

Special issue: Stainless Steel Rebar



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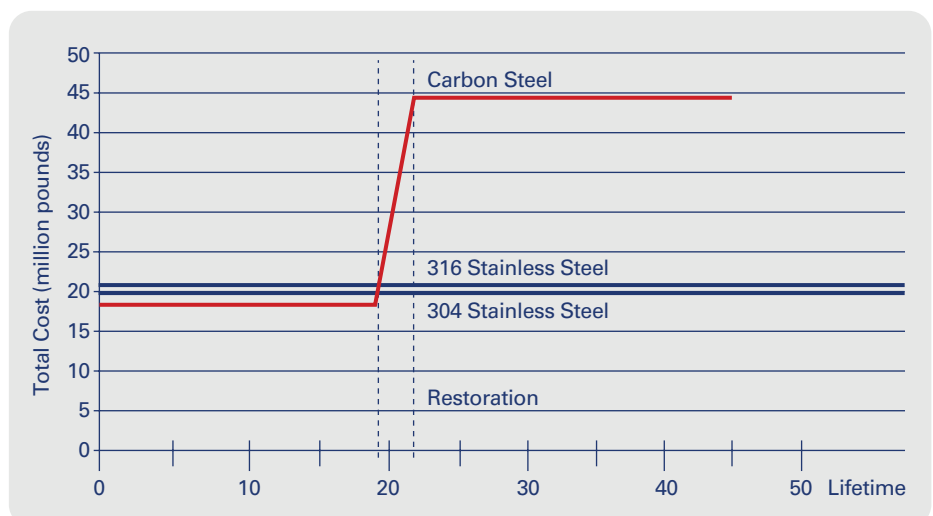
Introduction

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Stainless steel rebar provides a more corrosion resistant alternative to carbon steels as reinforcement of structures. Even though carbon steel is normally passive in the alkaline concrete environment, chlorides present in seawater or de-icing salts penetrate the concrete and cause the carbon steel reinforcement to corrode. Since the corrosion products are more voluminous than the rebar itself, the concrete experiences mechanical stress which causes the outer layers of the concrete to spall off. This exposes the carbon steel rebar to the surrounding environment, which is often even more aggressive. Although methods exist to prevent corrosion of the carbon steel rebar, such as the use of cathodic protection, such systems require careful monitoring. Stainless steel rebar offers a solution which is maintenance free and provides a high corrosion resistance.

Corrosion of the carbon steel reinforcement is the main reason why structures show premature failure today. The annual direct cost of corrosion to bridges alone in the USA, is estimated to be US\$ 5.9 billion to US\$ 9.7 billion [1]. If indirect costs were to be included, i.e. loss of economic revenue, the report forecasts that this could be as much as ten times higher. In Western Europe, the figures are not much better, an estimation in a Nordic report stated that €5 billion is spent yearly for repair of corroding concrete infrastructures [2]. With those figures in mind, it is easy to understand why more corrosion resistant reinforcement is needed and that the slightly higher initial cost of stainless steel rebar easily can be paid-off in a longer perspective. A paper published by the Bahrain Society of Engineers in 1995 [3] looked at two examples where the higher initial cost of stainless steel rebar is easily outweighed by the cost of concrete repairs. The first example, shown in Figure 1, is the lifecycle cost analysis (LCC) of the Swedish bridge Ölandsbron that was made for stainless steel rebar. The cost profile indicates an estimated cost of approximately £3m for using stainless steel rebar but a first intervention repair schedule costing approximately £25m.

Fig. 1 LCC of stainless steel reinforcement. From Kilworth and Fallon [3]

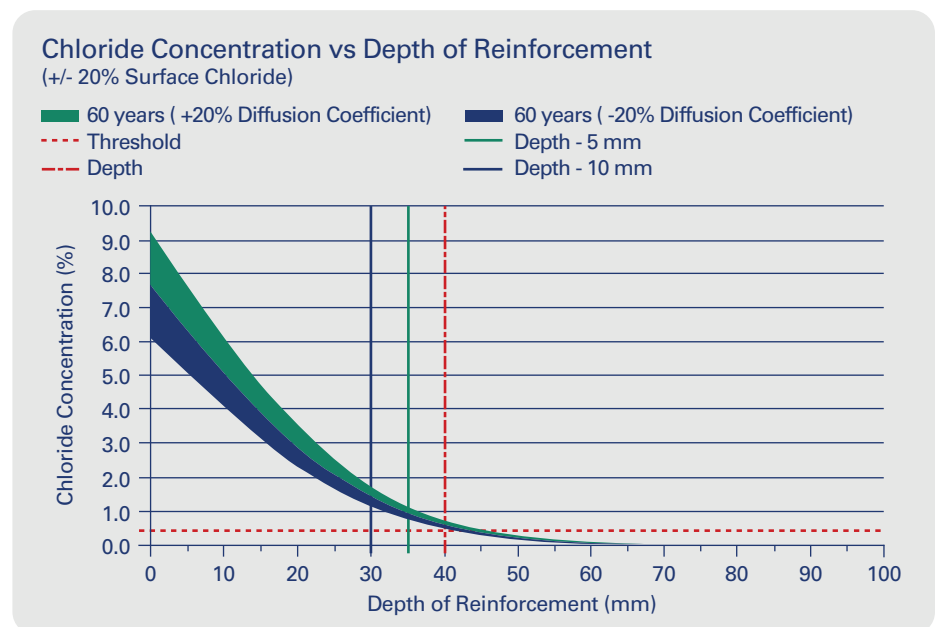


The second example given was the Midland Links motorway scheme in the UK where stainless rebar was not used. Again the initial additional cost of stainless rebar was in the order of £3m over a rebar cost of £28m and the cost of actual repairs was given as £45m to 1989. This scheme is still being repaired today.

An important point is that only the outermost layers of reinforcement need to be

replaced by the more corrosion-resistant stainless steel rebars. This is one of the reasons why the investment cost is only slightly increased when using stainless steel selectively compared to a complete use of carbon steel, but the depth to which the carbon steel has to be exchanged needs to be determined. Since chlorides penetrate the structure from the surface, a diffusion profile such as the one seen in Figure 2, will develop. Given a certain life-time, temperature and surface chloride concentration, it is possible to calculate the depth at which the chlorides will exceed the critical chloride threshold level (CCTL) for carbon steel and thus the depth to which stainless steel rebar should be used. Examples of commercially available predictive models include TR 61 [4] and LIFE 365 [5] and further refined models are used in nearly all major projects to design the durability of the structure. The Simple Representative Model (SRM), used in Figure 2, helps explain the parameters involved and should be used in conjunction with the accompanying report [6]. Both are available on the Outokumpu web site [7].

Fig. 2 Diffusion profile after 60 years. Chlorides measured as weight percent of the mass of cement.



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Critical chloride threshold levels for stainless steel reinforcement in pore solutions

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Summary

Selective use of stainless steel reinforcing bars (SSR) in parts of reinforced concrete (RC) structures that will be subject to chloride exposure is becoming more scientific in its application. Since original advice on where to use SSR and steel designation choice was given, concrete mixes have been specified for their durability for a given service life. With data available for the apparent chloride diffusion coefficient for the most used concretes and the chloride surface levels for different exposure conditions are known, it is only the Critical Chloride Threshold Level (CCTL) of the SSR designation to withstand the predicted chloride level at depth for the design life of the structure that needs to be defined. During the years, many researchers have measured the CCTL for a number of different steels. However, since a number of methods have been used, most of them using synthetic pore solutions; the existing CCTL data are diverse and lack the correlation between cast-in testing with in solution testing. This paper aims to clarify and compare results from some literature data for pore-solution and cast-in methods. It further reports the CCTLs of the following designations; 304L, 316L, and 2304 and carbon steel.

Keywords: Stainless steel reinforcement, Critical chloride threshold levels, Pore solutions

1. Introduction

In recent years, standards and codes of practice have been developed around the world to varying degrees of complexity in order to protect the passive oxide layer on carbon steel for attack from carbon dioxide or chloride ingress for a given design life [1]. These standards have taken a prescriptive approach to specifying the main parameters of concrete cover, cement type, and water to cement ratio for given bands of exposure conditions. In more recent times, reinforced concrete structure designers have been increasingly using predictive models such as Life-365 [2] or TR61 [3] to either take advantage of fine-tuning their knowledge of the exposure conditions or to design outside of the design life range of the existing standards. Predictive models offer a performance based solution either on a deterministic basis [2, 3] or on a probabilistic basis such as Duracrete [4], to concrete durability designs. Where concrete alone cannot provide the durability, predictive models offer the designer guidance on where to selectively replace carbon steel rebar with a more corrosion resistance reinforcement. This is particularly relevant to chloride exposures and the selective use of stainless steel reinforcement (SSR). Put simply, the process involves the specification where carbon steel needs to be replaced by SSR [4] and the critical chloride threshold level (CCTL) the SSR will be exposed to since this will determine the SSR designation required.

