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Inner relative humidity and degree of saturation in high-performance concrete stored in water or salt solution for 2 years

Quanbing Yang*

Division of Building Materials, Lund Institute of Technology, Lund, Sweden

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Abstract

The inner relative humidity (RH) and degree of saturation (S) of high-performance concrete cured for 2 years in water or 3% NaCl solution were measured at three different levels from the concrete surface (outer layer 0 to 16 mm, middle layer 16 to 32 mm, and inner layer 32 to 50 mm). The effects of many factors, such as water-to-cement (w/c) ratio, content of silica fume, and air content, were investigated. Results show that 1) inner RH values of high-performance concrete decrease with decrease in w/c ratio and with increase in silica fume content; 2) RH and S values of the outer layer of concrete are higher than those of the inner layer, and the difference increases with decrease in w/c ratio and with increase in the silica fume content; 3) air content has little influence on RH of the inner layer, but, as expected, because air pores do not 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 are higher than for concrete cured in water, and the S values of the three layers of concrete are markedly higher than for concrete cured in water; and 5) theoretical calculations indicate that the increase in molar concentration of soluble ions in concrete and the fractions of interlayer water, absorbed water, and gel water in the evaporable water could be the main factor behind the decrease of RH values or so-called self-desiccation of concrete with low w/c ratio and concrete with silica fume cured in water.

Keywords: Humidity; High-performance concrete; Self-desiccation; Curing; Silica fume

Self-desiccation has attracted little interest in previous concrete research because its effects are negligible in normal concrete with ordinary or high water-to-cement (w/c) ratio. However, with the development of superplasticizer technology and because of growing interest in high-performance concrete (HPC), the situation has been changed in recent years. The internal relative humidity (RH) level of HPC can be reduced dramatically when the 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 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 often is very big because of the finer pore structure that leads to a flatter sorption isotherm [6]. The lower the w/c ratio 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 sometimes, for HPC, it 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 concrete stored in water the chemical shrinkage leads to an ingress of extra water. The maximum amount of water sucked into the concrete corresponds exactly 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 the 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 con-

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* Quanbing Yang's present address, College of Materials Science and Engineering, Tongji University, 100 Wu Dong Road, Shanghai 200433, People's Republic of China.

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crete. However, measurements have shown that the inner part of HPC can be self-desiccated 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 ratio within the range 0.27 to 0.40 stored in pure water or 3% NaCl solution for about 2 years. The effects of silica fume and air-entraining agents (AEAs) also are studied. Self-desiccation is measured as a reduction in RH and degree of saturation.

1. Experimental

1.1. Raw materials

Portland cement with 0.6% Na_2O and 2% C_3A is used. The aggregate consists of crushed quartz sandstone 8 to 16 mm together with natural gravel 0 to 8 mm. In some concretes, silica fume was used. Silica fume is mainly an amorphous silica with a fineness of 17.5 m^2/g. The naphthalene sulphonate superplasticizer (V33) and vinsol resin AEA (Cementa 88L) are used. The mix proportions and some properties of concrete are listed in Table 1.

The concrete were made in connection with another study at the Division of Building Materials at Lund Institute of Technology and had been stored in water or 3% NaCl solution for about 2 years.

1.2. Curing conditions

Cylinder specimens (diameter 100 mm, length 250 mm) were cast and membrane cured for 1 day, and then stored for about 2 years under the following conditions:

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

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

The present research is part of other works on the frost resistance of HPC, investigating the effects of these treatments on frost resistance and self-dessication of HPC.

1.3. Experimental methods

1.3.1. Cutting specimens

A 10-mm thick slice is sawn from the cylinder with the wet saw as shown in Fig. 1a. A 7-cm cylinder will be used for salt-frost test in fields. The slice is surface dried immediately after sawing. The slice is quickly cut into 24 pieces using special equipment (Fig. 2). The pieces are taken from three layers (eight pieces in every layer) as shown in Fig. 1b. The pieces in the same layer are crushed with a hammer into many smaller pieces less than 10 mm. Then the smaller pieces are placed in a glass tube (volume about 50 mL), which is sealed with a tight rubber plug and weighed (Q_o). Layers 1, 2, and 3 are the inner layer 32 to 50 mm, middle layer 16 to 32 mm, and outer layer 0 to 16 mm, 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.

