RESISTENCIA AL CONGELAMIENTO Y DESCONGELAMIENTO DEL CONCRETO DE ALTA RESISTENCIA CON CENIZA VOLANTE CON ALTO CONTENIDO DE CALCIO Y MICROSILICA CONDENSADA

por

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Sinopsis: Se está desarrollando un estudio experimental sobre la resistencia a la compresión y al congelamiento de concretos de alta resistencia con varios niveles de sustitución de ceniza volante (0 a 80%) y un porcentaje prestablecido de microsílica (10%). Se añadió aire incluido a la mezcla para propósitos de comparación. Se estableció la relación agua/adherente óptima a un valor bajo de 0.27 por consideraciones de resistencia y trabajabilidad. Se usó superfluidificante para proporcionar una trabajabilidad adecuada y se mantuvo en un rango de 1.5 a 2.2%. Las relaciones agregado/cemento y agregado grueso/fino se mantuvieron en 5 y 1.22, respectivamente.

El programa de ensayes consistió en evaluar la resistencia a la compresión y dos series de especímenes fueron expuestos a pruebas de congelamiento y descongelamiento. Se encontró que un período de curado de 14 días, como lo especifica el Procedimiento A de ASTM C 666, era inadecuado para las mezclas con alto contenido de ceniza volante debido a la lenta ganancia de resistencia de ese tipo de mezclas. De modo que, todos los especímenes fueron curados en agua con cal por 28 días, antes de someterlos a ciclos de congelamiento y descongelamiento. La primera serie no tenía aire incluido, mientras que las segunda contenía ya sea 4 u 8% de aire incluido.

Los resultados de los ensayes han mostrado que el concreto con hasta un 60% de sustitución de ceniza volante con 10% de microsílica y sin aire incluido, indicaron igual o superior resistencia a la compresión a los 28 y 56 días, cuando se compararon con una mezcla de control con 100% de cemento. Las sustituciones de cemento de hasta 35% de ceniza volante y 10% de microsílica, indicaron una mejora en la resistencia al congelamiento, sin nada de aire incluido. La adición de 8% de aire incluido en la mezcla de 20% de ceniza volante + 10% de microsílica, aumentó el factor de durabilidad en cerca de 10%. También se proporcionan otros resultados incluyendo un estudio utilizando un microscopio electrónico de barrido (SEM).

Palabras clave: Resistencia al congelamiento, compresión, ceniza volante con alto contenido de calcio, superfluidificante, intrusión de aire, durabilidad, SEM.

Freezing and Thawing Resistance of High Strength Concrete containing High Calcium Fly Ash and Condensed Silica Fume

by

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Synopsis: An experimental study was undertaken on the compressive strengths and frost resistance of high strength concrete containing various levels of fly ash replacements(0 to 80%) and a fixed percentage of silica fume(10%). Air-entrainment was added to some of the mixtures for comparison purposes. Optimum water/binder ratio was fixed at a low value of 0.27 for strength and workability considerations. Superplasticizer was used to give proper workability and was maintained in the range of 1.5 to 2.2%. Aggregate/cement and coarse/fine aggregate ratios were maintained at 5 and 1.22, respectively.

The test program consisted of evaluating compressive strength in cylinders and two series of specimens were exposed to freezing and thawing tests. A curing period of 14 days, as specified by ASTM C 666 Procedure A, was found inadequate for the high fly ash mixtures because of the slow strength gain of such mixtures. Hence, all specimens were cured in lime water for 28 days, before subjecting them to freezing and thawing cycles. The first series had no entrained air whereas the second series contained either 4 or 8% entrained air.

The test results have shown that concrete with upto 60% fly ash replacement with 10% silica fume and without entrained air, indicated superior or similar 28 and 56-days compressive strengths, when compared to the 100% cement-control mixture. Replacement of cement by upto 35% fly ash and 10% silica fume, indicated enhanced frost resistance, without any air-entrainment. The addition of 8% air-entrainment in the 20% fly ash + 10% silica fume mixture increased the durability factor by about 10%. Other results were found. A study of matrix morphology and microstructure bonding, using the scanning electron microscope (SEM), helped to explain the observed test results in a comprehensive manner.

