EARLY AGE PROPERTIES OF HIGH PERFORMANCE CONCRETE WITH TERNARY BINDERS

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ABSTRACT

Use of silica fume in high strength concrete adversely affects the autogenous shrinkage properties and increase the risk of cracking at early ages. In order to compensate for the adverse effects of silica fume, ultrafine fly ash was incorparated into the binder phase of the high strength concrete in this work. Part of cement and part of silica fume were replaced by ultrafine fly ash and early age properties of the mixes with these ternary binders were compared. Strength gain was followed by compression test and, autogenous shrinkage properties were tested under free and restrained conditions.

It is seen that ternary binders can decrease the autogenous shrinkage strains and increase the crack resistance, while keeping the early strength gain at comparable level. Results of the Thermogravimetric (TGA) analysis showed that mixes with ternary binders had a similar hydration rate compared to the mix with silica fume only. Mercury intrusion porosimetry (MIP) proved that the amount of finer pore volume, one of the major reasons of autogenous shrinkage, was decreased with the incorporation of ultrafine fly ash.

Keywords: High strength concrete, Ternary binders, Supplemantary materials, Autogenous shrinkage, Porosity.

INTRODUCTION

High strength concrete has a high early strength gain but is also prone to early age shrinkage cracking, especially when silica fume is used as a supplemantary cementitious material. Silica fume improves concrete properties by a filler effect in which the silica fume particles bridge the spaces between cement grains and aggregates; and by reacting pozzolanically with calcium hydroxide to produce a greater solids volume of calcium silicate hydrate gel, leading to an additional reduction in capillary porosity during hydration.

Autogenous shrinkage is the result of fine pores in the microstructure of the cement matrix, caused by self-desiccation and water consumption by the cement hydration. The total volume of solid and liquid phases decrease during the hydration. As a hardened structure is formed after the setting of cement, the decrease in the volume of hardened matrix is compensated for by the formation of pores in the microstructure[1]. The early stage and long term hydration products contain fine pores formed during the setting and hardening of concrete. The amount of free water slowly decreases as the hydration proceeds and fine pores are formed in the hardened cement matrix. Therefore self-desiccation occurs, as the water vapor pressure reduces and the relative humidity in fine pores decreases. Self-desiccation and autogenous shrinkage are strongly influenced by the hydration process and formation of the fine gel pores in the microstructure[2, 3].

It was found that ultrafine fly ash is a promising cementitious supplement with higher degree of reactivity compared to fly ash and slag. Due to its particle size distribution and high specific surface area, ultrafine fly ash can improve the early and later age properties of the concrete. It was seen that the autogenous shrinkage was the highest at the end of the first day when silica fume was used. The first day autogenous shrinkage of ultrafine fly ash was approxiamately zero and swelling was observed with the plain concrete. At later ages, the autogenous shrinkage of the silica fume was substantially higher compared to the plain mix. The autogenous shrinkage of the ultrafine fly ash mix at later ages was similar to the plain mix. It was also demonstrated that the material composition can be used in order to influence the development of porosity, compressive strength and shrinkage strains. It was concluded that replacement of cement with a relatively inert ultrafine fly ash decreases the rate of hydration, increases the free water in the mix, reduces the volume of fine pores, and thus reduces the autogenous shrinkage[4, 5].

This study investigates the effects of a ternary binder system with cement, silica fume and ultrafine fly ash, on the early age properties of high strength concrete. Ternary binders can be optimized with a synergistic effect, allowing component ingredients to compensate for any mutual shortcomings[6]. The use of silica fume in all mixes ensures an early age strength, where, use of ultrafine fly ash has a potential to reduce the shrinkage by restructuring the pore system. The degree of hydration and pore size distribution were measured in order to explain the properties and mechanism of autogenous shrinkage and formation of the microstructure.

EXPERIMENTAL WORK

Two replacement systems were investigated and compared. The control concrete was cast with a binder consisting of 10% silica fume and 90% cement.This concrete is coded as 90-10. In the first system, part of cement was replaced by ultra fine fly ash, and thus, the binder consisted 10% silica fume, 10% ultra fine fly ash and 80% cement. This concrete is coded as 80-10-10. In the second system, part of silica fume was replaced by ultra fine fly ash and thus, the binder consisted 5% silica fume, 5% ultra fine fly ash and 90% cement. This concrete is coded as 90-5-5. The water/cementitious materials ratio was 0.31 and the superplasticizer used was 1.5% by the weight of cementitious materials in the mixes.

