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# In situ leaching investigation of pH and nitrite concentration in concrete pore solution

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## Abstract

Holes 3- to 5-mm in diameter were drilled in concrete and mortar specimens with and without calcium nitrite corrosion inhibitor. The holes were partially filled with distilled water to leach out soluble ions from the surrounding pores. The pH in the solution inside the holes was periodically monitored with a micro-pH glass electrode and a silver-silver chloride reference electrode. A small fraction of the solution ($\sim$10 μL) was also periodically extracted for spectrophotometric nitrite content determination. The terminal nitrite and pH values of the water in the holes matched the pore water compositions obtained in confirmatory tests using a conventional pore solution expression technique. The specimens without corrosion inhibitor yielded terminal pH $\sim$ 13.4. Specimens with nitrite inhibitor had pH $\sim$ 0.3 units lower than those without inhibitor. The terminal solution nitrite ion content was $\sim$8,000 ppm, which indicated that $\sim$10% of the total admixed nitrite was present in the pores. The pH drop was found to be quantitatively related to limited solubility of $Ca(OH)_2$ and its precipitation upon introduction of $Ca(NO_2)_2$. © 1999 Elsevier Science Ltd. All rights reserved.

*Keywords:* pH; Pore solution; Corrosion; Diffusion; Nitrite

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Calcium nitrite is increasingly being used as an inhibitor to protect reinforcing steel bars in concrete from chloride-induced corrosion [1,2]. The extent of corrosion inhibition is expected to be related to the portion of the inhibitor actually dissolved in the pore solution. The dissolved portion can be a small fraction of the total, as was observed in the case of sodium nitrite [3]. Another important corrosion initiation aspect of the pore water chemistry is its pH [4,5], which may be reduced upon the introduction of a highly soluble calcium salt. The objective of the investigation described here was to use a recently developed in situ leaching method [6] to determine the pH and nitrite concentration of the pore solution in concrete and mortar specimens containing a commercial calcium nitrite corrosion inhibitor. The results were compared with those obtained by conventional pore water expression procedures.

## 1. Experimental methods

### 1.1. Specimen preparation

### 1.1.1. Concrete specimens

The in situ leaching method employed has been described earlier [6] in detail. Cylindrical specimens (100 × 200 mm) with and without corrosion inhibitor were cast as part of large mix batches (>0.26 $cm^3$ each) according to the mix design shown in Table 1. The admixed corrosion inhibitor was a commercial product of W.R. Grace & Co.-Conn. (DCI™ S Corrosion Inhibitor, Cambridge, MA, USA), which consists of a water solution with about 30% weight (max) of calcium nitrite and 5% weight (max) of calcium nitrate. The mixing water reported in Table 1 included the amount of water from the inhibitor solution. The specimens were cast in plastic molds, demolded after 24 h and then cured in limewater for 160 days. (Separate tests with duplicate specimens showed that some nitrite loss to the limewater during curing did take place. However, total nitrite recovery was found to be above $\sim$86% at $\sim$1 cm below the lateral cylinder surface.) One cylinder from each mix was then cut transversely in half with a diamond saw. Three holes $\sim$5 mm in diameter and $\sim$30 mm deep were drilled

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Table 1
Concrete and mortar specimen mix design

| | Concrete control (CCTR) | Concrete with inhibitor (CDCI) | Mortar control (MCTR) | Mortar with inhibitor (MDCI) |
|---|---|---|---|---|
| Cement type | II | II | I | I |
| Cement content (kg/m$^3$) | 391 | 391 | 708 | 702 |
| Alkali (as $Na_2O$) in cement (wt.%) | 0.51 | 0.51 | 0.39 | 0.39 |
| Water (kg/m$^3$) | 149 | 160 | 319 | 315 |
| Fine agg. (sand) (kg/m$^3$) (SSD) | 709 | 696 | 1173 | 1164 |
| Coarse agg. (kg/m$^3$) (SSD) (limestone, max. agg. size 1 cm) | 957 | 948 | 0 | 0 |
| Inhibitor (L/m$^3$) | 0 | 22 | 0 | 37 |
| Water/cement ratio | 0.38 | 0.41 | 0.45 | 0.45 |

