

DURABILITY OF ALKALI-ACTIVATED SLAG CONCRETE



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The study consists of a series of experimental investigations concerning the microstructural, permeability and durability properties of alkali-activated slag concrete. The object of study is the so-called F-concrete. The basic material of F-concrete is finely ground slag that is activated by a combination of alkali metal compounds and rendered consistent in its fresh state by means of lignosulphonates.

The study was conducted at the Concrete and Silicate Laboratory of the Technical Research Centre of Finland. The series of investigations formed one part of a Nordic project entitled "Durability of alkali-activated slag concrete".

Keywords activation, slag, concrete, microstructure, permeability, durability

1. INTRODUCTION

The object of the studies reported here was F-concrete, the binder of which is finely ground blast furnace slag. Finely ground slag was activated by sodium hydroxide and sodium carbonate. In addition to alkali compounds the F-additive contained lignosulphonates, which act as dispersing agents. Set-controlling and antifoaming agents were also added.

In earlier studies carried out by the Concrete and Silicate Laboratory of the Technical Research Centre of Finland, the mechanical properties of F-concrete were found to be good and, according to the results, the heat treatment of fresh F-concrete was found to be favourable. The results of the earlier studies are summarized by Häkkinen (1986). The purpose of the investigations reviewed here has been to study the microstructure of hardened F-concrete compared with Portland cement concrete and to determine the influence of the structure of F-concrete on its permeability properties and to further study the durability properties of F-concrete.

2. MICROSTRUCTURE

Specific surface areas of the samples were determined by means of a nitrogen gas adsorption apparatus and calculated on the basis of the BET equation. Results are shown in Table 1. The age of mortar samples was three months and the age of paste samples was one year.

Table 1. Specific surface area (Häkkinen et al. 1987).

Paste	Mortar	Water-binder ratio	Aggregate-binder ratio	Curing conditions *)	Specific surface area (m ² /g)
F	-	0.23	-	T 20 RH 100	0.24
F	-	0.23	-	T 20 RH 70	0.16
P	-	0.23	-	T 20 RH 70	4.14
-	F	0.25	4	T 20 RH 70	0.78
-	F	0.43	5	T 20 RH 70	1.34
-	F	0.43	5	T 20 RH 70	1.34
-	F	0.51	6	T 20 RH 70	2.13
-	P	0.43	5	T 20 RH 70	3.22

*) T 20 RH 100 Curing at 20 °C, RH > 95 %
 T 20 RH 70 During the first 7 days: curing at 20 °C, RH > 95 %.
 Subsequent curing at RH 70 %.

Since the surface areas of sand and unhydrated binder are much smaller than that of hydrated paste, it can be said that the specific surface area of hydrated slag paste was significantly smaller than the surface area of hydrated Portland cement paste. The degree of hydration (bound water of the weight of binder) was at the same level at the same time. On the basis of the results it can be concluded that hydrated slag paste is much more compact than Portland cement paste such that the portion of small capillaries is less in slag paste than in Portland cement paste (Häkkinen et al. 1987). Also according to the studies of Jumppanen and co-workers (1986) the amount of small capillaries of F-paste samples accessible to N₂-molecules was clearly smaller than that of Portland cement paste. The normal hardened F-paste specimens had such a low content of N₂-accessible micropores that it was impossible to obtain reliable pore size distributions of them.

Pore size distribution curves of concrete samples were determined by means of mercury porosimetry. Table 2 lists the volume portions of microscopic and colloidal pores in F-samples and in Portland cement samples. According to the results the relative amount of microscopic pores increased as the hydration of slag proceeded. The behaviour of Portland cement samples was very different in that the relative amount of microscopic pores was always about 10 %. The increasing portion of large capillaries in slag samples can be due to the cracking of slag in the hydration process. As the slag binder reacts with water, it produces a dense structure with only a minimal amount of small capillaries and the shrinkage of the paste results in the cracking of the structure (Häkkinen et al. 1987).

Structural studies of concrete were also carried out by means of thin section analysis. The studies concentrated upon the appearance of cracks in the concrete structure (Fig. 1).

On the basis of the studies concerning the effect of preparation techniques on the appearance of cracks, and also on the basis of the strong cracking of the moist-cured slag paste specimens, it was concluded that the cracks in the alkaliactivated slag concrete were at least not entirely the result of drying (Häkkinen et al. 1987).

Table 2. Volume portions of pores measured 10 - 1 μm and 1 - 0.01 μm (Häkkinen et al. 1987).
Precuring of samples at 20 °C and RH ~ 100 %.

