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1997

Citation for published version (APA):
Yang, Q. (1997). *Inner RH and degree of saturation in high performance concrete cured in water or salt solution for 2 years*. (Report TVBM (Intern 7000-rapport); Vol. 7115). Division of Building Materials, LTH, Lund University.

Total number of authors:
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LUND INSTITUTE OF TECHNOLOGY
Division of Building Materials

INNER RH AND DEGREE OF SATURATION IN HIGH PERFORMANCE CONCRETE CURED IN WATER OR SALT SOLUTION FOR 2 YEARS

Yang Quanbing

Report TVBM-7115

September 1997

Preface

The author, Yang Qanbing, is associate professor at the Tongji University in Shanghai. He is also working at the Laboratory of the Shanghai Institute of Building Materials under the leadership of Professor Huang Shiyuan who is well-known to Swedish concrete researchers after his two years as guest researcher at the Swedish Cement and Concrete Research Institute in Stockholm.

Mr. Yang spent three months as a guest researcher at our division during the period June-August 1997. This report is one of the results of his work with us. He also made a freeze-thaw study of concrete made with two different types of air-entraining agents. This study will be published in a separate report.

The report presents measurements of the so-called self-desiccation of concrete with low water-binder ratio. The measurements were made on concrete specimens that had been used in a previous study on the frost resistance of high performance concrete. That study was part of the National Swedish Programme on High Performance Concrete that was closed formally in June 1997. A large number of specimens prepared at that study had been left in a water bath, or in a 3% sodium chloride solution, for almost 2 years. These specimens could be directly used for the study presented below.

The results are quite interesting since they show that a dense concrete remains fairly dry also at a few centimeter depth from the water exposed surface. This, of course, has a very big significance for durability problems, such as reinforcement corrosion and internal frost attack, since drying strongly affects the rate of deterioration and the service life of the concrete. These aspects of self-desiccation will be treated in other ongoing work at our division.

I sincerely thank Mr. Yang for this good work which was performed during a short time and with great effort.

Lund, 24 September 1997

Göran Fagerlund
Head of Division

INNER RH AND DEGREE OF SATURATION IN HIGH PERFORMANCE CONCRETE CURED IN WATER OR SALT SOLUTION FOR 2 YEARS

Yang Quanbing

ABSTRACT

The inner RH and the degree of saturation (S) of high performance concrete (HPC) cured in water or 3 % NaCl solution for 2 years are measured on three different levels from the concrete surface (outer layer, middle layer and inner layer). Effects of many factors, such as W/C ratio, content of silica fume and air content are investigated. Results show that, (1)inner RH values of HPC decrease with the decrease in W/C and with the increase in the content of silica fume; (2)RH and S values of the outer layer of concrete are higher than those of the inner layer, and the difference increases with the decrease in W/C and with the increase in the content of silica fume; (3)the air content has little influence on RH of the inner layer, but as expected, since airpores don't readily absorb water, the air content reduces S of the concrete; (4)for concretes cured in 3 % NaCl solution, the RH values of the inner layer is higher than those for concrete cured in water and the S values of the three layers of concrete are markedly higher than those for concrete cured in water; (5)RH values are not directly related to S values, and the degree of saturation is a better tool to evaluate the content of the evaporable water in concrete than RH; and (6)theoretical calculations indicate that the increase in the molar concentration of soluble ions in concrete and the fractions of interlayer water, absorbed water and gel water in the evaporable water could be a main reason behind the decrease of RH values or so-called self-desiccation of concrete with low W/C and concrete with silica fume.

1. INTRODUCTION

Self-desiccation has attracted little interest in previous concrete research because its effects are negligible in normal concrete with ordinary or high W/C. However, with the development of superplasticizer technology and because of growing interest in high performance concrete, the situation has been changed in recent years. The internal RH-level of high performance concrete can be dramatically reduced when te W/C ratio is far below 0.40 and silica fume is used[1, 2].

In a concrete with sealed curing there will always be a certain desiccation caused by the "chemical shrinkage" of hydrate water. Thus, after a certain hydration time an extra air filled pore space has appeared and the degree of saturation is reduced. This phenomenon is called "self-desiccation". The volume of air pores created is $\Delta W=0.0625\cdot\alpha\cdot C$ where α is the degree of hydration and C is the cement content[3].

The self-desiccation always causes a reduction in RH of the sealed concrete[4,5]. For a normal concrete the effect is very small due to the very steep sorption isotherm at high RH.

This in turn depends on the rather coarse pore structure. However, for HPC the RH reduction is often very big because of the finer pore structure which is leading to a more flat sorption isotherm[6]. The effect is shown schematically in Fig 1. It clearly shows that the reduction of evaporable water in NC (ΔW_{NC}) is much bigger than that in HPC (ΔW_{HPC}) in order to reduce ΔRH from 100%RH. The lower the W/C and the higher the amount of silica fume, the finer the pore structure and the bigger the reduction of RH[7].

Thus, for a sealed concrete the phenomenon "self-desiccation" always corresponds to a reduction in the degree of saturation, and it sometimes - for HPC- corresponds to a reduction in RH. The first effect is positive with regard to frost resistance. The second effect is negative with regard to shrinkage and microcracking[8].

For unsealed conrete stored in water the chemical shrinkage leads to an ingress of extra water. The maximum amount of water sucked into the concrete exactly corresponds to the volume of self-desiccated pores, $\Delta W=0.0625\cdot\alpha\cdot C$. Therefore, all capillaries will be filled and RH will be 100% under this condition. In a normal concrete the inflow of water is so rapid that one can assume that no self-desiccation occurs. For HPC the inflow in the outmost millimeters probably is complete leading to RH=100 % at the surface part of concrete. Measurements however have shown that the inner part of HPC can be self-desiccated also after a long period of water storage due to a very low rate of water transport.

In this study some tests are made on the self-desiccation effect of concrete with W/C within the range 0.27 to 0.40. The concretes were stored in pure water or 3 % NaCl solution for about 2 years. The effect of silica fume and air-entraining agents are also studied. Self-desiccation is measured both as a reduction in RH and as a reduction in the degree of saturation. Some estimates are also made of the effect of self desiccation on the inner ion concentration of the pore solution and its effect on the measured RH values.

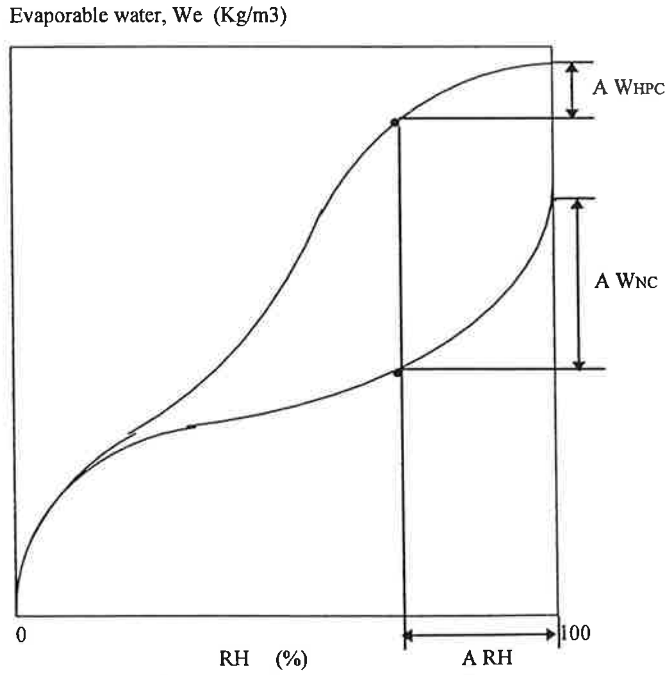


Fig 1 Schemetic effect of self-desiccation of sealed concrete
HPC = High Performance Concrete
NC = Normal Concrete

2. EXPERIMENTAL PROCEDURES

2.1 Raw materials

Portland cement with 0.6 % alkali and 2 % C_3A is used. The aggregate consists of crushed quartz sandstone 8~16 mm together with natural gravel 0~8 mm. In some concretes silica fume was used. Slica fume is mainly an amorphous silica with a fineness of 17.5 m^2/g. The naphthalene sulphonate superplasticizer (V33) and vinsol resin air-entraining agent (Cementa 88L) are used. In Table 1, the mix proportions and some properties of concrete are shown.

