Air-entraining Admixtures for Use with Fly Ashes Having High Carbon Contents

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Synopsis: New air-entraining admixtures (AEA), suitable for use with concrete containing fly ashes having levels of unburned carbon higher than the typical 2-4% allowed in the concrete industry, have been tested in this study.

A number of new AEA were selected using a mortar test. Results obtained on mortar were validated on concrete. The criteria for the evaluation of the admixtures in concrete were the dosage required for a specific air content, the sensitivity of the admixture to the carbon content of the fly ash, and the stability of the air in the fresh concrete during the first hour after the contact between the binder and the water. The air-void system of the hardened concrete was determined for the product found to be the most promising.

A full testing program in concrete of the selected air-entraining admixture was then undertaken including durability testing. Concrete having three different water-to-binder ratios were used (0.5, 0.42 and 0.32). The fly ash content of the concrete were 30% for the two higher water-to-binder ratios and 55% for the lower water-to-binder ratio concrete which was a typical high volume fly ash concrete. The new air-entraining admixture's family is suitable for fly ash having high carbon content, but it showed a poor compatibility with sulfonated water reducing admixtures. When used in combination with polycarboxylate-based water reducing admixtures, no special problem was experienced with the air entrainment. Generally, the new air-entraining admixture's family does not affect negatively the properties of the fresh concrete. The measured durability parameters and all other properties of the hardened concrete are very satisfying.

Keywords: Air-entraining agents; air bubbles; activated charcoal; admixtures; air-void parameters; carbon content; durability; fly ash; concrete; mortars; portland cement; water-reducing admixtures; superplasticizers.

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INTRODUCTION

Due to the increased concern in the industry for it to comply with the Clean Air Act Amendments imposed in 1990 by the US Environment Protection Agency (EPA), many utilities have changed their conventional burners to low-NOx burners (LNBs) in power plants to meet the EPA proposed regulation on NOx emission. As a result, the characteristics of the fly ash generated have been affected, and the increase in the residual carbon content is one of the examples (1, 2).

Currently available air-entraining admixtures (AEA) have considerably reduced effectiveness when used with fly ash with high level of residual carbon. Specified air contents are thus more difficult to achieve and maintain during concrete placement (3). This problem precludes the use of millions of tons of fly ash currently available in the US and Canada that otherwise meet the ASTM C 618 requirements.

The desired characteristics of the new AEA are that it should be able to produce adequate stable air-void parameters in concrete incorporating fly ashes that contain high levels of carbon. Ideally, the dosage of the new AEA should be similar to or lower than that of the currently commercially available AEA, and should not be significantly affected by normal variations in the carbon content of the fly ash. Also, the new AEA should be compatible with other chemical admixtures for concrete such as water-reducing admixtures and superplasticizers, and should not affect other properties of concrete such as workability of the fresh concrete and mechanical properties, and durability of the hardened concrete.

OBJECTIVES

The objective of this project was to develop a new air-entraining admixture that is effective in concrete incorporating fly ash with high carbon contents. The main responsibility of ICON/CANMET was to evaluate a new AEA developed by a Canadian admixtures producer, provide this company with feedback to help them make adjustments to the products, and then evaluate the most promising final product in concrete.

SCOPE OF THE WORK

The project was divided into several phases and tasks. First, a number of fly ashes covering a range of carbon contents were selected across the U.S.A., and characterized for their chemical and mineralogical compositions, and physical properties. The carbon in the fly ash was also characterized since it is important to explain how the carbon in fly ash affects the air-entraining admixture and this is especially helpful in the development of new admixtures (3). The following task was to select the most promising AEA based on testing in mortar. The results were then validated in concrete for the selected AEA that showed the most promising results. The criteria for the evaluation in concrete of the admixtures were the dosage required for a specific air content, and the stability of the air. The effect of the selected AEA on the air content of fresh and hardened concrete was determined.

MATERIALS

Cement

A commercially available CSA Type 10 normal portland cement (equivalent to ASTM Type I) was used in all the mortar and concrete mixtures. Its chemical composition and physical properties are shown in Table 1.

Aggregates

The sand for the mortars was standard graded sand meeting the requirements of ASTM C 778. The fine aggregate for the concrete mixtures was a natural sand. The coarse aggregate was a crushed limestone. The properties and grading of the fine and coarse aggregates used in the concrete mixtures are given in Tables 2 and 3.

Charcoal

A commercial activated charcoal having a specific surface of 500 m^2/g as determined by BET method was used in some concrete mixtures to determine the effect of carbon content on the dosage of the air-entraining admixtures.

Air-Entraining Admixtures

A total of seven families of surfactants were investigated as potential new air-entraining admixtures (AEA) in this project. Two commercially available admixtures were used as references in the mortar and the concrete mixtures. A first series of four new AEA were produced and sent by the admixture producer for evaluation. These products, identified as L4 (sulfate ether-based admixture), ND, NS and NA (sulfonates-based admixtures), were evaluated both in mortars and concrete. An additional admixture, ND_b, which was a modified version of ND with less residual sulfates content and lower solid contents (20%) was subsequently produced and evaluated in concrete.

Fly ashes

Nine fly ashes (generated from low-NOx burners) covering a range of carbon contents (LOI) from 1.5 to 21.5% have been selected from utilities in the USA. Corresponding information on the type of the burner system, operating conditions and the parameters of the power station from which the fly ashes are generated were collected. The Table 4 presents the above information as collected by the Electrical Power Research Institute, Palo Alto, California, U.S.A.

CHARACTERIZATION OF FLY ASHES

Composition of the fly ashes

The fly ashes selected were characterized by determining their chemical composition using X-ray fluorescence spectroscopy for CaO, SiO_2, Al_2O_3, Fe_2O_3, MgO, Na_2O, K_2O, and SO_3 content. Gravimetry measurements were used for loss on ignition and the carbon content in the fly ashes was determined using Leco combustion technique. The chemical analysis of the fly ashes is given in Table 5. The mineralogical composition of the fly ashes was determined by X-ray diffraction. All the fly ashes contain the same crystalline components that are Quartz (SiO_2), Mullite ($3Al_2O_3.2SiO_2$) and Magnetite (Fe_3O_4).

Physical properties of the fly ashes

The physical properties such as fineness, specific gravity and soundness of the fly ashes were determined according to ASTM standard tests. The fraction of the fly ashes retained on 45µm sieve (No. 325) was determined according to ASTM C430. The water requirement and the strength activity were determined according to ASTM C311. The physical properties of the fly ashes of this study are shown in Table 6.

MORTAR TEST RESULTS AND DISCUSSION

The air content in mortar was determined according to C185-01 ASTM standard. 20 % of the cement was replaced by the fly ash in mortar incorporating fly ashes. The results obtained on mortar mixtures showed that ND and NA admixtures performed better than the other AEA investigated including the reference admixtures (Table 7). In particular, the ND admixture demonstrated the best performance entraining the target air content (20% or more) in all the mortars regardless of the fly ash used, even for the mortar made with the Shawville-2 fly ash that has a very high carbon content of 13.4% (Figure 1). Surprisingly the reference 1 AEA, which was supposed to be designed for use in concrete incorporating fly ash with high carbon content, did not perform well.

Table 8 shows results obtained with ND and NA admixtures, and compared to the reference-2 admixture, using eight fly ashes having a carbon content ranging from 0.4% to 13.4 %. The ND air-entraining admixture performed very well showing a similar air content regardless of the fly ash used (Figure 2).

Although the dosage of 1 ml used for the ND admixture is high compared to 0.1ml used for NS and L4 AEA or 0.5 ml used for both NA and the reference 2, the ND admixture appears the most promising since it is the only one that was not affected by the type of the fly ash used. Also, the dosage used for this admixture was the same as that used for the reference 1 admixture which was specifically developed for high carbon content fly ashes.

