sulphate and result in precipitation of ettringite or AFm [31–33]. After one day, the hydroxide concentration and pH values are slightly increased over time due to continued hydration of the clinker phases which results in releasing almost constant amount of alkalis in the solution [2].

Wan et al. reported the pH of cement paste after 3, 7 and 14 days for samples with water to cement ratios of 0.5 and 0.7 using a digital pH metre [30]. They concluded that there was no significant difference between the pH of the mixtures with w/c of 0.5 and 0.7 at the age of 7 days. This is consistent with the pH values which were reported by Larbi et al. for neat OPC pastes with w/c of 0.40, 0.45 and 0.56 from 10 min to 28 days [10].

Broad acceptance of the expression method amongst most of the concrete experts has resulted in using this method for studying effects of chemical and mineral additives on the chemistry of the pore solution [2,6,7,9,10,12,17,25,34]. Although many researchers believe that the expression method is the only reliable technique for acquiring concrete pore solution and to perform ion concentration analysis and pH measurements [6,9–11,19,26,27,30,34,35], some researchers emphasized its limitations [21,23,28,36]. According to Li et al. [28], two crucial limitations of the expression method are the necessity of prior water saturation of the samples as well as the impracticality of performing this method for concrete specimens with low water to binder ratios, such as high-strength concrete, due to inadequate acquired pore solution even under high pressure. Furthermore, Räsänen and Penttala reported that this method is not appropriate for determining the
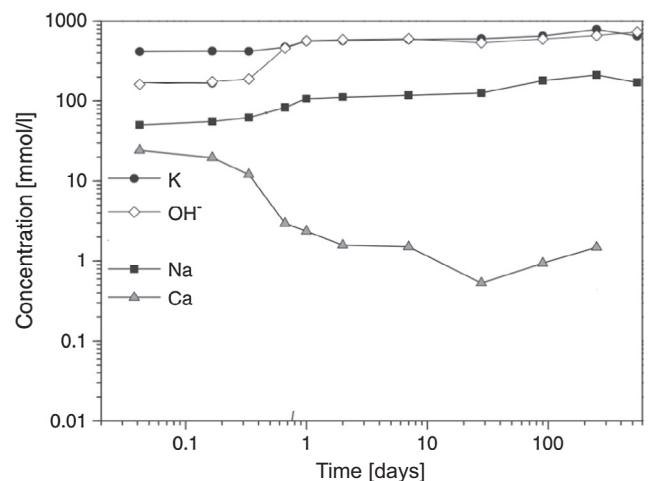

Fig. 5. Evolution of the alkali and hydroxide ions of the OPC samples with water to cement ratio of 0.5 [2].

accurate time to cover concrete slabs with adhesives, which need to be applied at a specific pH values of the concrete floor, because using special high-pressure devices is almost impractical in construction sites [23]. For measuring the pH of concrete surfaces prior to application of coatings, the standard method described in ASTM D4262-05 [37] and ASTM F710-05 [38] (see Section 3.1.2) is recommended.

In addition, Chatterji discussed that one of the test method's assumptions may lead to inaccuracy, namely that all significant materials pass through a liquid phase which is extracted under pressure [36]. He mainly considered very low concentrations of calcium ions in the extracted pore solution versus the important role of the calcium ion in the alkali-silica reaction and concluded that the expression method "may give a deceptive picture with regard to the rate of transport of the ions concerned". Therefore, he suggested that "most of the ions are transported through overlapping water layers adjacent to and strongly bound to solid particles". However, this suggestion may result in acquiring higher concentrations of the ions by applying higher pressure on concrete samples which is inconsistent with the reported results of the ion concentration of the extracted pore solution at different hydraulic pressures [18,22]. Furthermore, Duchesne and Berube showed that the very low concentration of the calcium ion in particular in the concrete pore solution is expected based on calculation of the calcium ion concentration considering the concentration of alkali ions and the solubility of calcium hydroxide [22].

Moreover, the published results of several comprehensive studies showed that there are reasonable relations between concentrations of different ions (including hydroxide) of the extracted concrete pore solution with the calculated values based on thermodynamic models [2,6,29]. However, some parts of ions might be bound for example, in the C–S–H and are not present in the concrete pore solution. Therefore, the authors believe that further research is needed for determining the significance of this phenomenon and its effect on the pH value and hydroxide concentration. To sum up, it can be concluded that there are some limitations and concerns about the expression method, however, it is the most reliable available test procedure for acquiring data on ion concentrations and pH of concrete and therefore the authors believe it needs to be standardized.

3.1.2. In-situ leaching method

Sagues et al. developed an in-situ leaching method for measuring the pH in concrete [21]. Fig. 6 shows a schematic view of the test setup, based on drilling a hole with a diameter of approximately 5 mm and a depth of 25 mm in the concrete sample. After drilling, the concrete powder was removed and 0.4 ml of deionized water was pipetted into the hole.
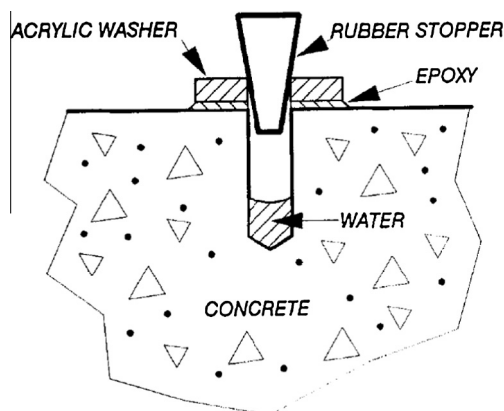

Fig. 6. Scheme of the test setup of the in-situ leaching method [21].

