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Chloride resistance of slag cement mortars

Etatsprogrammet Varige konstruksjoner 2012-2015

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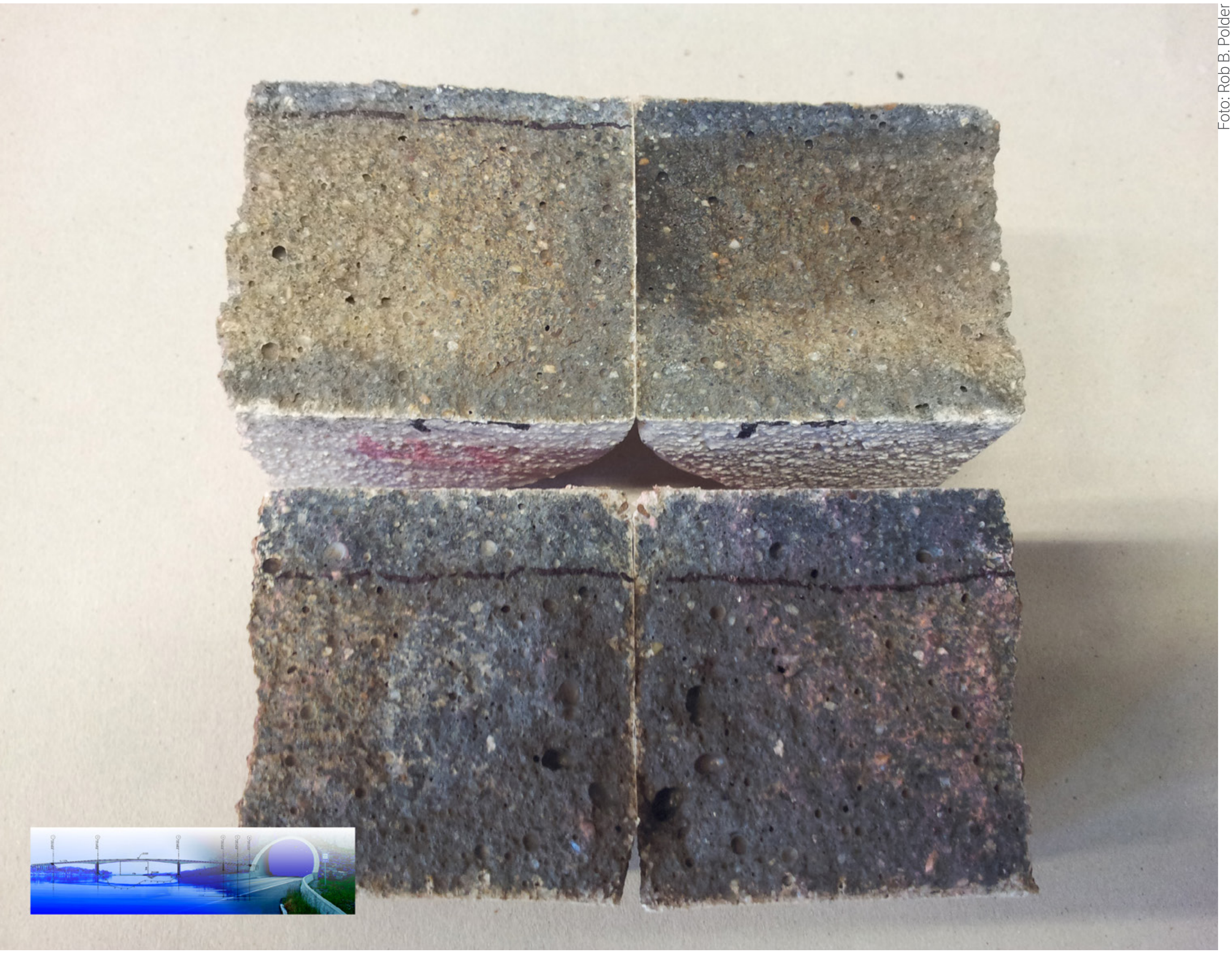

Foto: Rob B. Polder

Statens vegvesens rapporter

NPRA reports
Norwegian Public Roads Administration

Tittel
Kloridmotstand for mørtler med slaggsement

Undertittel
Varige konstruksjoner 2012-2015

Forfatter
Rob B. Polder

Avdeling
Trafikksikkerhet, miljø- og teknologiavdelingen

Seksjon
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Prosjektnummer
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Rapportnummer
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Prosjektleder
Synnøve A. Myren/ Sølvi Austnes

Godkjent av
Bård Pedersen

Emneord
levetid, armeringskorrosjon, slaggsement, kloridinntrengning, resistivitet, karbonatisering

Sammendrag
Et eksperimentelt program ble gjennomført for å studere egenskaper til fem mørtelblandinger med: CEM III / B (to typer); en CEM III / A (med 50% slagg) med silikastøv ; og en CEM I og en CEM II / A-V (flygeaskesement), begge med silikastøv. Rapid Chloride Migration (RCM) og elektrisk motstand ble testet i aldere mellom to dager og ett år. RCM- verdier viste konsistent nedgang og resistivitet viste økning mellom to dager og ett år. Forsøkene vil pågå i 3 år. Hensikten er å gi et bedre grunnlag til å vurdere bruk av slaggsementer i Norge som et virkemiddel for å oppnå mer bestandige betongkonstruksjoner. Rapporten inneholder data opp til 1 år.

Antall sider 22

Dato Februar 2016

Title
Chloride resistance of slag cement mortars

Subtitle
Durable structures 2012-2015

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Key words
service life, reinforcement corrosion, blast furnace slag cement, chloride penetration, resistivity, carbonation

Summary
An experimental program was carried out to study the properties of five mortar mixes made with: CEM III/B (two brands); a CEM III/A (with c. 50% slag) with silica fume; and a CEM I and a CEM II/A-V (fly ash cement), both with silica fume. Rapid Chloride Migration (RCM) and electrical resistivity were tested at ages between two days and one year. RCM values showed consistent decrease and resistivity showed consistent increase between two days and one year. The program is intended to collect data up to three years age. The ultimate goal is to provide a basis for evaluating the use of slag cement in Norway for durable concrete structures. The report contains data up to 1 year.

Pages 22

Date February 2016

Forord

Denne rapporten inngår i en serie rapporter fra **etatsprogrammet Varige konstruksjoner**. Programmet hører til under Trafikksikkerhet-, miljø- og teknologiavdelingen i Statens vegvesen, Vegdirektoratet, og foregår i perioden 2012-2015. Hensikten med programmet er å legge til rette for at riktige materialer og produkter brukes på riktig måte i Statens vegvesen sine konstruksjoner, med hovedvekt på bruer og tunneler.

Formålet med programmet er å bidra til mer forutsigbarhet i drift- og vedlikeholdsfasen for konstruksjonene. Dette vil igjen føre til lavere kostnader. Programmet vil også bidra til å øke bevisstheten og kunnskapen om materialer og løsninger, både i Statens vegvesen og i bransjen for øvrig.

For å realisere dette formålet skal programmet bidra til at aktuelle håndbøker i Statens vegvesen oppdateres med tanke på riktig bruk av materialer, sørge for økt kunnskap om miljøpåkjenninger og nedbrytningsmekanismer for bruer og tunneler, og gi konkrete forslag til valg av materialer og løsninger for bruer og tunneler.

Varige konstruksjoner består, i tillegg til et overordnet implementeringsprosjekt, av fire prosjekter:

Prosjekt 1: Tilstandsutvikling bruer
Prosjekt 2: Tilstandsutvikling tunneler
Prosjekt 3: Fremtidens bruer
Prosjekt 4: Fremtidens tunneler

Varige konstruksjoner ledes av Synnøve A. Myren. Mer informasjon om prosjektet finnes på vegvesen.no/varigekonstruksjoner

Denne rapporten tilhører **Prosjekt 3: Fremtidens bruer** som ledes av Sølvi Austnes. Prosjektet skal bidra til at fremtidige bruer bygges med materialer bedre tilpasset det miljøet konstruksjonene skal stå i. Prosjektet skal bygge på etablert kunnskap om skadeutvikling og de sårbare punktene som identifiseres i Prosjekt 1: Tilstandsutvikling bruer, og skal omhandle både materialer, utførelse og kontroll. Prosjektet skal resultere i at fremtidige bruer oppnår forutsatt levetid med reduserte og mer forutsigbare drift- og vedlikeholdskostnader.

