RESEARCH AND DEVELOPMENT

Corrosion "Aspects" of Galvanic Coupling Between Carbon Steel and Stainless Steel in Concrete





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Corrosion Aspects of Galvanic Coupling between Carbon Steel and Stainless Steel Reinforcement in Concrete

INTRODUCTION

Stainless steel derives its corrosion resistance from a naturally occurring chromiumrich oxide film, which is present on its surface. As this invisible film is inert, tightly adherent to the metal and, most importantly, in an environment where oxygen is present, even at relatively low levels, the film reforms instantly if the surface is damaged.

Carbon steel has normally a lower corrosion resistance than stainless steel, but if embedded in concrete, carbon steel will not normally corrode due to the formation of a protective iron oxide film, which passivates the steel in the strongly alkaline conditions of the concrete pore water.

There are, however, aggressive environments (e.g. carbonation or ingress of chlorides) that can give rise to breakdown of the passive layer on carbon steel, resulting in corrosion of the unprotected surface. Corrosion of steel in chloride-contaminated or carbonated concrete can be avoided by using corrosion-resistant alloys, such as stainless steel, instead of carbon steel. Stainless steel can be used for complete or partial substitution of carbon steel in new structures exposed to aggressive environments, or when a very long service life (more than 120 years) is required. Stainless steel can also be used in the repair of reinforced concrete structures damaged by corrosion in order to guarantee long-term effectiveness of the repair work.

Over the past years, there has been considerable development in the chemical composition of stainless steels, in their physical and mechanical properties and in the types of reinforcement available. Furthermore, it was shown that, depending on the chemical composition and microstructure (austenitic, ferritic, martensitic or duplex), a suitable type of stainless steel from mild to aggressive environment could be found.

At the same time, stainless steel was getting cheaper, although, still, today (1998), 5-8 times more expensive than uncoated carbon steel (black steel). Therefore, both an economically and technically attractive approach could be to substitute carbon steel with stainless steel in critical areas, such as the lower section of a column on a highway bridge exposed to de-icing salt, the splash zone for coastal structures, or an edge beam on a highway bridge. This form of application includes coupling between stainless steel and carbon steel. Especially engineers, with regard to the risk of galvanic corrosion, have expressed concern when stainless steel is used as partial substitution to carbon steel.

Therefore, the effect of the connection between stainless steel and carbon steel must be investigated in order to study the consequences of galvanic coupling for corrosion in concrete structures, in which stainless steel bars are supposed to be used for limited parts of the reinforcement. In this connection, it is necessary to highlight some most important aspects about corrosion of both stainless steel and carbon steel when both are embedded in concrete.

Stainless steel freely exposed to seawater may, if in galvanic contact with a less noble metal, such as carbon steel, initiate a galvanic type of corrosion of the less noble metal. The corrosion rate will depend on the area ratio between carbon and stainless steel. The otherwise slow cathodic oxygen reduction at the stainless steel surface is a catalyst for bacterial slime, which forms after a few weeks in seawater.

When stainless steel is cast into concrete, however, the cathodic reaction is a very slow process, since no such catalytic activity takes place on a stainless steel surface. A research project recently conducted at the FORCE Institute has indicated that the cathodic reaction is inhibited on stainless steel embedded in concrete, as compared to the cathodic reaction on carbon steel reinforcement in galvanic contact with corroding carbon steel.

As a consequence, connection between stainless steel and carbon steel should not promote significant galvanic corrosion. As long as both metals are in the passive condition, their potentials will be more or less the same when embedded in concrete. Even if there should be minor differences in potential, both carbon and stainless steel can be polarized significantly without any serious risk of corrosion, as their potentials will approach a common value without the passage of significant current.

Therefore, assuming the correct use of stainless steel, which means in all places where chloride ingress and subsequent corrosion might occur, the two metals can be coupled with no problem. This behaviour, and the fact that stainless steel is a far less effective cathode in concrete than carbon steel, makes stainless steel a useful reinforcement material for application in repair projects.

When a part of the corroded reinforcement, e.g. close to the concrete cover, is to be replaced, it could be advantageous to use stainless steel instead of carbon steel. Due to being a poor cathode, the stainless steel should minimize the possibility of problems occurring in adjacent corroding and passive areas after repair.

