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Accelerated Testing for Chloride Threshold of Reinforcing Steel in Concrete

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Abstract. Testing for the chloride threshold (also called critical chloride content) for corrosion initiation of steel in concrete has been found difficult and, at best, time consuming. Nevertheless, the chloride threshold is an important parameter in service life design of new structures and for evaluation of the remaining service life of existing structures. This paper reports on an accelerated test on mortar specimens that produces results within one week to a few weeks. It is based on accelerating chloride penetration by a mild electrical field while the steel potential is monitored. Upon corrosion initiation, specimens are sampled to obtain the chloride content that initiates corrosion. Results are reported of testing in CEM I (OPC) mortar on multiple specimens. Results for reference mortar are compared to specimens with application of a hydrophobic surface treatment. The results show that in reference CEM I mortar values for the critical threshold were obtained that agree well with previous experiments using the same method. This is taken as a validation of the method. The method is thought to be suitable for comparative chloride threshold studies of different binders, without or with corrosion inhibiting additions. Results for mortar with surface applied hydrophobic treatment, however, are unexpectedly low, which is taken to suggest that the method is not suitable for (e.g. surface treated) material with inhomogeneous electrolytic conduction.

Keywords: Service life · Reinforcement corrosion · Chloride threshold · Critical chloride content

1 Introduction

Designing new concrete structures or assessing existing structures for a quantified service life in chloride contaminated environment requires (at least) a value for the critical (or threshold) chloride content that initiates corrosion (Polder et al. 2017; Bertolini et al. 2013; and van der Wegen et al. 2012). However, its experimental determination has been found difficult and, at best, time consuming, see e.g. (Lollini et al. 2016, Pacheco and Polder 2016). Wide variations for the threshold have been found in the literature (Angst et al. 2009), among others due to different test methods. Recent work in RILEM TC 235-CTC has not provided a satisfactory test setup for concrete. On the other hand, recent studies have shown that an accelerated test on mortar may provide a suitable method. The test is based on acceleration of chloride

penetration into the mortar by applying a DC voltage, causing corrosion initiation in a relatively short period of time. The test method applied here is based on work by (Yang 2015, Yang et al. 2016) which is a further development of work by (Castellote et al. 2002, Andrade and Rebolledo 2012). Yang has demonstrated the beneficial effect of a corrosion protective addition to the bulk of CEM I mortar in terms of increased chloride threshold and increased time to corrosion initiation. This paper reports setup, execution and results of such testing on reference Portland cement mortar and on mortar with a surface applied hydrophobic treatment.

2   Experimental Setup

Principle. The material to be tested is Portland cement-sand mortar, as a proxy for concrete. The test principle is as follows. Mortar prisms with a single bar of reinforcing steel are subjected to accelerated chloride penetration from one side. Acceleration is obtained by applying a low DC voltage across the specimen, using a copper cathode in a $CuCl_2$ + NaCl solution and a stainless steel anode at the opposite side of the specimen, embedded in water. In the $CuCl_2$ + NaCl solution, the cathodic reaction is Cu^{2+} + 2 e → Cu (s). This has the advantage that no hydroxyl ions are formed in the solution, which would affect the transport of chloride ions into the mortar. The steel potential is monitored using an activated titanium (Ti*) reference electrode in the $CuCl_2$ + NaCl solution. The accelerating voltage is switched off twice a day for about half an hour. Steel potentials are monitored continuously, both with voltage on and off. The time development of the steel potential measured about half an hour after each instance of switching off is considered diagnostic for corrosion initiation. The criterion for corrosion initiation is a drop of at least 100–150 mV compared to the previous "off" measurement. Upon its corrosion initiation, a specimen is taken out of the setup and subsequently sampled for chloride at the depth of the steel. This chloride content is considered the critical or threshold content for the specimen. The expected time-to-corrosion-initiation is one to two weeks.

Additional Testing. Electrical resistances were measured using two steel plates on opposite sides of the mortar bars (two electrode method, TEM), or between copper cathodes and stainless steel anodes; or between Ti* and steel rebars, depending on the phase the specimen was in.