The concrete were made in connection with another study at the Department and had been stored in water or 3 % NaCl solution for about 2 years.

2.2 Curing conditions

Cylinder specimens (diameter 100 mm, length 250 mm) were cast and membrane cured for one day, and then stored for about 2 years under the following conditions:

Condition 1 membrane cured for 2 weeks + 4 weeks in water + one freezing-thawing cycle + 8 weeks in water + one freezing-thawing cycle + cured in water until the test. The freeze-thaw was made at moisture sealed condition

Condition 2 3 cycles consisting of wetting in 3 % NaCl solution for 2 weeks following by drying at 40 °C for 2 weeks + cured in 3 % NaCl solution until the test

Table 1 Mix proportions and some properties of the concrete

No	W/C	Cement + SF Kg/m^3	Gravel 0/8mm Kg/m^3	Quartzite 8/12mm Kg/m^3	2/16mm Kg/m^3	SP (dry weight) g/m^3	AEA Kg/m^3	Fresh Air content %	Density d Kg/m^3	Strength at 28d MPa
A1/a1	0.40	454 + 0	701	526	526	1.7	0	1.0	2425	88
a2		412+ 40	698	523	523	2.1	0	1.1	2409	102
A3		412 + 0	696	523	523	0	0.2	4.6	2253	65
B1/b1	0.35	492 + 0	703	528	527	3.9	0	0.6	2449	98
B2/b2		442+ 45	697	522	522	4.4	0	0.9	2446	117
B3		486 + 0	675	506	506	3.6	1.5	3.6	2376	88
D1/d1	0.33	485 + 0	706	529	529	4.8	0	1.7	2450	105
D2		460+ 25	705	529	529	5.5	0	1.3	2453	117
d3		438+ 45	702	527	527	7.5	0	1.3	2445	116
D4		487 + 0	686	514	514	4.9	0.2	3.5	2419	103
E1/e1	0.30	501 + 0	535	624	624	10.0	0	1.1	2482	122
E2/e2		455+ 45	533	622	621	11.2	0	0.8	2469	129
E3		500+ 0	525	613	613	6.0	0.3	2.6	2432	106
F1/f1	0.27	556 + 0	527	613	613	13.9	0	0.3	2502	133
F2		536+ 25	518	605	604	15.2	0	0.6	2493	138
f3		497+ 45	516	603	603	12.6	0	1.2	2463	140
F4		549 + 0	505	589	589	8.2	0.5	3.5	2421	110

Note: SF— silica fume SP— superplasticizer AEA— air-entraining agent
Capital letters (A1~F4) — stored in water Lower case letters (a1~f3) — stored in 3 % NaCl

2.3 Experimental methods

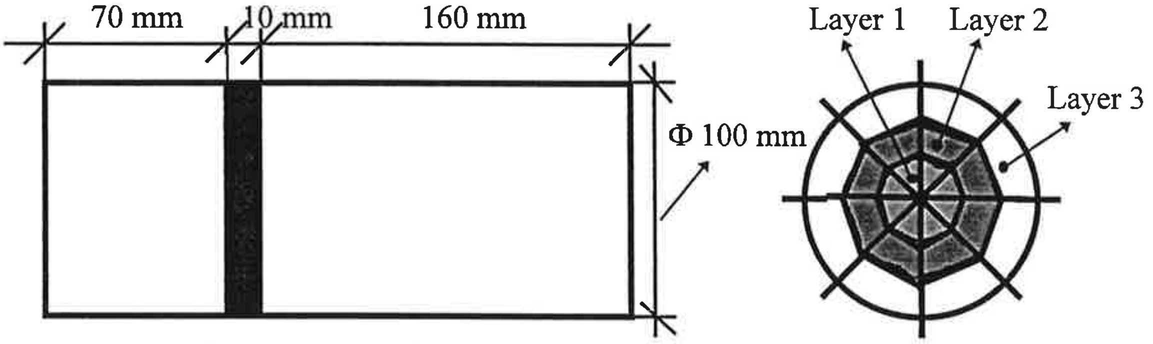
2.3.1 Cutting specimens

A 10 mm thick slice is sawn from the cylinder with the wet sawing according to Fig 2(a). The slice is surface-dried immediately after sawing. The slice is quickly cut into 24 pieces with a special equipment (see Fig 3). The pieces are taken from 3 layers (8 pieces in every layer) according to Fig 2(b). The pieces in the same layer are crushed with a hammer into many smaller pieces with a size below 10 mm. Then the smaller pieces are placed in a glass tube (the volume about 50 ml) which is sealed with a tight rubber plug and weighed (Qo). Layer 1, 2 and 3 are the inner, middle and outer layer respectively.

The specimens must be cut as quickly as possible because the RH of the air in the room is very low compared with that of the specimens.

2.3.2 Measuring RH[9]

For high performance concrete, the pieces for the measurement of RH must be as small as possible in order to reach the equilibrium of moisture more easily. The measurement is carried



(a) Sawing a slice from the cylinder

(b) Cutting the slice into pieces

Fig 2. The method of cutting a specimen into pieces

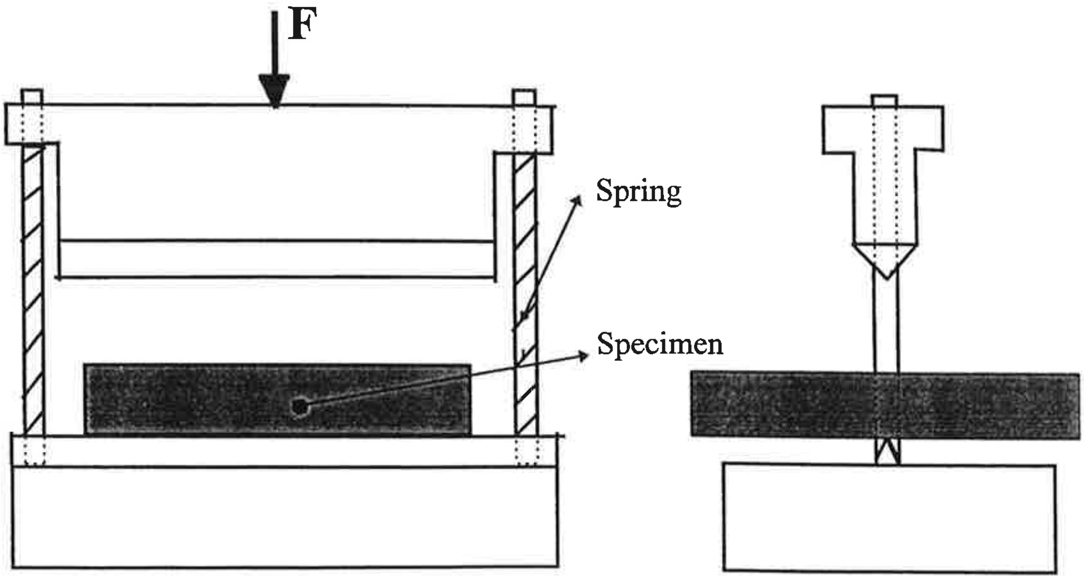


Fig 3. Set-up of the cutting equipment

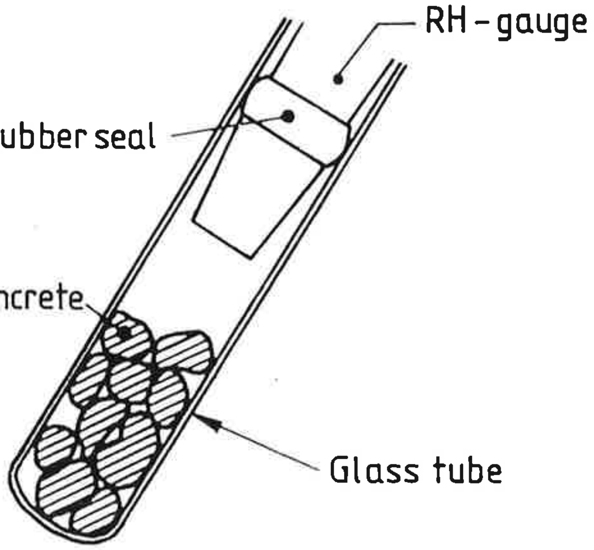


Fig 4 The measurement of RH

out in the room where there is a constant temperature of 18.2 ± 0.2 °C and relative humidity of 62.2 ± 0.2 %.

