ELSEVIER

Available online at www.sciencedirect.com

SCIENCE DIRECT®

Cement and Concrete Research 35 (2005) 277–283

CEMENT AND CONCRETE RESEARCH

# Ex situ leaching measurement of concrete alkalinity☆

Lianfang Li[a], Jingak Nam[b], William H. Hartt[b],*

[a]W.R. Grace & Co.-Conn, 62 Whittemore Avenue, Cambridge, MA 02420, USA
[b]Florida Atlantic University, SeaTech Campus, 101 North Beach Road, Dania Beach, FL 33004, USA

Received 12 June 2003; accepted 27 April 2004

## Abstract

A new technique involving ex situ leaching (ESL) of concrete particles in deionized water and chemical analysis of the resulting leachant was developed to determine the concrete pore water alkalinity. A water-to-concrete powder ratio no higher than 1 and a leaching time no less than 3 days were mostly used. The concrete pore water hydroxide ion concentration ($[OH^-]_{pore}$) was then calculated based upon a protocol that included several assumptions. It was found that $[OH^-]_{pore}$ was proportional to the cement equivalent alkali content but relatively insensitive to the concrete water-to-cement ratio. Determinations of $[OH^-]_{pore}$ were compared with (1) results from parallel, conventional pore water expression (PWE) experiments using concrete from the same batch, (2) a theoretical estimate of this parameter based upon mix design and cement chemistry of the concretes employed for ESL, and (3) data from the literature. All of these comparisons either directly or indirectly confirmed the validity of the proposed method. However, applicability of the ESL method, as proposed, to concrete containing pozzolans or highly soluble inorganic salts (or both) needs to be further explored.

*Keywords:* pH; Alkalis; Pore solution; Corrosion; Leaching

## 1. Introduction

Pore water alkalinity is now generally recognized as a parameter that affects service longevity of concrete structures. On the one hand, high alkalinity is essential for preservation of embedded steel reinforcement passivation and achieving an acceptably low corrosion rate. Evidence exists that as the pH of concrete pore water increases, the chloride-induced corrosion threshold also increases [1,2]. On the other hand, high pore water alkalinity promotes a reaction with certain alkali-reactive aggregates, which leads to the expansion and possibly the cracking of concrete [3].

The measurement of pore water pH provides a direct indication of concrete alkalinity. Pore water expression (PWE), whereby a cement paste, mortar, or concrete sample is subjected to a sufficiently high pressure that solution is squeezed from the material, has evolved to become the most commonly employed procedure for acquiring pore water for pH analysis [4–6]. Limitations associated with the method include the following: (1) prior water saturation of samples is required; (2) the method is more useful for pastes and mortars since expression yields for concrete, particularly high performance ones, are low.

Methods based upon leaching are alternatives to PWE. Thus, it is generally known that water-soluble species in concrete can be leached by their transport through the porous cementitious structure in response to a chemical potential gradient. The amount of alkaline species in pore water can then be determined indirectly by measuring their concentration in the leachant. Because of path tortuosity, this transport is usually slow; although it is thought to be describable, at least approximately, in terms of an appropriate solution to Fick's second law of diffusion. On this basis, the effective diffusion coefficient, $D_{eff}$, of chloride ions in concrete has been determined to normally be in the range $10^{-10}$ to $10^{-13}$ m$^2$/s, which is several orders of magnitude lower than in bulk liquid solutions. Diffusion data for alkaline ions in concrete are scarce, but a similar transport pattern and comparable $D_{eff}$ to that of chloride ions is expected [7].

An in situ leaching (ISL) method for pore water pH determination has been developed by Sagüés et al. [8] and

---

☆ The findings and opinions expressed here are those of the authors and not necessarily of the supporting organization.

* Corresponding author. Tel.: +1-954-924-7243; fax: +1-954-924-7270.
*E-mail address:* hartt@oe.fau.edu (W.H. Hartt).

0008-8846/$ – see front matter © 2004 Published by Elsevier Ltd.
doi:10.1016/j.cemconres.2004.04.024

Li et al. [9]. Here, a small quantity of distilled water is placed in a small cavity drilled in a concrete specimen. Subsequent to equilibration, the pH of this water is measured and assumed to have approached that of the concrete pore water. Similar to PWE, the ISL method can be employed to chemically analyze for soluble species in addition to $OH^-$ that might be of interest (e.g., $K^+$, $Na^+$, $Ca^{2+}$, $Cl^-$, and $NO_2^-$). Limitations of ISL include the following: (1) moisture saturation is also required, (2) relatively long experimentation times are required to assure equilibration, and (3) the extent to which the pH of the test sample approaches that of the pore water is a concern.

