Abstract
A new non-destructive chloride sensitive sensor element is presented for use in cement based porous materials. The sensor element determines the free chloride content in solutions and in porous cement based materials. It has been calibrated in synthetic pore solution and showed excellent long term stability, reproducibility and linearity (following the Nernst law). The sensor element has been used to monitor the water and chloride uptake into mortar blocks. The results show that the kinetics of the water and chloride ingress are different, the water front arrives earlier at a specific depth of the mortar cover. Good agreement between the free chloride content determined by the sensor and by pore water expression has been found.

Key-words: Chloride Penetration, Sensor, Monitoring, Resistivity, Kinetics

1. Introduction

Corrosion of the rebars due to chloride ions from deicing salts or sea water is the main cause of damage and early failure of reinforced concrete structures. High chloride concentrations in the concrete cover result in depassivation, the localized disruption of the protective passive film of the rebars. This situation represents a high corrosion risk in otherwise sound structures, corrosion attack becomes possible in the presence of oxygen and humidity on the steel surface. Severe corrosion attack usually occur when alternating drying / wetting cycles take place, typically in the splash zone of a structure. Chloride penetration into concrete determines the time to depassivation (initiation phase of localized corrosion) and is thus one of the most decisive processes for durability and service life of reinforced concrete structures. Water and chlorides are transported rapidly into concrete by capillary suction, thus besides the dominating influence of concrete porosity and pore size distribution the rate and amount of chloride ingress is related to the humidity gradients present in the concrete member.

Whereas active corrosion of the rebars can be detected in the laboratory and on-site by non-destructive electrochemical techniques as potential measurements [1, 2], no such possibility exists for the detection and quantification of chloride ions in concrete. Only qualitative informations on chloride distribution can be obtained from potential mappings [3]. From a scientific point of view the following factors are complicating the problem:
- **chloride analysis:**
  the determination of chloride content and chloride profiles till today are based on cores or powder taken from concrete samples in the lab or on structures. These analysis are destructive, costly, subject to experimental problems [4] and do not allow any continuous information on changes in chloride content and profile with time and during climatic changes.

- **free chloride:**
  Most of the data available linking chloride content and corrosion of the rebars refer to total (acid soluble) chloride content in concrete. It is however well known that for corrosion of the rebars only the free chloride content in the pore solution is relevant [5, 6] and has to be put in relation to the pore water composition, especially OH-content. Determination of the free chloride content is possible by pore water expression [7] of cores.

A non-destructive way to measure the free chloride concentration in-situ would thus be highly desirable both for on site monitoring and research purposes. In this paper a chloride sensitive sensor element based on a solid AgCl (silver chloride) electrode and a reference electrode for use in cement paste, mortar or concrete is presented. Results of experiments to test long term stability, reproducibility and calibration of the sensors in synthetic pore water solutions are reported. The sensor elements were embedded in mortar blocks at different heights in order to follow the chloride activity during chloride ingress, the electrochemical potential of embedded rebars and the electrical resistivity between the sensors was measured in parallel. The results of chloride activity determined by the sensors are compared to data obtained from pore water expression and from analysis of the total chloride content at different depths of the mortar blocks. It is shown that free chloride content can be determined in a non-destructive way, in-situ and continuously with good accuracy.

2. **Theory**

Chloride sensitive elements are used in analytical chemistry and different fields of modern technique either to determine chloride content quantitatively or to monitor chloride content continuously in water, waste water etc. Usually, silver chloride (AgCl) single crystals or AgCl deposited on silver wires are used. Due to the very low solubility of AgCl in aqueous solutions, the dependance of the interfacial potential \( E \) at the electrode \( \text{Ag}/\text{AgCl} // \text{Chloride solution} \) follows the Nernst law

\[
E (\text{AgCl}/Cl^-) = E_0 + RT/nF \ln ([Cl^-]/[AgCl])
\]  
(1)

which, at room temperature (\( T = 298 \) K) and for \( n = 1 \) becomes

\[
E (\text{AgCl}/Cl^-) = E_0 + 0.059 \times \log [Cl^-]
\]  
(2)

This potential can be measured against a stable reference electrode (e.g. saturated calomel electrode, SCE) in the same solution. In general, the term \( [Cl^-] \) refers not to chloride concentration \( c_{Cl^-} \) but to the chloride activity \( a_{Cl^-} \) linked by the activity coefficient \( \gamma_{Cl^-} \)

\[
a_{Cl^-} = c_{Cl^-} \times \gamma_{Cl^-}
\]  
(3)
When using concentrated solutions (CISA, constant ionic strength adjustors), the value of $\gamma_{\text{Cl}}$ can be taken reasonably as $\gamma_{\text{Cl}} = 1$ and thus chloride concentration is determined directly from eq. 2.