Execution. Ten specimens were tested untreated as reference (denoted reference) and ten specimens were treated with a hydrophobic agent (denoted H). Mortar bars of 110 × 40 × 40 mm were made using Ordinary Portland cement, CEM I 42.5, standard 0–2 mm (siliceous) sand and sand:cement:water ratios of 3:1:0.5. Each specimen contained a single (ribbed) reinforcing bar of 8 mm diameter. Steel bars were derusted by wire brushing to clean metal. Casting took place on May 25, 2016. Top surfaces were finished by trowelling. Moulds were covered with plastic; after one day specimens were unmoulded and transferred to a climate room at 20 C and 80% RH. At four weeks age, mortar resistances were measured through opposite 110 × 40 mm sides using 120 Hz AC and their resistivity was calculated using a geometrical cell factor
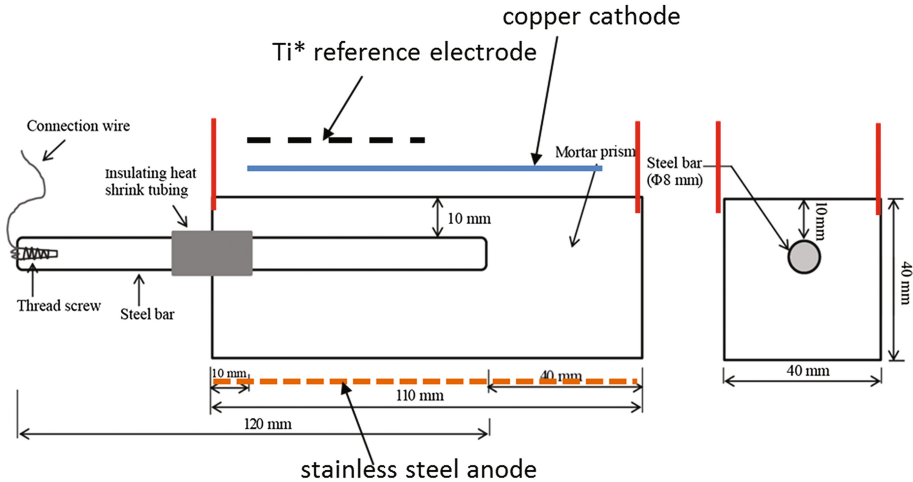
Fig. 1. Specimen layout; the four vertical lines indicate the pond on the top surface

(Polder 2001), neglecting the effect of the embedded steel bar. At 6 weeks age, a commercial hydrophobic agent H was applied to the top surfaces of specimens H. Subsequently, all specimens were provided with an epoxy coating on the sides and with PVC sheets around the top surface to form ponds, as shown in Fig. 1.

At 3 months age specimens and electrodes (cathodes, anodes, reference electrodes) were installed as illustrated in Fig. 1. Ponds were filled with 0.4 M $CuCl_2$ + 0.6 M NaCl electrolyte. The pH of the $CuCl_2$ + NaCl solution was measured using a pH electrode. Resistances between steel bar and Ti* electrodes were measured. A voltage of 6.0 V was applied. Steel potentials were logged using a datalogger at five minute intervals. After three hours the voltage was switched off for half an hour and potentials without voltage applied were measured as baseline. On the following days, the voltage was switched off twice a day for 30 to 45 min and potentials were measured. After three days the first specimens showed corrosion initiation. Subsequently, most specimens showed corrosion initiation in the next two to three weeks. Temperatures in the laboratory varied from 20 C up to 27 C.

