EFFECT OF WATER STORAGE TIME ON FROST RESISTANCE OF CONCRETE

High performance concrete

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Abstract

In high performance concrete (HPC) with low water-cement ratio, cement reaction will cause substantial drying expressed in terms of relative humidity (RH) of the pore water. This phenomenon is called self-desiccation. The RH-values as low as 85% have been measured in dense concretes that have been stored for more than 18 months in water. This means that there is almost no freezable water in the concrete until very low temperatures are reached. It also means that freeze-thaw tests made with young concrete might give results on the unsafe side. In this report some results from a bigger study of the effect of long-term water storage on the frost resistance of HPC are presented. The results show that previously self-desiccated concrete absorbs water when it is stored for a long time in water. Dilation tests during freezing indicate that concrete that was frost resistant when tested during the first months might become non-frost resistant after a long period of water storage. This must be considered in the design of freeze-thaw test methods.

Keywords: Frost resistance, high-performance concrete, self-desiccation, water absorption

1 Introduction

Test standards for frost resistance of concrete normally specifies that the concrete shall be about 28 days old at the start of the test. Besides, it is often specified that the concrete shall be water-stored from the casting until start of the test. It is questionable whether the result of such a freeze-thaw test is always representative for the real structure. In reality many concrete structures are exposed to more than 50 years of continuous water storage in combination with repeated freezing and thawing cycles. Examples are bridge pillars in the splash zone, and hydraulic structures. After some time, the water content in such structures will probably be considerably higher than in the test specimen. In high performance concrete (HPC) there is a self-desiccation that further lowers the water content in the specimen and thereby increases the frost resistance. One cannot exclude, however, that this self-desiccation gradually disappears in the real structure due to the inflow of water that is not compensated for by desiccation caused by the gradually slower cement reaction.

In this investigation the effect on the frost resistance of long-term water storage before start of the freeze-thaw test was investigated. Water storage was extended to 3 years. The HPC, with and without entrained air, was investigated. The w/c-ratio varied between 0.27 and 0.40. Only a few results are presented here. The rest of the study will be presented in reports from the division.

2 Self-desiccation and its potential effects

The specific volume of chemically bound water in cement paste is only about 0.75 litre/kg (Powers 1962). Thus, when a moisture-insulated cement reacts with water, an air-filled pore space is created. It can be calculated by

$$a = 0.25 \cdot w_n \qquad \mathbf{(1)}$$

where a (litre) is the air-space created, and w_n (litre) is the amount of chemically bound water. For Portland cement, the maximum amount of chemically bound water when all of the cement has hydrated is about $0.25 \cdot C$ where C (kg/m^3) is the cement content. Then, using the assumption that the degree of hydration α is proportional to the amount of chemically bound water, the air space can be calculated by

$$a = 0.25 \cdot 0.25 \cdot \alpha \cdot C = 0.0625 \cdot \alpha \cdot C \qquad \mathbf{(2)}$$

where C (kg/m^3) is the cement content in one cubic metre of concrete. Examples: (1) For a normal concrete with the cement content 300 kg/m^3 and the degree of hydration 80% the air space formed is 15 litres/m^3. (2) For HPC with the cement content 500 kg/m^3 and the degree of hydration 40% the air space is 12.5 litres/m^3. This means that the self-desiccation expressed in terms of the volume of air space formed is not bigger in HPC than in normal concrete due to the lower degree of hydration reached in HPC. However, in terms of the reduction in RH, self-desiccation is considerably larger in HPC; see below.

This self-desiccation is essential for protection of the concrete against early freezing. In fact, it is the reason why concrete can be placed with success during cold weather conditions. This is further treated by Fagerlund (1997).

For normal weight concrete (w/c > 0.40) the self-desiccation will not significantly change the internal relative humidity (RH) of the pore water. The desorption isotherm of such concrete is too steep at high values of RH. This in turn depends on the fairly coarse pore structure of normal concrete. For concrete with lower w/c ratios (HPC), the pore structure is finer, and therefore the sorption isotherm is more horizontal at high RH-values. This means that the internal drying caused by the cement hydration will lead to a significant reduction of the internal RH. For concrete with silica fume this characteristics is even more pronounced due to the more refined pore-structure caused by silica fume. The difference between normal concrete and HPC is shown in Fig 1.