Rapporten er utarbeidet av Rob B. Polder, TNO, Nederland, som del av et samarbeidsprosjekt mellom TNO og Statens vegvesen.

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TNO report

TNO 2015 R11427

Report on Laboratory testing of slag cement mortars for RCM and other properties up to one year of age

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Contents

1 Introduction

The Norwegian Public Roads Administration (Staten's Vegvesen; NPRA) is currently reviewing the durability performance of concrete mixes in existing bridges and tunnels and considering possible future concrete mixes for the next generation of bridges and tunnels. The research is part of NPRA's research program *Durable structures*.

The Netherlands have almost a century experience in the use of ground granulated blast furnace slag (GGBS) cements with high slag content, comparable to current CEM III/B (66-80 % slag) as defined in EN 197-1 (2011) for major infrastructure, including marine concrete. Over decades in practice and in abundant laboratory investigations, CEM III/B concrete has demonstrated considerably better performance on durability issues such as chloride induced reinforcement corrosion and alkali-silica reaction than pure Portland cement.

The NPRA and TNO have established a collaboration in order to make this Dutch experience and knowledge available for evaluation within the aforementioned context, and identify possible knowledge gaps with regard to durability performance and needs for future research relevant to the aforementioned Norwegian research programme. In 2013 a state-of-the-art review of experience with CEM III/B cement in concrete in the Netherlands was written and published as NPRA report 270 [1]. Following discussion of the state-of-the art review, it was considered useful to collect experimental data on materials incorporating slag, based on binders that could potentially be available on the Norwegian market. This report documents the results of the experiments up to the age of one year.

This study is part of the collaboration was between NPRA and TNO under agreement 2012082035 “RnD Collaboration Durable Structures – FB1 Durability of concrete with slag cement”, as agreed in document 2012/082035-003 of August 28, 2013.

2 Materials, methods and testing schedule

2.1 General

The experimental program agreed on was the following.

The overall goal was to obtain data over time, from relatively young age up to several years, in order to document chloride penetration resistance, electrical resistance and carbonation of the different binders over time.

To this end, mortar specimens were to be made with five binders and were to be tested for chloride penetration resistance at ages between 2 days and three years. In addition, electrical resistivity was to be tested between 2 days and three years, and carbonation was to be tested at ages one, two and three years. Moreover, specimens were to be sent to NPRA for RCM and resistivity testing at 90 days and at one year age.

Materials used are described in section 2.2, methods applied in section 2.3 and the overall testing schedule in section 2.4.

2.2 Materials

Specimens were prepared using binders (see below) and sand according to the standard for testing of cement, NEN-EN 196-1-2005 [2], with the following deviation: a water-to-binder ratio was used of 0.40 instead of 0.50 in order to stay close to common Norwegian concrete technology. This means that mortar with composition cement:sand:water equals 1:3:0.4 (by mass) was made using rounded siliceous sand of 0-2 mm grain size. Mixing and casting were carried out according to the standard. A superplasticiser Cugla HR (35% solids) was added in order to obtain the same workability of all mixes. Its dosage was determined using trial mixes. Mix compositions are reported in detail in Annex A.

Binders used were:

- CEM I 52.5 N (LA) Rapid from Aalborg with 5% silica fume, denoted as A-CEM I+5%SF.
- CEM II/A-V 42.5 N Anlegg FA from Norcem, with 5% silica fume, mix code B-CEM II/A-V+5%SF.
- CEM III/B 42.5 N from NL (ENCI), mix code C-CEM III/B(NL).
- CEM III/B 42.5 N-SR/LH/NA from Cemex (Germany), mix code D-CEM III/B(D).
- CEM III/A 42.5 N-NA from Cemex with 5% silica fume, mix code E-CEM III/A+5%SF.

All binder materials were obtained via NPRA except the Dutch slag cement. Properties of the cements used are reported in Annex A.

2.3 Methods

RCM testing
Specimens were tested for chloride penetration resistance using the rapid chloride migration (RCM) test according to NTBuild 492 [3]. For RCM testing, specimen moulds were PVC cylinders with approximate inner dimensions of 100 mm diameter and 50 mm height. After casting, the moulds were covered with plastic foil and stored in the laboratory at 20 °C and 95% RH for 24 hours. After 24 hours the specimens were demoulded and then immersed in saturated lime solution until the time of testing.

The test description involves vacuum saturation of cylindrical specimens (100 x 50 mm), mounting between chambers with electrodes filled with NaOH or NaCl solutions, and applying a DC voltage for a certain time. Voltage and time must be chosen from a table based on the initial current flowing through a specimen when 30 V is applied. After application of the voltage for the designated time, the specimens are split and sprayed with silver nitrate, upon which the chloride penetration front becomes visible. From the average penetration depth, the voltage and the time, the chloride migration coefficient is calculated.

The test was applied with the following deviations:

- Vacuum saturation was omitted for specimens up to 180 days age, considering that the specimens would not dry out significantly because they were stored at high humidity; and that vacuum treatment might cause damage to the microstructure, in particular at young ages; specimens tested at 360 days age were vacuum saturated.
- Voltage and time were chosen based on previous experience with young mortars [4] and with slag cements; in practice this means an extension of Table 1 given in NTBuild 492 to the high side for very dense mortars (Table 2) and to the lower side for young mortars (Table 3). Note 2 below Table 1 was neglected. The overall objective of choosing voltage and time is to obtain about 25 mm of penetration.

In addition, the following details of casting and testing specimens are given. Specimens were cast as discs with mix codes written on the finished (top) surface. The (non-marked) bottom-of-the-mould surface was exposed to the chloride solution (cathode side) in the RCM test. For the test, possible defects in the bottom surface are sealed by silicone sealant to prevent leakage.
Specimens sent to Norway for testing by NPRA were removed from the lime solution and packed in plastic to prevent drying out as much as possible.

Table 1 Settings for time and voltage according to NTBuild 492

Initial current I_{30V} [mA] (at 30 V)	Applied Voltage U [V] (after adjustment)	Possible new initial current I_o [mA] (at adjusted voltage U)	test duration t [h]
< 5	60	< 10	96
5-10	60	10-20	48
10-15	60	20-30	24
15-20	50	25-35	24
20-30	40	25-40	24
30-40	35	35-50	24
40-60	30	40-60	24

60-90	25	50-75	24
90-120	20	60-80	24
120-180	15	60-90	24
180-360	10	60-120	24
> 360	10	> 120	6

Note 1: the original Table in NTBuild 492 is titled: Test voltage and duration for concrete specimens with normal binder content.
Note 2: The Table has a note stating: For specimens with a special binder content, such as repair mortars or grouts, correct the measured current by multiplying by a factor (approximately equal to the ratio of normal binder content and actual binder content) in order to be able to use the above table.

Table 2 Suggested voltage and time based on experience with dense (slag) concrete specimens

initial current I_{30V} [mA] (at 30V)	applied voltage U [V] (adjusted)	expected new initial current I_o [mA] (at adjusted voltage U)	test duration t [h]
< 2	60	< 5	168
2-5	60	5-10	96

Table 3 Suggested voltage and time based on experience with young mortars [4]

age [day]	CEM I		CEM III/B		Other binders with 5% SF	
	Volt	Time	Volt	Time	Volt	Time
1	10	150 min	10	150		
2	15	240 min	15	240 min	15	240 min
7	15	24 hour	15	24 hour	15	24 hour
≥ 14	Measure current at 30 V and test (voltage and time) according to Table 1					

Note 1: testing at 1 day is not foreseen.
Note 2: testing of pure CEM I is not foreseen.

