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# A method for measuring the chloride threshold level required to initiate reinforcement corrosion in concrete

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## ABSTRACT

Information on the chloride threshold level that is necessary to initiate corrosion of steel reinforcement in concrete is required for service life calculations and performance testing of concrete. This paper proposes a method for determining the chloride threshold level causing the corrosion of steel in concrete. The method takes into account the need for accelerated chloride ingress and limitation of possible corrosion of steel parts not intended to act as anode.

## RÉSUMÉ

*Le niveau de chlorures au-delà duquel la corrosion des armatures en acier est déclenchée dans le béton renforcé, est un paramètre dont la connaissance est nécessaire aussi bien lors de la conception, que des essais de performance du béton. Une méthode de détermination de ce seuil est proposée dans cet article. La méthode tient compte à la fois de l'accélération induite du flux d'ions chlorure et des limitations liées à une possible corrosion de l'acier.*

## 1. INTRODUCTION

The prediction of service life for a reinforced concrete structure exposed to chlorides requires knowledge of the chloride ingress rate as well as the chloride concentration at which reinforcement corrosion is initiated; the so-called critical chloride concentration or chloride threshold level [1, 2]. Considerable research has been carried out on factors affecting the chloride transport in concrete with the aim of predicting the chloride ingress rate. However, limited research has been published on factors affecting the chloride threshold level for steel reinforcement in concrete [3-5].

Methods for determining chloride threshold levels have been the subject of a number of research projects [6-8]. However, no standard method for the determination of chloride threshold levels has been established. The current trend towards performance requirements, calls for a reliable test method.

One of the experimental difficulties to be dealt with is the time needed to obtain a critical chloride concentration at the depth of the reinforcement. This time can be long, even though the concrete cover of the test specimens is reduced to a thickness of only 5 mm. Furthermore, the chloride ingress rate during exposure is often significantly decreased by formation of a dense impermeable layer of calcium carbonate at the exposed surfaces [9].

In earlier attempts to determine chloride threshold levels these experimental difficulties have been dealt with by adding chlorides to the initial concrete mixture. Later, after recognizing that this method may result in erroneous results, strong saline solutions (compared with sea water) have been used as exposure solution in order to accelerate the chloride ingress, sometimes combined with cyclic wetting and drying. Electrical potential gradients have also been used to accelerate the chloride ingress [7]. However, none of these approaches have resulted in an approved standardized method that can be used to determine reliable chloride threshold levels within a reasonable test period, when a concrete relevant for marine structures is used.

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*Prof. Mette R. Geiker is a RILEM Senior Member. She participates in RILEM TCs 189-NEC 'Non-destructive evaluation of the 'covercrete' (concrete cover)', 196-ICC 'Internal curing of concretes' and RFC 'Rheology of cement based materials such as fresh concrete'.*

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Another issue of concern is the unwanted corrosion attacks that are often initiated at parts of the test specimens not intended as anode (protruding reinforcement bars, electrical connections, etc.) as a result of long exposure times often combined with strong saline exposure solutions.

This paper presents a method for determination of chloride threshold levels, for which these experimental difficulties have been dealt with. The method was developed as part of a recent study on the effect of steel-concrete interface defects on the chloride threshold level for reinforcement corrosion in concrete [10].

## 2. EXPERIMENTAL CONSIDERATIONS

The test method is based on: a) corrosion activity monitoring of the steel bars in reinforced concrete specimens subjected to accelerated chloride ingress. b) determination of the chloride concentration in the concrete adjacent to the corroding steel bars at the time of corrosion onset *i.e.*, the chloride threshold level. In order to determine chloride threshold levels within a reasonable test period the earlier encountered experimental difficulties (see introduction) are solved as follows:

