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16. Abstract The objective of this study was to determine the potential for reductions in carbon dioxide emissions in Texas by substituting high volumes of fly ash in concrete production and to identify the resulting benefits and challenges.  Researchers reviewed the literature and determined that high volume fly ash (HVFA) can improve the properties of both the fresh and hardened concrete. It can improve workability, heat of hydration, strength, permeability, and resistance to chemical attack. A laboratory investigation was performed to investigate the potential of HVFA concrete in mitigating the effects of alkali-silica reactivity, which was recently a serious concern in Texas. The laboratory study showed high volumes of Class F ash are very effective in reducing the alkali-silica reaction from a potentially reactive state to an innocuous state.  Researchers compiled data for 18 power plants located throughout Texas and determined that a total of 6.6 million tons of fly ash are produced annually in Texas and about 2.7 million tons (or 40%) are generally sold for use in concrete or other end products. Researchers estimated production of concrete in Texas and determined that if 60 percent of the portland cement used in Texas concrete production were replaced with fly ash, carbon dioxide emissions could potentially be reduced by 6.6 million tons annually by the year 2015.  More education is needed for design engineers and for the concrete industry regarding the performance and environmental benefits which can be realized through increased use of fly ash in concrete.					
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**POTENTIAL FOR REDUCED GREENHOUSE GAS  
EMISSIONS IN TEXAS THROUGH THE USE OF  
HIGH VOLUME FLY ASH CONCRETE**

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## ABSTRACT

The objective of this study was to determine the potential for reductions in carbon dioxide emissions in Texas by substituting high volumes of fly ash in concrete production and to identify the resulting benefits and challenges.

Researchers reviewed the literature and determined that HVFA can improve the properties of both the fresh and hardened concrete. It can improve workability, heat of hydration, strength, permeability, and resistance to chemical attack. A laboratory investigation was performed to investigate the potential of HVFA concrete in mitigating the effects of alkali-silica reactivity, which was recently a serious concern in Texas. The laboratory study showed high volumes of Class F ash are very effective in reducing the alkali-silica reaction from a potentially reactive state to an innocuous state.

Researchers compiled data for 18 power plants located throughout Texas and determined that a total of 6.6 million tons of fly ash are produced annually in Texas and about 2.7 million tons (or 40%) are generally sold for use in concrete or other end products. Researchers estimated production of concrete in Texas and determined that if 60 percent of the portland cement used in Texas concrete production were replaced with fly ash, carbon dioxide emissions could potentially be reduced by 6.6 million tons annually by the year 2015.

More education is needed for design engineers and for the concrete industry regarding the performance and environmental benefits which can be realized through increased use of fly ash in concrete.



## EXECUTIVE SUMMARY

Current trends show that infrastructure needs will continue to require large amounts of low cost building materials, such as portland cement concrete. This need will have to be balanced with the need for environmental preservation, natural resource conservation and pollution reduction. Portland cement concrete has clearly emerged as the material of choice for modern infrastructural needs. The world consumption of portland cement has risen from less than two million tons in 1880 to 1.3 billion tons in 1996 and is projected to increase to 2 billion tons by the year 2010.

The production of each ton of portland-cement clinker is accompanied by the release of approximately one ton of the greenhouse gas carbon dioxide. Besides other raw materials, each ton of portland cement requires approximately 1.5 tons of limestone, and considerable amounts of both fossil fuel and electrical energy.

The objective of this study was to determine the potential for reductions in carbon dioxide emissions in Texas by substituting high volumes of fly ash in concrete production and to identify the resulting benefits and challenges.

Researchers compiled data for the 18 power plants located throughout Texas and determined that a total of 6.6 million tons of fly ash are produced annually in Texas and about 2.7 million tons (or 40%) are generally sold for use in concrete or other end products. Therefore, almost 4 million tons of fly ash are landfilled. Just over half of the fly ash produced in Texas is a Class F ash. About 25 percent of the Class F ash is currently being sold or used and almost 60 percent of the Class C ash is sold or used

Fly ash can improve the properties of fresh concrete and the hardened concrete. Most concrete today contains some fly ash. The fly ash may typically replace no more than about 15 to 30 percent of the portland cement. Fly ash can improve the workability and reduces the heat of hydration in fresh concrete. It can improve the strength, permeability, and resistance to chemical attack of the hardened concrete. Canadian research has led to the development of high volume fly ash (HVFA) concrete. In this concrete, up to 60 percent of the portland cement is replaced with Class F fly ash. HVFA concrete exhibits excellent strength, workability, and low temperature rise. One barrier perceived by industry is that it takes a longer time to set. This can, however, be a distinct advantage during a typical Texas summer.

Throughout the course of this research study, the Texas Department of Transportation (TxDOT) experienced some serious problems with premature failure of concrete attributed to alkali-silica reactivity (ASR). There was some belief that Class C fly ash which was

being used in concrete was a contributing factor in the problem. Researchers investigated the potential of Class F ash used in high volumes at mitigating ASR through a laboratory investigation. An aggregate was chosen from Texas which was known to be potentially reactive with the alkalis in cement. Samples were made using a low and high alkali cement in immersed in NaOH for 28 days to monitor their expansion. In some of the samples, the cement was replaced with 58 percent Class F ash. In the samples containing the high alkali cement and 58 percent replacement with Class F ash, a distinct reduction in expansion was observed at all stages. An expansion reduction was also observed when a low alkali cement was blended with 58% Class F ash. This confirms the effectiveness of high volumes of Class F ash in reducing the alkali-silica reaction from a potentially reactive state to an innocuous state.

Researchers used data from the United States Geologic Services (USGS) on the amount of crushed stone, sand and gravel which is used for production of concrete to estimate quantities of concrete in Texas. The USGS also reports the amount of portland cement produced in Texas. In 2001, it is estimated that about 39 million tons of concrete was produced in Texas and about 30 percent or 12 million tons was attributed to the TxDOT market.

The production of one ton of cement produces about one ton of carbon dioxide. Therefore, every ton of portland cement that is replaced with fly ash, could result in a one-ton reduction in the emission of carbon dioxide. In this study, projections are made to the year 2015 on the quantities of fly ash available for use in concrete in Texas and the estimated potential reduction of carbon dioxide emissions associated with concrete production in different scenarios is shown below:

<u><i>Potential Carbon Dioxide Emission Reductions</i></u>	<u><i>Year 2005</i></u>	<u><i>Year 2015</i></u>
15% Cement Replaced	1,462,500 tons	1,650,000 tons
30% Cement Replaced	2,925,000 tons	3,300,000 tons
60% Cement Replaced	5,850,000 tons	6,600,000 tons

The concrete industry has accepted fly ash use in concrete. Most concrete plants have a silo which contains fly ash that is used routinely for concrete production. However, high volumes of fly ash in concrete is an unknown technology to many. Many plants produce concrete mixes with a Class C ash. It is not feasible for concrete plants to build an additional silo so that they could also have a Class F ash available to produce HVFA concrete. Some report this investment for a silo to be as high as \$1 million. There is currently no incentive for the concrete industry to change current ways.

Another barrier to the increased use of fly ash are the limitations placed by agency specifications. TxDOT as well as many other agencies allow a maximum of 35 percent fly ash replacement in concrete.

Almost half of the fly ash produced in Texas is a Class C ash. More research is needed to develop the performance characteristics of HVFA concrete produced with a Class C ash.

More education is needed for design engineers and for the concrete industry regarding the performance and environmental benefits which can be realized through increased use of fly ash in concrete.



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## **DISCLAIMER**

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# CHAPTER 1.0 INTRODUCTION

## 1.1 BACKGROUND

Current trends show that infrastructure needs will continue to require large amounts of low cost building materials, such as portland cement concrete. This need will have to be balanced with the need for environmental preservation, natural resource conservation and pollution reduction. Portland cement concrete has clearly emerged as the material of choice for modern infrastructural needs. The world consumption of portland cement has risen from less than two million tons in 1880 to 1.3 billion tons in 1996 and is projected to increase to 2 billion tons by the year 2010.

The production of each ton of portland-cement clinker is accompanied by the release of approximately one ton of the greenhouse gas carbon dioxide (CO<sub>2</sub>). Besides other raw materials, each ton of portland cement requires approximately 1.5 tons of limestone, and considerable amounts of both fossil fuel and electrical energy.

Eighty per cent of CO<sub>2</sub> emissions come from the combustion of fossil fuels, and approximately 30% of those emissions are from the transportation sector. The next largest source of CO<sub>2</sub> emissions is from the manufacture of cement and account for approximately 10% of all CO<sub>2</sub> emissions<sup>1</sup>. When faced with the challenge to reduce greenhouse gas emissions, policy makers have traditionally targeted the transportation sector and fossil fuel combustion, the largest CO<sub>2</sub> sources. This task has been difficult. A promising alternative is to target reductions in CO<sub>2</sub> emissions from cement manufacture through the substitution of fly ash (a coal combustion by-product).

Canadian researchers have determined that CO<sub>2</sub> emission reductions can be accomplished by substituting high volumes of fly ash (a material that is otherwise landfilled) as a replacement for cement<sup>2</sup>. Their research has shown that this high-volume fly ash (HVFA) concrete exceeds the requirements of conventional portland cement concrete and has all of the attributes of high-performance concrete. Use of fly ash in cement manufacture may also achieve complementary goals by reducing the waste stream, increasing material recycling and conserving energy. This can be accomplished without a significant economic impact to cement manufacturers or consumers.

To achieve sustainable development in the cement and concrete industry, we need to understand and appreciate what has happened to the world during our lifetime<sup>3</sup>. R.N. Swamy<sup>3</sup> states that, “the world at the end of this century is very different from the world that we inherited at the beginning of the century. There have been unprecedented social changes, unpredictable upheavals in world economy, uncompromising societal attitudes, and pollution and damage to our natural environment. In global terms, the societal transformations that have occurred can be categorized in terms of population growth,

technological revolutions, worldwide urbanization and uncontrolled pollution and creation of waste.”

The impact of global urbanization is not merely on the demand for construction materials but also on world energy demand, which again impinges finally on the construction industry<sup>3</sup>. In the present context of the world, 25% of the world’s population live in industrialized nations but they account for nearly 75% of the global energy consumption<sup>3</sup>.

Whatever its limitations, concrete as a construction material is still rightly perceived and identified as the provider of a nation’s infrastructure and indirectly, to its economic progress and stability because it is so easily and readily prepared and fabricated into all sorts of structural systems in the realms of infrastructure, habitation and transportation<sup>3</sup>.

In spite of the excellent known performance of concrete in normal environments, there are two aspects of the material that have tarnished its image: its environmental impact and its durability<sup>3</sup>. The construction industry has a direct influence on world resources, energy consumption, and on carbon dioxide emissions. The record of concrete as a material of everlasting durability has been greatly impaired by the material and structural degradation that has become common in many parts of the world<sup>3</sup>. We have assumed that the relative impermeability of concrete and protection of the embedded steel will be adequately provided for by the cover thickness and the presumed quality of the concrete<sup>3</sup>. However, our experience has shown that neither can be achieved as a normal and natural consequence of the process of concrete fabrication<sup>3</sup>.

Even when adequate concrete cover and concrete quality are achieved in practice, there is a high risk of premature corrosion deterioration in concrete structures exposed to aggressive salt-laden environments. The strong implication here is that with current design codes, premature deterioration due to steel corrosion is likely to continue. There is a need for a fundamental change in our thinking about concrete and concrete quality made of portland cement concrete<sup>4-7</sup>.

The high strength which has traditionally been desirable in concrete may give misleading ideas of durability. Although strength is clearly the result of the pore-filling capability of the hydration products, there is considerable evidence to show that there is no direct relationship between concrete strength and impermeability, and hence durability<sup>8</sup>.

Extensive research has now established that the most direct, technically sound and economically attractive solutions to the problems of reinforced concrete durability lies in the incorporation of finely divided siliceous materials in concrete. The fact that these cement replacement materials, or supplementary cementing materials, such as fly ash, ground blast furnace slag, silica fume, rice husk ash, natural pozzolans, and volcanic ash are all either pozzolanic or cementitious make them ideal companions to portland cement. Portland cement is the best chemical activator of these siliceous admixtures. Portland cement combined with fly ash can result in high quality concrete with intrinsic abilities for high

durability with immense social benefits in terms of resources, energy and environment - the only way forward for sustainable development<sup>3</sup>.

The objective of this study was to determine the potential for reductions in CO<sub>2</sub> emissions in Texas by substituting high volumes of fly ash in concrete production and to identify the resulting benefits and challenges.



## CHAPTER 2.0 FLY ASH PROPERTIES, PRODUCTION, AND AVAILABILITY

### 2.1 CHARACTERISTICS OF FLY ASH

Fly ash is a by-product of the combustion of coal in thermal power plants. It is a fine, powdery material that would “fly” out of the power plant’s stacks if it were not captured. But power plants today collect their fly ash particles through the dust collection system before they are discharged into the atmosphere.

These fly ash particles are typically spherical, ranging in diameter from less than 1  $\mu\text{m}$  up to 150  $\mu\text{m}$ . The type of dust collection equipment determines the range of particle sizes in a particular fly ash. The types and amounts of incombustible matter in the coal determines the chemical composition of the fly ash. Most of the fly ash contain compounds from the elements silicon, aluminum, iron, calcium, and magnesium. Fly ash produced from the burning of subbituminous coal contains more calcium and less iron than fly ash from bituminous coal. Unburned coal also collects with the fly ash as carbon particles. Fly ash from subbituminous coals contains very little unburned carbon.

There are two general classes of fly ash: Class C, which is normally produced from lignite or subbituminous coals and Class F, which is normally produced from bituminous coals. These two ashes differ in the ways they function in concrete mixtures. Class C ashes differ from Class F ashes in that they are self-hardening even without the presence of cement. In addition, Class C ashes contain higher levels of calcium. It should be noted that the American Society for Testing Materials (ASTM) specifications for fly ash (C618) do not make reference to the level of calcium in the ash as shown in Table 1. The different levels of calcium has led to the use of an alternative terminology commonly used: high-calcium and low-calcium ash for Class C and Class F, respectively.

**Table 1. ASTM C618-98 Specifications for Fly Ash.**

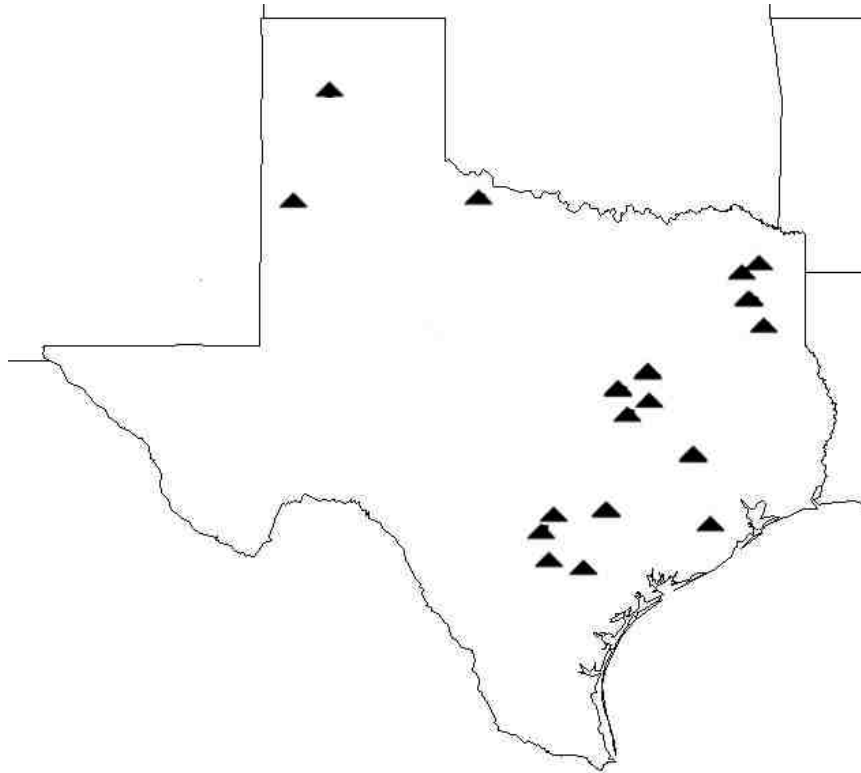
Class of Ash	ASTM Specification
Class C	$\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3 > 50\%$
Class F	$\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3 > 70\%$

One important characteristic of fly ashes is that they exhibit pozzolanic activity. A pozzolan is a siliceous or siliceous/aluminous material which in itself possesses little or no cementitious value but which will, in finely divided form and in the presence of moisture, chemically react with calcium hydroxide at ordinary temperatures to form compounds possessing cementitious properties.

Historically, Class C ash has been used much more in construction applications than Class F, primarily due to the self-hardening characteristics inherent in the Class C ash.

## 2.2 PRODUCTION AND AVAILABILITY OF FLY ASH IN TEXAS

There are 18 coal-fired power plants located throughout Texas as shown in Figure 1. Utilities must report the production of coal combustion by-products at their facilities annually to the Department of Energy. Researchers compiled these data as presented in Table 2. While this is the production for a single year, it is typical for annual production. Of interest to this study, is the production of fly ash. Approximately 6.6 million tons of fly ash are produced annually in Texas and about 2.7 million tons (or about 40%) are generally sold to use in concrete and/or other end products as illustrated in Figures 2 and 3. As shown in Figure 4, just over half of the fly ash produced in Texas is a Class F ash. About 25 percent of the Class F ash is currently being sold or used and almost 60 percent of the Class C ash is sold or used (Figure 5).