Table 1
Mix proportions and properties of concrete

Type	w/c	Cement + SF (kg/m^3)	Gravel 0/8 mm (kg/m^3)	Quartzite 8/12 mm (kg/m^3)	Quartzite 2/16 mm (kg/m^3)	SP (dry weight) (kg/m^3)	AEA (kg/m^3)	Fresh air content (%)	Density (d) (kg/m^3)	Strength at 28 days (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

AEA, air-entraining agent; SF, silica fume; SP, superplasticizer.

Capital letters (A1–F4), stored in water; lower case letters (a1–f3), stored in 3% NaCl.

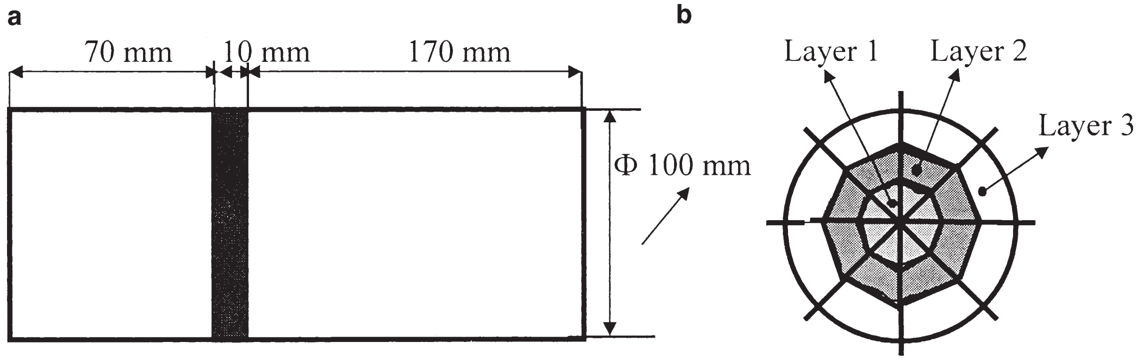

Fig. 1. Method of cutting a specimen into pieces. (a) Sawing a slice from the cylinder. (b) Cutting the slice into pieces.

1.3.2. Measuring RH [9]

For HPC, the pieces used for measurement of RH must be as small as possible to reach the equilibrium of moisture easily. The measurement is carried out in the room where there is a constant temperature of 18.2 ± 0.2°C and RH of 62.2% ± 0.2%. All tubes with specimen are put in the room at least for 4 days before the measurement. All RH sensors are calibrated according to ASTM E 104-85 before measurement. In the test, dew point meters of type Protimeter are used. The RH sensor is inserted in the tube and sealed by a rubber plug, so that the concrete pieces are protected from the outside air. The sensor is kept in the tube for at last 22 h to get the exact result, even though the equilibrium was found to be reached after about 16 h. All the RH sensors are placed in the room at least 4 h before the start of the next measurement, to decrease the eventual error caused by the moisture hysteresis of the sensors.

There are some systematic and random errors that may occur in during calibration and measurement of RH, such as temperature difference, drift in the RH meter, and calibration error. To reduce the uncertainty, RH measurement is repeated at least four times. The total uncertainty is about $\Delta RH = \pm 0.5\%$ RH after considering many errors [10].

1.3.3. Measuring the degree of saturation

After measurement of RH, all tubes with specimens are dried at 105°C for 2 days and weighed (Q_d), and then water is poured into the tubes. These tubes are stored for 5 days in vacuum of about 20 mmHg and another 5 days at atmosphere, and then weighed (Q_s). The weight Q_s is nearly constant and is equal to that measured by the common method [11] after 2 days. It is assumed that the vacuum procedure is sufficient to completely saturate all pores in the concretes. The measurement precision of the balance is 0.001 g. The degree of saturation of concrete is calculated by Eq. (1):

$$S = (Q_o - Q_d)/(Q_s - Q_d) \quad (1)$$

where S is the the degree of saturation of the specimen, Q_s is the weight of the tube with the specimen saturated with water, Q_d is the weight of the tube with the specimen dried at

