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Use of Class C Fly Ash in High-Volume Fly Ash Concrete Applications

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REPORT SUMMARY

Although the use of fly ash in concrete is a well-established practice, the volume of high-calcium Class C ash used lags behind that of low-calcium Class F ash. Because Class C may be the only type of ash produced in some western states, this disparity can significantly limit its use potential. The literature results presented in this report represent the first phase of a longer term research effort to provide technical information supporting the increased use of Class C ash in concrete applications.

Background

Fly ash has been used as an ingredient in concrete in the United States for more than half a century—the first major use being the construction of the Hungry Horse Dam in Montana in 1948. Since that time, the use of fly ash has grown steadily, with almost 15 million tons of fly ash used in concrete, concrete products, and grouts in 2006. The utilization of the material has been accompanied by extensive research on its composition and properties and on the way in which it influences the properties of concrete.

Traditionally, the amount of fly ash used in concrete has been in the range of 15 to 25% by mass of the cementing material, although higher levels have been used in certain applications. Over the past decade or so, there has been a trend to use higher levels of fly ash in concrete, largely in response to various government and industry incentives to improve concrete’s sustainability. Most research in these applications has supported uses for low-calcium Class F ashes; however, a need exists to develop suitable applications for the use of high-calcium Class C ashes in a wider range of concrete applications.

Objectives

- To summarize existing information on the use of Class C fly ash as a supplementary cementitious material in concrete, particularly in HVFA concrete
- To identify data needs and recommend research to fill those needs

Approach

The authors performed a detailed survey of the extensive literature on the use of fly ash to replace portland cement in concrete. They summarized key findings, with particular emphasis on the benefits and disadvantages of using high volumes of Class C fly ash. They considered all aspects of concrete performance, including fresh concrete properties such as workability and early strength gain, mechanical properties such as compressive strength and drying shrinkage, and durability characteristics such as resistance to alkali-silica reactions and attack by sulfate and chloride. Based on the review, the authors developed a prioritized list of research needs to advance the use of Class C ash in concrete.

Results

There is an extensive literature base on the use of ash in concrete. In general, the research is more extensive for low-calcium ashes than high-calcium ones. The results of the review were used as an indication of whether the use of HVFA concrete made with Class C fly ash is beneficial, disadvantageous, or has an uncertain effect for each property of the concrete. Because each fly ash is unique, the actual behavior of concrete made with any specific fly ash should be verified with respect to the following general statements:

- Class C ash has a beneficial or possible beneficial effect on the following HVFA concrete properties: workability, heat of hydration, late-age strength, delayed ettringite formation, permeability, and chloride resistance.
- Use of Class C ash can be a disadvantage or possible disadvantage with respect to the following HVFA concrete properties: bleeding, air entrainment, setting time, early-age strength, external sulfate attack, and carbonation.
- Significant uncertainty or disagreement exists with respect to the effect on the following properties: Young's modulus of elasticity, drying shrinkage, alkali-silica reactions, and salt scaling resistance.

Highest priority research needs were identified in the following areas:

- Developing performance criteria for quality control
- Comparing the performance of different ashes
- Improving early strength gain
- Evaluating deicer salt resistance
- Mitigating carbonation effects

EPRI Perspective

Concrete is currently the largest market for the beneficial use of fly ash. However, Class C ash is underused in concrete applications, partially because of perceived drawbacks of using Class C ash stemming from an incomplete understanding of the effects of Class C ash on concrete properties. This effectively defines geographic constraints on the use in concrete, particularly in western states where Class C is the dominant type of ash produced. The EPRI research is designed to provide the technical information necessary to support the increased use of and overcome existing barriers to the use of Class C ash in concrete by addressing the highest priority research needs.

Keywords

Fly ash
Class C
Concrete
Ash use

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INTRODUCTION

Fly ash has been used as an ingredient of concrete in the United States for more than half a century, the first major use being the construction of the Hungry Horse Dam in Montana (U.S. Bureau of Reclamation, 1948). Since that time, the use of fly ash has grown steadily, and according to the American Coal Ash Association (2006), almost 15 million tons of fly ash were used in concrete, concrete products, and grouts in the year 2005. The utilization of the material has been accompanied by extensive research on its composition and properties and on the manner in which it influences the properties of concrete. There are literally thousands of technical publications on the use of fly ash in concrete, and the literature generally supports the statement that the appropriate use of fly ash to replace part of the portland cement component of concrete can result in the following technical benefits:

- Improved fresh concrete properties – i.e., improved workability, reduced water demand, better cohesion, and improved pumpability
- Reduced heat of hydration, and hence reduced temperature rise in large pours
- Improved long-term strength
- Reduced permeability and improved resistance to the penetration of damaging entities such as chlorides and sulfates
- Improved resistance to alkali-silica reaction
- Improved resistance to chemical attack

However, the precise impact of fly ash on any single property of concrete depends on a number of parameters including, among other things, the composition and quantity of fly ash used, the properties and proportions of the other concrete-making materials, the conditions during placement, the quality of the workmanship, the nature and extent of curing, and the loading and environmental conditions to which the concrete is exposed. If all other things remain constant, the changes in the physical, mineralogical, and chemical properties of the fly ash or changes in the level of fly ash used in the concrete can have a very significant impact on the performance of the concrete.

The composition of fly ashes that are commercially available in the United States varies widely. For example, the calcium content of fly ash, expressed as calcium oxide (CaO), can range from less than 1% to more than 30% CaO. Fly ashes low in calcium behave very differently from those with high calcium contents, tending to be more efficacious in terms of controlling temperature rise, preventing expansion due to alkali-silica reaction (ASR) and increasing the resistance to sulfate attack (Thomas et al., 1995, 1999a; Shehata and Thomas, 2000;

Shashiprakash and Thomas, 2001). Research has shown that fly ashes with high calcium contents can be used to control internal temperature rises during hydration and to prevent ASR damage provided they are used at much higher replacement levels (Thomas et al., 1995; Shehata and Thomas, 2000). Furthermore, laboratory testing has shown that ternary cements containing modest levels of silica fume (3 to 5%) with moderate levels of high-calcium fly ash (20 to 30%) can be effective in controlling ASR and sulfate attack (Shashiprakash and Thomas, 2001; Shehata and Thomas, 2002; Thomas et al., 1999b).

Traditionally, the amount of fly ash used in concrete has been in the range of 15 to 25% by mass of the cementing material, although higher levels have been used in certain applications. However, over the past decade or so, there has been a trend to use higher levels of fly ash in concrete, largely in response to various government and industry incentives to improve the sustainability of concrete. Fly ash is an industrial by-product, and its use in concrete results in a reduced consumption of portland cement, the production of which results in the emission of greenhouse gases (GHG). Thus, the use of higher levels of fly ash results in a concrete with increased recycled material or recovered mineral content, and a reduced GHG footprint (Mehta, 2002; Malhotra, 2002).

Research has shown that concrete containing up to 50% (or more) Class F fly ash by mass of the total cementitious material can be produced with adequate short-term strength and excellent long-term strength, low permeability, and excellent resistance to chemical attack and corrosion, providing it is properly proportioned and adequately cured (e.g., Bilodeau and Malhotra, 2000). Such concretes may be suitable for many applications (Langley and Leaman, 1998)**.** However, the use of high levels of fly ash may also result in concrete with a reduced resistance to certain deterioration processes such as deicer-salt scaling and carbonation (Zhang et al., 1998; Bouzoubaâ et al., 2004; Thomas and Matthews, 1992b; 2000). Most of the available research data for concrete containing high levels of fly ash has been collected from studies using fly ash with relatively low calcium contents.

What Is Fly Ash?

Fly ash is produced in coal-burning electricity generating stations. It is the non-combustible material that is carried away from the burning zone of the boiler by the flue gases and is collected from those gases by mechanical or electrostatic precipitators. At the high temperature in the boiler (~ 1500°C), the non-organic matter (e.g., clays, calcite, pyrite, feldspar, gypsum, etc.) intimately associated with the coal forms molten droplets, and as these droplets are drawn away with the flue gases they are rapidly cooled (quenched), forming glassy spheres. Fly ashes produced from burning bituminous and anthracite coals are low in calcium and the glass that forms is essentially an aluminosilicate glass. The glass content of the fly ash is typically 60 to 90%, with the remainder being various crystalline phases. In low-calcium fly ashes, the crystalline phases form within the glass matrix, at the centre of larger glass particles (where the rate of cooling is lower), or sometimes on the surface of the glassy spheres. The principal crystalline components of low-calcium fly ashes are quartz, mullite, and hematite, which are chemically inert when mixed with water or mixed in concrete. As the calcium content of the fly ash increases, the glass changes to a calcium aluminosilicate glass (Roy et al., 1985), and its reactivity increases. It has been suggested that high-calcium fly ashes (> 20% CaO) may contain calcium-aluminate glass which is likely significantly more reactive than the glass in low-lime fly ashes (Diamond, 1983) and may participate in reactions with sulfate phases. The increase in calcium also influences the crystalline phases that form as the fly ash cools. High-calcium fly ashes may contain a wide range of crystalline phases, including tricalcium aluminate (C_3A), dicalcium silicate (C_2S), anhydrite, free CaO and MgO, merwinite, mellilite, various sodalite structures, and alkali sulfates (ACI, 2003; McCarthy et al., 1984, 1987; Roy et al., 1985), many of which are chemically reactive with water or in the alkaline pore solution of concrete.

Low-calcium fly ash is a pozzolanic material, which means that it will react with calcium hydroxide [$Ca(OH)_2$] and water at normal temperatures to produce calcium-silicate hydrates (C-S-H) and calcium-aluminate hydrates (C-A-H) with cementing properties. This reaction is beneficial in portland cement concrete, since the hydration of portland cement produces approximately 25% by mass of calcium hydroxide, which has limited cementitious properties. Thus, the incorporation of a pozzolan can increase the amount of C-S-H and C-A-H in the concrete, leading to improved long-term strength and reduced permeability (among other benefits). Low-calcium fly ash does not generally react with water of neutral pH; i.e., it is not a hydraulic material. Even at high pH with abundant calcium hydroxide present, as is the case within concrete, the rate of reaction of the aluminosilicate glass is relatively slow at normal temperature, and the partial replacement of portland cement with low-calcium fly ash will extend the setting time of concrete and retard the early-age strength development. However, at later ages, the continued pozzolanic reaction will increase the ultimate strength of the concrete. The rate of reaction is significantly accelerated by increases in temperature or increases in the pH within the concrete. High-calcium fly ashes are also pozzolans in the sense that they will react with the calcium hydroxide resulting from the hydration of portland cement and produce C-S-H and C-A-H. However, these fly ashes are also hydraulic in nature, as they will react directly with water to form a range of hydration products, and a mix of such fly ash and water will set, harden, and gain strength even in the absence of portland cement (or other activator). Indeed, it is possible to produce concrete of reasonable strength with some Class C fly ashes without portland cement (Cross et al., 2005). This behavior results from the hydraulic nature of the crystalline products and also the dissolution and reaction of the glass due to the presence of soluble alkalis and calcium within the fly ash. The hydraulic nature of Class C fly ash coupled with the increased reactivity of the glass phase usually means that it can be used to partially replace portland cement in concrete with a reduced impact on the early-age strength development when compared with low-calcium fly ash.

Classification of Fly Ash

ASTM C 618, *Standard Specification for Coal Fly Ash and Raw or Calcined Natural Pozzolan for Use in Concrete*, divides fly ash into two classes based on its composition and the rank of coal from which it was produced, as follows:

Table 1-1
ASTM Standard Specification for Class C and Class F Ash

Class	Description	Chemical Requirements
F	Fly ash normally produced from burning anthracite or bituminous coal that meets the applicable requirements for this class as given herein. This class of fly ash has pozzolanic properties.	$SiO_2 + Al_2O_3 + Fe_2O_3 \geq 70\%$
C	Fly ash normally produced from lignite or sub-bituminous coal that meets the applicable requirements for this class as given herein. This class of fly ash, in addition to having pozzolanic properties, also has some cementitious properties. Note: Some Class C fly ashes may contain lime contents higher than 10%.[1]	$SiO_2 + Al_2O_3 + Fe_2O_3 \geq 50\%$

[1] This note in ASTM C 618 is misleading as most, if not all, Class C fly ashes contain more than 10% CaO and many contain more than 20% CaO (see figure 1)

However, some fly ashes produced from lignite and sub-bituminous coals meet the chemical requirements of Class F fly ash; these fly ashes may be classed as either Class F or Class C fly ashes, and it is not uncommon to hear them described as a “Class F-C” or “Class C-F” fly ash. In Canada, CSA A3000 (CSA 2003) classifies the fly ash solely on the basis of the calcium content of the fly ash, the three classes being Type F (< 8% CaO), Type CI (8-20% CaO) and Type CH (> 20% CaO). The rationale for this approach is that the calcium content of the fly ash is considered to provide a reasonable indication of how the fly ash will perform in concrete (Thomas et al., 1999a).

Figure 1-1 shows the composition in terms of CaO and the sum of the oxides $SiO_2 + Al_2O_3 + Fe_2O_3$ for 110 different fly ash sources in North America (Thomas 2007). Class C fly ashes that do not meet the chemical requirement for Class F fly ash, i.e., the sum of the oxides $SiO_2 + Al_2O_3 + Fe_2O_3$ for the ash is less than 70%, are characterized by high calcium contents that are invariably greater than 15% CaO and usually greater than 20% CaO. Most of these fly ashes would be classified as Type CH in Canada, although a few sources would be classified as Type CI.

Some power plants use a blend of different coals, and the chemical composition of the resulting fly ash will obviously vary depending on the proportions and composition of the coals used. It is likely that a fly ash produced from a blended coal will behave in the same manner as a fly ash of the same composition produced from a single coal; however, there has been no definitive study to demonstrate that this is the case.

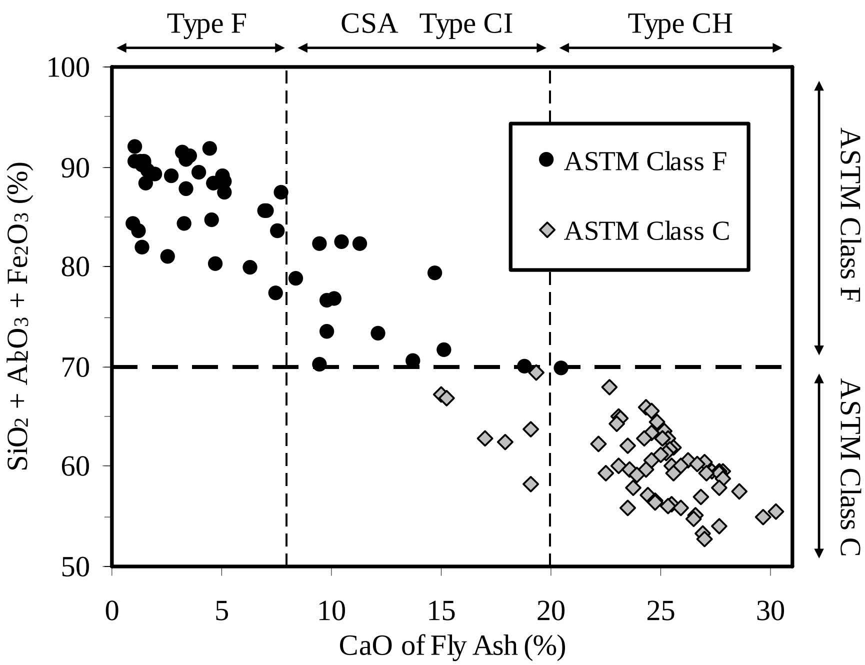

Figure 1-1
Composition (CaO versus SiO_2+Al_2O_3+Fe_2O_3) for fly ashes (from 110 sources in North America) (Thomas 2007).

High-Volume Fly Ash Concrete

The concept of using high levels of fly ash (e.g., ~ 50%) is not new. Indeed, in one of the first published studies on the use of fly ash, Davis and coworkers concluded the following (Davis et al., 1937):

> *For ordinary construction it appears that fly ash of moderately low carbon and moderately high fineness may be employed as replacements for portland cement in percentages up to 30 without in any way impairing the qualities of the concrete. For heavy concrete construction it appears that such fly ashes may be employed as replacements for portland cements in percentages as high as 50, with the advantages of substantially lower temperature rise due to hydration of the cement and of higher ultimate compressive strength.*

Thus, these early pioneers not only advocated the use of high levels of fly ash (up to 50%) but also introduced the notion of optimizing the amount of fly ash used for different types of construction.

Since the first major use of fly ash in the Hungry Horse Dam in Montana (constructed between 1948 and 1952) and until the 1980s, the use of relatively high levels of fly ash was restricted to massive concrete structures. In such structures, the main incentive for using large amounts of fly ash was to reduce the autogenous temperature rise resulting from the hydration of cement, and the low early-age strengths associated with these concretes were usually not a major concern. The proposition to use high fly ash contents in structural concrete began to emerge in the 1980s.

The development of “high fly ash content concrete” (or HFCC) in the U.K. occurred during the period 1977 to 1983 (Dunstan, 1983; 1986; Dunstan et al., 1992). In the late 1970s, it was realized that the use of high levels of fly ash (70 to 80% of the volume of cementitious material) could significantly improve the performance of roller compacted concrete (RCC); this idea was later implemented in the construction of the Upper Stillwater Dam in Utah in the early 1980s. In 1978, a concrete mix containing high levels of fly ash (50% by volume) was successfully used to slipform the vertical facing element during a full-scale RCC trial (Dunstan, 1983), and this led to the initiation of testing at three laboratories to develop HFCC (with up to 80% fly ash by volume) suitable for placement by immersion vibration. The first major placement of HFCC (with 51% and 56% fly ash by mass of cementitious material) compacted by immersion vibration was in 1981 in the construction of access roads to carry heavy plant equipment at the Didcot Power Station in Oxfordshire, U.K. (Dunstan, 1983). The success of this project led to the use of HFCC in a series of projects between 1982 and 1984, including the foundation slabs and retaining wall for an oil tank storage area (51% fly ash by mass), a marine slipway (52%), a sewage-treatment works (54%), and a concrete viaduct (35 to 65%). Five of these HFCC structures were evaluated by visual examination and testing of cores approximately 10 years after construction and were found to be in excellent condition (Dunstan et al., 1992). The concrete viaduct is a particularly interesting case, as the concrete mixtures were proportioned to optimize the amount of fly ash based on its cost and quality, and the strength and workability requirements for the project (Concrete Society, 1991). This resulted in different amounts of fly ash being used in the various components of the structure, with 35% fly ash being used in the post-tensioned precast units, 50% in columns and piers, 60% in pile caps, and 65% in piles as a precaution against sulfate attack (Concrete Society, 1991).

In the mid 1980s, a number of researchers from different countries embarked on studies of concrete containing high levels (e.g., 50% or more) of both Class F and Class C fly ash for various applications ranging from lean concrete to pavements; the parameters investigated included methods of mixture proportioning, use of lightweight aggregate, setting behavior, workability, heat development, strength (including the role of curing), creep, permeability, resistance to freezing and thawing, and chloride ion penetration (Ghosh and Timusk, 1981; Munday et al., 1983; Ravina and Mehta, 1986; 1988; Yuan and Cook, 1983; Majko and Pistilli, 1984; Haque et al., 1986; Joshi et al., 1986; Nasser and Al-Manaseer, 1986; 1987; Papayianni, 1986; Swamy and Mahmud, 1986; Tse et al., 1986; Johnston and Malhotra, 1987; Naik and Ramme, 1987a; Roselle, 1987; Sivasundaram et al., 1987). Despite the flurry of research activity, few structures were built in North America during this period using concretes containing high levels of fly ash. Two demonstration projects were conducted by Wisconsin Electric in September and November 1984, where 70% Class C fly ash was used in the concrete (Naik and Ramme, 1987b; 1989). In the first project, over 1000 yd^3 (765 m^3) of high fly ash content concrete was used to pave a truck access road at the Pleasant Prairie Power Plant in Wisconsin, and in the second project 50 yd^3 (38 m^3) of concrete was used in transformer foundations at a substation in Milwaukee County. Problems with slow strength gain and cracking between saw-cut joints were encountered with the paving project, but no problems were encountered with the second project. Wisconsin Electric has since constructed a number of high fly ash content concrete pavements with great success (e.g., Naik et al., 1995).

The term "high-volume fly ash concrete" (or HVFA concrete) was introduced to the concrete industry in 1986 (Malhotra, 1986). Malhotra and coworkers at the Canada Centre for Mineral and Energy Technology (CANMET) began work on HVFA concrete in 1985 and in the next twenty years, CANMET conducted extensive research on the properties of this product; these studies culminated in a plethora of technical publications. A detailed review of the CANMET HVFA concrete system was published by Malhotra and Mehta in 2005 (Malhotra and Mehta, 2005). This system is characterized by having low water and cement contents (typically 115 kg/m^3 water and 155 kg/m^3 cement), high levels of fly ash (typically 55% to 60%), and high doses of superplasticizer to maintain a high flow at the low water content. The resulting low water-to-cementing materials ratio (typically 0.28 to 0.32) means that moderate early-age strengths are achievable despite the use of the high levels of fly ash. The first field application of CANMET's HVFA concrete was in 1987, and the first major commercial use was for the construction of a shopping, cinema, and office complex in downtown Halifax, Canada, which was completed in 1988 and used 26,000 m^3 of concrete with specified design strengths from 30 to 50 MPa (Langley and Leaman, 1998). Since this time, HVFA concrete with similar proportions has been used on a number of other projects in North America (e.g., see Langley and Leaman, 1998; Malhotra and Mehta, 2005), including the recent construction of a monolith foundation of a Hindu Temple in Hawaiian Island of Kauai, which has a design life of 1000 years (Mehta and Langley, 2000).

There are increasing pressures to reduce the environmental impact of construction (and other industrial activities), and today's engineers and architects strive to build "green buildings" that endorse the principals of "sustainable development." The U.S. Green Building Council (USGBC) and the Canada Green Building Council (CaGBC) are consensus organizations dedicated to promoting environmentally responsible construction. Both organizations have developed LEED[1] rating systems to measure the performance of buildings in terms of human and environmental health: sustainable site development, water savings, energy efficiency, materials selection, and indoor environmental quality (USGBC, 2006). The use of fly ash and other supplementary cementing materials (SCMs) can contribute to LEED points, as they are considered to be a recycled material and, in many cases, a locally available material, both of which are encouraged for use by the LEED systems. The USGBC LEED system awards points for "Innovation in Design," and currently measures that lead to a 40% reduction in the portland cement content of concrete (e.g., through the use of fly ash) are included in this category. Detailed information on the LEED rating system and the contributions that can be made through the appropriate use of concrete is provided in a LEED Reference Guide produced by the National Ready Mixed Concrete Association and the Portland Cement Association (SWA, 2005).

High fly ash content or high-volume fly ash concrete has now become synonymous with "green concrete," and examples of construction projects that have incorporated high levels of fly ash in the concrete are becoming more commonplace. Although in some of these cases the mixture proportions have strictly followed the CANMET HVFA concrete concept using 55 to 60% fly ash, with very low water contents, very high levels of superplasticizers, and a water to

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[1] LEED – Leadership in Energy and Environmental Design

cementitious material ratio (W/CM) below 0.35, the trend has been toward a less rigorous approach where the level of fly ash and other mixture proportions are selected on a case-by-case basis (i.e., materials and proportions have been optimized for the specific application).

For the purposes of this report, high-volume fly ash concrete is considered to be concrete containing more than 30% fly ash by mass of cementing material, and high-calcium fly ash is considered to be fly ash that contains more than 15 to 18% CaO and meets the requirements of ASTM C 618 Class C fly ash, but not Class F fly ash (i.e., $50\% \leq SiO_2 + Al_2O_3 + Fe_2O_3 < 70\%$).

Research Needs – Classification / composition of fly ash

- Research is needed to accurately identify and quantify the mineralogical composition (glass and crystalline components) of fly ash, especially for ASTM Class C or high-calcium fly ashes. The objective is to develop a new classification correlating the compositional characteristics of ashes with their performance in concrete.

2

EFFECT OF CLASS C FLY ASH ON FRESH CONCRETE PROPERTIES

This section discusses how fly ash, in general, and certain fly ashes in particular, affect the fresh properties of concrete, such as workability, pumpability/finishability, bleeding, and air content. Whenever possible, distinctions are made between the behavior of Class F and Class C fly ashes, and the differences between high-volume fly ash mixtures (i.e., greater than 30 percent by mass replacement of cement) and mixtures with lower fly ash contents are highlighted.

