

# Corrosion inhibitors for reinforced concrete structures: a study of binary mixtures

**Andrea BRENNA<sup>1</sup>, Fabio BOLZONI<sup>2</sup>, Maria Vittoria DIAMANTI<sup>3</sup>,  
MariaPia PEDEFERRI<sup>4</sup>, Marco ORMELLESE<sup>5</sup>**

<sup>1</sup>*Politecnico di Milano, Dipartimento di Chimica, Materiali e Ingegneria Chimica “Giulio Natta”, Milan, Italy, andrea.brenna@polimi.it*

<sup>2</sup>*Politecnico di Milano, Dipartimento di Chimica, Materiali e Ingegneria Chimica “Giulio Natta”, Milan, Italy, fabio.bolzoni@polimi.it*

<sup>3</sup>*Politecnico di Milano, Dipartimento di Chimica, Materiali e Ingegneria Chimica “Giulio Natta”, Milan, Italy, mariavittoria.diamanti@polimi.it*

<sup>4</sup>*Politecnico di Milano, Dipartimento di Chimica, Materiali e Ingegneria Chimica “Giulio Natta”, Milan, Italy, mariapia.pedefferri@polimi.it*

<sup>5</sup>*Politecnico di Milano, Dipartimento di Chimica, Materiali e Ingegneria Chimica “Giulio Natta”, Milan, Italy, marco.ormellese@polimi.it*

## Abstract

To prevent or delay corrosion of steel reinforcement in concrete corrosion inhibitors may be used. Available commercial products are calcium nitrite based (considered the most effective product), or organic mixtures based on amines, alkanolamines, fatty acids and carboxylic substances. During the last 15 years in our laboratories, an intense experimental research has been carried out, aimed at identifying new organic substances or mixtures thereof that might have greater inhibiting effectiveness on corrosion by chlorides.

This paper presents the results of electrochemical tests carried out in alkaline solution. Tests were performed on binary mixtures made with organic substances (amines, carboxylates and amino-acids), varying the relative percentage concentration of the two compounds: 10/90, 30/70 e 50/50. Electrochemical tests (namely potentiodynamic and potentiostatic polarisation) were carried out in alkaline solution at increasing chlorides concentration. Some of the mixtures exhibited a marked synergistic effect in both potentiodynamic polarisation tests, with a clear-cut increase in the pitting potential, and in potentiostatic polarisation tests, with an increase in the critical chloride concentration for the initiation of localised corrosion.

## Keywords

Critical chloride content; electrochemical test; inhibitor; mixture; rebar corrosion.

## **Introduction**

Durability of reinforced concrete structures depends on carbon steel rebars corrosion. The two main causes of corrosion are concrete carbonation, due to the ingress of CO<sub>2</sub>, which reduces concrete pore solution pH to 8, and ingress of chlorides [1]. In the latter case, corrosion occurs if at the rebar level, chloride concentration exceeds a threshold value, which is influenced by the chemical composition of the rebar, concrete pH and rebar electrochemical potential, as clearly described by the “Pedeferrri Diagram” for cathodic protection and prevention [2]. Corrosion prevention is achieved during the design phase by making a high quality concrete mixture proportion, with a low water/cement ratio, by performing a correct curing and casting, and by using an appropriate cover. The European standards set out the threshold values of such parameters in relation to environmental aggressiveness [3-4]. With regard to structures exposed to very corrosive environments, or for structures with a design life over 50 years, it would be appropriate to use additional protective methods: blended cements, corrosion-resistant reinforcements, inhibitors, concrete coatings and cathodic protection.

Corrosion inhibitors may be used as a corrosion-prevention method, if added directly to fresh concrete, or as a restoration method for corroding rebars, when applied on the external surface of concrete and left to migrate inside [5]. Both inorganic products (based on calcium nitrite) and organic formulations are available. Calcium nitrite based inhibitors are internationally regarded as the most effective against corrosion: their inhibiting mechanism is well known, and the dosage is indicated in relation to the content of chlorides in concrete [5-6]. Organic commercial inhibitors, available since 1980s, are mixtures of amines, alkanolamines and carboxylate compounds. Literature data report an increase in the critical chloride content up to maximum 1.5% with respect to cement weight [5, 7-11].