At the same time, it is very important for the intelligent use of stainless steel that it is combined with carbon steel in quantities that guarantee both an optimal performance and cost-effective solution. The cost-effectiveness of the intelligent use of stainless steel for new structures has previously been demonstrated.

Recently presented results from a Danish project conducted by Rambøll, Arminox and FORCE Institute have also proved the cost-effectiveness of the intelligent use of stainless steel for repair of 25 to 30 year-old concrete columns on highways and coastal bridges. This analysis has been performed by comparing different repair strategies with and without the use of stainless steel.

In connection with the above-mentioned life cycle, cost analysis experiments have been performed to examine the corrosion aspects when connecting stainless steel and carbon steel in concrete.

AIM OF THE CORROSION TEST

The aim of the corrosion experiments described in this report is to define objectives for the use of stainless steel in repair of corroding reinforcement. The effect of galvanic coupling between the passive stainless steel and the existing carbon steel, in some case passive and in some cases corroding, is investigated in order to demonstrate that use of stainless steel for this purpose might even have a beneficial effect.

EXPERIMENTAL

Test samples

All test samples have the dimensions $300x170x70 \text{ mm} (\sim 12x7x3 \text{ in}. (length x width x height))$ and are cast from an ordinary Portland cement concrete of w/c ratio = 0.5 and without addition of fly ash and microsilica. All samples contain 5 reinforcement bar pieces in full sample length. These bars are either made of carbon steel or austenitic stainless steel (AISI 316). Additionally, the test samples contain two small pieces of the austenitic stainless steel or carbon steel, which correspond to 5% to 10% of the total steel volume. The 5% and 10% chosen for the samples represent the percentages of stainless steel to be used in example a) (10%) and example b) (5%). All bars have a diameter of 6 mm (~1/4 in.). In each sample, a reference electrode of the MnO₂-type is embedded. A total of 10 concrete samples are cast and they are divided into groups as follows:

Group 1: Three concrete samples, each containing five carbon steel rebars and two short (6 mm (\sim 1/4 in.)) stainless steel rebars corresponding to 5% and 10% of the total volume of the steel in the sample. The stainless steel rebars are closest to the concrete surface that is to be exposed to the aggressive environment. The carbon steel rebars are located behind the stainless steel, at different but defined depths from the exposed concrete surface.

Group 2: One reference concrete sample containing six pieces of carbon steel rebars that are located as the rebars in the samples in group 1.

Group 3: Three concrete samples, each containing the same number and volume of carbon steel and stainless steel rebars as the samples in group 1. The only difference is that all rebars are located at the same depth from the exposed concrete surface (cover is approximately 20 mm (\sim 3/4 in.)) to ensure that both the stainless steel and carbon steel are exposed under identical environmental conditions with more or less the same oxygen access.

Group 4: Three concrete samples, each containing five pieces of stainless steel rebars and two short pieces of carbon steel rebars corresponding to 5% and 10% of the total steel volume. All rebars are located at the same depth from the exposed concrete surface.

Figure 1 and Figure 2 show the above-described samples and the principle of measurements. Figure 3 and Figure 4 show photos of the test set-up.



Figure 1 Experimental model. See also Figure 3 and Figure 4.



Figure 2 Exposed area for groups 1 and 2 (top) and for groups 3 and 4 (bottom).



Figure 3 Experimental set-up for group 1 and group 2.



Figure 4 Experimental set-up for group 3 and group 4. The dark areas are red corrosion products.

Exposure conditions and measurements

One month after casting, all samples were exposed in a concentrated solution of NaCl (165 g NaCl/litre) with addition of $Ca(OH)_2$. In order to accelerate the chloride ingress, this exposure is a cycle of two days wetting in NaCl-solution and five days drying in laboratory atmosphere [9]. The following measurements are conducted:

• Macrocouple current between one of the short rebars (usually the one corresponding to the 5% of the total steel volume in the sample) connected to the remaining five rebars. The macrocouple current is measured by means of a specially constructed Zero-Ohm-Ammeter.

- Electrochemical potentials by means of an embedded MnO₂ reference electrode.
- Corrosion rate of chosen carbon steel bars and stainless steel bars by means of a polarization technique called galvanostatic pulse method.
- Visual inspection by means of a destructive method after conclusion of the test.