perpendicular to each of the freshly cut surfaces with a masonry drill bit. The holes were equidistant to the center of the cylinder and ~30 mm apart from each other. The holes were carefully cleaned after being drilled to remove all traces of dust. An acrylic washer was then attached to the rim of each hole with a fast curing epoxy. Immediately after that, 0.4 mL of distilled water was injected into each hole with a syringe, and rubber stoppers were pushed into the acrylic washers. The solution inside the hole was thus completely separated from the outside environment. The prepared specimens (Fig. 1) were then placed inside a closed ~100% relative humidity (RH) chamber so that the concrete remained saturated with water (the preparation procedure was performed quickly to minimize evaporation). A tray filled with saturated calcium hydroxide solution was placed inside the chamber to act as a $CO_2$ trap.

#### 1.1.2. Mortar specimens

Small mortar cylinders (15 × 60 mm) and mortar cubes (50 × 50 × 50 mm) with and without inhibitor were cast according to the mix designs in Table 1. The specimens were kept in their molds for 24 h and then cured inside a 100% RH chamber for 9 days. Three holes with a diameter of ~3 mm and depth of 30 mm were drilled on the top surface of each cube. There were two cubes in each group. The preparation procedure was the same as in the concrete specimens except that the holes were 3 mm in diameter and only 0.2 mL of distilled water was injected into each hole. The small mortar cylinders were used only for pore solution expression experiments after a curing period of 2 weeks.

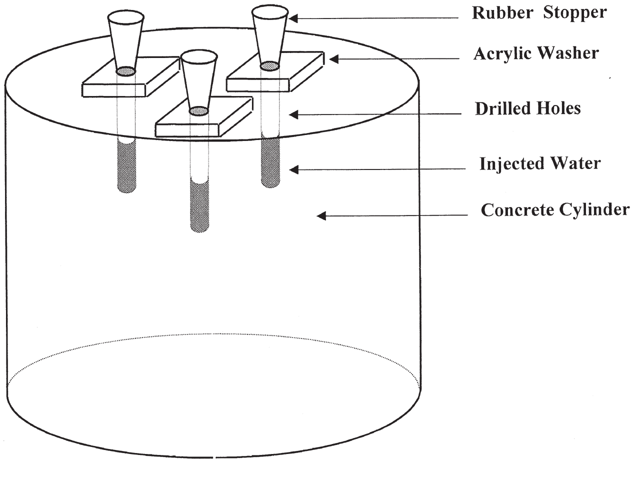

Fig. 1. Concrete cylinder arrangement for pH and nitrite measurements.

### 1.2. pH measurement

The pH of the solution in the holes was measured by means of a MI-405 micro-pH glass electrode and a silver-silver chloride reference electrode. Both electrodes had an outside diameter of ~2 mm. The holes on the concrete cylinders were wide enough that both electrodes could be inserted into the same hole to measure the pH. However, the holes on the mortar cubes were not large enough for the two electrodes to be inserted together. Hence, one of the holes on each cube was always used for the reference electrode while the pH electrode was inserted into either of the other two holes. The pH was calculated from inter-electrode potential measurements made with a Corning Model 140 pH meter (Scientific Instruments, Science Products, Corning Glass Works, Medfield, MA, USA) (input impedance ~$10^{12}$ Ω, bias current 1 pA) in the voltmeter mode. An external multimeter was connected to the electrometer output to achieve a resolution of 0.1 mV. Since the solution resistance between two holes on the mortar specimen was many orders of magnitude smaller than the input resistance of the electrometer, ohmic potential drop errors were negligible. Switching the position of the pH and reference electrode revealed no artifacts from junction potential difference of similar sources. The purpose of using small-sized holes was to accelerate equilibration between the solution in the hole and the surrounding pore water, as discussed in detail in Sagüés et al. [6]. Before and after each potential measurement, the electrodes were tested in standard pH 10, 12, and 13 buffer solutions. An effective calibration slope was obtained that minimized the alkaline error in the range of interest and was used to calculate the in situ pH. The change in the pH of the buffers due to temperature fluctuation was accounted for in the pH calculation. The room temperature