In the last decade, there has been a growing interest in studying new compounds capable of preventing or delaying corrosion, and understanding the inhibition mechanism [12-20]. Studies have been conducted on non-commercial compounds, both inorganic (zinc oxide, molybdates, borates, stannanes, phosphates) and organic (benzoate and its derivatives, carboxylate substances, quaternary ammonium salts, citrate and amine-based substances).

This paper presents the results of electrochemical tests (cyclic potentiodynamic polarisation and potentiostatic polarisation tests) performed on binary mixtures made with two organic substances and sodium nitrite in order to verify a possible synergistic effects in the inhibition of chloride induced corrosion. The organic substances have been selected in a prior research, during which 100 organic compounds containing amino or carboxylic groups have been tested [21-24].

## **Materials and Methods**

### **Potentiodynamic polarisation tests**

Potentiodynamic polarisation tests were performed in a standard 1 L electrochemical cell.

The working electrode was a carbon steel rebar with improved adhesion (nominal diameter 10 mm, length 40 mm). The two ends of the sample were shielded with a polymeric self-amalgamating sheath in order to obtain an exposed surface of 10 cm<sup>2</sup>. The surface was sandblasted to remove the passivation film. The samples were then assembled on a sample holder as illustrated in Figure 1.

A saturated calomel electrode (SCE, +244 mV vs the standard hydrogen electrode) was used as reference electrode. A platinum electrode was the counter electrode.

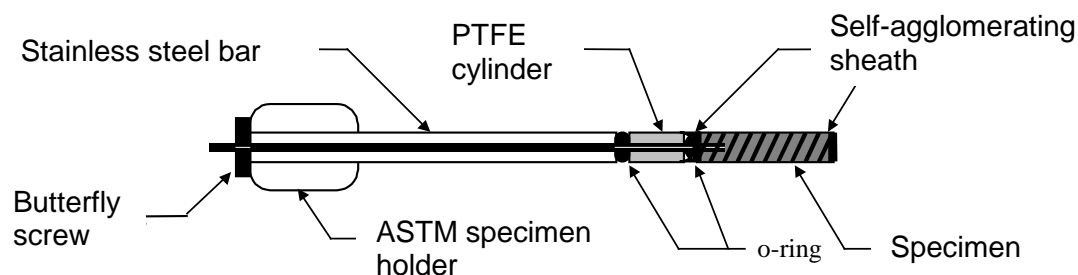


Figure 1: Assembly of the test specimen on the sample-holder

Tests were performed according to ASTM G61 [25], by increasing the potential with a scan rate of 10 mV/min, starting from -1.20 V SCE. Once a maximum current density of  $10 \text{ A}\cdot\text{m}^{-2}$  was reached, the potential scan was reversed to -1.20 V SCE. The test began 30 minutes after sample immersion. A 352 SoftcorrIII software measured the circulating current density and carbon steel potential. Cell temperature was  $20 \pm 2^\circ\text{C}$ . All tests were repeated at least twice to ensure data reproducibility, and in case of disagreement, more replicates were performed.

Samples were immersed in an saturated calcium hydroxide solution (pH 13), simulating the concrete pore solution: distilled water +  $2 \text{ g}\cdot\text{L}^{-1} \text{ Ca}(\text{OH})_2 + \text{NaOH } 0.1 \text{ M}$ .

