

# **EFFECTIVENESS AND MECHANISM OF CORROSION INHIBITING ADMIXTURES**

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## **ABSTRACT**

Steel reinforced concrete is one of the most durable and cost effective construction materials but it can suffer in high chloride environments from corrosion due to chloride induced break down of the normal passive layer protection. One way of protection embedded steel reinforcement from chloride induced corrosion is by the addition of corrosion inhibiting admixtures (CIA) to the concrete mixes.

In this paper, the effectiveness of various corrosion inhibiting admixtures (CIA), namely calcium nitrite and sodium benzoate, admixed with OPC mortar on fresh parameters (initial flowability and rate of flowability loss), microstructure related properties (cement-phase composition, capillary porosity and permeation) and reinforcement corrosion activity are reported. The role of these CIA on the mechanical properties (such as compressive, tensile and bond strength) of OPC matrix was also studied. Therefore, various 0.50 w/c OPC mortars made with 0, 2, 4 and 5% of either calcium nitrite or sodium benzoate were prepared and then assessed using mortar flow table, thermo-gravimetric analysis de-sorption test, initial surface absorption test and half-cell apparatus.

The results suggest that the beneficial role of corrosion inhibiting admixtures on enhancing the resistance of reinforcement against corrosion is dependent on the modifications that occur to the microstructure of OPC matrix as a result of inclusion of CIA. The use of calcium nitrite and sodium benzoate had reduced the capillary porosity and rate of water flow into OPC matrix and increased the amount of C-S-H. The amount of enhancement in the microstructure related properties is generally increased with CIA content. Also, the tensile and bond strength are significantly improved as a result of admixing calcium nitrite in OPC mix, while, all studied mechanical properties (compressive, tensile and bond strength) have been degraded when sodium benzoate was utilized.

## **INTRODUCTION**

There is no doubt that, the corrosion of reinforcing steel embedded in concrete is considered as a major world-wide problem. This problem takes place because of the effect of the chlorides, sulphates or carbonation. It has been estimated that the annual cost of repair to UK concrete structures due to reinforcement corrosion is about £500 million, while in the USA, the associated repair due to reinforced corrosion for concrete bridges alone has been estimated at \$ 50 billion per annum. In the Middle East, 74% of reinforced concrete structures show significant corrosion damage after as little as ten to fifteen years, and many structures have to be rebuilt every ten years or so unless extensive rehabilitation or repair is carried out [1,2]. Generally, chlorides are the principal cause of reinforcement corrosion in concrete structures. If the concentration of chlorides exceeds a threshold value, the passive oxide film on the surface of the reinforcement can be disrupted, in the presence of oxygen and moisture [2,3].

Therefore, a number of corrosion protection systems, such as corrosion inhibitors, epoxy-coated reinforcing steel, stainless steel, surface impregnation of concrete and cathodic protection are introduced to address corrosion of steel in reinforced concrete. From among them, the paper discusses the use of chemical corrosion inhibitors as concrete admixtures [4,5].

The possible mechanisms of corrosion inhibitors in reinforced concrete exposed to chloride have been discussed [5,6,7]. The inhibitor can delay the onset of corrosion by a) reducing the rate of ingress of aggressive ions (chlorides) by increasing the rate of chemical binding of chlorides and/or raising the chloride threshold value for corrosion initiation, and b) reducing the rate of corrosion once it is initiated. However, there is a lack of experimental evidence to confirm these above-mentioned mechanisms. Moreover, to the authors' knowledge, no attempt has been made in literature to elaborate the effectiveness of CIA on pore structure, cement-phase composition and permeation properties of concrete. If such elaborations are available, the mechanism of CIA on the corrosion activity of reinforcement will be clearly understood and identified. Consequently, there is a need for carrying out such study to find a scientific explanation for the mechanism of CIA and then provide a reasonable explanation to its effectiveness on various fresh and mechanical properties of OPC matrix.