Ex situ leaching (ESL), whereby pH of initially near-neutral distilled water is measured subsequent to its equilibrating with a ground paste, mortar, or concrete sample, provides a third option. In this case, leaching time is relatively short compared to that for ISL since the particulate nature of the sample reduces transport distances. The purpose of the present article is to describe methodology based upon this approach.

## 2. Experimental Procedure

### 2.1. Ex situ leaching

A series of 11.5 × 15.2 × 28.0 cm concrete blocks was made by the Florida Department of Transportation State Materials Office in Gainesville using three different water-to-cement ratios (w/c = 0.37, 0.41, and 0.50) and cements of three different alkalinities. Table 1 lists the composition of the cements and shows that the total alkali content expressed as %$Na_2O$ equivalent (denoted by $Na_2O_e$%) was 0.355, 0.519, and 0.972. These are subsequently designated as “low alkali,” “normal alkali,” and “high alkali,” respectively. Table 2 provides a listing of mix designs and specimen categories. The procedure involved form curing for 3 days followed by air curing indoors in non-air-conditioned space for approximately 3 months. The blocks were then transported to Florida Atlantic University where they were located in air-conditioned space. At this time, the four side faces were coated with epoxy, a bath was mounted on the top 11.5 × 28.0-cm face, and cyclic (1 week wet/1 week dry) ponding with 15 w/o NaCl commenced.

Table 1
Chemical composition (wt.%) of the three cements

| Compound | Low | Normal | High |
|---|---|---|---|
| $SiO_2$ | 21.93 | 21.88 | 20.63 |
| $Al_2O_3$ | 5.16 | 5.64 | 4.44 |
| $Fe_2O_3$ | 3.70 | 3.87 | 2.56 |
| CaO | 65.02 | 64.42 | 63.39 |
| MgO | 1.39 | 0.98 | 3.85 |
| $SO_3$ | 2.38 | 2.87 | 3.96 |
| $Na_2O$ | 0.099 | 0.164 | 0.192 |
| $K_2O$ | 0.39 | 0.54 | 1.19 |
| Equivalent alkali | 0.355 | 0.519 | 0.972 |

Table 2
Concrete mixture proportions

| Specimen designation | Cement alkalinity | w/c | Cement content (kg/m$^3$) | Coarse aggregate (limestone) (kg/m$^3$) | Fine aggregate (silica sand) (kg/m$^3$) |
|---|---|---|---|---|---|
| HA 0.37 | high | 0.37 | 400 | 1004 | 761 |
| HA 0.41 | high | 0.41 | 400 | 1004 | 719 |
| HA 0.50 | high | 0.50 | 400 | 1004 | 625 |
| NA 0.37 | normal | 0.37 | 400 | 1004 | 760 |
| NA 0.41 | normal | 0.41 | 400 | 1004 | 719 |
| NA 0.50 | normal | 0.50 | 400 | 1004 | 625 |
| LA 0.37 | low | 0.37 | 400 | 1004 | 761 |
| LA 0.41 | low | 0.41 | 400 | 1004 | 719 |
| LA 0.50 | low | 0.50 | 400 | 1004 | 625 |

### 2.2. Sample preparation and leaching

After approximately 2 years of cyclic ponding, horizontally oriented cylindrical 5.0-cm-diameter by 11.5-cm-long cores were extracted close to the bottom specimen face where acid solubility analyses indicated that the concrete was chloride-free. The top 1 cm layer of each core was discarded to avoid material that was possibly carbonated. The cores were then crushed and pulverized until all material passed a #50 sieve. The resultant powder from individual cores was then stored in airtight HDPE bottles.

For leaching, approximately 50 g samples of prepared concrete powder were weighed to an accuracy of ± 0.01 g, placed in individual air-tight HDPE bottles, and then mixed with various amounts of deionized water so that the water-to-concrete weight ratio (denoted by $\varphi$) was 0.7, 1.0, 2.0, and 4.0. For most of the leaching experiments, $\varphi = 1.0$ was selected. Leaching was sustained for periods of 1, 3, 10, and 30 days, during which the mixtures were periodically stirred. At the end of the leaching periods (3 days in most cases), the samples were filtered to remove particulates. In cases where some white solid particle suspension remained, a second filtering was performed. The resultant solution was divided into two approximately equal parts, each of which was immediately titrated first for $OH^-$ and then for $Ca^{2+}$ concentration, as will be described later.