Three inhibitors were studied: dimethylethanolamine (DMEA,  $(\text{CH}_3)_2\text{N}(\text{OH}-\text{CH}_2\text{CH}_2)$ ), sodium benzoate ( $\text{C}_6\text{H}_5-\text{COO}^-\text{Na}^+$ ) and sodium nitrite ( $\text{NaNO}_2$ ). Binary mixtures (A + B) were prepared maintaining a total constant 0.1 M concentration of inhibiting substances, with the following molar ratio:

- A 0.09 M + B 0.01 M
- A 0.05 M + B 0.05 M
- A 0.01 M + B 0.09 M

The mixture nitrite-benzoate was also tested at the ratio benzoate 0.07 M + nitrite 0.03 M.

For comparison purposes, tests were carried out on pure compounds (dosage 0.1 M) and in the alkaline solution without added inhibitors.

All tests were performed adding chlorides 0.1 M.

#### Potentiostatic polarisation tests

Potentiostatic polarisation tests were performed on the same binary mixtures, by immersing 13 carbon steel specimens (same configuration of Figure 1) in a 3 L cylindrical cell (20 cm in diameter). Specimens were polarized at 0 mV SCE, using an activated titanium net-wire as counter-electrode placed on the bottom of the cell. The polarisation potential simulated the corrosion behavior of carbon steel rebar in pristine concrete exposed to atmosphere. The current flowing in each sample was monitored through a series of shunts.

The alkaline solution with inhibitors was initially chlorides free: as soon as current density reached typical passive conditions values (passive current density lower than  $1 \text{ mA}/\text{m}^2$ ), chlorides were periodically added every 80-90 h to the solution (0.05, 0.1, 0.2 up to 0.8 M). A sharp increase in the current and visual inspection revealed corrosion occurrence.

## Results and discussion

### Potentiodynamic polarisation tests

The cyclic potentiodynamic tests allowed identifying pitting potential values (potential at which a clear-cut increase in the anodic current density was recorded) and the repassivation potential (potential at which the return curve intersects the passivity interval). Since only sodium nitrite showed an effect on the repassivation potential, in the following this parameter will not be discussed.

Table 1 summarizes the pitting potential values obtained in all the tested conditions. Carbon steel pitting potential in tests carried out in alkaline solution without inhibitors with chloride content 0.1 M was -200 mV SCE. In the presence of pure substances, the following values were obtained:

- Sodium nitrite +500 mV SCE
- Sodium benzoate +25 mV SCE
- DMEA -145 mV SCE

*Table 1 – Pitting potential values (mV SCE).*

Component A	Dosage (% - Moles)						Component B
	100 - 0	90 - 10	50 - 50	30-70	10 - 90	0 - 100	
<i>mol/L Component A</i>	<i>0.1</i>	<i>0.09</i>	<i>0.05</i>	<i>0.03</i>	<i>0.01</i>	<i>0</i>	
NITRITE	500	435	350	570	270	25	BENZOATE
NITRITE	500	455	150		-135	-145	DMEA
BENZOATE	25	100	30		70	-145	DMEA

The effectiveness of the binary mixtures in inhibiting chloride-induced corrosion was assessed by comparing pitting potentials with results achieved in the reference solution without inhibitors and in the presence of pure substances.

The pitting potential data of the binary mixtures were compared with the potentials that would prevail if the inhibitory effects of the two components were linearly combined. In the absence of synergistic or antagonistic effects, in fact, we may assume a theoretical pitting potential of every mixture obtained as average of the pitting potentials of the two constituents weighted in accordance with their respective concentration:

$$(1) \quad E^*_m = X_A \times E_A + X_B \times E_B$$

where  $E^*_m$  is the pitting potential of the theoretical A + B mixture,  $X_A$  e  $X_B$  represent the molar fraction of A and B in the mixture, and  $E_A$  e  $E_B$  are the pitting potentials of pure A or B components, with a 0.1 M content.

