

Self-desiccation mechanism of high-performance concrete^{*}

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Abstract: Investigations on the effects of W/C ratio and silica fume on the autogenous shrinkage and internal relative humidity of high performance concrete (HPC), and analysis of the self-desiccation mechanisms of HPC showed that the autogenous shrinkage and internal relative humidity of HPC increases and decreases with the reduction of W/C respectively; and that these phenomena were amplified by the addition of silica fume. Theoretical analyses indicated that the reduction of RH in HPC was not due to shortage of water, but due to the fact that the evaporable water in HPC was not evaporated freely. The reduction of internal relative humidity or the so-called self-desiccation of HPC was chiefly caused by the increase in mole concentration of soluble ions in HPC and the reduction of pore size or the increase in the fraction of micro-pore water in the total evaporable water (T_e/T_{te} ratio).

Keywords: High-performance concrete, Autogenous shrinkage, Self-desiccation, Relative humidity
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INTRODUCTION

The self-desiccation phenomenon has attracted more and more interest with the reduction of W/C ratio and the application of ultra-fine mineral materials such as silica fume in high-performance concrete. This phenomenon will result in the reduction of internal relative humidity (RH) and the autogeneous shrinkage of HPC (McGrath and Hooton, 1990; Persson and Fagerlund, 1997; Powers, 1947). McGrath and Hooton (1990) and Persson (1996) proved that the autogeneous shrinkage might be high enough to cause HPC internal cracking and therefore decreased the strength, especially the split tensile strength. Moreover, big prestress loss will occur in prestressed concrete with high strength if its autogeneous shrinkage is

not considered during designing.

The autogeneous shrinkage of HPC is considered to be related or equal to the chemical shrinkage in literatures (Mjornell, 1994; Persson, 1998). The chemical shrinkage is caused by the reduction in the absolute volume of cement and water during the hydration of cement. However, the chemical shrinkage does not answer all questions on the autogeneous shrinkage.

Hedenblad (1994) and Mjornell (1994)'s studies on the effect of alkali ions on RH showed that alkali ions had some influence on the reduction of RH in concrete, but that the measured effect was lower than that calculated by Raoult's law. Nilsson (1980)'s result indicated that for HPC the RH reduction was often very big because of the finer pore structure, which causes a flatter sorption isotherm. Furthermore, lower W/C and higher amount of silica fume lead to finer pore structure and bigger reduction of RH (Sellevold and Justnes, 1992).

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EXPERIMENTAL DETAILS

Raw materials and mix proportions

Portland cement with 0.54% Na₂O and 3.2% C₃A was used. The aggregate consisted of 5~20 mm crushed sandstone and 0~5 mm natural quartz sand. An amorphous silica fume (SF) with specific area of 20.5 m²/g and 98.2% SiO₂ was used. A powder product of naphthalene sulphonate superplasticizer (SP) was also used for enhancing the workability of HPC.

The mix proportions and properties of HPC are shown in Table 1. In order to investigate the mechanisms of self-desiccation easily, the sum of cementing materials in HPC was kept constant. The 100 mm cubic specimens for measuring compressive strength were stored in 20 °C water after being demoulded.

Test methods

(1) Autogeneous shrinkage

After casting, a curing membrane was coated on the surfaces of specimens in order to prevent water from evaporating. The Φ 60 mm×300 mm cylinder specimens for measuring the autogeneous shrinkage were demoulded and coated with soft butyl rubber around them as soon as possible after the concrete was finally set, about 8 hours after casting. Then the specimen length was measured immediately and this value was regarded as the initial length during calculation of the autogeneous

shrinkage. The specimen was placed in a room with constant temperature of (20±1) °C and relative humidity of 65%±2% after the length was measured. This treatment can ensure the weight of the specimen kept constant during the self-desiccation test.

(2) Internal relative humidity

Cylinder specimens (Φ 60 mm×300 mm) were molded in PVC pipes. One end of the pipe was stuffed up with a tight rubber plug, and the other end was sealed with butyl rubber. A 20 mm thick slice was rapidly cut from the cylinder specimens after some ageing and crushed with a hammer into 2.5~10 mm smaller pieces, which were then immediately placed into a 100 ml glass tube with a tight plug.