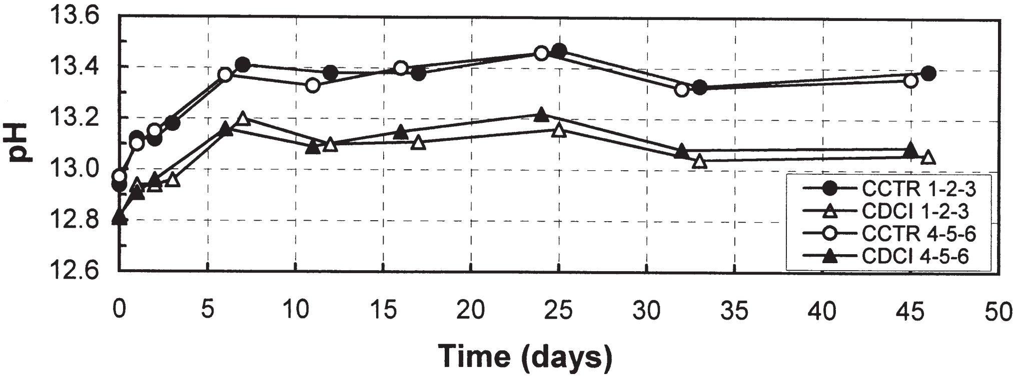

Fig. 2. Evolution of pH in concrete holes (calibrated to 21°C).

was 21 ± 2°C during the testing period. The pH of pore solution expressed from the mortar cylinders was also measured with the same two electrodes and the method described above.

Accuracy of pH measurements was verified by separate tests with diluted samples of the solution in the holes. The tests used the same set of electrodes in a range where alkaline error was negligible (a slope of 59 ± 1 mV/decade was obtained in that range). After dilution correction, the separate tests returned pH values typically within 0.05 of the in situ measurements.

### 1.3. Pore solution expression

A 20-mm bore pore solution expression piston was used to apply a nominal pressure of ∼650 MPa in gradual steps over ∼20 min. The procedure was similar to that described by Barneyback and Diamond [7]. Approximately 0.5 to 1 mL of pore solution was obtained from each mortar cylinder. The expressed pore solution was used for pH measurement and nitrite concentration analysis.

### 1.4. Nitrite concentration analysis

A small pipette was used to extract ∼10 μL of the solution from the holes on the concrete cylinders and mortar cubes at various time after the initiation of the experiment. The amount of extracted solution was determined to an accuracy of 0.1 mg while transferred into a 100-mL volumetric flask bottle placed on an analytical balance. The flask was then filled to 100 mL with distilled water. Further dilution was made when necessary. Nitrite in the resulting dilute sample was determined through formation of a reddish purple azo dye produced at pH 2.0 to 2.5 by coupling diazotized sulfanilamide with N-(1-naphthyl)-ethylenediamine dihydrochloride [8]. The intensity of the color was measured with a Milton Roy Spectronic 20D spectrophotometer (Milton Roy Co., Ivyland, PA, USA) at the wavelength of 543 nm. Calibration was performed with 0–250 μg/L $NO_2^-$-N sodium nitrite stock solution. Regression on the standard calibration curve in that range yielded a slope (calibration factor) of 0.0035 L/μg and a coefficient of determination ($R^2$) of 0.9999. Based on replicate analyses of extracted samples, the relative standard deviation (RSD) of this method was 2%. The expressed pore solutions from the mortar cylinders were also analyzed for nitrite in the same manner after appropriate dilution.

## 2. Results

### 2.1. pH in concrete and mortar cavities

Fig. 2 shows the evolution of pH of the solution inside the concrete holes prepared as described in section 1.1.1.

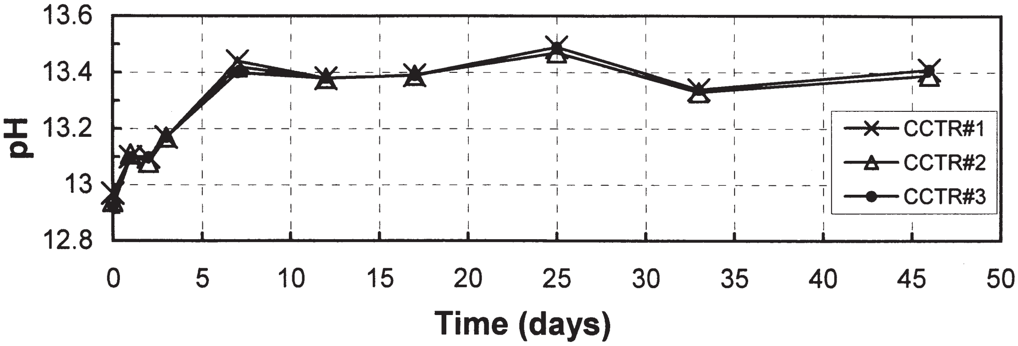

Fig. 3. pH evolution of the solution inside three holes on the same concrete cylinder CCTR1-2-3 showing similar behavior (calibrated to 21°C).

