

# USE OF NITRITE SALT AS CORROSION INHIBITOR ADMIXTURE IN REINFORCED CONCRETE STRUCTURES IMMERSSED IN SEA-WATER

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## Abstract

Sodium nitrite is supposed to be a corrosion inhibitor of reinforced concrete structures in contact with chlorides. In the present work the effect of 4% sodium nitrite by weight of cement on the corrosion process of cracked reinforced concrete specimens ( $w/c=0.50$ ) immersed in sea-water has been studied. It has been found that in cracked concrete specimens corrosion becomes more severe in the presence of sodium nitrite. The effect is quicker the larger the crack width of the concrete. Sodium nitrite does not substantially modify the chloride diffusion through uncracked concrete specimens, so that the above negative effect of sodium nitrite should be expected even in uncracked reinforced concrete areas but after longer immersion time in sea-water.

Key words: Corrosion inhibitor, Nitrite, Cracked reinforced concrete, Sea-water chloride diffusion.

## 1 Introduction

Nitrite salt is considered to be a corrosion inhibitor admixture for reinforced concrete structures containing chlorides (1). The available commercial nitrite salts are alkali nitrites such as sodium nitrite or calcium nitrite. The preferred form of nitrite should be the calcium salt when reactive aggregates are suspected to be present in a concrete, since sodium nitrite could aggravate the alkali-aggregate reaction effects. However if reactive aggregates are excluded, no substantial difference between sodium nitrite and calcium nitrite, at least for the inhibitive action, should be expected. The amount of nitrite required to counteract adequately the corrosive action increases when the amount of chlorides in the concrete is augmented. If the amount of nitrite is less than the required value, corrosion could act more severely than in its absence (2-4).

Therefore, the utilization of nitrite as a corrosion inhibitor could be to a certain extent successful only when the amount of chlorides in concrete is definitely known. This occurs when chloride is put into the mix as an impurity of one or more concrete ingredients (sand, mixing water,

etc.). On the other hand, when chloride is diffusing into the concrete from the environment (sea-water or areas exposed to deicing salts), it is very difficult to evaluate the exact amount of chloride and then the required amount of nitrite. Some papers have been published on the effect of nitrite on the steel corrosion promoted by chloride. However, these works have been carried out by examining the behaviour of a steel bar in a calcium hydroxide saturated solution simulating the aqueous phase into the concrete, and by studying a steel bar immersed in a cement paste or mortar (5-9).

The main purpose of the present paper was to study the effect of nitrite on the chloride steel corrosion of reinforced concrete specimens immersed in sea-water. This approach appears to be more realistic, since a steel bar immersed in a water solution, cement paste, or mortar, does not reproduce the reinforced concrete structure, because the contact between coarse aggregate and steel reinforcement could change significantly the local electrochemical behaviour of the system. Moreover, the passivity current density of steel has been found to be much lower in concrete than in calcium hydroxide saturated aqueous solution (10,11).

The other important aim of the present paper was to examine the effect of cracks on the steel corrosion of reinforced concrete specimens immersed in sea-water. Indeed, in cracked reinforced concrete structures chloride should penetrate easily and quickly through cracks. Therefore chloride could attain to high concentration near the reinforcement, so that a very high and unrealistic amount of nitrite should be required to counteract the corrosion action.

## 2 Experimental part

Two concrete mixes with the same composition (\*) were manufactured, the only difference being the absence or presence of sodium nitrite (4% by weight of cement). Since no reactive limestone aggregates were used, sodium nitrite was chosen as a potential corrosion inhibitor admixture.

Cubic specimens (100 mm) were produced by using the two above concrete mixes for compressive strength measurements at 1 to 28 days. Cubic specimens were also immersed in sea-water after a 45 days curing time, to determine the electrical resistivity and chloride penetration depth as a function of immersion time. The electrical resistivity was determined by measuring the current after inducing known voltages between two opposite faces covered by aluminium

(\*) water = 150 Kg/m<sup>3</sup>; type I Portland cement = 300 Kg/m<sup>3</sup>; sand = 735 Kg/m<sup>3</sup>; coarse aggregate = 1200 Kg/m<sup>3</sup>; max size of coarse aggregate = 19.1 mm.

plates. The chloride penetration depth was determined through a colorimetric test by spraying fluorescein and silver nitrate after splitting the cubic specimen in two pieces. Pink and black coloured surfaces correspond to concrete areas penetrated by chloride or not respectively (12).