The reduction in RH will reduce the amount of freezable water. A relation between RH of capillary water and its freezing point is

$$\ln(RH) = \left(\frac{\Delta H}{R \cdot 293}\right)\ln\left(\frac{T}{T_0}\right) \tag{3}$$

where ΔH (J/kmole) is the molar heat of fusion of water ($\Delta H = M(334+2\cdot q)10^3$ where q is the temperature in degrees Celsius), R is the gas constant, T (°K) is the freezing temperature and T_0 (°K) the freezing temperature of bulk water (273 °K). This means that water in equilibrium with 92% RH, 85% RH or 79% RH will not freeze until -10°C, -20°C and -30°C respectively.

Consequently, if an HPC reaches an internal RH of 85% due to self-desiccation there will be no water that can freeze until the temperature is below -20°C.

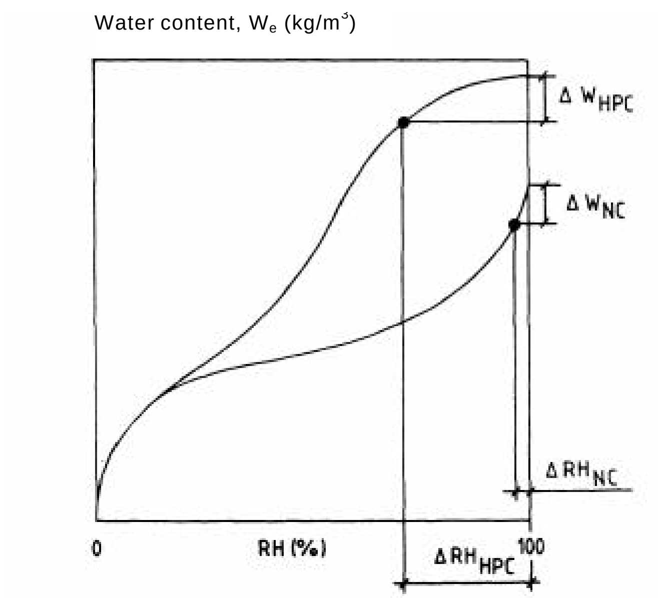

Fig. 1: Shape of the sorption isotherm of normal concrete (NC) and high-performance concrete (HPC) ΔRH is the self-desiccation caused by the hydration ΔW.(Fagerlund 1998)

Theoretically, the self-desiccation will prevail only if the concrete is moisture insulated so that no water can enter the concrete from the surroundings. If the concrete is open to external water, which is normally the case, it will absorb some water, which will raise its internal RH. Tests have shown, however, that a dense concrete can stay dry for a very long time even during very moist conditions. There is even a possibility that a concrete which was once self-desiccated will never become saturated again.

A freeze-thaw test often starts within one or two months after casting of the specimen. This means that one can assume that the internal parts of the freeze-thaw specimens are more or less dry when the test starts. This also applies in cases where the concrete has been stored in water. During the test, a certain moisture ingress might occur, especially if the test is very moist. One cannot exclude, however, that there is less freezable water in the specimen during the test than what might appear in the real structure. Frost damage will only occur when a critical moisture content is transgressed. Freeze-thaw tests, therefore, always must be made with concrete that have a moisture content that is representative for the prevalent field conditions. A representative moisture condition in HPC can only be reached by prolonged water storage, or by forcing water in by over-pressure. In the actual study, the prolonged water storage was used.