Gaidis [7] and Brown et al [8] have investigated the effect of corrosion inhibitors, such as calcium nitrite and sodium benzoate, on slump, setting time and compressive strength of concrete. Their results have shown that the addition of such inhibitors has led to decreasing the slump and accelerating the initial and final setting time. However, there is a lack of information regarding their effectiveness on the other aspects of fresh concrete, rate of flowability loss of concrete.

Hansson et al [6] and Berke and Hicks [9] had recently studied the effect of calcium nitrite and sodium benzoate as CIA on the early-age compressive strength of OPC concrete. They found that the inclusion of calcium nitrite on OPC concrete had led to a slight increase in the compressive strength of concrete. An opposite finding was obtained by Batis et al [10] when they used sodium benzoate as CIA. However, the effectiveness of CIA on the other mechanical properties of concrete (such as tensile and bond strength) has not been fully investigated yet.

Therefore, the main aims of this study can be summarized as follows:

- 1- To investigate the role of CIA (calcium nitrite and sodium benzoate) on cement- phase composition, pore structure and permeation characteristics of OPC matrix.
- 2- To clarify the role of CIA on the various mechanical properties (compressive, tensile and bond strength) and fresh parameters (initial flowability and rate of flowability loss) of OPC matrix.
- 3- To signify the importance of using CIA on reducing the corrosion activity of reinforcing steel.

## **EXPERIMENTAL**

Mixes were prepared using locally produced ordinary Portland cement (OPC), complying with BS12 (1978) and ESS 373 (1991). The chemical analysis of the cement used is summarized in Table 1. Natural siliceous sand was used as fine aggregate in all mixes considered in this experimental program. Tap water was used for mixing and curing. 10 and 16 mm diameter mild steel (grade 24/37) complying with ESS 262 (2000) were used for corrosion potential and bond strength measurements, respectively. Sodium chloride (NaCl) was used as a source of chloride ions. Calcium nitrite and sodium benzoate were used as corrosion inhibiting admixtures, which are denoted by N and B, respectively. The applied dosages of calcium nitrite and sodium benzoate were 0, 2, 4, and 5% (by weight of OPC).

Seven OPC mortar mixes made with different contents of calcium nitrite and sodium benzoate were prepared according to BS 5075 part 2 (1982). Constant w/b ratio of 0.5 and binder/sand of 1: 2.75 were considered. These mixes were used for mortar flow test, 28-days compressive, tensile and bond strength testing, initial surface absorption test and corrosion potential measurements.

Another seven OPC cement paste mixes of 0.50 w/c made with the same dosages of CIA mentioned above were prepared for thermo-gravimetric analysis and de-sorption test.

Table 1 Chemical analysis of OPC

$SiO_2$	$Al_2O_3$	$Fe_2O_3$	$CaO$	$MgO$	$Na_2O$	$K_2O$	$SO_3$	$LOI$	<i>Insoluble residue</i>
21.72	4.80	3.78	62.9	1.94	0.45	0.3	2.2	1.01	0.90

Mortar flow table apparatus was used for determining the initial flowability (measured at zero time from mixing) and rate of flowability loss of OPC mortar mixes, as described in ASTM C 230-80. The rate of flowability loss was determined by recording the instant flow at various elapsed periods from mixing, 0, 30, 60, 90 and 120 min.

Six cube specimens (70x70x70 mm), six specimens of a briquette shape, six cylinders (100 mm diameter, 200 mm height) and six cube specimens (100x100x100 mm) were taken from each mortar mix, demolded, cured in water for 27 days ( $20 \pm 2^\circ C$ ), and then subjected to compressive strength, tensile strength, bond strength and initial surface absorption test, respectively. The initial surface absorption test was carried according BS 1881: parts 5 (1970).

For corrosion potential measurements, three reinforced prismatic mortar specimens (80x80x100 mm) were prepared from each mortar mix. Four steel bars (10 mm diameter) with 100 mm length were embedded in each specimen during its casting such that 80 mm was fixed inside the mortar while the reminder 20 mm was kept outside. The thickness of the cover was kept constant, 20 mm. After 28 days of water curing, the specimens were submerged in 3% NaCl solution for 3 days and followed by drying the specimens in air for another 11 days. This cycle of wetting/ drying was repeated up to one year. The corrosion potential of the imbedded reinforcing steel bars in mortar was determined every two weeks using half-cell device, according to the procedures described in ASTM C876 (1980).