Results on mortars, that tend to demonstrate the superior performance of ND admixture are in line with those obtained by the researchers from the University of Sherbrooke during the development of the new products (4). However, these need to be validated in concrete tests.

PRELIMINARY CONCRETE TEST RESULTS AND DISCUSSION

Dosage of AEA

The first phase of the testing in concrete consisted essentially in validating the mortar test results by comparing the dosage of the different AEA for obtaining a target air content (5 to 7%) in concrete incorporating the different fly ashes.

Concrete having a water-to-binder ratio of 0.5 and a coarse aggregates content of 40% of the total volume of the concrete were made. The concrete incorporated 30% of fly ash in replacement of the cement.

The concrete tests were performed on concrete incorporating four fly ashes: Bowen, Crist, Portland and Shawville-2, covering a wide range of carbon contents. Figure 3 shows that, in the case of the Bowen fly ash (3.3% of C), the dosage of the reference 1 admixture was 360 ml/100 kg of binder to obtain an air content of 8%. This dosage is very high compared to that used with all the other admixtures tested. Consequently, it was decided to discard this admixture for the rest of the study, and use only the reference 2 admixture. In fact the dosage of the reference 2 admixture required to obtain an air content of 5.2% was 90 ml/100 kg of binder, which is acceptable. For ND, NS, NA and L4 admixtures provided by the admixtures producer, dosages of 30, 45, 75 and 90 ml/100 kg of binder were needed to obtain air contents of 5.6%, 8.0%, 5.1% and 4.8%, respectively. The L4 admixture, which required the same dosage as the reference 2 admixture, but produced a slightly lower air content was also discarded at this stage of the study. The same trend was observed with the mixtures incorporating Crist fly ash (8.7% of C), but the dosages were significantly higher in this case (Figure 4). Table 9 summarizes the dosages required and air contents achieved for the concrete mixtures using the different AEA and fly ashes. Each data is an average value of two or more test results.

The results tend to demonstrate that three new AEAs are promising as they performed better than the reference admixtures. These three admixtures are ND, NS and NA. The ND admixture performed better than NS and NA, and this is in agreement with the results obtained on the mortar mixtures. The reference 1 admixture showed the worst performance.

The Crist fly ash (carbon content of 8.7%) affected the dosage of AEA more than Shawville-2 fly ash, which has a significantly higher carbon content (13.4%). This behavior is in line with results obtained at the University of Sherbrooke (4), and is possibly related to the characteristics of the carbon in that fly ash. In fact the specific surface of this fly ash, as determined by the BET method is significantly higher than that of the three other fly ashes (Table 10).

In contradiction with the results on mortar, the dosage of all the AEA tested, including ND, were significantly affected by the fly ash used in the concrete, and therefore, most probably by the carbon content of the fly ash. However, in spite of the fact that the results on concrete are not as encouraging as those obtained on mortar, it appears that the ND family of admixtures provides the most promising new air-entraining admixtures tested so far in this study. A new version of the ND was developed at this stage (ND_b) and included in the study; its performance was very similar to that of the initial ND admixture with a better stability of the entrained air, as it will be discussed later (Fig.9).

Effect of carbon content of a fly ash

The purpose of the second phase of testing on concrete was to isolate the effect of the carbon content of the fly ash on the dosage of air-entraining admixture by adding carbon artificially to a specific fly ash thus eliminating the effect of other parameters such as the chemical composition and the fineness of the fly ash that can also influence the AEA requirement. This would then provide additional information about which AEA is less affected by the carbon, and consequently which one is the most promising.

An attempt was made to obtain from the industry a sample of fly ash previously separated from its carbon content by triboelectrostatic process, as well as a sample of the carbon removed from the ash (5,6). It would have then been possible to reintroduce the carbon in specific proportions in the fly ash. However, after some contacts with the industry this was not possible. Our solution was to use the charcoal even if we knew that it's surface activity might be higher compared to that of the carbon from the fly ash. Selected amount of charcoal, 1, 2, 3 and 4% by weight of the fly ash were added to the Bowen fly ash, which has a relatively low initial carbon content of 3.3%. The specific surface of the Bowen fly ash mixed to charcoal is given in figure 5.

The results showed that all the admixtures tested are sensitive to the charcoal addition (Fig. 6). It is possible that the addition of charcoal was too demanding for the admixtures and does not reflect well the reality when the carbon content of the fly ash may vary from load to load and cause problems to a concrete producer. However, results confirm that the ND admixture appears the most promising, since it’s dosage remains lower compared to other admixtures.

Effect of the Concentration of the AEA Admixture

The effect of the concentration of the ND_b admixture on the air content of the concrete was studied. Results are presented in figures 7 and 8. Generally, the higher is the dosage of the admixture, the higher is the air content in the concrete. For the ND_b admixture however, we have seen that an optimum dosage is needed to achieve a certain amount of air in the fresh concrete incorporating fly ash or not, but beyond this concentration there is very small increase of the air content of the concrete. This is interesting because a possible error in the dosage of this admixture will not lead to discard the concrete.

Stability of air entrained

Two fly ashes were used to determine the stability of the air entrained in the concrete: Bowen (3.3 % of carbon content) and Portland (6.8% of carbon content). The three remaining admixtures in the study, ND, NS and NA in addition to the reference 2 admixture were used initially. The new version of the ND admixture, ND_b, was also included in the study later on.

The air content, the unit weight and the slump of the concrete were monitored during the first hour following the contact between the mixing water and the cementitious material (cement + fly ash). Measurements were made at 10 minutes, 30 and 60 minutes.

Results are summarized in Table 11. The initial air entrained by ND, NS and NA admixtures was high, but quickly decreased with time. The concrete made using the reference 2 kept it's entrained air significantly better than the concrete made with ND and NS admixtures. Among these new admixtures, NA performed the best (Figure 9). The new version of ND (ND_b) performed better than the initial ND, the NS and the NA admixtures. The air produced with this new admixture was quite stable, similar to the result obtained with the reference 2 admixture.

Air-void parameters of hardened concrete

Preliminary analysis of air-void parameters of the hardened concrete was undertaken according to ASTM C 457 standard (Modified Point Count) on concrete made with the ND_b admixture. Results are presented in Table 12. The spacing factor ($\bar{L}$) and the specific surface of the air bubbles were determined. For the concrete analyzed so far, the spacing factors are lower than 230 μm, the value specified by the CAN A 23.1 standard as the mean value for this parameter to achieve a suitable behavior of the concrete exposed to severe conditions of freezing and thawing. The specific surface of the air bubbles, (α), was higher than 25 mm^{-1}, the minimum value recommended by the CAN A 23.1 standard, which means that the air entrained by this new admixture is formed by small bubbles well dispersed into the concrete mass as desired (7).

TESTING RESULTS ON CONCRETE

After the producer has completed all the desired adjustments of the ND admixtures, we have undertaken a full program of testing of this admixture in concrete. The Bowen fly ash, which incorporates 3.3 % of carbon was used in most of the mixtures.

Two series of four concrete mixtures each have been made with water-to-binder ratios of 0.50 (C1 to C4) and 0.42 (C5 to C8) respectively. In each series the concrete mixtures included one non-air entrained control mixture without fly ash (C1 and C5), one air-entrained control mixture without fly ash (C2 and C6) and two air-entrained mixtures incorporating 30% of fly ash. Two air-entrained admixtures, ND and a reference product (concrete C3 and C8) were used for the fly ash concrete mixtures. The Portland fly ash having a carbon content of 6.8 % was used in two concrete mixtures C9 and C11.