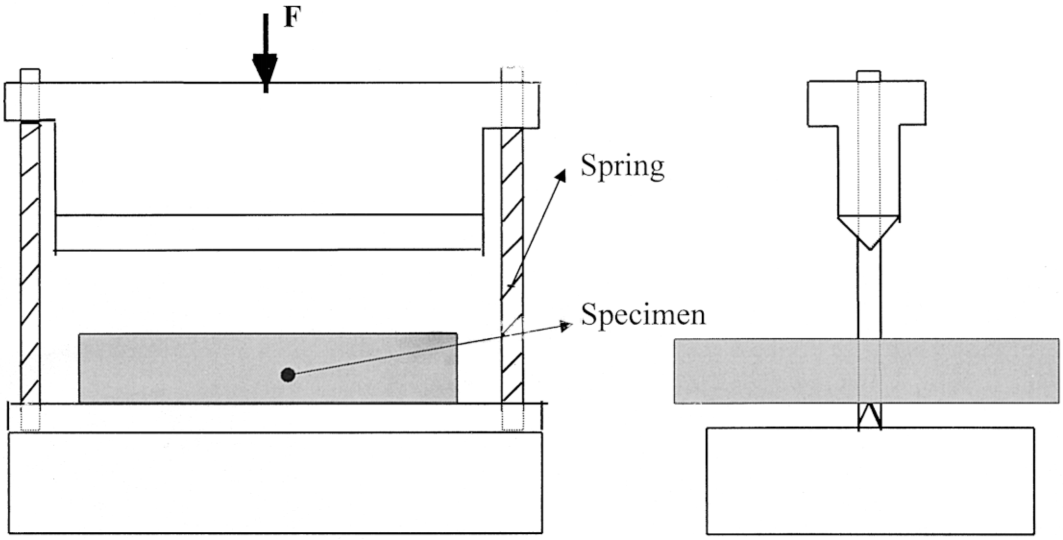

Fig. 2. Set-up of the cutting equipment.

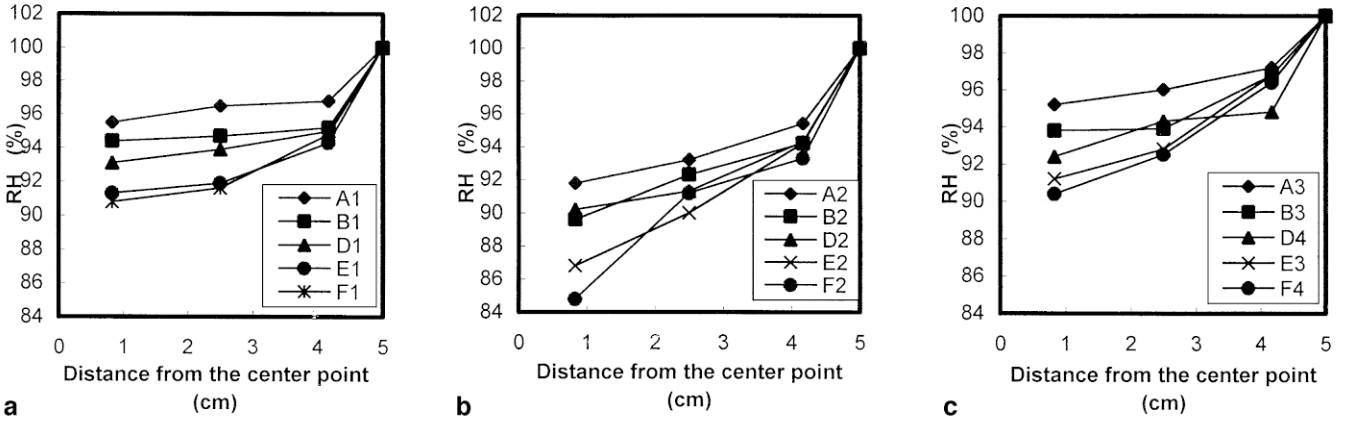

Fig. 3. Distribution of RH of HPC stored in water for 2 years (mix proportions A1–F4 , see Table 1). (a) Distribution of RH in concretes with various w/c ratios. (b) Distribution of RH in concretes with silica fume. (c) Distribution of RH in concretes with AEA.

