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New method to measure the rapid chloride migration coefficient of chloride-contaminated concrete

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Abstract

The apparent chloride diffusion coefficient, D_{app}, which is obtained by fitting chloride profiles as the result of time-consuming immersion tests can be substituted in a model on chloride ingress by the rapid chloride migration (RCM) coefficient of concrete, D_{RCM}, which is determined under electrically accelerated conditions. Until now, it was not possible to measure D_{RCM} of chloride-contaminated concrete, as already inherent chlorides interfere with the common colorimetric indicator used for penetration depth measurements. Furthermore, carbonation may also interfere with the penetration depth reading. To overcome these problems, the regular test has been modified by using iodide as penetrating ion and iodate–starch acetic acid as indicator. A strong linear relationship between the regular RCM test and the newly developed Rapid Iodide Migration (RIM) Test was found. Carbonated specimens can be tested using the RIM test without additional interference. Thus, the new method enables the quantification of the actual concrete quality sampled from existing structures during a condition assessment.

Keywords: Transport properties; Iodide; Chloride; Modeling

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1. Introduction

The apparent chloride diffusion coefficient D_{app} is an input parameter for a full probabilistic model on chloride-induced corrosion, which is physically based on Fick's second law of diffusion [1]. This input parameter may be determined using time-consuming immersion tests. However, D_{app} can be substituted by the rapid chloride migration (RCM) coefficient D_{RCM}, measured using an electrically accelerated migration test, as both parameters show a strong linear correlation [1,2]. For durability design purposes, a chosen concrete composition can be mixed and tested at a specific age in very short time to determine the parameter D_{RCM}, which is introduced to the model stating the mean value μ, standard deviation σ and corresponding statistical distribution type [1,3].

For existing structures, the model may be applied to estimate the residual service life of a structural component, with the advantage that the actual on-site concrete quality can be tested hereby improving the model precision. The service life of a recently constructed object can be checked using data of the as-built condition within a quality control system ("birth certificate" of a structure). For structures already exposed for longer periods to an environment containing chlorides, the residual service life may be used as the basis for an optimization process in a life cycle management system [4]. Cores of the concrete cover, which is strongly influenced by the workmanship, curing regime and environmental exposure history, would need to be drilled from the existing structure to be subjected to the RCM test.

Unfortunately, the above-described procedure of data updating for existing structures was until now not applicable in a straightforward manner, as concrete exposed to an environment containing chlorides or concrete produced with chlorides in the mixing water cannot be tested with the conventional RCM method. This is because already inherent chlorides will:

- also move during migration tests
- react with the common silver nitrate indicator.

Thus, the penetration depth of chlorides, measured subsequent to RCM testing, will be overestimated. This prob-

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Table 1
Investigated combinations of penetrating ions or molecules and corresponding indicators

Ion	Indicator	Color change in vitro
SCN^-	$Fe(NO_3)_3 + HAc$	orange
S^-	$Co(NO_3)_2 \cdot 6H_2O$	black precipitation
S^-	Zn	white
S^-	$C_8H_{14}Cl_2N_2 + FeCl_3$	dark blue
$KMnO_4$	None (color of dissolved $KMnO_4$)	violet
I^-	$(NH_4)_2S_2O_8 + C_6H_{10}O_5 + HAc$	light blue
I^-	$KIO_3 + C_6H_{10}O_5 + HAc$	dark blue

lem cannot be avoided by collecting dust samples after RCM testing for chloride analysis, as already present and newly penetrated chlorides can hardly be distinguished.

The proposed solution in this paper is to substitute chlorides in the migration test with a different ion with similar properties and to find an adequate indicator for detection, which fulfill the following conditions:

(a) The ion to be transported is not already contained in considerable quantities in the concrete constituents.
(b) The indicator solely reacts with the ion introduced to the test solution.
(c) The ion/indicator combination must produce an unambiguous color change on the surface of a split concrete specimen.

