Effect of rebar and cement type on the critical chloride content of cementitious materials

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Abstract:
The effects of rebar and cement type on the critical chloride content ($C_{\text{crit}}$) for rebar corrosion initiation were investigated in laboratory experiments. The tested rebars consisted of 'Top12' stainless steel bars (1.4003) with rolling skin, poorly pickled or well-pickled surfaces. Conventional, hot-rolled carbon steel bars (B500B) were tested as the reference in these experiments. The rebars were tested inside mortar samples with either CEM I 52.5R or CEM II/B-M (S-T) 42.5R as binder. The results show that the rebar steel grade as well as the surface quality had a large effect on $C_{\text{crit}}$: For the studied stainless steel rebars with rolling skin, $C_{\text{crit}}$ was about 2 times larger than the one for the carbon steel rebars. For the stainless steel rebars with well-pickled surface, $C_{\text{crit}}$ was about 3 times larger than the one for the carbon steel rebars. The experimental series with CEM II (and, additionally, with much longer passivation times) produced significantly higher $C_{\text{crit}}$-values than those found in the series with CEM I.

The effect of enhanced $C_{\text{crit}}$ (by a factor 2 or 3) on the corrosion-free service life of reinforced concrete is illustrated by DuraCrete-like lifetime predictions using input parameters as defined in Swiss standards. If the ageing factor ($n$) for chloride ingress in concrete is taken as $n = 0$, then a doubled or tripled $C_{\text{crit}}$ leads approximately to a doubled or tripled service lifetime. If the ageing factor $n = 0.45$, then a doubled or tripled $C_{\text{crit}}$ increases the service lifetime by approximately a factor 3 or 7, respectively.

Keywords: Critical chloride content; corrosion; stainless steel; cement type; DuraCrete modelling

Introduction

A means to increase the corrosion-free service life of reinforced concrete in salty environments is to use stainless steel instead of ordinary carbon steel for the first reinforcement layer(s) [1]. Although stainless steel is more expensive than ordinary rebar steel, the total costs over the required service life (i.e., life-cycle costs) may be reduced when the former are used. A higher corrosion resistance of the reinforcement leads to higher durability (corrosion-free service life) with less maintenance and repair costs. Different stainless steel types exist and these vary in price strongly. The question to be answered is how much improvement of rebar corrosion resistance (i.e., which stainless steel grade) would be needed for achieving the lowest life-cycle costs?

The critical chloride content ($C_{\text{crit}}$) is a parameter that expresses the increased durability of concretes containing a rebar type with increased corrosion resistance. $C_{\text{crit}}$ is defined as the chloride concentration in concrete at which corrosion (depassivation) of the reinforcement steel starts. Various service life prediction models used the parameter $C_{\text{crit}}$ as an input parameter [2]. The corrosion resistance of stainless steel bars has been commonly measured by placing the bars directly into a chloride solution that mimics the pore solution in concrete (e.g., [3-6]). Such studies showed that the corrosion resistance of (high-grade) stainless steel is up to an order of magnitude higher than the one for ordinary carbon steel [3].
Measurements of $C_{\text{crit}}$ of stainless steel embedded in concrete or other cementitious materials are less frequently reported. An experimental study of $C_{\text{crit}}$ for different stainless steels with different surface conditions reports values in the range of 1 to 8% by weight of cement [7]. The reference measurements on ordinary carbon steel showed $C_{\text{crit}}$-values of <0.5% under the same testing conditions [7].

In this laboratory study we measured the critical chloride content of a hot-rolled ferritic stainless steel type 1.4003 (called 'Top12' in this paper) with rolling skin or pickled surface embedded in mortar specimens. As a reference experiment, the $C_{\text{crit}}$ of conventional carbon steel rebar was measured parallel to the stainless steels under the same conditions. Apart from the rebar type, also the effect of cement type and passivation time was investigated in this study.