3 Investigations

3.1 Introduction: Tested concrete

Between 1992 and 1998, there has been a large national project in Sweden on high-performance concrete. As a part of this project, 26 different types of HPC specimens were cast in 1995 (Svensson 1995). The water/binder-ratio varied between 0.40 and 0.27 and the amount of air was between 1 and 9%. The cement was a low-alkali ($K_2O+Na_2O \approx 0.6\%$) sulphate resistant ($C_3A \approx 2\%$) standard portland cement. The aggregate consisted of gravel 0-8 mm, quartzite 8-12 mm and quartzite 12-16 mm. The air-entrainment agent used was vinsol-resin. The concretes were cast in plastic pipes with a diameter of 103 mm and a length of 250 mm. Seven specimen of each type of mixture were were cured in seven different ways. The cylinders were stored either in limewater or 3% sodium chloride solution. An extensive testing of these cylinders is going on. The testing includes measuring of length change during freeze/thaw cycles due to ice-formation and melting, self-desiccation and field studies of specimens exposed to de-icing salts along a Swedish road. Additional results will be published during 1999. This report contains results from measurements on specimen listed in Table 1. The investigation includes water absorption and freeze/thaw tests of specimen stored in limewater for three years.

Specimen in italics was part of a study of the internal self-desiccation performed by Fagerlund and Yang (Fagerlund and Yang 1998). The last number in the designation is connected to how the specimen was cured. 1 stands for storage in limewater since its de-moulding. 4 signifies that de-moulding was followed by two weeks of membrane curing which then was followed by storage in limewater.

3.2 Self-desiccation

In a study (Fagerlund and Yang 1998) the self-desiccation of high-performance concrete stored for two years in limewater was investigated. The specimens came from the large study described above. At a distance of 70 mm from the cylinder end a slice of 10 mm thickness was sawn. The slice was cut into three layers (inner, middle and outer) and the pieces from each layer were crushed by a hammer and placed in glasstubes. The tubes were put in a climate chamber (18.2 °C±0.2 °C, 62.2 ±0.2% RH) for four days before the RH-measurements started by using sensors placed in the tube. The RH was measured after the sensor had come to equilibrium with the air in the tube after about 24 hours. The results are seen in Figures 2 and 3.

Table 1: Tested concretes

Specimen Number	w/c-ratio	Air-content in fresh concrete (%)
0.40:0:0:1	0.40	1.0
0.40:0:5:1	0.40	4.6
0.35:0:0:1	0.35	0.6
0.35:0:4:1	0.35	3.6
0.33:0:0:1	0.33	1.7
0.33:0:3:1	0.33	2.5
0.33:0:4:1	0.33	3.5
0.33:0:9:1	0.33	9.2
0.30:0:0:1	0.30	1.1
0.30:0:3:1	0.30	2.6
0.27:0:0:1	0.27	0.3
0.27:0:3:1	0.27	3.5
0.40:0:0:4	*0.40*	*1.0*
0.40:0:5:4	*0.40*	*4.6*
0.35:0:0:4	*0.35*	*0.6*
0.35:0:4:4	*0.35*	*3.6*
0.33:0:0:4	*0.33*	*1.7*
0.33:0:4:4	*0.33*	*3.5*
0.30:0:0:4	*0.30*	*1.1*
0.30:0:3:4	*0.30*	*2.6*
0.27:0:0:4	*0.27*	*0.3*
0.27:0:3:4	*0.27*	*3.5*

The lower the w/c-ratio, the lower is the RH-value inside the concrete. In specimens with silica fume (not shown here), the RH-value was even lower. This is of great importance for the expansions during the freeze/thaw tests of the specimen, which will be presented in Section 3.5.

If this type of concrete is stored in water for a long time, there is a larger possibility that the self-desiccated pores will become filled with water. The concrete has a very low permeability but theoretically water transport does not stop until the moisture content is equal over the entire cross-section. When water reaches the inner parts of the concrete, the self-desiccated pores will be filled. This will lower the possibility of the concrete to withstand freeze/thaw cycles.

3.3 Long-term water absorption in specimens without air-entrainment

The specimens were weighed at ages of 1, 3, 33 and 36 months. The specimens were kept in saturated limewater all the time except during the freeze/thaw tests (see section 3.5) which were conducted in a moisture sealed condition.

