Durability of Resource Saving "Green" Types of Concrete

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Summary

One of the impediments for the use of resource saving "green" types of concrete on a larger scale is the lack of documentation of durability properties. The Danish Centre for Resource Saving Concrete has carried out durability investigations to encourage the use of green concrete. This article presents the results of an investigation of frost resistance, carbonation and chloride ingress for five types of green concrete. The investigation shows that the tested types of green concrete can be evaluated using the same accept criteria as for ordinary types of concrete. Some of the residual products lower the effect of the chemical additives, e.g. the air entraining agent, and therefore it can be difficult to obtain an air void structure with sufficient fineness to ensure frost resistance. However, it seems possible to produce green concrete, which is just as durable as ordinary concrete.

Introduction

In Denmark, a Centre for Resource Saving Concrete Structures was formed in 1998. The aim is to gain more knowledge about environment-friendly – so-called "green" - types of concrete and to develop technical solutions, so green concrete can be used in modern building technology. Fulfilment of the objectives of the centre calls for different kinds of expertise. Therefore, the centre involves partners from all sectors related to concrete production, i.e. cement and aggregate producers, a contractor, a ready mix plant, a consultant and a building owner besides Danish Technological Institute and the two technical universities in Denmark.

The ways to sustainable concrete design are manifold. The Centre aims for

- concrete with minimal clinker content
- concrete with green types of cement and binders
- concrete with inorganic residual products
- operation and maintenance technology for green concrete structures
- green structural solutions and structural solutions for green concrete

The centre has initiated five development projects corresponding to the five targets. The three first mentioned all imply changes of the traditional concrete mix design. Investigation of different concrete mix designs has been carried out in different phases: The first phase consisted of a screening of more than 30 different mix designs. Among these, the most promising mix designs were selected for a comprehensive test programme in the second phase. The results presented in this article originate from this second phase, from investigations of the durability of five green types of concrete intended for use in aggressive environment.

In the year 2001 the practical use of green concrete and green structural solutions will be demonstrated, when the results of the development projects are incorporated in a highway overpass project.

Environmental goals and intentions

The Centre for ressource saving concrete has laid down a list of environmental goals:

- CO₂ emission caused by concrete production must be reduced by at least 30%.
- The concrete must consist of at least 20% residual products, used at aggregates.
- The concrete industry's own residual products must be used in concrete production
- New types of residual products, previously landfilled or disposed of in other ways, must be used in concrete production
- CO₂-neutral, waste-derived fuels must replace at least 10% of the fossil fuels in cement production.

The Centre defines "green" concrete as concrete which satisfies one or more of the environmental goals. Moreover, a green type of concrete has to meet all of the environmental intentions listed below:

- avoid the use of materials which contain substances on the Danish Environmental Protection Agency's list of unwanted materials
- do not reduce the recycling ability of green concrete compared to conventional concrete (today, 95% of the concrete is reused)
- do not increase the content of hazardous substances in discharge water from concrete production

The environmental aspects of the project is described in greater detail in [1].

Test programme

Objectives

Depending on the environmental action the concrete will be subjected to most concrete codes state demands on e.g. maximum w/c ratio, minimum strength and minimum filler content (see for example DS 481 [2]). We know by experience that these requirements will lead to dense and durable concrete structures. But how do we know that these requirements are sufficient for types of concrete differing from conventional concrete, e.g. green types of concrete, where we have very limited experience? Therefore, in order to encourage the use of green types of concrete, one important task is to provide documentation of their durability properties and to prove that they have adequate service lives.

A number of standard test methods have been developed to test concrete resistance against specific deterioration mechanisms, e.g. salt surface scaling and chloride ingress. When testing new types of concrete using standard test procedures prepared for conventional concrete, one may face two problems:

- The test results approve non-durable concrete or disqualify durable concrete, because the accept-criteria are not adjusted to the present type of concrete.
- The standard tests do not uncover new durability problems introduced with new types of concrete, because the standard tests only relate to deterioration mechanisms relevant for conventional concrete.

The chemical composition of the green constituents in the concretes in this study has been thoroughly examined. In the light of this examination, it is believed that the concretes tabled in the next paragraph will not present any new durability aspects, so therefore this investigation is focused on the classical durability issues of frost resistance, chloride ingress, and carbonation.

