

Chloride transport in mortar at low moisture concentration

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Abstract. Chloride penetration into cementitious structures with a steel reinforcement results in corrosion of the steel. Concrete columns of bridges, which are in frequent contact with sea water, are an example of these structures. Understanding the chloride transport in cementitious materials can lead to improving their durability. In this paper, the chloride transport driven by moisture transport in various specimens is compared experimentally. Standard mortar specimens, with a water cement ratio of 0.5, are immersed into sodium chloride solutions to obtain specimens with the chloride mass percentage of 2.0%. The specimens, with initial chloride of 2.0%, are exposed to relative humidities of 55% at the top and 70% at the bottom, to obtain a moisture transport through the specimen, during 10 months. The chloride profiles before and after the experiment are compared. The concentration is measured with three techniques; Titration, Ion Chromatography and XRF. The results show that the chloride concentration measurement with Titration and Ion Chromatography are similar while the measurement with XRF is approximately 30% higher. Furthermore, due to the moisture transport through the specimen during 10 months, the total chloride content of the specimen seems to be decreased. Although that at the beginning of the experiment the chloride concentration at the surface is higher than the average concentration, this surface concentration at the end of the experiment is surprisingly lower than the average concentration.

1 Introduction

Chloride transport is one of the important mechanisms to determine the durability of the steel reinforced concrete. When chloride reaches steel rebar's, corrosion occurs, and this can lead to the end service life of a structure.

The steel reinforcement in concrete is normally well protected against corrosion. This protection is based on the alkalinity of the pore water of concrete. The high pH generates a thin layer on the steel surface. This passivation layer inhibits the corrosion process. This layer can be lost due to the chloride [1-2].

The corrosion of the reinforcements is clearly detected at the marine structures in the splash and tidal zones [3-5]. The corrosion of the marine structures begins with the wetting phase, in which the concrete cover layer is saturated with a chloride solution by capillary adsorption. In the drying phase, the water evaporates leaving chloride behind [6]. During the next wetting phase, the pores are again filled with seawater, which dissolves salts already present in the pore. Therefore the concentration of chloride rises and this leads to corrosion of the steel reinforcement [7]. In these structures, there is always an interaction between the moisture transport and the chloride transport.

In this paper, the influence of moisture transport on the chloride transport is investigated by transporting moisture through a specimen with a known chloride concentration profile during a period of time. The

chloride concentration profiles after the experiment are measured and compared with the profiles from the start of the experiment.

2 Experiment

An experiment is designed to create a moisture flux through mortar specimens with chloride. The moisture flux through the specimens is obtained by creating a low and a high relative humidity, as it is shown in Figure 1.

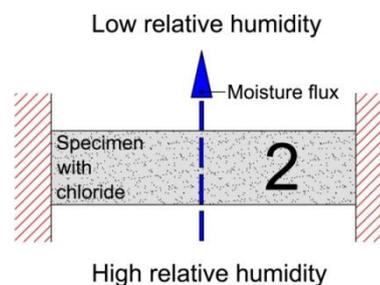


Fig. 1. A moisture flux is created by applying a high relative humidity below the specimen and a low relative humidity above the specimen.

The desired relative humidity is obtained by using oversaturated salt solutions. An equilibrium relative humidity of 54% at 20 °C is obtained by using magnesium nitrate and 75% at 20 °C by sodium chloride

[8]. The specimens are cylinders with a diameter of 100 mm and thickness of 10 mm. The side of the specimens is sealed to ensure a one dimensional flux. As shown in Figure 2, the specimens are fixed on a glass container with the oversaturated sodium chloride solution.

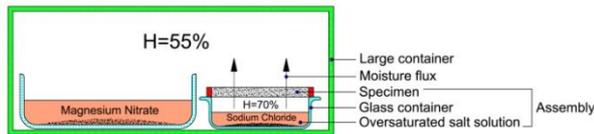


Fig. 2. Schematic view of the experiment set-up

The glass container is placed in a large container with the oversaturated magnesium nitrate solution. The duration of this experiment is 10 months. The chloride profiles before and after the experiment are measured and compared.