Resistivity was tested using an AC resistance meter (ESCORT LCR) at 120 Hz following either one or both of two procedures (see section 2.4 and Table 4):

- The cell resistance was measured after a specimen had been inserted in an RCM cell, before the actual application of the (initial) voltage; the cell resistance was also measured after the RCM test; the resistivity was calculated from the initial cell resistance by multiplying with the geometrical cell constant (surface area/length); the result is denoted **Rrcm**.
- The resistance of a specimen was measured (after surface drying) by placing it between two steel plates with wetted cloth, after removal from the saturated lime solution; the resistivity was calculated using the geometrical cell constant (surface area/length); the result is denoted **Rtem**.

The geometrical cell constant is given by π $(0.05)^2/0.05$ equals 0.157 m. Minor deviations from nominal dimensions are neglected.

Carbonation testing

For carbonation testing, specimens were 160 x 40 x 40 mm^3 mortar bars cast in steel moulds. They were demoulded at 24 hours and stored in saturated lime solution. At seven days age, they were placed on the roof of the TNO laboratory building without shelter.

Carbonation depths were determined by splitting off a part of the prisms and spraying the freshly broken surface using phenolphthalein.

2.4 Testing schedule

The time schedule for testing is given in Table 4.

Table 4 Planned testing schedule; for RCM: 3 specimens tested

age	RCM and Rrcm $	resistivity Rtem &	Carbonation depth
2	yes	yes	-
7	yes	yes	-
14	-	yes	-
28	yes	yes	-
56	-	yes	-
60 - 90	-	yes (all specimens)	-
90# @	yes	yes	-
180	yes	-	-
270	-	yes (all specimens)	-
360@	yes	yes (all specimens)	yes
2y %	yes	yes	yes
3y %	yes	yes	yes

carried out at 133 days age at TNO and at 120 days at NPRA.
@ specimens were sent to NPRA for testing at their laboratory
$ Rrcm denotes resistivity tested on specimens in the RCM cell before the voltage was applied
& Rtem denotes resistivity tested on discs between steel plates
% testing at 2 and 3 years age is foreseen, but is not included in this report

Rrcm was measured on all specimens subjected to the RCM test. Rtem was measured on planned occasions, in principle on three specimens. Measurements on 56 days age were not reported. In April 2014, Rtem was measured on all available 19 specimens per mix. The age of specimens then was between 60 and 90 days. Rtem was measured on January 29, 2015 on all remaining discs. Specimen age was between 360 and 385 days.

3 Results

3.1 Casting dates

Mortars were coded, prepared and cast as indicated in Table 5. For the first mix a trial mix was made, which was very stiff. Subsequently, a superplasticiser was added in order to get a plastic mix. For subsequent mixes, superplasticiser dosage was determined by trial and error for similar workability. Dosages used are reported in Table 5. Full mix proportions are reported in Annex A. Mixing batches were relatively small; a complete group of specimens for each mix (36 cylinders and 3 prisms) was composed of about 20 batches.

Table 5 Mix codes and casting information

mix code	binder	casting date (2014)	superplasticiser dosage
A-CEM I+5%SF	CEM I + 5% SF	January 14	0.65%
B-CEM II/A-V+5%SF	CEM II/A-V + 5% SF	January 21	0.33%
C-CEM III/B(NL)	CEM III/B (NL)	January 28	0.13%
D-CEM III/B(D)	CEM III/B (D)	February 4	0.13%
E-CEM III/A+5%SF	CEM III/A + 5% SF	February 11	0.22%

3.2 RCM results

An overview of RCM results is given in Table 6. The testing that was originally planned at 90 days' age was moved to c. 130 days due to the moving of the laboratory. Penetration depths are added for 360 days age specimens for more detailed comparison with measured NPRA data. The RCM results are graphically shown in Figure 1 on linear and log-log scales. The linear plot shows a strong decrease during the early stages, the log-log plot better shows the development over a year.

Table 6 Overview of RCM results obtained at TNO; mean and standard deviation in (); penetration depth in specimens at 360 days

mix code	A-CEM I 5%SF	B-CEM II/A-V 5%SF	C-CEM III/B NL	D-CEM III/B D	E-CEM III/A 5%SF
age (day)	Drcm (10^{-12} m^2/s) mean and standard deviation ()				
2	23 (2.8)	44 (1.9)	119 (10)	49 (4.9)	40 (2.4)
7	18 (0.9)	21 (1.2)	7.8 (0.3)	6.3 (0.5)	8.3 (0.6)
28	2.8 (0.3)	6.9 (0.7)	4.0 (1.5)	2.5 (0.15)	2.5 (0.4)
133	1.4 (0.2)	1.4 (0.0)	1.5 (0.1)	0.83 (0.05)	0.60 (0.15)
185	1.5 (0.1)	1.5 (0.2)	1.7 (0.4)	1.5 (0.2)	0.66 (0.1)
360 #	0.87 (0.15)	0.68 (0.1)	0.43 (0.1)	0.57 (0.03)	0.37 (0.01)
	penetration depth (mm)				
360 #	11 *	9 *	6 *	15 $	10 $

#specimens were vacuum saturated before testing

* polarised for three days
$ polarised for five days
Note: for practical purposes, RCM results are commonly rounded to 0.5 unit or to 1 unit above a value of 10; here we have rounded to 0.1 unit (for values below 10) or 0.01 (for values below 1) in order not to lose information