Prismatic reinforced specimens (400x150x100 mm) were also produced. These specimens were reinforced by a steel plate (320x130x1 mm) placed at 30 mm from the side of the concrete specimen containing a preformed notch 10 mm deep (Fig. 1). By loading the specimens on the surface opposite the notch, a flexural stress was induced and consequently, specimens were middle-cracked. The presence of the steel plate and different values in the load allowed the crack width to be controlled in the following ranges: 0.03-0.04, 0.25-0.40 and 0.95-1.10 mm.

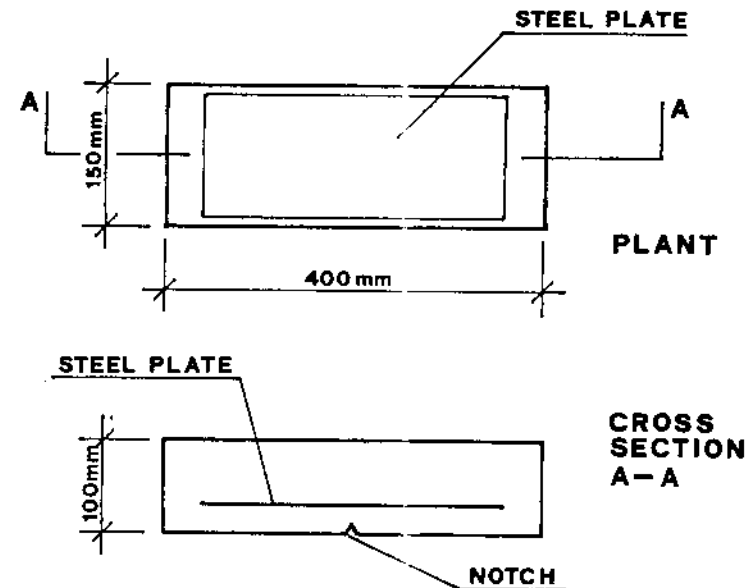


Fig. 1. Prismatic reinforced specimen.

Finally cracked reinforced specimens have been immersed in sea-water to evaluate the formation, the nature and the morphology of corrosion products by visual observations as well as to determine the corrosion extent and depth by microscopic measurements.

## 3 Results and discussion

The results of both plain concrete specimens and reinforced ones will be examined.

### 3.1 Plain concretes

Figure 2 indicates that 4% sodium nitrite addition reduces the concrete compressive strength by about 25%. The effect is similar to that of other sodium salts, such as sodium carbonate or sodium silicate, which accelerate set but retard cement hardening. Since the w/c ratio is the same for the plain mix and that containing sodium nitrite, the reduction in the compressive strength could be ascribed to a decrease in the degree of hydration and therefore, to a higher capillary porosity or a change in the cement paste microstructure.

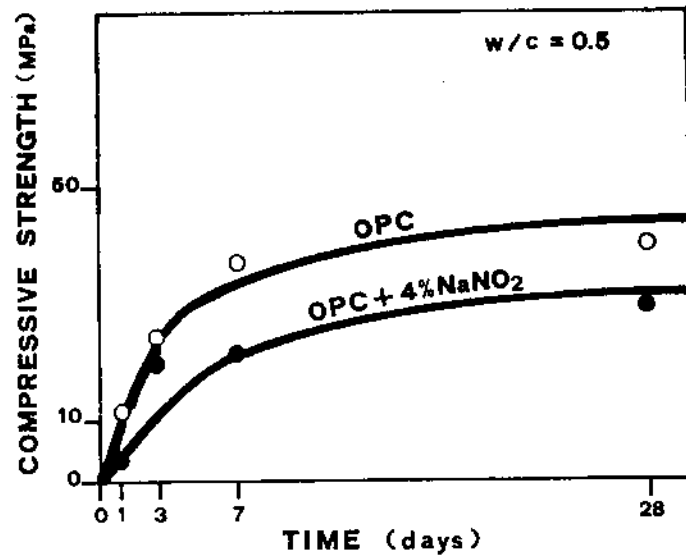


Fig. 2. Compressive strength versus time.

Figure 3 shows chloride penetration into the concrete as a function of immersion time in sea-water and indicates that chloride diffusion is not modified by sodium nitrite addition. These results would demonstrate that the degree of cement hydration and the capillary porosity of the cement paste is not changed by sodium nitrite. Alternatively, if one supposes that the degree of hydration is reduced and the capillary porosity is increased, then it should be admitted that the presence of Na<sup>+</sup> and NO<sub>2</sub><sup>-</sup> ions in the capillary pores counterbalances the higher porosity of the cement paste, so that chloride diffusion becomes equal even if the capillary porosity is different. Figure 4 shows the change in concrete electrical resistivity as a function of

immersion time in sea-water. For both concrete mixes, after immediate decrease, due to penetration of ions coming from sea-water, the electrical resistivity slightly increases. The precipitation of brucite crystals (13) into capillary pores could explain the slight resistivity increase. At a given immersion time in sea-water, sodium nitrite concrete always shows a lower electrical resistivity because of the higher ionic strength probably due to the presence of Na<sup>+</sup> and NO<sub>2</sub><sup>-</sup> ions in the aqueous phase filling the capillary pores.