The pH measurement was done by using a MI-405 glass pH micro electrode and an Ag/AgCl electrode was used as the reference electrode. The potential difference between working and reference electrode was measured and converted to pH values using a linear potential interpolation/extrapolation from the calibration points. Fig. 7 shows the pH evolution of different concrete mixes versus time. The pH values which were measured a few hours after first injection of water into the hole (day 0) were between 12.4 and 12.8. Then, the pH increased quickly and reached values between 12.8 and 13.4 after two weeks to one month. According to Sagues et al. [21], the average of the last 30 days of testing (apparent terminal pH value) for mixes A and F (100% OPC) and E (with the highest cement replacement ratio of 30%FA + 8%SF) was in the range of 12.8–12.9. The apparent pH value for other mixes (20% and 30% FA replacement and 20%FA + 8%SF replacement) was approximately 13.1. Therefore, they concluded that in-situ leaching is a reliable method for measuring pH values [21]. Li et al. used the in-situ leaching method for measuring the pH and nitrite concentration of the pore solution of mortar and concrete with and without a corrosion inhibitor [24].

The corrosion inhibitor was a commercial product based on calcium nitrite (max 30% weight) and calcium nitrate (max 5% weight). They drilled three holes with a diameter of 3 and 5 mm and a depth of 30 mm in the surface of each mortar and concrete specimen, respectively. The pH of the solution inside the holes was measured by using an Ag/AgCl reference electrode and an MI-405 micro-pH glass electrode which was calibrated at 21 °C. Fig. 8 shows the pH evolution in concrete and mortar. It should be noted that the first measurement was done approximately four hours after injecting distilled water into the holes which was set as day 0 in Fig. 8.

The pH of mortar and concrete without corrosion inhibitor (MCTR and CCTR) was approximately 13.1 and 12.95 at day 0, respectively. After one week, the pH of the solution of the mortar and concrete samples reached to about 13.3 and 13.4, respectively, which seemed a near-equilibrium value between the solution in the hole and the surrounding concrete and the rate of pH improvement was almost constant after that [24]. Furthermore, the pH values of concrete and mortar samples containing corrosion inhibitor (MDCI and CDCI) was approximately 0.3 and 0.2 pH units lower than the corresponding values of the concrete and mortar samples without corrosion inhibitor, respectively. In general, the pH measurements of the mortar samples showed a similar trend compared to the pH values of the concrete samples. This similarity between pH of mortar and concrete which was reported by Li et al. [24] using in-situ leaching is in agreement with the results which were reported by Leemann et al. [12] and Duchesne and Berube [22]. In general, the in-situ leaching method is an easier and cheaper method in comparison with the expression method which requires a special steel die and the application of high pressures. Also, there is no risk of failure due to lack of obtained pore solution as it can happen when using the expression method. However, the expression method is widely accepted as a reference method and it is recommended to compare each new test method with the expression method for showing its conformity. Li et al. compared results of their pH measurements by using the in-situ leaching method with the expression method as shown in Fig. 9 [24]. The pH value of the expressed pore solution (average of two tests) was very close to the pH value which was measured by in-situ leaching (average of four holes) for the mortar samples without corrosion inhibitor. Furthermore, the reported difference between pH of the mortar samples containing corrosion inhibitor obtained by these two methods was around 0.1 pH unit. These results are consistent with the results which were reported by Sagues et al. [21].

However, there are some limitations concerning the in-situ leaching method. First, this method needs pre-conditioning of the
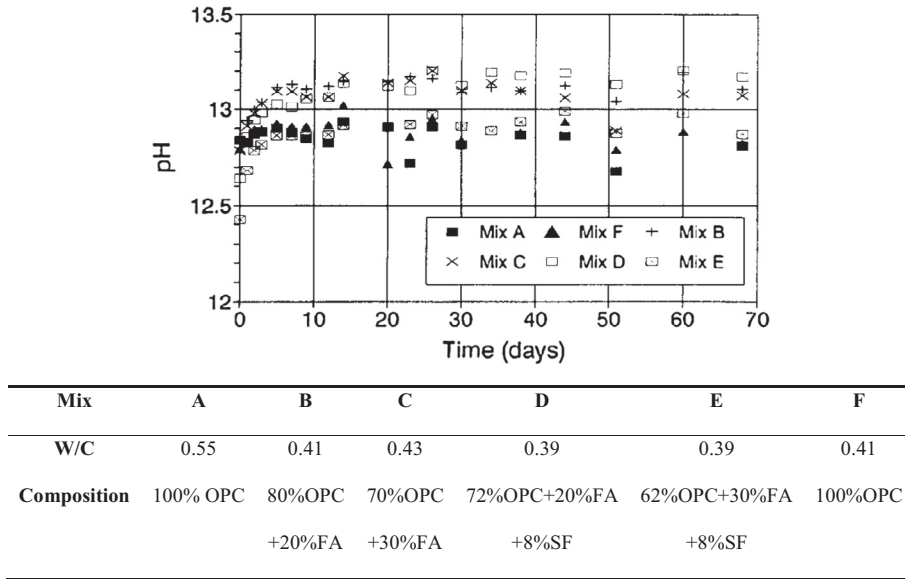
Mix	A	B	C	D	E	F
W/C	0.55	0.41	0.43	0.39	0.39	0.41
Composition	100% OPC	80%OPC +20%FA	70%OPC +30%FA	72%OPC+20%FA +8%SF	62%OPC+30%FA +8%SF	100%OPC

Fig. 7. pH evolution of different concrete mixes measured by in-situ leaching versus time [21].