The increase in the degree of saturation (ΔS) is calculated according to equation (4) (Fagerlund 1977).

$$\Delta S = \frac{V_w}{V_p} \tag{4}$$

where: V_w (m^3) is the increased volume of water in the specimen related to the volume of water after four weeks of water storage, and V_p (m^3) is the calculated paste pore volume; the calculation is based on equation (5).

$$V_p = C\left(\frac{w}{C} - 0.19 \cdot \alpha\right) \quad \textbf{(5)}$$

where: C (kg/m^3) is the amount of cement, w (kg/m^3) is the amount of mixing water and, α is the degree of hydration which is supposed to be 0.8 for all of the specimens.

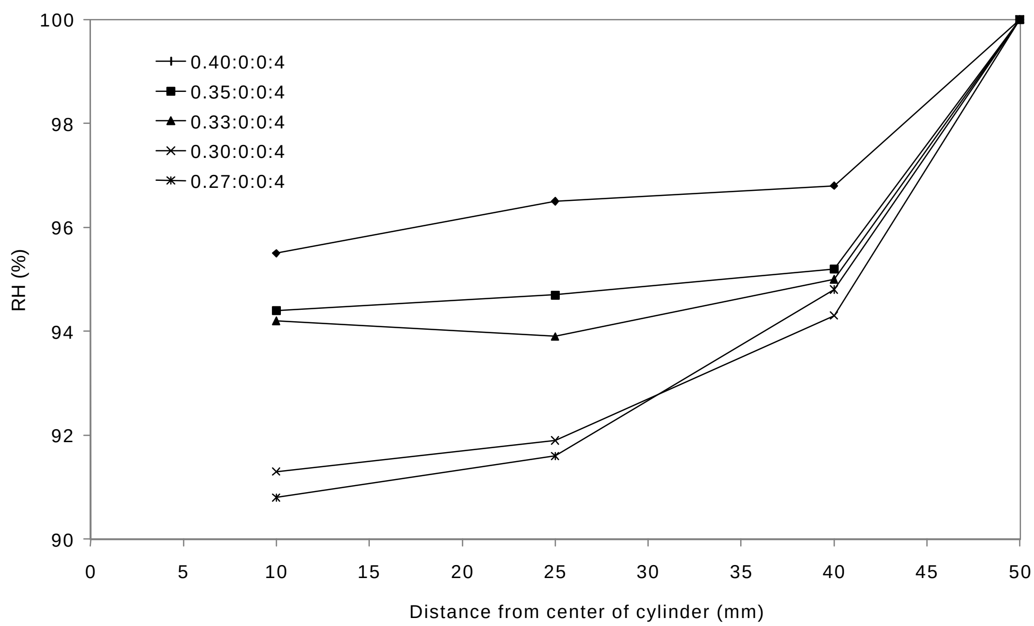

Fig. 2: The distribution of RH in specimen without air-entrainment

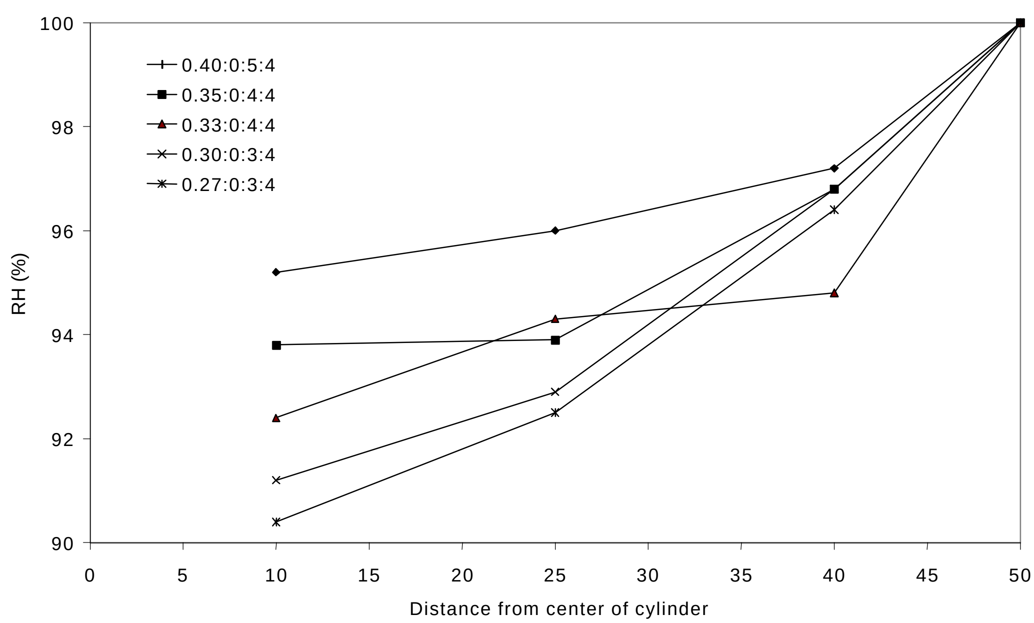

Fig. 3: The distribution of RH in specimen with air-entrainment

All of the specimens show an increase in the degree of saturation (Fig 4). The lowest w/c ratios show the largest absorption, which might depend on the fact that they had the largest self-desiccation. For these concretes, the rate