Concrete	Water-binder ratio	Age	Chemically bound water (loss of ignition at 650 °C) (% by wt. of binder)	Volume portions of the pores %	
				10 - 1 μm	0.01 - 1 μm
F	0.4	3 d	10.1	16	84
F	0.4	7 d	12.3	25	75
F	0.4	11 d	17.7	25	75
F	0.4	21 d	-	35	65
P	0.4	3 d	13.2	9	91
P	0.4	11 d	20.3	10	90
P	0.4	21 d	-	10	90

Water-cement ratio

Air-water ratio

0.05

0.15

0.5

0.4

0.32

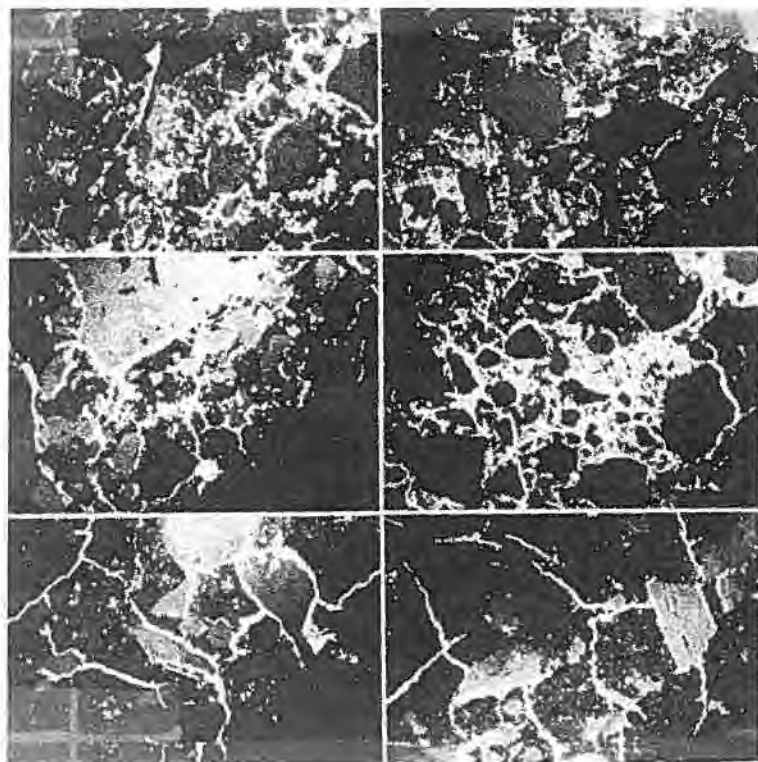


Fig. 1. Microstructure of F-concrete samples (Vesikari 1987). Each figure represents an area of ~ 2 mm x 3 mm. Thin section fluorescence microscopy.

According to Vesikari (1987) one can conclude from the shape of microcracks in F-concrete that the cause of cracking must be shrinkage and not swelling of the cement paste. Withdrawal of water from concrete stored in dry air causes drying shrinkage. Unless the entire concrete block is free to contract, shrinkage cracking will appear. Normally the cracks caused by drying shrinkage are perpendicular to the surface and their width decreases with increasing depth from the surface. This is due to the moisture gradient during the drying process. In the case of cracks in F-concrete there seems to be no resemblance to a normal cracking pattern in drying shrinkage. Instead, the cracks are randomly distributed around the concrete section and their direction is haphazard. The possible difference in crack size near the surface and in the centre of the concrete block could be attributed to drying shrinkage but their original formation must have taken place during the hydration process caused by the early hydration shrinkage (Vesikari 1987).

In order to discover the effect of the components of the F-additive on the appearance of the cracks, the composition of the additive was modified. The effect of the composition of alkali compounds, the amount of alkali compounds and the amount of lignosulphonates and sodium gluconate were studied. None of these seemed to have a significant influence on the structure of F-concrete. The water-binder ratio and the heat treatment both had a slight effect on the appearance of the cracks. The most clearly influential factor was the chemical composition of the slag (Häkkinen et al. 1987).

3. STRENGTH AND SHRINKAGE

Compression and tension in bending and splitting strength values of F-concrete and reference concrete made of normal hardening Portland cement are presented in Table 3.

After breaking the specimens surplus pieces were dried at 105 °C and ignited at 650 °C in order to determine the amount of chemically bound water (Table 4).

On the basis of the results shown in Table 3, no significant differences between the strength properties of F-concrete and Portland cement concrete could be seen.

The results of shrinkage measurements are shown in Fig. 2 (Häkkinen et al. 1987). The F-concrete specimens shrank by about 0.10 - 0.15 o/oo during the 5 days of moisture curing after demoulding of the specimens. Drying shrinkage during the two weeks of curing at 40 % RH was almost similar in F-concrete and Portland cement concrete.

Table 3. Strength properties of F-concrete and Portland cement concrete (Häkkinen et a. 1987).