**(a) MCTR: control samples,
MDCI: samples with corrosion inhibitor**

**(b) CCTR: control samples,
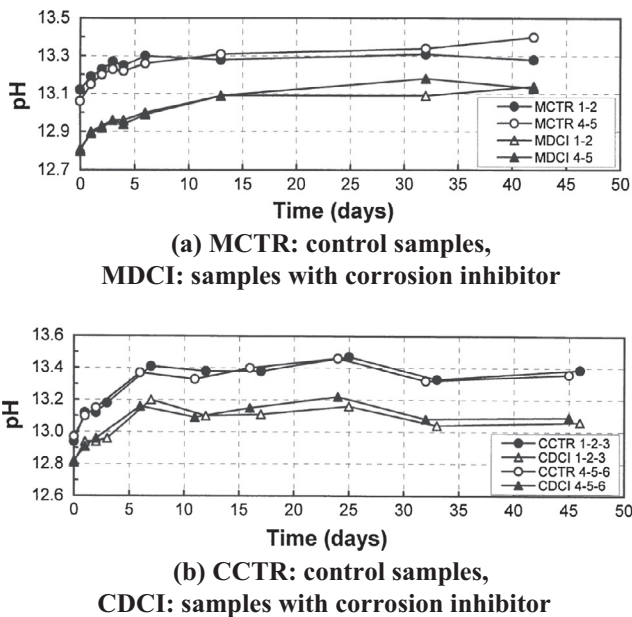CDCI: samples with corrosion inhibitor**

Fig. 8. pH evolution in (a) mortar and (b) concrete with and without corrosion inhibitor [24].
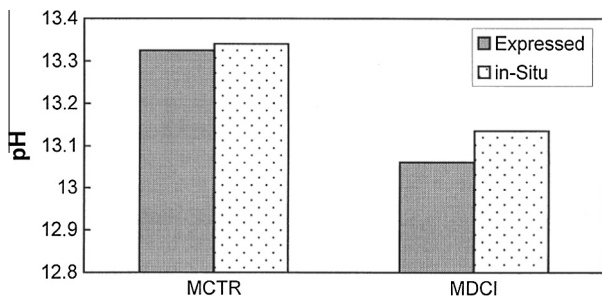

Fig. 9. Comparison between pH values obtained by the expression and in-situ leaching method for mortar with (MDCI) and without (MCTR) corrosion inhibitor [24].

samples by saturation before the measurements can start, which is a similar limitation as what was mentioned for the expression method.

Furthermore, the in-situ leaching method is time-consuming due to the required time for reaching equilibrium between the water added inside the hole and the surrounding concrete pore solution. This time span varies depending on the amount of water and the dimensions of the hole up to one week [21,24]. In addition, there is always a risk of carbonation of the water inside the hole which is in direct contact with available CO_2 in the air [21]. It should be noted that there is no standardized test procedure for performing the in-situ leaching method for concrete and consequently, test parameters such as the size of the hole and the amount of water inside the hole are still arbitrary. However, Sagues et al. developed a model based on inward diffusional transport of the pH-determining species in the surrounding concrete pore solution and concluded that the cavity size, cavity water content and exposure to atmospheric CO_2 should be minimized to measure the pH value of the water inside the hole which is in equilibrium with the surrounding concrete pore solution [21].

Other in-situ leaching methods, which are in fact methods to be considered merely as non-destructive methods, are the ones described in ASTM D4262-05 [37] and ASTM F710-05 [38]. The standardized method described in ASTM D4262-05 is used to determine the alkalinity of chemically cleaned and etched concrete surfaces prior to coating. To make sure that residual chemicals were removed by water rinsing, the pH of the water used for rinsing is determined by a pH test paper, a pH pencil or a pH metre. In ASTM F710-05, the pH of concrete surfaces is determined by placing several drops of distilled water on the surface in which a pH paper is dipped after about 60 s. However, the latter standardized method was criticized by Grubb et al. [39] and Kakade [40]. They mentioned that by using this method not the pH of the concrete surface but the pH of the distilled water is measured. They proposed an alternative method, which should merely be classified as a kind of non-destructive ex-situ leaching method, where powder is gathered from the concrete surface by hand-sanding a pre-defined area with 50-grit sandpaper. Afterwards the collected powder should be used for pH measurements with pH strips.

3.1.3. Ex-situ leaching method

Another method for measuring the pH of concrete is based on using a given amount of powder suspension of a ground concrete sample with a solvent after their equilibration which is known as the ex-situ leaching method [23,28,35].

This is a frequently used method for measuring the pH of soil [41] and ASTM D4972 [42] "Standard Test method for pH of Soils" recommends a method based on using this technique for soil. In terms of concrete, a similar method is routinely used for determining the free chloride content [19,43,44]. Table 3 presents different conditions which were used by different researchers for using the ex-situ leaching method for pH determination [45]. It can be seen that there is no standardized or even common test procedure for measuring the pH of the concrete by using the ex-situ leaching method. Only for measuring pH of limestone, quicklime and hydrated lime, a standard method, based on ex-situ leaching, exists as described in ASTM C25 [46]. For example, for cementitious materials, the concrete powder to water ratio varied in a broad range between 1/0.67 and 1/50. Another parameter is the leaching time which varied between 3 min and even up to 30 days whereas different stirring times were applied as well. However, Grubb et al. [39] reported that factors such as particle size, amount of sample and soaking time only have a minor influence, while dilution ratio and temperature seem to be non-negligible factors. Acceptable reliability levels of the ex-situ leaching method were reported by comparing it with the expression method [23,28,45]. Fig. 10 shows results which were reported by Räsänen and Penttala [23] when comparing the pH values of normal strength concrete measured by the ex-situ leaching technique (named "suspension") and the expression method (named "extracted"). The water to cement ratio was 0.75 in this study and the numbers after the name of the method (0.5 and 0.8) represent the portions of concrete powder in the total weight of the mixtures.