After corrosion initiation, specimens were removed from the setup, ponds were removed and 30–35 mm of the part without steel bar was cut off. Subsequently, a horizontal slice was sawn at 7.5–12.5 mm depth from the top surface of the cut off part, corresponding to the position of the upper surface of the steel bar, as illustrated in Fig. 2. These slices were crushed and ground and analysed for chloride after dissolution in hot nitric acid by Volhard's titration. Chloride content was calculated by mass of cement assuming 18% of the acid soluble fraction was hydration water. After cutting off the part for chloride analysis, the remaining parts of the specimens were tested for resistance (by TEM, through the top-bottom faces) and subsequently their cut surface was tested for water repellence by wetting and recording the depth of the lighter (hydrophobic) and darker (hydrophilic) parts. Some specimens were subsequently split to examine the steel bars for corrosion.
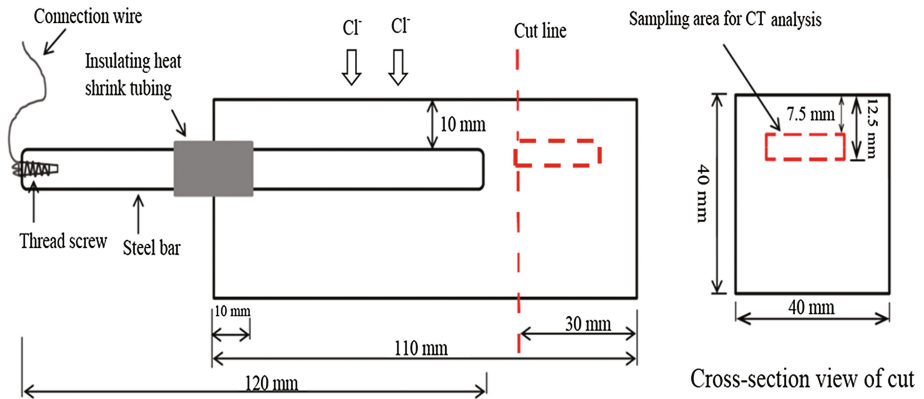
Fig. 2. Sampling for chloride analysis after corrosion initiation indicated by the hatched rectangle, corresponding with upper level of rebar

3   Results

The average resistivity at 28 days age, after storage in 20 C and 80% RH was 240 Ohm*m, its standard deviation (stdev) was 50 Ohm*m. The amount of hydrophobic agent applied on specimens H was c. 300 ml/m², which was achieved in two or three coats. The average potential difference between Ti* and steel rebar for reference specimens was −310 mV (stdev 90 mV) and for H specimens −270 mV (stdev 40 mV). Steel potentials changed slightly during the c. 30 min after switching off the voltage. Potential changes were −10 mV or less for reference specimens. Typical changes for treated specimens H were + or −10 mV except for the first few days, when they were +50 to 150 mV. Average resistance between Ti* and steel rebar was 0.66 kOhm (stdev 0.17 kOhm) for reference and 1.49 kOhm (stdev 0.38 kOhm) for H specimens. Figure 3 shows steel potentials 30 min after switching off the voltage as a function of time over the testing period

Corrosion initiation in reference specimens occurred between 4 and 7 days with an average of 5 and a stdev of 1 day; in treated specimens H after 5 to 18 days (average 13 d, stdev 5 d). Corrosion initiating (threshold) chloride contents in reference specimens varied between 0.8% and 1.2% chloride by mass of cement with an average of 0.97% and a standard deviation of 0.25%. For H treated specimens the threshold varied between 0.1 to 0.7% with an average of 0.48% (stdev 0.24%). H treated specimens had a water repellent top layer of typically 2–4 mm thickness. Resistivity for reference specimens was 135 O*m, for H specimens 550 O*m. Three specimens from each group were split to, at least partially, inspect the steel bar and the mortar/steel interface. No general pattern was visible to the naked eye: some specimens did and others did not show corrosion spots; some contained air bubbles in the steel/mortar interface, however, without clear correlation to corrosion spots.