3 Experimental

3.1 Chloride sensitive sensor elements
The sensor elements are shown in figure 1. The central, active chloride sensitive element is a silver wire coated with electrochemically deposited silver chloride (AgCl) appearing black. This coated wire is mounted in a stainless steel (DIN 1.4301) tube-case, the electrical isolation between the AgCl coated wire and the stainless steel tube is obtained by a small, flexible teflon tube. An epoxy resin is used as sealer to prevent ingress of solution into the stainless steel or teflon tube. Each sensor element has two electrical connections, one to the silver wire (chloride sensor) and one to the stainless steel tube (allows measurement of potential and resistivity).

3.2 Calibration of the sensor elements
The calibration of the sensor elements was performed in synthetic pore water solutions, in saturated Ca(OH)$_2$ and in distilled water. Pore water was expressed from samples of cement paste w/c 0.4 (solution A) and PC mortar w/c 0.75 (solution B) and analysed by ICP-AES spectroscopy (table 1). The synthetic pore solutions were prepared without Fe and Al ions. All calibration measurements were done with eight sensors, potentials were measured versus a saturated calomel (SCE) electrode. Chloride ions were added to the solutions as NaCl in a concentration range from 0.001 to 4 Mol/l. In addition to the potential of the chloride sensors conductivity and pH of the solutions were measured.

![Figure 1: Chloride sensitive sensor element (total length ca. 12 cm)](image)

Table 1: Composition of the expressed pore solutions from cement paste w/c 0.4 (A) and mortar w/c 0.75 (B)

<table>
<thead>
<tr>
<th>Solution</th>
<th>Al$^{3+}$</th>
<th>Ca$^{2+}$</th>
<th>Fe$^{2+}$</th>
<th>K$^+$</th>
<th>Na$^+$</th>
<th>SO$_4^{2-}$</th>
<th>OH$^-$</th>
</tr>
</thead>
<tbody>
<tr>
<td>B, w/c 0.75</td>
<td>mg/l</td>
<td>46</td>
<td>5.3</td>
<td>2.8</td>
<td>8500</td>
<td>800</td>
<td>930</td>
</tr>
<tr>
<td>mMol</td>
<td>1.7</td>
<td>0.13</td>
<td>0.05</td>
<td>217.95</td>
<td>34.78</td>
<td>9.69</td>
<td>158.5</td>
</tr>
<tr>
<td>A, w/c 0.4</td>
<td>mg/l</td>
<td>8</td>
<td>25</td>
<td>0.7</td>
<td>22800</td>
<td>1380</td>
<td>537</td>
</tr>
<tr>
<td>mMol</td>
<td>0.3</td>
<td>0.63</td>
<td>0.01</td>
<td>584.6</td>
<td>60</td>
<td>5.59</td>
<td>501.2</td>
</tr>
</tbody>
</table>

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3.3 Mortar blocks, chloride uptake, measurements
The mortar blocks (Figure 2) were prepared from ordinary PC with a w/c ratio of 0.75, a sand/cement ratio of 2. After casting and demoulding the blocks were cured 28 days in the humidity cabinet and afterwards dried for 10 days at 50 deg. The total porosity determined from MIP was 20±1 %. Each mortar block contained four rebars (cover 15, 20, 30 and 75 mm), 16 chloride sensitive sensor elements and an embedded MnO₂ reference electrode (ERE 20, Force Institute, Copenhagen). During the chloride uptake experiments (600 h) the mortar blocks were immersed 3 mm in a NaCl solution, the mortar block 1 in a 3 molar, block 2 in a 1 molar solution. The potential of the chloride sensors was measured versus a calomel electrode (SCE) put into the NaCl solution and versus the MnO₂ electrode, readings were taken for each sensor every 8 minutes with a programmable high impedance voltmeter (Keithley 2001, switch system 7001). The resistance between the neighbouring stainless steel tubes of the sensor elements was determined with an LCR meter (Escort ELC-131D) at 1 kHz.

3.4 Chloride analysis
At the end of the experiments cores (d = 40 mm) were taken from the mortar blocks for pore water expression and total chloride analysis. Chloride profiles (10 to 90 mm) were determined on powder obtained from four holes of 6 mm diameter. The powder was dissolved in dilute nitric acid, chlorides were determined by direct-potentiometry in a CISA solution [8].
4. Results

4.1 Calibration of the chloride sensitive sensor elements

The potential of the chloride sensitive sensors (average of eight sensors) measured for the different chloride contents in the synthetic pore solutions (fig. 3), in saturated Ca(OH)₂ (fig. 4a) and in distilled water (fig. 4b) decreases linearly with increasing logarithm of the chloride concentration:

\[ E \ (V \ SCE) = M_0 + M_1 \times \log c_{Cl^-} \]  

