

Analysis of the trend of pH changes of concrete pore solution during the hydration by various analytical methods

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Abstract

The pH is an important parameter in concrete health monitoring. Many studies have been conducted to investigate the environmental elements that influence the pH value of concrete. This study focussed on the investigation of the pore solution in concrete throughout the hydration process during a 90-day timeframe. The concrete pore solution was extracted by ex-situ leaching methods (ESL) including cold water and hot water extraction (CWE and HWE). The pH of the solutions was obtained by various techniques such as titration, direct measurement by pH electrode, back calculation method, and the thermodynamic modelling based on the measured alkali concentrations. For both ex-situ leaching processes, the changes in pH and alkali concentration appear to be similar. Due to the dilution effect of water addition, direct pH measurement with a pH electrode and titration method underestimates the real pH value. The results obtained from the measured alkali concentrations were more reliable and indicated that the pH of the fresh concrete was around 13.1 and increased gradually up to 13.8 with time. Back calculation of the pH of the concrete using the dilution of the H⁺ ions show the high pH values. Therefore, the actual pH of the concrete pore solution can be evaluated using a thermodynamic modelling based on the alkali content of the extracted solution.

Keywords: Concrete, pH, pore solution, Thermodynamic calculations

1 1. Introduction

2 The pH is a critical factor in determining the health of concrete, since it influence the corrosion of
3 reinforced steel bars. Many research studies reveal that the corrosion of the steel bar is initiated when
4 the pH of the concrete pore solution drops below a certain level [1]. The concrete matrix contains its
5 pores aqueous solution called as pore water or pore solution [2,3]. Oxides of alkali metals such as
6 sodium and potassium present in the cement, remain partially in the pore solution resulting in high
7 pH values [4]. The pH of the pore solution in concrete varies between 12.5 and 13.9 depending on the
8 cement type, the water to cement ratio, and the amount of alkali metal oxides present in the concrete
9 mixture [5–7]. The concentration of alkali metal hydroxides in the concrete pore solution generally
10 ranges from 0.15 to 0.85 mol L⁻¹ [7]. Moreover, the production of calcium hydroxide (Portlandite)
11 during the hydration of cement, stabilizes the pH at least 12.5. Carbonation and/or alkali leaching can
12 reduce the pH and facilitate the corrosion of the steel bar. Continuous exposure of the concrete
13 surface to water e.g rain or groundwater and carbon dioxide from the atmosphere can accelerate the
14 pH reduction rate in concrete [8].

15 The high pH environment protects the steel bar from corrosion and increases the durability of
16 concrete. However, high pH and high alkali concentrations can cause the so-called alkali-silica reaction
17 (ASR). ASR is the reaction between the silicate materials present in the aggregates and the OH⁻ ions in
18 the pore solution of concrete [9]. The alkali-silicate gel formed due to ASR can result in expansion and
19 cracking in the concrete structure [4]. The pH value of the concrete pore solution can also affect the
20 composition of the hydrates form in a concrete [10]. In particular, the Ca²⁺ concentration can affect
21 the composition and stability of calcium silicate hydrates (C-S-H), ettringite, and AFm phases [11][10].
22 The amount of alkali ions and the quantity of the free water are key parameters affecting the pH in
23 the pore solution of concrete. Various methods have been reported previously to measure the pH of
24 the cementitious system including destructive and non-destructive methods [6,10,12–15]. Non-
25 destructive methods such as an embedded potentiometric electrode and fibre optic sensors can be
26 effective for real-time application in the monitoring of pH. However, there are some drawbacks to
27 using these sensors. Most of the chromophores or compounds used in the sensor probe have poor
28 stability and short life span in a high alkaline environment like concrete [16]. On the other hand, only
29 a few fiber optic sensors have been developed for a concrete application. Hence, further, development
30 should be carried out to overcome current obstacles in using the sensors[17].

31 The pore-water expression (PWE) method is the most commonly used destructive method to extract
32 the pore solution from pastes [18–20]. The pore solution is extracted by pressing the sample using a
33 hydraulic press device. The composition and concentration of ions of the extracted solution in the
34 PWE method are almost equal to the composition and concentration of ions present in the pore
35 solution. While this method is well applicable to pastes (and mortars) it is very difficult to press out
36 pore solutions from concrete samples due to the presence of large aggregate such that other methods
37 have to be used for concrete samples. Moreover, the use of the PWE method requires the presence
38 of sufficient pore water to be pressed out physically, such that this method cannot be used to extract
39 the concrete pore fluid from well-dried concrete blocks.