105°C for 2 days, and Q_o is the actual weight of the tube with the specimen.

2. Results

2.1. RH of HPC over the cross-section

2.1.1. Distribution of moisture

For HPC with sealed curing, the inner distribution of moisture is even due to no ingress of extra water. During this condition, RH has been found to decrease significantly with the decrease of w/c ratio [1,5].

However, the present study shows that, for HPC stored in water for a long time, the internal distribution of moisture is uneven because extra water gradually permeates into concrete from the surface. The reason is the very low permeability of HPC. Fig. 3 clearly shows that RH of concrete decreases from outside to 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.

2.1.2. Effect of w/c ratio

It has been found that 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]. Water for 2 years decreases with the decrease of w/c ratio, but the effect of w/c ratio on RH values of the outer layer of concrete is negligible (Fig. 4). It is also seen that the RH values of the inner layer of concrete are much higher than those of concrete in the sealed curing. The values for sealed curing are taken from another study where the same types of cement and silica fume were used [5].

2.1.3. Effect of 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 produces extra C-S-H. Therefore, the the cap-

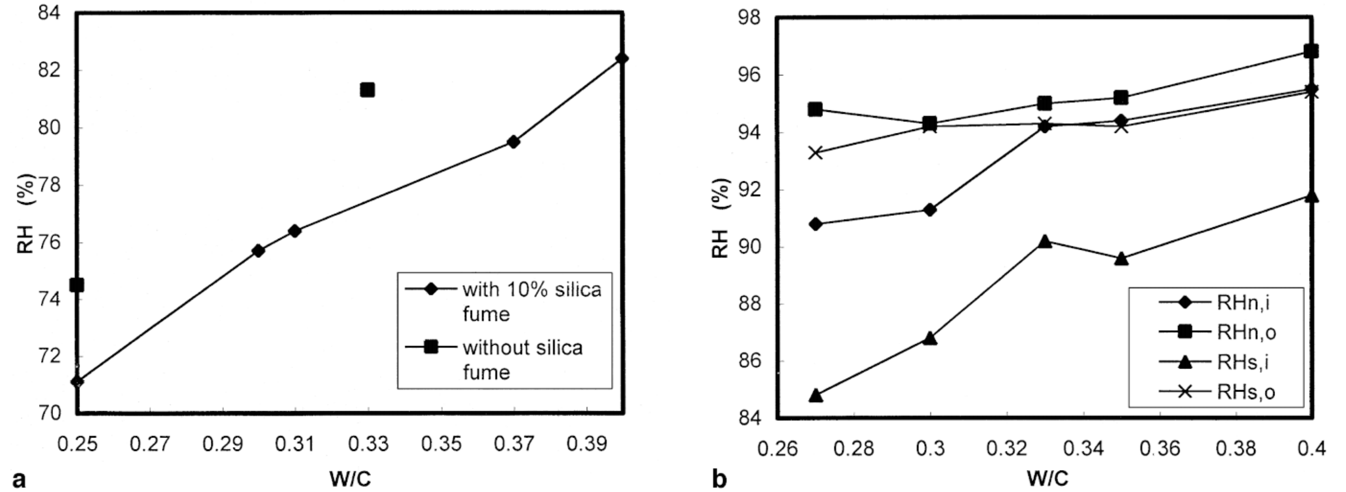

Fig. 4. Effect of w/c ratio on RH of HPC cured in sealed condition or stored in water for 2 years. (a) Sealed curing [5]. (b) Stored in water. i, inner layer; n, without SF and AEA; o, outer layer; s, with SF.

