Self-Desiccation of Portland Cement and Silica Fume Modified Mortars

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The internal relative humidity of sealed cement mortar prisms was measured, and self-desiccation was observed. Lowering the water-to-cement plus silica fume ratio (W/C+S) increases self-desiccation, as does increased content of silica fume and age of curing. Mechanisms of self-desiccation are discussed with regard to silica fume addition, W/C+S ratio and age. Reduction of relative humidity appears to contribute to increased freezing and thawing durability. Durability factors for cement mortar prisms (obtained by ASTM C666) are compared to internal relative humidity of wet cured prisms of similar dimensions. Results are consistent with expected behavior.

Introduction

Uptake of water is necessary in order to maintain saturation as hydration of cement proceeds since the volume of the new solid is less than the combined volumes of the cement and water of the initial paste. The high surface area of the reaction products adsorbs a great deal of water to its surface thus reducing free water available for chemical reaction. If the system is sealed against the ingress of water or the reaction products produce a discontinuous pore structure (reducing the permeability), the water available for reaction (free water) will be reduced until there is not enough to saturate the solid surfaces and the internal relative humidity will be reduced.[1]

The term "self-desiccation" in this context was described by Powers and Brownyard.[2] Earlier attempts to measure the humidity in concrete were made by Gause and Tucker.[3] Using a lithium chloride electric hygrometer they measured relative humidity at various depths into blocks of drying concrete and over hermetically sealed cement pastes. They found that the relative humidity of the sealed pastes dropped to between 88% and 79% in 28 days for moderate heat of hydration cement and high early strength cement, respectively. The extent of self-desiccation in cement pastes was later quantified by Copeland and Bragg.[1] They found a monotonic decrease with time of the relative humidity of chips of cement paste sealed in glass vials. The limiting value of relative humidity was lower for lower water/cement ratio pastes.

Recent concern over the accelerated deterioration of concrete in many modern structures has brought about keen interest in the development and use of more durable materials and improved methods of construction. It is conventionally thought that the use of supplementary cementing materials (fly-ash, blast furnace slag, silica fume) as partial replacements for cement results in increased durability in many aggressive environments because of reduced permeability to aggressive fluids (due to a finer pore structure) and increased consumption or dilution of the leachable byproduct calcium hydroxide. While this undoubtably plays a major role, it is suggested that some of the resistance may result from the combination of a reduced permeability and internal self-desiccation.[4] This effect may help explain the apparently anomalous good resistance to freezing and thawing of some non-air-entrained high strength silica fume concretes.[4]

This study has expanded on the work of Copeland and Bragg[1] by using more up to date instrumentation and a greater array of mix parameters and related test procedures. The effects of silica fume content and W/C+S at various ages were measured. Humidity was measured with very precise capacitance-based humidity sensors placed inside sealed cavities. In addition a closed loop air circulation system was developed to prevent condensation on the humidity sensors caused by minor temperature differentials. Companion samples were tested for freezing and thawing durability in accordance with ASTM C666 (Procedure A).

Mix Design

The nine mortar mixes used in the investigation are detailed in Table I. Three silica fume contents were chosen (0, 7.5, and 15% replacement by mass of cement) to bracket quantities used in industry (e.g., 7% was used for 70 MPa high strength concrete on the Scotia Plaza project in Toronto). All data is tabulated in relation to cement plus silica fume. Ignoring entrapped air

Table I. Mix Designs

Mix	W/C+S	A/C+S	Silica Fume (%)	Super-plasticizer (% of C+S mass)	Calculated C+S Content (kg/m^3)
D32	0.32	2.00	0.0	1.5	720
E32	0.32	2.00	7.5	2.0	716
F32	0.32	2.00	15.0	3.0	712
D45	0.45	2.25	0.0	0.0	622
E45	0.45	2.25	7.5	0.5	619
F45	0.45	2.25	15.0	1.0	616
D60	0.60	2.25	0.0	0.0	568
E60	0.60	2.25	7.5	0.0	566
F60	0.60	2.25	15.0	0.0	564

Table II. Composition of Cementing Materials

	Portland Cement	Silica Fume
CaO (%)	62.15	0.30
SiO_2	21.25	93.89
Al_2O_3	4.54	0.19
Fe_2O_3	3.03	0.32
MgO	3.68	0.71
SO_3	2.97	0.28
Na_2O	0.15	0.13
K_2O	0.47	0.93
Na_2O (equiv)	0.46	0.74
Loss on ignition (plant)	1.76	2.72
Loss on ignition (lab)	3.70	1.40
Bogue C_3A	6.9	
Relative density	3.15	2.32
Nitrogen BET surface area (m^2/kg)		23 000

contents, the total cementing materials content of the mortar mixes based on volumetric mix calculations is given in Table I. Three water-to-cement + silica fume ratios (0.32, 0.45, 0.60) were chosen to try and cut across a limiting value at which self-desiccation may become significant.