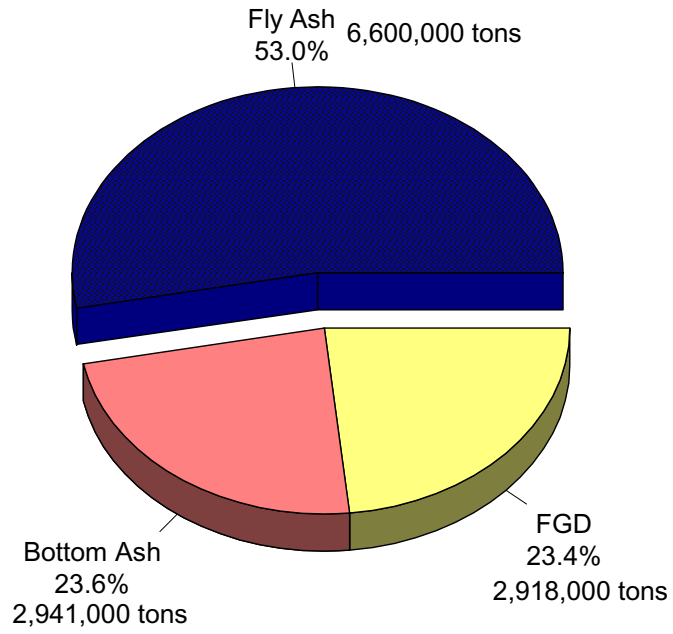


**Figure 1. Location of Coal-Fired Power Plants in Texas.**

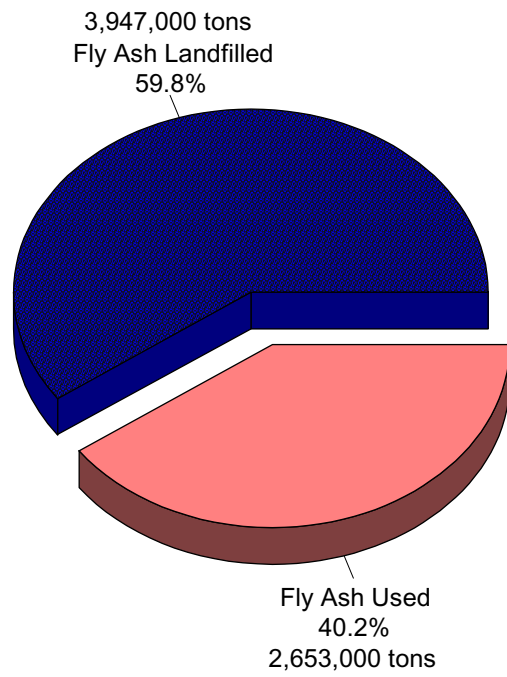
**Table 2. Coal Combustion By-Products Produced and Sold by Texas Power Plants for the Year 2000.**

Plant Code (DOE)	Plant Name	County	Total Fly Ash Produced thousand short tons	Total Fly ash Sold, thousand short tons	Total Bottom Ash Produced, thousand short tons	Total Bottom Ash Sold, thousand short tons	Total FGD or Gypsum Produced, thousand short tons	Total FGD or Gypsum Sold, thousand short tons
127	Oklaunion	Wilbarger	110.8	110.8	43.1	43.1	0	0
298	Limestone*	Limestone	191.0	191.0	485.8	36.4	1278.9	0
3470	WA Parish	Fort Bend	344.0	296.7	115.8	40.2	48.2	47.8
3497	Big Brown*	Freestone	576.0	189.7	229.8	24.4	0	0
6136	Gibbons Creek	Grimes	69.9	69.6	23.3	13.7	0	0
6139	Welsh	Titus	211.5	188.3	25.8	25.8	0	0
6146	Martin Lake*	Rusk	1165.4	425.8	574.0	30.3	603.4	0
6147	Monticello*	Titus	1355.5	192.8	553.7	8.4	47.6	0
6178	Coletto Creek	Goliad	118.8	24.3	29.7	0	0	0
6179	San Seymour	Fayette	238.0	212.0	102.0	36.0	37.0	4.0
6181	JT Deely	Bexar	127.2	126.2	38.1	19.7	0	0
6183	San Miguel	Atascosa	688.9	5.8	229.6	0	338.1	0
6193	Harrington Station	Potter	197.3	185.6	49.3	49.3	0	0
6194	Tolk Station	Lamb	186.2	152.4	52.5	49.6	0	0
6648	Sandow*	Milam	352.0	97.9	150.9	27.7	134.5	0
7030	TNP One	Robertson	252.8	92.8	103.9	18.4	0	0
7097	JK Spruce	Bexar	92.3	91.5	26.8	13.8	46.3	46.3
7902	Pirkey	Harrison	323.3	0	107.8	0	384.4	0
<b>Total</b>			<b>6600.9</b>	<b>2653.2</b>	<b>2941.9</b>	<b>436.8</b>	<b>2918.4</b>	<b>98.1</b>

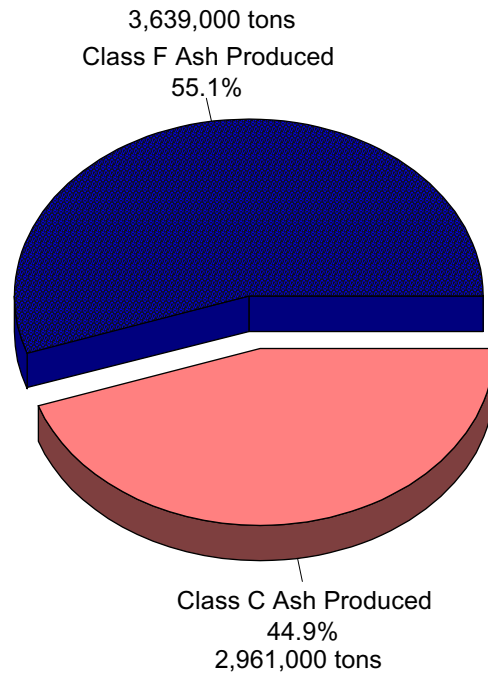
Based on information reported by utilities to the EIA DOE on form 767. \*Produces a Class F fly ash.



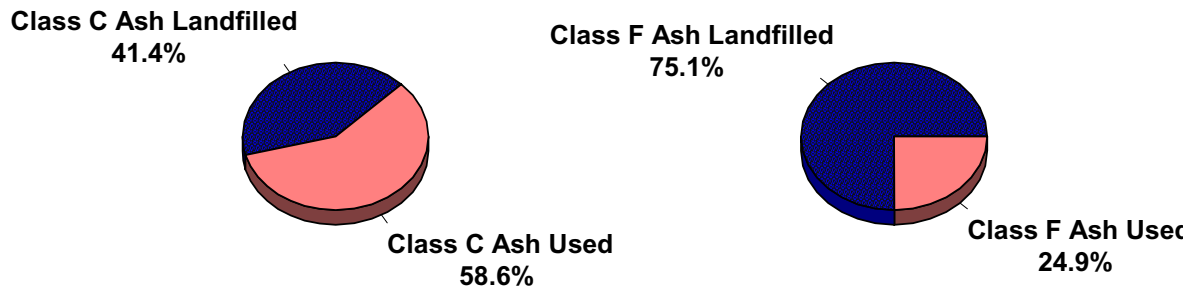
**Figure 2. Typical Annual Production of Coal Combustion By-Products in Texas.**



**Figure 3. Typical Annual Use of Fly Ash in Texas.**



**Figure 4. Typical Annual Production of Class C and Class F Fly Ash in Texas.**



**Figure 5. Typical Annual Use of Class C Ash versus Class F Fly Ash in Texas.**

### 2.3 TYPICAL COMPOSITION OF FLY ASHES FROM PLANTS IN TEXAS.

Composition of fly ashes will vary from plant-to-plant. Table 3 shows fly ash compositions from selected plants in Texas.

**Table 3. Fly Ash Composition and Properties.**

Chemical Analysis	<i>Class C Ash, W.A. Parish Plant</i>	<i>Class F Ash, Limestone Plant</i>	<i>Class F Ash, Big Brown</i>
Silicon Dioxide, %	33.39	57.03	56.38
Aluminum Oxide, %	1.57	19.08	6.8
Iron Oxide, %	6.27	10.03	20.82
$SiO_2 + Al_2O_3 + Fe_2O_3$ , %	59.23	86.14	84.00
Magnesium Oxide, %	5.27	1.89	2.57
Sulfur Trioxide, %	2.24	0.67	0.64
Moisture Content, %	0.06	0.01	0.11
Loss on Ignition, %	0.23	0.01	0.41
Available Alkalis as Na <sub>2</sub> O, %	1.29	0.19	1.12
<i>Calcium Oxide, %</i>	<i>27.45</i>	<i>7.66</i>	<i>11.57</i>
<b>Physical Analysis</b>			
Fineness: Amount retained on 325 sieve, %	10.40	34.17	16.11
Water Requirement, % control	94	95	93
Specific Gravity	2.63	2.38	2.44
Autoclave Expansion, %	-0.01	-0.03	-0.03
Strength Activity Index with Portland Cement, %, 28 day	93	80	97

## 2.4 FUTURE OF FLY ASH IN TEXAS

One of the concerns for engineers and officials responsible for specifying the use of fly ash in concrete regards the consistency of quality and future availability of that product. A recent trend for some of the plants in Texas is to supplement or replace their current coal source with Powder River Basin coal from Wyoming due to its low cost. This raises the question, “how will this new coal source in varying quantities affect the chemistry of the ash and thus the properties of concrete?” A plant which burns Powder River Basin coal will produce a Class C ash. What happens, though, when a plant which burns lignite coal and produces an F ash begins to supplement that coal with Powder River Basin coal which produces a C ash? This is also of concern to Texas Department of Transportation (TxDOT) officials who have recently been concerned about the use of Class C ash and would like to specify a Class F ash. The following is a discussion of a realistic scenario to show that supplementing lignite coal with Powder River Basin coal may produce no effective change in the quality of the fly ash.

### *Scenario:*

The TXU Martin Lake Plant has historically burned lignite coal mined in Texas. TXU has at least 10 years of lignite deposits at their mine to support this plant. This type of plant is not capable of handling 100% Powder River Basin (PRB) coal and TXU officials have stated they could never supplement the lignite coal with more than 25% PRB at this plant.

If the Martin Lake plant burns 75% lignite coal and 25% PRB, what is the effect on the CaO content of the ash? Due to the efficiency of PRB coal, it only produces about 80 lbs of fly ash per ton of coal; whereas, lignite produces about 200 lbs of fly ash.

*One ton of lignite coal produces about 200 lbs of fly ash with a CaO content of about 10% for a total of 20 lbs of CaO.*

*One ton of PRB coal produces about 80 lbs of fly ash with a CaO content of about 30% for a total of 24 lbs of CaO.*

If the plant uses 75% lignite and 25% PRB what is the CaO content of the blend?

$$\begin{aligned} 0.75 (20 \text{ lbs of CaO}) &= 15 \text{ lbs (for lignite)} \\ 0.25 (24 \text{ lbs of CaO}) &= \underline{6 \text{ lbs (for PRB)}} \\ &21 \text{ lbs of CaO} \end{aligned}$$

Therefore, a ton of lignite coal produces 20 lbs of CaO and a blend of lignite and PRB (75/25) produces only 21 lbs of CaO which is not enough of a difference to affect the performance characteristics of the fly ash.



## CHAPTER 3.0 FLY ASH USAGE IN CONCRETE PRODUCTION

### 3.1 REASONS TO USE FLY ASH IN CONCRETE

There are many benefits to using fly ash in concrete and the benefits associated with it being a recycled by-product is secondary to most engineers. Fly ash can improve the properties of fresh concrete and the hardened concrete. It reduces the amount of portland cement required in concrete which makes its use cost-effective. Typically, 15 to 30 percent of the portland cement in most concrete is replaced with fly ash.

#### Effects of Fly Ash on Properties of Fresh Concrete

Fresh concrete is a concentrated suspension of particulate materials of widely differing densities, particle sizes, and chemical compositions in a solution of lime and other components<sup>9</sup>. When cement and water are mixed, chemical reactions occur which increases the temperature of the concrete. To effectively mix and place concrete, a certain degree of fluidity, or workability, is needed. Fly ash plays a role in these factors as described below.

***Improved Workability/Decreased Water Demand.*** Fly ash is a very fine-grained, powder-like material consisting of spherical, glassy particles. These very small, spherical particles provide a lubricating effect in the concrete resulting in improved workability of the fresh concrete. This improved workability allows the amount of water used in the concrete to be reduced.

***Reduced Heat of Hydration.*** When concrete begins to set or hydrate, a temperature rise occurs. Use of fly ash as partial replacement for portland cement reduces the temperature rise in the concrete as shown in Figure 6. Cooling which occurs after a large temperature rise can lead to cracking in mass concrete.

#### Effects of Fly Ash on Properties of Hardened Concrete

***Strength Development and Ultimate Strength.*** As mentioned previously, fly ash is available in two general types: Class C and Class F. Class C ash (high in calcium) is cementitious even in the absence of portland cement. When Class C ash is used, the rate of strength development in concrete is only slightly affected by the ash. Much of the early research on fly ash concrete was performed using Class F fly ash. In this early work, the ashes came from older plants producing a coarse particle size and were relatively inactive as pozzolans. These ashes showed a slow rate of strength development leading to the thinking that “fly ash reduces strength at all ages”.<sup>9</sup> More recent research indicates that concrete containing fly ash has the potential to produce satisfactory compressive strength-development. The influence of the class of fly ash on the long-term compressive strength of the concrete is not significant.

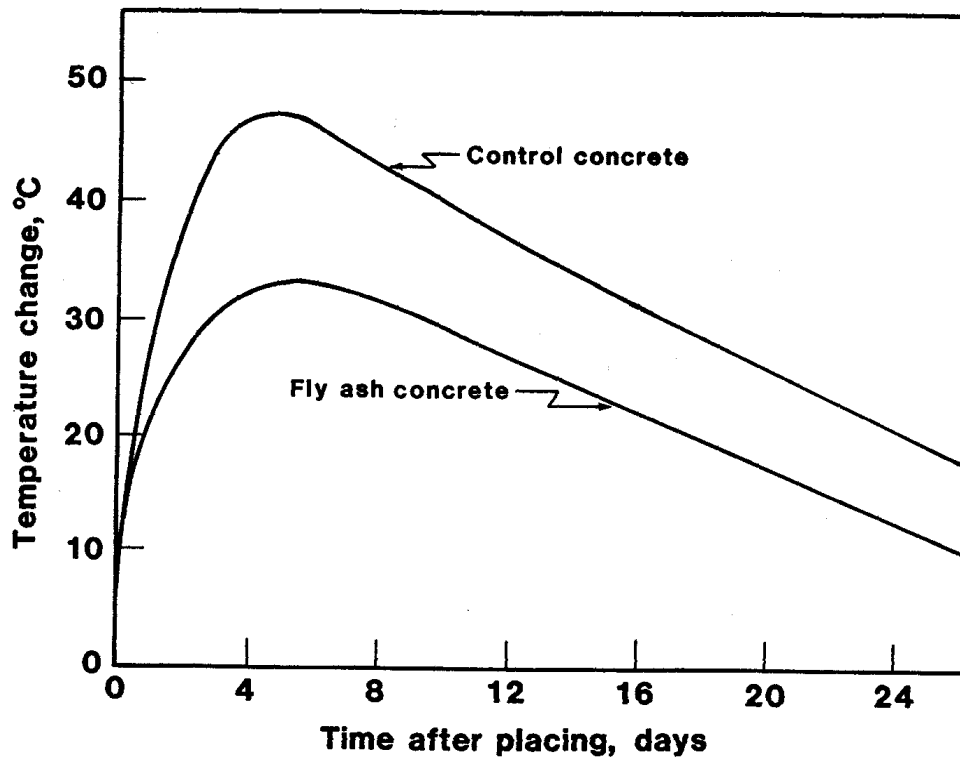
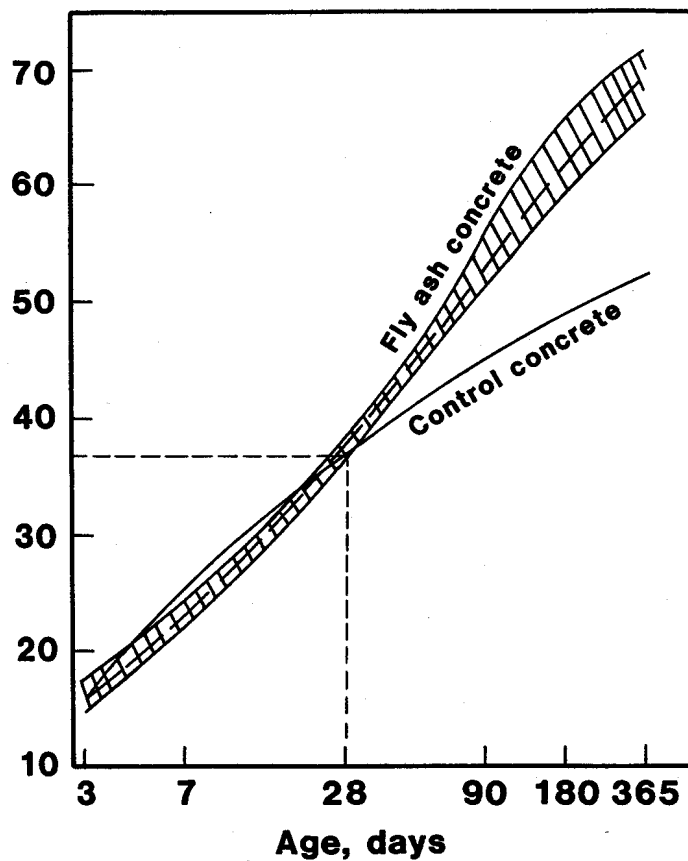


Figure 6. Temperature Change in Concrete with Time (After Reference 49 and 9).

In general, the compressive and flexural strengths of fly ash concretes is slightly lower at early ages than those of control concretes but exceeds those of concrete without fly ash at later ages.

The additional binder produced by the fly ash reaction with available lime allows fly ash concrete to gain strength over time. Mixtures designed to produce equivalent strength at early ages will ultimately exceed the strength of straight cement concrete mixtures as shown in Figure 7.



**Figure 7. Typical Strength Gain of Fly Ash Concrete (after Reference 48 and 9)**

**Permeability.** The key to a sustainable transportation infrastructure is in using materials with exceptional durability. The lack of durability in concrete is often related to excessive permeability. For concrete to remain durable it must be impervious to the aggressive environments in which it may be used. Concrete is often used in harsh marine environments. It is also sometimes in contact with sulphate and acidic waters. A permeable concrete pavement is also very susceptible to deterioration where salts are used by maintenance crews for deicing bridges and roadways.

The movement of aggressive solutions into concrete play a primary role in determining the rate of concrete deterioration caused by chemical attack. The use of fly ash in concrete decreases the required water and this combined with the production of additional cementitious compounds reduces the permeability of the concrete. This reduced permeability results in improved long-term durability and resistance to various forms of deterioration.

**Resistance to ASR and Sulfates.** Fly ash also improves the resistance of concrete to alkali-silica reactivity (ASR) which will be described later in detail. It also improves resistance to sulfate attack by inducing three phenomena:

- fly ash consumes the free lime making it unavailable to react with sulfate,
- the reduced permeability prevents sulfate penetration into concrete,
- replacement of cement reduces the amount of reactive aluminates available.

### **3.2 HIGH-VOLUME FLY ASH (HVFA) CONCRETE**

The quantity of fly ash use in concrete generally ranges from 15 to 30 percent replacement of the portland cement. In 1985, the Canada Centre for Mineral and Energy Technology (CANMET) initiated studies on structural concrete incorporating high volumes (>50%) of low calcium fly ashes<sup>9</sup>. This research resulted in HVFA concrete with adequate early-age strength and workability, low temperature rise, and high late-age strength.

#### **Setting Time**

One of the barriers to using HVFA concrete by the industry is its reduced time to set. Malhotra and Ramazanianpour<sup>9</sup> report that research was performed to measure times of set in accordance with ASTM C403. Test results show that *initial* setting times were 7.5 hours which comparable to those of control concrete made with the same water content and water to cementitious ratio. However, final setting times were delayed by about 3 hours compared with the control concrete. These delays may be related to the problem of compatibility between cementitious materials and superplasticizers. This delay in setting time may be viewed by the industry to pose a scheduling problem. This could be a problem during winter construction; however, the delayed set can be a distinct advantage in a Texas summer.

