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# A study on corrosion inhibitors for concrete application

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**Abstract**

The inhibiting behavior of many organic and inorganic substances against steel corrosion was evaluated in an alkaline chloride solution, constituted by a saturated calcium hydroxide solution containing 0.1 M chloride ions. Besides 0.05 M sodium nitrite (SN), among the tested substances, only 0.005 M 5-hexyl-benzotriazole (C6BTA), 0.05 M sodium β-glycerophosphate (GPH), and saturated dicyclohexylammonium nitrite (DCHAMN) were able to prevent pitting corrosion over 30-day exposures to the aggressive electrolyte. Moreover, very good results were obtained with steel specimens coated by DINITROL AV 30®, which is a commercial corrosion inhibitive filming product. Chloride-polluted mortars embedding steel rods were also prepared to assess the influence of the most promising inhibitors, added either as admixtures or as impregnation agents, under conditions closer to those experienced in concrete. The inhibiting efficiencies (IE) were tested by Electrochemical Impedance Spectroscopy (EIS). Good results were obtained with admixed tungstosilicic acid (TSAH), with GPH or DCHAMN penetrated from the outside or in the presence of DINITROL AV 30® coating. © 2000 Elsevier Science Ltd. All rights reserved.

*Keywords:* Corrosion; Corrosion inhibitors; Mortar; Electrochemical properties; Chloride

## 1. Introduction

Besides calcium nitrite, which is the traditional commercial inhibitor used for application in reinforced concrete structures [1,2], many substances have been tested as inhibitors against the corrosion of reinforcing steel rebars [3–5].

Sodium monofluorophosphate has been widely studied and applied in the field to prevent the onset of corrosion or to reduce the corrosion rates, both in the presence of chlorides [6,7] and in the presence of carbonation [8]. It is used by penetration from the concrete surface because, as an admixture, it induces a strong retardation of the concrete setting and can be transformed into insoluble compounds.

Alkanolamines such as diethanolamine, dimethylpropanolamine, monoethanolamine, dimethylethanolamine, methyldiethanolamine, and triethanolamine were tested as corrosion inhibitors and their effect on the concrete mechanical properties was evaluated [9]. An inhibitive effect was experienced particularly with triethanolamine, monoethanolamine, and methyldiethanolamine. Alkanolamine salts of organic and inorganic salts were also found to reduce the steel corrosion rates and to be compatible with the concrete matrix [10]. Alkanolamines are the active agent in many proprietary inhibitive formulations [4].

Other organic substances, which are claimed to have an inhibitive effect, are based on ternary mixtures of aldonic acid, benzoic acid, and a triazole [11], carboxylic or bicarboxylic acids [12,13], tannins [14].

In this article, many substances were evaluated as possible inhibitors of the concrete reinforcement corrosion, first in an alkaline chloride solution, then in chloride-polluted mortars, where their influence on the corrosion rate was investigated by Electrochemical Impedance Spectroscopy (EIS).

## 2. Methods

Specimens were cut from AISI 1033 rods (chemical composition: C=0.3%; S=0.03%; $P<0.01\%$; Si=0.04%; Mn=0.96%; Ni=0.2%; Cu=0.02%; Al=0.07%; balance Fe), used as concrete reinforcement. Steel sheets of similar compositions were used for weight loss measurements in simulated concrete pore solutions.

Three types of specimens were used:

1. Cylinders with exposed area about 4.5 cm$^2$, for electrochemical tests in simulated concrete pore solutions;

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2. Sheets with area of approximately 26 $cm^2$, for weight loss measurements in simulated concrete pore solutions;
3. Cylinders with exposed area of approximately 26 $cm^2$ for EIS tests in mortars.

The specimens were always prepared by surface grinding with emery papers, from nos. 120 to 600, washed with double distilled water and degreased with acetone. On type 1 and type 3 steel specimens, an electrical contact was ensured by a threaded rod screwed into a threaded hole on the top of the cylinders, properly screened from the aggressive environment.

### *2.1. Tests in alkaline solutions*

Preliminary tests were carried out in a saturated calcium hydroxide solution containing a chloride concentration of 0.1 M. The solution was filtered to avoid solid suspension and showed a pH value of about 13. The substances tested as corrosion inhibitors are reported in Table 1, with the adopted abbreviations, while the concentrations are indicated in Section 3. The additives producing insoluble calcium salts in this environment were tested in a modified alkaline environment, constituted by a 0.1 M NaOH solution, containing 0.1 M chlorides. They were oleic (OLA) and linoleic (LIOLA) acids.