### 2.3. Chemical analysis

The $OH^-$ concentration was determined by measuring the potential of a combination pH electrode in the leachant as it was titrated with 0.1 N HCl in 0.4-ml increments. The endpoint for $OH^-$ titration was selected as 7.0 so that any $OH^-$ species that might have already been carbonated during the sample preparation stage were also accounted for. Accordingly, the hydroxide concentration in the leachant ($[OH^-]_{lch}$) was calculated from the expression

$$[OH^-]_{lch} = \frac{V_{HCl}0.1}{V_1} \tag{1}$$

where $V_{HCl}$ is the endpoint volume (in ml) of 0.1 N HCl and $V_l$ is the volume (in ml) of the leachant sample under titration.

Immediately after the $OH^-$ titration, the resulting solution was first adjusted to pH>13 by adding 1 M NaOH solution. It was then titrated for $Ca^{2+}$ concentration employing 0.01 N disodium ethylenediamine tetraacetate dihydrate (EDTA) with hydroxy naphthol blue as the indicator. The endpoint was defined by a change of the solution color from purple to blue. The calcium ion concentration in the leachant ($[Ca^{2+}]_{lch}$) was calculated from the expression

$$[Ca^{2+}]_{lch} = \frac{V_{EDTA}0.01}{V_l} \qquad (2)$$

where $V_{EDTA}$ is the endpoint volume (in ml) of the 0.01 N EDTA. After $[OH^-]_{lch}$ and $[Ca^{2+}]_{lch}$ were obtained, the $OH^-$ concentration and pH of the concrete pore water were calculated according to procedures that are presented in Section 3.2.1.

To assess the accuracy of the titration methods, five solution samples obtained from a saturated $Ca(OH)_2$ solution were separately titrated for $[OH^-]$ and $[Ca^{2+}]$. The standard error for both $[OH^-]$ and $[Ca^{2+}]$ was less than 1%, and the electrical charge of the cation ($Ca^{2+}$) was balanced by that of the anion ($OH^-$) to 99%. Based upon this, it was concluded that the titration methods were sufficiently accurate to be employed for the purposes of this investigation.

### 2.4. Pore water expression

To evaluate the validity of the current ESL method, PWE and ESL were performed on a concrete that was made from a common batch (cement 335 kg/m$^3$, stone 1160 kg/m$^3$, sand 830 kg/m$^3$, and w/c = 0.52). A Type I cement with $Na_2O_e\%$ = 0.99% was used. Subsequent to setting, the concrete was moist cured in a fog room of 100% relative humidity for 28 days. The PWE procedure was the same as has been described previously [9] except that the maximum pressure exerted on a concrete sample was approximately 200 MPa. Since the amount of pore water from each expression was not enough for an accurate $OH^-$ titration, the pH of the expressed samples was measured using a micro-pH electrode following the same procedure as described previously [8,9].

## 3. Results and discussion

### 3.1. Concrete porosity

Fig. 1 shows the measured concrete porosity values based on water absorption capacity [10]. This indicates that concrete porosity increased with increasing w/c but was essentially independent of cement alkalinity content.

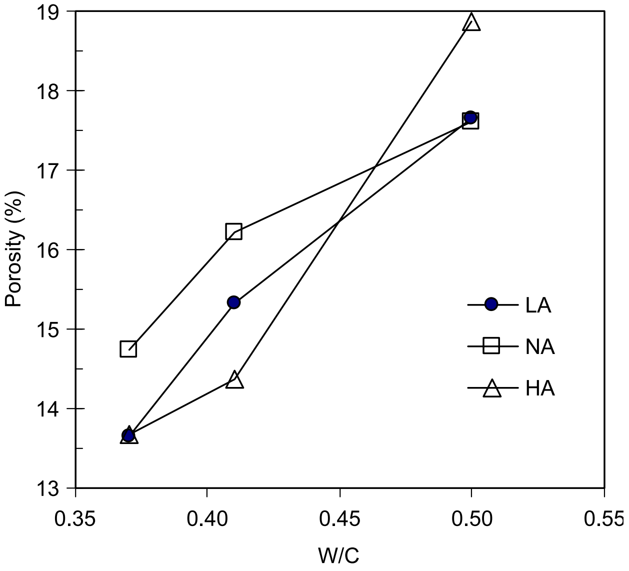

Fig. 1. Measured porosity of the various concrete mixes.