There are a number of discussion points concerning the measurement of $C_{\text{crit}}$ [8]: How should it be measured in the laboratory and to what extent are laboratory measurements of $C_{\text{crit}}$ representative for reinforced concrete structures in the field? The determination of an accurate (absolute) $C_{\text{crit}}$ representing field conditions is surely important for making reliable service life predictions. However, laboratory experiments can also be setup in a way to merely determine relative differences in $C_{\text{crit}}$. Such relative measurements can be used as an input for a DuraCrete-like model to predict the service life improvement as will be shown in the last part of this paper.

**Materials and Method**

**Sample type and test duration**

A wide range of methods have been used to measure $C_{\text{crit}}$ in the laboratory. A review of the available methods and results for $C_{\text{crit}}$ can be found in literature [8]. For normal concrete with conventional rebar carbon steel, experimentally determined $C_{\text{crit}}$-values range between 0.1 and 3% (of binder content), depending on used method and materials [8,9].

At TFB a $C_{\text{crit}}$-method has been developed on the basis of existing techniques (e.g., [9-11]) and our own experiences. The sample type is as follows: A steel bar with a diameter of 10 mm and a length of $\geq$10 cm is embedded in a mortar specimen with a diameter of 30 mm in order to obtain a cover thickness of 10 mm (Fig. 1). One steel end lies in the mortar specimen while the other end extends outside of the sample. Both ends of the steel in the mortar are covered with a 2-layer protection system of a cement paste product (Zentrifix KMH) covered with an epoxy coating to avoid crevice corrosion or corrosion of the cut steel surface. These so-called lollipop-samples were placed in a salt solution and the chloride entered the specimen by diffusion.

Given an anticipated chloride migration coefficient and $C_{\text{crit}}$ for the test mixtures, a cover thickness of 10 mm was predicted to produce a reasonable test duration by using the diffusion error-function (eq. 1 & 2 on page 7). For the mortars with CEM I the 10 mm cover produced actual average test durations of 9 to 60 days for the series with the lowest to highest $C_{\text{crit}}$-values. For the mortar with CEM II the average test durations with a 10 mm cover were underestimated and ranged from 58 to 240 days for the series with the lowest to highest $C_{\text{crit}}$-value. These much longer test durations point towards a strong effect of cement type on the diffusive ingress rate of chloride in the experiments.
Materials
The mortars were standard mixtures prepared according to Swiss standard [12], but with adjusted w/c-ratio and maximum grain size. The mortars were prepared using a high water-cement ratio (of 0.6) to increase the chloride ingress rate (i.e., lower test duration). Standard CEN sand was sieved to obtain the fractions with a maximum grain size of 1 mm, in order to create uniform specimens with a cover/aggregate size ratio of approximately 10.

The tested rebar types were as follows:
• ordinary concrete rebar of hot-rolled carbon steel B500B (Ø = 10 mm);
• Top12 with rolling skin (Ø = 10 mm);
• Top12 with poorly pickled and poorly cleaned surface (Ø = 10 mm);
• Top12 with well-pickled and well-cleaned surface (Ø = 12 mm).

Top12 is a hot-rolled ferritic stainless steel type 1.4003 with approx. 12.2 mass-% chromium and a martensitic-ferritic structure. The Top12 with poorly pickled surface was macroscopically somewhat brown due to incomplete removal of the rolling skin and slightly corroded surface, and/or due to renewed corrosion after pickling. Remains of the pickle liquid may have remained on the surface and have facilitated some minor corrosion. The age of the pickled steel surface at time of the first test series with CEM I was approximately 3 months.

In this first series of experiments, the mortar samples were prepared with ordinary Portland cement (CEM I 52.5R). In the second series the mortar samples contained a CEM II/B-M (S-T) 42.5 R binder with slag and burned shale.

Corrosion experiment
The lollipop samples were cured in a saturated lime solution (without salt) for durations \((t_c)\) of 7-98 days in the first series (CEM I) and 214 or 244 days in the second series (CEM II) in order to develop a passive film on the steel bar in the mortar.