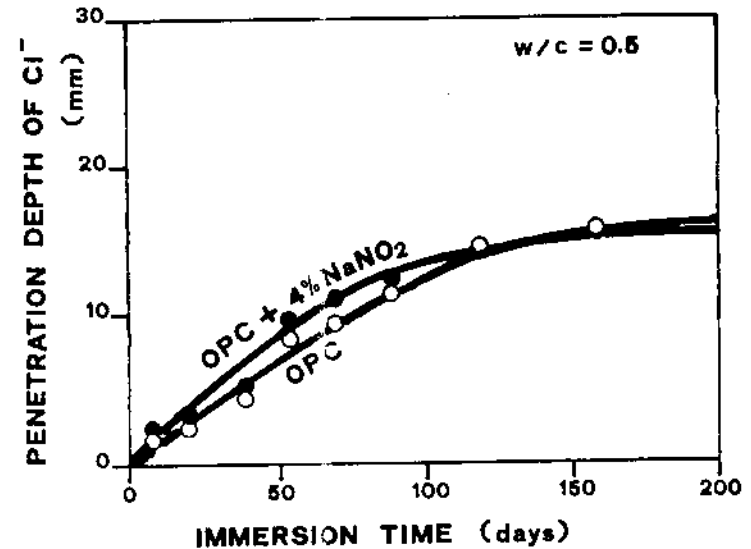


Fig. 3. Chloride penetration as a function of the immersion time in sea-water.

### 3.2 Reinforced concrete specimens

Table 1 summarizes all the tests carried out to evaluate the effect of sodium nitrite on the corrosion promoted by chloride penetration into the cracked concrete specimens. After 90 days of immersion in sea-water no corrosion product was observed in concrete specimens with cracks of 0.30 mm in width or less. Only in concrete specimens having cracks of 1 mm corrosion occurred. However, in concrete containing sodium nitrite, the corrosion of the embedded steel plate appeared to be much more severe: the corrosion products were incoherent and brown coloured, like FeOOH, with low extension but with deep attack (0.2 mm) for the corroded

area (Fig. 5). On the other hand in the sodium nitrite free concrete, the corrosion products were dense and black coloured, like  $Fe_3O_4$  with a higher extension and less deep attack (0.05 mm) for the corroded area (Fig. 6).

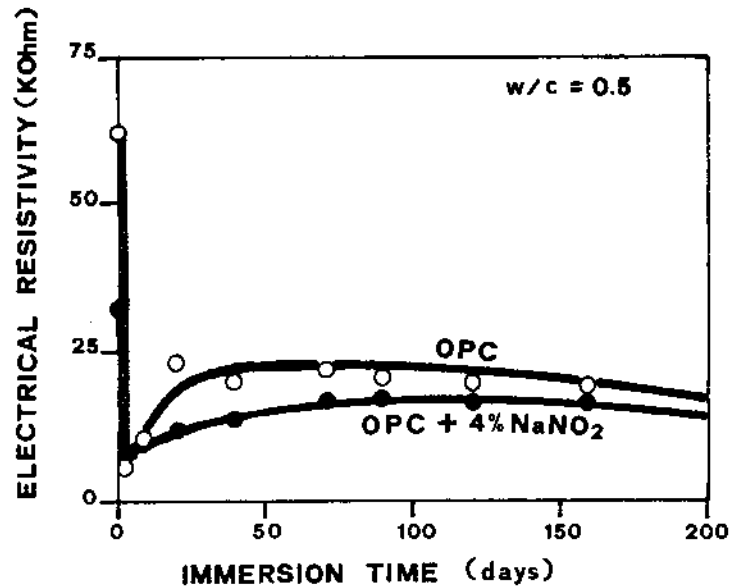


Fig. 4. Electrical resistivity as a function of the immersion time in sea-water.

These results demonstrate that sodium nitrite aggravates the local corrosion process when a large amount of chloride ions reaches the steel reinforcement.

