

# REVIEW OF METHODS TO DETERMINE THE pH AND THE FREE ALKALI CONTENT OF THE PORE SOLUTION IN CONCRETE

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## Abstract

Alkali-silica reaction (ASR) in concrete is known to be induced by the dissolution reaction where the reactive silica in aggregates is dissolved by the pore solution in the concrete, followed by a precipitation reaction leading to a gel formation. The rate of the dissolution reaction depends on the pH of the pore solution, which is linked to its alkali content. It is assumed that ASR only can occur if the pH is above a critical limit called “alkali threshold”. The knowledge of the pH in a given concrete is of importance for durability. This paper presents a literature review of different methods to determine the pH and the free alkali content in pore solution and discusses their advantages and drawbacks.

**Keywords:** ASR, pore solution, pH, free alkali content, concrete

## 1 INTRODUCTION

A pore solution with high pH is - together with the presence of reactive aggregates and sufficient amount of moisture - needed for alkali-silica reaction (ASR) to occur in concrete. ASR may lead to the expansion and cracking of the concrete. The pH in a concrete with conventional Portland cement ranges between approx. 12.5 and 13.8 [1, 2], depending on e.g. the alkali content of the cement itself [3]. The addition of supplementary cementitious materials can lead to a reduction in the pH [2]. A pH higher than 12.5, which is the pH of a solution saturated in respect to  $\text{Ca}(\text{OH})_2$ , is obtained in presence of alkali such as Na and K. ASR only occurs when the pH is above the “threshold” limit. This threshold depends on the aggregates present in the concrete [4]. Measurement of the pH and the free alkali content of concrete is thus of great importance. Several methods can be employed for determining the pH and the free alkali content [5-9], but each of them exhibit different drawbacks. The lack of internationally accepted and reliable measurement method is still an issue of concern. This paper presents a review of existing methods to determine the pH and/or the free alkali content of the pore solution of a concrete. Initially, the paper describes and discusses the methods. A brief comparison and preliminary recommendations follow.

## 2 LITERATURE REVIEW

This section gives an overview of various methods reported in the literature.

### 2.1 Pore water expression

#### *Description*

During pore water expression (PWE) a high pressure equipment compresses the hardened cementitious material sample, resulting in the expression of the pore solution. This procedure is the most commonly employed and is often used as a reference method for comparison with results obtained by other techniques [10-17]. PWE, first described by Longuet et al. [18] and Barneyback and Diamond [19], requires a specific device, presented in FIGURE 1, which is placed under a mechanical press. The applied pressure varies from one author to another, ranging between 200 and 1000 MPa. If the size of the sample is slightly smaller than the cavity under the piston, it can be placed directly in this cavity. Otherwise, the sample must be crushed into smaller pieces (with various sizes and masses) as reported in [1]. However, the authors of the present paper have observed that crushed samples

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seem to yield lower amounts of solution. This could be due to the sample volume since pieces are difficult to pack in the cavity. Once the sample is introduced in the device, the pressure is applied and the solution is recovered and filtered. In order to avoid carbonation, the solution should be analyzed directly after the expression.

#### *Influence of the preconditioning*

PWE can be used for cement paste, mortar and concrete samples; however, the applicability can be restricted due to the limited amount of free water available, particularly for older samples, dense samples with low water/binder ratio and samples containing a lot of aggregates. For mortar samples of approx. 250 g only few milliliters can be obtained from specimens older than one day [19]. In order to increase the amount of obtained solution for crushed concrete samples, Alonso et al. [1] proposes the addition of a small amount of water by spraying just before the expression. There is no standard for the sprayed water volume as it varies depending on the initial moisture content of the sample. But no free water in excess should be present on the surface of the sample. The hydration of unreacted cement is supposed to be limited due to the short interaction time. By spraying water, the obtained solution will thus be diluted, which should result in an underestimation of the pH when measured directly on the extracted solution.