#### **Temperature Rise**

Because of the low cement content in HVFA concrete, the rise in temperature during the first few days is minimal. This makes its use ideal in the construction of massive structures such as concrete dams.

#### **Compressive Strength**

High volume fly ash concrete exhibits adequate strength development at both early and late ages. Research in Canada has shown that the one-day compressive strength is more than adequate for formwork removal at normal temperatures and comparable to the strength of portland cement concrete. Twenty-eight day compressive strengths are also comparable to the values for normal portland cement concrete. Due to the slow pozzolanic reaction, the HVFA concrete achieves significant improvements in its mechanical properties at later ages compared to conventional portland cement concrete.

## **Durability**

The water permeability of HVFA concrete is very low. Tests performed on 50-mm thick concrete discs under uniaxial flow and pressure conditions indicate a permeability less than or equal to  $10^{-13}$  conditions<sup>2</sup>.

Air-entrained, high-performance, HVFA concrete shows excellent resistance to repeated cycles of freezing and thawing. After 1000 cycles in ASTM C 666 Procedure A test (freezing and thawing in water), the durability factors are in excess of 90; conventional air-entrained portland cement concrete is considered satisfactory if it can withstand 300 cycles<sup>2</sup>.

The high-performance, HVFA concrete shows very high resistance to the penetration of chloride ions in tests performed according to ASTM C 1202. Its resistance is considerably higher than conventional portland cement concrete of similar strength. The charge measured on HVFA concrete usually ranges from 500 to 2000 coulombs at 28 days, and from 200 to 700 coulombs at 91 days. A value of less than 600 coulombs is indicative of very high resistance, and hence, very low permeability<sup>2</sup>.

The drying shrinkage strains of HVFA concrete are comparable to, or lower than that of conventional portland cement concrete, with measured values of the order of  $500 \times 10^{-6}$  after 64 weeks of air drying<sup>2</sup>.

### **3.3 CONCERN REGARDING ALKALI-SILICA REACTIVITY IN TEXAS**

Throughout the course of this research study, the Texas Department of Transportation (TxDOT) experienced some serious problems with premature failure of concrete attributed to alkali-silica reactivity (ASR). There was some belief that Class C fly ash which was being used in concrete was a contributing factor in the problem. Researchers investigated the potential of Class F ash used in high volumes at mitigating ASR through a laboratory investigation as presented in Chapter 5. A description and discussion of ASR is presented in the following chapter.



## CHAPTER 4.0 UNDERSTANDING PERFORMANCE ISSUES RELATED TO ALKALI SILICA REACTIVITY

### 4.1 GENERAL

In the late 1930's, a disturbing type of damage in the form of map or pattern cracking was observed in concrete structures along the coast of California. The California Department of Transportation was the first to suggest that the deterioration of the concrete was due to a reaction between the alkalis in the cement and certain reactive siliceous elements of the aggregates.

This discovery initiated a series of experiments, primarily in the United States, and a few years later in Australia, England and Denmark. Thereafter, from 1960 onwards, this reaction received global attention, and international and concurrent research was launched. The first task was to establish a limit on the alkali content in Portland cement to prevent the deleterious reaction from occurring.<sup>10</sup> Preliminary work by numerous researchers had indicated that expansive reaction was unlikely to occur when the alkali content of the cement was below 0.6%  $\text{Na}_2\text{O}_{\text{eq}}$  by weight of the cement. However, researchers such as Stark and some other researchers<sup>11-13</sup> proved that this value might be conservative in many cases.

Unfortunately, in order to reduce the alkalis in cement by 0.15%, there is a 300% increment in energy consumption during cement manufacture.<sup>14</sup> Additionally, the Environmental Protection Agency (EPA) does not permit alkalis to be expelled from the kiln chimney and pollute the atmosphere or to be buried underground because it is a potential ground water pollutant.<sup>10</sup>

So, the research efforts were then directed to demonstrate that portland cement containing higher than the permissible alkali content (according to ASTM C 150) could be safely used in combination with pozzolans such as fly ash or slag using reactive aggregates.<sup>10,15,16</sup> In addition, many forms of siliceous aggregates have been found to be reactive while sources of truly "non-reactive" aggregates are not readily available in some locations. This has led to efforts to devise ways to control the reaction when reactive siliceous aggregates are used.

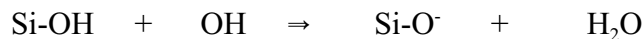
Fly ash has been reported by several researchers to reduce expansion due to ASR. However, the current level of knowledge in this area is still insufficient. There is still a considerable difference of opinion about the effectiveness of fly ash and other supplementary cementing materials like slag in controlling expansion due to ASR. There is much concern about the alkalis present in the fly ash itself and whether these are available for the deleterious reaction. So, there is an urgent need to improve our present knowledge about the mechanism in which fly ash helps to prevent damage due to ASR. In reality, no definite guidelines are available at present for engineers to determine the type and amount of fly ash to be used in combination with a given combination of cement and aggregate.

## 4.2 DEFINITION OF ALKALI-SILICA REACTIVITY

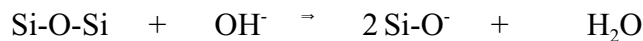
The alkali-silica reaction is a slow reaction between the hydroxyl ions in the pore solution of the concrete and certain siliceous components of the aggregate. The alkalis, sodium (Na) and potassium (K), in concrete are primarily derived from cementitious materials. Calcium also an alkali available in concrete, is a contributor to the pore solution alkalinity.

The reactive silica is not directly attacked by the alkalis (Na + K). The alkalis contribute initially to the high concentration of hydroxyl ions in the solution and later to the formation of an expansive alkali-silica gel.<sup>17</sup> The cement paste of concrete contains interconnected microscopic pores through which water or ion in solution can migrate. The concrete pore solution is alkaline in nature and its pH value increases as the alkali content of the cement increases. The reaction products of ASR have a great affinity for moisture. The cement paste of concrete contains interconnected microscopic pores through which water or ions in solution can migrate. In absorbing water, the gel induces pressure and expansion and cracking of aggregate and surrounding paste ensues.

Dent Glasser and Kataoka<sup>18</sup> proposed that there is an acid-base reaction between the hydroxyl ions in solution and the acidic silanol (Si-OH) groups as follows:



As further hydroxyl ions penetrate the structure, some of the siloxane linkages (Si-O-Si) also attacked:



The negative charges on the oxygen atoms are balanced by alkali cations (Na<sup>+</sup> and K<sup>+</sup>) that simultaneously diffuse into the structure. The disruption of siloxane bridges weakens the structure and if sufficient reserves of alkali hydroxide are available, the process continues to produce an alkaline-silicate reaction.

## 4.3 MECHANISM OF EXPANSION DUE TO ASR

Hansen<sup>19</sup> proposed that the mechanism of expansion followed the osmotic theory in the sense that the cement paste surrounding the reactive grains of the aggregates, behaves like a semi-permeable membrane through which water (or pore solution) may pass but not the larger complex silicate ions of the reactive aggregate. The water is drawn into the reacting grain where its chemical potential is lowest. An osmotic pressure cell is formed and increasing hydrostatic pressure is exerted on the cement paste, inevitably leading to the cracking of the surrounding mortar.

On the other hand, researchers like McGowan and Vivian<sup>20</sup>, argued that the classical osmotic theory based on cracking of the surrounding cement paste 'membrane' due to ASR would relieve hydraulic pressure and prevent further expansion. Their experiments showed that

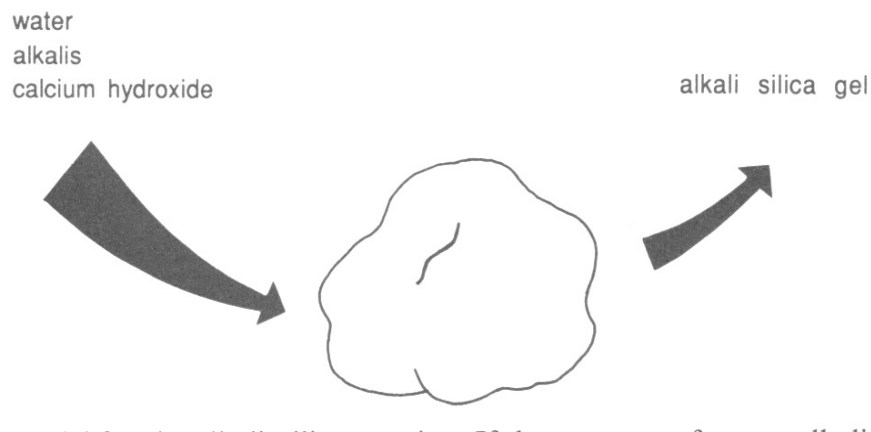
expansion was accompanied by formation and widening of cracks due to mechanical absorption rather than hydraulic forces. So, they proposed an alternative mechanism based on the physical absorption of water by the alkali-silica gel and subsequent swelling of the gel.

Powers and Steinour<sup>21</sup> proposed a ‘compromise’ theory suggesting that both osmotic and mechanical pressure may be generated depending on whether the alkali-silicate complex is fluid or solid. Swelling is caused by the entry of water into a region where the effect of a solute reduces its free energy.

Diamond<sup>22</sup> proposed a theory which consists of the following four steps:

Initial alkaline depolymerization and dissolution of reactive silica.

- Initial alkaline depolymerization and dissolution of reactive silica.
- Formation of a hydrous alkali-silica gel.
- Attraction of water by the gel.
- Formation of a fluid solution (a dilute suspension of colloidal particles).



**Figure 8. A Model for ASR.** (After Reference 22)

Figure 8 shown above indicates a model for the alkali-silica reaction. It implies that if the amount of water, alkali hydroxide and calcium hydroxide entering the reactive particle are larger than the amount of alkali-silica gel seeping out, the particle expands and cracks the surrounding cement paste.

#### **4.4 ROLE OF CALCIUM**

Most of the early ASR research work did not consider calcium in the primary mechanism of reaction and expansion. Chatterji<sup>23,24</sup> proposed an ASR expansion mechanism with a clearly defined role of  $\text{Ca}(\text{OH})_2$ . He suggested that expansion occurs in concrete when the net amount

of material entering a reactive silica grain ( $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{OH}^-$ ) exceeds the amount of material leaving the grain ( $\text{Si}^{4+}$ ). The calcium concentration in the pore solution surrounding the grain controls the rate of diffusion of silica away from the reactive site. At high levels of calcium, the migration of silica is prevented, leading to expansion of the reactive grain.

Thomas et al.<sup>25</sup> demonstrated that the alkali-silica gel in concrete containing fly ash show no expansion or cracking. These gels are relatively low in calcium compared to that in ordinary portland cement (OPC) concretes without fly ash. The gel in fly ash concrete formed by the reaction between the cement alkalis and reactive silica in the aggregate was initially low in calcium and high in alkali. This gel is relatively fluid and readily disperses into the cement paste. However, in OPC concrete, the alkali in the gel may be replaced by calcium producing a more viscous product which is less able to dissipate when it swells on contact with water. This swelling of the high calcium gel may lead to tensile stresses to develop in concrete leading to its disruption. The lower availability of calcium in fly ash concrete, due to reduced  $\text{Ca}(\text{OH})_2$  content, prevents the formation of the damaging form of gel. Consequently, the gel remains in a fluid state and disperses through the pore structure rather than creating internal stresses.

#### **4.5 FACTORS AFFECTING ASR**

For the alkali-silica reaction to occur, three conditions must be present<sup>17</sup>:

- Reactive forms of silica in the aggregate,
- High alkali (pH) pore solution,
- Sufficient moisture.

The amount of gel formed in the concrete depends on the amount and type of silica, and alkali hydroxide concentration. Natural aggregates contain various forms of silica minerals, which have varying reactivities – a measure of the readiness of the silica to react with the alkali. The exact composition of the gel reaction product may vary, but the gel always contains alkali, calcium, silica and water<sup>26</sup>.

#### **Reactive Silica in Aggregate**

Reactivity is a function of the type and form of constituents comprising the aggregate. Forms of silica are generally related to the rate at which volcanic magma cooled during the formation of the rock. Forms of siliceous minerals in aggregates range from amorphous or glassy (non-crystalline) to cryptocrystalline, microcrystalline, and crystalline, listed in order of decreasing cooling rate. During the formation of quartz crystals, some strain may be introduced. Aggregate containing strained quartz tends to be reactive. Opal is an amorphous form of silica with a variable amount of water in its structure. It is considered to be a very reactive form of silica.

In crystallographic terms, the reactivity of silica is related to the degree of order in the crystal structure. One of the convenient ways of classifying reactive silica minerals is as follows<sup>17</sup>:

Metastable group: opal, cristobalite, intermediate glass and acid glass.

Quartz: cryptocrystalline quartz, chalcedony group which includes chalcedony, chert, agate, flint and jasper.

Aggregates containing silica minerals in the metastable group typically react more rapidly than those in the quartz group. An aggregate that presents a large surface area for reaction – poorly crystalline, many lattice defects, amorphous, glassy, microporous – is susceptible to reaction<sup>27</sup>. According to the *Guide Specifications for Concrete Subject to Alkali-Silica Reactions*<sup>28</sup>, fine and coarse aggregate containing more than the following quantities of constituents are considered potentially reactive:

- Opal - more than 0.5% by mass;
- Chert or chalcedony - more than 3.0%;
- Tridymite or cristobalite - more than 1.0%;
- Optically strained or microcrystalline quartz - more than 5.0%;
- Natural volcanic glasses - more than 3.0%.

### **High-Alkali Content Pore Solution**

Alkali hydroxides in solution react readily with reactive forms of silica in aggregate. As the aggregate reactivity increases, the gel reaction products can be formed with lesser concentrations of alkali. This is precisely why low-alkali cements alone may not be sufficient to control ASR with highly reactive aggregates containing minerals such as opal. As the pH, or the alkalinity of the pore solution increases, potential for ASR increases. At higher concentrations, even the more stable forms of silica are susceptible to attack<sup>26</sup>. If the alkali concentration is great enough, the alkali hydroxides break stronger silicon bonds found in less reactive aggregates to form the gel reaction product. This is the reason why aggregates that are considered to be non-reactive, sometimes exhibit ASR<sup>17</sup>.

Repeated cycles of wetting and drying can create high localized concentrations of alkalis. As moisture travels through the concrete, dissolved alkalis move in solution, and are retained when the moisture evaporates from the concrete surface. This process, called as alkali-migration, can cause high alkali concentrations at an evaporative surface even when the overall concrete alkali content is low.

### **Sufficient Moisture**

Absorption of moisture by the gel reaction products is the fundamental step causing expansion due to ASR<sup>29</sup>. Water has a dual role in the alkali-silica reactivity; firstly it is a ‘carrier’ of alkali cations and hydroxyl ions and secondly, it is absorbed by the hygroscopic gel which swells. This swelling develops pressure sufficient to crack the concrete<sup>30</sup>. Therefore, deleterious ASR does not occur in concrete that is dry in service. If moisture in the concrete is too tightly held by cement hydration products, expansion will not occur even if the reaction between the alkaline pore solution and siliceous aggregate has occurred.

Relative humidity (RH) is a convenient measure of indicating moisture availability for absorption by ASR gel. Stark<sup>31</sup> determined that RH values greater than 80 percent, referenced to 70 to 75° F, indicates that sufficient moisture is available for absorption by the ASR gel and under such circumstances, expansion can occur. In general, higher the RH above 80 percent, greater the possible level of expansion in a given concrete. At 100 percent RH, the volume increase of the gel can vary significantly, depending upon the water-cement ratio and porosity of the aggregate. Thus, the RH values, which reflect thermodynamic free energy levels of the moisture are most convenient for indicating the moisture availability for expansive ASR<sup>29</sup>. Experimental and case study investigations have shown that below 70 percent RH, expansive reaction is negligible but above 80 percent RH, the expansive effects increase dramatically.

The two-stage process of reaction and of adsorption of water by the gel reaction product can be demonstrated in the laboratory. If an alkali-silica reactive concrete prism is prepared in the laboratory, but not stored in a humid environment, expansion due to development of the gel will be negligible. However, if a specimen stored in humid conditions is removed, rapid expansion will result such that within a few days it will have expanded to approximately the same extent as an identical prism, which had been stored in moist condition throughout. These observations imply that although the reaction may occur at relatively low humidities, high moisture levels are required in order for the gel formed by the reaction to absorb water and increase in volume.

### **Concrete Alkali Content**

As the alkali content of the concrete increases, the potential for ASR also increases. Only the alkalis from the cement or cementitious materials are included in the determination of the total alkali content of the concrete. This is because the contribution of alkalis from other ingredients is usually small.

The total alkali content of concrete is calculated as follows:

$$(\text{lb. cement per cu. yd.}) \times (\text{Na}_2\text{O equivalent}^* \text{ in cement}) / \text{lb. alkali per cu. yd.}$$

\* = The total (acid soluble) alkali content of portland cement includes both sodium oxide (Na<sub>2</sub>O) and potassium oxide (K<sub>2</sub>O), but is expressed as equivalent sodium oxide as follows:

$$\text{Na}_2\text{O}_{\text{eq}} = \text{Na}_2\text{O} + 0.658 (\text{K}_2\text{O}).$$

The sodium and potassium oxides are determined by the chemical tests outlined in ASTM C 150.

Generally, in the United States, the method used to control the concrete alkali content is to specify a low-alkali content. However as previously noted, concrete made with low-alkali cement can still exhibit expansive ASR, particularly if moisture movement concentrates the alkalis in one location<sup>32</sup>. This may be further aggravated if alkalis are provided by certain mineral and chemical admixtures or mixing water or if the total alkali content of concrete is high.

According to ASTM C 150-72, a portland cement can be classified as follows:

- EA extra low alkali  $\leq 0.4\% \text{Na}_2\text{O}_{\text{eq}}$
- LA low alkali  $\leq 0.6\% \text{Na}_2\text{O}_{\text{eq}}$
- MA medium alkali  $\leq 0.8\% \text{Na}_2\text{O}_{\text{eq}}$
- HA high alkali  $> 0.8\% \text{Na}_2\text{O}_{\text{eq}}$

### External Alkalis

Common sources of external alkalis are deicing salts, seawater, groundwater and water from industrial processes. Sodium chloride deicing salts and seawater in particular can provide unlimited amounts of alkali<sup>33</sup>. Immersing concrete prisms containing reactive aggregates in a sodium chloride solution had demonstrated increases in expansion and deterioration of concrete, especially at elevated temperatures<sup>34,35</sup>.

The use of supplementary cementitious materials and a low water-cementitious materials ratio reduces concrete permeability and slows the ingress of external alkalis and thus reduces the potential for ASR expansion. Similarly, protective coatings and sealers also provide a barrier to deicing salts, seawater and other sources of alkalis. Regular cleaning, although not a very practical solution, may be helpful too, so that the unwanted salts are carried away before they have a chance to enter the concrete and contribute to the reaction.