of water absorption is still high. This indicates that some of the pores created by the self-desiccation have started to absorb water. When the degree of saturation exceeds the critical degree of saturation, the concrete will be damaged during a freeze/thaw attack. If the water absorption continues at this rate, that degree of saturation will be reached sooner or later.

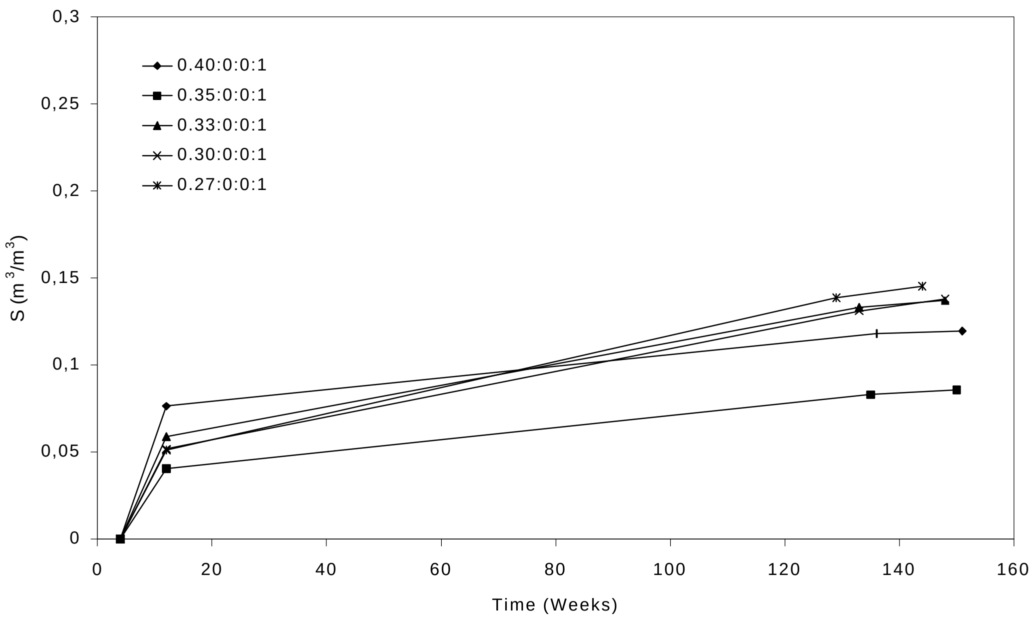

Fig. 4: Increase in degree of saturation for specimens without air-entrainment

3.4 Long-term water absorption in specimens with air-entrainment

These specimens have been treated in the same way as the specimen without air-entrainment with two exceptions; concretes 0.33:0:4:1 and 0.33:0:9:1 have only been subjected to three freeze/thaw tests. What can be clearly seen is that the degree of saturation is higher for all of the specimens with air-entrainment compered to those without air-entrainment (Fig 5). This is an indication that water absorption also occurs in the air pores. This is very dangerous for the frost resistance of the concrete.