Results are presented in Figures 2-4. In each graph the following characteristic values are plotted:

- $E_r$  = pitting potential of the reference solution without inhibitors (= -200 mV SCE)
- $E_A, E_B$  = pitting potential of the solution with pure inhibitor A or B
- $E_m$  = experimental pitting potentials of the mixture (red spot)
- $E^*_m$  = pitting potential of the mixture expected in the absence of synergistic effects (dotted blue line)

The inhibitor effectiveness was accordingly assessed as follows:

- increase in the pitting potential of the mixture compared to a linear sum of the effects of single constituents ( $\Delta E_{m-m}^*$ )
  - $\Delta E_{m-m}^* > 0$  mixture with synergistic effect
  - $\Delta E_{m-m}^* < 0$  mixture with antagonistic effect
- increase in the pitting potential of the mixture compared to the reference solution ( $\Delta E_{m-r}$ )
  - $\Delta E_{m-r}^* > 300$  mV significant inhibitory effect

The nitrite–benzoate mixture exhibits synergistic effects at low nitrite concentrations (<50%), reaching the maximum values for mixtures with approximately 30% of nitrite ( $\Delta E_{m-m}^* \approx 450$  mV, see Figure 2). The pitting potential approximates 600 mV SCE, with an increase by 800 mV with respect to the pitting potential of the reference solution without inhibitors.

The trend of the results for nitrite–DMEA mixtures is shown in Figure 3. In this case, the lack of a synergistic effect between the two substances is evident. The trend of the measured pitting potentials is nearly overlapped to the dotted line. The results are affected by the poor performance of DMEA, already highlighted by other authors and by the same research group [5, 23, 24]

In the case of benzoate–DMEA mixtures, the synergistic effect occurs for all the composition range, although the value of pitting potential is well lower (about 300 mV) with respect to the results obtained in the presence of benzoate–nitrite mixtures.

#### Potentiostatic polarisation tests

Due to poor performance of the mixture benzoate–DMEA, only nitrite–benzoate and nitrite–DMEA mixtures were tested.

Figure 5 and Figure 6 report the percentage of corroded carbon steel samples as a function of the added chlorides.

In the case of the reference solution, more than 80% of the samples corroded just after the first chloride addition (0.05 M). All samples corroded at the second chloride addition (0.1 M). All the three pure substances showed an inhibitive effect, the nitrite being the most efficient, showing the onset of corrosion at the following chlorides content:

- Sodium nitrite 0.5 M – 0.8 M chlorides
- Sodium benzoate 0.2 M – 0.4 M chlorides
- DMEA 0.1 M – 0.2 M chlorides

Both tested mixtures were able to improve the critical chloride content. The best performance was observed in the presence of 0.07 M benzoate – 0.03 M nitrite (Figure 6), in agreement with the results of the potentiodynamic polarisation tests (Figure 2). First sample corroded at a chloride content 0.3 M, last samples corroded at chloride content 0.5 M.

The mixture nitrite 0.5 M – benzoate 0.5 behaved as the pure benzoate 0.1 M.

The mixture nitrite 0.5 M – DMEA 0.5 showed a trend in between the two pure compounds.

In any case, it seems that the synergistic effect found in potentiodynamic polarisation tests is not so evident in the potentiostatic polarisation tests.