Alkali-silica reaction in a salt environment, appear to be very complex and may involve complex mechanisms. In general cases, the dissolved sodium chloride in concrete may undergo a partial conversion to sodium hydroxide to form a chloride-bearing equivalent of monosulfoaluminate as is commonly found in many concretes. In rare cases, a chloride-bearing ettringite can also be formed in the paste<sup>29</sup>. The formation of such compounds and the consequent removal of chloride ions from the pore solution imply a one-to-one increase in the hydroxyl ion concentration of the solution. This causes the pH to rise, thus accelerating any ASR reaction that may be taking place. Moreover, some of the dissolved sodium chloride remains as  $\text{Cl}^-$  ions in the pore solution, This causes the onset or acceleration of steel corrosion<sup>29</sup>. This residual chloride may also cause the acceleration of the ASR reaction by a mechanism involving the uptake of chloride into the early-stage ASR reaction product.

### Wetting and Drying

Dry exposure reduces the potential for expansive cracking due to ASR. Concrete that has high initial water content may maintain a high internal relative humidity if it is not permitted to dry. High humidities can sustain the ASR reaction. Alkali migration can occur with alternate wetting and drying, concentrating alkalis near the drying zone and inducing reaction in that region<sup>32</sup>. Providing good drainage can help minimize both the available moisture and wet-dry cycles.

## **Temperature**

The ASR rate usually increases with increasing temperature<sup>32</sup> so that the structures in warmer exposures are more susceptible to ASR than those in colder exposures. The effect of high or low temperatures on ultimate expansion is aggregate-dependant, with most aggregates reacting more at higher temperatures<sup>17</sup>.

## **Gel Reaction Product**

The reaction between alkali and the reactive silica in the presence of moisture produces an alkali-silica gel, which swells on the absorption of water. The gel varies considerably in composition, depending upon the composition of the alkali pore fluids, the nature of the particular form of reactive silica, temperature of reaction and concentration of the reactants<sup>21</sup>.

When a sample of concrete affected by ASR, is exposed by cracking open the concrete, the gel is usually transparent and resinous in appearance, with a viscosity between that of thick motor oil and resin. Typically, the gel carbonates with time and exposure to air, becoming white and hard with desiccation cracks similar to those observed in thin layers of dried mud. Therefore, it is advisable to look for gel immediately upon breaking a fresh surface.

Gel viscosities also exhibit a wide range of values, and can produce pressures extending up to 11 MPa. The gel at first is very viscous, but as it absorbs moisture from the pore fluids and swells, it gradually becomes less viscous until eventually it becomes fluid enough to flow along cracks, fill voids and permeate the micropores in the cement paste.

## **4.6 VISUAL SYMPTOMS OF EXPANSIVE ASR**

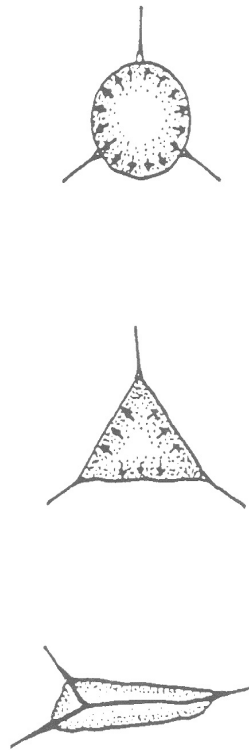
In order to diagnose ASR and to assess its impact on a structure, a step-by-step procedure needs to be followed. This procedure includes: 1) site inspection and testing, 2) sampling, 3) laboratory investigation, 4) evaluation, and 5) risk assessment of future reaction<sup>36</sup>. Visual inspection of the structure becomes an important part of this process.

## **Expansion**

Map cracking is a very common indicator of ASR. This is usually followed by spalling of the concrete surfaces and even relative displacement of different portion of a structure. The risk of catastrophic failure is low as the deterioration due to ASR is slow. ASR can exacerbate other deterioration problems such as those that occur in freeze-thaw, deicer or in sulfate environments. Similarly, cracking from other mechanisms may allow ingress of alkalis and aggravate ASR damage.

## Cracking

A well-developed network of map cracking is a typical pattern associated with ASR. While inspecting a structure for ASR, the inspection should consider the location, length, width, apparent depth, and continuity of cracks, and whether the cracks go through or around the aggregate<sup>17</sup>. Fine cracks are not always visible but can be seen fairly easily on a wet surface that is beginning to dry. As the ASR gel absorbs water, it exerts a fairly uniform pressure up to around 1450 psi or more in all directions<sup>37</sup>. This pressure exceeds the tensile strength of conventional concrete and the concrete generally cracks in a star pattern. This cracking is usually enough to relieve the stress and accommodate the resulting increase in volume. As this process continues, the cracks radiating form a pattern resembling a map. Figure 9 below indicates the development of crack pattern in the concrete due to ASR.



**Figure 9. Development of Crack Pattern in Concrete Due to ASR.**  
(After Reference 37)

## **Surface Deposits (Efflorescence)**

The deposits of ASR gel can be found around the cracks in concrete, leaving a deposit on the surface, which may be white or dark gray in color. These deposits are sometimes called efflorescence. However, their presence is not indicative of ASR or other mechanisms. A chemical analysis is generally helpful to determine if ASR gel is present in the deposit.

## **Popouts**

A popout is generally a portion breaking out of the surface of the concrete, leaving a hole behind. Popouts caused by fine aggregates are much smaller than those caused by coarse aggregates. A fractured aggregate particle can often be found at the bottom of the hole<sup>17</sup>. The number, size and location of the popouts provide important information about the reactivity of the aggregate in the concrete. The gel at the site of a popout is a strong indication of ASR.

## **Color Change**

Surface discoloration is common in conjunction with map cracking. The areas along cracks may be bleached or brownish in color. Darkened and blotchy areas are often associated with ASR.

## **4.7 PREVENTATIVE MEASURES FOR ASR**

The methods for minimizing the risk of damaging ASR reaction may include the following, although not in the priority in which they are listed.

- Use of non-reactive aggregates,
- Use of low-alkali cement,
- Limit alkalis in concrete,
- Use of supplementary cementing materials like fly ash, slag and silica fume.

### **Use of Non-Reactive Aggregates**

The use of a non-reactive aggregate is ideal but not always practical. However, non-reactive aggregates may not be available in many locations and importing non-reactive aggregates is not always a viable option. ASR has also been found to occur in some cases where the aggregates were thought to be inert. The best way to predict aggregate performance is a good service record, but this information may not always be available. Some measures like blending the reactive aggregate with non-reactive aggregate are adopted to mitigate the deleterious effects of ASR.

### **Use of Low-Alkali Cement**

According to early work of Stanton<sup>38</sup>, expansive reaction is unlikely to occur when the alkali content of the cement is below 0.6%  $\text{Na}_2\text{O}_{\text{eq}}$ . This value has been fairly successful with

slightly reactive to moderately reactive aggregates. ASTM C 150 has adopted this limit. The drawback of this criterion is that it does not take into account the cement content of the concrete, which governs the alkali content of concrete. However, low alkali cements are not available in all areas. Even low alkali cement is known to cause ASR. Stark<sup>39</sup> reported damage in highway structures constructed with alkali contents of 0.35% to 0.60%. Some testing using low-alkali cement has showed delayed expansion and cracking after longer periods than with high alkali cements.

### **Limit Concrete Alkalis**

Some of the national specifications have taken into account the fact that merely specifying the limit on the alkali content of cement may not be enough. European and Canadian experiences indicate that expansion does not take place when reactive aggregates are used in concrete containing less than 5 lb per cu. yd. of alkali<sup>40</sup>. In Canada, CSA Standard A23.1-94-Appendix B, dictates the requirement of supplementary cementing material to control ASR. According to it, the supplementary cementing material may be used to control ASR provided that it meets two criteria: (1) it must conform to certain chemical requirements and (2) it must be used at or above the minimum dosage specified. If less than the required minimum amounts are used, then the mortar-bar accelerated expansion test (CSA Test Method A23.2-25A) or the concrete prism expansion test (CSA Test A23.2-14A) needs to be run in order to verify the materials effectiveness in controlling expansion. As per the chemical requirements, fly ash can have a maximum total alkali content of 4.5% (as  $\text{Na}_2\text{O}_{\text{eq}}$ ) and a maximum water-soluble alkali content of 0.5%. Similarly, the minimum dosages for fly ash are 20%-30%, depending upon the alkali content of the ash and combined silica plus alumina content.

The Appendix B of CSA A23.1-94 states that restricting the concrete alkali content to 5 lb per cu. yd. may not be effective specially when concrete is to be used in mass concrete structures that can not tolerate even slight expansions.

### **Use of Supplementary Cementing Materials**

Supplementary cementing materials like fly ash have been used in concrete for many decades and have proved adequate to control ASR. Laboratory research over the years has confirmed this. The type of fly ash, its alkali content, chemical composition and dosage, all affect the effectiveness of the fly ash to control expansion<sup>8</sup>. ASTM C 618 Class F fly ashes have proved to work better than Class C fly ashes. Class F ash has a higher silica content and lower lime content. These properties have shown to increase the ability to control expansive ASR.

Experiments and field research have amply demonstrated that ASR expansion decreases as the ash content increases. The dosage of fly ash depends on the chemical composition, alkali content of the concrete and the reactivity of the aggregate. Some laboratory results have shown that certain high alkali/high calcium fly ashes are not only ineffective at normal dosages to control ASR, some of these materials may even exacerbate ASR expansion when

used at lower amounts<sup>29, 42</sup>. ASTM C 311, *Method for Sampling and Testing Fly Ash or Natural Pozzolans for Use as a Mineral Admixture in Portland Cement Concrete*, specifies an optional chemical requirement of a maximum limit of 1.5% on available alkalis. The effectiveness of fly ash in reducing the damage due to ASR is presented in the following chapter.

## CHAPTER 5.0 A LABORATORY INVESTIGATION OF HIGH VOLUME FLY ASH TO MITIGATE ASR IN CONCRETE

### 5.1 GENERAL

A laboratory investigation was initiated in this research effort to identify the potential of a high volume of Class F fly ash incorporated in concrete on ASR using a reactive aggregate and a low and a high alkali portland cement.

### 5.2 TESTING PROGRAM

The shortcomings of ASTM C 227 and C 289 prompted the development of a rapid test method for assessing potential reactivity of aggregate. ASTM C 1260, *Test Method for Potential Alkali Reactivity of Aggregates (Mortar-Bar Method)*, offers a relatively rapid test to supplement the lengthier test methods. The test measures the potential aggregate reactivity, and not the reactivity of specific cement-aggregate combinations or the effectiveness of supplementary cementitious materials to control ASR in concrete<sup>42</sup>.

This test involves measuring the length change of mortar bars made with the sample aggregate stored in a strong alkaline solution at an elevated temperature 176° F (80° C). Aggregates having a mean mortar-bar expansion of 0.10% or less at 14 days are considered as innocuous. Expansions of more than 0.20% are indicative of reactive aggregates by this rapid screening method. Between 0.10% and 0.20%, the aggregates may be potentially reactive; they might exhibit either innocuous or deleterious behavior in field performance. Due to the severe test conditions, aggregates with good field performance and no history of ASR can sometimes test to be reactive. The reason for this is that aggregates in field concrete are rarely exposed to the severe alkali and temperature conditions of the test method. Thus, aggregates identified as potentially reactive by ASTM C 1260 can perform well in practice when exposed to more reasonable alkali levels. One distinct advantage of C 1260 is that slowly reacting aggregates can be identified by this test due to its severity.

Therefore, it is necessary to refine the ASTM C 1260 so that it can be closely identified with actual field conditions and verify if different cementitious materials-aggregate combinations can be tested for potential ASR, by using this test<sup>42</sup>. Stark<sup>29</sup> has suggested modifications and improvements of the C 1260 test by varying the concentration of the NaOH solution to match the pore solution of the concrete. These tests, by varying concentrations of NaOH solution, could then determine safe cement or concrete alkali levels for a particular aggregate.

The variables included in the testing procedure were:

- Total alkali content of the cement;
- Normality of the solution.

The water-cement ratio and the temperature of the exposure conditions were kept constant as per ASTM C 1260. The percentage of cement replaced by fly ash was kept at a high volume

constant of 58%. Three specimens per mix were typically prepared. All the mortar-bar specimens were of 1”x 1”x 11-1/4” size, as specified by ASTM C 1260. The molds used for casting the specimens were in accordance to ASTM C 490, *Standard Practice for Use of Apparatus for the Determination of Length Change of Hardened Cement Paste, Mortar, and Concrete*.

## **Materials Used**

**Cement.** The alkali-silica reaction is dependent mainly upon the reaction between the alkali in the cement and the reactive silica in the aggregates. For this reason, two types of cement; one low alkali cement and another high alkali cement were used in the entire test program. Both the cements met the requirements of ASTM C 150. The cement used was passed through a No. 20 (850- $\mu$ m) sieve in order to avoid using cement having lumps.

The first source of cement had an alkali content of 0.51% as  $\text{Na}_2\text{O}_{\text{eq}}$  and this was designated as “low alkali content cement” for this study. The second source of cement had an alkali content of 0.58% as  $\text{Na}_2\text{O}_{\text{eq}}$ , which was designated as the “high alkali content cement.” The percentage of alkalis for the high alkali content cement, 0.58% is close to the 0.6% limit specified in ASTM C 150. All material properties are included in Appendix A.

**Aggregates.** The aggregate chosen for the laboratory study was a quartz from the Murphy Pit and was known to be potentially reactive according to TxDOT published results. The degree of straining in quartz is one of the ways by which reactivity is defined. The measurement of the angle between the onset and completion of undulatory extinction of strained quartz grains in polarized light estimates the reactivity in a potentially reactive aggregate<sup>30</sup>. The aggregate was dried before sieving. The fine aggregates were graded as per ASTM C 1260 and stored in air-tight containers to prevent ingress of moisture.

**Fly Ash.** Class F fly ash was used for the entire test program. The fly ash had an available alkali content, expressed as  $\text{Na}_2\text{O}_{\text{eq}}$ , of 0.4%. The alkali content of the fly ash is quite low as compared to the maximum permissible limit of 1.5% as per ASTM C 618. The properties and chemical composition of the fly ash is given in Appendix A.

**Water.** Distilled water was used to avoid the effect of ions from the water to the pore solution by water.

## Preparation of Mortar Prisms

**Preparation of Molds.** The molds were thoroughly cleaned before use. ASTM C 1260 specifies that the interior surfaces of the mold be covered with a release agent. A Teflon, light-coat release agent, serves this purpose well and was sprayed in the molds evenly. Gage studs were placed on the inside of the molds to enable the measurement of length changes.

**Proportioning and Mixing of Mortar.** As per ASTM C 1260, for making three specimens of size 1"x 1"x 11-1/4", 440 grams of cement and 990 grams of aggregate were mixed. The water-cement ratio was 0.47.

The mixing of mortar was done according to ASTM C 305, *Practice for Mechanical Mixing of Hydraulic Cement Pastes and Mortars of Plastic Consistency*. The procedure is summarized as below.

The total amount of water was first placed in the mixing bowl. The cementitious materials were then added and mixed on low speed for about 30 seconds. The total amount of aggregate was then added over a period of 30 seconds while the mixer continued to mix. The mortar was then allowed to mix for another 30 seconds at medium speed and then the mix was allowed to stand for about 60-90 seconds. The mold specimens were then molded, after adequate compacting by a tamper. The top surface was finished smooth.

**Storage and Measurements.** After casting, the test specimens were kept immediately in a moist room and retained in the molds for 24 hours. On the next day, they were demolded, identified properly and an initial reading was taken with a vertical length comparator instrument, as per ASTM C 490. To maintain consistency of readings, the same end of the specimens was kept up each time. After tabulating the readings, the specimens were immersed in water in a sealed container, which was placed in an oven kept at a constant temperature of 80° C (176° F). It is pointed out that the prisms were kept in water at room temperature for 2-3 hours and then the container was introduced in the oven at 80° C (176° F). This was to avoid thermal shock to the prisms. After 24 hours in the oven, the prisms were taken to a room, which had ambient temperature (about 23° C), and before significant cooling took place, their lengths are measured. This was the zero reading. After the zero reading, the prisms were immersed in either 1/0.5/0.25 N NaOH solution kept at 80° C (176° F). This solution was stored in a tightly covered plastic container, which was large enough to totally immerse all the prisms. The prisms were measured at approximately the same time of the day every 3 days. The linear expansion was calculated and expansion was monitored for at least 28 days. The expansion was reported to the nearest 0.001%.

Shayan et al.<sup>43</sup> suggested that considerable care must be taken to prevent the specimens from cooling appreciably when they are removed from the NaOH solution for measurement. They found out that a delay of 5 minutes caused an average temperature drop of about 15° C for the mortar bars. After correlating this information to various aggregates, they found out that the temperature drop of about 15° C, caused a length change of about 0.016% for the mortar

bars, which is quite significant. Therefore, they recommended that after removal from the NaOH solution, the elapsed time be limited to 30 seconds before taking the measurements of the mortar bars.

### 5.3 DISCUSSION OF TEST RESULTS

Concrete made from each of the two different alkali cements and reactive aggregates was tested for compressive strength before testing for ASR. This was done to ascertain if the reactive aggregates or the percentage of internal alkalis in the cement influenced the strength of concrete. The concrete mixture proportions are given in Table 4 and the compressive strength test results in Table 5.

**Table 4. Concrete Mix Proportions**

Mix No.	$\frac{W}{C + F}$	$\frac{F}{C + F}$	Water (kg/m <sup>3</sup> )	Cement (kg/m <sup>3</sup> )	Fly Ash (kg/m <sup>3</sup> )	Fine Aggr. (kg/m <sup>3</sup> )	Coarse Aggr. (kg/m <sup>3</sup> )	HRWA (kg/m <sup>3</sup> )
P1	0.35	-	130	369	-	620	1275	9.1
P2	0.35	0.58	130	155	214	620	1275	5.9
P3	0.35	-	130	369	-	620	1275	9.1
P4	0.35	0.58	130	155	214	620	1275	5.9

Notations in table:

- P1 Low alkali cement (control)
- P2 Low alkali cement and 58% Class F fly ash
- P3 High alkali cement (control)
- P4 High alkali cement and 58% Class F fly ash
- HRWA High Range Water Reducing Admixture
- W Water
- C Cement
- F Fly Ash

Dr. Malhotra and his colleagues have done extensive research on concrete using high volumes of fly ash, mostly Class F fly ash. The contribution of Dr. Malhotra to the area of high volume fly ash concrete has been significant and has been globally accepted. The results from the compressive tests from this test program were in agreement with Dr. Malhotra's research for the role of high volumes of fly ash in concrete<sup>44</sup>. The general trend of strength development pattern in Table 5 indicates that the strength of high volume fly ash concrete (HVFA) is slightly lower than that of plain cement concrete up to 28 days, irrespective of the alkali content of the cement. Although concrete mixture P1 containing low alkali cement demonstrates higher strength than its counterpart concrete mixture P3, the difference on strength is more likely due to the lower alkali content in concrete mix P1.