40 The pH of a solution obtained from the PWE method can be measured easily using a suitable pH
41 electrode, although the alkaline error of pH meter and calibration of pH meter using high alkaline
42 buffer solution should be considered in these measurements [21]. Alternatively, the pH can also be
43 measured indirectly by titrating the solution with an acid [22–24]. However, the pH values based on
44 the titration method may somewhat overestimate the actual pH value of the solution due to the
45 protonation of additional ions in the solution [5].

1 The in-situ leaching (ISL) method was first described by Sagüés et al. [25] for the pH measurement of
2 concrete. ISL approach involves drilling small cavities in the sample's surface, filling the cavities with a
3 small, known amount of deionized water, and then equilibrating the solution in the cavities.
4 Equilibrium is assumed to be achieved when the pH of the solution inside the cavity is stable, which
5 can take one or two weeks [25,26]. This method, however, will not provide accurate results for
6 concretes with a dense micro-structure [27]. Furthermore, a prolonged equilibration time might result
7 in carbonation and incubation process in alkali leaching and, as a result, a reduction in pH [28,29].

8 The ex-situ leaching (ESL) method is another destructive method to measure the pH of the concrete
9 pore solution. According to the test results by Plusquellec et al.[10], the pH of the concrete pore
10 solution can be calculated based on the measured free alkali metal content in the leachate with the
11 help of thermodynamic modelling. ESL methods include Cold-Water Extraction (CWE) and Hot Water
12 Extraction (HWE).

13 A common process of ESL methods involves the leaching of a powdered concrete sample into a known
14 volume of water, extraction of filtrate after a certain time, and analysis of the extract. Different
15 researchers have used a different process for the CWE. Alonso et al. [6] have recommended that the
16 particle size of the powdered sample lesser than 80 μm , a liquid/solid ratio of 1, and a leaching time
17 of 5 min. In the HWE method, the sample is pulverized to get the particle size below 160 μm , powdered
18 sample (10 g) is mixed with deionized water (100 mL). Then the suspension is boiled for 10 minutes
19 and left to stand for overnight at room temperature. The solution is filtered and the volume was
20 adjusted to 100 mL [30].

21 Alkalis are released from alkali sulphate and carbonates present in Portland cement/cementitious
22 materials when they are mixed with water. The alkali fraction bound in clinker will be released during
23 the hydration. The released alkalis will be partitioned between the solid hydrates (mainly on C-S-H)
24 and the pore solution [12,31]. The OH^- concentration in the pore solution can be directly correlated to
25 the total alkali content (Na_2O_e) and to the parameter $\text{Na}_2\text{O}_e \cdot \text{CaO}/(\text{SiO}_2)^2$ [32]. Both of these can be
26 derived from the chemical composition of the cement. The $\text{CaO}/(\text{SiO}_2)^2$ ratio represents the ability of
27 C-S-H to bind to alkalis. If the total alkali content in the pore solution decreases, alkalis will be released
28 from C-S-H to maintain the equilibrium between liquid-solid phase. The majority of the free alkalis
29 present in the pore solution will be released when the hardened cement is immersed in water with a
30 neutral pH. Therefore, the liquid/solid ratio, and leaching time are important parameters if the alkalis
31 in the pore water are measured.

32 Most of the published researches on pH measurement of hardened concrete has been focused on
33 carbonation and corrosion of steel bar, but not on the pH changes during the hydration of concrete.
34 Thus, the present work focuses on the determination of pH changes of concrete during hydration in
35 an inert atmosphere. In this work, the CWE and HWE procedures were modified slightly to improve
36 the accuracy of the extraction and the liquid to solid ratio was maintained in 2:1 ratio. The water used
37 in the extraction was divided into three parts and the extraction was carried out three times for one
38 sample.

39 40 2. Materials and Methodology

41 Blended hydraulic fly ash cement (SLS 1247/ ASTM C595) containing limestone was used in this
42 experiment. The chemical composition was acquired by X-ray fluorescence (XRF; S8 TIGER, Bruker)
43 and is given in Table 1. River sand was used as a fine aggregate. Organic debris in the river sand was
44 removed carefully by hand, and then the sand was passed through a steel mesh (2 mm) to get the

1 sand size below 2mm. Then it was purified by washing with distilled water followed by an oven drying
 2 at 100 °C. Crushed granite stone was used as coarse aggregate. Crushed granite stones were passed
 3 through 10 mm and 8 mm metal sieves to obtain the size between 8 to 10 mm. The small size of coarse
 4 aggregates was used to reduce the error that can be caused by weight since the number of coarse
 5 aggregates enclosed in each sample may vary. The maximum weight of an aggregate was about 1g.
 6 The double-distilled water was used in all processes and was obtained from Aquatron A4000 double
 7 distilled water plant from the Department of Chemistry, Eastern University, Sri Lanka (Conductivity \approx
 8 6.80 $\mu\text{s}/\text{Cm}$).

