Initiation and Corrosion Propagation of Stainless Steel Reinforcements in Concrete Structures

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Abstract

The use of stainless steel is a suitable method to increase the corrosion resistance of rebars in concrete structures. These steels have a higher corrosion resistance than galvanised rebars and are not sensitive to defects contrary to epoxy coated rebars. Nevertheless stainless steel reinforcement is not widely used due to the high costs compared to ordinary steel. Chromium reinforcing steels (e.g. X2NiCr12) exemplify the actual intent to lower the initial material costs during construction by optimizing the alloy content and the manufacturing process of the steels without risking the long-term durability of the concrete structures. The present contribution shows a practical method to characterize and compare the corrosion behaviour of stainless steels in concrete. A chromium steel (1.4003), a duplex stainless steel (1.4462) and an ordinary carbon steel as reference were investigated. For a first characterization tests in concrete pore solution with different chloride concentrations, pH-values and surface qualities of the steel were performed. To determine critical chloride concentrations for pitting corrosion rebar probes were fixed together with chloride sensors in mortar blocks, which were immersed in a NaCl-solution for suction test. The main part of these test series was the application of the stainless steels in field test under natural alternating exposure conditions. Samples of ordinary carbon steel, chromium steel and duplex steel were fixed in a large concrete block, which was deposited in the splash zone between two columns of a highway gallery. Additionally chloride and resistance sensors as well as temperature sensors were built in the concrete. A special data acquisition system for the continuous recording of potential, macrocell current, concrete resistance and concrete temperatures was used. With this online-monitoring the time of the initiation and the corrosion propagation of the different steels could be measured. After three years of exposure the steel samples were removed from the concrete block for visual inspection. Depth of corrosion attack and anodic area on the steels were compared and correlated with the continuously measured data.

Keywords: stainless steel reinforcement, concrete, monitoring, field test
1. Introduction

It is a matter of common knowledge that stainless steel reinforcements have a higher corrosion resistance than ordinary carbon steels or galvanised rebars. However, in most research projects the corrosion initiation of stainless steels was in the foreground [1, 2]. The corrosion propagation of stainless steels in concrete was not widely examined so far. Certain information is available e.g. from long standing outdoor tests [3]. A main part of this research work was the continuous measuring of the corrosion propagation of a chromium steel and the analysis of the corrosion attacks compared to an ordinary carbon steel.

2. Tested Steels

For both, laboratory and field tests two stainless steels and an ordinary carbon steel (reference) were investigated: a ferritic stainless steel TOP12 (X2Cr12, basis 1.4003), developed by von Moos Stahl AG Switzerland, a duplex stainless steel (X2CrNiMoN22-5-3, 1.4462) and an unalloyed reinforcement steel (S500). The rebars had a diameter of 10 and 16 mm. TOP12 is manufactured by a new production process, where the material properties are achieved by only two production steps: hot rolling of the billets in several steps to the final product and controlled cooling [4]. The chemical composition of the investigated steels is given in table 1.

Table 1 chemical compositions of the investigated steels [m-%]

<table>
<thead>
<tr>
<th></th>
<th>S500</th>
<th>TOP12</th>
<th>1.4462</th>
</tr>
</thead>
<tbody>
<tr>
<td>C max.</td>
<td>0.15</td>
<td>0.03</td>
<td>0.03</td>
</tr>
<tr>
<td>Mn max.</td>
<td>0.59</td>
<td>1.50</td>
<td>2.00</td>
</tr>
<tr>
<td>S max.</td>
<td>0.43</td>
<td>≤ 0.015</td>
<td>≤ 0.015</td>
</tr>
<tr>
<td>Cr min./max.</td>
<td>0.09</td>
<td>10.50/12.50</td>
<td>21.00/23.00</td>
</tr>
<tr>
<td>Ni min./max.</td>
<td>0.12</td>
<td>0.30/1.00</td>
<td>4.50/6.50</td>
</tr>
<tr>
<td>Mo min./max.</td>
<td>0.02</td>
<td></td>
<td>2.50/3.50</td>
</tr>
<tr>
<td>N min./max.</td>
<td></td>
<td>0.030 (max.)</td>
<td>0.10/0.22</td>
</tr>
</tbody>
</table>