A commercially available Type I Portland cement and silica fume was used in the casting of high strength concrete. Ultra fine fly ash replaced Portland cement and silica fume by volume. The silica fume used in the slurry form, containing 50% solid and 50% water, to ensure adequate dispersion in the mix. Its specific gravity is 2.2 gr/cm^3 and average particle size is 0.3 μm. The mix water was adjusted to account for the water in the slurry. The average particle size of the class F (ASTM C618) ultra fine fly ash Micron^3, supplied by Boral Material Technologies, was 3 μm and has a specific gravity of 2.57 gr/cm^3. Over 90% of the ultra fine fly ash particles passed from a 7 μm sieve.

3 mm river sand and 9.5 mm pea gravel were used as fine aggregate and coarse aggregate, respectively. Effective absorption of the fine aggregates and coarse aggregates were 2.3% and 1.3%, respectively. Aggregates were dried for 24 hours at 230^{o}C prior to mixing.

Specimens for compression test were demolded after 24 hours and cured in a controlled environment chamber at 22^{o}C, and 100% relative humidity until the age of testing.
The compressive strength of cylindical concrete specimens of 100 x 200 mm was determined at 1, 3, 7 and 28 days.

Free shrinkage test was performed with concrete specimens of 50 x 100 x 400 mm. Stainless steel gage studs were embedded on both sides of the fresh concrete, providing a gage length of 350 mm. Two detachable mechanical gages were used for measuring shrinkage from the time of initial setting up to 24 hours. After 24 hours, shrinkage measurements were determined according to ASTM C 341. Immediately after demolding the specimens for the autogeneous shrinkage measurements, specimens were sealed with adhesive aluminum sheets and kept under controlled temperature (22^{o}C) and humidity (50%) chamber. Length changes were recorded to measure the autogeneous shrinkage strains.

In the restrained shrinkage tests, ring specimens were used for simulating an infinitely long slab. Specimens with a 3.5 cm thickness, 30.5 cm inner diameter and 14 cm height were cast around a rigid steel ring. The exterior mold was removed 24 hours after casting. With these dimensions the concrete ring was assumed to be under uniform internal pressure provided by the ring with a relatively uniform axial tensile state of stress. The specimes were sealed with adhesive aluminum sheets and were kept under controlled temnperature at 22^{o}C. Daily visual inspections were performed. The day at which the cracking starts and the width of the cracks were measured. The crack width is measured as the average of the three locations (bottom, middle and top) of each crack. A microscope was used for measurements.

TGA test was done in order to evaluate the hydration process of the concretes. This technique allows quantification of the bound water in concrete. It is assumed that points of inflection or horizontal regions on the weight loss vs. temperature curve distinguish the weight losses due to seperate phases in the cement phase[7]. The limit between free and bound water is defined at 105^{o}C. The bound water content can be calculated by the difference between the water loss at 1000 ^{o}C and 105 ^{o}C, and is directly correlated with the cement hydration. The degree of hydration can be calculated by the ratio of percentage of bound water to the percentage of water needed for total hydration, 0.24. Thermogravimetry also can be used to estimate the pozzolanic reactivity.

In order to evaluate the pore size distribution and volume, MIP test was performed. Paste samples were put in acetone for several days to stop the hydration, and dried in an oven at 80 ^{o}C for 24 hours. Samples of known weight were sealed in the porosimeter and mercury was forced into the pores of the concrete by a steadily increasing pressure. The volume of mercury intruding the sample was recorded as the pressure increased. It is possible to evaluate the pore size versus pore volume curve from the amount of pressure applied and the amount of mercury intruded. Since the maximum pressure that can be applied is 200 MPa, it is possible to access the pores as small as 6 nm. The maximum of the derivative of pore volume with respect to pore radius, dV/dlogR, gives the critical pore size, under which the pore system is assumed to be interconnected. Under the critical pore size, the pore volume drastically increases as the pore radius decreases.

TEST RESULTS

The strength test results are presented in Table 1. Replacement of cement with 10% ultra fine fly ash (80-10-10) decreased the first day strength of the conventional high strength mix (90-10) by 13%. Replacement of silica fume by 5% ultra fine fly ash (90-5-5) did not have any significant effect on the strength of the conventional high strength concrete (90-10). The strength gain during the 3, 7 and 28 days were the same for all the concretes, which reached to a 28-day strength of above 70 MPa.