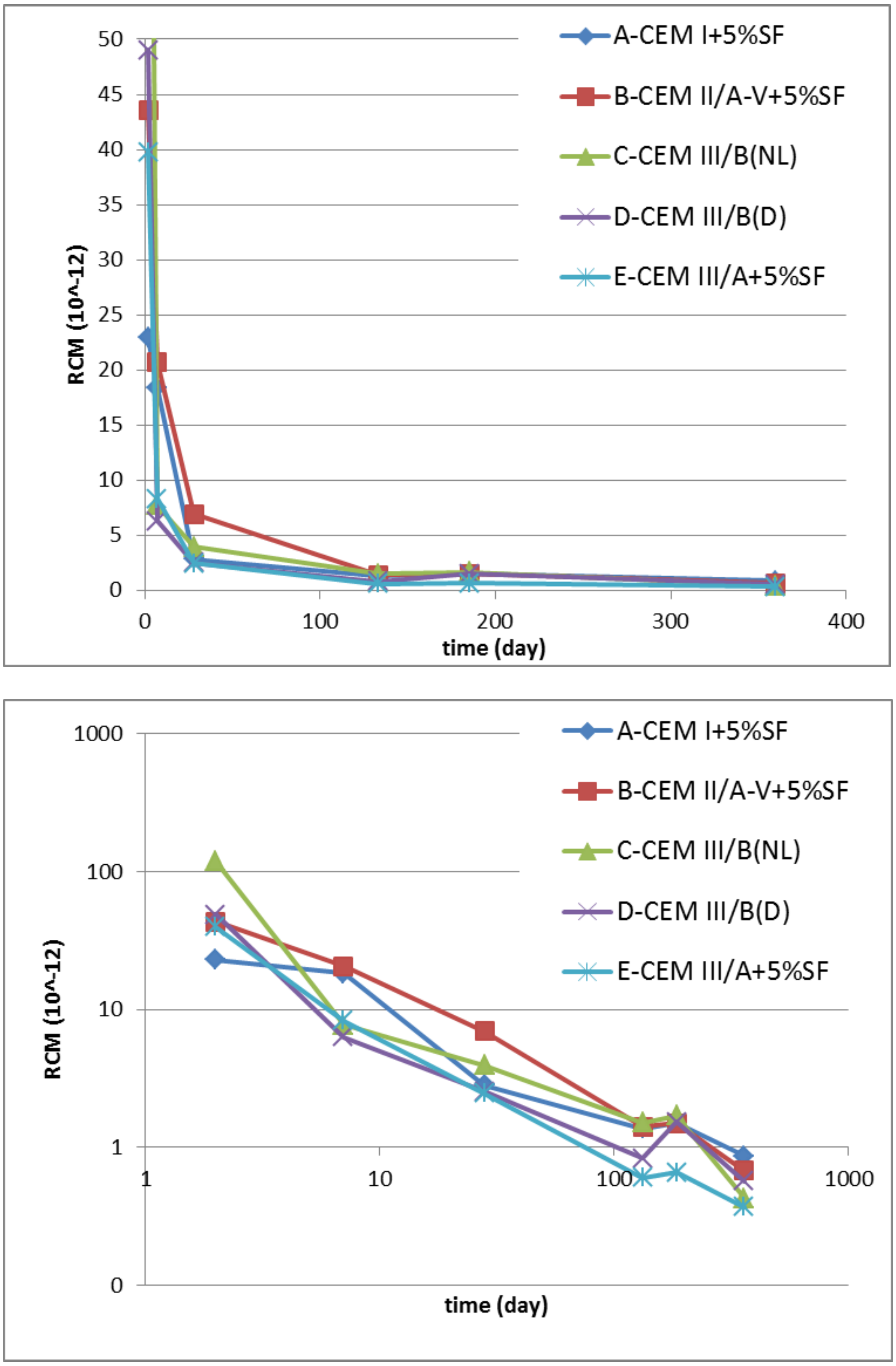


Figure 1 RCM results up to 360 days; top: linear plot, bottom log-log plot.

Full experimental details of RCM testing up to 360 days are given in the Annex B. They can be summarised as follows. Chloride penetration depths ranged from 5 to 31 mm, with a few less than 10 mm and the majority between 20 and 30 mm. Generally, correspondence between three tested samples was good, with one exception. Variation coefficients (VC, 100%*standard deviation/average) were about 10%. The only exception was mix C-CEM III/B(NL) at 28 days, which had individual values of 3, 3 and 6 * 10^{-12} m^2/s, resulting in a coefficient of variation (VC) of 38%.

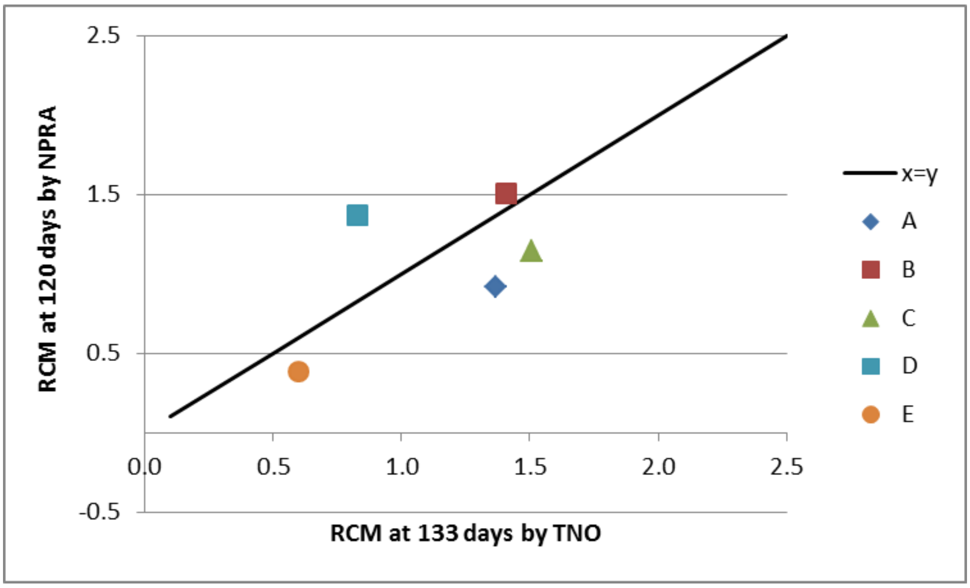
The 2 day specimens of mix A were tested at 15 V for 4 hours, as suggested in Table 3. The penetration depths were small (5 mm), so for the following batches of age 2 days the testing time was increased or the voltage was set at 30 V.

Table 7 provides an overview of RCM results obtained by NPRA at 120 and 360 days age. Experimental details include vacuum saturation before testing. Figure 2 provides a comparison of NPRA's results at 120 days to TNO's results at 133 days; and results from both laboratories at 360 days.

Table 7 Overview of RCM results obtained at 120 and 360 days age by NPRA

mix	A-CEM I 5%SF	B-CEM II/A-V 5%SF	C-CEM III/B NL	D-CEM III/B D	E-CEM III/A 5%SF
			120 days		
Average RCM (10^{-12} m^2/s)	0.92	1.51	1.14	1.37	0.39
St.dev. RCM (10^{-12} m^2/s)	0.04	0.22	0.09	0.10	0.04
VC (%)	5	15	8	7	10
			360 days		
Average RCM (10^{-12} m^2/s)	0.80	0.62	0.73	0.88	0.31
penetration depth (mm)	7.2	11.0	6.6	7.8	5.8

Note: rounded to 0.01 unit in order not to lose information



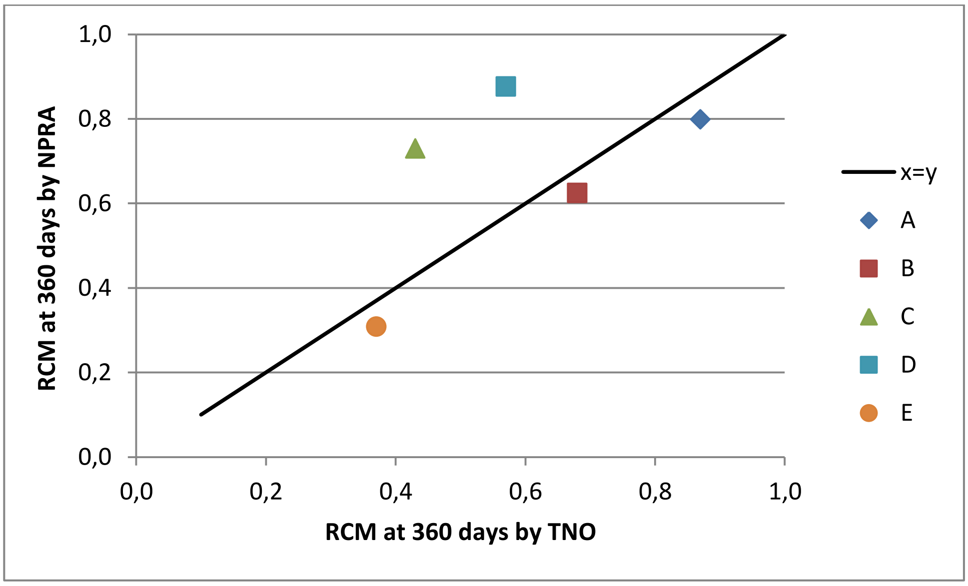


Figure 2 Comparison of NPRA's RCM results at 120 days to TNO's results at 133 days (top) and in both laboratories at 360 days (bottom) (in 10^{-10} m^2/s).

Note: For two of the mixes, a mistake was made reading out the chloride penetration of tests after 180 days. Initially the penetration depths were recorded as c. 40 mm. The calculated RCM values were quite high (higher than at 130 days). This led to additional investigations. The hypothesis was made that the penetrated part of the specimens (here typically 10 mm) had been taken as the non-penetrated part (typically 40 mm). This was tested by carefully examining the split specimens (half-cylinders). A clear distinction could be made based on colour. The halves were then split (into quarter cylinders) and the newly split surface was sprayed with silver nitrate. After a few minutes, a clear colour difference was observed; one zone was more blue-greyish (ca. 10 mm), the other zone (c. 40 mm) was more dark-brown. Supposedly, the former is the part penetrated by chloride, the latter the non-penetrated part. In addition, a drop of chloride solution (3.5% NaCl) was applied to the supposedly non-penetrated part, which immediately changed from brown to blue-greyish. This was taken as evidence that indeed, originally the two zones had been swapped, resulting in erroneous values. The results reported in Table 6 are the correct ones.
These events are reported here for two reasons:

- Mistakes of this type are possible, which may have significant effects on the results.
- A simple method is available for control of correct readout of the chloride penetration in case of suspect results.

