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Nitrite binding in cement

J. Tritthart[a,*], P.F.G. Banfill[b]

[a]University of Technology, Stremayrgasse 11, 8010 Graz, Austria
[b]Heriot-Watt University, Riccarton, Edinburgh EH14 4AS, UK

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Abstract

Pore solution has been pressed out of hardened cement pastes prepared with the addition of nitrite-containing corrosion inhibitors. The binding of nitrite was assessed by comparing the concentration in the mixing water with that in the pore solution in both the presence and absence of chlorides. The results indicate that a major controlling mechanism is the adsorption of nitrite and chloride ions on the surface of hydration products. However, there is clear competition between adsorption of nitrite and chloride on cement and as a result at the presence of chloride there is more free nitrite available to inhibit steel corrosion. Using calcium nitrite results in lower free nitrite and hydroxyl ion concentrations than when sodium nitrite is used because precipitation of calcium hydroxide is enhanced and therefore higher dosage rates are needed. All this information enables guidance for the satisfactory use of nitrite inhibitors to be produced. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Pore solution; Corrosion inhibitors; Nitrite; Chloride; Cement paste; Concrete

1. Introduction

Nitrite salts are the basis for corrosion inhibitors used in significant quantities worldwide as admixtures in concrete for protecting embedded steel from corrosion initiated by chlorides [1]. In 1995, the British Board of Agrèment [2] inspected 11 reinforced concrete structures containing nitrite inhibitors, which were all performing satisfactorily and Gonzalez et al. [3] reported that the presence of 2% sodium nitrite decreased the corrosion current in laboratory mortars to 10% of that observed in control specimens.

Clearly only the nitrite ions dissolved in the pore solution of the cement matrix are free to migrate to the steel and inhibit corrosion and therefore recommended addition rates have been established to ensure that the minimum concentration necessary to passivate the steel surface is exceeded. Since nitrite ions bound by cement cannot be effective the influence of chloride ions on nitrite binding in cement is of great practical interest to users of concrete. However, apart from an article by Kawamura et al. [4], which reported the effect of age on ionic concentrations in the pore solution of mortars and their resulting electrochemical corrosion behaviour when made at a single addition rate of sodium and calcium nitrite, a literature survey failed to reveal any systematic research results. This article describes an investigation that aimed to generate experimental data on the influence of nitrite content and counter-ion type, age, water/cement ratio, and the presence of chlorides on the free nitrite concentration in the hardened pastes of typical cements. Such a database of information was expected to be of considerable benefit to concrete users.

2. Experimental

Three different Austrian cements, a normal portland cement (PZ-375-EZ), a cement containing about 30% BFS (EPZ) and a sulfate-resisting cement (HS-cement), and a British portland cement (grade 42.5N) were used. The chemical compositions of the cements are given in Table 1.

The salts were dissolved in the appropriate quantity of mixing water before the cement was added and the paste

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* Corresponding author. Tel.: +43-316-873-7158; fax: +43-316-873-7650.

E-mail address: tri@tvfa.tu-graz.ac.at (J. Tritthart).

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Table 1
Cement composition and fineness

	PZ-375-EZ	EPZ	HS-cement	British 42.5N
Loss on ignition (1000°C)	2.6	1.9	1.2	nd
Insoluble residue	0.7	0.6	0.6	nd
SiO_2	19.9	24.7	21.2	20.5
Al_2O_3	4.6	7.9	3.2	4.6
Fe_2O_3	2.7	1.7	4.8	3.3
CaO	61.9	54.1	63.1	63.5
MgO	2.4	3.4	1.4	2.1
SO_3	2.9	2.6	2.4	1.2
Na_2O	0.3	nd	nd	<0.05
K_2O	1.0	nd	nd	0.5
C_3A (Bogue)	nd	nd	0.3	nd
Specific surface (Blaine)	3550	2900	2850	3480