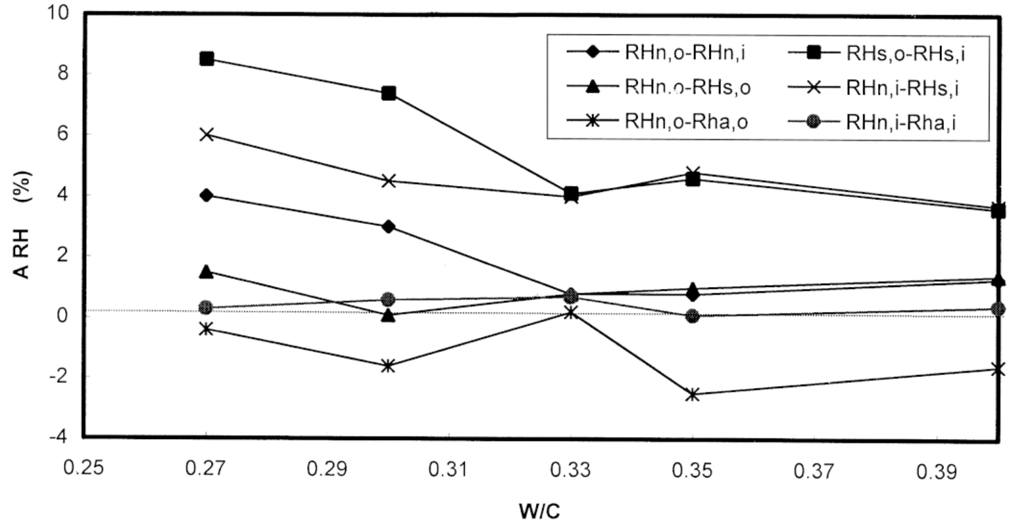

Fig. 5. Effect of silica fume and AEA on RH of HPC cured in water for 2 year. i, inner layer; n, without SF and AEA; o, outer layer; s, with SF. [ARH (%) in Y-axis actually ΔRH.]

illary pores becomes much smaller and the permeability of the concrete decreases significantly [12].

For concrete with silica fume, the difference in RH between the outer and inner layers is much larger than that without silica fume (Figs. 3 and 5). 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 ratio, which means that silica fume has a big influence on the reduction of RH in the inner layer. However, the effect of silica fume on RH in the outer layer is very small. 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 the RH value high and, therefore, diminishes the effect of self-desiccation.

2.1.4. Effect of air content

The effect of AEA on RH values is negligible for all concretes and for all locations, as shown in Fig. 5.

2.1.5. 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 three drying-wetting cycles. Figure 6 shows that the internal RH of some concretes without silica fume is gradually reduced from inside to outside, which is contrary to the results shown in Fig. 3. However, the difference in RH between the inside and the outside is rather small. For concretes with silica fume, the distribution of RH is very different from that without silica fume (Fig. 6). The difference in RH between concrete without silica fume and concrete with silica fume (Fig. 7) is similar to the results for concretes stored in pure water (Fig. 5).

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 slightly lower than those of concretes cured according to condition 1 (Fig. 7).

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

2.2. Degree of saturation of concrete

The degree of saturation (S) is also an important parameter to express the moisture in concrete, especially for evaluating the frost resistance of HPC. In fact, the self-desiccation can create an extra air space [3] and, therefore, reduce the degree of saturation. S values of the inner layer are

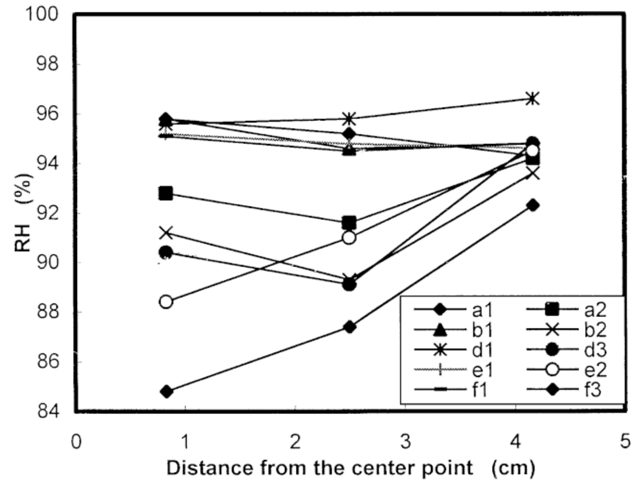

Fig. 6. Distribution of RH of HPC cured in 3% NaCl for 2 years (proportions a1–f3, see Table 1).

much lower than those of the outer layer for various concretes and curing conditions (Table 2). The difference in S values between the outer and inner layers obviously increases in the presence of silica fume and AEA compared to concrete without these additions. This is similar to the RH determinations. These results clearly demonstrate that self-desiccation of HPC still occurs even after storage in water for 2 years.

