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Influence of pre-rusting on steel corrosion in concrete

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Abstract

Steel specimens in three different superficial states (machined, scaled, and pre-rusted) were embedded in concrete blocks (OPC) with various chloride contents (0.0, 0.4, and 2.5 wt.%/cement) and exposed to different levels of relative humidity (60–100%). Electrochemical methods for corrosion monitoring were applied for a period of 4 years. The concrete blocks were broken and mass changes of steel specimens were determined. The average corrosion rate of machined and scaled steel was lower than 1 μm/year in concrete with a low chloride content (≤ 0.4 wt.%). The pre-rusted steel in concrete even without any chloride content showed technically unacceptable average corrosion rate (> 1 μm/year). For all steel specimens, corrosion was localized. The corrosion rate at these spots reached values up to 65 μm/year. Mass-loss data confirmed electrochemical results (polarization resistance), i.e. that the corrosion rate of pre-rusted steel reinforcement was unacceptable even in noncarbonated concrete without any chlorides present. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Corrosion; Chloride; Reinforcement; Concrete; Pre-rusted steel

1. Introduction

Literature data relating to the problem of pre-rusted steel [1–8] were not definite. Inhibitive action of pre-rusted surface was observed by Al-Tayyib et. al [2], Hansson and Sørensen [3], and Mehmood et al. [5], but their experiments were performed in concrete with high chloride contents, where activation is observed in all cases after some time; pre-rusted surface only somewhat delays heavy steel activation. On the contrary, results of John et al. [1], Avila-Mendosa et al. [4], and Gonzales et al. [6] witness to stimulating influence of rust. Our previous results [7,8] have as yet testified to the undesirable corrosion effect of pre-rusted steel surface in concrete with low chloride content.

A passive layer forms on the metallic surface spontaneously in alkaline cement, and in this case, the corrosion rate is lower than 0.1 μm/year. The average corrosion rate from 1 to 2 μm/year is usually still considered as state of "non-corrosion." The aggressiveness of the electrolyte, which originates in concrete in the presence of humidity, depends primarily on the content of substances, which stimulate corrosion attack of iron and cause the breakdown of the passive layer. The corrosion rate of steel in the active state is in the order of 10^1 μm/year, which is unacceptable in terms of technical requirements of its users. The corrosion attack on the steel reinforcement surface is mostly nonuniform. This means that, apart from the sites at which the steel is in the active state, there are also sites where the steel is passive. The corrosion rate of steel in the active state is limited by oxygen transport to the metal surface. However, oxygen reduction occurs primarily on the passive cathodic surface where it is easier [9]. This distribution of anodic and cathodic processes leads to an undesirable combination of a small anode and a large cathode, and also to undesirable increase in the electrolyte's aggressiveness at anodic sites (drop of pH in consequence of the hydrolysis of Fe^{2+} ions and increase in the concentration of chloride ions due to their migration).

2. Experimental

Steel specimens (rods Ø 1 cm, 30 cm^2) were embedded in concrete (18.8 wt.% OPC, 0.58 w/c), with a covering layer of 2 cm (Fig. 1). Each concrete block contained two rods of scaled and machined carbon steel (0.26 wt.% C) and two rods of pre-rusted and machined carbon steel (0.06

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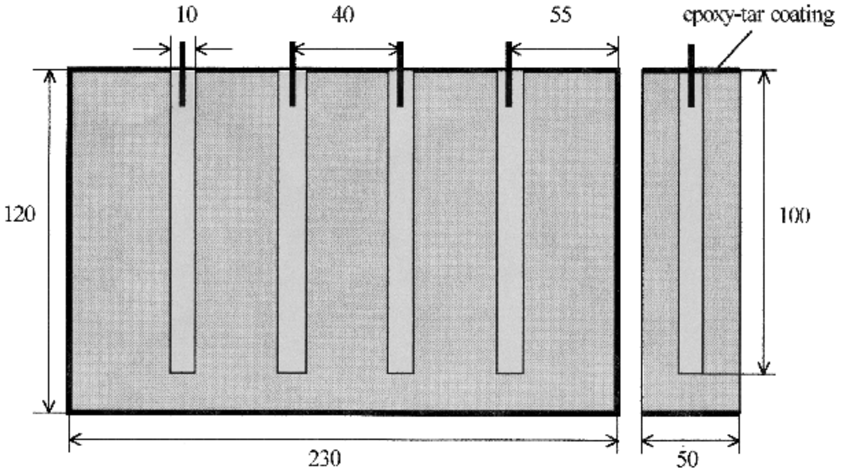

