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# Binding of Nitrite in Concrete, Cement Mortar and Paste

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Binding of Nitrite in Concrete, Cement Mortar and Paste


by


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## DEDICATION

I would like to dedicate this work to my parents, Awad AlShehri and Zainh AlShehri, who always kept me in their prayer. Also, to my wife, Amirh. AlShehri, who supported me in my Master's journey. Last, but not least, to my two lovely daughters Jana and Ghina.

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## ABSTRACT

Calcium nitrite as a corrosion inhibitor is mainly used to protect steel reinforcement in concrete by reducing its corrosion rate. Hence the effectiveness of calcium nitrite depends on its availability as a free nitrite in the pore solution. The present research work aims to determine the concrete mixture component mostly responsible for nitrite binding in concrete. Firstly, the experimental program included testing of nitrite binding in cement paste. Secondly, the effect of adding the fine aggregate (mortar mix) on nitrite binding was assessed. Finally, the mix with coarse aggregate (concrete mix) was evaluated. In-situ leaching method was used to obtain the pore solution that was needed.

Measurement of pore solution with the In-situ leaching method and after an average of 48 days showed that concrete specimens have the most nitrite binding capacity. Then, the binding of nitrite was less in mortar and paste specimens respectively. Therefore, concrete specimens bind more nitrite compared to the paste and mortar specimens. The binding ratio increased whenever the nitrite addition level increased. Nevertheless, the free nitrite were similar in the case of the lowest nitrite addition for all types of mix. The pH levels for the mixes with nitrite present, were lower than those of the control mixes.

# CHAPTER 1: INTRODUCTION

## 1.1 Background

Concrete has been used for many years as a building material. Concrete is characterized by being strong in compression conditions and weak in tension conditions. Therefore reinforcing bars, as steel is strong in tension, are used to overcome that weakness. Unfortunately, the corrosion of reinforcing steel is one of the main causes of failure in these reinforced concrete structures. Therefore, protection measures have been developed to stop or reduce reinforcement corrosion such as cathodic protection and corrosion inhibitors. Research on corrosion inhibitors has increased over the last 25 years, particularly on its performance and the degree of protection that it can provide.

Calcium Nitrite (CN) is one of the most commonly used inhibitors and it merits special attention. The Nitrite ion ($NO_2^-$) is present in both a bound condition (chemically or physically attached with hydrated cement components) and a free condition as a part of the pore solution in the concrete. Corrosion of steel rebar starts when the passive film, which is a thin protective surface layer formed around the rebar due to the high alkalinity of concrete, is damaged. Instantly, the free nitrite ion is expected to react with the steel substrate and assist in repairing the damaged passive film. This highlights the importance of the free nitrite participation in the repassivation process.

The literature review showed that there is very little research done on how much free nitrite would be available in the concrete pore solution.

**1.2 Objective**

Free nitrite ions in concrete are expected to be the ones that participate in the repassivation of the passive film, which will lead to reduce the corrosion rate. So in principle the more free nitrite, the better should be the effect on decreasing the corrosion rate. In this study, we seek to control the mix and test paste, mortar, and concrete simultaneously (which has not been sufficiently done in any previous studies) and change the corrosion inhibitor content.

It may be hypothesized that the cement is the main concrete component that reacts with nitrite since it is chemically more reacting than the aggregate. However, it is also possible that nitrite may physically attach to aggregate especially in the transition zone; around the coarse aggregate; which would reduce further the amount of the free nitrite in the pore solution.

This investigation intends to

- Further investigate the above hypothesis by obtaining additional experimental data to find the binding extent of nitrite in paste, mortar, and concrete. The effect on binding will be better elucidated by using for all mixes the same water/cement (w/c) ratio and cement to fine and coarse aggregate ratio.
- Find free nitrite concentration level in concrete by incorporating different levels of total (free plus bound) corrosion inhibitor content.

**CHAPTER 2: LITERATURE REVIEW**

**2.1 Introduction**

A review of the literature on calcium nitrite as a corrosion inhibitor was performed to establish the latest knowledge on its use in reinforced concrete structures. The literature concentrates mainly on how the nitrite inhibitor performs in reducing the corrosion of steel in concrete in different environments.

ISO 8044 (1989) defines the inhibitors as a chemical substance that reduces the corrosion rate once it is available in a suitable amount in the corrosion system without changing any other corrosion agent. The inhibitor that will be discussed here is the inhibitor which is added to water during the mix of concrete as opposed to an inward migrated inhibitor applied to the surface of hardened concrete.

Calcium nitrite for concrete was introduced in the early 1970s and since then it has been the admixed inhibitor for reinforced concrete to be most extensively tested. Also, it has a long record of use in Japan, the US and the Middle East (Elsener, 2011).

**2.2 Mechanism of Corrosion Inhibitor Protection**

In order for the corrosion to occur, four requirements should be present:

- Anodic site: $Fe \rightarrow Fe^{+2} + 2e^-$ anodic reaction

- Cathodic site: $2e^- + H_2O + 1/2O_2 \rightarrow 2OH^-$ cathodic reaction

- Electrolyte: water in the concrete pores will represent the path for ions

- Electrical path: steel will represent the path for electrons to go from anode to cathode

Due to the high alkalinity of concrete, a passive film will be formed around the steel. Once the passive film breaks down (for example due to slow chloride ion contamination of the concrete in seawater), steel corrodes (anodic reaction). Several reactions will take place before rust is formed (Broomfield, 2007). Hence, corrosion inhibition has become one of the protection methods that are used to overcome the corrosion problem.

Corrosion inhibitors can be classified as an anodic, cathodic, or mix type inhibitors based on their mechanism of action. Calcium nitrite is classified as an anodic inhibitor since it acts on the anodic side of the corrosion cell (Koichi, Takao, 2003). Rosenberg reported that calcium nitrite reacts with ferrous ions to form ferric oxide (Eq. (1)):

$$2Fe^{2+} + 2OH^- + 2NO_2^- = Fe_2O_3 + 2NO + H_2O \quad (1)$$
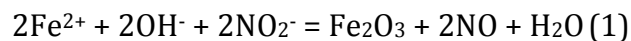
This oxide will repair and stabilize the broken passive film (Rosenberg, Gaidis, 1979). So, corrosion rate will decrease because the reactions that follow the release of the ferrous ion, which is the first corrosion product, are interrupted once ferrous ion reacts with nitrite (M. Balonis and Glasser, 2011).

## 2.3 Effect of Corrosion Inhibitor on Corrosion Rate

McCarthy, Giannakou and Jones (2004) compared different protection measures in reinforced concrete: including a calcium nitrite solution for corrosion inhibition (admixed at 20 L/m$^3$); silane/siloxane for hydrophobic surface treatment; waterproofing admixture and finally the use of controlled formwork permeability. These were used to either delay chloride ingress or mitigate corrosion. Reinforced concrete panels with w/c= 0.55 (incorporating each protection measure separately) were cast. After curing, panels were exposed to wet and dry cycles in a tank that has 3.0 M NaCl exposure. Corrosion potentials,

current densities, chloride level of panels were monitored over the 25 weeks of exposure. Most of the calcium nitrite panels showed no signs of corrosion compared to the other protection measures panels. On visual inspection, after splitting open the panels, rebar conditions confirmed corrosion potential results. It was concluded that nitrite seems to modify the chemistry around the steel rebars, promoting the reaction between the nitrite and ferrous ions, which result in delaying the corrosion initiation.

The State of Hawaii Department of Transportation (HDOT) sponsored a research project at the University of Hawaii at Manoa to study the durability of reinforced concrete in the marine environment and evaluate different admixtures (Joshua and Robertson, 2012).  This project was initiated in 2002 by casting reinforced concrete panels with different admixture including: Fly ash, silica fume, DCI (Darex Corrosion Inhibitor, which is a commercial product that contains about 30% by weight of calcium nitrite as corrosion inhibitor, marketed by W.R. Grace (W.R. Grace 2008)), FerroGard 901, and Rhocete CNI. The water to cement ratio ranged from 0.35 to 0.4.  Panels were located at Pier 38 in Honolulu Harbor on the island of Oahu and exposed to tidal conditions. These panels were removed from the Pier in 2012 for assessment. According to the visual inspection and the half-cell potential readings, which were carried out during the exposure time, only a fewwere showing signs of corrosion. All panels with DCI 20L/m$^3$ and w/c=0.4 were in good conditions  Also,  one of the three silica fume panels, that had 5% replacement of cement and  w/c=0.36 and two of the three fly ash panels that had15% replacement of cement and w/c=0.36 were in good condition. Also, chloride concentration along the concrete cover was evaluated (Robertson, Newtson, 2009) and the chloride concentrations in fly ash and

silica fume panels were significantly lower than the control panels. Moreover, there was no difference in pH between specimens with calcium nitrite or without.

A paper, published in 2005 by S.A. Civjan et al., discussed the effect of admixture combination in inhibiting the corrosion in structural concrete. The test specimens consisted of non-cracked and pre-cracked slabs (180× 305× 305 mm) reinforced at top and bottom with a No. 5 steel bar. There was a control mix and 13 combination mixes of up to three of the following admixtures: calcium nitrite (14 l/m$^3$ addition), disodium tetrapropenyl succinate (1/2% of cement weight), fly ash (15% replacement), silica fume (6% replacement), blast furnace slag (25% replacement). The water/cement ratio was 0.4 for all mixes except two with 0.47. The mix with w/c=0.47 ratio would produce specimens with high permeability which allow for an additional acceleration of testing. The specimens were exposed to a 24 week cycle for 4 1/2 times. In the first 12 weeks, the cycle were as follows: 4 days ponding with 15% NaCl solution followed by 3 days drying. In the second 12 week period, specimens were continuously ponded with 15% NaCl solution (these conditions represent the severe environment). Four tests were used in this study including potential readings, visual inspections, and macro-cell corrosion readings. The paper concluded that calcium nitrite alone provided protection against corrosion in non-cracked concrete but not so in the pre-cracked concrete. The study recommended using double or triple combinations of admixture along with calcium nitrite.

Another study was carried out by I. Kondratove, P. Montes and T. Bremner (2003) to assess the performance of corrosion inhibitors in uncracked and pre-cracked concrete. Reinforced concrete slabs were made with a 0.4 water/cement ratio and an organic inhibitor or calcium nitrite inhibitors. The crack width was either 0.2 or 0.4 mm. After 28

days of moist curing, slabs were installed at a marine environment (at Treat Island, Maine) at the mean high tide that would represent aggressive conditions. Linear polarization resistance was used to monitor the corrosion rate annually. After three years of exposure, for uncracked slabs both inhibitors helped to reduce the corrosion rate compared to the control. For pre-cracked slabs, the corrosion current densities were high in the first 12 months of exposure. Also, the steel rebar surface had a localized pitting corrosion. The study concluded that using corrosion inhibitors in cracked concrete was ineffective.

A study of the effectiveness of corrosion inhibitors in four different types of contamination of concrete was investigated. The four contaminated concrete mixes were as follows: 0.8% chloride, 0.8% chloride +$SO_3$, seawater and brackish water.(O.S. B. Al-Amoudi et al., 2003). Four types of corrosion inhibiting admixture (calcium nitrite, calcium nitrate, and two organic admixtures) were tested in these contaminated concrete types. The specimens with 0.8% chloride and seawater contaminations were partially immersed in 5% NaCl solution and also other specimens were immersed partially in different solutions representing harsh environment. As the study progressed, calcium nitrite specimens were showing a noticeably effect in delaying corrosion compared to other admixture inhibitors. Corrosion current densities of specimens with inhibitors indicated that the passivity of steel was maintained for longer (122 days) than the specimens without corrosion inhibitors (31 days).

## 2.4 Stability of Corrosion Inhibitor

The degree of protection provided by calcium nitrite depends on its availability in concrete once corrosion starts. Thus, H. Liang, N. Poor and A. Sagüés (2003) conducted an experiment to measure the apparent diffusion of nitrite in concrete. Specimens were cast

with Type II cement. Other components were varied such as the water/cement ratio ranging from 0.4 to 0.49 and calcium nitrite (DCI) 11 or 22 L/m$^3$. A 20% of fly ash (as cement replacement) was used in one of the mixes. Specimens were cured in limewater for 60 to 180 days. The leaching experiment was executed in accordance with the specifications of ANSI/ANS16.1-1986 with minor changes (e.g the liquid volume and solution renewal period). Three leaching solutions were used: deionized (DI)water, limewater and synthetic water at temperature either 35-37 $^o$C or 22$^o$C. The leaching time for most specimens was 90 days. The results showed that the apparent diffusion coefficient value is more sensitive to the water/cement ratio than to the leaching solution or the DCI dosage. Also they concluded that adding the fly ash or increasing curing time would reduce the apparent diffusivity.

## 2.5 Binding of Nitrite

The literature review shows that there is a little work that has been done in the binding of nitrite in concrete. Binding of nitrite in concrete may be described on first approximation (Li, et al., 1999) as having a relationship between bound and free nitrite in the form of the Langmuir isotherm:

$$C_B^{-1} = (K\,C_F)^{-1} + C_L^{-1} \qquad\qquad\qquad \text{(Eq-2)}$$

where $C_B$ is the bound nitrite concentration, $C_F$ is the free nitrite concentration, K is the Langmuir absorption coefficient (the binding slope) and $C_L$ is a limiting bound concentration limit.

Li, Sagüés and Poor investigated the binding degree of nitrite in concrete and mortar along with measuring the apparent diffusion coefficient of nitrite in concrete (Li, et al., 1999). Concrete and mortar specimens with and without calcium nitrite have been studied.

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Holes were drilled in each specimen, partially filled with water and kept in a closed chamber ($\sim$100% relative humidity). Periodically, $\sim$10 μL of the hole solution was extracted and analyzed in a spectrophotometer for nitrite content. The results were as follows: after 102 days for concrete and 82 days for mortar, free nitrite in the pore solution was 8,000 ppm and 7,100 ppm respectively. The paper concluded that $\sim$10% of the admixed nitrite was found free (unbound) in pore solution.

Tritthart and Banfill assessed the free nitrite in the presence and absence of chloride. They compared the free nitrite result from paste specimens and water where both mixed with nitrite (Tritthart and Banfill, 2001). The nitrite content was determined by using a spectrophotometer and the chloride content was also determined by potentiometric titration with 0.01 M $AgNO_3$. The results showed that there was a competition between chloride and nitrite for binding with a cement hydration product. The study concluded that the ratio between chloride/nitrite should stay below 1.5 (the authors emphasized that all chloride sources should be taken in consideration).

Also, the chloride/nitrite ratio was addressed by N.S. Berke (Berke, N. and Hicks, M., 2004). N.S. Berke collected a data over 20 years from site and laboratory research that showed the ratio could be varied depend on how much corrosion inhibitors (DCI) were added and the content of Chloride ion in concrete. The highest and lowest ratios were 1.5 and 1.2 respectively (for a 15 l/m³ DCI, Max. Chloride ion 5.9 kg/ m³ & for a 30 l/m³ DCI & Max. Chloride ion 9.5 kg/ m³ respectively).