3. Laboratory Tests

Tests in Solution

Solution tests were made in a synthetic pore solution (pH value 13.5) with different chloride concentrations. The pore solution was carbonised by flooding CO₂ to lower the pH. To characterise the corrosion behaviour of the steel samples in synthetic pore solution, potentiodynamic current potential curves (propagation rate 0.2 mV/sec) were performed. To determine corrosion resistance the pitting potential was used as criteria. A special cell with flexible sealings was constructed to perform experiments on the rolling skin of ribbed rebars. For rebars with a diameter of 10 mm the surface exposed to the electrolyte was 23 cm², for rebars with a diameter of 16 mm 35 cm². The samples were polarised cathodically for five minutes in advance at a potential of -600 mV_SCE. The chloride contents, pH values and surface qualities were chosen as follows:

- chloride concentrations: 0/0.3/0.5/1/2/3/5 mol/l
- pH-values: 13.5/12.5/11.8/10.5/9.5/8.0
- surface qualities: grinded (320 grid)/sandblasted/as received
Suction tests with mortar blocks

The set-up of the mortar blocks for suction tests is illustrated in fig. 1. Two rebars and two chloride sensors (Ag/AgCl) were installed at the same level in mortar blocks with w/c ratio 0.6 and max. grain size of 4 mm. After a preliminary saturation time in water the mortar blocks were immersed in NaCl solution and ventilated on the top side to obtain a slow and continuous uptake of the salt solution. Initiation and chloride concentrations could be determined by potential measurements with a saturated calomel electrode [5].

4. Field Study

For the field study, a concrete beam (pc, w/c 0.6, max. grain size 16 mm) with dimension 100 x 30 x 20 cm was prepared. Eight samples (diameter 10 mm) of ordinary carbon steel, TOP12 and duplex steel were installed in the concrete block. Concrete cover was 10 mm. Furthermore, the beam contained chloride sensors at rebar level, resistivity and temperature sensors in different depths, reference electrodes (MnO₂) and a rebar mat of S500 as cathode on the backside (concrete cover 100 mm). The concrete beam was exposed to salted splash water in a Swiss highway gallery (A13). A data acquisition system for the continuous recording of potential, macrocell current, concrete resistivity and concrete temperature was used [6]. After three years of exposure the steel samples were removed from the concrete beam for visual inspection (depth of corrosion attack, anodic area) and measuring of the weight loss.

5. Results and Discussion

5.1 Laboratory Tests

Tests in Solution

Fig. 2 show the pitting potentials of untreated samples of S500, TOP12 and duplex steel at pH 13.5 und 10.5. TOP12 has a higher corrosion resistance than S500 at pH 13.5. Duplex stainless steel is resistant up to chloride concentrations of more than 3 mol/l. At pH 10.5 (corresponds to carbonated concrete) almost no difference in corrosion behaviour of S500 and TOP12 could be detected. The pitting potentials are below 0 mV SCE even with chloride concentrations <0.1 mol/l. Only the duplex steel is passive up to a chloride content of 1 mol/l.
To test the influence of surface quality of TOP12 steel, the rolling skin was removed by sandblasting. This treatment leads to a significant higher corrosion resistance at pH 13.5. The pitting potentials increase about 100 mV with 0.3 and 1 M NaCl. At pH 10.5 this effect disappears and the steels are active at open circuit potential [7]. The negative influence of rolling skin on the corrosion resistance was also reported in [2]. More results of the solution tests can be found in [7].

**Suction Tests**

Examples of results of the suction tests are given in fig. 4. Due to the chloride ingress into the mortar corrosion initiation starts as soon as the chloride content on the rebar level exceeds a critical value. This leads to an abrupt decrease of the corrosion potential of the steel samples. The results of the suction tests are presented in table 2. The critical chloride content of TOP12 with rolling skin is between 0.5 und 1.5 mol/l (mean 0.85 mol/l) and it is two to three times
higher as for S500 (mean 0.33 mol/l). TOP12 samples with sandblasted surface show a higher critical chloride content (>3 mol/l). This confirms the results of the solution tests.

![Graph of potential vs. time with critical chloride concentrations marked](image)

**Fig. 4** Critical chloride content for corrosion initiation of TOP12 (as received) and S500 in mortar

**Table 2** Max./min. and mean values of the critical chloride content for ordinary carbon steel (S500), TOP12 and duplex stainless steel (1.4462) in mortar (pH ≈ 13.5). Values in brackets: Cl⁻ [m%/cement]

