

CORROSION INVESTIGATION OF STEEL REINFORCEMENTS IN THE PRESENCE OF VARIOUS ADDITIVES AND INHIBITORS¹

Pál HENCSEI¹ and Ádám JANTAI²

¹Department of Inorganic Chemistry
Technical University of Budapest

H-1521 Budapest, Szt. Gellért tér 4., Hungary

²FTV KEMOKORR Ltd

H-1116 Budapest, Építész u. 40-44, Hungary

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Abstract

The corrosion of steel reinforcement was investigated in the presence of various chloride contents and inhibitors. The corrosion sensitivities of steel reinforcements of ten different qualities were determined via polarization potential measurements. The inhibitor effects of two organosilicon compounds soluble in water were tested in saturated $\text{Ca}(\text{OH})_2$ solutions containing chloride in various concentrations. A potassium-methyl-siliconate-based inhibitor was found to reduce the aggressive effect of chloride. The positive results obtained in model solutions were also verified by a test series carried out with concrete specimens. The critical value of chloride ion concentration was determined: up to a chloride content of 2%, a dose of 3% of the tested inhibitor ensures corrosion protection of steel reinforcements of various qualities.

Keywords: corrosion, steel reinforcement, concrete, inhibitor.

Introduction

The corrosion of steel reinforcements in concrete is determined by the material quality of steel on the one hand, and by the aggressive ambience in concrete, on the other [1, 2]. The aggressive ambience is conditioned by the reduction of pH via carbonation caused by air, the water content, oxygen diffusion, aggressive ions of additives as well as chloride ions getting into the ready-made structure from outside. As a consequence of the carbonation reaction, the protection ensured by the strongly basic character of concrete ceases at the surface double layer of steel reinforcement, the boundary layer will be depassivated and an even corrosion damage can be experienced. Water and ions dissolved in water increase the electrical conductivity of concrete thereby intensifying corrosivity. Oxygen diffusion is determined by the thickness, compactness and water content of the concrete layer. The greatest problem concerning deterioration of reinforced

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concrete structures is caused by chloride ions. Chloride ions attack locally the surface double layer of steel and cause hole-corrosion in a basic agent. In carbonated concrete chloride ions speed up corrosion of steel reinforcement because they do not become fixed in the carbonated zone at all.

The aim of our research has been to investigate the mechanism of corrosion at the surface of steel reinforcements in the presence of various additives and silicon-containing inhibitors and for various steel qualities.

Considering the methodology of investigation, tests were done in model solutions on reinforced concrete specimens modelling truly the real ambience and electrochemical and analytical methods were applied to follow the processes occurring.

Protection of Reinforcing Steel against Corrosion

Protection of reinforcing steel against corrosion can be achieved in various ways. These procedures can be classified into the following groups [3, 4]:

1. Reduction of Ambience Aggressiveness

The aim of the methods in this group is primarily to reduce the effect of chloride ions. This can be done by reducing the amount of chloride ions or by replacing them in concrete additives by other, less corrosive materials, or by adding inhibitors which reduce or eliminate the harmful effect of chlorides. Another possibility is inactivation of chloride present in corrosive materials getting inside the structure from outside. Ice melting materials, mostly NaCl get into concrete structures in greatest quantities with road salting in the winter. Several ice melting materials have been elaborated recently, e.g. new types are calcium-magnesium-acetate and other salts with inhibitor content, which are less corrosive but the general use is limited by their high prices [5].

2. Indirect Protection of Concrete

Here belong methods which improve concrete quality (primary protection: concrete covering, limitation of cracks) and formation of surface protecting coatings on the surface of concrete (secondary protection) [6].

3. Direct Protection of Reinforcement Steel against Corrosion

Corrosion damage can almost totally be stopped with application of corrosion-proof steel reinforcements even in an agent with high chloride content. As the price of corrosion-proof steels is 4-5 times higher than that of common steels, their application is reasonable in special cases only [7, 8]. Protection of steel reinforcements can be solved also with coatings. Among metal coatings first of all zinc will be applied, galvanised reinforcement is advantageous where it is located partially in air, partially in concrete or in porous, frequently carbonating concrete [3]. From among plastic coatings epoxide coating in powder form is considered to be the best, its application has been proposed with bridges, sea structures and cooling towers [8-10].