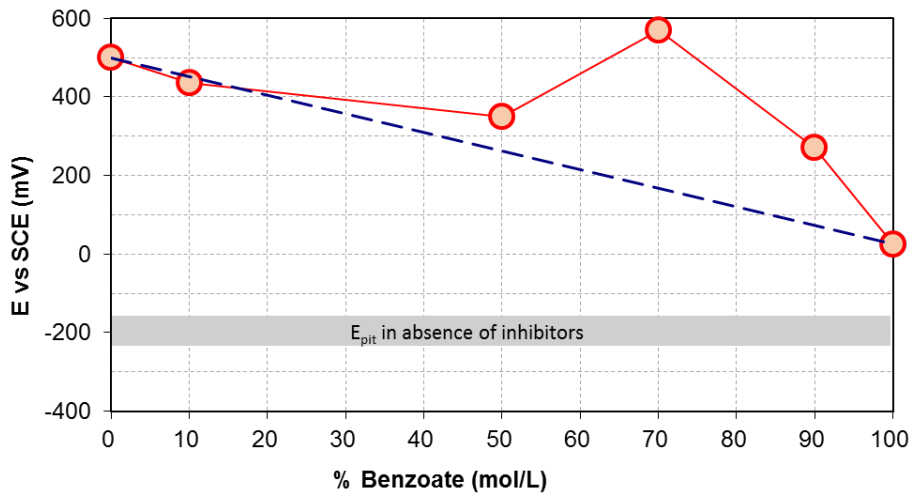


Figure 2: Effect on pitting potential of the nitrite – benzoate mixture

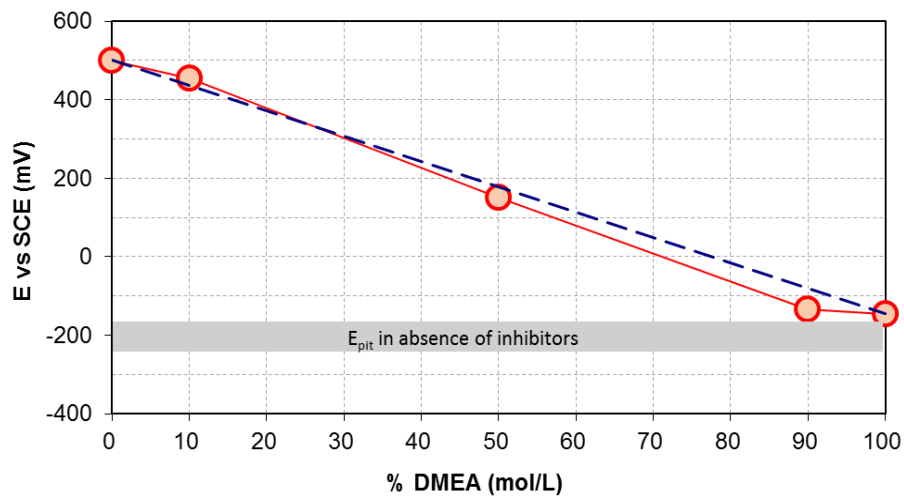


Figure 3: Effect on pitting potential of the nitrite – DMEA mixture

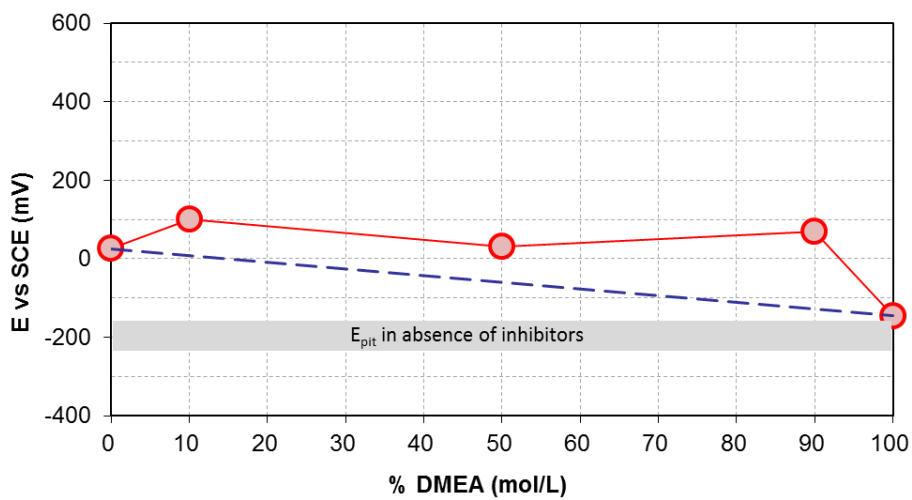


Figure 4: Effect on pitting potential of the benzoate – DMEA mixture

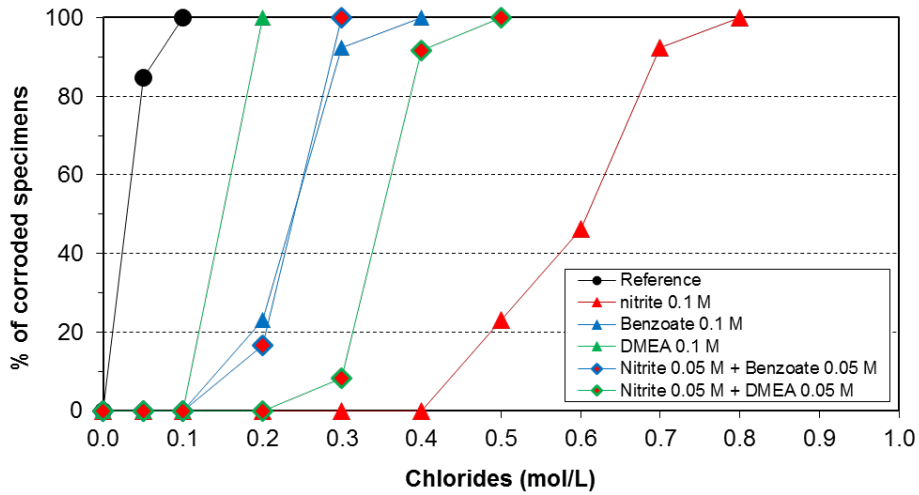


Figure 5: Percentage of corroded samples obtained by potentiostatic polarisation tests

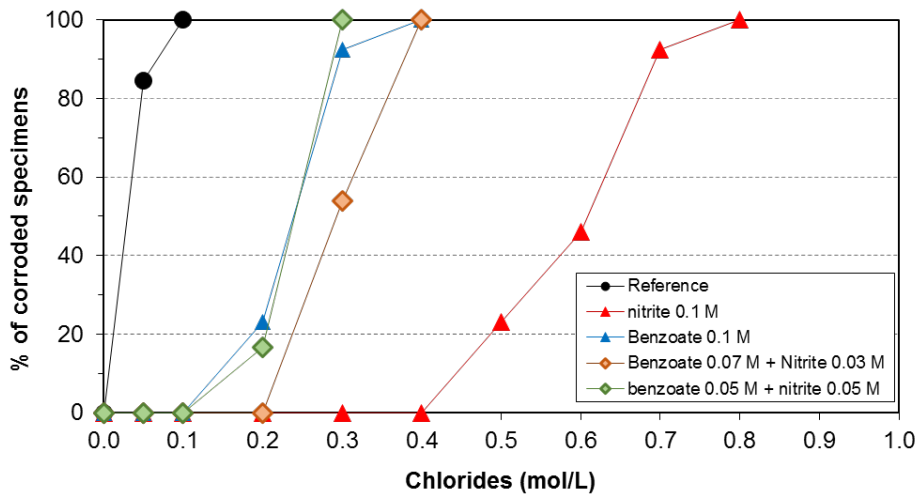


Figure 6: Percentage of corroded samples obtained by potentiostatic polarization tests: effect of nitrite-benzoate concentration

The same approach used to highlight the efficiency of the mixtures in increasing the pitting potential was used to process the data of critical chloride concentration. Results are reported in Figure 7 and Figure 8: dotted line is the expected critical chloride trend of the mixture in the absence of any synergistic effects, while red spots are the experimental values (error bars represent the minimum and maximum values). No significant synergistic effect is evident: in the case of nitrite–benzoate mixture there is even an antagonistic effect for low benzoate concentration, while additive effect is prevailing at higher concentration (Figure 7). The behaviour of the nitrite–DMEA mixture is additive and this result is in agreement with those of potentiodynamic polarisation tests (compare Figure 8 with Figure 4).