Specimen sizes:

- 500 × 100 × 100 mm³ in bending
- 100 × 100 × 100 mm³ in splitting
- area of compression 100 × 100 mm².

Water-binder ratio 0.40.

Aggregate-binder ratio 4.

Melamine resin based admixture was used as a water-reducing agent in Portland cement concrete.

Age and curing conditions	Strength values (MPa)		Tension strength values (% by value of compression)	
	F-concrete	Portland cement concrete	F-concrete	Portland cement concrete
7 days at RH 100 % compression	44.4	44.7	-	-
bending	6.2	6.7	14.0	15.0
splitting	2.9	4.1	6.5	9.2
24 days at RH 100 % compression	59.0	56.1	-	-
bending	8.4	6.7	14.2	11.9
splitting	3.4	3.8	5.7	6.8
7 days at RH 100 % 17 days at RH 40 % compression	59.5	61.5	-	-
bending	4.8	5.4	8.1	8.8
splitting	3.4	4.3	5.6	7.0
24 days at RH 100 % 6 days at 40 °C compression	62.0	57.6	-	-
bending	4.7	4.6	7.6	8.0
splitting	3.2	3.9	5.2	6.8

Table 4. Loss on ignition (at 650 °C) of concrete samples (Häkkinen et al. 1987).

Curing conditions	Loss on ignition (% by wt. of binder)	
	F 40 (16)	P 40 (16)
7 days at RH 100 %	13.1	14.9
24 days at RH 100 %	13.5	15.2
7 days at RH 100 % and 17 days at RH 70 %	13.0	15.1

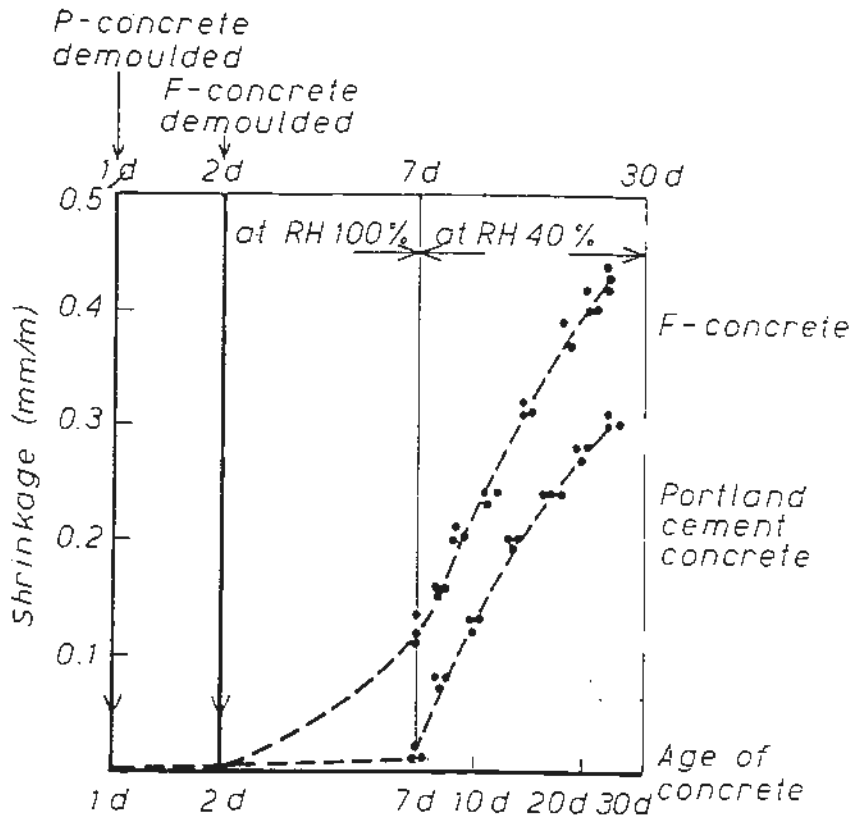


Fig. 2. Shrinkage of F-concrete and reference concrete made from Portland cement (Häkkinen et al. 1987).
Specimen size $100 \times 100 \times 500 \text{ mm}^3$.
Water-binder-aggregate ratio 0.4:1:4.
Melamine resin based admixture was used as a water-reducing agent in Portland cement concrete.

4. PERMEABILITY AND CARBONATION

4.1 Capillary suction

The coefficient of capillary suction and the total porosity of the specimens were determined by means of the capillary suction of water. The specimens were precured for one week at 20°C and RH $\sim 100\%$ and for three weeks at 20°C and RH 70 %. Subsequently the specimens were dried at 50°C . After the test, the specimens were dried at 105°C and ignited at 650°C in order to determine the amount of chemically bound water. The results of the test series are shown in Table 5.