3.3 Resistivity results

An overview of resistivity results measured on specimens in migration cells before the start of the test (Rrcm) is given in Table 9. Unfortunately, some values noted in the test files showed strong deviations from expected values by at least an order of magnitude. These are probably due to measuring errors. For those cases, the applied cell voltage *U* was divided by the cell current I_o to obtain an approximate (estimated) resistivity value (marked red in Table 9). Table 9 provides average values of three specimens and also standard deviations and VC's, except for estimated values. Figure 3 provides a log-log plot of resistivity values. As a side note: in TNO's experience, for properly made and tested specimens the coefficient of variation for resistivity measurements is normally of the order of 10%. This is valid for all sets of values reported here.

Table 9 Overview of resistivity measured on specimens in RCM cells, (Rrcm, in Ωm); values in ***red/bold/italic*** were obtained from cell voltage/current

mix	age (day)	2	7	28	133	185	360
A-CEM I 5%SF	average	***34***	***70***	179	***314***	441	465
	stdev			4		22	18
	VC (%)			2		5	4
B-CEM II/A-V 5%SF	average	31	38	108	428	***450***	354
	stdev	5	8	3	33		26
	VC (%)	16	21	3	8		7
C-CEM III/B NL	average	26	120	289	525	***369***	324
	stdev	13	14	4	81		14
	VC (%)	50	12	1	15		04
D-CEM III/B D	average	33	118	317	482	501	543
	stdev	0	7	3	27	5	2
	VC (%)	0	6	1	6	1	0
E- CEM III/A 5%SF	average	31	80	242	***900***	1077	945
	stdev	3	4	7		108	79
	VC (%)	10	5	3		10	8

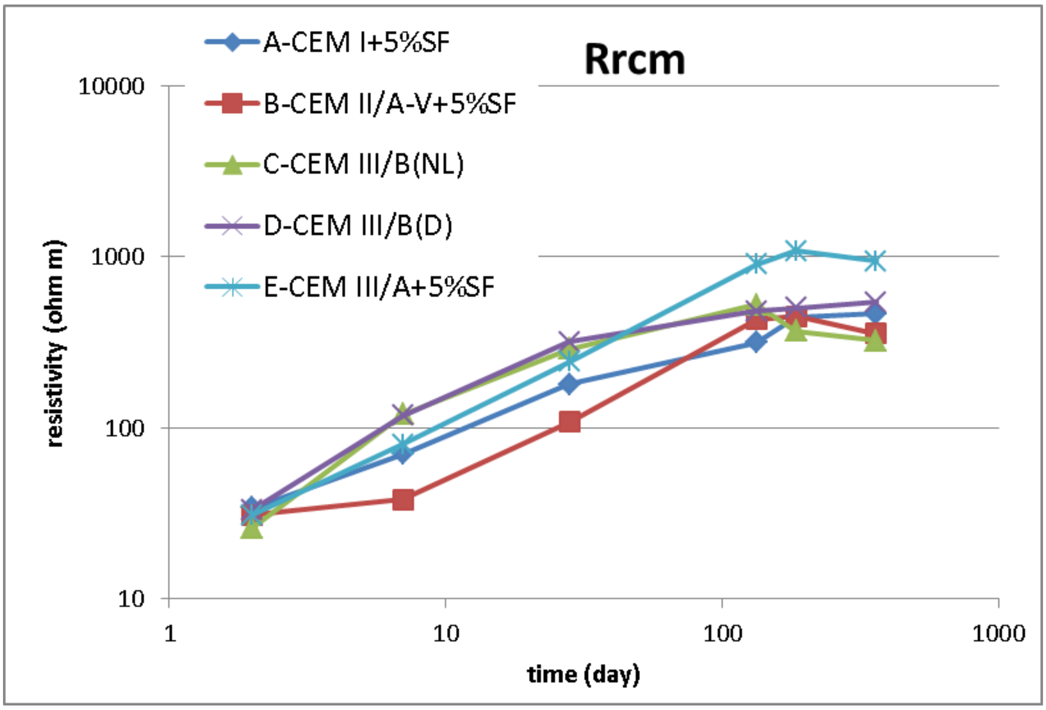


Figure 3 Log-log plot of resistivity values measured on specimens mounted in migration cells (Rrcm) as a function of age.

Resistivities were also measured using the two-electrode method (TEM) on specimens taken out of the saturated lime water, generally on three specimens. These tests were carried out at the age of 2, 7, 14 and 28 days. Unfortunately, records of measurements at 56 days were lost. However, around that age, measurements were carried out in a single campaign in April, 2014, when specimens had ages between 60 and 90 days (depending on individual mixes' casting date). For simplicity, their age is averaged at 75 days. These results are reported in Table 10. Resistivity (Rtem) was not measured at 180 days age. Resistivity measured at about one year age is reported in Table 11.

Resistivities (Rtem) measured between 2 and 360 days are reported in Table 12. Figure 4 provides a log-log plot of all TEM results up to 360 days age.

Table 10 Resistivity by TEM (Rtem, in Ωm) of 18 or 19 specimens measured in April 2014 at ages between 60 and 90 days

mix	mean	stdev	VC (%)	test date	cast date	age
A-CEM I 5%SF	530	40	8	9-apr	9-1-2014	90
B-CEM II/A-V 5%SF	419	52	12	17-apr	16-jan	91
C-CEM III/B NL	534	45	9	9-apr	23-jan	76
D-CEM III/B D	526	70	13	9-apr	30-jan	69
E- CEM III/A 5%SF	591	49	8	8-apr	6-feb	61

Table 11 Resistivity measured by TEM (Rtem, in Ωm) at one year age at TNO and NPRA

	TNO				NPRA
mix	mean	stdev	VC (%)	age (day)	mean
A-CEM I 5%SF	479	30	6	385	601
B-CEM II/A-V 5%SF	802	58	7	378	1246
C-CEM III/B NL	781	80	10	371	1159
D-CEM III/B D	658	77	12	364	862
E- CEM III/A 5%SF	1251	50	4	357	1478

Table 12 Resistivity measured by TEM (Rtem, in Ωm) between 2 and 360 days age

age (day)	A-CEM I+5%SF	B-CEM II/A-V+5%SF	C-CEM III/B(NL)	D-CEM III/B(D)	E-CEM III/A+5%SF
2	30	28	19	35	29
7	114	37	121	137	84
14	154	59	198	212	140
28	203	110	296	339	244
75	530	419	534	526	591
270	560	802	843	666	1439
360	479	802	781	658	1251