Several research projects have been carried out to determine CCTL values of SSR designations over the years. The most published values for CCTL have been what have become known as the “Pedferri” diagrams, which were the product of earlier work, by Bertolini et al. [5], which in turn references Sorensen et al. [6] The common theme was

determining the CCTL by holding a rebar specimen at a constant potential ($+200 \text{ mV}_{\text{SCE}}$) and increasing the chloride level until corrosion is observed. More recently a similar method has been used by Hurley and Scully [7]. However, in the main, these test methods have evolved, as has the understanding of their applicability, along with the development of SSR. This has meant that not all tests have been suitable for their application to SSR and not all have been carried out on what is now commercially produced SSR. For example some have been on plain annealed bar, others on hot rolled SSR pickled in the laboratory, and indeed the manufacturing process itself has developed from cold ribbing annealed plain bar to pickled hot rolled and straightened SSR, and it is well known that surface roughness and improper pickling can affect the corrosion resistance. This paper seeks to discuss the various testing methods carried out in the past and then presents initial results on the most prudent method. Moreover it marks the beginning of manufacturer SSR corrosion testing and research and understanding into the various parameters affecting SSR CCTL values.

1.1 The Critical Chloride Threshold Level (CCTL)

Many attempts to define a critical chloride threshold level (CCTL) for different reinforcements have been made, both in concrete, cement and synthetic pore solutions. Although many articles, reports etc. have been written on the subject, there are still some issues that remain, namely:

1.1.1 How to define and report CCTL

Although the name itself is a definition, it must be agreed whether it is the free or total chloride level that should be measured and at what maximum distance from the reinforcement. This is especially important when the chlorides are not heterogeneously added to a concrete or cement block specimen. Since part of the chlorides are chemically bound to the cement phases and physically adsorbed to the concrete pore walls, there is only part of the chlorides that take part in the corrosion reaction. Although this makes a free chloride measurement advantageous, local pH variations could result in a release of the bound chlorides into the solution [8–10]. A local increase of the free chlorides would not be detected by normally used post-test free chloride measurement and it would result in lower and more diverse CCTL values.

There are mainly two ways of reporting the chloride level in concrete tests, the $[\text{Cl}^-]/[\text{OH}^-]$ level and "percent chlorides by weight of cement or concrete". Arguments in favour of both of these methods can be found, and a more expanded discussion can be read in a recent review by Ann [8]. The $[\text{Cl}^-]/[\text{OH}^-]$ ratio is suggesting that the inhibiting effect is given by the hydroxyl ion while the detrimental effect is given by the chloride ion. Although this ratio also takes the fact that corrosion is a combined effect of pH and chloride level, the chloride binding is pH dependent, which result in a higher hydroxyl concentration as well as a decrease in chloride concentration when pH is increased and make the $[\text{Cl}^-]/[\text{OH}^-]$ exponentially dependent on the hydroxyl ion concentration. The total chloride level is adopted in many standards as the way to measure chlorides. Although this method does not take the carbonation into account as the $[\text{Cl}^-]/[\text{OH}^-]$ ratio does, it accounts for local pH drops, that can occur when a pit is nucleated. Moreover, the effect of the cement matrix is taken into account, which in a way is a measure of the inhibiting effect.

1.1.2 How to measure CCTL

This is the most complex and difficult point to solve. Since concrete structures are expected to have a lifetime of several hundreds of years, accelerated testing is necessary. Accelerated testing itself has some limitations, since it is assumed that there are no long-term effects beyond the test-period. Furthermore, CCTL must be measured not only for each steel designation, but also for each cement type, since it has been shown that different cement types have different CCTLs. This is mainly explained by the pH but other effects such as buffering capacity, chloride binding, pore-structure also needs to be clarified.

There are today many different ways to measure the CCTL. The difference between measuring in concrete and in simulated pore-solutions is the most obvious. Although

measuring CCTLs in concrete is closer to the real application, there are also a larger number of uncontrollable parameters, such as voids, water/cement ratios, bound/free chlorides etc., which can cause unexpected results and larger scattering of data. The concrete measurements are also more time-consuming since there is a need to cast all specimens. On the other hand, when measuring in a simulated pore-solution the CCTL needs to be “translated” into a concrete-CCTL. The concrete also has a certain buffering capacity and lower transport rates, if the chlorides are ponded rather than cast-in, that can cause the CCTL level to vary between concrete and pore-solutions.

In natural conditions, the chloride concentration slowly increases with time, since it is a result of a diffusion process, so many investigations instead use concrete to which chlorides are added via the water added to the cement. For a cast-in method, the ingress of chlorides through ponding will be time-consuming and take several months. For a pore-solution the problem is less complicated since chlorides can be added [5, 7], but it is then assumed that the effect of the increasing chloride concentrations are the same as for the cast-in samples.

The final critical point is the potential of the rebar. Certain authors define the CCTL as the chloride level where no corrosion occurs independent of the potential or current density for evaluation, whereas other researchers uses a defined potential for which the current density should be low. Both potentiodynamic as well as potentiostatic testing are found in literature.

In the potentiodynamic testing, the potential is slowly increased (typically 10–20 mV·min⁻¹) from the corrosion potential (open circuit potential, typically -100 to -200 mV_{SCE}) up to a certain potential where a sudden current increase is seen and thereafter the scan is reversed. The formation of a hysteresis loop normally indicates that local corrosion has occurred, while a direct decrease upon a reverse could indicate either oxygen evolution or transpassive corrosion. In the alkaline environments the potential for oxygen evolution on the stainless steel is lower (around +600 mV_{SCE}) than in neutral environments and transpassive corrosion is therefore seldom observed.

In a potentiostatic experiment, the potential is increased to a certain potential and thereafter either the temperature or the chloride level is increased to make the environment more severe. The third and most used method, applicable to cast-in testing is to study the corrosion at E_{corr} . Although this method is the most realistic, it is time-consuming and the onset of corrosion is difficult to observe.

1.1.3 Significance to the real application

This is probably the most important aspect of the CCTL value, since it should reflect the chloride tolerance in the construction. The CCTL should not only rank different designations for use as reinforcement but also guide designers for material selection in a concrete construction. Although this seems to be an advantage of “real” tests where the information can be interpreted directly, tests similar to the real application will be time-consuming and leave many parameters uncontrolled, which can cause different results, under apparently the same conditions.

1.2 Cast-in methods

Cast-in methods are the methods that are closest to the real application, thus the CCTL achieved can directly be translated into the highest chloride level that a certain type of reinforcement can withstand. However, cast-in methods are often more time-consuming than pore solution tests, and uncontrolled parameters such as voids near the rebar can affect the CCTL measured, which causes a larger spread of the data. This is the argument against using highly porous blocks, also a factor which affects the relative merits of cast-in mortar blocks and cast-in concrete blocks. Two different methods to add chlorides are normally used in these tests, mixed-in chlorides and ponding.

1.2.1 Mixed-in chlorides

Mixed-in chlorides have been used by several authors and result in a constant chloride level in the concrete or mortar block [6, 12–15]. In the method, chlorides are added to

the cement mixing water and in most cases the chlorides are also measured post-test, to confirm the chloride levels achieved. In the article by Pedefferri et al. both galvanically coupled and non-coupled carbon steel were investigated and potentiostatic control was used when the steels did not initiate corrosion at the corrosion potential.

Sørensen et al. [6] investigated the CCTL in mortar prisms (size 40x40x160 mm) with 0–8% Cl. Both carbon steels as well as stainless steels (304 and 316) were investigated and the rebars were tested in both welded and unwelded condition in a Portland cement. Two different electrochemical methods were used; potentiodynamic scans up to +200 mV_{SCE} as well as a series of potentiostatic experiments at +200 mV_{SCE}. The criterion for corrosion was set as the chloride content necessary to cause the current to be in the order of 10⁻² A·m⁻². The results are seen in Table 1. Two sets of experiments were also done, in an outdoor environment for 5 months and a carbon dioxide-rich environment respectively, and were visually inspected. A comparison with the pond-test was also performed, by immersing mortar samples at 0 mV_{SCE} in a solution of 1 M NaCl. The time to corrosion varied between 82–255 days, for those samples that corroded (experiment was interrupted after 175–285 days).

1.2.2 Pond-test

The pond-test is the cast-in method that mostly closely resembles the application and causes a slowly incremental increase of chlorides at the rebar surface. A pond of a concentrated chloride-containing solution is put on top of cement or concrete blocks in which rebars are cast-in. The method is described in the standard ASTM G109 [16] and has been used by some researchers [17–20]. Despite its resemblance to the real application, the method is time-consuming, and it often takes several months to perform an experiment.

