Variation in steel-mortar bond strength and microstructure in cathodically protected specimens after two-year exposure

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ABSTRACT

Steel embedded in concrete passivates due to the formation of an oxide film that may be broken by exposure to aggressive environments. In such cases, reinforcing bars need to be cathodically protected.

There are several criteria to select the adequate protection potential. In this paper it is proposed that steel could be polarised with three different potentials, -850, -1000 and -1250 mV, taken with respect to the saturated calomel electrode (SCE). Two electrolytes were employed: tap water and 3% sodium chloride solution. Mortar specimens were polarised for two years and, then, subjected to a pullout test in order to determine bond strength variations at the steel-mortar interface. It was found that steel-mortar adhesion diminished 10% when specimens were polarised at -1250 mV. These changes may be related to hydrogen evolution and to changes in the crystalline microstructure of the cement paste.

RÉSUMÉ

Dans le béton armé, l'acier est passivé à cause de la formation d'une pellicule d'oxyde qui, en présence d'un milieu agressif, peut être abîmée. Dans ce cas, l'acier de renforcement doit être cathodiquement protégé.

Il y a divers critères pour la sélection du potentiel de protection le plus approprié. Dans ce travail, il est proposé que l'acier peut être polarisé dans trois valeurs du potentiel: -850, -1000 et -1250 mV, mesurées par rapport à l'électrode de calomel saturé.

Des éprouvettes de mortier, plongées soit dans de l'eau du robinet, soit dans une solution contenant 3% de NaCl, ont été polarisées pendant deux ans avant d'être soumises à un essai de traction pour évaluer la variation de la tension d'adhérence dans l'interface acier/béton. Dans le cas où les éprouvettes ont été polarisées à -1250 mV, la tension d'adhérence a été inférieure de 10% par rapport à celles non polarisées mais maintenues dans les mêmes conditions. Cette variation peut être reliée non seulement à la génération d'hydrogène mais encore aux changements dans la microstructure cristaline de la pâte de ciment.

1. INTRODUCTION

Reinforced concrete combines several properties of two different materials, concrete itself and steel. Concrete is a low-cost material which, if properly manufactured, is highly stable to external or internal damage and protects steel which is bound to be corroded even in low aggressive environments. Steel embedded in concrete passivates easily due to the alkaline conditions and the formation of an oxide film that builds up onto it and largely decreases its corrosion rate. There are other factors that contribute to increase structure durability such as an adequate mortar cover thickness on steel bars, low mortar porosity (low water/cement, w/c, ratio or air incorporation), good steel-mortar bond, minimum cracking and the possibility of steel repassivation. The passive film can be partially or totally broken by exposure to chloride-rich environments,

concrete carbonation, etc. In such cases, reinforcing bars may be cathodically protected by the application of a potential negative enough to bring the material to either the immunity or the passivity zone [1, 2].

One of the drawbacks associated with cathodic protection is the possible loss in bond strength at the steel-mortar interface. There is not much information on this subject in the literature and there is still controversy about the loss in bond strength when the potential required for hydrogen evolution on steel bars is attained. To avoid this phenomenon, Vrable and other researchers [3, 4] have suggested that the polarisation potential should be below -1.1 V with respect to CSE (copper/copper sulphate electrode). Tache and Lemoine [5] found that the steel-mortar bond was not affected by polarisation of reinforcing bars during a 300-day test period with a potential between -900 and -1500 mV

(measured against SCE, saturated calomel electrode). The bond strength value was independent of the type of exposed surface, which could either contain lamination oxides, be sandblasted or show signs of corrosion induced by a strong anodic polarisation.

The aim of this work is to study bond strength variations at the steel-mortar interface of cathodically polarised specimens. Three polarisation potentials were selected to conduct this research, -850, -1000 and -1250 mV. Specimens were polarised for two years in order to determine the variation in steel – mortar bond strength. A pull-out test was developed in accordance with well-known standards to determine steel-mortar bond strength. The cement paste microstructure and the rebar surface were studied by scanning electron microscopy (SEM) and correlated with changes in mortar bond strength.