mixed with a spoon. The sodium nitrite and sodium chloride used were of analytical quality, whereas the calcium nitrite was the commercially available corrosion inhibitor DCI (a concentrated aqueous solution — Grace Construction Products) and a crystalline product from an unknown supplier. In both of the latter cases, the nitrite content was determined beforehand so that pastes of the required addition rate could be prepared. The fresh cement pastes were filled into tightly closed plastic bottles, which were mounted in a rotary frame. The samples were rotated overnight to prevent water separation before setting, after which the bottles were removed and stored at 20°C until required for testing. The pore water press used in Graz is described in Ref. [5] and that used in Edinburgh was developed from the one first described in Ref. [7]. The OH^- and $NO_2{}^-$ concentrations of the expressed pore solutions were determined as follows. The OH^- concentration was determined by titration with 0.1 M HCl against *m*-cresol purple (Merck). The $NO_2{}^-$ concentration was determined by a spectrophotometer (Milton Roy spectronic 1201) using α-naphthylamine/sulfanilic acid at 530 nm and the Cl^- concentration by potentiometric titration (ORION 960) with 0.01 M $AgNO_3$.

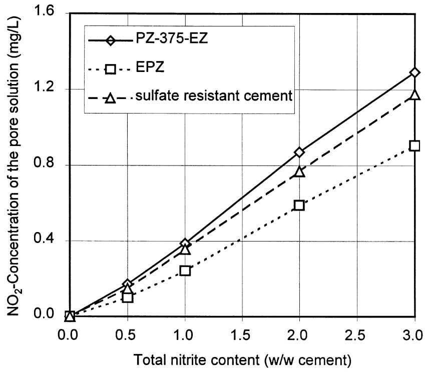

Fig. 1. Nitrite concentration of the pore solution versus total nitrite content.

3. Results and discussion

3.1. *Effect of total nitrite content (sodium salt) on the nitrite and hydroxide concentration of the pore solution*

Fig. 1 shows that the nitrite concentration of the pore solutions obtained from the three Austrian cements (water/cement ratio of 0.6) mixed with sodium nitrite increases with increasing total nitrite content. The pore solution of the sulfate-resisting cement has a somewhat lower nitrite concentration than the PZ-375-EZ, indicating that it has bound more nitrite. The EPZ has clearly bound the most nitrite.

It is clear that the interaction between nitrite and C_3A in cement is not significant, otherwise the nitrite concentration of the pore solution of the low C_3A cement would have been much higher than that of the other cements. This was confirmed by pore solution investigations of clinker samples to which various amounts of gypsum were added. The factor that the hydrated EPZ, which has bound the most nitrite, had most probably a higher specific surface area as a result of its slag content suggests that the main mechanism of binding is adsorption of nitrite ions at the surface. The steady increase in nitrite concentration in the pore solution with increasing total nitrite content confirms this. If it were instead due only to chemical binding the nitrite concentration of the pore solution would be expected to remain low up to a critical total nitrite content corresponding to total consumption of the nitrite-binding component (this would depend upon its solubility product). At higher nitrite contents than the critical value, it would be expected to increase sharply with increasing total nitrite content and since this behaviour is not observed chemical binding can be discounted.

Fig. 2 shows that the hydroxyl concentration of the different cements follows no regular trend with total nitrite content. The shape of the curve in Fig. 2 for the PZ-375-EZ is similar to that observed in previous work on chloride binding [8] where the initial increase of hydroxyl concen-

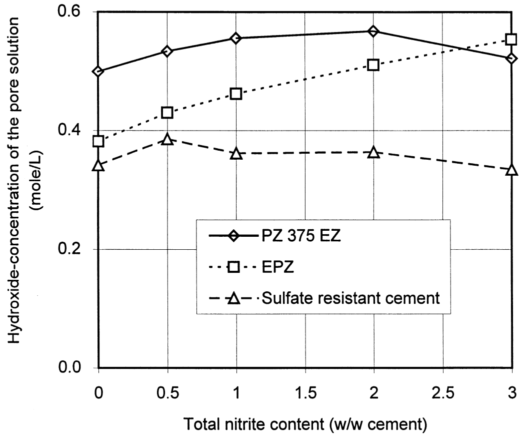

Fig. 2. Hydroxyl concentration of the pore solution versus total nitrite content.

tration was attributed to competitive adsorption between chloride and hydroxyl. Evidently, this behaviour is not restricted only to chloride and this is further support for the adsorption of nitrite on to hydrated cement. For the slag-containing EPZ, the increasing trend continues to a nitrite content higher than that tested here, while for the low C_3A cement, the increase is restricted to low-nitrite contents only.