Workability and Water Demand

A recognized benefit of using fly ash in concrete is the reduced water demand (to achieve a target slump) and overall increase in workability. Figure 2-1 illustrates the impact of fly ash on water demand in concrete, for a range of different fly ash sources and dosages (Whiting, 1989). This reduction in water demand can be attributed to the spherical particle shape of fly ash, which has a lubricating or "ball bearing" effect on concrete rheology. Furthermore, the median size of fly ash particles is on the same order as portland cement, so unlike silica fume particles, which are much smaller than cement grains, fly ash does not increase the available surface area and concomitant demand for water. It should be mentioned that all fly ash sources are different, and not all have the same water-reducing effect on concrete. Factors such as particle size distribution and carbon content will have a role in determining the water-reducing capability for a given fly ash.

When considering the water reductions that are typically possible when using fly ash, it should be noted that this can be taken advantage of when proportioning a given mixture. Specifically, the water-reducing effect can be integrated into the design of the mixture, allowing for a reduction in mix water and a parallel reduction in the W/CM for the mixture. This modification in W/CM can be quite effective in trying to offset the early-age strength reduction that typically results from fly ash usage, especially when fly ash is used at high dosages (e.g., greater than 30 percent).

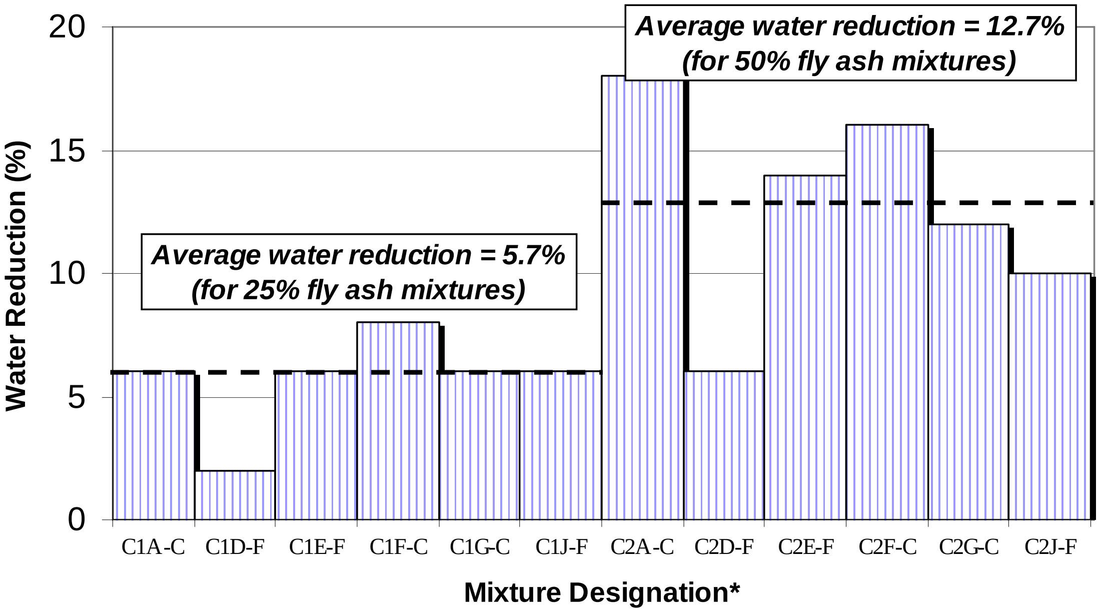


Figure 2-1
Water reductions for various fly ashes (after Whiting, 1989).
[Note that mixture designations are same as those used by Whiting (1989): "1" = 25 percent fly ash mixture; "2" = 50 percent fly ash mixture; A, D, E, F, G, J refer to different fly ash samples; for last term, C = Class C fly ash, F = Class F fly ash.]

Finishability and Pumpability

Concrete containing fly ash will tend to be easier to finish and pump, provided that the mixture is well proportioned. This improvement in finishability and pumpability is a hallmark of fly ash technology and makes its usage in field applications more readily accepted from the contractor community. Fly ash increases the cohesiveness of concrete and typically provides a "creamy" texture on the surface of a slab, allowing for easier finishing and texturing. Pumpability is improved through the enhanced cohesion, as well as by the spherical particle size of fly ash, which helps to lubricate the mixture and make it easier to pump, with lower pump pressures and less wear and tear on pumping equipment.

Bleeding

In most applications, fly ash will reduce the bleeding of concrete, including both the amount and rate of bleeding. This effect will vary from fly ash to fly ash and will also be influenced by overall mixture proportions and characteristics. The reduction in bleeding can be problematic in hot, dry, windy conditions, where plastic shrinkage cracking is a concern, and this can be exacerbated when fly ash is used in relatively high dosages, where bleeding is further reduced and setting time is further extended (as described later in this report). Under these conditions, the early-age tensile strength gain of the concrete will be quite slow, and the lack of bleed water at the top surface of a slab, for example, will lead to more rapid shrinkage as water is drawn from below the surface of the slab to the drier air above the slab. This can be dealt with in the field with proper early curing practices, such as fog misters, and by optimizing the finishing operations. Although increasing the early strength gain of fly ash mixtures by lowering the W/CM (to take advantage of water-reducing effect of fly ash) can be beneficial in offsetting the tensile stresses triggered by plastic shrinkage, one should be aware that this approach will also typically further reduce bleeding, again highlighting the need to protect fly ash concrete from rapid evaporation at early ages.

Air Entrainment

The use of fly ash in concrete tends to increase the required air-entraining admixture (AEA) needed to obtain a target air content, when compared to a control portland cement mixture. Each fly ash will have a different impact on AEA demand, depending on the chemical and physical characteristics of the fly ash, the dosage used, and other mixture-related factors (e.g., alkali content of cement, presence of other chemical admixtures, etc.).

In general, Class F fly ashes have more of an impact on AEA demand than Class C fly ash, and some Class C fly ashes with relatively high water-soluble alkali contents may even require less AEA than mixtures without fly ash (Pistilli, 1983). Although Class C fly ashes generally tend to be less problematic than Class F fly ash with regard to impact on AEA demand, the authors' experience is that when problems are encountered with Class C fly ash, the effects can be substantial. The authors have encountered a handful of high-CaO ashes over the past 20 years that have had profound effects on AEA demand, and further, these specific ash sources tend to vary with time and are quite sensitive to these changes, when considering AEA demand.

The most significant factor affecting AEA demand is the presence of unburned carbon in fly ash. This carbon is typically quantified by using the loss-on-ignition (LOI) test, which is not completely accurate, because other materials are also burned off as ashes are heated to such high temperatures (greater than 700°C). Nevertheless, LOI is a reasonable index of the carbon content of fly ash. However, LOI does not take into account the specific chemical nature or reactivity of the carbon, and it has been clearly shown that not all carbons act the same in concrete (Hill and Folliard, 2006). Some fly ashes contain very active carbon, with high surface areas, and these ashes tend to more significantly impact AEA demand. This has especially been the case in recent years, as low-NOx burners have been introduced into coal-burning power plants to reduce environmental impact. These low-NOx burners have, in some cases, drastically altered the nature of the unburned carbon, with major increases in surface area and tendency to increase AEA demand, and to a lesser extent water demand, in concrete.

Hill and Folliard (2006) compared several fly ashes and highlighted the impact of low-NOx burners on AEA demand, as shown in Figure 2-2. In this figure, it can be seen that some fly ashes with highly absorptive carbon have major impacts on AEA demand in concrete, even when the LOI is quite low, less than 1 percent (see fly ashes "C" and "E" in Figure 2-2). This behavior is in sharp contrast to other fly ashes, where the increase in LOI has a much less substantial impact on air entrainment (fly ash "H," for example, in the same figure). For these types of fly ash sources that exhibit relatively linear and mildly sloped relationships between LOI and AEA demand (or air content for a fixed AEA dosage), using LOI as a predictive index is useful and quite feasible in the field. However, for fly ashes with very high reactivity, such as ashes "C" and

"E" in Figure 2-2, LOI is not a meaningful or accurate index or predictor of AEA demand in concrete. Work is in progress at the University of Texas at Austin and Cornell University (funded under TxDOT Project 5207) to attempt to develop quick screening tests for these highly absorptive ashes that are generated at power plants that have recently been retrofitted with low-NOx burners.

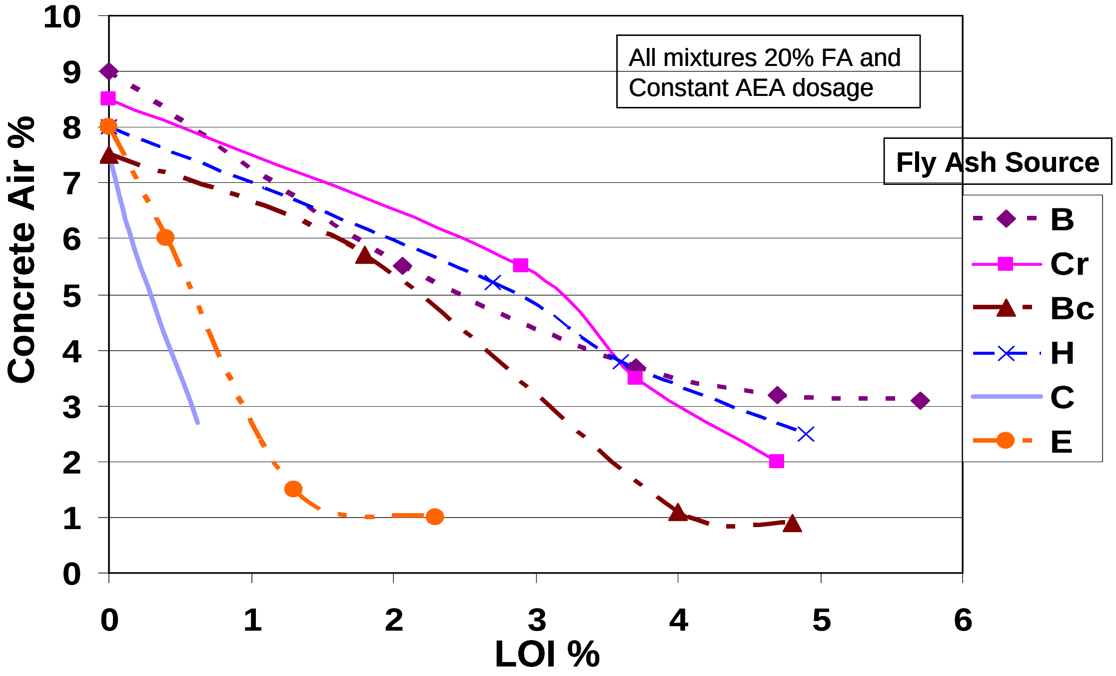


Figure 2-2
Relationship between LOI of various fly ashes and impact on air content in concrete (after Hill and Folliard, 2006).

Various beneficiation technologies have been developed and implemented in recent years to try to combat the effects of unburned carbon on AEA demand, including electrostatic separators (more effective for high-LOI ashes), carbon burn out (CBO), and chemical treatment of the ash with a surfactant to satisfy the carbon's absorption capacity, thereby minimizing the tendency for AEA absorption onto high-surface-area carbon (Hill and Folliard, 2006).

Research Needs – Air entrainment

- Rapid / reliable screening tests are needed to serve as indices for efficiently / reliably evaluating the impact of a subject fly ash on air-entraining agent demand. This seems to be particularly critical in the case of some Class C fly ashes where small changes in LOI were found to result in huge changes on air entrainment capacity. This is also important for fly ashes that have been modified by low-NOx burners, where the reactivity (surface area, absorption tendencies, etc.) has been changed and makes entraining air a challenge.

Setting Time

In reviewing available literature on the effects of fly ash on setting time, there is a clear consensus that fly ash increases both the initial and final set times of concrete. The amount of retardation, however, is quite dependent on the type and dosage of fly ash used, as well as other mixture-related factors. The retardation will, in general, be more significant at lower ambient temperature, as shown by Chevrier and Bilodeau (2001). These authors have determined the setting time of concrete incorporating 0, 30, 40, and 50 percent fly ash at different ambient temperatures of 23, 14, and 5°C. The different concrete mixtures were designed to achieve similar 28-day compressive strength at normal 23°C curing temperature. The fly ash used met the requirements of ASTM Class F fly ash but had a relatively high CaO content of 13.4 percent (CSA Class CI fly ash). Results of their study are given in Table 2-1 and illustrated in Figure 2-3.

Table 2-1
Setting Time of Concrete Incorporating Different Percentages of Fly Ash at Different Ambient Temperatures (Chevrier and Bilodeau, 2001)

Ambient Temperature	Setting Time, hours:minutes							
	Control		30% Fly Ash		40% Fly Ash		50% Fly Ash	
	Initial	Final	Initial	Final	Initial	Final	Initial	Final
23°C	06:00	07:20	07:05	08:50	07:50	09:50	07:00	09:40
14°C	07:45	10:05	08:55	11:50	09:50	13:05	11:20	14:30
5°C	11:55	16:30	16:25	22:20	18:05	26:40	18:45	27:25

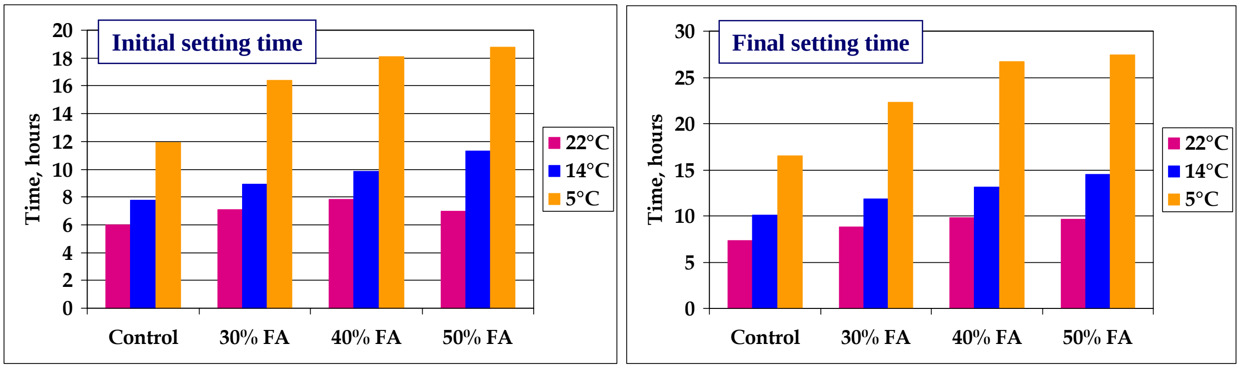


Figure 2-3
Initial and final setting time as a function of temperature and fly ash content (from Chevrier and Bilodeau, 2001).

The data show that at normal ambient temperature (23°C), the setting time of the fly ash concrete is relatively longer compared to that of the control and that, in general, it increases with the increased percentage of fly ash. In this study, the effect of increasing the percentage of fly ash on the setting time was partially offset by the reduction of the W/CM of the mixtures required to achieve similar compressive strength at 28 days. At lower ambient temperature, the setting time of the fly ash concrete was significantly more retarded than that of the control concrete.

Gebler and Klieger (1986) evaluated four Class C fly ashes and six Class F fly ashes and found that the increase in set time for mixtures containing 25 percent fly ash (by mass replacement of cement) was the following: Class F fly ashes – average of 35 minute increase in initial set time and 75 minute increase in final set time; Class C fly ashes – average of 30 minute increase in initial set time and 45 minute increase in final set time. Based on this data, Class C fly ash did not retard setting time nearly as much as Class F fly ash. However, the author's experience, based on laboratory and field evaluations and trials, is that Class C fly ashes tend to retard set time more than Class F fly ash. This experience has recently been confirmed in a comprehensive study funded by the Texas Department of Transportation (TxDOT Project 4563), and the main findings related to set time and heat of hydration are summarized by Poole (2007). Using a three-parameter model proposed and applied to hydration modeling (Pane and Hansen, 2002; Schindler and Folliard, 2005) as shown in Equation 1,

$$\alpha(t_e) = \alpha_u \cdot e^{-\left[\frac{\tau}{t_e}\right]^{\beta}} \qquad \text{Equation 1}$$

where $\alpha(t_e)$ = degree of hydration at equivalent age t_e, τ = hydration time parameter (hours), β = hydration shape parameter, and α_u = ultimate degree of hydration. This three-parameter model is represented graphically in Figure 2-4. This figure shows a typical hydration curve and highlights what impact an increase in each of the three parameters would have on the shape of this curve. The time parameter, τ, is particularly relevant to this section on setting time as it is, in essence, an index of setting time or the onset of heat generation and increased concrete rigidity. In the section on heat of hydration, the other aspects of heat generation will be discussed. In tying Figure 2-4 to previous discussions on fly ash, it is well established that the setting time, and hence, hydration time parameter (τ) increases when using fly ash at typical dosages used in concrete construction.

The recently completed study at the University of Texas at Austin has attempted to better quantify this effect and to further delineate the differences between different fly ash types and dosages using both isothermal and semi-adiabatic calorimetry. Some of these findings, relative to setting time, are discussed next, and other findings related to overall heat development are discussed later in this report.

The University of Texas study confirms the consensus found in literature that using fly ash tends to retard concrete setting (as evidenced by increasing β values), with the retardation increasing as fly ash dosage increases (up to a dosage of 40 percent fly ash mass replacement of cement, the upper bound limit evaluated in the study). In addition, this study showed that the amount by which fly ash increases retardation increases as the CaO content of the fly ash increases, which agrees with previous work by Schindler and Folliard (2005). The increase in retardation was most pronounced for Class C fly ashes, perhaps due to mineralogy of the fly ash and/or the impact on early pore solution chemistry (e.g., availability and reactivity of C_3A and sulfates in solution). More work is needed to definitively identify the causes of retardation in high-CaO ashes and to relate fly ash characteristics to setting time behavior.

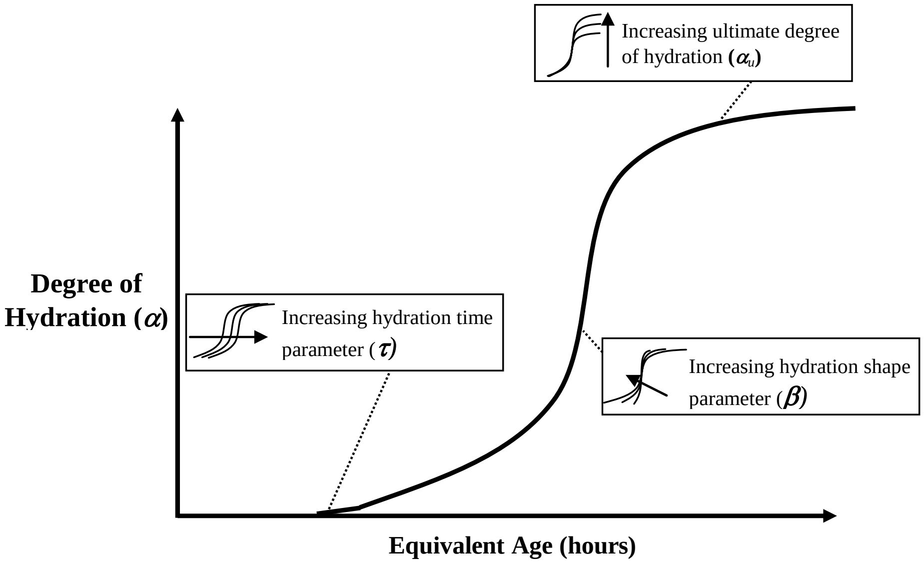


Figure 2-4
Graphical depiction of three-parameter model for describing hydration of concrete.

Based on the findings of the University of Texas study, as summarized by Poole (2007), a statistical model has been developed, relating the characteristics and dosage of cementitious materials (portland cements and various SCMs) to the hydration time parameter (τ) or degree of retardation. For brevity, this overall equation and details thereof are not provided herein, but Figure 2-5, which deals specifically with fly ash dosage and chemistry, is included. In this figure, one can see that the impact of fly ash is based on the dosage, as well as the CaO content. This equation is based on a wide range of concrete mixtures, tested using semi-adiabatic calorimetry, and incorporating fly ashes with a range of CaO from 0.7 to 28.9 percent.

This model for predicting τ, as well as the other two hydration parameters described in Figure 2-4, is surprisingly quite accurate, given that only the CaO content of the fly ash is taken into account, without the incorporation of detailed mineralogical parameters. Unfortunately, as discussed elsewhere in this report, one cannot use CaO as a stand-alone predictor of behavior when considering sulfate resistance. Furthermore, as described next, the infamous case of the “never-setting concrete” cannot be predicted solely by the CaO content of the ash, as this extreme behavior involves a unique compatibility issue that arises with a very specific combination of fly ash chemistry (and mineralogy), cement chemistry, admixture type and dosage, and placement temperatures.

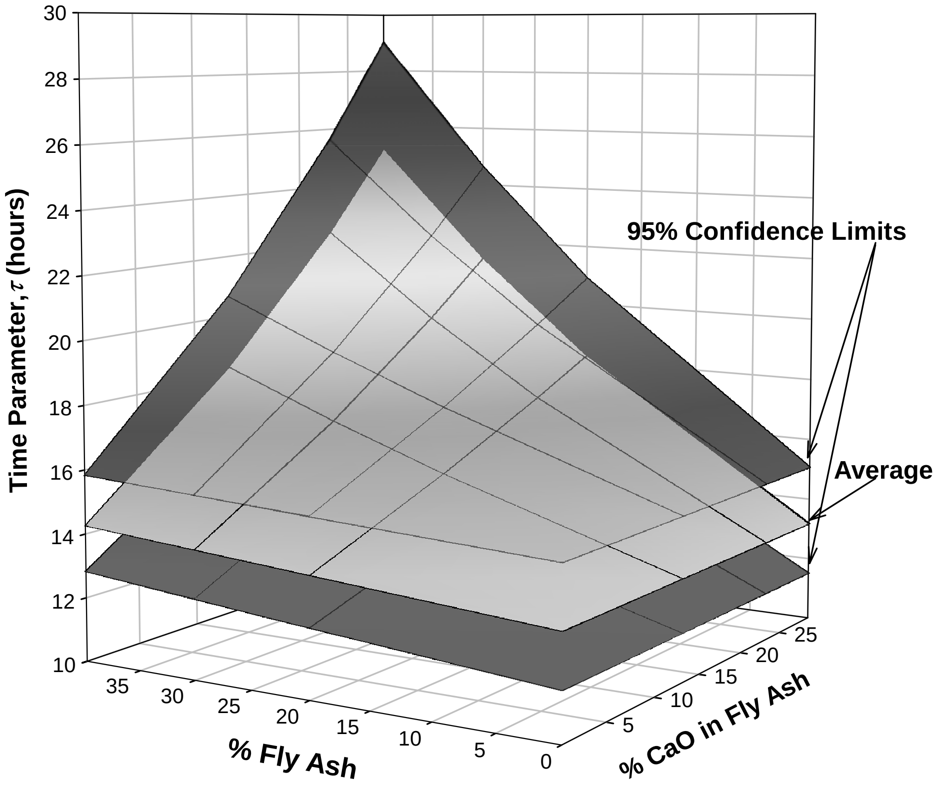


Figure 2-5
Effect of fly ash dosage and CaO content on retardation, as characterized by time parameter, τ (Poole, 2007).

Over the past two to three years, there have been a number of reported cases of concrete exhibiting extraordinarily long setting times in summer placements. This extreme setting behavior has been euphemistically called the case of the "never-setting concrete," although in reality, the concrete does eventually set, albeit it after several days or more. These problems have been observed particularly in the southern part of the United States in recent years, especially during times of cement shortage and subsequent importation of foreign cements, and have been detailed in the literature (Sandberg and Roberts, 2005; Roberts and Taylor, 2007). Based on literature and the authors' direct experience with these field problems, the following can be identified as factors contributing to this extreme increase in setting time:

- Presence of Class C fly ash, specifically reactive fly ash used at relatively high dosages (e.g., 25-35 percent).
- Presence of normal water reducers, again used at relatively high dosages.
- Presence of "undersulfated" cements (undersulfated with regard to the combined system, but not necessarily if cements were used in absence of fly ash and water reducer). By way of background, sulfates, in the form of gypsum or anhydrite, are added to portland cement clinker to control setting times. The amount of sulfates added is based on an "optimal sulfate" concentration, as described in ASTM C 150. This optimal sulfate concentration is actually expressed as a range of allowable sulfate contents. As defined above, "undersulfated" cements are those that are produced at the low end of the allowable sulfate

range, and these cements generally behave satisfactorily in the vast majority of applications; however, when combined with the system described above (in combination with Class C fly ash and normal water reducers) they may exhibit symptoms of severe set retardation.