Table 1. Average compressive strengths of the concretes (MPa)

Days	Strength (MPa)		
	90-10	90-5-5	80-10-10
1	45.4	46.7	39.6
3	51.5	52.3	48.8
7	61.8	60.8	59.5
28	71.7	73.6	71.6

The development of the free autogenous shrinkage strains are shown in Table 2. The cracking days and the crack widths of the concretes, measured from the restrained shrinkage test, are given in Table 3. It can be seen that the free shrinkage strains are higher at early ages since the hydration rate is also faster. With the replacement of cement with 10% ultra fine fly ash (80-10-10) the autogenous shrinkage of the conventional high strength concrete (90-10) was decreased by 46% in the first 24 hours. The total decrease in autogeneous shrinkage at the end of 28 days was 34%. The cracking day was delayed by 3 days and the size of the crack width was decreased by 34%. Replacement of silica fume by 5% ultra fine fly ash (90-5-5) decreased the autogenous shrinkage of the conventional high strength concrete (90-10) by 27% in the first 24 hours. The total decrease in autogeneous shrinkage at the end of 28 days was 20%. The cracking day was also delayed by 3 days and the size of the crack width was decreased by 23%.

Table 2. Measured strains of autogous shrinkage from the free shrinkage test (units in microstrains)

Days	90-10	90-5-5	80-10-10
1	293	214	157
3	413	279	212
7	548	374	312
28	703	564	462

Table 3. Cracking days and crack widths, measured from the restrained shrinkage test.

	90-10	90-5-5	80-10-10
Cracking Day	16	19	19
Crack Size (mm)	0.26	0.20	0.17

The results of the TGA test are given in Table 4. The percentage of bound water and degree of hydration is calculated between 105^{o}C and 1000 ^{o}C for 1st, 3rd, and 7th days.

Table 4. Bound water and degree of hydration from the TGA experiment (units in %)

	105-1000^{o}C			Degree of Hydration		
Days	90-10	90-5-5	80-10-10	90-10	90-5-5	80-10-10
1	12.3	13.9	12.8	51	58	53
3	14.4	15.1	15.9	60	63	66
7	16.0	16.1	16.4	67	67	68

It can be seen that the amount of bound water increases with the increasing age, since more water is bound during the process of hydration. It can also be seen that there is no significant change in the hydration process of the concretes, with respect to the binder type used. The slightly higher hydration degree calculated for the 80-10-10 mix is due to the reaction between ultrafine fly ash and $Ca(OH)_2$ to form calcium silicate hydrates.

The capillary pores can be classified as the pores between 6 to 50 nm in diameter. Pores larger than 50 nm are considered as large-diameter pores[8]. Capillary pores can be further divided in to finer (6~20 nm) and larger (20~50 nm) capillaries. It is these finer capillaries and the gel pores (1.5~6 nm) that are the reason for autogenous shrinkage strains during the self-desiccation process of the hardened matrix. The total pore volume and the critical pore size calculated from the MIP test are given in Table 5 for 1st, 3rd, and 7th days of hydration.

Table 5. Critical pore diameter, total and finer porosity of the cement matrices calculated from MIP test

	Specimen	1. Day	3. Day	7. Day
D_{cr} (nm)	90-10	16.7	9.6	9.6
	90-5-5	14.1	9.3	10.8
	80-10-10	14.3	8.4	8.1
Total Porosity 10^{-2} (cm^3/cm^3)	90-10	22.8	16.0	12.9
	90-5-5	17.1	12.5	11.9
	80-10-10	16.5	12.6	10.0
Porosity Smaller than Dcr 10^{-2} (cm^3/cm^3)	90-10	14.3	8.8	6.3
	90-5-5	10.0	7.6	5.9
	80-10-10	11.2	6.8	5.5
Porosity Smaller than 20 nm 10^{-2} (cm^3/cm^3)	90-10	16.8	14.0	10.5
	90-5-5	14.2	11.4	9.3
	80-10-10	13.7	10.9	8.1

It can be seen that as the hydration proceeds in time, both the critical size and the total volume of the capillary pores reduce. The fine capillary pore size, under which high autogenous shrinkage strains occur, is considered as the volume of the pores smaller than the critical pore size of the cement matrices. The fine capillary system under the critical pore size can be considered as a continous network. Thus, the volume of the pores smaller than the critical pore size is the most influential factor, because of both their size and volume, in the development of shrinkage strains due to water consumption and decrease in the relative humidity.