Tests done on fresh concrete included the slump measurement, air content, unit weight, bleeding and temperature of the concrete. Tests done on the hardened concrete included setting time (ASTM C 403), compressive strength (1, 7, 28 and 91 days according to ASTM C 39), flexural strength (ASTM C 78) and Young's modulus of elasticity (ASTM C 469) at 28 days, resistance to chloride ions penetration (ASTM C 1202) at 28 and 91 days, air voids system measurements (ASTM C 457) and resistance to the freezing and thawing cycling (ASTM C 666). The results obtained for hardened concrete of these two series are given in Table 17. The durability results for these concrete are presented in Table 19. For the concrete with W/B = 0.42, two water-reducing admixtures have been used: a lignosulfonate-based water-reducer and a carboxylic acid-based water-reducer.

A third series of three high-volume fly ash concretes (HVFAC) was done to verify if the new admixture is compatible with superplasticizers. Two types of superplasticizers have been used in the high-volume fly ash concrete: a naphthalene-based and a polyacrylate-based superplasticizer. One HVFAC mixture used the reference 2 as air-entraining admixture whereas the two other concrete mixtures used the ND air-entraining admixture. Results obtained for the high-volume fly ash concretes are summarized in Tables 18 and 20. The mixtures proportions and properties of the fresh concrete for the three series of mixtures are given in Table 13 to Table 16.

Properties of fresh concrete

The properties of the fresh concrete are given in Table 13 for the first two series of mixtures. The values of the initial slump and the air content targeted for these two series of concrete were 100 ± 20 mm and 5 ± 1% respectively. All mixtures had the required initial slump (Table 13).

The air content of the concrete made with the reference admixture is within the limits of the targeted values (5.2 and 6.5%). Concrete made with the ND air-entraining admixture had a little bit more air (6.6 to 8.0%) than the targeted value even if the dosage used for the ND admixture (15 to 30 ml/100 kg of the binder) is much lower than the dosage of the reference admixture (80 to 90 ml/100 kg of the binder). This is in agreement with the results obtained previously on mortar and concrete with these types of new admixtures. The dosage of the ND admixture in the concrete incorporating fly ash is twice the dosage used in the control concrete without fly ash (8). For HVFA concrete made with the polysulfonated-based superplasticizer, the air content of the concrete is low.

Setting time and bleeding of the concrete

The bleeding and the setting time of the fresh concrete were determined for all the mixtures: results showed that concrete made with the new admixture bleed less than that made with the reference admixture (Table 15). The initial and the final setting time of concrete made with the new admixtures (C4, and

C7) are shorter than that of the concrete incorporating the reference admixture (C3 and C8) for the same water-to-binder ratio even if the air content for the former concrete is higher. The dosage of the new admixture is 3 times lower than that of the reference admixture, which can explain this interesting behavior.

Compatibility with water-reducing admixtures

Concrete having a W/B of 0.42 needed the use of a water-reducing admixture to obtain the desired slump. Two types of water-reducing admixtures were used, a lignosulfonate-based water-reducing admixture for concrete C5 and C6 and a carboxylic acid-based water-reducing admixture for concrete C7 and C8. The dosage of the two water-reducing admixtures varied from 265 to 330 ml/100 kg of the binder. For concrete C6 and C7 the ND air-entraining agent was used. The air content obtained for the two concrete (7.6 and 7.1 % respectively) indicates that the ND air-entraining admixture is compatible with the two types of water-reducing admixtures. Other properties of the fresh concrete including the setting time and the bleeding are not negatively affected by the combination of the ND air-entraining agent and the two water-reducing admixtures (Table 15).

Properties of the hardened concrete

Compressive strength

Compressive strength and other properties of the two series of concrete are presented in Table 17. Cast specimens for mechanical testing (100x200 mm cylinders, prisms, etc.) were cured in moist conditions. Values of 1-day and 7-days compressive strength of concrete made with the ND admixture is higher than that made with the reference AEA admixture for both W/B. The higher dosage of reference AEA admixture is possibly responsible of this decrease of the compressive strength as a consequence of the longer setting time observed on the fresh concrete. At later ages (28 and 91 days) the compressive strengths of the concrete made with both admixtures are quite similar. Concrete incorporating fly ash develops lower compressive strength than the control without fly ash at early ages, but at 91-days both types of concrete had the same strength. Control mixtures C1 (W/B = 0.5) and C5 (W/B = 0.42) without fly ash and entrained air had the higher compressive strength at all ages.

For High Volume Fly Ash (HVFA) concrete the compressive strength is very low after one day, 10.5 MPa for C9, 10.7 MPa for C10 and 11.6 MPa for C11 (Table 18). This is due to the combined use of a high fly ash content and the needed presence of a superplasticizer to achieve a desired initial slump of 200 ± 20 mm. However the superplasticizer had not have much effect on the setting time of the concrete.

The later age compressive strength was low compared to the two first series of concrete, but the strength development rate is higher for the HVFA concrete, which anticipates an ultimate higher compressive strength (9). There is no significant difference due to the type of air-entraining admixture used.

Flexural Strength and Young's Modulus of Elasticity

The flexural strength and Young's modulus of elasticity of the first two series of concrete were measured after 28 days of curing of the specimens. Results are shown in Table 17. No significant difference is observed between the concrete made with both air-entraining admixtures for the two W/B. A similar trend for both parameters measured is observed in High Volume Fly ash concrete (Table 18).

Resistance to Chloride-ions penetration

The resistance of concrete to the Chloride-ions penetration was evaluated according to ASTM C 1202 standard. Results are presented in Table 17. Permeability of concrete is fundamental in determining the rates of mass-transport relevant to destructive chemical action of aggressive agents. The resistance to chloride ions penetration, expressed as the charge passing through the specimen in coulombs, is higher for fly ash concrete for both water-to-binder ratios as expected. At 91 days, the total charge passing is less than 875 coulombs for the fly ash concretes, whereas that of the control is more than 2600 coulombs. Fly ash concrete is more compact than the control due to the pozzolanic reaction of the fly ash (10). Results show that there is no impact of the air-entraining agent on this parameter as concrete made with the two air-entraining admixtures presented similar values of passing charge at all ages.

The High Volume Fly Ash series (Table 18) showed low values of total charge passed: 870 and 880 coulombs at 28 days for the two concrete made with the ND admixture (C10 and C11) and 1120 coulombs for the concrete made with the reference admixtures. Very low values of 380, 420 and 480 coulombs respectively were obtained for the three mixtures. The very low W/B and the microstructure refinement due to the pozzolanic reaction between the fly ash and the lime produced by the cement hydration is responsible of this high resistance to the Cl-ions penetration (11).

Air voids parameters

The air-void parameters of the hardened concrete were measured according to ASTM C 457 standard (Modified Point Count). This is the most important test, which gives the efficiency of an air-entraining admixture (12). Concrete having adequate air voids parameters will be durable when exposed to freezing and thawing cycling. Results for the first two series of mixtures are presented in Table 17. The air content in the hardened concrete is 5% or more for the six air-entrained concretes. This means that the stability of the air is excellent for both air- entraining admixtures. The spacing factor ($\bar{L}$) and the specific surface (α) of the air bubbles were determined. For all the concrete analyzed, the spacing factors ranged from 100 (C3) to 186 (C8). These figures are lower than 230 μm, the limit value specified by the CAN A 23.1 standard as the mean value for this parameter to achieve a suitable behavior of the concrete facing severe conditions of freezing and thawing. In all cases the specific surface of the air bubbles, (α), is higher than 25 mm^{-1}, the minimum value recommended by the CAN A 23.1 standard, which means that the air entrained by both admixture is formed by small bubbles well dispersed into the concrete.