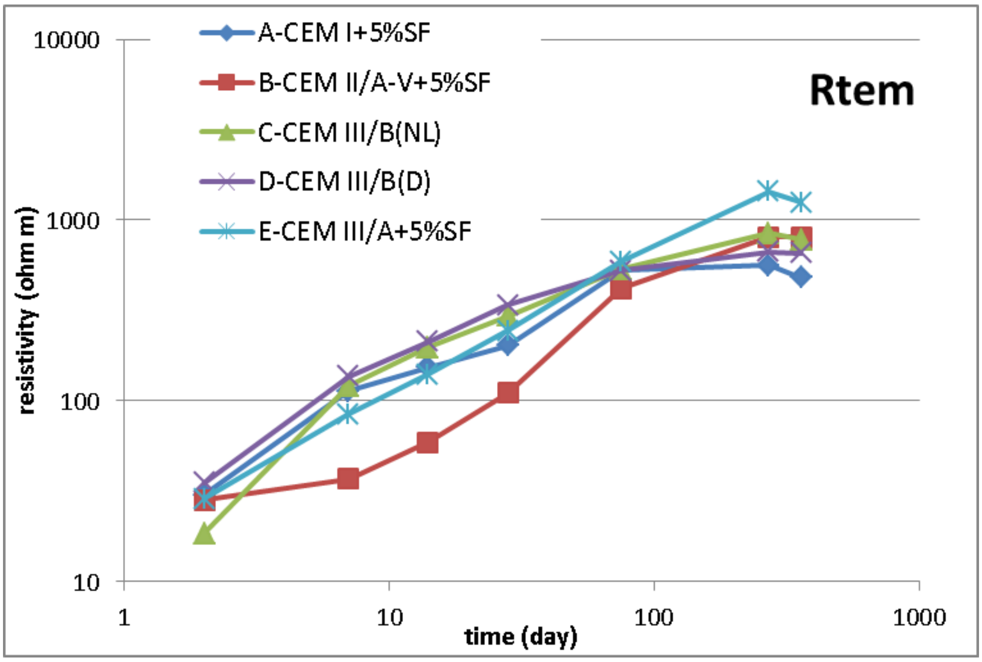


Figure 4 Log-log plot of resistivity values measured on specimens between steel plates (Rtem) as a function of age.

The resistivity-time plots measured by these two procedures (Rrcm in the RCM cell versus Rtem between steel plates) are quite similar, which is confirmed by a comparison of results up to 360 days' age provided in Figure 5.

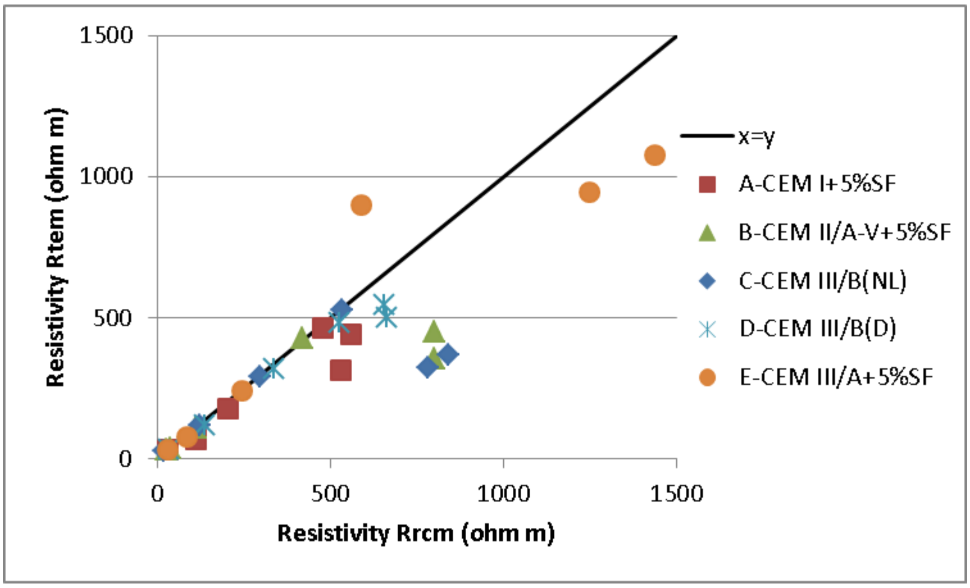
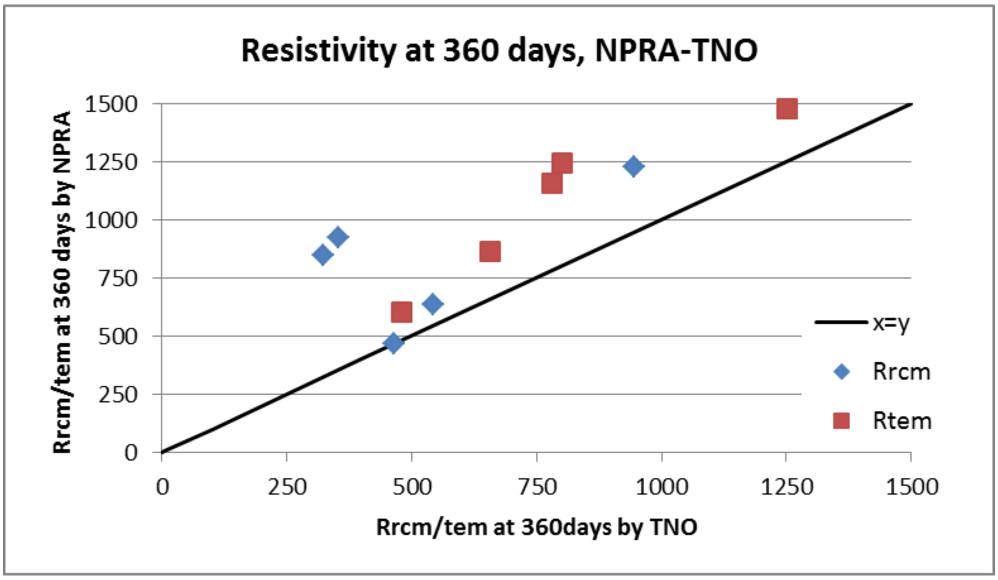


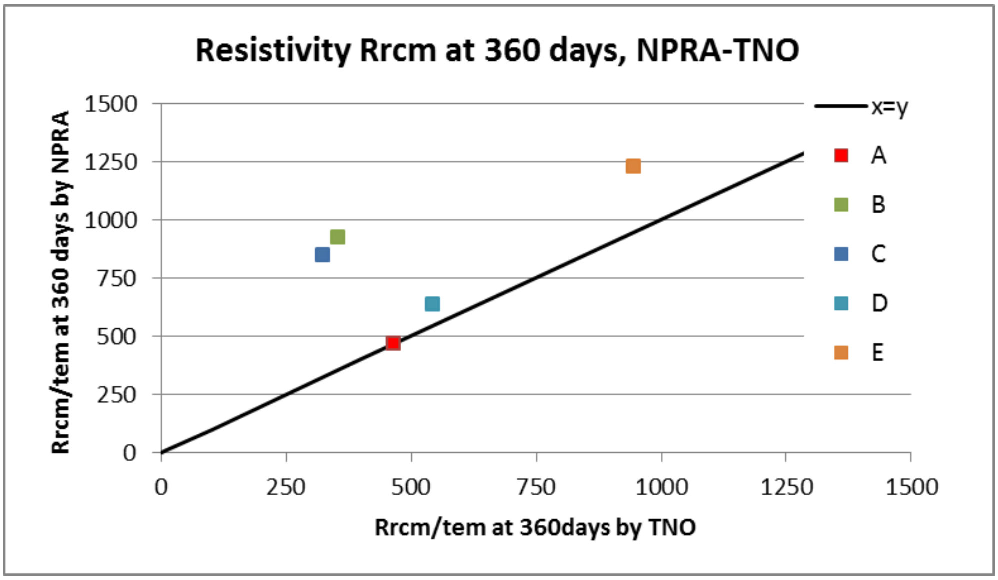
Figure 5 Resistivity measured in migration cells (Rrcm) versus those measured on specimens between steel plates (Rtem) up to 28 days age in Ωm and line of equality.

Table 13 provides an overview of resistivity results obtained by NPRA at 120 and 360 days age. R(1) was measured at 1 kHz prior to water saturation; results for three specimens were reported and the average value was corrected for temperature towards 20 C. R(2) was calculated from the ratio of a voltage of 30 V and the initial cell current (U/I) prior to RCM testing (only one value reported). TNO also vacuum saturated the 360 day RCM specimens before testing. Consequently, R(1) corresponds to Rtem as measured by TNO; and R(2) to Rrcm (only 360 day specimens). A comparison of NPRA's Rtem and Rrcm results with TNO's results measured at 360 days is given in Figure 6, in an overview plot and two separate plots making individual mixes recognisable.