The pore structure of hardened cement pastes (in terms of capillary porosity) and cement-phase composition (amount of bound water and CSH) were measured by de-sorption test and thermo-gravimetric analysis, respectively, using the same test procedures described elsewhere [11,12]. For each test, six discs (25 mm thick and 50 mm diameter) were taken from each cement paste mix, cured in water for 27 days ( $20 \pm 2^\circ C$ ), and subjected to the specified test procedures. The average result of six samples was then regarded for each case of study.

## RESULTS AND DISCUSION

### *Microstructure and Permeation Related Properties*

In this study, the microstructure related properties of OPC matrix admixed with or without corrosion-inhibiting admixtures (CIA) were investigated by assessing the amount of bound water (representing degree of hydration), CSH and amount of interconnected pores (expressed by capillary porosity), using thermo-gravimetric analysis and de-sorption test. These two tools of assessment have been successfully used for such purposes [11,12]. If these related properties were clarified, the role of CIA on the permeation, mechanical and reinforcement corrosion characteristics of reinforced concrete will be better understood.

Therefore, the amount of bound water and weight loss due to decomposition of CSH (deduced from thermo-gravimetric analysis) and amount of inter-connected pores (deduced from de-sorption test) of OPC hardened cement paste admixed with or without CIA (calcium nitrite and sodium benzoate) were estimated as described earlier [11,12]. The estimated results are listed in Table 2. It can be seen from these results that the amount of bound water and CSH of OPC mortar containing calcium nitrite (N) were reasonably increased with increasing the content of calcium nitrite.

Meanwhile, sodium benzoate (B) had caused a slight increase in CSH and negligible effect on the amount of bound water, as compared to the effect of calcium nitrite.

Regarding the effect of CIA on the amount of interconnected pores, it is clear from the data illustrated in Table 2 that both inhibitors (N and B) had reduced the capillary porosity of OPC mortar. The amount of reduction in the amount of the interconnected pores is increased with increasing the dosage of CIA content. Generally, the use of calcium nitrite has led to reducing the capillary porosity of OPC mortar more than the use of sodium benzoate.

Table 2 Bound water, decomposition loss due to C-S-H and capillary porosity of OPC hardened cement pastes containing different contents of CIA.

Code	Corrosion inhibitor		Bound water, %	Decomposition due to C-S-H, %	Capillary porosity, %
	Type	Content			
Control	-	-	18.9	5.6	2.4
2N	Calcium nitrite	2%	22.1	6.8	1.7
4N		4%	26.7	7.3	1.6
5N		5%	28.0	8.5	1.5
2B	Sodium benzoate	2%	20.5	6.3	2.0
4B		4%	19.0	6.2	1.9
5B		5%	17.5	6.0	1.9

These results agree with those obtained in previous study carried out by Batis et al [10], who found that, for light weight mortar at w/C=0.5, cement/ sand = 1: 3, the total water porosity of OPC mortar were decreased by using sodium nitrite or sodium benzoate and the amount of decrease was increased with an increase of the inhibitor content. This beneficial effect of the corrosion inhibiting admixtures on the pore structure of OPC matrix may be attributed to their significant role on the cement-phase composition (especially CSH), as discussed above.

In this study, the permeation properties of OPC matrix made with CIA were investigated by measuring the initial surface absorption (ISA) using initial absorption test (ISAT). The ISAT is considered as one of the most common, simplest, and longest established method for measuring the absorptivity of concrete, by providing data to indicate the water flow into the surface of dry concrete [13].

The ISAT was carried out, as described elsewhere [13], on different OPC mortars containing either calcium nitrite or sodium benzoate. The results of this investigation are demonstrated in Figure 1. It is clear that the use of both inhibitors had led to reducing the value of ISA, compared to control mix. The amount of reductions increased with increasing the dosage of CIA, up to 4%.

