Analysis of the Rapid Chloride Migration test

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ABSTRACT: In this study the Rapid Chloride Migration test (RCM) standardized as NT Build 492 and BAW-Merkblatt is reviewed. Since the traditional natural diffusion tests are laborious, time consuming and costly, they are not always preferred from a practical point of view. To overcome these disadvantages, several accelerated tests have been developed. Among the accelerated chloride migration tests, the Rapid Chloride Migration test (RCM) seems to be the most promising test to use in the prediction of the chlorides progression into concrete. Nevertheless, because of deficiencies in the theoretical background, the test has received some criticism. The largest issue of the test concerns the assumption of the chloride concentration profile in concrete after the migration test. The “S-shaped” abrupt chloride penetration front, assumed in the theoretical model, has not been observed in reality. This leads to a wrong estimation of the chloride ion migration coefficient – D_RCM. Moreover, the effect of the polarization of electrodes used in the test and the differences in the quality of concrete from the inner layers (the tested part of concrete in the RCM test) and outer layers (the concrete which is the real barrier against the chlorides test) have not been studied sufficiently and are considered to have a significant effect on the RCM test results. The investigations presented in this paper include results of the measurements of the polarization of electrodes, the influence of curing of concrete on the quality of concrete cover, the differences in quality between concrete in the inner and outer layers and the discussion of the consequences of assuming an incorrect chloride penetration front in the RCM model. Considering the investigations, some modifications of the RCM test procedure are proposed and a further direction of research is outlined.

1 INTRODUCTION

In view of problems with chloride-induced corrosion of reinforcing steel, there is a need for quantified information on chloride transport properties of concrete. Thus, a reliable prediction model of chloride ingress into the concrete cover is considered as the key point for an assessment of the long-term behaviour of concrete exposed to sea water or de-icing salts. Several laboratory testing methods (both long-term and short-term) have been developed to quantify the chloride transport in concrete. The long-term methods are usually not preferred from the practical point of view because they are laborious, time consuming and costly. To overcome these disadvantages, an accelerated test - the Rapid Chloride Migration test (RCM) with the associated resulting D_RCM (chloride-ion migration coefficient) has been developed by Tang (1996). NT Build 492 and BAW-Merkblatt describe in detail the execution of the test. Within the European DuraCrete project the D_RCM has been introduced into service
life model for concrete (using correction factors), which has lately resulted in even higher popularization of the test method. However, 10 years after the standardization of the RCM test, there are still some major concerns regarding its theoretical principles.

This paper points out the biggest controversy of the theoretical RCM model: the sharp free-chloride concentration profile, assumed by Tang (1996) to compute the final output of the test - $D_{RCM}$. Experimental chloride concentration profiles presented by Stanish (2002), Castellote et al. (1999, 2002) or Yuan (2009) are not that sharp but very similar in shape to the “natural” diffusion profiles, thus the equations developed should be treated carefully, as they lead to an incorrect estimation of the migration coefficient. This might be a reason for the discrepancies between $D_{RCM}$ and $D_{app}$ obtained from the non-steady-state “natural” diffusion test methods. Moreover, in this paper, the problem of the polarization of electrodes is investigated. The electrochemical phenomenon of polarization of the stainless-steel electrodes, which appears during RCM testing, causes a difference between the values of the potential applied by the power source and the potential across the tested concrete specimen. Knowing the exact value of the polarization potential makes it possible to calculate the $D_{RCM}$ coefficient in a more accurate way. The polarization effect of titanium electrodes is also investigated, as titanium could be a more suitable material for the electrodes.

The final analysis presented in this paper concerns the differences in quality between outer and inner layers of concrete and the influence of curing on the $D_{RCM}$ value. The RCM test procedures are prescribing the testing of concrete from inner layers (as they must be free of chlorides prior to testing) rather than the outer layers. However, the resistance against intrusion of chloride ions is different for the different parts of concrete, thus testing the inner and outer layers will result in different $D_{RCM}$ values. In practice this means that an inappropriate part of concrete is tested for the chloride ion migration - not the outer one but the inner one which often has better properties. This can lead to an overestimation of the quality of concrete and finally to an overestimation in predicting its service life.