All the acid compounds were neutralized by equivalent sodium hydroxide amounts.

Anodic polarization curves, recorded after 45 min of immersion in the various solutions under free corrosion conditions, were used to evaluate the pitting potentials (potential scanning rate 0.5 mV $s^{-1}$). Crevice corrosion was avoided by properly varnishing the contact region between the electrode and the gasket.

Some of the substances were also tested for their influence on the steel corrosion behavior during 30-day immersions in the presence of chlorides. At the end of the immersions, weight losses were evaluated and the occurrence of localized corrosion attacks was recorded.

### *2.2. Tests in mortars*

Ordinary Portland Cement mortar specimens, each embedding two steel electrodes of type 3 (at a distance of about 2.5 cm from each other), were cast in polyethylene moulds (size 7 × 8 × 10 cm). Both ends of the electrodes were masked with epoxy to leave a known exposed surface area.

Table 1
Additives investigated as corrosion inhibitors in alkaline solution

| Inhibitor | Abbreviation | Group |
|---|---|---|
| Triethanolamine | TEOA | Alkanolamines |
| 6-Amino-1-hexanol | HOA | |
| Tetraethylammonium chloride | TEAM | Quaternary ammonium derivatives |
| Tetrahexylammonium chloride | THAM | |
| Benzyltriethylammonium chloride | BEAM | |
| Benzyltriethylammonium tetrafluoroborate | BEAMB | |
| Benzyltributylammonium chloride | BBAM | |
| Tetraethylphosphonium chloride | TEPH | Quaternary phosphonium derivatives |
| Benzotriazole | BTA | BTA and its derivatives |
| 5-Methyl-benzotriazole | C1BTA | |
| 5-Butyl-benzotriazole | C4BTA | |
| 5-Hexyl-benzotriazole | C6BTA | |
| Sodium gluconate | GLU | Organic acids or their salts |
| D-Saccharic acid, monopotassium salt | SAC | |
| Calcium α-D Eptagluconate | EGLU | |
| Phthalic acid, monopotassium salt | PHTA | |
| Lactic acid | LAC | |
| Maleic acid | MAL | |
| Suberic acid | SUB | |
| Adipic acid | ADI | |
| Sodium benzoate | BEN | |
| Sodium nitrite | SN | Inorganic acids or their salts |
| Tungstosilicic acid hydrate | TSAH | |
| Phosphomolybdic acid | PMA | |
| Ammonium tetrathiotungstate | AMTT | |
| Ammonium tetrathiomolybdate | AMTM | |
| Monofluorophosphoric acid | MFP | |
| Dicyclohexylammonium nitrite | DCHAMN | Miscellaneous |
| Dicyclohexylamine | DCHA | |
| Sodium β-glycerophosphate | GPH | |
| 2-Mercaptobenzimidazole | MBI | |
| Phloroglucinol | PHLO | |

Table 2
Chlorides and inhibitors content of the different mortar mixes, all characterized by a water/cement weight ratio of 0.5 and a sand/cement weight ratio of 3

| Type | $Cl^-$/cement weight ratio | Inhibitor(s) | [Inh]/[$Cl^-$] molar ratio |
|---|---|---|---|
| 1 | 0 | – | – |
| 2 | 0.02 | – | – |
| 3 | 0.02 | SN | 0.05 |
| 4 | 0.02 | SN | 0.5 |
| 5 | 0.02 | GPH | 0.05 |
| 6 | 0.02 | GPH–SN | 0.05–0.05 |
| 7 | 0.02 | C6BTA–SN | 0.05–0.05 |
| 8 | 0.02 | TSAH | 0.0035 |
| 9 | 0.02 | –[a] | –[a] |
| 10 | 0.02[b] | – | – |
| 11 | 0.02[b] | DCHAMN | 0.5[b] |
| 12 | 0.02[b] | GPH | 0.5[b] |
| 13 | 0.02[b] | C6BTA | 0.05[b] |

[a] Electrodes coated by DINITROL AV 30®.

[b] Penetrated in the mortar from an external alkaline solution after mortar setting.

A hole in the mortar, in a symmetrical position with respect to the electrode couple and close to both electrodes, allowed the insertion of a reference electrode.

The different mortar mixes investigated are reported in Table 2. In mortar types (m.t.) 3–8, additives and chlorides were added to the mixing water, at the [inhibitor]:[$Cl^-$] molar ratios indicated in the table. The m.t. 2 is the corresponding blank mortar, as no additive is present.