9 A concrete mixture of M20 grade was prepared at a water-cement ratio of 0.45 and it was cast in
 10 polypropylene cups (A 100) to give approximately 250 g samples. Then the cups were closed and
 11 sealed by Sellotape airtightly. Subsequently, six samples were placed in plastic bags filled with N_2 gas
 12 and stored at room temperature about 30°C. In this manner, 11 batches containing 6 samples were
 13 prepared and stored. Pore fluid was extracted at a specific period of hydration as 1h, 3h,5h,7h,9h, 1
 14 day, 3 days, 7 days, 14 days, 28 days, and 90 days.

15 One batch of samples was opened and transferred into a desiccator containing soda lime. The initial
 16 weight of all the samples was measured and two samples were placed in an oven at 105°C to obtain
 17 the free water content. The two samples were subjected to cold water extract and another two
 18 samples were subjected to hot water extract.

19 *Table 1: Characterization of the cement used in this experiment*

Chemical composition of the cement (mass %)	
SiO₂	18.65
Al₂O₃	4.21
Fe₂O₃	2.91
Cr₂O₃	0.009
MnO	0.053
TiO₂	0.293
P₂O₅	0.192
CaO	59.95
MgO	1.39
K₂O	0.50
Na₂O	0.26
SO₃	2.28
LOI	9.14
Total	99.76
Total C	2.13

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32 2.1. Coldwater extraction (CWE)

33 The concrete sample of hydration time \leq 9h was placed in a stainless-steel container directly while the
 34 rest of the samples (older than 9h) were crushed in a powder using steel mortar and pestle (Please
 35 note that all the aggregates were crushed in this procedure). 250 mL of freshly prepared CO_2 -free
 36 double-distilled water at room temperature was added to the whole crushed sample and stirred by a
 37 stainless-steel rod by hand for 3-4 minutes. After that, and the filtrate was extracted by vacuum
 38 filtration using Whatman filter paper (Grade 40, pore size-8 μm). Then the residue was again subjected

1 to the same process using 125 mL of water two times. Then all filtrate was transferred into a
2 volumetric flask (500 mL) by adjusting the volume to 500 mL using double distilled water.

3 2.2. Hot water extraction (HWE)

4 The hot water extraction process used in this experiment is different from the process described by
5 Berube et al. [30]. The same process as used for the cold-water extraction was repeated in HWE,
6 except for the temperature of the water. The temperature of the double distilled water used in hot
7 water extract was around 70°C. After the extraction of pore fluid, it was transferred into a volumetric
8 flask (500 mL) by adjusting the volume to 500 mL using double distilled water and it was closed and
9 labelled. Both CWE and HWE processes were duplicated for every experiment.

10

11 2.3. Determination of free water content

12 The amount of free water in the concrete sample is important in the measurement of the pH of the
13 pore fluid of concrete. The sample that is subjected to the pore water analysis cannot be used for the
14 determination of free water. Therefore, another sample in the same batch is used to measure the free
15 water content. The average value of the free water content of two parallel samples is assumed to be
16 equal to the water content of the sample that is subjected to the pore water extraction process. All
17 samples have experienced the same environmental condition and same hydration period. Therefore,
18 the free water content of all samples is similar. The free water content determination process is based
19 on the method described by Farstad et al. [33]. The initial weight of the individual sample was
20 measured, then it was broken into small pieces carefully without any sample loss. All broken parts
21 were dried in an oven at 105°C until a constant weight is obtained. However, drying at 105°C induces
22 the loss of some of the crystalline water of the ettringite and C-S-H). The free water content of the
23 samples was calculated using the following equation eq (1).

$$\text{Percentage of free water} = \frac{M_{\text{initial}} - M_{\text{Final}}}{M_{\text{Initial}}} \times 100 \quad \text{eq (1)}$$

24

25 2.4. pH measurement

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27 2.4.1. Direct measurement

28 The pH meter was calibrated with standard buffer solutions (pH 4.01, 7.00, and 10.01) before taking
29 the measurements. The temperature was recorded between 30 to 32 °C during the calibration and
30 the pH measurements. The pH of the extracted pore fluid was recorded using the pH meter (Eutech
31 pH 700). All pH measurement were recorded after the pore water extract had reached thermal
32 equilibrium with room temperature (around 30-32 °C).