After the preconditioning, the specimens were transferred to a saturated \((\approx 5 \text{ M}_\text{NaCl/l})\) NaCl- and lime solution at constant temperature. The solution was refreshed once per month and salt precipitates on the specimen surfaces removed. The chlorides entered the specimens by diffusion.
The passivation/depassivation state was monitored by a continuous measurement of the open circuit potential. The reference electrode for the measurements of potential was a silver/silver-chloride electrode (SSE). The onset of corrosion (depassivation) was indicated by a large drop in potential (in the range of 100 to 300 mV).

At the point of depassivation, the samples were taken out of the solution and dried at 50°C for 2 hours. Subsequently, the steel was detached from the mortar by splitting the sample into several parts. All samples steel and mortar surfaces were checked for corrosion signs under a microscope. Rebars with corrosion pits or rust were photographed.

**Chloride content measurement**

The chloride concentration surrounding the steel bars was measured from a powder sample that was collected by grinding off the rib texture on the mortar surface. The ribs contained between 1.2-1.6 gram mortar, a sample amount that was sufficient for chloride content measurement using XRF in compliance with a Swiss standard [13].

The chloride content measured is the weight fraction of the mortar material in the ribs. It is common to calculate the chloride content as a weight percentage of the cement content in mortar or concrete. Since compositional gradients exist at contact surfaces (due to wall effects), the chloride content could not be simply calculated from the mixture composition. In this study the actual cement paste content of a number of ribs in two samples was determined as explained below. It was assumed that this content is equal for all samples with the same added w/c-ratio and sand content.

The sand content in ribs was measured by means of image analyses of scanning electron microscopy images (Fig. 2). The ribs contain an average 31.6 vol-% quartz sand and 68.4 vol-% cement paste, which correspond to 41.8 and 58.2 weight-%, respectively (for a mortar with quartz sand and a w/c-ratio of 0.6). It follows that the cement content of the mortar ribs was 36.4 weight-%. The measured chloride contents in the mortar therefore was multiplied by a factor 100/36.4 = 2.75 to obtain the approximate chloride content as a percentage of the binder weight.

**Fig. 2:** (a) SEM-BSE image of a rib cross-section with sand consisting of predominantly quartz. (b) Rib with sand grains and air-bubbles highlighted in white, the remaining material being cement paste with hydration products, unhydrated cement and capillary porosity.
Results and Discussion

The measured $C_{\text{crit}}$-values for the four steel types and two cement types are presented in Fig. 3. Two samples from the CEM II series (#4 with rolled skin rebar, and #3 with well-pickled rebar) showed a (very) early drop in potential, but no signs of corrosion. We believe that the recorded potential drop was an artefact and excluded these two measurements from the series average. The results are then as follows:

- For the samples with the same or similar passivation time ($t_c = 212-244$ days) and CEM II, the average $C_{\text{crit}}$ of the Top12-steel with well-pickled surface was a factor 3.4 larger than $C_{\text{crit}}$ for ordinary carbon steel. The Top12 with rolled skin or poorly pickled surface had a $C_{\text{crit}}$ of 2.2 or 2.3 times larger, respectively, than the one for the carbon steel rebar.

![Fig. 3. Effect of rebar type on the critical chloride content as measured in mortar samples using CEM I (top diagram) or CEM II/B-M (S-T) 42.5 R (bottom diagram).](image)
• The samples with CEM I showed a similar trend as was seen for CEM II samples, but the differences between the first and last two series was larger in the CEM I experiments. This could (partly) be a result of the difference in passivation time (7 & 22 days versus 98 days). Longer passivation may lead to relatively larger \( C_{\text{crit}} \)-values due to the formation of a thicker or more stable passivation film on the steel surface. Steel passivation is a time-dependent phenomenon [14].

• If passivation time \( (t_c) \) has an effect on \( C_{\text{crit}} \) then this effect could possibly also explain the absolute differences observed between the corresponding series in the CEM I and CEM II experiments. That is, the higher \( C_{\text{crit}} \)-values for the CEM II samples are a result of the longer passivation times. The difference in cement type (CEM I vs. CEM II) may also have contributed to the differences in \( C_{\text{crit}} \) observed between both series. However, for CEM II mortar lower instead of higher \( C_{\text{crit}} \)-values are possibly to be expected, since the pore solution in CEM II mortars is expected to be less alkaline [15].