Protection of steel reinforcement can be achieved with various inhibitors, too. In practice $\text{Ca}(\text{NO}_2)_2$, NaNO_2 and other inorganic salts soluble in water are used which are charged to the make-up water. Inhibitors cannot ensure a durable protection because they may be washed away with moisture and may migrate to the surface of structures [3, 6, 8]. For protection of steel reinforcement of new structures also cathodic protection can be applied [11]. With this method the main problem is the selection of the suitable protecting potential, since the appropriate potential is different in the air, the moist and underwater zones, it depends on the moisture content and on climatic conditions and varies with time, too.

Experimental Part

In the first section of our work the corrosion sensitivities of steel reinforcements of various qualities were determined via polarization potential measurements. The change in polarization potential of the steel reinforcement with respect to a calomel electrode was measured by means of a galvanodynamic method according to the Hungarian Standard MSZ 17215-6:1984 [12]. The potential was plotted in diagrams as a function of the electrical charge on the active area of the steel. The scheme of the instrument used can be seen in *Fig. 1*. Ten different steel reinforcements were tested, of which nine were different reinforcement steels and span wires widely applied in building industry, the tenth was a corrosion resistant steel sample [13]. Characteristic data of samples are listed in *Table 1*.

For the measurements, a surface of 5 cm^2 area was left free on the steel samples, other parts were coated by a paint. Following degreasing, the samples were put into a saturated solution of $\text{Ca}(\text{OH})_2$ of pH 12.4. After 24 hours the pH was reduced by bubbling air through, while CaCO_3 precipitated. At $\text{pH} < 12.0$ carbonation was ensured by storage in air.

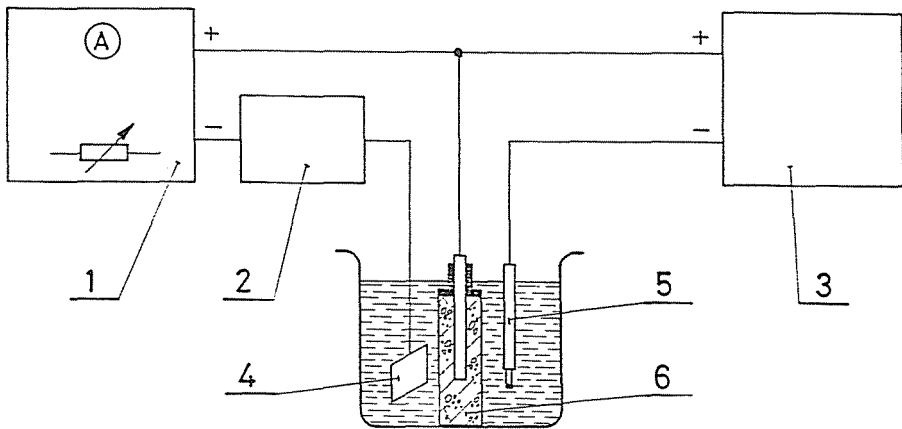


Fig. 1. The scheme of the instrument used. 1 : current generator, 2 : coulometer, 3 : compensograph, 4 : platinum electrode, 5 : saturated calomel electrode (SCE), 6: steel reinforcement sample (investigated electrode)

Table 1
Reinforcement samples

Symbol	Character	Tensile strength N/mm ²
B 38.24	hot rolled steel	
B 50.36	hot rolled steel	
B 60.40	hot rolled steel	
BHS 55.50	cold drawn reinforcement, steel wire	
1500.5	guy wire	1630
1800.25 S	guy wire	1820
Fp-93	cold drawn guy wire	1770
Fp-100	cold drawn guy wire	1770
Fp-139	cold drawn guy wire	1670
KO-1	ferritic corrosion resistant steel	

The polarization potential and pH were measured simultaneously every 8–15 hours in the course of 8 days. Sudden changes in polarization potential simultaneously with the appearance of corrosion were observed at different pH values for various steel samples. On the surface of steel samples the starting of corrosion could be observed visually, following the sudden reduction in polarization potential. From the data we determined a polarization potential of -350 mV (SCE) – as a limit value of active corrosion damage for the tested steels, i. e. a more negative value than this indicates

corrosion. The most unfavourable result was obtained for sample B 50.36: protection ceased at pH = 11.1. The span wire sample 1500.5 proved to be the best (pH = 10.5) while steel KO-1 exhibited complete protection in the investigated range, in accordance with expectations. These results are shown in *Fig. 2*.