Ann et al., studied the effect of addition of calcium nitrite-based inhibitors on corrosion, chloride transport, setting time and compressive strength (Ann et al., 2006). For corrosion assessment, four levels of calcium nitrite and five levels of chloride were used.

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Mortar specimens were cast with an embedded steel rebar and the water/cement ratio of 0.5. Then, specimens were cured and stored in a chamber with relative humidity of 95% for 28 days. The corrosion rate measurement using the polarization method showed that the corrosion rate decreased with the addition of calcium nitrite compared to the control specimens. Also, the chloride threshold level increased in the specimens with calcium nitrite. For the highest addition of 12 L/ $m^3$: chloride threshold ranged from 0.73% to 1.95% by weight of cement compared to the control specimens with a range of 0.18% to 0.33% by weight of cement. It is worth mentioning that results from the concrete specimens with corrosion inhibitors showed that the compressive strength after 900 days almost matched the results of 28 days.

Generally, various studies agreed that whenever the nitrite based corrosion inhibitors were added to the mix the chloride threshold would increase. The issue of how much of the nitrite is in free form in the pore water was addressed in the literature but to a relatively small extent. Also, another limitation of the previous studies that they were done with variable conditions (different w/c ratio, different type of cement, different addition of the DCI, at el.), supporting the desirability of the present investigation, where uniform conditions were used for comparison.

## CHAPTER 3: METHODOLOGY

### 3.1 Experimental Approach

The experimental program is intended to achieve the objectives by determining the concentration of free nitrite in paste, mortar, and concrete specimens. By measuring the free nitrite in specimens consisting of cement and water (paste), cement, water and sand (mortar) and cement, water, sand and coarse aggregate (concrete), the extent of the free nitrite in pore solution was determined for each mix. Then, the results were compared to each other to find which of mixes did bind more nitrite. Also, the effect of aggregate on binding was investigated.

The Specimens were cast in the laboratory with admixed commercial calcium nitrite inhibitor additions, which were 25, 20, 15 and 10 L/m$^3$ along with control specimens without inhibitor addition. Specimens were cured at $\sim$ 22$^o$C.After curing, three holes were drilled in each specimen and filled with $\sim$2ml DI water. Then, the specimens were stored vertically in closed chambers where relative humidity was $\sim$100%. The in-situ leaching method was used in this investigation (Sagüés et al., 1997, Li et al., 1999 and L. Cáseres et al., 2006). A spectrophotometer was used to measure the intensity of color of the extracted amount after dilution and adding the color reagents; thus providing a reading of the nitrite content via a calibration constant. The pH of the pore solution was also determined for each mix. The results of this experiment help to better understand the binding of nitrite in paste, mortar, and concrete.

## 3.2 Materials and Specimens

The experiments were conducted using paste, mortar, and concrete specimens admixed with DCI. Type II cement was used for all mixes. Also, deionized water was used in each mix instead of tap water to eliminate the possibility of increasing nitrite content in the experiment from nitrites present in the treated tap water. All mixes used 0.5 as the water to cement ratio.

All the specimens of paste, mortar, and concrete were cured and kept in their molds, to avoid the leaching of nitrite to the exterior. After 14 days of curing (Powers,1959), three holes 3 mm × 30 mm (diameter × height) were drilled with a masonry drill bit on the top, exposed surface of each cylindrical specimen.  The aim for using small diameter was to accelerate the equilibrium between the injected solution (that would be added later) and the surrounding pore solution (Sagüés et al., 1997). Then each hole was carefully cleaned to remove any remaining dust. After that, an acrylic washer was attached to each hole with a fast-set epoxy. Immediately, 0.2 ml of deionized water were injected into the hole and the top of the acrylic washer was covered with a rubber stopper (see figure 3.1). The solution inside the hole was thus isolated from the surrounding environment (Sagüés et al., 1997 and Li et al., 1999).

The specimens were stored vertically in their molds leaving the outer surface exposed in sealed containers at a laboratory temperature of ~ 22 °C. These containers contained a layer of tap water at the bottom to maintain the relative humidity at ~ 100% so that the exposed top surface of the specimens would not dry, and also to minimize any carbonation of the surface region from air renewed each time the container was open.

Carbonation is known to proceed only at a very slow rate in highly humid concrete (Bertolini et al., 2004).

**3.2.1 Paste Specimens**

Five different mixes of paste were used. Table 3.1 summarizes the mix design and the paste properties of the specimens. Four of these mixes contained corrosion inhibitor DCI dosages which were 25, 20, 15 and 10 L/ m3 respectively.
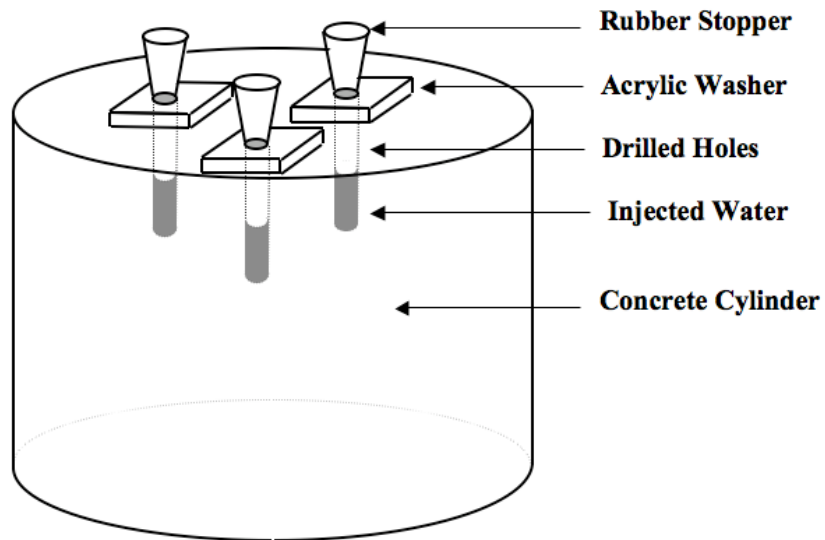


Figure 3.1 Specimen setup for nitrite and pH measurements (Li,L. et al., 1999).

Control specimens were cast without DCI addition. Three cylinders having dimensions of 2 in × 4 in (diameter × height), made using standard plastic sample molds, were cast for each mix. In these and in the other specimen formulations, to keep the w/c ratio the same, the amount of water added was reduced whenever inhibitor was added to account for the water content of the inhibitor. The adjustment was made based on the factor 0.84 water kg/DCI Liter, as listed by the manufacturer (W.R. Grace 2008).

Table 3.1 Paste properties and mix design

| Specimen | Paste A | Paste B | Paste C | Paste D | Paste Control |
|---|---|---|---|---|---|
| Cement, kg/m³ | 1223 | 1223 | 1223 | 1223 | 1223 |
| DCI, kg/m³ | 32.5 | 26.0 | 19.5 | 13.0 | 0.0 |
| Water, kg/m³ | 591 | 595 | 599 | 603 | 612 |
| Water/cement ratio | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 |
| Unit weight, Kg/m³ | 1846 | 1844 | 1842 | 1840 | 1835 |
| Batch weight, kg | 1.551 | 1.549 | 1.547 | 1.545 | 1.541 |

### 3.2.2 Mortar Specimens

For the mortar specimens, five mixes (four with corrosion inhibitor DCI and one control) were also used. The fine aggregate was sand in saturated surface dry (SSD) condition so it would not absorb water from the mix. Table 3.2 lists all the mortar properties of specimens. Three cylinders having dimensions of 2 in × 4 in were cast for each mix.

Table 3.2 Mortar properties and mix design

| Specimen | Mortar A | Mortar B | Mortar C | Mortar D | Mortar Control |
|---|---|---|---|---|---|
| Cement, kg/m^3 | 775 | 775 | 775 | 775 | 775 |
| Fine aggregate, kg/m^3 | 953.3 | 955.4 | 957.5 | 959.6 | 963.8 |
| DCI, kg/m^3 | 32.5 | 26 | 19.5 | 13 | 0 |
| Water, kg/m^3 | 366.5 | 370.7 | 374.9 | 379.1 | 387.5 |
| Water/cement ratio | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 |
| Unit weight, Kg/m^3 | 2127 | 2127 | 2127 | 2127 | 2126 |
| Batch weight, kg | 1.787 | 1.787 | 1.787 | 1.786 | 1.786 |

### 3.2.3 Concrete Specimens

Limestone coarse aggregate with a maximum size of 3/8 in was used in all the five concrete mixes (see table 3.3 for concrete mix design).

Four mixes were with DCI addition and one control. Coarse aggregate was also in SSD condition. Three cylinders having dimensions of 2 in × 4 in were cast for each mix.

Table 3.3 Concrete properties and mix design

| Specimen | Concrete A | Concrete B | Concrete C | Concrete D | Concrete Control |
|---|---|---|---|---|---|
| Cement, kg/m^3 | 500 | 500 | 500 | 500 | 500 |
| Fine aggregate, kg/m^3 | 612.2 | 614.3 | 558.7 | 560.7 | 622.8 |
| DCI, kg/m^3 | 32.5 | 26 | 19.5 | 13 | 0 |
| Water, kg/m^3 | 229 | 233.2 | 237.4 | 241.6 | 250 |
| Coarse aggregate, kg/m^3 | 950 | 950 | 950 | 950 | 950 |
| Water/cement ratio | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 |
| Unit weight, Kg/m^3 | 2324 | 2324 | 2266 | 2265 | 2323 |
| Batch weight, kg | 1.952 | 1.952 | 1.903 | 1.903 | 1.951 |

### 3.3 Nitrite Analysis

The holes in the specimens were periodically monitored for water retention and refilled if found dry until sufficient water for extracting a sample was retained. A pipette was used to extract an average of about 0.01 g of pore solution from each hole, typically 30 days after last injecting DI water in the cavities. The extracted amount was transferred to a 100-ml volumetric flask placed on an analytical balance having 50mL DI water. A two drops of phenolphthalein indicator was added and the solution was neutralized after that by

adding a two drops of hydrochloric Acid. Then the solution was treated with sulfanilic acid (2.00mL). Later, it was coupled with N-( 1-Naphthyl) phenophalein Ethylenediamine Dihydrochloride (2.00mL) which produce a pink azo dye color (purple color) and the flask was topped up with DI water to its set volume. After that, the solution was placed in a 13.27 $cm^3$ cuvette and a spectrophotometer (a Milton Roy Spectronic 20D) was used to measure the intensity of the color by determining absorption at 540nm wavelength (Jeknavorian, A. A., et al., 1995). The solution was diluted since the extracted solution concentration was higher than the concentration that spectrophotometer can detect.

A 2500 ppm sodium nitrite ($NaNO_2$ from Fisher Scientific company) solution was prepared and used as a stock solution to perform a calibration. The same reagent used in the present experiment were also used here which are sulfanilic acid, N-( 1-Naphthyl) Ethylenediamine Dihydrochloride. After averaging three analyses, a calibration curve was obtained with a slope of 1.0938 ppm (North Carolina Department of Transportation, 2005). This procedure was used to analyses free nitrite in all specimens. The calibration curve and data table are shown below (table 3.4 and figure 3.2).

All measurements are reported as the difference in absorption between that of the solution to be tested and that of a blank that consisted of distilled water with the addition of the color reagent normally used to react with the nitrite.  The blank absorption was typically in the order of 0.05.  In initial experiments there was some aging in the measured value of the absorption of a blank solution that was kept otherwise unchanged. Consequently, the recorded absorption of samples with the extracted pore solution was updated against that current value of the blank solution.  For later experiments a fresh blank solution was prepared every time.

Table 3.4 Data of three samples for calibration curve

| Nitrite concentration (ppm) | Absorption | | | |
|---|---|---|---|---|
| | Sample 1 | Sample 2 | Sample 3 | Average |
| 0.186 | 0.22 | 0.207 | 0.218 | 0.215 |
| 0.373 | 0.424 | 0.42 | 0.414 | 0.419 |
| 0.560 | 0.622 | 0.62 | 0.564 | 0.602 |

## 3.4 pH Measurements

The pH measurements of the solution inside the hole were taken by means of a pH sensing electrode; which was made with titanium wire covered with a mixed metal oxide (MMO) (Castro et al., 1996). The potential of the wire was measured against a thin-bodied Ag/AgCl reference electrode. Since the hole diameter would not be able to accommodate both electrodes, one hole in each cylinder was used to place the Ag/AgCl reference electrode, whereas the MMO reference electrode was inserted into either of the other two holes (Li et al., 1999). Then with a Corning pH meter 140 Model in voltmeter mode to measure the potential difference, the pH was calculated. Before any measurements, the electrodes were calibrated in standard buffer solutions pH11, pH12 and pH13 respectively. Then, a manipulation formula was used to find pH of each hole. After that, pH of each mix was based on an average of 6 pH readings. The laboratory temperature during the test was $23\pm2$ °C.
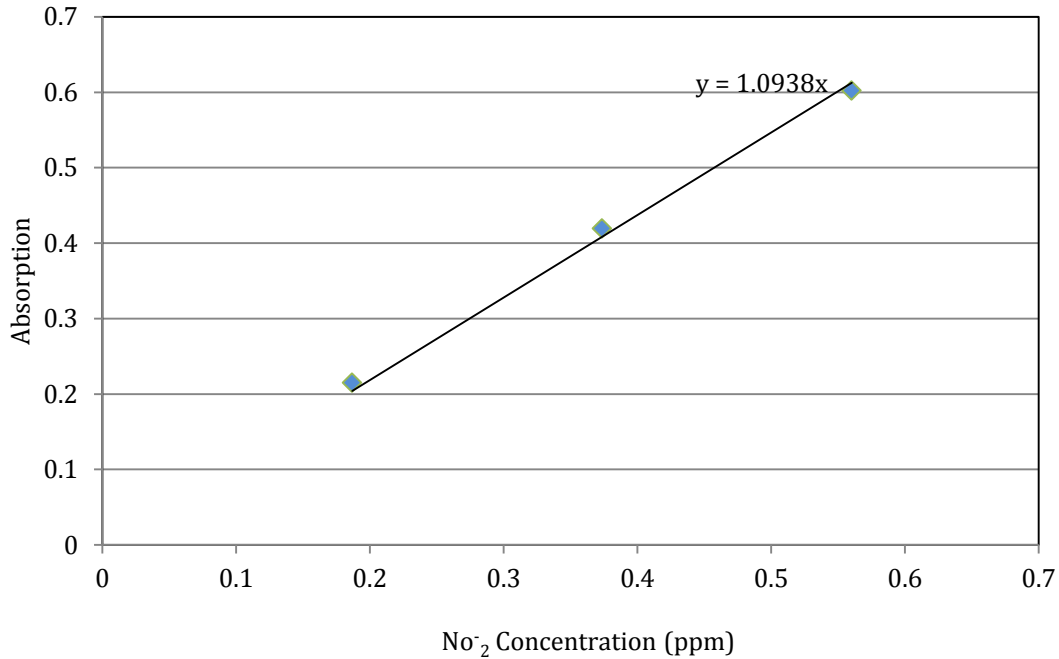
Figure 3.2 Average result of the three calibration tests, forcing intercept at the origin.