- Hot weather conditions (e.g., greater than 90°F).

The above combination of factors has led to numerous problems in the southern part of the United States in recent years, although the problem seems to have disappeared in the past year, as has the national cement shortage. Nevertheless, it is included in this report because the presence of Class C fly ash has been identified as a critical component of the situation. In particular, the Class C fly ashes that have led to this problem have been very reactive, from an early strength gain perspective. Fly ashes of this variety would also tend to be those that are most prone to sulfate attack and those most suitable for use in "FlashFill," a type of controlled low-strength material comprised only of fly ash, sand, and water (without cement). Not all Class C fly ashes fit in this category, and furthermore, fly ashes with identical CaO contents may not have similar effects, whether discussing setting time behavior, sulfate resistance, or suitability for "FlashFill." This overall picture reinforces the need for being able to better quantify fly ash mineralogy, as opposed to just relying on bulk chemical composition. This desire to accurately determine fly ash mineralogical composition is perhaps one of the most important research needs today, given the applicability to such critical and diverse aspects of concrete behavior.

Heat of Hydration

A major benefit of using fly ash in concrete is the reduction in heat of hydration, especially for large concrete elements. The effects on heat generation are highly dependent on the specific fly ash used and the amount of portland cement being replaced. A review of the published literature shows that there are far more papers/reports that have focused on Class F fly ash rather than Class C fly ash. An exhaustive literature review is not the intention here, as there have been a wide range of papers on the benefits of using fly ash to reduce heat generation. Rather, this section highlights some of the studies related to fly ash and heat of hydration, with emphasis on the effects of fly ash chemistry and dosage on heat generation.

Dunstan (1984) reported that the rate of heat development generally increased with the CaO content of the fly ash, and some high-CaO ashes, when used at typical field dosages, imparted little or no reduction in heat generation. Thomas et al. (1995) used conduction calorimetry to show that fly ashes with a range of CaO contents (3 to 27 percent CaO content) yielded results similar to Dunstan's, namely that the 7-day heat of hydration for various cement/fly ash combinations was linked strongly to the CaO content of the ash. Thomas et al. (1995) also showed that in order to achieve a given amount of heat reduction, fly ashes with high CaO contents had to be used at higher replacement levels.

Although moderate amounts of high-CaO fly ash (Class C) may not profoundly reduce heat generation, high dosages of high-CaO fly ash have been used to control the temperature rise in mass concrete foundations. An example is the concrete raft foundation (10,000 m^3) for the Windsor Courthouse (Anon., 1996), in which concrete with 50% Class C fly ash was used to control temperature and thermal cracking.

Poole (2007), in a summary of work performed under Texas Department of Transportation-funded research, showed that low-CaO fly ashes tend to reduce the heat of hydration of the mixture primarily through dilution of the portland cement. They reduce the slope of the accelerating portion of the hydration curve as well. Higher-CaO fly ashes also reduce the heat of hydration, but also show some hydraulic properties beyond pure dilution of the portland cement. They reduce the slope of the accelerating portion of the hydration curve, and they increase the duration of the induction period of the mixture. The overall findings from this comprehensive study have been integrated into a software package (ConcreteWorks) that primarily relies upon fly ash dosage and CaO content to model the hydration time parameter, hydration slope parameter, ultimate degree of hydration, and activation energy. It is beyond the scope of this report to summarize all these aspects of heat modeling when using fly ash, but as an example, Equation 2 shows how the ultimate heat of hydration can be calculated for a combination of portland cement (with specific chemistry defined by either Bogue's calculations or Rietveld analyses) and various SCMs.

$$\begin{aligned} H_u &= H_{cem} \cdot p_{cem} + 461 \cdot p_{GGBF-100} + 550 \cdot p_{GGBF-120} \\ &+ 1800 \cdot p_{FA-CaO} \cdot p_{FA} + 330 \cdot p_{S.F.} \end{aligned} \quad \text{Equation 2}$$

where H_u = total heat of hydration (J/gram), H_{cem} = heat of hydration of the cement (J/gram), p_{cem} = cement mass to total cementitious content ratio, $p_{GGBF-100}$ = % Grade 100 blast furnace slag (GGBF slag) in mixture, $p_{GGBF-120}$ = % Grade 120 blast furnace slag (GGBF slag) in mixture, p_{FA} = fly ash mass to total cementitious content ratio, p_{FA-CaO} = fly ash CaO mass to total fly ash content ratio, and $p_{S.F.}$ = % silica fume in mixture.

Poole (2007) reported that the activation energy (E_a) or heat sensitivity of cement pastes was affected by fly ash, with Class F fly ash tending to reduce E_a; Class C fly ash may either lower or raise E_a, depending on the C_3A and SO_4^{2-} content of the cement that is paired with the fly ash. As a general trend, the amount of change in E_a roughly correlates with the CaO content of the fly ash.

Research Needs – Setting time and heat of hydration

- Work is needed to accurately predict the setting time / strength gain / heat of hydration of high-volume Class C fly ash concrete systems, especially in different environmental (temperature) conditions. The CaO content of fly ash appears to be a good index for heat of hydration development but it doesn't take into account mineralogy (i.e., C_3A) or particle size. Work should thus focus on a range of Class C fly ashes with varying "reactivity" (glassy vs. crystalline components).
- There is a need to better understand the mechanism(s) of retardation in Class C fly ash concrete mixtures and to determine why Class C fly ash does retard more than Class F fly ash. For instance, Class C fly ash coupled with water reducer and under-sulfated cement was found to lead to excessive set times. Work is needed to understand such behavior and to establish how can this be predicted before it happens, and thus be prevented.

- Tools / practices / products need to be developed to regulate the setting behavior and improve the early-strength gain of concrete containing Class C fly ash, especially when high dosages are used. These improvements in constructability will help to ensure that the major benefits of fly ash usage are realized and that contractors' concerns over construction schedule can be reduced. Understanding how fly ash characteristics impact the fresh and hardened properties of concrete is key to this objective.

3

EFFECT OF CLASS C FLY ASH ON THE MECHANICAL PROPERTIES AND DIMENSIONAL STABILITY OF CONCRETE

Compressive Strength

It is well accepted that, for a given W/CM, concrete incorporating fly ash as partial replacement for cement will demonstrate lower early-age strength as compared to control portland cement concrete; the higher the replacement level is, the lower the early-age strength of the fly ash will be. In general, for concrete incorporating up to about 50% fly ash, at some point in time, under moist-curing conditions, the strength of the fly ash concrete will equal that of the control portland cement concrete, and then, at later ages, will be significantly higher than that of the control concrete.

Normally, concrete will be designed to achieve a certain minimum strength at a specific age, typically 28 days. In general, to achieve a specific strength at 28 days, the W/CM of the fly ash concrete will have to be lower than that of the control concrete; the higher the percentage of fly ash will be, the lower the W/CM will have be. In the case of high-volume fly ash concrete, very low W/CM, ranging from 0.30 to 0.35 may be required.

A number of studies indicate that the compressive strength development of concrete incorporating large volumes of ASTM Class C fly ash is faster at early ages than that of ASTM Class F concrete having similar mixture proportions (Yuan and Cook, 1983; Gebler and Klieger, 1986; Tse et al., 1986; Naik et al., 2003b; Zhang et al., 1998). In their study on concrete incorporating 20, 30, and 50 % ASTM Class C fly ash, Yuan and Cook stated that the slow strength gain at early ages, typical of concrete made with ASTM Class F fly ash, was not evident for the Class C fly ash concrete (Yuan and Cook, 1983). Their results also showed that the rate of strength development of the ASTM Class C fly ash concrete was comparable to that of the portland cement concrete at any time for the given mixtures. Although their study dealt with concrete incorporating 25% fly ash, which does not meet the definition for high-volume fly ash concrete within this report, Gebler and Klieger showed that, in general, moist-cured concrete with Class C fly ash was developing slightly higher early strengths than concrete with Class F fly ash but that the long-term (91 days and beyond) compressive strength was not significantly different for the two classes of fly ash, and this would probably apply to concrete incorporating larger amounts of fly ash (Gebler and Klieger, 1986). In the same study, Gebler and Klieger investigated the effect of moist curing on the strength development of the fly ash concrete. Their results indicated that the concrete containing Class F fly ash would require slightly more moist curing for long-term compressive strength development as compared to concrete made with

Class C fly ash. Their results also showed that the strength development of concrete made with Class C fly ash subject to air curing was similar to that of the control concrete.

Although it appears that concrete incorporating Class C fly ash may develop strength significantly faster at early ages than concrete made with Class F fly ash, higher replacement levels of cement by Class C fly ash in concrete may still result in early-age strength values significantly lower than that of concrete without fly ash. This has been shown by Naik and Ramme in their study on concrete incorporating one Class C fly ash in proportions ranging from 20 to 60 percent (Naik and Ramme, 1989). Their results showed that the early-age strength of the concrete incorporating 50 to 60 percent Class C fly ash was very low. However, at 28 days and beyond, the specified strength of the concrete was met and the strength of the fly ash concrete was, at later ages, higher than that of the control. They stated that the source of Class C fly ash investigated could be used for structural concrete in quantities up to at least 40 percent replacement of cement, and that if early-age strength was not an important consideration, then even higher amounts of that fly ash, such as 60 percent replacement, could be used.

In a different study, Naik et al. (1997) investigated high-volume fly ash concrete with three different ASTM Class C fly ashes. The cement replacement levels used were 40, 50, and 60 percent, and the water-to-cementitious materials ratio was kept constant at 0.30. They found that, in general, at ages up to 7 days, the fly ash mixtures exhibited lower strength compared to the reference mixture. Also, concrete incorporating 40 and 50 percent of the Class C fly ash showed equivalent or higher strengths than the reference concrete except at the very early ages.

Flexural and Splitting-Tensile Strengths

There is not much data available on the flexural and splitting-tensile strengths of concrete incorporating large volumes of ASTM Class C fly ash and on how they compare to those of either reference concrete or concrete incorporating large volumes of Class F fly ash. However, it seems that, in general, the trend found for the compressive strength development applies also for the flexural and splitting-tensile strengths. Both the flexural and splitting-tensile strengths of concrete incorporating large volumes of Class C fly ash are, in general, slightly lower at early ages but similar at later ages to those of control concrete of equivalent compressive strength (Naik et al., 1995; Naik et al., 1997; Naik et al., 2003b; Zhang et al., 1998; Carrasquillo 1987). Also, as compared to the performance of Class F fly ash concrete, the strengths of the Class C fly ash concrete may be slightly higher at early ages.

Young's Modulus of Elasticity

Similarly to flexural and splitting-tensile strengths, the relationship between the Young's modulus of elasticity and compressive strength is not significantly affected by conventional amounts of fly ash in the concrete. In general, when compared to control concrete, the modulus of elasticity of fly ash concrete will follow a similar trend as that of compressive and other strength properties, i.e., lower at early ages and higher at later ages for a given specified strength.

As for high-volume fly ash concrete, it is reported that the modulus of elasticity of this type of concrete is relatively higher than that of control concrete of similar strength (Malhotra and Mehta, 2005). These authors suggest that the high modulus values of the high-volume fly ash concrete may be due to a considerable portion of unreacted fly ash acting as a fine aggregate. However, there is not much data available on the modulus of elasticity of high-volume fly ash concrete made with Class C fly ash. Naik et al. (1997) have tested high-volume fly ash concrete mixtures incorporating 40, 50, and 60% of Class C fly ash. Three different Class C ashes with CaO contents ranging from 27.6 to 31.9% were used. The data showed that similarly to their compressive strength test results, the modulus of elasticity of the high-volume fly ash concrete at early ages up to 7 days was lower than that of the reference concrete, but that at 28 days and beyond, both types of concrete had similar modulus of elasticity values. These data partially contradict the observations made by Malhotra and Mehta (2005) about the higher modulus of elasticity of high-volume fly ash concrete. It should be mentioned that this general observation made by Malhotra and Mehta was made mainly on concrete incorporating Class F fly ash. The results from the Naik et al. study could be an indication that for modulus of elasticity properties, Class C fly ash behaves slightly differently from Class F fly ash. However, Carette et al. (1993), in their investigation using eight different fly ashes, including two that would be classified as Class C fly ash by ASTM, found no significant difference in behavior between the two types of fly ash.

Drying Shrinkage

Malhotra and Mehta (2005) reported that the drying shrinkage strains of high-volume fly ash concrete are lower than that of control concrete. However, this statement is based essentially on the CANMET's HVFA concrete system. Also, Malhotra and Mehta do not differentiate between the two classes of fly ash and, in fact, their observations are mostly based on data on high-volume fly ash concrete made with Class F fly ash.

In this report, the definition of high-volume fly ash concrete is different from that of Malhotra and Mehta, but still, there is not much data available on the drying shrinkage of this type of concrete made with Class C fly ash, and it is difficult to draw clear conclusions on this subject. Some authors (Yuan and Cook, 1983; Carasquillo, 1987) have found that the drying shrinkage of high-volume fly ash concrete made with Class C fly ash was similar to that of the control concrete, but others (Naik et al., 1997) have found that the former was significantly higher than the latter. When compared to high-volume fly ash concrete made with Class F fly ash, it appears that the high-volume fly ash concrete made with Class C fly ash demonstrates similar shrinkage values, as shown in Figure 3-1 (Carette et al., 1993), or higher shrinkage values (Naik et al., 1995; Carasquillo, 1987).

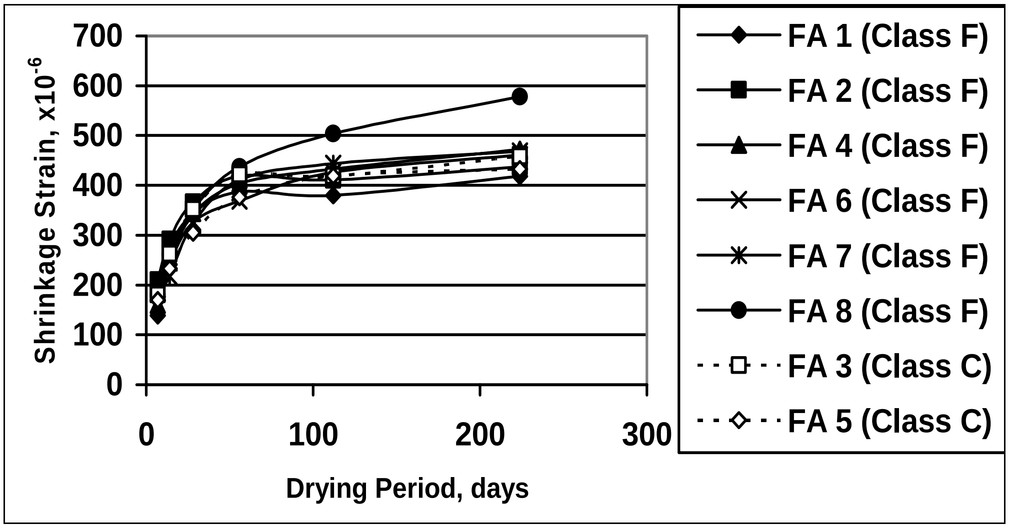


Figure 3-1
Drying shrinkage of high-volume fly ash concrete made with Class F and Class C fly ashes (Carette et al., 1993).

Research Needs – Mechanical properties

- Work is needed to evaluate the effect of various factors [e.g., fly ash compositional characteristics, exposure conditions (e.g., temperature)] on the early-age strength development in concrete incorporating high levels of Class C fly ash.
- The use of accelerating admixtures (or other materials) to increase early-age strength should be further evaluated.

4

EFFECT OF CLASS C FLY ASH ON THE DURABILITY OF CONCRETE

Alkali-Silica Reaction (ASR)

Alkali-silica reaction (ASR) is a chemical reaction between various forms of silica present within fine and/or coarse aggregate particles and the alkali hydroxides (Na,K – OH) from the concrete pore solution. During this internal chemical attack, the “reactive” silica progressively transforms into an alkali-silica gel that absorbs water, thus inducing pressure within and around aggregate particles and, in turn, inducing cracking and possible loss in serviceability of the affected concrete member. ASR can take from 2 to more than 25 years to develop to a significant extent in concrete structures, depending on a number of factors such as the nature and reactivity level of the aggregate, the environmental conditions to which the structure is exposed (humidity, temperature, etc.), the original alkali content in the concrete and the potential contribution of alkalis from other sources than the cement (e.g., aggregates, chemical admixtures, SCM, de-icing salts, sea water, etc.), the restraint to which the structure/element is subjected, and so on. Over the past few decades, numerous investigations have shown that expansion due to ASR can be prevented by: 1) using non-reactive aggregates, 2) reducing the total alkali content in concrete under threshold values that vary from one aggregate to another, and 3) judiciously selecting a sufficient proportion of effective supplementary cementing materials (SCM) (e.g., fly ash, ground granulated blast-furnace slag, natural pozzolans, silica fume, etc.) or lithium-based admixtures.

Performance Evaluation of SCM to Prevent ASR Expansion

Thomas et al. (2006) recently reviewed the various test methods for evaluating the efficacy of SCM for controlling expansion due to ASR in concrete. The Concrete Prism Test (CPT) (ASTM C 1293) is considered by many to be the most reliable laboratory test for determining the potential alkali-reactivity of aggregates and the efficacy of preventive measures (e.g., fly ash) for controlling expansion. When the test is used to evaluate preventive measures, test prisms, 75 x 75 x 300 to 400 mm in size, are made from a concrete mixture incorporating a total cementitious materials content of 420 kg/m^3 and where the SCM to be investigated is used as replacement, by mass, of the high-alkali concrete cement. Additional alkali is added, in the form of NaOH, to bring the cement alkali content to 1.25% Na_2O equivalent for acceleration purposes. The test prisms are then stored in sealed plastic containers at 38°C (100^{o}F) and R.H. > 95% and their length change monitored regularly over a period of two years; an expansion limit of 0.04% is used to identify safe combinations of SCM and reactive aggregates. However, the duration of this test is judged too long for most practical purposes. More recently, an accelerated version of the CPT in which test prisms are stored at 60°C (140°F) was proposed as a way to accelerate the expansion process in the CPT and get faster results (Fournier et al., 2004; Ideker et al., 2006). Extensive work is currently in progress in the authors' laboratories to evaluate the reliability of this accelerated version of the test.

Originally developed to evaluate the potential alkali-reactivity of concrete aggregates, the ASTM C 1260 accelerated mortar bar test (AMBT) (ASTM C 1260) has in recent years been modified in order to evaluate the performance of different combinations of materials for controlling ASR expansion; this modified method is known as ASTM C 1567. In that test, mortar bars 25 x 25 x 280 mm in size are cast from a mortar mixture in which the SCM to be investigated is used, as replacement, by mass, of the control cement. The test prisms are then stored in a 1N NaOH solution at 80°C (176°F) and their length change monitored regularly over a period of 14 to 28 days. The expansion limit and the testing period vary from one organization to another. Thomas et al. (2007) recently demonstrated that using an expansion limit of 0.10% at 14 days generally correlated well with the results obtained in the CPT or observed in field structures incorporating reactive aggregates and various proportions of SCM.

Efficacy of Fly Ash in Controlling ASR Expansion in Binary and Ternary Cementitious Systems

It is now well established that low-calcium Class F fly ashes are effective in controlling expansion due to ASR when used at moderate levels of replacement (i.e., 15 to 30%, depending on degree of reactivity of the aggregate to counteract). However, Class C fly ashes with higher calcium contents (i.e., > 20% CaO) tend to be less effective in this role, at least at similar replacement levels, in comparison to Class F ashes (Diamond and Lopez-Flores, 1981; Dunstan, 1981; Buck and Mather, 1987; Klieger and Gebler, 1987; Shehata and Thomas, 2000; Fournier 2002). Shehata and Thomas (2000) indeed showed that the expansion of concrete prisms (ASTM C 1293) containing a reactive siliceous limestone (Spratt aggregate) and high-alkali cement (raised to 1.25% Na_2Oe) partially replaced with 25% fly ash was strongly influenced by the calcium content of the fly ash, as shown in Figure 4-1 (with additional unpublished data from Shehata and Thomas). Generally, fly ashes with calcium contents above 20% CaO were not able to control the two-year expansion of concrete to below 0.04% when used at a 25% replacement level. Note that fly ashes with high alkali contents (e.g., > 5% Na_2Oe) were also unable to control expansion regardless of the calcium content. The same study showed that the high-calcium fly ashes were effective in controlling expansion in the concrete prism test, provided the fly ashes were used at higher levels of replacement (e.g., 50 to 60%), as shown in Figure 4-2.

Fournier et al. (1997) selected two highly reactive aggregates from Canada to be tested in control concrete mixtures made with high- and low-alkali ASTM Type I portland cements, and in mixtures incorporating high volumes (i.e., 56%) of selected Canadian fly ashes. These ashes had CaO and Na_2Oeq contents ranging from about 2 to 26% and 1.3 to 9.5%, respectively. The nominal cementitious materials content and the water-to-binder ratio for the high-volume fly ash (HVFA) concrete mixtures were 375 ± 10 kg/m^3 and 0.31 ± 0.01, respectively. Figure 4-3 shows that the effectiveness of fly ash in reducing expansion due to ASR in the HVFA system was a function of the chemical composition of the fly ash used, in particular its calcium and alkali contents.

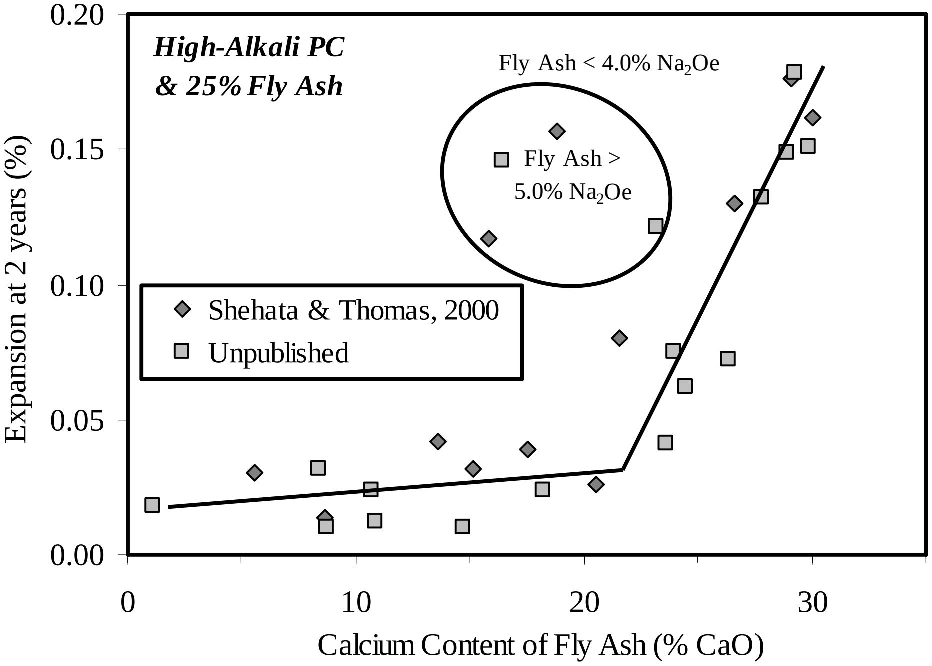


Figure 4-1
Effect of the calcium content of fly ash on the expansion of concrete prisms with Spratt aggregate.