Keywords: Frost resistance, compression, high calcium fly ash, superplasticizer, air entrainment, durability, SEM.

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INTRODUCTION

Chemical and / or mineral admixtures are used widely in concrete production in North America for enhanced performance[1]. The increase in use of two such admixtures in concrete, namely, fly ash and silica fume, has been encouraged over the past several years, in order to produce high performance concrete (HPC). In general, high performance is defined by not high strength alone but by high durability and economy as well. In Canada, durability against freezing and thawing is often of overriding importance.

Cracking and loosening up of the binding matrix caused by expansion of freezing water in the void system of the cement paste or the aggregates, is the major deterioration process of frost action on concrete. Detailed discussion, on some of the existing mechanisms are available in the papers published by Powers et al., Litvan and Meier et al.[2, 3, 4].

The use of fly ash in concrete in regulated amounts can enhance the frost resistance of concrete [5]. Fly ash alters the principal frost-damage parameters : namely, porosity and strength of paste, amounts of freezable water and number of voids, in a favorable way by producing a denser and stronger paste due to secondary pozzolanic reactions between the fly ash particles and the $Ca(OH)_2$ [6, 7].

The use of condensed silica fume along with large volumes of lignite fly ash (ASTM type C) in concrete, have been limited worldwide. The work reported herein is part of a research program being conducted on concrete containing 10% silica fume and several levels of fly ash replacements, in order to identify and explain the frost durability aspects of such concrete.

EXPERIMENTAL PROGRAM

Six concrete mixtures were made with CSA Type 10 normal portland cement (ASTM Type 1), Saskatchewan (lignite) fly ash and condensed silica fume. Fly ash content of the mixtures was either 20, 35, 50, 60, 70 or 80% of the weight of binder. Silica fume used was held constant at 10% of the weight of binder. In addition, two control mixtures, one made of 100% CSA type 10 cement and the other of 10% silica fume + 90% CSA type 10 cement, were also made and subjected to the same freezing and thawing tests. The aggregate to binder ratio and the coarse/fine aggregates ratio by weight, were maintained at 5 and 1.22 respectively. The weight of superplasticizer was varied between 1.5 and

2.2% of the weight of cement while the water to binder ratio was maintained at a low value of 0.27. No air entrainment was added initially, to any of the eight mixtures, so as to delete the effect of air-entrainment on strength. However, a second series consisting of 20 and 50% flyash + 10% silica fume with 4% and 8% entrained air, was tested under the same freezing and thawing conditions in order to understand the effect of air entrainment on frost resistance of flyash + silica fume concrete. For the air entrained mixtures, regular liquid organic air entraining agent MB-AE10 meeting ASTM C260 specifications, was used. Physical and chemical analysis of cement, fly ash and condensed silica fume are given in Table 1.

Mixing of concrete was carried out in a pan mixer in accordance with ASTM C 192. Initially, the pan was wetted and the mixer was started. Then the mixing sequence followed was that recommended by CANMET, Ottawa : coarse aggregate, part of water, cement and silica fume (if any), fly ash (if any), remaining part of water, fine aggregate, and finally superplasticizer (if any). The mixing was continued for three minutes, left to rest for two minutes and then remixed for another two minutes to prevent false setting. The air entraining agent was dissolved in the mixing water prior to mixing, whenever air entrainment was used.

The mixtures were tested according to ASTM C 666 Procedure A (rapid freezing and thawing in water). Before subjecting to freezing and thawing cycles, the 90x110x400 mm (3.5x4.5x16 in.) prism specimens were moist cured in lime water for 28-days since, 14 days of curing, as specified by ASTM C 666, was found inadequate for the high flyash mixtures because of the slow strength gain of such mixtures. Besides the freezing and thawing specimens, thirty 75x150 mm (3x6 in.) cylinders were cast in cardboard moulds, for every mixture, in accordance with ASTM C 31 and C 193, and they were moist cured. The cylinders were later tested for compressive strengths at 1, 3, 7, 14, 28 and 56 days. Also, from every batch, three 75x150 mm compressive strength test specimens were cast for the accelerated K-5 strength testing. Details of the physical properties of fresh and hardened concrete are presented in Table 2. The accelerated strength test cylinders were cast in three stainless steel moulds of the K-5 tester which contained plastic linings. Then they were mounted onto the K-5 tester and kept at a temperature of 160 deg.C (300 ± 5 deg.F) and a pressure of 10.34 ± 0.17 MPa (1500 ± 25 psi) for 3 hours and were tested after 2 hours of cooling.