## 3.5 Porosity

The porosity of paste, mortar, and concrete specimens was found using an adaptation of the method described in ASTM C 642-2006 (ASTM, 2006). Two cylinders from each mix, with or without nitrite, were weighted and then placed in an oven at a temperature of 100 to 110 $^\circ$C for 24 to 60 hours. The oven-dry mass (A) of each specimen was recorded after removing it from the oven and allowed to cool in temperature 20 to 25 $^\circ$C. Then, the specimen was immersed in water at a temperature of about 21 $^\circ$C for not less than 48 hours. This was repeated until two values showed an increase of 0.5% in the mass. The surface-dry mass after immersion (B) was recorded after drying the surface with a towel. Next, the specimens were placed in a boiler covered with tap water and boiled for approximately 5 hour. The specimens were then removed and left to cool at laboratory temperature.

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The saturated mass after boiling was recorded after removing the moisture from the surface (C). Finally, the specimens were suspended by wire in water and the immersed apparent mass (D) was recorded. The following relationship was used to find the porosity of specimens (ASTM C 642, 2006):

Volume of permeable pore space $= (C - A)/(C - D) \times 100$

Table 3.5 Calculation of the porosity of the paste specimens

| Mix Type | Sample number | Weight After the 3rd 24 h in Oven | Weight After the 2ed 24 h Submerged | Saturated Mass after Boiling | Immersed Apparent Mass | Volume of Permeable Pore Space (voids) % |
|----------|---------------|-----------------------------------|-------------------------------------|------------------------------|------------------------|------------------------------------------|
| Paste | A-1 | 290.1 | 372 | 373.6 | 174 | 41.8 |
| | A-2 | 291 | 373.2 | 374.5 | 174.6 | 41.8 |
| | B-1 | 291 | 373.5 | 375 | 174.5 | 41.9 |
| | B-2 | 290.9 | 374.5 | 376.9 | 174.3 | 42.4 |
| | C-1 | 285.8 | 370.1 | 371.9 | 171.4 | 42.9 |
| | C-3 | 287.7 | 371.2 | 372.6 | 172.9 | 42.5 |
| | D-1 | 286.2 | 366.9 | 368.4 | 170.5 | 41.5 |
| | D-3 | 285.3 | 367.3 | 369 | 170.9 | 42.3 |
| Average | | | | | | 42.1 |

The porosity of paste, mortar, and concrete were found to be 42.14, 29.37 and 20.0% respectively. These nominal porosities were used to express the nitrite content per cubic meter of each mix. Tables 3.5, 3.6 and 3.7 show the porosity calculation for paste, mortar, and concrete specimens respectively.

Table 3.6 Calculation of the porosity of the mortar specimens

| Mix Type | Sample number | Weight After the 3rd 24 h in Oven | Weight After the 2ed 24 h Submerged | Saturated Mass after Boiling | Immersed Apparent Mass | Volume of Permeable Pore Space (voids) % |
|---|---|---|---|---|---|---|
| Mortar | A-1 | 343.7 | 403.9 | 404.7 | 204.5 | 30.5 |
| | A-2 | 347.8 | 408.1 | 408.8 | 207.2 | 30.3 |
| | B-1 | 355.3 | 412.5 | 413.9 | 212 | 29.0 |
| | B-2 | 354.8 | 412.1 | 412.8 | 211.4 | 28.8 |
| | C-1 | 358.5 | 415 | 416 | 214.1 | 28.5 |
| | C-2 | 364.6 | 421.4 | 422.2 | 217.9 | 28.2 |
| | D-1 | 354.6 | 413.7 | 415.1 | 212.5 | 29.9 |
| | D-2 | 352.2 | 410.7 | 412.5 | 211 | 29.9 |
| Average | | | | | | 29.4 |

Table 3.7 Calculation of the porosity of the concrete specimens

| Mix Type | Sample number | Weight After the 3rd 24 h in Oven | Weight After the 2ed 24 h Submerged | Saturated Mass after Boiling | Immersed Apparent Mass | Volume of Permeable Pore Space (voids) % |
|---|---|---|---|---|---|---|
| Concrete | A-1 | 405.3 | 447.4 | 447.9 | 234.1 | 19.9 |
| | A-3 | 400.3 | 442.1 | 442.3 | 238.9 | 20.6 |
| | B-1 | 301.1 | 329.7 | 330.1 | 179.9 | 19.3 |
| | B-3 | 340.9 | 376 | 376.5 | 204.4 | 20.7 |
| | C-1 | 399.9 | 441 | 441.2 | 237.9 | 20.3 |
| | C-3 | 254.9 | 278.6 | 278.9 | 152.3 | 18.95 |
| | D-1 | 404.1 | 445.1 | 445.6 | 240.5 | 20.2 |
| | D-3 | 403.7 | 444.4 | 444.5 | 240.0 | 19.95 |
| Average | | | | | | 20.0 |

# CHAPTER 4: RESULTS AND DISCUSSION

## 4.1 Free Nitrite

During the first ~63 days following preparation of the specimens DI water was added periodically to the holes in the test specimens, replenishing any absorbed water. Afterwards water absorption was less noticeable and water addition was discontinued. Two sets of free nitrite measurements were taken. The first set was obtained for each mix about 30 days after last injecting DI water in the cavities. The second set was taken about 52, 45, and 47 days after last injecting DI water for paste, mortar, and concrete respectively, by which time about half of the holes in each specimen had begun to become dry again.

The pore solution from control specimens was also analyzed. The difference between control sample results and the deionized water with color reagents (the blank solution) results was small and therefore neglected. Only results for specimens with admixed nitrite are discussed in the following.

It is noted that some absorption measured values were somewhat greater than the max level in the prepared calibration curve. Then, in this case the calibration curve extrapolated to cover these measured values with understanding that those numbers are to be considered approximate.

Results for the first set of measurements are given in Figures 4.1, 4.2, and 4.3 which show the pore solution nitrite concentration in paste, mortar, and concrete respectively.
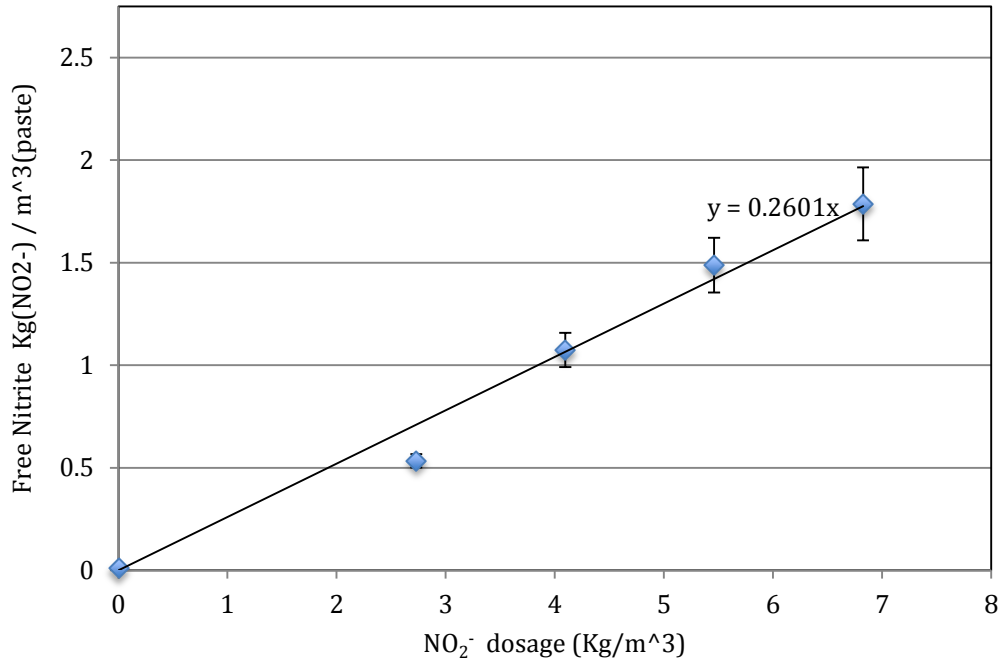
Figure 4.1 Relation between the admixed nitrite content and the free nitrite content in paste pore solution (porosity=42.1% and cement content =1223 kg/m³). Result from the first set of measurements.
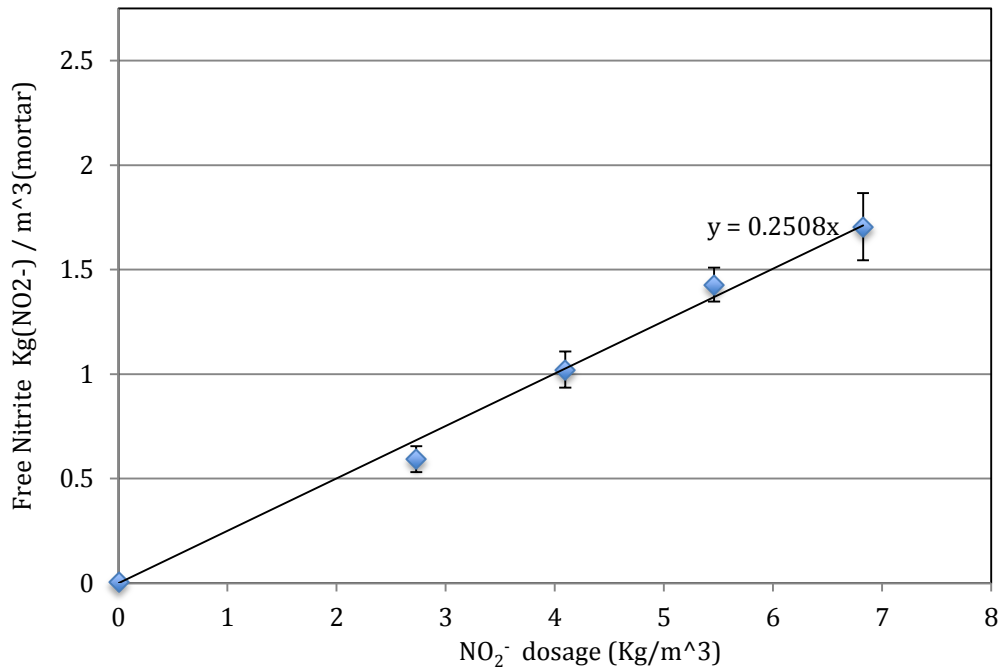


Figure 4.2 Relation between the admixed nitrite content and the free nitrite content in mortar pore solution (porosity=29.4% and cement content =775 kg/m³). Result from the first set of measurements.
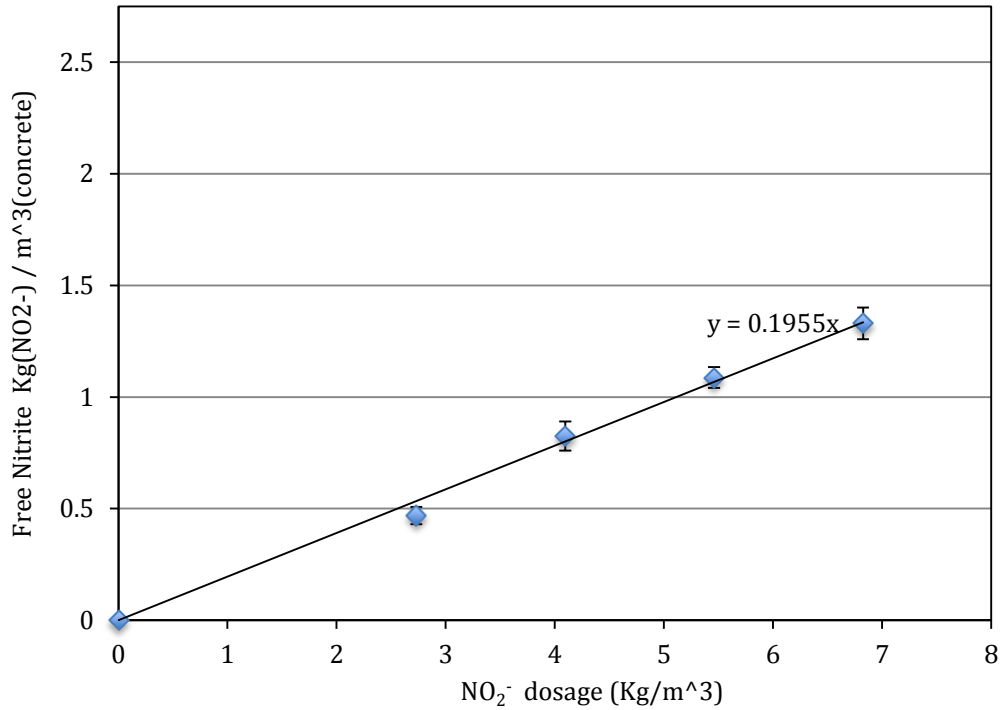
Figure 4.3 Relation between the admixed nitrite content and the free nitrite content in concrete pore solution (porosity=20.0% and cement content =500 kg/m³). Result from the first set of measurements.

Each point in the graphs represents an average of 8 to 9 readings. Error bands in these and subsequent figures represent + - one standard deviation. For this first set , the nitrite concentration in the pore solution of paste, mortar, and concrete specimens that were cast with 25 L/m³ DCI was found to be ~1.79, 1.71, and 1.33 Kg ($NO_2^-$)/m³ (mix) respectively.