According to [23], the difference between the results of these two methods was 0.04 and 0.14 pH units on average for powder to suspension ratios of 0.5 and 0.8, respectively. Although Fig. 10(a) shows that the difference between the methods is very small, Fig. 10(b) demonstrates broader scattering of results for normal strength concrete with OPC type II 42.5R (NSC). However, Räsänen and Penttala recommended the ex-situ leaching method as a reliable method for measuring the pH of concrete [23]. Furthermore, Li et al. measured pH values and hydroxide ion concentrations of concrete by using the ex-situ leaching method and reported acceptable conformity with results obtained by the concrete solution expression method as the reference method [28]. In the meantime, they compared their results using ex-situ leaching with results which were reported by other researchers using the expression method as shown in Fig. 11. Due to the use of different cements with varying alkali contents, the hydroxide ion concentrations were compared versus equivalent Na_2O percentages. Li et al. concluded that there is no evidence that the ex-situ leaching method overestimates the hydroxide ion concentration of the concrete pore solution [28].

Table 3
Different conditions which were used by different researchers for performing the ex-situ leaching method [45].

| No.	Equipment	Material	Curing or pre-conditioning	Solid/water	Leaching time	Filtration	pH measurement	Ref.
1	No special	Concrete		1:3.5 to 1:4	24 h	Yes	Electrode	Haque and Kayyali [19]
2	No special	Concrete	De-moulded at 24 h and cured in distilled water for 7 days	1:2	1 h	Yes	Electrode	Arya et al. [43]
3	No special	Paste	Sealed for 35 days	1:2, 1:5 and 1:50	1, 6 or 24 h (different stirring times)	Yes	OH titration	Arya and Newman [44]
4	Special device with N_2 inlet	Mortar	100% RH	1:0.67	30 s stirring, resting for 24 h and stirring again	Yes	OH titration	Alonso et al. [45]
5	No special	Mortar and concrete	In plastic at 45% RH at 20 °C	1:1.5 to 1:0.67	15 min	No	Electrode	Räsänen and Penttala [23]
6	No special	Concrete	–	1:0.7–1:1–1:2–1:4	1, 3, 10, 30 days	No	OH titration	Li et al. [28]
7	(CO_2 protection)	Paste, mortar and concrete	100% RH	1:1	3 min (continuously stirring)	No	Electrode	Thangavel and Rengaswamy [47]
8	In N_2	Paste and mortar	–	1:9	Slow stirring. Monitoring pH value till stabilization	No	Electrode	Pavlik [48]
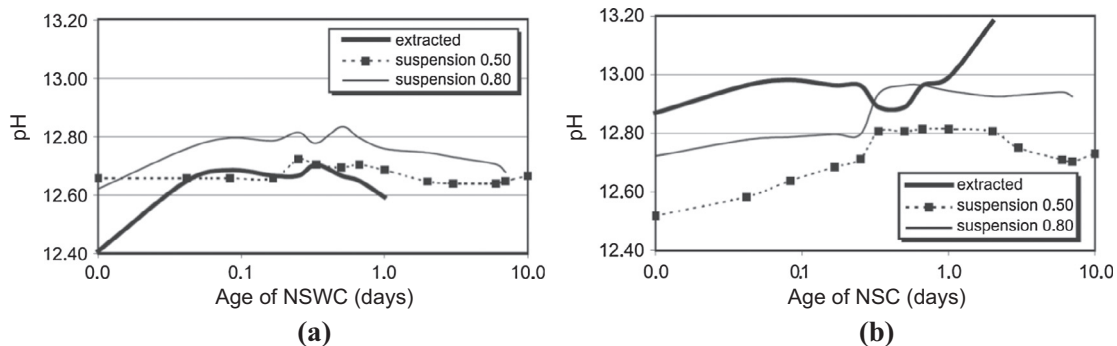
Fig. 10. Comparison between pH values of normal strength concrete with (a) CEM I 52.5 (NSWC) and (b) CEM II 42.5R (NSC) measured by the ex-situ leaching (suspension) and expression (extracted) method (numbers after the name of the method (0.5 and 0.8) are portions of concrete powder in the total weight of the suspension) [23].
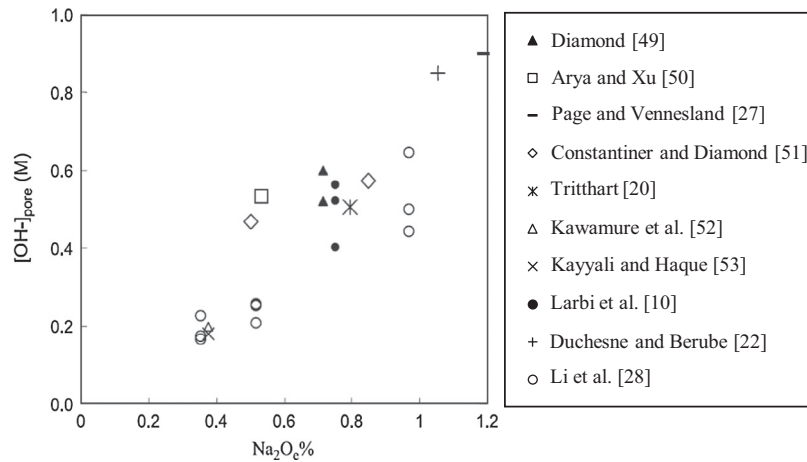
Fig. 11. Comparison between hydroxide concentrations of concrete mixes measured by ex-situ leaching [28] and the expression method at different Na$_2$O$_e$ percentages [28].