The portland cement used for all the specimens was a low alkali, moderate C_3A, CSA Type 10 (similar to ASTM Type I); the oxide contents and other material properties are given in Table II. Condensed silica fume was from SKW Canada Limited's Becancouer, Quebec plant. The analysis of a similar sample of silica fume from this source is also shown in Table II. The sand was granitic with a relative density of 2.68 and a fineness modulus of 1.8.

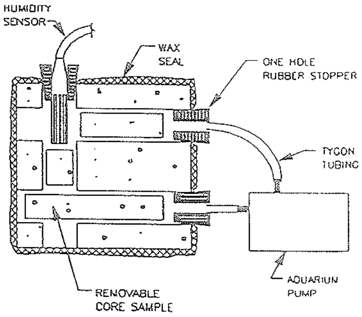
Mixing was carried out in a 0.08 m^3 (3 ft^3) flat pan mixer. Varying dosages of a powdered naphthalene sulphonate based superplasticizer (from 0% to 3% by mass of cementing materials) were added to increase the workability of the stiffer mixes as shown in Table I.

Humidity Measurement

Internal relative humidity of the cement mortar was measured inside 20 mm diameter humidity wells or cavities cored into 100 × 100 × 215 mm prisms. The apparatus is shown in Fig. 1. A system of three intersecting holes created a humidity well for inserting the probe and circulating the internal atmosphere. The system accommodated a combined electrical capacitance type relative humidity and thermistor temperature probe which is removable to prevent deterioration of the sensor. A closed loop pumping system circulated air over the cement mortar and past the sensor to prevent condensation on the sensor tip at high relative humidity due to minor temperature differences in the test equipment. All test equipment exposed to the internal atmosphere of the humidity well was made of non hygroscopic material, i.e., does not desorb water into or adsorb water from the test atmosphere. Continuity of the pore structure was preserved so that effects of capillary suction were maintained throughout the depth of the specimen.

Specimens were allowed to cure for 24 hours at which time three sets of humidity wells were diamond drilled in each block. Small 19 mm diameter core samples were stored in the cavity and removed at a later date for other tests such as porosity, degree of saturation, and moisture content (not reported here). Solid rubber stoppers were used to seal the holes and the remaining exterior surfaces of the prisms were sealed with wax to prevent moisture movement in or out of the samples.

Humidity was measured at ages of 14, 28, 56, and 91 days by inserting the relative humidity probes into the cavities for a period of one hour with the air circulation system on. Temperature and humidity were closely monitored during



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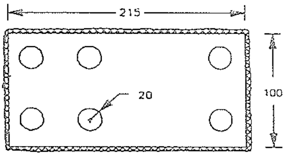

PROFILE

Fig. 1. Humidity blocks.

the test to check for system errors such as condensation on the sensor (excessively high humidity or erratic temperature fluctuation) or air leakage (rapidly falling humidity). After initial calibration tests, equilibrium was assumed to occur after one hour.

An important part of the process was careful calibration of the humidity sensors with saturated salt solutions. This was done every few weeks during the test program to keep errors in the readings to a minimum. All humidity readings were adjusted by applying a correction factor based on a linear interpolation between two calibration points obtained from reference standards and a second interpolation between two calibration dates, i.e., before and after the reading was taken. Saturated salts used for calibration and their equilibrium vapor pressures are shown in Table III. Readings were not corrected for temperature as it was assumed that the effect of temperature on internal relative humidity of concrete was small. Results showing relative humidity of sealed blocks are shown in Figs. 2 and 3.