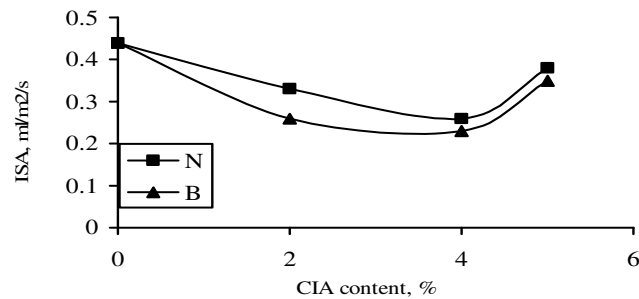


Figure 1 Initial surface absorption of OPC mortars containing various CIA.

This means that the inclusion of both inhibitors under study would minimize the rate of flow of aggressive fluids into the cover concrete. Such observation may be attributed to the densification effect of CIA on the pore structure of OPC matrix through reducing the amount of interconnected pores, as proved above by capillary porosity results shown in Table 2.

### Corrosion Activity

Such modifications in the microstructure and permeation related properties of OPC matrix as a result of inclusion CIA, described in the above section, can also lead to reducing the amount of aggressive ions that would reach the reinforcement, thus reducing the risk of reinforcement corrosion. However, an experimental proof has to be provided to confirm this opinion. This led the authors to extend their work to study the corrosion activity of reinforced OPC mortar incorporating CIA. In this study, the corrosion activity of reinforcement was assessed by monitoring its corrosion potential at regular periods, using half-cell device according ASTM C876.

The relationship between the corrosion potential measurements of reinforcement embedded in OPC mortars subjected to 3% NaCl environment and exposure period was depicted, as shown in Figure 2. Two stages were observed with such a relationship. The first stage represents the period at which the corrosion potential varied between  $-0.2\text{V}$  and  $-0.35\text{V}$ , CSE, i.e., greater than 90% probability that corrosion does not occur as specified by ASTM C876 limits. While, stage II represents the period at which the corrosion potential varied between  $-0.35\text{V}$  and  $-0.50\text{V}$ , CSE i.e., greater than 90% probability that corrosion occur according to ASTM C876 limits. The duration of these two stages was denoted by  $T_1$  and  $T_2$ , and can be referred as “stage of onset of corrosion and stage of corrosion propagation, respectively”.

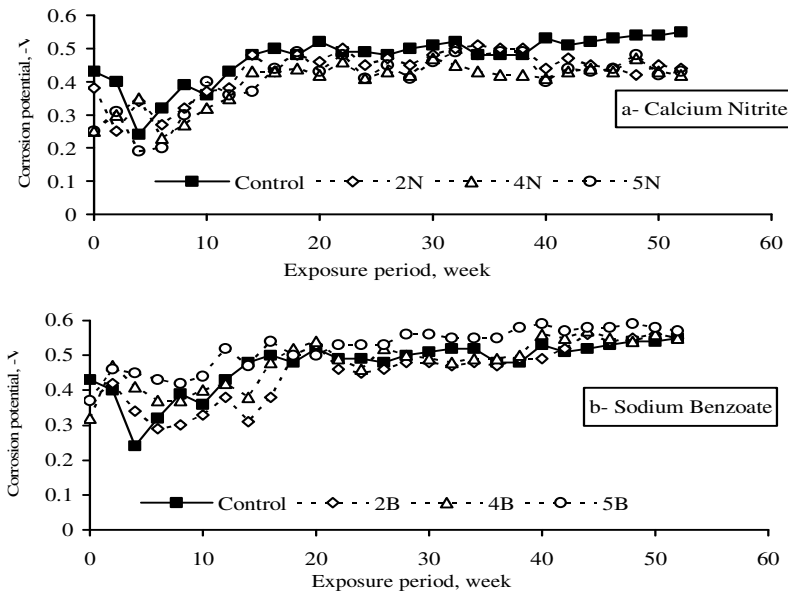


Figure 2 Corrosion potential of OPC mortars made with either a) calcium nitrite or (b) sodium benzoate and exposed to 3% NaCl environment.