2. Investigated ions and corresponding indicators

Various ions and molecules, which may behave similarly in concrete compared to chlorides, and corresponding indicator systems were tested first in vitro. All in vitro tests were performed with a saturated calcium hydroxide solution to simulate the alkaline pore solution of concrete. Ion indicator combinations, which showed good visibility in vitro, were then sprayed in various concentrations onto concrete surfaces to check whether a change in color would be sufficiently detectable as well, Table 1.

Amongst all investigated combinations, the most suitable solution fulfilling all of the conditions (a) to (c) given above was the reaction of iodide with iodate to form iodine, which in a second step produces an iodine–starch complex when in contact with starch. Iodide does not react with iodate in an alkaline solution. Hence, the pH value of the concrete surface must be decreased by means of an acid sprayed onto the split concrete surface:

- Diluted sulfurous acid will cause gypsum to precipitate.
- Iron constituents within the concrete form a yellowish, brownish precipitation with diluted hydrochloric acid.
- The least amount of precipitation was found when applying acetic acid (HAc). The reaction of acetic acid with the calcium hydroxide of the pore solution produces calcium acetate, which is highly soluble and only produces a white precipitation when the surface is drying (Eq. (1)):

$$2HAc + Ca(OH)_2 \rightarrow 2H_2O + Ca(Ac)_2 \qquad (1)$$

Moreover, the white color of the acetate precipitation even provides the additional advantage that a stronger contrast to the iodine–starch reaction is obtained, which facilitates the measurement of the iodide penetration depth.

The conventional RCM test is conducted by introducing chloride in the form of sodium chloride to the test solution. Hence, iodide as the substituted penetrating ion is also given to the modified test solution as sodium iodide. Potassium was chosen as the counter ion for iodate in the indicator solution. In an acidic environment, the reaction product of sodium iodide and potassium iodate will be molecular iodine (Eq. (2)):

$$10NaI + 2KIO_3 + 12HAc \rightarrow 6I_2 + 10NaAc + 2KAc + 6H_2O \qquad (2)$$

It is assumed that chains of approximately 10 to 20 iodine molecules are formed, which are then embedded into the channels of starch helixes contained in the indicator solution [5]. This iodine–starch complex causes the concrete to turn dark compared to the iodide-free concrete (Fig. 1).

3. Properties of chloride and iodide

3.1. Physical and chemical properties

Both chlorine and iodine are part of the seventh main group (halogens) in the periodic system. However, signifi-

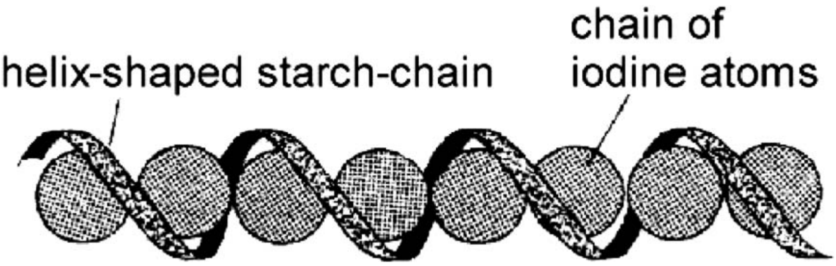

Fig. 1. Iodine–starch complex [5].

Table 2
Comparison of chloride and iodide ion [6,7]

Property	Chloride	Iodide
Relative atomic mass [g/mol]	35.45	126.90
Ionic radius [pm]	181	216
Solvation number [–]	2.9	1.2

cant differences can be found, which may lead to a different transport behavior within concrete (Table 2).

The relationships between the ionic radius, the concentration-dependent solvation number, being the average number of water molecules surrounding the particular ion [7], the binding behavior of a regarded ion and its rate of transportation within the concrete pore solution are very complicated. A reliable comparison of the transport properties of iodide and chloride in concrete must thus still be based on experiments.

3.2. Binding of iodide

The binding of chloride in concrete has been a large research issue within the last decades. A review of this process would be out of the scope of this paper. Regarding iodide, little research seems to be conducted so far. This is because a contact of iodide with concrete is rather uncommon in practice.