For the lower DCI addition amount (10 L/m³), the nitrite concentration in the pore solution of paste, mortar, and concrete specimens were found to be ~0.53, 0.59, and 0.47 Kg ($NO_2^-$)/m³ (mix) respectively.
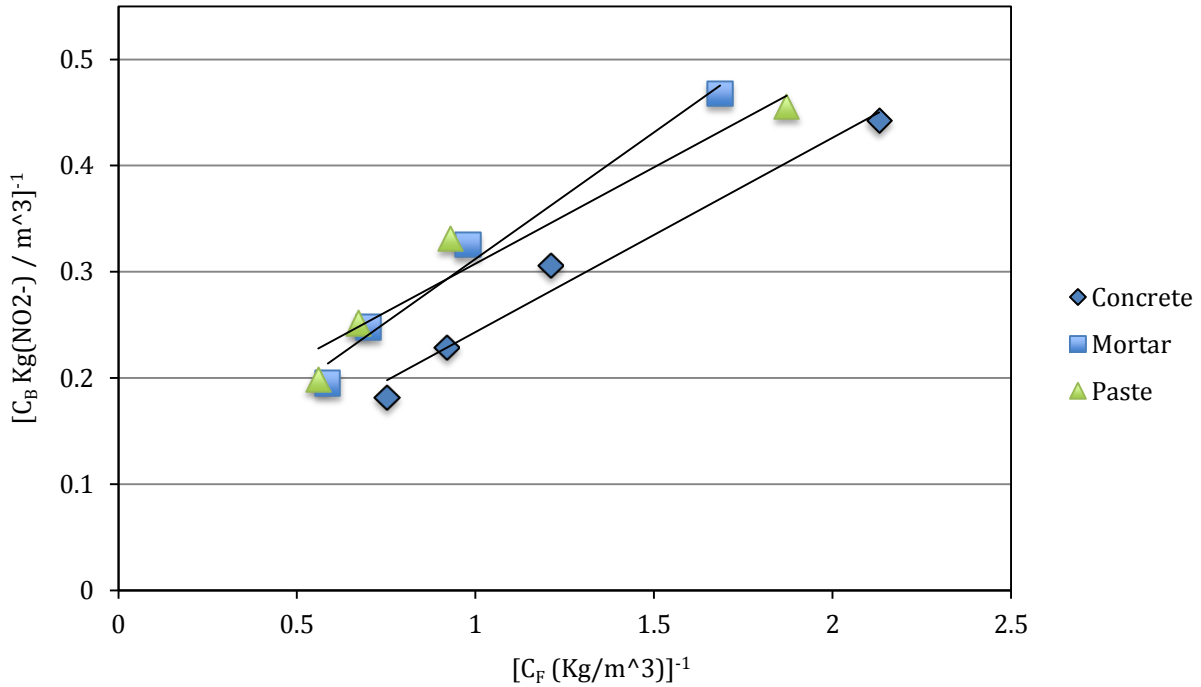
Figure 4.4 Nitrite binding isotherms for the first measurements of paste, mortar and concrete specimens (Appendix 5: table I-1)
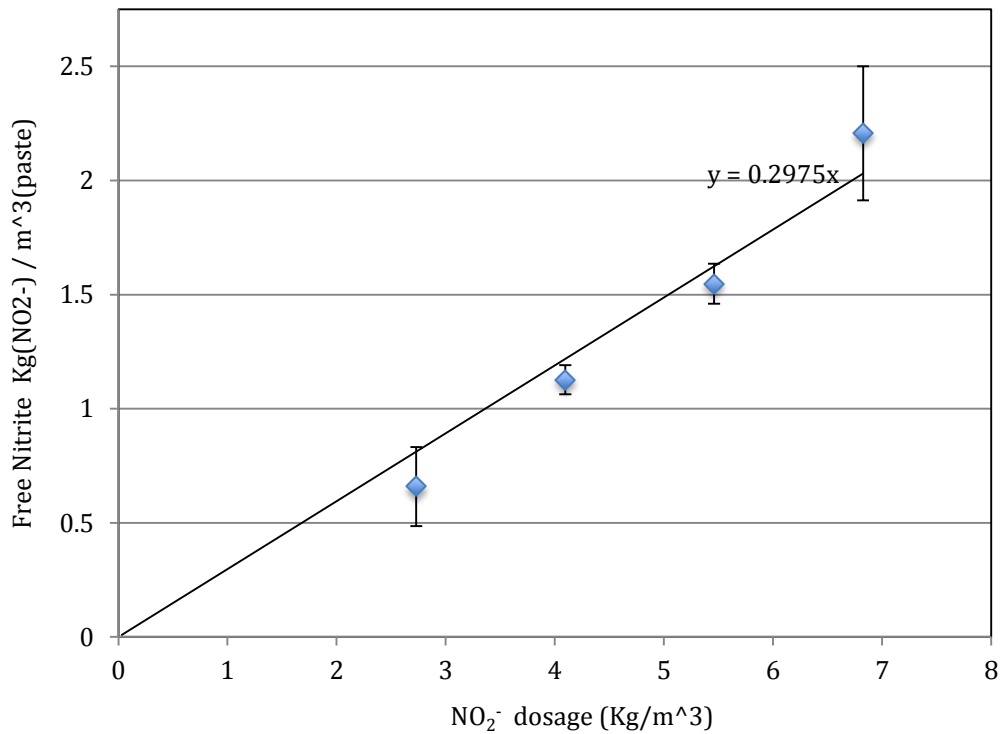


Figure 4.5 Relation between the admixed nitrite content and the free nitrite content in paste pore solution (porosity=42.1% and cement content =1223 kg/m³). Result from the second set of measurements.

The results in Figures 4.5, 4.6, and 4.7 compared with those in Figures 4.1, 4.2, and 4.3 indicate that for a given mixture and nitrite addition level there was a slight increase in nitrite concentration with time. These results were in agreement with other results that were mentioned in the literature review regarding the increase in the nitrite concentration with time in the pore solution (Li, et al., 1999).
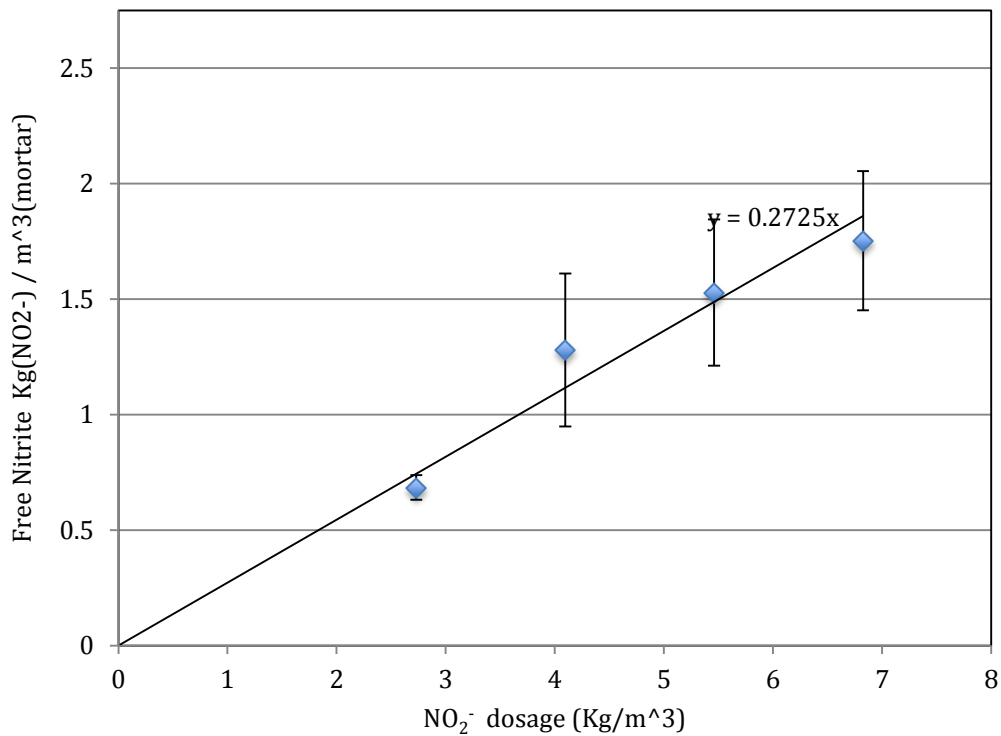


Figure 4.6 Relation between the admixed nitrite content and the free nitrite content in mortar pore solution (porosity=29.4% and cement content =775 kg/m$^3$). Result from the second set of measurements.

In the first set of measurements, the results showed that the average of binding in paste and mortar specimens were almost similar. However, concrete specimens showed a higher binding for all level of DCI addition compared to the other two specimens.

For the second set of measurements, the results for the lowest addition of DCI 10 L/m$^3$ (~0.66 Kg (NO$_2^-$)/m$^3$ in paste ,~0.68 Kg (NO$_2^-$)/m$^3$ in mortar ~0.64 Kg (NO$_2^-$)/m$^3$ in concrete) showed little difference between the free nitrite concentrations in paste, mortar,

and concrete. However, for the highest DCI additions the amounts of free nitrite

concentration in paste ($\sim$2.21 Kg ($NO_2^-$)/m$^3$), mortar ($\sim$1.75 Kg ($NO_2^-$)/m$^3$), and concrete

($\sim$1.53Kg ($NO_2^-$)/m$^3$) specimens were clearly differentiated.
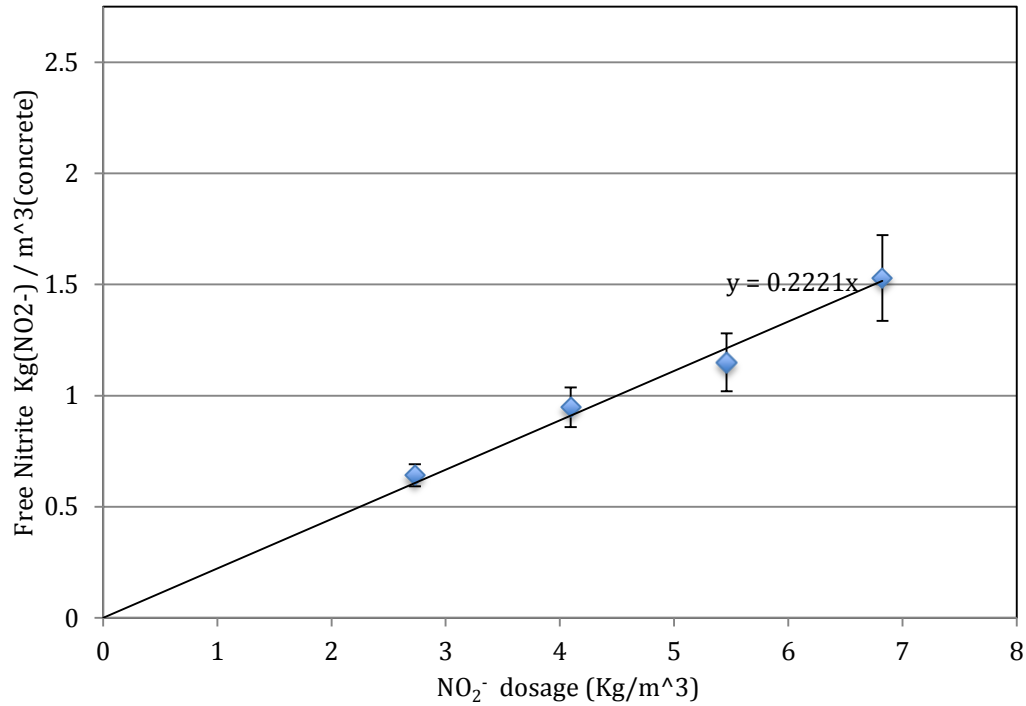


Figure 4.7 Relation between the admixed nitrite content and the free nitrite content in concrete pore solution (porosity=20.0% and cement content =500 kg/m$^3$). Result from the second set of measurements.

Figure 4.4 shows for the first set of measurements of paste, mortar and concrete

specimens the nitrite binding isotherms were plotted to the inverses of bound and free

nitrite to see to what extent they may match the behavior expected for a Langmuir

isotherm per Eq.(2). Figure 4.8 shows the same for the second set.  The data for both sets

fitted reasonably the Langmuir behavior, and the parameters K and $C_L$ were obtained by

simple linear fit. Results are given in Table 4.1. Results from other sources in the literature

are shown there as well.
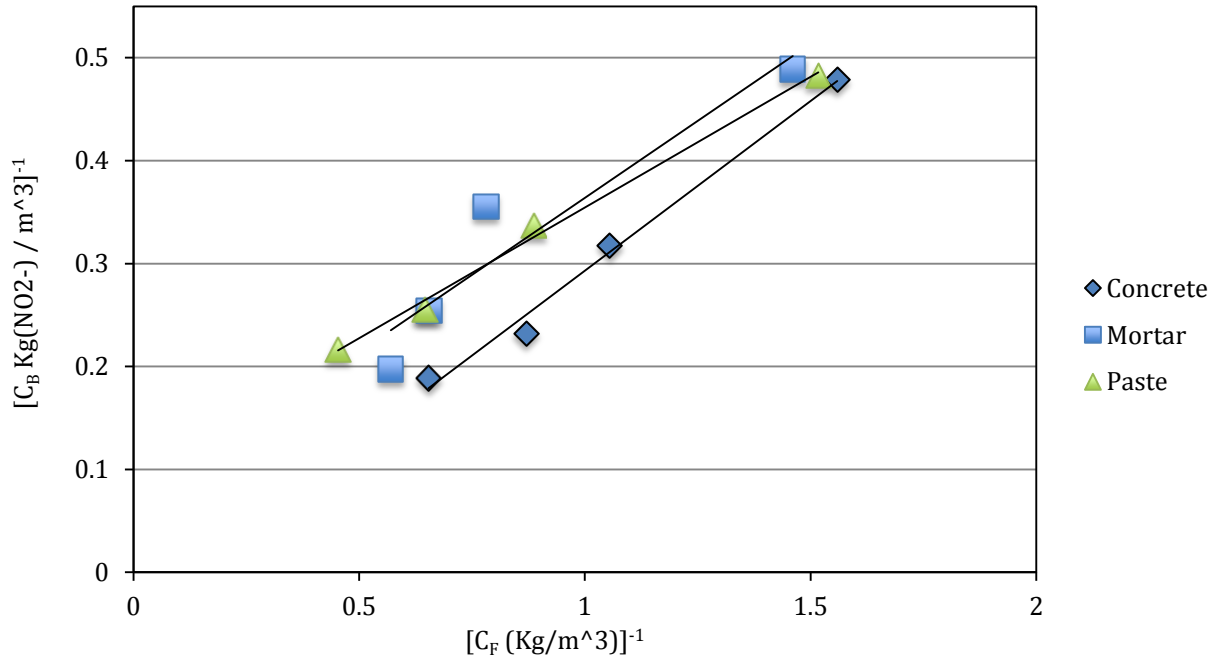
Figure 4.8 Nitrite binding isotherms for the second measurements of paste, mortar and concrete specimens (Appendix 5- table I-2)

Table 4.1 Comparison between the absorption coefficient (K) and the limiting bound concentration ($C_L$) with other studies.

| | First measurements | | | Second measurements | | | Li, et al., 1999 | Tritthart, et al., 2001 |
|---|---|---|---|---|---|---|---|---|
| | Concrete | Mortar | Paste | Concrete | Mortar | Paste | Mortar | Paste |
| K~ | 6 | 5 | 6 | 3 | 3 | 4 | 7 | ~5* |
| $C_L \sim$ (Kg/m$^3$) | 17 | 14 | 8 | 27 | 25 | 10 | - | - |

*Estimated from values shown in that work and the missing parameters were assumed as follows: the density of pore water=1.0128g/ml and cement factor= 1212.5 and porosity=30%.