RESULTS AND DISCUSSION

Macrocouple Current

The macrocouple current was measured by means of a specially constructed Zero-Ohm-Ammeter. This instrument provides very exact values of current densities, as the measurements are independent of the ohmic resistance.

At the start of the measuring when carbon steel and stainless steel are embedded in concrete, which is not contaminated with chlorides, both metals are passive and have very similar electrochemical potentials. Therefore, the current, which is dependent of the differences in potential between the coupled metals, is very low.

When the samples become contaminated with chlorides and the chloride concentration reaches the critical value for carbon steel, this metal starts to corrode. At the same time, the electrochemical potential of carbon steel drops rapidly.

The rapid drop in potential of the corroding metal causes a significant increase in macrocouple current when the corrosion process starts. Thus, an electromotive force between two metals with different electrochemical potentials is created and this results in the electrical current (corrosion current) flowing between them, Figure 5.



Figure 5 Macrocouple current as function of exposure time for test specimens in group 3, where one specimen has started to corrode and two other specimens are still passive. Therefore, the measured macrocouple current for these two specimens is close to zero.

By systematic registration of the macrocouple current in each test sample it is possible to determine time to corrosion initiation. It is supposed that only carbon steel will start to corrode at the chloride concentrations reached by exposure under the above-described conditions. This postulate is later confirmed by visual investigation after conclusion of the exposure of samples in chloride-contaminated solution.

Among other parameters, the increase in macrocouple current after initiation of corrosion depends on the type of passive material (cathode). This is because the macrocouple current flows through concrete from the steel with the more negative potential (acting as anode) to that with the more positive potential (cathode). Such a current stimulates corrosion on the anode.

Since the passive film on stainless steel is much more stable than that of carbon steel, and, thus, can be passive in a wider range of conditions, stainless steel can influence the galvanic coupling phenomena that can occur in reinforced concrete.

It is expected that the current will be much lower when the corroding carbon steel is connected to a passive stainless steel, compared to the current registered between active and passive bars of carbon steel. Because of this, the increase in corrosion rate on carbon steel due to galvanic coupling with stainless steel will be significantly lower than in the case of carbon steel.

The experimental results shown on Figure 6 confirm this behaviour. When the current is measured between the carbon steel rebar starting to corrode and a small rebar (5%) of carbon steel that is still passive, a current density value of approx. 4.3 μ A/cm² is registered. If the same corroding carbon steel rebar is connected to the small rebar (5%) of stainless steel, the measured current density value is reduced to only 0.27 μ A/cm². This means a reduction in current density by an approx. factor of 15, which will result in the same decrease in corrosion rate.



Figure 6 Macrocouple current for stainless steel and passive carbon steel.

The increase in corrosion rate on carbon steel embedded in chloride contaminated concrete due to galvanic coupling with stainless steel is significantly lower than the increase induced by coupling with passive carbon steel. The lower macrocouple current density for stainless steel compared to passive carbon steel is a consequence of its cathodic behaviour. Under a previously performed investigation, it was found that compared to carbon steel, stainless steel has a higher over-voltage for the cathodic reaction of oxygen reduction. The high cathodic over-voltage on stainless steel means that when stainless steel is polarized to a negative potential owing to galvanic coupling with corroding carbon steel, it can produce a current density several times lower than the passive carbon steel can generate. Thus, the consequence of coupling with stainless steel is generally negligible, since passive areas of carbon steel always surround the area where corrosion takes place.

This behaviour has been proved during the present investigations. In one of the samples with small bars of stainless steel, the remaining bars of carbon steel, which had started to corrode, were coupled to the still passive small bars of carbon steel from another sample. This resulted in the remarkable increase in macrocouple current. This current started to decrease when the primary connection between carbon steel and stainless steel was reestablished. The results of this test are shown in Figure 7.



Macrocouple current . Sample 10

Figure 7: Influence of cathode material on the macrocouple current

The macrocouple current for the remaining samples is plotted on the figures included as Enclosure 1 to this report.

As a consequence of these findings, stainless steel is even considered to be a better reinforcement material for use in repair projects, when part of the corroded reinforcement is to be replaced, compared with usual carbon steel. Due to being a poor cathode, the stainless steel will minimize eventual problems that could occur in neighbouring corroding and passive areas after repair.