(4)

The standard deviation of the potential readings as well as the results of the linear regression performed for the four solutions are summarized in table 2. The sensor ele-

![Figure 3: Calibration curve of the chloride sensitive sensor elements in synthetic pore solutions. A: cement paste w/c = 0.4, B mortar w/c = 0.75](image)

![Figure 4: Calibration curve of the chloride sensitive sensor elements in solutions. A: saturated Ca(OH)₂, B distilled water](image)
Table 2: Results of statistical analysis of the calibration of the sensor elements

<table>
<thead>
<tr>
<th>solution</th>
<th>slope M1 [V/decade]</th>
<th>axis M0 [V SCE]</th>
<th>R</th>
<th>STD dev [V SCE]</th>
</tr>
</thead>
<tbody>
<tr>
<td>pore solution A</td>
<td>-0.053</td>
<td>-0.002</td>
<td>0.997</td>
<td>0.0021</td>
</tr>
<tr>
<td>pore solution B</td>
<td>-0.054</td>
<td>-0.006</td>
<td>0.998</td>
<td>0.0007</td>
</tr>
<tr>
<td>sat. Ca(OH)2</td>
<td>-0.059</td>
<td>-0.004</td>
<td>0.996</td>
<td>0.0004</td>
</tr>
<tr>
<td>dist. water</td>
<td>-0.050</td>
<td>-0.005</td>
<td>0.998</td>
<td>0.0003</td>
</tr>
</tbody>
</table>

Results of statistical analysis of the calibration of the sensor elements show very good reproducibility and stability as shown from the cyclic immersion experiments (fig. 5). The long term stability of the sensors, tested at 0.5 M NaCl in synthetic pore solution B, is documented in figure 6. Changes of less then ±1 mV were observed over a period of nearly 100 days. No effect of the length of the exposed AgCl wire on the potential readings was found.

4.2 Chloride uptake into mortar blocks
The potential readings of the chloride sensitive sensor elements at different depths in the mortar block 2 (1 M NaCl) is shown in figure 7 as a function of time of immersion. The chloride sensors at depth 4, 5 and 7 mm show immediately low potentials (ca. 0 V SCE), sensors at higher depths initially showed positive potentials (ca. 0.15 V SCE) and dropped to values at ca. 0.05 V SCE after about 1 h (cover 15 mm), after 6h for cover 27 mm and after 23 h for 42 mm. The sensor at the highest depth (61 mm) drops more slowly at a time interval of 60 to 100 hours.

4.3 Corrosion behaviour of the rebars
The corrosion potential of the embedded rebars (figure 8) with low minimum cover (10 mm, 15 mm) dropped within less than one hour from initially passive values (ca. 0 V SCE) to the active state (< -0.4 V). The rebar with 25 mm cover showed the transition to the active state after 15 hours. The corrosion potentials as well as visual inspection at the end of the experiment showed that all the rebars were actively corroding.
4.4 Resistance of the mortar
The resistance between the stainless steel tubes of neighbouring sensor elements was initially, in the dry mortar blocks, very high (> 100 kΩ). A sharp drop to values of about 60 Ω was observed when water reached the sensors, for higher cover depths longer times to reach the drop in resistance were necessary. The sharp decrease in resistance occurred always before the corresponding chloride sensor showed the drop in potential (figure 9).

4.5 Results of chloride analysis
The free chloride concentration determined in the pore solution expressed from cores of the mortar blocks are shown in table 3 together with the chloride activity determined by the sensors based on the calibration curve of the pore solution B (fig. 3b). The free chloride concentration determined in the pore solution of the bottom of the two mortar blocks is close to the concentration of the solution (3 resp. 1 molar). At the top of the blocks lower chloride concentrations are measured.

Table 3: Free chloride concentrations in the expressed pore solutions and determined by the chloride sensors. "Bottom" means the lower 5 cm, "top" the upper 5 cm of the height of the blocks.

<table>
<thead>
<tr>
<th>location</th>
<th>measured pore solution mg Cl / ml</th>
<th>activity [Mol/l]</th>
<th>sensors activity [Mol/l]</th>
</tr>
</thead>
<tbody>
<tr>
<td>MPK1 bottom A</td>
<td>109.6</td>
<td>3.09</td>
<td>2.9 ± 0.3</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>102.2</td>
<td>2.89</td>
</tr>
<tr>
<td>MPK1 top A</td>
<td>92.9</td>
<td>2.60</td>
<td>2.0 ± 0.5</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>90.7</td>
<td>2.56</td>
</tr>
<tr>
<td>MPK2 bottom A</td>
<td>52.2</td>
<td>1.48</td>
<td>1.1 ± 0.2</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>39.5</td>
<td>1.11</td>
</tr>
<tr>
<td>MPK2 top A</td>
<td>17.4</td>
<td>0.49</td>
<td>0.5 ± 0.1</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>22.5</td>
<td>0.63</td>
</tr>
</tbody>
</table>
5. Discussion

The results of this work are discussed with respect to the calibration and stability of the sensors, the kinetics of water and chloride ingress into cement based porous materials, the relationship between steel depassivation and chloride content and the possibility of the chloride sensors used to determine the free chloride content in mortar or concrete.