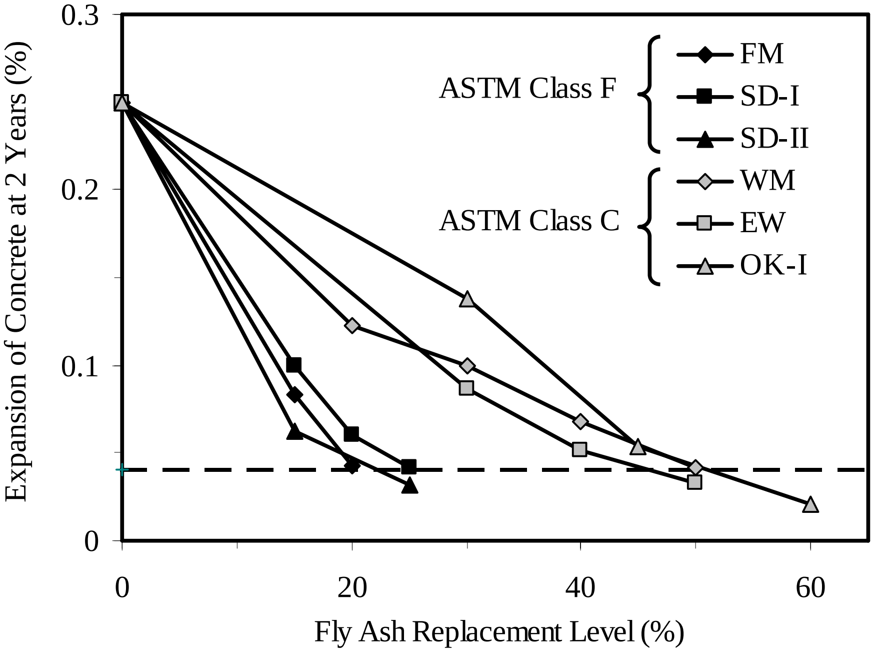


Figure 4-2
Effect of the replacement level of fly ash on the expansion of concrete prisms with Spratt aggregate (Shehata and Thomas 2000).

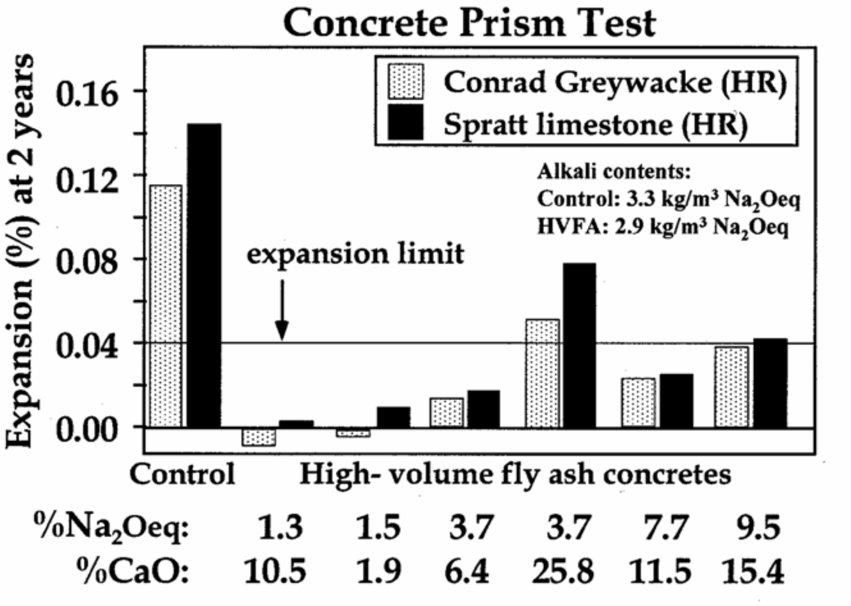


Figure 4-3
Concrete prism expansion data after two years of testing at 38°C and R.H. > 95% for control concretes and HVFA concretes (56% replacement level) incorporating the highly reactive Spratt limestone and Conrad greywacke aggregates (Fournier et al., 1997).

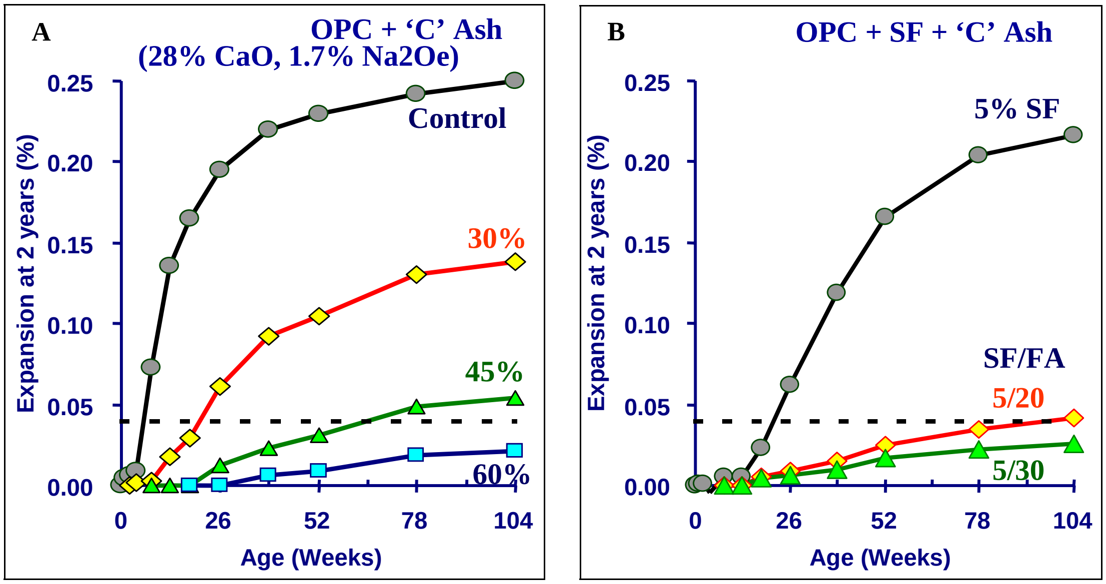


Figure 4-4
Expansion as a function of time for sets of concrete prisms incorporating a highly reactive siliceous limestone (Spratt) and different proportions of Class C fly ash (Shehata and Thomas 2002).
(A) Control and binary systems incorporating 30 to 60% Class C fly ash.
(B) Concrete incorporating 5% silica fume only and ternary systems incorporating 20 and 30% Class C fly ash and 5% silica fume.

Shehata and Thomas (2002) showed that more moderate levels of high-calcium fly ash (20 to 30%) could be used to control expansion due to ASR when they were used in a ternary cement blend that also contained high-alkali cement and moderate levels of silica fume (~5%) (Figure 4-4).

Since 2002, Fournier and coworkers at CANMET, University of New Brunswick, and the University of Texas at Austin have been carrying out a comparative laboratory [accelerated mortar bar test and concrete prism tests (at 38 and 60°C)] and field (outdoor exposure site) testing program to evaluate the effectiveness of fly ash in binary and ternary (in combination with silica fume) systems in reducing expansion due to ASR (Fournier et al., 2004, 2005, 2006). Fly ashes with CaO contents ranging from 1 to 28% and reactive aggregates from different locations in Canada and the United States were selected for the study. The fly ash contents investigated range from 15% (with low-calcium ashes) to 60% (with the high-calcium ashes). ASTM C 1567 was first used as a screening test. Based on the results thus obtained, several combinations were reproduced in the Concrete Prism Test (ASTM C 1293); test prisms were monitored for expansion for 2 years at 38°C (standard test) and up to 9 months at 60°C (accelerated test). Table 4-1 summarizes the results obtained to date using the AMBT. The results confirm that the minimum fly ash necessary to control expansion due to ASR varies as a function of the composition of the ash and the type of reactive aggregate to counteract.

Table 4-1
Summary of AMBT Data Obtained as Part of the EPRI-ICAR-PCA Project (Fournier et al., 2005). The minimum fly ash content is given for which an AMBT expansion of < 0.10% (i.e., acceptable level) is obtained either in binary (fly ash only) or ternary (in combination with 5% silica fume) cementitious systems, for the various aggregates tested in the study. A black box indicates that the fly ash, at that replacement level, was ineffective in controlling expansion with that particular aggregate.

FA composition	FA1		FA2		FA3	
%CaO →	0.90		13.20		16.80	
%Na$_2$Oe →	1.75		0.74		10.45	
% FA in the system	Binary	Ternary	Binary	Ternary	Binary	Ternary
15			Qtz	Wt,Pen,Wy		
20	Wt,Wy, Qtz,Pen		Wy			Qtz,Wy
25		NM	Wt,Pen	NM		Pen,Sp
30	NM					
35			NM			
40						NM
50					Sp, NM, Wy,Qtz,Pen	

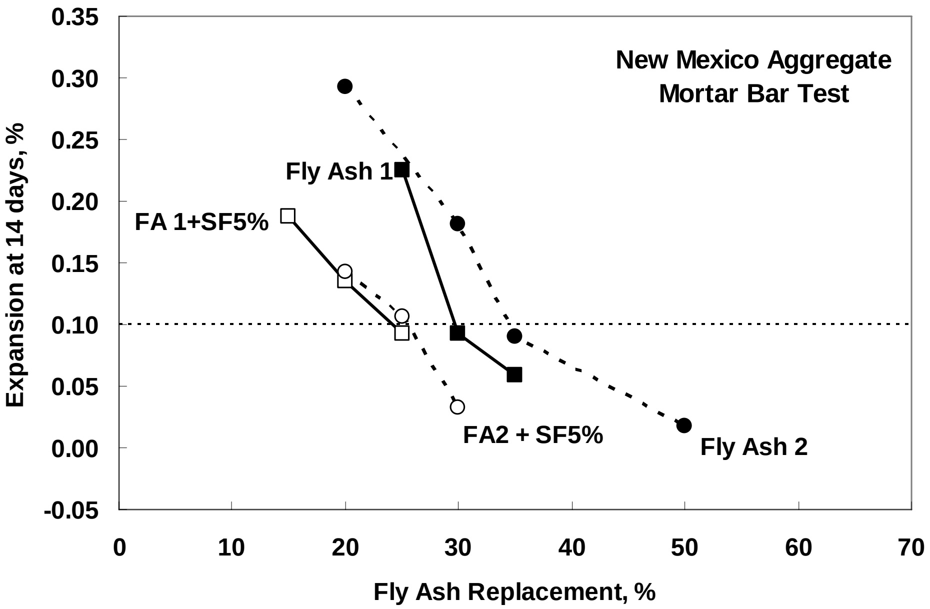
Table 4-1 (continued)
Summary of AMBT Data Obtained as Part of the EPRI-ICAR-PCA Project (Fournier et al., 2005). The minimum fly ash content is given for which an AMBT expansion of < 0.10% (i.e., acceptable level) is obtained either in binary (fly ash only) or ternary (in combination with 5% silica fume) cementitious systems, for the various aggregates tested in the study. A black box indicates that the fly ash, at that replacement level, was ineffective in controlling expansion with that particular aggregate.

FA composition	**FA4**		**FA5**		**FA6**	
%CaO →	22.50		21.00		28.10	
%Na$_2$Oe →	2.30		5.83		1.95	
% FA in the system	Binary	Ternary	Binary	Ternary	Binary	Ternary
15		Wy,Qtz		Qtz		Wt
20		Sp,Wt,Pen				Qtz
25				Wt,Wy,Pen		Pen
30	Wt,Qtz					Wy
35		NM				
40	Sp(±)			NM	Wt,Qtz	NM
50	NM,Wy,Pen		Wt(±),Wy,Qtz		Wy	
60			NM,Pen(~)		NM,Pen	

Note: NM: New Mexico gravel (highly reactive); Wt: Wright sand (Texas) (highly reactive); Wy: Wyoming gravel (highly reactive); Sp: Spratt limestone (Ontario) (highly reactive); Qtz: Minnesota quartzite (moderately reactive); Pen: Pennsylvania greywacke (highly reactive).

As indicated in Table 4-1 and illustrated in Figures 4-5 and 4-6 for two highly reactive (NM and Wy gravels) aggregates, the addition of 5% silica fume in ternary systems was beneficial (but not always sufficient in the proportions tested) in further reducing accelerated mortar bar expansions. This was particularly the case in the presence of high-calcium/high-alkali fly ashes, which had shown some limitations in their effectiveness at controlling expansion due to ASR in the 20-30% range commonly used in practice. The above observations are also confirmed by the concrete prism data presented in Figure 4-7.

Recent tests at University of New Brunswick have also shown that combinations of Class C fly ash with either Class F fly ash or slag are also effective. However, at the time of writing, only data from accelerated tests were available; the results of this study will be reported when ongoing concrete prism tests are completed.



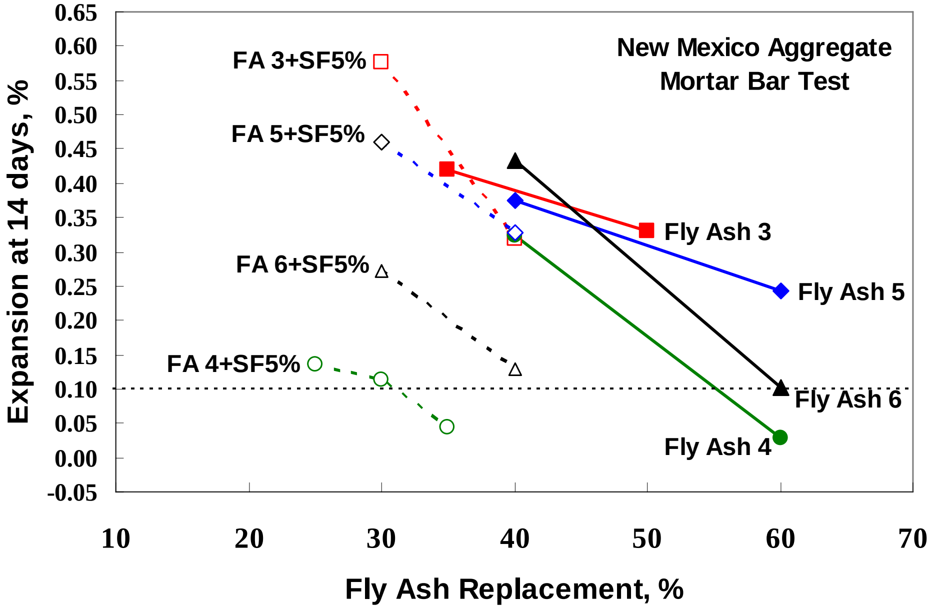
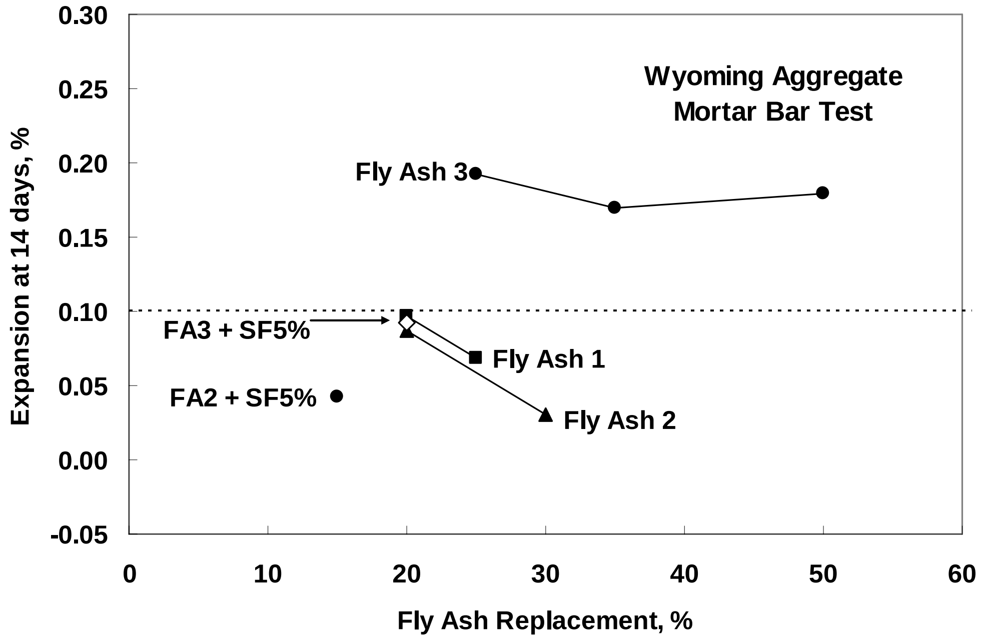


Figure 4-5
Accelerated mortar bar test results for mortar systems incorporating the highly reactive New Mexico gravel and six fly ashes with CaO contents ranging from 0.90 to ~30% (see Table 4-1) (from Fournier et al., 2005).



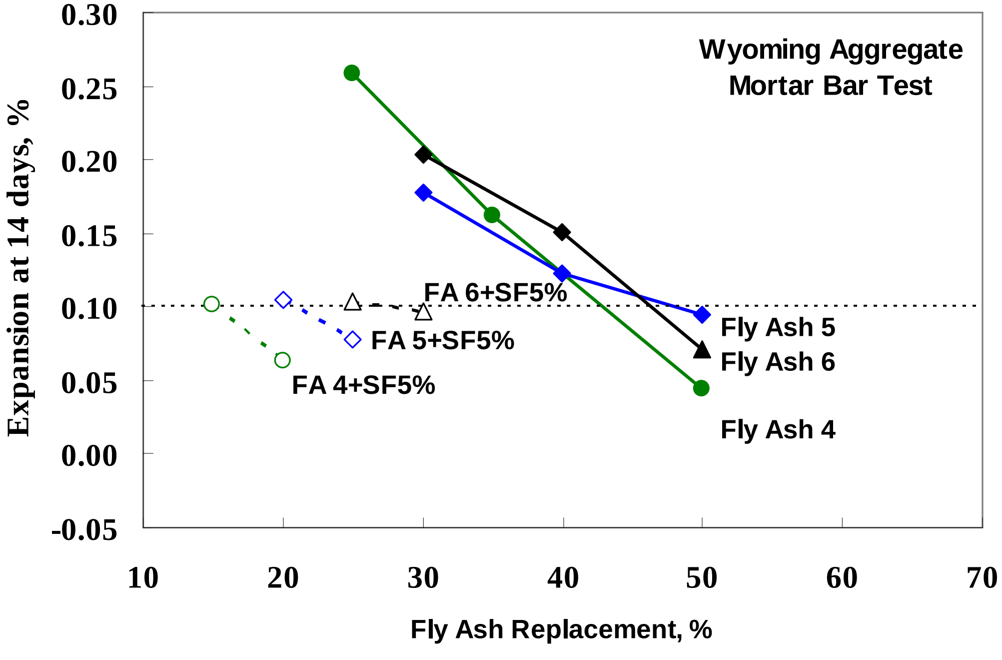


Figure 4-6
Accelerated mortar bar test results for mortar systems incorporating the highly reactive Wyoming gravel and six fly ashes with CaO contents ranging from 0.90 to ~30% (see Table 4-1) (from Fournier et al., 2005).

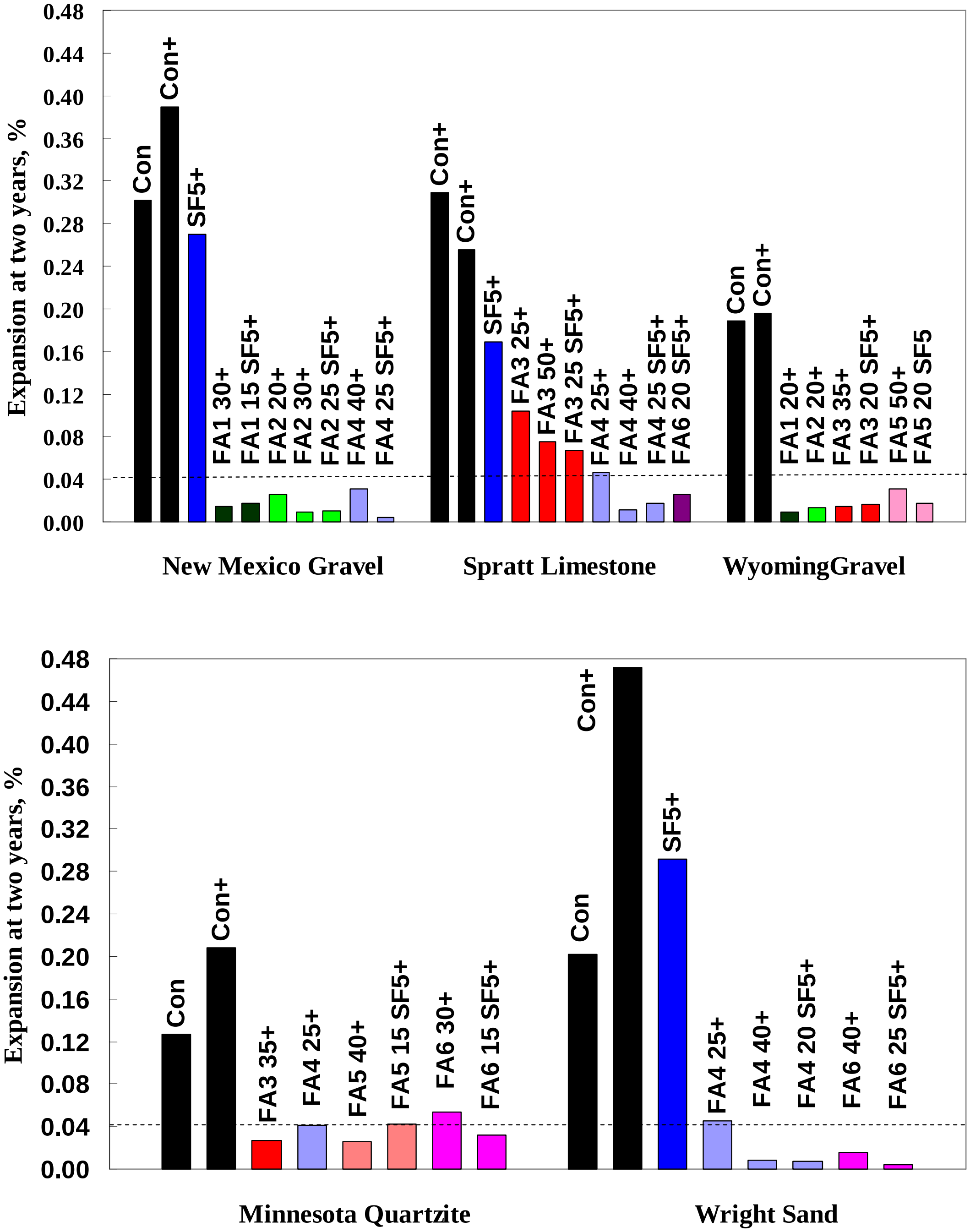


Figure 4-7
Concrete prism test results for concrete systems incorporating moderately to highly reactive aggregates and six fly ashes (i.e., FA1 to FA6) with CaO contents ranging from 0.90 to ~30% (see Table 4-1) (from Fournier et al., 2006). As per ASTM C 1293, the total cementitious materials content is 420 kg/m^3. The abbreviation "Con" means control mixtures (i.e., with no fly ash). Mixtures with fly ash (FA) and/or silica fume (SF) are identified with the replacement level used (e.g., FA5 15 SF5+: mixture with 15% fly ash FA5 and 5% silica fume). The "+" suffix used for control and fly ash mixtures means that the alkali content corresponding to the portland cement part in the mixture has been raised to 1.25% Na_2Oeq by the addition of NaOH to the mixture water.

Folliard et al. (2006) described a comprehensive research program focusing on the construction of a “Showcase Bridge” to be constructed by the Texas Department of Transportation (TxDOT), in which each of the twelve spans of the bridge would entail different mitigation measures to prevent ASR-induced expansion of concrete containing a highly reactive aggregate from Corpus Christi. Table 4-2 shows the results of AMBT, CPT, and exposure blocks performed in the program. Within this table, identical designations are used for the various materials as were used in Folliard et al. (2006). Specifically, F7 is a highly reactive aggregate from Texas, FA2-F is a Class F fly ash with a CaO content of 10.8 percent, FA4-C is a Class C fly ash with a CaO content of 24.6 percent, UFFA is an ultra-fine fly ash (from the same power plant as FA2-F), and SF is condensed silica fume.

The mixtures shown in Table 4-2 reflect the mixtures that were selected for the proposed bridge, and each mixture containing SCM or lithium nitrate was based on selecting the lowest dosage of the materials to attempt to optimize early-age strength gain and to control the economic feasibility in the case of lithium-based products. Note that the control mixture is not proposed to be used in the actual bridge, but will be included in a small-scale test bridge located near the actual bridge.