3.2. Influence of age and water/cement ratio

Fig. 3 shows the nitrite and hydroxyl concentration of the pore solution obtained from samples of different ages (water/cement ratio of 0.6). The nitrite concentration decreased over the first 7 days from the concentration in the mixing water and then increased again to slightly higher values. The hydroxyl concentration increased sharply over the first 7 days due to the dissolution of alkalis from the cement and then increased more slowly but exactly in parallel with the increase in nitrite concentration. The parallel increase suggests that both increasing concentrations are due to the reduction in the free water by continuing hydration, which makes the pore solutions more concentrated. This is also an indication that nitrite is bound only in the early stages of hydration. The results agree with the situation in chloride binding, which is practically complete within 14 days [6,8].

Fig. 4 shows that, as expected, nitrite and hydroxyl concentration decreased with increasing water/cement ratio. Experimental error is the most probable explanation of the increase of the nitrite curve between water/cement ratio of 0.5 and 0.6, which does not fit this picture.

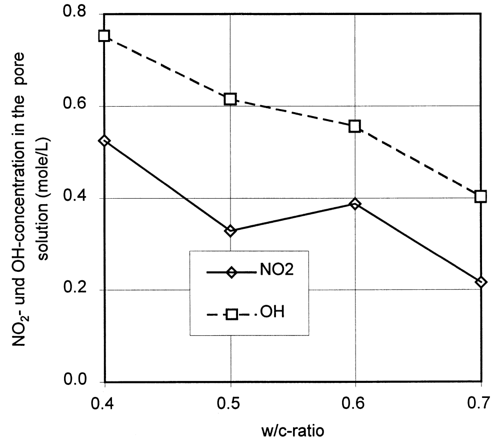

Fig. 4. Ion concentration in the pore solution versus water/cement ratio.

3.3. Comparison of chloride and nitrite binding with sodium salts

Fig. 5 is a comparison of the pore solution concentration of samples containing added chloride and nitrite at water/cement ratio of 0.6. The chloride results were obtained from a previous investigation using the same cement (PZ-375-EZ), same water/cement ratio, and the same age [6]. The PZ-375-EZ cement is a commercially available blend in equal parts of the “PZ-375” cements available from all Austrian cement factories and its composition changes very little with time. As a result, the chloride concentration data can be directly compared and this is confirmed by two identical samples from the programmes. In each case, a sample containing 1.0% chloride (w/w cement) but no nitrite was analysed and the chloride concentrations in the pore solutions were 10,880 ppm (0.3068 mol/l) in the present study and 10,300 ppm (0.2905 mol/l) in the previous study.

The abscissa of Fig. 5 shows nitrite and chloride contents in moles per kilograms of cement because the different molecular weights make it impossible to present the data as a percentage of cement. The results show that chloride is bound to a higher degree: at all abscissa values, the chloride concentration is lower than the equivalent nitrite concentration. This difference can also be seen in a comparison between the pore solution concentrations and the concentration in the mix water. The chloride concentration in the pore solution is always much lower than that in the mix water, whereas the nitrite concentration is in the same range. With

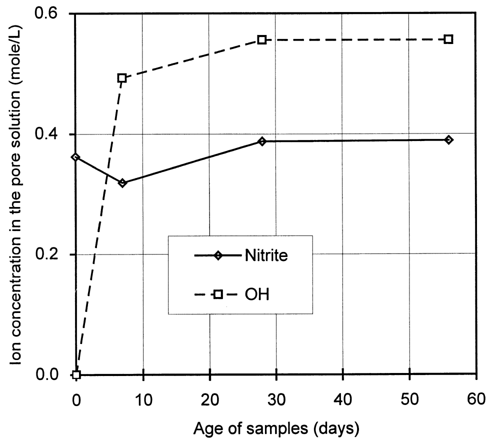

Fig. 3. Ion concentration in the pore solution versus age of samples.