5.1 Calibration and stability of the sensor elements

The sensor elements were first tested in different solutions. As is shown in table 2, the standard deviation averaged over eight sensors and all the concentrations measured in one solution is very low, the sensors show a very good reproducibility. This is further confirmed with the cyclic experiments (fig. 5) performed in the synthetic pore solution B. The sensor elements showed the expected dependence of the potential on the chloride concentration (eq. 2) up to a concentration 1 M NaCl (fig. 3, 4). The value measured for a concentration of 1 M NaCl was -0.004 ± 0.002 V SCE, thus practically identical in all the solutions tested. The slope dE/dlog [Cl⁻] was found to be -0.054 V/decade in the two synthetic pore solutions A and B with high ionic strenght (table 1), the difference to the theoretically expected value (-0.059 V) may be explained by the fact that no correction for the activity of chloride ion has been made. For the further calculations the calibration curve of solution B is taken to convert potential to free chloride concentration in the pore solution.

The possible influence of a junction potential has been checked, the difference between a calomel electrode in solution and one on top of the mortar blocks was 0.008 V, each junction SCE/mortar is thus associated with 4 mV of potential drop.

5.2 Kinetics of water and chloride ingress

The results of this work allow to follow the uptake of both, water due to capillary suction by the sharp drop in resistance when water arrives in the pore system (see 4.4) and of the free chlorides (chloride sensors, fig. 7) as a function of immersion time of the mortar blocks. As is shown in figure 10, the time when the water front arrives as well as the
time when the chloride sensors measure a potential of 0.05 V SCE (corresponding to ca. 0.1 Mol/l) show a square root behaviour, \( x = k \sqrt{t} \), as expected for this type of mortar with 20% porosity. It is however interesting to note the huge difference in the kinetics of water and chloride ingress: at a depth \( x \) the free chlorides are detected much later than the water. This shows that the pore system of cement based materials retards the ingress of chloride ions by physical and chemical binding. The "time lag" between water front and free chlorides increases strongly with increasing cover depth. From earlier experiments [9] it is known that ratio between the uptake of water (determined by weight measurements) and total chloride content (acid soluble) corresponds to the concentration of the solution.

5.3 Initiation of rebar corrosion
All the rebars in the two mortar blocks initially showed potentials in the passive range (fig. 8). When free chlorides arrived at the level of the bars, the potential dropped to values in the active range (< 0.4 V SCE). This passive/active transition occurred immediately for bars with a minimum cover of 10 mm (axis of bar 14 mm, radius 4 mm), after about one hour for a cover with 15 mm and after ca. 15 h at 25 mm cover. From the free chloride content in the pore solution at the depth of the bars (fig. 7) at time of depassivation (fig. 8), a free chloride concentration necessary for depassivation between 0.44 Mol/l (27 mm) and 0.65 Mol/l (21 mm) can be calculated for the bar with cover 25 mm. This concentration is reached after ca. 1 hour after the start of the experiment at a depth of 15 mm and immediately at 10 mm.

5.4 Bound and free chloride
The chloride activity measured in-situ by the chloride sensors and the free chloride concentration determined in the expressed pore water solutions (table 3) showed a good agreement of the results. At the bottom of both mortar blocks the concentration of the immersion solution was found within the accuracy of the technique and the scatter of the results. The evaluation of the ratio bound/free chloride is ongoing.

6. Conclusions
A new non-destructive chloride sensitive sensor element for use in cement based porous materials has been fabricated and tested in solutions and in mortar blocks. The results have shown:

1. The sensors show excellent stability and reproducibility. They follow the Nernst law with good linearity in a range from 0.01 to 4 Mol/l chloride concentration.
2. The chloride content measured in-situ by the sensors is in good quantitative agreement with that determined by pore water expression.
3. Measuring the resistance between two neighbouring sensors the water uptake can be monitored continuously.
4. The sensors allow to follow in-situ and continuously the chloride penetration, it is clearly shown that the kinetics of the water and chloride ingress are different: the water front arrives much earlier at a specific depth than the free chlorides.
References


[8] IBWK Laboratory guide for chloride determination with ion selective electrodes (1993)