Table III. Saturated Salt Solutions for Humidity Probe Calibration

Saturated Salt	Relative Humidity at 25°C
NaCl	75.1
$(NH_4)^2SO_4$	80.2
K_2CrO_4	86.5
$BaCl \bullet 2H_2O$	90.3
K_2SO_4	97.0

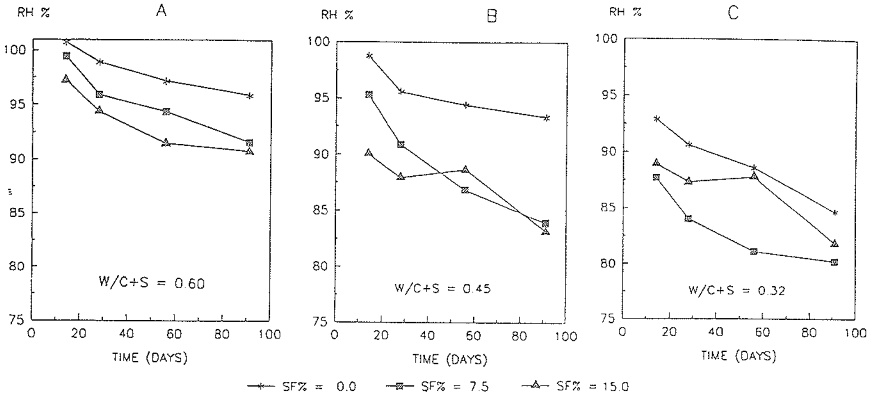

Fig. 2. Relative humidity vs time for sealed blocks.

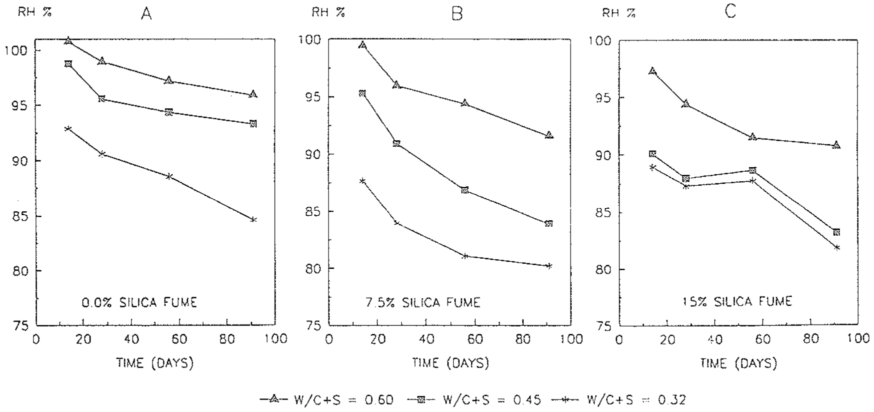

Fig. 3. Relative humidity vs time for sealed blocks.

Freezing and Thawing Tests

Specimens for ASTM C666 (Procedure A) were cast in steel molds measuring 100 × 75 × 400 mm. Stainless steel studs for length measurements were embedded in the ends for length change measurements. All mixes were non-air-entrained. After casting, the prisms were trowelled smooth, covered with wet burlap and plastic, and left overnight in the laboratory air. The molds were stripped the next morning and the specimens were placed in saturated limewater. After fourteen days of curing, the beams were weighed in the saturated surface dry condition, and the external dimensions measured. To prevent further hydration prior to test, the beams were stored in a deep freeze, each beam being wrapped in plastic to prevent sublimation of water.

The nine primary mixes were made of a sand known to be durable to freezing and thawing. The ASTM C666 tests were performed in Logan automatic freezing and thawing machines. Included in the testing were loss of mass, ultrasonic pulse velocity, and length change in addition to dynamic modulus.

Results of the ASTM C666 Procedure A tests are shown in Table IV. Figure 4 compares the durability factors to the average internal relative humidity of companion samples moist cured for 14 days. The probes were 60 mm from the cured surface. This depth was chosen for comparison since it approximated the distance to the center of the ASTM C666 prisms.

Discussion

Relative humidity of all sealed blocks reduced monotonically with time. Lowering W/C+S increased self-desiccation, as did increased content of silica fume and age of curing. Equilibrium was not yet established after 91 days of sealed curing.

Figure 2 shows plots of relative humidity vs time for each of the nine mixes. Each data point represents an average of the readings from the three humidity wells in each sealed block. Each plot is at a constant silica fume content and the three curves are for different W/C+S ratios. Each curve shows a monotonic decrease in relative humidity, suggesting that an equilibrium humidity is being approached. This trend is more evident in the upper three curves which have the highest W/C+S ratio. Possible reasons for this monotonic decrease being more pronounced in higher W/C+S ratio mortars are:

1. The more open structure of high W/C+S ratio mortars allows for freer movement of water within the paste structure to the unreacted cement grains. Also, there is an abundance of water; thus, hydration is more immediate and equilibrium relative humidity is established at an earlier age.