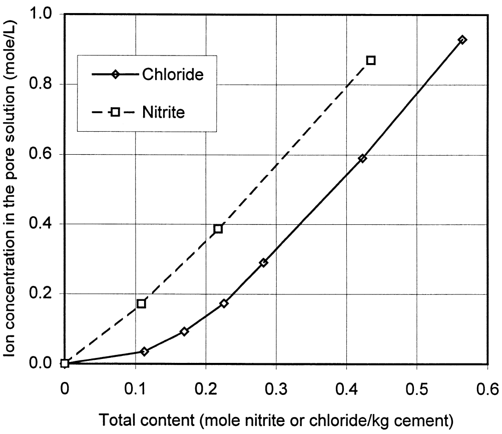

Fig. 5. Ion concentration in the pore solution versus total content.

regard to the degree of binding, expressed as a percentage of the total, only a qualitative assessment based on several assumptions can be given as follows.

After 28 days of hydration at 0.60 water/cement ratio, the bound water (bound both physically and chemically) will account for about 25–30% by weight of the cement. Therefore, the free water content (i.e., that which can, in principle, be expressed in the pore press) will be 30–35% by weight of the cement. Assuming that all unbound chloride or nitrite is uniformly distributed throughout the free water, the proportion of bound nitrite at 1% total nitrite content, i.e., 0.217 mol NO_2/kg cement, can be estimated to be 53–60%. In the same way, the proportion of bound chloride at 1% total chloride content, i.e., 0.283 mol Cl/kg cement, can be estimated to be 62–67%.

3.4. Influence of chloride on the nitrite concentration in the pore solution (sodium salts)

Fig. 6 shows the variation of nitrite concentration in the pore solution with total nitrite content in samples of British cement at water/cement ratio of 0.5 and made without and with 1% chloride w/w cement (added as NaCl). At total nitrite contents up to 1%, the nitrite concentration in the pore solution was consistently higher when chloride was present, whereas at 2% total nitrite the opposite was found. In samples made with the Austrian cement PZ-375-EZ at water/cement ratio of 0.6, the same effect was observed but was less pronounced.

Fig. 7 shows that the chloride concentration of the pore solution in samples made with PZ-375-EZ (water/cement ratio of 0.6) and containing 1% total chloride increases up to 1% total nitrite and remains constant at higher nitrite levels. The chloride concentrations in the British cement samples are higher because of the lower water/cement ratio in these samples but there is hardly any effect of nitrite content on the chloride concentration of the pore solution. Unfortunately, there is no result for chloride concentration at zero nitrite content.

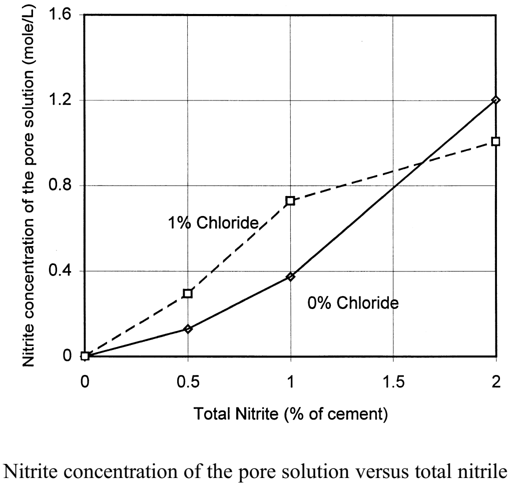

Fig. 6. Nitrite concentration of the pore solution versus total nitrile content.

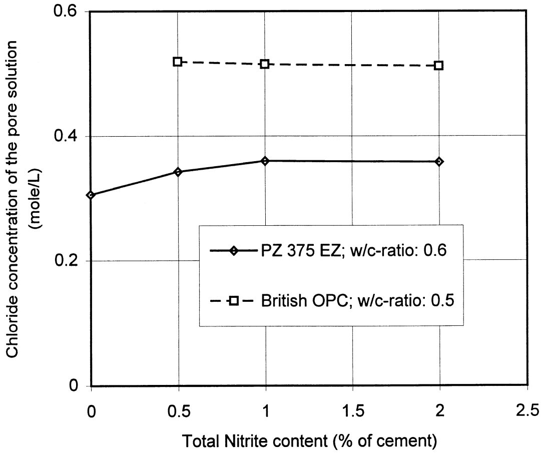

Fig. 7. Chloride concentration of the pore solution versus total nitrile content.