By prolonging the immersion time in sea-water up to 150 days even the crack with the lowest width (0.03 mm) was to a certain extent involved in the corrosion process providing that sodium nitrite was present. Whereas, no corrosion was recorded in the absence of sodium nitrite (Table 1).

Figures 7 and 8 show the pitting corrosion and the absence of corrosion in the steel plate belonging to the concrete with and without sodium nitrite respectively. Again, the more severe steel corrosion in reinforced concrete specimens caused by sodium nitrite is confirmed even in concrete with low width cracks. To explain the negative effect of sodium nitrite on the corrosion process in the experimental conditions of the present work, it should be admitted that:

(a) a large amount of chloride ions penetrates through the cracks in a period of time which depends on the crack

Table 1. Visual observations and microscopic measurements on reinforced concrete specimens.

Crack width (mm)	Immersion time (days)	With NaNO <sub>2</sub>		Without NaNO <sub>2</sub>	
		Microscopic measurement	Visual observation	Microscopic measurement	Visual observation
1	90	0.2 mm corrosion depth 1.5 cm <sup>2</sup> corroded area	incoherent brown corrosion products (FeOOH)	0.05 mm corrosion depth 0.6 cm <sup>2</sup> corroded area	extensive compact black corrosion products (Fe <sub>3</sub> O <sub>4</sub> )
0.3	90	No corrosion		No corrosion	
0.03	90	No corrosion		No corrosion	
0.03	150	Pitting corrosion		No corrosion	



Fig. 5. Micrograph of the corrosion depth in the plate (cross section) embedded in the concrete with NaNO<sub>2</sub> after three months of immersion in sea-water.

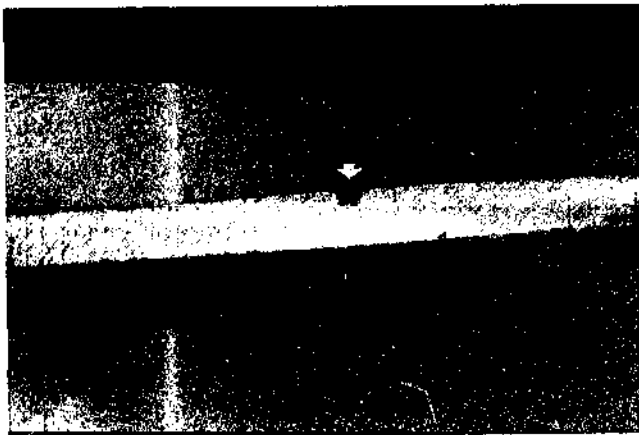


Fig. 6. Micrograph of the corrosion depth in the plate (cross section) embedded in the plain concrete after three months of immersion in sea-water.



Fig. 7. Corrosion traces on the concrete (left) and on the steel plate (right) embedded in the concrete containing  $\text{NaNO}_2$  after five months of immersion in sea-water.

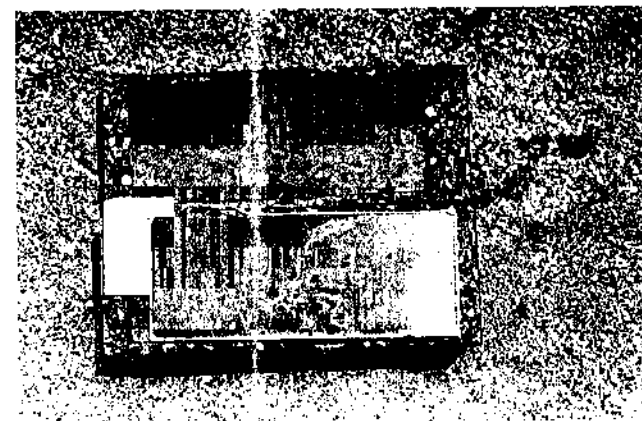


Fig. 8. Steel plate embedded in the plain concrete after five months of immersion in sea-water (no corrosion trace).

width;

(b) the chloride/nitrite concentration ratio near the steel reinforcement becomes so high that the corrosion inhibitor effect of nitrite is therefore vanished;

(c) the different exposure conditions of steel reinforcement in cracked areas and those near sound uncracked concrete cause an electrical potential difference which is greater in the presence of nitrite.

#### 4 Conclusions

In cracked reinforced concrete specimens immersed in sea-water the presence of sodium nitrite, supposed to be a corrosion inhibitor, really makes chloride corrosion more severe.

The narrower the crack width, the longer the time required to record such a negative effect. Since sodium nitrite does not affect chloride diffusion in uncracked concrete specimens, one can expect that the above mentioned negative effects of sodium nitrite could be found even in uncracked areas but at longer times of immersion.

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