It can be seen that the critical pore size, the total volume of the capillary pores and the volume of smaller capillaries were decreased with the addition of ultra fine fly ash particles, in mixes 80-10-10 and 90-5-5 (Table 5). At the first day of hydration, the decrease in the finer capillaries was 22% for the 80-10-10 mix and 30% for the 90-5-5 mix, compared to the 90-10 mix. A continuous particle size distribution was achieved since the average particle size of ultra fine fly ash (~3 microns) is in between of silica fume (~0.3 microns) and of cement (~15 microns). This results in a microstructure with less volume of porosity, and a smaller critical pore size.

The fine capillary size can also be defined simply as the size of the pores in between 6 nm and 20 nm. It can be seen from the Table 5 that, again the 90-10 mix contains 15% more volume of these fine pores compared to the both 90-5-5 and 80-10-10 mixes.

DISCUSSION

The experimental results indicate that, partial replacement of both silica fume and cement with ultra fine fly ash reduces the autogenous shrinkage strains, delays the cracking, although does not prevent, and reduces the crack size without any significant decrease in the compressive strengths. Although the first day strength of the mix with 10% ultra fine fly ash was lower, the third day strength caught up with the other high-strength mixes.

The hydration rates of all the mixes were comparable, indicating that the lower autogeneous shrinkage of high strength mixes with ultra fine fly ash, used in this research work, was a result of a physical property, i.e. the pore system, rather than a chemical process, i.e. rate and products of hydration. Use of ultra fine fly ash, together with silica fume, resulted in similar hydration rates. The relation between the hydration rate and autogenous shrinkage is presented in Fig. 1. Although the shrinkage is directly related to the hydration and consumption of water in the concrete, the reason for different values of autogenous shrinkage strains with respect to the same hydration degree is the pore structure of the concrete. This result is in accordance with previous studies[2]. The relation between the autogenous shrinkage and the volume fraction of fine pores, at different ages, are presented in Fig. 2. The larger volume of finer capillary pores with the silica fume mix is the reason for the development of higher autogenous shrinkage strains and early cracking. Due to a continous particle size distribution with the use of ultra fine fly ash, the total volume, finer size capillary volume were smaller compared to the conventional high strength mix at the early days of hydration. Although the hydration rates were similar, the initial autogenous shrinkage was decreased by the addition of ultra fine fly ash. Since the finer pore system in the hydrating cementitious paste is responsible for the strains that develop during the self-desiccation and decrease in the relative humidity, higher autogenous shrinkage strains were measured for the conventional high strength concrete at early days.