Table IV. ASTM C666 (Procedure A) Test Results

Mix	W/C+S	Silica Fume (%)	Air (%)	Mass Loss (%)	Length Change (%)	Cycles to 60% Eo	Durability Factor 300 Cycles
D60.1	0.60	0.0	1.8	2.15	0.69	36	7.2
D60.2	0.60	0.0	1.8	0.67	0.37	25	5.0
E60.1	0.60	7.5	2.5	0.64	0.17	34	6.8
E60.2	0.60	7.5	2.5	-2.16	0.67	75	15.0
F60.1	06.0	15.0	3.2	0.25	0.16	77	15.4
F60.2	06.0	15.0	3.2	0.59	0.08	34	6.8
D45.1	0.45	0.0	6.5	0.91	0.30	32	6.4
D45.2	0.45	0.0	6.5	1.06	0.41	28	5.6
E45.1	0.45	7.5	5.5	1.32	0.41	74	14.8
E45.2	0.45	7.5	5.5	0.85	0.16	54	10.8
F45.1	0.45	15.0	5.1	0.44	0.05		72.0
F45.2	0.45	15.0	5.1	0.55	0.21		78.0
D32.1	0.32	0.0		-0.03	0.01		102.3
D32.2	0.32	0.0		0.00	0.01		102.3
E32.1	0.32	7.5		0.0	0.01		101.1
E32.1	0.32	7.5		0.0	0.02		98.8
F32.1	0.32	15.0		-0.12	0.01		100.0
F32.2	0.32	15.0		-0.12	0.01		98.8

2. The air circulation system has a tendency to reduce the relative humidity below approximately 88% RH. Since lower W/C+S ratio mortars have a lower overall humidity, an exaggerated drop in humidity results.

3. Higher W/C+S ratio mortars have a greater volume of capillary water. Thus any minor drying through the sealant would not result in a significant drop in humidity, while lower W/C+S ratio samples may be showing drying with time.

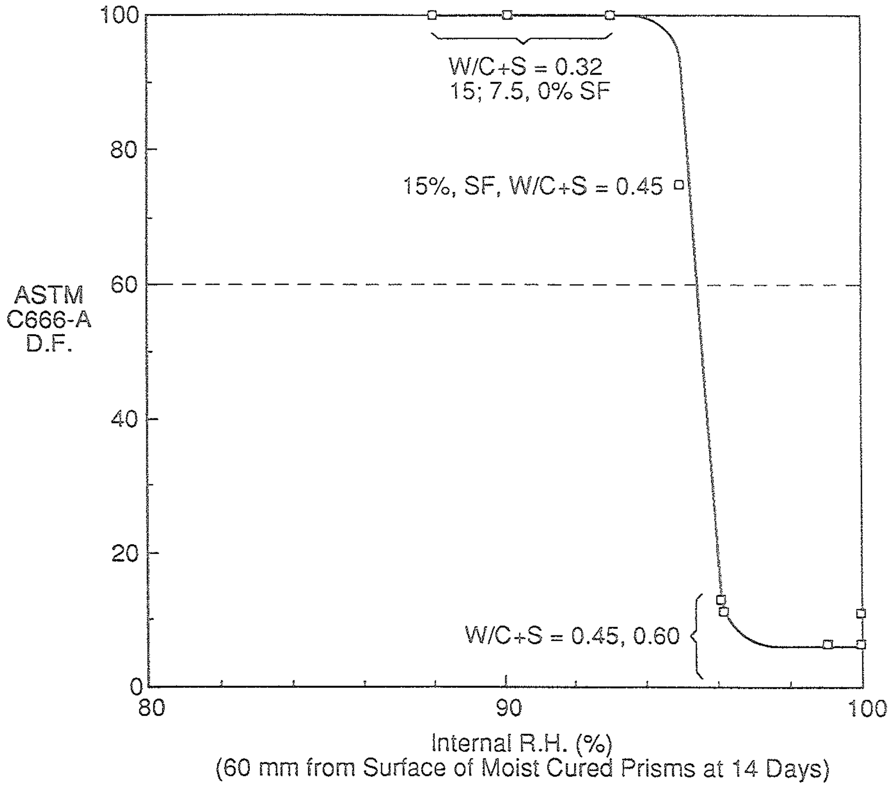

Fig. 4. Influence of self-desiccation on freezing and thawing performance.

The data can be compared to those of Copeland and Bragg[1] who measured the relative humidity of sealed cement paste and found that relative humidity was reduced to 94% for a 0.44 W/C sample at ages of 100 days and longer. The relative humidity of mix D45, which had a W/C ratio of 0.45, was reduced to 93.3% RH in 91 days. Recently Nilsson[6] measured the relative humidity samples with a W/C ratio of 0.4 and 10% silica fume. Humidity was reduced to 70% after six months.