From the shape of the graphs (figures 4.4 and 4.8) and table 4.1, it can be seen that

binding was nearly linear as the values of $C_L$ are quite large, so the Langmuir isotherm

could be reduced to a simple straight line with $C_L^{-1} \sim 0$. Then, the relationship between

bound and free nitrite would be,

$$C_B = K \, C_F$$

Comparisons in Table 4.1 show also that the values of K obtained here are in the general range of the values reported from previous investigations.

**4.2 Discussion of Nitrite Results**

Readings of the first set of measurements were generally more numerous compared to those of the second set. (an average of 8.5 concentration values from each mix compared to an average of 4.5 concentration values respectively, with greater variability). Nevertheless, some overall trends became apparent.

In general and as expected, free nitrite concentration in pore solution increased whenever the addition of DCI was increased. The increasing trend was noticed in all mixes (see figures 4.1, 4.2 and 4.3).

Table 4.1 shows that the binding slope K of the first set of measurements was greater by about 50% to 100% than that of the second set. However there was relatively little differentiation in this parameter between the concrete, mortar and paste in both the first and the second tests when looking at the total amount of free nitrite (Table 4.2).

Table 4.2 The evolution of nitrite in pore solution for the two set of measurements.

| DCI (L/m$^3$) / mix type | First measurements (Kg/m$^3$) | | | Second measurements (Kg/m$^3$) | | | The increment (%) | | |
|---|---|---|---|---|---|---|---|---|---|
| | Concrete | Mortar | Paste | Concrete | Mortar | Paste | Concrete | Mortar | Paste |
| 25 | 1.33 | 1.70 | 1.79 | 1.53 | 1.75 | 2.21 | 15.04 | 2.94 | 23.46 |
| 20 | 1.09 | 1.43 | 1.49 | 1.15 | 1.53 | 1.55 | 5.50 | 6.99 | 4.03 |
| 15 | 0.83 | 1.02 | 1.07 | 0.95 | 1.28 | 1.13 | 14.46 | 25.49 | 5.61 |
| 10 | 0.47 | 0.59 | 0.53 | 0.64 | 0.68 | 0.66 | 36.17 | 15.25 | 24.53 |

In both the first and second set of measurements, the free nitrite concentration in paste and mortar specimens was about the same but on average distinctly higher (about 20% to 30% more) for all addition levels than that of the concrete specimens. Hence, the fine aggregate appeared to have had no major effect on nitrite binding, but the coarse aggregate (concrete) appeared to have increased binding to some extent.

All the nominal porosity values were relatively high compared to the values normally seen with similar mixture proportions. The reason could be that the specimens were not extensively cured, as the water fill on the cylinder molds during curing was only applied to the top side of the specimens. In addition, the high water-cement ratio (0.5.) that were used could be also a reason of getting a high porosity

**4.3 Effect of Coarse and Fine Aggregate on Nitrite Binding**

The effects of adding coarse aggregate on nitrite binding were observed. The free nitrite concentration in pore solution for each DCI addition was reduced whenever the mix had a coarse aggregate. The measurements showed that fine aggregate has a little effect on the free nitrite concentration. Generally for all the DCI addition levels, concrete specimens showed the lowest free nitrite concentration in the pore solution compared to the paste and mortar specimens. Hence, coarse aggregate played a factor in binding nitrite in concrete. A possible cause for that behavior is that in concrete the free nitrite could have been absorbed to some extent in the highly porous transition zone between coarse aggregate and the surrounding matrix (Mindess, S. & Young, JF, 2003).

The total nitrite amounts added to paste, mortar and concrete mixes were similar and the highest addition of nitrite was 6.825 $Kg/m^3$ (25 L/ $m^3$). In the second set of measurements, the free nitrite concentration were 2.21 $Kg/m^3$, 1.75 $Kg/m^3$ and 1.53 $Kg/m^3$

in paste, mortar and concrete specimen respectively. With a porosity of 42.1, 29.4 and 20 % for paste, mortar and concrete specimens respectively, 32%, 26% and 22% of the added nitrite was present in the pore solution of paste, mortar and concrete respectively. These values are higher (typically twice or more) than those reported in other studies (Li, et al., 1999 and Tritthart and Banfill, 2001)

The reasons for the high concentration of the free nitrite in the pore solutions compared to other the studies could be the high porosity of these specimens. Powers, R.G. et al., (2002) mentioned on their interim report about the corrosion inhibitors in concrete that the fraction of free nitrite in pore solution would increase whenever the porosity of the specimen is large. This is consistent with the results obtained in the present study..

Furthermore, there was a difference in the concentration of nitrite in the pore solution between the first and second sets of measurements, implying that the concentration of the free nitrite was affected by the hydration of the cement. As the hydration of cement continued, the pore solution size decreased. Consequently, the concentration of the pore solution increased and the same would have happened for the concentration of free nitrite.

## 4.4 pH Analysis and Discussion

The pH levels of pore solution for paste, mortar, and concrete were measured as described in the methodology after 30 days from casting the specimens (see figure 4.9, 4.10 and 4.11). The results suggested that paste, mortar, and concrete specimens with admixed corrosion inhibitor had generally pH values slightly lower compared to those of the control specimens, which were cast without inhibitor. Each pH value on the graph represented an average of 4 to 6 pH measured readings.

The observation of lowered pH on nitrite addition was noted by Li [Li, et al., 1999] who ascribed it to the limited solubility of calcium ions. With high pH solution, the solubility of $Ca(OH)_2$ will limit the concentration of calcium ions. Part of calcium ions in specimens with nitrite would react with $OH^-$ and produce $Ca(OH)_2$. Accordingly, pH value would be reduced.

The average of the pore solution pH of the concrete control specimens was ~ 13.03 while the pH of the concrete specimens with the higher corrosion inhibitor addition was ~ 12.72.
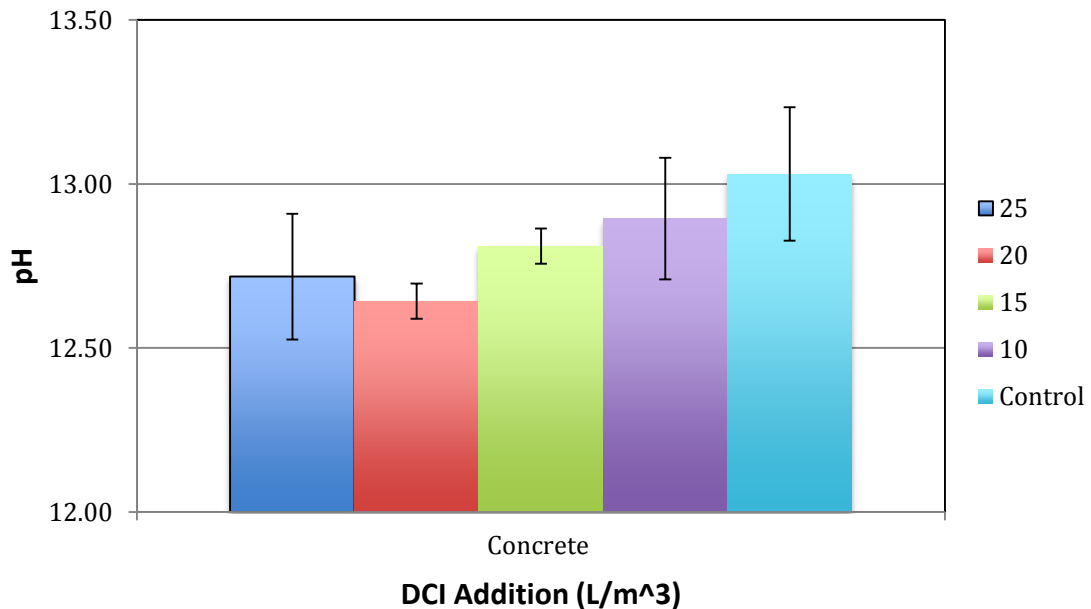


Figure 4.9 pH levels of pore solution for concrete specimens (30 days)

For mortar specimens, control pH was ~13.00 which is higher than the specimens with corrosion inhibitors ($25L/m^3$) by ~ 0.1, an amount that may not be significant given the scatter of the results.

Moreover, pH of paste specimens that were cast with higher level of corrosion inhibitors was ~12.79 which is less than the pH of the control specimens by ~ 0.25, again with a significant degree of uncertainty.
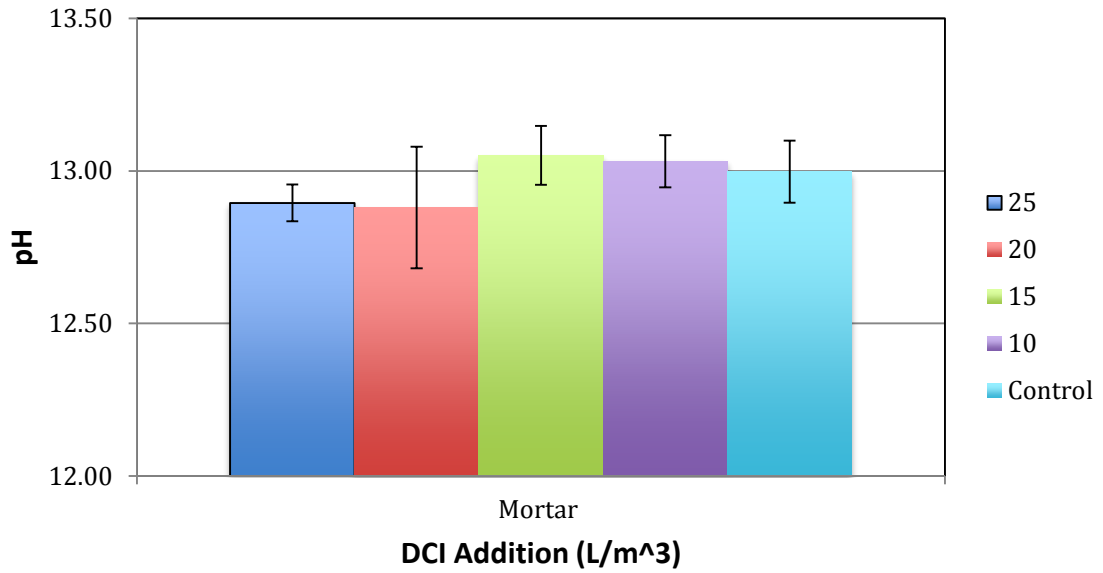


Figure 4.10 pH levels of pore solution for mortar specimens (30 days)
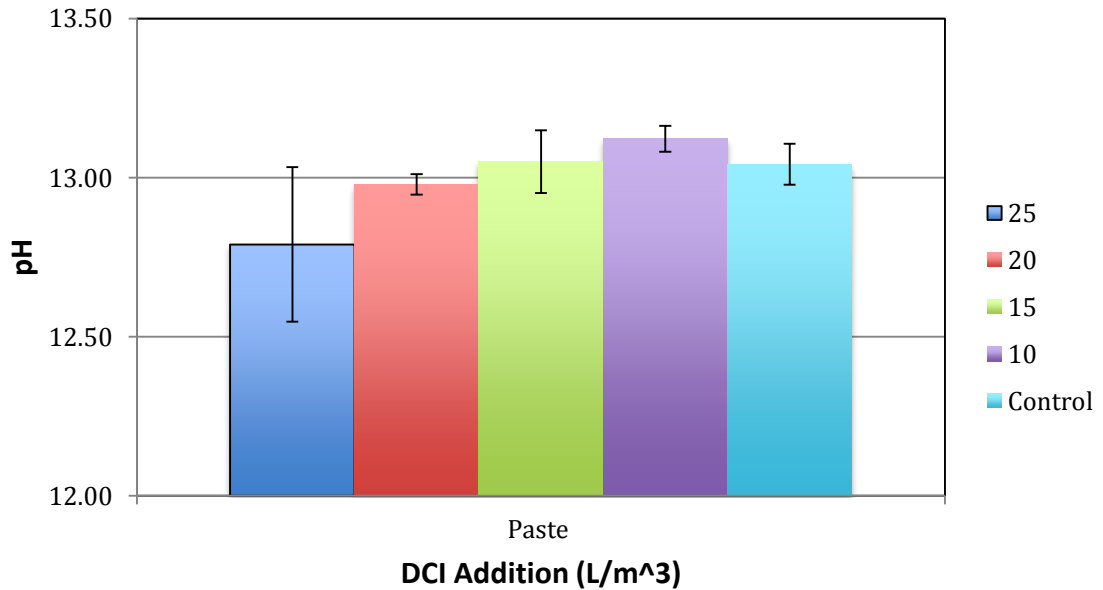


Figure 4.11 pH levels of pore solution for paste specimens (30 days)

The slight drop in the pH, compared to the control, suggested by the results would moderately decrease the corrosion threshold. However, by adding nitrite to the mix in the level used, the corrosion threshold would be expected to increase by amounts in the order-of-magnitude range (Federal Highway Administration, (2000)).  Thus the effect of the pH change would not be important by comparison.

## CHAPTER 5: CONCLUSIONS

### 5.1 Conclusion

- Free nitrite increased with the increase of the DCI dosage.

- Langmuir binding isotherm parameters for paste, cement and concrete were found to be comparable for all 3 materials and in the order of K~3 to 6 (bound to free nitrite ratio when concentrations are expressed per unit volume of the cured material), and with a high limit value CL in the order of 8 to 27 kg/m3, hence indicating that the binding was approximately linear.

- Coarse aggregate has an effect in nitrite binding. The free nitrite concentrations in pore solution that were observed in concrete specimens were somewhat lower than those in the paste and mortar specimens. Hence, the results suggest that cement is not the only component that binds with nitrite.

- It is proposed as an explanation that nitrite was absorbed at the transition zone around the coarse aggregate.

- Fine aggregate appears to have little effect on the free nitrite binding compared to coarse aggregate.

- Porosity was high compared to the literature review data. The expected reason is that these specimens were not well cured since curing was just to the top side of the specimen.

- Generally, the pH of specimens with DCI appeared to have slightly lower values compared to the control sample.

## 5.2 Future Work

Current research confirms that small fraction of nitrite will be available in pore solution, the rest is bound. Future work to be done based on the results and conclusions of this research is to investigate the degree of nitrite binding of mixes that have a pozzolanic addition such as fly ash and silica fume as partial replacement of cement, to determine if in those cases the extent of free nitrite can be increased, for more efficient corrosion control.

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**APPENDICES**

## Appendix 1 Permission for Use of Table and Figures

The license applies to Figure 3.1.