In the ASTM G109 standard [16], a pond is placed on top of the concrete specimen (101.6 x 152.4 mm) containing 400 ml of 3 weight percent NaCl. Three rebars are placed in the concrete specimen, an upper one that will experience a higher chloride level than the two rebars below. The test assumes that the chlorides reaches the upper bar before the lower bar; hence the upper rebar will be active, while the two lower rebars will be passive and act as cathodes. The potential and current are measured and time to failure is defined as the time where the current reaches 10 µA and at least half the samples exhibit currents greater than 10 µA. The concrete specimens are cured for 28 days in a moist room and thereafter further dried for two weeks (RH 50%) and the test should be started one month after they are taken out from the moist room. The solution is then put on top of the block for two weeks, and thereafter vacuumed off and this cycle is repeated until the experiment is stopped. The test was originally developed for determining the effect of chemical admixtures on the corrosion of steel in concrete, and the determination of CCTL by this method can be cumbersome since the chloride concentration is heterogeneous throughout the block.

Page et al. [17, 20] used the pond method with different chloride concentrations in the pond, and also varied the cycle time, with an exposure time up to two years. The specimens were exposed to a weekly or monthly wet-dry cycle in four different concrete types (OPC paste, OPC limestone, OPC quartzite and SRPC quartzite.) In the second paper, the influence of wet-dry cycles was further compared, and a set of slabs with admixed chlorides was used (0–2% NaCl). Measurements of E_{corr} and the polarisation resistance were performed (from which I_{corr} was calculated). The pond test with monthly wet-dry cycles and the SRPC concrete resulted in the highest corrosion rates of the carbon steel tested.

Castellote et al. [18] used small mortar specimens for their test. A stainless steel plate was placed as a cathode in the pond above the rebar, and a steel plate at the bottom as the anode. The transport rate of chlorides into the mortar block was increased by an electrical field (13 V) that was applied across the block. Currents were measured by LPR, which is a common method to measure the corrosion rate.

The pond-test method has also been used by Hartt and Nam [19], who tested carbon steel in both low alkalinity (LA) and high alkalinity (HA) cements with one-week cycles. The time to corrosion was defined as the first time the potential was below -280 mV_{SCE}. For LA this time was between 13 and 60 days, while in the case of HA it was between

CCTL of different alloys determined by cast-in methods

Table 1

Ref.	Steel	Test	Environment	Temp.	CCTL value given
[6]	304	Pot. stat. 0 mV _{SCE}	Portland cement	RT	5–8% weight cement
	304 + res. weld ¹				3.5–5% weight cement
	304 + weld ²				3.5–5% weight cement
	316				>8% weight cement
	316 + weld ²				>5.8% weight cement
	316 + res. weld ¹				3.5–5% weight cement
	CS				<0.5% weight cement
[6]	304	Pot. stat. +150 mV _{SCE}	Portland cement	RT	3.5–5% weight cement
	304 + res. weld ¹				1–2% weight cement
	304 + weld ²				1–2% weight cement
	316				3.5–5% weight cement
	316 + res. weld ¹				2–3.5% weight cement
	316+ weld ²				1–2% weight cement
	CS				<0.5% weight cement
[6]	304	Pot. stat. +200mV _{SCE}	Portland cement	RT	3.5–5% weight cement
	304 + res. weld ¹				1–2% weight cement
	304 + weld ²				1–2% weight cement
	316				3.5–5% weight cement
	316 + res. weld ¹				1–2% weight cement
	316+ weld ²				1–2% weight cement
	CS				–
[6]	304	Pot. dyn. to 0 mV _{SCE}	Portland cement	RT	>8% weight cement
	304 + res. weld ¹				5% weight cement
	304 + weld ²				3.5–5% weight cement
	316				>8% weight cement
	316 + res. weld ¹				5–5.8% weight cement
	316+ weld ²				>5% weight cement
	CS				0.5% weight cement
[6]	304	Pot. dyn. to +200mV _{SCE}	Portland cement	RT	5–8% weight cement
	304 + res. weld ¹				2–3.5% weight cement
	304 + weld ²				1–2% weight cement
	316				>8% weight cement
	316 + res. weld ¹				3.5–5% weight cement
	316+ weld ²				1–2% weight cement
	CS				<0.5% weight cement
[6]	304	Pot. stat. +0 mV _{SCE} Immersion in 1 M NaCl	Portland cement	RT	0.77% weight mortar
	304 + res. weld ¹				0.47% weight mortar
	304 + weld ²				0.47±0.9% weight mortar
	316				–
	316 + res. weld ¹				–
	316+ weld ²				0.27% weight cement
	CS				0.26±0.13% weight cement
[11]	CS	E _{corr}	OPC	20	1.1–1.2% weight binder
[11]	CS	E _{corr}	OPC	35	1.1–1.2% weight binder
[11]	CS	E _{corr}	OPC	50	1.1–1.2% weight binder
[11]	CS	E _{corr}	OPC +10%Si fume	20	0.6–1.1% weight binder
[11]	CS	E _{corr}	OPC +10%Si fume	35	0.6–1.1% weight binder
[11]	CS	E _{corr}	OPC +10%Si fume	50	0.6–1.1% weight binder
[18]	CS	Pond-test	IV-B-32.5 SR/BC	RT	Cl _{tot} 0.152; Cl _{free} 0.330; Cl ⁻ /OH ⁻ 2.0

¹res. weld: Resistance welding ²weld: MIG/MAG welding

112–197 days. The shorter time in case of the LA cement was explained by the high w/c ratio and an expected dry concrete, which caused fast ingress of chlorides.

Manera et al. [11] used a method that was an intermediate between the mixed-in chlorides and the pond-test method. The method was based on a three-layer concrete block where mixed-in chlorides are put in a separate layer between two layers of non-chloride concrete. Measurements of the half-cell potential versus a MnO_2 reference electrode as well as determination of corrosion currents by LPR were performed during the experiment. The temperature was held at 20°C for 3 months; it was thereafter increased to 35 and 50°C for 15 days at each temperature. The results showed that the addition of 10% silica fume decreased the CCTL, defined as the chloride concentration at which the macro-cell currents were in the range of 1–2 $\text{mA}\cdot\text{m}^{-2}$ combined with a potential lower than $-200 \text{ mV}_{\text{SCE}}$.

1.3 Pore solution tests

The simulated pore solution should resemble the environment to which the rebar is exposed. A homogenous chloride concentration as well as a faster material transport speeds up the test time and significantly limits the number of uncontrollable parameters. However, since the CCTL in concrete and CCTL in pore solutions cannot be assumed to be the same, “translation problems” between the two CCTLs are expected.

Although there are a lot of different cements, not many researchers have adjusted the content of the pore solutions to reflect a certain type of cement, except for the use of hydrocarbonate and carbonate ions to simulate carbonation. Data concerning the chemical content of pore-solutions can be found in references [9, 21–24].

1.3.1 Potentiostatic methods

Potentiostatic methods are used in references [5] and [7]. Bertolini et al. [5] performed potentiostatic tests at $+200 \text{ mV}_{\text{SCE}}$ as well as potentiodynamic tests at four different pore solutions with four different pHs. In the potentiostatic tests, the chloride content was continuously increased by 0.5% every 48th h until 10% was reached. The critical chloride level was considered to be reached when corrosion gave an increase in current density to more than $0.5 \text{ mA}\cdot\text{m}^{-2}$. The steels investigated were CS, 304, 304L, 316, 316L, 254SMO, the martensitic grade 410 and a duplex grade (23Cr4Ni). The results are seen in Table 2. As stated earlier, the results are probably the origin of the often-published “Pedeferr-diagram”.

In the potentiostatic method used by Hurley and Scully [7], the potential was again set to $+200 \text{ mV}_{\text{SCE}}$, and the method very similar to that used by Bertolini et al. [5]. The definition of breakdown was defined as the chloride content where the current density exceeded $1\text{--}2 \mu\text{A}\cdot\text{cm}^{-2}$. The chloride content in the solution was increased by 0.1 M NaCl every 24th hour, starting without chlorides. Constant chloride potentiostatic tests were also performed, using the same test parameters as above. The constant chloride potentiostatic test resulted in slightly lower CCTL than the incremental chloride tests. Considering the diffusion profile of chlorides in the real application, the incremental chloride test should resemble the practical situation better than the constant chloride test.

The American standard ASTM A955 [25] uses a pore solution consisting of 974.8 g H_2O , 18.81 g KOH and 17.87 g NaOH. One bar is placed in a pore solution containing 15% NaCl, and two bars are placed in another beaker only containing pore solution at RT. A gel-salt bridge connects the two beakers, and should limit the amount of chlorides transported through the salt bridge. The solution should be changed every five weeks. Readings of the voltage drop over a $10\text{-}\Omega$ resistor should be made every day the first week, thereafter weekly. Although this is not a potentiostatic test in the sense that the potential is controlled, the corroding rebar will experience an elevated potential since it is galvanically coupled to passive carbon steel.