The results shown in Figure 2 indicated that, compared to control mix, calcium nitrite (N) was more effective in reducing the corrosion potential measurements than sodium benzoate (B). Increasing the content of CIA from 2 to 4 or 5% had no significant effect on corrosion potential measurements. It seems also from the data represented in Figure 2 that the inclusion of either N or

B in OPC matrix resulted in extending both stages of corrosion,  $T_1$  and  $T_2$ . The estimated values of  $T_1$  and  $T_2$  of specimens made with N seems to be higher than that of specimens made with B, where the values of  $T_1$  were 6, 8, 12, 8 and 10 weeks for 0%, 2%N, 4%N, 5%N and 2% B, respectively, and the values of  $T_2$  were 40, 52, 52, 52, 42, 40 and 22 weeks for 0%, 2%N, 4%N, 5%N, 2%B, 4% B and 5% B, respectively. These findings may be attributed to the effective role of CIA on the cement-phase composition, pore structure and permeation properties of OPC matrix, as described in the previous section.

### ***Fresh and Mechanical Properties***

To the authors' knowledge, there is a little information in literature regarding the effectiveness of CIA on the loss of fresh parameters and most of mechanical properties of OPC matrix, e.g. compressive, tensile and bond strength. This led the authors to conduct this study to cover such aspects. Consequently, the effectiveness of calcium nitrite and sodium benzoate on the initial flowability (measured at zero time from mixing) of OPC mortar mixes was investigated and the results are demonstrated in Figure 3. As seen, compared to control mix, sodium benzoate inhibitor has reasonably reduced the initial flowability of OPC mortar and the highest reduction was produced when 4% of sodium benzoate was utilized. While, the effect of calcium nitrite was not significantly notable. Generally, the initial flowability of OPC mortar made with N was greater than that made with B. However, these observations are contradictory with those made earlier by Brown et al [8] who found that the use of calcium nitrite had led to reducing the slump of concrete.

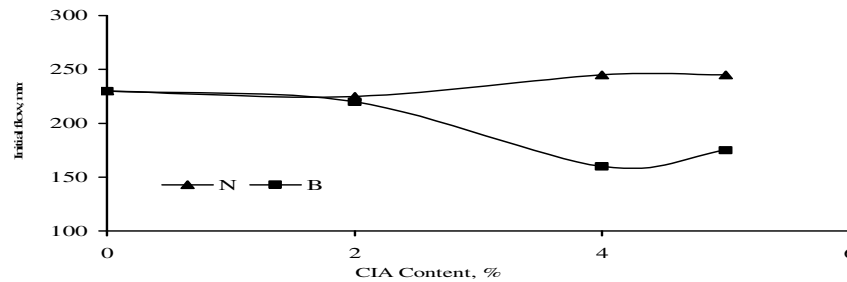


Figure 3 Flowability of OPC mortar made with various corrosion inhibitors.

The influence of corrosion inhibiting admixtures on the rate of loss in fresh properties of concrete is very important for engineers on site in order to determine the suitable period between mixing and casting. Therefore, the effect of CIA on the rate of flowability loss of OPC mortar was studied, as shown in Figure 4. It is noted that, the % instant/initial flow of OPC mortars containing 0, 2, 4 and 5% calcium nitrite decreased with increasing the elapsed period from mixing. After 120 min from mixing, the amount of loss in flowability reached 33%, 29%, 29% and 24% for mixes containing 2, 4 and 5 % N, respectively. Similar effect was produced when 2% sodium benzoate was used. These findings agree with the results reported by Gaidis [7] and Brown et al [8], who noted that the inclusion of 1 and 2% of N had led to decreasing the initial and final setting time of OPC concrete.

On the other hand, the dosage of 4 and 5% sodium benzoate seems to retard the setting time of OPC matrix, where the % instant/initial flow values were always greater than 100%. This means that no flowability loss would occur at such dosages during the considered time of testing. However, a rheological study is required to find an explanation for such phenomena.