#### *Influence of the applied pressure*

Several studies have been performed on the effect of the applied pressure during PWE on the composition of the extracted solution. Duchesne and Bérubé [20] observed no influence of the pressure on the alkali concentration of the extracted pore solution of cement pastes and mortars with a fixed water/binder ratio of 0.5 at 7 and 28 days old. Various pressure intervals were investigated: 0-200, 200-560 and 0-560 MPa. Similarly, Cyr et al. [17] did not observe changes in the concentration of K, Na, Ca and Si for PWE using the following upper limits for the pressure: 300, 500, 750 and 1000 MPa. However, in [10] Bérubé and Tremblay did observe a pressure dependency of the composition of the extracted pore solution for cement paste samples containing  $\text{LiNO}_3$ . For the pressure intervals, 0-200, 200-400 and 400-1000 MPa, the total measured Na and K concentrations are respectively 0.87, 0.91 and 1.07 mol/L. A similar increase is also observed for Li. In addition, they noticed that [Na] increases more than [K] with the applied pressure, i.e. an increase of approx. 30 % and 20 %, respectively, when comparing the results obtained at 200 and 1000 MPa. The representativity of the pore solution obtained by PWE can be questioned due to the pressure dependency of its composition. According to the review of Vollpracht et al. [2], the use of a pressure higher than 250 MPa results in a significant modification of the pore solution, while Bérubé and Tremblay [10] suggest an upper limit of 400 MPa. There is thus no consensus on the effect of the pressure.

## **2.2 In situ leaching**

### *Description*

In situ leaching (ISL) consists of drilling small cavities from the surface of the sample, adding small and known amount of deionized water in the cavities and then analyzing the solution in the cavities after equilibration. The equilibrium is supposed to be reached when the pH of the solution inside the cavity is stable, which is depending on the sample and takes about one to two weeks [5, 21]. Figure 2 presents a sketch of the ISL arrangement. ISL was first described by Sagüés et al. [5] and Li et al. [21], mainly for pH measurements. Moreno [22] applied ISL to study the pH in carbonated concrete. Cáseres et al. [13] used this method to obtain information regarding the spatial distribution of chlorides in concrete samples. First, the samples have to be water saturated. E.g. Sagüés et al. [5] suggest to place them in an acclimatized chamber at 100 % RH and  $22 \pm 2$  °C until constant mass is reached. After this pre-conditioning, the experimental procedure is divided into four steps: 1) cavities are dry drilled (between 3 - 5 mm in diameter and 25 - 35 mm deep) using a drill from the upper surface; 2) distilled water (0.2 - 0.4 ml) is injected inside the cavities after removing dust and debris. Each cavity is isolated from the environment by using an acrylic washer, affixed with a fast-setting epoxy, and a tapered rubber stopper; 3) the sample is placed back in the 100 % RH chamber and kept there for monitoring; 4) The pH of the solution in each cavity is measured periodically: a micro pH electrode is put in one cavity while the micro reference electrode is placed in another cavity until equilibrium is reached, assuming identical solution in both cavities. Part of the solution can also be pipetted for other chemical analysis.

#### *Influence of the preconditioning*

ISL requires water saturated samples, or the added water will be absorbed by the surrounding material. However, water saturation by exposing samples above water or in a fog chamber might lead to leaching of alkali and thus to a reduction in pH due to condensation of water on the surfaces [23]. Bokern [23] observed a reduction in the potassium content of concrete samples between 20% and 40% after 28 days of curing in a fog chamber or above water. The analyses were done on the water below the sample or on the water dropped from the sample into a basin (for the fog chamber). Lindgård et al. [24] also observed extensive alkali leaching on concrete samples exposed over water, depending on sample size, binder type and exposure temperature. Hence, the water-saturation has to be realized with great care in order to prevent leaching.

#### *Limitations of use*

Cáseres et al. [13] pointed out that ISL is not accurate for concretes with a very dense micro-structure. Full saturation cannot be reached for large and dense concrete samples, generating a loss of the cavity water into the concrete. In addition, a slow equilibration of the solution inside the cavities with the surrounding concrete could lead to an underestimation of the final measured pH if the equilibrium is not reached. A long equilibration time can also lead to carbonation issue and thus a decrease of the pH [5].

### **2.3 Ex situ leaching methods**

All ex situ leaching methods (ESL) rely on the same principle (FIGURE 3): 1) grinding the concrete to a powder, 2) leaching of the powdered sample by introducing it to a known amount of deionized water for a certain amount of time, 3) separating the liquid from the solid and 4) analyzing the solution, called the extracted solution. The objective is to extract the elements present in the pore solution and only those, i.e. not the elements sorbed on the hydrated phases or the ASR gel, and not to dissolve hydrates or anhydrous phase. Three variants of ESL methods are discussed below.