<table>
<thead>
<tr>
<th></th>
<th>$C_{\text{crit}}^{\text{max}}$ [mol/l]</th>
<th>$C_{\text{crit}}^{\text{min}}$ [mol/l]</th>
<th>$C_{\text{crit}}^{\text{mean}}$ [mol/l]</th>
</tr>
</thead>
<tbody>
<tr>
<td>S500</td>
<td>0.4</td>
<td>0.3</td>
<td>0.3 (0.5)</td>
</tr>
<tr>
<td>TOP12 rolling skin</td>
<td>1.4</td>
<td>0.6</td>
<td>0.9 (1.0)</td>
</tr>
<tr>
<td>TOP12 sandblasted</td>
<td>3.7</td>
<td>3.0</td>
<td>3.4 (&gt;3)</td>
</tr>
<tr>
<td>Duplex Steel</td>
<td>&gt;5.0</td>
<td>&gt;5.0</td>
<td>&gt;5.0 (&gt;5)</td>
</tr>
</tbody>
</table>

**5.2. Field study**

**Potentials**

Die field tests were started in October 2000 and lasted until summer 2003. At the beginning of the measurements some steel samples were connected to the rebar mat at the backside of the concrete beam. Potential measurements were performed with the rest of the rebars, which were isolated from the cathode. After 13 months the steels connected to the rebar mat were separated from the cathode to prevent a possible cathodic protection of the remaining samples. Fig. 5 shows the potential development of three samples with different steel qualities. It is visible that the S500 steel activates during the first winter (January 2000). Before stable initiation a larger amount of activation and repassivation processes occur with the TOP12, which are probably caused by the rolling skin. The potential of the duplex steel remains passive during the entire test stage (no initiation processes were detected). The maximum potential drop between active and passive state of S500 amounts to about 450 mV and 250 mV for TOP12. The critical chloride content for initiation could be determined with the chloride sensors in the same way as in the suction tests. In general a good correlation with the laboratory results were found [7]. All of the eight S500 samples were active after seven months and all the TOP12 rebars after 22 months.
Fig. 5  Potential of isolated steel samples (ordinary carbon steel S500, TOP12, duplex steel) over time in a concrete beam exposed to salted splash water in a Swiss highway gallery (A13)

**Chloride contents**

After three years of exposure the chloride content in the concrete beam was analysed in the laboratory. Fig. 6 shows three chloride profiles on the front- and the backside of the beam. It is clear that the chloride content on rebar level is above 1.5 m.%/c. The depth of the chloride front reaches about 70 mm. In a depth of 40 mm the chloride content is above 0.4 m.%/c. As expected, the chloride content on the backside of the concrete block was considerably lower. Therefore, the chloride front did not reach the cathode.

Fig. 6  Chloride profiles after three years in a concrete beam (front and backside) exposed to salted splash water in a Swiss highway gallery (A13)
Concrete resistivities

The fast and deep reaching chloride ingress can be documented by means of resistivity measurements. Fig. 7 shows an example of the temperature compensated resistivities over time (1 September 2002 to 3 June 2003) for three different depths. As it is known from other research projects [6] the deep reaching chloride ingress into the concrete together with splash water due to capillary suction takes place during short time intervals (large incidents). These incidents occur with low temperatures and high relative humidity [9]. On the basis of the resistivity measurements it can be concluded that the amount of chlorides in fig. 6 entered the concrete at three large incidents (one in each winter). Generally, the concrete resistivities increased slightly during the entire test stage of three years due to hydration of the concrete.

Macrocell currents

The macrocell current of corroding steel samples is a measure for the material loss due to corrosion processes and gives information on the corrosion propagation. Fig. 8 shows the weight loss calculated with Faraday’s law of four S500 and three TOP12 samples. The zero point on the time scale corresponds to the point of initiation. It is visible that the corrosion rate (weight loss per time) of S500 is much higher than the one of TOP12. However, it has to be considered that the maximum attack depth can not be derived from the mass loss directly, because the anodic area is not known. Therefore the steel samples were removed from the concrete beam after the test period of three years for further investigations.

Fig. 7 Temperature compensated concrete resistivities in three different depths over time (sep 2002 to june 2003) in a concrete beam exposed to salted splash water in a Swiss highway gallery (A13)
Fig. 8 Mass loss over time of ordinary carbon steel and TOP12 samples in a concrete beam exposed to salted splash water in a Swiss highway gallery (A13)

**Investigations of the steel samples**

After the removal of the steel samples corrosion products were removed in an ultrasonic bath with pickling solution. Afterwards the corroded area, the weight loss and the max. attack depth were measured. The mean values of the anodic areas and the max. attack depts for S500 and TOP12 steel are given in table 3. It has to be noticed that the time of corrosion (TOC) of most samples was different (varying initiation times). After 27 months about one third of the surface of S500 was corroded, 10% on the TOP12 after approximately 12 months. The attack on both steel types was very inhomogeneous. On the S500 rather wide shallow pits were visible whereas the attacks on the TOP12 were limited on smaller areas.