The measurement was carried out in a room with constant temperature of (20±1) °C and relative humidity of 65%±2%. All glass tubes with specimens were put for at least 4 days in the room and all RH sensors were calibrated according to ASTM E104-85 before the measurement. A dew point meter (Testo 650) with precision of 1% RH was used for measuring RH. The RH sensor was inserted in the tubes, sealed with a rubber plug, and kept in the tube for at least 20 hours to get the exact result, and then the RH was measured every two hours. The RH measurement was ended when three consecutive values of RH measurement were constant. The sensors were placed in the room at least 4 hours before the next measurement in order to de-

Table 1 Mix proportions and properties of HPC

Mix	W/C	Cement+SF (kg/m ³)	Sand (kg/m ³)	Stone (kg/m ³)	SP (kg/m ³)	Air (%)	Slump (mm)	Density (g/cm ³)	Strength (MPa)	
									28 d	360 d
A0	0.40	500+0	489	1165	1.6	1.0	225	2.432	87	94
A1		450+50	486	1160	2.0	1.2	215	2.415	98	108
B0	0.37	500+0	503	1190	3.5	0.9	220	2.451	95	101
B1		450+50	500	1185	4.0	0.8	225	2.446	114	126
C0	0.33	500+0	522	1223	4.5	1.3	195	2.459	106	111
C1		450+50	519	1218	5.0	1.1	190	2.448	118	132
D0	0.30	500+0	536	1248	9.1	1.2	200	2.481	117	123
D1		450+50	533	1243	9.9	0.9	210	2.470	129	140
E0	0.25	500+0	556	1293	12.5	0.7	190	2.494	136	141
E1		450+50	553	1288	13.0	1.2	185	2.472	140	155

crease the error caused by moisture hysteresis.

(3) Evaporable water

Before the RH measurement, the tube with specimen was weighed (M_0). After the RH measurement, the tube was dried and pumped in a vacuum of 25 mm Hg for 24 hours and then weighed (M_r) again. Finally, the tube with specimen was dried at 105 °C for 1 day to constant weight and weighted (M_d), and then the tube without specimen was weighed (M_t). The total evaporable water (T_{te}) and the residual evaporable water at a vacuum of 25 mm Hg in the specimen (T_r) could be calculated as follows:

$$T_{te}=(M_0-M_d)/(M_0-M_t)\times 100\% \quad (1)$$

$$T_r=(M_r-M_d)/(M_0-M_t)\times 100\% \quad (2)$$

Results on the evaporable water are shown in Table 2.

TEST RESULTS AND DISCUSSION

Internal relative humidity

Results on the effect of curing age and W/C ratio on the internal relative humidity (RH) of HPC are shown in Fig.1 and Fig.2. Fig.1 shows that the RH of HPC was significantly reduced before 50 days. The RH of HPC without SF decreased little after 100 days, but the RH of HPC with 10% SF still decreased with the increase in the curing age. Analysis of the self-desiccation in the following discussions was based on one-year HPC data.

Fig.2 shows that the RH of one-year HPC decreased nearly linearly with the reduction of W/C ratio, but the RH of HPC with 10% SF was much lower than that of HPC without SF.

Autogenous shrinkage

Effects of W/C and SF on the autogenous

Table 2 Results on the evaporable water, mole concentration of soluble ions and relative humidity in HPC

Mix	T_{te} (%)	T_r (%)	S (mol/L)	S_a (mol/L)	Relative humidity* (%)		
					RH	RH_c	RH_a
A0	3.48	2.83	1.15	6.15	88.1	98.0	89.6
A1	3.24	2.80	1.12	8.23	83.7	98.0	86.4
B0	2.79	2.26	1.42	7.55	84.6	97.5	87.4
B1	2.70	2.38	1.33	10.81	81.5	97.6	82.6
C0	2.30	1.90	1.71	9.88	82.3	97.0	83.9
C1	2.30	2.01	1.55	12.32	77.6	97.3	80.4
D0	2.08	1.73	1.88	11.25	79.1	96.7	81.9
D1	2.01	1.78	1.75	15.11	74.8	96.9	74.6
E0	1.65	1.37	2.34	13.78	75.3	95.9	78.3
E1	1.66	1.46	2.12	17.82	70.8	96.3	72.8

Note: *RH measured by the meter; RH_c and RH_a calculated by Raoult's law according to S and S_a respectively