Even in m.t. 9, containing admixed chlorides, no inhibitor was used: the steel rods were coated by a wax-based Corrosion Inhibitive Compound (CIC) containing an alkylbenzene sulphonate salt, as corrosion protection agent (DINITROL AV 30®), which is usually employed against the atmospheric corrosion in the aeronautic field.

After 24 h in the moulds, the mortar specimens were completely immersed in saturated calcium hydroxide solutions periodically renewed and kept in contact with the laboratory atmosphere for 1 year.

Some results are also described on the effect of saturated dicyclohexylammonium nitrite (DCHAMN, m.t. 11), sodium β-glycerophosphate (GPH, m.t. 12), and 5-hexylbenzotriazole (C6BTA, m.t. 13) penetrated in the mortars from an external alkaline solution, after 1 day mortar curing (Table 2). The solutions were allowed to penetrate completely before the mortars were immersed in a saturated calcium hydroxide solution polluted by chlorides. The chloride amount in the latter solution was the same as in the other mortar mixes. M.t. 10 was obtained with the same method adopted for m.t. 11–13, but in the absence of any inhibiting additive.

The EIS tests were carried out by a Solartron 1260/1287 FRA/Electrochemical Interface and a Compaq Prolinea 4/50 PC for data logging and analysis. The measurements were carried out with applied sinusoidal potential waves of 10 mV amplitude around the corrosion potential, with frequencies ranging from $10^6$ Hz (or higher) down to $10^{-3}$ Hz and more frequently $10^{-4}$ Hz. As a reference electrode, a low-impedance Ag/AgCl wire was used to avoid the distortion of the high frequency part of the spectra.

All the potentials quoted in the text are referred to the saturated calomel electrode (SCE).

## 3. Results and discussion

### 3.1. Tests in alkaline solutions

Table 3 collects the $E_{cor}$ and $E_{pit}$ values measured from the anodic polarization curves and the width of the passive

Table 3
Data collected from the anodic polarization curves in saturated calcium hydroxide solution, containing a 0.1 M chloride concentration

| Inhibitor | Concentration (M) | $E_{cor}$ ($V_{SCE}$) | $E_{pit}$ ($V_{SCE}$) | ($E_{pit}$–$E_{cor}$) (V) |
|---|---|---|---|---|
| –[a] | – | −0.249 | 0.607 | 0.856 |
| – | – | −0.294 | 0.056 | 0.350 |
| TEOA | 0.05 | −0.281 | −0.149 | 0.132 |
| HOA | 0.05 | −0.296 | −0.009 | 0.287 |
| TEAM | 0.05 | −0.370 | −0.280 | 0.090 |
| THAM | 0.05 | −0.521 | −0.521 | 0 |
| BEAM | 0.05 | −0.291 | 0.055 | 0.346 |
| BEAMB | 0.05 | −0.294 | −0.084 | 0.210 |
| BBAM | 0.05 | −0.290 | 0.031 | 0.321 |
| TEPH | 0.05 | −0.309 | 0.012 | 0.321 |
| BTA | 0.005 | −0.343 | −0.343 | 0 |
| C1BTA | 0.005 | −0.305 | −0.170 | 0.135 |
| C4BTA | 0.005 | −0.285 | 0.077 | 0.362 |
| C6BTA | 0.005 | −0.340 | 0.332 | 0.672 |
| GLU | 0.05 | −0.397 | −0.250 | 0.147 |
| SAC | 0.05 | −0.415 | −0.415 | 0 |
| EGLU | 0.05 | −0.395 | −0.395 | 0 |
| PHTA | 0.05 | −0.238 | −0.089 | 0.149 |
| LAC | 0.05 | −0.447 | −0.447 | 0 |
| MAL | 0.05 | −0.253 | 0.122 | 0.375 |
| SUB | 0.05 | −0.267 | 0.050 | 0.317 |
| ADI | 0.05 | −0.281 | −0.281 | 0 |
| BEN | 0.05 | −0.269 | −0.038 | 0.231 |
| SN | 0.005 | −0.207 | 0.100 | 0.307 |
|  | 0.05 | −0.308 | 0.410 | 0.718 |
| TSAH | sat. | −0.360 | 0.130 | 0.490 |
| PMA | 0.00055 | −0.257 | −0.117 | 0.140 |
| AMTT | 0.01 | −0.436 | −0.281 | 0.155 |
| AMTM | 0.005 | −0.429 | −0.038 | 0.391 |
|  | 0.01 | −0.462 | −0.163 | 0.299 |
| MFP | 0.05 | −0.436 | −0.436 | 0 |
| DCHAMN | sat. | −0.206 | 0.084 | 0.290 |
| DCHA | sat. | −0.262 | 0.512 | 0.774 |
| GPH | 0.05 | −0.310 | 0.090 | 0.400 |
| MBI | 0.005 | −0.213 | −0.019 | 0.194 |
| PHLO | 0.05 | −0.307 | −0.307 | 0 |
| SUB+HOA | 0.05+0.05 | −0.243 | −0.243 | 0 |
| MAL+HOA | 0.05+0.05 | −0.272 | 0.028 | 0.300 |
| GLU+BEN | 0.05+0.05 | −0.329 | −0.180 | 0.149 |
| GLU+BEN +C1BTA | 0.05+0.05 +0.05 | −0.234 | −0.234 | 0 |