33 The pH value corresponds to the negative logarithm of the H⁺ activity (a_{H⁺}) as shown in eq (4). The
34 ionic activity can be related to H⁺ ions concentration using eq (2), where a_i is the activity of ion, m_i is
35 the concentration in molal units, and γ_i is the activity coefficient. The activities of H⁺ and OH⁻ are
36 related according to eq (3), the K_w given corresponds to 30 °C as all experiments have been conducted
37 at the laboratory temperature around 30 °C.

$$38 \quad a_i = m_i \gamma_i \quad \text{eq (2)}$$

$$a_{\text{H}^+} a_{\text{OH}^-} = K_w = 1.47 \times 10^{-14} \quad \text{eq (3)}$$

$$\text{pH} = -\log a_{\text{H}^+} \quad \text{eq (4)}$$

2.4.2. Titration method

Extracted pore fluid (10.0 mL) was transferred into a titration flask and it was titrated against standard HCl (0.01 mol L⁻¹) using methyl red as an indicator. The required volume of diluted HCl solution was obtained and that used to calculate the pH in the extract using Eq. (3) and Eq. (4). The concentration of OH⁻ and pH in the concrete pore fluid was obtained as detailed below in section 2.5.

2.4.3. pH calculated based on the free alkali metal content

For an alkaline solution, the concentration of OH⁻ is much larger than that of H⁺ and thus determines the pH of the solution. The concentrations of OH⁻ depend to a large extent on the K and Na concentrations, thus pH values can be calculated based on measured Na and K concentrations. Extracted pore fluid (5.0 mL) and 3.4 mL HNO₃ (1.5 mol L⁻¹) were transferred into a volumetric flask (50 mL). The total volume of the mixture was adjusted to 50 mL by adding double-distilled water to prevent the precipitation. The solution was analysed for Na⁺ and K⁺ using Atomic Absorption Spectrophotometer (AAS) with the model- GBC SensAA-Dual, using Air-acetylene flame. [10,12].

Thermodynamic modelling studies were carried out based on the procedure suggested by Plusquellec et al. [10] by considering only the free alkali metal content (Na and K) in the concrete pore fluid. The pore solution was extracted through the CWE/ HWE methods and the concentration of free alkali metals in the concreted pore fluid was back-calculated using the results obtained by the AAS considering the dilution as detailed below in section 2.5. Calculated results were incorporated into PHREEQC program and pH was calculated using the updated thermodynamic database Cemdata 18 provided by Lothenbach and co-workers [34]. The methodology to run the program is described by Plusquellec *et.al.* [35] and is briefly described as follows. A temperature of 30°C was used in the PHREEQC calculations to correspond to the average laboratory temperature in Sri Lanka. The back calculated alkali concentration was used as the "Individual element input" in the program in mmol/kg water and the pH was calculated in PHREEQC based on charge balancing the Na and K concentrations.

2.5. Calculation of alkali content in the concrete pore solution

In the concrete, the amount of pore solution has a large impact on the alkali concentrations and thus the pH values. Thus, direct measurement of alkali concentration in the HWE or CWE extract will not represent the actual alkali concentration of the pore solution since water is added during the process of pore water extract and needs to be corrected taking into account the amount of additional water added.

The alkali concentration in the pore solution (C_p) of the concrete can be calculated based on eq (5) using the alkali concentration in the HWE or CWE extract, where C_f corresponds to the alkali concentration measured in the extract, V_f to the volume of the extract (500 mL), and V_p to the volume of pore solution (free water) in the concrete.

$$C_p = \frac{C_f \times V_f}{V_p} \quad \text{eq (5)}$$

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2 3. Results and discussion

3 3.1. Determination of free water content

4 The percentage of free water content based on drying at 105° was calculated by using Eq. 1. The
 5 average value of the free water percentage and dry weight of samples at different hydration times is
 6 given in Table 2 and Fig. 1.