All tubes with specimen are put in the room at least for four days before the measurement. All RH-sensors are calibrated according to ASTM E 104-85 before the measurement. In this test, dew point meters of type Protimeter are used. The RH-sensor is inserted in the tube and the sensor is sealed by a rubber plug so that the concrete pieces are protected from the outside air, see Fig 4. The sensor was found to be kept in the tube for at last 22 hours in order to get the exact result, even though equilibrium is reached after about 16 hours. All the RH-sensors are placed in the room at least 4 hours before the start of the next measurement, in order to decrease the eventual error caused by the moisture hysteresis of the sensors.

There are some systematic and random errors that may occur in calibration and measurement of RH, such as temperature difference, drift in the RH meter and calibration error etc. In order to reduce the uncertainty, the measurement of RH is repeated at least 4 times.The total uncertainty is obtained after considering many errors, see Table 2[10].

Table 2 Overall uncertainty in RH measurement (Sc is a safe margin)

Measurement Times	Uncertainty U=ΔRH (%RH)		
	Sc=0.28	Sc=0.54	Sc=0.65
1	0.56	1.08	1.30
2	0.4	0.8	0.9
3	0.3	0.6	0.8
4		0.5	0.7
5		0.5	0.6
6		0.4	0.5
7			0.5

2.3.3 Measuring the degree of saturation

The degree of saturation is also an important parameter to express the moisture in concrete. After the measurement of RH all tubes with specimens are dried at 105 °C for two days and weighed (Qd), and then water is poured into the tubes. These tubes are stored at the vaccum of about 25 mmHg for five days and another five days at the atmosphere, and then weighed (Qs). The degree of saturation of the concrete is calculated by:

$$S = (Qo - Qd) / (Qs - Qd) \qquad \text{..................................} \quad (1)$$

S	the degree of saturation of the specimen
Qs	the weight of the specimen saturated with water
Qd	the weight of the specimen dried at 105 °C for two days
Qo	the actual weight of the specimen

The measurement precision of the balance is 0.001g. The total weight of a dried sample is at least 15 g. It is assumed that te vaccum-procedure is sufficient to completely saturate all pores in the concretes.

3. RESULTS

All results are shown in Appendix 1.

3.1 RH of high performance concrete

3.1.1 Distribution of moisture over the cross section

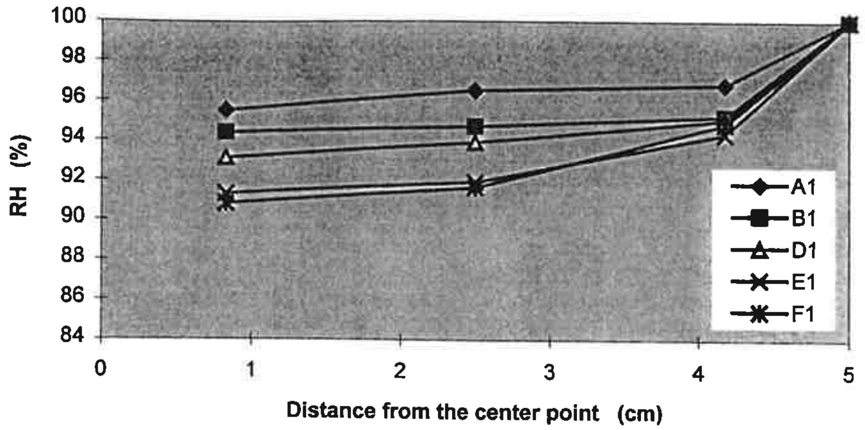
For high performance concrete with sealed curing, the inner distribution of moisture is even due to no ingress of extra water. During this condition, RH has been foundd to decrease significantly with the decrease of W/C[1,5].

However, the present study shows that for HPC cured in water for a long time, the internal distribution of moisture is uneven because extra water caused by the "chemical shrinkage" of the chemically bound water gradually permeates into concrete from the surface. The reason is the very low permeability of HPC. Fig 5 clearly shows that RH of decreases from the outside to the inside, and the difference of RH between outside and inside increases with the decrease in W/C ratio and with the increase in the amount of silica fume and air. However, the differences of RH in the outer layer among the various mix proportions are very small, which means that there must be an ingress of extra water in the outer layer.

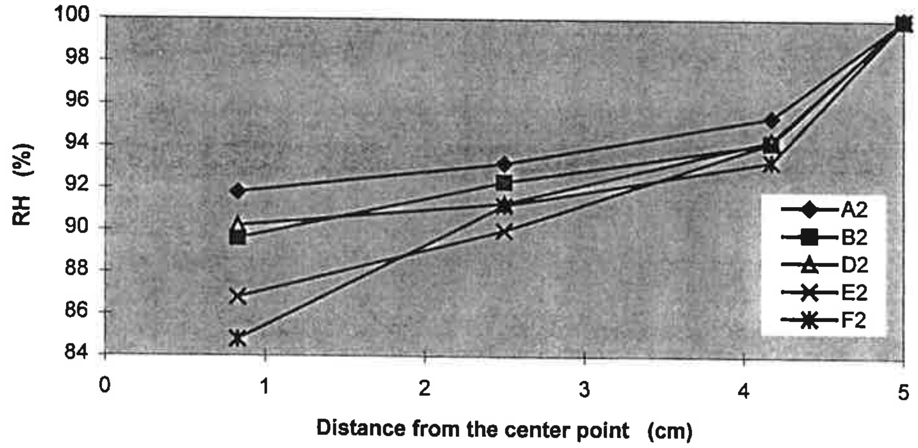
3.1.2 Effect of W/C

The effect of self-desiccation of concrete with sealed curing substantially increases when the W/C ratio is far below 0.40, so RH can be reduced considerably[2,5]. From Fig 6 it is also seen that RH of concrete stored in water for 2 years decreases with the decrease of W/C, but the effect of W/C on the RH values of the outer layer of concrete is negligible. It is also seen that the RH values of the inner layer of concrete are much higher than those of concrete with sealed curing. The values for sealed curing are taken from another study where the same types of cement and silica fume were used[5].