3 Specimen preparation

In this experiment, mortar specimens with a water cement ratio of 0.5 and cement type of CEM I 42.5 N is used. Composition and properties of the specimens are shown in Table 1.

Table 1. Composition and properties of the specimens

Materials	Mortar	
	Volume (m ³)	(kg/m ³)
CEM I 42,5N	159.47	502.18
Sand	568.51	1506.54
Water	251.09	251.09
Superplasticizer	0.93	1.01
Air	20	-
w/c	0.5	
Porosity (%)	17	
1-day compressive strength (MPa)	10.26	
7-days compressive strength (MPa)	42.07	
28-days compressive strength (MPa)	56.83	

The mortar specimen is cast in PVC tubes with a diameter of 100 mm. After one day, the mortar is demoulded and cured for 28 days. Specimens of 10 mm thickness are cut from the mortar cylinder, and provided with a chloride mass percentage 2.0%. These chloride concentrations, C_t (kg_{Cl} / 100kg_{solid}) or (%), are calculated as [9]

$$C_t = \frac{\phi \cdot c_{Cl} + C_{Cl_s} \cdot (100 - \phi) \cdot \rho_s}{\rho_m}, \quad (1)$$

where ϕ (m³_{solution} / 100 m³_{mortar}) is the porosity, c_{Cl} (kg_{Cl} / m³_{solution}) the concentration of free chlorides, C_{Cl_s} (kg_{Cl} / kg_{solid}) the concentration of bound chlorides, ρ_s

(kg_{solid} / m³_{solid}) the specific density and ρ_m (kg_{solid} / m³_{mortar}) the apparent density, where the subscript mortar includes the solid and the pore solution.

It is assumed that C_{Cl_s} is a function of c_{Cl} given by

$$C_{Cl_s} = K \cdot c_{Cl}^n, \quad (2)$$

where K (m³ⁿ / kgⁿ) is the chloride binding capacity and n (-) the chloride binding intensity parameter.

Sodium chloride solutions are used to provide the specimens with chloride. In order to obtain a 2.0% chloride content of the mass of mortar specimen, c_{Cl} is calculated from Eqs. (1) and (2) for $K = 0.53 \times 10^{-3}$ m³ⁿ / kgⁿ [10], $n = 0.52$ [10], $\phi = 17$ m³_{solution} / 100 m³_{mortar} (Table 1), $\rho_s = 2062$ kg_{solid} / m³_{solid} and $\rho_m = 2412$ kg_{solid} / m³_{mortar}, so that $c_{Cl} = 144$ kg_{Cl} / m³_{solution}.

Due to the use of the sodium chloride solution, the values of the concentration of free chlorides c_{Cl} are recalculated. To obtain 2.0% chloride, 237 kg/m³ of the solution sodium chloride is used.

Vacuum saturation is used for penetrating chloride into the mortar specimen. The procedure starts by placing the specimens in a desiccator. An air pressure of 4 kPa is applied on the specimens for 3 h to remove the air from the specimen. After the salt solution is added to the specimens in the desiccator after 3 h, the pressure is maintained for another hour, and the specimens are then left in the salt solution for 20 h.

The chloride concentration profiles of mortar specimens are measured in five positions in the specimens [11]. The procedure of measuring chloride concentration profiles starts with grinding layers of 1 mm with Profile Grinder 110. The obtained powder is dried at 100 °C to a constant mass and cooled down to room temperature. From each layer, 2 g is placed in a beaker. After adding 35 ml of distilled water and 2 ml nitric acid of 1M, the beaker is shaken manually for 1 min. The solution is brought to boil, cooled afterwards, and poured onto filter paper. The obtained solution is adjusted to 100 ml, and used for the determination of the concentration of chloride. The concentration is measured by Metrohm MET 702 automatic titration. A silver nitrate solution of 0.01 mol/l is used as a titration solution.