Freezing and thawing Test

After moist curing in lime water for 28-days, four specimens of each mixture, were put inside long, vertical, rectangular, prismatic metal containers which were filled with water and placed inside the freezing and thawing tank, as shown in Fig. 1. Spacers of narrow rods were inserted between the four sides of each specimen and the corresponding faces of the container walls to ensure that the specimens were completely surrounded by approximately 3 mm (1/8 in.) of water on all sides. The specimens were placed on a flat piece of wire mesh at the bottom of the metal container to facilitate water and heat circulation next to the specimen.

The specimens were weighed and their natural frequencies were determined so as to evaluate their relative dynamic modulus of elasticity. The same process was repeated periodically (i.e. after every 23 and 32 cycles). The instrument for measuring the frequencies was a "Sonic Star" assembled in the Engineering Shops with a Type 602 Display Unit of Tektronix, Oregon, as outlined in ASTM C 666 and C 215. Every time the specimens were taken out, they were thoroughly washed in lukewarm water and were surface dried by wiping with a dry bath towel. The containers were also rinsed. The specimens were returned to the containers, turning them end-for-end (that is, top and bottom ends reversed), so that the same ends of the specimens do not always remain at either the bottom or at the top, during the entire freezing and thawing test. A predetermined rotation scheme was employed to shift the specimens to different locations inside the tank, so as to ensure that each specimen was subjected to conditions that prevailed in all parts of the freezing and thawing tank.

The freezing and thawing cycles were stopped after 300 cycles or until the relative dynamic modulus of elasticity reached 60 % of the initial modulus, whichever happened first. The durability factor was calculated as per ASTM C 666. The visual appearance of the specimens and any defect that developed were noted. Photographs of the specimens and their surfaces were taken before and after the freezing and thawing test. The surfaces were examined for texture, cracks, scaling off and exposure of the aggregates. A microstructure study with the help of a scanning electron microscope (SEM) was carried out on samples taken from the specimens, before and after the freezing and thawing tests.

Scanning Electron Microscopy

At the end of the freezing and thawing tests, small samples of about 1 cm^3 (0.06 in^3) each, were taken from the control specimens and from the mid-section of the freezing and thawing specimens, for the scanning electron microscopy (SEM) tests. Each sample was coated with a very thin layer of gold as an electrical conductor and its microstructure was examined under a Philips SEM 505 scanning electron microscope. The results of the SEM study will be discussed later so as to explain changes in microstructure as a result of freezing and thawing. Microprobe Analysis was also performed on some of the specimens in order to identify the elemental composition of the crystals. JEOL : JXA - 860 Superprobe was used for this purpose. The Energy Dispersion Spectrums (EDS) obtained are presented in the next section.

TEST RESULTS AND DISCUSSION

Workability and Compressive Strength

The optimum water to binder ratio was obtained from preliminary testings for maximum compressive strength and proper workability. A water/binder ratio of 0.27 was found suitable and was used for all subsequent testings. The water content of a fresh mixture (used for determination of water/binder ratio), was calculated by subtracting from the total

water added, the water absorbed by the coarse aggregates, and adding the water in the superplasticizer that was used in the mixture. The water content of the concrete mixtures containing high quantities of fly ash were slightly reduced so as to maintain close consistency and workability values. Table 2 indicates the properties of fresh and hardened concrete mixtures.

All mixtures with fly ash and silica fume generally showed lower strength than the control, at the age of 7 days (Table 2). However, with an increase in age, concrete with 20 to 60% fly ash along with 10% silica fume, gave 28 and 56-days strengths similar to that of the control specimens (HP C0-100% cement concrete), as shown in Fig. 2. With further increase in fly ash content beyond 60%, the strength level dropped, possibly due to poor matrix bonding because of the presence of too many unreacted fly ash particles, as evident from SEM micrographs to be discussed later. The 10% silica fume + 90% cement concrete, as well as the 10% silica fume + 20% fly ash + 70% cement concrete, had superior strengths compared to the control, at all ages. Table 2 also indicates that compressive strengths of the air-entrained 20% and the 50% fly ash concretes show lower values compared to their non air-entrained mixtures. Also, high air entrainment (8%) lowers the compressive strengths of the 20 and 50% fly ash mixtures, at all ages.