The use of silica fume and AEA decreases 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. It is interesting to note that w/c ratio has little influence on the S values of the concrete. However, for concretes cured according to condition 2, the S values are much larger than those of concretes cured in condition 1, even though RH values in the outer layer cured in condition 2 are somewhat lower than those cured in condition 1. Consequently, it is necessary to add AEA for HPC subjected to frost and salt, otherwise the HPC is not automatically frost resistant, which was proved by Petersson [13].

3. Discussion

3.1. Relative humidity

First, is the amount of water in the specimens large 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 calculated as shown in Eq. (2):

$$\Delta W = (1 - 0.622) \times 15(g/m^3) \times 50 \times 10^{-6}(m^3) = 2.8 \times 10^{-4}\ g \quad (2)$$

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

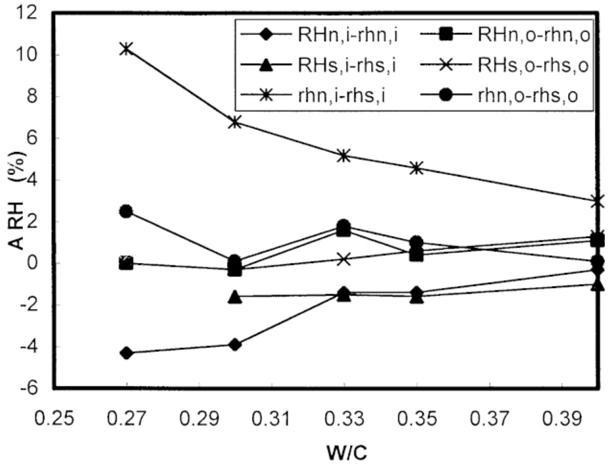

Fig. 7. Difference of RH between concretes cured in water and in 3% NaCl solution. rh, stored in 3% NaCl; RH, stored in water. [ARH (%) in Y-axis actually ΔRH.]

The minimum amount of water in the specimen is 0.428 g. Thus, only 0.065% of the water in the specimen needs to be evaporated. Therefore, the RH measurement should be correct provided the calibration of the gauges is correct. It also shows that there is enough water to keep 100% RH in the specimens if the water is pure water and can be evaporated freely.

Second, can the ions solved in water explained the observed RH values in HPC? To evaluate and calculate the effect of soluble ions, it is necessary to make some assumptions:

1. The molar number of all ions in concrete that are soluble into water, such as Na^+, K^+, Ca^{2+} OH^-, SO_4^{2-}, etc., is equal to that of 1% Na_2O in cement weight (in fact, the cement used here contains about 0.6% Na_2O).
2. All evaporable water β of various states (in pores with various sizes) has the same effect on RH and the soluble ions [Eq. (3)]:

$$\beta = (Q_o - Q_d) \div (Q_d - Q_t) \quad (3)$$

where Q_t is the weight of the tube without the specimen.

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

1. The molar number of all soluble ions or solutes (mole) [Eq. (4)]:

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

2. The amount of evaporable water in the specimen (g) [Eq. (5)]:

$$We = \beta \times d \times 10^3 = [(Q_o - Q_d) \div (Q_d - Q_t)] \times d \times 10^3 \quad (5)$$

Table 2
Results on S values of concretes

Curing condition	Type	Position	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

where d is the density of moist concrete

3. The molar concentration of the soluble ions in the concrete (M) [Eq. (6)]:

$$M = N \div (W_e \times 10^3) = 3.23 \times 10^{-4} C \div [(Q_o - Q_d) \div (Q_d - Q_t)] \times d \quad (6)$$

According to Raoult's law, the vapor pressure of a volatile component in an ideal solution is equal to a product of the mole fraction of the component in the solution and the vapor pressure of the pure component at the same temperature. 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.

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 the pore solution is shown in Fig. 8. The RH values decrease with the increase in molar concentration of the solution. This indicates that a certain part of the reduction of internal RH in HPC depends on the effect of the molar concentration in pore solution on the vapor pressure.

Fig. 8 also shows that the use of AEA has little influence on the relationship between RH and the molar concentration of solution. However, for the same molar concentration, 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 must be related to changes in structure of the hydrates and an increase in the amount of interlayer pore, gel pore, and fine pore.