- Accelerated chloride ingress is obtained by first subjecting the test specimens to drying in a controlled climate after which the specimens are exposed to a saline solution allowing capillary suction of the solution as illustrated in Fig. 1. As accurate chloride threshold levels can not be determined during capillary suction due to the fast moving chloride front, the rapid chloride ingress should be limited to the concrete cover, *i.e.* chlorides should not reach the reinforcement at a critical level during the capillary suction. By using this method the problem with formation of a dense impermeable calcium carbonate layer, due to otherwise long exposure times, is also solved.
- Unwanted corrosion attacks are avoided by the design of the test specimens used (see Figs. 2 and 3), which effectively restricts the access of saline exposure solution to the protruding ends of the steel bars. Furthermore, an epoxy coating is applied to the protruding ends and all non-exposure surfaces (after drying) in order to further minimise the risk of crevice corrosion at the protruding ends and electrical connections.

Although the moisture profile after the drying in a controlled climate can be determined, it may not be possible to accurately predict the chloride profile that would be obtained from the capillary suction of the saline solution. Therefore, test specimens with different concrete covers are used in order to obtain a range of chloride concentrations from "above threshold" (*i.e.*, certain corrosion) to "below threshold" (*i.e.*, no probability of corrosion) at the depth of the steel bars after the capillary suction has ceased. Based on [11] the target chloride content at the depth of the steel bars with the smallest cover "above threshold" should not be lower than 0.2 mass percent of sample whereas the chloride content at the depth of the steel bars with largest cover "below threshold" should not be higher than 0.05 mass percent of sample (see Fig. 1). Using this method, rapid chloride ingress limited to the cover is obtained by capillary suction, after which chloride ingress until corrosion onset is caused by a transport mechanism approximating diffusion.

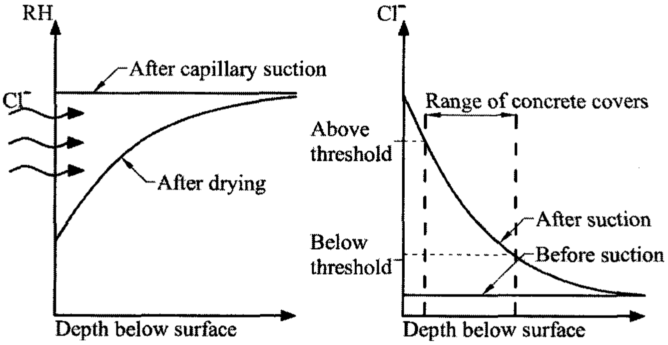

Fig. 1 - Schematic illustration of the effect of conditioning on the relative humidity and chloride profiles.

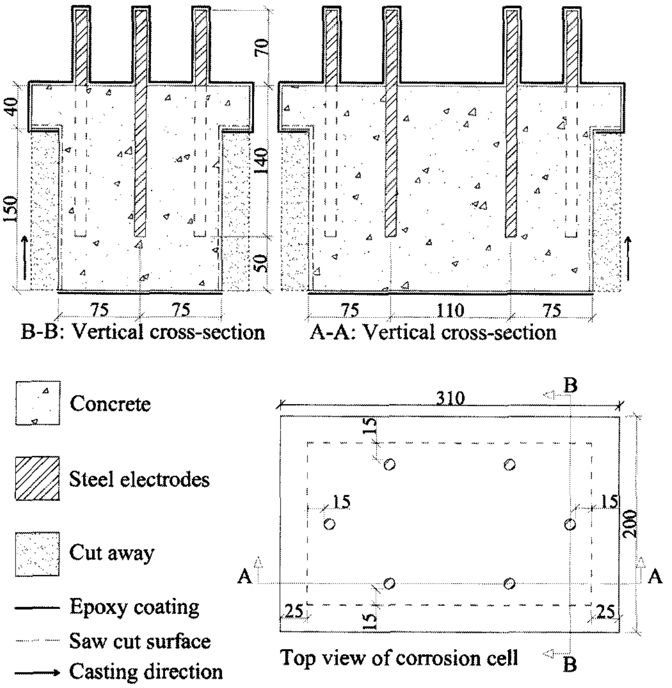

Fig. 2 - Geometry of the corrosion cell (here shown with a concrete cover of 15 mm). All measures are given in mm. The steel electrodes are exposed to chloride from the saw cut surfaces.