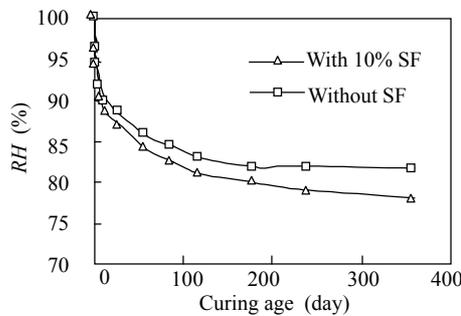


Fig.1 Effect of curing age on the internal humidity RH of HPC with W/C of 0.33

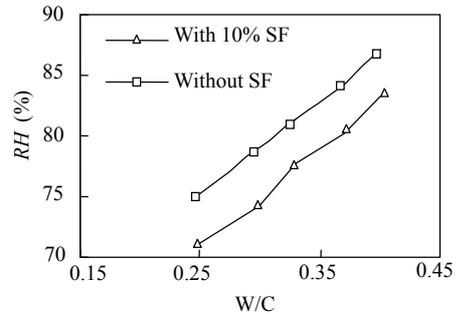


Fig.2 Effect of W/C ratio on the RH of one-year HPC

shrinkage of one-year HPC are shown in Fig.3 showing that the autogenous shrinkage was obviously reduced with W/C, but that the shrinkage of HPC with 10% SF was much larger than that of HPC without SF.

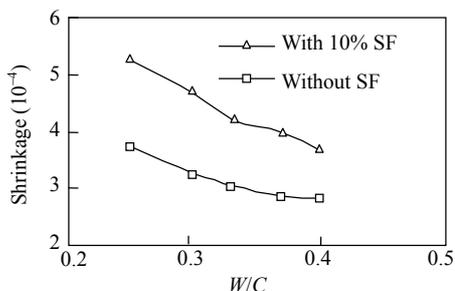


Fig.3 Effect of W/C on the autogenous shrinkage of one-year HPC

Mechanisms of self-desiccation

The autogenous shrinkage of HPC is considered to be related or equal to the chemical shrinkage reported in many literature. If this viewpoint is correct, the autogenous shrinkage is certainly enhanced with the increase in the hydrated degree of cement and the amount of hydrates. Based upon Powers and Brownyard (1948)'s results, the maximum hydrated degree of cement α_{\max} depends on the W/C ratio of concrete, i.e., $\alpha_{\max} = (W/C)/0.39$. In other words, at the same content of cement, the hydrated degree of cement and the amount of hydrates decrease with the reduction of W/C, i.e., the autogenous shrinkage should decrease with W/C. However, the actual results are just opposite.

Fig.4 shows that the autogenous shrinkage of one-year HPC increased with the reduction of RH,

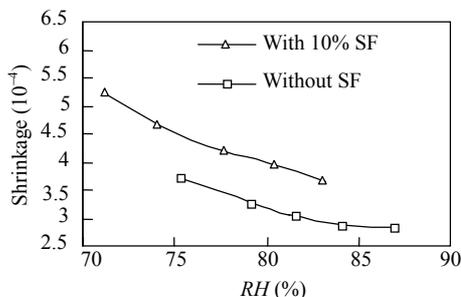


Fig.4 Relationship between RH and autogenous shrinkage of one-year HPC

and that the shrinkage of HPC with SF was much larger than that of HPC without SF. It is reasonable to infer that the effect of reduction of the internal relative humidity on HPC was just like that of HPC being placed in environment with low RH. Why is the internal relative humidity reduced with the reduction of W/C and the addition of silica fume?

(1) Evaporable water

Results on the effect of total evaporable water T_{te} on RH in HPC are shown in Fig.5 clearly indicating that RH in HPC was reduced with T_{te} , and that the effect of T_{te} on RH in HPC with 10% SF was larger than that in HPC without SF. Their regression equations were as follows:

$$\text{Without SF } RH = 6.865T_{te} + 65 \quad (\text{correlative coefficient } r = 0.978) \quad (3)$$