The resistance of water penetration in capillary suction was considerably smaller in F-concrete than in reference concrete made of Portland cement or blended cement with the same water-binder ratio and strength level (Table 6) (Häkkinen et al. 1987). The resistance coefficient of F-concrete was also quite insensitive to changes in water-cement ratio (Vesikari 1987).

Table 5. Pore constants of F-concrete and reference concretes (Häkkinen et al. 1987)
Water-binder-aggregate ratio 0.4:1:4.

Concrete	Binder	Total pore volume (l/m ³)	Density (kg/m ³)	Coefficient of capillary suction w_k *) (kg/m ² s ^{1/2})	Resistance of penetration M *) (s/mm ²)	Amount of bound water (% by wt. of binder)
F	Oxelösund slag	151.3	2280	0.017	22.53	15
F	Rautaruukki slag	143.0	2290	0.022	15.37	12
B	Normal hardening Portland cement 80 % by wt. and Rautaruukki slag 20 % by wt.	152.2	2300	0.012	26.82	-
P	Normal hardening Portland cement	148.5	2290	0.011	53.79	14

*) Coefficient of capillary suction $w_k = k / t$
 w_k is amount of capillary water (kg)
 t is time of suction (s)
 Resistance of penetration $M = t/Z^2$
 Z is rising height of water (mm).

Table 6. Influence of binder on the strength of concrete (Häkkinen et al. 1987).
Water:Binder:Aggregate ratio 0.4:1:4.
Curing conditions:
7 d at 20 °C, RH > 95 %, subsequent curing at RH 70 %.

Binder	Strength, 28 d			Strength, 91 d		
	Compression	Flexure	Ratio	Compression	Flexure	Ratio
F (Oxelösund slag)	70.6	8.7	12.3	78.8	8.9	11.3
F (Rautaruukki slag)	53.5	5.7	10.7	62.7	5.9	9.4
B (Blended cement, see Table 5)	57.4	7.7	13.4	-	-	-
P (Normal hardening Portland cement)	71.5	10.5	14.7	74.5	11.7	15.7

4.2 Water tightness

Water tightness of concrete specimens was tested according to standard SFS 4476 (1980). In the water tightness equipment the specimens were influenced by about 1 MPa water pressure for 24 h. The strength values of the test and reference concretes were at the same level (Table 3). The specimens were either wet (at RH 70 %) or dry (at 40 °C). The penetration depth of water in Portland cement specimens was fairly even but in F-concrete specimens, both dry and wet, water had almost or totally penetrated through the specimens in a surface layer the depth of which was about 10 - 30 mm. Drying of specimens

had a marked influence on the penetration of water into F-concrete specimens, but had little or no influence on water penetration into Portland cement specimens. Results are shown in Table 7 and Fig. 3.

Table 7. Coefficient of water penetration for F-concrete and reference concrete made of normal hardening Portland cement (Häkkinen et al. 1987). See Fig. 3.
Water: binder: aggregate ratio 0.4:1:5.
Specimen size 300 × Ø 150 mm.

Curing conditions		F-concrete	Coefficient of water penetration = $\frac{2 \times \text{max. penetration (mm)}}{100 \text{ mm}}$ P-concrete
4 d at RH > 95 %	20 d at RH 70 %	0.1 - 0.7	0.0 - 0.1
4 d at RH > 95 %	14 d at RH 70 %	See Fig.	0.1 - 0.2
6 d at 40 °C			