1.3.2 Potentiodynamic tests

The potentiodynamic tests used by Bertolini et al. [5] consisted of a slow sweep ($20 \text{ mV}\cdot\text{min}^{-1}$) in the pore solutions specified in Table 2. They started 200 mV below the corrosion potential and continued until the current density exceeded $0.5 \text{ mA}\cdot\text{cm}^{-2}$. The same method was later used by CAPCIS on behalf of CARES UK, when the corrosion resistance of

various SSR designations was tested, among them LDX 2101[®] [26]. The authors stated that this test method can only be used for ranking of various designations and that it is difficult to relate to concrete-CCTL due to the impossibility to convert percent chlorides in a solution to percent chloride by weight of cement/concrete. Also Moreno et al. [27] have performed potentiodynamic testing in the pore solutions with the same composition as Bertolini et al. [5]. Their criterion for CCTL was when a breakdown potential is observed.

Hurley and Scully [7] also performed a number of potentiodynamic sweeps to define the chloride threshold. In their potentiodynamic scans, that started 50 mV below the corrosion potential and increased the potential in the anodic direction at a rate of $10 \text{ mV} \cdot \text{min}^{-1}$, their definition of CCTL was the chloride concentration at which the pitting potential was below $200 \text{ mV}_{\text{SCE}}$, i.e. well below the oxygen evolution potential, occurring at around $+600 \text{ mV}_{\text{SCE}}$. Interestingly, the results from the potentiodynamic sweeps are different from their potentiostatic sweeps. For the stainless steels tested, 316LN and S32101, it was not possible to find a CCTL with the potentiodynamic method, although the chloride concentration exceeded 2 M. The explanation given was that the potentiodynamic test was too fast to cause corrosion, and there was a risk that potentiodynamic testing caused an overestimation of the CCTL.

Bautista et al. [28] investigated the influence of welding and weld-cleaning by using potentiodynamic testing in saturated $\text{Ca}(\text{OH})_2$ with addition of 0.5% NaCl and with bubbling of CO_2 -enriched air to simulate carbonation. The electrochemical measurements were performed by polarisation curves with a scan rate of $10 \text{ mV} \cdot \text{min}^{-1}$. Since the purpose of the article was to study the influence of welding and weld cleaning, no CCTL values were published, but instead the pitting potentials were recorded. One of the results was that weld cleaning is important to the corrosion resistance in the alkaline environment.

One of the drawbacks with performing potentiodynamic sweeps is the evaluation potential. Since oxygen evolution occurs at a potential around $600 \text{ mV}_{\text{SCE}}$, pitting corrosion occurring above this potential can be confused with the competing oxygen evolution. To distinguish between pitting corrosion and oxygen evolution many researchers perform a reversed sweep and check if a hysteresis loop is formed, which indicates corrosion rather than oxygen evolution. However, the pitting potential cannot be evaluated if oxygen evolution occurs since it cannot be determined which of the processes occurred first. This matter is also discussed in the article by Hurley and Scully [7], which is one of the few articles performing potentiodynamic sweeps that address this issue.

1.3.3. Tests performed at the corrosion potential

In addition to potentiodynamic sweeps, Moreno et al. [27] also investigated the CCTL in different pore-solutions at the corrosion potential, while continuously performing LPR measurements to determine the corrosion rate. Their definition of CCTL from the corrosion potential measurements was a corrosion current density a magnitude higher than it was without chlorides, i.e. in the range of $10^{-6} \text{ A} \cdot \text{m}^{-2}$. Uniform corrosion was found in the mildly carbonated environment (pH 9), even when no chlorides were present and the carbon steel used was not found to be passive at this pH.

As seen in Table 2, there are many different methods to measure the CCTL, all of them with their advantages and drawbacks. In the present work a potentiostatic method, resembling the method used by Bertolini et al. [5] and Hurley and Scully [7], was selected to evaluate the CCTL for industrially produced rebars in pore solutions. Three different stainless steel designations were selected in this first step, 304L, 316L and 2304, all of them industrially produced and pickled. The grade 2304 has a different micro-structure than the first two grades since it is duplex while the others have an austenitic structure. The duplex grades are advantageous compared to the austenitic grades with a more stable price due to lower nickel content and higher yield strength compared to an austenitic grade with the same corrosion resistance.

CCTL of different alloys determined in simulated pore-solutions

Table 2

Ref.	Steel	Test	Environment	T/°C	pH	CCTL value given	
[5]	CS	Pot. Stat +200 mV _{SCE}	Ca(OH) ₂ + incr. Cl ⁻	20 (40)	12.6	0.8 % (<0.5%)	
	AISI 410					2% (2%)	
	304					>10% (5%)	
	304L					5% (4.5%)	
	316					>10% (>10%)	
	316L					4.5% (5%)	
	23Cr4Ni					10% (3%)	
	254SMO®					>10% (>10%)	
[5]	CS	Pot. Stat +200 mV _{SCE}	0.9 M NaOH + incr. Cl ⁻	20 (40)	13.9	6% (7%)	
	AISI 410					>10% (7%)	
	304					>10% (10%)	
	304L					>10% (>10%)	
	316					>10% (>10%)	
	316L					>10% (>10%)	
	23Cr4Ni					>10% (>10%)	
	254SMO®					>10% (>10%)	
[5]	CS	Pot. Stat +200 mV _{SCE}	0.3M NaHCO ₃ 0.1M Na ₂ CO ₃ or 0.015M NaHCO ₃ 0.005M Na ₂ CO ₃ + incr. Cl ⁻	20 (40)	9	0.5% (-%)	
	304					2.5% (1%)	
	304L					3% (3%)	
	316					3.5% (3%)	
	316L					3.5% (1.5%)	
	23Cr4Ni					2.5% (1.5%)	
	254SMO®					>10% (10%)	
	[5]					CS	Pot. Stat +200 mV _{SCE}
AISI 410		0.5% (1%)					
304		1% (1%)					
304L		1% (1%)					
316		1.5% (1%)					
316L		1% (1.5%)					
23Cr4Ni		1% (1.5%)					
254SMO®		>10% (>10%)					
[7]	CS	Pot. Dyn. Ev. Pot. +200 mV _{SCE}	Sat. Ca(OH) ₂	RT	12.6	Cl ⁻ /OH ⁻ : 0.287	
	Fe 9%Cr					Cl ⁻ /OH ⁻ : 2.87	
	LDX 2101®					Cl ⁻ /OH ⁻ : >57.7 (nothing but susp. O ₂ ev. observed)	
	316L					Cl ⁻ /OH ⁻ : >57.7 (nothing but susp. O ₂ ev. observed)	
[7]	CS	Pot. Stat. +200 mV _{SCE}	Sat. Ca(OH) ₂ + const. Cl ⁻	RT	12.6	Cl ⁻ /OH ⁻ : 0.05	
	Fe9%Cr					Cl ⁻ /OH ⁻ : 0.5	
	LDX 2101®					Cl ⁻ /OH ⁻ : 3	
	316L					Cl ⁻ /OH ⁻ : 12	
[7]	CS	Pot. Stat. +200 mV _{SCE}	Sat. Ca(OH) ₂ + incr. Cl ⁻	RT	12.6	Cl ⁻ /OH ⁻ : 0.25	
	Fe9%Cr					Cl ⁻ /OH ⁻ : 2.5-4	
	LDX 2101®					Cl ⁻ /OH ⁻ : 7-10	
	316L					Cl ⁻ /OH ⁻ : 15-30	
	Clad w. SS					Cl ⁻ /OH ⁻ : 5-7	
	Clad w. SS + exposed end					Cl ⁻ /OH ⁻ : 0.7-1	
[27]	CS	E _{corr} + LPR	0.9 M NaOH	RT	13.9	1%	
			0.3M NaHCO ₃			9.0	0.1-1%
			0.1M Na ₂ CO ₃			9.0	Uniform corrosion w/o Cl ⁻
			0.015M NaHCO ₃				
			0.005M Na ₂ CO ₃				
Sat. Ca(OH) ₂	12.5	0.02%					
[27]	CS	Pot. Dyn. Const. Cl ⁻	0.9 M NaOH	RT	13.9	3%	
			0.3M NaHCO ₃			9.0	0.05%
			0.1M Na ₂ CO ₃			9.0	Uniform corrosion w/o Cl ⁻
			0.015M NaHCO ₃				
			0.005M Na ₂ CO ₃				
			Sat. Ca(OH) ₂			12.5	0.05%

2. Experimental observations

The selected method for determining the CCTL levels was a potentiostic method which was used for ranking as well as giving an indication of how the stainless steel grade should behave in a chloride-containing concrete environment. The potential was +200 mV vs. SCE, a potential that have been selected by other research groups [5–7], which gives very conservative results. The potential corresponds to an overpotential of more than 400 mV, since normal open circuit potentials in this highly alkaline environment are around -200 mV_{SCE}. The pore solution was selected to resemble real pore-solutions pressed from an Ordinary Portland Cement and the composition was taken from Andersson et al. [21]. The content of ions is similar to other results from solution pressed from OPCs [9, 29]. Compared to this data, the ion strength in the selected pore-solution is relatively mild, which again will result in rather conservative results.