[a] In the absence of chlorides.

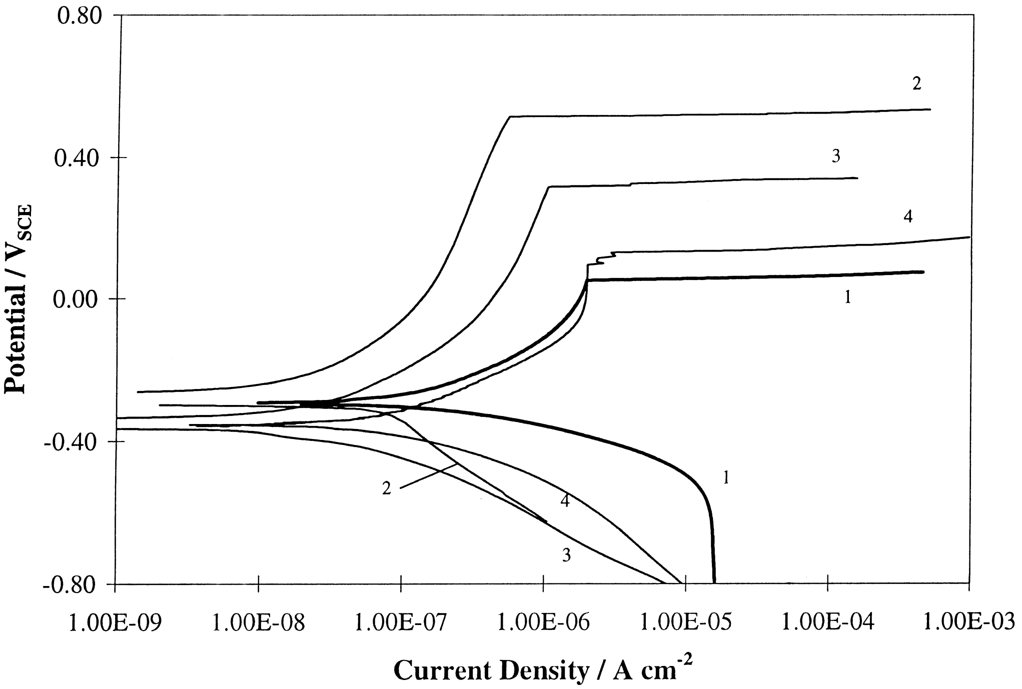

Fig. 1. Polarization curves recorded in saturated $Ca(OH)_2$ solutions in the absence (1) or in the presence of the following additives: saturated DCHA (2), 0.005 M C6BTA (3), or saturated TSAH (4).

range calculated from their difference. In the absence of additives, chloride reduces the width of the passive range to less than one-half. No additive allowed a passive range as wide as that measured in the absence of chlorides. However, sodium nitrite (SN) and a few other substances were able to increase $E_{pit}$ and $E_{pit}-E_{cor}$. The following is the decreasing pitting potential sequence: sat. DCHA>0.05 M SN>0.005 M C6BTA>sat. tungstosilicic acid (TSAH)>0.05 M MAL>0.005 M SN>0.05 M GPH>sat. DCHAMN>0.005 M C4BTA>Blank.

Among these substances, TSAH exhibited a limited increase in the pitting potential probably owing to its limited solubility in the aggressive environment. The possibility to increase the inhibiting efficiencies (IE) by increasing the additive concentration was precluded also in the case of saturated DCHA solution and in the case of 0.005 M C4BTA or C6BTA solutions, which were close to the saturated conditions. On the contrary, saturated DCHAMN solution was almost 0.05 M.