#### *Cold water extraction*

Cold water extraction (CWE), often referred to in literature as “ex situ leaching”, has been used in several studies [1, 6, 11, 12, 14-16, 25-29]. For the CWE procedure, the extraction solution is deionized water at room temperature. The extracted solution is either completely analyzed or the pH can be measured directly in the suspension using an electrode designed for that purpose [1]. There are numerous variations of the CWE procedure. One can for example agitate the suspension or not during the leaching step, one can vary the particle size, the liquid to solid ratio (L/S) and/or the leaching time. Alonso et al. [1] studied the influence of the most commonly used parameters and suggested to use the following: stirring, particle size below 80  $\mu\text{m}$ , L/S = 1.0, and leaching time = 5 min.

#### *Hot water extraction*

Hot water extraction (HWE) is described by Bérubé et al. [9, 30]. The sample is pulverized to have a particles size below 160  $\mu\text{m}$ . Ten grams of this powder is mixed with 100 mL of deionized water. This suspension is boiled for 10 minutes and then let to stand overnight at room temperature. The suspension is filtered and the solution is adjusted to 100 mL before analyzing the free alkali content.

#### *Espresso*

HWE was modified by Fournier [Personal communication], leading to the “Espresso” method. Ten grams of the ground sample is put into a Buchner filter covered by a filter paper and the filtration unit is connected to a vacuum pump. About 300 mL of deionized boiling water is then added progressively onto the bed of particles and the vacuum filtration starts immediately. The solution is cooled down and topped up to 500 mL with distilled water before analysis. Espresso is less time consuming and also presents a better repeatability than the classical HWE [Fournier, Personal communication].

#### *Influence of various parameters*

##### *- Sample size and representability*

The size of the sample has to be chosen in order to ensure a good representability of the material. This parameter is especially important for ESL for which a small amount of material is used, and particularly while studying concrete with large aggregates. The aggregate/paste content of the

sample has to be representative of the entire material. It is recommended to have a large enough sample, especially in the case of concrete, and to grind it entirely, even though only a small amount of sample is needed for the ESL test.

- Influence of the presence of aggregates

For the analysis of concrete samples, the influence of the presence of aggregates has to be verified. During testing, the fine ground aggregates can also release elements such as alkali metals in the extracted solution [30]. Hence, a parallel leaching test on only the aggregates should be performed and the results obtained when analyzing the extracted solution should be corrected accordingly [9].

- Addition of water

For ESL methods, the addition of water to the ground material has other consequences besides dilution. The unhydrated part of the cement can be hydrated with the additional water. This secondary hydration leads to a release of OH<sup>-</sup> ions into the solution which might give rise to a higher pH as observed in [6, 12, 16]. Partial dissolution of the hydrated phase can also occur when adding water. A phase prone to dissolution is Portlandite [31], resulting in the release of OH<sup>-</sup> into the solution. This can lead to an overestimation of the pH.

- Particle size and extraction time

The samples need to be ground prior to extraction. Logically the extraction time is closely linked to the particle size [1]: for larger particles, a longer extraction time is required in order to have a proper extraction. However, longer extraction time allows for further dissolution of hydrated phases and/or the secondary hydration. Similarly, fine particles provide a higher specific surface which promotes dissolution of hydrates and secondary hydration products. Hence a good compromise between those two parameters has to be chosen e.g. Alonso et al. [1] suggested for particles below 80 μm an equilibration time of five minutes under stirring.

- Liquid to solid ratio

Some authors [1, 6, 11, 15] measure the pH directly in the suspension. However, the authors of the present paper suggest that for ESL methods, the pH should be calculated based on the elemental composition of the solution as described in section 4. Due to dilution induced by the addition of water, the pH of the pore solution cannot be measured directly on the suspension in a reliable way. In addition, the liquid to solid ratio (L/S) should be high enough to allow extraction e.g. by filtration or centrifuging. On the other hand, it should be low to limit dissolution of phases. A good compromise is L/S = 1.0, according to Räsänen and Penttala [6], Hidalgo et al. [11], Li et al. [12] and Alonso et al. [24].