To deal with the influence of chloride on the binding of nitrite, Figs. 6 and 7 suggest that competition between the ions for available adsorption sites is one possible, but not the only, explanation of the observed phenomena. This is because at 0.5% and 1% total nitrite content, the nitrite concentration in the pore solution was higher in the presence than in the absence of chloride and also the chloride concentration in the pore solution was higher in the presence than in the absence of nitrite. Furthermore, the hydroxyl ion concentrations in the pore solutions obtained from PZ-375-EZ prepared with and without salt support this proposal. With no salt, the hydroxyl concentration was 0.500 mol/l, with 0.5% nitrite it was 0.534 mol/l, and with both 0.5% nitrite and 1.0% chloride together it was 0.660 mol/l and this suggests competition between all three anions for adsorption sites. If this competition were the only explanation for the results, an increase in the content of one ion would be expected to result in an increased

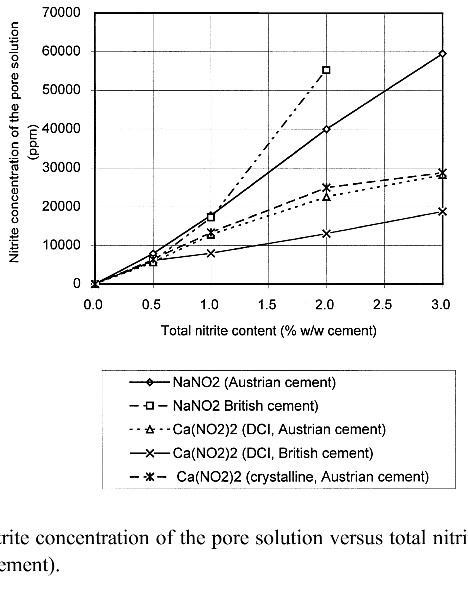

Fig. 8. Nitrite concentration of the pore solution versus total nitrite content (% w/w cement).

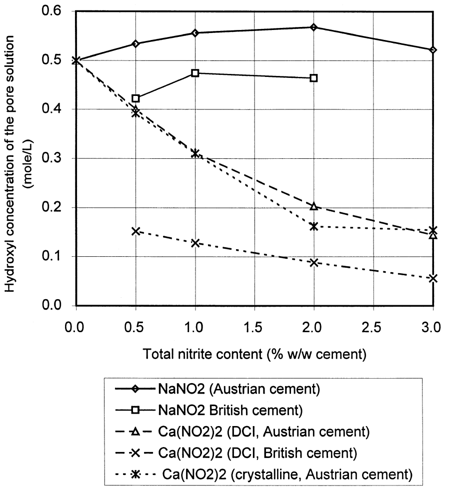

Fig. 9. Hydroxyl concentration of the pore solution versus total nitrite content (% w/w cement).

concentration of the other ions in the pore solution. For example, the nitrite concentration of the pore solution of a chloride-containing sample would be expected to be higher at 2% total chloride content than in a chloride-free one, but this was not the case (Fig. 6). Therefore, adsorption cannot be the only explanation for the observed concentrations of ions in the pore solution and there must surely be some influence of chemical binding.

3.5. Influence of the nitrite salt counter-ion

Fig. 8 shows the nitrite concentration and Fig. 9 the hydroxyl concentration in pore solutions expressed from pastes of PZ-375-EZ and the British cement (28 days old, water/cement ratio of 0.6) containing varying amounts of sodium and calcium nitrite. In the case of the Austrian cement, the nitrite concentration is similar with both calcium salts but calcium nitrite gives much lower concentrations than sodium nitrite. This can be explained by the fact that calcium ions are insoluble at the high pH value but take up hydroxyl ions from the pore solution and precipitate as $Ca(OH)_2$ thus reducing the hydroxyl concentration of the pore solution. The British cement exhibited the same effect to a more pronounced degree. Obviously, adsorbed calcium ions affect the whole hydration mechanism and the controlling equilibrium for the ion concentration in the liquid phase is affected differently in different cements. In our case, this is most probably concerned with the low alkali content of the British cement and further studies are required to clarify the effect.