The standard test procedures chosen are

Frost resistance: Surface scaling according to a modified SS 13 72 44 (Borås method) [3], and air void analysis according to DS/EN480-1 [4].

Carbonation: NT-BUILD 357 [5].

Chloride ingress: CTH-method [6].

All these methods prescribe testing of time dependent properties at fixed deadlines, e.g. 28 days after casting. However, in the preliminary testing of green concretes it has been observed that the development of strength for some of the green types of concrete deviate from strength development of conventional concrete, and it is most likely that the development of other properties will deviate too. For this reason, measurements of surface scaling and chloride diffusion coefficient have been carried out at more than one concrete age.

Concrete mix designs

The investigation includes five green types of concrete. In addition, a reference concrete, AR, is included in the test programme. AR is a normal Danish concrete intended for aggressive environment. AR is produced with extra low alkali, highly sulphate resistant cement, a moderate fly ash content as well of a moderate content of silica fume. It fulfils the Danish code DS 481 [2] and the specification for concrete work of the Danish Road Directorate [7].

The five green types of concretes are:

- A0 Concrete with low alkali, moderate sulphate resistant cement. Change of cement type lowers the energy consumption of cement production. The same cement type is used for A1 and A3. A0 fulfils DS481, but not the specification of the Danish Road Directorate.
- A1 Concrete with a high amount of fly ash (40% of powder b.w.)
- A3 Concrete with sewage sludge incineration ash instead of ordinary fly ash
- *A5* Concrete with concrete slurry
- A6 Concrete with stone dust

The compressive strengths of the green types of concrete are all comparable to the strength of *AR*. The concrete mix designs are listed in Table 1.

Constituent	Description	AR	AO	A1	A3	A5	A6
Cement	Aalborg Portland	287.6	-	-	-	-	-
LASR cement							
	(CEM I 42.5 HS/EA)						
	Aalborg Portland	-	286.5	188.6	277.0	-	-
	RAPID [®] cement (CEM						
	I 52.5 MS/LA)						
	Cementa	-	-	-	-	398.0	397.2
	ANL cement						
	(CEM I 42.5 HS/LA)						
Ordinary	Danaske B1	33.7	32.3	137.4	-	-	-
fly ash							
Silica fume	Elkem	17.4	17.0	17.8	17.0	-	-
Residual	Fly ash/sewage plant	-	-	-	34.7	-	-
product	Concrete slurry	-	-	-	-	14.6	-
	(weight of dry matter)						
	Stone dust 0/2						462
Water		149.0	155.4	131.7	143.3	147.9	150.0
Plastizicer	Conplast 212	2.39	2.50	2.42	2.23	-	
	Peramin V	_	_	_	_	-	1.98
Super	Conplast SP 605	-	-	3.40	3.18	-	-
plastizicer							

Table 1: Mix design for the tested concretes (according to the batch report from the ready mix plant). All constitutents are noted by weight [kg/m³].

Constituent Description		AR	AO	A1	A3	A5	A6
	Peramin F	-	-	-	-	3,95	-
	CEM 92M	-	-	-	-	-	6.78
Air-entraing	Conplast 316 AEA 1:5	1.01	0.73	0.50	0.31	-	-
admixture HPa		-	-	-	-	0,12	0,15
Sand	0/4 A, Nr. Haldne	621	629	646	640	-	-
	0/8 Östervang					832	457
Coarse	4/8 A, Uddevalla	244	245	251	249	-	-
aggregate	8/16 A, Uddevalla	855	858	871	865	-	-
	8/16 Östervang					200	197
	16/25 Östervang					718	693

AR, A0, A1, and *A3* is produced by a Danish ready mix plant, whereas *A5* and *A6* is produced by a Swedish concrete producer.

The above mentioned concretes present a mix of different ways to lower the environmental impact of concrete production. Substitution of cement with fly ash (A1) is the traditional way to minimise the clinker content. A0, A1, and A3 are produced with a green type of cement, where 9% of the fuel for cement production comes from renewable resources. A3, A5, and A6 introduce new residual products in concrete production, A5 and A6 from the concrete industry itself, A3 from other industries. An evaluation of the environmental goals is given in Table 2.

