# Chloride Migration Coefficients from Non-Steady-State Migration Experiments at Environment-Friendly "Green" Concrete

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# Abstract

The Centre for Resource Saving Concrete Structures was established in 1998 by a number of mainly Danish companies and educational and research institutions. One of the main targets of the centre is to develop technologies, which encourage the use of resource saving concrete ("green" concrete), i. e. concrete with minimal clinker content, concrete with high amounts of cement replacement materials, such as fly ash, silica fume and other pozzolans and concrete with waste materials such as stone dust and inorganic residual products.

Among others one important task of the project is to prove the service life of the "green" concrete. This includes an investigation of the ability to withstand chloride ingress when exposed to aggressive environment. For these purposes the chloride ingress behaviour of the "green" concrete will be determined using a rapid chloride migration test method. This paper presents the first test results obtained during the first stage of the project.

### Introduction

In 1998 the Danish Centre for Resource Saving Concrete Structures initiated a research project on "green" concrete which concerns the entire life of a concrete structure. The aim is to

• develop more environmentally friendly types of cement and concrete, e.g. concrete with reduced consumption of cement and binders or concrete with recycled inorganic residual products from concrete production or other types of production.

Edvardsen , Chloride Migration, 1 of 7 Fax: +45 45 97 21 14 E-mail: cle@cowi.dk • develop technological solutions for performance and maintenance adjusted to the new green types of concrete and green construction technology for already known types of concrete.

The Centre comprises different projects for development of technologies, which can be used directly by the industry and thereby encourage for example the use of "green" concrete. The development projects are supported by a number of technical activities, which combine research and development. One important task is to prove the service life of the "green" concrete. This includes an investigation of the ability to withstand chloride ingress when exposed to aggressive environment and for this purpose there is a demand for a test method, which can provide reliable information about such properties.

#### **Test method**

For this project the rapid chloride migration method was used to determine the chloride migration coefficient from migration experiments at "green" concrete, see Fig. 1. Among the different rapid test methods available, the rapid chloride migration (RCM) method elaborated by Tang /1/ has been revealed in /2,3/ to be theoretically the clearest, experimentally the most simple and with regard to precision (repeatability) the most promising tool.

Conventional methods to determine the chloride ingress e. g. by immersion of concrete specimens in chloride-contaminated solutions (i.e. APM 302, NT Build 443, AASHTOO T259-80) have the disadvantage that they are very time-consuming (2-4 months). In contrast the rapid chloride migration method is extremely fast. The test period is limited to some few days. Because of this, diffusion migration coefficients can be determined as a function of the concrete age. Chloride migration coefficients from migration tests at early age may be measured too.

The repeatability of the method has been investigated systematically, e.g. by round-robin test /2,3/. The determined coefficients of variation (CoV) are in the range of 5-9%. (for comparison: COV for NT Build 443 lays in the rang of 8-14%).

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Fig.1: Test arrangement of the rapid chloride migration test /1/

The specimens for testing must be a water-saturated cylinder of 100 mm in diameter and 50 mm in thickness. The sample will be given in a sealing tape, ensuring that the tape will extend above the top surface of the specimen about 150 mm so as to hold reagents A (anolyte solution), which is free of chlorides. Subsequently, the sealed specimen will be located in the chloride containing reagents B (catholyte solution) by setting on a plastic support followed by the location of anodic stainless steel plate.

A potential of  $30\pm0.2$  V (DC) is applied across the specimen for a period of time which will be fixed in dependency of the recorded initial current. After the fixed test duration the anode has to be removed.

Immediately after the end of the test, the specimens are split into two half cylinders parallel to the height. The fractured surfaces are sprayed with an  $AgNO_3$  solution to detect the depth of chloride penetration by colorimetric method.

# Results

During autumn 1999 (first phase of the project) the first tests have been carried out on three different mix designs

- two mix designs (A and B) with raised contents of fly ash (FA), 18% and 40% of the powder respectively
- one mix design, where ordinary fly ash is substituted with ash originating from the combustion of sludge from a sewage plant (C)

Edvardsen , Chloride Migration, 3 of 7 Fax: +45 45 97 21 14 E-mail: cle@cowi.dk The concrete was mixed on ready mix plants. Therefore in each case the basis for the mix design was the local mix design for a so-called A-concrete; that is concrete complying with the directions for concrete exposed to aggressive environment stated by the Danish Standard DS481 /4/. The mix design was then modified after the following the principles

- the cement type has been changed from a low alkali sulphate resistant cement to a rapid cement (in order to reduce the amount of energy used for cement production)
- the volume of paste has not been changed
- the equivalent water/cement ratio has not been changed  $\left(\left(\frac{w}{c}\right)_{aa} = \frac{w}{c+0.5FA+2.5F}\right)$
- the type and amount of aggregates have not been changed

After mixing the concrete was poured into a lorry mixing drum. After 60 seconds of rotation the slump and the air content of the fresh concrete were measured. If the measured values differed significantly from a slump of 100 mm and an air content of 5.5%, the mix design was adjusted and a new mix was prepared.