Fig. 1. Concrete block with steel bars (mm).

wt.% C). Scaled and pre-rusted surfaces were in the state as received from the supplier. The average thickness of rust on pre-rusted bars was approximately 50 μm. The pre-rusted surface was in a state following half-year exposure in outdoor atmosphere (C4 according to ISO 9223). The average thickness of scale (Fe_3O_4) on scaled bars was between 10 and 20 μm, with the scale regular and adherent on the whole surface. The pre-rusted surface was covered with a brown, partially nonadherent layer on the black base. Narrow peripheral walls of concrete blocks were insulated with two-component epoxy–tar coating (200 μm), with non-coated concrete surface left only on the two side walls of each block. This ensured relatively uniform access of both the liquid (during saturation with chlorides) and the atmosphere (during exposition) to the surface of all the exposed steel specimens.

Various chloride contents were introduced after the curing period into dry concrete blocks by way of their immersion to the sodium chloride solutions for 7 days. The blocks were then dried (at 50°C) to the required water content corresponding to the chosen humidity level. Two concrete blocks with the same chloride content were placed together into glass cabinets with atmosphere of different relative humidity provided for by water vapour pressure of various saturated salt solutions (60% RH, NaBr; 70% RH, $NH_4Cl + KNO_3$ (1:1); 80% RH, NH_4Cl; 90% RH, $ZnSO_4$; 100% RH, H_2O). The salt solutions were not in contact with the concrete blocks. There was no temperature control and the measured temperatures were in the range of 12–26°C. Temperature and humidity were measured during the whole period of exposure. Two parallel, identical concrete blocks were exposed for every humidity level (70, 80, 90, and 100%) and chloride content (0.4 and 2.5 wt.%/cement), with only one set exposed for RH 60% and 0.0 wt.% Cl^-/cement. Altogether, 23 concrete blocks were exposed with 92 steel specimens (2×36 of them in parallel sets). A constant water content in all concrete blocks (checked by weighing) was reached after 4 months of exposure. The average equilibrium water content [% of dry concrete mass (±1%)] was 4% for 60% RH, 4.7% for 70% RH, 5.4% for 80% RH, 7.3% for 90% RH, and 10.2% for 100% RH. After 6 months of exposure, chlorides were practically evenly distributed in concrete under 90% and 100% RH, while under lower RH values, the chloride content at the steel level was rather lower than in concrete close to its surface. Chloride concentration of 0 wt.% means that the chloride content was lower than 0.05 wt.%/cement for all RH levels, average concentration of 0.4 wt.% means that chlorides at the steel level were in the interval of 0.37–0.53 wt.%/cement, and for the value of 2.5 wt.%, the chloride content was in the interval of 2.14–2.71 wt.%/cement. Chloride distribution in every concrete block was measured by an analysis of concrete drilled perpendicularly every 10 mm to the free surface of the concrete block after 2, 6, and 48 months of exposure.

Corrosion behavior of carbon steel specimens in concrete was monitored periodically by way of measuring the free corrosion potential (E_{corr}) and linear polarization resistance (R_p)(± 10 mV vs. E_{corr}, 0.1 mVs^{-1}) under laboratory conditions in the course of 4 years. Corrosion measurement systems (CMS 352/273 EG & G or CMS 100/PC3 Gamry) were used for the electrochemical measurement and data analysis. Platinum wire was used as a counter electrode, placed parallel to the measured steel specimen and on the opposite side of the concrete block, which was in contact with a saturated calomel electrode (SCE).

The exposure of 14 concrete blocks (4x14 steel specimens) was terminated in the 42nd and 48th month, respectively. The parallel set is still under exposure. The blocks were broken and the steel specimens were taken out. The corrosion attack was evaluated visually, based on the mass loss. In order to determine mass changes, the specimens were pickled according to ASTM G1 (C.3.1). In order to determine the original metal mass of the scaled or pre-rusted specimens, mass corrections to the original oxide layer were made on series of nonexposed original reinforcement specimens. Given the variance of values, these corrections lowered the accuracy of the corrosion rate determination in pre-rusted specimens to ±0.5 μm/year. In the case of machined and scaled specimens, however, mass changes allowed us to determine the corrosion rate after 4-year exposure with an accuracy of 0.1 μm/year. After breaking the concrete blocks, the depth of carbonation was determined using phenolphthalein.