				0		
Eı	nvironmental goal	AO	A1	A3	A5	A6
•	CO ₂ reduction	27% (🗸)	52% 🗸	29% (🗸)		
•	Residual products as					1
	aggregates					
•	Residual products from				~	1
	the concrete industry					
•	Residual products from			1		
	other sources					
•	Waste-derived fuels	9% (🗸)	9% (🗸)	9% (🗸)		

Table 2: Evaluation of environmental goals.

A0 is accepted as a green type of concrete; though it does not fulfil any of the goals, it is close to fulfilling two of the five goals.

Resistance against frost deterioration

Results

The test method used is an accelerated frost-thaw test according to SS 13 72 44, except each 7^{th} frost-thaw cycle is replaced by 24 hours at constant temperature (20°C), which enables registration of ultrasound transmission time and dilation of the test specimens [3].

The measurements of scaling are shown in Figure 1.



Figure 1: Results of surface scaling test according to SS 13 72 44 (modified). Left:Exposure to frost-thaw cycles started 31 days after casting (standard procedure). Right: Exposure to frost-thaw cycles started 59 days after casting.

The concretes were also subjected to an air void analysis according to DS/EN480-1, see Table 1.

Table 5. Results of all vola analysis							
		AR	A0	A1	A3	A5	A6
Air content in hardened concrete	[vol-%]	6.18	5.86	5.23	6.44	4.04	3.94
Paste content	[vol-%]	26.1	27.0	26.3	25.6	28.2	27.1
Powers spacing factor	[mm]	0.13	0.18	0.33	0.30	0.17	0.35
Volume of micro air voids (diameter < 300 μm)	[vol-%]	3.00	2.25	0.84	0.83	2.03	0.72

Table 3: Results of air void analysis

Comments

Normally the salt scaling test is performed in a way that the exposure to frost-thaw cycles starts 31 days after casting. In this case, the accept criterion according to DS481 is that at least one of the following two requirements has to be fulfilled:

- The scaling after 56 freeze-thaw cycles is less than 0.2 kg/m^2
- The scaling after 56 freeze-thaw cycles is less than 0.5 kg/m² and the proportion between the amount scaled of after 56 cycles and the amount scaled of after 28 cycles is less than 2.

As can be seen in Figure 1, all concretes except *A1* (concrete with high fly ash content) can be accepted.

A1 probably fails due to the high spacing factor. According to the Danish concrete code, the spacing factor of a concrete, which is not subjected to a frost-thaw test, must not exceed 0.20 mm. If A1 had fulfilled this requirement, it would probably also show sufficient frost resistance. A review of relevant litterature shows that it is possible to make frost resistant concrete with high fly ash contents if the fineness of the air void system is adequate (see e.g. [8]).

A6 has an even higher spacing factor than A1, though nearly no scaling was observed. At first sight this seems contradictory, but observations made by Pigeon can explain this [9]: Pigeon showed that the critical spacing factor is not a fixed quantity valid for all types of concrete. The critical spacing factor is lower, the denser the concrete is. In addition to fly ash, A1 also contains silica fume, and A1 is expected to be denser than A6 without silica fume. For this reason the critical spacing factor of A1 may be lower than 0.33, whereas the critical spacing factor of A6 is higher than 0.35.

Effect of age of concrete, when the scaling test is performed

According to the standardised test procedure of the scaling test, the concrete is exposed to frost action for the first time 31 days after casting. In this study, a similar test has been run, where the age of the test specimens was 59 days, before they were exposed to frost. The results are shown in Figure 1 (to the right).

A comparison of results shows that the scaling of AI is reduced, when the concrete age is increased before frost action. However, the scaling of AI is still not satisfactory.

For A3 a slight increase of scaling is observed at the later age. For the rest of the concretes, the amount of scaling is more or less unchanged. For all concretes except A1 it is difficult to draw conclusions about the time dependent development of frost resistance, because it is not possible to detect a significant change, when the scaling in both tests were low.

Inner damage

Parallel to the scaling test, the test specimens were inspected by measuring ultra sound transmission time and dilation to reveal if any inner damage had occurred. However, the changes in ultrasound transmission time and the length changes were small, so there is no sign of inner deterioration.