2 RAPID CHLORIDE MIGRATION TEST – THEORETICAL AND EXPERIMENTAL CHLORIDE CONCENTRATION PROFILES

The Rapid Chloride Migration test (RCM), also known as CTH or RMT, proposed initially by Tang (1996) and standardized as NT Build 492, is currently often used to investigate the durability of concrete. The RCM is an electrically-accelerated test method which yields the rapid chloride migration coefficient.

As mentioned above, the RCM test is based on the forced ionic migration induced by the external electrical voltage applied across the Ca(OH)$_2$-saturated concrete specimen. Due to the potential difference between the electrodes, chloride ions move from the upstream solution (10% NaCl), through the concrete specimen, towards the downstream solution (0.3N NaOH), for a certain time. Afterwards, the specimen is split open and sprayed with AgNO$_3$ – an indicator for chlorides. Finally, the chloride penetration depth is measured and based on this value the $D_{RCM}$ is calculated.

The RCM governing equations, presented by Tang (1996) are based on the Nernst-Planck equation, describing the flux of chloride ions under the action of chemical and electrical potential:

$$J = J_M + J_D = -D \frac{\partial c}{\partial x} + \frac{zFE}{RT} c,$$  \hspace{1cm} (1)

where: $J$ – total flux of chlorides [kg/(s*m$^2$)], $J_M$ – flux of chloride due to electrically forced migration [kg/(s*m$^2$)], $J_D$ – flux of chlorides due to diffusion [kg/(s*m$^2$)], $D$ – chloride ion migration coefficient [m$^2$/s], $c$ – free-chloride concentration [g/dm$^3$], $x$ – depth in concrete [m], $z$ – ion valence, $F$ – Faraday constant [9.65*10$^4$ C/mol], $R$ – gas constant (8.314 J/mol*K), $T$ – temperature [K], $E$ – electrical field [V/m].

For a non-steady state process Eq. (2) is used as follows:
where: \( c_t \) – total chloride concentration, \( c_b \) – bound chloride concentration, \( J_0 \) – flux of chlorides through a unit area of solution, \( D_0 \) – migration rate of chlorides through pore solution in concrete, \( t \) – duration of test.

It is worth emphasizing that the binding process included in the chloride transport model as term \((1 + \partial c_b / \partial c)\) is assumed constant, which represents either: no binding or a linear binding with an instantaneous equilibrium between free and bound chlorides.

Solving Eq. (2) with the following conditions:

\[
\begin{align*}
    c &= 0, x > 0, t = 0 \\
    c &= c_0, x = 0, t > 0 \\
    c &= 0, x \to \infty, t = t_M
\end{align*}
\]

where: \( c_0 \) – concentration of chlorides in bulk solution, \( t_M \) – large finite number, gives the exact analytical solution:

\[
c(x,t) = \frac{c_0}{2} \left[ e^{ax} \text{erfc} \left( \frac{x + aD_{RCM}t}{2\sqrt{D_{RCM}t}} \right) + \text{erfc} \left( \frac{x-aD_{RCM}t}{2\sqrt{D_{RCM}t}} \right) \right],
\]

where: \( a = zFE/RT \); \( \text{erfc} \) – complement to the error function: \( \text{erfc} = (1-\text{erf}) \).