Table 1 presents an overview of the main results, together with some of Yang's. The latter illustrate that adding an inhibitor releasing substance, modified hydrotalcite (MHT), to mortar, increased threshold values were obtained.
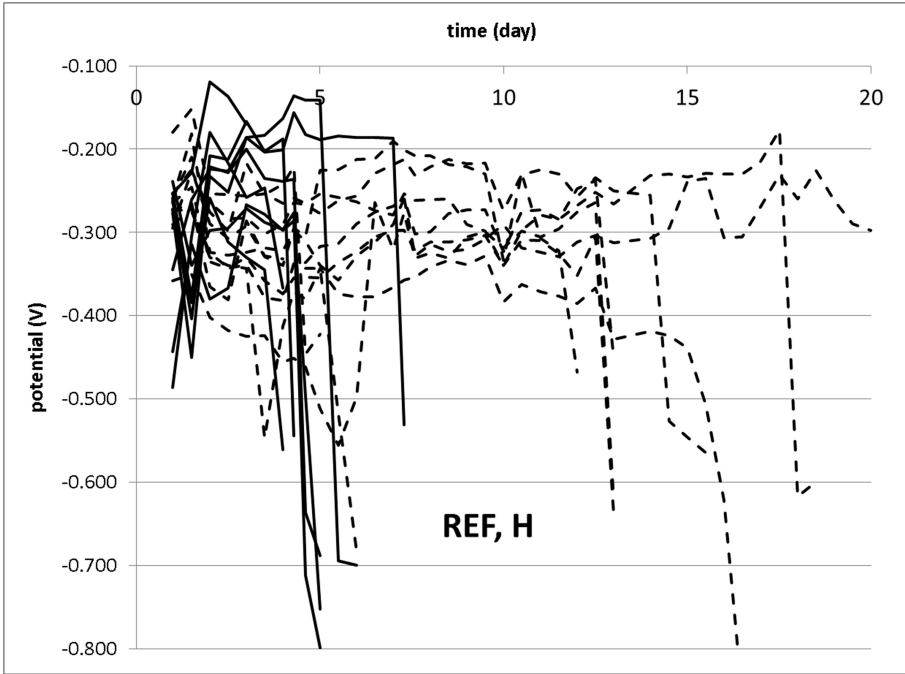
Fig. 3. Steel potential (with Voltage off) as a function of testing time (days), solid lines reference, hatched lines H

Table 1. Main results from this work and Yang's; t-t-c time to corrosion, Ct chloride threshold; mean values (stdev)

	t-t-c (day)	Ct (%)	Remark
reference	5 (1)	0.97 (0.25)	this work
H	13 (5)	0.48 (0.24)	this work
reference	3 (0.1)	0.93 (0.1)	Yang 2015; Yang et al. 2016
5% MHT-pAB	3.6 (0.1)	1.24 (0.15)	ditto, bulk inhibitor 5%
10% MHT-pAB	3.3 (0.6)	1.36 (0.1)	ditto, bulk inhibitor 10%

4   Discussion

Resistivity. The 28 days resistivity of 250 ± 50 Ohm*m is reasonable for CEM I mortar, considering that some drying out had taken place during storage in 20 C 80% RH. A typical value in water saturated condition is c. 150 Ohm*m (Souza 2016). The standard deviation is reasonable or slightly above typical (Polder 2001). At the end of the experiment, due to re-wetting, reference resistivity was 135 Ohm*m, as expected. Treated specimens had a higher apparent resistance: 550 Ohm*m. This high value for surface treated specimens does not reflect a high "bulk" resistivities, but is a composite of a high-resistive surface layer and a lower resistive bulk.

Potentials. Steel potentials upon installation were around −300 mV versus Ti*. Due to the low pH of the catholyte (c. 3) in which the Ti* is embedded, these values should not be compared to "normal" potentials in concrete, with much higher pH, typically 13. Nevertheless, all initial potentials can be taken as indicative of steel passivity, as no chloride is present and the mortar is alkaline.

Sometime after the voltage was applied, most (off) potentials dropped by c. 200 mV or more within one day or less (Fig. 3). A few specimens showed a more gradual change of potential or remained rather constant, others were more erratic. Nevertheless, in both groups the large majority behaved as expected, with a sudden potential drop indicating corrosion initiation.

Time-to-Corrosion. The time-to-corrosion-initiation for reference specimens, 5 days on average, corresponds very well with Yang's results (Yang 2015; Yang et al. 2016). For surface treated specimens it took 13 days on average to develop corrosion. The surface treatment clearly delayed the initiation of corrosion.