<table>
<thead>
<tr>
<th></th>
<th>anodic area [cm²]</th>
<th>[% of total area]</th>
<th>max. attack [mm]</th>
<th>TOC [month]</th>
</tr>
</thead>
<tbody>
<tr>
<td>S500</td>
<td>3.7 ± 1.2</td>
<td>30 ± 10</td>
<td>0.7 ± 0.4</td>
<td>27 ± 1</td>
</tr>
<tr>
<td>TOP12</td>
<td>1.2 ± 1.1</td>
<td>10 ± 9</td>
<td>0.5 ± 0.3</td>
<td>12 ± 3</td>
</tr>
</tbody>
</table>

For the further evaluation is has to be considered that only the macrocell current between the steel sample and the reinforcement mat could be measured (external macrocell). The macrocell on the sample itself (internal macrocell) could not be recorded (fig. 9).
From the measured macrocell current, weight loss, max. attack depth, TOC and the circumstance that some samples were isolated from the external cathode during the entire test stage, mean values of the mass loss rate (mg/d) for the external and internal macrocell and the max. pit growth rate (mm/y) could be calculated (table 4). It can be concluded that the weight loss of S500 is determined from the external and internal macrocell by one half each. The internal macrocell portion of TOP12 is about three times higher. This means that the current spread of the corrosion process of TOP12 is smaller. On the one hand this is due to the lower potential difference between the active and passive state (see 5.2 potentials) and on the other hand the cathodic current density of TOP12 is higher than for S500 [7]. The totally smaller material loss of TOP12 compared to ordinary carbon steel S500 can be explained by the lower voltage drop active/passive and the less soluble corrosion products with chromium ions.

The mean pit growth rate of S500 and TOP12 are similar. This result signifies that the total material loss of TOP12 is lower than the weigh loss of S500 but the corrosion attack is more localised and proceeds more into depth. This can be explained by the pH drop around the attack zone in case of local corrosion processes. The passive film of ordinary carbon steel is less resistant to acidic environment than the passive film of a chromium steel. Therefore, the lateral growth of corroding zones is more pronounced and results in rather wide shallow pits in the case of ordinary carbon steel S500.

Table 4 Mean ± sdev of the weight loss over time for the external (mcint) and internal (mcext) macrocell and the mean value of the max. pit growth rate of S500 and chromium steel TOP12

<table>
<thead>
<tr>
<th></th>
<th>weight loss mcint [mg/d]</th>
<th>weight loss mcext [mg/d]</th>
<th>max. pit growth mcext +int [mm/year]</th>
</tr>
</thead>
<tbody>
<tr>
<td>S500</td>
<td>2.07 ± 0.30</td>
<td>2.33 ± 1.04</td>
<td>1.21</td>
</tr>
<tr>
<td>TOP12</td>
<td>1.13 ± 0.45</td>
<td>0.32 ± 0.16</td>
<td>1.18</td>
</tr>
</tbody>
</table>

6. Conclusions

From the results of the presented investigations the following conclusions can be drawn:

- Results of solution-, suction tests and field investigation show a good correlation concerning the corrosion behaviour of ordinary carbon steel S500, ferritic stainless steel TOP12 and duplex stainless steel
- At pH 13.5 the critical chloride content of TOP12 chromium steel is about two to three times higher than for ordinary carbon steel S500. Duplex steel is resistant up to a chloride concentration of at least 3 mol/l
- Corrosion resistance of all steels depends strongly on the pH value. In carbonated concrete with chlorides there is almost no difference in corrosion behaviour between TOP12 and S500
The removal of the rolling skin by sandblasting results in significantly higher corrosion resistance of the TOP12 steel.

For chloride induced corrosion the weight loss of chromium steel is lower compared to ordinary carbon steel. Instead the attacks are more localised and a similar increase of attack depth can be expected.

By measuring macrocell currents corrosion propagation can be underestimated perspicuously.

7. Acknowledgements

This research project was financially supported by KTI Switzerland and the Graubünden highway administration, canton of Grisons Switzerland.

8. References


8. H. Ungricht, F. Hunkeler and H. Böhni, “Chloride Ingress into Concrete under Natural Alternating Exposure Conditions”, in: see [7], p. 247-256