Nevertheless, it was found that calcium aluminate hydrates and iodide form complexes ($3CaO{\cdot}Al_2O_3{\cdot}CaI_2{\cdot}8H_2O$), which are quite similar to the well-known Friedel's salt. These complexes crystallize forming hexagonal plates [8]. Fischer [9] stated that hydroxide ions within the Friedel's salt may be exchanged by other anions, forming quite similar phases. This leads to the conclusion that iodide may also be incorporated into Friedel's salt in exchange of hydroxide.

Allard et al. [10] investigated the sorption of iodide in the cement paste matrix. The extent of sorption decreased with increasing pH value. Hence, it can be assumed that iodide is physically bound by calcium silicate hydrates in a similar manner as is the case for chlorides.

3.3. Iodide diffusion coefficient of concrete

The influence of the temperature and of the w/c ratio on the iodide diffusion coefficient has been reported in [11]. The comparison with data for the chloride diffusion coefficient revealed a very similar behavior of both ions.

4. Rapid migration testing with chloride and iodide

4.1. Setup of rapid migration test

The general setup of the test was developed by Tang [2], also known as the CTH method. This paper will detail only the modifications of Tang's [2] test method. In the following, the modified migration test with iodide will be referred to as Rapid Iodide Migration (RIM) Test, whereas the test with chlorides is referred to as RCM test. Principal of both test methods, depicted in Fig. 2 for the RIM test, is the acceleration of ions by means of a voltage gradient.

For both tests, the molar concentration of the test solution is identical. In the RCM test, the aqueous test solution is composed of 0.2 M KOH + 0.51 M NaCl (3.0% sodium chloride). In the modified RIM test, the test solution contains 0.2 M KOH + 0.51 M NaI (7.695% sodium iodide).

The current measured at the beginning of the test, I_0, indicates the test duration necessary to achieve a penetration depth approximately equal to half of the specimen length. The values for the test duration, which are based on experimental experience of Tang [2], are only valid for concrete specimens with a diameter of $d = 100$ mm and a length of $L = 50$ mm. For different specimen geometry, as may be due to limitations at the sampling site, the measured current I_0 can be corrected according to Eq. (3) in order to use the values given in Eq. (2).

$$I_{0,d=100\ \mathrm{mm},\ L=50\ \mathrm{mm}} = I_0 \frac{100^2}{d^2} \times \frac{L}{50} \qquad (3)$$

where d is the diameter in millimeter and L is the length in millimeter of a concrete core.

At the end of the assigned test duration, the concrete samples are split in half. To detect the chloride penetration depth (RCM test), the specimen is first sprayed with an aqueous fluoresceine solution (1 g/l in 70% ethyl alcohol). After the surface has slightly dried for a couple of seconds, an aqueous silver nitrate solution (0.1 M) is immediately applied. The specimens of the RIM test are likewise split and sprayed with the indicator solution. One liter indicator

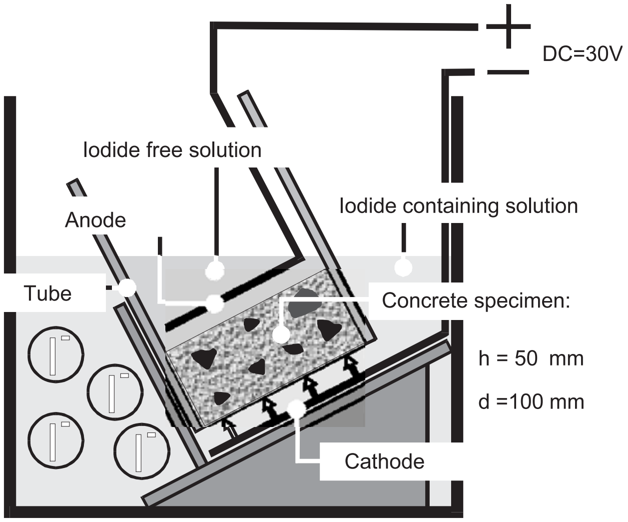

Fig. 2. Experimental setup of RIM test.