(a) the distribution of RH in concretes with various W/C ratio



(b) the distribution of RH in concretes with silica fume



(c) the distribution of RH in concretes with air-entraining agent

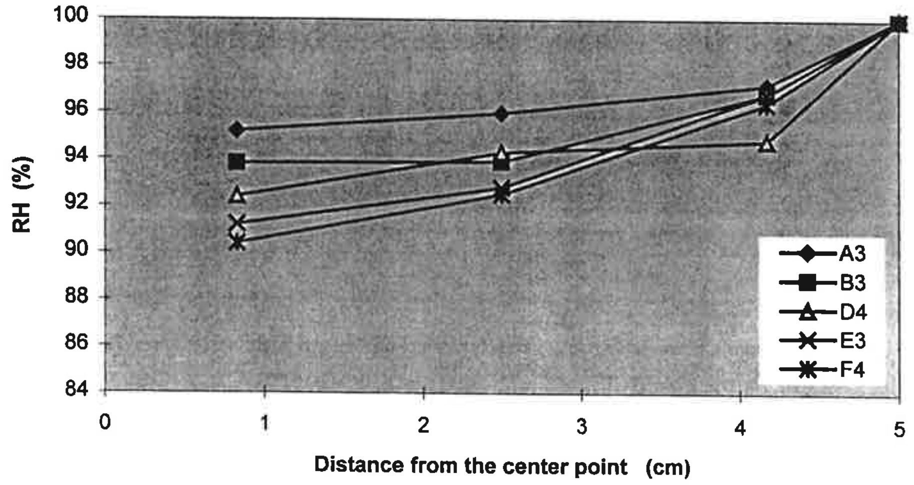
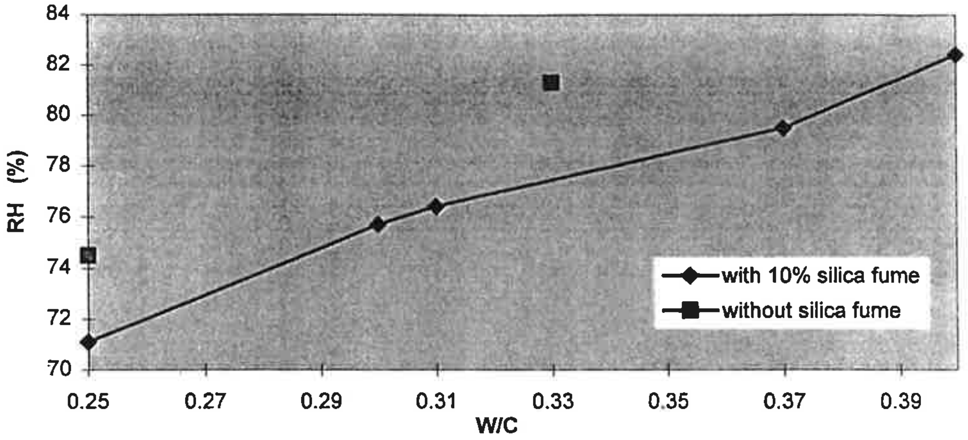


Fig 5 Distribution of RH of HPC stored in water for 2 years
(mix proportions A1~F4 , see Table 1)

(a)sealed curing[5]



(b)stored in water

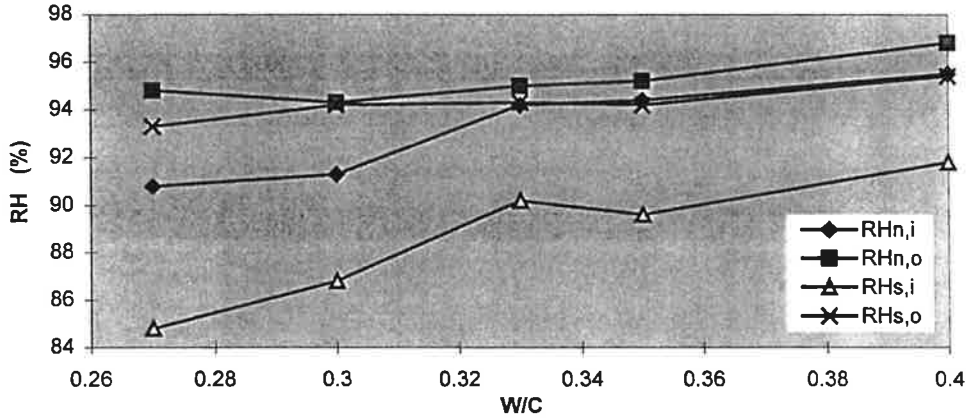


Fig 6 Effect of W/C ratio on RH of HPC stored in seeled condition or in water for 2 years (n—without SF and AEA, s—with SF, i—inner layer, o—outer layer)

3.1.3 Silica fume

The use of silica fume causes changes in the internal pore structure of concrete because SiO_2 of silica fume reacts with $Ca(OH)_2$ and therefore produces extra C-S-H. Therefore, the size of the capillary pores becomes smaller and the permeability of the concrete decreases significantly [11].

For concrete with silica fume, the difference in RH between the outer layer and the inner layer is much larger than that without silica fume, see Fig 7. The RH difference of the inner layer between concrete without silica fume and with silica fume is also very big, and increases with the decrease of W/C. However, the RH difference of the outer layer between concrete without silica fume and concrete with silica fume is very small, and the effect of W/C on the difference is neligible. These results show that it is much more difficult for water to permeate into concrete with silica fume than that without silica fume, but the outer layer of concrete can still get enough water to keep RH value high diminishing the effect of self-desiccation.

3.1.4 Air content

Fig 7 shows that the effect of AEA on RH is neligible for all concretes and for all locations.

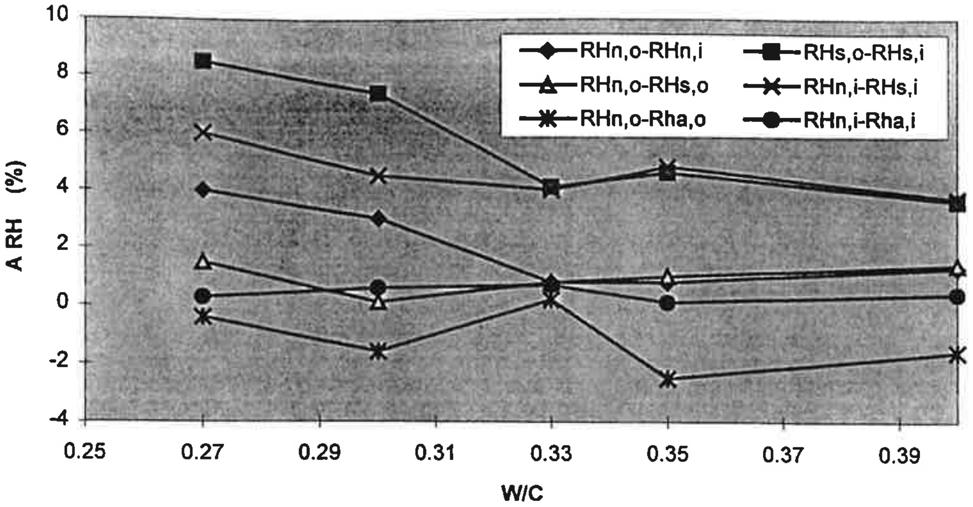


Fig 7 Effect of silica fume and AEA on RH of HPC stored in water for 2 years (n—without SF and AEA, s—with SF, a—with AEA, i—inner layer, o—outer layer)

3.1.5 Effect of Salt solution

The distribution of moisture in HPC is very complex when it is stored in 3% NaCl solution for 2 years after 3 drying-wetting cycles according to **condition2.** Fig 8 shows that the internal RH of the concrete without silica fume for some concretes is gradually reduced from the inside to the outside, just in contradiction to the results in Fig 5. The difference in RH beween the inside and the outside is however rather small. For concretes with silica fume, the distribution of RH is very different from that without silica fume, see Fig 8. The difference in RH between concrete without silica fume and concrete with silica fume (see Fig 9) is similar to the results for concretes stored in water, see Fig 7.

However, for concretes cured according to **condition 2**, the RH values of the inner layer obviously are higher than those of concretes cured according to **condition 1**, but the RH values of the outer layer are somewhat lower than those of concretes stored according to **condition 1**, see Fig 9.