Resistance to Freezing and Thawing

Mather [8] observed that non-air-entrained concrete with a low water to binder ratio, will be durable against freezing and thawing if it has a compressive strength of about 24 MPa (3500 psi) when subjected to freezing and thawing; this strength reflects the desired strength of the paste which can withstand the pressure in the concrete due to volumetric expansion of the freezing water under frost action. Also, if the water to binder ratio is quite low, all mixing water can combine with the cementitious material and the concrete will develop low permeability; hence producing a condition in which it will be quite unlikely that the paste will critically saturate when freezing takes place. If the paste does not critically saturate on freezing, a satisfactory air-void system is not required for concrete to resist frost. In the present program the water to binder ratio was maintained at a low value of 0.27 and the majority of the concrete specimens were non-air entrained. The 28-days strength of the specimens of all mixtures was higher than 40 MPa (5714 psi) except for the 80% fly ash mixture which had a strength of 28 MPa (4000 psi), when they were subjected to rapid freezing and thawing cycles.

From visual inspection of the specimens after 300 freezing and thawing cycles, significant surface damage and cracks, exposed aggregates and substantial weight loss was observed, for the specimens with 50% or higher fly ash replacement levels. However, compared to the control, the 20% and the 35% fly ash replacement concretes along with 10% silica fume, performed better with regards to loss of dynamic modulus and surface damage. The 10% silica fume concrete showed a very good resistance to freezing and thawing and did not suffer any surface damage, except for minor cracks, after 300 freezing and thawing cycles, as evident in Fig. 3. The average weight loss of specimens of all series versus the mixture-type is shown in Fig. 4. The results for weight loss and

durability of the air-entrained 20% and 50% fly ash concretes, have been plotted in Fig. 4 and 5, respectively, alongwith results of the non air-entrained specimens for better comparison. The average weight loss of the air-entrained mixtures was found to be 20 to 38% lower than the non air-entrained mixtures indicating lesser surface spalling under freezing and thawing cycles, as evident from Fig. 6.

Yuan and Cook [9] observed that durability of non-air-entrained concrete increases as the percentage of fly ash replacement increases up to 30%. In the present series of tests non-air-entrained concrete was used in the majority of the mixtures. The durability factor at 300 cycles (DF_{300}), was computed from the measured relative dynamic modulus and the results for all series were plotted against the fly ash replacement levels as shown in Fig. 5. Concrete with either 20 or 35% fly ash + 10% silica fume and also the 10% silica fume concrete exhibited better performance compared to the 100%-cement control concrete, after 300 freezing and thawing cycles. Durability of 50% fly ash concrete (with 10% silica fume) was found to be comparable to the durability of 100%-cement control concrete. Fly ash replacement beyond the 50% level reduced the frost resistance of concrete substantially and exhibited "poor" performance as per Neville's[10] acceptance recommendation. The 50% fly ash mixture did not show any appreciable increase in its durability factor, upon inclusion of 4 to 8% air-entrainment in the mixture. However, the 20% fly ash mixture with 8% air-entrainment showed a 10% increase in its frost durability factor.

Considering the frost durability factor of concrete (DF) with respect to the presence of silica fume, it is evident from Fig. 5 that the DF decreased linearly as the percentage of fly ash in the mixture was increased. Hence, the presence of fly ash in the mixture did not enhance the frost resistance of CSF concrete at all. However, compared to the frost durability factor of the control (100% type 10 cement) concrete (d_o), the presence of fly ash alongwith 10% CSF, did enhance the frost durability factor (DF) upto a fly ash content of 35% only, as shown in the same figure.

Discussion of microstructure and its effects on bonding and matrix morphology as evident from SEM micrographs, are presented next.