3. Results and discussion

Average values were calculated from the R_p and E_{corr} values for the whole time of exposure for each steel specimen in concrete blocks ($\bar{R}_p$, $\bar{E}_{corr}$) (Table 1). The free corrosion potential of the pre-rusted steel reinforcement reached values, which did not correspond in all cases to the extent of the corrosion attack (according to ASTM C 876). At low aggressiveness of the pore solution in concrete (0.0% or 0.4% Cl^-/cement), the measured potential seemed to reflect the oxidation conditions on the rust surface rather than the corrosion process on the metal–rust interphase itself. For pre-rusted specimens, R_p values were always low, regardless of the chloride content. For all superficial states of steel, the corrosion rate calculated from mass loss was lower than 1–2 μm/year at $\bar{R}_p$>30 Ω.m^2. The results of electrochemical measurements and the corrosion rates calculated on the basis of mass loss are compared in detail in our paper [11].

In concrete with a low chloride content (0.0 and 0.4 wt.% to cement), the specimens with the originally pre-rusted surface exhibited the highest average corrosion rates (up to about 5 μm/year). Specimens with surface originally scaled and machined exhibited average corrosion rates in the order of 10^{-1} μm/year. In concrete with a high concentration of chlorides (2.5 wt.% to cement), all exposed steel specimens, regardless of the initial state of their surface, exhibited high average corrosion rates (above 1 μm/year). At this chloride concentration, we could also observe the highest average corrosion rate at a relative humidity of 70% to 90%. Lower corrosion rates at 100%RH is due to difficult access of oxygen, and at 60%RH, by the low conductivity of concrete.

The specimens whose corrosion rate was below 1 μm/year either did not show any visible corrosion attack, or the attack was limited to 2% of the surface maximum. An attack on 2–10% of the surface was recorded at average corrosion rates between 1 and 4 μm/year. An attack affecting more than 10% of the surface corresponded to corrosion rates above 2 μm/year. The recalculation of the recorded mass loss solely to the area attacked by corrosion showed the highest corrosion rates in the order of 10^1 μm/year (up to 65 μm/year). We may assume that the pH of concrete at the surface of the specimens did not change significantly over the whole period of the exposure due to carbonation. This was so because at humidities above 60%, the depth of carbonation was even less than one-half of the cover layer thickness (20 mm) over all 4 years of the exposure. Traces of corrosion products in concrete were observed only in blocks with a chloride content of 2.5% Cl^-/cement. These proved that rust precipitation and oxidation of Fe^{2+} ions occurred at certain spots up to several millimeters from the metal surface. This testified to a considerable drop of pH in this area due to hydrolysis as compared with the original value of concrete. At lower chloride concentrations, rust traces in concrete were indistinct even for pre-rusted specimens, although they exhibited unacceptably high corrosion rates under the given conditions.

Table 1
Average values of mass-loss corrosion rate (v_{corr}), polarization resistance ($\bar{R}_p$), and free corrosion potential ($\bar{E}_{corr}$) of steel in different superficial states after 4-year exposure in concrete

			Pre-rusted			Scaled			Machined		
Cl^- (wt.%/cement)		RH (%)	v_{corr} (μm/year)	$\bar{R}_p$ (Ω.m^2)	$\bar{E}_{corr}$ [V (SCE)]	v_{corr} (μm/year)	$\bar{R}_P$ (Ω.m^2)	$\bar{E}_{corr}$ [V (SCE)]	v_{corr} (μm/year)	$\bar{R}_p$ (Ω.m^2)	$\bar{E}_{corr}$ [V (SCE)]
<0.05		60	5	22	+0.082	0.2	34	+0.077	≤0.1	142	+0.051
		80	3	4	+0.011	≤0.1	42	+0.062	0.2	202	+0.034
		90	3	2	+0.013	≤0.1	38	+0.019	≤0.1	194	+0.012
		100	4	2	−0.030	≤0.1	48	−0.074	≤0.1	152	−0.118
0.4	0.42	60	≤1	61	+0.046	≤0.1	69	+0.052	≤0.1	148	+0.030
	0.43	70	2	5	+0.005	0.2	40	+0.018	≤0.1	106	−0.050
	0.37	80	4	4	−0.008	0.2	50	+0.009	≤0.1	109	−0.038
	0.39	90	2	5	−0.155	0.2	57	−0.086	0.3	129	−0.147
	0.53	100	5	2	−0.187	0.2	32	−0.183	0.2	104	−0.239
2.5	2.14	60	2	18	−0.262	2.4	24	−0.254	1.1	52	−0.234
	2.39	70	11	5	−0.293	10.6	6	−0.424	7.4	13	−0.343
	2.44	80	10	4	−0.259	13.3	3	−0.346	7.0	14	−0.419
	2.71	90	8	2	−0.499	61.6[a]	1	−0.456	5.5	8	−0.505
	2.65	100	5	1	−0.262	1.9	4	−0.474	1.6	36	−0.338