Table 4-2
Mixtures Evaluated and Proposed for Showcase Bridge (Under TxDOT Project 4085, as Detailed in Folliard et al., 2006)

	AMBT	CPT	Exposure Blocks	
Showcase Bridge Mixtures - F7	**14 days Expansion (%)**	**2 years Expansion (%)**	**Average Expansion (%)**	**Age (days)**
Control - F7 (1.25% Na_2O_e)	**0.29**	**0.205**	**0.9064**	1397
20% FA2-F	0.04	0.016	0.0159	1395
40% FA4-C	0.08	0.007	0.0247	1122
15% UFFA	0.02	0.005*	0.0216	1134
10% Metakaolin	0.03	0.017	0.0201	1134
40% Slag	**0.12**	0.027	0.0192	1395
75% $LiNO_3$	0.01	0.028	0.0212	1393
35% FA4-C & 5% SF	0.06	0.013	-0.0039	1115
30% FA4-C & 5% UFFA	0.06	0.017	0.0216	1115
20% FA2-F & 5% SF	-	0.013	0.0077	1317
30% FA4-C & 75% $LiNO_3$	0.02	0.025	**0.0463**	1314
35% Slag & 5% SF	0.07	0.023	0.0138	1338
Low Alkali Cement (0.52% Na_2O_e)	**0.23**	0.001**	-0.0021	1357

Bold *indicates data that failed the test or exhibits cracking in the field.*
**measurement at 18 months*
***measurement at 1 year*

It should be noted that this bridge has not yet been built, due to environmental permitting issues unrelated to this project, but it is anticipated that this bridge or a similar one will be constructed using most or all of the mixtures shown in Table 4-2. With regard to fly ash use in this proposed bridge, the requisite dosage for Class C fly ash was double that of the Class F fly ash. Although not shown in this table, concrete prisms and exposure blocks cast with 30 and 35 percent Class C fly ash (FA4-C) exceeded expansion limits under ASTM C 1293 after two years and exhibited cracking in exposure blocks. Lastly, it should be noted that the combination of 30% Class C fly ash and 75% lithium nitrate solution (based on standard 100 percent dosage being equal to 0.55 gallons of 30% $LiNO_3$ solution per pound of alkalis from the portland cement only) expanded and cracked significantly in the exposure block (stored outdoors in Austin, Texas). It appears that there is no synergy between Class C fly ash and lithium nitrate (a chemical admixture also used to control ASR expansion in concrete), unlike what has been observed in Class F fly ash/lithium mixtures. It is likely that the dosage of lithium needs to be adjusted to also take into account some or all of the alkalis present in Class C fly ash. More work is in progress now by the authors to determine requisite dosages of fly ash when used with lithium compounds, but suffice it to say that there does not seem to be any synergy when combining Class C fly ash with lithium nitrate.

Comparison of Testing Methods for Evaluating the Efficacy of SCM Against ASR

Thomas et al. (2007) have shown that the AMBT (ASTM C 1567), using an expansion limit of 0.10% at 14 days, provides an acceptable evaluation of the efficacy of SCM in controlling expansion due to ASR. This is illustrated in Figure 4-8 based on the results of the EPRI study currently in progress (Fournier et al., 2006, 2007). Figure 4-8 shows that most data fall into the pass-pass and fail-fail quadrants; however, one can see that the AMBT overestimates, for a number of the combinations tested (data in the upper left quadrant), the amount of fly ash that would be required to control ASR expansion based on the corresponding expansions obtained in the CPT. This suggests that using the AMBT would represent a safe approach, at least in the case of the various combinations illustrated in Figure 4-8.

Regarding the use of the accelerated concrete prism test (60°C) for evaluating the efficacy of fly ash for controlling ASR expansion, Figure 4-9 shows that a 9-month, 0.040% expansion limit could be used, which represents a significant acceleration compared to the two-year testing period required in the conventional test performed at 38°C. Once again, the expansions obtained in the 60°C test seem to overestimate the amount of fly ash required for ASR control for a number of the combinations tested (data in the upper left quadrant), which suggests that the test would also represent a safe approach for selecting safe proportions of fly ash for ASR control.

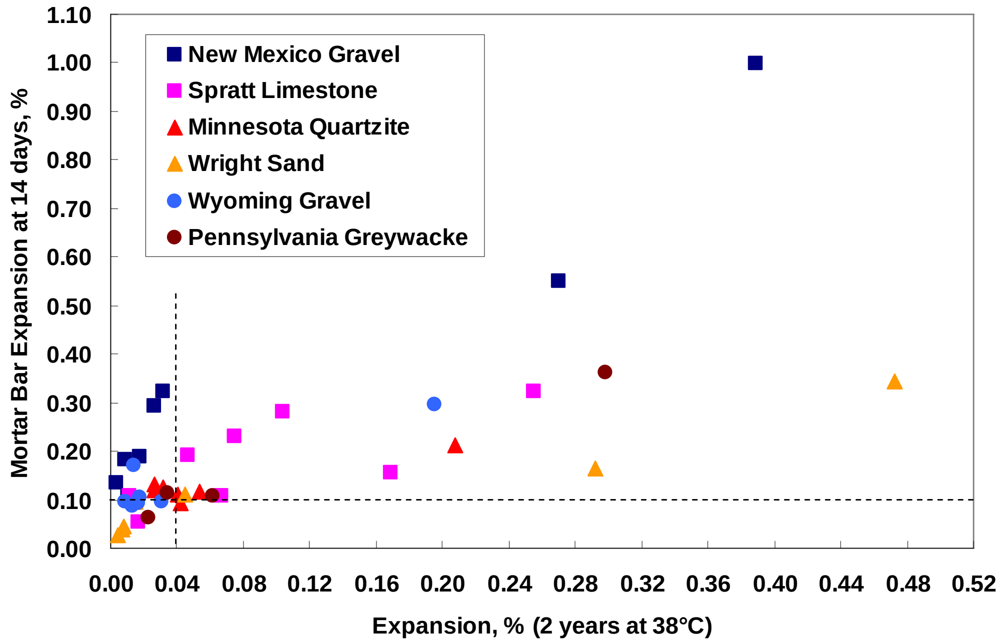


Figure 4-8
14-day accelerated mortar bar expansions plotted against two-year concrete prism expansion for various binary and ternary combinations tested by Fournier et al. (2006).

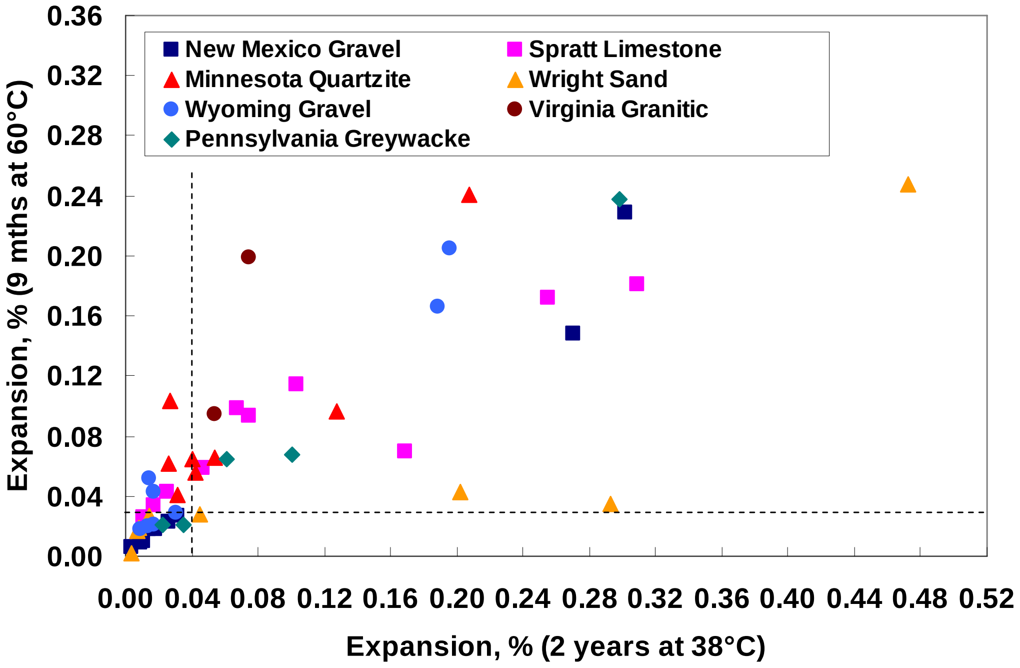


Figure 4-9
9-month accelerated concrete prism expansions (60°C, R.H. > 95%) plotted against two-year concrete prism expansion (38°C, R.H. > 95%) for various binary and ternary combinations tested by Fournier et al. (2006).

Past research has shown that for the most part, the alkalinity of portland cement has little or no impact on the expansion of aggregates using the accelerated mortar bar test (ASTM C 1260). However, research at the University of Texas at Austin over the past several years has shown that the effects of cement alkalinity may be more pronounced when testing fly ash in conjunction with reactive aggregates. Specifically, work conducted by Bauer (2002) and Pugh (2003) has shown that higher-alkali cements actually result in lower expansion values, compared to similar tests using lower-alkali cement. Clearly, this is counterintuitive and not likely to be the case for actual field concrete. It is well established that higher alkali contents of cement, combined with fly ash at a given dosage, contribute more to ASR than lower-alkali cements. Thus, it is more than likely a side effect of the ASTM C 1260 testing regime. It is particularly relevant given that some agencies have in the past specified, or still do specify, the use of a “job site” mixture in ASTM C 1260 test conditions. In these instances, the actual fly ash and cement of interest were used in the test, and if multiple cement sources were available to a contractor/producer, one could test each cement in the test series and would more than likely end up showing that the highest-alkali cement was most efficient in reducing expansion.

Typical data from the University of Texas program are shown in Table 4-3, in which the higher-alkali cement consistently yielded lower expansions than low-alkali cement, and in some cases, the cement selection made the difference between passing or failing the test (using a 0.10 percent expansion limit at 14 days).

Table 4-3
14-Day Expansions for Highly Reactive TX Fine Aggregate Combined with Fly Ashes of Different CaO Contents

Fly Ash Designation*	CaO of fly ash (%)	Replacement by mass of cement (%)	14-day Expansion high-alkali cement (Na_2O_e=0.89%)	14-day Expansion low-alkali cement (Na_2O_e=0.52%)
FA6-F	13.12	20	0.05	0.09
FA7-F	0.69	20	0.02	0.13
FA8-C	23.13	30	0.09	0.13
FA9-C	28.91	40	0.11	0.13

* designations consistent with TxDOT Project 4085 Final Report (Folliard et al., 2006)

Similar data were presented to the ASTM Task Group on ASR Performance Limits, and the interactions between cement and fly ash were discussed in detail. At the end of these discussions, it was decided that the issue may be a concern when specifications directly tie the cement/fly ash combination from ASTM C 1260 (or currently ASTM C 1567) to those to be used in a specific field application, because higher-alkali cements may do better in the laboratory using the accelerated mortar bar test but they will perform worse in field applications. Despite this inherent concern, deliberations within ASTM have arrived at the fact that this cement/fly ash interaction only has a minor impact on test results, perhaps suggesting that five percent less fly ash might be needed than what is actually indicated by the test. It was postulated that this “error” is overcome by the inherently conservative nature of testing SCM using ASTM C 1260. Specifically, ASTM

C 1260 generally overpredicts by about five percent how much fly ash is needed to control expansion, when compared to ASTM C 1293 test results. Thus, the two effects tend to cancel each other out, and the end result should still be reasonable. More work is still warranted to flush out the details of this cement/fly ash interaction, but it is quite possible that the effects observed in this test are due to alkali activation of fly ashes, which would mean a higher-alkali cement would “kick in” a given fly ash more effectively in the first day or so of the mortar bar test, resulting in a mixture that is less permeable and slows the ingress of the NaOH host solution into the bars. Given the desire in today’s concrete industry to generate data as quickly as possible, this interaction deserves future attention.

Mechanism of Beneficial Action of Fly Ash for Controlling ASR

The effect of fly ash composition on the expansion of concrete can be explained on the basis of the composition of the pore solution (Shehata et al., 1999). Low-calcium fly ashes are more effective in binding alkalis and reducing the concentration of alkalis in the pore solution, and higher-calcium fly ashes have to be used at greater levels of replacement to produce the same effect (Figure 4-10). The fact that more moderate levels of high-calcium fly ash (20 to 30%) are found to control expansion due to ASR when used in a ternary cement blend with moderate levels of silica fume (~ 5%) (Shehata and Thomas, 2002) can also be explained on the basis of how the combination of silica fume and high-calcium fly ash influenced the pore solution.

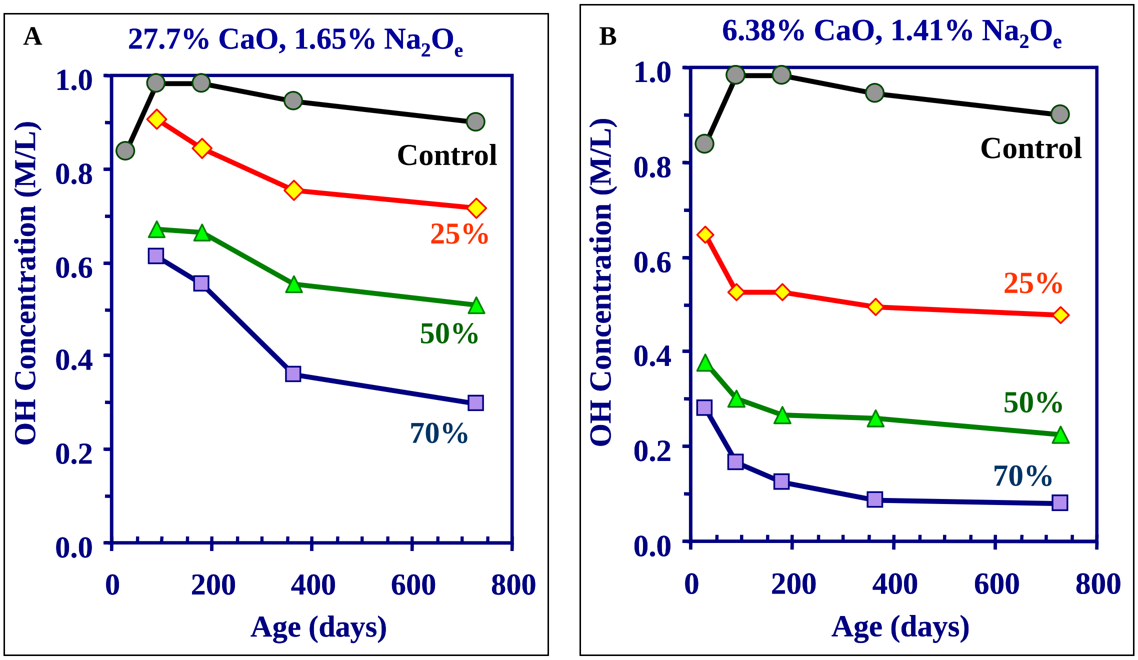


Figure 4-10
Concentration of hydroxyl ions (OH-) in the pore solution of pastes incorporating various proportions of high-calcium (A) and low-calcium (B) fly ashes (Shehata et al., 1999).

Later studies by Thomas and Shehata (2004) showed that the alkali and hydroxyl ion concentration of the pore solution extracted from 2-year-old hardened cement paste samples

(W/CM = 0.50) was a function of the chemical composition of the blend, and an excellent linear relationship was established between the OH concentration of the solution and the parameter $(Na_2Oe \times CaO)/SiO_2$ calculated for 79 different blends of portland cement, fly ash, slag, and silica fume. This relationship is shown in Figure 4-11. However, more research is required to determine the precise relationship between fly ash composition, aggregate reactivity, cement alkalinity, and the minimum “safe” level of fly ash required to prevent deleterious reaction.

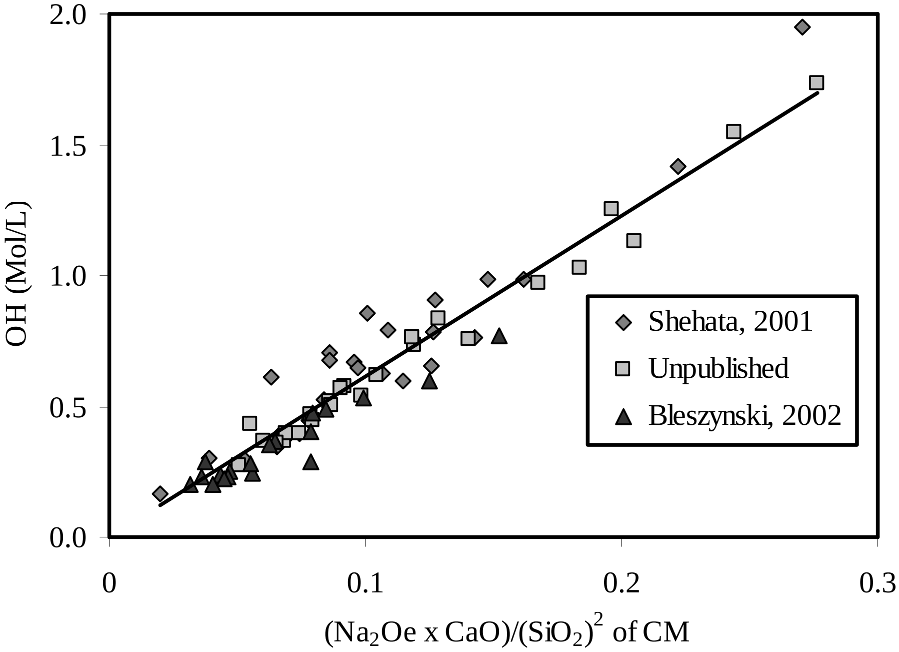


Figure 4-11
Relationship between chemical composition of the cementing materials and the pore solution extracted from hardened cement paste (Thomas and Shehata, 2004).

Integrated Approach for the Selection of Preventive Measures Against ASR

Malvar et al. (2002) recently proposed a state-of-the-art review of recommendations for ASR mitigation from a number of organizations, including a few U.S. state departments of transportation (California, New Mexico, Washington State), AASHTO, Portland Cement Association, Federal Aviation Administration, American Concrete Institute, Canadian Standards Association, RILEM, etc. The various groups evaluated all recommend the use of fly ash for controlling ASR; however, only a few have specific recommendations regarding the use of Class C fly ash. CALTRANS, for instance, indicates that fly ash with more than 10% CaO is unsuitable for mitigating ASR; recommendations include using 30% of a fly ash with a CaO content ranging from 2 to 10%. The New Mexico DOT preferentially requires the use of Class F fly ash with reactive aggregates but allows the use of Class C ash; both ashes need to have < 10% CaO, < 1.5% available alkalis, and LOI < 3%. The International Center for Aggregate Research (ICAR) reports an approach allowing a number of different options for the prevention of ASR, one of those being the use of 35% of Class C fly ash.

Canadian Standards Association developed two Standard Practices (i.e., CSA A23.2-27A and CSA A23.2-28A) (CSA 2004a, 2004b) to help selecting preventive measures against alkali-aggregate reaction in concrete (Fournier et al., 1999). The first (i.e., 27A) is a step-by-step approach based on a risk analysis. The risk of poor performance of concrete due to ASR is first classed according to the degree of reactivity of the aggregates, the size of the concrete element, and the humidity of the environment. The need for and level of preventive measure is then determined according to the required service life of the concrete structure. The type and level of preventive action is then selected from among the following options: (1) reject the proposed aggregate, (2) limit the alkali content of the normal portland cement concrete, and (3) use effective SCM (or an effective combination of SCM) in sufficient amounts. When SCM are to be used without the need or opportunity for confirmatory testing, the specific type of constituents (i.e., fly ash, slag, silica fume) and the minimum proportion needed are proposed based on past field experience and extensive laboratory investigations using known Canadian reactive aggregates. The minimum amount of SCM to be used depends on: (1) the type of SCM used, (2) the level of prevention of ASR, and (3) the composition of the SCM, e.g., its alkali and CaO contents for fly ash. Table 4-4 gives an extract from Standard Practice A23.2-27A (CSA 2004a); it provides prescriptive recommendations for the use of fly ash for controlling ASR expansion in concrete. One can see that there is no prescriptive recommendation for fly ash with a CaO content > 20% and that the appropriate amount of such material can be determined only through laboratory testing, which is covered by Standard Practice A23.2-28A.

Table 4-4
Use of SCM for Counteracting ASR (from CSA 2004a)

Type of SCM	Total Alkali Content of SCM % Na_2Oeq	Chemical Composition Requirement (% oxides)	Cement Replacement Level (% by mass) [a]		
			Prevention Level W	Prevention Level X	Prevention Level Y & Z
Fly Ash	< 3.0	CaO < 8%	•15	• 20	• 25
		CaO = 8-20%	• 20	• 25	• 30
		CaO > 20%	See [b]	See [b]	See [b]
	3.0 – 4.5	CaO < 8%	• 20	• 25	• 30
		CaO = 8-20%	• 25	• 30	• 35
		CaO > 20%	See [b]	See [b]	See [b]
	> 4.5	See [b]			

Na_2Oeq = sodium oxide equivalent = $Na_2O + [0.658 \times K_2O]$

[a] In order to control the total alkali content of the concrete mixture, the maximum alkali content of the cement used in combination with any SCMs should be < 1.0% Na_2Oeq.

[b] In the presence of reactive or potentially reactive aggregates, blast furnace slag and silica fume with alkali contents > 1.0% Na_2Oeq, and fly ash with alkali contents > 4.5% Na_2Oeq and/or with CaO contents > 20% may be used when their effectiveness in reducing expansion due to ASR is demonstrated in accordance with CSA Standard Practice A23.2-28A. In this respect, test results have indicated that higher-alkali fly ashes (but not high-CaO ashes), when used in large quantities (e.g., > 50% as cement replacement by mass), can reduce expansion to an acceptable level.

The type and proportion of SCM to be used with "job" aggregates can be determined through a laboratory investigation program, as described in CSA A23.2-28A (CSA 2004b). The approach is also used to evaluate the effectiveness of materials not meeting the compositional requirements given in Table 4-4 (e.g., blast furnace slag with alkali contents > 1.0% Na_2Oeq, silica fume with alkali contents > 1.0% Na_2Oeq and/or SiO_2 content < 85%, fly ash with alkali contents > 4.5% Na_2Oeq and/or with CaO contents > 20%) and of blends of different SCM in controlling expansion due to ASR. The testing program in the laboratory involves the use of the accelerated mortar bar test (ASTM C 1567) and the Concrete Prism Test (ASTM C 1293).

Research Needs – Alkali-silica reaction

- Despite the fact that there has been significant work done on Class C fly ash and ASR, there is still a strong need to focus on correlating the effect of the compositional characteristics of Class C fly ashes with their efficacy in reducing expansion due to ASR.
- Most of the work to date relating to the evaluation of the efficacy of fly ash for controlling ASR expansion has been in high-alkali systems. There is a need to look at the use of Class C fly ash in lower-alkali systems, i.e., systems that are much closer to typical "job mix designs" commonly used in field structures.
- In low-alkali systems, the contributions of "available" alkalis from fly ashes in HVFA (Class C) systems will need to be evaluated, as alkalis from the fly ash may contribute to long-term expansion processes in such systems.
- Testing in low-alkali systems will be a challenge for laboratory testing; consequently, links will be required between accelerated testing performed in the laboratory and field performance (including exposure blocks).

De-icing Salt Scaling Resistance

The de-icing salt scaling resistance of fly ash concrete remains a controversial subject. Numerous studies, based on laboratory test data, have demonstrated that concrete incorporating more than about 20-25 percent fly ash performs unsatisfactorily when exposed to freezing and thawing in the presence of de-icing salts. On the other hand, as stated by Thomas (1997), there is clearly a lack of consistency between the performance of fly ash concrete under accelerated and field conditions. That author reported a number of cases of field placements containing relatively large amounts of fly ash that performed satisfactorily after several years of exposure to de-icing salt.