Figure 3 shows the same data except that each plot is for constant W/C+S ratio and the three curves represent different silica fume contents. By comparing the second set of plots (Figs. 3(*a*), (*b*), and (*c*)) to the previous set of plots (Figs. 2(*a*), (*b*), and (*c*)) it can be seen that for the ranges of values

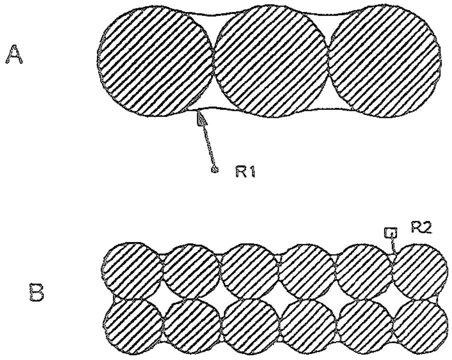

Fig. 5. Two pore structures with the same volume and water content, yet different equilibrium vapor pressure (Ref. 8).

tested, that W/C+S has a more significant influence on relative humidity than the silica fume content.

The question of whether or not self-desiccation has occurred is complicated by the fact that the internal structure of the paste is likely very different for different mixes. As well, the structure of the paste is likely to change with time. Mercury porosimetry results indicate that silica fume tends to refine the pore structure and possibly increase the internal surface area.[5,7,8] Scanning electron micrographs indicate a more open, large grain structure at higher W/C+S ratios. Figure 5 helps explain how two equal volumes and masses of a solid can contain the same quantity of water and yet can have different equilibrium vapor pressures. If by lowering the water cement ratio or by increasing the silica fume content the initial pore structure is refined, then a lower relative humidity may not be due to the quantity of pore water as much as the nature of the pore water. Nevertheless, it is hard to imagine that the time dependent change in relative humidity is due only to changes in internal surface area. Mercury porosimetry results only showed a slight change in internal surface area with time.[8]

Sellevold[5] provided the following explanation for increased self-desiccation of silica fume mixes. He found that pastes with the same W/C ratio and varying additions of silica fume produced a structure with the same porosity (by water displacement). Thus he reasoned that the chemical shrinkage of silica fume paste must be greater than that of ordinary paste. As a result, restricted hydration will cause a greater vapor pressure depression as silica fume content is increased.

The closed loop circulation system worked very well at preventing condensation at high humidity levels (up to 98% RH). It is believed that the data would not have been possible to obtain without this system. However, below approximately 88% RH, the circulation system failed to give better results than by simply using the probes alone.

ASTM C666 tests were carried out to observe the effect of self-desiccation and the addition of silica fume on the durability of non-air-entrained cement mortars. Denser pore structures created by low water/cement ratios and additions of silica fume means that the capillary porosity is reduced and thus the quantity of freezable water is also reduced (it is estimated that growth of ice in cement hydrate interstices, or gel pores, cannot occur above –78°C[2]). Self-desiccation might also further reduce the capillary saturation.

Mixes with lower W/C+S ratios had higher durability factors. Increased silica fume content also tended to increase the durability factor. Unfortunately the air content was not controlled and the effect of naturally entrapped air cannot be neglected. Results are split between very high and very low durability factors as is typical of this test. However, self-desiccated specimens tended to have higher durability factors and, as shown in Fig. 4, a relative humidity of 95% seems to have divided good and bad performance. Critical saturation measurements were not obtained because gravimetric measurements from core samples were not consistent.

Conclusions

1. Self-desiccation or internal self-drying due to hydration was measured, the effect being greater with reducing water-to-cementitious material ratios and increasing silica fume content.
2. A closed loop air circulation system was developed and evaluated, which proved useful in preventing condensation on the humidity sensors and provided greater precision at high humidity levels (above approximately 88% RH).
3. Prisms were cast for the ASTM C666 freezing and thawing durability test to examine the hypothesis that non-air-entrained mixes might prove durable if internal self-desiccation, measured as a drop in relative humidity, reduced the quantity of freezable water and the degree of saturation. Specimens exhibiting reduced internal relative humidities of less than 95% survived the standard 300 cycles of testing.

Acknowledgments

This work was funded by a grant from the University of Toronto. The cement was supplied by Lafarge Canada Limited and the silica fume was

supplied by SKW Ltd. Freezing and thawing tests were performed by Ontario Hydro Civil Research Department.

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