### 3.2. Pore water hydroxide ion concentration

### 3.2.1. Method of calculation

After the concentrations of $Ca^{2+}$ and $OH^-$ in the leaching solution are determined, the $OH^-$ concentration in the pore water of the concrete (denoted by ($[OH^-]_{pore}$) under a fully water-saturated condition can be calculated. This involves the following assumptions:

**Assumption I:** The major cations in the leaching solution are $Ca^{2+}$, $Na^+$, and $K^+$, whereas $OH^-$ is the only major anion. By neglecting other species, the following equation applies:

$$2[Ca^{2+}]_{lch} + [Na^+]_{lch} + [K^+]_{lch} = [OH^-]_{lch} \qquad (3)$$

**Assumption II:** Similarly, the following equation holds for ionic species in concrete pore water before leaching:

$$2[Ca^{2+}]_{pore} + [Na^+]_{pore} + [K^+]_{pore} = [OH^-]_{pore} \qquad (4)$$

**Assumption III:** During the leaching process, equilibrium is established between alkali ions in the concrete pore water and those dissolved into the leaching water. Alkali ions that may be physically or chemically bound to the cement paste are not released into the leaching solution.

**Assumption IV:** Prior to leaching, the cement in the concrete samples is either fully hydrated or the effect of extra cement hydration after concrete pulverizing and remixing with water during leaching is negligible.

It is known that calcium hydroxide crystals constitute 20–25% of the volume of the solids in hydrated cement paste [11]. Nevertheless, the solubility of $Ca(OH)_2$ in high pH concrete pore water is very low, such that at pH>13, the soluble $[Ca^{2+}]$ is much less than that of $[Na^{+}]+[K^{+}]$. Accordingly, Eq. (4) can be simplified as

$$[OH^{-}_{pore}] \cong [Na^{+}]_{pore} + [K^{+}]_{pore} \tag{5}$$

However, $[Ca^{2+}]_{lch}$ in Eq. (3) cannot be neglected because some solid calcium hydroxide crystals are likely to have dissolved when a significant amount of external leaching water is mixed with concrete powder. Based on Assumption III and material balance, the hydroxide concentration in fully water-saturated concrete pore water will be

$$\begin{aligned}[OH^{-}]_{pore} &= [Na^{+}]_{pore} + [K^{+}]_{pore} \\ &= ([Na^{+}]_{lch} + [K^{+}]_{lch})\frac{V_{lch}}{V_{pore}} \end{aligned} \tag{6}$$

where $V_{lch}$ is the total volume of leaching water plus the volume of preexisting pore water in the concrete sample under the exposure conditions and $V_{pore}$ is the total capillary pore volume of the water saturated concrete sample, as calculated by the following equation:

$$V_{pore} = W\rho/d \tag{7}$$

where $W$, $d$, and $\rho$ are the weight, density, and capillary porosity of the concrete sample, respectively. By employing Eq. (3), Eq. (6) can be expressed as

$$[OH^{-}]_{pore} = ([OH^{-}]_{lch} - 2[Ca^{2+}]_{lch})\frac{V_{lch}}{V_{pore}} \tag{8}$$

Lastly, pH of the concrete pore water is calculated as

$$pH = 14 + \log(\gamma[OH^{-}]_{pore}), \tag{9}$$

where $\gamma$ is the activity coefficient of $OH^{-}$, which is approximately 0.7 when $[OH^{-}]_{pore}$>0.1 mol/L [12].

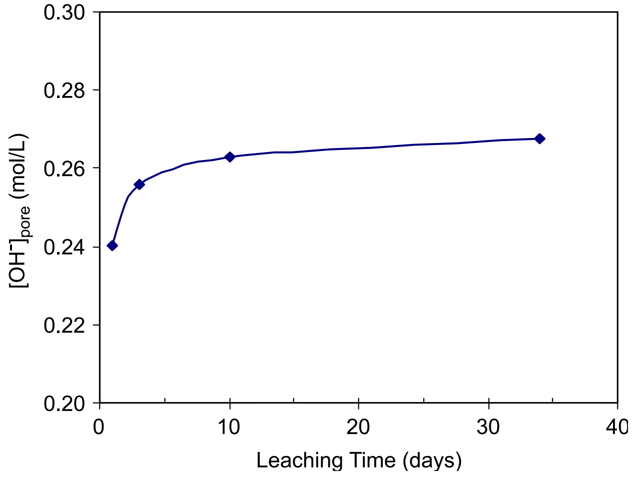

Fig. 2. Effect of leaching time on $[OH^{-}]_{pore}$ of NA 0.50 concrete ($\varphi = 1.0$).