The ASTM C 672 test, sometimes with some slight modifications, is the test mostly used for determining the de-icing salt scaling resistance of concrete. Several investigations using that test have shown that concrete incorporating fly ash had lower resistance to de-icing salts compared to that of control concrete. High-volume fly ash concrete incorporating large percentages of fly ash (≈ 50%) performed, in general, very poorly in that test, even when the W/CM of the concrete was kept very low at about 0.32. As for the effect of the type of fly ash, Thomas (1997) has indicated in his review paper that Class C fly ash tends to perform better than Class F fly ash. However, some others have results showing the opposite (Zhang et al., 1998). As stated above, there are several examples of fly ash concrete, sometimes high-volume fly ash concrete, field placements performing adequately when exposed to de-icing salt. Given this, several authors suggested that the ASTM test is possibly too severe or, at least, does not adequately represent the actual performance in the field of fly ash concrete, and pointed out the necessity to develop a new test method, or a modified version of the ASTM test.

Some investigators have attempted to identify the factors explaining the lower performance of fly ash concrete in the ASTM test. One approach is to identify the differences in the casting, finishing, and curing procedures between the field and the test that would affect the scaling resistance of concrete in the test. For some reasons, the fly ash concrete would be more sensitive to those differences than the concrete without fly ash. This could lead to the development of a more realistic test procedure for the evaluation of the potential performance of fly ash concrete mixtures to be used in applications exposed to de-icing salts. This could lead also to clear identification of procedures or field practices that would ensure adequate field performance of fly ash concrete exposed to de-icing salt.

In their study, Bouzoubaâ et al. (2004) have compared the laboratory and field performance of concrete incorporating various percentages of supplementary cementing materials, including concrete incorporating 25 and 35 percent fly ash. This investigation consisted of placing sidewalk sections using different concrete mixtures and different finishing and curing practices. For each mixture, a number of specimens were cast, and several others were cored from the sidewalk sections. The specimens were then tested for de-icing salt scaling resistance. Both the ASTM test and a standard test (BNQ NQ 2621-900) used in the Province of Quebec, Canada, which is a variation of the ASTM test, were used. The main differences between the ASTM and BNQ tests are the following:

- The BNQ standard does not require brushing after the bleeding, i.e., the slabs are simply covered with a plastic sheet immediately after finishing with a wooden trowel.
- The BNQ standard requires a moist curing period of thirteen days followed by a fourteen-day period of air drying and a seven-day period of resaturation of the surface with a solution of 3% NaCl.
- The BNQ standard requires that the scaling residues are collected and weighed after 7, 21, 35, and 56 cycles of freezing and thawing, and the cycles continue during the weekends.

The fly ash concrete mixtures performed relatively poorly in the ASTM test but performed well when tested in accordance with the BNQ test. The performance in the field of the fly ash concrete mixtures was acceptable according to the visual evaluation of the sidewalk sections. The results of the BNQ test were significantly more in line with the field performance than were the results of the ASTM test. The same study confirmed what was reported by a number of other investigations, as the use of curing compound (membrane) instead of wet curing considerably improved the scaling resistance of fly ash concrete.

Generally speaking, considering the variability of the test results, it appears reasonable to say, in accordance with Thomas (1997), that fly ash concrete is likely to perform relatively well in the ASTM test if the W/CM of the fly ash concrete does not exceed 0.45 and the fly ash content does not exceed about 30 percent, although there might be exceptions. The limited information available indicates that concrete meeting these criteria would probably perform well in the BNQ standard scaling test. Consequently, given the number of examples of satisfactory performance of fly ash concrete in the field, including some examples involving concrete incorporating larger percentages of fly ash, it is reasonable to suggest that fly ash concrete meeting the above criteria should also perform adequately in the field, provided that proper placing, finishing, and curing procedures are used.

Ongoing research at a number of institutions has indicated that certain anti-icing salts, such as potassium acetate, can exacerbate alkali-silica reaction (ASR) when applied to concrete containing reactive aggregate. However, few data have been published at this time and the mechanisms of the interaction between the anti-icing salt and the concrete, and the role of typical ASR preventive measures, such as using fly ash, are not fully understood.

Research Needs – De-icing salt scaling resistance

- Examine the effect of placing, finishing, and curing practices on the scaling resistance of high-volume Class C fly ash concrete.
- Develop or recommend suitable test methods for evaluating the scaling resistance of concrete, especially concrete containing high levels of SCMs.
- Conduct field trials with high-volume Class C fly ash concrete in sidewalks and pavements. Also, run laboratory testing using various accelerated tests (compare ASTM C 672 and BNQ).

Sulfate Attack

This section describes the effects of fly ash on the resistance of concrete to sulfate attack. Discussion will be provided on external sulfate attack, physical salt attack, and internal sulfate attack [or delayed ettringite formation (DEF)].

External Sulfate Attack

The first reported case of external sulfate attack dates back to the early 19th century in Europe, and according to Mehta (2000), the formation of ettringite from calcium- and alumina-bearing phases of portland cement paste was implicated as the cause of expansion and cracking as far as back as 1892. In 1915, Wig and Williams published their observations on sulfate attack in the western United States (Mehta, 2000). Since then, occurrences of sulfate attack have been widespread throughout the United States, especially in California. External sulfate attack is such a concern mainly because of the prevalence of sulfates from a range of sources, including soil, groundwater, industrial waster, fertilizers, and marine sources.

When considering external sulfate attack, it is convenient to separate the types of attack into chemical attack (described in this section) and physical attack (described in the next section on physical salt attack). Chemical sulfate attack results from chemical attack on cement paste by an external sulfate source. External sulfates typically take the form of sodium sulfate, magnesium sulfate, or calcium sulfate. Often, the actual salts are mixtures of the above. The chemical attack by sulfates is strongly dependent on the cation type, and in fact, the reaction products that form may be significantly different, depending on the type of sulfate(s) involved. There are various manifestations of sulfate attack, including concrete expansion, loss of mass, popouts, map cracking, efflorescence, and spalling. It is generally believed that ettringite formation leads to expansion, whereas gypsum formation leads to a loss of mass, although there is some debate about each of these statements. The decomposition of C-S-H generally leads to softening and disintegration (Taylor, 1997; Taylor and Gollop, 1997).

According to Shashiprakash and Thomas (2001), concrete resistant to chemical sulfate attack can be produced using at least one (usually a combination) of the following approaches:

1. Use a sulfate-resistant portland cement
2. Use supplementary cementing materials
3. Produce a low-permeability concrete (typically needs SCMs to fully realize benefit)

With regard to the first method, the use of a sulfate-resistant cement, it has long been known that the most important portland cement characteristic affecting sulfate resistance is the C_3A content (Mather, 1968). This is the basis for the development of moderately and highly sulfate-resistant cements (Type II and Type V, respectively). In general, Type II (or Type I/II) cement is readily available in many locations across the United States, but there is a general lack of Type V cement (with the main exception being in California). The general lack of availability of Type V cements in the United States (and the world) has been triggered by the movement toward using SCMs to control sulfate attack, as described next.

The first reference to using fly ash to suppress expansion and deterioration due to sulfate attack was by Davis et al. in 1937. Fly ash can prevent sulfate attack by:

- Reducing concrete permeability.
- Reducing calcium hydroxide content in concrete through pozzolanic reaction (produces C-S-H at the expense of CH). CH is one of the phases attacked most often in sulfate attack.
- Reducing ionic mobility.
- Reducing C_3A content of cementitious system by dilution effect (except for when using some Class C ashes that contain high amounts of C_3A).

Not all fly ashes behave the same way when used in concrete subjected to external sulfates. The use of Class F fly ash (CaO content less than 15-18 percent) has long been found to be effective for sulfate resistance when dosages between 25 and 35% by mass are used. However, some high-lime Class C fly ashes produce concrete with poor sulfate resistance, sometimes even worse than control mixtures without fly ash (Dunstan, 1980; Mehta, 1986; von Fay and Pierce, 1989; Tikalsky and Carrasquillo, 1992). More recently, Shashiprakash and Thomas (2001) proposed the following reasons why high-lime ashes were less effective than low-lime ashes in controlling sulfate attack:

- Some high-calcium fly ashes contain C_3A (also some CH)
- Lower consumption of lime due to reduced pozzolanicity

- Presence of reactive calcium-aluminates in glass phase
- Production of reactive aluminate hydrates (e.g., Dunstan's gehlenite)

Figure 4-12 shows the strong relationship between the CaO content of the fly ash and the expansion at six months in ASTM C 1012 testing (Shashiprakash and Thomas, 2001). It is important to note in Figure 4-12 that there is a general trend between expansion and CaO content, but some high-lime ashes (e.g., CaO around 30 percent) actually perform better than expected. More research is needed to better differentiate the behavior of different high-lime ashes; using CaO as an index of potential expansion does not hold for high-CaO ashes. An example that highlights this is shown in Figures 4-13 and 4-14, which present unpublished data from a University of Texas sulfate attack research project (a joint project with University of New Brunswick, funded by TxDOT) on two Class C ashes with quite similar chemistries but significantly different behaviors when tested using ASTM C 1012. The CaO contents for these two ashes were 21.6 and 23.5 percent for Figures 4-13 and 4-14, respectively. Clearly, the fly ash shown in Figure 4-13 was more effective in reducing expansion than the fly ash shown in Figure 4-14, especially when used in lower dosages (i.e., 20 or 25 percent by mass replacement of cement). This is just one example of ashes that behave differently, despite similarities in chemical composition, but it highlights the need to better characterize the mineralogy of fly ash to gain better insight into sulfate resistance.

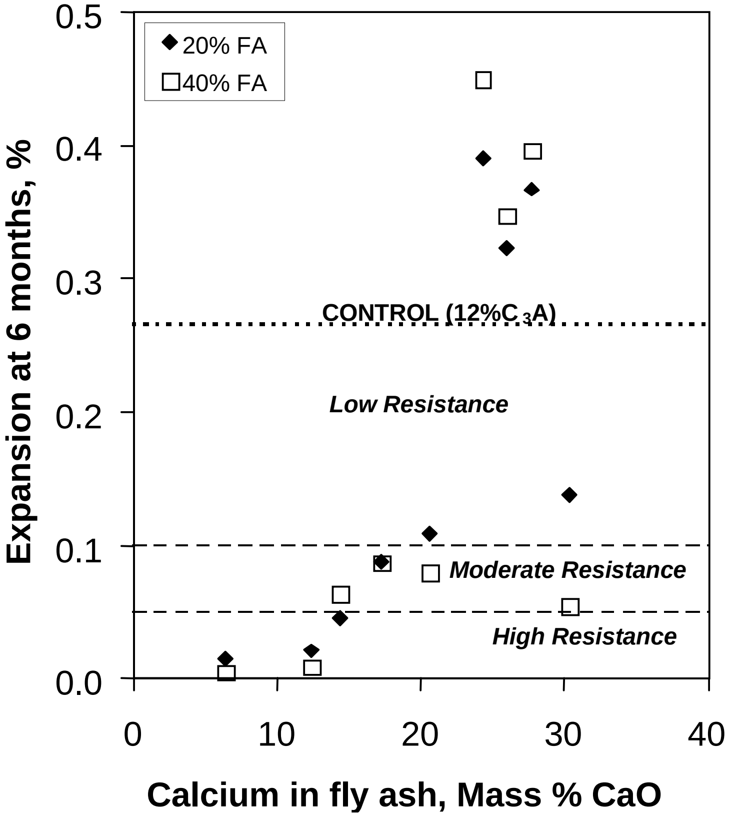


Figure 4-12
Effects of CaO content of fly ash on sulfate-induced expansion using ASTM C 1012 (after Shashiprakash and Thomas, 2001).

Research is underway at the University of Texas and University of New Brunswick to develop more accurate means of identifying and quantifying the mineralogical composition of fly ashes. Determining the mineralogy of fly ash is not only important with regard to sulfate attack, but also in relation to heat of hydration, early-age strength gain, and delayed ettringite formation.

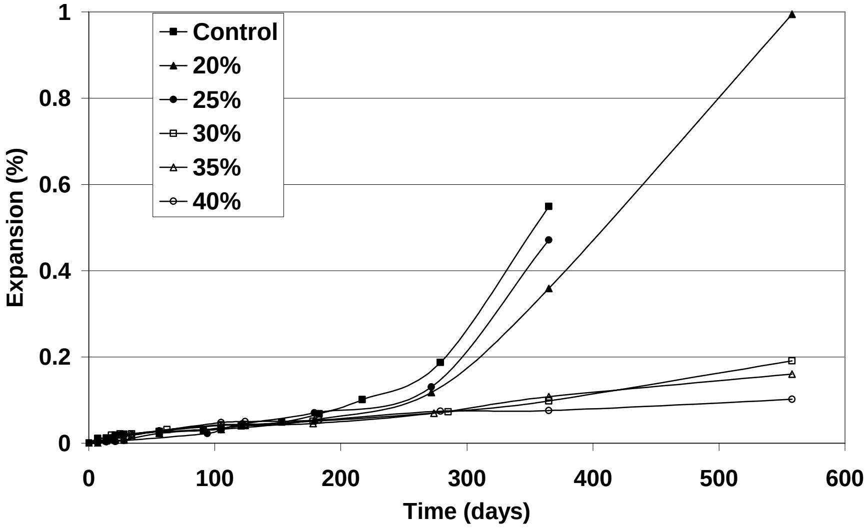


Figure 4-13
Effects of various dosages (by mass replacement of cement) of Class C fly ash (CaO=21.6) on expansion using ASTM C 1012 (unpublished data, University of Texas).

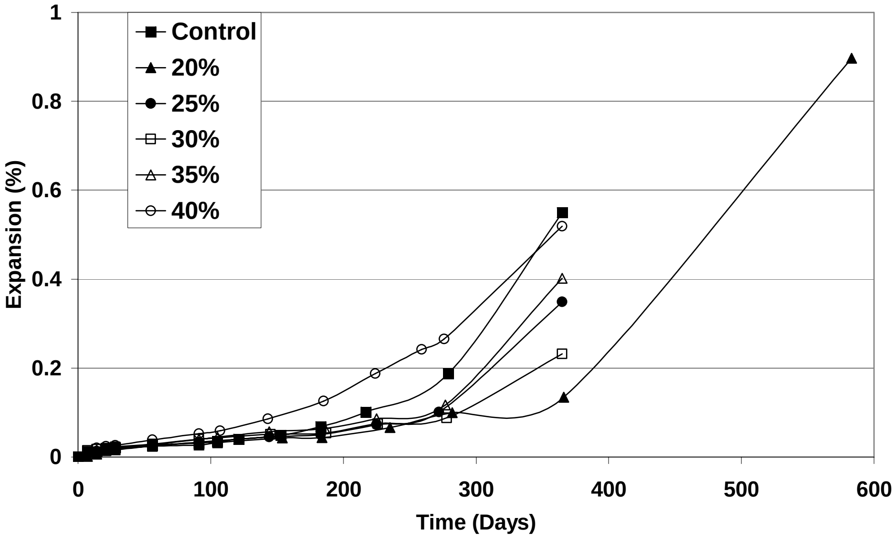


Figure 4-14
Effects of various dosages (by mass replacement of cement) of Class C fly ash (CaO=23.5) on expansion using ASTM C 1012 (unpublished data from University of Texas).

When evaluating the results of ASTM C 1012 or other accelerated sulfate test methods, it should be noted that the failure of mortar containing Class C fly ash can be quite dramatic, with complete loss of cohesion and mass, even at relatively low levels of expansion. Figure 4-15 illustrates this behavior, showing mortar bars containing a high-CaO fly ash after only a few weeks in 5 percent sodium sulfate solution. Work is still needed to elucidate the cause of this extreme behavior for certain Class C fly ashes.

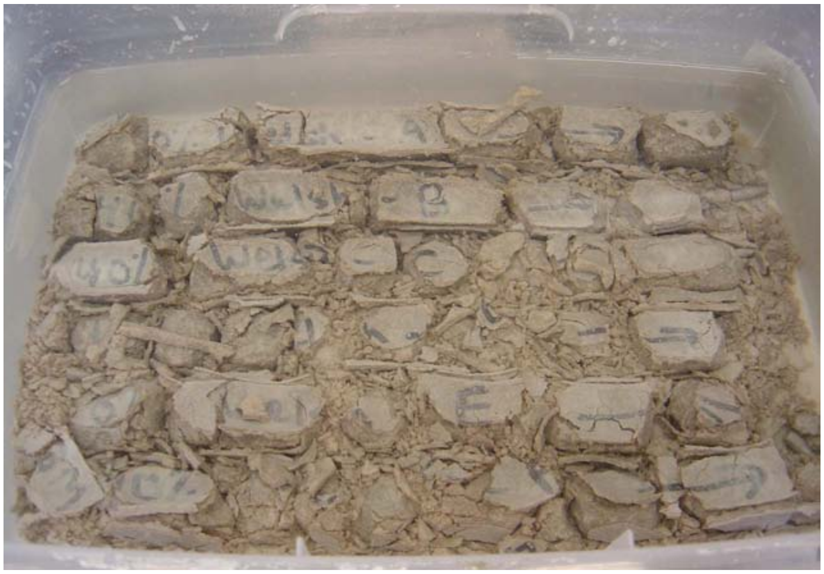


Figure 4-15
Typical failure mode of Class C fly ash mortars tested using ASTM C 1012, illustrating complete loss of cohesion and mass, even at relatively low levels of expansion (photo from testing at University of Texas).

In addition to linking the mineralogy and chemistry of fly ashes to sulfate resistance, Shashiprakash and Thomas (2001) also performed significant research on combining high-CaO ashes with silica fume, with emphasis on mixtures with between 3 and 6 percent silica fume (by mass of total cementitious materials). It was found that just a small dosage of silica fume (3 percent) significantly increased the sulfate resistance of mortar containing high-calcium fly ash. A recent study by Obla et al. (2003) found that 12 to 16% ultra-fine fly ash (UFFA) was sufficient to suppress sulfate-induced expansion. Ongoing work at the University of Texas and University of New Brunswick is further evaluating the benefits of adding silica fume or ultra-fine fly ash, in relatively small dosages, to increase the sulfate resistance of mortar/concrete containing high-CaO fly ash. These efforts also include less accelerated and more realistic testing regimes for sulfate resistance, including the use of wetting and drying cycles and the use of an outdoor exposure site in Austin, Texas, in which over 30 concrete mixtures are being evaluated in trenches containing 5 percent solutions of calcium sulfate, sodium sulfate, and magnesium sulfate. The final results of this study are not yet published, but some preliminary conclusions can be drawn. Sodium sulfate appears to be slightly more damaging than magnesium sulfate, when considering the outdoor exposure conditions. Calcium sulfate or gypsum has caused essentially no expansion in almost all of the mixtures under evaluation; there is, however, some minor mass loss observed for some mixtures, especially those with higher W/CM ratios. Class C fly ash mixtures are currently performing quite well in a gypsum-rich environment, although failure is quite severe and rapid in the outdoor sodium sulfate exposure.

Physical Salt Attack

Physical salt attack results from physical attack on cement paste by external sulfate sources, without any chemical degradation of the concrete. This phenomenon, known as salt crystallization or physical salt attack (note that this term is used in this report), is caused by salt solutions, particularly sodium sulfate, entering the concrete and undergoing volume changes as the ambient temperature changes, somewhat similar to freezing and thawing damage (Folliard and Sandberg, 1994). Folliard and Sandberg reported that external sulfates (e.g., sodium sulfate) can penetrate into relatively porous concrete, and as the ambient temperature changes, so does the volume of the sodium sulfate solution within the concrete. The sodium sulfate solution inside the concrete, which is present as either thenardite (Na_2SO_4) or mirabilite ($Na_2SO_4 \cdot 10H_2O$), will typically increase in volume as the temperature decreases, due to precipitation from a supersaturated solution. A total volume expansion of about 3 percent was reported by Folliard and Sandberg, and this amount of internal expansion was enough to completely destroy some concrete mixtures. This damage occurred without any chemical change in the concrete and without the temperature ever reaching the freezing point of water. Interestingly, the types of temperature fluctuations needed to cause this type of distress (e.g., ambient temperature swings between roughly 5 and 23^{o}C) are quite moderate and normal in many parts of the world. This physical phenomenon is also responsible for the destruction of solid rocks.

There have been only limited studies on methods of preventing physical salt attack. Folliard and Sandberg (1994) reported that low W/CM concrete mixtures are quite effective in preventing physical salt attack, especially when SCMs are used. Folliard and Sandberg also showed that air entrainment is helpful in reducing although not eliminating physical salt attack. With time, it was shown that air-entrained voids ultimately become filled with salts, and they are no longer accessible to the salt solution as it increases in volume. Haynes et al. (1996) recommend a maximum W/CM of 0.45, along with a pozzolan for improved durability to physical salt attack. Research is limited on the use of fly ash to prevent physical salt attack, and it remains to be seen how well high-CaO ashes will perform in accelerated salt attack tests. Intuitively, one would expect the chemistry/mineralogy of fly ash to be less important in this case, as the attack is physical, not chemical, in nature. Research is needed to determine how the chemical, mineralogical, and physical characteristics of fly ash impact resistance to physical salt attack.

Internal Sulfate Attack (DEF)

Delayed ettringite formation (DEF) is another form of internal chemical degradation. Generally, it is accepted that DEF may occur in concretes that were initially subjected to temperatures in excess of 70°C (158°F) during curing. High temperatures may inhibit the normal formation of ettringite ($C_4A\check{S}_3H_{32}$[*]) and accelerate the formation of calcium silicate hydrate (C-S-H) during cement hydration. The sulfate (and to a lesser extent aluminate resulting from the incongruous

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[*] In cement chemistry notation, where C = CaO, S = SiO_2, $\check{S}$ = SO_3, A = Al_2O_3, and H = H_2O.

dissolution of ettringite) that would usually form ettringite at normal temperatures is instead absorbed by the rapidly forming C-S-H. Later, the sulfate and aluminate ions absorbed by the C-S-H are released into the pore solution of the hardened cement paste to react with available monosulfate to form ettringite, resulting in expansion and cracking.

When concrete is subjected to excessively high curing temperatures, DEF can be chemically suppressed by incorporating sufficient dosages of SCMs (Ramlochan et al., 2003; Folliard et al., 2006). Concrete containing greater than 20-25 percent Class F fly ash or 35-40 percent Class C fly ash has been shown to be essentially immune from DEF, even when curing temperatures approach 95°C (200°F). Figure 4-16 shows the beneficial effects of adding fly ash to heat-cured mortars (Folliard et al., 2006). Ramlochan et al. (2003) proposes that the alumina content of SCMs is a key characteristic impacting DEF, and this explains why both Class F and Class C ash inhibit DEF, whereas silica fume, which is essentially devoid of alumina, is relatively ineffective under similar testing. It is likely that SCMs impact the early hydration kinetics, slowing down C-S-H formation and impacting the timing and preferred stability of monosulfate and ettringite.

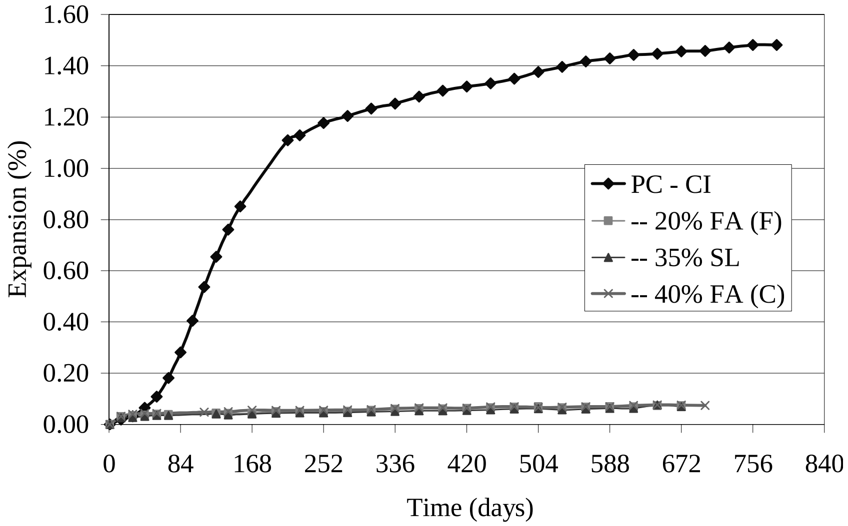

Figure 4-16
Effects of fly ash and slag on expansion of mortars cured at 95°C (200°F), after Folliard et al. (2006). Note the following: PC-CI is a high-C3A cement, FA(F) is a Class F fly ash, SL is slag, and FA(C) is a Class C fly ash.