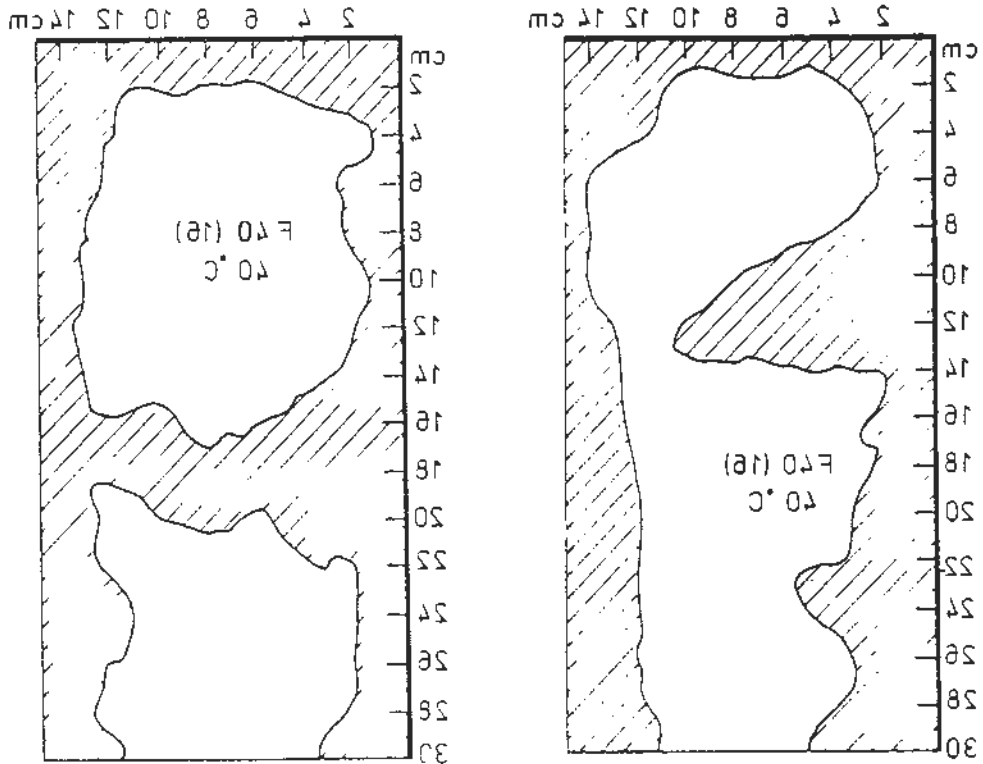


Fig. 3. Examples of the cross-section diagrams of F-concrete cylinders cured at 40 °C (Häkkinen et al. 1987). Areas of water penetration have been darkened.

4.3 Gas permeability

In order to measure the specific gas permeability of concrete samples compressed air was passed from an air bottle to the heads of specimens situated in metal cylinders. The openings between the specimens and the walls of the cylinders were tightened with bitumen. The air flow through the specimens was guided into measurement equipment which consisted of water-filled capillary tubes. The results of the test are presented in Table 8.

Table 8. Gas permeability of F-concrete and Portland cement concrete (Häkkinen et al. 1987).

Water:binder:aggregate ratio 0.4:1:5.

Curing of specimens:

Heat treatment 14 h at 40 °C, 3 d at 20 °C, RH ~ 100 %.

Subsequently either 11 d at 70 % RH or 7 d at 70 % RH and 6 d at 40 °C.

Specimen size 60 × ø 150 mm.

Concrete	Coefficient of gas permeability (m ²) ***)			
	F *)	F	P **)	P
Precuring	70 % RH	4D °C	70 % RH	40 °C
Δp = 1 bar	1.2 × 10 ⁻¹⁷	1.9 × 10 ⁻¹⁵	1.7 × 10 ⁻¹⁸	1.0 × 10 ⁻¹⁷
Δp = 3 bar	1.8 × 10 ⁻¹⁷	3.0 × 10 ⁻¹⁵	2.0 × 10 ⁻¹⁸	1.2 × 10 ⁻¹⁷
Δp = 5 bar	2.8 × 10 ⁻¹⁷	4.5 × 10 ⁻¹⁵	2.8 × 10 ⁻¹⁸	1.1 × 10 ⁻¹⁷

*) Compressive strength 43.4 MPa (specimen size 100 × 100 × 100 mm).

**) Compressive strength 47.0 MPa (specimen size 100 × 100 × 100 mm).

***) $D_s = \frac{\eta \cdot \phi \cdot l}{A \cdot \Delta p}$

where η dynamic viscosity of air (Ns/m²)
 ϕ volume flow of air (m³/s)
 l thickness of the specimen (m)
 A surface area of the specimen (m²)
 Δp pressure difference (N/m²).

The permeability of F-concrete cured at 70 % RH was about 10 times higher than that of Portland cement concrete. The drying of concrete considerably influenced the permeability of F-samples, far above that of the Portland cement concrete. It is obvious that the cracks in the F-concrete form a continual pore network, which makes the concrete permeable as the pores are empty of water (Häkkinen et al. 1987).

4.4 Carbonation

The influence of slag binder on the carbonation rate of concrete was studied by accelerating the carbonation process (Häkkinen et al. 1987). All the specimens were precured for seven days at 20 °C and RH > 95 % and for five weeks at RH = 70 %. Subsequently one part of the specimens was left in precuring conditions while another part was moved to a carbon dioxide box, where the specimens were kept for either three or six months. In the carbon dioxide box the gas flowed freely. The concentration was measured occasionally and was verified as being about 3 %. At the end of the test series all the specimens were broken and the depth of carbonation was measured by dyeing with phenolphthalein solution. Carbonation results are presented in Table 9.

Table 9. Carbonation coefficients and strength results for F-concrete and reference concrete made of normal hardening Portland cement (Häkkinen et al. 1987).