## 3. MATERIALS AND MANUFACTURE OF TEST SPECIMENS

The geometry of the test specimens (referred to as corrosion cells in the following) is shown in Figs. 2 and 3d. Each corrosion cell consisted of a concrete specimen with six 10 mm diameter smooth reinforcement bars (referred to as steel electrodes in the following) with a length of

210 mm of which 140 mm was embedded in the concrete specimen. The chemical composition of the steel electrodes is given in Table 1.

The corrosion cells were cast upside down as box shaped specimens (310 × 200 × 190 $mm^3$) with a cover thickness of 40±0.1 mm. The accurate positioning of the steel electrodes was secured by fixing the steel electrodes in the bottom plate of the moulds (see Fig. 3a).

A concrete with a w/c of 0.45 was selected for the experiment. The mix composition and selected properties are given in Table 2. The cement used was white Portland cement (CEM I 52.5) with the Bogue composition given in Table 3.

After casting the corrosion cells were stored in the moulds for one day at 20°C, demoulded and cured at 20°C in curing tanks with saturated lime for seven days and subsequently at 30°C until a maturity of 28 days was obtained. The maturity equivalent to the age at 20°C was calculated from the maturity function presented in [12] and activation energy of 22 KJ/mol [13].

## 4. PREPARATION AND CONDITIONING OF TEST SPECIMENS

After curing, the lower 150 mm of the concrete cover was reduced by diamond cutting. Corrosion cells with a concrete cover of 5, 10, 15, 20 and 25 mm were produced (see Figs. 2 and 3c). By removing minimum15 mm of the outermost concrete from the cast surfaces, the concrete between the saw cut exposure surface and the steel electrodes should be approximately similar to the bulk concrete. The uppermost 40 mm of the cover was not cut off in order to increase the distance from the protruding steel electrodes to the nearest chloride exposed surface and hereby preventing unwanted corrosion attacks (crevice corrosion) at the protruding ends of the steel electrodes.

The saw cut corrosion cells were placed in a drying chamber at 22±5 % RH and 30±1 °C. Selected additional dummy corrosion cells were mounted with RH sensors in drilled holes at a depth of 5, 10 and 20 mm below the saw cut surface allowing monitoring of the RH profile in the concrete during the drying. Based on an estimation of the empty pore space as a function of RH, which would be available for subsequent filling with saline solution by capillary suction, the specimens were kept in the chamber for 60 days until an RH of approximately 60 % was measured at a depth of 10 mm below the saw cut surface.

After drying, RH profiles were determined as function of depth below the exposure surface by sampling concrete from selected dummy corrosion cells by means of hammer and chisel. The RH of the samples was measured in RH measuring cells at 30±0.1 °C immediately after sampling.

Wires were connected to the protruding steel electrodes after which all non-exposure surfaces, the protruding steel electrodes and the wire connections were coated with a transparent chloride proof epoxy resin allowing visual examination of the protruding steel electrodes (see Fig. 3d).

**Table 1 - Reinforcing steel composition [mass %]**

| C | Si | Mn | P | S | Fe |
|---|---|---|---|---|---|
| 0.13 | 0.18 | 1.3 | 0.009 | 0.015 | Re. |
| Cr | Ni | Cu | Al | N | |
| 0.04 | 0.03 | 0.02 | 0.001 | 0.004 | |