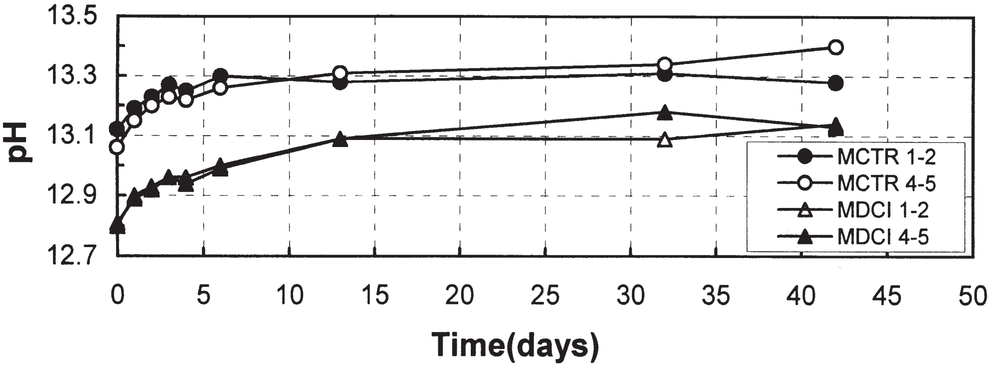

Fig. 4. Evolution of pH in mortar holes (calibrated to 21°C).

The first measurement took place ~4 h after the distilled water was injected into the holes. Each data point represents the average pH measurements from three holes on the same cylinder. As can be seen in Fig. 3, the individual pH values for the three holes in a given specimen were very close to each other. For the two control cylinders without any corrosion inhibitor (CCTR 1-2-3 and CCTR 4-5-6, each number in the specimen name representing a hole on that specimen), the pH rapidly approached 12.95 in day 0. The pH then increased over a week to ~13.4, after which the hydroxides seemed to have reached near-equilibrium between the hole solution and the surrounding concrete. For concrete cylinders with corrosion inhibitor (CDCI 1-2-3 and CDCI 4-5-6), the pH reached ~12.8 (close to that of $Ca(OH)_2$) in day 0. After that, pH increased over a week to ~13.15 and stayed near ~13.1 for the rest of the testing period. The results clearly indicate that the pH value with corrosion inhibitor was ~0.3 lower than that without corrosion inhibitor.

The results of pH measurements from mortar cubes (Fig. 4), were very similar to those from concrete cylinders. Each data point represents the average of two holes on the same cube. The initial pH for the two control cubes without any corrosion inhibitor (MCTR 1-2 and MCTR 4-5) was ~13.1. The pH then increased over a week to a near-equilibrium value of ~13.3. For mortar cubes with corrosion inhibitor (MDCI 1-2 and MDCI 4-5), the pH was ~12.8 at day 0, and then increased slowly to a terminal value of ~13.13. The terminal pH for mortar cubes with corrosion inhibitor was ~0.2 less than that for cubes without corrosion inhibitor.

### 2.2. Nitrite in concrete and mortar cavities

The concrete and mortar specimens showed similar behavior. The measured nitrite concentrations inside the concrete cylinder holes with corrosion inhibitors are shown in Fig. 5. The first measurement was taken at day 5. The nitrite concentration in the solution was found to be ~2,000 ppm. The nitrite concentration increased slowly and appeared to reach a terminal level of ~8,000 ppm in 102 days. The nitrite concentration in the holes on the mortar cubes (Fig. 6) reached ~2,200 ppm at day 0. After that, the concentration