Carbonation

Method

35 days after casting, the test specimens are placed in a climate chamber with a CO_2 enriched atmosphere (3% CO_2 , 60% RH). The carbonation depth is measured 4, 8, and 12 weeks after the specimens have been placed in the chamber (the carbonation depth is made visible by means of phenolphthalein, according to NT-BUILD 357).

Results

The results (mean values of carbonation depth) are shown in Figure 2.



Figure 2: Carbonation depths measured according to NT-BUILD 357.

Comments

The carbonation depths of A0 and A3 are at about the same level as the carbonation depth of the reference concrete AR. The carbonation is more pronounced for A1 and less pronounced for A5 and A6.

Calcium hydroxide, Ca(OH)₂, is formed during cement hydration, and because of the high alkalinity of calcium hydroxide, the presence of calcium hydroxide will ensure a high pH-

value in the concrete. The pH-value is roughly constant, as long as calcium hydroxide is present, no matter the content of calcium hydroxide.

During the carbonation process, calcium hydroxide reacts with carbon dioxide, CO_2 , from the atmosphere. When all calcium hydroxide in an area has reacted, the pH-value in the area decreases. If two types of concrete have different initial contents of calcium hydroxide, the one with the lowest content will be most sensitive to carbonation, because the carbonation front will travel faster. That means that the initial content of calcium hydroxide in hardened concrete expresses a kind of carbonation potential.

The initial content of calcium hydroxide has been calculated for the six types of concrete in this study by calculating the amount of calcium hydroxide formed during cement hydration and correcting the result by the amount of calcium hydroxide consumed during a pouzzolanic reaction with fly ash or silica fume. The calculation shows that the initial content of calcium hydroxide is about the same for AR, A0, and A3 (~30 kg/m³ concrete). The amount of fly ash in A1 is so high that it can eliminate all the calcium hydroxide. For A5 and A6 the initial content of calcium hydroxide is higher than that of the reference AR (~110 kg/m³). These results indicate that A1 will be more sensitive to carbonation than AR, A0, and A3, whereas A5 and A6 will be far less sensitive. This agrees very well with the experimental findings, though in A1 there is still an amount of calcium hydroxide left after the puzzolanic reaction, which can be observed because there is still an area with high pH-value in front of the carbonated area.

It is important to notice that the difference in carbonation potential between AR and A5 and A6 does not come from the green elements in A5 and A6 (concrete slurry and stone dust, respectively). According to the explanation given above, the difference is due to differences in Danish and Swedish concrete practice: Swedish concrete has a higher cement content and contains no puzzolans, and therefore it will in general be more resistant to carbonation than Danish concrete.

Chloride ingress

Test Method

For this part of the project, a rapid chloride migration test method was used [6]. The method, which is developed at Chalmers University of Technology, is known as *the CTH-method*, but it is also an Nordtest standard (NT-BUILD 492). This test method was considered the most advantageous for the purpose in this project for the following reasons:

- Most other rapid test methods (i.e. AASHTO T277) measure the charge passing the specimen when a voltage is applied over it. The charge is very dependent on the ion content in the pore solution, not only the chloride ions. The ion composition in the pore solution may vary a lot from one green type of concrete to another, because of e.g. the residual products used, and therefore a comparison of results would be difficult. Using the CTH-method, the chloride diffusion coefficient is evaluated from a measurement of chloride penetration depth. That is, the result is based on a direct measurement of chloride ions present in the sample.
- Ponding tests (e.g. NT-BUILD 443) register the chloride profile after exposure to a salt solution. The test period is often several months, which means that the registered resistance against chloride ingress is a kind of average resistance during the test period. In contrast, the test period of the CTH-method is limited to some hours, which enables measurement of the resistance against chloride ingress at a certain age.
- In general, the CTH-method is theoretically clear, experimentally simple, and it has shown good repeatability.

Results

For each type of concrete, the chloride diffusion coefficient is measured 28 days, 3 months and 1 year after casting. The measured chloride diffusion coefficients are shown in Figure 3.



Figure 3: Left: Chloride diffusion coefficients measured with the CTH-method at different concrete ages. Right: Same data, pressented in logarithmic mapping.