Note: Re. = Remaining

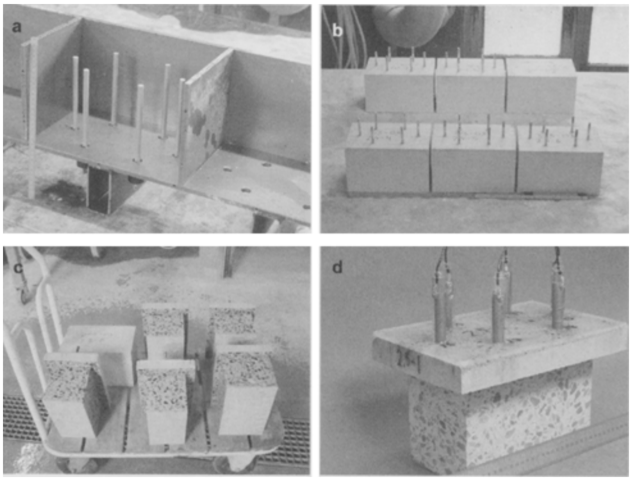

Fig. 3 - Production of corrosion cells: a: The steel electrodes are fixed in the bottom plate of the mould before casting (mould side removed for better view). b: Five corrosion cells and a "dummy" specimen after demoulding. c: Specimens after reducing the cover by diamond cutting. d: Specimen with wires and epoxy coating – ready for exposure.

**Table 2 - Mix design and selected properties of the concrete**

| Component | Amount | Unit |
|---|---|---|
| Cement | 319 | $Kg/m^3$ |
| Water | 144 | $Kg/m^3$ |
| Aggregate (0-16 mm) | 1863 | $Kg/m^3$ |
| Air content* | 9 | Vol.% |
| Compressive strength** | 34 | MPa |

* In accordance with EN 12350-7.

** At the age of 28 maturity days in accordance with EN 12390-3.

**Table 3 - Bogue composition of cement [mass %]**

| $C_3S$ | $C_2S$ | $C_3A$ | $C_4AF$ |
|---|---|---|---|
| 64.0 | 23.0 | 4.5 | 1.0 |

The corrosion cells were then exposed to a saline solution containing 0.165 kg NaCl per litre solution, corresponding to 10 mass percent $Cl^-$. The corrosion cells were immersed to a depth corresponding to the height of the exposure surfaces. A ratio of approximately 2.5 between the exposed area ($m^2$) and the volume of the saline solution ($m^3$) was used for the exposure. The duration of the capillary suction was determined by monitoring the weight gain of selected dummy corrosion cells. When a mass change of less than 0.01 mass percent per day relative to the weight of the immersed specimen was obtained, the capillary suction was defined as stopped and the corrosion cells as re-saturated.

RH and chloride profiles were determined after the capillary suction: RH profiles by sampling concrete as described above and chloride profiles by profile grinding in

2 mm steps and Volhard titration of the powder samples in accordance with NT Build 208 [14]. Thin sections of the cover concrete were prepared and investigated by petrographic examination before and after the drying in order to determine for possible adverse effects of the drying.

## 5. TESTING

The testing was started four days after the corrosion cells were placed in the saline solution for re-saturation by capillary suction. The corrosion activity of each steel electrode was monitored by potentiostatic control. The steel electrodes were maintained at a potential of 0 mV SCE during the test period, hereby limiting the influence of the applied potential on the determined chloride threshold levels as shown in [5]. Here it was found that the chloride threshold is independent of the potential for values ranging from +250 to -250±50 mV SCE whereas for potentials lower than -200±50 mV SCE the threshold progressively increases with decreasing potential. A Mixed Metal Oxide (MMO) titanium mesh and a SCE electrode were employed as a counter and reference electrode respectively. Both electrodes were placed in the exposure solution.

The current applied to maintain the steel electrodes at their fixed potentials was recorded on an hourly basis during the test. The current was in the range of 0-10 μA when the steel electrodes were in the passive state and increased abrupt when corrosion was initiated. Corrosion initiation was defined as an increase to more than 50 μA. During the test no activation-repassivation cycles were observed before stable active corrosion was initiated contrary to what has been observed by others [3].