As can be seen from Figs. 8 and 9, the free nitrite concentration was highest with the addition of the sodium salt. The lowest nitrite concentrations were found in the pore solution of the British cement with the calcium salt. When comparing the hydroxyl and nitrite curves, it is striking that the nitrite concentration has comparatively little effect on the hydroxyl concentration when sodium nitrite is used. However, the hydroxyl concentration decreases as the nitrite concentration increases when calcium nitrite is used and this confirms the effect described above. The effect of hydroxyl concentration on nitrite binding is probably a result of the competition between the two ions for adsorption sites on the solid surface. When fewer adsorption sites are occupied by hydroxyl, more nitrite can be adsorbed and this reduces the free nitrite concentration in the liquid phase. The continuing increase in free nitrite concentration with increasing total nitrite addition can be explained in a similar way through chemical binding.

3.6. Influence of chloride on the free nitrite concentration

Fig. 10 shows the nitrite concentration in pore solutions expressed from pastes (water/cement ratio of 0.6) containing varying amounts of nitrite, with and without 1% chloride,

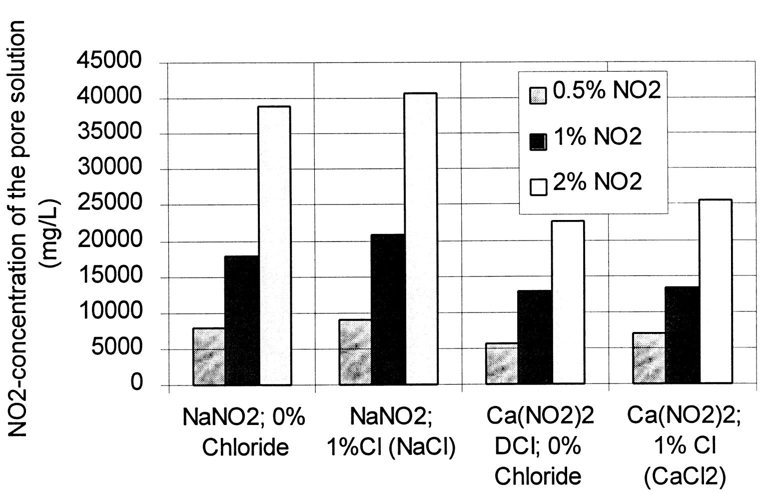

Fig. 10. Nitrite concentration of the pore solution of cement pastes containing different amounts of nitrite and 0% or 1% chloride.

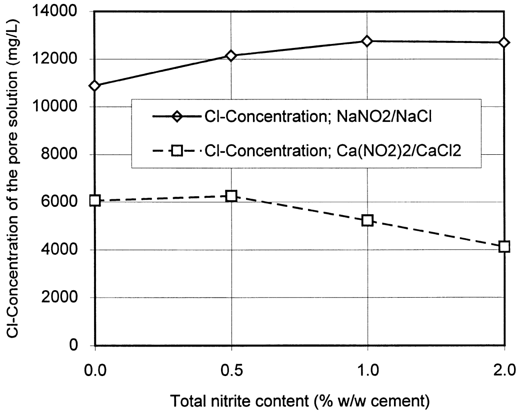

Fig. 11. Chloride concentration of the pore solution versus total nitrite content (% w/w cement).

calculated by weight of cement. The nitrite concentration in chloride-containing pastes is rather higher than in the corresponding chloride-free pastes. Fig. 11 shows the free chloride concentrations from samples with 1% chloride. When sodium salts are used, the chloride concentration increases up to 1% nitrite addition but then remains practically constant to 2% nitrite. When calcium salts are used the curve increases only as far as 0.5% nitrite before decreasing again relatively steeply.

In view of the influence of chloride on the binding of nitrite, which brings the concentration curves quite close together, the competition between these ions for adsorption sites can be seen as the preferred but not the only explanation. The higher nitrite concentration in pore solutions of chloride-containing pastes compared to those in chloride-free samples can be interpreted as competition in this way. In this scenario, increasing nitrite content increases the chloride concentration with sodium salts but decreases it with calcium salts, as shown in Fig. 11. However, only limited conclusions about the type of binding can be drawn from the pore solution analyses for samples prepared with different salts, because the type and amount of salt influences the composition and/or the physical characteristics of hydration products and consequently their ability to bind ions.