7 *Table 2: The amount of free water and sample weight at different hydration times.*

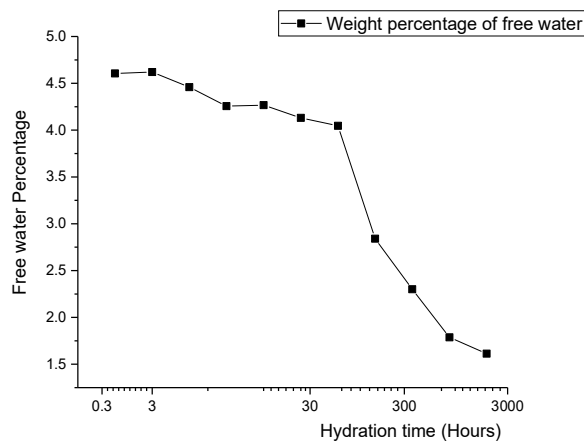
Hydration Time (hours)	Free water content (g)	Percentage of free water content	The average dry weight of the samples	
			CWE	HWE
1	11.27	4.6	233.4	233.6
3	11.22	4.6	231.6	232.1
5	10.82	4.5	231.8	231.3
7	10.32	4.3	232.2	232.4
9	10.33	4.3	231.8	231.9
24	10.02	4.1	232.6	232.3
48	9.76	4.0	231.5	231.8
168	6.81	2.8	232.9	232.8
336	5.5	2.3	233.6	233.8
672	4.26	1.8	234.2	233.3
2160	3.82	1.6	233.1	232.9

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9 The results show that the percentage of free water is reduced from 4.6 to 1.6 % due to the hydration
 10 process as expected. The free water content plays an important contribution to the recalculated
 11 values. Hence, a careful measurement of free water content is an essential part. The 10% error in
 12 measuring the free water content can bring about a 10% error in the back-calculated parameters.
 13 Further, it can cause approximately 0.3% of error in the calculated pH value. The effect of ±10% error
 14 in the measurement of free water content is described in Fig. 6.

15 The dry weights of the individual samples show some variations as they contain some coarse
 16 aggregates. The average dry weight of all samples used for both CWE and HWE is 232.6 g.

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Fig. 1 – Decrease in free water content during hydration of the concrete.

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3.2. Direct pH measurement by pH electrode

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The pH values recorded from the CWE and HWE are summarised in Supplementary information (SI) and displayed in Fig. 2. No systematic difference could be observed between the pH values obtained by CWE and HWE. This indicates that the temperature of the water used during the extraction procedure has no significant effect.

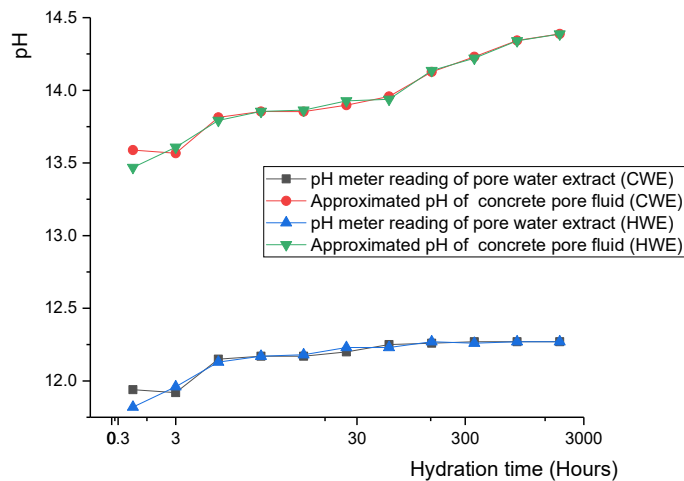
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Some researchers [6,13] have directly used the pH measured in the extract as an approximation for the pH in the pore solution of the concrete, neglecting the effect of dilution. In many cases, such a simplification will not provide an adequate estimation of the effective pH value in the pore solution. To illustrate the problems, also the concentration of H^+ in the concrete pore solution was calculated directly based on the amount of free water in the concrete and based on the additional water used during the extraction procedure using Eq. 5 and the result is plotted in Fig. 2. The directly calculated pH values of the pore solution are 1.5 to 2 pH units higher than the values measured in the extract, due to the dilution. The difference increases with hydration time as less pore solution is present leading to a higher dilution of the original pore solution and thus to higher back-calculated pH values. The pH obtained by back-calculation of directly measured pH values increase up to pH 14.4, which is higher than the usual range of pH values 13 -13.6 observed in pressed out pore solution [5] indicating that the back-calculation of the pH measured in the extract overestimates the real pH value of the pore solution of the concrete, in agreement with the experimental findings for paste samples reported by Plusquellec et al. [10]. Realistic pH values will not be obtained by considering only the simple dilution of H^+ ion, which provides absurd pH values greater than 14. There is a substantial difference in pH values obtained from pH electrode for extracted solution and back calculated results, indicating that results achieved by focusing solely on dilution are inconsistent.