Table 13 Resistivity measured by NPRA at age 120 and 360 days; R(1) corresponds to Rtem (Table 11); R(2) corresponds to Rrcm (Table 9)

	120 days				360 days	
	R(1) (in Ωm)			R(2) (in Ωm)	R(1) (in Ωm)	R(2) (in Ωm)
mix	average	st.dev	VC (%)	average	average	average
A-CEM I 5%SF	577	93	17	449	601	466
B-CEM II/A-V 5%SF	569	86	16	390	1246	925
C-CEM III/B NL	676	30	5	615	1159	849
D-CEM III/B D	559	51	10	478	862	638
E- CEM III/A 5%SF	1247	36	3	802	1478	1226





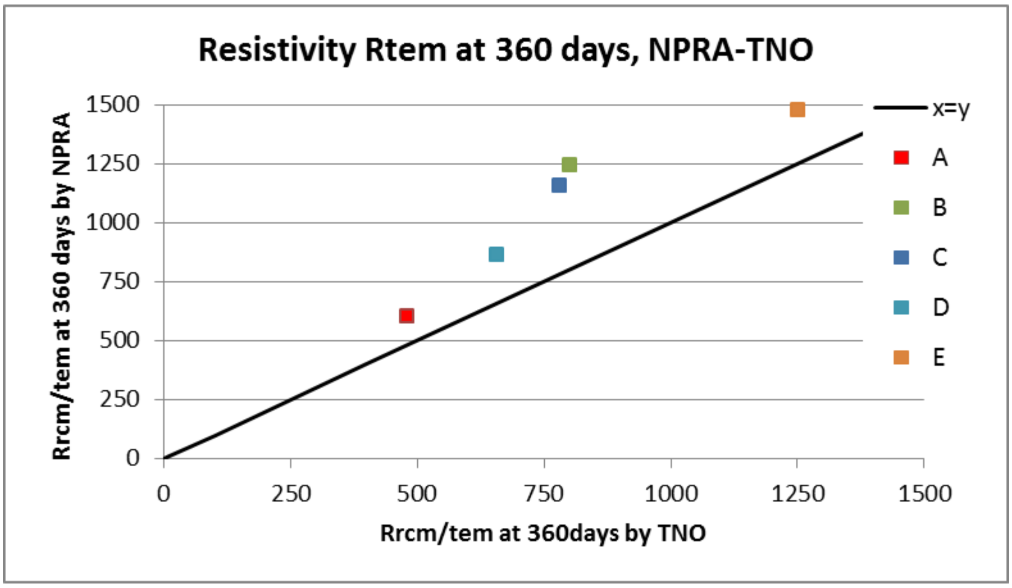


Figure 6 Comparison of resistivity results in Ωm between TNO and NPRA at 360 days for Rtem (non-vacuum saturated) and Rrcm (vacuum saturated) (TOP); only Rrcm with mixes marked separately (MIDDLE); only Rtem with mixes marked (BOTTOM).

3.4 Carbonation results

Carbonation depths were measured at one year age of prisms. It should be noted that, from 7 days age on, the prisms had been fully exposed (not sheltered) on the roof of the (old) laboratory until the end of 2014. In February 2015 they were placed outside the (new) laboratory under a shelter.
Table 14 reports carbonation depths as measured on the prisms.

Table 14 Carbonation depth at 360 days

mix	A-CEM I 5%SF	B-CEM II/A-V 5%SF	C-CEM III/B NL	D-CEM III/B D	E-CEM III/A 5%SF
carbonation depth (mm)	0	0	2	4	1

4 Discussion

The most important general observations and trends in the results are:

- The migration coefficient (RCM) decreases with increasing specimen age, which is according to the expectation, due to continued hydration of cementitious materials.
- At 28 days all mixes have roughly the same RCM, except mix B-CEM II/A-V+5%SF, whose value is about twice of that of the other mixes (the difference is far beyond the scatter); this is attributed to the relatively slow hydration of fly ash in this mix, which has not really taken off yet at 28 days. Slag reacts more strongly within the first 28 days than fly ash (mixes C, D, E). This is according to expectation. The Dutch slag mix (C) has a relatively high RCM value at 28 days, which is probably caused by one specimen deviating from the other two due to unknown causes.
- At 360 days age, all RCM values are below $1*10^{-12}$ m^2/s. Mix A-CEM I 5%SF has the highest value, followed by mix B-CEM II/A-V 5%SF; mixes C-CEM III/B NL, D-CEM III/B D and E-CEM III/A 5%SF have quite similar (low) values, with mix E-CEM III/A 5%SF having the lowest value. Differences between A, B and (C, D, E) are statistically significant (about one standard deviation); differences between C, D and E are probably not significant. From these results, it can be inferred that hydration of slag continues rather long. For mix A without slag or fly ash, it remains to be seen if the value will further reduce with time. For mix B, there may be further potential for reduction due to continued hydration of fly ash.
- Vacuum saturation before testing of specimens at later ages was found to be useful.
- Resistivity increases with age, with mix B-CEM II/A-V+5%SF having the lowest value at 7 and 28 days; this mix is catching up around 270 days age and beyond; mix E-CEM III/A 5%SF has the highest resistivity at 360 days. The lower early values of mix B reflect slower hydration of fly ash, as observed for the RCM values. The same remarks can be made for further potential of resistivity increase for individual mixes as for further RCM reduction.
- Resistivity measured in RCM cells is comparable to resistivity measured on specimens between steel plates.
- Reproducibility for RCM is about 10-15%, for resistivity about 10%, which are good values for these kind of tests.
- The correspondence of results from TNO and NPRA is generally good. Part of the differences found is thought to be related to differences in pre-treatment (vacuum saturation or not). Initially TNO did not perform vacuum saturation. When TNO did apply vacuum saturation the differences between the RCM results of TNO and NPRA became less.
- Carbonation depth after one year of mainly outdoor exposure was negligible for mixes A, B and E; small for mix C and slightly above the expected (low) value for mix D. It should be noted that non-sheltered outdoor exposure results in rather wet specimens. Under those conditions, carbonation should be expected to be low. From one year age exposure will be outdoors sheltered, which will result in some drying out of the material. Consequently, increase of carbonation depths in the second year can be expected.

5 Conclusions and recommendations

5.1 Conclusions

Five mortar mixes have been tested over one year for rapid chloride migration (RCM), electrical resistivity and carbonation in outdoor exposure conditions. The mixes comprised different binders: Portland cement plus silica fume (5%), Portland plus fly ash (15-25%) and silica fume (5%); high blast furnace slag (more than 65%, with cement from two different producers) and medium slag (c. 50%) plus silica fume (5%). The water/binder ratio was 0.40 in all cases. The test data allow the following conclusions to be drawn.

RCM was tested from two days age up to one year. At early ages differences occurred between mixes. At 28 days all values were rather low, with the fly ash mix having the highest values. From 28 days until one year age, a strong reduction occurred in all mixes. At one year age (after vacuum saturation), all results were quite low, with Portland plus silica fume and Portland, fly ash and silica fume having comparatively higher results. At one year, the mix with a medium slag content and silica fume (mix E-CEM III/A+5%SF) has a very low value.

These trends over time reflect continued hydration of cementitious materials and densification of the pore structure of the mortar.

The development of electrical resistivity confirms the trends observed in the RCM testing: resistivities become higher with time, further supporting that densification of the material is ongoing.

Carbonation was low in all specimens; only one high slag mix (mix D-CEM III/B) had slightly deeper carbonation than expected. The overall low carbonation depth is probably due to the specimens being fully exposed (non-sheltered) to outdoor conditions. As further exposure will be in outdoor sheltered conditions, increased carbonation is expected.