2. EXPERIMENTAL

2.1 Preparation of test specimens.

Cylindrical mortar specimens were cast. A grooved rebar of ordinary hardness (6 mm diameter, 25 cm long) was inserted along the axis of each specimen. The rebar had a deformation pattern similar to that shown in Fig. 1 of ASTM C 234-91a. Its chemical composition was similar to AISI 1040 steel but with a high Mn content (C: 0.40; Mn: 1.00%; Si: 0.40-0.50%; P and Si < 0.02%). The mortar was manufactured with a 1:3 cement/sand ratio by weight and a water/cement ratio equal to 0.5. Ordinary portland cement (ASTM C 150 Type I) and ordinary graduated siliceous river sand (similar to ASTM C 778) were used. The moulds, 5 x 10 cm in size, were filled in three layers, pressing each layer with a tamper and being careful to leave a flat upper surface to avoid stress concentration during the pullout test. In the first 24 h, specimens were left in their moulds, in the humid chamber (> 95% RH and 23 ± 2°C). They were then removed from their moulds and kept under lime water to complete the 28-day curing period under the same conditions of relative humidity and temperature.

2.2 Specimen polarisation

There are several criteria for selecting the right protection potential [3-4, 6-8]. One of the most widely applied suggests a -850 mV polarisation potential in relation to CSE [4-6]; as an alternative this value may be taken when the polarisation is cut off to discount the ohmic overpotential [7]. Other criteria take the corrosion potential of the reinforcing bar as the starting point and consider that the protection potential should be shifted -100, -300 mV, etc., with respect to the corrosion potential [9]. The open circuit potential of reinforcing bars, however, may vary from one point to another in the structure and with ambient conditions [10, 11], so it cannot be taken as a valid reference point. Based on previous studies [12], three polarisation potentials were selected to conduct this research,
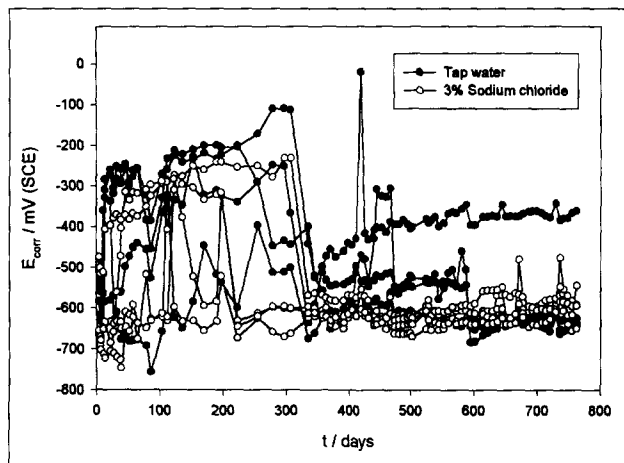

Fig. 1 – Rebar corrosion potential as a function of time in tap water and in 3% sodium chloride solution.

-850, -1000 and -1250 mV; the -1250 mV potential being sufficient to cause appreciable hydrogen evolution. Hydrogen evolution at this potential was previously reported by several researchers [4, 12] and is consistent with data reported by Pourbaix [13].

A set of eight specimens was polarised at each of the above mentioned potentials by means of a potentiostat, to be then subjected, after a two-year exposure, to a pull-out test in order to determine the bond strength variation at the steel-mortar interface. Specimens were placed in a plastic container, 60 x 40 x 25 cm in size, immersed in the selected electrolytes: tap water, of moderately high resistivity and low resistivity 3% sodium chloride. Platinum anodes were employed to polarise the specimens. A similar set of specimens was left unpolarised, in the same electrolytes, in order to be used as a control test and discount the effect of ageing. The rebar potential was monitored continuously for two years.

Test temperature was 20 ± 5°C.

2.3 Variation in steel-mortar bond strength

Pullout Test. This test consists in removing a steel bar embedded in mortar by applying an increasing stress to pull the rebar out of the specimen. The test was developed in accordance with ASTM C 234-91a, varying mainly the specimen size (5 x 10 cm) and the steel bar diameter (6 mm) and was employed previously by other researchers [14, 15].