On the other hand, Haque and Kayyali reported that the average hydroxide ion concentration measured by the powder suspension (ex-situ leaching) method was about 13 times more than its average value measured by the expression method with a broad fluctuation of 7.4–27 times [19]. They concluded that this is maybe because of further hydration of unhydrated cement particles after sampling which resulted in an unrealistic increase of the hydroxide ion concentration. In contrast with [19], Sagues et al. reported that ex-situ leaching underestimates hydroxide ion concentration likely because of the dilution effect [21]. Such controversy can be expected with regard to several crucial parameters which affect the results of the in ex-situ leaching method. The main factors are the solvent/solid ratio, the fineness of the concrete powder, the solution filtration, the extraction time, the stirring time and the temperature of the powder and solvent [23,28,35]. Like other methods, the ex-situ leaching method has some advantages and drawbacks. This is a very simple, fast and cheap method which does not need any complicated setup like embedded metal/metal oxide electrodes or any particular equipment like the expression method (special steel die and high capacity hydraulic machine). Basically, this method is more common than the in-situ leaching method and consequently, well-developed in concrete engineering for measuring chloride concentration compared to pH measurements. In terms of pre-conditioning which is a principle in in-situ leaching for the samples and usually required in the expression method for samples of old concrete and high-strength concrete, the ex-situ leaching method does not require such pre-treatments. Furthermore, this method does not need long stabilizing time for obtaining equilibrium in the solution and surrounding concrete in contrast with the in-situ leaching method. On the other hand, possible dilution and carbonation during the measurement can result in significant deviations. Another crucial issue is the difference between dissolution rates of different hydrated phases and alkalis including potassium, sodium and calcium ions. In general, the ex-situ leaching method is still not a standardized method and there is a conflict between published results so that according to the authors further work is needed to finalize the procedure, including practical aspects and critical parameters such as solvent/solid ratio, fineness of concrete powder, solution filtration, extraction time, stirring time and temperature of powder and solvent.

3.2. Non-destructive methods

Although extraction of pore solution is the most common method for measuring the pH of concrete, this is a time-consuming and destructive procedure, and researchers have attempted to develop non-destructive, in-situ methods using embedded sensors so that it is possible to measure pH values based on continuous real-time monitoring. In general, different sensors have been developed for replacing common glass electrodes which are not appropriate for miniaturizing and robust designing. These novel sensors can be categorized in different types such as ion-sensitive-field-effect transistor (iSFET) [49,50], fibre optic [51,52], hydrogel film [53] and solid-state pH sensors [54,55]. This section critically reviews the use of embedded metal/metal oxide potentiometric electrodes and fibre optic sensors since those have been used for pH measurements in concrete.

3.2.1. Embedded potentiometric electrodes

The glass membrane electrode is the electrode which is most commonly used for measuring the pH of solutions, due to its superior performance with regard to slope, selectivity, detection limit and insensitivity versus redox systems [1]. However, these electrodes are not suitable to be embedded in concrete for in-situ pH measurements of hardened concrete because of the lack of long-term stability, alkaline error and fragility [56,57]. Therefore, some researchers have worked to develop potentiometric methods using embedded sensors [58,59] and electrochemical impedance spectroscopy [60] for measuring pH values or pH dependent processes in structural materials. In particular, metal/metal oxide electrodes have been considered suitable for overcoming the mentioned barriers due to their remarkable stability and robustness, prompt response and their flexibility in size for making micro to macro pH sensors. The theoretical background of using the metal oxide electrodes for measuring pH, relies on reversibility of their redox reaction in aqueous solutions. In general, different researchers developed different metal oxide electrodes including oxides of iridium, platinum, palladium, rhodium, titanium, tin, aluminium and rhenium [61–64]. However, iridium oxide electrodes are the most developed electrodes amongst them. This can be attributed to their higher stability in a broad pH range, higher resolution, less stabilizing time and faster response even in difficult conditions such as high temperatures, high pressure and aggressive media [65]. In the meantime, Huang et al. reported their results on developing a flexible pH sensor using an iridium oxide sensing film [66]. An iridium/iridium oxide (Ir/IrO$_2$) electrode can be prepared by using different methods such as electrochemical oxidation [67], electrochemical deposition [68], sputtering coating [69] and thermal oxidation in carbonate [56]. Kinoshita and Madou described the theoretical principle of functionality of an Ir/IrO$_2$ electrode in Eqs. (1) and (2) [69]. Therefore, it can be concluded that the equilibrium potential of an Ir/IrO$_2$ electrode relies only on the pH of the solution at a specific temperature so that it is possible to calculate

the pH of the solution by measuring the potential of the Ir/IrO$_2$ sensor.

$$IrO_2 + H^+ + e^- \rightarrow \frac{1}{2}Ir_2O_3 + \frac{1}{2}H_2O \tag{1}$$
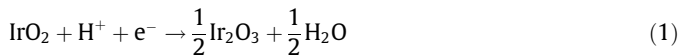
$$E = E^0 + \frac{RT}{F}\ln[H^+] = E^0 - 0.0592\,pH \quad (V\ vs\ SHE, 298\ K) \tag{2}$$

E: measured potential, E^0: standard electrode potential, R: universal gas constant,
T: absolute temperature, F: Faraday constant. SHE: standard hydrogen electrode.