Further measurements of electrochemical potentials and corrosion rates should confirm that this is good and safe practice.

Electrochemical Potentials

When both carbon steel and stainless steel are passive, which is normally the case in chloride free concrete, and when this concrete is aerated, these two types of steel have

almost the same free corrosion potential. Indeed, in this environment, carbon steel is normally slightly nobler than stainless steel. In this particular test, the free corrosion potentials of stainless steel in chloride free concrete were in the range between -300 to -350 mV vs. MnO₂ reference electrode. For carbon steel, the free corrosion potentials in chloride free concrete were measured just below -300 mV vs. MnO₂ reference electrode.

Both metals will also remain passive after connection in chloride free concrete. In chloride-contaminated concrete, stainless steel will remain passive and maintain the potential values mentioned above. However, carbon steel will start to corrode when the chloride concentration exceeds the critical value, often stated to be above 0.5 % w/w of concrete. Due to the start of corrosion, the potential of carbon steel will change to the more negative values. The potential of the corroded carbon steel will depend on the aeration condition of the concrete. In the present investigation, these potentials were found between -400 to -700 mV vs. MnO₂ reference electrode.



Electrochemical potentials before and after exposure in chloride solution

Figure 8: Electrochemical potentials registered on stainless steel and carbon steel before and after exposure in chloride solution

When both metals were connected in chloride-contaminated concrete, the potentials of the macrocouple were found to be between the values measured for the passive stainless steel and corroded carbon steel. In water-saturated samples, the macrocouple potential became stable shortly after connection of both metals. In dried concrete, the potential of the macrocouple showed a progressive change towards less negative values, and the macrocouple current registered under these conditions was also decreasing compared to the values measured during exposure in chloride solution.

Determination of Corrosion Rate by Means of Galvanostatic Pulse Method

Galvanostatic pulse method is a transient polarization technique working in the time domain. A short-time anodic current pulse is imposed galvanostatically on the reinforcement from the counter electrode placed on the concrete surface. The applied current is usually in the range of 10 to 200 microampere and the typical pulse duration is up to 10 seconds. The reinforcement is polarized in anodic direction compared to its free corrosion potential.

The resulting change in potential is dependent on the state of corrosion in the reinforcement, and can be expressed by means of polarization resistance, ohmic resistance, double layer capacitance and the impressed current. Thus, it is possible to calculate the polarization resistance and, moreover, the corrosion current. When the area of polarized reinforcement is known, it is also possible to calculate the instantaneous corrosion rate from the values of the corrosion current.

In the case of the present investigation, the area of polarized reinforcement was known exactly. However, the small size of the rebar in the investigated samples caused another problem. Even the smallest current that could be applied by means of the galvanostatic pulse device was found to be too big to achieve the optimal polarization conditions (reinforcement should only be polarized to maximum 20 mV from the free corrosion potential when the ohmic resistance is subtracted).

Therefore, the rather high current applied for polarization influences the obtained results. This high current has a special effect on the values of the corrosion rate determined for passive rebars (mostly stainless steel). These values are higher than could be expected for steel in the passive condition, but, still, the calculated corrosion rate values are more than one decade lower for passive stainless steel compared to the active corroding carbon steel.

Some typical values of instantaneous corrosion rate calculated from galvanostatic pulse measurements are collected in Table 1.

Sample	Reinforcement material ⁽¹⁾	Free Corrosion Potential (mV vs. MnO ₂)	Average Corrosion rate (µm/year) ⁽²⁾	Actual Corrosion rate (µm/year) ⁽³⁾
3	1- Stainless Steel (5%)	-263	2.0	2,0
	Stainless Steel	-223	1,1	1,1
	(10%)	-175	7,7	385
	2- Carbon Steel	-162	7,6	23
	3- Carbon Steel	-237	3,3	9,8
	4- Carbon Steel	-185	3,9	3,9
	5- Carbon Steel	-180	2,9	2,9
	6- Carbon Steel			
6	1- Carbon Steel (5%)	-575	2,0	2,0
	Carbon Steel (10%)	-553	1,1	1,1
	2- Stainless Steel	-280	7,7	385
	3- Stainless Steel	-278	7,6	23
	4- Stainless Steel	-276	3,3	9,8
	5- Stainless Steel	-270	3,9	3,9
	6- Stainless Steel	-274	2,9	2,9
9	1- Stainless Steel (55)	-199	7,9	7,9
	Stainless Steel	-262	0,7	0,7
	(10%)	-554	18	359
	2- Carbon Steel	-570	56	845
	3- Carbon Steel	-643	42	422
	4- Carbon Steel	-586	34	508
	5- Carbon Steel6- Carbon Steel	-625	80	161