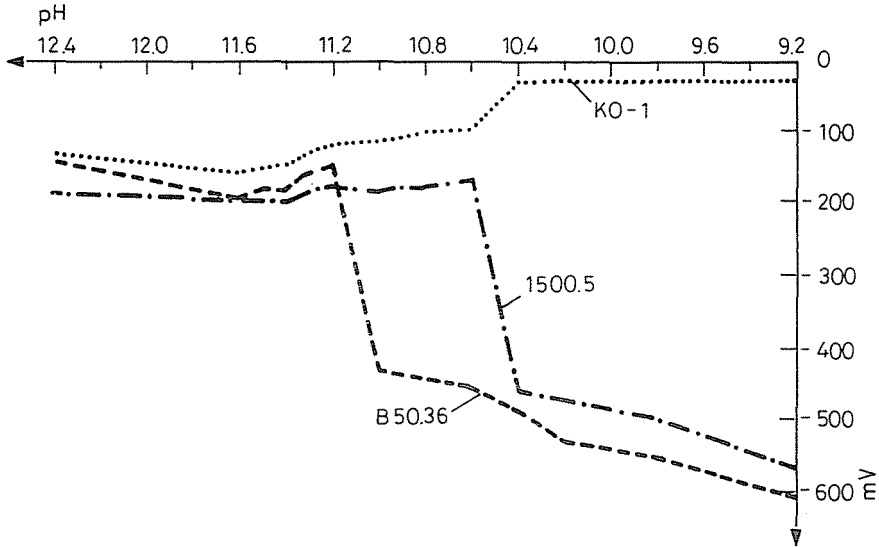


Fig. 2. Polarization potentials of different reinforcement samples versus pH in saturated $\text{Ca}(\text{OH})_2$ solution

The corrosion sensitivity of steel reinforcements was also tested as a function of the chloride ion concentration. Polarization diagrams were taken in saturated $\text{Ca}(\text{OH})_2$ solution containing chloride at a concentration of 150–900 mg/dm^3 . From the course of the curves the starting of the spot-corrosion range, where corrosion appears, was determined, as well as the limit of the aggressive range where a green discolouration due to formation of FeCl_2 can be observed on the steel surface. Of the steel samples, Fp 139 appeared to be the most sensitive, while the most favourable result was obtained for sample 1500.5 (see *Fig. 3*). In *Fig. 4* the protection, in *Fig. 5* the appearance of spot corrosion and in *Fig. 6* the aggressive effect can be observed.

In further tests the behaviour of three steel samples (B 38.24, 1500.5, Fp 139) was studied in saturated $\text{Ca}(\text{OH})_2$ solutions containing chloride at a concentration of 600 – 1200 – 2000 mg/dm^3 [14]. The surfaces of the steel samples were visually observed and the appearance and amount of green