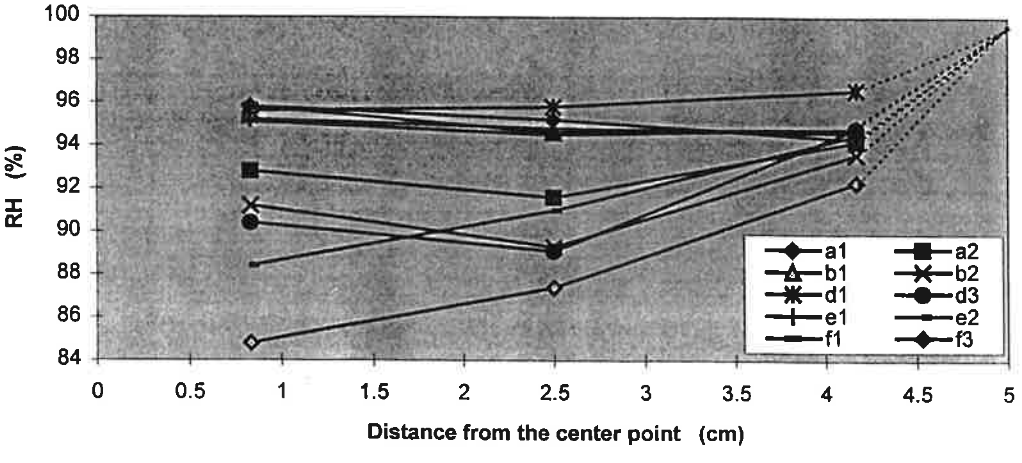


Fig 8 Distribution of RH of HPC cured in 3 % NaCl for 2 years (mix proportions a1~f3, see Table 1)

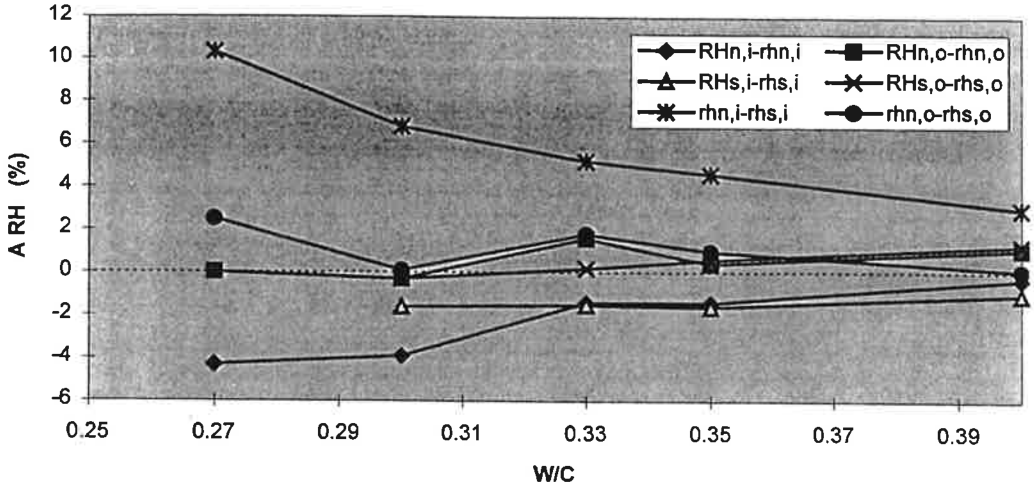


Fig 9 Difference of RH between concretes cured in water and in 3 % NaCl solution (RH—stored in water, rh—stored in 3 % NaCl solution, s—with SF n—without SF and AEA, i—inner layer, o—outer layer)

Table 3 Results on S values of concretes

Curing conditions	Types	Positions	W/C ratios				
			0.27	0.30	0.33	0.35	0.40
Condition 1 (in water)	Without SF and AEA	Inner layer	64.2	63.8	81.4	69.4	66.7
		Middle layer	70.6	70.7	78.9	72.6	70.3
		Outer layer	86.1	74.1	79.2	80.3	80.4
	With SF	Inner layer	58.8	58.7	68.3	59.2	
		Middle layer	70.9	64.9	70.0	59.2	
		Outer layer	81.8	73.4	76.4	74.4	
	With AEA	Inner layer	57.1	63.5	62.0	60.8	62.4
		Middle layer	63.4	69.7	74.3	63.1	64.8
		Outer layer	70.9	77.0	80.2	79.0	67.0
Condition 2 (in 3%NaCl)	Without SF and AEA	Inner layer	72.6	70.5	82.4	71.8	74.3
		Middle layer	76.7	77.3	83.6	73.7	73.0
		Outer layer	78.8	85.1	94.3	84.5	81.2
	With SF	Inner layer	72.5	69.1	77.6	65.5	70.6
		Middle layer	75.6	71.2	76.3	72.1	71.8
		Outer layer	85.0	82.6	83.8	83.1	85.7

The results therefore show that NaCl solution permeates into concrete, and the influence of salt on RH is much bigger than that expected. Moreover, the ingress of NaCl solution and the 3 drying-wetting cycles in the early age probably influence the hydration of clinker and the internal structure of concrete.

3.2 Degree of saturation of concrete (S)

In Table 3 is shown that S values of the outer layer are much higher than those of the inner layer for various concretes and curing conditions. The difference in S between the outer layer and the inner layer significantly increases in the presence of silica fume and AEA compared to concretes without these additions. This is similar to the RH determinations. These results clearly demonstrate that self-desiccation of HPC occurs.

The use of silica fume and AEA decrease the S values of concretes, and the effect of these additions on S of the inner layer is obviously larger than the effect on S of the outer layer. However, for concretes cured according to **condition 2,** the S values are larger than those of concretes cured in **condition 1,** which corresponds to other results[12]. It is interesting to note that W/C has little influence on the S values of the concrete.

3.3 Relationship between RH and S

Fig 10 clearly shows that for the same concrete stored in water, the RH values increase with the increase in the S values, somewhat like the relationships in Fig 1. The curves in Fig 10 become much flatter with the decrease in W/C and with the uses of AEA and SF. This is to be expected since different mixes have different sorption isotherms and different air contents.

4. DISCUSSION

4.1 Basic knowledge

4.1.1 Equilibrium vapor pressure

The pressure of the vapor of a liquid in equilibrium with the liquid is called the equilibrium vapor pressure of the liquid. The equilibrium vapor pressure is a characteristic property of a substance and is independent of the quantity of liquid present, i.e. it depends on the intermolecular forces in the liquid and on temperature, but does not depend on the volume of the vapor or the volume and surface area of the liquid[13].

4.1.2 Relative humidity

The concentration of water vapor in air is usually expressed in terms of relative humidity. The relative humidity (RH) is defined:

$$RH = \frac{Pv}{Pev} \quad \cdots\cdots\cdots\cdots \quad (2)$$

Pv the partial pressure of water vapor in the air
Pev the equilibrium vapor pressure of water at same temperature

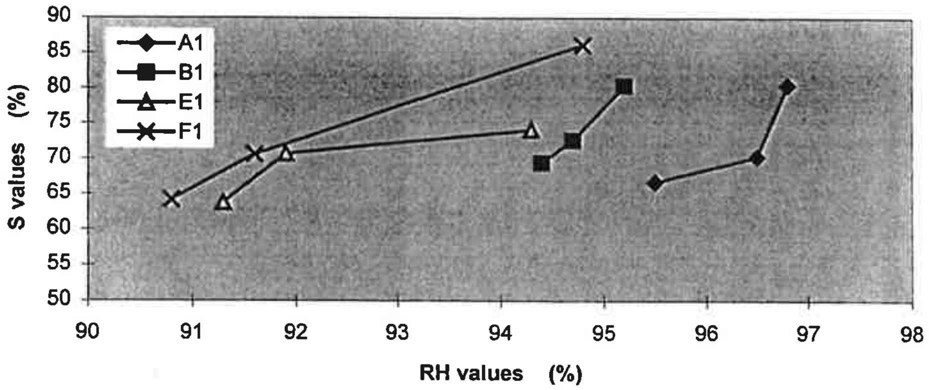
Because the equilibrium vapor pressure of water increases as temperature increases, the relative humidity of a sample of air decreases as temperature increases[14].