Du et al. [56] used an iridium oxide electrode for measuring pH fluctuations at the interface of a reinforcing steel bar and mortar which was kept in a 3.5% NaCl solution over time up to 60 days (Fig. 12). The mortar was made with a water/cement and sand/cement ratio of 0.6 and 3, respectively. The results of their measurements of the local pH in the vicinity of a rebar inside concrete are shown in Fig. 13.
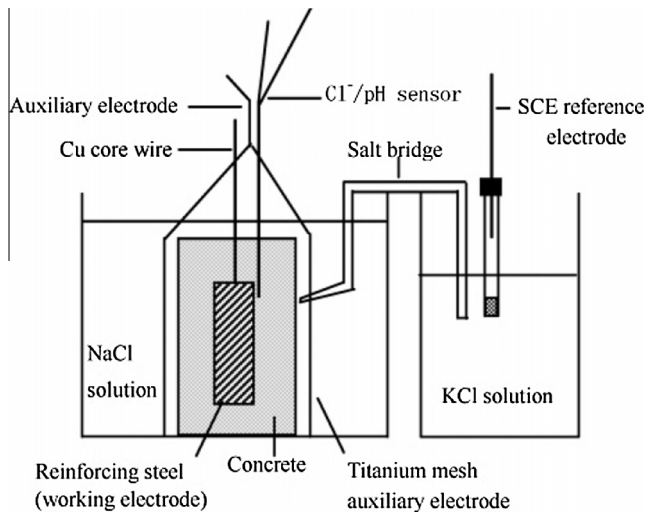

Fig. 12. Test setup for measuring pH fluctuations at the interface of a reinforcing steel bar and mortar in a solution of 3.5% NaCl [56].
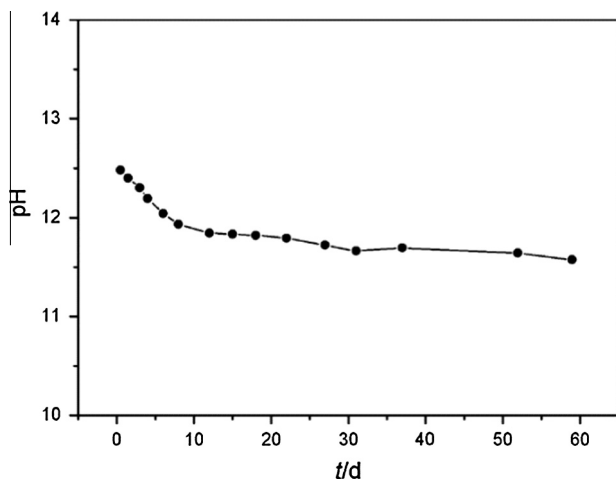

Fig. 13. pH values measured by Ir/IrO$_2$ electrode at the interface of the steel bar and concrete in a 3.5% NaCl solution over time (days) [56].

According to [56], the pH drop at the interface of the concrete and the rebar during the first days is due to diffusion of hydrogen and hydroxide ions which is attributed to the difference of their concentrations. This decreasing trend of the pH becomes significantly slower by further neutralization of the alkali environment of concrete by the formation of acid. Dong et al. developed a multifunctional sensor consisting of pH and chloride sensors as shown in Fig. 14 [70].

They embedded this multifunctional sensor in the concrete at a depth of approximately 10 mm and measured the pH variation at the interface between rebar and concrete while the sample was subjected to a cyclic exposure condition of 2 days immersing in 3.5% NaCl solution and 2 days of drying. The concrete mix proportion was 1:0.4:1.57:2.36 (ratios of cement: water: sand: coarse aggregate). The concrete samples with the embedded multifunctional sensor were cured at room temperature and 95% RH for 28 days before starting the potential measurements. Fig. 15 shows the pH fluctuations over a period of 250 days. As can be seen, first the pH value was around 13.2 and showed a slight decrease due to leaching of alkalis into the surrounding solution. However, the main pH drop was reported after 120 days due to a high carbonation degree.

By comparing the above mentioned works, it can be seen that different initial trends for pH variation were reported by [56,70] which may be mainly attributed to different test conditions. Du et al. [56] immersed samples in a 3.5% NaCl solution whereas Dong et al. [70] applied cycles of 2-day wetting and 2-day drying. Furthermore, they used different materials Du et al. [56] used mortar whereas Dong et al. [70] measured the pH of concrete samples. Although using this type of pH sensor seems advantageous, there are several concerns for using them. For example, the effect of changing some parameters such as the ionic strength of the concrete pore solution, concrete porosity, moisture content and temperature have not been clarified yet. Furthermore, these methods do not measure active ion concentration directly and their measurements are influenced by total ionic strength. Therefore, it is possible that the real pH in concrete is different from the measured pH. Another problem is the high pH value within concrete, while these methods are mainly developed for other applications such as in-vivo applications where the maximum applicable pH is lower than the pH of a concrete solution (around 13). Furthermore, there are several obstacles for developing embedded pH sensors in concrete. For example, they cannot be calibrated in situ over a long period of time and consequently, the values obtained may be measured by significant errors; or they can simply be broken inside the concrete element. Furthermore, the performance of the embedded electrodes does not seem reliable enough when the concrete is dry. In addition, it must be guaranteed that the sensor has a close contact to the pore solution in the concrete to measure pH changes.

3.2.2. Fibre optic sensors

Recently, a novel type of pH measuring sensors have been developed for concrete by using fibre optics [59,71–75]. Different methods are developed based on optical or spectroscopic characteristics including absorbance, reflectance, fluorescence and refractive index [76–78]. Furthermore, some researchers reported the feasibility of using sol–gel based optic fibre pH sensors for measuring pH in concrete [77–80]. In general, the required setup for measuring pH with fibre optic sensors consists of a light source, a coupler, a fibre switch, a spectrometer, a sensor and a computer as shown in Fig. 16 [81].