3.5 Expansions during freezing

At four times during the three year period since casting, the specimens have been subjected to single cycles of freezing and thawing. The cycle is presented in Fig 6. The specimens were tested at the age 1, 3, 18 and 30 months. During the four freeze/thaw tests, the temperature and the length changes were measured. The temperature was recorded by a thermocouple in the centre of the specimen. A displacement transducer recorded the length changes. It was fixed on the invar-frame in which the specimen was placed. The maximum expansion is measured as the maximum deviation of the measured dilation from the extrapolated curve of linear thermal contraction. In (Fig 7), this is presented for specimens without air-entrainment. The expansion increased with increasing water-storage time.

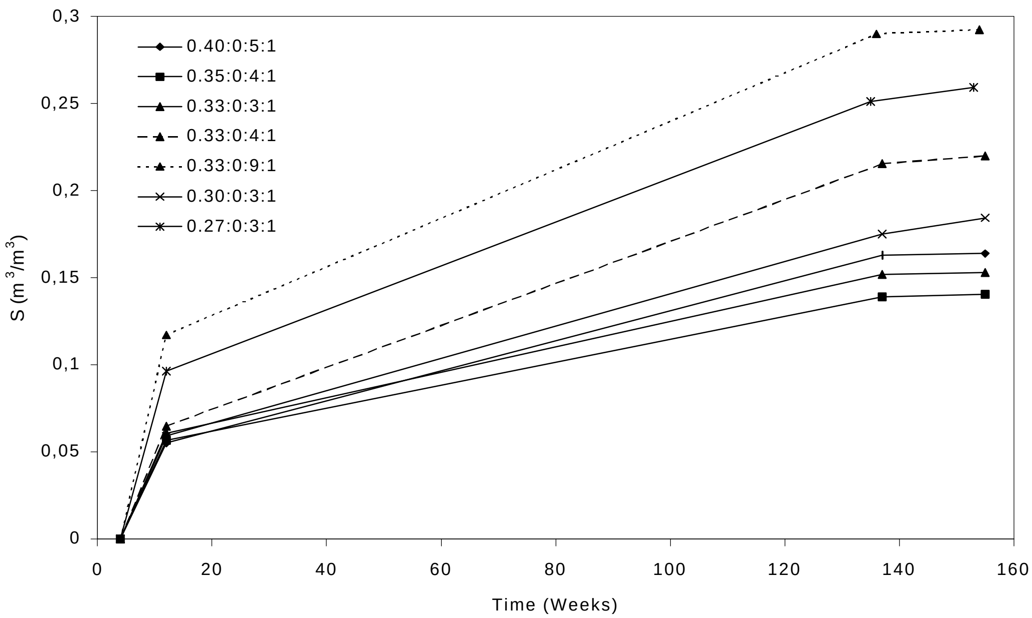

Fig. 5: Increase in degree of saturation for specimens with air-entrainment

Concrete with air-entrainment shows smaller expansions (Fig 8). The reason probably is that a large portion of the air-pore system stays air-filled after long-time water absorption. The large absorption in concretes with air-entrainment is therefore not big enough to cause damage. After very long time of water storage, however, even concrete with air-entrainment might become vulnerable to frost.