The test was carried out by applying a load of about 20-30 $kg.cm^{-2}.min^{-1}$, recording the loads required to cause slips of 0.1, 0.2, 0.3, 0.4 and 0.5 units (or more, if possible) and the maximum pullout load. Three types of rupture may occur, which indicates the end of the test: 1) the bar slips at least 2.5 mm in relation to the mortar; 2) the specimen mortar breaks as the bond strength is higher than the mortar tensile strength and 3) the steel bar plastically deforms or breaks. The first failure mode is desirable. Bond strength, T ($kg.cm^{-2}$), is estimated from the expression:

$$T = \frac{P_{(kg)}}{S_{(cm^2)}}$$

Table 1 – Steel-mortar bond strength in cathodically protected specimens after two-year exposure					
Electrolyte	Potential mV vs. ECS.	Average steel-mortar bond strength [kg.cm^{-2}]			
		1-year	% variation	2-year	% variation
Tap water	---	69.5	---	103	---
	- 850	72.0	+4	105	+2
	- 1000	75.6	+9	100	-3
	- 1250	61.8	-11	94.3	-8
3% sodium chloride	---	65.5	---	98.0	---
	- 850	66.8	+2	95.2	-3
	- 1000	73.1	+12	98.0	0
	- 1250	61.1	-7	88.5	-10

Notes: steel-mortar bond strength variation is consigned as percentage variation with respect to the controls (non-polarised specimens). Results are given with an uncertainty of ± 3.5 kg.cm^{-2}.

Where P is the load required to cause a certain slip and S is the bar lateral surface area. In this research work T was determined as an average of the loads required to cause strains in 0.1 unit increments up to 0.5 units. Results in Table 1 are given with an uncertainty of ± 3.5 kg.cm^{-2}. Being comparative tests and employing the same batch of cement and the same batch of sand throughout the experiment, it is considered that the individual moduli of elasticity of both the mortar and steel will remain constant for all the specimens.

Visual inspection of polarised reinforcing bars. After the pullout test, reinforcing bars were visually inspected in order to determine their degree of corrosion.

2.4 Analysis of the reinforcing bar-mortar interface

Chemical analysis and X-ray diffraction patterns of the mortar paste. The mortar paste surrounding the rebar was scraped off from the corresponding specimen piece and then subjected to chemical analysis to determine the insoluble residue in hydrochloric acid, the active silica content and the calcium oxide content. At the same time, the X-ray diffraction pattern of this material was also obtained.

Scanning electron microscopy of the mortar paste and the rebar surface. The mortar surface just below the rebar, as appeared by simple fracture, was examined by scanning electron microscopy (SEM) to determine the cement paste microstructure. Observations were made in comparison with mortars from non-polarised specimens that had been kept immersed for 2 years in the selected electrolytes. The rebar surface resulting from the pull-out test was also scanned to determine its morphology.

3. RESULTS AND DISCUSSION

3.1 Specimen polarisation

The selected polarisation potential values are shifted, as an average, -100, -250 and -500 mV, respectively,

from the most negative value of rebar corrosion potential in tap water and in 3% sodium chloride. Rebar corrosion potential in both electrolytes fluctuated among negative and positive potentials during the test period (Fig. 1).

3.2 Variation in steel-mortar bond strength

The variation of steel-mortar bond strength in polarised specimens, at the end of two-year exposure, is shown in Table 1. Results are given with an uncertainty of +3.5 kg.cm^{-2}. For the sake of comparison, the values corresponding to one-year exposure, reported in previous work [16], were also included. During the first year and for the lowest cathodic potentials (-850 and -1000 mV), bond strength of specimens immersed in tap water increased slightly. The measured values were 72.0 and 75.6 kg.cm^{-2}, which represent a variation of about +4 and +9%, respectively, with reference to non-polarised specimens (blanks). This means that there are no significant differences between polarised steel-mortar specimens and blanks. When the applied potential was -1250 mV, bond strength decreased to 61.8 kg.cm^{-2}, that is to say -11% with respect to the blanks. Results obtained after two-year polarisation showed the same tendencies. Rebars polarised at -850 mV showed a 2% increase in steel-mortar strength, being the absolute value of 105 kg.cm^{-2}. When the applied potential was -1000 mV the steel mortar bond strength was found to be equal to 100 kg.cm^{-2} and it decreased to 94.3 kg.cm^{-2} when the polarisation potential was -1250 mV. The variation, with respect to the blanks, was -3 and -8%, respectively.

When the electrolyte was 3% sodium chloride, slightly different bond strength values with respect to those of tap water were obtained at the end of the first year of exposure. For the lowest cathodic potentials employed in this research, -850 and -1000 mV, bond strength was 66.8 and 73.1 kg.cm^{-2}; so variations of +2 and +12%, respectively, were encountered. When the applied potential was -1250 mV the bond strength decreased to 61.1 kg.cm^{-2} (7% with respect to the blanks). At the age of two years, bond strength decreased to 95.2 and to 88.5 when the applied potentials were -850 and -1250 mV, being the variation -3 and -10%, respectively. No changes were detected when the applied potential was -1000 mV.