Research Needs – Sulfate attack

- A better understanding is needed of the effect of the compositional characteristics (mineralogical, chemical, physical, etc.) of fly ash and their performance regarding sulfate attack, especially in high-volume systems. The effect of exposure conditions (e.g., wet-dry cycles) should also be investigated.
- More accurate and applicable sulfate tests are needed, especially given that ASTM C 1012 is the primary test used and has several issues. The expansion limits and test durations are not necessarily based on correlation to field performance. Because some Class C ashes show poor sulfate resistance, an accurate test is needed to ensure that durable mixtures are selected that contain appropriate Class C fly ashes or combinations of Class C fly ash with other SCMs, such as silica fume or ultra-fine fly ash.

Acid Attack

It is generally accepted that portland cement concrete can only be resistant to mild acids, and for applications where concentrated and/or strong acids are present, specialty cements should be used. For applications where mild acids are occasionally expected, a dense concrete with low W/CM is recommended. SCMs, especially silica fume, that are effective in reducing calcium hydroxide (the first phase to be attacked by acids) can help to improve resistance to mild acids (Sellevold and Nilson, 1987).

Water Permeability and “Rapid Chloride Permeability”

In its strictest sense, fluid permeability is the measure of the rate of flow of a fluid under pressure through a porous material. The water permeability (also known as the hydraulic conductivity) of concrete can be measured by applying a hydraulic gradient across a saturated concrete sample and measuring the rate of flow. In a similar manner, the gas permeability can be measured by applying gas pressure to one face of a concrete sample and measuring the flow of gas from the opposite face. For gas to flow through a porous material like concrete, the pores must be at least partially empty, in other words the sample cannot be saturated with water. The gas permeability of concrete is strongly influenced by the degree of water saturation of the sample at the time of test.

The incorporation of fly ash into properly cured concrete results in a refinement in the pore structure due to the pozzolanic reaction and resulting creation of additional calcium-silicate and calcium-aluminate hydrates, and this results in a reduction in the permeability (Manmohan and Mehta, 1981). Many researchers have demonstrated that the permeability of well-cured concrete, mortar, or cement paste decreases with increasing fly ash content (Marsh et al., 1985; Thomas and Matthews, 1992a); however, the permeability of fly ash concrete is more sensitive to curing and in improperly cured concrete the use of fly ash may increase permeability (Thomas and Matthews, 1992a).

Coefficients of water permeability become increasingly difficult to measure as the permeability of concrete decreases, and there are few data available for high-volume fly ash concrete, which can be expected to have a very low permeability provided it is well cured. Bilodeau et al. (1994) reported very low water permeability coefficients for HVFA concrete with 58% fly ash and very low water content (W/CM = 0.33). Eight different fly ashes were used in this study. Two of these would be classified as Class C fly ashes by ASTM, because the sum of the oxides SiO_2 + Al_2O_3 + Fe_2O_3 was marginally less than 70%, being just 69.5% and 69.1%, for fly ashes with calcium contents of 14.9% and 19.3% CaO, respectively. All of the concretes had very low permeability, and in many cases, including some of the concrete mixes containing Class C fly ash, a steady state of water flow could not be achieved even after test periods of up to 6 months. The authors speculate that in these cases the coefficient of water permeability is less than 1.6×10^{-14} m/s. Such values are one to two orders of magnitude lower than typical values measured for good quality portland cement concrete.

Due to the difficulty in measuring the permeability of concrete in general (and the particular difficulty in measuring the permeability of low-permeability concrete), indirect measurements of permeability have been developed. The most commonly used of these methods is ASTM C 1202, *Standard Test Method for Electrical Indication of Concrete's Ability to Resist Chloride Ion Penetration*, which measures the amount of electrical charge passed (in Coulombs) during a six-hour period with a potential difference of 60 V (D.C.) across a 50-mm thick slice taken from a 95-mm diameter core (other sizes may be used with appropriate correction factors). The amount of charge passed will depend on the electrical conductivity of the concrete, not the permeability. However, despite this, the test has become known as the "rapid chloride permeability test" or RCPT. The electrical conductivity of concrete depends on the structure of the pores and the composition of the solution within the pores. The ability of concrete to resist chloride ion penetration is also dependent on pore structure, but is further influenced by the composition (and binding capacity) of the hydrates rather than the pore solution. Consequently, the use of the RCPT or other electrical measurements as an indicator of the transport properties of concrete has been criticized by some workers (e.g., Shi, 2004). Other workers (e.g., Stanish et al., 2001) have shown that there is a reasonable correlation between the RCP test and more rigorous chloride transport tests such as the bulk diffusion test (discussed below).

The impact of HVFA (56% fly ash with ~ 13% CaO) on RCPT results for concrete can be seen in Figure 4-17 for data from Thomas et al. (2001). At early ages (28 days) there is little difference between the charge passed for HVFA concrete and portland cement concrete of the same W/CM. However, the RCPT value for HVFA concrete decreases rapidly with age and after 4 years the values are between 70 and 110 Coulombs. The RCPT value for the portland cement concrete also decreases with age, but not to the same extent, and after 4 years the charge passed ranges from 600 to 2900 Coulombs, depending on the W/CM. Thus, the fly ash is effective in reducing the long-term RCP from between 10 to 20 times compared to concrete without fly ash at a similar W/CM.

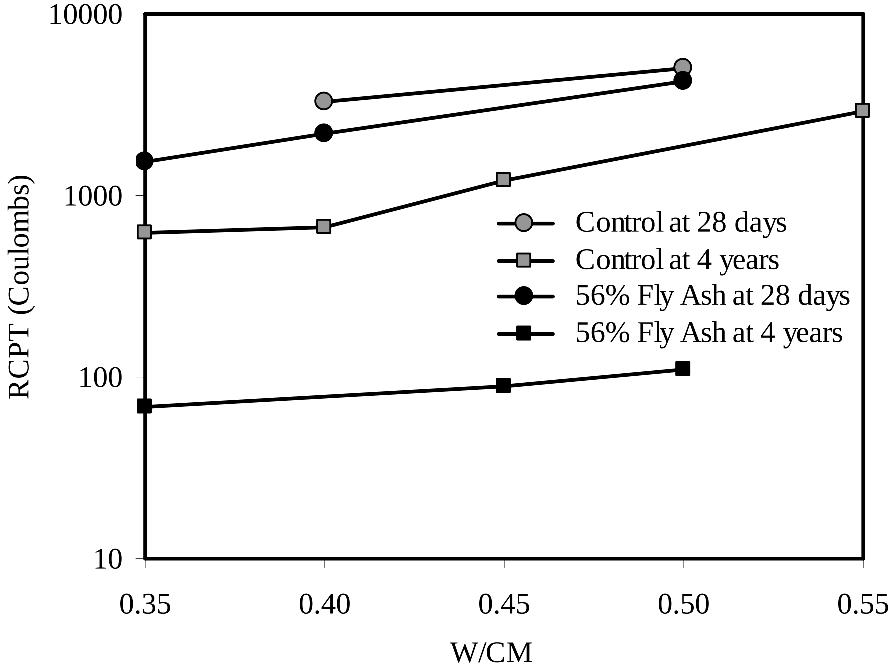

Figure 4-17
Effect of age on RCPT results for HVFA concrete (Thomas et al., 2001).

Figure 4-18 shows the change in RCPT value with age for HVFA concretes (W/CM = 0.33) containing 58% fly ash from eight different sources, including two Class C fly ashes. Between 28 days and 1 year the RCPT decreases on average by approximately 10 times. There is no consistent effect of the fly ash composition for these fly ashes with calcium contents ranging from 1.8 to 19.3% CaO. That the RCPT continues to decrease with age was demonstrated by a study by Malhotra et al. (2000) on cores taken from 10-year-old large blocks stored outdoors under cover from direct precipitation. RCPT test results are shown in Table 4-5. The HVFA concrete (W/CM = 0.29) with 57% Class F fly ash had a measured RCP of 0 (zero) Coulombs after 10 years exposure, which was considerably lower than the other concretes with and without different SCMs.

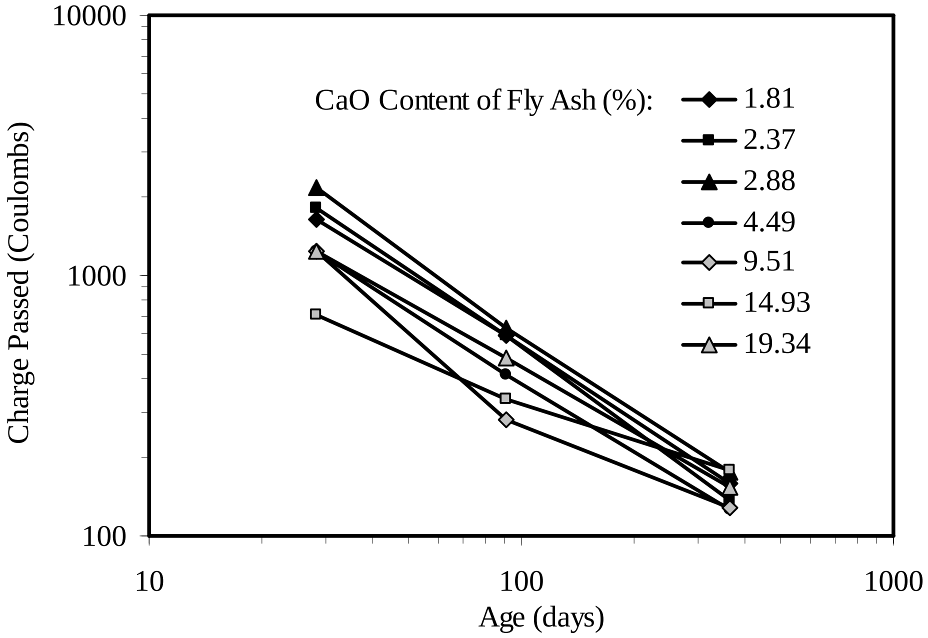

Figure 4-18
Effect of age and fly ash composition on RCPT (results for HVFA concrete – Bilodeau et al., 1994).

Table 4-5
"Rapid Chloride Permeability" Data for Cores Taken from 10-Year-Old Concrete Blocks (Malhotra et al., 2000)

Mix	Supplementary Cementing Materials in Mix	Cementitious Content (kg/m3)	W/CM	RCPT at 10 Years (Coulombs)
1	7% Silica Fume + 28% Slag	485	0.29	100
2	35% Slag	484	0.28	235
3	8% Silica Fume	488	0.27	565
4	12% Silica Fume	486	0.27	120
5	57% Fly Ash	350	0.29	0
6	100% Portland Cement	485	0.27	380

RCP test results were reported by Naik et al. (2003a) for cores taken from 6 concrete pavements at ages of between 7 and 14 years. These pavements contain between 19 and 70% Class F fly ash (3.6% CaO) and 35 to 67% Class C fly ash (28.9% CaO). The results are shown in Table 4-6. These values do not approach the zero value reported by Malhotra et al. (2000), but do demonstrate that very low RCPT numbers can be achieved in mature field concretes with high volumes of either Class F or Class C fly ash. The data in Table 4-6 show that the RCPT is generally lower for HVFA concrete with Class F fly ash compared to that with a similar amount of Class C fly ash. Further cores from these structures were taken in Summer 2005 and are being tested at University of New Brunswick to determine the chloride diffusion coefficient (according to test method ASTM C 1556).

Table 4-6
"Rapid Chloride Permeability" Data for Cores Taken from Concrete Pavements (Naik et al., 2003a)

Mix	Fly Ash	Cementitious Content (kg/m^3)	W/CM	Age (years)	RCPT (Coulombs)
A-1	70% Class C	335	N/A	14	113
B-5	50% Class C	350	0.26	8	217
C-4	19% Class C	350	0.29	8	566
D-2	67% Class F	400	0.31	7	65
E-3	53% Class F	389	0.31	7	77
F-6	35% Class F	416	0.31	8	155

These data demonstrate that HVFA concrete can achieve very low RCPT numbers at later ages. However, these advantages may not be realized in short-term studies, and HVFA concrete may actually be prohibited from use by specifications that place maximum limits on the RCP value at early ages (e.g., 28 days). One approach for overcoming this problem may be to utilize an accelerated curing procedure to predict later-age "chloride permeability." Such an approach was proposed by Lane and Ozyildirim (1999) and has been adopted by Virginia DOT. Concrete cylinders for RCPT testing are cured for 7 days at 23°C and then for 21 days at 38°C. The results of 28-day tests are compared in Figure 4-19 with results from tests conducted on cylinders cured continuously at 23°C for either 28 days or 1 year. The data show that the 28-day tests on concrete (with up to 35% fly ash or 60% slag) subjected to elevated-temperature curing give a good indication of the long-term performance of the concrete.

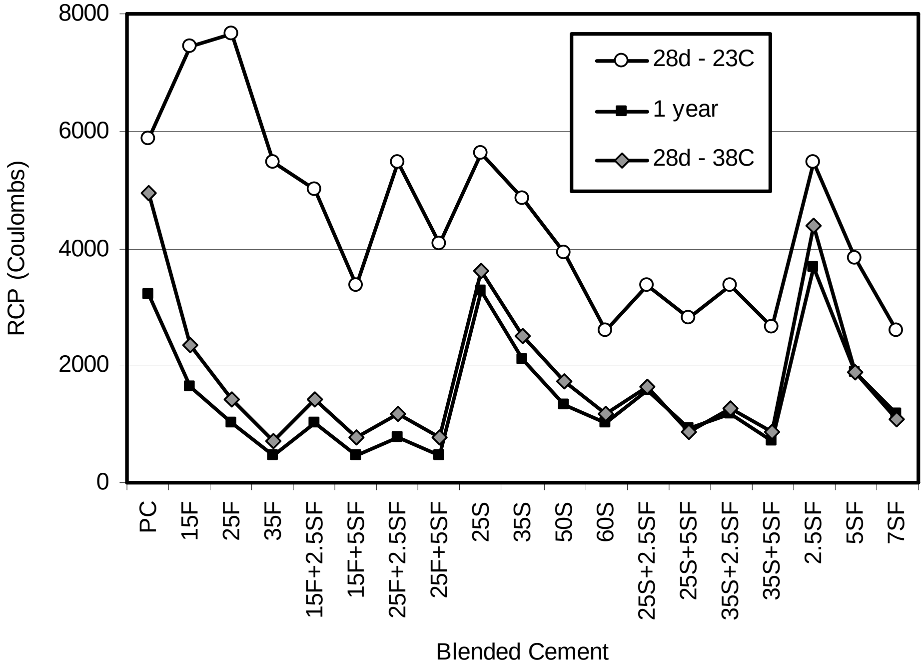

Figure 4-19
Effect of elevated-temperature curing on RCPT (Lane and Ozyildirim, 1999).

Research Needs – Chloride resistance and permeability

- ASTM C 1556 testing on concrete with high volumes of Class C fly ash (long-term to determine change with time)
- Examination of other transport processes
- Monitoring of chloride profiles in slabs exposed to de-icing salts (scaling study)
- Marine exposure
- Testing to determine chloride-binding isotherms for Class C fly ash
- RCPT results for concrete subjected to elevated-temperature curing compared with long-term RCPT data on cores taken from field-exposed concrete blocks to confirm that the values obtained in accelerated tests are eventually achieved in field concrete

Resistance to Chloride Ingress, Carbonation, and Corrosion of Embedded Steel

When reinforcing steel is embedded in concrete, the high-pH environment favors the formation of a passive layer of iron oxide on the steel surface, which protects the underlying steel from corrosion. This phenomenon, known as passivation, will protect the steel indefinitely unless the passive layer is destroyed, either by the presence of an excessive amount of chloride ions at the location of the steel or by the reduction of the pH in the vicinity of the steel due to the penetration of carbon dioxide from the environment (a process known as carbonation). The penetration of chlorides or CO_2 into the concrete does little harm to the concrete itself; however, once either compound has penetrated the full depth of cover and reached the steel, the passive layer is lost and corrosion of the steel is initiated. The corrosion process involves the conversion of metallic iron to various ferric and ferrous compounds (oxides and hydroxides), which occupy much greater volumes than the original metal. Thus, the formation of the corrosion products results in cracking, spalling, and delamination of the concrete cover. The corrosion process also results in a loss of the cross-section of the steel reinforcement and consequently a reduction in load-carrying capacity. However, in most cases, the cracking and spalling of the cover is noticeable well in advance of any significant loss of structural performance.

The ability of the concrete cover to resist the penetration of chloride ions or CO_2 is an important property, as it defines the duration for which the concrete is able to provide protection to the steel. Once corrosion initiates, the rate of corrosion will also depend on the quality of the concrete, corrosion occurring more rapidly in concrete of high permeability. However, even in good quality, low-permeability concrete the time between the initiation of corrosion and the appearance of visible damage (often referred to as the propagation period) is relatively short compared with the initiation period, which is the time from construction to the onset (or initiation) of the corrosion process. Thus, in this report the focus will be on the rate of chloride ingress and carbonation of high-volume concrete rather than on the rate of corrosion of steel embedded in such concrete.

Chloride Resistance

There are two standardized ASTM tests for directly measuring the resistance of concrete to chloride ion penetration. One is the bulk diffusion test (ASTM C 1556), which involves exposing pre-saturated concrete to a chloride solution for a certain period of time and then measuring the chloride-concentration profile and determining a bulk diffusion coefficient. The second method is known as the chloride ponding test (ASTM C 1543) and involves ponding a chloride solution on an unsaturated concrete specimen and measuring the depth of chloride penetration after a specified period of time. The standard conditions used in this test are to moist cure the concrete for 14 days, allow it to air dry for 14 days, and then to pond chlorides on one surface for 90 days; however, other conditions are permitted. The precise conditions used have a very significant impact on the penetration of chlorides. The standard ponding test is not particularly useful for determining the influence of fly ash for the following reasons: (1) the standard curing period (14 days) is not sufficient for significant pozzolanic reaction to have taken place prior to first exposure, (2) the drying period makes it difficult to deconvolute the effects of the different transport mechanisms at work (i.e., ionic diffusion and capillary suction), and (3) the combination of the 90-day soaking period and the coarseness of the profiling procedure (10-mm or ½-inch intervals) is not sensitive enough to compare low-permeability concrete (i.e., little penetration to second interval). Other methods for determining chloride resistance are to expose concrete samples to chloride environments (e.g., marine exposure sites) and to determine chloride penetration after various periods of exposure. This review will focus on data published from bulk diffusion and long-term natural exposure tests.

As with many other properties of concrete, determining the influence of fly ash is complicated by the fact that the influence is extremely age-dependent, and the impact of age (or maturity) becomes more significant as the level of replacement increases. This can be seen in the steady-state diffusion tests performed by Page and coworkers on cement paste samples. In short-term tests they reported that 20 to 30% fly ash reduced the diffusion coefficient by about 2.5 times (Ngala et al., 1995), whereas in more mature systems reductions of up to 10 times were observed. Testing of concrete exposed to marine environments has also shown that the resistance of fly ash concrete to chloride-ion penetration increases significantly with the duration of exposure (Bamforth, 1999; Thomas and Bamforth, 1999; Thomas and Matthews, 2004).

Thomas and coworkers (Thomas and Matthews, 2004) placed reinforced concrete prisms from a series of concrete mixtures in the tidal zone of a marine exposure site on the Thames estuary in southeastern England. These mixtures contained various levels of Class F fly ash (0, 15, 30, and 50%) and within a given mix series, concretes with and without fly ash were designed to achieve the same standard-cured 28-day compressive strength. This resulted in decreasing W/CM with increasing fly ash content for concretes of the same strength. Figure 4-20 shows the chloride profiles for concrete without and with 50% fly ash designed to achieve a specified 28-day strength of 35 MPa. At early ages there is a relatively rapid ingress of chlorides into both concretes, partly because the concretes were unsaturated when they were first placed at the site. However, at later ages it is clear that the concrete with 50% fly ash has a much greater resistance to chloride penetration. Figure 4-21 compares profiles after 10 years exposure for concretes of various strengths produced without and with 50% fly ash. The strength of the concrete appears to have little consistent impact on the chloride profiles at this age, whereas the presence of fly ash has a substantial effect. Figure 4-22 shows the chloride content in the depth interval from 21 to 26 mm beneath the surface for 35-MPa concretes with different amounts of fly ash exposed for various periods of time. The chloride penetrated to this depth rapidly in the control concrete without fly ash. The rate of chloride penetration decreased significantly with fly ash content, and the chloride content at this depth barely increased at all beyond the initial 28-day period for the concrete with 50% fly ash.

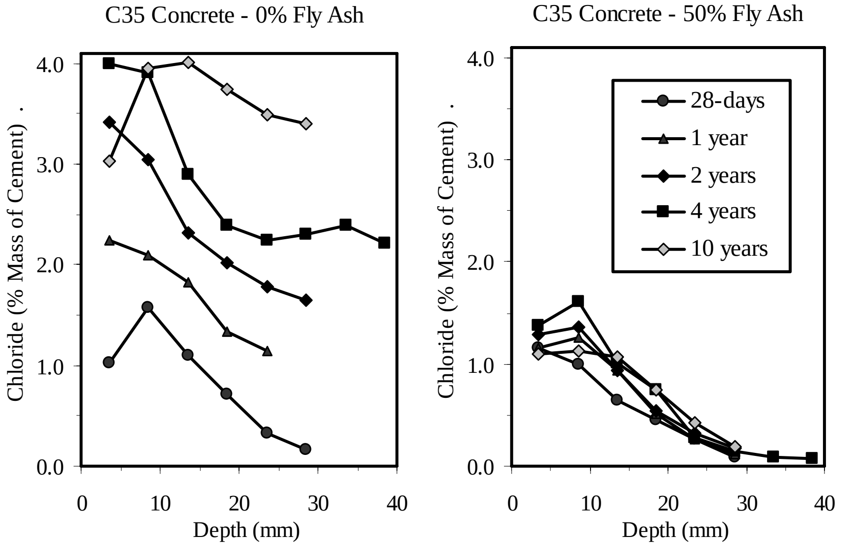

Figure 4-20
Chloride profiles in concrete after various exposure periods in a marine tidal zone (Thomas and Matthews, 2004).

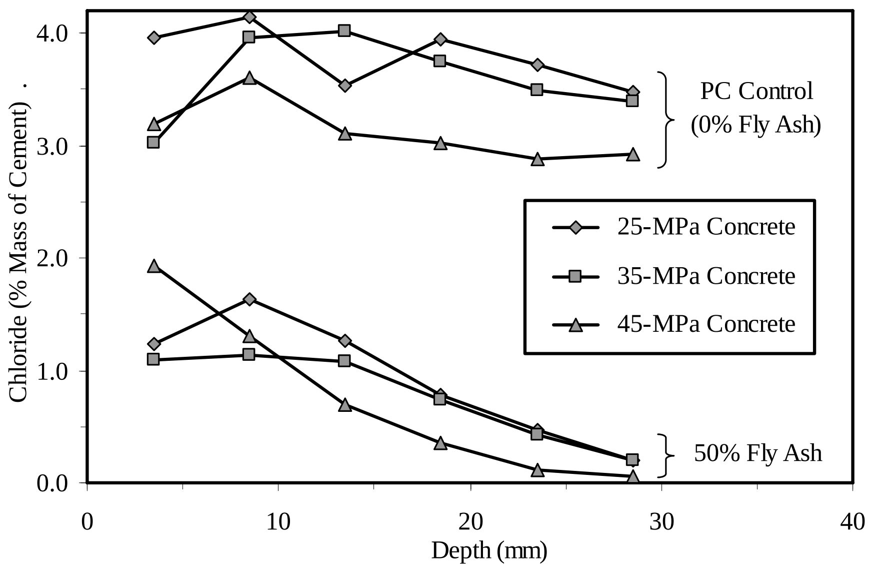

Figure 4-21
Chloride profiles in concrete after 10 years in a marine tidal zone (Thomas and Matthews, 2004).