When corrosion was initiated, the corrosion cell containing the respective steel electrode was removed from the test setup and the part of the corrosion cell containing the corroding steel electrode was removed by diamond cutting (See Figs. 4a, b). A typical pit initiation observed when removing the steel electrodes is shown in Fig. 5.

The remaining corrosion cell was reconnected to the test setup and placed in the saline solution for further exposure. The cut out section (approximately 100 × 100 × 50 $mm^3$) was opened by cutting two tracks along the steel electrode after which the back of the section was removed allowing visual examination of the steel electrode.

In order to determine chloride threshold levels for design purposes (as used in *e.g.* [1]) the approach in [8] was used; the chloride threshold level was defined as the chloride concentration in the infinitesimal layer at the depth of the reinforcement in the bulk concrete at the time of corrosion onset. The chloride threshold levels were therefore determined by grinding off material on each side of the steel electrode at the cover depth ±0.5 mm parallel to the steel electrode *i.e.* a layer of 1 mm was ground off (see Fig. 4c). A sample of approximately 5 g of dry powder was obtained from each side. The chloride content was determined by Volhard titration in accordance with [14] (mass percent of sample) and potentiometric titration as described in [15] (mass percent of binder).

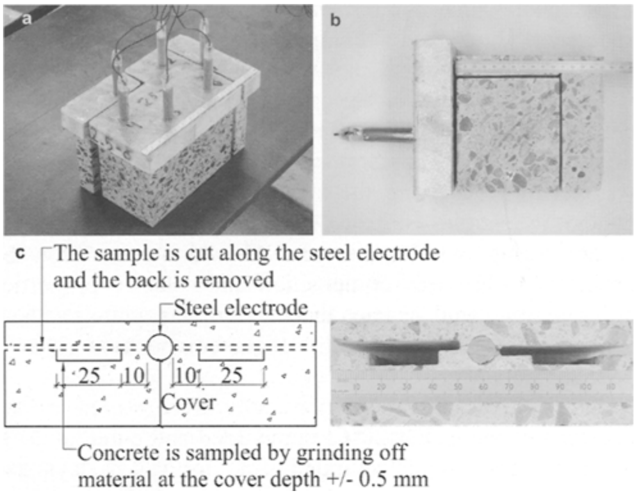

Fig. 4 - Sampling after corrosion initiation: a: Two steel electrodes are removed. b: The middle section is cut out. c: The back of the section is cut loose, removed and material ground off on each side of the electrode for chloride analysis.

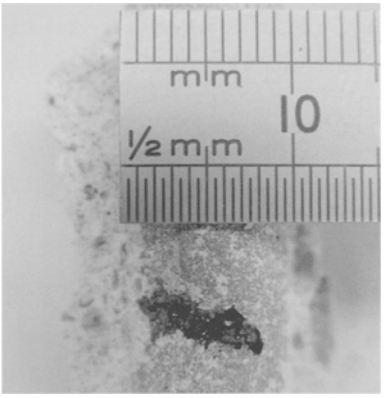

Fig. 5 – Typical corrosion pit on a steel electrode removed from a corrosion cell immediately after detection of corrosion initiation. The pit is faced towards the exposure surface *e.g.* the concrete surface (the back of the electrode is covered with hunks of concrete).

## 6. RESULTS AND DISCUSSION

The cumulative weight of the solution absorbed, recorded until the capillary suction had stopped is presented in Fig. 6. The RH profiles determined before and after the capillary suction are presented in Fig. 7 and the chloride profiles determined after the capillary suction in Fig. 8.

The cumulative rate of absorption decreased to a low level after approximately 150 hours (~6 days) and was defined as stopped after 216 hours (~9 days) where an absorption rate below 0.01 mass percent per day (corresponding to $7\times10^{-3}$ $kg/m^2\times day$) was recorded.