**Appendix 2 First Absorption Data and Calculation of Nitrite Concentration**

Table A-1: Calculation of nitrite concentration in paste (25 L/m$^3$)

| Date | Type of specimen | Addition ratio of DCI (L/m$^3$) | Specimen name | Hole # | Extracted amount (g) | Dilution (mL) | Absorption | Concentration (g/g) | Mass of nitrite in the beaker (g/g) | Nitrite in (Kg(NO$_2^-$))/(m$^3$ (paste) | Average |
|------|------------------|-------------|---------------|--------|----------------------|---------------|------------|---------------------|----------------------------------------|-------------------------------------------|---------|
| 30-Jan-14 | Paste | 25 | A-1 | 1 | 0.0152 | 100 | 0.624 | 5.7E-07 | 5.7038E-05 | 1.58131435 | |
| | | | | 2 | 0.0101 | 100 | 0.516 | 4.72E-07 | 4.7166E-05 | 1.96791138 | |
| | | | | 3 | 0.0224 | 100 | 1.120 | 1.02E-06 | 0.00010238 | 1.92595978 | |
| | | | A-2 | 1 | 0.0108 | 100 | 0.588 | 5.37E-07 | 5.3748E-05 | 2.09715621 | |
| | | | | 2 | 0.0113 | 100 | 0.500 | 4.57E-07 | 4.5704E-05 | 1.70438919 | 1.78659602 |
| | | | | 3 | 0.0104 | 100 | 0.468 | 4.28E-07 | 4.2779E-05 | 1.7333638 | |
| | | | A-3 | 1 | 0.0171 | 100 | 0.806 | 7.37E-07 | 7.3675E-05 | 1.81558314 | |
| | | | | 2 | 0.0226 | 100 | 0.960 | 8.78E-07 | 8.7751E-05 | 1.63621362 | |
| | | | | 3 | 0.0231 | 100 | 0.970 | 8.87E-07 | 8.8665E-05 | 1.61747272 | |

Table A-2: Calculation of nitrite concentration in paste (20 L/m$^3$)

| Date | Type of specimen | Addition ratio of DCI (L/m$^3$) | Specimen name | Hole # | Extracted amount (g) | Dilution (mL) | Absorption | Concentration (g/g) | Mass of nitrite in the beaker (g/g) | Nitrite in (Kg(NO$_2^-$))/(m$^3$ (paste) | Average |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 30-Jan-14 | | 20 | B-1 | 1 | 0.0133 | 100 | 0.517 | 4.73E-07 | 4.7258E-05 | 1.49732512 | |
| | | | | 2 | 0.0129 | 100 | 0.514 | 4.7E-07 | 4.6984E-05 | 1.53479586 | |
| | | | | 3 | 0.0221 | 100 | 0.798 | 7.29E-07 | 7.2943E-05 | 1.39087412 | |
| 31-Jan-14 | | | B-2 | 1 | 0.0013 | 100 | 0.102 | 9.32E-08 | 9.3236E-06 | | |
| | | | | 2 | 0.0166 | 100 | 0.630 | 5.76E-07 | 5.7587E-05 | 1.46187309 | 1.48762748 |
| | | | | 3 | 0.0096 | 100 | 0.368 | 3.36E-07 | 3.3638E-05 | 1.47656917 | |
| | | | B-3 | 1 | 0.0126 | 100 | 0.424 | 3.88E-07 | 3.8757E-05 | 1.2962015 | |
| | | | | 2 | 0.0119 | 100 | 0.458 | 4.19E-07 | 4.1865E-05 | 1.48250349 | |
| | | | | 3 | 0.0105 | 100 | 0.480 | 4.39E-07 | 4.3876E-05 | 1.76087751 | |

Table A-3: Calculation of nitrite concentration in paste (15 L/m³)

| Date | Type of specimen | Addition ratio of DCI (L/m³) | Specimen name | Hole # | Extracted amount (g) | Dilution (mL) | Absorption | Concentration (g/g) | Mass of nitrite in the beaker (g/g) | Nitrite in (Kg(NO$_2^-$))/(m³ (paste) | Average |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 31-Jan-14 | | 15 | C-1 | 1 | 0.0101 | 100 | 0.324 | 2.96E-07 | 2.9616E-05 | 1.23566528 | |
| | | | | 2 | 0.0214 | 100 | 0.580 | 5.3E-07 | 5.3016E-05 | 1.0439782 | |
| | | | | 3 | 0.0110 | 100 | 0.322 | 2.94E-07 | 2.9433E-05 | 1.12756191 | |
| | | | C-2 | 1 | 0.0011 | 100 | 0.030 | 2.74E-08 | 2.7422E-06 | 1.05052352 | |
| | | | | 2 | 0.0097 | 100 | 0.283 | 2.59E-07 | 2.5868E-05 | 1.12380746 | 1.07436049 |
| | | | | 3 | 0.0125 | 100 | 0.340 | 3.11E-07 | 3.1079E-05 | 1.04772212 | |
| | | | C-3 | 1 | 0.0109 | 100 | 0.307 | 2.81E-07 | 2.8062E-05 | 1.08489845 | |
| | | | | 2 | 0.0099 | 100 | 0.240 | 2.19E-07 | 2.1938E-05 | 0.93379868 | |
| | | | | 3 | 0.0109 | 100 | 0.289 | 2.64E-07 | 2.6417E-05 | 1.02128876 | |

Table A-4: Calculation of nitrite concentration in paste (10 L/m$^3$)

| Date | Type of specimen | Addition ratio of DCI (L/m$^3$) | Specimen name | Hole # | Extracted amount (g) | Dilution (mL) | Absorption | Concentration (g/g) | Mass of nitrite in the beaker (g/g) | Nitrite in (Kg(NO$_2^-$))/(m$^3$ (paste) | Average |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1-Feb-14 | | 10 | D-1 | 1 | 0.0088 | 100 | 0.129 | 1.18E-07 | 1.1792E-05 | 0.56465639 | |
| | | | | 2 | 0.0024 | 100 | 0.030 | 2.74E-08 | 2.7422E-06 | 0.48148995 | |
| | | | | 3 | 0.0109 | 100 | 0.152 | 1.39E-07 | 1.3894E-05 | 0.53714842 | |
| | | | D-2 | 1 | - | 100 | -0.002 | -1.83E-09 | -1.828E-07 | | |
| | | | | 2 | 0.0224 | 100 | 0.304 | 2.78E-07 | 2.7788E-05 | 0.52276051 | 0.53428672 |
| | | | | 3 | 0.0176 | 100 | 0.234 | 2.14E-07 | 2.1389E-05 | 0.51213021 | |
| | | | D-3 | 1 | 0.0094 | 100 | 0.144 | 1.32E-07 | 1.3163E-05 | 0.59008129 | |
| | | | | 2 | 0.0120 | 100 | 0.168 | 1.54E-07 | 1.5356E-05 | 0.53926874 | |
| | | | | 3 | 0.0117 | 100 | 0.160 | 1.46E-07 | 1.4625E-05 | 0.52675823 | |

Table A-5: Calculation of nitrite concentration in paste (0 L/m³)

| Date | Type of specimen | Addition ratio of DCI (L/m³) | Specimen name | Hole # | Extracted amount (g) | Dilution (mL) | Absorption | Concentration (g/g) | Mass of nitrite in the beaker (g/g) | Nitrite in (Kg(NO$_2^-$))/(m³ (paste) | Average |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 13-Feb-14 | | 0 | C-C-1 | 1 | 0.0169 | 100 | 0.003 | 2.74E-09 | 2.7422E-07 | 0.00683773 | |
| | | | | 2 | 0.0089 | 100 | 0.003 | 2.74E-09 | 2.7422E-07 | 0.012984 | |
| | | | | 3 | 0.011 | 100 | 0.003 | 2.74E-09 | 2.7422E-07 | 0.01050524 | |
| | | | C-C-2 | 1 | 0.0111 | 100 | 0.003 | 2.74E-09 | 2.7422E-07 | 0.01041059 | |
| | | | | 2 | 0.0109 | 100 | 0.003 | 2.74E-09 | 2.7422E-07 | 0.01060161 | 0.00978337 |
| | | | | 3 | 0.0134 | 100 | 0.003 | 2.74E-09 | 2.7422E-07 | 0.0086237 | |
| | | | C-C-3 | 1 | 0.0186 | 105 | 0.003 | 2.74E-09 | 2.7422E-07 | 0.00621277 | |
| | | | | 2 | 0.0119 | 105 | 0.003 | 2.74E-09 | 2.7422E-07 | 0.00971072 | |
| | | | | 3 | 0.0095 | 100 | 0.003 | 2.74E-09 | 2.7422E-07 | 0.01216396 | |

Table B-1: Calculation of nitrite concentration in mortar (25 L/m³)

| Date | Type of specimen | Addition ratio of DCI (L/m³) | Specimen name | Hole # | Extracted amount (g) | Dilution (mL) | Absorption | Concentration (g/g) | Mass of nitrite in the beaker (g/g) | Nitrite in (Kg(NO$_2^-$))/(m³ (mortar) | Average |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 7-Feb-14 | Mortar | 25 | A-1 | 1 | 0.0212 | 100 | 1.380 | 1.26E-06 | 0.00012614 | 1.74755096 | |
| | | | | 2 | 0.0106 | 100 | 0.784 | 7.17E-07 | 7.1664E-05 | 1.98562312 | |
| | | | | 3 | 0.0147 | 100 | 0.885 | 8.09E-07 | 8.0896E-05 | 1.61626497 | |
| | | | A-2 | 1 | 0.0116 | 105 | 0.632 | 5.78E-07 | 5.777E-05 | 1.46266784 | |
| | | | | 2 | 0.0144 | 100 | 0.815 | 7.45E-07 | 7.4497E-05 | 1.51943365 | 1.70511039 |
| | | | | 3 | 0.0102 | 110 | 0.648 | 5.92E-07 | 5.9232E-05 | 1.70553823 | |
| | | | A-3 | 1 | 0.0102 | 100 | 0.652 | 5.96E-07 | 5.9598E-05 | 1.71606624 | |
| | | | | 2 | 0.0108 | 100 | 0.698 | 6.38E-07 | 6.3803E-05 | 1.73507516 | |
| | | | | 3 | 0.0125 | 100 | 0.865 | 7.91E-07 | 7.9068E-05 | 1.85777331 | |

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Table B-2: Calculation of nitrite concentration in mortar (20 L/m$^3$)

| Date | Type of specimen | Addition ratio of DCI (L/m$^3$) | Specimen name | Hole # | Extracted amount (g) | Dilution (mL) | Absorption | Concentration (g/g) | Mass of nitrite in the beaker (g/g) | Nitrite in(Kg(NO$_2^-$))/(m$^3$ (mortar) | Average |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 8-Feb-14 | | 20 | B-1 | 1 | 0.0091 | 100 | 0.480 | 4.39E-07 | 4.3876E-05 | 1.4160757 | |
| | | | | 2 | 0.0095 | 100 | 0.490 | 4.48E-07 | 4.479E-05 | 1.38471086 | |
| | | | | 3 | 0.0096 | 100 | 0.486 | 4.44E-07 | 4.4424E-05 | 1.35910078 | |
| | | | B-2 | 1 | 0.0118 | 100 | 0.652 | 5.96E-07 | 5.9598E-05 | 1.4833793 | |
| | | | | 2 | - | 100 | -0.003 | -2.74E-09 | -2.742E-07 | | 1.42783944 |
| | | | | 3 | 0.0129 | 100 | 0.636 | 5.81E-07 | 5.8135E-05 | 1.32359168 | |
| | | | B-3 | 1 | 0.0135 | 100 | 0.714 | 6.53E-07 | 6.5265E-05 | 1.41987812 | |
| | | | | 2 | 0.0117 | 100 | 0.632 | 5.78E-07 | 5.777E-05 | 1.45016641 | |
| | | | | 3 | 0.0086 | 100 | 0.508 | 4.64E-07 | 4.6435E-05 | 1.58581268 | |

Table B-3: Calculation of nitrite concentration in mortar (15 L/m$^3$)

| Date | Type of specimen | Addition ratio of DCI (L/m$^3$) | Specimen name | Hole # | Extracted amount (g) | Dilution (mL) | Absorption | Concentration (g/g) | Mass of nitrite in the beaker (g/g) | Nitrite in (Kg(NO$_2^-$))/(m$^3$ (mortar) | Average |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 8-Feb-14 | | 15 | C-1 | 1 | 0.0126 | 100 | 0.502 | 4.59E-07 | 4.5887E-05 | 1.06959607 | |
| | | | | 2 | 0.0174 | 100 | 0.710 | 6.49E-07 | 6.4899E-05 | 1.09545798 | |
| | | | | 3 | 0.0173 | 100 | 0.728 | 6.65E-07 | 6.6545E-05 | 1.12972282 | |
| | | | C-2 | 1 | 0.0166 | 100 | 0.630 | 5.76E-07 | 5.7587E-05 | 1.01887073 | |
| | | | | 2 | 0.0085 | 100 | 0.282 | 2.58E-07 | 2.5777E-05 | 0.89066996 | 1.0218483 |
| | | | | 3 | 0.0206 | 100 | 0.752 | 6.87E-07 | 6.8739E-05 | 0.9800252 | |
| | | | C-3 | 1 | 0.0228 | 100 | 0.752 | 6.87E-07 | 6.8739E-05 | 0.88546137 | |
| | | | | 2 | 0.0112 | 105 | 0.438 | 4E-07 | 4.0037E-05 | 1.04988737 | |
| | | | | 3 | 0.0174 | 100 | 0.698 | 6.38E-07 | 6.3803E-05 | 1.0769432 | |

Table B-4: Calculation of nitrite concentration in mortar (10 L/m$^3$)

| Date | Type of specimen | Addition ratio of DCI (L/m$^3$) | Specimen name | Hole # | Extracted amount (g) | Dilution (mL) | Absorption | Concentration (g/g) | Mass of nitrite in the beaker (g/g) | Nitrite in (Kg(NO$_2^-$))/(m$^3$ (mortar) | Average |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 9-Feb-14 | | 10 | D-1 | 1 | 0.0143 | 100 | 0.323 | 2.95E-07 | 2.9525E-05 | 0.60639151 | |
| | | | | 2 | 0.0090 | 100 | 0.217 | 1.98E-07 | 1.9835E-05 | 0.64729738 | |
| | | | | 3 | 0.0103 | 100 | 0.211 | 1.93E-07 | 1.9287E-05 | 0.54996095 | |
| | | | D-2 | 1 | 0.0121 | 100 | 0.312 | 2.85E-07 | 2.8519E-05 | 0.69223866 | |
| | | | | 2 | 0.0132 | 100 | 0.289 | 2.64E-07 | 2.6417E-05 | 0.58777422 | 0.59349976 |
| | | | | 3 | 0.0140 | 100 | 0.337 | 3.08E-07 | 3.0804E-05 | 0.64623204 | |
| | | | D-3 | 1 | 0.0099 | 100 | 0.182 | 1.66E-07 | 1.6636E-05 | 0.49354052 | |
| | | | | 2 | 0.0122 | 100 | 0.245 | 2.24E-07 | 2.2395E-05 | 0.53912923 | |
| | | | | 3 | 0.0147 | 100 | 0.317 | 2.9E-07 | 2.8976E-05 | 0.57893333 | |