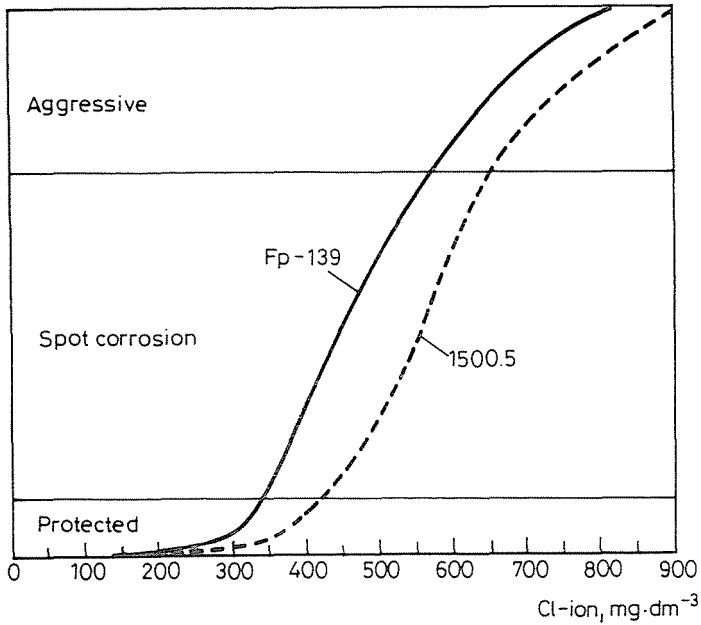


Fig. 3. Corrosion risk of steels as a function of the chloride concentration

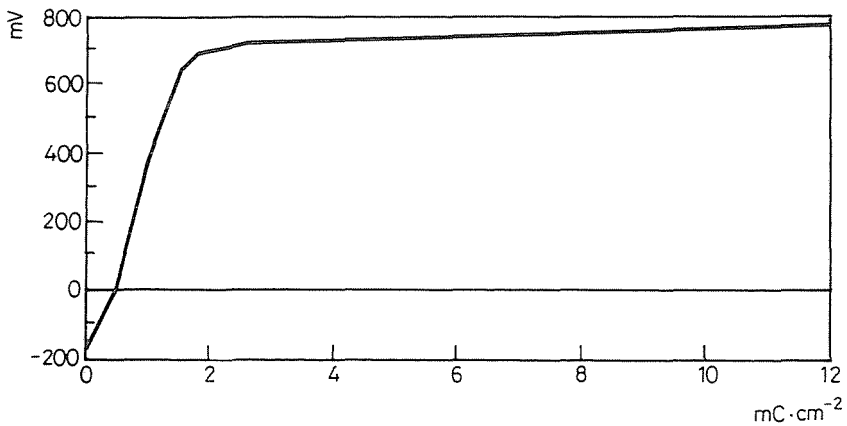


Fig. 4. The change of polarization potential of different reinforcement samples (ref: SCE) as a function of the electrical charge on the active area of the steel in saturated $\text{Ca}(\text{OH})_2$ solution

discolouration, corrosion stains and spot corrosion faults were evaluated. On the basis of the results the following sequence was obtained concerning

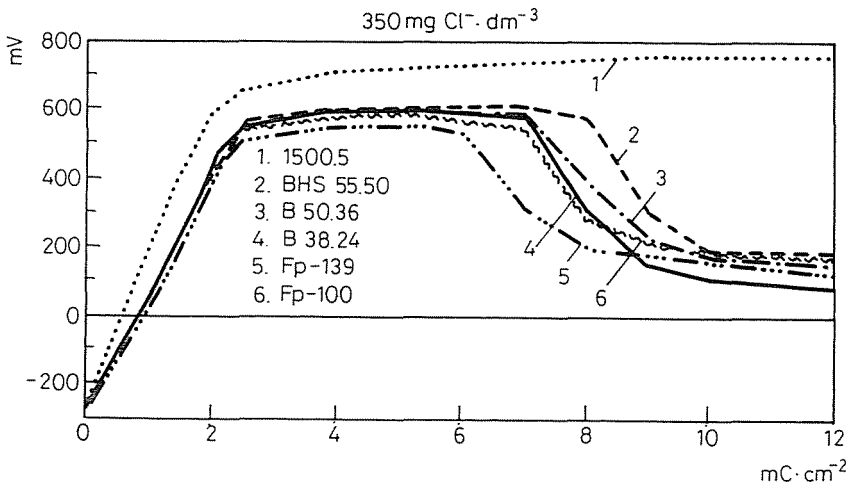


Fig. 5. The change of polarization potential of different reinforcement samples (ref: SCE) as a function of the electrical charge on the active area of the steel in saturated Ca(OH)₂ solution containing 350 mg/dm³ Cl⁻

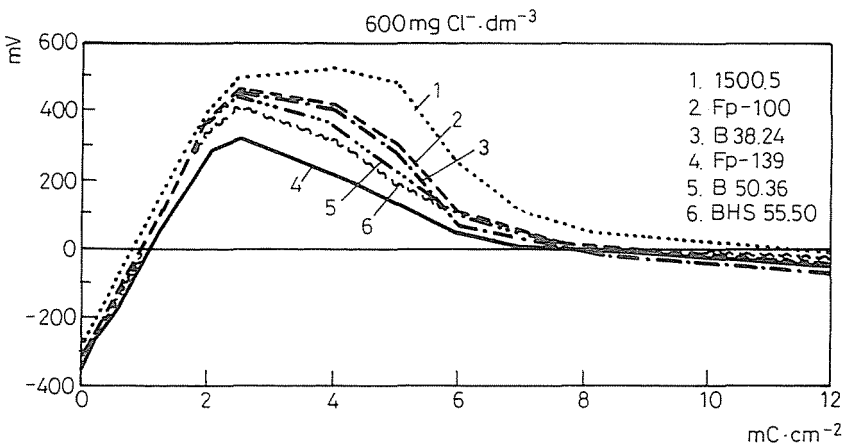


Fig. 6. The change of polarization potential of different reinforcement samples (ref: SCE) as a function of the electrical charge on the active area of the steel in saturated Ca(OH)₂ solution containing 600 mg/dm³ Cl⁻

the corrosion resistance of steel reinforcements:

$$1500.5 > B 38.24 > Fp139$$

Afterwards, the inhibitor effect of the following two organosilicon compounds soluble in water were tested [15]:

- S-1: $\text{CH}_3\text{Si}(\text{OH})_2\text{OK}$ dry material content 42.6%, pH=13.6
 S-2: $\text{CH}_3\text{Si}(\text{OH})_2\text{ONa}$ dry material content 33.8%, pH=13.8

The compounds were used in concentrations of 1, 3 and 5%. The polarization diagrams indicated that both materials had anti-corrosive effect. At a concentration of 1%, the inhibitor S-1 ensured protection at a chloride content of 600 mg/dm^3 while a dose of 3% at a chloride content of 1200 mg/dm^3 was not enough to provide protection. However, 5% inhibitor in an agent of 1200 mg/dm^3 chloride content provided perfect protection, no rust was formed. Although S-2 also had inhibitor effect, but the effect was weaker than that of the inhibitor S-1. In Figs. 7-10 polarization diagrams taken for the steel sample B 38.24 in the presence of inhibitor S-1 in various concentrations are shown. The corrosion effects of concrete additives (antifreeze, solidifying, flow-accelerator) were also investigated. If these additives are used in the recommended dose (4 to 6% of the cement), no corrosion damage occurs and the polarization diagrams are practically identical with those recorded in saturated $\text{Ca}(\text{OH})_2$ solution.

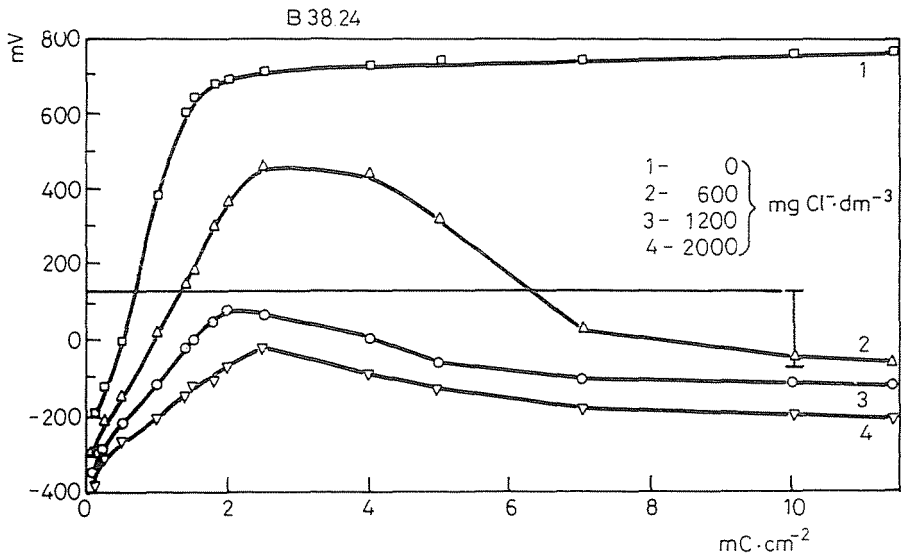


Fig. 7. Polarization diagrams (B 38.24 reinforcement sample, saturated $\text{Ca}(\text{OH})_2$ solution, at various Cl^- ion concentrations)