The analysis of the above values reveals that only when a potential equal to -1250 mV was applied, a decrease by about 8-10% in steel-mortar bond strength is attained. Being this potential the only one corresponding to the hydrogen evolution zone, hydrogen is thought to be partly responsible for the loss in bond strength. For the other applied potentials, which correspond to the oxygen reduction wave, the tendency for steel mortar bond strength is to remain unchanged with respect to non-polarised specimens (blanks). The most important

Table 2 – Chemical analysis of mortar samples taken from the steel mortar interface

Electrolyte	Tap water				3% Sodium chloride			
Polarisation potential (mV)	0	-850	-1000	-1250	0	-850	-1000	-1250
Insoluble Residue (%)	45.5	45.1	54.8	52.3	48.3	50.7	47.5	55.0
Soluble silica, SiO_2 (%)	8.36	7.02	6.50	7.67	9.78	7.55	7.84	7.39
CalciumOxide, CaO (%)	10.8	10.4	9.41	9.88	12.1	9.95	9.88	8.70
CaO/SiO_2 Ratio	1.29	3.00	1.45	1.29	1.24	0.79	1.26	1.18

difference found among these results and those encountered by Tache and Lemoine [5] is a decrease by about 10% when the hydrogen evolution potential is attained.

Visual inspection of polarised reinforcing bars. A visual observation of reinforcing bars subjected to polarisation revealed that specimens that had been polarised at -850 mV (ECS) exhibited some pitting throughout the bar when the electrolyte was 3% sodium chloride, while in the remaining instances the bar surface was found to be protected. Therefore, according to these results, the criterion which establishes that steel is protected in the range -710 to -810 mV with respect to CSE [3] (-636 to -736 mV with respect to SCE) would only be acceptable when well-kept steel mortar is concerned, but in practice this is not the usual case when protection is needed. The -850 mV potential in relation to CSE (-776 mV with respect to SCE) [4-7] also seems to be insufficient to achieve an adequate protection of steel in concrete. These potential values are very close to

those for which pitting corrosion of reinforcing bars was reported to occur in chloride containing media [17]. This fact is also understandable because these potential values do not fall in the immunity zone of Pourbaix's diagrams [13]. In this sense, several authors recommend more negative potentials to achieve adequate cathodic protection [2].

3.3 Analysis of the reinforcing bar-mortar interface.

Chemical analysis and X-ray diffraction patterns of the mortar paste. It was found that a thin layer of fine granulometry mortar paste surrounded the rebar and that its composition differed from that of bulk mortar. It contained 50 ± 5% of quartz material and a calcium oxide: silica ratio (Table 2) lower than that of the original cement (2,99).