McPolin et al. reported a pH probe which was made by coating sol–gel, including a cresol-red indicator dye (pH range 8–13), onto the plastic clad silica fibre with a core diameter of 600 µm [82]. First, they investigated the accuracy of the sensor using a specific setup. Two holes with depth of 5 and 10 mm and diameter of
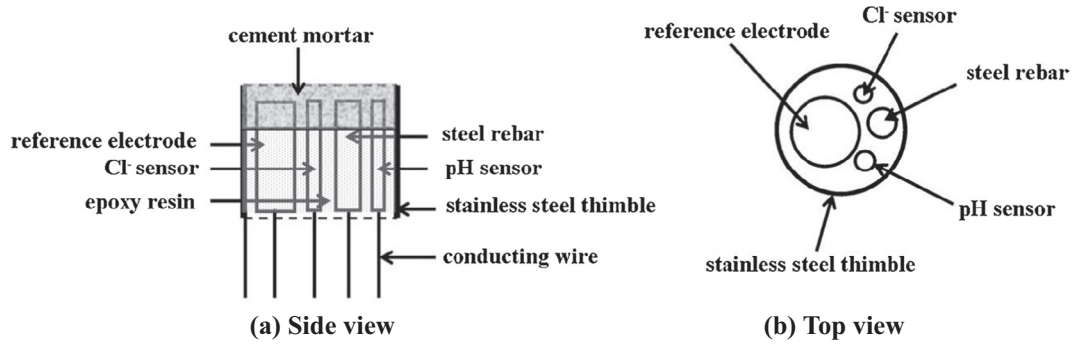
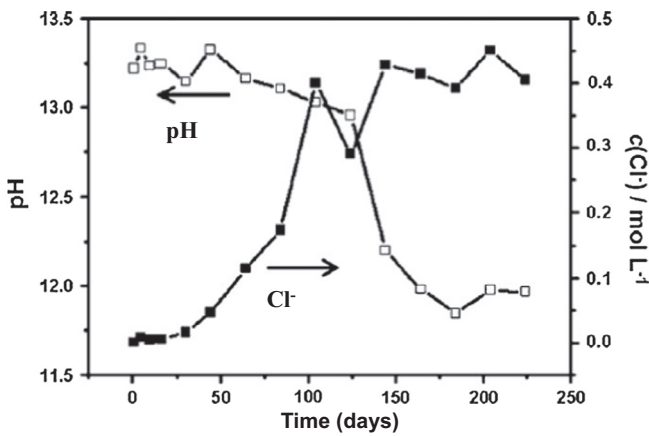**Fig. 14.** (a) Side view and (b) top view of multi-functional pH and chloride sensor [70].

Fig. 15. pH variation at the interface between rebar and concrete of samples subjected to cyclic immersion in 3.5% NaCl solution and drying [70].
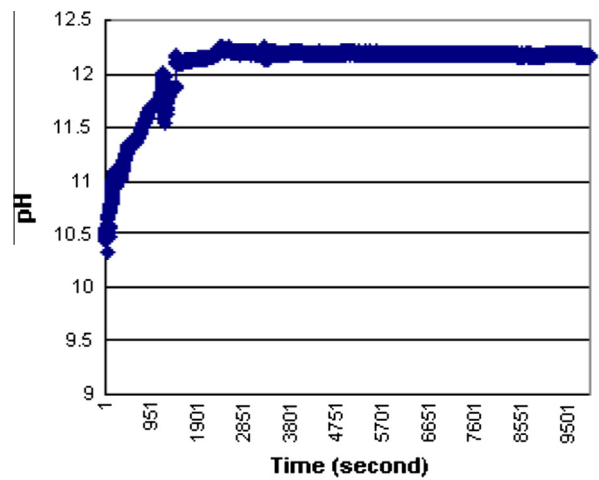

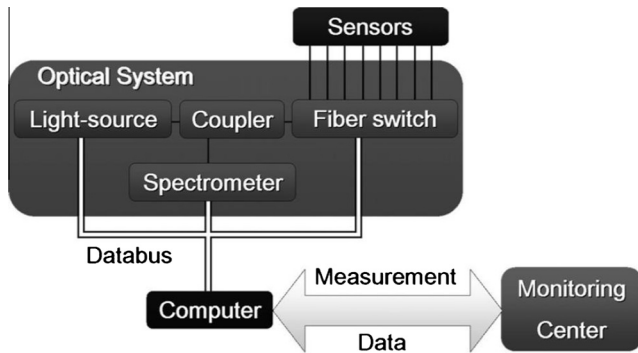**Fig. 17.** pH measurements in carbonated mortar by using a sol–gel based pH probe [82].

Fig. 16. Setup for measuring pH by using fibre optic sensors [81].

6 mm were drilled in a mortar sample (w/c: 0.42) which was exposed to unidirectional accelerated carbonation (5% CO_2, 55% RH and 20 °C). After filling the hole with water to a depth of 5 mm, the probe was inserted in the hole and the pH value was measured. Fig. 17 shows the results of the pH measurements for the hole with depth of 10 mm. It can be seen that the sol–gel probe needed more than half an hour to stabilize after insertion. Although the average depth of carbonation was 4 mm using the phenolphthalein solution (pH indicator in the range of 8.0–9.8), the measured pH value using the probe was around 12.2 for the hole with depth of 10 mm. This higher pH value can be attributed to leaching of alkalis from partly carbonated and uncarbonated areas into the water in the hole. After checking the functionality of the sensor in the cement mortar, they embedded the optic fibre

probe in the sample before casting and monitored pH fluctuations of a carbonated specimen until 18 months [82]. Instead of using phenolphthalein as pH indicator, as done in the previously mentioned study, Martin-del-Rio et al. [83] suggested the use of alizarin yellow R and indigo carmine to indicate the pH of concrete.