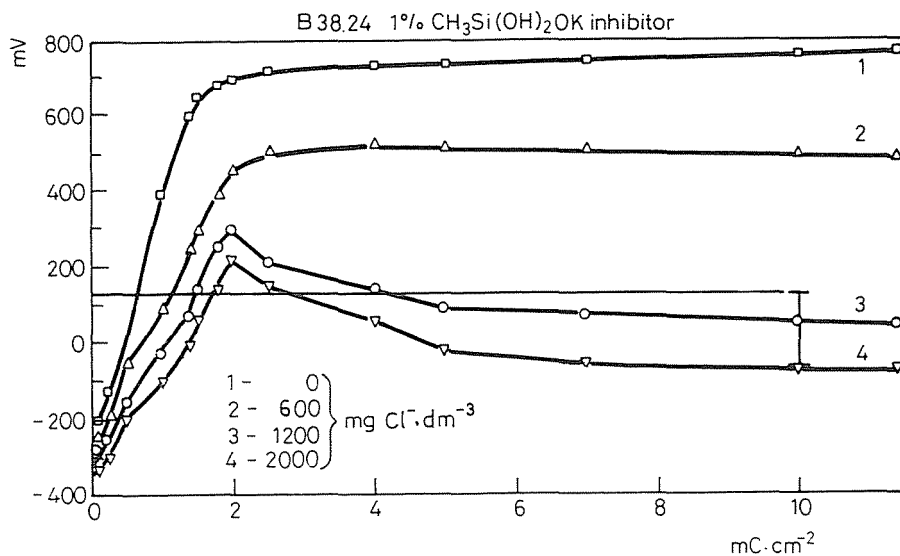


Fig. 8. Polarization diagrams (B 38.24 reinforcement sample, saturated $\text{Ca}(\text{OH})_2$ solution, 1% K-methyl-siliconate based inhibitor, (relative to cement) various Cl^- ion concentrations)

Tests in model solutions have been followed by tests on concrete specimens [16]. Steel reinforcements of three different qualities were embedded into concrete of given composition at varying chloride and inhibitor concentrations. The concrete mixtures were prepared according to the mentioned standard from cement of quality 350 kspc 20, (dose of 320 kg/m^3) and with the use of an additive (1790 kg/m^3) with a maximum grain size of $\text{O}4 \text{ mm}$ and a w/c -factor equal to 0.6. This concrete mixture corresponds to concrete quality C 16. After storing for 1 month, the prepared specimens were put into saturated $\text{Ca}(\text{OH})_2$ solution and the polarization diagrams were recorded.

The test series made with concrete specimens confirmed the positive results obtained in model solutions. Protection against corrosion of steel reinforcements embedded in concrete specimens was achieved and more favourable results were obtained than in the case of model solutions. No corrosion was detected on the steel reinforcements after having broken the specimens. The inhibitor S-1 proved to provide protection. Different sensitivities to corrosion of various steel qualities were indicated also in the concrete specimens but differences were smaller than in the case of model

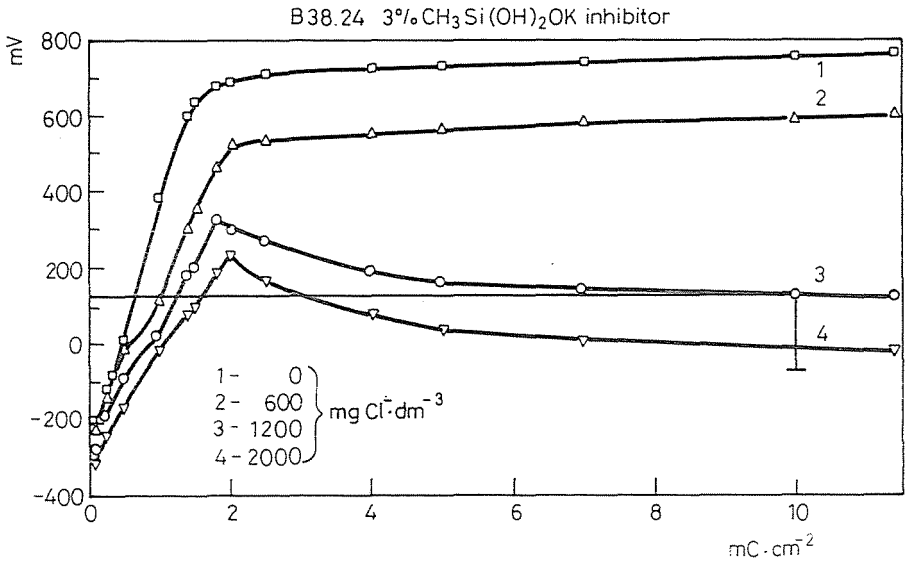


Fig. 9. Polarization diagrams (B 38.24 reinforcement sample, saturated Ca(OH)₂ solution, 3% K-methyl-siliconate-based inhibitor (relative to cement) various Cl⁻ ion concentrations)

solutions. A few characteristic results of tests on concrete specimens are illustrated in *Figs. 11* and *12*.

In order to determine the critical chloride concentration the above mentioned test series was supplemented as follows. The inhibitor S-1 was applied at a concentration of 3% beside 2 or 3% chloride for all three steel reinforcements. 2 or 3% (related to cement content) correspond to chloride contents of 2800 and 4200 mg/kg concrete, respectively.