SEM Examination

COMPRESSIVE STRENGTH:

From the compressive strength test results presented in Table 2 and Fig. 2, it is evident that the low fly ash + silica fume mixtures exhibit higher strengths than the 100% cement control concrete. However, increasing fly ash contents upto 50% or more in the mixture brings about a loss of compressive strengths. SEM micrographs presented in Fig. 7, 8 and 9 may explain the observed results. Fig. 7 shows the matrix of a 100% cement control concrete. Well formed platy crystals of $Ca(OH)_2$, are evident in the microstructure. In contrast, the SEM micrograph of Fig. 8 shows a dull, dense matrix of 20% flyash + 10% silica fume concrete with no trace of $Ca(OH)_2$ platelets. The $Ca(OH)_2$ appears to have

been consumed up in the secondary pozzolanic reactions, thereby providing a denser matrix of additional CSH gel deposition. This dense paste structure of flyash + silica fume concrete provides for higher compressive strengths. However, very high fly ash content in the mixture, say 50% or more, leaves numerous rounded unreacted fly ash particles in the matrix after 28 days of moist curing. This is evident in the SEM micrograph of 50% flyash + 10% CSF concrete presented in Fig. 9. The unreacted flyash particles do not bond well with the paste and a very fine gap seems to exist in between the paste and the flyash particle. This presence of too many unreacted flyash particles with poor bonding to the paste, brings about a loss of compressive strengths of the high fly ash concrete mixtures. Fig. 10 shows the microstructure of 20% flyash + 10% silica fume concrete containing 8.3% entrained air, after 28 days of moist curing. Comparing with the microstructure of non air entrained 20% flyash + 10% silica fume concrete as presented in Fig. 8, it is clear that Fig. 10 reveals a honeycombed matrix with numerous air voids, which bring about a loss of compressive strength of the air-entrained mixtures.

SPECIMENS SUBJECTED TO FREEZING AND THAWING:

The microstructure of the paste which influenced the amount of freezable water in the matrix, played a definite role in affecting the frost resistance. The following principal parameters control the frost damage to concrete - porosity of the paste which determines the amount of freezable water in the matrix; paste microstructure and strength and the number of air-voids and cavities. Concrete mixtures with 10% silica fume + 90% cement and mixtures with 20 and 35% fly ash + 10% silica fume, exhibited a relatively dense microstructure, compared to the 100%-cement control concrete (Fig. 11, 12 and 13), due to additional deposition of CSH gel because of secondary pozzolanic reaction. From their dense cementitious matrix, it could be inferred that they contained very little freezable water and hence, were resistant to freezing and thawing cycles. A similar kind of dense matrix was observed in concrete with 50% or more fly ash. However, the presence of unreacted and unhydrated fly ash particles (as evident from the spherical particles and the rounded sockets in Fig. 14a), weakened the matrix bonding thereby adversely affecting the frost resistance. Nonetheless, 50% fly ash concrete exhibited comparable frost resistance to the 100%-cement control concrete . But, with 50% or more fly ash replacement, the presence of too many unreacted fly ash particles brought about early disruption of concrete when subjected to rapid freezing and thawing cycles. Based on the SEM micrographs of Fig. 11 through 16, the following distinct observations and frost deterioration mechanisms may be proposed :

100%-cement control concrete - With decrease in temperature, portlandite migrates through capillaries to cracks and pores and deposits platy $Ca(OH)_2$ over hydration products scattered throughout the matrix (Fig. 15), thereby loosening up the binding matrix.

10% silica fume + 90% cement concrete - Exhibits a dark dense matrix due to additional CSH gel formation as a result of secondary pozzolanic reaction. No platy $Ca(OH)_2$ crystals are evident (Fig. 12). The dense matrix made this concrete very resistant to frost cycles.

Fly ash + silica fume concrete - The densification of matrix due to additional CSH formation from secondary pozzolanic reactions and the absence of platy $Ca(OH)_2$, was also observed in this concrete (Fig. 13 and 14a). Hence, fly ash + silica fume concrete (upto 35% fly ash) exhibited good frost resistance. However, with increasing fly ash contents, the presence of unreacted fly ash particles (Fig. 14a), which did not bond well with the matrix (Fig. 9), weakened the microstructure bonding thereby adversely affecting the frost resistance of such concrete. The Energy Dispersion Spectrum (EDS) on the surface of an unreacted flyash particle is shown in Fig. 14b. Heavy presence of silicon, some aluminium and very little calcium marks the spectrum. The needle-like crystals, strewn across the matrix of 50% flyash + 10% CSF concrete as shown in Fig. 14a, were identified as ettringite crystals from the EDS shown in Fig. 14c. Calcium, sulphur and aluminium in the spectrum confirmed the presence of ettringite which is calcium sulphoaluminate.