The X-ray diffraction patterns exhibited all the peaks corresponding to quartz ($2\theta \sim 20.8$, 26.6, 36.6, 39.5 [doublet], 42.6, 45.8, 50.0, 55.2) and several peaks ($2\theta \sim$ 18.06, 28.6, 34.10, 47.10, 50.9) corresponding to calcium hydroxide (CH). Eventually some peaks assigned to calcite were found ($2\theta \sim 29.4$, 31.4); the formation of this compound was attributed to the action of atmospheric carbon dioxide. All the samples showed the bands at $2\theta \sim 29$-$32°$ and $2\theta \sim 50°$ corresponding to amorphous hydrated calcium silicate hydrate (CSH). The main components of the mortar paste were dicalcium silicate hydrate (peaks at $2\theta \sim 26.4$, 27.4, 29.4, 32.6, 34.4, 41.2) and tricalcium silicate (peaks at $2\theta \sim 23.0$, 29.4-30.2 [doublet], 32.4, 34.2, 41.4, 45.8-46.8, 49.8, 51.75, 56.0); this last compound was found especially in specimens polarised at -1250 mV. Late formation ettringite (E) was also found ($2\theta \sim 9.12$). The increase in the number of peaks as a consequence of the formation of different calcium silicate hydrates of a better ordered structure is more pronounced in water than in 3% sodium chloride. As an example, the X-ray diffraction pattern obtained for specimens kept in tap water was shown in Fig. 2. This fact correlates well with the observation of the mortar paste by SEM in the sense that a larger amount of more ordered structures was observed
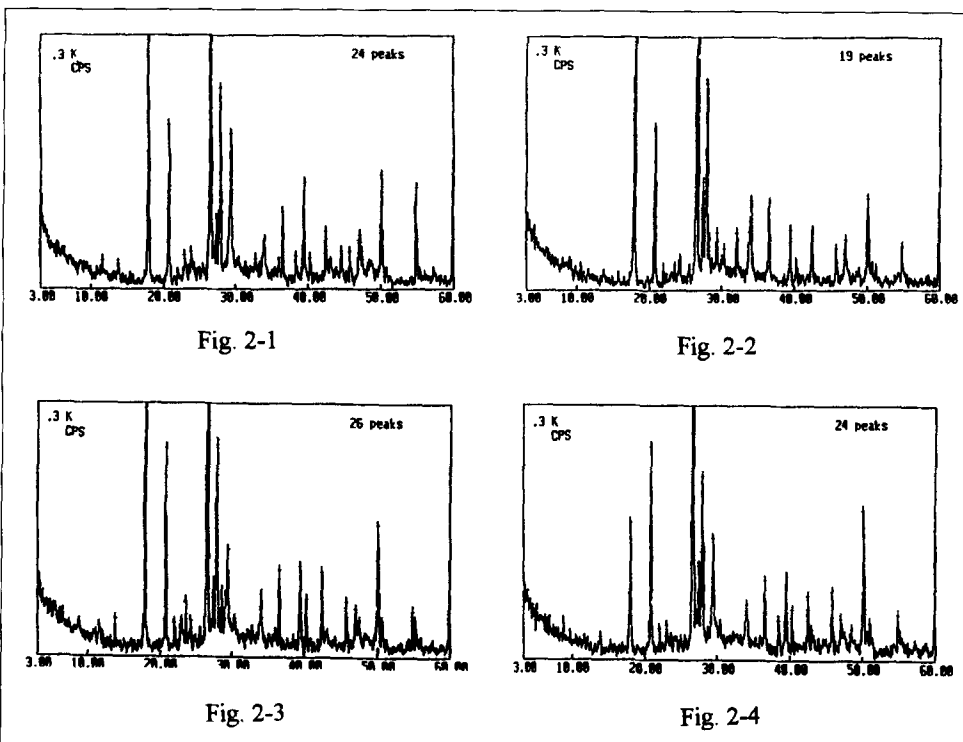