This procedure lead to the mix designs listed in Table 1. The measured chloride migration coefficients and the related concrete age at the time of testing are listed at the bottom of the table.

Table 1: Mix design for the tested types of concrete. All constituents are noted by weight  $[kg/m^3]$  in a saturated, surface dry condition.

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Constituent	Description	Α	$\mathbf{B1}^1$	$\mathbf{B2}^1$	С
		18% FA	40% FA	40% FA	19 %
					ash from
					sewage
					plant
Cement	Aalborg Portland RAPID <sup>®</sup> cement (CEM I 52.5 MS/LA)	272.3	189.9	188.3	279.1
Ordinary fly	Danaske	63.6	137.6	134.7	-
ash	Dunuske	05.0	157.0	151.7	
Fly ash from		-	-	-	68.5
sewage plant					
Silica fume	Elkem	17.6	17.1	16.8	14.3
Water		140.0	118.1	119.0	133.2
Plastizicer	Conplast 212	-	-	-	2.63
	Conplast 214	3.21	2.42	2.39	-
Super plastizicer	Peramin F	-	-	-	1.27
	Conplast SP 430	-	3.44	2.78	-
Air-entraing admixture	Conplast 316 AEA 1:9	-	-	-	1.14
	Conplast 316 AEA 1:11	1.41	1.73	4.74	-
Sand		637.1	667.10	649.6	584.2
Coarse		1141.7	1176.0	1168.6	1102.0
aggregate					
					2
(w/c) <sub>eq</sub>	[-]	0.42	0.42	0.44	$0.40^{2}$
Concrete age	[d]	40	40	28	28
at chloride					
migration					
testing					
Chloride	$[10^{12} \text{ m}^2/\text{s}]$	4.9	6.8	6.5	20.1
migration					
coefficient					
from					
I migration test	1	1	1	1	

1. After curing of B1 for 28 days the air content of the hardened concrete turned out not to be sufficient to ensure frost resistance. Therefore the casting was repeated with a slightly changed mix design to increase the artificial air pore content (B2). The water/cement ratio has been calculated as if the fly ash from the sewage plant was ordinary fly ash.

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As still no acceptance criteria exist for the chloride diffusion coefficient, the inventor of the rapid chloride migration test Mr. Tang /1/ has given the following guidelines for the chloride migration coefficient D measured by the RCM method:

- $D < 2 \cdot 10^{-12} \text{ m}^2/\text{s}$ : very good resistance against chloride ingress
- $D < 8 \cdot 10^{-12} \text{ m}^2/\text{s}$ : good resistance against chloride ingress
- D<16·10<sup>-12</sup> m<sup>2</sup>/s: *moderate resistance* against chloride ingress
- $D>16\cdot10^{-12}$  m<sup>2</sup>/s: not suitable for aggressive environment

# **Discussion and Perspective**

Beside concrete mix C (concrete with ash from sewage plant) the "green" concrete shows a good resistance against chloride ingress. Thus, the results confirm the results obtained at similar investigations /5/ performed at concrete consisting of Portland cement and high amounts of fly ash (up to 40% FA). In the latter, the investigations have revealed that the chloride migration coefficient from migration test will be significantly reduced with increasing fly ash content and advanced concrete age.

One possible cause for this increased resistance to chloride ingress is the so-called "pore-blocking effect" due to the puzzolanic reaction of the fly ash. Another cause seems to be the increased chloride binding capacity of concrete consisting of fly ash.

The result for concrete C foreshadows that the addition of ash coming from sewage plant may have a negative effect on the chloride resistance. Parallel to the durability testing, the compressive strength was measured at different concrete ages (7, 14, 28 and 56 days). These measurements showed that concrete C has a slower development of mechanical properties than the other types of concrete, and this may indicate that the development of properties such as chloride resistance is slower too. Though, it can not be excluded that at a later stage the chloride resistances of concrete C and conventional concrete will be equal. This raises the question: Do we reject "green" concrete with sufficient chloride resistance by using the same acceptance criteria as for conventional concrete?

A verification of these phenomena requires additional investigations. In the next phase of the research project a more comprehensive testing of the chloride resistance of "green" concrete is foreseen which comprise among other things chloride migration testing at different concrete ages (including concrete at ages >>1 year). Further, an investigation of the chloride binding capacity of "green" concrete is under consideration, e. g. by testing the ad- and de-sorption behaviour of binder specimens which will be submerged into chloride solutions.

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