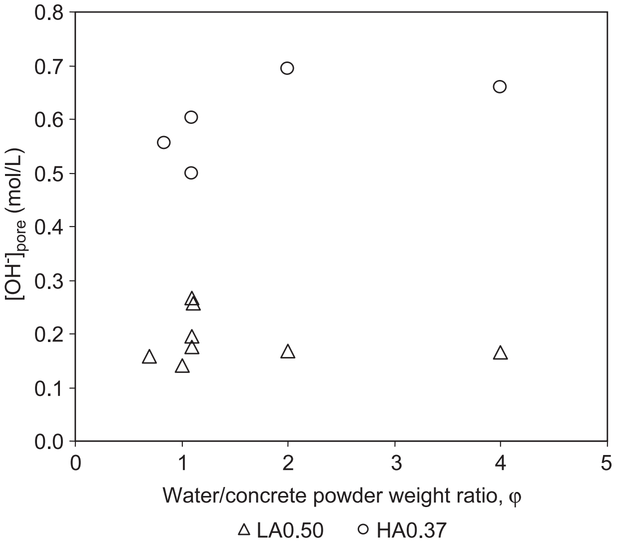

Fig. 3. Effect of $\varphi$ on $[OH^{-}]_{pore}$ for LA 0.50 and HA 0.37 concrete (total leaching time = 3 days).

### 3.2.2. Effect of leaching time on $[OH^{-}]_{pore}$

Fig. 2 shows the effect of leaching time on $[OH^{-}]_{pore}$ for NA 0.50 concrete samples with $\varphi = 1.0$. The data show relatively pronounced accumulation of $OH^{-}$ in the leachant during the initial 3 days; however, the additional increase with more prolonged leaching was modest. Consequently, all subsequent experiments for determination of $[OH^{-}]$ and pH utilized a 3-day leaching period.

### 3.2.3. Effect of relative amount of water during leaching

Fig. 3 shows the effect of $\varphi$ on the measured values of $[OH^{-}]_{pore}$ for the LA 0.50 and HA 0.37 concretes. All samples were subjected to a leaching period of 3 days. For the LA 0.50 concrete, $[OH^{-}]_{pore}$ was relatively unaffected by $\varphi$. For the HA 0.37 concrete, however, a higher $\varphi$ (increased relative amount of water during leaching) increased the measured $[OH^{-}]_{pore}$. This observation for the HA 0.37 concrete may have resulted from hydration of previously unhydrated cement particles in the samples, which caused additional alkali ions to be released into the leaching solution and, hence, to an overestimation of $[OH^{-}]_{pore}$. To minimize this overestimation, $\varphi$ should be maintained as low as possible. For practical proposes, however, $\varphi = 1$ was selected as a compromise so that, on the one hand, sufficient leaching solution is extracted for chemical analysis and, on the other hand, any $[OH^{-}]_{pore}$ overestimation is minimized.

### 3.2.4. Effect of cement alkalinity on $[OH^{-}]_{pore}$

Fig. 4 shows the measured $[OH^{-}]_{pore}$ for the different concrete mixes as a function of $Na_2O_e$%. The $[OH^{-}]_{pore}$ was apparently insensitive to w/c; however, this parameter increased with increasing $Na_2O_e$%. The average $[OH^{-}]_{pore}$ was 0.19 M for the low alkali concrete, 0.24 M for the normal alkali, and 0.53 M for the high alkali.

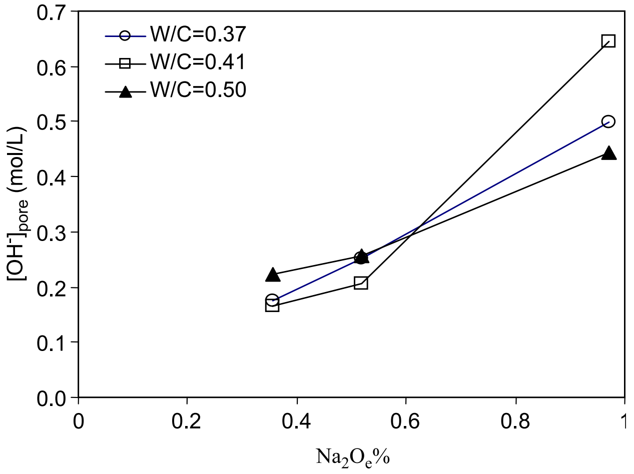

Fig. 4. Measured pore water $[OH^-]$ of the various concrete mixes.