In the case of High Volume Fly Ash mixtures, C9, C10 and C11, air content in the hardened concrete is 4.5, 3.3 and 6.0% respectively (Table 18). Spacing factor values of 120, 230 and 101 μm respectively and specific surface of air bubbles of 25.4, 38.7 and 41.1 mm^{-1} respectively were measured for the concrete. The poor compatibility between the polysulfonated-based superplasticizer and the ND air-entraining admixture is possibly responsible for the low air content and the poor characteristics of the air void system of the concrete mixture C10. On the contrary, the air void system of the concrete C11 which was made with an acrylic-based superplasticizer had excellent characteristics even if this mixture incorporated a fly ash having a high carbon content (6.8%). This is an indication of the good compatibility between the ND admixtures and the acrylic-based superplasticizer. Concrete C9 used the reference product as an air-entraining admixture.

Resistance to Repeated Cycles of Freezing and Thawing

The durability parameters of the concrete were evaluated by submitting the specimens to freezing and thawing cycles according to ASTM C 666 standard, Procedure A. Results expressed as percent of change in length, weight, resonant frequency, pulse velocity and the calculated durability factor of the concrete are presented in Table 19 for the first two series of concrete. For each concrete, a reference prism not submitted to freezing and thawing cycles and cured in a moist environment is tested along with the specimens submitted to freezing and thawing cycles. Residual flexural strength was also determined for the reference and the specimens submitted to freezing and thawing cycles (Table 19). Concrete with adequate air voids parameters must have a good frost resistance. It is for this purpose that air-entraining admixtures were developed. It has been demonstrated in many works at CANMET that fly ash has no apparent ill effects on the frost resistance of concrete when a proper volume of air is entrained and the characteristics of the air-void system meet the generally accepted criteria (13,14,15). Results obtained in this study indicate a very good performance of all the concrete tested for both water-to-binder ratios. The durability factor is within 100 and 104 for the concrete, which is excellent. The residual flexural strength of the specimens submitted to freezing and thawing, expressed as a percentage of the flexural strength of the reference prism not submitted to freezing and thawing, is very good for the fly ash concrete made with the new air entraining agent (C4, C7) with values varying from 94 to 98% compared to 87.5% and 90% for the two concrete mixtures (C3 and C8) made with the reference admixture.

In the case of High Volume Fly Ash Concrete (Table 20), the durability factor is sligtly lower for the concrete C10, made with a polysulfonated-based superplasticizer and the ND air-entraining admixture compared to the other concrete because the air content in the concrete is very low (3.3%). The air void system parameters for this concrete with a spacing factor and a specific surface of the bubbles of 230 µm and 25.4 mm^{-1} respectively are at the limit of generally accepted criteria. Durability data of the concrete C11 made with an acrylic-based superplasticizer and the ND air-entraining agent are very good: the durability factor has an excellent value of 104. The characteristics of the air voids are excellent for this concrete. The air content in the hardened concrete is 6.0% (7.2% in the fresh concrete) and the spacing factor and the specific surface of the bubbles are 101 µm and 41.1 mm^{-1} respectively even if this concrete incorporated the Portland fly ash which had a carbon content of 6.8%. Concrete C9, made with the reference admixture and a naphthalene polysulfonated-based superplasticizer showed good durability data. This concrete was done with the Portland fly ash. The residual flexural strength after 300 cycles of freezing and thawing is low for this series of mixtures due to the low strength development of the concrete submitted to repeated cycles of freezing and thawing compared to the relatively high strength development of the reference prisms not submitted to freezing and thawing cycling. The percentage of the flexural strength of the specimens tested compared to the reference prisms cured in a moist environment was 60.9% for the C10 mixture, 65.7% for the C9 and 72% for the C11 mixture. The residual flexural strength is negatively affected by low air content and a poor air void system, which is the case for the concrete C10.

CONCLUDING REMARKS

The objective of this study was to evaluate the potential use of a series of new air-entraining admixtures in concrete incorporating fly ashes with a high carbon content. After many tests on mortars and concrete, adjustments were made by the producer on the most promising admixture to finally obtain an admixture as suitable as possible for use in concrete incorporating fly ash with a high carbon content. The final product (ND_b) showed real potential in producing adequate air content in fresh concrete and a very good air void system in the hardened concrete. The difference in the air content of the fresh and the hardened concrete is not high, which indicates a good stability of the air entrained. The new air-entraining admixture is less sensitive to the over-dosage compared to the reference product, which is interesting from a practical point of view for concrete producers.

All properties of fresh concrete evaluated along with the mechanical properties of the hardened concrete are similar for the new admixture and the reference. There is no ill effect to use this admixture in concrete, even if the fly ash content of the concrete is as high as 55%.

The resistance to chloride ions penetration and the frost-resistance of concrete made with this new admixture are excellent: this admixture did not affect negatively the durability of the concrete.

The only problem remaining to solve is the poor compatibility of this new admixture with polysulfonate-based high-range water reducing admixtures. However the compatibility with acrylic-based water-reducing agents is very good.

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Table 1 – Chemical composition and physical properties of the cement

	CSA Type 10 (ASTM Type I)
Chemical Composition, % SiO_2 Al_2O_3 Fe_2O_3 CaO MgO Na_2O K_2O TiO_2 MnO SO_3 LOI	 20.33 4.36 2.99 62.92 2.72 0.27 0.83 0.19 0.04 3.23 2.32
Physical Properties Passing 45 µm, % Blaine, cm^2/g Specific Gravity Compressive strength on cubes, MPa 3 days 7 days 28 days	 93.2 402 3.15 28.2 33.0 40.8

Table - 2 Grading of aggregates

Coarse Aggregate			**Fine Aggregate**		
Sieve size		Cumulative Percentage Retained	Sieve size		Cumulative percentage retained
mm	(in)		mm		
19.0	(3/4)	0	4.75	(No.4)	0
12.7	(1/2)	30	2.36	(No.8)	10.0
9.5	(3/8)	70	1.18	(No.16)	32.5
4.75	(No.4)	100	0.60	(No.30)	57.5
			0.30	(No.50)	80.0
			0.15	(No.100)	94.0
			pan		100.0

Table - 3 Physical properties of aggregates

	Coarse Aggregate	**Fine Aggregate**
Specific gravity	2.72	2.70
Absorption	0.5	0.8

Table 4 - Information on Fly Ashes

Location	Company	Plant	Boiler Type	Burner Type	Coal Type	Class	LOI (%)	C (%)
Portland Pennsylvania	Southern Co.	Portland	ABB C-E Tangential Fired	ABB C-E Low Nox level	Western Pa. Pittsburgh seam bituminous	F	10.1	6.8
New Florence Pennsylvania	Southern Co.	Steward	ABB C-E Tangential Fired	No low NOx burner	Western Pa. bituminous	F	4.1	3.3
Shawville Pennsylvania	Southern Co.	Shawville	B&W Front Fired	B&W DRB-XCL Low NOx	Western Pa. bituminous	F	21.5	19.3
			ABB C-E Tangential Fired	C-E LNCFSlllOver fired air	Western Pa. bituminous	F	15.8	13.4
			ABB C-E Tangential Fired	C-E LNCFSlllOver fired air	Western Pa. bituminous	F	6.4	4.8
Taylorsville Georgia	Georgia Power (Southern Co.)	Bowen	C.E. Boiler	Low NOx Burner	Sub-bituminous coal from Kentucky	F	4.8	3.3
Pensacola Fl	Gulf Power Co. (Southern Co.)	Crist	Foster-Wheeler Opposed wall Fired	Foster-Wheeler Low NOx Burner	Blend (South America, Appalachian and Illinois basin)	F	10.5	8.7
Laughlin, NV	Edison Int.	Mohave	-	-	Bituminous	F	1.6	0.4
Denver, Co.	Public Service of Colorado	Pawnee	Foster Wheeler	Front-rear wall low NOx	Sub-bituminous	C	1.5	0.4