However, after determination of the RH profiles it was revealed that the corrosion cells were not fully re-saturated throughout the depth of the concrete at the time of investigation (see Fig. 7). Although the absorption had decreased to a low level, a further but slow inward moisture flow would be expected, moving the chlorides deeper into the concrete.

The decreasing degree of saturation through the depth of the concrete is assumed to be caused by entrapped air; the entrapped air is slowly dissolved in the pore solution resulting in further, but slow solution absorption. After being dissolved in the pore solution, the air is transported by diffusion first to the larger pores and subsequently to the concrete surface [16].

Comparing the RH profiles with the obtained chloride profiles it is observed that although the RH in the concrete was affected to a depth greater than 60 mm below the exposed surface, the chloride content in the concrete had only been affected to a depth of approximately 20 mm. The depth of the ingress and the distribution of chlorides after the capillary suction are mainly subscribed to the amount of saline solution absorbed. However, chloride binding is assumed to be another contributing factor causing a gradual decrease in the chloride concentration of the saline solution during the capillary suction [17, 18].

As expected, corrosion was initiated on the steel electrodes with a "thin cover" during the capillary suction. Before the capillary suction had stopped, corrosion was initiated at the steel electrodes with a concrete cover of 5, 10 and 15 mm, whereas the steel electrodes with a cover of 20 and 25 mm were still in the passive state (see Table 4).

Thus, a shorter drying period could have been used providing more electrodes for corrosion measurements (or the need for a smaller range of covers) and reducing possible adverse effects of drying and re-saturation.

With the method used chloride threshold levels were determined within a period of 130 days including casting and curing, even though a concrete quality of "practical relevance" was used (*i.e.*, realistically low w/c). This was only obtained as a result of the method used to accelerate the chloride ingress. Furthermore, unwanted corrosion was avoided by the design of the corrosion cells used.

However, as for any other accelerated method the possible adverse effects of the conditioning, mainly the drying, should be considered. From the petrographic examination of the thin sections made before and after the drying it was found that the drying had resulted in a carbonation depth of only 0.7 mm below the exposure surfaces. Furthermore, no signs of crack formation or other defects were found. Although no significant adverse effects were found in the examinations, it is assumed that the drying has resulted in an increase in larger pores at expense of the smaller pores, *i.e.*, a "coarsening of the pore system" [19].

Another effect of the drying and subsequent re-saturation is that the amount of air filled pore space is increased due to incomplete re-saturation. As described in [4] air voids in the steel-concrete interface zone decreases the chloride threshold level, increasing the probability of corrosion.

**Table 4 - Exposure time till corrosion initiation**

| Concrete cover [mm] | Time to corrosion [days] |
|---|---|
| 5 | < 4 |
| 10 | < 4 |
| 15 | 4-7 |
| 20 | 31-50 |
| 25 | -* |

* Corrosion was not initiated within the test period.

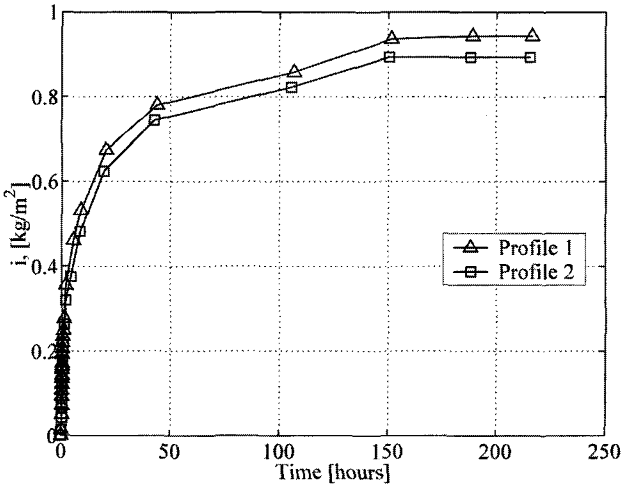

Fig. 6 - Cumulative absorption of the saline exposure solution during re-saturation of the corrosion cells by capillary suction (two independent profiles).