4.1.3 Degree of saturation

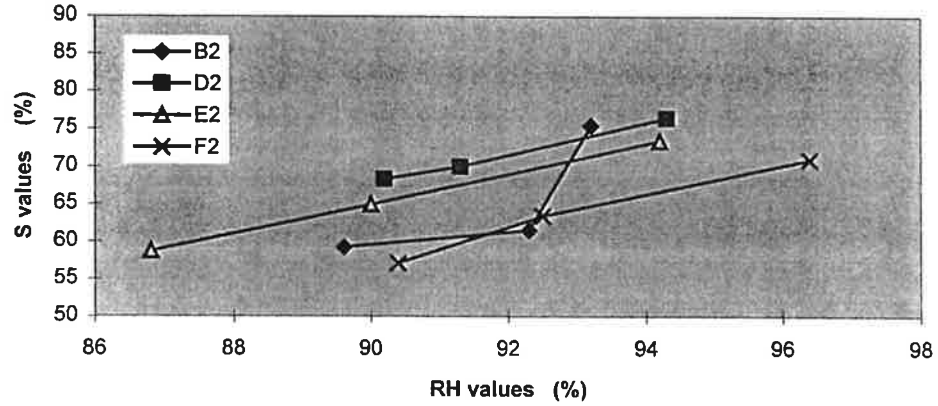
According to Fagerlund, the degree of saturation of concrete can be defined[15]:

$$S = \frac{Vw}{Vp} \quad \cdots\cdots\cdots\cdots \quad (3)$$

(a)Without SF and AEA



(b)With SF



(c)With AEA

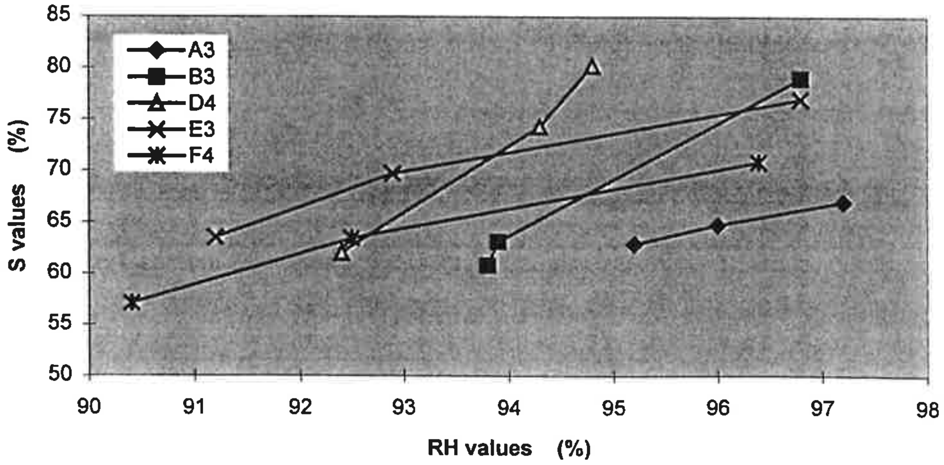


Fig 10 Relationship between RH and S of concretes stored in water for 2 years (mix proportions A1~F4, see Table 1)

where *Vw* is the total water volume evaporable at +105°C and *Vp* is the total open pore volume. It is very important that in *Vp* are included all pores in the concrete, thus also the entrained air pores, the compaction pores and the aggregate pores. S only depends on the quantity of water present, and is independent of various ions dissolved in the water and is also independent on whether water is in the free or in the adsorbed state, just in contradiction to RH. It must be noted, however, that the specific volume of the water depends on the presence of dissolved ions and to some extent on the location of the water.

4.2 Discussion

4.2.1 Relative humidity (RH)

Firstly, is the amount of water in the specimen big enough to give a correct RH value? The net air volume of the glass tube is about 50 ml. The RH of the air in the tube is about 62.2 % when the specimen is placed in it. The temperature is about 18.2 °C. Thus the amount of water needed to increase RH from 62.2 % to 100 % is :

$$\Delta W=(1-0.622)\times 15\ (g/m^3)\times 50\times 10^{-6}(m^3)=2.8\times 10^{-4}\ g$$

(15 g/m^3 is the vapor content in air at 100 %RH and +18°C)

The minimun amount of water ΔQ in the specimen is 0.428 g (specimen E2-1, see Appendix 1). Thus only 0.065% of the water in the specimen needs to be evaporated. Therefore, the RH measurement ought to be correct provided that the calibration of the gauges is correct.

Secondly, can the ions solved in water explain the observed RH values in HPC? In order to evaluate and calculate the effect of soluble ions, it is neccessary to make some assumptions:

1. The molar number of all ions in concrete that are soluble into water is equal to that of 1 % Na_2O in cement weight.
2. All evaporable water β of various states (in pores with various sizes) has the same effect on RH and the soluble ions, $\beta=(Qo-Qd)\div Qd$.

Then, the concentration of the ions in the pore solution of the concrete can be calculated and expressed as the molar concentration of NaOH, shown in Appendix 1. The following calculations are made based on one litre of concrete:

1. The molar number of all soluble ions (mole):

   $$N=2\times 0.01C\div 62\ (\text{atomic mass of } Na_2O)=3.23\times 10^{-4}C \quad \cdots\cdots\cdots\cdots\ (4)$$

2. The amount of evaporable water in the specimen (g):

   $$We=\beta\times d\times 10^3=((Qo-Qd)\div Qd)\times d\times 10^{34}C \quad \cdots\cdots\cdots\cdots\ (5)$$

3. The molar concentration of the soluble ions in the concrete (M):

   $$M=N\div(We\times 10^{-3})$$
   $$=3.23\times 10^{-4}C\div((Qo-Qd)\div Qd)\times d)\quad (\text{d is the density of concrete})\ \cdots\cdots\ (6)$$

According to Raoult's law, the vapor pressure of a volatile component in an ideal solution is equal to the product of the mole fraction of the component in the solution and the vapor pressure of the pure component at the same temperature[16]. The calculated increase in the molar concentration of ions in the solution can explain part or all of the measured decrease of the RH values. Generally, a solution with the molar concentration of below 1 M is assumed to an ideal solution. Appendix 1 shows that the molar concentrations in the concretes are larger than 1 M, so the measured decrease of RH values is somewhat larger than that calculated with Raoult's law.

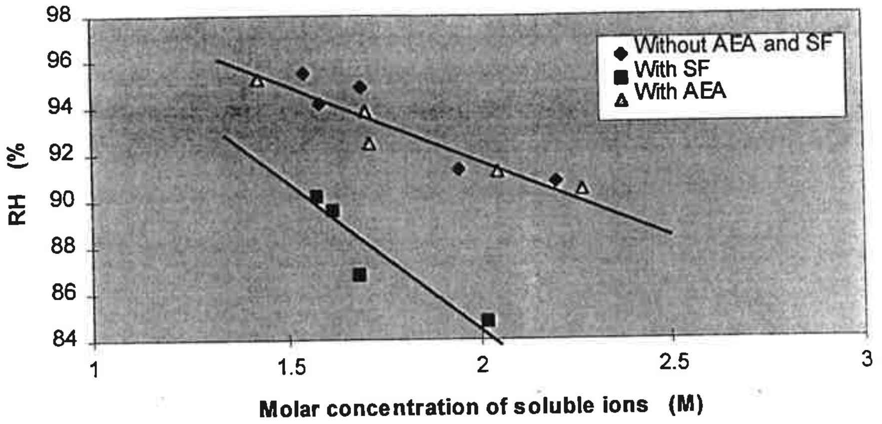


Fig 11 Relationship between RH and the molar concentration of solution of the inner layer in concrete stored in water for 2 years

Because the curing condition of concrete has big influence on the water content and thus on the ion concentration in the outer layer of concrete, the calculated molar concentration is different from the actual value. For example, for the concrete cured in water, it is sure that the molar concentration of the outer layer decreases very much due to the leaching-out of the ions and the ingress of extra water, especially for low W/C. Finally, at the surface, the concentration reaches an equilibrium with the molar concentration of the curing water.