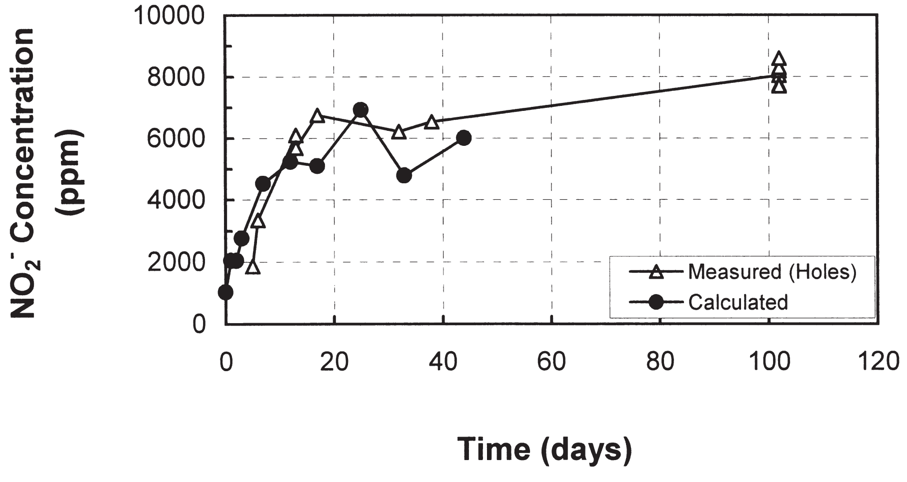

Fig. 5. Evolution of $NO_2^-$ concentration in concrete holes. (Data from day 0 to day 45 represent the average of two holes from CDCI 1-3, and data for day 102 represent the six holes from CDCI 1-2-3 and CDCI 4-5-6.)

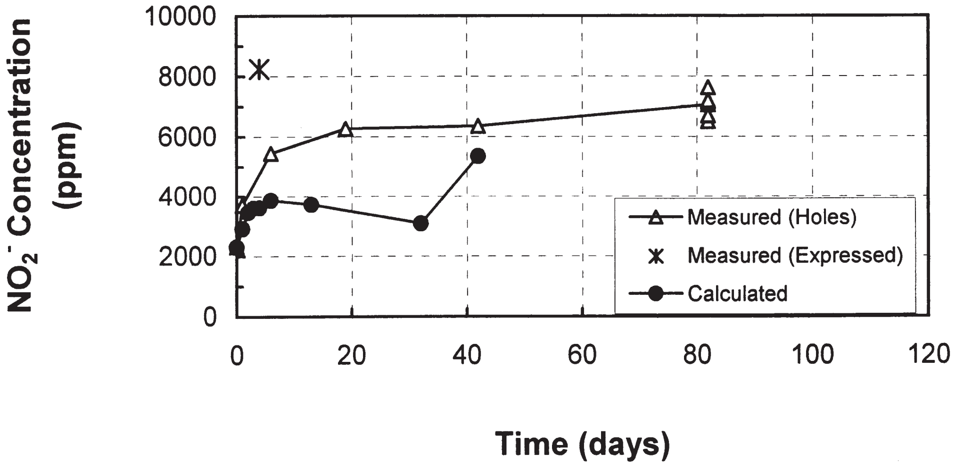

Fig. 6. Evolution of $NO_2^-$ concentration in mortar. (Data from day 0 to day 42 represent the average of two holes from MDCI 4-5, and data for day 82 represent the six holes from MDCI 1-2-3 and MDCI 4-5-6.)

gradually increased and reached ~7,100 ppm at day 82. (The pH measurement was not performed after 50 days because the amount of water left inside most of the cavities was insufficient for a pH measurement.)

### *2.3. pH and nitrite in expressed mortar pore solutions*

The pH values of pore solutions expressed from small mortar cylinders (average of two tests) with and without inhibitor were very close to those measured on mortar cubes from the same batch with the in situ leaching method (average of four holes), as shown in Fig. 7. The nitrite concentration in the expressed mortar pore solution (average of two tests) was ~8200 ppm (shown in Fig. 6), which was close to the terminal values measured with the in situ leaching method.

## 3. Discussion

### *3.1. Evolution of pH and nitrite concentration in the cavities*

The basic aspects of the in situ leaching technique have been presented in a recent publication by Sagüés et al. [6]. The time evolution observed here of pH within the cavities is in agreement with that previous work. The predictive model by Sagüés et al. [6] suggests that after approximately a week the pH in cavities of the size and water content used here may reasonably approach the pH of the pore water.