• An outlier of the general trends observed in these experiments is the series of poorly pickled and poorly cleaned steel with CEM II, by not having a systematically higher \( C_{\text{crit}} \) as for the other rebar types with CEM II. A possible explanation is that the poorly pickled and poorly cleaned Top12 surfaces were contaminated by the pickling liquid that slowly degraded the steel surface over time. The CEM II series started about a year after the start of the CEM I series.

The obtained \( C_{\text{crit}} \)-values for conventional rebar carbon steel are higher (by a factor 2 to 3) than the values commonly used in technical specifications and standards [16]. The measured \( C_{\text{crit}} \)-values do compare to those reported in other studies (e.g., [8,17]). There could be a number of reasons why laboratory measurements of \( C_{\text{crit}} \) are higher than those measured directly in the field. The quality of laboratory concretes can be unrealistically good (without defects), and environmental effects like drying and carbonation do usually not occur in laboratory experiments. It has also been suggested that a size effect (i.e., steel sample length) has an effect on the magnitude of \( C_{\text{crit}} \) and leads to an overestimation of \( C_{\text{crit}} \) in the laboratory if short steel samples are used [17]. Moreover, the effect of cold-rolled versus warm-rolled steel is expected to be important (conf. [18]), and needs to be considered when laboratory and field results are being compared.

The difference in \( C_{\text{crit}} \) for hot-rolled carbon steel and hot-rolled Top12 (without pickling) was a factor of about 2 in both series (CEM I + short \( t_c \) and CEM II + long \( t_c \)). The factor 2 was also found for these rebar types in solution experiments [19,20].

After the experiments, all steel rods and surrounding mortar were checked for corrosion signs under a microscope. From the 40 tested samples there were 22 showing a clear isolated corrosion pit with the formation of black and red rust (Fig. 4). Since the rust penetrated the mortar material, these corrosion pits and products are clearly related to the depassivation of the rods in the chloride solution. The other samples did not show clear pitting or rust, but only small superficial roughness or corrosion patches that in some cases may have been pre-existing.
Fig. 4. Example of clear corrosion signs in the Top12 rebar with rolling skin (sample #1) at the moment of depassivation. (a) Corrosion products on the mortar surface (black/red rust); (b) Corrosion pits and corrosion products on the steel surface.

**DuraCrete Modelling**

The results showed an important effect of reinforcement steel type and surface processing on the critical chloride content ($C_{\text{crit}}$) in mortar specimens. The critical chloride content of Top12-steel with rolling skin was approximately twice as large as the one for conventional rebar steel. For a Top12 with a well-pickled surface, $C_{\text{crit}}$ was roughly 3 times larger than the one for the conventional rebar. How much does the increased critical chloride content (by a factor 2 or 3) increase the corrosion-free service life of reinforced concrete in salty environments? This was calculated by using a DuraCrete-like prediction model for chloride ingress in road environments with deicing salts [16].

The basis of many chloride ingress models for concrete is the solution of Fick’s second law under the assumption of constant diffusion coefficient ($D$) and chloride surface concentration ($C_s$), i.e., the error-function solution:

$$C(x,t) = C_{x,\text{app}} \cdot \text{erfc} \left( \frac{x}{2 \sqrt{D_{\text{app}} t}} \right)$$  \hspace{1cm} (1)

$D$ and $C_s$ are referred to as apparent diffusions coefficient ($D_{\text{app}}$) and apparent surface concentration ($C_{s,\text{app}}$) in these prediction models, since these parameters are not time-independent in reality.