Table 5 - Chemical composition of the fly ashes

Fly ashes	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	P_2O_5	TiO_2	SO_3	LOI	C
	%											
Portland	44.7	24.4	12.5	2.8	0.8	0.9	1.6	0.3	1.1	2.1	10.1	6.8
Steward	49.4	27.8	9.9	1.8	0.8	0.3	2.4	0.5	1.5	0.4	4.1	3.3
Shawville 1	39.6	21.8	11.8	0.9	0.6	0.2	2.0	0.3	1.1	0.8	21.5	19.3
Shawville 2	41.2	22.8	12.9	1.0	0.7	0.2	2.2	0.3	1.2	0.8	15.8	13.4
Shawville 3	49.6	26.7	11.7	1.2	0.8	0.3	2.6	0.3	1.4	0.6	6.4	4.8
Bowen	54.6	28.3	5.4	1.1	0.9	0.4	2.8	0.2	1.6	0.4	4.8	3.3
Crist	47.1	23.3	7.5	2.4	1.1	1.4	2.8	0.6	1.2	0.7	10.5	8.7
Mohave	52.9	22.6	5.1	10.2	1.9	2.6	0.6	0.2	1.2	0.8	1.6	0.4
Pawnee	32.7	18.4	5.4	29.9	5.9	2.5	0.3	1.2	1.6	2.7	1.5	0.4

Table 6 - Fly Ash Physical Properties

Fly Ash	**Specific Gravity**	**Blaine cm^2/g**	**45 µm % Passing**	**Strength Activity Index**		
				% H2O	**7 days**	**28 days**
Portland	2.40	3270	85.9	101.2	82.5	89.2
Steward	2.39	2430	79.0	97.1	75.5	81.4
Shawville-1	2.16	-	64.9	-	-	-
Shawville-2	2.24	-	61.7	-	-	-
Shawville-3	2.31	2857	82.2	99.2	78.2	85.4
Bowen	2.21	2125	80.2	97.1	76.5	83.1
Crist	2.25	3194	84.1	98.3	77.4	86.7
Mohave	2.18	2586	73.1	97.1	78.3	86.5
Pawnee	2.70	2935	82.5	95.9	92.0	97.0

Table 7 - Air content (%) in Mortar Mixtures

Mixture	Carbon content %	Ref.1 (1 ml)*	Ref.2 (0.5 ml) *	L4 (0.25 ml) *	ND (1 ml) *	NS (0.1 ml) *	NA (0.5 ml) *
Control	-	22.4	22.4	25.5	21.1	20.9	21.5
Bowen	3.3	20.5	17.0	25.1	21.7	12.3	21.0
Portland	6.8	17.8	15.1	22.2	21.5	13.7	21.0
Crist	8.7	11.3	7.9	11.1	22.6	6.8	13.0
Shawv.-2	13.4	12.2	10.6	11.1	20.5	7.6	14.4

***The dosage used for the mixtures (target air for the control: 20-25%); Fly ash is at 20% replacement of cement**

Table 8 - Air Content of Mortar Mixtures made with 8 fly ashes

Mixture	**Carbon content** (%)	**Reference 2** (0.5 ml)	**ND** (1 ml)	**NA** (0.5 ml)
Control	-	22.4	21.1	21.5
Bowen	3.3	17.0	21.7	21.0
Steward	3.3	19.1	22.2	21.7
Portland	6.8	15.1	21.5	21.0
Crist	8.7	7.9	22.6	13.0
Shawville-2	13.4	10.6	20.5	14.4
Shawville-3	4.8	14.7	21.9	12.6
Mohave	0.4	20.5	21.2	19.7
Pawnee	0.4	21.8	20.2	20.8

Note: The values are an average of 2 tests. Fly ash is at 20% replacement of cement.

Table 9 - Air Content of concrete made with 4 selected fly ashes

Fly ash		**Control**	**Bowen**	**Crist**	**Portland**	**Shawville-2**
Carbon	(%)	100% cement	3.3	8.7	6.8	13.4
Admixture		Air Content (%); dosage by 100 kg of binder				
Reference 2	% air		5.2	8.5	4.3	4.0
	Dosage		*90 ml*	*530 ml*	*130 ml*	*300 ml*
ND	% air	9.8	10.5 (5.6)	8.5	8.5	8.4
	Dosage	*15 ml*	*45 m l* *(30 ml)*	*180 ml*	*90 ml*	*120 ml*
NS	% air	8.0	8.0	9.2	6.6	4.5
	Dosage	*15 ml*	*45 ml*	*180 ml*	*60 ml*	*120 ml*
NA	% air		5.1	3.8	6.0	3.2
	Dosage		*75 ml*	*180 ml*	*90 ml*	*135 ml*
NDb	% air		5.9	-	6.0	-
	Dosage		*40 ml*	-	*60 ml*	
L4	% air		4.8	-	-	-
	Dosage		*90 ml*	-	-	-
Reference 1	% air	3.1	8.0	5.0	-	-
	Dosage	*90 ml*	*360 ml*	*660 ml*	-	-

Note: The values are an average of 2 tests or more. Fly ash is at 30% replacement of cement

Table 10 - Specific surface of fly ashes and a fly ash with carbon added

Fly ash	**Carbon content** (%)	**Specific surface** (m^2/g)
Portland	6.8	2.84
Crist	8.7	6.82
Shawville-2	13.4	4.87
Bowen	3.3	1.53
Bowen + 0.5% charcoal	3.8*	4.47
Bowen + 1% charcoal	4.3*	7.60
Bowen + 2% charcoal	5.3*	16.08
Bowen + 3% charcoal	6.3*	25.42
Bowen + 4% charcoal	7.3*	32.59

*** The charcoal used has a specific surface of about 500 m^2/g.**

Table 11 - Air content and slump of concrete made with the Portland fly ash and the new AEAs.

Time	**ND** *(45ml)*		**NS** *(60 ml)*		**NA** *(90 ml)*		**Reference 2** *(150 ml)*		**ND$_b$** *(60 ml)*	
min	Air	Slump	Air	Slump	Air	Slump	Air	Slump	Air	Slump
	%	mm	%	mm	%	mm	%	mm	%	mm
10	6.7	100	8	110	6.2	110	6.0	90	6.0	100
30	4.7	70	6.6	80	5.2	100	5.6	70	5.4	100
60	3.6	50	5.0	60	4.9	80	4.9	50	5.1	80

Note: The values are an average of 2 or more tests. Dosage of AEA by 100 kg of the binder

Table 12 - Air-void parameters of hardened concrete (W/B = 0.42)

Admixture	**Fly Ash (30%)**	**% air Fresh***	**% Air Hardened****	**α (mm^{-1})**	**Spacing factor (μm)**
ND$_b$	Bowen (3.3% C)	3.6	2.8	33.7	177
	Portland (6.8% C)	5.0	3.5	29.3	186
	Shawville-2 (13% C)	4.8	3.5	25.5	225
		6.1	4.3	29.1	172
	Control (0% F.A)	6.1	5.1	27	185

***Air in fresh concrete after 60 minutes; **Specimens cast after the air content measurement.**

Table 13 – Composition and Properties of Fresh Concrete (First Two series)

Concrete identification		**C1**	**C2**	**C3**	**C4**	**C5**	**C6**	**C7**	**C8**
W/B		0.50	0.50	0.50	0.50	0.42	0.42	0.42	0.42
Binder Composition (%)	*Cement*	100	100	70	70	100	100	70	70
	Fly ash	0	0	30	30	0	0	30	30
Total binder (kg/m³)		340	340	340	340	380	380	380	380
Water (l/m³)		170	170	170	170	160	160	160	160
Coarse aggregate (kg/m³)		1095	1080	1025	1065	1045	1045	1045	1025
Fine aggregate (kg/m³)		790	720	740	715	760	760	740	740
Water reducer (l/100 g of binder)	*Ligno*					265	330		
	Carbo.A.							265	265
Air-entraining agent type			ND	Ref.2	ND		ND	ND	Ref.2
Dosage (ml/100 kg of binder)			15	90	30		15	25	80
Air content- 60 min (%)		1.8	6.6	6.5	8.0	2.1	7.6	7.1	5.2
Unit weight (kg/m³)		2440	2310	2275	2230	2405	2260	2275	2260
Slump (mm)-10 min		80	100	125	110	80	80	80	105