25 mm rebars of the stainless steel designations 304L, 316L and 2304, with nominal composition seen in Table 3, were cut in 100 mm lengths and a hole for electrical contact was drilled in one of the ends of the rebar. The rebars were thereafter ultrasonically cleaned in acetone for 20 min, and thereafter covered with Lacomit (Agar Scientific) in both ends. The rebars were thereafter hanged in a beaker, and 1 l of OPC pore-solution was added. The pore-solution consisted of 2.61 g·l⁻¹ NaOH, 9.04 g·l⁻¹ KOH and 0.17 g·l⁻¹ Ca(OH)₂. To promote stirring, air, scrubbed through a wash bottle filled with saturated Ca(OH)₂ was bubbled through the solution.

Nominal composition of the stainless steel grades used

Table 3

Steel designation	Microstructure	Cr	Ni	Mo	C
304L	Austenitic	18.1	8.1	–	0.02
316L	Austenitic	17.2	10.1	2.1	0.02
2304	Duplex	23	4.8	0.3	0.02

The open circuit potential was measured for 1 h before the experiment started, and the potential was thereafter increased to the final potential (+200 mV_{SCE}) with a sweep rate of 10 mV·min⁻¹. The potential was held at least 10 h before the chlorides were added in the form of sodium chloride. The chloride concentration was increased by 0.2 M every day, divided on two separate additions of 0.1 M with at least 8 h between the additions. After ensuring that three chloride additions per day the first two days did not affect the final CCTL result, this chloride addition rate was used to speed up the measurements. Two sets of experiments were performed, at room temperature (20–23°C) and at 40°C. The CCTL was defined as the chloride content at which the current density exceeded 10 µA·cm⁻² for 5 h. pH was measured as soon as corrosion had started with a pH meter (Jenway 3345 Ion meter) equipped with a pH electrode (Schott pH electrode Blue line) calibrated with fresh buffer solutions at pH 7.0, 10.0 and 12.0 (Merck).

The results for CCTL levels at room temperature are seen in Table 4. The chloride levels are for all investigated SSR designations were above 5.7% chlorides by weight of solution

CCTL in weight percent chlorides measured at room temperature for different steels and comparison with literature data using similar methods

Table 4

	This article	Bertolini et al. [5]	Hurley and Scully [7]
Stainless steel product	Industrially produced and pickled rebar	Not mentioned	Industrially produced rebar, laboratory pickled
pH	12.8–12.9	12.6	12.6
Carbon steel	<0.4	0.1–0.6	–
304L	6.0	5.0	–
316L	5.7	5.5	around 4.5
2304	6.7	≥10	–

CCTL in weight percent chlorides measured at 40°C for different steels and comparison with literature data using similar methods

Table 5

	This article	Bertolini et al. [5]
Stainless steel product	Industrially produced and pickled rebar	Not mentioned
pH	~13.3	12.6
CS	<0.4	0.4
304L	2.8	4.5
316L	2.1	4.5
2304	2.1	3.5

for the room temperature experiment, more than ten times higher than the CCTL level for carbon steel rebar. For the series at 40°C, presented in Table 5, the CCTLs are lower, but the chloride tolerance is still much higher than for the carbon steel rebar. It should be noted that the carbon steel corroded at the lowest level of chloride addition in both the RT and the 40°C experiment, so the CCTL could be lower than 0.4% at this pH. To investigate the influence of the potential, an experiment was performed with 316L at +100 mV_{SCE} at 20°C. The CCTL for this lower potential was slightly higher, 6.4% compared to 5.7% when the potential was held at +200 mV_{SCE}. Although the difference in potential was rather small it indicates that these are very conservative results.

3. Discussion

Comparing the results from the test performed in this article with those from Bertolini et al. [5] and Hurley and Scully [7] performed on similar stainless steel designations, as seen in Table 4, it can be observed that the values are in the same range, considering the pH and steel designation. In this investigation, the pH was slightly higher than the pH for saturated calcium hydroxide solution. Measuring the [Cl⁻]/[OH⁻] ratio instead of the weight percentage of chlorides, the values for 316L would be between 18–25 compared to a ratio of around 20 in the work by Hurley and Scully. The conclusion is thus that the method gives reasonable values with different alkaline solutions and between different research groups and can therefore be used as a comparative and accelerated method for evaluating the corrosion resistance of stainless steel rebar. The present results at room temperature do not even differ significantly from those of Bertolini et al., in spite of the fact that the latter work involved a lower pH and contained no specification of the steels tested. However, at 40°C, the CCTL levels in the present work are lower than those of Bertolini et al.

The evaluation of the dependence of the potential on the measured CCTL revealed that the potential does play a role. Future work will evaluate if +200 mV_{SCE} results in too conservative values for input to predictive models, and if a lower potential should be used instead. Since the corrosion potential of stainless steel rebars are found to be around -200 to -250 mV_{SCE}, the resulting overpotential of around 400 mV, is quite large and may be excessive. This is further exacerbated by the fact that some authors claim that the pore-solution environment itself is more aggressive than the concrete structure. The conservative values are, however, not necessarily a drawback since they easily could be accounted for in a translation from a pore-solution CCTL to a cement-CCTL. This conversion is a further question that needs to be clarified, since pore-solution CCTL values need to be translated into cement CCTL values and there exist few works that has performed the same experiments in both pore-solutions as well as in cement structures. Comparing the values given in reference [5] with the graph in reference [30] gives a conversion factor of around 0.7 for transforming a pore solution-CCTL for pH 12.6 into a cement-CCTL, which also seems to be in agreement in with the results from Sorensen et al. [6] for stainless steel reinforcement. However, this transformation factor needs to be further clarified and understood, also adapted to account for the effect of voids, small cracks and other heterogeneities found in larger cement and concrete structures.

4. Conclusions

In this paper, the CCTL of rebars in different stainless steel designations have been investigated with a potentiostatic method in a synthetic pore-solution. The investigation shows that the critical chloride threshold levels for the grades 304L, 316L and 2304 do not differ to a large extent between the designations, but are in the range of 5–7 wt% chlorides, with the duplex grade 2304 having the highest CCTL at room temperature. Comparing with the values found in literature, the values measured in this work seems reasonable, also considering that this is an industrially produced reinforcement. The method itself has shown to be reliable and efficient. It can therefore be a suitable method to rank stainless steel rebars and give a relatively rapid indication of the corrosion resistance. A possible drawback with the method is that it gives too conservative values to put in predictive models, since it uses a high overpotential to measure the CCTL. This disadvantage could however be easily accounted for when developing conversion factors to compare pore-solution CCTLs to cement-CCTLs.

5. Acknowledgement

Maria Lundberg and Anette Wallin Luukas are gratefully acknowledged for help with specimen preparation and help during the experiments.

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This paper was originally presented as paper 046 at Corrosion and Prevention 2009, Coffs Harbour, NSW, Australia, 15-18 November, 2009, organized by the Australasian Corrosion Association. The permission to republish this paper is highly appreciated.

Corrosion properties of stainless steels as reinforcement in concrete in Swedish outdoor environment

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Abstract

Stainless steels are finding increasing use as reinforcement in repair work with original carbon steel reinforcement as well as new construction in aggressive environments. This work examines the corrosion properties of austenitic stainless steels 304L, 316L and duplex stainless steels, S32101, S32205. Cast-in stainless rebars were tested alone and coupled to carbon steel rebars to investigate the influence on the corrosion rates of the carbon steel. Chlorides were added to the concrete in amounts ranging from 0.3% to 3% by mass of cement. The macro-cell current between stainless steels and carbon steel showed a galvanic effect at the beginning of the exposure but this declined to very low values after some time. No corrosion was detected on any of the stainless steel rebars in contact with the concrete after two years exposure outdoor. Moreover, the coupling of the carbon steel to a stainless steel was seen to only have a minor effect on the corrosion rate of the carbon steel, indicating that the stainless steel acted as a weak cathode in this environment.