Fig. 2-1

Fig. 2-2

Fig. 2-3

Fig. 2-4

Fig. 2 – X-ray diffraction pattern (Cu K_α line) of the cement paste adjacent to the rebar corresponding to specimens kept in tap water. 1) non-polarised; 2) -100 mV; 3) -250 mV; 4) -500 mV.
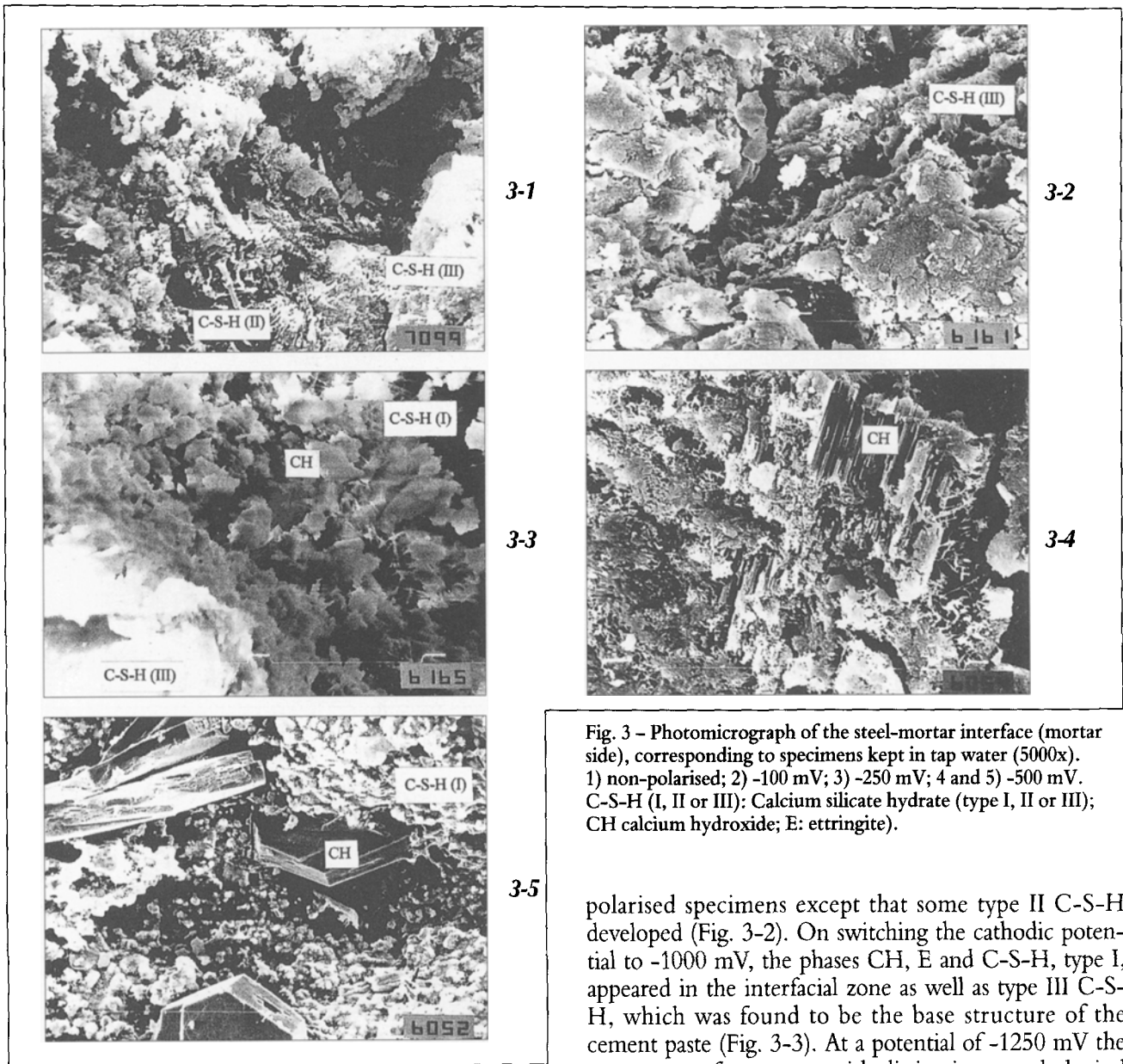
Fig. 3 – Photomicrograph of the steel-mortar interface (mortar side), corresponding to specimens kept in tap water (5000x).
1) non-polarised; 2) -100 mV; 3) -250 mV; 4 and 5) -500 mV.
C-S-H (I, II or III): Calcium silicate hydrate (type I, II or III); CH calcium hydroxide; E: ettringite).

at the highest applied cathodic potential.

Scanning electron microscopy of the mortar paste and the rebar surface. The mortar surface just below the rebar, as appeared by simple fracture, was examined by SEM (5000X). The structures in the cement paste were identified according to patterns reported in the literature [18-22].

Non-polarised specimens, kept in tap water, showed the typical cement paste morphology constituted by calcium silicate hydrate (C-S-H), type III (late formation), as reported by Diamond (Fig. 3-1). Far away from the zone adjacent to the rebar, small amounts of ettringite (E) and calcium hydroxide (CH) crystals, together with C-S-H, types I and II, were also found. It must be pointed out that type I C-S-H grows radially around the cement particle and C-S-H, type II, shows a reticulated pattern.

On polarising with the lowest selected cathodic potential no important changes were detected in the mortar paste microstructure with respect to non-

polarised specimens except that some type II C-S-H developed (Fig. 3-2). On switching the cathodic potential to -1000 mV, the phases CH, E and C-S-H, type I, appeared in the interfacial zone as well as type III C-S-H, which was found to be the base structure of the cement paste (Fig. 3-3). At a potential of -1250 mV the appearance of structures with distinctive morphological features was intensified; lamellar CH and acicular E were also detected (Fig. 3-4). Singular structures such as hexagonal CH in a bed of C-S-H, type I, were encountered on moving a bit away from the interface (Fig. 3-5, 1000X). It was also noticed that far away from the rebar, the applied potential caused E and C-S-H type II to develop.

For non-polarised specimens, kept in 3% sodium chloride, it was observed that E, lamellar CH and some C-S-H, type II, formed (Fig. 4-1). Type III C-S-H was the predominant phase far away from the interfacial region. For the lowest cathodic potential (-850 mV), some HC and C-S-H, type II, together with the base compound C-S-H, type III, were found (Figs. 4-2 and 4-3). When the applied potential was -1000 mV acicular E formed (Fig. 4-4). As the potential was switched to -1250 mV, CH and C-S-H type I structures developed and the amount of E increased.