Fig. 1 compares, as an example, the polarization curves obtained in the blank solution (curves 1) to those obtained in the presence of either DCHA (no. 2) or C6BTA (no. 3) or TSAH (no. 4). As can be seen, besides increasing the pitting potential, C6BTA and particularly DCHA markedly reduce the anodic passive current densities and inhibit the cathodic reaction connected to the oxygen reduction. This last effect is also shown by TSAH.

In the modified alkaline environment, highly scattered pitting potential values were measured in the absence of any additive, while in the presence of the additives the reproducibility is acceptable (Table 4). The tested acids were unable to afford an inhibitive effect, whereas some mixtures showed promising results.

In the hypothesis that some substances could develop an inhibiting effect for contact times between the metal and the solution longer than 45 min, 30-day immersions were carried out, not only in the presence of the substances indicated in the sequence, but also in the presence of other additives whose structure appeared promising to afford corrosion inhibition. Immersion tests lasting 30 days were also carried out on steel specimens coated by DINITROL AV 30®.

Table 5 collects the gravimetric corrosion rates obtained in the blanks (calcium or sodium hydroxide solutions, with 0.1 M chlorides) and in the inhibited solutions. This table shows that some substances, which appeared as promising inhibitors according to the ($E_{pit}-E_{cor}$) values reported in

Table 4
Data collected from the anodic polarization curves in 0.1 M NaOH solution, containing a 0.1 M chloride concentration

| Inhibitor | Concentration (M) | $E_{cor}$ ($V_{SCE}$) | $E_{pit}$ ($V_{SCE}$) | ($E_{pit}-E_{cor}$) (V) |
|---|---|---|---|---|
| – | – | −0.380 ± 45 | 0.410 ± 0.192 | 0.790 ± 0.165 |
| OLA | 0.05 | −0.409 | −0.084 | 0.325 |
| LIOLA | 0.05 | −0.305 | −0.070 | 0.235 |
| OLA + TEOA | 0.05 + 0.05 | −0.450 | 0.600 | 1.050 |
| OLA + HOA | 0.05 + 0.05 | −0.276 | 0.615 | 0.910 |
| LIOLA + TEOA | 0.05 + 0.05 | −0.293 | −0.032 | 0.261 |
| LIOLA + HOA | 0.05 + 0.05 | −0.353 | 0.600 | 0.953 |

Table 5
Gravimetric corrosion rates obtained after 30-day immersions

| Solution | Corrosion rate ($\mu$m y$^{-1}$) | Inhibiting efficiency (%) | Comments |
|---|---|---|---|
| Blank[a] | 11.7 | – | Pitting/crevice |
| Blank + 0.005 M SN | 13.1 | no effect | Pitting |
| Blank + 0.05 M SN | 1.26 | 89 | – |
| Blank + sat. DCHA | 9.02 | 23 | Pitting |
| Blank + sat. DCHAMN | 0.372 | 97 | – |
| Blank + 0.05 M BEAM | 12.5 | no effect | Pitting/crevice |
| Blank + 0.05 M TEPH | 20.4 | stimulation | Pitting/crevice |
| Blank + 0.05 M GPH | 0.94 | 92 | – |
| Blank + 0.005 M GPH+0.005 M SN | 3.52 | 70 | Pitting |
| Blank + 0.005 M C6BTA | 3.81 | 67 | Pitting |
| Blank + sat.TSAH | 9.95 | 15 | Pitting/crevice |
| Blank + 0.05 M MAL | 11.9 | no effect | Pitting |
| Blank/DINITROL AV 30® | 2.60 | 78 | Micropitting |
| Blank[b] | 4.8 | – | Pitting/crevice |
| Blank[b] + 0.05 M OLA+0.05 M TEOA | 2.7 | 44 | Pitting |
| Blank[b] + 0.05 M OLA+0.05 M HOA | 1.3 | 73 | – |
| Blank[b] + 0.05 M LIOLA+0.05 M TEOA | 12.6 | stimulation | General corrosion |
| Blank[b] + 0.05 M LIOLA+0.05 M HOA | 3.2 | 33 | Pitting/crevice |

[a] Blank = $Ca(OH)_2$ sat. + [$Cl^-$] 0.1 M.

[b] Blank = NaOH 0.1 M + [$Cl^-$] 0.1 M.