As noted above, the high pH of concrete pore water is a result of the release of alkali ions into pore water during cement hydration. Stochiometrically, the reaction of each mole of cement alkali oxide produces 2 mol of hydroxide, as represented by the following simplified reaction:

$$Na_2O + H_2O \rightarrow 2NaOH \tag{10}$$

On this basis, the theoretical $[OH^-]_{pore}$ is,

$$[OH^-]_{pore} = \frac{C \cdot Na_2O_e\% \cdot h}{50M\rho} \tag{11}$$

where $C$ is the cement content of a concrete mix (kg/m$^3$), $h$ is the degree of cement of hydration (fraction), and $M$ is the molecular weight of $Na_2O$ (g/mol).

By assuming cement full hydration ($h = 1.0$) and no binding of alkali ions to hydrated cement paste, theoretical $[OH^-]_{pore}$ values for concrete with $C = 400$ kg/m$^3$ and $\rho = 0.10$, 0.15, and 0.20 were calculated and are plotted as lines in Fig. 5, in comparison to measured $[OH^-]_{pore}$ values for the concrete mixes investigated here. The theoretical lines lie above the measured values, suggesting that full cement hydration had not been achieved, even with the powdered concrete samples exposed to distilled water for 3 days. On the one hand, additional hydration during leaching may have been minimal, consistent with the concrete powder particulate size being much larger than the cement particle size. Alternatively, the difference between the measured and theoretical $[OH^-]_{pore}$ may partly be due to the binding effects of alkali ions similar to that of chlorides in concrete [13,14].

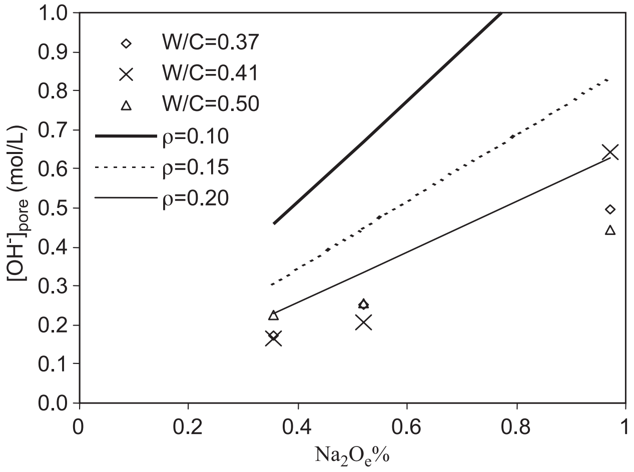

Fig. 5. Comparison of measured $[OH^-]_{pore}$ and theoretical values for concrete with $C = 400$ kg/m$^3$ and $\rho = 0.10$, 0.15, or 0.20 while assuming full hydration and no binding.

### 3.2.5. Comparison between ESL and PWE

As mentioned earlier, the validity of the current method (ESL) was evaluated by comparing the calculated pore water pH based upon it with that measured from PWE for concrete samples from the same batch ($C = 335$ kg/m$^3$, w/c = 0.52, and $Na_2O_e\% = 0.99$). The pH determined by ESL was 13.52 and by PWE, 13.62, indicating general agreement between the two and no significant tendency, if any, for overestimation by the former method.