Table 14 – Composition and Properties of Fresh HVFA Concrete

Concrete identification			**C9**	**C10**	**C11**
W/B			0.32	0.32	0.32
Binder Composition (%)	*Cement*		45	45	45
	Fly ash	*Bowen*	-	55	-
		Portland	55	-	55
Total binder (kg/m³)			380	380	380
Water (l/m³)			122	122	122
Coarse aggregate (kg/m³)			1025	1070	1070
Fine aggregate (kg/m³)			775	775	775
Superplasticizer (l/m³)	*PNS**		4.5	4.7	
	Polyacrylate		-	-	4.3
Air-entraining agent type			Ref.2	ND	ND
Dosage (ml/100 kg of binder)			120	70	50
Air content- 60 min (%)			4.8	3.9	7.2
Unit weight (kg/m³)			2350	2360	2275
Slump (mm)-10 min			220	210	210

***PNS is the polysulfonated-based superplasticizer**

Table 15 - Bleeding and Setting time of the first two series of concrete

Concrete identification		**C1**	**C2**	**C3**	**C4**	**C5**	**C6**	**C7**	**C8**
W/B		0.50	0.50	0.50	0.50	0.42	0.42	0.42	0.42
Binder Composition (%)	*Cement*	100	100	70	70	100	100	70	70
	Fly ash (Bowen)	0	0	30	30	0	0	30	30
Air content- 60 min (%)		1.8	6.6	6.5	8.0	2.1	7.6	7.1	5.2
Air-entraining agent type		-	ND	Ref.2	ND	-	ND	ND	Ref.2
Unit weight (kg/m^3)		2440	2310	2275	2230	2405	2260	2275	2260
Bleeding (ml/cm^2)		0.052	0.019	0.114	0.048	0.105	0	0.019	0.090
Setting time (hours)	*Initial*	3.8	5.0	5.3	4.9	4.9	5.8	5.0	6.3
	Final	*5.1*	6.3	7.1	5.9	6.3	7.1	6.3	7.8

Table 16 - Bleeding and Setting time of High Volume Fly Ash Concrete

Concrete identification			**C9**	**C10**	**C11**
W/B			0.32	0.32	0.32
Binder Composition (%)	*Cement*		45	45	45
	Fly ash	*Bowen*	-	55	-
		Portland	55	-	55
Air content- 60 min (%)			4.8	3.9	7.2
Unit weight (kg/m^3)			2350	2360	2275
Bleeding (ml/cm^2)			0.01	0.009	0
Setting time (hours)	*Initial*		6.5	5.6	5.8
	Final		8.3	7.3	7.5

Table 17 - Properties of the Hardened Concretes (First Two Series)

Concrete identification		**C1**	**C2**	**C3**	**C4**	**C5**	**C6**	**C7**	**C8**
W/B		0.50	0.50	0.50	0.50	0.42	0.42	0.42	0.42
Binder Composition (%)	*Cement*	100	100	70	70	100	100	70	70
	Fly ash (Bowen)	0	0	30	30	0	0	30	30
Unit weight (kg/m^3)		2420	2305	2290	2245	2425	2305	2320	2300
Air voids system readings	*% Air*		5.7	5.9	6.5		5.1	6.3	5.2
	$\bar{L}$ (µm)		148	100	112		185	103	186
	α (mm^{-1})		28.6	42	34.3		27	32.4	25.7
Compressive strength (MPa)	1d	24.8	19.5	8.7	9.9	26.4	27.2	17.4	15.6
	7d	36.1	29.9	21.7	18.9	39.9	39.9	30.3	28.2
	28d	44.5	34.6	30.2	28.0	47.8	46.5	39.7	39.3
	91d		39.2	36.7	35.1		48.7	50.1	49.3
Flexural strength (MPa)	*28d*	6.2	5.9	5.4	5.2	6.6	6.6	6.7	6.5
Elastic Modulus (GPa)		34.1	30.9	27.5	26.6	35.1	31.2	30.5	30.0
Cl ions penetration (Coulomb)	*28d*	4260	4600	2750	4460	3890	3820	2000	2580
	91d		3050	760	875		2640	560	760

Table 18 - Properties of the hardened High Volume Fly Ash Concrete

Concrete identification			**C9**	**C10**	**C11**
W/B			0.32	0.32	0.32
Binder Composition (%)	*Cement*		45	45	45
	Fly ash	*Bowen*	-	55	-
		Portland	55	-	55
Unit weight (kg/m^3)			2350	2360	2270
Air voids system readings	*% Air*		4.7	3.3	6.0
	$\bar{L}$ (µm)		120	230	101
	α (mm^{-1})		38.7	25.4	41.1
Compressive strength (MPa)	1d		10.5	10.7	11.6
	7d		26.6	25.6	26.6
	28d		39.8	40.5	40.2
	91d		50.3	50.6	49.8
Flexural strength (MPa)	*28d*		6.5	6.2	6.4
Elastic Modulus (GPa)			31.0	34.1	30.5
Cl ions penetration (Coulomb)	*28d*		1120	870	880
	91d		480	380	420

Table 19 - Durability data of concretes (First Two Series)

Concrete identification		**C1**	**C2**	**C3**	**C4**	**C5**	**C6**	**C7**	**C8**
W/B		0.50	0.50	0.50	0.50	0.42	0.42	0.42	0.42
Binder Composition (%)	*Cement*	100	100	70	70	100	100	70	70
	Fly ash (Bowen)	0	0	30	30	0	0	30	30
% change at the end of the freezing and thawing cycles (300 cycles)	*Length*		0.015	0.010	0.014		0.016	0.014	0.007
	Weight		-0.05	-0.46	-0.22		0.20	0.07	-0.31
	Pulse velocity		-1.27	-1.33	-1.87		-1.28	-2.00	-3.19
	Resonant Frequency		0	1.09	0		0	1.09	2.08
	Durability Factor		100	102	100		100	104	104
Flexural strength (MPa) at the end of 300 cycles of freeze/thaw	*Reference (0 cycle)*		5.9	5.6	5.1		7.1	6.2	5.0
	Samples (300 cycles)		5.6	4.9	4.8		6.0	6.1	4.5
	% of change		94.9	87.5	94.1		84.5	98.4	90.0
Cl ions penetration (Coulomb)	*28d*	4260	4600	2750	4460	3890	3820	2000	2580
	91d		3050	760	875		2640	560	760

Table 20 - Durability data of High Volume Fly Ash Concrete

Concrete identification		**C9**	**C10**	**C11**
W/B		0.32	0.32	0.32
Binder Composition (%)	*Cement*	45	45	45
	Fly ash	55	55	55
% change at the end of the freezing and thawing cycles (300 cycles)	*Length*	-0.007	0.047	0.013
	Weight	-1.004	-0.95	-0.50
	Pulse velocity	-1.0	-1.40	-0.31
	Resonant Frequency	2.00	-3.54	1.92
	Durability Factor	102	92.8	104
Flexural strength (MPa) at the end of 300 cycles of freeze/thaw	*Reference (0 cycle)*	6.7	6.4	8.2
	Samples (300 cycles)	4.4	3.9	5.9
	% of change	65.7	60.9	72.0
Cl ions penetration (Coulomb)	*28d*	1120	870	880
	91d	480	380	420