From the foregoing discussion, it may be deduced that the mortar paste morphology depends on both the applied potential and the selected electrolyte. On polar-
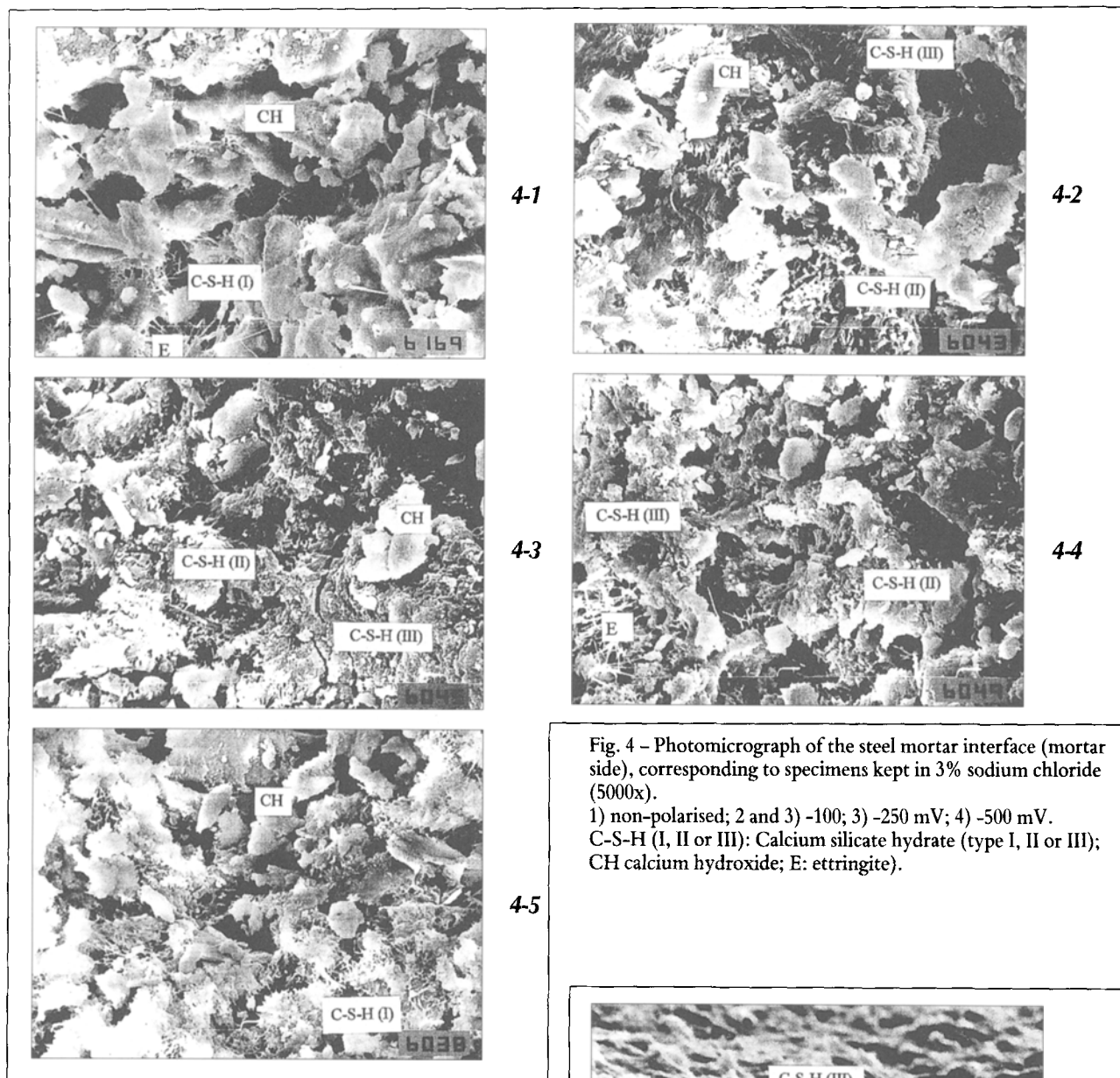
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4-5

Fig. 4 – Photomicrograph of the steel mortar interface (mortar side), corresponding to specimens kept in 3% sodium chloride (5000x).
1) non-polarised; 2 and 3) -100; 3) -250 mV; 4) -500 mV.
C-S-H (I, II or III): Calcium silicate hydrate (type I, II or III);
CH calcium hydroxide; E: ettringite).