Concrete	Water-binder ratio	Thermal treatment	Carbonation coefficient B mm/a ² *)	Compressive strength MPa Age 7 months, CO ₂ curing
F	0.35	60 °C	1.5	81
F	0.43	60 °C	2.3	71
F	0.51	60 °C	3.5	63
F	0.43	-	1.0	86
P	0.43	-	0.7	77
P	0.43	60 °C	0.6	65
P	0.51	60 °C	0.8	49

*) $L_c = B \sqrt{t}$
 where L_c is depth of carbonation (mm)
 t time (year)
 B carbonation coefficient (mm/year).

The carbonation rate of F-concrete was in every case considerably greater than that of reference concrete. The carbonation of concrete samples was also optically analysed (Table 10). Carbonation of F-concrete differed from that of Portland cement concrete in that carbonation penetrated the concrete along the microcracks. In X-ray diffraction and thermoanalytical studies the carbonates in CO₂-treated specimens were found to be calcium carbonates (Häkkinen et al. 1987).

Table 10. Carbonation depths in CO₂-treated (three months) specimens measured in thin sections.

Concrete	Water-binder ratio	Heat treatment	Carbonation depth	
			variation (mm)	mean (mm)
F	0.35	60 °C	2 - 10	4
F	0.43	60 °C	8 - 14	9
F	0.43	-	3 - 6	3
F	0.51	60 °C	12 - 18	13
P	0.43	-	1 - 3	1.5

5. FROST RESISTANCE

The freeze-thaw test was carried out using an automatic freeze-thaw cabinet, where freezing takes place in air and thawing in water. The temperature falls to -20 °C during the freezing stage and rises to +20 °C during thawing. Five freeze-thaw cycles could be performed within a day. The total amount of cycles was 700. The shape and conditions were checked during the test by visual inspection and by measuring the ultrasonic pulse velocity through the specimens. At the end of the test the compressive strength and flexural strength were determined. The strength results of concretes are presented in Table 11 (Vesikari 1987).

Table 11. Strength values determined after 700 cycles in the freeze - thaw test (Vesikari 1987).
Test specimens 100 × 100 × 500 mm.

Water-cement ratio		Air-water ratio	
		0.05	0.15
0.50	<u>Compressive strength</u>		
	- test, MPa	48.5	no result
	- ref., MPa	55.5	
	- ratio, %	87	
	<u>Flexural strength</u>		
	- test, MPa	3.72	no result
- ref., MPa	4.80		
- ratio, %	78		
0.40	<u>Compressive strength</u>		
	- test, MPa	57.0	48.5
	- ref., MPa	60.8	50.0
	- ratio, %	94	97
	<u>Flexural strength</u>		
	- test, MPa	3.57	4.05
- ref., MPa	5.38	4.65	
- ratio, %	66	87	
0.32	<u>Compressive strength</u>		
	- test, MPa	72.5	67.5
	- ref., MPa	77.8	75.5
	- ratio, %	93	89
	<u>Flexural strength</u>		
	- test, MPa	4.22	4.52
- ref., MPa	5.85	5.95	
- ratio, %	72	76	

For concrete with a water-cement ratio below or equal to 0.4, the frost resistance seems to be good. The air content has little influence on the test results (Vesikari 1987).

The frost-salt tests were performed at two ages of concrete. At the beginning of the tests the age of concretes was 35 d in the first test serie and 230 d in the second test serie. Prior to the test the specimens had been stored at first for 7 d at 100 % RH and at last for 7 d in water and for the rest at 70 % RH. The results of the frost-salt tests are presented in figures 4 and 5 (Vesikari 1987).