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Table B-5: Calculation of nitrite concentration in mortar (0 L/m³)

| Date | Type of specimen | Addition ratio of DCI (L/m³) | Specimen name | Hole # | Extracted amount (g) | Dilution (mL) | Absorption | Concentration (g/g) | Mass of nitrite in the beaker (g/g) | Nitrite in (Kg(NO₂⁻))/(m³ (mortar) | Average |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 10-Feb-14 | | 0 | B-C-1 | 1 | 0.0156 | 100 | 0.002 | 1.83E-09 | 1.8282E-07 | 0.00344185 | |
| | | | | 2 | 0.0141 | 100 | 0.002 | 1.83E-09 | 1.8282E-07 | 0.003808 | |
| | | | | 3 | 0.0170 | 100 | 0.002 | 1.83E-09 | 1.8282E-07 | 0.0031584 | |
| | | | B-C-2 | 1 | 0.0109 | 100 | 0.002 | 1.83E-09 | 1.8282E-07 | 0.00492595 | |
| | | | | 2 | 0.0206 | 100 | 0.002 | 1.83E-09 | 1.8282E-07 | 0.00260645 | 0.00431042 |
| | | | | 3 | 0.0239 | 100 | 0.002 | 1.83E-09 | 1.8282E-07 | 0.00224656 | |
| | | | B-C-3 | 1 | - | 100 | | | 0 | | |
| | | | | 2 | 0.0093 | 100 | 0.002 | 1.83E-09 | 1.8282E-07 | 0.00577343 | |
| | | | | 3 | 0.0063 | 100 | 0.002 | 1.83E-09 | 1.8282E-07 | 0.00852268 | |

Table C-1: Calculation of nitrite concentration in concrete (25 L/m$^3$)

| Date | Type of specimen | Addition ratio of DCI (L/m$^3$) | Specimen name | Hole # | Extracted amount | Dilution (mL) | Absorption | Concentration (g/g) | Mass of nitrite in the beaker (g/g) | Nitrite (Kg(NO2-))/(m^3(concrete) | Average |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 6-Feb-14 | Concrete | 25 | A-1 | 1 | 0.0100 | 100 | 0.778 | 7.1E-07 | 7.1E-05 | 1.4223 | |
| | | | | 2 | 0.0265 | 100 | 1.850 | 1.7E-06 | 0.00017 | 1.27626 | |
| | | | | 3 | 0.0120 | 100 | 0.830 | 7.6E-07 | 7.6E-05 | 1.26447 | |
| | | | A-2 | 1 | 0.0137 | 100 | 0.950 | 8.7E-07 | 8.7E-05 | 1.2677 | |
| | | | | 2 | - | 100 | -0.014 | -1.3E-08 | -1.3E-06 | | 1.32982 |
| | | | | 3 | 0.0118 | 100 | 0.812 | 7.4E-07 | 7.4E-05 | 1.25802 | |
| | | | A-3 | 1 | 0.0105 | 100 | 0.806 | 7.4E-07 | 7.4E-05 | 1.40333 | |
| | | | | 2 | 0.0123 | 100 | 0.945 | 8.6E-07 | 8.6E-05 | 1.40456 | |
| | | | | 3 | 0.0141 | 100 | 1.035 | 9.5E-07 | 9.5E-05 | 1.34194 | |

Table C-2: Calculation of nitrite concentration in concrete (20 L/m³)

| Date | Type of specimen | Addition ratio of DCI (L/m³) | Specimen name | Hole # | Extracted amount | Dilution (mL) | Absorption | Concentration (g/g) | Mass of nitrite in the beaker (g/g) | Nitrite (Kg(NO2-))/(m^3(concrete) | Average |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 6-Feb-14 | | 20 | B-1 | 1 | 0.0149 | 100 | 0.875 | 8E-07 | 8E-05 | 1.07358 | |
| | | | | 2 | 0.0158 | 100 | 0.910 | 8.3E-07 | 8.3E-05 | 1.05292 | |
| | | | | 3 | 0.0099 | 100 | 0.636 | 5.8E-07 | 5.8E-05 | 1.17445 | |
| | | | B-2 | 1 | 0.0119 | 100 | 0.728 | 6.7E-07 | 6.7E-05 | 1.1184 | |
| | | | | 2 | 0.0207 | 100 | 1.190 | 1.1E-06 | 0.00011 | 1.05097 | 1.08727 |
| | | | | 3 | 0.0209 | 100 | 1.260 | 1.2E-06 | 0.00012 | 1.10214 | |
| | | | B-3 | 1 | 0.0167 | 100 | 1.005 | 9.2E-07 | 9.2E-05 | 1.10018 | |
| | | | | 2 | 0.0246 | 100 | 1.380 | 1.3E-06 | 0.00013 | 1.02555 | |
| | | | | 3 | - | 100 | -0.010 | -9.1E-09 | -9.1E-07 | | |

Table C-3: Calculation of nitrite concentration in concrete (15 L/m$^3$)

| Date | Type of specimen | Addition ratio of DCI (L/m$^3$) | Specimen name | Hole # | Extracted amount | Dilution (mL) | Absorption | Concentration (g/g) | Mass of nitrite in the beaker (g/g) | Nitrite (Kg(NO2-))/(m^3(concrete) | Average |
|------|------|------|------|------|------|------|------|------|------|------|------|
| 6-Feb-14 | | 15 | C-1 | 1 | 0.0247 | 100 | 1.070 | 9.8E-07 | 9.8E-05 | 0.79195 | |
| | | | | 2 | 0.0121 | 100 | 0.504 | 4.6E-07 | 4.6E-05 | 0.76148 | |
| | | | | 3 | 0.0132 | 100 | 0.646 | 5.9E-07 | 5.9E-05 | 0.89469 | |
| | | | C-2 | 1 | 0.0104 | 100 | 0.484 | 4.4E-07 | 4.4E-05 | 0.85079 | |
| | | | | 2 | 0.0207 | 100 | 0.890 | 8.1E-07 | 8.1E-05 | 0.78602 | 0.82551 |
| | | | | 3 | 0.0132 | 100 | 0.532 | 4.9E-07 | 4.9E-05 | 0.7368 | |
| | | | C-3 | 1 | 0.0134 | 100 | 0.690 | 6.3E-07 | 6.3E-05 | 0.94136 | |
| | | | | 2 | 0.0104 | 100 | 0.478 | 4.4E-07 | 4.4E-05 | 0.84025 | |
| | | | | 3 | 0.0177 | 100 | 0.800 | 7.3E-07 | 7.3E-05 | 0.82628 | |

Table C-4: Calculation of nitrite concentration in concrete (10 L/m$^3$)

| Date | Type of specimen | Additio n ratio of DCI (L/m$^3$) | Specime n name | Hol e # | Extracte d amount | Dilutio n (mL) | Absorptio n | Concentrati on (g/g) | Mass of nitrite in the beaker (g/g) | Nitrite (Kg(NO2- ))/(m^3(concret e) | Averag e |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 7-Feb-14 | | 10 | D-1 | 1 | 0.0097 | 100 | 0.245 | 2.2E-07 | 2.2E-05 | 0.46175 | |
| | | | | 2 | 0.0102 | 100 | 0.266 | 2.4E-07 | 2.4E-05 | 0.47675 | |
| | | | | 3 | 0.0213 | 100 | 0.472 | 4.3E-07 | 4.3E-05 | 0.40511 | |
| | | | D-2 | 1 | 0.0112 | 100 | 0.310 | 2.8E-07 | 2.8E-05 | 0.50601 | |
| | | | | 2 | - | 100 | -0.013 | -1.2E-08 | -1.2E-06 | | 0.4694 |
| | | | | 3 | 0.0106 | 100 | 0.305 | 2.8E-07 | 2.8E-05 | 0.52603 | |
| | | | D-3 | 1 | 0.0104 | 100 | 0.247 | 2.3E-07 | 2.3E-05 | 0.43419 | |
| | | | | 2 | 0.0107 | 100 | 0.269 | 2.5E-07 | 2.5E-05 | 0.4596 | |
| | | | | 3 | 0.0140 | 100 | 0.372 | 3.4E-07 | 3.4E-05 | 0.48577 | |

Table C-5: Calculation of nitrite concentration in concrete (0 L/m$^3$)

| Date | Type of specimen | Addition ratio of DCI (L/m$^3$) | Specimen name | Hole # | Extracted amount | Dilution (mL) | Absorption | Concentration (g/g) | Mass of nitrite in the beaker (g/g) | Nitrite (Kg(NO$_2^-$))/(m$^3$(concrete) | Average |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 10-Feb-14 | | 0 | A-C-1 | 1 | dry | 100 | -0.022 | -2E-08 | -2E-06 | | |
| | | | | 2 | 0.0131 | 100 | -0.001 | -9.1E-10 | -9.1E-08 | -0.0014 | |
| | | | | 3 | 0.0063 | 100 | -0.001 | -9.1E-10 | -9.1E-08 | -0.0029 | |
| | | | A-C-2 | 1 | 0.0070 | 100 | -0.001 | -9.1E-10 | -9.1E-08 | -0.00261 | |
| | | | | 2 | 0.0061 | 100 | -0.001 | -9.1E-10 | -9.1E-08 | -0.003 | -0.0021 |
| | | | | 3 | 0.0164 | 100 | -0.001 | -9.1E-10 | -9.1E-08 | -0.00111 | |
| | | | A-C-3 | 1 | 0.0063 | 100 | -0.001 | -9.1E-10 | -9.1E-08 | -0.0029 | |
| | | | | 2 | 0.0077 | 100 | -0.001 | -9.1E-10 | -9.1E-08 | -0.00237 | |
| | | | | 3 | 0.0352 | 100 | -0.001 | -9.1E-10 | -9.1E-08 | -0.00052 | |

## Appendix 3 Second Absorption Data and Calculation of Nitrite Concentration

Table D-1: Second calculation of nitrite concentration in paste (25 L/m$^3$)

| Date | Type of specimen | Addition ratio of DCI (L/m$^3$) | Specimen name | Hole # | Extracted amount (g) | Dilution (mL) | Adjusted Absorption | Concentration (g/g) | Mass of nitrite in the beaker (g/g) | Nitrite in (Kg(NO$_2^-$))/(m$^3$ (paste) | Average |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 22-Feb-14 | Paste | 25 | A-1 | 1 | | | | | | | |
| | | | | 2 | | | | | | | |
| | | | | 3 | 0.0048 | 100 | 0.314 | 2.87E-07 | 2.8702E-05 | 2.51979738 | |
| | | | A-2 | 1 | | | | | | | 2.20723002 |
| | | | | 2 | | | | | | | |
| | | | | 3 | | | | | | | |
| | | | A-3 | 1 | 0.0106 | 100 | 0.596 | 5.45E-07 | 5.4479E-05 | 2.16579628 | |
| | | | | 2 | 0.0152 | 100 | 0.764 | 6.98E-07 | 6.9835E-05 | 1.93609641 | |
| | | | | 3 | | | | | | | |

Table D-2: Second calculation of nitrite concentration in paste (20 L/m$^3$)

| Date | Type of specimen | Addition ratio of DCI (L/m$^3$) | Specimen name | Hole # | Extracted amount (g) | Dilution (mL) | Adjusted Absorption | Concentration (g/g) | Mass of nitrite in the beaker (g/g) | Nitrite in (Kg(NO$_2^-$))/(m$^3$ (paste) | Average |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 22-Feb-14 | | 20 | B-1 | 1 | 0.0173 | 100 | 0.692 | 6.33E-07 | 6.3254E-05 | 1.54076782 | |
| | | | | 2 | 0.0134 | 100 | 0.582 | 5.32E-07 | 5.3199E-05 | 1.6729979 | |
| | | | | 3 | | | | | | | |
| | | | B-2 | 1 | | | | | | | |
| | | | | 2 | | | | | | | 1.54771027 |
| | | | | 3 | 0.0058 | 100 | 0.226 | 2.07E-07 | 2.0658E-05 | 1.50092038 | |
| | | | B-3 | 1 | 0.0155 | 100 | 0.594 | 5.43E-07 | 5.4296E-05 | 1.47615498 | |
| | | | | 2 | | | | | | | |
| | | | | 3 | | | | | | | |

Table D-3: Second calculation of nitrite concentration in paste (15 L/m³)

| Date | Type of specimen | Addition ratio of DCI (L/m³) | Specimen name | Hole # | Extracted amount (g) | Dilution (mL) | Adjusted Absorption | Concentration (g/g) | Mass of nitrite in the beaker (g/g) | Nitrite in (Kg(NO$_2^-$))/(m³ (paste) | Average |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 22-Feb-14 | | 15 | C-1 | 1 | 0.0152 | 100 | 0.466 | 4.26E-07 | 4.2596E-05 | 1.18091744 | |
| | | | | 2 | 0.0219 | 100 | 0.640 | 5.85E-07 | 5.8501E-05 | 1.12567512 | |
| | | | | 3 | 0.0231 | 100 | 0.610 | 5.58E-07 | 5.5759E-05 | 1.01717356 | |
| | | | C-2 | 1 | | | | | | | |
| | | | | 2 | | | | | | | 1.12696796 |
| | | | | 3 | 0.0049 | 100 | 0.140 | 1.28E-07 | 1.2797E-05 | 1.10054845 | |
| | | | C-3 | 1 | 0.0123 | 100 | 0.379 | 3.46E-07 | 3.4644E-05 | 1.18689229 | |
| | | | | 2 | 0.0056 | 100 | 0.173 | 1.58E-07 | 1.5814E-05 | 1.18996801 | |
| | | | | 3 | 0.0187 | 100 | 0.528 | 4.83E-07 | 4.8263E-05 | 1.08760082 | |

Table D-4: Second calculation of nitrite concentration in paste (10 L/m$^3$)

| Date | Type of specimen | Addition ratio of DCI (L/m$^3$) | Specimen name | Hole # | Extracted amount (g) | Dilution (mL) | Adjusted Absorption | Concentration (g/g) | Mass of nitrite in the beaker (g/g) | Nitrite in (Kg(NO$_2^-$))/(m$^3$ (paste) | Average |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 22-Feb-14 | | 10 | D-1 | 1 | 0.0080 | 100 | 0.109 | 9.96E-08 | 9.9634E-06 | 0.52482404 | |
| | | | | 2 | | | | | | | |
| | | | | 3 | 0.0033 | 100 | 0.077 | 7.04E-08 | 7.0384E-06 | 0.89878123 | |
| | | | D-2 | 1 | | | | | | | 0.65900082 |
| | | | | 2 | | | | | | | |
| | | | | 3 | | | | | | | |
| | | | D-3 | 1 | 0.0220 | 105 | 0.384 | 3.51E-07 | 3.5101E-05 | 0.67233505 | |
| | | | | 2 | | | | | | | |
| | | | | 3 | 0.0097 | 100 | 0.136 | 1.24E-07 | 1.2431E-05 | 0.54006295 | |

The specimens were dry. Therefore, no results were reported for the Second calculation of nitrite concentration in paste (0 L/m3)