**Table 5. Compressive Strength of Concrete Mixtures.**

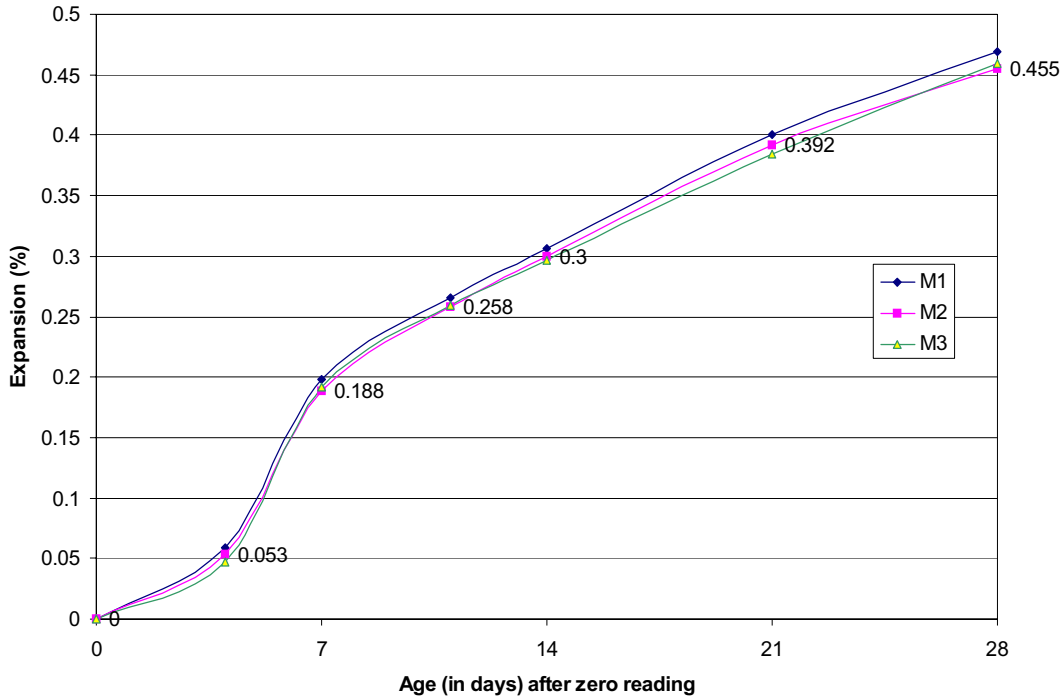
Mix No.	$\frac{W}{C + F}$	$\frac{F}{C + F}$	Slump (inches)	Average Compressive Strength of Cylinders, Mpa (psi)		
				3-day	7-day	28-day
P1	0.35	-	4.5	25.5 (3695)	34.1 (4945)	48.6(7035)
P2	0.35	0.58	6	16.9 (2450)	23.8 (3440)	37.8 (5475)
P3	0.35	-	4	22.4 (3240)	31.2 (4520)	46.2 (6700)
P4	0.35	0.58	6.5	21.3 (3085)	27.9 (4045)	41.6 (6020)

Three specimens per mix were typically cast. After the initial and the zero readings were made, readings were taken at 4 day, 7 day, 11 day, 14 day, 17 day, 21 day, 24 day and 28 days. Such a close monitoring of the expansion was done so as to detect the process of expansion as controlled by the alkali content of the cement, the effect of the presence of Class F fly ash and the alkalinity of the storage conditions. The expansions are reported in Appendix B and will be discussed subsequently in this chapter. The test results for prisms immersed in 1.0 N and 0.5 N NaOH solutions are discussed here in this chapter in detail.

The initial expansion, i.e., up to 4 days, even though stored in 1 N NaOH solution was quite nominal. A very steep rise is seen from 4 days up to 7 days, indicating that the expansion is evident and that sufficient alkali level has been achieved to the pore solution of the mortar specimen to cause expansion. At the end of 7 days, the expansion is almost equal to 0.2%, which is the potential reactivity level a reactive aggregate reaches in 14 days. This indicates very high reactivity. At 14 days, the observed average expansion is 0.3%, which is one and a half times the potential reactivity of 0.2% expansion.

From 7 days to 28 days, the slope of the expansion is fairly constant indicating that the rate of expansion is fairly consistent over that period of time. The observed average expansion at 28 days is about 0.45%, which is the highest expansion among all the mixes for the project. The slope of the curve also indicates that further expansion is possible beyond 28 days.

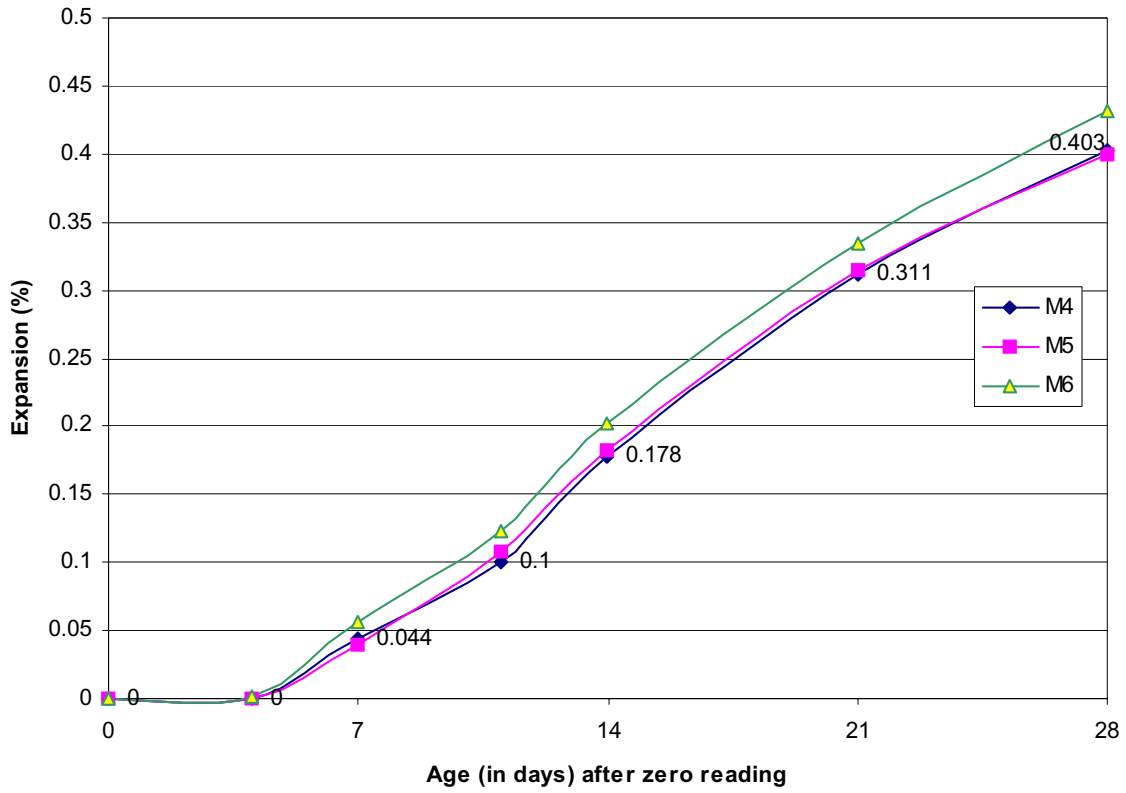
Elevated temperatures (80° C) and enhanced alkali levels have been most commonly used in the past to identify the reactivity of aggregates in the laboratory in a short period of time. The enhanced alkali levels have usually been achieved by storage of specimens in alkali-bearing solutions, like sodium hydroxide in this case. Figure 10 clearly indicates that the two factors, enhanced alkali levels and elevated temperatures have been successful in accelerating the alkali-silica reaction in order to identify the reactivity of the aggregates in a short period of time.



**Figure 10. Expansion of Mortar Prisms Cast Using High Alkali Cement and Immersed in 1.0 N NaOH Solution.**

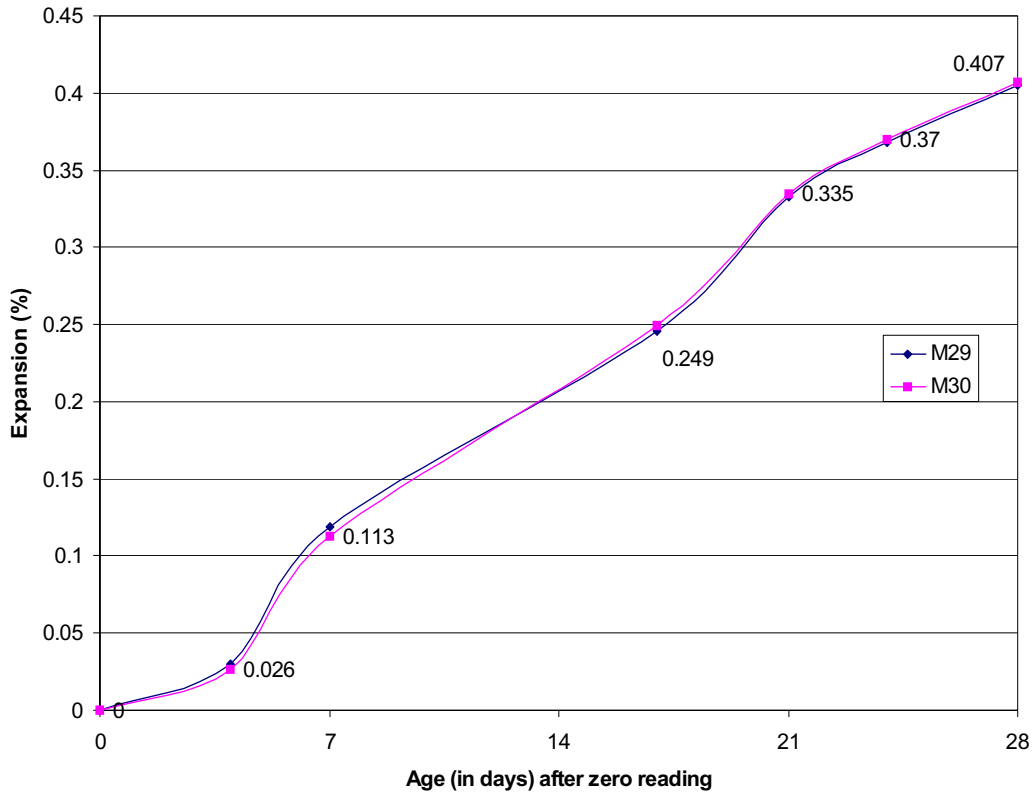
When the normality of the sodium hydroxide (NaOH) solution is reduced by 50%, no expansion is observed at the corresponding early age (up to 4 days) as seen in Figure 11. This should suggest that the elevated temperature alone is not sufficient at early ages to accelerate ASR. However, from then (4 day) onwards, a steady increase in expansion, as seen with the 1 N NaOH solution, is observed. At 14 days, the average expansion of the prisms was close to the potential reactivity level of 0.2%.

In comparison, the average expansion of prisms immersed in 1 NaOH solution is almost 1.5 times more, i.e., 0.3% expansion at 14 days. This suggests that when the prisms are immersed in 0.5% N NaOH solution, there is definite indication of reactivity at 14 days; but which is substantially lower than what is observed for 1 NaOH solution. At 28 days, the average expansion recorded is about 0.40%, which is only 10% less (0.40% vs. 0.45%) than compared to prisms immersed in 1.0 N NaOH solution. This indicates that there is a rise in the reactivity from 14 days up to 28 days. A constant rise in slope is seen from 4 days to 28 days, specifying that the increase in the potential reactivity is fairly gradual.



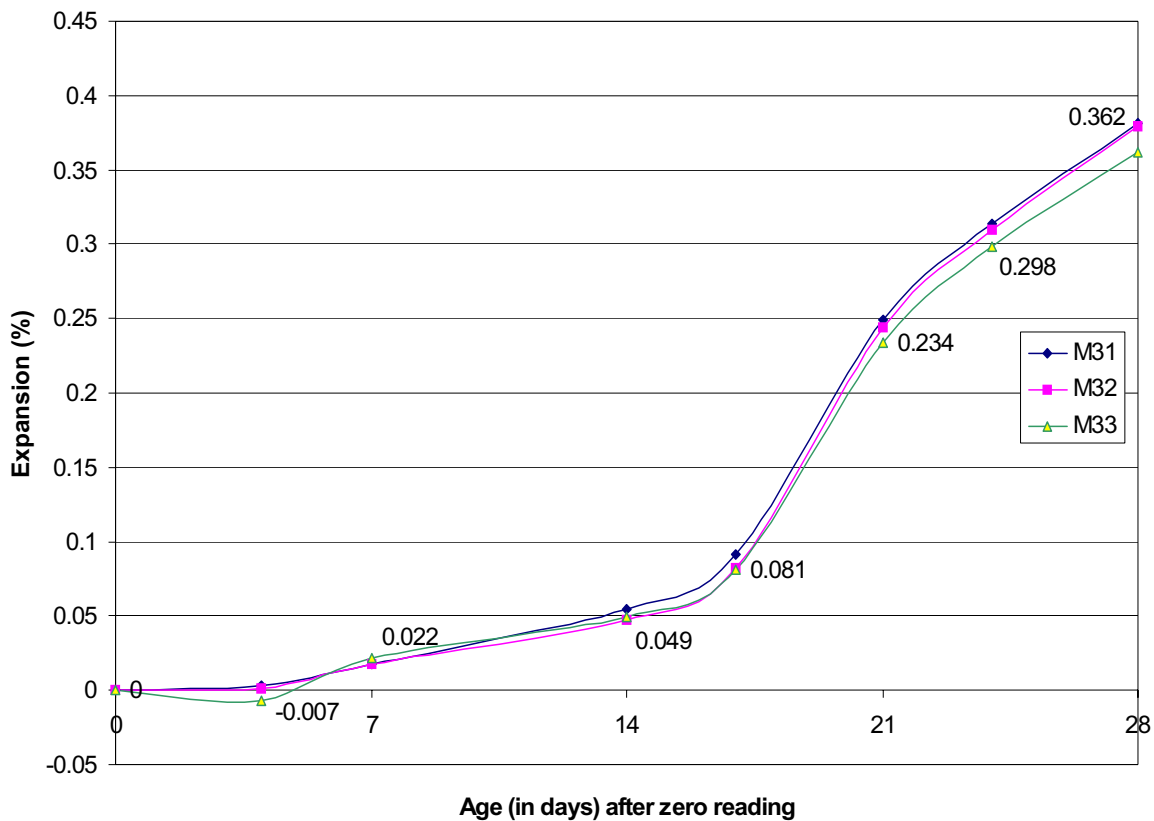
**Figure. 11. Expansion of Mortar Prisms Cast Using High Alkali Cement and Immersed in 0.5 N NaOH Solution.**

As seen in Figure 12, the slope and pattern of expansion for prisms made with the low-alkali cement control mix, are fairly similar to those prisms made with the high-alkali cement control mix. The average expansion observed at 14 days is about 0.20% which is less than the expansion observed (0.3%), when the high-alkali cement control mix prisms are immersed in 1 N NaOH solution, but more average expansion than observed (0.19%) when the high-alkali cement control mix prisms are immersed in 0.5 N NaOH solution. This point indicates that the internal alkalis in the cement are not playing a big role in influencing the expansion due to the alkali-silica reaction.



**Figure. 12. Expansion of Mortar Prisms Cast Using Low Alkali Cement and Immersed in 1.0 N NaOH Solution.**

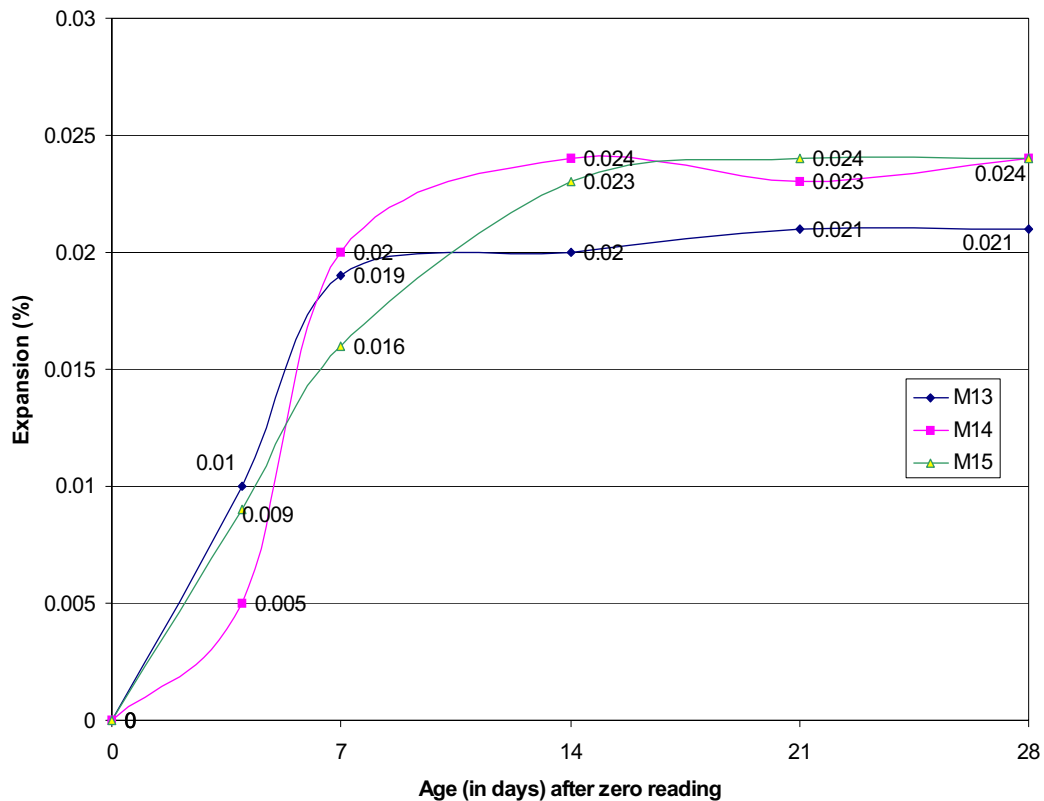
Figure 13 shows that the expansion observed up to 14 days is very nominal (0.05%) which is four times less than the limit of 0.2% at 14 days for potential reactivity. After 17 days, the expansion takes off a very steep increase, steeper than any of the observed specimens. The average expansion at the end of 28 days is 0.36% which is only 10% less than the corresponding expansion in prisms made with the high-alkali cement control mix and stored in similar 0.5 N NaOH solution. The expansion at the end of 28 days proves that the alkalis in the cement are not playing a big role in the reaction.



**Figure 13. Expansion of Mortar Prisms Cast Using Low Alkali Cement and Immersed in 0.5 N NaOH Solution.**

There is a distinct reduction in the expansion all throughout the 28-day period of the test as compared to the control mixes as seen in Figure 14. The steep rise in expansion till 7 days indicates that the fly ash has not yet begun to participate in the hydration reaction. After 7 days, very limited expansion (20% increase over a period of next 21 days) took place. This suggests that longer moist curing of high volume fly ash cementitious binders might help to reduce the expansion at early ages. This aspect of the effect of moist curing is presently under study, as a part of a larger program.