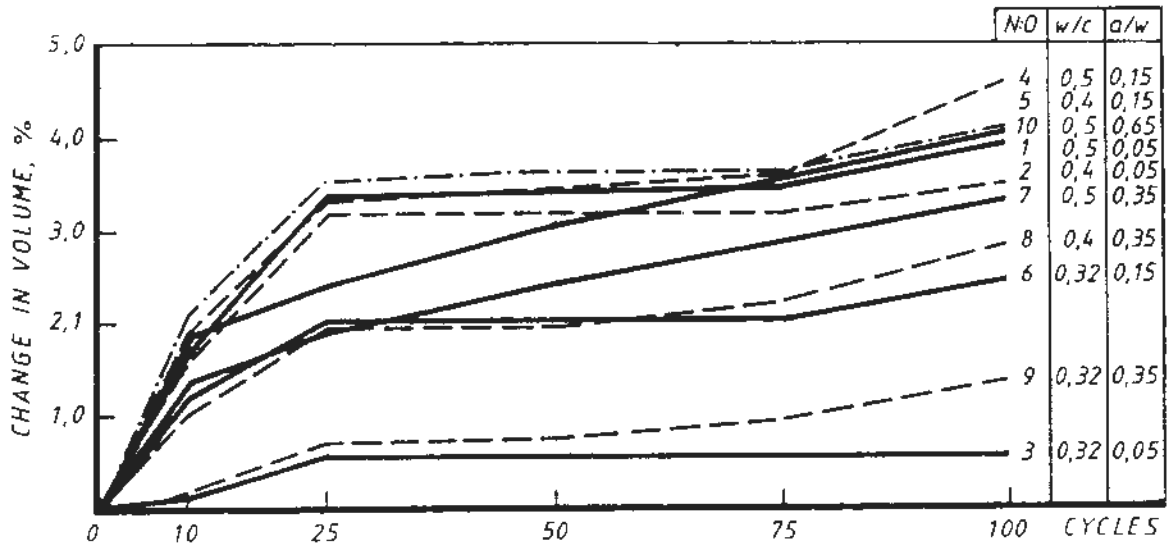


Fig. 4. Results of the frost-salt test (1st series) (Vesikari 1987). The age of concrete at the beginning of the test was 35 d. Test specimens 100 × 100 × 100 mm. Test arrangement (Werse 1976).

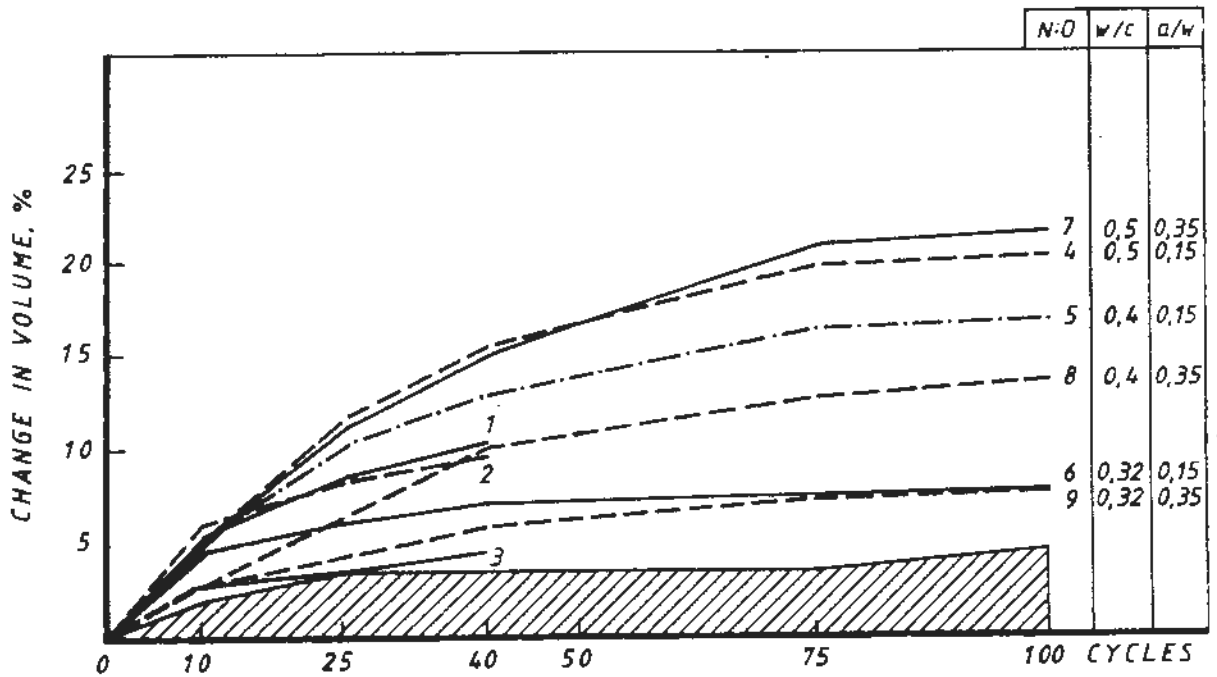


Fig. 5. Results of the frost-salt test (2nd series) (Vesikari 1987). The age of concrete at the beginning of the test was 230 d. The area under the curves of the 1st test series is depicted by the shadowed area.

In the frost-salt test the reduction in volume of specimens was relatively large during the first 25 cycles. After this primary scaling stage the rate of scaling slows down considerably or even stops. After 75 cycles the rate of scaling once again slowly begins to accelerate. The influence of the water-cement ratio on the results of the frost-salt test is clear. The air content does not appear to have much influence on the rate of scaling (Vesikari 1987).