For the concretes stored in water for 2 years, the relationship between the RH values of the inner layer and the calculated molar concentration of solution is shown in Fig 11. There is a good relation between the molar concentration of the solution and the RH values. The RH values decreases with the increase in the molar concentration of the solution. This indicates that a certain part of the reduction of the internal RH in HPC can depend on the effect of the molar concentration in pore solution on the vapor pressure. It is evident that the self-desiccation of HPC causes an increase in the molar concentration of ions in the pore solution. The regression curves are as follows:

Concretes without AEA or with A: $RH=105.8-7.14M$ ($n=5, \gamma=0.96$) …………… (7)
Concretes with 5 or 10 % SF $RH=107.8-11.5M$ ($n=4, \gamma=0.92$) …………… (8)

where n is the number of samples and γ is the regression coefficient.

Fig 11 also shows that the use of AEA has little influence on the relationship between RH and the molar concentration of solution, which is reasonable since AEA has little effect on the amount of soluble ions. This is also one reason that the effect of AEA on RH values is negligible. However, for the same molar concentration, the RH values of the concretes with silica fume are much lower than those of the concretes without silica fume even though silica fume also has little effect on the soluble ions. This may be related to changes in pore structure changing te desorption isotherm.

The evaporable water includes interlayer water, absorbed water, gel water, capillary water and air bubble water. In the calculation above, it is assumed that all evaporable water could be used as solvent. It may be that the water in gel pores, the adsorbed water by hydrate gel particles, and the interlayer or zeolitic water can not be used as solvent. Therefore, the adjusted molar concentration can be calculated by the sum of evaporable water minus the interlayer water, the absorbed water and some gel water.

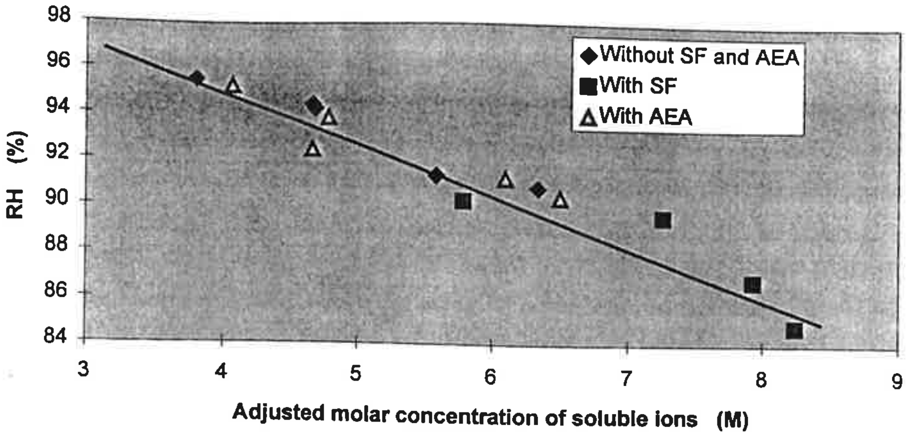


Fig 12 Relationship between RH values and the adjusted molar concentration of ions of the inner layer in concrete stored in water for 2 years

After measuring the degree of saturation the specimen is kept in a vaccum of 20 mm Hg for 6 hours and then stored 16 hours without opening the air vent valve after closed the vaccum pump, and another 2 hours at the atmosphere. If the residual water β_r in the specimen is defined as the amount of water that can not be used as solvent, the adjusted molar concentration can be calculated as follows:

$$M_{adj}=M\div(1-(\beta_r\div\beta)) \quad \text{.........................} \quad (9)$$

In Appendix 1 it is seen that the β_r/β values of different layers in the same specimen is similar and the effect of W/C on the β_r/β value is small. The use of silica fume obviously increases the β_v/β value, which indicates an increase in the amount of interlayer water, absorbed water and gel water. Fig 12 shows that the relation between the RH values and the adjusted molar concentraion is very good for all mix proportions of concretes stored in water. The regression curve is:

$$RH=104.2-2.25\ M_{adj} \qquad (n=14, \gamma=0.93) \quad \text{..................} \quad (10)$$

4.2.2 Degree of saturation S

According to section 4.1.3, the degree of saturation only depends on the quantity of the evaporable water in concrete, so the change of the fractions of the interlayer water, absorbed water and gel water in all vaporable water have no influence on S. Certainly, the entrained air pores have great influence on S, and therefore an increase in the air content reduces the degree of saturation of concrete.

From the analysis in the section 4.2.1, it is seen that the RH values are largely affected by the concentration of solube ions and the frations of interlayer water, absorbed water and gel water. Futhermore, the measuring conditions, such as temperature and quality of the RH sensor etc. have big influence on the precision of RH value, especially for RH values higher than 98%. On the contrary, all the factors have no influence on the precision of the S values. Therefore, the degree of saturation in concrete is a better tool for evaluating the content of the evaporable water than RH and therefore is also a better tool for describing self desiccation.

4.2.3 Salt

According to Raoult's law RH of a solution is reduced compared to pure water. Therefore, salt such as NaCl contained in the pore system of a concrete increases the hygroscopicity. This means that the equilibrium moisture content at a certain RH is higher in a concrete containing salt. This is confirmed in the present investigation where it was found that RH was higher in concretes stored in 3 % NaCl solution (**condition 2**).

5. CONCLUSIONS

For HPC stored in water for 2 years, the RH and S values of the inner layer in HPC are much lower than those of the outer layer, which clearly confirms that the self desiccation in the interior occurs and that a certain inflow of water occurs at the surface.

The difference of the RH and S values between the outer layer and the inner layer increases with the decrease of W/C and with the increase in the amount of silica fume. This depends on a reduction of the permeability of the concrete. However, the difference of the RH values in the outer layer among concretes with various mix proportions is very small, which shows that the ingress of extra water at the surface diminishes these differences. Futhermore, the RH values of concrete cured in water are much higher than those of concrete with sealed curing.

The RH values significantly decrease with the increase of silica fume and the decrease of W/C, but the use of AEA has little influence on RH values. However, the S values are obviously reduced by the use of AEA, which is reasonable since air pores do not contain water.

S values of concrete with salt are much larger than those without salt, the effect of salt on RH values is however very complex.

The relation between the measured RH values and the calculated molar concentration of soluble ions in concrete is very good. The regression equations are as follows providing all evaporable water can be used as solvent:

Concretes without AEA or with AEA	$RH=105.8-7.14M$	$(n=10, \gamma=0.95)$
Concretes with 5 or 10 % SF	$RH=107.8-11.54M$	$(n=4, \gamma=0.92)$

If only capillary water is assumed to be used as solvent, i.e. no interlayer water, absorbed water and gel water, the calculated molar concentration can be adjusted. For all concretes stored in water, the relationship between the measured RH values and the calculated adjusted molar concentration is good. The regression equation is as follows:

$$RH=104.2-2.25\ M_{adj} \qquad (n=14, \gamma=0.93)$$

A certain part of the reduction of the internal RH in HPC probably depends on the increase in the molar concentration of the pore solution. The fine pore structure in HPC is probably the reason in the reduction of RH values.

The RH values of self-desiccation are not related to the S values. The degree of saturation S is a better tool for evaluating the content of evaporable water in concrete than the relative humidity and therefore is also a better tool for describing self-desiccation.

ACKNOWLEDGEMENTS

The research work presented in this paper is carried out under the suggestion and supervision of Professor Göran Fagerlund. I am highly indebted to Professor Göran Fagerlund not only for his kind support and invaluable guidance, but also for his correcting the original manuscript patiently .