Keywords: Stainless steel reinforcement, Chloride-containing concrete, Outdoor exposure, Galvanic corrosion

Introduction

The corrosion of carbon steel reinforcements in concrete structures is the main reason why concrete structures show premature failure. Although the carbon steel should be passive in the concrete structure due to an alkaline pH of 13–14 in the concrete, chloride ions originating from seawater or spread on the roads for deicing can cause corrosion of the carbon steel. The attack can be further aggravated by carbonation, in which carbon dioxide dissolved in the pore water decreases the pH to 9, resulting in an increased sensitivity of the steel to chlorides. The corrosion of the steel reinforcement can result in severe damage of the construction affected necessitating expensive reparation work.

To protect the carbon steel from corroding, techniques such as epoxy coatings and galvanization, have been developed [1]. Although these can give good corrosion resistance, cracks and defects in the coating can cause the corrosion rate to increase appreciably. Stainless steels have therefore become attractive as reinforcement in concrete during recent years, since they have low corrosion rates even in chloride-containing concrete [2]. Despite their higher initial cost compared to the normally-used carbon steel, the total lifetime cost can often be lower, due the lower maintenance cost and extended lifetime resulting from the lower corrosion rates [3]. An even more cost-effective solution can be to limit the use of stainless steels to the areas in which the concrete is contaminated by chlorides.

Although stainless steel shows good corrosion resistance, there have been concerns

about galvanic corrosion of the carbon steel, when used together with stainless steel since the latter has a slightly higher electrochemical potential than carbon steel and may thus act as a cathode in a galvanic couple. Recent findings [4, 5] show however that the use of new passive carbon steel in repair work can be more damaging due to a higher cathodic efficiency of the passive carbon steel compared to the stainless steel.

The stainless steel grades considered as reinforcements have often been 304L, 316L or S32205 [2–7]. The first two have an austenitic microstructure while the third has a duplex microstructure containing both austenitic and ferritic phases. In neutral environments, the corrosion resistance of the three grades is S32205>316L>304L [8] and in seawater, all three grades are likely to suffer from pitting corrosion. At alkaline pHs, for example concrete, the environment is less aggressive, and studies have shown these three grade are corrosion resistant in concrete environments with moderate chloride additions [2, 4, 6, 7]. Although the grades show satisfying corrosion behavior, the initial cost of the stainless steel is still a disadvantage and there is still need for a stainless steel with similar corrosion resistance in concrete structures at a lower cost.

A new duplex stainless steel has been introduced to the market, LDX 2101® (Outokumpu Stainless Trade Name, UNS S32101, EN 1.4162), which has a higher mechanical strength than 304L and 316L, an equal or better corrosion resistance than 304L in chloride-containing environments, and a similar or slightly lower cost. Tests in pore solutions have shown that the corrosion resistance of rebars in this material was similar to 304L [9] and the combination of strength, corrosion resistance and cost makes this stainless steel grade an interesting alternative for use as reinforcement in concrete structures.

This study presents results from a 2-year investigation of four different stainless steel grades used as reinforcements in concrete blocks with various chloride additions and exposed to a Swedish outdoor environment [10]. The concrete blocks contained both stainless steels and carbon steel, both galvanically coupled and non-coupled as well as a reference electrode to measure the individual potentials of the different steels. The concrete blocks were broken apart after one or two years and the corrosion rate was measured and compared to the galvanic currents obtained during the exposure.

Grade, microstructure and chemical composition in weight percent of the stainless steels used

Table 1

Quality (UNS)	Quality (EN)	Microstructure	Cr	Ni	Mn	N	Mo	C	Fe
304L	1.4301	austenitic	18.12	8.64	1.43	0.066	0.31	0.027	bal.
316L	1.4401	austenitic	16.60	11.03	1.45	0.051	2.05	0.017	bal.
S32101	1.4162	duplex	21.49	1.43	4.84	1.430	0.14	0.028	bal.
S32205	1.4462	duplex	22.24	5.32	0.99	0.171	3.13	0.023	bal.

Chemical composition in weight percent of the carbon steel used

Table 2

C	Si	Mn	P	S	Cr	Ni	Mo	Cu	N	Fe
0.122	0.18	0.82	0.016	0.028	0.18	0.20	0.02	0.38	0.041	bal.

Experimental

The evaluated stainless steel (SS) grades, their microstructure and chemical composition are seen in Table 1 and the composition of the carbon steel is seen in Table 2.

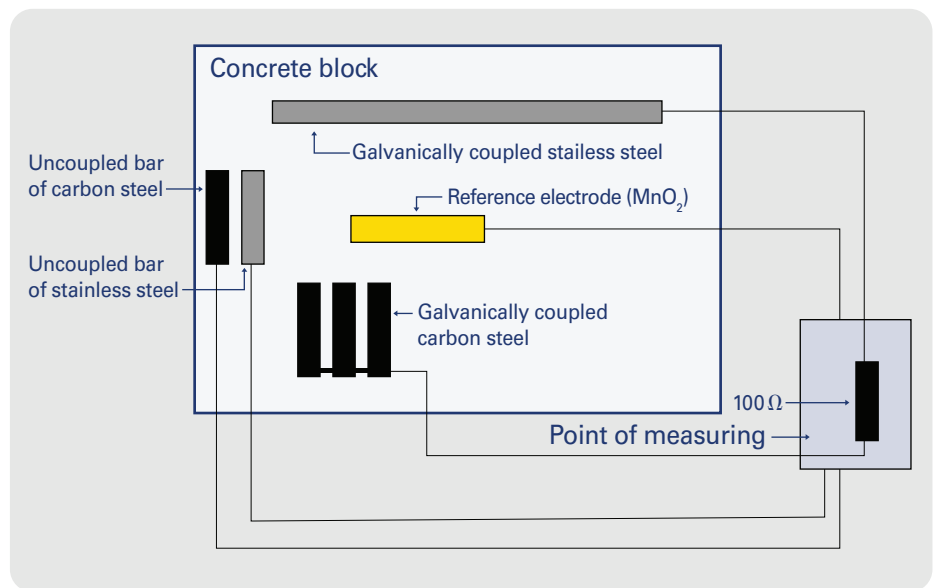
The bars used had a diameter of 10 mm (S32101, S32205, carbon steel) or 16 mm (304L, 316L). The length of the bars was 100 mm (CS, SS) or 300 mm (SS) and all bars were weighed before casting in the concrete blocks.

The concrete used was a repair concrete that was mixed with Stockholm tap water to which sodium chloride was added. Four different chloride concentrations were tested,

ranging from 0.3 to 3 weight percent chloride per kg cement and the chloride content was also measured after the test. The chloride content referred to hereafter will be the chloride content measured after testing. The water cement ratio was 0.5 and the concrete cover had a thickness of 15 mm.

The steels were cast in such a way that both galvanically coupled and uncoupled steel bars were tested at the same time, and a schematic view of the experimental setup is seen in Figure 1. In addition to the steel bars, a MnO_2 reference electrode was put in each concrete block to measure the electrochemical potential of the bars. This reference electrode has an electrochemical potential +0.396 vs. SHE in a saturated $\text{Ca}(\text{OH})_2$ solution [11].

Fig. 1 Experimental setup of the concrete blocks that had a size of 400x280x45 mm



To accelerate carbonation of the concrete blocks, the blocks were exposed to an atmosphere consisting of 99.5% CO_2 for six weeks. The carbonation depth was thereafter measured with a solution of phenolphthalein. Although the concentration of carbon dioxide was much higher than in air (around 400 ppm), the carbonation depth was only a few millimeters, which is believed to be because there is little possibility for carbon dioxide to diffuse in the air-filled pores in wetted concrete. After these six weeks the carbonation process was interrupted and the concrete blocks were exposed to the outdoor environment.

Potentials of both the uncoupled and coupled stainless and carbon steels were continuously recorded with respect to the MnO_2 reference electrode during the exposure time. In addition to the electrochemical potential, the galvanic current density was continuously measured during the two years the concrete blocks were exposed, by measuring the potential difference over a resistor of 100 Ω . To ensure that this did not affect the current density, the current was sometimes measured with a zero-resistance amperometer. Measurements of the potential and galvanic currents were performed continuously, however, during winter the measurements were performed only on days when the outside temperature was above zero.

After one and two years of exposure to Swedish urban environment, the concrete blocks were broken apart and the steels were removed and pickled to determine the weight loss. To completely remove the concrete remains and any corrosion products, the stainless steels were pickled in 20% HNO_3 whereas the carbon steels were pickled in Clark's solution (conc. HCl with addition of 20 g Sb_2O_3 and 60 g $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ per litre).