The mean expansion at the end of 28 days is about 0.023% which is around 20 times less than that observed in prisms made with the high-alkali cement control mix and stored in 1.0 N NaOH solution. This confirms the effectiveness of high volumes of Class F fly ash in reducing the alkali-silica reaction from a potentially reactive state to an innocuous state.



**Figure 14. Expansion of Mortar Prisms Cast Using High Alkali Cement and 58% Replacement by Class F Fly Ash, Immersed in 1.0 N NaOH Solution.**

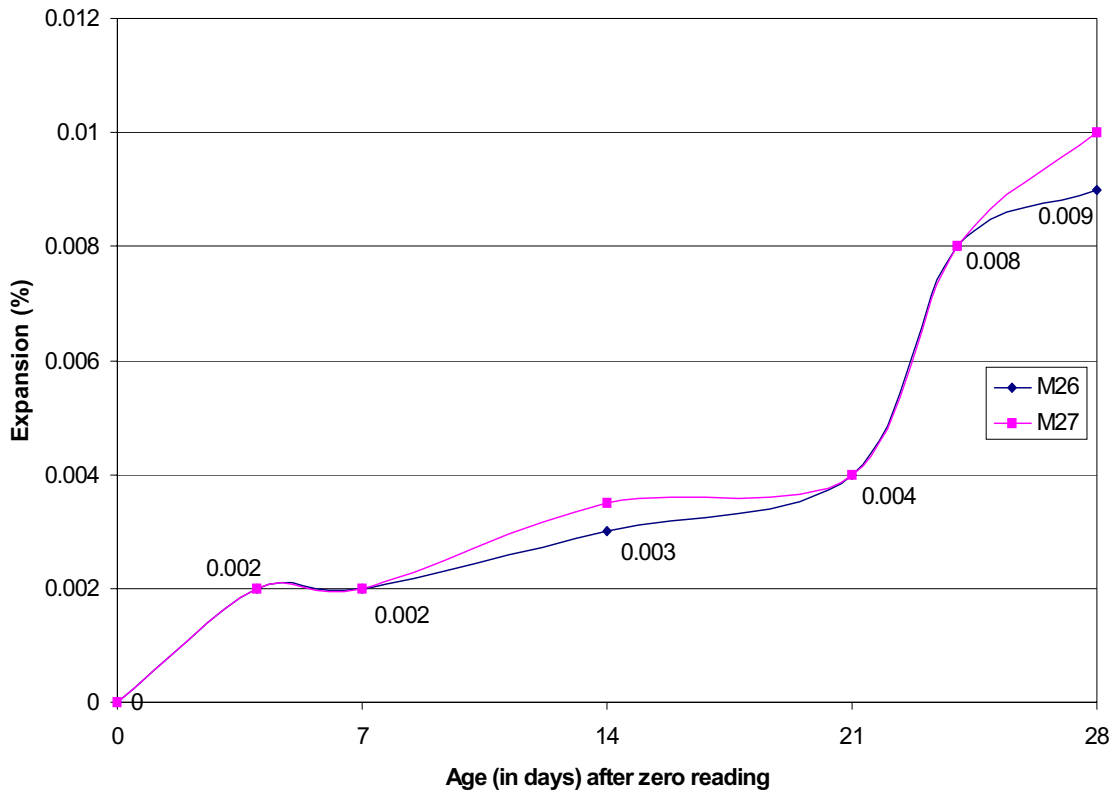
Long-term results presented by Shayan et al.<sup>45</sup> have indicated that a measurable amount of chemical shrinkage occurred in the first few months in concretes containing fly ash and with high alkali contents based on six-year observations. The analysis of the pore solution of the mortar specimens containing fly ash indicated that the fly ash was found to be very effective in reducing the alkalinity of the pore solution.

Reducing the alkalinity of the pore solution and thus the concentration of one of the initial reaction products (OH<sup>-</sup> ions)<sup>46</sup> is of the accepted mechanisms by which fly ash reduces the damage due to ASR and it seems to be the governing mechanism in this case, too.

The salient features of the expansion curve when 58% of high-alkali cement was replaced with Class F fly ash were:

- The expansion remained almost constant after the first 7 days.
- The expansion at 7 days reduced by more than 90% as compared to the control mix.
- Expansion at 14 days reduced by more than 92%.
- Expansion at 28 days reduced by more than 94%.

As seen in Figure 15, the maximum expansion observed at the end of 28 days is approximately 0.1%. In general, the expansion at all the stages is too low and is beyond proper interpretation. Again the effectiveness of high volume of Class F fly ash is evident in controlling the expansion due to ASR.



**Figure 15. Expansion of Mortar Prisms Cast Using High Alkali Cement and 58% Replacement by Class F Fly Ash Immersed in 0.5 N NaOH Solution.**

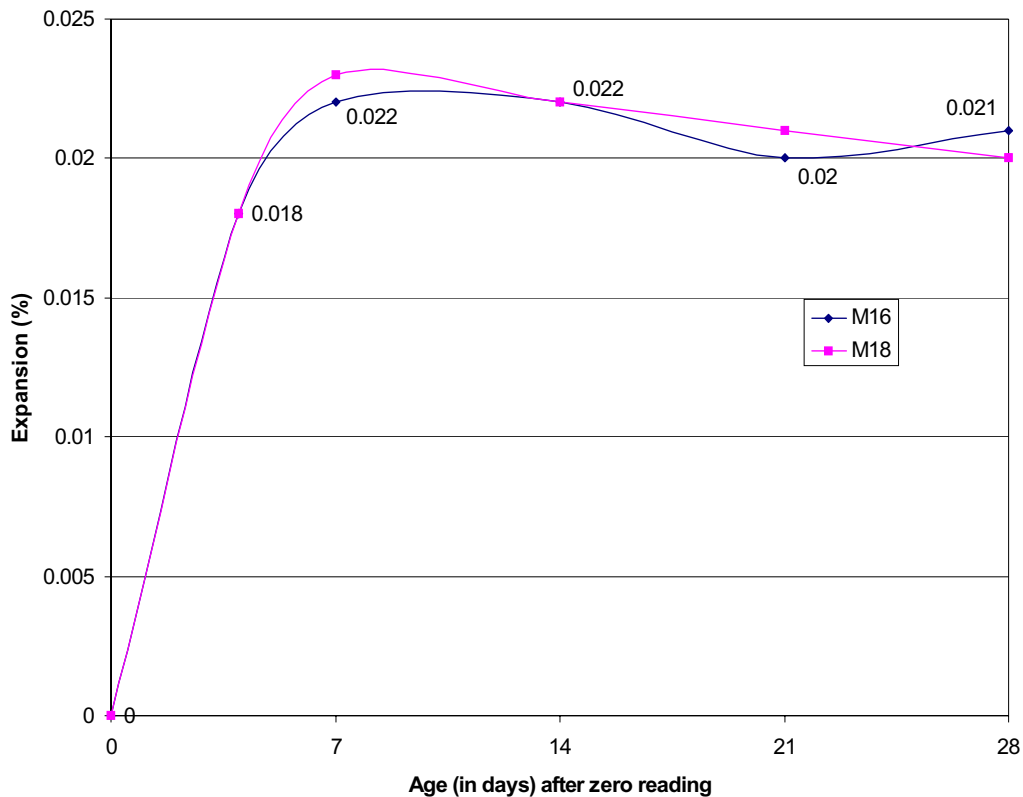
The observed expansions of this low-alkali cement and 58% replacement by Class F fly ash mix as seen in Figure 16, are pretty similar to those prisms made with high-alkali cement and 58% replacement by Class F fly ash. Very little expansion occurred after 7 days suggesting once again that the moist curing of high volume fly ash cementitious binders might help to reduce the expansion at early ages.

The mean expansion at the end of 28 days was 0.021% which is only about 15% less than that seen in the prisms made up with high-alkali cement and 58% replacement by Class F fly ash. This once again implies that the alkalis in the cement are not contributing much to the alkali-silica reaction.

The salient features of the expansion curve when 58% of low-alkali cement was replaced with Class F fly ash were:

- Expansion remaining almost constant after 7 days as seen with high alkali cement control mix.
- The expansion at 7 days reduced by more than 80% as compared to the control mix.
- Expansion at 14 days reduced by more than 89%.
- Expansion at 28 days reduced by more than 94%.

High volumes of Class F fly ash are, thus, effective in controlling expansion due to ASR even with low-alkali cement. The comparative expansion for prisms made with different mixes at various ages is shown in Table 6.

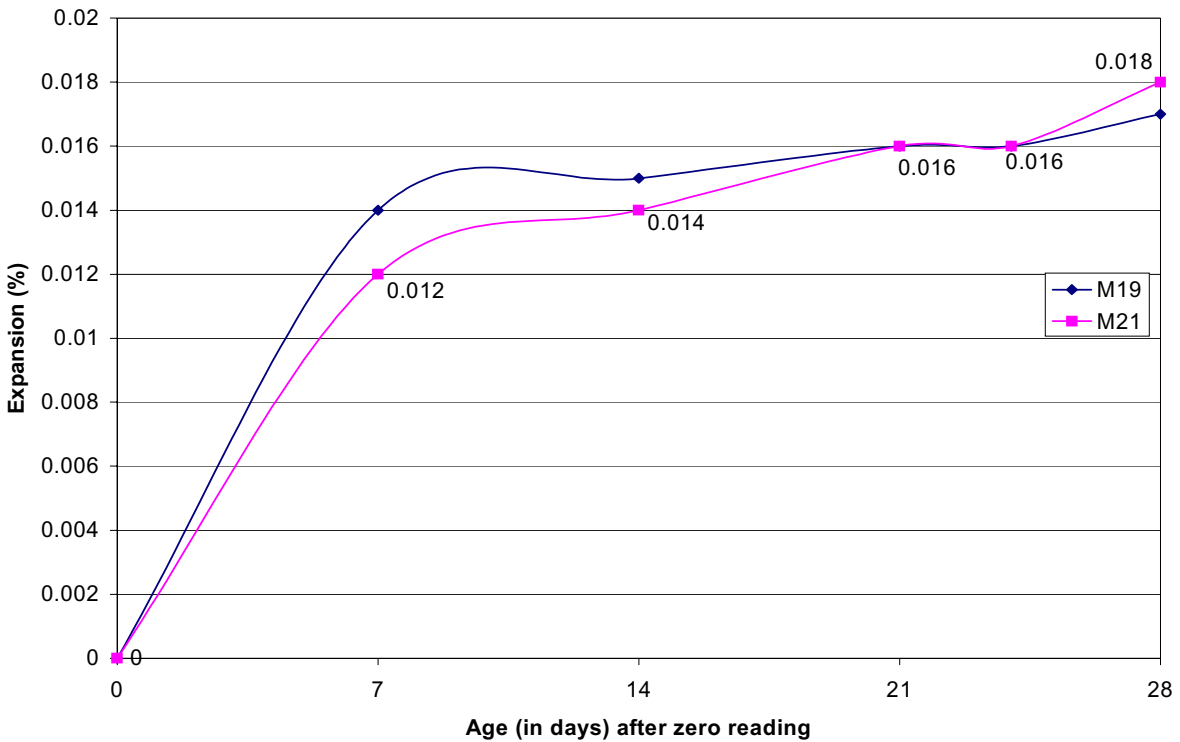


**Figure 16. Expansion of Mortar Prisms Case Using Low Alkali Cement and 58% Replacement by Class F Fly Ash Immersed in 1.0 N NaOH Solution.**

**Table 6. Comparative Percent Expansion for Prisms Made with Different Mixes at Various Ages.**

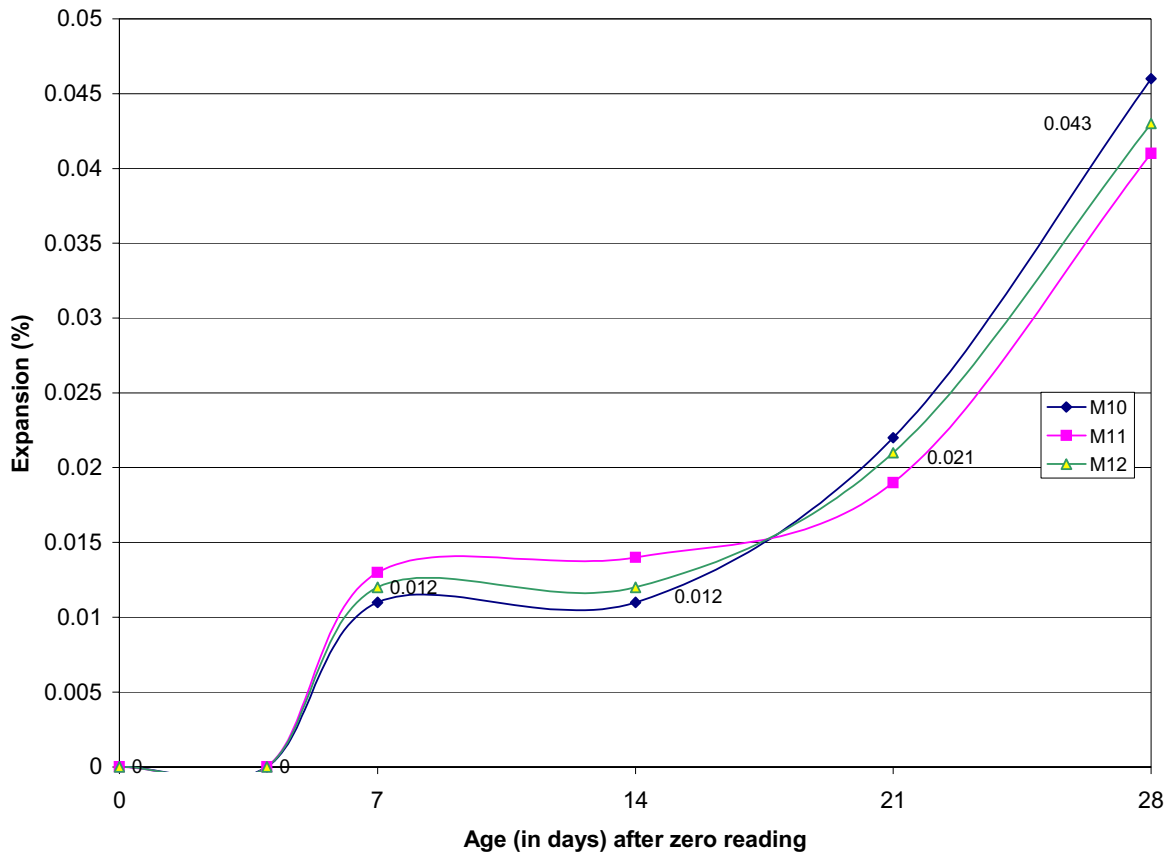
Age in Days	High Alkali Cement	Low Alkali Cement	High Alkali Cement + 58% Class F Fly Ash	Low Alkali Cement + 58% Class F Fly Ash
7	0.046	0.022	0.002	0.013
14	0.193	0.05	0.0033	0.015
21	0.415	0.356	0.0095	0.018

From Figure 17, it is evident that the mean expansion observed at 14 days is about 0.014%. This is around 5 times more than that observed in prisms made with the high-alkali cement and 58% replacement by Class F fly ash but still about 40% less than the potential reactivity level of 0.2% expansion.



**Figure 17. Expansion of Mortar Prisms Cast Using Low Alkali Cement and 58% Replacement by Class F Fly Ash Immersed in 0.5 N NaOH Solution.**

The maximum expansion observed at the end of 28 days is approximately 0.18%, which is almost twice as much as observed in prisms made with high-alkali cement and 58% replacement by fly ash. This implies that the expansion is more when the alkali content of the Portland cement is low and fly ash is present. Figure 18 shows that expansion at all stages in this mix, immersed in 0.25 N solution is too low and is beyond proper interpretation. The 0.25 N NaOH concentration appears to be too low to achieve the alkali levels needed to accelerate ASR.



**Figure 18. Expansion of Mortar Prisms Cast Using High Alkali Cement and Immersed in 0.25 N NaOH Solution.**

## 5.4 EFFECT OF EFFECTIVE ALKALI CONTENT ON EXPANSION

An effort is made to correlate the effective alkali content of the mix to the expansion observed in the prisms. In this regard, work done by Kollek is found to be useful. His work comprised of mortar bars tested in accordance to ASTM C 227, but stored at 20° C. Kollek's results demonstrated that if the effective alkalis derived from Portland cement are taken as 100%, then those derived from fly ash can be taken as 17%. This was to normalize the equation for the contribution of the alkalis. He postulated that the total effective alkali content of a hydraulic binder is the sum of the effective alkali content of the Portland cement and the effective alkali content of the mineral additive that may be intermixed with it and can be written as:

$$A_{TE} = k_c \cdot A_c (1-p) + k_e \cdot A_e \cdot p$$

where

$A_{TE}$  = total effective alkali content of the mix,

$A_c$  = total alkali content of the Portland cement,

$A_e$  = total alkali content of the mineral additive, i.e., fly ash or slag,

$p$  = the level of cement replaced by a mineral additive,

$k_c$  = coefficient of alkali effectiveness in Portland cement,

$k_e$  = coefficient of alkali effectiveness in the mineral additive,

It should be borne in mind that the alkali is assumed to be reactive and that the aggregate might contribute alkalis to the mix. However, Kollek's paper does not cover this critical issue. As the contribution of alkalis from Portland cement are taken as 100% and that from fly ash as 17%, the constants,  $k_c$  and  $k_e$  are taken as 1.0 and 0.17 respectively. Kollek assumed  $k_c = 1$ , for simplifying his argument. Table 7 gives a summary of the total effective alkali content with contributions from cement and fly ash.