The preparation and investigation of concrete specimens, evaluation of polarization diagrams and tests after having broken the specimens were carried out as described above. It was stated that for all three steel reinforcements an inhibitor content of 3% provided protection against corrosion at a chloride content of 2%. There was no corrosive change on the surface of steel reinforcements. Steel reinforcements of specimens containing 3% chloride exhibited corrosion damage. The polarization diagram of span wire marked 1500.5 indicates a very weak protection, it is at the limit of corrosion danger. After having broken the specimens, two small spot corrosion changes were found on the surface of the steel reinforcements. Diagrams of samples B 38.24 and Fp 139 are characteristic of point corrosion danger, evaluation points indicate damage. On the surfaces of steel reinforcements taken out of broken specimens several spot corrosion damages of 0.5–1 mm²

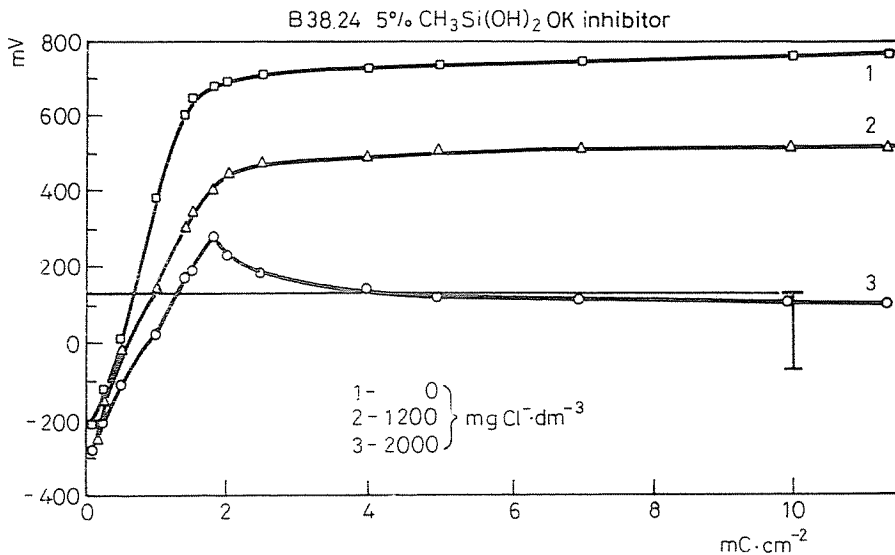


Fig. 10. Polarization diagrams (B 38.24 reinforcement sample, saturated $\text{Ca}(\text{OH})_2$ solution, 5% K-methyl-siliconate-based inhibitor (relative to cement) various Cl^- concentrations)

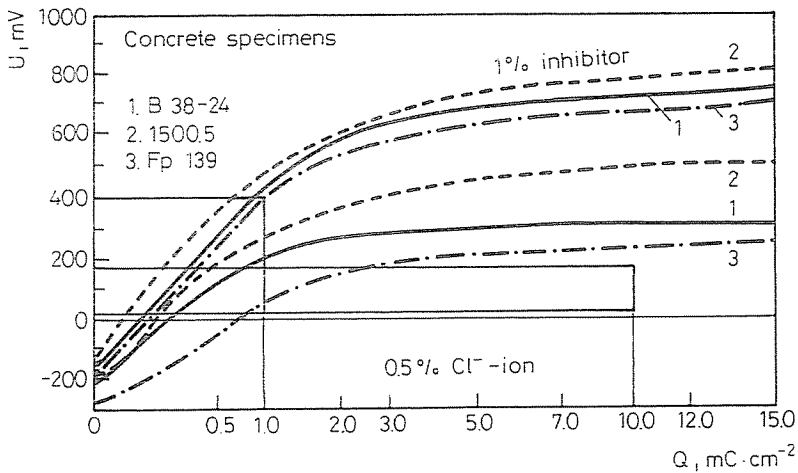


Fig. 11. Polarization diagrams of concrete specimens containing different steel reinforcements (0.5% Cl^- , 0 and 1% inhibitor S-1)