Assuming that the electrical field (E) and the penetration depth (x) are large enough, the first \( \text{erfc} \) term on the right side tends to zero, thus Eq. (4) can be simplified to:

\[
c(x,t) = \frac{c_0}{2} \text{erfc} \left( \frac{x-aD_{RCM}t}{2\sqrt{D_{RCM}t}} \right),
\]

In Fig. 1 a graphical solution of Eq. (5) is plotted, where the free-chloride concentration changes rapidly from the bulk concentration \( (c_0) \) to 0 within a small distance. Based on this profile the following relationship is obtained:

\[
x_f = x_d - \alpha \sqrt{x_d},
\]

\[
\alpha = 2 \sqrt{\frac{RT}{zFEU}} \left[ \frac{1}{\text{erf}^{-1} \left( 1 - \frac{2c_d}{c_0} \right)} \right],
\]

where: \( \alpha \) – laboratory constant, \( x_d \) – chloride penetration depth indicated by the colorimetric indicator, \( c_d \) - chloride concentration at which the colorimetric indicator changes the color, \( x_f \) – inflection point of the front.
Introducing Eq. (6) and (7) into Eq. (5) and solving for $D_{RCM}$ finally results in:

$$D_{RCM} = \frac{RL * x_d - \alpha \sqrt{x_d}}{zFU \ t},$$  \hspace{1cm} (8)

The output of the test – $D_{RCM}$ – is a direct chloride ion transport parameter expressed in m$^2$/s.

As mentioned above, in the theoretical basis of RCM a sharp chloride concentration profile is assumed in order to compute the $D_{RCM}$. However, several authors have obtained softer profiles. In Fig. 2 an experimental RCM chloride profile presented by Stanish (2002) is shown.

Similar experimental chloride profiles were presented in Castellote et.al. (1999, 2002) and Yuan (2009). It is clear that this shape of profile is not that sharp in comparison to the theoretical one (Fig. 1), but very similar to the “natural” diffusion profiles. This difference between the theory and the experimental results gives serious evidence of the incorrectness of the chlorides transport model presented by Tang (1996). Thus, the developed equation system should be treated carefully, as it leads to an incorrect estimation of the migration coefficient. This might be the reason of the discrepancies between $D_{RCM}$ and $D_{app}$ obtained from the non-steady state “natural” diffusion test methods.

4 THE EFFECT OF THE POLARIZATION OF ELECTRODES

An exact value of the electrical field across the concrete specimen is required for calculations of the chloride ion migration coefficient ($D_{RCM}$). However, due to the polarization effect of the electrodes, the potential applied by the power source is not equal to the potential difference across the concrete specimen. This effect is only included in the NT Build 492 procedure.
(BAW-Merkblatt does not take it into account) and assumed to have a value of 2V. Nevertheless, this value of polarization can vary, depending on the value of the current flowing in the circuit, so on the quality of concrete.

To measure the polarization potential of electrodes, the test set-up shown in Fig. 3 was constructed (C. Helm (2009)). The potentiodynamic measurements of current were performed for stainless-steel electrodes (SS) and for mixed-metal-oxides coated titanium (MMO-Ti) electrodes. The scan rate yielded a value of ± 0.056 mV/s. Ag/AgCl and MMO-Ti electrodes were used as standard reference electrode and counter electrode, respectively. The measurements were performed in a 0.2N KOH + 0.17N NaCl water solution (anolyte) and a 0.2N KOH water solution (catholyte). The results are presented in Fig. 4 and Fig. 5.

The results obtained on the SS and MMO-Ti electrodes show the polarization effect in a wide range of DC currents flowing in the circuit (10⁻⁸A ÷ 0.3A). Nevertheless, during the RCM testing, the value of current usually remains within the range of 10 ÷ 100 mA (bold sections of curves in Fig. 4 and Fig. 5). To estimate the total polarization potential, the absolute values of the polarization potentials of both electrodes, relevant to the current flowing in the circuit, should be read out from the presented figures and summed up. For the SS electrodes, in a range of current of 10 ÷ 100 mA, the total polarization effect can vary from 1.8V up to 2.2V.

If the value of current exceeds 100 mA, the polarization effect could be considerably higher. The assumption of 2V polarization adopted in NT Build 492 seems to be correct, while it is
close enough to the real polarization value in the investigated range of current. It is also clear that in BAW-Merkblatt procedure a calculation error is introduced because the polarization effect is not included. For an application of 30V external voltage, the error may reach 7% for 100mA since the potential difference over the concrete specimen yields 27.85V instead of 30V. Knowing the exact polarization value, it is also possible to insert it directly into the final $D_{RCM}$ calculation, so that the final test result is more accurate.