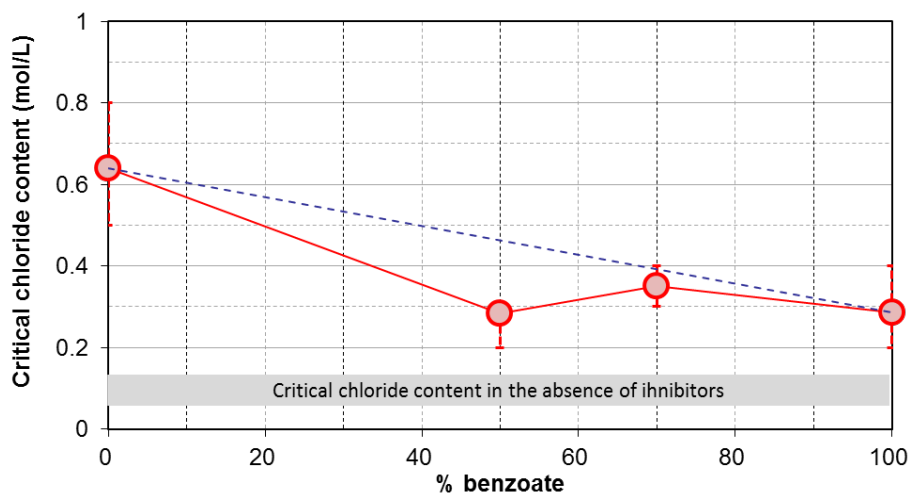


Figure 7: Effect on critical chloride content measured in potentiostatic polarisation tests for nitrite – benzoate mixtures

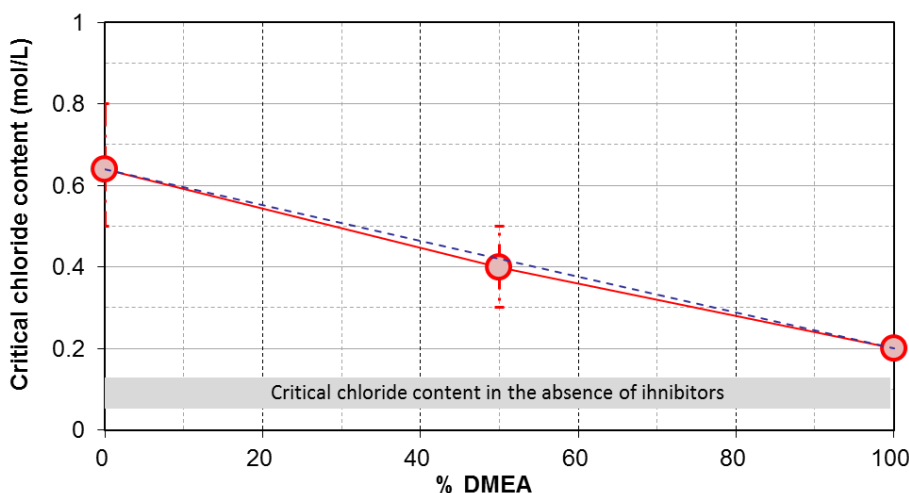


Figure 8: Effect on critical chloride content measured in potentiostatic polarisation tests for nitrite – DMEA mixtures

### **Conclusions**

The paper describes the results of electrochemical tests (potentiodynamic and potentiostatic polarisation) carried out on binary mixtures obtained by combining sodium benzoate and DMEA with sodium nitrite. Molar ration of the two constituents of each mixture was rage from 10/90, 30/70 and 50/50.

Only the mixture sodium benzoate 0.07 M – sodium nitrite 0.03 M showed the best inhibition efficiency, with a clear synergistic effect. Pitting potential increased about 800 mV with respect values measured in the reference solution without any inhibitor. Nevertheless, this mixture did not confirm the same trends in potentiostatic polarisation tests, in which additive effects were shown for higher benzoate concentration, with even a pejorative effect for lower concentration of benzoate.

The nitrite–DMEA mixture did not show any interesting effect in both potentiodynamic and potentiostatic polarisation tests; the worst results is surely affected by the low performance of DMEA. Also in these mixtures, additive behaviour prevails.