$$\text{With 10\% SF } RH = 8.263T_{te} + 58 \quad (r = 0.982) \quad (4)$$

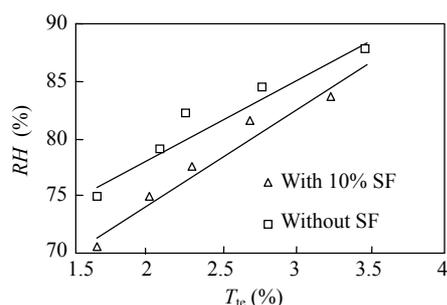


Fig.5 Effect of total evaporable water T_{te} on RH in one-year HPC

However, even for HPC with W/C of 0.25, there was enough evaporable water to maintain 100% RH in the HPC if the evaporable water was pure water and could be evaporated freely. In fact, the RH and temperature of the air in the 100 ml glass tube was about 65% and 20 °C when the specimen was placed in it, so the amount of water needed to increase RH from 65% to 100% was:

$$\begin{aligned} \Delta W &= (1 - 0.65) \times 17.3 \text{ (g/m}^3\text{)} \times 100 \times 10^{-6} \text{ (m}^3\text{)} \\ &= 6.06 \times 10^{-4} \text{ g} \end{aligned} \quad (5)$$

17.3 g/m³ is the vapor content in air at 100% RH and 20 °C.

Consequently, HPC only needed very little water to keep 100% RH. In fact, the minimum amount of evaporable water in the specimen for

measuring RH was 0.126 g. Consequently, it can be reasonably inferred that the reduction of RH in HPC was not due to shortage of water, but because the evaporable water in HPC was not evaporated freely.

(2) Mole concentration of soluble ions

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. In other words, the increase in the molar concentration of soluble ions in the specimen will cause the reduction of RH in the specimen. In order to evaluate and calculate the effect of soluble ions, it is necessary to make some assumptions:

i) The number of moles of all ions in one-year concrete that are soluble into water, such as Na^+ , K^+ , Ca^{2+} , OH^- , SO_4^{2-} , etc., is equivalent to that of 0.6% Na_2O in cement weight.

ii) All evaporable water of various states (in pores with various sizes) has the same concentration of the soluble ions and the same evaporating ability.

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

i) The number of moles of all soluble ions or solutes (mole):

$$N = 2 \times 0.006C / 62 \quad (\text{atomic mass of } \text{Na}_2\text{O}) \\ = 1.94 \times 10^{-4}C \quad (C, \text{ cement content}) \quad (6)$$

ii) The amount of total evaporable water in the specimen W_{te} (g):

$$W_{te} = T_{te} \times d \times 10^3 \\ (T_{te} \text{ shown in Eq.(1); } d, \text{ density, g/cm}^3) \quad (7)$$

iii) The molar concentration of the soluble ions in the concrete (S):

$$S = N / (W_{te} \times 10^{-3}) = 1.94 \times 10^{-4}C / (T_{te} \times d) \quad (8)$$

The relationship between the internal relative humidity and the calculated molar concentration S of soluble ions in HPC is given in Fig.6 showing that the RH values decreased linearly with the increase in the molar concentration. Their regressive equations were as follows:

$$\text{Without SF} \quad RH = -3.06S + 96.82 \\ (\text{correlative coefficient } r=0.97) \quad (9)$$

$$\text{With 10\% SF} \quad RH = -4.73S + 98.36 \\ (r=0.99) \quad (10)$$

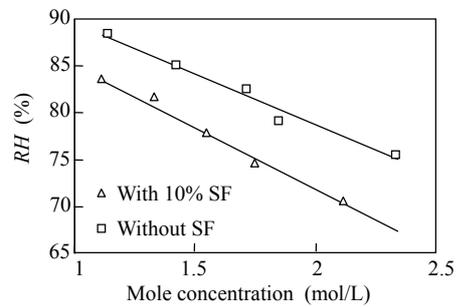


Fig.6 Relationship between the RH and the molar concentration of soluble ions in HPC

These results indicated that a part of the reduction of the internal RH in HPC was certainly due to the increase of the molar concentration in HPC. Raoult's law and S values were used to calculate values of RH_c caused by the increase of S as presented in Table 2 indicating that only 16~19 percent of reduction of the internal RH was caused by the increase of S for HPC without SF, 12%~13% for HPC with 10% SF. This implies that factors other than the mole concentration had much bigger influence on the internal relative humidity of HPC, which may be related to the pore structure of HPC.