According to studies of Vesikari (1987) the behaviour of F-concrete in the frost-salt test is different from that of Portland cement concrete but similar to that of slag cement concrete. The scaling curve for Portland cement concrete is either straight or curves slightly upwards (Fig. 6). Silica concrete with Portland cement as the main binding agent behaves in principle in the same way as pure Portland cement concrete but the rate of scaling is smaller. F-concrete and slag cement concrete have an S-shaped scaling curve with a large amount of primary scaling (0...25 cycles), after which almost no scaling occurs (25...50 cycles); finally the rate of scaling slowly accelerates (after 50 or 75 cycles). The concretes in Figure 6 have approximately the same water-cement ratio (between 0.4 and 0.48) and air content (between 4.8 and 6 %), so that the difference in scaling curves are mainly due to the binding agent (Vesikari 1987).

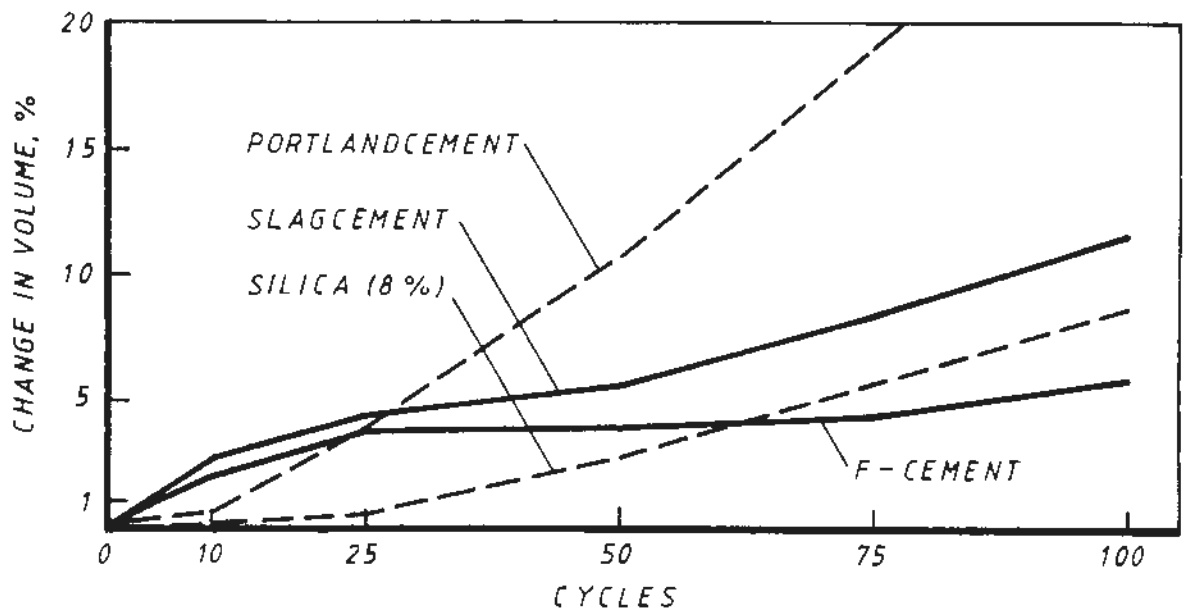


Fig. 6. Effect of binding agent on the shape of the scaling curve (Vesikari 1987).

The results of the 2nd series of frost-salt tests show that primary scaling increases with the age of the specimens. Primary scaling averaged 4 times that in the 1st series at 25 cycles and 5.5 times that at 75 cycles (Vesikari 1987). The reason for primary scaling in F-concretes and slag cement concretes is probably carbonation. Carbonation reduces the resistance of both F-concrete and normal slag cement concrete. The resistance of Portland cement concrete may slightly increase under the influence of carbonation (Vesikari 1987).

6. CONCLUSIONS

According to the results the hardened slag paste is very dense having only a small amount of small capillaries, but the structure contains microscopic cracks due to hydration shrinkage. The effect of the cracks on the permeability properties was found to be significant. The resistance of water penetration in capillary suction is considerably smaller in F-concrete than in reference Portland cement concrete. The resistance coefficient of F-concrete is also quite insensitive to changes in water-cement ratio. The carbonation rate of F-concrete is considerably greater than that of reference concrete. Carbonation penetrates the F-concrete along the microcracks.

On the basis of strength results it is possible to produce F-concrete with very good mechanical properties.

The frost resistance and frost-salt resistance of F-concrete are good whenever the water-cement ratio is smaller than or equal to 0.4. The air content does not have much influence on the frost resistance or frost-salt resistance of F-concrete. However, in the frost-salt test a rapid primary scaling takes place and the amount of this primary scaling increases with an extended age of concrete. This phenomenon is common to other slag cement concretes and is probably related to the carbonation at the surfaces of test specimens. Cracking does not have a clearly detrimental effect on the frost resistance of F-concrete.

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