![Figure 5: Polarization curves for mixed-metal-oxides coated titanium electrodes](image)

The polarization effect of the MMO-Ti electrodes is shown in Fig. 5. These electrodes are made of titanium and coated with mixed precious active metal oxides. The special coating prolongs the life of the electrodes and provides excellent corrosion resistance. The polarization effect of the MMO-Ti electrodes is lower in comparison to the SS electrodes and yields $1.5 \div 1.8V$. Due to the lower polarization potential and higher corrosion resistance, the MMO-Ti electrodes can successfully replace the SS electrodes. Thus, applying the Ti-MMO electrodes in the test set-up described in BAW-Merkblatt could reduce the introduced error by decreasing the overestimation of the potential difference across the specimen.

5 QUALITY OF INNER AND OUTER LAYERS OF CONCRETE, INFLUENCE OF CURING OF CONCRETE ON THE CHLORIDE ION MIGRATION COEFFICIENT

The available RCM test procedures prescribe the testing of concrete from inner layers of structures or testing cubes. It is required to avoid the surface effects (bleeding, wall effect) and prior chloride contamination. However, some properties of inner and outer layers of concrete are different due to the differences in their microstructure. This fact implies that resistance against intrusion of chloride ions is different for individual parts of concrete. In case of concrete prepared and cured under laboratory conditions, these differences can be minimized due to thorough preparation and good curing. Nevertheless, for real concrete structures, the outer layer – so the layer which is directly exposed to chlorides action and is the real barrier against harmful substances – usually is characterized by worse properties than the inner layers. This is usually caused by the big-scale production process, weather curing etc. In practice this means that an inappropriate part of concrete is tested for the chloride ion migration - not the outer one but the inner one, often having better properties. This can lead to an overestimation of the quality of concrete and finally to an overestimation in predicting the service life of reinforced concrete structures.

The following experiment was performed (J.Gulikers (2009)) to show the differences between quality of concrete cured under laboratory (inner layer) and real construction-site conditions (outer layer). Four concrete mixes were prepared – two having a potentially good quality (low w/c ratio) and two with a potentially poor quality (high w/c). Concrete mix proportions are presented in Table 1. Concrete cubes (15cm x 15 cm) and a test wall (1m x 1m x 30 cm) were cast from each batch. The cubes were stored in water (22 °C), while the test panels were kept
outside, exposed to the weather conditions. To represent the real construction-site curing, one side of each test wall was demoulded after 1 day from casting and left free for the weather exposure (wind, rain, changes in temperature – poor curing) and the opposite side of walls were covered by a plastic foil and demoulded after 7 days from casting (to represent better curing). Cores were drilled out from each cube and test panel after 26 days from casting.

Table 1: Concrete mix proportions (J. Gulikers (2009))

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Cement [kg/m³]</th>
<th>Water [kg/m³]</th>
<th>Sand 0-2 mm [kg/m³]</th>
<th>Sand 0-4 mm [kg/m³]</th>
<th>Gravel 4-16 mm [kg/m³]</th>
<th>w/c</th>
<th>Density [kg/m³]</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1</td>
<td>Cem I 52.5R, 360</td>
<td>137</td>
<td>0</td>
<td>837</td>
<td>1132</td>
<td>0.38</td>
<td>2466</td>
</tr>
<tr>
<td>C2</td>
<td>Cem III/B, 42.5N, 360</td>
<td>137</td>
<td>0</td>
<td>828</td>
<td>1120</td>
<td>0.38</td>
<td>2445</td>
</tr>
<tr>
<td>C3</td>
<td>Cem I 52.5R, 360</td>
<td>216</td>
<td>72</td>
<td>679</td>
<td>1015</td>
<td>0.6</td>
<td>2342</td>
</tr>
<tr>
<td>C4</td>
<td>Cem III/B, 42.5N, 360</td>
<td>216</td>
<td>0</td>
<td>742</td>
<td>1003</td>
<td>0.6</td>
<td>2321</td>
</tr>
</tbody>
</table>

After 28 days from casting the RCM testing were performed (following the NT Build 492 manual). The tests were performed on the inner layers of concrete cured in laboratory (to represent potential quality) and on the outer layers of concrete cured on the construction-site (to represent the real quality). The results are presented in Fig. 6.