Fig. 5 – Photomicrograph of the protective film developed on steel in cathodic polarised specimens after two-year exposure (2000x).
1) normal aspect; 2) oxide growing underfilm; 3) globular iron oxide disrupting the film.
C-S-H (I, II or III): Calcium silicate hydrate (type I, II or III);
CH calcium hydroxide; E: ettringite).

5-2

5-1

5-3
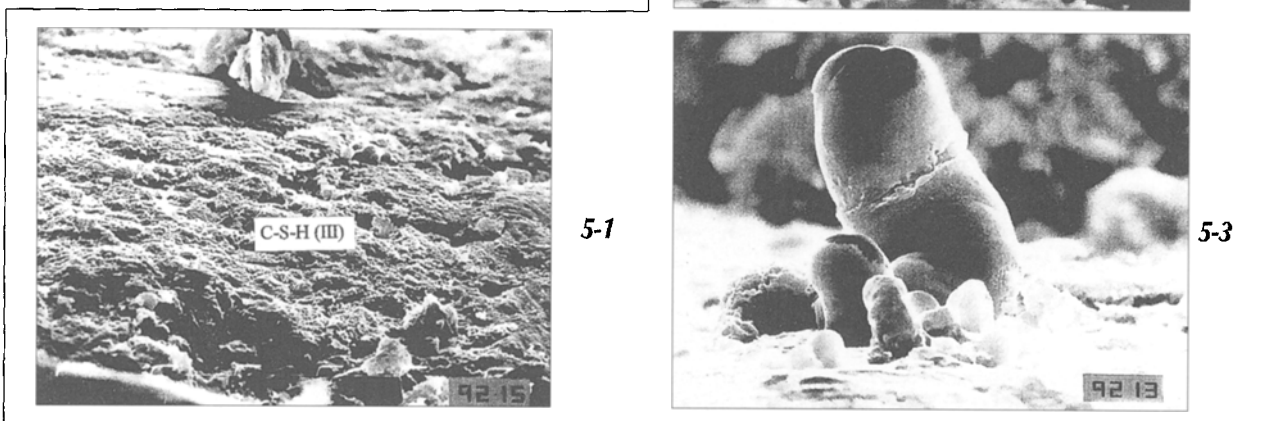
ising the rebar calcium ions migrate towards the rebar (cathode) and at the same time hydroxil ions are produced; the combined action of both ions may induce the formation of more ordered structures in the rebar-mortar interface [2]. This phenomenon is more noticeable at -1250 mV and was related to the appearance of a larger number of peaks in the X-ray pattern. Moreover, the increasing amount of better ordered structures as cathodic potential increased and the developing of lamellar CH crystals coincided with the diminishing in steel mortar bond strength. This led us to think that not only hydrogen evolution but also crystal growth may be responsible for the reported adherence loss in cathodically polarised specimens.

The protective layer on rebars was mainly composed of C-S-H, type III, (Fig. 5-1), which is similar to that of the mortar paste. The fractured surface exhibited E and C-S-H type I formations. Exceptionally, in discontinuities and failure zones, hexagonal CH plates and alveolar formations were found.

Some of the samples immersed in 3% sodium chloride and polarised with the lowest cathodic potentials (-850 mV) showed elevations due to underfilm oxide growth (Fig. 5-2). Sometimes oxide caused the protective layer to break and it exhibited different more or less expansive morphologies (Fig. 5-3). Photomicrographs of rebar protective layers have a 2000X magnification.

4. CONCLUSIONS

Based on the experiments run for two years, the following conclusions can be drawn:

1. An applied potential of -850 mV (SCE) was not high enough to protect steel bars in mortar specimens stored in 3% sodium chloride because pitting corrosion may occur.

2. Steel-mortar bond strength values are affected in a different way depending on the applied potential. A decrease in the steel-mortar bond strength by about 10% was observed when the applied potential was -1250 mV, while for the lower potentials employed in this research (-850 and -1000 mV) a slight increase in the steel-mortar bond can be observed, as compared with non-polarised specimens.

3. Polarisation also affected the cement paste microstructure and the observed modifications appeared to be potential dependent.

4. The loss of adherence between steel and mortar, for the highest applied potential, was interpreted to occur as a consequence of hydrogen evolution and modifications of the cement paste microstructure.

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