3.7. The chloride/nitrite ratio in pore solutions

Fig. 12 shows the Cl^-/NO_2^- mole ratio for pore solutions in specimens (water/cement ratio of 0.6) with nitrite additions between 0.5% and 2%, all of which contained 1% chloride and where the counter-ions were variously the same or different. At equal chloride content the Cl^-/NO_2^- ratio decreased with increasing nitrite addition. For each nitrite addition the Cl^-/NO_2^- ratio was highest when both nitrite and chloride were sodium salts and lowest when they were both calcium salts. This shows that the binding of both ions is influenced by the type of salt. Kawamura et al. [4] determined the Cl^-/NO_2^- ratio in specimens with 1% addition of chloride (as NaCl) and 1% nitrite salt, added either as $NaNO_2$ or $Ca(NO_2)_2$. The NO_2 content was therefore 0.67% in the former case and 0.70% in the latter. The Cl^-/OH^- ratio in the pore solution of 28-day-old samples was found with 0.90 (1% $NaNO_2$) and 0.81 (1% $Ca(NO_2)_2$) [4]. Although a direct comparison with our results is not possible because we added 1% chloride and 0.5%, 1.0%, or 2.0% nitrite, Kawamura et al.'s [4] results show not only the same trend but the values lie in a range that is consistent with our results at the somewhat different NO_2^- contents.

4. Discussion

This investigation set out to demonstrate how much free nitrite is present in the pore solution to protect embedded steel. The results show that this is affected in a complicated way by the cement composition, the chloride concentration present, and the type of nitrite salt. There appears to be competition for adsorption sites between nitrite, chloride, and hydroxyl ions, which suggests that the amount of free nitrite will be higher at higher chloride and/or hydroxide concentrations. Nitrite ions are bound by cement to a much

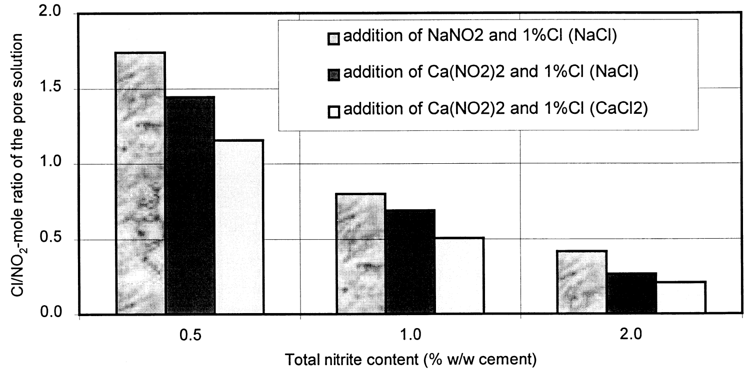

Fig. 12. Cl/NO_2 ratio of the pore solution at different total nitrite content (% w/w cement).

lesser degree than chloride ions and this is encouraging for the effectiveness of nitrite ions as inhibitors in chloride-contaminated concrete, provided that the binding is not so weak that the nitrite leaches out of the concrete entirely.

While both sodium and calcium nitrite have been used in this investigation, it is important to note that it is calcium nitrite that is used in commercial practice and that the free nitrite concentration, when the latter is used, is approximately half that when sodium nitrite is used at the same rate of addition. In addition the free hydroxyl ion concentration decreases significantly as a result of using calcium nitrite, in contrast to the nearly constant concentration when the sodium salt is used. These factors need to be taken into account when guidance for users is formulated.

Gianetti [1] interprets the addition rates quoted in the British Board of Agrèment test certificate for DCI [2] as being consistent with a maximum permissible chloride/nitrite ratio to ensure inhibition of steel corrosion of 1.2–1.5. The certificate gives addition rates and the corresponding chloride levels at the reinforcement against which DCI confers protection. Figs. 5, 6, and 7 show that with sodium salt the free chloride concentration is always less than the free nitrite. In practice, the chloride will enter the concrete usually as NaCl and the nitrite is added as the calcium salt. With these salts, the chloride/nitrite ratio decreases from about 1.5 at low added nitrite to about 0.3 at 2% nitrite addition (Fig. 12). Therefore, this protection criterion is always achieved for the cements in this investigation. Even with the low-alkali cement (referred to as British cement in the figures), for which competitive adsorption gives a low free nitrite concentration, 3% nitrite added as DCI gives ~0.4 mol/l free nitrite representing protection against up to 0.6 mol/l free chloride. This is approximately 20 times the protection offered by the alkalinity of the pore solution of the same cement paste alone (0.056 mol OH^-/l): using Haussmann's [9] Cl^-/OH^- threshold for corrosion of 0.6, 0.056 mol/l hydroxyl would protect against ~0.03 mol/l free chloride in concrete.