Comments

Time dependent diffusion coefficient

When the measured values are mapped in a system of co-ordinates with logarithmic axes (see Figure 3, to the right), the chloride diffusion coefficient as a function of time can be approximated with a straight line. This means, that the time dependency can be described by the following formula (suggested by Tang and Nilsson [10]):

$$D(t) = a \cdot t^{-b} \tag{1}$$

where

- *t* is the concrete age (days after cating)
- *a* and *b* are constants evaluated by regression. In a physical interpretation of the formula, *a* is the chloride diffusion coefficient one day after casting, whereas *b* expresses how fast the chloride diffusion coefficient is changing.

The *a*- and *b*-values for the six different types of concrete are listed in Table 4.

	AR	A0	A1	A3	A5	A6
a	34.3	29.5	74.8	15.9	27.9	25.15
b	0.435	0.452	0.728	0.350	0.196	0.114

Table 4: a- and b-values for the tested types of concrete.

It can be observed in Figure 3 (and deduced from the figures in Table 4) that at all times chloride diffusion coefficients of A0 and A3 are at the same level as the diffusion coefficient of AR or even a little bit lower.

28 days after casting, the chloride diffusion coefficient of A1 is at the same level as AR. But the reduction of the diffusion coefficient of A1 is quicker, resulting in a diffusion coefficient of A1 of less than 50% of the diffusion coefficient of the reference concrete one year after casting. The explanation of the very good chloride resistance is probably an increased chloride binding caused by the high fly ash content.

The diffusion coefficients of A5 and A6 are from the beginning of the test series (28 days after casting) at a higher level than the diffusion coefficients measured for the rest of the concretes. The development of the chloride diffusion coefficient is also slower. However, a check up on the development of the chloride diffusion coefficient of a normal Swedish concrete which was not originally a part of the test programme gave a result similar to the results of A5 and A6. Just like in the case of carbonation, the differences between on the one hand AR and on the other hand A5 and A6 are not due to the green initiatives (concrete slurry and stone dust). The

reason for the differences is the general differences between Danish and Swedish concrete tradition, where concrete in Sweden is produced without fly ash and silica fume.

Accept criterion

In the Danish and Swedish concrete codes, no acceptance criteria are stated for the chloride diffusion coefficient. Tang Luping has given the following guidelines for the chloride diffusion coefficient D measured with the CTH-method 28 days after casting:

- $D < 2 \cdot 10^{-12} \text{ m}^2/\text{s}$: Very good resistance against chloride ingress
- $D < 8 \cdot 10^{-12} \text{ m}^2/\text{s}$: Good resistance against chloride ingress
- $D < 16 \cdot 10^{-12} \text{ m}^2/\text{s}$: Moderate resistance against chloride ingress
- $D > 16 \cdot 10^{-12} \text{ m}^2/\text{s}$: Not suitable for aggressive environment

According to these guidelines, AR, A0, A1, and A3 show good resistance against chloride ingress, whereas A5 shows moderate resistance and A6 just exceeds $16 \cdot 10^{-12}$ m²/s and therefore is characterised as being not suitable for aggressive environment.

For practical reasons, we need accept criteria at an early age (e.g. 28 days after casting), though the diffusion coefficient at a later stage, e.g. one year after casting, is more relevant for the chloride ingress during the whole service life of the structure. When stating limits for the chloride diffusion coefficient 28 days after casting, we assume a "normal" further development of the diffusivity. But as it was demonstrated in the previous paragraph, the time dependency of the chloride diffusion coefficient may vary quite a lot.

Conclusion

In the study, the durability of five different types of green concrete and a reference concrete were investigated as regards frost action, carbonation, and chloride ingress. The five green types of concrete represent different green strategies, i.e. concrete with minimal clinker content, concrete with green cement and binder, and concrete with inorganic residual products.

All concretes except concrete with high fly ash content showed good frost resistance. The concrete with high fly ash content failed because the air void system was too coarse. Concerning frost resistance, nothing in the test results indicate that we cannot use the normal test procedures and acceptance criteria when testing green concrete.

A high content of fly ash also makes the concrete vulnerable to carbonation. It is possible to roughly forecast the susceptibility to carbonation by calculating the amount of calcium hydroxide in the hardened concrete.

The green types of concrete showed just as good resistance against chloride ingress as ordinary concrete. However, the study also made it clear that it is difficult to put forth strict limits for the chloride diffusion coefficient at an early concrete age (e.g. 28 days after casting), because green changes in the mix design may influence the development in time of the chloride diffusivity.

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