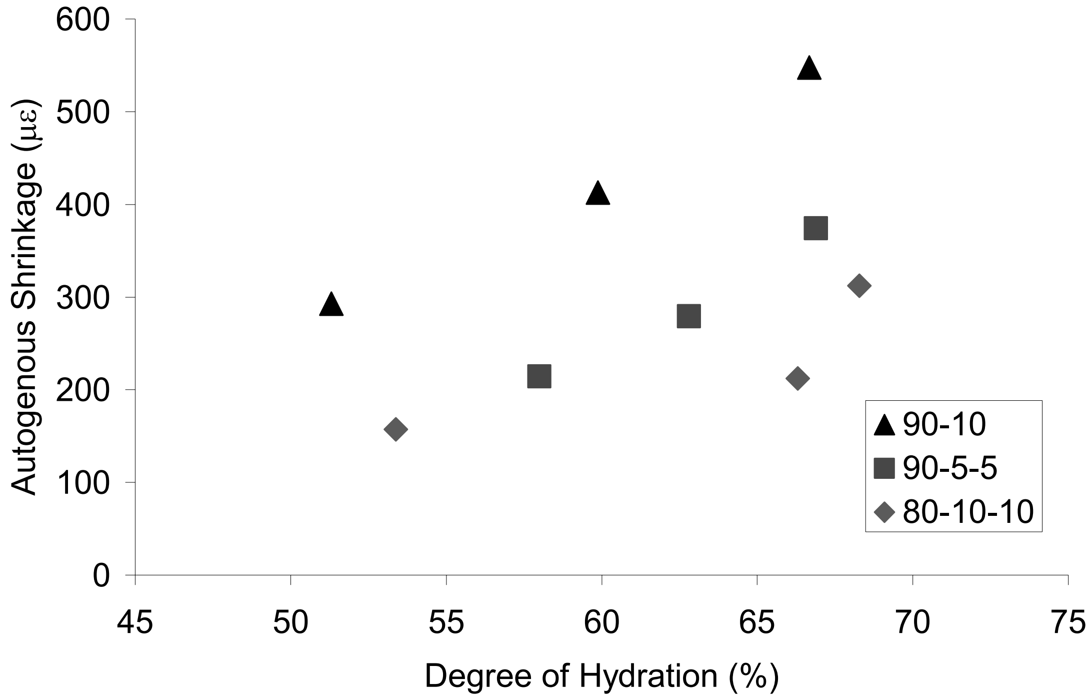

Fig. 1. Relation between the autogenous shrinkage and the degree of hydration

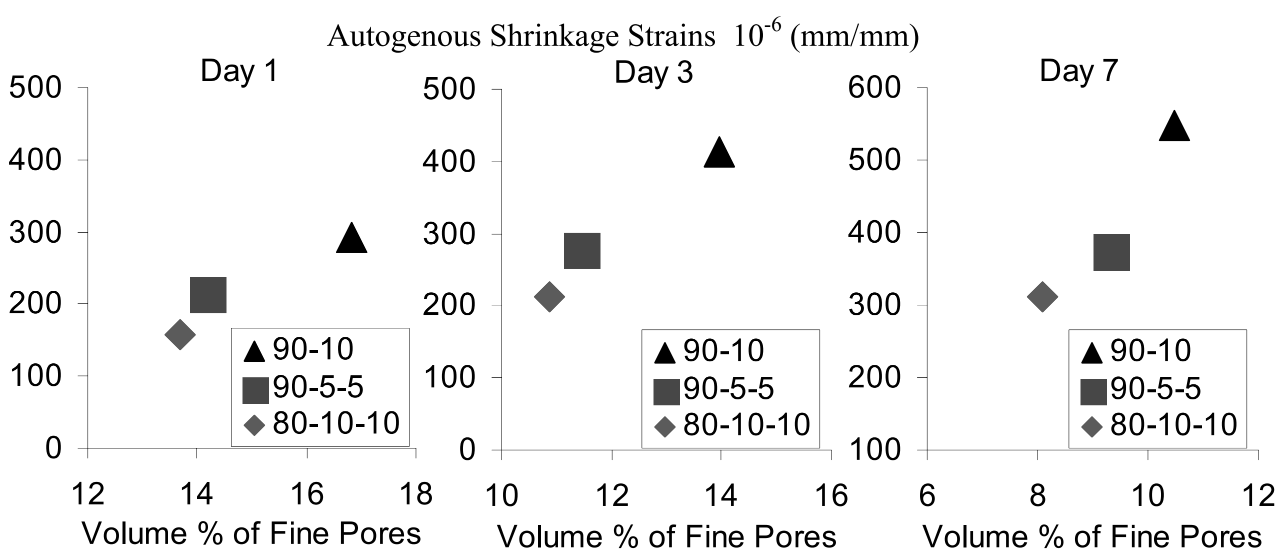

Fig. 2. Relation between the autogenous shrinkage and the volume of finer capillaries (of radius smaller than the critical pore diameter).

The major increase in the fine porosity was measured at the end of one day. Later, the gap between the fine pore volumes was smaller. The major increase in the autogenous shrinkage of silica fume concrete without ultrafine fly ash was measured at the end of 1st day. The rate of increase in the autogenous shrinkage was similar at later ages, proving the link between the fine pore structure and autogenous shrinkage development.

CONCLUSION

By combining supplemantary cementitious materials with different properties, it is possible to tailor the pore microstructure and autogenous shrinkage properties of the high strength concrete. Autogenous shrinkage greatly depends on the pore structure of the hydrating paste. Incorporation of ultrafine fly ash, together with silica fume, restructures the pore system by decreasing the finer pore volume and critical pore size, which in turn, reduces the shrinkage strains that develop during the self-desiccation and relative humidity decrease. This reduces the autogenous shrinkage of high strength concrete, delays the cracking and decreases the crack size without any significant change in the strength gain and hydration rate.

Since the fine pore volume is of importance, further studies are needed in order to understand the effect of gel pores, of diameter smaller than 6 nm, on the autogenous shrinkage. Further studies are also needed to understand the mechanism of the capillary pore formation starting from the early hours of hydration.

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