Tables 3 and 4, fail to hinder the corrosion process during longer exposures. In fact, the ($E_{pit}-E_{cor}$) values afforded by 0.05 M SN, DCHA, and C6BTA were high and similar to each other, but the IE after 30-day immersions were different: only 0.05 M SN was able to completely avoid the onset of localized corrosion. The same happened for MAL, TSAH, GPH and 0.005 M SN: only GPH completely inhibited the formation of corrosion product spots. Among the mixtures that gave promising results in sodium hydroxide solution, only OLA/HOA keeps its good IE against pitting corrosion, while OLA/TEOA and LIOLA/HOA show a poor inhibitive action. These discrepancies are to be expected when the reinforcement of the passive film induced by the inhibitor is temporary. High IE are detected in this case after short time immersions, while average corrosion rates calculated by weight losses over long exposure times are higher, as quicker chloride penetration into the passive film is allowed.

An opposite behavior is detected in the case of saturated DCHAMN, which shows only a small passive potential range after 45 min of immersion and exhibits an excellent IE after a 30-day immersion, better than that afforded by 0.05 M SN. This indicates that it needs a relatively long time to build up a protective passive film on the steel surface.

The long time immersion tests confirm that quaternary ammonium or phosphonium compounds do not inhibit the corrosion of steel in alkaline chloride media.

### 3.2. Tests in mortars

All the impedance spectra obtained in mortars were interpreted according to the equivalent circuit shown in Fig. 2, reputed acceptable for the steel–concrete and steel–mortar systems [15–17]. $R_s$ should be the solution resistance between the reference electrode and the mortar. The first parallel RC combination should correspond to the dielectric properties of the mortar cover. The second parallel RC combination, not always observed, can be due to an inorganic film adherent to the steel electrodes, constituted by a lime-rich film [16,18,19] or a corrosion product film [20,21]. The last RC combination, which in many cases also contains a Warburg diffusion element in series to the resistive element, is related to the electrochemical properties of the corroding steel rebar.

The parameters of the EIS spectra obtained in the different mortars, after 1 year (m.t. 1–9) or 6 months (m.t. 10–13) of exposure to aerated $Ca(OH)_2$ solutions are collected in Table 6. In some cases, the deformation of the high frequency arc in the Nyquist spectra prevented the independent evaluation of $R_s$ and $R_c$. Where they can be distinguished, it can be noticed that $R_s$ values are in the range 500–1000 Ω cm$^2$ for m.t. 1–10, while they are lower (310–440 Ω cm$^2$) in the case of m.t. 11–13, probably as a consequence of a limited permeability of the inhibitor-impregnated mortars, which reduces the chloride ingress from the external solution. $R_c$ values of about 1700 Ω cm$^2$

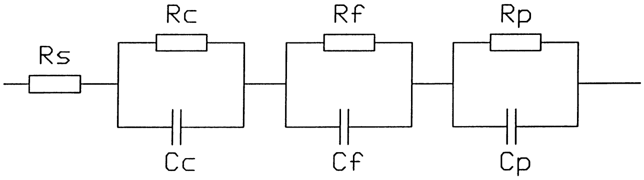

Fig. 2. Equivalent circuit adopted to interpret the EIS spectra obtained in mortars.

Table 6
Parameters of the equivalent circuit of Fig. 2 evaluated from the EIS spectra recorded on the different mortars after 1 year (m.t. 1–9) or 6 months (m.t. 10–13) of continuous immersion in aerated $Ca(OH)_2$ solutions
nd = not detectable.

| Mortar type | $R_s$ ($\Omega$ cm$^2$) | $R_c$ ($\Omega$ cm$^2$) | $C_c$ (pF cm$^{-2}$) | $R_f$ ($\Omega$ cm$^2$) | $C_f$ (nF cm$^{-2}$) | $R_p$ ($\Omega$ cm$^2$) | IE (%) |
|---|---|---|---|---|---|---|---|
| 1 | 890 | 1700 | 60 | 400 | 25 | $2.5\cdot10^6$ | |
| 2 | 875 | 500 | 220 | – | – | $1.3\cdot10^5$ | |
| 3 | | 1360[a] | nd | – | – | $4.4\cdot10^5$ | |
| 4 | 500 | 600 | 160 | 130 | 50 | $1.5\cdot10^6$ | 83 |
| 5 | 1000 | 510 | 270 | – | – | $>1.5\cdot10^5$ | |
| 6 | 830 | 670 | 200 | – | – | $>3\cdot10^5$ | |
| 7 | 770 | 1100 | 70 | – | – | $2.5\cdot10^5$ | |
| 8 | | 1400[a] | nd | – | – | $6.9\cdot10^5$ | 62 |
| 9 | | 1100[a] | nd | – | – | $>10^6$ | >74 |
| 10 | 720 | 1250 | 80 | – | – | $6.3\cdot10^5$ | |
| 11 | 310 | 950 | 170 | – | – | $1.1\cdot10^7$ | 88 |
| 12 | 370 | 1000 | 70 | – | – | $1.3\cdot10^7$ | 90 |
| 13 | 440 | 1350 | 110 | – | – | $8.0\cdot10^5$ | |