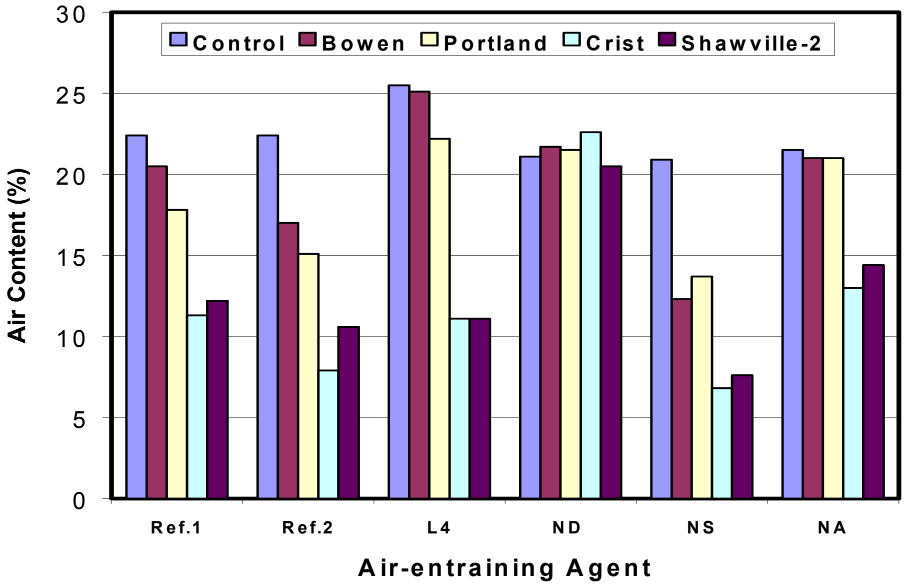

Figure 1 - **Air content of mortars containing different Air Entraining Agents**

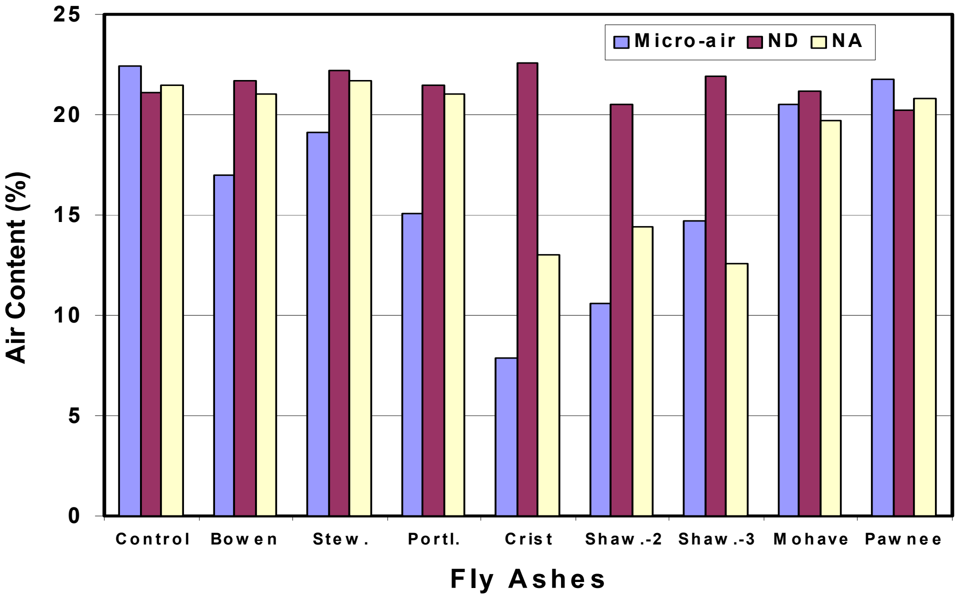

Figure 2 - **Air content in mortars containing different fly ashes for 3 AEAs**

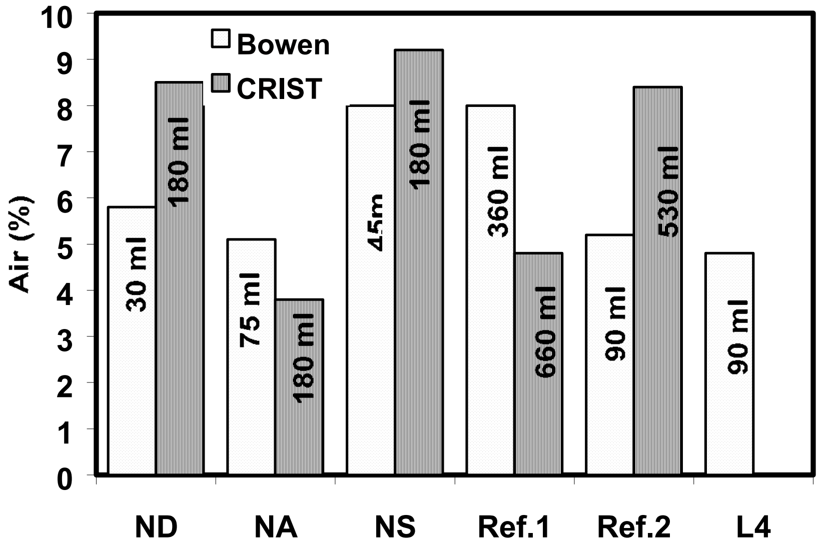

Figure 3 – Air entrained in concrete made with Bowen and CristFly Ash. (Dosage of AEA by 100 kg of binder).

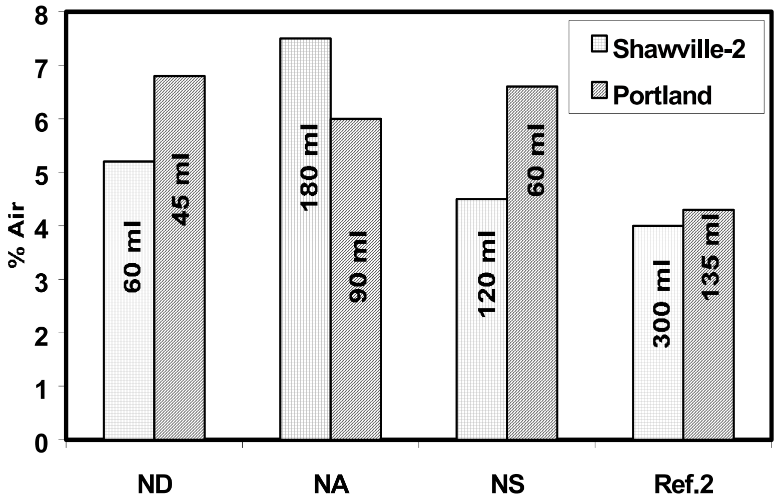

Figure 4 - Air entrained by the 4 admixtures in concrete made with the Portland and the Shawville-2 fly ashes: 30 % of total binder. (Dosage of AEA by 100 kg of binder).