Previous investigators [5] observed that under freezing and thawing cycles, air-entrained fly ash concrete deteriorated by migration of ettringite and $Ca(OH)_2$ from the paste structure to the air-voids in the concrete, thereby weakening up the matrix. In the present series, majority of the tests were non-air entrained concrete and the deposition of needle-like ettringite and $Ca(OH)_2$ in the air-voids were not evident since very little air-voids were present. However, needle-like ettringite crystals were found scattered throughout the matrix (Fig. 14a) and over the unreacted fly ash particles (Fig. 16) after the freezing and thawing tests. From the above observation, the following process is postulated : With depletion of $Ca(OH)_2$ due to secondary pozzolanic reactions, the solubility of ettringite increased. And, with the freezing of water due to frost cycles, volumetric expansion occured and the excess of water, now containing dissolved ettringite is expelled from the pores, through capillaries, into micro-cracks and fine gaps (Fig. 9) in between the unhydrated fly ash and the CSH matrix. The migration of ettringite in solution, weakens the binding matrix. The fine water gaps which were observed by other investigators too [6, 11, 12], failed to close even after 28-days of lime water curing (Fig. 9) and thus played a role in the frost deterioration mechanism.

For the air entrained mixtures, the presence of 8.2% entrained air in the 20% fly ash concrete, enhanced the frost durability factor by about 10%. Fig. 17 show the matrix of 20% flyash concrete before and after the freezing and thawing cycles. In contrast to Fig. 13 which exhibits dense non air-entrained matrix of 20% flyash concrete, Fig. 17 shows a honeycombed like structure caused by rounded sockets of entrained air in the 20% flyash air-entrained concrete. This brought about an average 12% loss of compressive strength of the air-entrained 20% flyash + 10% silica fume concrete. However, for the 50% fly ash concrete, air-entrainment of the order of 8.7% did not enhance its frost durability appreciably, as the presence of too many unreacted fly ash particles in the matrix with poor bonding to the paste, brought about early disruption of such concrete (Fig. 9). The presence of too many unreacted fly ash particles in high fly ash concrete could be either due to lack of $Ca(OH)_2$ as a result of fast pozzolanic reactions of condensed silica fume, or due to insufficient curing time of only 28 days. Hence, freezing and thawing resistance of high fly ash concrete warrants further research to fully understand its frost deterioration mechanism.

CONCLUSIONS

Based on the analysis of the test results and the microscopic analysis of concrete microstructure, the following conclusions are drawn :

1. Concrete with 10% CSF and high quantities of fly ash showed low early strengths. However, beyond 28 days, concrete with upto 60% fly ash and 10% CSF showed superior or at least equal compressive strengths to the type 10 cement-control concrete. The high compressive strengths of fly ash + CSF mixtures was attributed to denser paste structures compared to the 100% cement-control concrete. Air entrained fly ash + silica fume concrete mixtures showed lower compressive strengths compared to the non-air entrained mixtures.

2. Using 10% CSF only, as a cement replacement, improved the strength and durability of concrete exposed to freezing and thawing cycles.

3. Using up to 35% fly ash and 10% condensed silica fume (CSF) by weight, in the binder, provided satisfactory frost durable concrete. Durability of 50% fly ash concrete (with 10% silica fume) was found to be comparable to the durability of 100%-cement control concrete. Fly ash replacement beyond the 50% level reduced the frost resistance of concrete substantially. Using air-entrainment of 4 to 8 % in concrete mixtures, enhanced the frost resistance of 20% fly ash + 10% CSF concrete. However, for the 50% fly ash + 10% CSF concrete, air entrainment did not enhance its frost resistance significantly.

4. The presence of too many unreacted fly ash particles in high fly ash + silica fume concrete, adversely affected its frost resistance. The presence of unreacted fly ash particles could possibly be due to the depletion of available $Ca(OH)_2$ as a result of the fast secondary pozzolanic reactions of condensed silica fume or due to insufficient curing time of 28 days.

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