[a] $R_s + R_c$.

are found in the absence of chlorides. Values in the range 500–1100 $\Omega$ cm$^2$ are found in m.t. 2–9, owing to the higher ion content of the mortar pore electrolyte. The slightly higher $R_c$ values obtained in m.t. 10–13 (950–1350 $\Omega$ cm$^2$) appear to confirm that the level of free chloride ions in these mortars is slightly lower than that obtained with admixed chlorides.

The presence of an inorganic film was detected at intermediate frequencies ($10^5$–$10^3$ Hz) only in two cases, which are shown in Fig. 3, where the high frequency portions of the impedance spectra are plotted in the complex plane. They are both characterized by low steel corrosion rates, indicating that the films should not be constituted by corrosion products. No inorganic film is evident in the case of inhibitors penetrating from the outside.

For the sake of simplicity, the $R_p$ values were extrapolated by fitting the low frequency portion of the spectra by the arc of a circle, whose low frequency intercepts with the real axis is reported in Table 6. In those cases where this fitting procedure was not suitable, the table indicates that the $R_p$ values are higher than the impedance modulus at the lowest investigated frequency (usually $10^{-4}$ Hz).

The comparison among $R_p$ values obtained in m.t. 2–9 suggests a good inhibition of the corrosion process in m.t. 4, 8, and 9, with IE of 83%, 62%, and >74%, respectively, as reported in the table. These IE values are calculated by the formula $IE = (R_{p\ inh} - 2R_{p\ blank})/R_{p\ inh}$ (which takes into consideration a $B$ value for the Stern–Geary relation of 26 mV in the case of corroding steel rebars and 52 mV for passive steel rebars [6]). Fig. 4

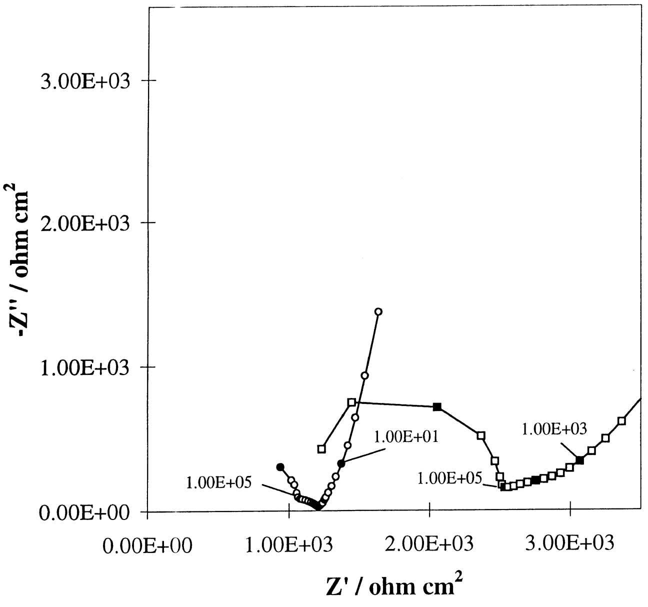

Fig. 3. High frequency portions of the impedance spectra obtained in m.t. 1 (squares) and 4 (dots). The solid symbols refer to integer frequency decades.

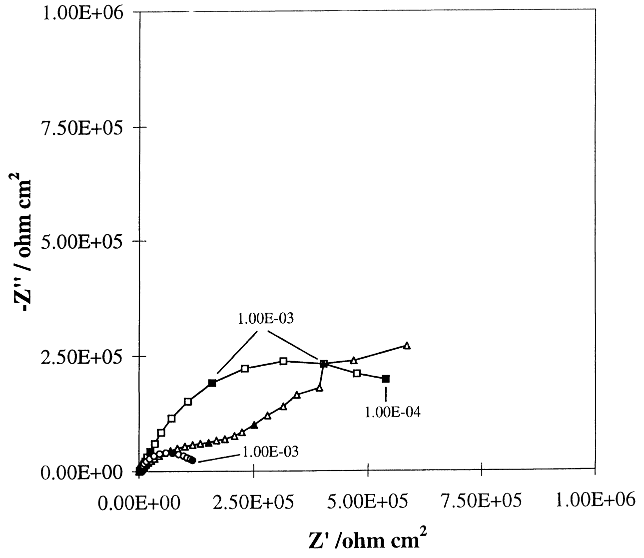

Fig. 4. Impedance spectra obtained in m.t. 2 (dots), 8 (squares), and 9 (triangles). The solid symbols refer to integer frequency decades.