The evaporable water includes the interlayer water, absorbed water, gel water, capillary water, and air bubble water. In the previous calculation, 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 zeolite water cannot 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.

After measuring the degree of saturation the specimen is kept in a vacuum of 20 mm Hg for 6 h and then stored 16 h without opening the air vent valve after the vacuum pump is closed, and another 2 h at the atmosphere. If it is considered that the effect of the amount of the residual water β_r in the specimen on RH is negligible and therefore β_r cannot be used as solvent, the adjusted molar concentration can be calculated as shown in Eq. (7):

$$M_{adj} = M \div [1 - (\beta_r \div \beta)] \quad (7)$$

Fig. 9 shows that the relation between RH values and adjusted molar concentration is very good for all mix proportions of concretes stored in water.

Based on M and M_{adj}, the calculated RH_c and the adjusted RH_{adj} values of specimens stored in water according to Rault's law are shown in Table 3. It can be seen that the RH_c values are much larger than the measured RH_m values, even though the increase in M values causes somewhat of a reduction of RH. However, the RH_{adj} values are near to the measured RH values, especially for the RH values in the inner layers. The measured RH_m values in the outer layers are always larger than the RH_{adj} values.

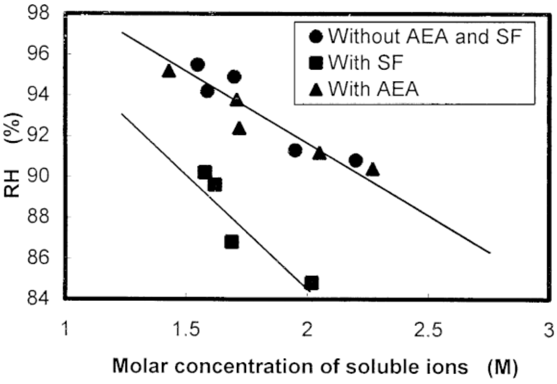

Fig. 8. Relationship between RH values and molar concentration of ions of the inner layer in concrete stored in water for 2 years.

From Table 3 and Figs. 8 and 9, it is easy to conclude that the increase in molar concentration of soluble ions in HPC is a main factor behind the reduction of RH and, therefore, is a main mechanism of self-dessiction. Meanwhile, the volume fraction (VF) of interlayer pore, gel pore, and fine pore in the sum volume of pores has a substantial influence on the increase in the molar concentration. Consequently, the amount of soluble ions and the VF values are key factors causing reduction of RH or self-desiccation in HPC, which, if true, easily explain the results.

First, due to the high content of cement and low w/c ratio, the amount of soluble ions and the VF values in HPC are much higher than those in ordinary concrete, so the reduction of RH or self-dessication is more obvious for HPC. Second, the addition of silica fume significantly enhances the VF value (this increase is much larger than that caused

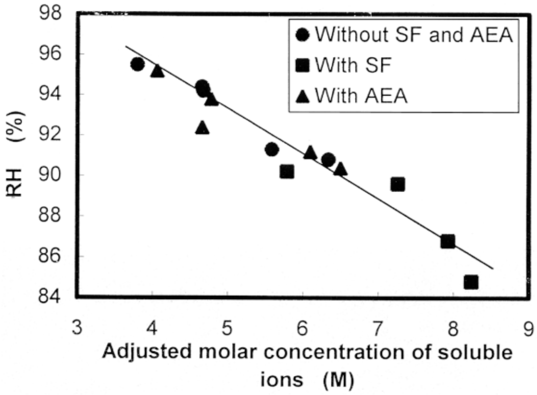

Fig. 9. Relationship between RH values and the adjusted molar concentration of ions of the inner layer in concrete stored in water for 2 years.