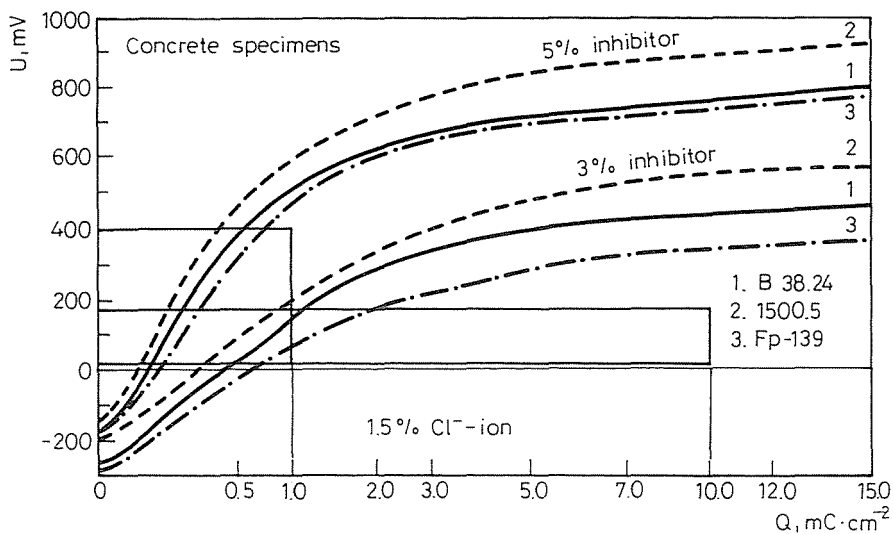


Fig. 12. Polarization diagrams of concrete specimens containing different steel reinforcements (1.5% Cl⁻, 3 and 5% inhibitor S-1)

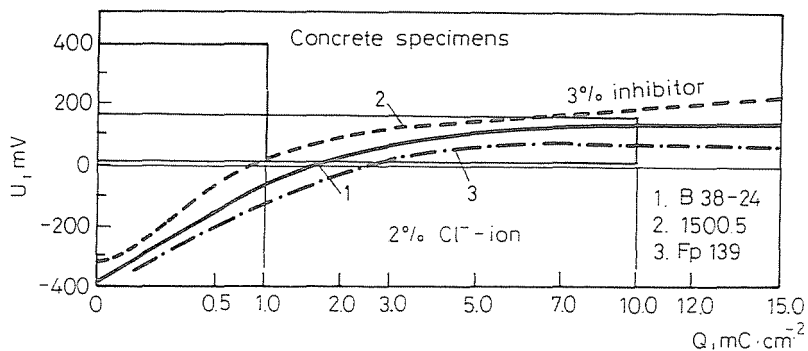


Fig. 13. Polarization diagrams of concrete specimens containing different steel reinforcements (2% Cl⁻, 3% inhibitor S-1)

area were found for both steel qualities. In Fig. 13 diagrams of specimens containing 2% chloride and 3% S-1 inhibitor are shown.

Summing up, it can be stated that the inhibitor S-1 applied at a concentration of 3% provides protection of steel reinforcements of various qualities up to a chloride content of 2%. With increase of chloride content the protection ceases and spot corrosion occurs.

References

1. BALÁZS, GY.- ERDÉLYI, A. - KOVÁCS, K. (1991): *Építőanyag*, Vol. 43, p. 82.
2. BALÁZS, GY.- ERDÉLYI, A. - KOVÁCS, K. (1991): *Építőanyag*, Vol. 43, p. 202.
3. *ACI Journal* (1985): Vol. 82, No. 1, p. 3.
4. *Beton* (1991): Vol. 41, No. 1, p. 33.
5. AGOOS, A. (1989): *Chemicalweek*, Vol. 144, No. 5, p. 18.
6. NÜRNBERGER, U. (1988): *VDI Berichte*, Vol. 653, p. 119.
7. HAYNES, J. (1984): *Civil Engineering* (London), No. 8, p. 23.
8. KOELLIKER, E. (1990): *Beton und Stahlbetonbau*, Vol. 85, No. 7. p. 186.
9. BARFOOT, J. (1987): *Concrete*, Vol. 21, No. 12, p. 11.
10. SCHIESSL, P. (1989): *Bauwirtschaft*, Vol. 43, No. 10, p. 862.
11. SEDERHOLM, B. - LINDER, B. (1994): *Proceedings of UK Corrosion and Eurocorr '94 Conference*, Bournemouth, Vol. 3, p. 189.
12. Hungarian Standard MSZ 17215-6 (1984): Corrosion Protection of Concrete and Reinforced Concrete Structures. Testing and Qualification of the Steel Protective Effect of the Concrete.
13. HENCSEI, P. - JANTAI, Á. (1993): *Építőanyag*, Vol. 45, No. 3, p. 90.
14. HENCSEI, P. - JANTAI, Á. (1994): *Építőanyag*, Vol. 46, No. 1, p. 8.
15. HENCSEI, P. - JANTAI, Á. :*ACH-Models in Chemistry*, in press.
16. HENCSEI, P. - JANTAI, Á.: *Korróziós Figyelő*, in press.