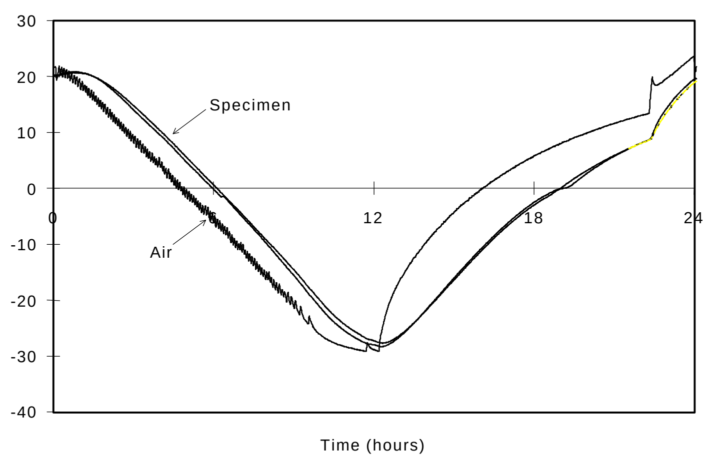

Fig. 6: Temperatures during freeze/thaw tests

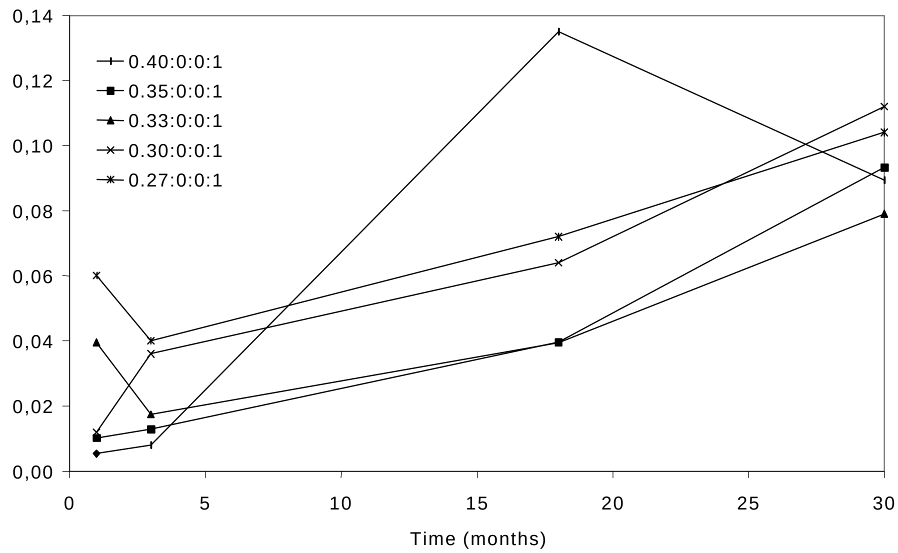

Fig. 7: Maximum expansion in specimens without air-entrainment

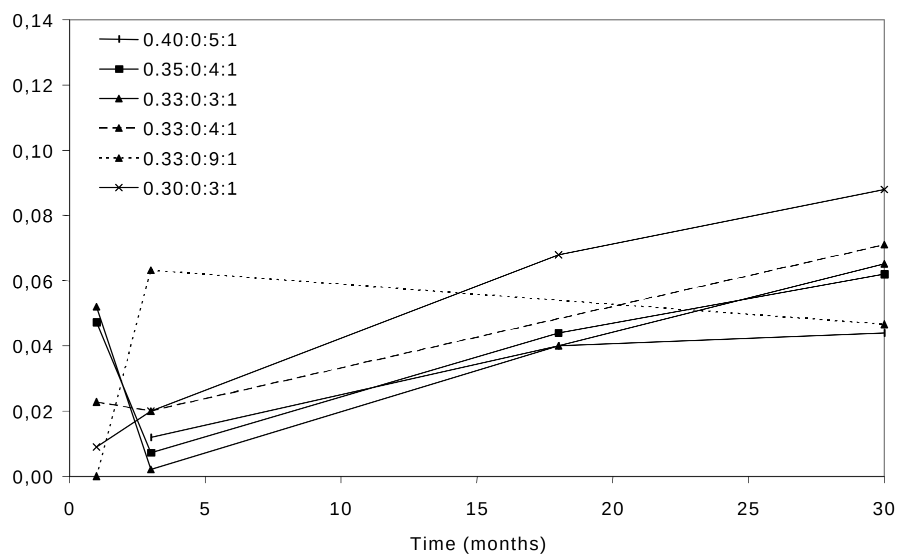

Fig. 8: Maximum expansion in specimens with air-entrainment

4 Conclusions

The effect of long time water storage on the frost resistance of high-performance concrete has been studied in this investigation. There are clear indications that self-desiccated pores might become re-saturated by long-term water storage and that air pores might absorb water. This emphasises the consideration of the long-term water absorption in self-desiccated concrete and air pores when designing freeze-thaw tests.

5 References

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