Khalil et al. reported their results on using meso-tetraarylporpholactone as an optical pH sensor in the pH range of the solution between 11.5 and 13.2 [84]. Habel and Krebber introduced their fibre optic pH sensor but it only worked in the pH range of 9–12 (Fig. 18) [85]. Srinivasan et al. used trinitrobenzene-sulfonic acid (TNBS) as the indicator that shows a change in optical properties in the pH range of 12–14 [73].

Azo-dye is also one of the pH indicators which has been used for monitoring pH by optical fibres. It is a weak acid which has two forms, protonated and deprotonated [81]. The colour of this material depends on the ratio of concentrations of its protonated and deprotonated forms. The deprotonated form has a bathochrome shift of absorption in comparison with the protonated one which causes a colour change from yellow to red. However, the ratio of concentrations of the protonated and deprotonated forms of the azo-dye is based on the pH of its surrounding material. Blumentritt et al. developed a set of five optical-fibre sensors by the use of azo-dye and calibrated the sensor by using KOH from pH of 10.40 [81]. While the absorption of these sensors was recorded every 30 s, the pH of the solution was gradually increased by adding KOH every five minutes until a pH of 12.24 was reached. However, the colour change of the azo-dye from yellow to red occurred in the pH range of 11–11.8. Fig. 19 shows their results which are reported almost identical in the calibrated range of the five pH sensors [81]. How-
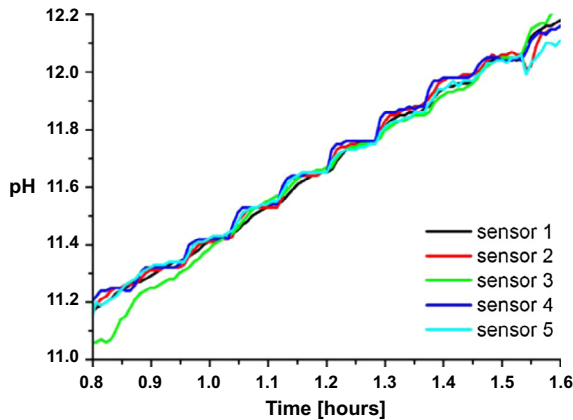
Fig. 18. Fibre optic pH sensor [85].

Fig. 19. Results of measured pH by 5 fibre-optical planar transmission sensors [81].

ever, the curves of the sensors drift remarkably for pH values out of the range of calibration of the sensors so that the sensor has to be calibrated for a wider range of pH values (see Fig. 19).

Evanescent field spectroscopy through optical fibres was used by Vimer et al. for in-situ pH measurement of cementitious materials [72]. They explained that it is possible to avoid frequent calibrations which are required due to long-term drifts and electric or magnetic interference by using optical spectroscopy. The sensing mechanism was based on the pH induced change in fluorescence intensity of a coumarin imidazole dye which was covalently attached to a polymer network by co-polymerization of the dye monomer with methacrylic acid co-monomer and 1,4-bis (acryloyl) piperazine cross-linker. Although research on using fibre optic probes for measuring pH in concrete is on-going, these probes are commercially available on the market for other applications. However, most of these probes are not appropriate for use in concrete applications mainly because of the low range of pH values which can be measured (usually up to 9–10). Recently, Nguyen et al. [75] reported about the design of a fibre optic pH sensor providing a response over a pH range of 10.00–13.00 which could be used for corrosion monitoring in concrete structures. In general, fibre optic pH sensors have several advantages such as eliminating reference electrode, low price, resistance to chemicals, feasibility of remote sensing and signal transmission over far distances, possibility for miniaturization and independence of electromagnetic interference. On the other hand, there are still some drawbacks for using this type of sensors. One of the main obstacles is the fact that only few fibre optic sensors have been developed for measuring pH values in high alkali environment such as concrete [75,86–90]. In the meantime, some of the reported sensors demonstrated significant overlap between their spectra at low and high pH measurements according to Khalil et al. [84]. Another limitation of some of currently available fibre optic pH sensors is their chemical instability of the chromophore at high pH [91,92] or dye leaching

and short life span [79]. Consequently, although fibre optic sensors seem very advantageous, further developments should be done for overcoming current barriers and making them more accurate, repeatable and reproducible.

4. Conclusion

Based on the evaluation of different destructive and non-destructive methods which have been developed for measuring the pH of concrete, it can be concluded that extraction of concrete pore solution by applying high pressure, which is known as the expression method, is the most common method amongst the destructive test methods. However, this method has several technical and practical concerns. On the other hand, non-destructive methods by using embedded metal/metal oxide electrodes and fibre optic sensors can be very effective for real-time monitoring of pH fluctuations over time at different conditions. However, these methods have been introduced recently and need further development to be considered as reliable and practical methods with an accurate level of resolution, repeatability and reproducibility. It should be noted that despite the broad range of used methods for measuring the pH of concrete, none of the investigated methods has been standardized yet. Therefore, the authors conclude that it is highly recommended that the required measures are taken for developing a specific standard test method for measuring the pH of fresh and hardened concrete with high level of repeatability and reproducibility due to the important role of pH with regard to durability of concrete structures.

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