RESULTS

Uncoupled steels

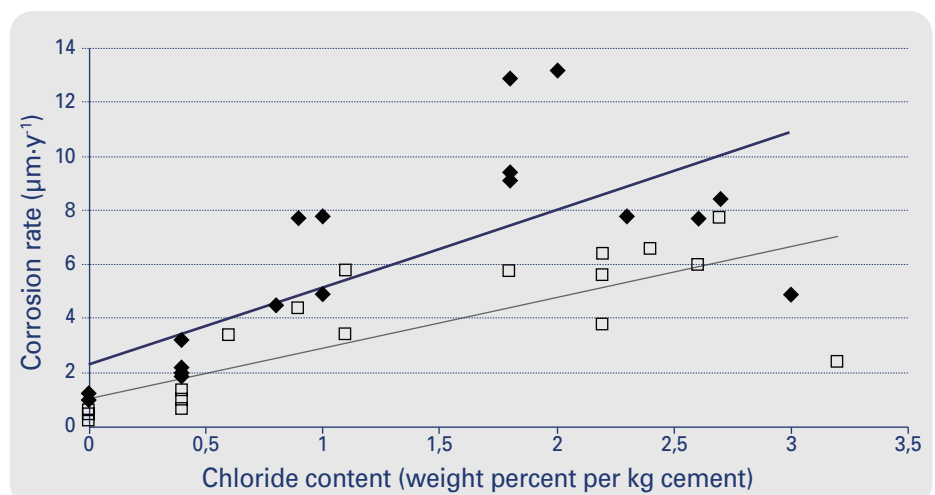
Figure 2 shows photographs of the uncoupled steels at the highest chloride concentrations after 2 years. No corrosion was seen on the uncoupled stainless steels where these were in contact with the concrete. This result was obtained independent of the chloride content, exposure time and stainless steel grade and is due to the high pH of concrete, which substantially increases the corrosion resistance. For comparison, in neutral freshwater systems the maximum chloride concentration that usually is recommended for 304L is around 400 ppm at 20°C [8]. Although this is the limit for which there is no risk for corrosion, and freshwater systems differ from concrete environments regarding oxygenation and stagnation, this gives an idea of the beneficial effect of the high pH. Some corrosion was seen under the protective tube covering the electrical connection. This type of corrosion was only seen on the bars with a larger diameter, and was due to a poor fitting of the tube, which resulted in the formation of a crevice.

Fig. 2 Uncoupled carbon steels (left) and stainless steels (right) after two years in a concrete block with a) 304L and 2.4% chlorides, b) 316L and 2.6% chlorides, c) S32101 and 2.6% chlorides and d) S32205 3.2% chlorides.



For the carbon steels, a small weight loss was observed even in the concrete without chloride additions and this increased with chloride content, as seen in Figure 3. At higher chloride concentrations, the scattering of the data points increased, a phenomenon also seen by others [1].

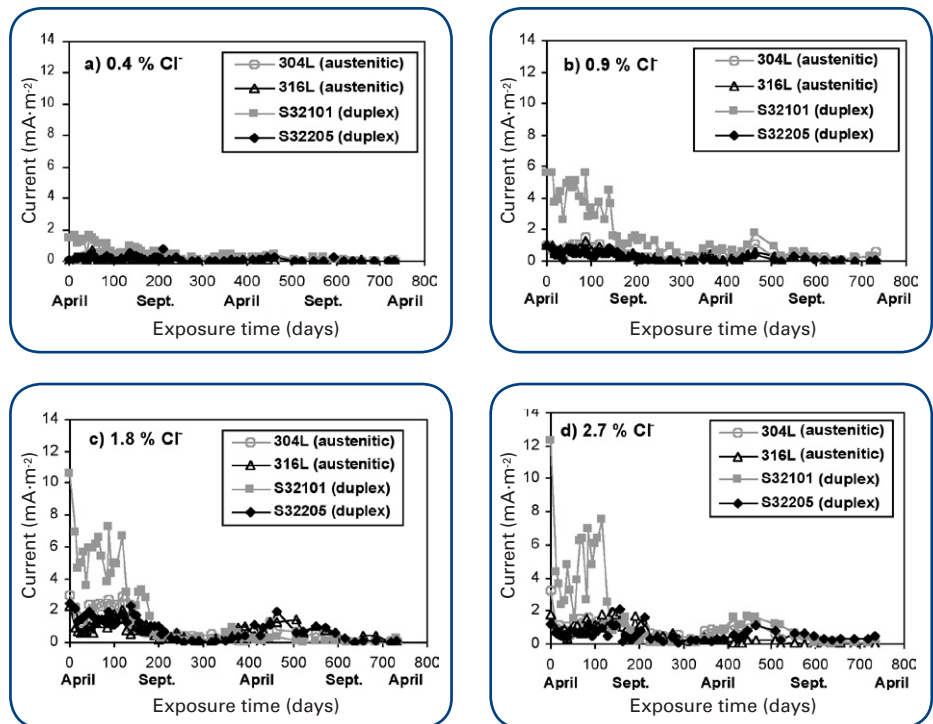
Fig. 3 Corrosion rates of uncoupled carbon steel bars measured by weight loss. Solid black diamonds (◆) with black trend line represent measurements performed after one year while open squares (□) combined with a grey trend line represent carbon steels exposed for two years.



Galvanically coupled stainless and carbon steels

When the stainless steels were electrically connected to carbon steel the corrosion rates of the stainless steels were unaffected. This is because they act as cathodes in this galvanic couple, whereas the carbon steel will act as an anode and corrode. Figure 4 shows the galvanic currents between the stainless steel and the carbon steel during the 2-year exposure. There is an initial macrocell current, especially between S32101 and carbon steel, but the current significantly decreases after the initiation period of 150 days and are thereafter very low for all couples. These results strongly indicate that galvanic corrosion between stainless steel and carbon steel occurs only to a very low extent in these environments.

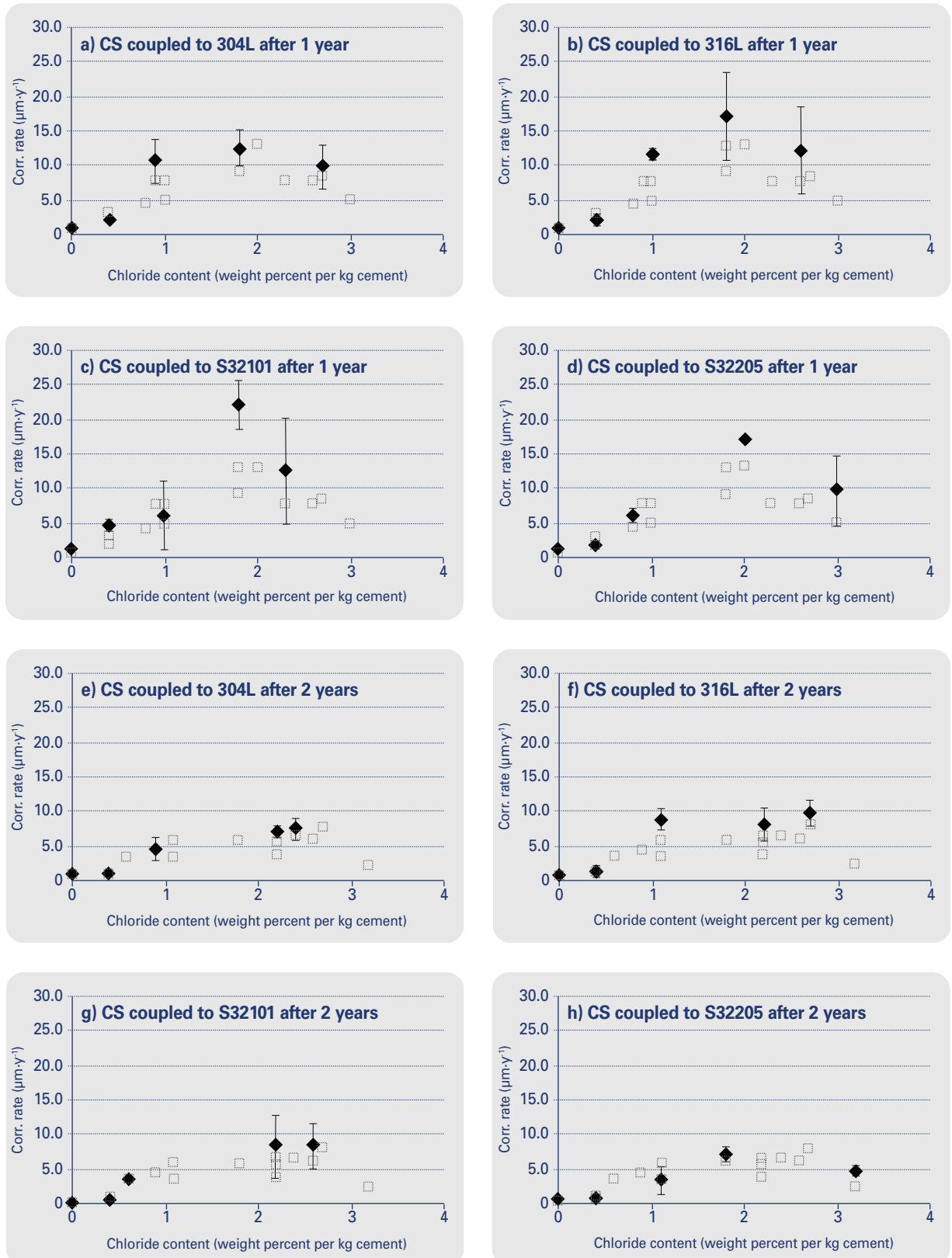
Fig. 4 Macro-cell currents in concrete blocks with carbon steels coupled to different stainless steels, all with a water:cement ratio of 0.5, and a concrete cover of 15 mm.