![Figure 6: Influence of curing of concrete on the chloride migration coefficient (D_{RCM})](image)

It is clear that the concrete cured under laboratory conditions has the lowest values of chloride ions migration coefficient. Furthermore, the influence of curing of the construction-site test panel on the D_{RCM} value is also noticeable – the side cured only for 1 day shows the lowest resistance against chlorides intrusion. From the designing point of view, it should be considered as necessary not only to rely on the RCM results obtained on concrete prepared/cured in laboratory scale, but also to test samples from real structures. It is also clear that the quality of concrete from the inner layers of concrete (laboratory curing) is higher than the quality of outer layers (construction-site curing). The results presented above show that the RCM test procedure should be modified to test the outer layer of concrete instead of the inner one. However, this would only be possible in the case of concrete elements which were not exposed to chlorides. The presence of chlorides on the concrete surface can be easily checked by spraying silver nitrate over the surface. In case of chloride contaminated concrete, it is possible to use the Rapid
Iodide Migration (RIM) test presented by Lay et.al. (2003) instead. The test is very similar to the RCM – with the mentions that the chloride-bearing solution is replaced by iodite solution and a different colorimetric indicator is used. The RIM test results are proved to be in a good agreement with results of the RCM test, thus the method can be used alternatively.

6 CONCLUSIONS

Although the RCM test is becoming a very popular test describing the durability of concrete, it is still necessary to improve its theoretical background and experimental procedure. The analysis of the RCM test presented in this paper includes a discussion of the consequences of assuming an incorrect chloride penetration front in the RCM model, results of measurements of the polarization of electrodes, influence of the curing of concrete on its quality and the differences in quality between inner and outer layers of concrete.

It has been pointed out that the equations governing the theoretical model of the RCM test should be treated carefully as the free-chlorides concentration profile assumed to compute the $D_{\text{RCM}}$ coefficient is different from the experimental profile. This can finally lead to an incorrect $D_{\text{RCM}}$ estimation and can explain the origin of differences between $D_{\text{RCM}}$ and $D_{\text{app}}$ obtained from the “natural” diffusion non-steady state tests. A new chloride transport model resulting in the theoretical chloride profile being in agreement with the experimental one should be developed so the $D_{\text{RCM}}$ could be calculated in an improved way.

Furthermore, results of the measurements of the polarization potential presented in this paper show that the assumption of 2V adopted in NT Build 492 procedure as the value of the stainless-steel electrodes polarization is correct, since it can vary from 1.8 up to 2.2 V for the current in range of $10 \div 100$ mA. Nevertheless, in the case of the BAW-Merkblatt procedure, the polarization effect is neglected, thus an error in $D_{\text{RCM}}$ calculation is introduced. Alternatively the MMO-Ti electrodes are proposed as titanium is a more suitable material for the electrodes.

The final investigation presented in this paper concerns the differences in quality between inner and outer layers of concrete and the influence of curing on the quality of concrete. The RCM test procedures – due to the surface effects and chloride contamination prior to testing - are prescribing to test only the inner layers of concrete. However, the quality of inner and outer layers of concrete is different, thus the $D_{\text{RCM}}$ results obtained on the inner and outer layers of the same concrete cannot be the same. The influence of curing on the quality of concrete is also of a vital importance from the durability point of view. As expected, concrete cured in a good way is characterized by an improved resistance against chloride intrusion in compare to the same concrete cured not so carefully. Thus, to obtain more reliable results, testing of the outer layers of concrete is proposed following either: standard RCM test procedures in case of chloride-free concrete or RIM test in case of chloride-contaminated concrete.

REFERENCES


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