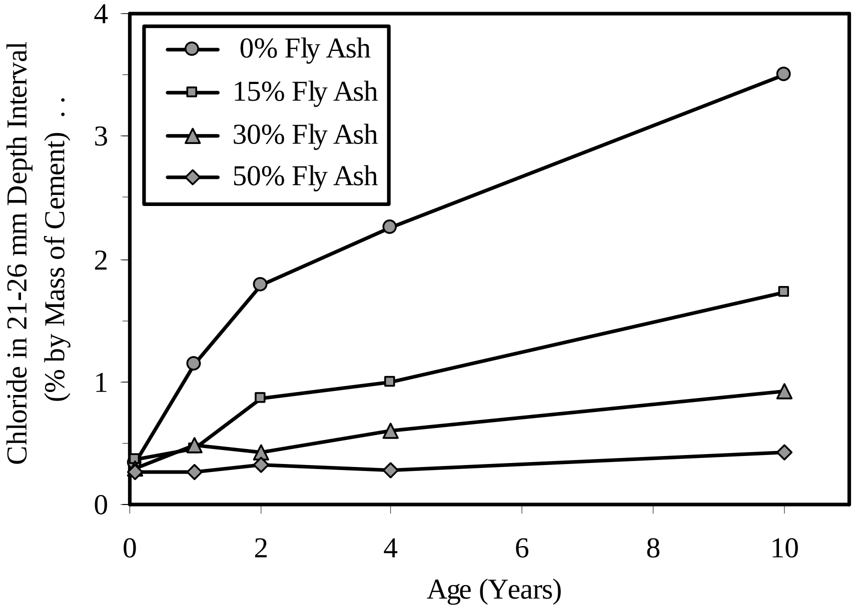

Figure 4-22
Chloride content at a depth of 21-26 mm in concrete after various exposure periods in a marine tidal zone (Thomas and Matthews, 2004).

The authors of this report are not aware of any similar studies on concrete with high volumes of Class C fly ash.

Research Needs – Chloride diffusion

- Work is needed to evaluate the chloride diffusion characteristics in high-volume Class C fly ash concrete systems, including field exposure tests (slabs subjected to frequent de-icing salt applications on exposure site) and marine-exposure studies (e.g., Treat Island).
- Cores should be taken from structures with high-volume Class C fly ash to measure diffusion coefficients.

Carbonation

The rate of carbonation of concrete will vary depending on the properties of the concrete (especially the W/CM and the type and quantity of supplementary cementing materials present), the amount of moist curing provided to the concrete, and the exposure condition. Well-cured portland cement concrete with low W/CM will show insignificant carbonation rates, regardless of the exposure condition. However, as the W/CM increases, the period of moist curing decreases, or the quantity of SCM increases, there will generally be an increase in the rate of carbonation. In a moist environment, concrete will carbonate slowly, because CO_2 cannot penetrate the water-filled pores. Concrete will carbonate more rapidly in dry environments, but in such conditions there is insufficient moisture to sustain corrosion of the steel once the CO_2 has penetrated the cover concrete, resulting in the loss of the passive layer. Consequently, concrete that is most vulnerable to carbonation-induced corrosion is concrete that is protected from direct contact with moisture but is exposed to periods of high relative humidity. This includes exterior elements that are protected from direct precipitation, such as the underside of balconies and beams. Many laboratory studies have used this type of environment to investigate parameters that influence carbonation (e.g., Thomas and Matthews, 1992b; 2000).

A number of researchers have shown that concrete containing up to 30% fly ash will carbonate at a similar rate as portland cement designed to have the same 28-day compressive strength (Tsukayama, 1980; Lewandowski, 1983; Matthews, 1984; Nagataki et al., 1986; Hobbs, 1988; Dhir, 1989; Collepardi et al., 2004). However, if concretes are proportioned for equal 28-day strength, this invariably means that the W/CM decreases with increasing fly ash content, especially for Class F fly ash. When compared on the basis of equal W/CM, fly ash concrete carbonates more rapidly, and the differences become quite marked in poorly cured, high-W/CM concrete with high levels of fly ash (Thomas and Matthews, 1992b; 2000 Burden, 2006). Even when compared on the basis of equal strength, concrete with fly ash (especially at high levels of replacement) may carbonate more rapidly in poorly cured, low-strength concrete (Ho and Lewis, 1983; 1987; Thomas and Matthews, 1992b; 2000).

Generally, the depth of carbonation, d, increases linearly with the square root of time, t, according to the equation $d = k\sqrt{t}$, where k is the carbonation-rate coefficient usually expressed in units of $mm/y^{0.5}$. The value of k depends on the concrete materials and proportions, on the curing period, and on the exposure environment (Parrott, 1987). Thomas (2004) established carbonation-rate coefficients for concretes with up to 50% fly ash on the basis of 10-year data collected at the Building Research Establishment (BRE) in the U.K.; these data are presented in Table 4-7.

Table 4-7
Effect of Strength, Curing, and Fly Ash Content on Carbonation Rates, *k* (mm/y^{½})

Strength Grade[1] (MPa)	Moist Curing (days)	Fly Ash Content (%)			
		0	15	30	50
18	1	6.82	8.28	8.25	10.18
	3	5.84	6.29	6.17	8.37
	7	4.91	4.60	5.32	7.10
25	1	4.85	4.93	5.17	6.38
	3	3.06	3.73	3.90	5.85
	7	2.44	3.28	3.20	4.83
32	1	2.39	2.80	2.97	3.87
	3	0.71	2.08	2.02	2.64
	7	0.28	1.28	1.23	1.86

[1] Strength grade based on characteristic 28-day cylinder strengths (converted from original cube strengths)

These data show that for concrete of the same 28-day strength, differences in the carbonation rates for concrete with 0 to 30% fly ash are generally small, although there is a slight increase with increasing fly ash content. Concrete containing 50% fly ash carbonates at a much faster rate despite having a significantly lower W/CM than concrete of the same strength without fly ash. To achieve similar rates of carbonation as concrete without fly ash, high-volume fly ash concrete needs either to be proportioned to achieve a higher compressive strength or to be provided with an extended period of moist curing.

A recent study reported carbonation data for the HVFA concrete system developed by CANMET (Bouzoubaa et al., 2006). In this study, the maximum carbonation coefficient for concrete with 56% fly ash and W/CM = 0.32 when moist cured for 7 days was 5.04 mm/y^{½} for indoor exposure and 2.51 mm/y^{½} for unprotected outdoor exposure. This compares with 1.14 mm/y^{½} and 0 mm/y^{½} (i.e., no measurable carbonation at 7 years) for portland cement concrete with the same W/CM, indicating that the use of high levels of fly ash resulted in much increased carbonation rates. However, it was concluded by the authors of this study that “carbonation is not an issue for well-cured HVFA concrete” based on the calculated time-to-corrosion (> 200 years) for reinforcing steel with a depth of cover of 40 mm[2] in concrete exposed outdoors.

The conclusion of Bouzoubaa et al. (2006) is only valid if the following conditions are met: (1) HVFA concrete is proportioned with very low W/CM (≤ 0.32), (2) concrete is moist-cured for at least 7 days, (3) concrete is directly exposed to moisture during service (i.e., not protected from precipitation), and (4) the specified minimum cover requirements (e.g., 40 mm) are met. If there

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[2] Minimum cover in Canadian specifications (CSA A23.1) for concrete exposed outdoors provided there are no chlorides present and the concrete is not cast against and permanently exposed to earth.

are changes in the mixture proportions, if the concrete is not directly exposed to moisture (e.g. it is protected from rainfall), and if 7-days curing and 40-mm cover are specified, but not achieved in practice, the time-to-corrosion will be reduced substantially. For example, the data in Table 4-7 show that 25-MPa concrete with 50% fly ash (W/CM = 0.41 for this mix) has a carbonation coefficient of $k = 5.85$ mm/y^{½} if it is only moist-cured for 3 days. If the cover actually achieved in practice is only 30 mm, corrosion of the steel will be initiated in just 26 years.

The data discussed above relate to studies using Class F fly ash. A recent study conducted at UNB (Burden, 2006), using concrete (W/CM = 0.34 to 0.50) with 30 to 50% fly ash (11 to 29% CaO) from various sources in North America, showed that the rate of carbonation was influenced by the source of fly ash used, but that there was no consistent trend with the chemical composition (e.g. CaO content) of the fly ash. Fly ash concrete carbonated significantly more rapidly than portland cement concrete of the same W/CM regardless of the source of fly ash, the differences being most notable for poorly-cured concrete at high W/CM.

Thomas and Matthews (1992b) observed that increasing the fly ash content of the concrete increased the rate of carbonation but decreased its permeability to gas. This apparent anomaly can be explained by the lower content of calcium hydroxide in concrete containing fly ash due to the dilution of the portland cement content and the consumption of calcium hydroxide by the pozzolanic reaction. A lower calcium hydroxide content means that less CO_2 is consumed by the carbonation reactions.

In summary, when high-volume fly ash concrete is used in areas prone to carbonation (i.e. sheltered outdoor exposure), particular attention must be paid to ensuring that the concrete mixture proportions, period of moist curing and depth of cover are adequate for the purpose.

Research Needs – Carbonation

- Carbonation susceptibility of concrete incorporating large volumes of Class C fly ash should be evaluated on large specimens exposed in natural environmental conditions prone to the development of this process. This should then be correlated with the susceptibility to carbonation measured under accelerated testing conditions in the laboratory.
- In order to develop practical data on carbonation, a field survey (carbonation profiling) of existing structures incorporating high volumes of Class C fly ash should be done.
- The effect of various parameters on the resistance to carbonation of concrete incorporating high volumes of Class C fly ash (e.g., curing membranes, curing compounds, anti-carbonation coatings, internal curing) should be evaluated.

5

SUMMARY AND RECOMMENDATIONS

The following is a summary of the information found in the literature regarding the physical, mechanical, and durability properties of concrete incorporating large volumes of ASTM C 618 Class C fly ash. However, since each fly ash is unique, the actual behavior of concrete made with any specific fly ash can differ significantly from that suggested by the general statements given hereafter. An indication is also provided whether the use of HVFA concrete made with Class C fly ash is beneficial, disadvantageous, or has an uncertain effect for each property of the concrete.

For the purposes of this report, high-volume fly ash concrete (HVFAC) is considered to be concrete containing more than 30% fly ash by mass of cementing material, and high-calcium fly ash is considered to be fly ash that contains more than 15 to 18% CaO and meets the requirements of ASTM C 618 Class C fly ash, but not Class F fly ash (i.e., $50\% \leq SiO_2 + Al_2O_3 + Fe_2O_3 < 70\%$).

Properties of Fresh Concrete

Workability

Concrete incorporating fly ash will tend to be easier to finish and pump, provided that the mixture is well proportioned.

Bleeding

In most applications, fly ash will reduce the bleeding of properly proportioned concrete, including both the amount and rate of bleeding. The reduction in bleeding can be problematic in hot, dry, windy conditions, where plastic shrinkage cracking is a concern; the problem can be exacerbated when fly ash is used in relatively high dosages, where bleeding is further reduced and setting time is further extended. This can be dealt with in the field with proper early curing and protection practices to minimize the loss of moisture due to evaporation (such practices include the use of fog misters), and by optimizing the finishing operations.

Air Entrainment

In general, the use of fly ash in concrete tends to increase the dosage of air-entraining admixture (AEA) needed to obtain a target air content, when compared to a control portland cement mixture. Although Class C fly ashes generally tend to be less problematic than Class F fly ash with regard to impact on AEA demand, the authors have encountered a handful of high-CaO ashes over the past 20 years that have had profound effects on AEA demand.

The most significant factor affecting AEA demand is the presence of unburned carbon in fly ash. It has been clearly shown that not all carbons act the same in concrete. Some fly ashes contain very active carbon, with high surface areas, and these ashes tend to more significantly impact AEA demand. This has especially been the case in recent years, as low-NOx burners have been introduced into coal-burning power plants to reduce environmental impact.

Setting Time

The use of fly ash increases both the initial and final set times of concrete. The amount of retardation, however, is quite dependent on the type and dosage of fly ash used, as well as other mixture-related factors. There are some contradictions in the literature. Some authors indicated that Class C fly ash did not retard setting time nearly as much as Class F fly ash, whereas others found that Class C fly ashes tend to retard set time more than Class F fly ash. For instance, over the past two to three years, there have been a number of reported cases of concrete exhibiting extraordinarily long setting times in summer placements. The following can be identified as factors contributing to this extreme increase in setting time:

- Presence of Class C fly ash, specifically “reactive” fly ash used at relatively high dosages (e.g., 25-35 percent)
- Presence of normal water reducers, again used at relatively high dosages
- Presence of “undersulfated” cements (undersulfated with regard to the combined system, but not necessarily if cements were used in absence of fly ash and water reducer)
- Hot weather conditions (e.g., greater than 90°F)

Therefore, precautions should be taken in presence of similar factors and conditions.

Heat of Hydration

A major benefit of using fly ash in concrete is the reduction in heat of hydration, especially for large/massive concrete elements. The effects on heat generation are highly dependent on the specific fly ash used and the amount of portland cement being replaced. Some authors reported that the rate of heat development generally increased with the CaO content of the fly ash, and some high-CaO ashes, when used at typical field dosages, imparted little or no reduction in heat generation. However, although moderate amounts of high-CaO fly ash (Class C) may not profoundly reduce heat generation, higher dosages of high-CaO fly ash have been used to control the temperature rise in mass concrete foundations.

Mechanical Properties

Early-Age Strength

It is well accepted that, for a given W/CM, concrete incorporating fly ash as partial replacement for cement will demonstrate lower early-age strength as compared to control portland cement concrete; the higher the replacement level is, the lower the early-age strength of the fly ash concrete will be. Although it appears that concrete incorporating Class C fly ash may develop strength significantly faster at early ages than concrete made with Class F fly ash, higher replacement levels of cement by Class C fly ash in concrete may still result in early-age strength values significantly lower than that of concrete without fly ash.

Later-Age Strength

In general, the compressive strength of concrete incorporating up to about 50% fly ash will, at some point in time, under moist-curing conditions, equal and then surpass that of the control portland cement concrete. This increase in later-age compressive strength is a definite advantage of HVFAC.

Young's Modulus of Elasticity

There are some contradictions in the literature about the Young's modulus of elasticity of HVAFC made with Class C fly ash, but in general, it follows the same pattern as for the strength properties.

Drying Shrinkage

There is not much information available, but it appears that the drying shrinkage of HVFAC made with Class C fly ash is, in general, similar to that of control concrete

Durability of Concrete

Alkali-Silica Reaction

It is well established that low-calcium (or Class F) fly ashes are effective in controlling expansion due to ASR when used at moderate levels of replacement (i.e., ~ 20 to 30% depending on the degree of reactivity of the aggregate to counteract). However, Class C fly ashes with higher calcium contents (i.e., > 20% CaO) tend to be less effective in this role than Class F fly ashes, at least at similar replacement levels. Some investigators have shown that the high-calcium fly ashes were effective in controlling expansion in the concrete prism test, provided the fly ashes were used at higher levels of replacement (e.g., 50 to 60%). Others have shown that more moderate levels of high-calcium fly ash (20 to 30%) could be used to control expansion due to ASR when used in combination with small amounts of silica fume (~5%) in ternary systems.

The minimum fly ash necessary to control expansion due to ASR varies as a function of the composition of the ash (e.g., alkali content), the alkali content of the concrete, and the type of reactive aggregate to counteract. However, in the case of Class C ashes, it is unclear how much of the alkalis in the ash may contribute to expansion, especially in low-alkali concrete systems. It also appears that there is no synergy between Class C fly ash and lithium nitrate (a chemical admixture also used to control ASR expansion in concrete), unlike what has been observed in Class F fly ash/lithium mixtures; the exact reason for that is uncertain. It may be that the dosage of lithium needs to be adjusted to also take into account some or all of the alkalis present in Class C fly ash.

De-Icing Salt Scaling Resistance

The de-icing salt scaling resistance of fly ash concrete remains a controversial subject, since there is clearly a lack of consistency between the performance of fly ash concrete under accelerated (i.e., laboratory) and field conditions. On the one hand, there are several examples of fly ash concrete, sometimes high-volume fly ash concrete field placements, performing adequately when exposed to de-icing salt. On the other hand, several authors have suggested that the ASTM test (C 672) for evaluating the de-icing salt scaling resistance of concrete is possibly too severe or, at least, does not adequately represent the actual performance in the field of fly ash concrete; these authors thus pointed out the necessity of developing a new test method, or a modified version of the ASTM test.

Generally speaking, considering the variability of the test results, it appears reasonable to say that fly ash concrete is likely to perform relatively well in the ASTM test if the water-to-cementing materials ratio (W/CM) of the fly ash concrete does not exceed 0.45 and the fly ash content does not exceed about 30 percent, although there might be exceptions. Consequently, given the number of examples of satisfactory performance of fly ash concrete in the field, and sometimes the satisfactory performance of concrete incorporating larger percentages of fly ash, it is reasonable to suggest that fly ash concrete meeting the above criteria should also perform adequately in the field provided that proper placing, finishing, and curing procedures are used.

External Sulfate Attack

The use of Class F fly ash (CaO content less than 15-18 percent) has long been found to be effective for sulfate resistance when dosages between 25 and 35% by mass are used. However, some high-lime Class C fly ashes produce concrete with poor sulfate resistance, sometimes even worse than control mixtures without fly ash. The sulfate resistance of concrete incorporating high-calcium fly ash is somewhat related to the composition of the ash; however, the exact correlation has yet to be established.

It was found that just a small dosage of silica fume (3 percent) significantly increased the sulfate resistance of mortar containing high-calcium fly ash.

Internal Sulfate Attack

When concrete is subjected to excessively high curing temperatures, delayed ettringite formation (DEF) can be chemically suppressed by incorporating sufficient dosages of SCMs. Concrete containing greater than 20-25 percent Class F fly ash or 35-40 percent Class C fly ash has been shown to be essentially immune from DEF, even when curing temperatures approach 95°C (200°F).

Water Permeability and "Rapid Chloride Permeability"

The incorporation of fly ash into properly cured concrete results in a refinement in the pore structure due to the pozzolanic reaction and resulting creation of additional calcium-silicate and calcium-aluminate hydrates, and this results in a reduction in the permeability. High-volume fly ash concrete, which in general should have low W/CM, can be expected to have a very low permeability provided it is well cured.

At early ages (28 days), there is little difference between the results of the rapid chloride permeability test (RCPT), i.e., the charge passed, for HVFA concrete and portland cement concrete of the same W/CM. However, the RCPT value for HVFA concrete decreases rapidly with age, and this type of concrete can achieve very low RCPT numbers at later ages.

Resistance to Chloride Ingress

Steady-state diffusion tests on paste specimens showed that 20 to 30% fly ash reduced the diffusion coefficient by about 2.5 times in short-term tests, whereas in more mature systems, reductions of up to 10 times were observed. Testing of concrete exposed to marine environments has also shown that the resistance of fly ash concrete to chloride-ion penetration increases significantly with the duration of exposure. However, the information on this property is based mainly on Class F fly ash concrete; there is very little information specific to Class C fly ash.

Carbonation

For concrete of the same 28-day strength, made with 0 to 30% fly ash, differences in the carbonation rates are generally small, although there is a slight increase with increasing fly ash content. Concrete containing 50% fly ash carbonates at a much faster rate despite having a significantly lower W/CM than concrete of the same strength without fly ash.

To achieve similar rates of carbonation as concrete without fly ash, high-volume fly ash concrete either needs to be proportioned to achieve a higher compressive strength or needs to be provided with an extended period of moist curing. The above observations relate to studies using Class F fly ash. A recent study using concrete (W/CM = 0.34 to 0.50) with 30 to 50% fly ash (11 to 29%

CaO) showed that the rate of carbonation was influenced by the source of fly ash used, but that there did not seem to be any consistent trend with the chemical composition (e.g., CaO content) of the fly ash. Fly ash concrete carbonated significantly more rapidly than portland cement concrete of the same W/CM, regardless of the source of fly ash, the differences being most notable for poorly cured concrete at high W/CM.

In summary, when high-volume fly ash concrete is used in areas prone to carbonation (i.e., sheltered outdoor exposure), particular attention must be paid to ensuring that the concrete mixture proportions, period of moist curing, and depth of cover are adequate for the purpose.

Principal Research Needs

The literature review presented in previous chapters identified a number of technical or research gaps regarding the use of high volumes of ASTM Class C fly ashes in concrete. Among those, the following are, in the authors' opinion, the most critical items that would require more work, as they often represent barriers against the use of such high-volume fly ash systems in concrete.

Research Need No. 1: Development of Performance Criteria for Quality Control

Research is needed to develop performance criteria for quality control in concrete incorporating high volumes of ASTM Class C fly ash. In order to achieve that goal, investigations should focus on: 1) developing better performance/screening test procedures and criteria, and 2) correlating the inherent properties [i.e., physical, chemical, mineralogical (e.g., glass and crystalline components), and micro-textural characteristics] of the ashes to their performance in such systems, especially regarding the following "controversial" issues:

- Setting time (including compatibility issues with admixtures, evaluation of the effect of cement composition, and temperature conditions).
- ASR expansion control. (One of the key issues will be to evaluate the impact of alkalis available from Class C ashes in high-volume systems incorporating cements of low to moderate alkali contents, which are closer to those in "job mix designs" commonly used in field structures.)
- Sulfate resistance. [The main issues to consider are 1) the effect of the compositional characteristics of fly ash and their performance in concrete exposed to sulfates, talking into account the effect of exposure conditions (e.g., wet-dry cycles), and 2) development of more accurate and applicable sulfate tests to ensure that durable mixtures are selected that contain appropriate Class C fly ashes or combinations of Class C fly ash with other SCMs, such as silica fume or ultra-fine fly ash.]
- Impact of the type and proportion of carbon in various Class C ashes on air entrainment demand and efficiency in high-volume concrete systems.

The research would set the basis that could result in the establishment of a new classification of fly ashes based on their performance in concrete.

Research Need No. 2: Comparison of the Performance of Different Ashes

Following the work designated as Research Need No. 1, research is needed to compare the performance of ashes resulting from different practices in thermal stations or in processing plants, such as:

- Blending Class C and F ashes thus producing an ash with moderate CaO content, the objective being to determine if the performance of this ash is comparable to that of a fly ash of similar composition but from a single source.
- Blending of fuels in thermal stations that can affect the composition of the ash and consequently its performance in high-volume systems.

In collaboration with EPRI, a survey could be carried out with utilities in selected regions of the United States to establish a list of practices in thermal stations that affect the ash composition; samples of ashes resulting from such processes could then be collected for further testing in the laboratory.

Research Need No. 3: Improving Early Strength Gain

Research is needed to evaluate new tools, practices, and products (e.g., accelerating admixtures, nanomaterials, etc.) that could be used to improve the early-strength gain of concrete containing high volumes of Class C fly ash. These improvements in constructability will help to ensure that the major benefits of fly ash usage are realized and that contractors' concerns over construction schedule can be reduced. Understanding how Class C fly ash characteristics impact the fresh and hardened properties in high-volume concrete systems is key to this objective.

Research Need No. 4: Evaluating Salt Scaling Resistance

In Northern regions, the perceived poor de-icing salt scaling resistance of concrete incorporating fair to large volumes of fly ashes is at least one barrier, if not the main barrier, against the use of fly ash in concrete. As there is limited data available on the de-icing salt scaling performance of Class C fly ash in high-volume systems, there is a need to carry out more work in the area, especially regarding the effect of placing, finishing, and curing practices on the scaling resistance of high-volume Class C fly ash concrete.

Work needs to be continued to develop a more suitable performance test method for evaluating the scaling resistance of concrete, especially concrete containing high levels of SCMs. This can best be done by conducting comparative field and laboratory trials with high-volume Class C fly ash concrete in sidewalks and pavements. Tests of chloride diffusion characteristics in high-volume Class C fly ash concrete systems should be carried out, including field exposure tests (slabs subjected to frequent de-icing salt applications on exposure site) and marine-exposure studies (e.g., Treat Island).

Research Need No. 5: Mitigating Carbonation Effects

Many reports have raised concerns about the increased susceptibility to carbonation of concrete incorporating large volumes of fly ash, which in turn can contribute to increasing the risk of corrosion in reinforced concrete members. Consequently, more research is needed on the susceptibility to carbonation of concrete incorporating large volumes of Class C fly ash using large specimens exposed in natural environmental conditions prone to the development of this process. This should then be correlated with the susceptibility to carbonation measured under accelerated testing conditions in the laboratory. In order to develop practical data on carbonation, a field survey (carbonation profiling) of existing structures incorporating high volumes of Class C fly ash should be done, while the effect of various parameters on the resistance to carbonation of concrete incorporating high volumes of Class C fly ash (e.g., curing membranes, curing compounds, anti-carbonation coatings, internal curing) should be evaluated.

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