Table 1: Average corrosion rate values calculated by means of galvanostatic pulse measurements and actual corrosion rate values obtained by the correction of the corroding surface area

Explanations:

- (1) Numbers before the reinforcement material indicates which bars have been galvanically connected. The bar without number has not been connected.
- (2) Values of corrosion rate calculated by means of galvanostatic pulse measurements without correction for the actually corroding surface area determined by means of the visual inspection
- (3) Values of corrosion rate after correction for the actually corroding surface area determined by means of the visual inspection

In order to verify the instantaneous and average corrosion rate values calculated by means of the galvanostatic pulse method, it was decided to conduct visual inspection of the investigated samples. By means of the visual inspection it was possible to determine the actual and corroding surface area. In normal case this area is smaller than the area covered by the guard ring in the galvanostatic pulse equipment. It is because corrosion is often started by one small pit and is not propagated as general attack on the whole surface. Knowing this area it possible to correct the average corrosion rate obtained by the non-destructive method to the actual corrosion rate concentrated only on the limited part of the exposed surface.

The results in table 1 show higher corrosion rate values for stainless steel bars (5%) in samples 3 and 9 which were connected to the carbon steel reinforcement than values of corrosion rate for the free exposed stainless steel (10%). It is due to the electrochemical behaviour of stainless steel. Due to this behaviour the measured current includes both a contribution from corrosion but also from depolarization. As soon as the stainless steel will be disconnected from the carbon steel the measured current will decrease and represent true corrosion current.

Visual Inspection of Test Samples

The seven of ten samples (except samples No. 4, 5 and 7) were broken by means of a pneumatic hammer. Concrete was removed from the reinforcement surface. Thereafter all reinforcement bars were inspected visually. The general observation from this inspection was that only the carbon steel reinforcements were corroded. The extent of the corrosion was different from sample to sample.

On the other hand it was easy to distinguish between reinforcement bars located at the different depths from the exposure surface. It means that the reinforcements closest to the exposure surface were more heavily corroded than the reinforcement bars located behind. Some of the carbon steel bars located in the long distance from the exposure surface with low chloride concentration remain still passive.

None of the inspected stainless steel bars show any sign of corrosion attack. No difference was noticed between stainless steel bars, which was galvanically connected to the carbon steel and stainless steel bars, which were only exposed to the high chloride concentration. This observation is in accordance with explanation of the reason for the higher values of corrosion current for stainless steel bars connected to carbon steel. As explained above the higher values of corrosion current for stainless steel bars connected to the carbon are caused by the electrochemical phenomena and are not representing the actual corrosion rate.

The results of the visual inspection are shown on Fig. 9, Fig. 10 and Fig. 11, on which are photos of reinforcement bars from sample No. 1, 6 and 9.



Fig. 9. Photo of the reinforcement bars from sample 3



Fig. 10 Photo of reinforcement bras from sample 6



Fig. 11 Photo of reinforcement bars from sample 9

Summary

The coupling of corroding carbon steel with stainless steel is generally without risk, and is negligible compared to coupling to passive carbon steel, which always surrounds the corroding area.

Stainless steel has a higher over-voltage for cathodic reaction of oxygen reduction with respect to carbon steel. Therefore, the increase in corrosion rate on carbon steel embedded in chloride-contaminated concrete due to galvanic coupling with stainless steel is significantly lower than the increase brought with passive carbon steel.

Therefore, assuming the correct use of stainless steel, which means in all locations where chloride ingress and subsequent corrosion may occur, the two metals, carbon steel and stainless steel, can be coupled without problem. This behaviour, and the fact the stainless steel is a far less effective cathode in concrete than carbon steel, makes stainless steel a useful reinforcement material in repair projects.

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