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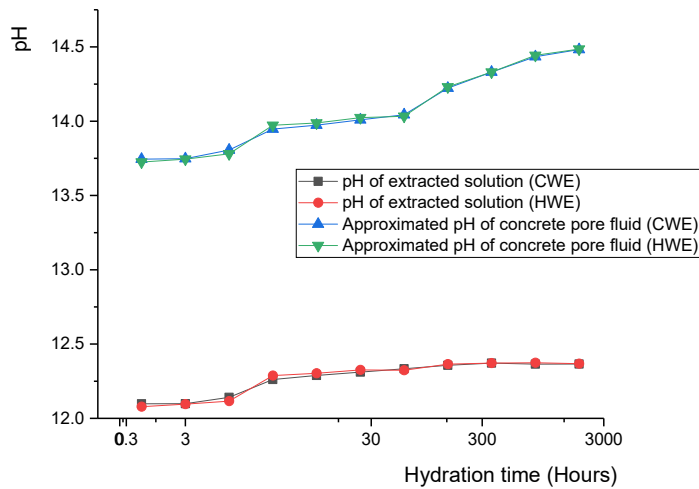


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Fig. 2: pH changes with hydration time measured by pH electrode in the CWE and HWE extract and back-calculated pH values in the concrete pore solution.

3.3. pH measurement by titration

9 The pH value in CWE and HWE extract was also obtained by titration with HCl. and based on these
 10 values the pH value of the concrete pore fluid was calculated based on the results obtained from the
 11 titration and are summarised in SI and Fig. 3. Titration instead of direct pH measurements has been
 12 previously used [36] and it has been suggested that titration could overestimate the real pH value as
 13 titration results include also hydroxides present as the protonation of different aqueous complexes
 14 such as CaOH^+ or HCO_3^- will contribute to the amount of acid needed [5]. In fact, the titration results
 15 (Fig. 3) were approximately 0.1 log units higher than the pH measured directly by an electrode (Fig.
 16 2). This corresponds to $\approx 20\%$ higher OH^- concentrations using a linear scale. This underlines that the
 17 titration method in fact moderately overestimates the effective pH value in the extract.
 18 Again, as stated above, there is a large difference between the pH measured in the extract and the pH
 19 value back-calculated to the pore solution, showing an overestimation of the pH in the pore solution
 20 based on the back-calculated results, indicating that these values do not represent the real pH value
 21 in the pore solution.



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Fig. 3: pH changes with hydration time obtained from titration in the CWE and HWE extract and back-calculated pH values in the concrete pore solution.

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3.4. Determination of pH based on measured alkali concentrations