**Table 7. Total Effective Alkali Content with Contribution from Cement and Fly Ash.**

Type of Cement Used	Effective Alkali Content of Cement, $A_c$ , %	Effective Alkali Content of Fly Ash, $A_e$ , %	Total Effective Alkali Content of Mix, $A_{TE}$ , %
High Alkali Cement	0.58	0.40	0.28
Low Alkali Cement	0.51	0.40	0.25

Here,

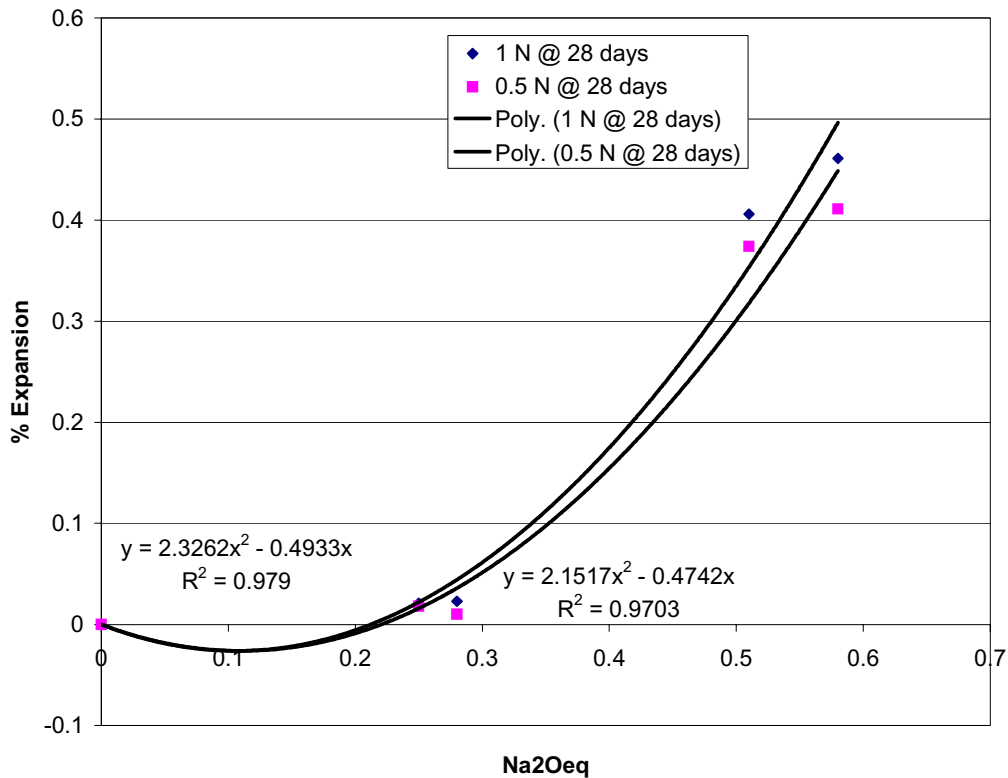
$p = 0.58$  (58% replacement of cement by fly ash),

$k_c = 1.0$ ,

$k_e = 0.17$ .

Thus, after the effective alkali content of the mix,  $A_{TE}$ , was calculated, a quadratic curve was fitted to predict the expansion if the alkali content if the mix is known. Plots were made to compare the expansion for prisms stored in 1.0 N and 0.5 N NaOH at 14 and 28 days, respectively. The underlying assumptions for these plots are that the aggregates used have a proven track record of reactivity and no contribution from the aggregates is assumed.

Figure 19 shows excellent results for prisms stored in 1.0 N as well as 0.5 N NaOH solution. This might be due to the fact that the fly ash has started to participate in the reaction suggesting that the effective alkali content of the mix might have indeed been reduced. The fit of the expansion data points stored in 0.5 N NaOH solution is suggestive that assuming there is reduction in the alkali content due to fly ash, 0.5 N NaOH storage might predict similar results to those stored in 1.0 N NaOH solution. This argument is further supported by the expansion results of prisms made with the control mixes (i.e., using low alkali or high alkali cement only, without the use of fly ash) which show the prisms exhibiting a variation of only around 10% when stored in 1.0 N and 0.5 N NaOH solutions, respectively.



**Figure 19. Rate of Expansion at 28 Days as a Function of Equivalent Alkalis for Mortar Prisms.**

## 5.5 MODEL FOR PREDICTING EXPANSION

A hyperbolic model was first used to predict the ultimate expansion for a given mix as stated below:

$$\%Exp = \%Exp_0 \left\{ \frac{t}{n+t} \right\}$$

where,

$\%Exp_t$  = %Expansion at time t,

$\%Exp_0$  = Predicted ultimate expansion,

t = Age in days,

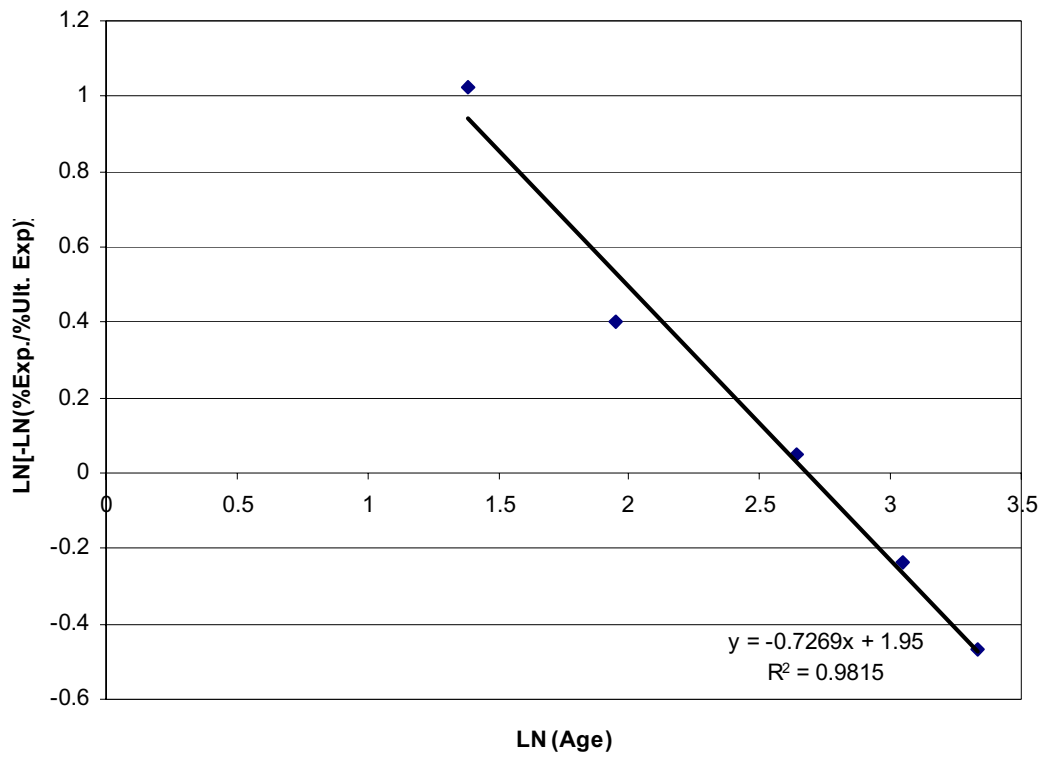
n = Half-time for the expansion

The ultimate expansion predicted from this model was used to calculate parameters  $\alpha$  and

$\beta$ , using the Weibull distribution, which is given by,

$$\frac{\%Exp_t}{\%Exp_0} = e^{-(\alpha/t)^\beta}$$

A plot for the high alkali cement (control mix) prisms immersed in 1.0 N NaOH solution is shown in Figure 20. Similar plots were obtained for all the eight mixes. The parameter,  $\alpha$ , is the y-intercept and  $\beta$  is the slope of the regression line. The values of  $\alpha$  and  $\beta$  along with their  $R^2$  values for all mixes are tabulated in Table 8. As can be seen, a good coefficient of determination ( $R^2$ ) was obtained for all of the prism mixes. This suggests that the estimated values of ultimate expansion as calculated from the model correspond well to the actual data obtained from the test program.



**Figure 20. Plot to Obtain  $\alpha$  and  $\beta$  Parameters for High Alkali Cement Mix Immersed in 1.0 N NaOH Solution.**

**Table 8. Parameters  $\alpha$  and  $\beta$  for the Different Mixes.**

Type of Mix and Storage Conditions for Prisms	$\alpha$	$\beta$	$R^2$
High alkali cement prisms in 1.0 N	1.95	-0.7269	0.9815
High alkali cement + 58% Class F fly ash prisms stored in 1.0 N	3.7217	-1.8375	0.9961
Low alkali cement prisms in 1.0 N	2.3045	-0.8134	0.9874
Low alkali cement + 58% Class F fly ash prisms stored in 1.0 N	Values not obtained	Values not obtained	Values not obtained
High alkali cement prisms in 0.5 N	1.5252	-9.338	0.9681
High alkali cement + 58% Class F fly ash prisms stored in 0.5 N	1.0719	-0.2995	0.8756
Low alkali cement prisms in 0.5 N	4.188	-1.401	0.8841
Low alkali cement + 58% Class F fly ash prisms stored in 0.5 N	1.1725	-0.9384	0.944

## CHAPTER 6.0 POTENTIAL FOR CARBON DIOXIDE EMISSION REDUCTIONS

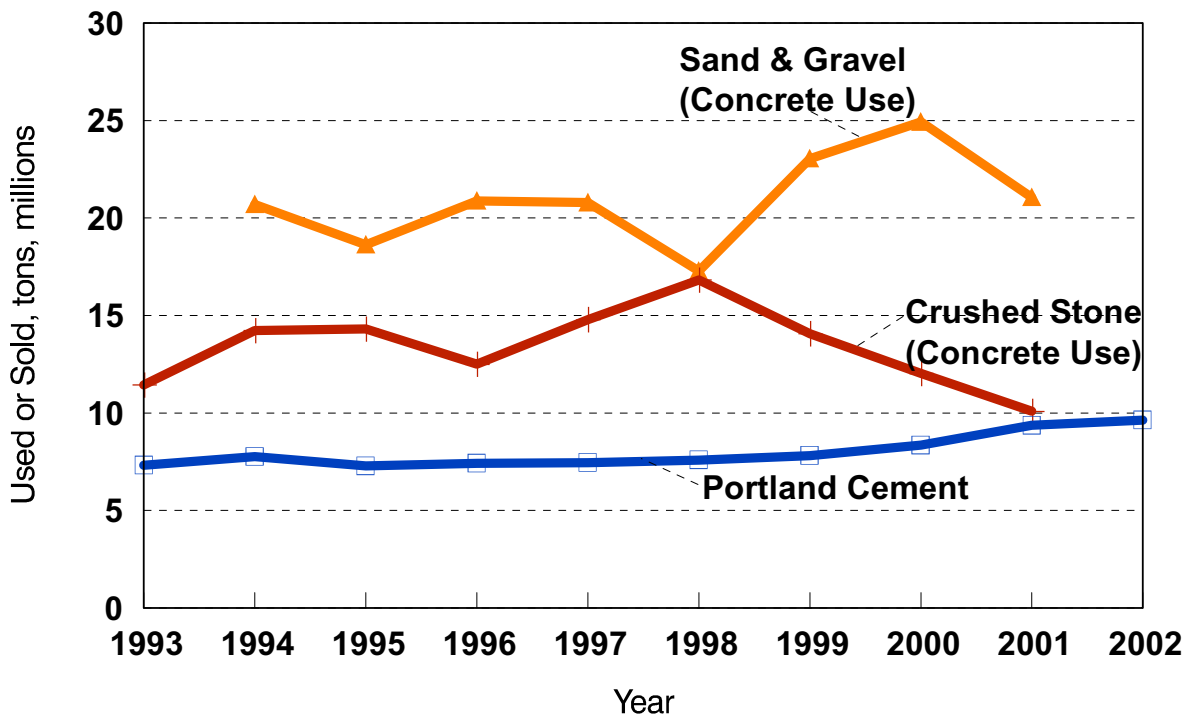
### 6.1 QUANTITY OF CONCRETE PRODUCED IN TEXAS

Several data sources were used to estimate the quantity of concrete produced in Texas. Some of the most reliable data comes from the United States Geologic Services (USGS) which annually publishes data on the amount of crushed stone and the amount of sand and gravel sold or used in Texas for the production of concrete<sup>47</sup>. These statistics are listed in Table 6.1 and shown graphically in Figure 6.1. Based on the quantity of aggregate sold for the production of concrete, an estimate was made on the quantity of concrete produced with these aggregates, also shown in Table 6.1.

The USGS also maintains data on the quantity of cement produced at cement plants in Texas as shown in Table 9 and Figure 21.

**Table 9. Amount of Concrete and Concrete Components Produced in Texas .**

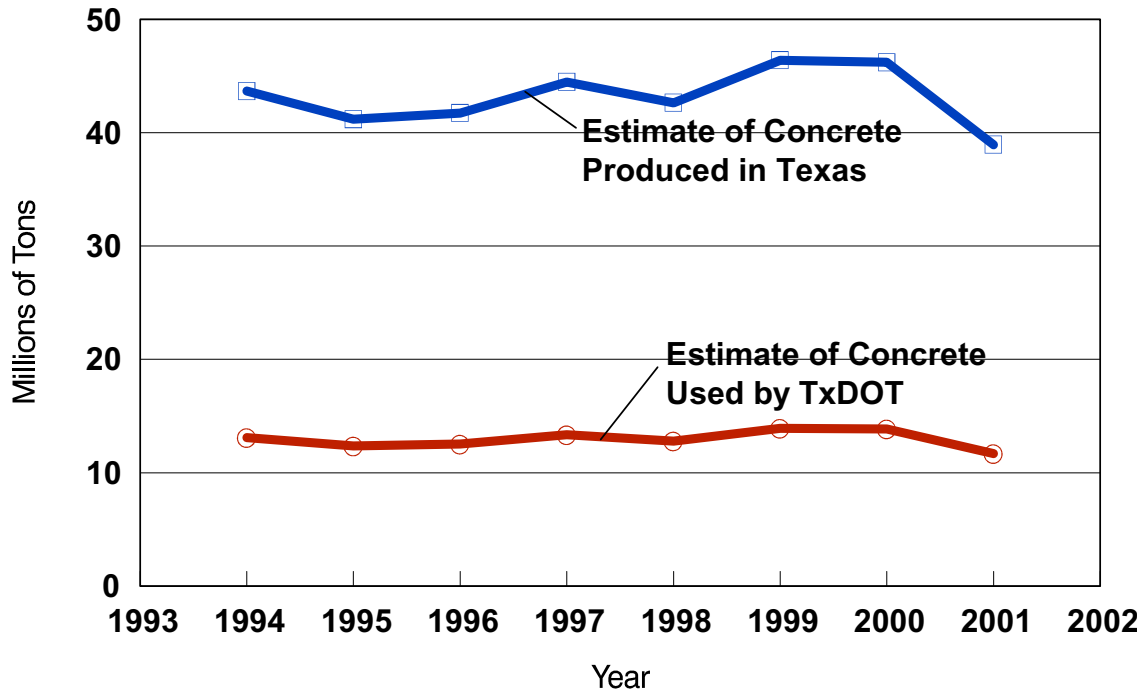
Year	Portland Cement Sold or Used in Texas, short tons	Crushed Stone Sold or used for Concrete Production in Texas, short tons	Sand and Gravel sold or used for Concrete Production in Texas, short tons	Estimate of Concrete Sold or Used in Texas, short tons
2002	9,630,000	Not Available	Not Available	Not Available
2001	9,360,000	10,089,000	21,060,000	38,936,000
2000	8,343,000	12,033,000	24,930,000	46,204,000
1999	7,812,000	14,067,000	23,040,000	46,383,000
1998	7,587,000	16,830,000	17,280,000	42,637,000
1997	7,452,000	14,787,000	20,790,000	44,471,000
1996	7,416,000	12,501,000	20,880,000	41,726,000
1995	7,281,000	14,310,000	18,630,000	41,175,000
1994	7,758,000	14,229,000	20,700,000	43,661,000
1993	7,317,000	11,439,000	Not Available	Not Available



**Figure 21. Annual Production of Portland Cement and Aggregate in Texas for Use in Concrete.**

For purposes of this study regarding use of the statistics given in Table 6.1, it is assumed that the aggregates and portland cement produced in Texas are used in Texas for concrete production and not exported to other states. This is probably a reasonable assumption in that there is no particular need for other states to use aggregates from Texas (except maybe near the borders where it is economically feasible). It is assumed, also, that the portland cement produced in Texas is likely to be used in Texas. This is assumed to be true because it is often difficult for cement plants to keep up with the demand during the busy construction seasons so there would be little need for transporting cement to other states. Also, the quantities of portland cement produced in the state correspond reasonably with the quantities of aggregate produced for concrete.

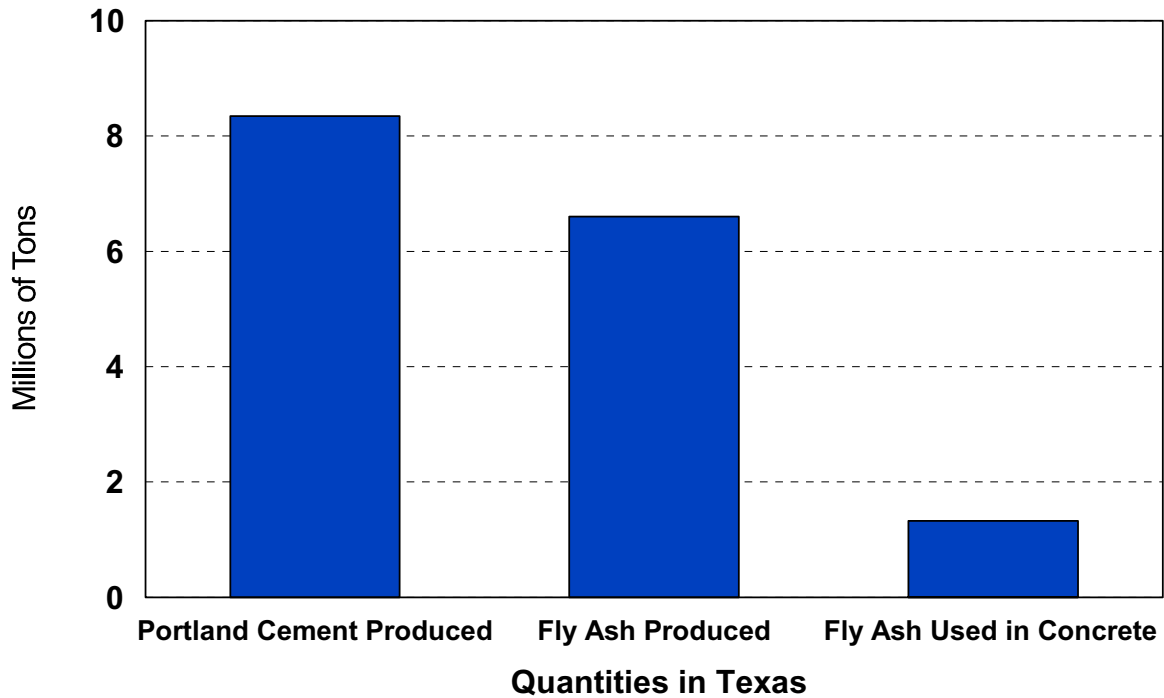
The estimated annual production of concrete is shown in Figure 22. In interviews with various industry representatives, it is estimated that about 30 percent of the concrete market is held by TxDOT projects as also shown in Figure 22.



**Figure 22. Estimated Production of Concrete in Texas and Portion Used by TxDOT.**

## 6.2. QUANTITY OF FLY ASH USED IN CONCRETE PRODUCTION

Most concrete which is produced in Texas contains some quantity of fly ash and it varies throughout the state. It is generally used to enhance the workability and economics of concrete without regard to the improved performance expected through the use of fly ash. It is estimated by industry representatives that concrete in Texas, on average, contains 10 to 15 percent fly ash replacement. This quantity can be verified to some degree by comparing to the quantity of fly ash sold as reported by the utilities in Table 2. In Table 2, it is reported that 2,653,200 tons of fly ash was sold in 2000; however, the end use for this fly ash is not documented. Some of this fly ash is used for stabilization purposes. It is also known from discussions with one of the utilities, that some Class F ash was railed to Florida for concrete production there. If all of the fly ash which was sold in Texas in 2000 was used in concrete production, it is estimated that this would comprise about 30 percent replacement of portland cement with fly ash in concrete production. If the actual use in concrete is closer to about 15 percent as estimated by industry representatives, then one can conclude that about half of the fly ash being sold (or 20% of that being produced) in Texas is for use in the production of concrete in Texas (see Figure 23).