The general level of free nitrite is broadly in agreement with the results of the limited investigation carried out by Li et al. [10]. They used calcium nitrite inhibitor cast into concrete and mortar specimens at about 1.5% by weight of nitrite ion and determined free ion concentrations by a novel leaching method, where small holes drilled into the solid concrete were filled with water and the amount of each ion dissolving in the water in each hole determined at intervals over 7 weeks. They claim good agreement between the results so obtained and those obtained by conventional pore water expression, as done in the present work. Inhibitor at this concentration reduced pH by 0.2–0.3 units compared to controls and produced a free nitrite concentration of 6500 ppm. These results agree best with the values for the British cement with calcium nitrite shown in Figs. 8 and 9. The alkali content of both cements in this comparison was low (British cement 0.05% and Li et al.'s cement 0.5% Na_2O) compared to the Austrian cement and this probably accounts for the similarity.

Since a maximum chloride/nitrite ratio must not be exceeded users of nitrite inhibitors must ensure that the admixture addition rate is sufficiently much higher to protect against both the chloride added in the raw materials (these must be analysed first) and the level of external chloride contamination anticipated during the lifetime of the structure.

5. Conclusions

Direct measurements of free ion concentrations are fundamentally important to establish the minimum dosages of nitrite inhibitors necessary to confer protection on steel in concrete. The analyses reported in this article show that nitrite and chloride ions adsorb competitively on cement and at higher chloride concentrations there is more free nitrite to inhibit the corrosion of embedded steel.

Users of nitrite inhibitors must be aware that a threshold free nitrite concentration needs to be achieved such that the chloride/nitrite ratio remains below 1.5. This requires all sources of chloride to be analysed for the concrete in question. The results can be used to give guidance for the satisfactory use of nitrite inhibitors.

Acknowledgments

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References

[1] F. Gianetti, Corrosion inhibitor, Concr. Eng. Int. (1998) 2–10 (March/April).

[2] British Board of Agrèment, DCI and DCI-S corrosion inhibitors, Agreement Certificate No 96/3232, October 1998, 7 pp.

[3] J.A. Gonzalez, E. Ramirez, A. Bautista, Protection of steel embedded in chloride containing concrete by means of inhibitors, Cem. Concr. Res. 28 (1998) 577–589.

[4] M. Kawamura, S. Tanikawa, R.N. Swamy, H. Koto, Pore solution composition and electrochemical behaviour of steel bars in mortars with nitrite corrosion inhibitors, Fifth CANMET/ACI International Conference on Superplasticizers and Other Chemical Admixtures in Concrete, (1997) 35–53.

[5] J. Tritthart, Chloride binding in cement: I. Investigations to determine the composition of pore-water in hardened cement, Cem. Concr. Res. 19 (1989) 586–594.

[6] J. Tritthart, Chloridinduzierte Betonstahlkorrosion (Chloride-induced corrosion of steel in concrete), Schriftenr. Strassenforsch. BMfwA 346 (1988) 117.

[7] R.S. Barneyback, S. Diamond, Expression and analysis of pore fluids from hardened cement pastes and mortars, Cem. Concr. Res. 11 (1981) 279–285.

[8] J. Tritthart, Chloride binding in cement: II. The influence of the hydroxide concentration in the pore solution of hardened cement paste on chloride binding, Cem. Concr. Res. 19 (1989) 683–691.

[9] D.A. Haussmann, Steel corrosion in concrete, Mater. Prot. 6 (1967) 19–23 (November).

[10] L. Li, A.A. Sagues, N. Poor, In-situ leaching investigation of pH and nitrite concentration in concrete pore solution, Cem. Concr. Res. 29 (3) (1999) 314–321.