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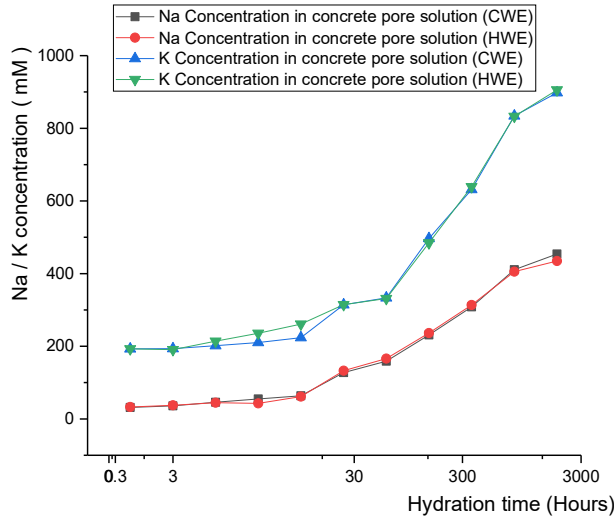
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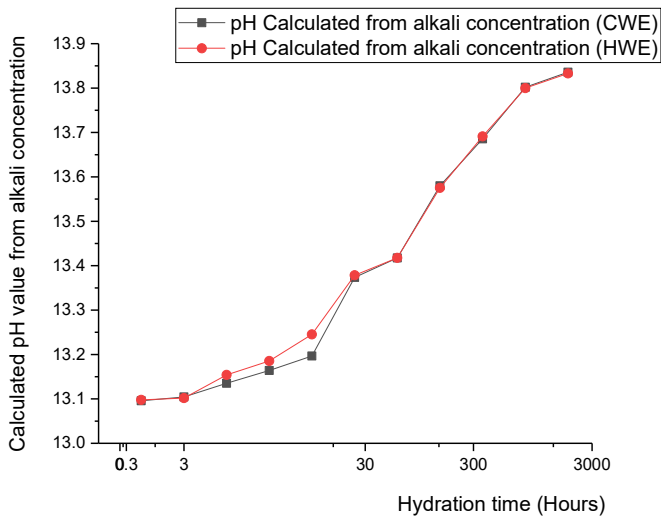
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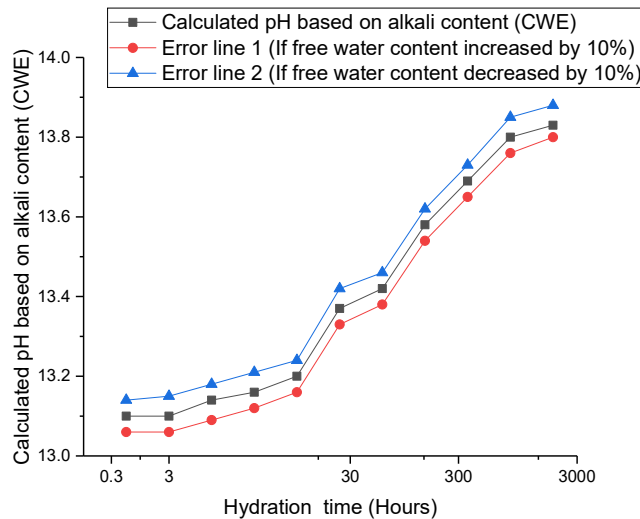
The concentration of Na^+ and K^+ can be used to calculate the pH of the concrete pore fluid, as the OH^- concentrations in the pore solution depends mainly on the alkali concentrations [5,10]. Thermodynamic modelling can be used to calculate the pH values from the measured Na and K concentrations as detailed in [10,35]. The alkali concentrations obtained in the extracts from CWE and HWE and the values calculated in the pore solution are tabulated in SI. The Na and K concentrations calculated in the pore solution are shown in Fig. 4. Again, no significant difference is observed between the hot and cold water extraction procedure. The Na and K concentrations increase with time in both extracts. Na and K concentrations started to increase significantly between 9 and 24 hours of hydration due to the release of alkali metals from the reaction of the clinker phases and the reduction of the amount of available water [12]. The calculated pH values in the concrete pore fluid are displayed in Fig. 5. The obtained pH values show a comparable increase as the alkali concentrations displayed in Fig. 4 and increase from pH 13.1 to 13.8, thus within the expected range of pH values in the pore solution of concrete [13,37].



1
 2 Fig. 4: Na and K concentration in the concrete pore solution during the hydration
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 5 Fig. 5: pH of concrete pore solution during hydration time calculated from alkali concentration
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2 Fig. 6: Effect of error in the measurement of free water content. Calculated pH value in Error line 1
3 and Error line 2 show deviation of -0.04 and +0.04 respectively with the actual line.

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3.5. Comparison of results

7 CWE and HWE give comparable results in all analyses indicating that the usage of hot water and cold
8 water for the extraction process has no significant effect. This absence of any effect of temperature
9 on the resulting pH in the extract agrees with the results obtained by Bérubé et al. [30] on concrete.

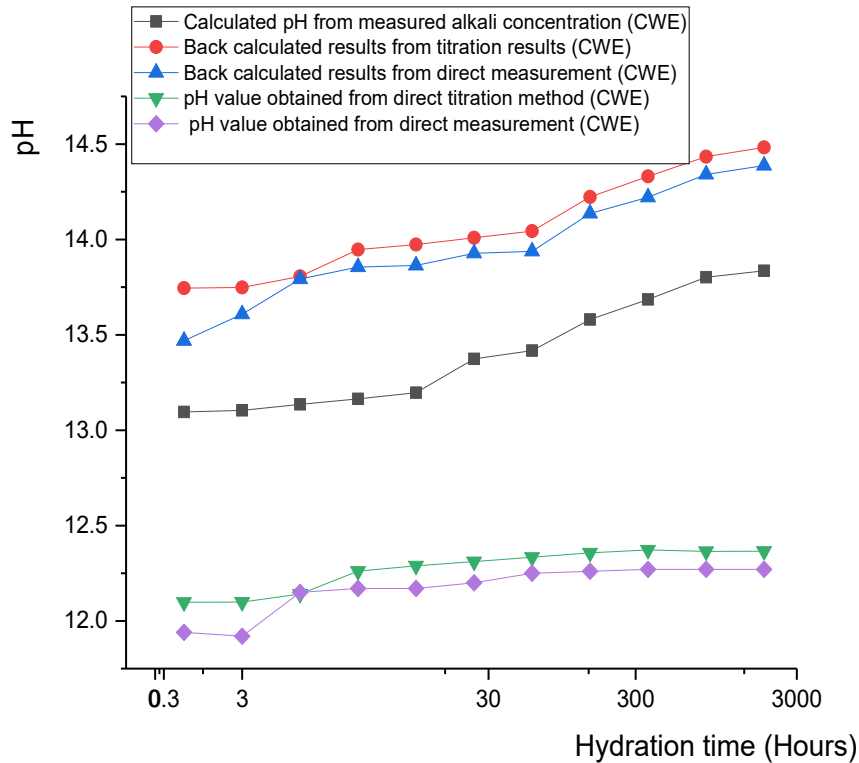
10 All the calculated and measured pH values of pore water extract and concrete pore fluid obtained
11 from CWE are summarised in Fig. 7. There are large differences between the pH values measured in
12 the extract and the pH values calculated for the pore solution in concrete. The pH values measured in
13 the extract were 1.5 to 2 log units lower than those recalculated for the concrete pore solution, as the
14 extracted solutions were strongly diluted. The pH values in the extracts (11.9 to 12.4) are much lower
15 than pH values observed in the pore solution of other Portland cement and mortars, indicating that
16 the values measured in the extract are not adequate for direct use to determine the pH values in the
17 pore solution of Portland cements.