During the whole period of the work, many colleagues at the Division have given me their help, which is greatly appreciated. Special thanks are directed to Dr. Göran Hedenblad and Mr. Bertil Persson for their introducing the technology of measuring RH and knowledges on the self-desiccation of concrete, to Mr. Bo Johansson and Mrs Katja Nordström for their help and cooperation during making specimens, to Mr. Tomas Ekström for his help in preparing the figures.

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Appendix 1 All results of this study

Type	RH (%)	RHc(%)	M(M)	ΔQ (g)	β (%)	β_r (%)	β_r/β (%)	S (%)
A1-1	95.5	97.1	1.55	0.922	3.90	2.31	59.2	66.7
A1-2	96.5	97.2	1.50	1.542	4.04			70.3
A1-3	96.8	97.8	1.19	1.783	5.08	2.94	57.9	80.4
A3-1	95.2	97.3	1.43	1.167	3.95	2.36	59.8	62.9
A3-2	96.0	97.5	1.37	1.434	4.12	2.53	61.4	64.8
A3-3	97.2	97.7	1.22	1.366	4.62	2.66	57.6	67.0
a1-1	95.8	97.4	1.40	1.088	4.33	2.35	54.3	74.3
a1-2	95.2	97.3	1.37	1.685	4.41	2.39	49.6	73.0
a1-3	94.3	98.3	0.93	1.846	6.48	3.45	53.2	81.2
a2-1	92.8	98.0	1.07	1.401	5.16	4.0	77.5	70.6
a2-2	91.6	98.0	1.08	1.878	5.11	4.02	78.1	71.8
a2-3	94.2	98.6	0.75	2.145	7.38	5.38	72.9	85.7
B1-1	94.4	96.8	1.70	1.270	3.81	2.42	63.5	69.4
B1-2	94.7	96.9	1.67	1.105	3.89	2.59	66.6	72.6
B1-3	95.2	97.6	1.28	1.527	5.06	3.15	62.3	80.3
B2-1	89.6	97.0	1.62	0.918	3.61	2.80	77.6	59.2
B2-2	92.3	97.0	1.59	1.475	3.67	2.94	80.1	59.2
B2-3	93.2	97.8	1.21	1.793	4.81	3.53	73.4	75.4
B3-1	93.8	96.8	1.71	0.610	3.86	3.12	64.2	60.8
B3-2	93.9	96.9	1.67	1.288	3.96	2.53	63.9	63.1
B3-3	96.8	97.5	1.36	1.398	4.84	3.18	65.7	79.0
b1-1	95.8	96.6	1.83	0.721	3.54	1.96	55.4	71.8
b1-2	94.6	97.3	1.36	1.404	4.76	2.30	54.0	73.7
b1-3	94.8	97.8	1.16	1.740	5.61	3.26	58.1	84.5
b2-1	91.2	97.0	1.59	0.817	3.67	2.70	73.6	65.5
b2-2	89.3	97.3	1.38	1.451	4.24	3.29	77.6	72.1
b2-3	93.6	98.0	1.11	1.683	5.26	3.80	72.2	83.1
D1-1	94.2	97.0	1.59	0.725	4.03	2.66	66.0	81.4
D1-2	93.9	96.9	1.65	1.216	3.87			78.9
D1-3	95.0	97.0	1.61	1.365	3.97	2.38	60.0	79.2
D2-1	90.2	97.0	1.58	1.079	3.84	2.79	72.7	68.3
D2-2	91.3	96.5	1.86	1.268	3.26	2.40	73.6	70.0
D2-3	94.3	97.4	1.40	1.493	4.34	2.99	68.9	76.4
D4-1	92.4	96.8	1.72	1.012	3.82	2.41	63.1	62.0
D4-2	94.3	96.7	1.77	1.402	3.71	2.44	65.8	74.3
D4-3	94.8	97.8	1.18	1.718	5.54	3.32	59.9	80.2
d1-1	95.6	97.3	1.42	1.098	4.50	2.51	55.8	82.4
d1-2	95.8	97.0	1.61	1.560	3.98	2.14	53.8	83.6
d1-3	96.6	97.8	1.18	1.620	5.44	2.88	52.9	94.3
d3-1	90.4	97.3	1.44	0.946	4.01	3.16	78.8	77.6
d3-2	89.1	97.3	1.39	1.578	4.16	3.23	77.6	76.3
d3-3	94.8	98.1	1.02	1.952	5.67	4.19	73.9	83.8

continued

continue Table 3

Type	RH(%)	RHc(%)	M(M)	ΔQ (g)	β (%)	β_r (%)	β_r/β (%)	S (%)
E1-1	91.3	96.3	1.95	0.706	3.35	2.18	65.1	63.8
E1-2	91.9	95.6	2.34	0.862	2.78	1.80	64.7	70.7
E1-3	94.3	97.0	1.63	1.107	4.01	2.50	62.3	74.1
E2-1	86.8	96.9	1.69	0.428	3.52	2.77	78.7	58.7
E2-2	90.0	96.5	1.87	0.998	3.18	2.43	76.4	64.9
E2-3	94.2	97.1	1.55	1.150	3.83	2.81	73.4	73.4
E3-1	91.2	96.1	2.05	0.828	3.24	2.15	66.4	63.5
E3-2	92.9	95.2	2.51	1.048	2.65	1.73	65.3	69.7
E3-3	96.8	97.0	1.60	1.445	4.16	2.41	57.9	77.0
e1-1	95.2	96.5	1.87	0.683	3.48	1.87	53.7	70.5
e1-2	94.8	97.2	1.52	1.328	4.30			77.3
e1-3	94.6	97.6	1.25	1.428	5.20	2.90	55.8	85.1
e2-1	88.4	96.2	1.99	0.752	2.99	2.27	75.9	69.1
e2-2	91.0	96.5	1.86	1.276	3.20	2.37	73.8	71.2
e2-3	94.5	97.3	1.43	1.525	4.17	2.96	71.0	82.6
F1-1	90.8	95.8	2.20	0.668	3.26	2.13	65.3	64.2
F1-2	91.6	96.2	1.97	1.391	3.64			70.6
F1-3	94.8	96.7	1.75	1.549	4.10	2.57	62.7	86.1
F2-1	84.8	96.1	2.02	0.716	3.43	2.59	75.5	58.8
F2-2	91.2	96.6	1.81	1.380	3.83	2.82	73.4	70.9
F2-3	93.3	96.8	1.69	1.398	4.10	2.96	72.2	81.8
F4-1	90.4	95.6	2.27	0.923	2.92	1.90	65.1	57.1
F4-2	92.5	95.9	2.16	1.012	3.07	2.18	71.0	63.4
F4-3	96.4	96.8	1.73	1.505	3.83	2.51	65.5	70.9
f 1-1	95.1	95.6	2.27	0.945	3.16	2.02	63.9	72.6
f 1-2	94.5	96.5	1.88	1.140	3.82			76.7
f 1-3	94.8	97.3	1.44	1.473	4.97	3.22	64.8	78.8
f 3-1	84.8	97.0	1.63	0.877	4.00	3.34	83.5	72.5
f 3-2	87.6	96.9	1.70	1.327	3.84	3.08	80.2	75.6
f 3-3	92.3	97.7	1.23	1.643	5.28	3.80	78.1	85.0

↑↑ ↑
| |These numbers represent the different positions from the center, see Fig 2
See Table 2.

RH	the measured relative humidity
RHc	the calculated RH values according to Raoult's law
M	the molar concentration of the solution (see eq. (6))
ΔQ	the weight of evaporable water in concrete (ΔQ=Qo-Qd)
β	the moisture content in concrete (β=ΔQ÷Qo)
β_r	the moisture content in concrete after minus interlayer water, absorbed water and gel water
S	the degree of saturation