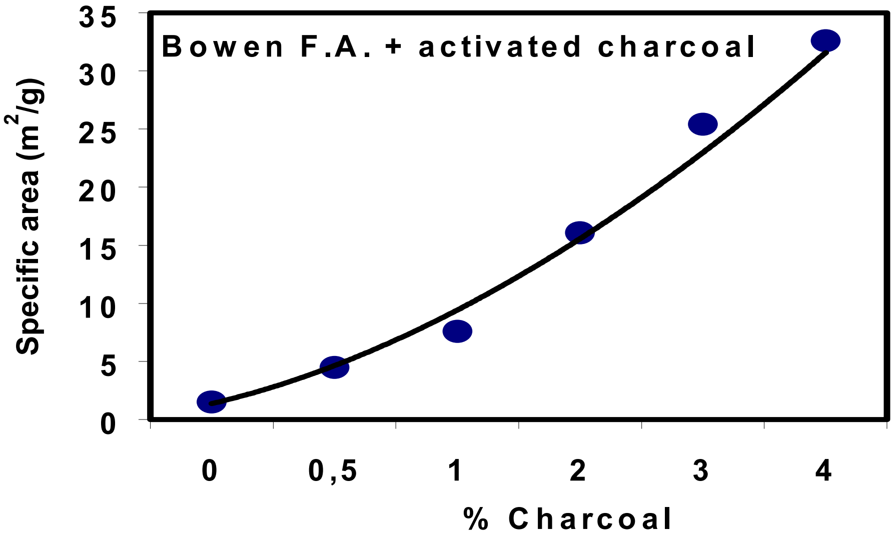

Figure 5 - Evolution of the specific surface of the Bowen fly ash mixed with charcoal

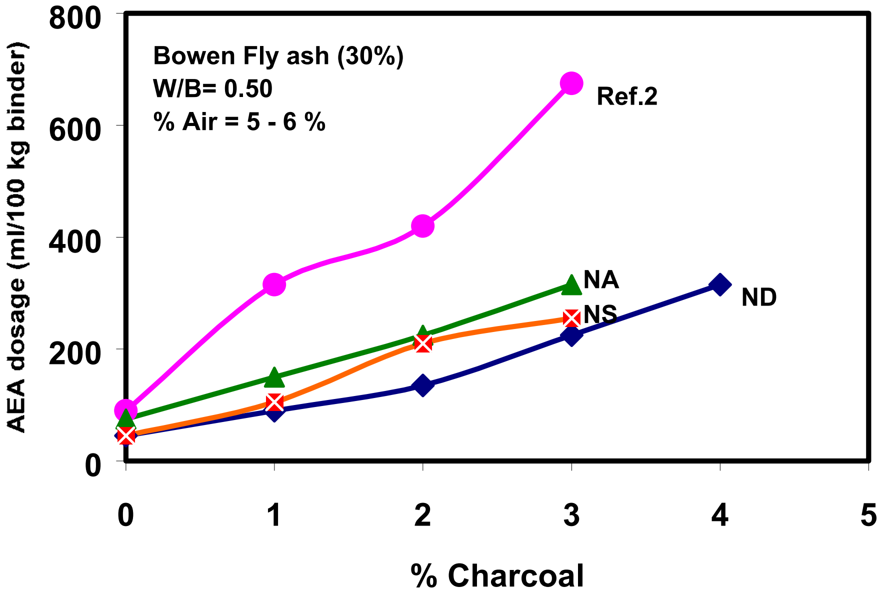

Figure 6 – Effect of the charcoal on the AEA demand of the Concrete.

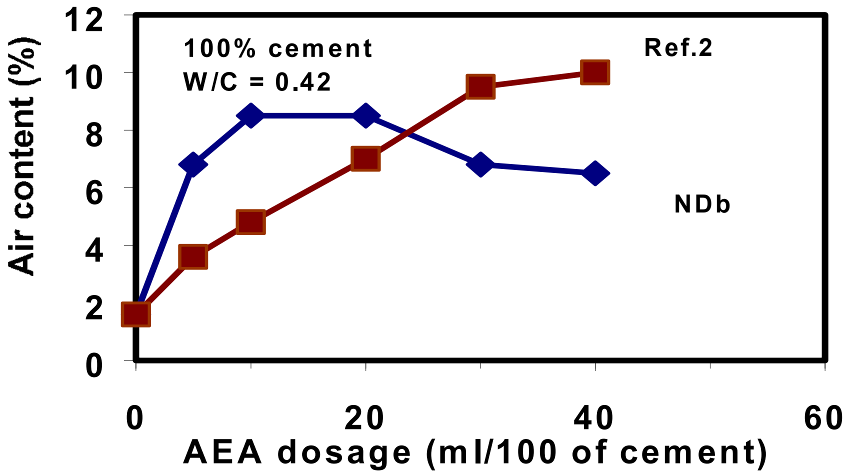

Figure 7 - Effect of the air-entraining admixture dosage on the air content of the concrete made with Cement only.

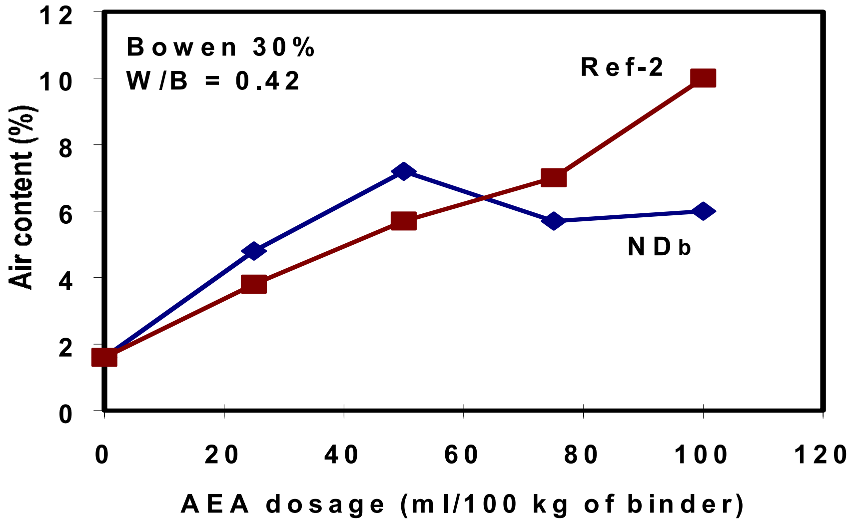

Figure 8 - Effect of the air-entraining admixture dosage on the air content of the concrete incorporating Fly Ash

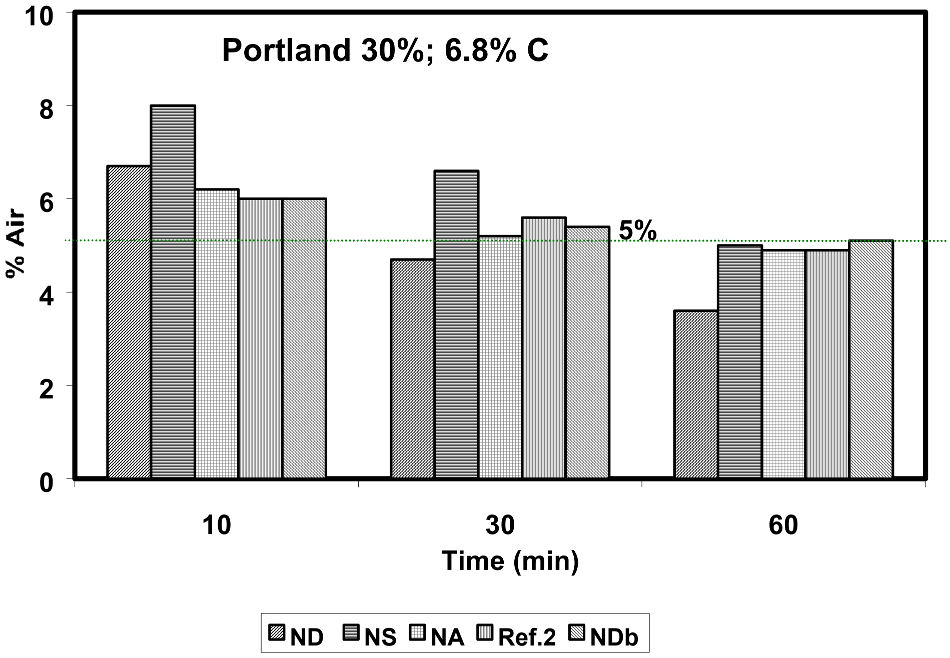

Figure 9 - **Stability of the air entrained in concrete made with 30% of the Portland fly ash for five admixtures.**