18 The pH values in the pore solution back-calculated from those extracts taking into account the
19 additional water, are with 13.5 to 14.2 higher than the expected pH values, indicating that the
20 measured pH values are affected by other factors. In fact, the pH of the extracted solution is not only
21 determined by the pH of the pore solution but also affected by the partial dissolution of portlandite,
22 C-S-H, ettringite and AFm phases during the CWE and HWE procedure resulting in an increase of
23 dissolved ions [10,38] and thus of pH value in the extract and thus also in the back-calculated pore
24 solution. A similar over-estimation of the pore solution pH has also been reported by Plusquellec
25 et al. [10], who could relate it to the presence of high Ca concentrations in the CWE and HWE extracts.
26 This high pH values underline that also the back-calculated pH values are not a good estimate for the
27 pH in the original pore solution.

28 The pH values calculated from the measured alkali concentrations, however, provide reliable results
29 of the pH in concrete resulting in pH values from 13.1 to 13.8. These pH values agreed with the pH
30 values observed in previous studies in paste samples [5,12,39], in mortar samples[10] as well as in
31 concrete samples [13,37]. In contrast, the simplistic approach considering only the dilution effect

1 based on the pH measured in diluted CWE and HWE overestimates the real pH values strongly and
 2 should be not be used. Further, it should also be mentioned that the amount of free water in the
 3 sample has a significant impact on the results obtained using this method.

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7 Fig. 7: Comparison of pH values obtained in the CWE extract (direct pH measurement and titration),
 8 back-calculated pH values (from direct pH measurement and titration) and pH values calculated form
 9 measured alkali concentrations.

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11 4. Conclusion

12 The changes in the pH of the concrete pore solution were followed up to 90 days. Concrete pore water
 13 was extracted using ex-situ leaching methods. In all cases an increase of the pH values with time was
 14 observed. There was no significant difference between the results obtained from the cold water
 15 extraction (CWE) and hot water extraction (HWE) method.

16 The pH of the extracts was analysed by different methods such as titration, direct pH measurement
 17 using a pH electrode and calculated from measured alkali concentrations using thermodynamic
 18 modelling. In general, the pH values using titration were approximately 0.1 log unit higher than the
 19 direct measurements with a pH electrode indicating a moderate overestimation of pH values by the
 20 titration method.

21 Direct pH measurement of the pore water extract using a pH electrode or titration method
 22 underestimated the actual pH value of the concrete pore solution by 1 to 1.5 pH units due to the high
 23 dilution of the original pore solution.

1 The pH values in the concrete pore solution were also back-calculated based on the amount of free
2 water in the concrete and the amount of additional water used during the extraction procedure. These
3 back-calculated pH values were with 13.5 to 14.2 higher than the actual pH values in the pore solution
4 of the concrete due to the partial dissolution of hydrates during the CWE and HWE procedure resulting
5 in an increase of dissolved ions [10,38] and thus of pH value in the extract and the calculated pH of
6 the pore solution.

7 In contrast, the calculation of the pH value based on the measured alkali concentrations using a
8 thermodynamic modelling tool, PHREEQC, provides reliable results with pH values from 13.1 to 13.8,
9 which are in good agreement with the previously published direct determination of pH values in
10 cementitious systems [10,12,39]. Careful measurement of the free water content plays an important
11 role in the calculation of pH values based on CWE and HWE extraction.

12

13

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19

20 **Conflict of interest**

21 The authors declare that there are no conflicts of interest.

22

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