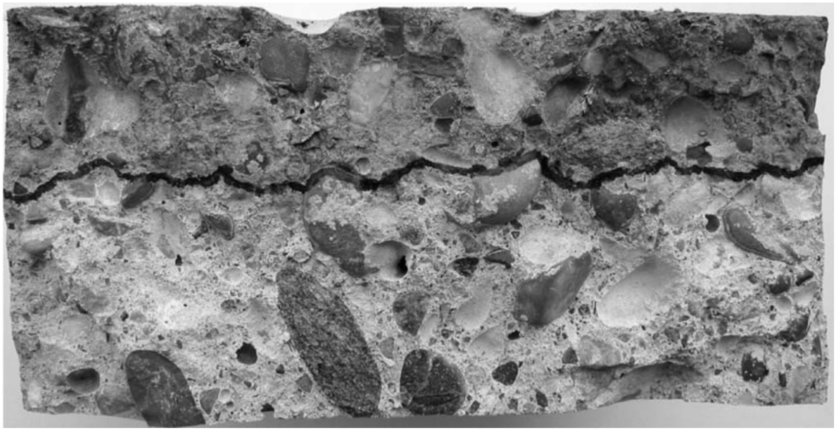

Fig. 3. Concrete specimen penetrated by iodide from topside in RIM test. Penetration front is marked by a dark line.

for detection of the iodide penetration front is composed of the following:

- 1.0 M aqueous potassium iodate (400 ml/l)
- 3% aqueous starch solution (400 ml/l)
- 50% acetic acid (200 ml/l)

The acetic acid in the indicator mainly protects the starch from a bacterial attack. A color change is therefore only weakly visible. Once the surface has slightly dried, a 50% aqueous acetic acid solution must be sprayed thoroughly onto the surface to reduce the pH value of the concrete, which will immediately enhance the color change of the concrete. The iodine-containing concrete appears brownish, whereas the iodine-free concrete becomes lighter (Fig. 3).

Further characteristics of the iodide indicator worth to be mentioned are as follows:

- The penetration depth of iodide is instantly visible after spraying of the indicator.
- The iodide indicator may be applied again even days after testing to recover the penetration depth once it has faded.

The penetration depth of chloride and iodide revealed by the color change is measured along the diameter in an interval of 1 cm. From these penetration readings, the mean value *m* and the coefficient of variation (CoV) are calculated for each test series.

4.2. Chloride and iodide profiles after rapid migration testing

Rapid migration tests with mortar specimens composed according to DIN EN 196-1 [12] were conducted with sodium chloride (NaCl) or sodium iodide (NaI) in the test solution. At the end of a 24-h testing, powder samples were collected by grinding one specimen of each test series in 0.5-mm intervals.

To determine the chloride content of the powder samples, these were dissolved in 18% nitric acid. The filtered solution was then analyzed using photometry. For analysis of the iodide content ion chromatography was used. When dissolving the powder samples of mortar containing iodide with nitric acid, the iodide will be oxidized to molecular iodine, which cannot be detected by ion chromatography. Therefore, hydrochloric acid with additions of zinc-(II)-chloride was used for dissolution of the concrete containing iodide, as in this reduced solution iodide remains stable.

For better comparison, the iodide content is expressed in chloride mass (multiplication by the ratio of molar masses $M_{\mathrm{Cl}}/M_{\mathrm{I}} = 35.45/126.9 = 0.279$) (Fig. 4).

As can be seen in the profiles of Fig. 4, the transport and binding behavior of iodide and chloride is very similar in an electrically accelerated migration test. This leads to the conclusion that for chloride and iodide, differences in the ion radius and in the binding behavior are negligible or at least seem to balance each other out.

Additional to the profiling, the two remaining specimens of each series were split into half and sprayed with the respective indicators. The penetration depth of iodide and chloride were $X_{d,\mathrm{Iodide}} = 17.5$ mm and $X_{d,\mathrm{Chloride}} = 17.0$ mm, respectively (Fig. 4). From these single results, it can already be deduced that the sensitivity of both indicator systems seems to be very similar.