v_{corr}>1 μm/year; $\bar{R}_p$<30 Ω m^2; $\bar{E}_{corr}$<−0.250 V (SCE).

[a] Concrete block was broken during exposure due to corrosion.

One of the causes of the high corrosion rate on a pre-rusted surface might be the contamination of the rust layer with sulfates during atmospheric exposure prior to the steel's embedding in concrete (we proved their presence in the rust layer). Sulfates can hardly act as a major stimulator of corrosion in an environment containing chlorides, but their presence on the steel surface at low chloride content may contribute to a high corrosion rate. However, its major cause rests in the porous rust acting as barrier for alkaline solution from concrete and also acts as crevice in which anions concentrate by migration to anodic sites. We assume that the transport of OH^- through rust increases pH under rust, but not on the level where spontaneous passivation occurs. Rust, actually, also acts as a barrier for chlorides and water, but it has only short-term positive influence. Hydrolysis of corrosion products leads to the further acidification of the occluded solution adjoining the metal surface.

The corrosion process in concrete in the active state is usually limited by the rate of the cathodic process, i.e. by the limiting current density of the reduction of oxygen or the surface layer of rust. Some authors [4] claim that the corrosion rate of steel in concrete in the active state exceeds the rate of the transport-governed oxygen reduction, and they consider a parallel course of the surface rust layer reduction to be inevitable, similarly as under atmospheric conditions [10]. The original rust, in our case a layer of about 50 μm, is able to ensure depolarization for an average corrosion rate of 1 μm/year for only a little more than 1 year. Hence it is obvious that the rust layer reduction could not play a major role in our case in which average corrosion rates reached up to 14 μm/year in the course of 4 years. In the case of periodical drying and moistening of concrete, however, the layer of rust may, to a certain extent, act as an "accumulator" of the system's reducible component. The corrosion products oxidize at the time of low concrete humidity and, consequently, easy oxygen access; on the contrary, rust is reduced and participates in depolarization at the time of increased humidity and, consequently, more difficult oxygen access. Pre-rusted steel surface seemed to create conditions in which the alkaline concrete solution was unable to change sufficiently the electrolyte under rust in order to passivate the metal.

4. Conclusions

Four-year exposure tests proved that steel reinforcement used in the manufacture of concrete components with a pre-rusted surface exhibited from mass-loss measurements unacceptable average corrosion rates. This applied to practically all relative atmosphere humidity levels (60–100%) and chloride contents, i.e. even in noncarbonated concrete with a very low concentration of chloride ions.

The behavior of a scaled surface of steel reinforcement was comparable with that of a machine-cleaned surface, and its corrosion rates at a low chloride content may be considered acceptable (<1 μm/year). In terms of corrosion control, a high content of chlorides in concrete (2.5 wt.% to cement) is unacceptable for scaled and machined surfaces as well. The highest average corrosion rates (about 10 μm/year) were detected in specimens embedded in concrete blocks with a high content of chlorides and exposed in atmosphere with a relative humidity of 70–90%. The local corrosion rate of steel specimens in concrete did not exceed 65 μm/year. One of the causes of the high corrosion rate on a pre-rusted surface might be the contamination of the rust layer with sulfates during atmospheric exposure prior to the steel's embedding in concrete. However, its major cause rests in the porous rust acting as barrier for alkaline solution from concrete and also as crevice in which corrosion stimulating anions concentrate by migration to anodic sites. The results achieved so far indicate that the share of the original rust reduction in the overall depolarization reaction, which accompanies steel corrosion in concrete at a constant humidity, is low, and that the rate of oxygen penetration through the cover layer of concrete is crucial for corrosion in the active state.

Acknowledgments

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