- Influence of the temperature

One of the differences between the presented ESL methods is the temperature of the extraction solution. The use of boiling water instead of water at 23° C does not seem to have any influence on the extracted alkali concentration when performing HWE as reported by Bérubé et al. [9]; however, the stability of various phases is compromised. This high temperature will lead to the dissolution of ettringite and potentially other hydrates. The possible dissolution of Ca(OH)<sub>2</sub> when adding water will be limited since the solubility is decreasing with temperature.

## 2.4 Fiber optic sensors

### *Description*

Fiber optic sensors (FOS) rely on the combination of an optic fiber with a sensing material which will exhibit different absorbance or fluorescence depending on the pH of the environment. The use of FOS for monitoring the pH of the pore solution of cementitious materials is a recent development [7, 32-36]. For the absorbance-based sensor, the sensing material is generally composed by a pH indicator fixed in a solid substrate (e.g. sol-gel). A color change will be observed if there is an evolution of the pH of the media. The sensing material of the fluorescence-based sensors is a polymer mixed with a dye. This dye presents protonated or deprotonated groups depending on the pH. In all cases, the signal can be calibrated by using the sensors on solutions at different pH. A FOS sensor can be embedded in the sample during the casting or placed in an existing structure [7]. In this latter case, a small cavity is drilled in the material and filled with water prior to the introduction of the sensor. It is then similar to the ISL method presented previously.

### *Limitations*

The solid substrate and the dye have to be chosen carefully according to the material which has to be analyzed. Afterwards, the dye has to be immobilized in a suitable solid substrate (cellulose, sol-gel or polymers). However, dye leaching could occur, leading to a drift of the signal and a gradual deterioration of the probe. For instance, the pH of the environment has to be taken into account. In their study, Nguyen et al. [32] observed a leaching at pH 13.5 and thus limited the study to the range 10 – 13.2. In this range, the chosen probe exhibited a better stability, i.e. 20 months. The choice of the solid substrate will also influence the leaching of the dye. Sol-gel are believed to be less effective than other substrates to prevent the leaching: the lifetime of the probe will then be reduced [Basheer, Personal communication].

## **2.5 Parameters affecting the determination of the pH and the free alkali content**

### *Influence of the filtration*

Filtration has been observed to influence the composition of the extracted solution. For example, the pH of the suspensions obtained after ESL methods has been found to be lowered by 0.1 pH unit after filtration with a nylon filter [1, 6]. Moreover, the slower the filtration the lower is the measured pH [6]. The decrease in pH is most likely caused by trapping OH<sup>-</sup>, Na<sup>+</sup> and/or K<sup>+</sup> ions in the filter. The type of filter seems to play an important role: Nylon, PVDF or PTFE filter appear to retain fewer ions compared to cellulose filters [1].

### *Description of the solution: spectrometry*

In order to determine the elemental composition of the solution (e.g. Na, K, S, Ca, Al, Si, Fe), various instruments can be used e.g. flame spectrometry or inductively coupled plasma spectrometry (ICP). The spectrometry techniques generally involve a complicated calibration which has to be done by matrix reconstruction because of interferences between the different species present in solution. Those interferences have a strong influence on the result, especially for concentrated solutions.

### *pH determination*

If the pH is measured directly with an electrode, e.g. after PWE, one has to keep in mind that the potential of an electrode reflects the activity of the ions and not the concentration. The activity of one element is dependent of the ionic strength of the solution. The activity of an ion in a solution with high ionic strength is always lower than its concentration. Some authors [28] determined the hydroxide concentration in a solution by HCl titration and then calculated the pH according to the formula  $\text{pH} = 14 + \log [\text{OH}^-]$ . This formula does not take into account the ionic strength of the solution and is thus only suitable for diluted solutions. Using it will lead to an overestimation of the pH as the ionic strength of the solution increases.

The calibration of the pH electrode has to be made using a proper range of pH buffers, e.g. 7, 10 and 13. One should also note that pH measurements involving electrodes also suffer from the effect called “alkaline error”. A pH electrode is designed to respond selectively to H<sup>+</sup>. However, alkaline ions can cause interference, especially at high pH, e.g. pore solutions of concrete. As the alkaline ions can replace H<sup>+</sup> in the outer gel layer of the glass membrane, it can result in an underestimation of the pH.