4.3. Calculation of the rapid migration coefficient

The calculation of the rapid migration coefficient for both the test with chloride or iodide is performed according to the analytical derivation in [2], see Eqs. (4) and (5):

$$D_{\mathrm{RCM},0} = D_{\mathrm{RIM},0} = \frac{RTL}{zFU} \times \frac{X_d - \alpha\sqrt{X_d}}{t} \tag{4}$$

$$\alpha = 2\sqrt{\frac{RTL}{zFU}} \times \operatorname{erf}^{-1}\left(1 - \frac{2c_d}{c_0}\right) \tag{5}$$

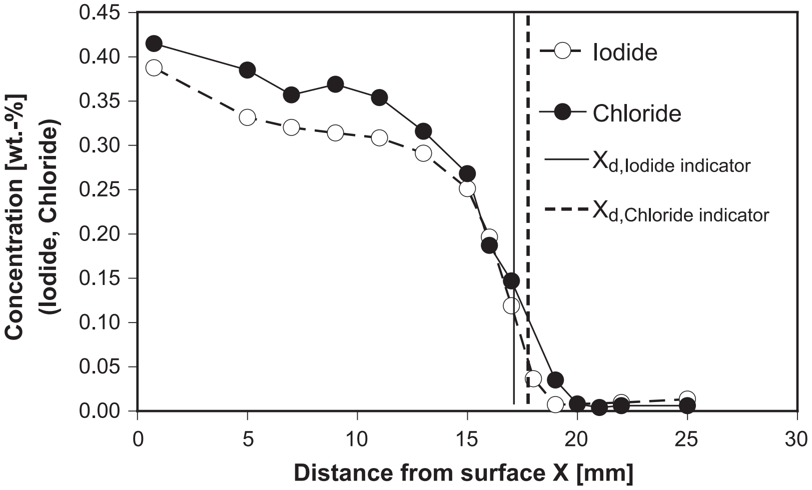

Fig. 4. Comparison of chloride and iodide profiles and average of penetration depth X_d revealed by chloride and iodide indicator after rapid migration test.

where $D_{\text{RCM},0}$: chloride migration coefficient [m^2/s], $D_{\text{RIM},0}$: iodide migration coefficient [m^2/s], R: universal gas constant, $R = 8.314$ [J/(Kmol)], T: temperature [K], L: length of specimen [m], z: valence, $z = 1$ for chloride and iodide [−], F: Faraday constant, $F = 96490$ [J/(Vmol)], U: direct current voltage, here $U = 30$ [V], X_d: penetration depth of chloride or iodide [m], α: auxiliary variable [−], t: test duration [s], erf^{-1}: inverse of error function, c_d: free iodide or chloride concentration at color change boundary of indicator (detailed below) [mol/l], c_0: chloride concentration of chloride or iodide in test solution, here $c_0 = 0.51$ [mol/l].

4.4. Free ion concentration at color change boundary of indicator c_d

According to Eqs. (4) and (5), c_d, which is the concentration of chloride or iodide in the pore water solution that will cause an unambiguous color change when reacting with the applied indicator, must be known. Ions will only react with an indicator if they are freely available in the pore solution. Otsuki et al. [13] prepared specimens with various chloride concentrations (0.1, 0.25, 0.5, 1.0, and 2.0% per cement) in the mixing water. After a storage period of 2 weeks in water, these samples were split and sprayed with indicator. Those specimens giving a clear color change were chosen for pore water extraction with subsequent chloride analysis. The free chloride concentration at the color change boundary was found to be 0.15 (% per cement).

As Otsuki et al. [13] published the chloride concentration at the color change boundary related to the cement content, Tang [14] assumed a pore volume of 0.3 ml/g cement, which yields $c_d = 0.14$ mol/l. Additionally, it was assumed that already bound chlorides were set free by the extraction process. Due to this effect, the chloride concentration was reckoned to be enriched by a factor of two when compared to a bulk solution, resulting in a value of $c_d = 0.07$ mol/l.