As a secondary assessment, Fig. 6 plots measured $[OH^-]_{pore}$ values determined by ESL as a function of $Na_2O_e\%$ for the present concrete mixes in comparison to data from the literature [6,15–23], which were determined using samples obtained by PWE. Regardless of the scatter,

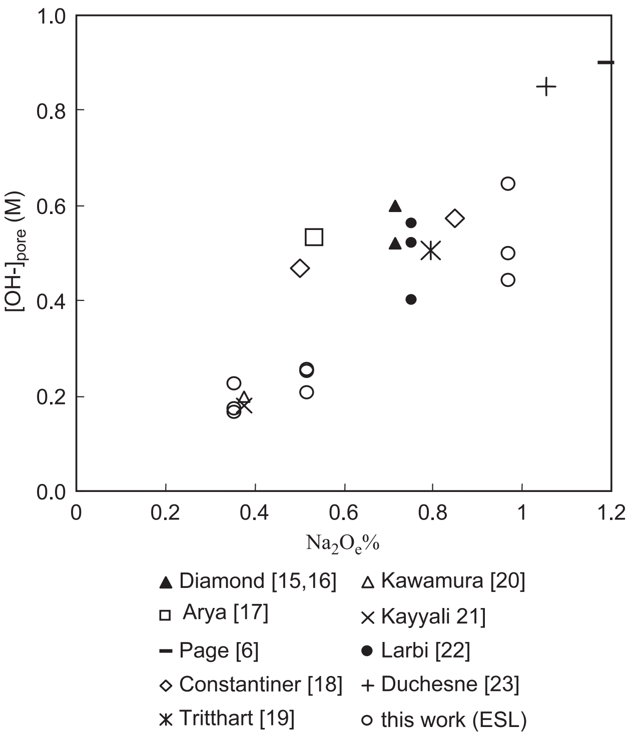

Fig. 6. Relationship between $[OH^-]_{pore}$ and $Na_2O_e\%$ for concrete mixes measured with ESL in this study and those measured with PWE in literature.

the data conform to a common trend in that $[OH^-]_{pore}$ increased with increasing $Na_2O_e$%. Again, there is no indication that the ESL method overestimated $[OH^-]_{pore}$. The simple linear regression for the ESL results shown in Fig. 4 yields the average $[OH^-]_{pore}$ about 0.53 times $Na_2O_e$%. In contrast, Diamond [24] found that $[OH^-]_{pore}$ was about 0.70 times $Na_2O_e$% based on literature data for w/c = 0.50 cement pastes and mortars using PWE. The lower $[OH^-]_{pore}$ values relative to $Na_2O_e$% for the current study compared with those of Diamond [24] may be due to the prolonged air drying for the concrete specimens used in ESL. This possibility is supported by the work of Rivard et al. [25] and Constantiner and Diamond [26] who reported that a portion of the alkali hydroxides that were previously soluble can become fixed onto solid surfaces after prolonged air drying and that such fixed hydroxides do not reenter the solution for a long time after subsequent saturation of the concrete.

An advantage of the ESL method compared to ISL and PWE, in addition to its applicability to high performance concretes and the fact that experimentation times are relatively short, is that it can be employed to calculate alkalinity of pore water in cases of undersaturation by assuming water occupies only a fraction of the available pore space (see Eqs. (7)–(9)). However, additional experimentation is necessary to determine applicability of the ESL method, as proposed, to concretes containing pozzolans or highly soluble inorganic salts (or both).

## 4. Conclusions

1. A new ESL method for determining concrete pore water alkalinity has been developed. The method is relatively simple and is applicable to concrete of various water-to-cement ratios. A water-to-concrete powder ratio of 1:1 and a minimum leaching time of 3 days are recommended.
2. Preliminary comparisons of pore water pH data using ESL with parallel PWE measurements and with data in the literature confirmed validity of the ESL method.
3. Concrete pore water hydroxide concentration (and hence pH) was found to be proportional to the cement equivalent alkali content but essentially independent of water-to-cement ratio.

## Acknowledgements

The authors acknowledge Dr. Alberto A. Sagüés at the University of South Florida for providing the equipment and necessary assistance in performing the pore water expression and associated pH measurement. Particularly appreciated is the financial support that was provided by the Florida Department of Transportation.