Threshold Values. The average "chloride threshold" for reference specimens is 0.97% chloride by mass of cement. The coefficient of variation is reasonable, c. 25%, which is quite normal for such measurements (Pacheco and Polder 2016). The threshold value for reference material agrees well with Yang's work (Yang 2015; Yang et al. 2016), with an average of 0.93% for similar cement mortar. This suggests that the test method produces reproducible results.

Further Considerations. All reference specimens showed the expected behaviour of a sudden potential drop of several hundreds of millivolts within a week. The potential change over 30 min after switching off was small, which suggests the absence of strong polarisation of the steel bars. This is a prerequisite for obtaining realistic threshold values in a test that applies a voltage for acceleration. Consequently, for electrically homogeneous cementitious materials the test is clearly validated. This test appears suitable for threshold testing different binders or materials with admixed (bulk) corrosion inhibitors.

On the other hand, in specimens with a hydrophobic surface treatment an average threshold of 0.48% was found, much lower than for reference specimens. This is unexpected for various reasons. The hydrophobic treatment extends only a few mm into the specimen, and certainly not to the depth of the rebar. Consequently, in terms of threshold concentration the rebar/mortar interface would be expected to behave similar as untreated material. A good explanation for this unexpected behaviour is presently lacking. There may be an influence of the varying resistivity in treated specimens, with a highly resistive top layer and a lower resistive bulk. The resulting non-homogeneous electric field may alter the transport of chloride and other (hydroxyl) ions. Alternatively, the surface treatment may have contained small imperfections (leaks). At such leaks the flow of ions would be strong, causing corrosion, while the sampled part is not influenced by the leak. However, the application of the hydrophobic agent in multiple coats renders this explanation improbable. Yet another possibility is that the moisture content around the steel, which is probably different for treated versus reference specimens, has an effect. In any case, the applicability of the test method for materials with a (hydrophobic) surface treatment is questionable. Further study on this topic is needed.

5 Conclusions

A recently developed method for determining the chloride threshold for corrosion initiation, based on chloride migration accelerated by an electrical field, was applied to CEM I mortar ("reference") and to the same mortar with a surface treatment using a hydrophobic agent ("H"). The potentials of embedded steel bars were monitored, and a drop in the off potential was taken as indication of corrosion initiation. Subsequently chloride was analysed at the depth of the steel bars, which was taken as the threshold value.

Specimens showed the expected potential drop related to corrosion initiation after 4 to 18 days, with shorter times for reference specimens and longer times for specimens with a hydrophobic surface treatment. Resistance measurement and wetting of cut surfaces showed that in the hydrophobically treated specimens a high-resistive surface layer of about 2–4 mm thickness on the average was present, corresponding with the expected hydrophobic effect of the treatment. This surface treatment clearly increased the time to corrosion initiation.

Corrosion initiating chloride ("threshold") levels of about 1% chloride ion by mass of cement were found in reference specimens, corresponding well with previous results obtained using this test method. However, lower threshold values of c. 0.5% were found in specimens with a surface treatment. This is contrary to expectation; at present a good explanation is lacking. In general, the unexpected results obtained may be due to (a) adverse effects of the surface treatment on the chloride threshold, (b) undesired effects of a hydrophobic surface layer on the test, or (c) a combination of both. Adverse effects of the surface treatment on the threshold are unlikely: the hydrophobic effect does not extend to the steel bar. It is more likely that an explanation exists in effects on the test or in the combination. It may have to do with the occurrence of a high-resistive surface layer, with defects in this layer, local effects or with different moisture contents.

Regarding the test method, the results support the present version as suitable for determining the chloride threshold for corrosion initiation in a relatively short time. This however, only applies to material with homogeneous electrical (ion transport) properties (resistivity). The method is expected to produce useful results for different binders or for admixed corrosion inhibitors. Possibly the effects of imperfections in the steel/mortar interface can be tested. At present, the test should be taken as comparative rather than absolute. We do not claim that results are representative for concrete. Further work is needed to establish correspondence to concrete in practice.

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