The value for c_d probably is not equal for every type of concrete. Thus, Tang [2] performed an error estimation to evaluate the effect of a deviation of the assumed from the actual concentration at the color change boundary. To do so, Eq. (4) can be differentiated for α, which includes c_d to obtain the CoV (Eq. (6)):

$$\text{CoV}(\Delta\alpha) = \left|\frac{\alpha}{\alpha - \sqrt{X_d}}\right| \cdot \left|\frac{\Delta\alpha}{\alpha}\right| \cdot 100[\%] \tag{6}$$

From Eq. (6), it can be seen that the CoV of α decreases with increasing penetration depth. Assuming a change of c_d by a factor of 2.5 results in a ratio of $\Delta\alpha/\alpha = 30\%$. When inserting this value to Eq. (6), one can see that for tests with a penetration depth X_d above 10 mm, the CoV is below 5%. As the penetration is controlled by the test duration to yield a value of approximately $X_d = 25$ mm, Tang [2] set the color change boundary constant to $c_d = 0.07$ mol/l regardless of the concrete type.

To determine the concentration of the color change boundary for the present reaction of iodide with the indicator solution composed of iodate, starch and acetic acid, mortar specimens according to Ref. [12] were prepared with various concentrations of iodide in the mixing water. After 7 days storage in water with identical iodide concentration as the mixing water, the specimens were split into half and sprayed with the indicator system (Fig. 5).

The specimens with 0.07 and 0.10 mol/l iodide in the mixing water were considered to show an unambiguous color change. From separate specimens prepared with these concentrations, pore water solution was extracted as described in Ref. [15] and analyzed for the iodide concentration applying ion chromatography (Fig. 5).

The concentrations of iodide causing a change in color were coincidentally fairly close to the concentration, which was used in Ref. [2] as the color change boundary for

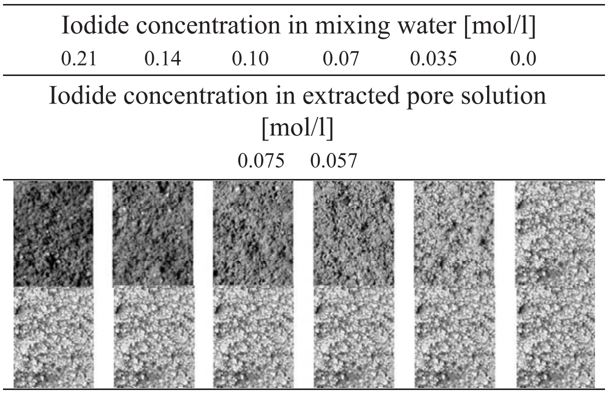

Fig. 5. Color change boundary of indicator system for detection of iodide; for better comparison, the photo of the iodide-free sample is added at the bottom.

chlorides with the silver nitrate and fluoresceine indicator. Of course, it must be remembered that prior bound iodide may have been set free during the extraction process. However, when considering

(a) the subjectivity for the determination of the color change boundary and
(b) the negligible small effect of an iodide enrichment during extraction on the result of the migration coefficient D_{RCM}, as detailed above for chlorides,

the iodide concentration causing a clear color change can be set constant to $c_d = 0.07$ mol/l. This enables a direct comparison with the conventional RCM method.

5. Application of colorimetric indicators to carbonated concrete

When applying silver nitrate on specimens of a carbonated concrete cover drilled from existing structures, it must be realized that carbonated and noncarbonated concrete react in a different manner [16]. When sprayed with the indicator solution, concrete with inherent chlorides will produce a color in between purple and brown. On the surface of chloride-free noncarbonated concrete, dark silver oxide is produced, which is darker compared to the chloride containing concrete [13].

In carbonated concrete, the indicator will not form dark silver oxide and remains light. This effect may thus feign a penetration front. Carbonated concrete should thus be treated with an alkaline solution prior to the application of the indicator [16].

Tests have shown that the newly developed indicator for iodide in concrete will not reveal the carbonated zone, since

(a) the indicator system contains acetic acid and thus reduces the pH value of the entire specimen surface, and
(b) reaction partners are missing.

However, slight differences in color may appear in the carbonated zone as the pore structure, and hence the drying behavior when wetted with indicator solution is altered by carbonation.

6. Correlation of rapid migration tests with chloride and iodide

For a certain mortar composition, the following was demonstrated above:

(a) The transport behavior, including binding processes, of iodide and chloride seem to be very similar in a rapid migration test.
(b) The sensitivity of both indicator systems can be considered as equal in sensitivity.