## References

[1] D.A. Hausmann, Steel corrosion in concrete—How does it occur? Mater. Prot. 6 (11) (1967) 19–23.
[2] L. Li, A.A. Sagüés, Chloride corrosion threshold of reinforcing steel in alkaline solutions: I. open-circuit immersion tests, Corrosion 57 (1) (2001) 19–28.
[3] M.H. Shehata, M.D.A. Thomas, The effect of fly ash composition on the expansion of concrete due to alkali–silica reaction, Cem. Concr. Res. 30 (7) (2000) 1063–1072.
[4] P. Longuet, La protection des armatures dans le béton armé élaboré avec des ciments de laitiers, Silic. Ind. 8 (1976) 321–328.
[5] R.S. Barneyback, S. Diamond, Expression and analysis of pore fluids from hardened cement pastes and mortars, Cem. Concr. Res. 11 (2) (1981) 279–285.
[6] C.L. Page, O. Vennesland, Pore solution composition and chloride binding capacity of silica fume cement pastes, Mater. Struct. 16 (1983) 19–25.
[7] J. Marchand, E. Samson, Y. Maltais, R.J. Lee, S. Sahu, Predicting the performance of concrete structures exposed to chemically aggressive environment—field validation, Mater. Struct. 35 (12) (2002) 623–631.
[8] A.A. Sagüés, E.I. Moreno, C. Andrade, Evolution of pH during in-situ leaching in small concrete cavities, Cem. Concr. Res. 27 (11) (1997) 1747–1759.
[9] L. Li, A.A. Sagüés, N. Poor, In-situ leaching investigation of pH and nitrite concentration in concrete pore solution, Cem. Concr. Res. 29 (3) (1999) 315–321.
[10] C642-97 Standard Test Method for Density, Absorption, and Voids in Hardened Concrete, American Society for Testing and Materials, Volume 04.02, West Conshohocken, PA., October 2001.
[11] P.K. Mehta, Concrete—Structure, Properties, and Materials, Prentice-Hall, Englewood Cliffs, NJ, 1986.
[12] E. Samson, G. Lemaire, J. Marchand, J.J. Beaudoin, Modeling chemical activity effects in strong ionic solutions, Comput. Mater. Sci. 15 (1999) 285–294.
[13] H.F.W. Taylor, A method for predicting alkali ion concentrations in cement pore solutions, Adv. Cem. Res. 1 (1) (1987) 5–16.
[14] S.Y. Hong, F.P. Glasser, Alkali binding in cement pastes: Part I. The C-S-H phase, Cem. Concr. Res. 29 (12) (1999) 1893–1903.
[15] S. Diamond, Effects of two Danish flyashes on alkali contents of pore solutions of cement–flyash pastes, Cem. Concr. Res. 11 (3) (1981) 383–394.
[16] S. Diamond, Effects of microsilica (silica fume) on pore-solution chemistry of cement pastes, Commun. Am. Ceram. Soc., (1983 May) C82–C84.
[17] C. Arya, Y. Xu, Effect of cement type on chloride binding and corrosion of steel in concrete, Cem. Concr. Res. 25 (4) (1995) 893–902.
[18] D. Constantiner, S. Diamond, Pore solution analysis: are there pressure effects?in: K.L. Scrivener, J.F. Young (Eds.), Mechanisms of Chemical Degradation of Cement-Based Systems, E&FN Spon, London, 1997, pp. 22–29.
[19] J. Tritthart, Chloride binding in concrete. II. The influence of the hydroxide concentration in the pore solution of hardened cement paste on chloride binding, Cem. Concr. Res. 19 (5) (1989) 683–691.
[20] M. Kawamura, O.A. Kayyali, M.N. Haque, Effects of a flyash on pore solution composition in calcium and sodium chloride-bearing mortars, Cem. Concr. Res. 18 (5) (1988) 763–773.
[21] O.A. Kayyali, M.N. Haque, Environmental factor and concentration of $Cl^-$ and $OH^-$ in mortars, J. Mater. Civ. Eng. 2 (1) (1990) 24–34.
[22] J.A. Larbi, A.L.A. Fraay, J.L. Bijen, The chemistry of the pore fluid of silica fume-blended cement systems, Cem. Concr. Res. 20 (4) (1990) 506–516.

[23] J. Duchesne, M.A. Berube, Evaluation of the validity of the pore solution expression method from hardened cement pastes and mortars, Cem. Concr. Res. 24 (3) (1994) 456–462.

[24] S. Diamond, Mechanisms of alkali–silica reaction, Alkali–Aggregate Reaction, . Proceedings of the 8th International Conference on Alkali–Aggregate Reaction, Kyoto. Elsevier, Oxford, UK, 1989, pp. 83–94.

[25] P. Rivard, M. Berube, G. Ballivy, J. Olliver, Effect of drying–rewetting on the alkali concentration of the concrete pore solution, Cem. Concr. Res. 33 (6) (2003) 927–929.

[26] D. Constantiner, S. Diamond, Fixation of alkalis in cement pore solutions, in mechanisms of degradation of cement based systems, in: K.L. Scrivener, J.F. Young (Eds.), E&FN Spon, London, 1997, pp. 67–74.