Table 3 represents the average results of 28-days compressive, tensile and bond strength of OPC mortar admixed with different contents of N and B. It is apparent that all mechanical properties of mortar made with N were always higher than the corresponding OPC mortars made with B. For OPC mortars made with N, the compressive, tensile and bond strength results were

enhanced with increasing dosage of N. However, the use of N had led to the reduction of compressive strength of OPC specimens, compared to control specimen (0% N), especially at low dosages (2% and 4%).

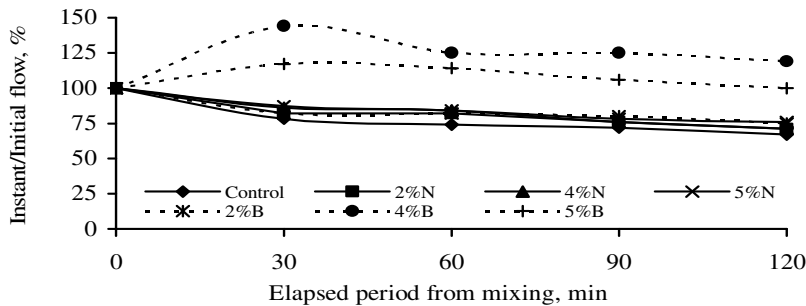


Figure 4 Rate of flowability loss of OPC mortar made with various CIA.

On the other hand, for specimens containing sodium benzoate (B), all mechanical properties significantly diminished as a result of inclusion B in OPC matrix, especially compressive strength. Such a diminishing effect increases with increasing B content. Therefore, it can be recommended that, from the mechanical properties of mortar point of view, the optimum ratio of calcium nitrite and sodium benzoate to be used in concrete industry are 5 and 2%, respectively, for achieving the highest possible mechanical properties. These two dosages can also be used successfully for inhibiting/delaying corrosion, see the results shown in Figure 2 and Table 2.

Table 3 28-days compressive, tensile and bond strength of OPC mortars containing different contents of CIA.

Code	Corrosion inhibitor		Compressive strength (kg/cm <sup>2</sup> )	Tensile strength (kg/cm <sup>2</sup> )	Bond strength (kg/cm <sup>2</sup> )
	Type	Content			
Control	-	-	360	21	45
2N	Calcium nitrite	2%	260	24	49
4N		4%	270	26	50
5N		5%	370	27	52
2B	Sodium benzoate	2%	270	20	45
4B		4%	210	18.5	44
5B		5%	150	16	41

The degrading effect of sodium benzoate on the various mechanical prosperities may be attributed to change of cation system of OPC matrix due to the presence of sodium ions in the inhibitor [7]. However, pore solution analysis is necessary to confirm such explanation. While, the beneficial effects of calcium nitrite on tensile, bond and compressive strength, especially at high dosages, may be due to the enhancement effect of calcium nitrite on cement-phase composition, as described by the data shown in Table 2.

## CONCLUSIONS

The following conclusions can be drawn from the present study:-

- 1- Inclusion of calcium nitrite into OPC mixes can lead to a significant modification in its microstructure and permeation related characteristics. Increasing the dosage of calcium nitrite resulted in enhancing the degree of hydration and amount of CSH, and reducing the amount of interconnected pores and rate of fluid transport. Meanwhile, sodium benzoate had a little effect on cement-phase composition when compared to calcium nitrite.
- 2- Calcium nitrite reasonably reduces the corrosion activity of reinforcement more than sodium benzoate. Generally, both stages of reinforcement corrosion (onset of corrosion and corrosion propagation) could be extended if these inhibitors are utilized in concrete mixes.
- 3- The initial flowability of OPC matrix is inversely affected with increasing the dosage of sodium benzoate and this effect would increase with increasing sodium benzoate content. While, calcium nitrite has an insignificant role on initial flowability, on the other hand, the rate of flowability loss is significantly increased with calcium nitrite in OPC mixes, compared to sodium benzoate.
- 4- The tensile and bond strength are significantly improved as a result of admixing calcium nitrite in OPC mixes and the amount of improvement increases with increasing its content. On the other hand, the studied mechanical properties (compressive, tensile and bond strength) have been degraded when sodium benzoate was used.

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