For the methods which do not allow direct pH measurement, e.g. ESL, the authors of the present paper recommend to calculate the pH based on the measured composition of the extracted solution by using thermodynamic modelling tools such as PhreeqC [37] or GEMS [38]. The authors recommend to use the Pitzer approximation to calculate the activity coefficients of the species in solution, as this approximation is valid for solution with high ionic strength such as the pore solution of concrete. For pH calculations based on the ESL results the dilution of ions has to be taken into account. The free water content of the sample is thus to be known. It can be determined by measuring the weight loss after drying to constant mass at 105° C by either TGA (thermogravimetric analysis) or oven drying. The calculated pH values will be strongly dependent on the determined free water content.

### *Free alkali content determination*

The free alkali content relative to the sample mass can be determined directly with ESL methods. The free water content will not influence the result significantly, as it is nearly negligible compared to the high amount of water added during the extraction. The free alkali content can also be calculated based on the composition of the pore solution obtained by PWE. However, the exact free

water content has to be known as it will strongly influence the determination of the free alkali content per gram of sample.

### 3 COMPARISON

TABLE 1 presents a brief overview of the different methods for determining the pH and the free alkali content of the pore solution of concrete. PWE is generally considered as the reference for the analysis of the pore solution. Most authors compare PWE with other methods. Li et al. [21] compare results obtained by ISL and PWE on the same samples. The authors conclude that the methods give comparable results, the difference between the values being lower than 0.2 pH unit. However, such a difference is significant at high pH (logarithmic scale). Another comparison between PWE and ISL performed by Sagiúes et al. [5] revealed that the latter method gives a slightly higher pH (0.08 pH unit). This indicates that the impact of dilution is weaker than e.g. hydration and/or dissolution which would lead to a higher pH.

Other authors compared the data obtained by PWE and CWE [1, 11]. They concluded that the methods give similar results, the pH obtained by PWE being 0.1 pH unit lower than the value obtained by CWE. This is surprising since CWE induces necessarily a dilution of the ions contained in the pore solution of the original samples. It has to be noticed that Alonso et al. [1] only made the study on low pH cement (around pH 11.3), which could explain why there is no significant difference between PWE and CWE: the low alkali concentration will be less influenced by the dilution. Hidalgo et al. [11] observed that the pH after CWE gets lower than after PWE if the L/S increases.

Bérubé and Tremblay [10] compared the amount of alkali in the pore solution obtained after PWE and HWE. The results show similar amount of K for both methods while PWE leads to lower amount of Na. The K/Na ratio was also found to be dependent on the water/cement ratio of the sample and on the pressure during PWE. This dependence with the water/cement ratio was not observed with HWE. Bérubé and Tremblay concluded that Na is more difficult to express than K during PWE and that HWE gives more realistic results.

### 4 RECOMMENDATIONS

Based on this review, some recommendations were established concerning the methods to determine the pH and the free alkali content of the pore solution in concrete (see TABLE 2).

Pore water expression (PWE) is recommended for direct pH measurements, using low pressure i.e. below 250 MPa. However, the applicability is questionable in the case of field concrete due to potential limited amount of free water. PWE may also be applied to determine the free alkali content relative to the sample mass, provided that the amount of free water is known.

Ex situ leaching (ESL) is preferred for free alkali content determination. The pH of the pore solution can be determined based on calculation using Phreeqc or GEMS software after chemical analysis of the extracted solution. However, the free water content of the sample has to be known to correct for the dilution.

Among all the presented methods, it appears that in situ leaching (ISL) should be avoided due to the requirement to have a water saturated sample, which can lead to leaching of ions. In addition, ISL requires long equilibration time, up to one month, during which carbonation can occur. The use of fiber optic sensor (FOS) in existing concrete structures suffers from similar drawbacks as ISL. This method could be of interest for the monitoring of structures, however issues regarding long term stability need to be resolved.

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## 7 FIGURES

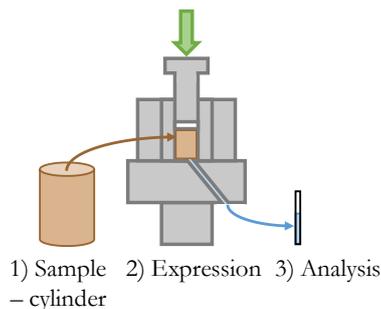


FIGURE 1: Pore water expression (PWE).