## References

1. L. Bertolini, B. Elsener, E. Redaelli, P. Pedferri, R. Polder, “Corrosion of steel in concrete: prevention, diagnosis, repair”, Wiley, Weinheim (2013).
2. P. Pedferri, *Construction and building materials*, **10** (1996) 391.
3. EN 206, “Concrete Part 1: specification, performance, production and conformity” (Brussels, Belgium; European Committee of Standardization).
4. EN 1992-1-1, “Eurocode 2: design of concrete structures - Part 1-1: general rules and rules for, buildings” (Brussels, Belgium; European Committee of Standardization).
5. B. Elsener, “Corrosion inhibitors for steel in concrete - State of the art report”, EFC Publications, Number 35 (2001).
6. N.S. Berke, T.G. Weil, in “Advances in Concrete Technology”, Int. Conf. CANMET, Athen, Greece (1992) p. 899–924.
7. C.K. Nmai, S.A. Farrington, G.S. Bobrowsky, *Concrete International* **14** (1992) 45.
8. U. Mader, *Concrete*, **9** (1999) 215–232.
9. W. Morris, M. Vazquez, *Cement and Concrete Research*, **32** (2002) 259.
10. L. Mechmeche, L. Dhouibi, M. Ben Oueddou, E. Triki, F. Zucchi, *Cement and Concrete Composites*, **29** (2007) 365.
11. T.A. Soylev, M.G. Richardson, *Construction and Building Materials*, **22** (2008) 609.
12. N.N. Andreev, D.S. Bulgakov, I.A. Gedvillo, A.S. Zhmakina, S.S. Vesely, *International Journal of Corrosion and Scale Inhibitors*, **3** (2014) 238.
13. C. Monticelli, A. Frignani, A. Balbo, F. Zucchi, *Materials and Corrosion*, **62** (2011) 178.
14. S.-H. Tae, *Construction and Building Materials*, **35** (2012) 270.
15. M. Cabrini, S. Lorenzi, T. Pastore, *Electrochimica Acta*, **124** (2014) 156.
16. F.L. Fei, J. Hu, J.X. Wei, Q. Yu, Z. Chen, *Construction and Building Materials*, **70** (2014) 45.
17. J.O. Okeniyi, O.A. Omotosho, O.O. Ajayi, C.A. Loto, *Construction and Building Materials*, **50** (2014) 448.
18. H.S. Ryu, J.K. Singh, H.M. Yang, H.S. Lee, M.A. Ismail, *Construction and Building Materials*, **114** (2016) 223-231.
19. W. Martinez, A. Torres, R. Hernández, E. Alonso, I. Mendoza, I. Martinez, *Anti-Corrosion Methods and Materials*, **63** (2016) 65-71.
20. N.N. Andreev, I.A. Gedvillo, A.S. Zhmakina, D.S. Bulgakov, S.S. Vesely, *International Journal of Corrosion and Scale Inhibitors*, **5** (2016), 319–324
21. M. Ormellese, F. Bolzoni, L. Lazzari, P. Pedferri, *Materials and Corrosion*, **59** (2008) 98.
22. M. Ormellese, L. Lazzari, S. Goidanich, G. Fumagalli, A. Brenna, *Corrosion Science*, **51** (2009) 2959.
23. M. Ormellese, F. Bolzoni, L. Lazzari, A. Brenna, M. Pedferri, *Materials and Corrosion*, **62** (2011) 170.
24. F. Bolzoni, A. Brenna, G. Fumagalli, S. Goidanich, L. Lazzari, M. Ormellese, M. Pedferri, *La Metallurgia Italiana*, **107** (2015) 53.
25. ASTM G 61, “Standard Test Method for Conducting Cyclic Potentiodynamic Polarization Measurements for Localized Corrosion Susceptibility of Iron-, Nickel-, or Cobalt-Based Alloys” (West Conshohocken, PA: ASTM International).