These aspects still had to be proven for a wider range of concretes. To answer the question whether independent of the concrete composition, a migration test with iodide can substitute the test with chloride in the test solution the correlation of both migration coefficients has been determined (Fig. 6).

Concrete and mortar specimens were produced and tested under variation of the binder type, w/c ratio and age with the objective of covering a wide range of migration coefficients. Each specimen type was tested at the same time in the same laboratory with the regular RCM test and the newly developed RIM test. The test conditions were identical with respect to specimen geometry (∅ = 104 mm, length $L = 50$ mm), test duration t, temperature T, direct current voltage U, concentration of chloride or iodide containing solution (0.51 M in a 0.2-M KOH solution) and testing age.

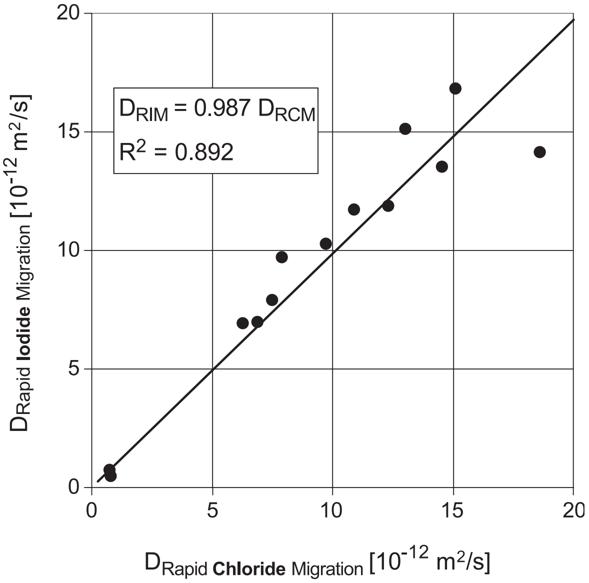

Fig. 6. Correlation of rapid migration coefficients determined for chloride and iodide.

As can be seen in Fig. 6, a strong linear relationship between the migration coefficients determined in the RCM and in the RIM test was obtained. The deviations from the regression line are in the range of the CoV of the rapid migration method being CoV = 20% [1,3].

Thus, in general, the RIM test can be applied as a substitute for the RCM test. This is of course not necessary for chloride-free noncarbonated specimens produced in the laboratory, as iodide is usually more expensive compared to chloride. However, for specimens drilled from existing structures, the method is currently the best available alternative.

7. Conclusions

Various ions, which are barely contained in concrete constituents, have been studied with respect to their detectability by a colorimetric indicator. The combination of iodide as the transported ion and an indicator consisting of an aqueous solution of iodate, starch and acetic acid was found to give good visibility on a concrete surface.

Electrically accelerated migration tests, which are commonly used for rapid determination of the apparent chloride diffusion coefficient, were conducted with iodide and chloride as the transported ion in concrete. After the rapid migration testing, the specimens were chemically analyzed for the concentrations of both ions versus penetration depth. The iodide and chloride profiles revealed that both ions posses very similar transport and binding properties in concrete when subjected to an electrical field. Measurement of the penetration depth of iodide and chloride within these samples using the respective indicators was very similar as well. This gives evidence that both indicator systems are fairly comparable in sensitivity.

The iodide concentration at the color change boundary of the iodate, starch and acetic acid indicator, which is necessary as an input for the calculation of the RIM coefficient D_{RIM}, has been determined by chemical analysis of extracted pore solutions. The results showed that the color change boundaries of both indicator systems for chloride and iodide can be set equal to $c_d = 0.07$ mol/l when considering the minor effect of a deviation from the actual value on the overall result.

Concrete of a wide range of qualities has been tested either with chloride or iodide as the transported ion at the same time under identical conditions. A strong linear relationship was found for the migration coefficients of both ions in concrete.

Whereas the indicator for chloride may feign a penetration front when applied to chloride-free but carbonated concrete, the newly developed iodide indicator is not affected by a pH reduction of the concrete.

In conclusion, an efficient technique is provided to measure the migration coefficient of chloride containing concrete, which is of special importance for the condition assessment of existing structures exposed to chlorides.

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