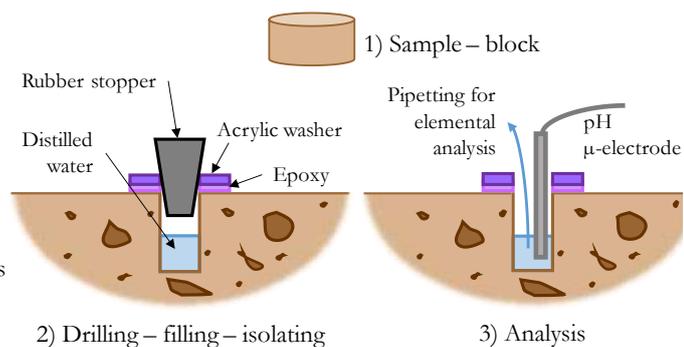


Figure 2: Schematic of the in situ leaching (ISL) arrangement.

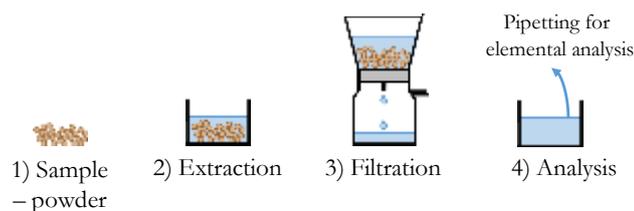


FIGURE 3: Ex situ leaching (ESL) methods. For the “espresso method”, steps 2 and 3 are combined.

TABLE 1: Overview of methods for determining the pH and the free alkali content in concrete

Method	Abbr.	Specimen	Liquid/solid (weight)	pH assessment *	Duration	Main advantages	Main drawbacks	References
Pore water expression	PWE	Cylinder (no pieces)	-	pH electrode or calculation	0.5 - 4 h	- No dilution effect	- Not applicable on relatively dry samples - Possible pressure dependence on the results	[10, 15, 17, 18, 19, 20]
In situ leaching	ISL	Block	-	pH electrode or calculation	1 - 2 months	- Spatial distribution possible	- Not applicable on non-saturated samples - Potential leaching during water saturation - Potential carbonation (long equilibration time)	[5, 13, 21, 22]
Ex situ leaching	ESL	Block	1	-	5 min	- Applicable on relatively dry samples	- Dissolution of solids (low)	[1, 6, 11, 12, 16, 27, 28, 29]
- Cold water extraction	CWE	Powder < 80 µm	-	-	≈ 12 h	- No water saturation required	- Dissolution of solids (medium)	[9, 30]
- Hot water extraction	HWWE	Powder < 160 µm	10	Calculation	5 min	-	- Dissolution of solids (high)	[Foumier, Personal communication]
- Espresso	-	Powder < 160 µm	50	-	-	-	-	[7, 32, 33, 34, 35]
Fiber optic sensor	FOS	Block	-	pH sensor	As required	- Applicable on-site	- Still in development - Limited probe lifetime	

TABLE 2: Recommendations for determining the pH and the free alkali content in concrete

Parameters/techniques	Concerned method	Point of consideration
pH determination	All	- PWE is preferred (the free water content has to be known when using ESL-methods) - For a direct measurement; proper calibration, i.e. constant temperature, pH buffers 7, 10 and 13, and special electrode for high pH - Calculation: the ionic strength has to be taken into account. Thermodynamic modelling tools coupled with the Pitzer database is recommended
Free alkalis content determination	All	- ESL is preferred (the free water content has to be known when using PWE)
Relatively dry samples	All	- ESL should be used (PWE and ISL are not applicable)
Water saturation	PWE, ISL	- Should not be performed (modification of the system, alkali leaching)
Pressure	PWE	- Pressure < 250 MPa (solutions could be more concentrated for higher pressure)
Aggregates	ESL	- Verification of the potential alkali release by ESL - Remove possible large aggregates before extraction
Filtration	All	- Verification of possible adsorption of ions by the filter
Spectrometry	All	- Calibration by matrix reconstitution.