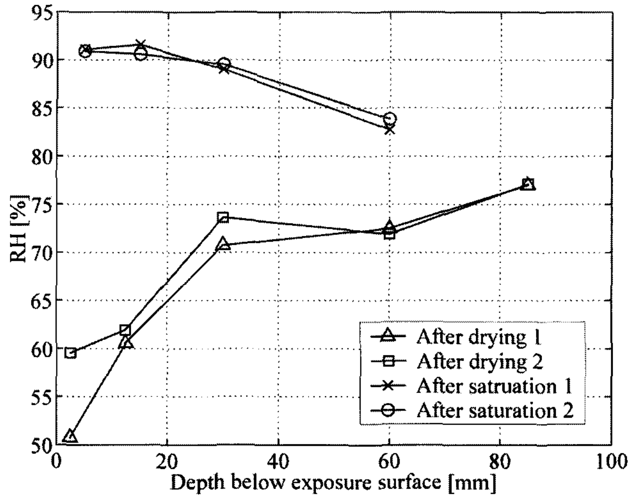

Fig. 7 - RH profiles after 60 days of drying and after the capillary suction was defined as stopped (two independent profiles at each condition).

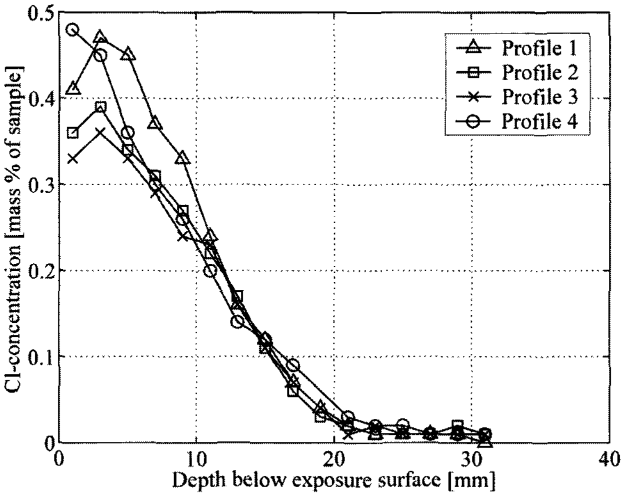

Fig. 8 - Chloride profiles determined after the capillary suction was defined as stopped (four independent profiles).

For determination of the optimal combination of drying and re-saturation for acceleration of chloride ingress, the possible adverse effects of a non-saturated pore system on the chloride threshold levels need further investigation.

Furthermore, the various accelerated methods proposed in the literature and their respective adverse effects should be evaluated in order to identify the most promising accelerated method on which a future reference method should be based.

Based on examination of the steel electrodes with a concrete cover of 20 mm, the concrete composition and test method used the chloride threshold level for the steel electrodes was found to range from 0.52 to 0.74 mass percent of binder (0.11 to 0.14 mass percent of sample) with an average value and std. dev. of 0.63 and 0.11 mass percent of binder (0.13 mass and 0.01 mass percent of sample), respectively. This is in the range of values found by other researchers [20] and indicates that the possible adverse effect of a non-saturated pore system is limited.

## 7. CONCLUSION

A test method for determination of chloride threshold levels for initiation of reinforcement corrosion has been proposed. The method has been shown to solve earlier encountered problems with crevice corrosion at parts of the test specimens that were not intended as anode. In addition, the testing procedure described in this paper can effectively accelerate the chloride ingress, reducing the time needed to obtain a critical chloride concentration at the depth of the reinforcement bars. With the method described in this paper, the concrete composition, reinforcement steel and exposure conditions used, the chloride threshold levels could be determined within a period of 130 days. The initial results are very positive. However, before considering this approach for standardization further developments should be investigated to reduce labour and further testing should be conducted to increase the statistical database as far as precision and reproducibility of the test method.

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