The chloride concentration is calculated as:

$$C_t = \frac{V_{AgNO_3} \cdot N_{AgNO_3} \cdot M_{Cl}}{m_s} \cdot 100, \quad (3)$$

where C_t (kg_{Cl} / 100 kg_{solid}) is the chloride concentration, V_{AgNO_3} (m³_{AgNO₃}) the volume of the titrated silver nitrate solution, N_{AgNO_3} (mol_{AgNO₃} / m³_{AgNO₃}) the molarity

of silver nitrate solution, M_{Cl} ($\text{kg}_{Cl}/\text{mol}_{Cl}$) the molar mass of chloride and m_s (kg_{solid}) the mass of the sample.

With Eq. (3), the chloride concentration is determined as a function of the position, as it is shown in Figure 3.

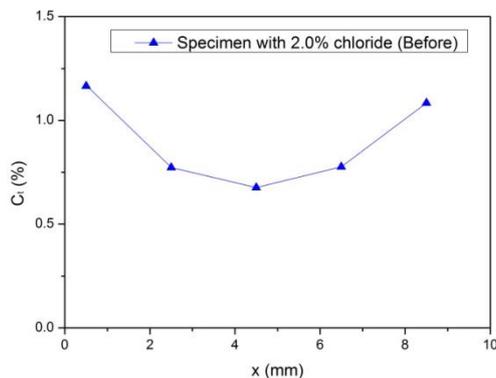


Fig. 3. Chloride concentration profiles

The high chloride concentration profile in the surface layer occurs due to the use of a specimen that was not completely dry in the beginning of the experiment. However, the drying procedure requires much attention because drying causes micro cracks in the specimen, which must be avoided in this experiment. Furthermore, the increased porosity at the surface of the specimen, which is generated during the cutting in layers of 10 mm, could also cause this effect. Another possible reason for the high chloride concentration in the surface layer is that part of the free-chloride entering the specimen can be bound in the external layers, and, therefore, the chloride concentration in the solution entering the deeper layers is automatically decreased.

4 Results

The chloride profiles in the mortar specimens are measured by titration before the experiment as shown in Figure 3. The chloride profile for two specimens after a moisture flux of 10 months through the specimen is also measured, as shown in Figure 4. The moisture flux during these 10 months is measured by the mass of the assembly. This mass decreases during the experiment. The moisture flow, which is the time derivative of the decreased mass, is calculated and is approximately 0.05 g/d.

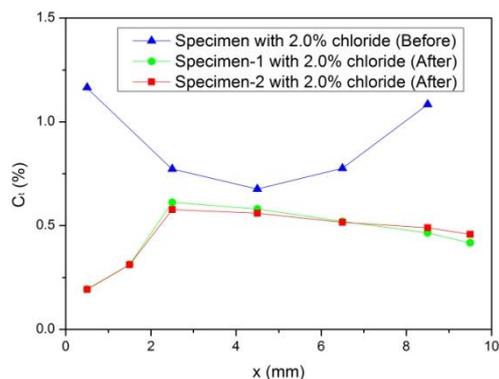


Fig. 4. Chloride concentration profiles before and after the experiment

Figure 4 shows two interesting behaviors after 10 months. Firstly, it shows that the average chloride concentration in the specimen is decreased. Secondly, the chloride concentration at the surface is also decreased. It is unclear how the chloride content decreased in the specimen. Due to the uncertainty of this result, the chloride concentrations after 10 months are measured with different methods other than titration. Ion chromatography is one of other techniques that are used to measure the chloride concentrations in the specimen. This technique is similar to titration due to the measuring the chloride ions in a liquid. With this technique, the first layers from the surface are measured, as it is shown in Figure 5.