Table 3
Measured RH_m, calculated RH_c, and adjusted RH_{adj} values of specimens stored in water

	w/c Ratios														
	0.40			0.35			0.33			0.30			0.27		
No.	RH_m	RH_c	RH_{adj}	RH_m	RH_c	RH_{adj}	RH_m	RH_c	RH_{adj}	RH_m	RH_c	RH_{adj}	RH_m	RH_c	RH_{adj}
N-I	95.5	97.1	94.8	94.4	96.8	93.5	94.2	97.0	93.5	91.3	96.3	90.9	90.8	95.8	91.3
N-M	96.5	97.2	96.0	94.7	96.9	93.1	93.9	96.9		91.9	95.6	92.3	91.6	96.2	
N-O	97.8	96.0		95.2	97.6	94.3	95.0	97.0	94.4	94.3	97.0	93.6	94.8	96.7	93.5
S-I				89.6	97.0	90.2	90.2	97.0	90.4	86.8	96.2	88.2	84.8	96.1	86.8
S-M				92.3	97.1	89.3	91.3	96.5	92.0	90.0	96.5	90.2	91.2	96.6	90.7
S-O				93.2	97.8	92.1	93.7	97.0	94.2	94.2	97.1	92.0	93.3	96.8	91.6
A-I	95.2	97.3	95.0	93.8	96.8	93.4	92.4	96.8	92.8	91.2	96.1	89.8	90.3	95.6	89.9
A-M	96.0	97.5	95.2	93.9	96.9	93.7	94.3	96.7	93.5	92.9	95.2	91.9	92.3	95.9	91.1
N-O	97.2	97.7	95.9	96.8	97.5	94.5	94.8	97.8	94.1	96.8	97.0	94.6	96.4	96.8	93.1

A, with AEA; I, inner; M, middle; N, without SF and AEA; O, outer; S, with SF.

by the reduction of w/c ratio), even though it does not enhance the amount of soluble ions, so the self-dessication of HPC with silica fume is very obvious. Third, the effect of AEA on RH is very small because it has little influence on the amount of soluble ions and the VF value. Finally, for HPC stored in water for 2 years, the concentration of soluble ions in the outer layer reaches an equilibrium with that of the curing solution due to the leaching-out of the ions and the ingress of extra water, so the changes of mix proportion have very small influence on RH of the outer layer.

3.2. Degree of saturation

Degree of saturation (S) only depends on the quantity of evaporable water in concrete, so the states of water in pores have no influence on S. Certainly, the entrained air pores have great influence on S; therefore, the increase in air content reduces the degree of saturation in concrete. These are contrary to the results of RH. Furthermore, in contrast to to RH values, the measuring conditions, such as temperature and moisture, etc., have little influence on S values. Therefore, the degree of saturation in concrete is a better tool for evaluating the content of evaporable water than RH and, therefore, is a better tool for evaluating the frost resistance of HPC if the air content is under control.

Because air content has a big influence on the S value of concrete, the difference of air content among different concretes must be considered when comparing their S values.

3.3. Salt

Salts such as NaCl have a strong hygrosecopicity; therefore, the presence of salt in concrete accelerates the ingress of water and enhances the S value, which was proved by Yang et al. [14]. Also, the early drying-wetting cycles may cause the S value increase. Consequently, except for the RH value in the outer layer, the RH and S values of concretes stored in condition 2 are larger than those stored in condition 1.

The RH values in the outer layer depend on the concentration of the curing solution. Clearly, the concentration of soluble ions in condition 2 is higher than that in condition 1, so the RH value of the outer layer stored in condition 2 is lower than that stored in condition 1.

4. 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 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 and inner layers increases with the decrease of w/c ratio and with the increase in the amount of silica fume. This depends on reduction of the permeability of 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 decreases these differences. Furthermore, 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 ratio. The S values are considerably reduced by the use of AEA, which is reasonable because air pores normally do not contain water. The S values of concrete with salt are much larger than those without salt. The effect of salt on the RH values is very complex and may be related to curing conditions at an early age. It is necessary to add AEA to HPC subjected to frost and salt because of the high degree of saturation.

According to Rault's law, the theoretical calculations show that the increase in molar concentration of soluble ions in HPC is a main reason for the reduction of RH and, therefore, for the self-desiccation. The increase in the VF of the interlayer pore, gel pore, and fine pore in the sum volume of pores has a substantial influence on the increase of molar concentration and, therefore, on the reduction of RH.

If air content is under control, the degree of saturation S is a better tool for evaluating the content of evaporable water in concrete than the RH and, therefore, is a better tool for evaluating the frost resistance of HPC.

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