Table E-1: Second calculation of nitrite concentration in mortar (25 L/m$^3$)

| Date | Type of specimen | Addition ratio of DCI (L/m$^3$) | Specimen name | Hole # | Extracted amount (g) | Dilution (mL) | Adjusted Absorption | Concentration (g/g) | Mass of nitrite in the beaker (g/g) | Nitrite in (Kg(NO$_2^-$))/(m$^3$ (mortar) | Average |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 24-Feb-14 | Mortar | 25 | A-1 | 1 | 0.0080 | 100 | 0.626 | 5.72E-07 | 5.7221E-05 | 2.10073355 | |
| | | | | 2 | | | | | | | |
| | | | | 3 | | | | | | | |
| | | | A-2 | 1 | 0.0011 | 100 | 0.167 | 1.53E-07 | 1.5265E-05 | 4.07577697 | |
| | | | | 2 | 0.0254 | 120 | 1.484 | 1.36E-06 | 0.00013565 | 1.56850826 | 2.33369658 |
| | | | | 3 | 0.0281 | 115 | 1.664 | 1.52E-06 | 0.0001521 | 1.58976754 | |
| | | | A-3 | 1 | | | | | | | |
| | | | | 2 | | | | | | | |
| | | | | 3 | | | | | | | |

Table E-2: Second calculation of nitrite concentration in mortar (20 L/m³)

| Date | Type of specimen | Addition ratio of DCI (L/m³) | Specimen name | Hole # | Extracted amount (g) | Dilution (mL) | Adjusted Absorption | Concentration (g/g) | Mass of nitrite in the beaker (g/g) | Nitrite in (Kg(NO$_2^-$))/(m³ (mortar) | Average |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 24-Feb-14 | | 20 | B-1 | 1 | | | | | | | |
| | | | | 2 | 0.0122 | 115 | 0.736 | 6.73E-07 | 6.7276E-05 | 1.61958822 | |
| | | | | 3 | | | | | | | |
| | | | B-2 | 1 | 0.0024 | 100 | 0.160 | 1.46E-07 | 1.4625E-05 | 1.78976234 | |
| | | | | 2 | | | | | | | 1.5284 |
| | | | | 3 | | | | | | | |
| | | | B-3 | 1 | | | | | | | |
| | | | | 2 | 0.0142 | 115 | 0.622 | 5.69E-07 | 5.6856E-05 | 1.17594948 | |
| | | | | 3 | | | | | | | |

Table E-3: Second calculation of nitrite concentration in mortar (15 L/m$^3$)

| Date | Type of specimen | Addition ratio of DCI (L/m$^3$) | Specimen name | Hole # | Extracted amount (g) | Dilution (mL) | Adjusted Absorption | Concentration (g/g) | Mass of nitrite in the beaker (g/g) | Nitrite in (Kg(NO$_2^-$))/(m$^3$ (mortar) | Average |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 24-Feb-14 | | 15 | C-1 | 1 | | | | | | | |
| | | | | 2 | | | | | | | |
| | | | | 3 | | | | | | | |
| | | | C-2 | 1 | 0.0092 | 100 | 0.388 | 3.55E-07 | 3.5466E-05 | 1.13221922 | |
| | | | | 2 | | | | | | | 1.27986594 |
| | | | | 3 | 0.0145 | 100 | 0.602 | 5.5E-07 | 5.5027E-05 | 1.11458993 | |
| | | | C-3 | 1 | 0.0316 | 100 | 1.304 | 1.19E-06 | 0.0001192 | 1.10784023 | |
| | | | | 2 | 0.0028 | 105 | 0.195 | 1.78E-07 | 1.7824E-05 | 1.86966244 | |
| | | | | 3 | 0.0069 | 100 | 0.302 | 2.76E-07 | 2.7605E-05 | 1.17501788 | |

Table E-4: Second calculation of nitrite concentration in mortar (10 L/m$^3$)

| Date | Type of specimen | Addition ratio of DCI (L/m$^3$) | Specimen name | Hole # | Extracted amount (g) | Dilution (mL) | Adjusted Absorption | Concentration (g/g) | Mass of nitrite in the beaker (g/g) | Nitrite in (Kg(NO$_2^-$))/(m$^3$ (mortar) | Average |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 24-Feb-14 | | 10 | D-1 | 1 | | | | | | | |
| | | | | 2 | 0.0060 | 100 | 0.166 | 1.52E-07 | 1.5174E-05 | 0.74275137 | |
| | | | | 3 | | | | | | | |
| | | | D-2 | 1 | | | | | | | |
| | | | | 2 | 0.0101 | 105 | 0.261 | 2.39E-07 | 2.3857E-05 | 0.69375441 | 0.68470527 |
| | | | | 3 | | | | | | | |
| | | | D-3 | 1 | 0.0102 | 100 | 0.233 | 2.13E-07 | 2.1298E-05 | 0.6132568 | |
| | | | | 2 | 0.0060 | 100 | 0.154 | 1.41E-07 | 1.4077E-05 | 0.6890585 | |
| | | | | 3 | | | | | | | |

The specimens were dry. Therefore, no results were reported for the Second calculation of nitrite concentration in mortar (0 L/m3)

Table G-1: Second calculation of nitrite concentration in concrete (25 L/m³)

| Date | Type of specimen | Addition ratio of DCI (L/m³) | Specimen name | Hole # | Extracted amount | Dilution (mL) | Adjusted Absorption | Concentration (g/g) | Mass of nitrite in the beaker (g/g) | Nitrite (Kg(NO$_2^-$))/(m³ (concrete) | Average |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 23-Feb-14 | Concrete | 25 | A-1 | 1 | 0.0065 | 100 | 0.564 | 5.15539E-07 | 5.15539E-05 | 1.586274786 | |
| | | | | 2 | | | | | | | |
| | | | | 3 | | | | | | | |
| | | | A-2 | 1 | | | | | | | |
| | | | | 2 | | | | | | | 1.5293497 |
| | | | | 3 | | | | | | | |
| | | | A-3 | 1 | 0.0048 | 100 | 0.428 | 3.91225E-07 | 3.91225E-05 | 1.630103595 | |
| | | | | 2 | 0.0281 | 100 | 1.910 | 1.74589E-06 | 0.000174589 | 1.242623953 | |
| | | | | 3 | 0.0056 | 100 | 0.508 | 4.64351E-07 | 4.64351E-05 | 1.658396448 | |

Table G-2: Second calculation of nitrite concentration in concrete (20 L/m³)

| Date | Type of specimen | Addition ratio of DCI (L/m³) | Specimen name | Hole # | Extracted amount | Dilution (mL) | Adjusted Absorption | Concentration (g/g) | Mass of nitrite in the beaker (g/g) | Nitrite $(Kg(NO_2^-))/(m^3$ (concrete) | Average |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 23-Feb-14 | | 20 | B-1 | 1 | | | | | | | |
| | | | | 2 | 0.0085 | 100 | 0.608 | 5.55759E-07 | 5.55759E-05 | 1.307667491 | |
| | | | | 3 | 0.0150 | 100 | 0.856 | 7.8245E-07 | 7.8245E-05 | 1.043266301 | |
| | | | B-2 | 1 | | | | | | | 1.1494632 |
| | | | | 2 | | | | | | | |
| | | | | 3 | | | | | | | |
| | | | B-3 | 1 | 0.0122 | 105 | 0.804 | 7.34918E-07 | 7.34918E-05 | 1.204783169 | |
| | | | | 2 | 0.0207 | 105 | 1.180 | 1.07861E-06 | 0.000107861 | 1.042135849 | |
| | | | | 3 | | | | | | | |

Table G-3: Second calculation of nitrite concentration in concrete (15 L/m³)

| Date | Type of specimen | Addition ratio of DCI (L/m³) | Specimen name | Hole # | Extracted amount | Dilution (mL) | Adjusted Absorption | Concentration (g/g) | Mass of nitrite in the beaker (g/g) | Nitrite (Kg(NO$_2^-$))/(m³ (concrete) | Average |
|------|------|------|------|------|------|------|------|------|------|------|------|
| 23-Feb-14 | | 15 | C-1 | 1 | 0.0088 | 100 | 0.502 | 4.58867E-07 | 4.58867E-05 | 1.042878511 | |
| | | | | 2 | 0.0127 | 100 | 0.670 | 6.12431E-07 | 6.12431E-05 | 0.964458967 | |
| | | | | 3 | 0.0182 | 100 | 0.806 | 7.36746E-07 | 7.36746E-05 | 0.809610864 | |
| | | | C-2 | 1 | 0.0041 | 100 | 0.212 | 1.93784E-07 | 1.93784E-05 | 0.94528916 | 0.94770615 |
| | | | | 2 | | | | | | | |
| | | | | 3 | 0.0071 | 100 | 0.331 | 3.02559E-07 | 3.02559E-05 | 0.852280042 | |
| | | | C-3 | 1 | 0.0164 | 100 | 0.870 | 7.95247E-07 | 7.95247E-05 | 0.969813172 | |
| | | | | 2 | | | | | | | |
| | | | | 3 | 0.0058 | 100 | 0.333 | 3.04388E-07 | 3.04388E-05 | 1.049612305 | |

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Table G-4: Second calculation of nitrite concentration in concrete (10 L/m$^3$).

| Date | Type of specimen | Addition ratio of DCI (L/m3) | Specimen name | Hole # | Extracted amount | Dilution (mL) | Adjusted Absorption | Concentration (g/g) | Mass of nitrite in the beaker (g/g) | Nitrite (Kg(NO2-))/(m3 (concrete) | Average |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 23-Feb-14 | | 10 | D-1 | 1 | | | | | | | |
| | | | | 2 | 0.0060 | 100 | 0.222 | 2.02925E-07 | 2.02925E-05 | 0.6764168 19 | |
| | | | | 3 | | | | | | | |
| | | | D-2 | 1 | | | | | | | 0.641414 37 |
| | | | | 2 | | | | | | | |
| | | | | 3 | | | | | | | |
| | | | D-3 | 1 | 0.0123 | 100 | 0.408 | 3.72943E-07 | 3.72943E-05 | 0.6064119 14 | |
| | | | | 2 | | | | | | | |
| | | | | 3 | | | | | | | |

The specimens were dry. Therefore, no results were reported for the Second calculation of nitrite concentration in concrete (0 L/m3)

## Appendix 4 Calculation Sheet

Table H-1 Example of the reported data and its calculation.

| Date | Type of specimen | Addition ratio of DCI (L/m³) | Specimen name | Hole # | Extracted amount | Dilution (mL) | Absorption | Concentration (g/g) | Mass of nitrite in the beaker (g/g) | Nitrite (Kg(NO$_2^-$))/(m^3(concrete) |
|------|------------------|------------------------------|---------------|--------|------------------|---------------|------------|---------------------|--------------------------------------|----------------------------------------|
| 6-Feb-14 | Concrete | 25 | A-1 | 1 | 0.0100 | 100 | 0.778 | 7.1E-07 | 7.1E-05 | 1.4223 |

Table H-2 Calculation of the total added nitrite in mix (25 L/m³ for concrete).

| DCI Dosage | 25 | DCI L/m^3 concrete |
|------------|-----|--------------------|
| DCI density | 1300 | kg/m^3 |

The calculation of the free nitrite in the pore solution is as follows:

- Conversion to total added DCI (kg NO$_2^-$/m³ concrete)

$$= \text{DCI Dosage} \times \text{DCI density}/1000$$

Total DCI = 32.5 kg NO$_2^-$/m³
Ca(No$^-_2$)$_2$ contains approximately 21% NO$_2^-$. Therefore,
Total added nitrite = 6.825 kg NO$_2^-$/m³

- A 0.01 g were extracted from the cavity # 1 cylinder#A-1. Where the extracted pore solution consists of extracted pore water and extracted free nitrite. Then, to find the concentration of free nitrite in the extracted solution, the following relation were used:

$$Cnc = \frac{Men}{Mct}$$

  - o  C nc = Concentration of free nitrite in cavity obtained from the calibration curve = 7.1×10$^{-7}$
  - o  M en = Mass of the measured nitrite in the extracted solution.
  - o  M ct = Mass of the amount of solution in the beaker (100 g)
  - o  M e = the total extracted amount of pore solution from the cavity, which equals   = 0.0100 g

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o   M en = $7.1 \times 10^{-5}$ g,

Then, $Cn$= The concentration of nitrite in pore solution

$$Cn = \frac{Men}{Me}$$

$Cn$ = $7.11 10^{-3}$ g $NO_2^-$/g pore solution

- Further, the concentration were expressed as part of the mix specimens porosity as follows:
  Concentration of nitrite in pore solution [Nitrite $(Kg(NO_2^-))/(m^3(concrete))$]:
  = The concentration of nitrite in pore solution × water density × porosity × 1000
    o   The concentration of nitrite in pore solution= 7.11E-03 g $NO_2^-$/g pore water
    o   Water density = 1g/ $cm^3$
    o   Porosity (concrete specimen)=0.2 $cm^3$ (pore water)/ $cm^3$(concrete)
    o   And multiplied by 1000 for conversion.
  = The concentration of nitrite in pore solution × water density × porosity × 1000 = 1.422 $Kg(NO2-)/m3(concrete)$

## Appendix 5 Data and Calculation of Nitrite Binding Isotherms

Table I-1 Nitrite binding isotherms for the first measurement of paste, mortar and concrete specimens solution

| DCI (L/m³) / mix type | Concrete | | Mortar | | Paste | |
|---|---|---|---|---|---|---|
| | (1/CF) (kg/m³) | (1/CB) (kg/m³) | (1/CF) (kg/m³) | (1/CB) (kg/m³) | (1/CF) (kg/m³) | (1/CB) (kg/m³) |
| 25 | 7.519 | 0.149 | 5.864 | 0.150 | 0.171 | 6.654 |
| 20 | 9.197 | 0.186 | 7.003 | 0.188 | 0.143 | 5.317 |
| 15 | 12.113 | 0.249 | 9.786 | 0.250 | 0.102 | 3.992 |
| 10 | 21.303 | 0.372 | 16.849 | 0.374 | 0.059 | 2.670 |

Table I-2 Nitrite binding isotherms for the second measurement of paste, mortar and concrete specimens solution

| DCI (L/m³) / mix type | Concrete | | Mortar | | Paste | |
|---|---|---|---|---|---|---|
| | (1/CF) (kg/m³) | (1/CB) (kg/m³) | (1/CF) (kg/m³) | (1/CB) (kg/m³) | (1/CF) (kg/m³) | (1/CB) (kg/m³) |
| 25 | 6.538 | 0.149 | 5.704 | 0.150 | 0.175 | 6.649 |
| 20 | 8.699 | 0.187 | 6.542 | 0.188 | 0.152 | 5.307 |
| 15 | 10.551 | 0.249 | 7.813 | 0.252 | 0.127 | 3.967 |
| 10 | 15.590 | 0.375 | 14.604 | 0.375 | 0.068 | 2.661 |