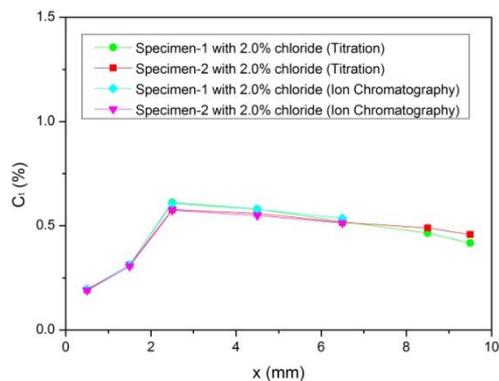


Fig. 5. Measurement of chloride concentration profiles with titration and Ion chromatography

The measurements with both techniques, titration and ion chromatography, are similar. From this result, it is clear that the amount of the free chloride in the solution is measured. But to measure the total chloride, the bound chloride must also be taken into account. It is assumed in the measurement with these two techniques that all the bound chloride is unbound by using nitric acid. To examine this, the powders of the grinded layers are measured again by XRF. XRF is a technique which can be used to determine chloride content. However, a calibration is needed to obtain reliable results. First measurement in powder form of the layer close to the surface is carried out to compare the three techniques

(Titration, Ion chromatography and XRF), as it is shown in Figure 6.

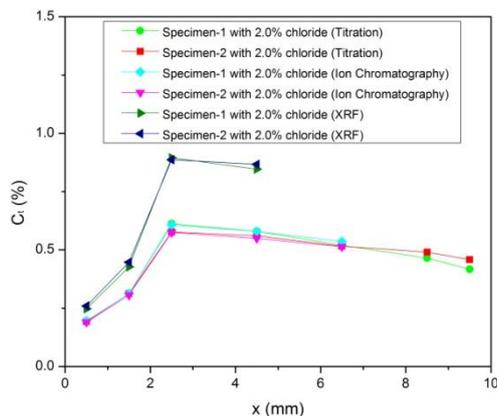


Fig. 6. Comparison of different techniques to measure chloride concentration profiles

The measurement of chloride concentration in the specimen with XRF shows a higher chloride concentration by approximately 30%, but with the same trend as the previous two techniques. The accuracy of this technique is however questionable as mentioned earlier. To obtain more reliable results, a calibration method is designed. Layer of mortar specimens without chloride is ground with the Profile Grinder 110. By adding a known amount of sodium chloride to the powder, the exact amount of chloride is then known. By measuring the chloride concentration of the mixed powder, the calibration of XRF can be obtained.

Furthermore, a new experiment is designed to examine the decrease of the chloride concentration towards the end of the experiment, as it is shown in Figure 4. In this experiment, the specimens will be saturated by the vacuum saturation method as explained before. Some of these specimens will be sealed to avoid moisture transport, and some others will be exposed to a moisture flux. The chloride concentration profiles will be measured and compared after 0, 5, and 9 months.

5 Conclusions

The influence of moisture on chloride transport in mortar is investigated in this paper. Specimens are exposed to chloride solutions to obtain specimens with 2.0% chloride of the mass of the specimen. The specimen is replaced in a surrounding in order to create moisture flux through the specimen. After 10 months, the chloride concentration profiles are measured by titration and compared with the chloride concentration profiles from the start of the experiment. The results show that the chloride concentration is decreased at the end of the experiment. Because of the seemingly disappearance of chloride, the chloride concentrations profiles are measured with different techniques.

Ion chromatography is used to measure the profiles. The result of this technique is similar to the titration technique. In these two techniques, the chloride is measured from liquid solution, where it is assumed that all the bound chloride is unbound due to the use of nitric acid. To investigate this, XRF technique is used to measure the chloride concentration profile. With this technique, chloride concentration can be measured in solid state, which means directly from the ground powder. Although this technique needs to be calibrated, accurate results can be obtained.

References

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