In the DuraCrete-approach, $D_{\text{app}}$ is calculated for a given exposure duration using the following expression:

$$D_{\text{app}} = K \cdot M_{28d} \cdot \left( \frac{t_0}{t} \right)^n$$  \hspace{1cm} (2)
with $M_{28d}$ being the chloride migration coefficient at a concrete age of 28 days (as measured in the laboratory). The time $t_0$ is the reference time (in years) at which $M$ is measured ($t_0 = 28$ days) or the age of first chloride exposure. The time $t$ is the exposure period in years. The correlation factor $K$ is a constant that links the experimentally measured $M$ to field performance ($D_{app}$). The factor $n$ is the ageing factor, describing how the apparent diffusion coefficient of a field concrete changes with time.

The effect of $C_{crit}$ on the calculated corrosion-free lifetime is shown in Table 1. For these calculations a maximum migration coefficient of $10 \cdot 10^{-12} \text{ m}^2/\text{s}$ as defined by Swiss standard SN EN 206-1 [21], and chloride surface content of 0.4% by concrete mass was used. This surface chloride content represents a relatively strong chloride supply in road environments with deicing salts [16]. The ageing factor $n = 0.45$ follows from benchmarking the above model to the results of various field experiments adjacent roads [16]. Note that the calculations in Table 1 are based on the common practical standard $C_{crit}$-value of 0.05% by concrete mass ($\approx 0.4\%$ by binder mass) for conventional carbon steel rebar, and not the (absolute) laboratory values presented in Fig. 3.

In the hypothetical case of no chloride ingress ageing ($n = 0$), the corrosion-free lifetime increases almost linearly with $C_{crit}$ for the investigated cases. In case of an ageing factor $n = 0.45$ for CEM I concrete, lifetime is an exponential function of $C_{crit}$: Doubling of $C_{crit}$ leads to an approximately three times larger lifetime, whereas a three times larger $C_{crit}$ leads to an approximately 7 times larger lifetime.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>CEM I without ageing</th>
<th>CEM I with ageing</th>
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<tbody>
<tr>
<td>$M_{28d} \left(10^{-12} \text{ m}^2/\text{s}\right)$</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>correlation factor $K$</td>
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<td>0.5</td>
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<tr>
<td>ageing factor $n$</td>
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<td>0</td>
</tr>
<tr>
<td>$C_{s,app}$ (% of concrete weight)</td>
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<td>0.4</td>
</tr>
<tr>
<td>time to reach $C_{crit} = 0.05%_{con}$</td>
<td>1.2 years</td>
<td>3.4 years</td>
</tr>
<tr>
<td>time to reach $C_{crit} = 0.10%_{con}$</td>
<td>2.2 years</td>
<td>6.0 years</td>
</tr>
<tr>
<td>time to reach $C_{crit} = 0.15%_{con}$</td>
<td>3.6 years</td>
<td>10.1 years</td>
</tr>
<tr>
<td>Lifetime increase by doubling of $C_{crit}$</td>
<td>x 1.8</td>
<td>x 1.8</td>
</tr>
<tr>
<td>Lifetime increase by tripling of $C_{crit}$</td>
<td>x 3</td>
<td>x 3</td>
</tr>
</tbody>
</table>

**Conclusions**

- The differences observed between the two experimental series with CEM I and CEM II seem to be better explained by the differences in passivation time (i.e., curing time before chloride exposure), rather than by the difference in cement type.
• The experimental durations to achieve depassivation were significantly longer in the CEM II series, and this suggests that there was a significant effect of cement type on the chloride ingress rate and/or chloride binding.

• For the series with CEM II, the curing (waiting) time before chloride exposure was long (approx. 8 months) and equal for all steel types. Under these conditions, the critical chloride content ($C_{crit}$) of the well-pickled Top12-rebar was a factor 3.4 times larger than for the conventional carbon steel rebar. Potentially, this larger corrosion resistance can lengthen the corrosion-free service life of reinforced concrete by a factor 7 compared to conventional rebars.

• The experiments showed that a well-pickled and cleaned Top12 rebar surface produced a significantly better and more robust corrosion resistance compared to Top12 rebars with no or poorly pickled (and cleaned) surface.

References


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