The in situ leaching method has been used here for the first time to examine corrosion inhibitor content in the pore water. The spectrophotometric analysis technique used had ample sensitivity to achieve good experimental resolution at the levels investigated. Extraction of ~10 μL samples of water was achieved routinely and accurately without specialized equipment. The procedure usually left enough remaining cavity water to allow for several subsequent extractions without need for replenishing. The results indicate that the characteristic time (to reach two-thirds of the terminal value) of nitrite concentration evolution in the cavity was approximately 10 days. Charge neutrality, other ionic coupling effects, and binding may be dominant in the transport of nitrite ions through concrete. Ignoring those effects, application of the model by Sagüés et al. [6] to the observed characteristic time and present conditions would yield $10^{-8}$ $cm^2$/sec as an order-of-magnitude estimate for the apparent nitrite diffusion coefficient.

### *3.2. Amount of nitrite present in the pore water*

The apparent terminal nitrite concentrations in the concrete and the mortar cavities were 8,000 ppm and 7,100 ppm, respectively, which can be compared with the 8,200 ppm observed in the pore water extraction from mortar samples. The leaching of nitrite from concrete into the cavity water was a slow process; near-equilibrium was reached in ~100 days. It is instructive to compare the nitrite amount present in the pore water with the total amount of nitrite added as an admixture. For simplicity, it may be assumed that concrete has a nominal porosity of 10% and there is no interaction between aggregates and inhibitor. A "total" nitrite concentration was then calculated by supposing that all

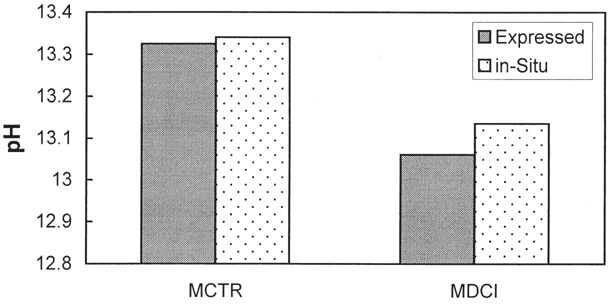

Fig. 7. Comparison of pH measured in expressed pore solution and with the in situ method.

the nitrite admixed per Table 1 had gone into the water-saturated pores. The "total" concentration thus calculated was ~70,000 ppm for both materials, implying that only ~1/10 of the admixed inhibitor was present in the pore solution. Much of the remaining inhibitor is expected to be present as reversibly bound to the concrete matrix, since extraction of a large percentage of the admixed nitrite is achieved by leaching powdered concrete in larger volumes of fresh water [9]. Measurements reported by Corbo and Farazam [3] of solutions obtained by pore water expression of mortar with admixed sodium nitrite inhibitor revealed a ratio of nitrite in pore solutions to "total" admixed nitrite similar to that obtained here.

### 3.3. Interplay between inhibitor concentration and pH of the pore water

The results showed that concrete and mortar specimens with admixed corrosion inhibitor had pH values of ~0.3 and 0.2 pH units, respectively, less than those of the corresponding mixes without inhibitor. The pH drop can be interpreted as a result of the limited solubility of $Ca^{2+}$ ions. Calcium nitrite is highly soluble in neutral water (46 g at 0°C and 89 g at 91°C in 100 mL of water for $Ca(NO_2)_2 \cdot 2H_2O$) [10]. However, in solutions of very high pH value the concentration of $Ca^{2+}$ ions is strongly limited by the solubility product of $Ca(OH)_2$ ($K_{sp} = 1.3 \times 10^{-6}$ at 25°C) [11]. For example, in a solution of pH 13 at 25°C the solubility of $Ca^{2+}$ is $\sim 8 \times 10^{-5}$ mol/L, which is about 1/200 of the concentration of a pH 12.6 solution containing only saturated $Ca(OH)_2$ at the same temperature. Since the concrete pore solution without corrosion inhibitor had pH ~13.4, the equilibrium amount of $Ca^{2+}$ ions was very small. The presence of calcium nitrite in the pore solution causes part of its $Ca^{2+}$ ions to react with the $OH^-$ ions in the solution to precipitate calcium hydroxide as in Eq. (1):