shows the spectra obtained in m.t. 2, 8, and 9. Only one low frequency arc is present in m.t. 2 (blank) and 8 (TSAH), while in m.t. 9 (DINITROL AV 30®), besides an initial portion overlapping the arc obtained in the blank mortar, the beginning of a second arc is visible, probably connected to diffusion through the protecting coating.

Fig. 5 compares the impedance spectra obtained in m.t. 11–13 to that obtained in m.t. 10 (blank with chlorides penetrated from the outside). The presence of a corrosion inhibiting effect is clearly evident in m.t. 11 (DCHAMN) and 12 (GPH). Table 6 shows that they induce IE% of 88% and 90%, respectively. These results are in agreement with previous ones [22], as far as the corrosion inhibiting capabilities of DCHAMN in this environment are concerned. Also, the steel corrosion inhibition afforded by GPH in alkaline solutions was already stressed in a previous work [23]. However, in mortars, it was possible to achieve a corrosion inhibiting effect, only in the presence of GPH/SN admixtures, in well-aerated mortars, where oxygen appeared to cooperate in maintaining passivity conditions on the steel rebars [19]. The addition of large amounts of GPH in mortars (to get an inhibitor/chloride molar ratio of 0.5, as in m.t. 11) was precluded, as it markedly slowed down the mortar set reactions. Therefore, its penetration from an external solution appears a possible solution to the problem, thanks to its high solubility in saturated calcium hydroxide solutions.

On the contrary, C6BTA (m.t. 13) does not reduce the reinforcement corrosion rates, in spite of the good IE afforded in alkaline solutions. Its loss by adsorption on the hardened cement paste has to be verified.

The mechanism of corrosion inhibition of these latter substances will be the subject of a next paper, in preparation in our laboratory.

## 4. Conclusions

A rapid screening test based on anodic polarization curve recording is a useful tool to select candidate inhibitors of steel corrosion during 30-day immersions in alkaline chloride solutions.

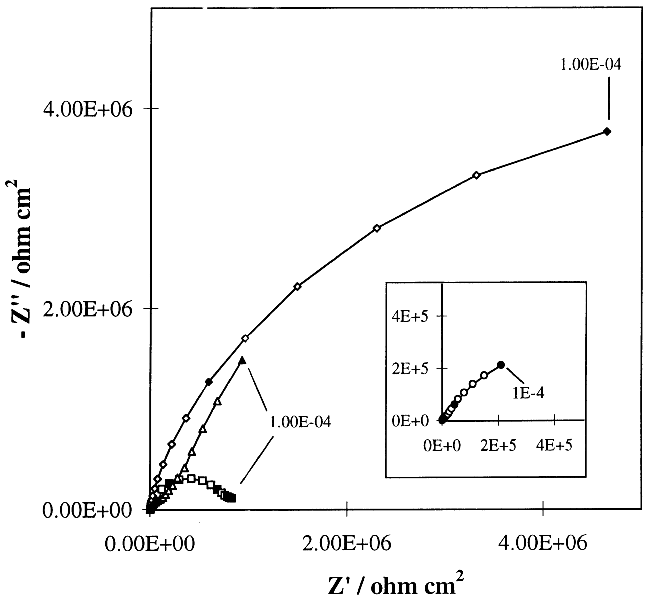

Fig. 5. Impedance spectra obtained in m.t. 10 (dots, in the insert), 11 (diamonds), 12 (triangles), and 13 (squares). The solid symbols refer to integer frequency decades.

Among the promising substances, only 0.05 M SN, 0.005 M C6BTA, 0.05 M GPH, and sat. DCHAMN are able to keep the inhibiting action throughout the exposure. Very good results are also obtained with steel specimens coated by DINITROL AV 30®.

Tests carried out in chloride-polluted mortars after 1 year of curing show that a good inhibiting action is achieved with admixed TSAH (IE% 62) or in the presence of the protective coating DINITROL AV 30® (IE%>74). Preliminary results obtained after 6 months of exposure to chloride-polluted mortars give IE% of 88 or 90 with GPH- or DCHAMN-impregnated mortars, respectively.

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