(3) Pore structure

According to Kelvin's law, the smaller the pore diameter is, the smaller is the vapor pressure of evaporable water in the pore, and therefore the lower is the relative humidity in the pore, and the more difficult is the evaporation of the water. In other words, evaporable water in smaller pore has smaller effect in enhancing the RH in HPC. The evaporable water includes the interlayer water, absorbed water, gel water, capillary water and air-bubble water. Obviously, the interlayer water,

absorbed water and gel water were more difficult to be evaporated than the capillary water and air-bubble water.

In order to estimate these effects intuitively, the solvent and the amount of total evaporable water must be adjusted during calculation of the mole concentration of soluble ions. If a part of the total evaporable water in a specimen is not evaporated at a vacuum of 25 mm Hg for 24 h, the effect of the residual evaporable water in HPC on RH is negligible and therefore this part of water must be taken out during calculation of the mole concentration. Consequently, a dummy molar concentration S_d can be calculated as follows:

$$S_d = S / (1 - T_r / T_{te})$$

(T_{te} and T_r are shown in Eqs.(1) and (2)) (11)

The relationship between the internal relative humidity and the dummy molar concentration of soluble ions in HPC is shown in Fig.7, clearly showing that the internal relative humidity in HPC only depends on the dummy molar concentration of soluble ions regardless of HPC with or without SF, and that the RH in HPC decreases linearly with the increase of S_d .

$$\text{With 0~10\% SF} \quad RH = -1.45S_d + 96.1$$

($r=0.99$) (12)

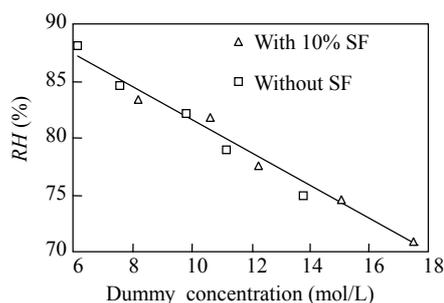


Fig.7 Relationship between the RH and the dummy molar concentration of soluble ions in HPC

Table 2 shows that the calculated RH_d was roughly similar to the measured RH, and that about 81~90 percent of reduction of the internal RH was caused by the increase of S_d for HPC without SF, about 84%~95% for HPC with 10% SF.

If S_d in Eq.(8) and S in Eq.(11) are taken into Eq.(12), and d is taken as the average of 10 density values in Table 1, 2.456 g/cm^3 , a new equation is obtained:

$$\text{With 0~10\% SF} \\ RH = -1.146 \times 10^{-4} \times C / (T_{te} - T_r) + 96.1 \quad (13)$$

Eq.(13) shows that the RH decreases with the increase of $1/(T_{te} - T_r)$, and therefore the increase in the fraction of T_r in T_{te} reduces the RH, and the more the increase is, the much more obvious is the reduction of the RH.

Based on the above results and analyses, it is easy to explain the effects of W/C and silica fume on the reduction of the RH. According to the results of Sellevold and Justnes (1992), the lower the W/C is and the higher the amount of silica fume is, the finer is the pore structure. Furthermore, the finer the pore is, the greater is the shrinkage due to the loss of water in the pore. From Kelvin's law it can be deduced that the fraction T_r in T_{te} increases much more when the pore structure becomes finer, and therefore the RH decreases more. Of course, the effect of silica fume on the reduction of pore size in HPC is much greater than that of W/C, and therefore the reduction of RH or autogenous shrinkage caused by silica fume is much greater than that caused by W/C.

Consequently, the reduction of internal relative humidity or so-called self-desiccation of HPC is chiefly caused by the increase in mole concentration of soluble ions in HPC and the reduction of pore size or the increase in the fraction of micro-pore water such as gel water, interlayer water, etc., in the total evaporable water (the fraction of T_r in T_{te}).

CONCLUSION

The autogenous shrinkage of HPC increases with the reduction of W/C and the increase in the curing age, whereas the internal relative humidity of HPC decreases. These phenomena are remarkably amplified by the addition of silica fume.

The autogenous shrinkage of one-year HPC

increases with the reduction of RH, and the shrinkage by the RH reduction of HPC with SF is much greater than that of HPC without SF.

Theoretical analyses and calculation showed that the reduction of RH in HPC is not due to shortage of water, but due to the fact that the evaporable water in HPC is not evaporated freely. The main reasons behind the reduction of internal relative humidity or so-called self-desiccation are the increase in mole concentration of soluble ions and the reduction of pore size or the increase in the fraction of micro-pore water in the total evaporable water (the fraction of T_r in T_{te}).

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