$$Ca^{2+} + 2OH^- \rightarrow Ca(OH)_2(s). \tag{1}$$

The precipitation of $Ca(OH)_2$ (and consequent reduction in pH) takes place until a new equilibrium is reached in accordance with the value of the solubility product. Charge neutrality has to be maintained by replacing $OH^-$ ions with an equal amount of $NO_2^-$ ions if the total alkali content in the pore solution is assumed to be unaffected by the introduction of calcium nitrite. The $NO_2^-$ concentration in the pore solution (8,000 ppm, or 0.17 M) greatly exceeds that of $Ca^{2+}$ in the pH range of interest. The pH depression due to the presence of the inhibitor can then be simply estimated from Eq. (2):

$$[OH^-]_n - [OH^-]_i = [NO_2^-] \tag{2}$$

where the subscripts *i* and *n* correspond to the conditions with inhibitor and without inhibitor, respectively. Therefore, in the pore solution, the nitrite concentration can be calculated according to:

$$[NO_2^-] = \frac{10^{(pH_n - 14)}}{\gamma_n} - \frac{10^{(pH_i - 14)}}{\gamma_i} \tag{3}$$

where $pH_i$ and $pH_n$ are the pH, and $\gamma_i$ and $\gamma_n$ are the activity coefficients of $OH^-$ ions in pore solution in concrete and mortar with and without inhibitor, respectively. Eq. (3) was applied for each test date to the results from the pH measurements of specimens with inhibitor (CDCI 1-2-3 and MDCI 4-5) and to the average of the corresponding specimens without inhibitor (CCTR 1-2-3 and MCTR 4-5) measured simultaneously. The results of the calculations by assuming $\gamma_i$ and $\gamma_n$ to be 1 are presented in Figs. 5 and 6 for comparison with the nitrite concentrations obtained by direct spectrophotometric analysis of the cavity water. The nitrite concentrations estimated from the pH difference approximate the direct nitrite measurements reasonably for the concrete specimens. There was only rough agreement between the calculated and measured nitrite values for mortar specimens, possibly because of difference in the hydration evolution between the control and nitrite specimens. Agreement for both concrete and mortar could be closer than indicated in Figs. 5 and 6 since the $OH^-$ activity coefficient (unknown but assumed to be 1 for the calculations) is likely to be approximately 0.7–0.8 [12]. The resulting higher calculated values would then better approach the measured nitrite concentrations.

### 3.4. Implications

The inhibitor presence at the level investigated here reduced pore water $[OH^-]$ by ~0.13 M. If that had been the only result of the calcium nitrite addition, the chloride concentration threshold $[C_T]$ of the pore water for steel corrosion initiation would have been expected to be reduced, since $[C_T]$ in the absence of other effects is proportional to $[OH^-]$ [4,5,13]. However, calcium nitrite protects steel by increasing the stability of the passive layer on steel surface to an extent that greatly overwhelms the pH reduction, resulting in a large net increase in $[C_T]$.

Measurements of the polarization behavior of steel in water solutions are often conducted to investigate the protection mechanism of calcium nitrite inhibitor and evaluation of its performance [14–17]. The above findings may serve as an indication of a representative level of inhibitor addition to the simulated pore solution. Chloride additions to simulate various levels of concrete contamination should likewise be made by recognizing that only a fraction of the total chloride in the concrete is present in the pore solution [18,19].

## 4. Conclusions

1. An in situ leaching technique provided representative estimates of the pore water nitrite ion concentration and pH of concrete and mortar specimens, in reasonable agreement with the results from conventional pore water expression experiments.

2. Commercial calcium nitrite inhibitor (30% $Ca(NO_2)_2$) addition of 22 L/$m^3$ of concrete resulted in a pore water nitrite ion concentration of ~8,000 ppm (0.17 M) in water-saturated concrete. This amount corresponds to about 1/10 of the admixed inhibitor, if the effective volume porosity is assumed to be ~10%.
3. The pH of the pore water was ~13.4 in concrete without inhibitor and ~13.1 with inhibitor. A comparable pH drop was also observed in the mortar specimens.
4. The pH drop was explained by the limited solubility of $Ca(OH)_2$, and its precipitation upon introduction of calcium nitrite. Calculations based on that mechanism, using the observed pH drop, yielded nitrite ion concentrations in reasonable agreement with those measured by direct analysis.

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