A significant decrease in corrosion rate during the second year was also observed for the corrosion rates measured by weight loss, as seen in Figure 5. The corrosion rates were for all steels and environments significantly lower for the blocks exposed during two years, compared to the blocks exposed for one year. This correlates well to the current density measurements, which showed higher current densities during the first year that thereafter decreased during the second year. From the corrosion rates determined by weight loss, it could in fact be seen that the 2-year corrosion rate in many cases was half the corrosion rate during the first year, which indicate the corrosion during the second year can be expected to be very close to zero.

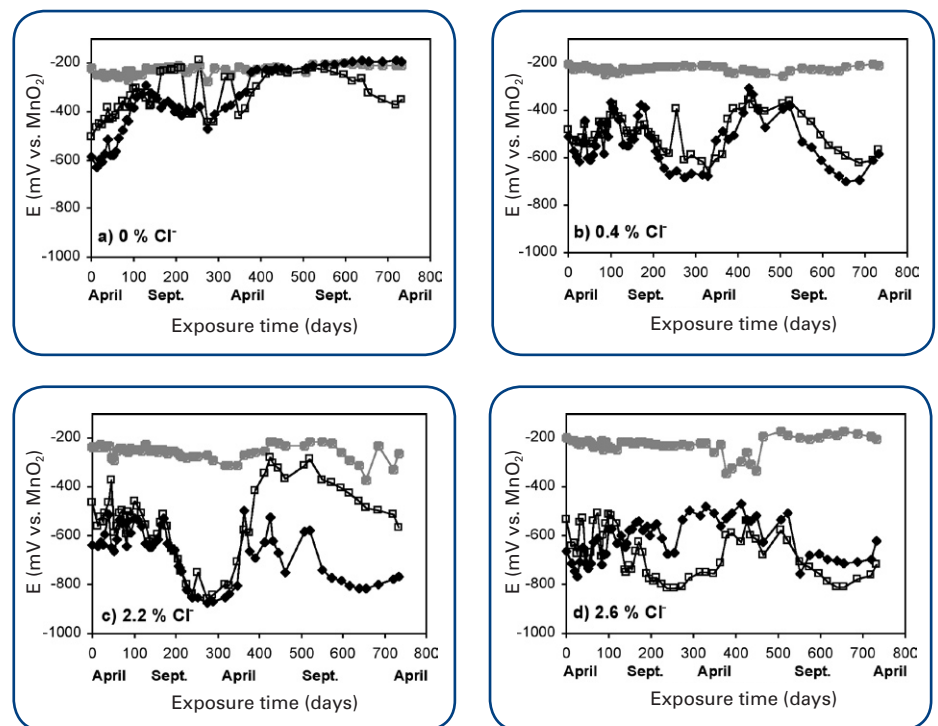
In line with Cui et al. [5] and Bertolini et al. [12], the galvanic coupling of stainless steels to carbon steel was found to affect the corrosion rate only to a very small extent. When comparing the weight losses of both coupled and uncoupled carbon steels, as seen in Figure 5, the corrosion rates are found to be slightly lower for uncoupled carbon steels, but are in most cases within the standard deviation of the galvanically coupled carbon steels.

Fig. 5 Corrosion rates measured by weight loss of carbon steels galvanically coupled to stainless steels. Graphs a–d represent corrosion rates after 1 year while graphs e–h represent corrosion rates after two years. Solid black diamonds (\blacklozenge) show the corrosion rate of carbon steels coupled to stainless steel and open grey squares (\square) represent uncoupled carbon steels. The stainless steel grade to which the carbon steel was coupled is written in each graph.



Open circuit potential measurements versus the MnO_2 reference electrode of the coupled and uncoupled stainless steels, revealed that the potential of the coupled stainless/carbon steel was similar to the potential of the carbon steel bars, as illustrated in Figure 6. The figure shows the results for S32101 but no significant differences between the different grades were found. Since the potential of the coupled SS/CS was similar to the carbon steel itself, it is further evidence that the carbon steel is not significantly affected by the presence of the stainless steel. Combined with the results of the low galvanic currents, seen in Figure 4, it can be concluded that the stainless steel is easily polarized to the potential of the carbon steel without a significant increase of the current density. Only in one case, the block containing 2.2 weight percent chloride per kg cement, the potential of the galvanically coupled steel differed from the carbon steel after 400 days. Although this could have indicated a higher corrosion rate, the galvanic currents and the corrosion rates measured by weight loss does not support that this is the case. When removing the couplings between carbon and stainless steels the potential increased for the stainless steels whereas the potential of the carbon steel slightly decreased. This phenomenon was also reported by Pérez-Quiroz et al. [6] who tested 304 in a solution containing saturated $\text{Ca}(\text{OH})_2$.

Fig. 6 Electrochemical potentials of the stainless steel S32101 (—●—), carbon steel (—◆—) and S32101 and CS galvanically coupled together (—□—). The four graphs show potentials of steels in blocks with different chloride content. All blocks had a water:cement ratio of 0.5 and a concrete cover of 15 mm.



Discussion

The presence of chlorides near the reinforcement is normally a result of a diffusion process, which causes a concentration profile with a higher concentration at the surface and a lower concentration near the reinforcement [1]. At a large depth from the surface there will be only negligible amounts of chloride, even after a long time. This means that stainless steels can be used where the diffused chlorides are present, while carbon steels can be used deeper in the structure, where no chlorides are present. In this study, the chlorides were mixed with the concrete from the beginning, and there was therefore no concentration profile. This is a simplified situation, which eliminates the need to estimate chloride diffusion distances and vary the thickness of the concrete cover and instead allows direct study of the effect of chloride content.

The results indicate that the long-term corrosion behavior of all four stainless steel grades investigated in this study are the same when exposed to Swedish outdoor environment with chloride contents up to 3 weight percent per kg cement. This can be explained by the fact that it is the passive layer that determines the electrochemical potential of the stainless steel as long as the stainless steels are in their passive state. The passive layer mainly contains chromium oxides and the composition does not vary to a large extent between the investigated grades, thus resulting in similar corrosion potentials.

Furthermore, this study shows that the lean duplex stainless steel grade S32101 can be used in chloride-containing concrete construction, confirming earlier indications from pore solution tests [9]. Since S32101 is a duplex grade, it has higher mechanical strength than 304L and 316L, which could be an advantage in some cases. Combined with the similar or slightly lower cost compared to other stainless steels, this makes it an attractive alternative in concrete construction that contains chlorides. Although the macro-cell current between carbon steel and stainless grade S32101 is higher during the first 150 days, the current density thereafter decreases significantly and it is therefore suggested that this process has little impact on the long-term corrosion behavior. The reason for the initial higher current is unclear, and it may be a statistical effect or due to a reduction process connected to the stainless steel grade.

The low galvanic currents measured between carbon steels and stainless steels has been proposed by Bertolini et al. and Cui et al. [5, 12] to be due to the stainless steel being a poor cathode with high overvoltages for the cathodic reaction. This is in line with what has been observed in this study, where low galvanic currents have been measured during the two years (Figure 4) and the potentials of the coupled SS/CS is close to the potential of the carbon steel (Figure 6). These two results imply that the potential difference between the uncoupled and coupled stainless steel does not result in high cathodic currents, a result which is typical for a stainless steel in its passive state.

Finally, the decreased macro galvanic currents after half a year, together with the lower corrosion rates during the second year for both coupled and uncoupled steels, show one of the risks with short-term testing in these environments. Although short-term testing can be valuable to determine certain properties of the reinforcement, it is necessary to perform longer studies in real concrete to be able to predict the corrosion rate after several years.

Conclusions

This study has investigated the corrosion behavior of the stainless steels 304L, 316L, S32101 and S32205 in concrete construction containing up to 3 weight percent chlorides by cement weight that have been exposed to Swedish outdoor environment for two years. Both uncoupled stainless steel bars as well as stainless bars coupled to carbon steel have been investigated. The results show that S32101 has comparable corrosion resistance with the other grades in this environment and that all grades are corrosion resistant. The results also indicate that galvanic corrosion has little influence of the corrosion rate on the carbon steel bars in these environments.

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