As a preliminary overall conclusion, it appears that in terms of performance under chloride load the three slag mixes are equivalent with or even slightly better than the “reference” mix B-CEM II/A-V 5%SF with fly ash and silica fume. In Dutch practice, fly ash cement would be used with at least 25% of fly ash (CEM II/B-V) without silica fume. Experience with silica fume is low in The Netherlands. On the other hand, a mix with 15% fly ash and 5% silica fume was tested in the laboratory in the 1990s and proved to have good chloride penetration resistance [1].

5.2 Recommendations

In view of the positive results obtained with five binders up to one year of age, continued exposure and testing for RCM and resistivity at later ages is recommended. It is possible that significant differences between the five mixes will develop. For RCM testing, vacuum saturation is strongly recommended. Furthermore for RCM testing, applying a high voltage (60 V) and a long testing time (5, 7 or even more days) is recommended. Continued exposure to natural carbonation should be continued (now outdoor sheltered) and testing at later ages is recommended. It is also recommended to characterise the microstructure of both carbonated and non-carbonated materials using microscopy.

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7 Signature

Delft, 16 December 2015

Prof.Dr. R.B. Polder
Author

Dr. M.R. de Rooij
Reviewer

M.D. Stamm MSc
Research manager
Structural Reliability

A Mix codes, cement properties and mortar mix compositions

Table A.1 Mix codes and binder type

mixture	binder	origin	SF	w/b
A	CEM I	Denmark	5%	0.4
B	CEM II/A-V	Norway	5%	0.4
C	CEM III/B	Netherlands	0%	0.4
D	CEM III/B	Germany	0%	0.4
E	CEM III/A	Germany	5%	0.4

Table A.2 Cement identification and properties

cement	CEM I 52.5 N (LA)	CEM II/A-V 42.5 N Anlegg FA	CEM III/B 42.5 N	CEM III/B 42.5 N-SR/LH/NA	CEM III/A 42.5 N-NA
Manufacturer /plant	Aalborg	Norcem	ENCI	Cemex/ Schwelgern@	Cemex Schwelgern@/
slag %	-	-	71	75	49
fly ash %	-	19	-		-
C_3A %	<8				
CaO %			45.3		
K_2O %					0.70
Na_2O %					0.23
Na_2Oeq %		0.6	0.7	0.66	0.70
SO_3 %	2.9 – 3.5	2.7	2.9		3.22
Cl % #	<0.04	<0.085		<0.08	<0.08
Blaine m^2/kg		390	524	470	450
density g/cm^3	3.09 – 3.19	2.99		2.95	3.00

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# water soluble

Table A.2 Mix compositions

Mix A			rho (kg/m^3)	mass (g)	volume (ml)
binder	Norway	CEM I	2950	450	152.54
SF	5%		2200	22.5	10.23
Standard sand			2650	1350	509.43
Super plasticizer	0.65%	35% solid weight		2.93	
w/b	0.40		1000	178.98	178.98
Total volume					851.19
Mix B					
binder	Norway	CEM II/A-V	2950	450	152.54
SF	5%		2200	22.5	10.23
Standard sand			2650	1350	509.43
Super plasticizer	0.33%	35% solid weight		1.5	
w/b	0.40		1000	179.98	179.98
Total volume					852.18
Mix C					
binder	Netherlands	CEM III/B	2950	450	152.54
SF	0%		2200	0	0.00
Standard sand			2650	1350	509.43
Super plasticizer	0.13%	35% solid weight		0.6	
w/b	0.40		1000	180.39	180.39
Total volume					842.37
Mix D					
binder	Germany	CEM III/B	3150	450	142.86
SF	0%		2200	0	0.00
Standard sand			2650	1350	509.43
Super plasticizer	0.13%	35% solid weight		0.6	
w/b	0.40		1000	180.39	180.39
Total volume					832.68
Mix E					
binder	Norway	CEM III/A	2950	450	152.54
SF	5%		2200	22.5	10.23
Standard sand			2650	1350	509.43
Super plasticizer	0.22%	35% solid weight		1.0	
w/b	0.40		1000	180.65	180.65
Total volume					852.85

Note: sand was CEN Standard sand (0-2)
Note 2: typical variations between batches are as follows: sand ± 5 g; cement and water ±0.5-1 g

B Experimental details of RCM testing up to 360 days per mix

Mixes
A-CEM I+5%SF
B-CEM II/A-V+5%SF
C-CEM III/B(NL)
D-CEM III/B(D)
E-CEM III/A+5%SF

Table B.1 Mix A-CEM I+5%SF

mix & age	A2	A7	A28	A133	A185	A360
Initial voltage (V)	15	30	30	30	30	30
Initial current (mA)	70	67	23	10	10	10
Adjusted voltage (V)	15	30	40	60	60	60
Adjusted current (mA)	71	67	32	26	20	20
Test duration (h)	4	24	24	24	24	72
Average penetration (mm)	5	21	9	6	7	11
Average RCM [10^{-12} m^2/s]	23	18	2.8	1.37	1.50	0.87
St.dev. RCM [10^{-12} m^2/s]	2.8	0.85	0.32	0.19	0.01	0.15
VC (%)	12	5	11	14	1	17

Table B.2 Mix B-CEM II/A-V+5%SF

mix & age	B2	B7	B28	B133	B185	B360
Initial voltage (V)	30	30	30	30	30	30
Initial current (mA)	196	130	120	10	9	5
Adjusted voltage (V)	30	15	20	60	60	60
Adjusted current (mA)	195	63	80	20	18	10
Test duration (h)	6	24	24	66	48	72
Average penetration (mm)	23	22	11	17	13	9
Average RCM [10^{-12} m^2/s]	44	21	6.9	1.4	1.5	0.68
St.dev. RCM [10^{-12} m^2/s]	1.9	1.2	0.68	0.01	0.16	0.1
VC (%)	4	6	10	1	11	15

Table B.3 Mix C-CEM III/B(NL)

mix & age	C2	C7	C28	C133	C185	C360
Initial voltage (V)	30	30	30	30	30	30
Initial current (mA)	268	35	14	8	8	5
Adjusted voltage (V)	15	35	60	60	60	60
Adjusted current (mA)	127	41	29	17	17	10
Test duration (h)	6	24	24	65	48	72
Average penetration (mm)	31	20	13	18	14	6
Average RCM [10^{-12} m^2/s]	120	7.8	4.0	1.5	1.7	0.43
St.dev. RCM [10^{-12} m^2/s]	9.9	0.28	1.5	0.01	0.43	0.1
VC (%)	8	4	38	1	25	2

Table B.4 Mix D-CEM III/B(D)

mix & age	D2	D7	D28	D133	D185	D360
Initial voltage (V)	30	30	30	30	30	30
Initial current (mA)	153	35	13	10	9	1.3
Adjusted voltage (V)	15	35	60	60	60	60
Adjusted current (mA)	72	41	27	22	17	2.8
Test duration (h)	6	24	65	65	48	145
Average penetration (mm)	14	16	28	10	13	15
Average RCM [10^{-12} m^2/s]	49	6.3	2.5	0.83	1.5	0.57
St.dev. RCM [10^{-12} m^2/s]	4.9	0.45	0.15	0.05	0.24	0.05
VC (%)	10	7	6	6	16	10

Table B.5 Mix E-CEM III/A+5%SF

mix & age	E2	E7	E28	E133	E185	E360
Initial voltage (V)	30	30	30	30	30	30
Initial current (mA)	135	160	18	5	5	0.5
Adjusted voltage (V)	30	15	60	60	60	60
Adjusted current (mA)	143	80	37	9	9	1.1
Test duration (h)	6	24	24	63	48	144
Average penetration (mm)	22	10	21	10	6	10
Average RCM [10^{-12} m^2/s]	40	8.3	2.5	0.60	0.66	0.37
St.dev. RCM [10^{-12} m^2/s]	2.4	0.59	0.40	0.15	0.1	0.01
VC (%)	6	7	16	25	16	2

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