**Figure 23. Production of Portland Cement and Fly Ash Produced in Texas in the Year 2000 Compared to Estimated Quantity of Fly Ash Used in Concrete.**

### 6.3. POTENTIAL FOR THE REDUCTION OF CARBON DIOXIDE EMISSIONS

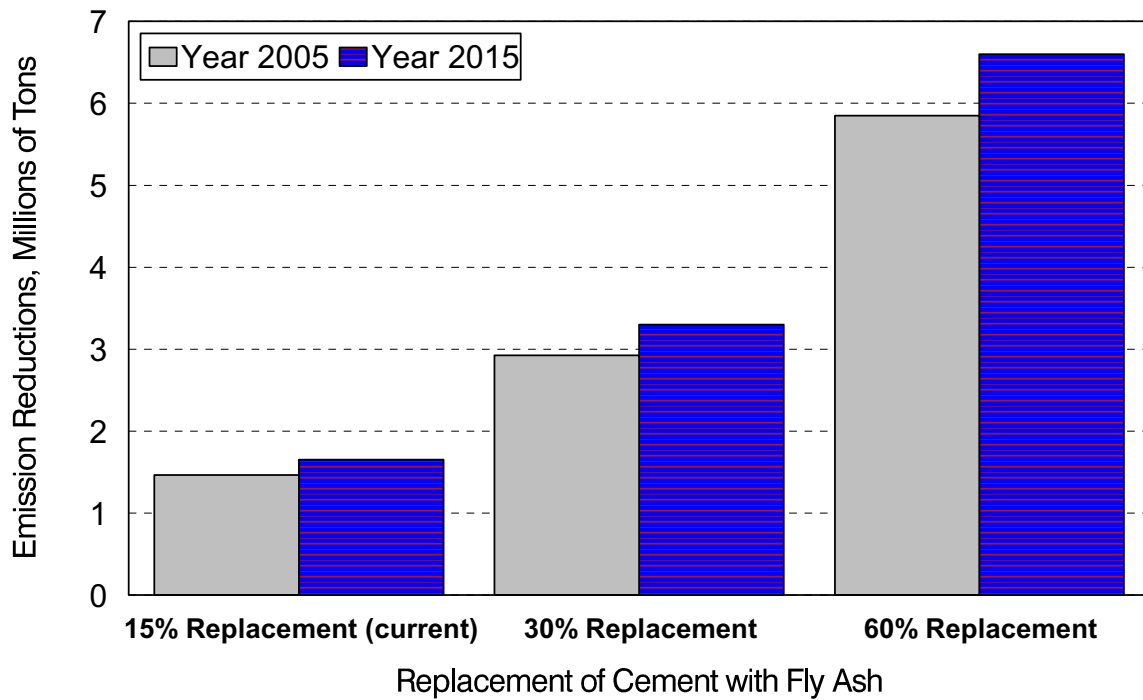
The production of one ton of cement produces about one ton of carbon dioxide. Therefore, every ton of portland cement that is replaced with fly ash, could result in a one-ton reduction in the emission of carbon dioxide. A similar study in Canada estimates a significant decrease in greenhouse emissions (up to 3.6 million tons by the year 2010) with fly ash replacing 60% of cement in concrete<sup>50</sup>. For the study presented herein, projections are made to the year 2015 on the quantities of fly ash available for use in concrete in Texas and the estimated potential reduction of carbon dioxide emissions associated with concrete production in the following scenarios:

- Scenario 1: fly ash continues to replace about 15 percent of portland cement in concrete,
- Scenario 2: fly ash replaces 30 percent of portland cement in concrete beginning in 2005, and
- Scenario 3: fly ash replaces 60 percent of portland cement in concrete beginning in 2005.

Based on a linear regression of the eight years of data shown in Figure 6.2 for the production of concrete, it is estimated that concrete production in the year 2005 would be 39 million tons and in 2015 would be about 44 million tons. According to the three scenarios

presented above, the potential for carbon dioxide emission reductions are presented as follows and in Figure 24:

<u>Potential Carbon Dioxide Emission Reductions</u>	<u>2005</u>	<u>2015</u>
Scenario 1	1,462,500 tons	1,650,000 tons
Scenario 2	2,925,000 tons	3,300,000 tons
Scenario 3	5,850,000 tons	6,600,000 tons



**Figure 24. Potential for Carbon Dioxide Emission Reductions.**

Figure 24 indicates that by the year 2015, carbon dioxide emissions associated with concrete production could be reduced by 6.6 million tons if 60 percent of cement were replaced with fly ash.

#### 6.4. FLY ASH AVAILABILITY VERSUS POTENTIAL DEMAND

Replacing portland cement with as much as 60 percent fly ash produces what is called a HVFA concrete as described in detail previously. Most of the research associated with HVFA concrete involves the use of a Class F fly ash. An obvious question regarding the use of HVFA concrete is, “Will there be enough Class F fly ash available to meet that level of demand?”

Based on the data presented in Table 2, about 3.1 million tons of Class F fly ash were produced in the year 2000. Using estimated quantities of concrete for the same year, a 60 percent replacement of cement with fly ash would require about 6.9 million tons. If TxDOT alone were using a HVFA concrete, about 2.1 million tons of Class F ash would be required. If all concrete purchased by TxDOT contained the maximum amount of fly ash allowed by TxDOT specifications (35% replacement), it is estimated that a total of 1.2 million tons of fly ash would be required. These data are presented in Figure 25.

Most of the research on HVFA concrete has been performed with Class F fly ash because the work was done in Canada where that is the type of ash available. However, there is also the potential for using high volumes of Class C ash in concrete but more research is needed in Texas to verify the performance properties.

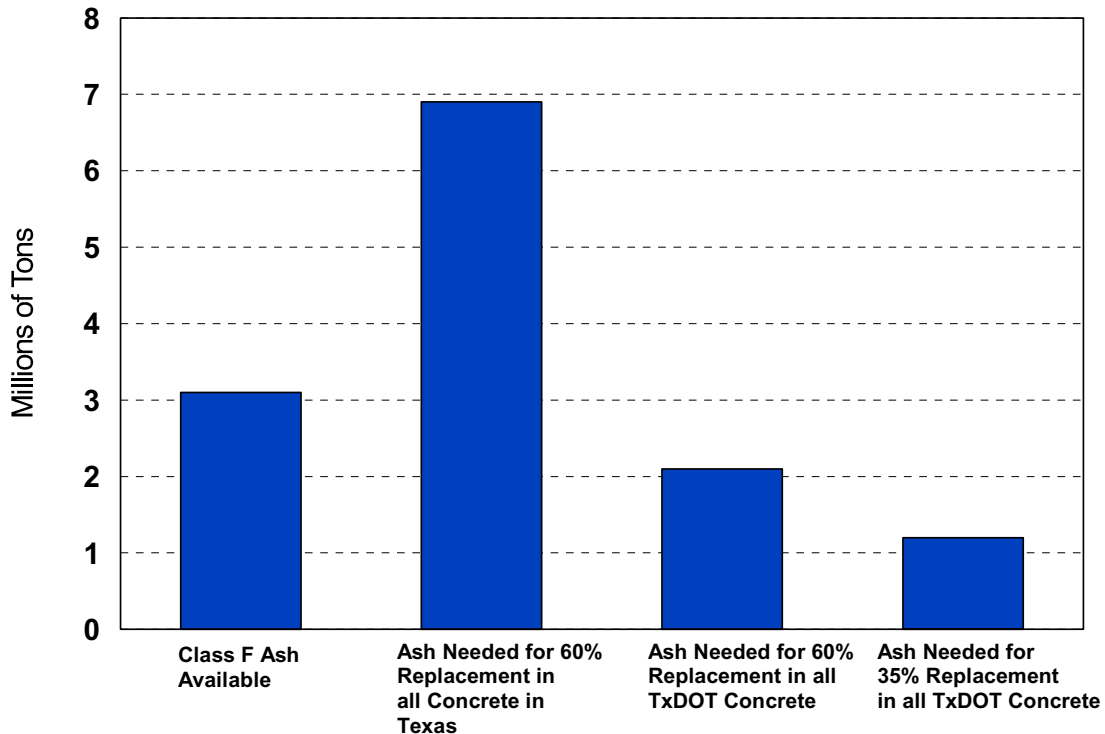


Figure 25. Availability of Class F Ash for Potential Demands.

## **CHAPTER 7.0 CONCLUSIONS AND RECOMMENDATIONS**

### **7.1. PRODUCTION AND AVAILABILITY OF FLY ASH IN TEXAS**

Researchers compiled data for the 18 power plants located throughout Texas and determined that a total of 6.6 million tons of fly ash are produced annually in Texas and about 2.7 million tons (or 40%) are generally sold for use in concrete or other end products. Therefore, almost 4 million tons of fly ash are landfilled. Just over half of the fly ash produced in Texas is a Class F ash. About 25 percent of the Class F ash is currently being sold or used and almost 60 percent of the Class C ash is sold or used

### **7.2 FLY ASH USAGE IN CONCRETE PRODUCTION**

Fly ash can improve the properties of fresh concrete and the hardened concrete. Most concrete today contains some fly ash. The fly ash may typically replace from about 15 to 30 percent of the portland cement. Fly ash can improve the workability and reduces the heat of hydration in fresh concrete. It can improve the strength, permeability, and resistance to chemical attack of the hardened concrete. Canadian research has led to the development of high volume fly ash (HVFA) concrete. In this concrete, up to 60 percent of the portland cement is replaced with Class F fly ash. HVFA concrete exhibits excellent strength, workability, and low temperature rise. One barrier perceived by industry is that it takes a longer time to set. This can, however, be a distinct advantage during a typical Texas summer.

### **7.3 ALKALI SILICA REACTIVITY**

Throughout the course of this research study, the Texas Department of Transportation (TxDOT) experienced some serious problems with premature failure of concrete attributed to alkali-silica reactivity (ASR). There was some belief that Class C fly ash which was being used in concrete was a contributing factor in the problem. Researchers investigated the potential of Class F ash used in high volumes at mitigating ASR through a laboratory investigation. An aggregate was chosen from Texas which was known to be potentially reactive with the alkalis in cement. Samples were made using a low and high alkali cement in immersed in NaOH for 28 days to monitor their expansion. In some of the samples, the cement was replaced with 58 percent Class F ash. In the samples containing the high alkali cement and 58 percent replacement with Class F ash, a distinct reduction in expansion was observed at all stages. An expansion reduction was also observed when a low alkali cement was blended with 58% Class F ash. This confirms the effectiveness of high volumes of Class F ash in reducing the alkali-silica reaction from a potentially reactive state to an innocuous state.

## **7.4 POTENTIAL FOR CARBON DIOXIDE EMISSION REDUCTIONS WITH THE USE OF HVFA CONCRETE**

Researchers used data from the United States Geologic Services (USGS) on the amount of crushed stone, sand and gravel which is used for production of concrete to estimate quantities of concrete in Texas. The USGS also reports the amount of portland cement produced in Texas. In 2001, it is estimated that about 39 million tons of concrete was produced in Texas and about 30 percent or 12 million tons was attributed to the TxDOT market.

The production of one ton of cement produces about one ton of carbon dioxide. Therefore, every ton of portland cement that is replaced with fly ash, could result in a one-ton reduction in the emission of carbon dioxide. In this study, projections are made to the year 2015 on the quantities of fly ash available for use in concrete in Texas and the estimated potential reduction of carbon dioxide emissions associated with concrete production in different scenarios is shown below:

<u><i>Potential Carbon Dioxide Emission Reductions</i></u>	<u><i>Year 2005</i></u>	<u><i>Year 2015</i></u>
15% Cement Replaced	1,462,500 tons	1,650,000 tons
30% Cement Replaced	2,925,000 tons	3,300,000 tons
60% Cement Replaced	5,850,000 tons	6,600,000 tons

## **7.5 BARRIERS TO INCREASED FLY ASH USE IN CONCRETE**

The concrete industry has accepted fly ash use in concrete. Most concrete plants have a silo which contains fly ash that is used routinely for concrete production. However, high volumes of fly ash in concrete is an unknown technology to many. Many plants produce concrete mixes with a Class C ash. It is not feasible for concrete plants to build an additional silo so that they could also have a Class F ash available to produce HVFA concrete. Some report this investment for a silo to be as high as \$1 million. There is currently no incentive for the concrete industry to change current ways.

Another barrier to the increased use of fly ash are the limitations placed by agency specifications. TxDOT as well as many other agencies allow a maximum of 35 percent fly ash replacement in concrete.

Almost half of the fly ash produced in Texas is a Class C ash. More research is needed to develop the performance characteristics of HVFA concrete produced with a Class C ash.

More education is needed for design engineers and for the concrete industry regarding the performance and environmental benefits which can be realized through increased use of fly ash in concrete.

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## APPENDIX A MATERIAL PROPERTIES

### Mill Certificates

#### Low Alkali Cement ASTM C 150 Type I Cement

<u>Chemical Composition</u>	<u>Percent</u>
Loss on Ignition (L.O.I)	1.09
Sulfur Trioxide (SO <sub>3</sub> )	3.17
Silica Dioxide (SiO <sub>2</sub> )	20.98
Ferric Oxide (Fe <sub>2</sub> O <sub>3</sub> )	1.8
Magnesium Oxide MgO	1.43
Aluminum Oxide Al <sub>2</sub> O <sub>3</sub>	4.85
<b>Equivalent Alkalis</b>	<b>0.51</b>
Calcium Oxide (CaO)	65.38
Tricalcium Silicate (C <sub>3</sub> S)	62.56
T r i c a l c i u m (C <sub>3</sub> A)	9.8
Aluminate	
Insoluble Residue (I.R.)	0.12
Surface Area Blaine (Sq. m/kg)	355
Wagner (Sq. m/kg)	186
Passing 325 Mesh	92.7
Soundness: Autoclave expansion	0.04
Entrained Air	5
Time of setting Gilmore	Vicat
Initial (Minutes) 183	123
Final (Minutes) 303	177
<b>C o m p r e s s i v e</b>	
<b>Strength</b>	
3 Day strength 3948 lbs./sq.in	
7 Day strength 5153 lbs./sq.in	

**(High Alkali Cement) - ASTM C 150-97a, AASHTO M 85-89 Type I Cement**

<u>Chemical Composition</u>		<u>Percent</u>
Loss on Ignition	(L.O.I)	0.9
Sulfur Trioxide	(SO <sub>3</sub> )	3.3
	(SiO)	20.1
Ferric Oxide	(Fe <sub>2</sub> O <sub>3</sub> )	3.2
Magnesium Oxide	MgO	0.7
Aluminum Oxide	Al <sub>2</sub> O <sub>3</sub>	5.4
Calcium Oxide	(CaO)	65.40
Insoluble Residue		0.33
Free Lime		0.8
Potential Compounds (%)		
C3S		63
C3A		9
<b>Equivalent Alkalis</b>		<b>0.58</b>
Surface Area	Blaine (Sq. m/kg)	371
	Wagner (Sq. m/kg)	204
Passing 325 Mesh		95.3
Time of setting	Gilmore	
Initial (Minutes)	150	
Final (Minutes)	270	
C o m p r e s s i v e		
Strength		
	psi	Mpa
1 Day strength	2510	17.3
3 Day strength	3760	25.9
7 Day strength	4770	32.9
28 Day strength	6360	43.9
False Set (% Free)		83
Air Content (% vol)		7
Autoclave expansion(%)		0.00

## Fly Ash - ASTM C 618

<u>Chemical Composition</u>	<u>Percent</u>
Loss on Ignition (L.O.I)	0.2
Sulfur Trioxide (SO <sub>3</sub> )	0.5
Silica Dioxide (SiO <sub>2</sub> )	58
Ferric Oxide (Fe <sub>2</sub> O <sub>3</sub> )	5.3
Magnesium Oxide MgO	2.5
Aluminum Oxide Al <sub>2</sub> O <sub>3</sub>	19.6
<b>Equivalent Alkalis</b>	<b>0.4</b>
Calcium Oxide (CaO)	10.9
Moisture Content	0.1
Specific Gravity	2.37



**APPENDIX B**  
**ACCELERATED MORTAR BAR PRISM EXPANSION RESULTS**

Mixture	High Alkali cement only – Control mix
Testing Condition	Mortar bars immersed in 1 N NaOH solution at 80° C

Days	% Expansion			Mean Expansion (%)
	M1	M2	M3	
0	0	0	0	0
4	0.059	0.053	0.047	0.053
7	0.198	0.188	0.192	0.193
14	0.306	0.300	0.297	0.301
21	0.400	0.392	0.384	0.392
28	0.469	0.455	0.459	0.461

Mixture	High Alkali cement only – Control mix
Testing Condition	Mortar bars immersed in 0.5 N NaOH solution at 80° C

Days	% Expansion			Mean Expansion (%)
	M4	M5	M6	
0	0	0	0	0
4	0	0	0.002	0.001
7	0.044	0.04	0.056	0.047
14	0.178	0.183	0.202	0.188
21	0.311	0.315	0.335	0.320
28	0.403	0.400	0.431	0.411

Mixture	High Alkali cement only – Control mix
Testing Condition	Mortar bars immersed in 0.25 N NaOH solution at 80° C

Days	% Expansion			Mean Expansion (%)
	M10	M11	M12	
0	0	0	0	0
4	0	0	0	0
7	0.011	0.013	0.012	0.012
14	0.011	0.014	0.012	0.012
21	0.022	0.019	0.021	0.021
28	0.046	0.041	0.043	0.043

Mixture	High Alkali cement + 58% Class F Fly Ash
Testing Condition	Mortar bars immersed in 1.0 N NaOH solution at 80° C

Days	% Expansion			Mean Expansion (%)
	M13	M14	M15	
0	0	0	0	0
4	0.010	0.005	0.009	0.008
7	0.019	0.020	0.016	0.018
14	0.020	0.024	0.023	0.022
21	0.021	0.023	0.024	0.023
28	0.021	0.024	0.024	0.023

Mixture	Low Alkali cement + 58% Class F Fly Ash
Testing Condition	Mortar bars immersed in 1 N NaOH solution at 80° C

Days	% Expansion		Mean Expansion (%)
	M16	M18	
0	0	0	0
4	0.018	0.018	0.018
7	0.022	0.023	0.023
14	0.022	0.022	0.022
21	0.020	0.021	0.021
28	0.021	0.020	0.021

Mixture	Low Alkali cement + 58% Class F Fly Ash
Testing Condition	Mortar bars immersed in 0.5 N NaOH solution at 80° C

Days	% Expansion		Mean Expansion (%)
	M19	M21	
0	0	0	0
4	0.008	0.007	0.008
7	0.014	0.012	0.013
14	0.015	0.014	0.015
21	0.016	0.016	0.016
28	0.017	0.018	0.018

Mixture	Low Alkali cement + 58% Class F Fly Ash
Testing Condition	Mortar bars immersed in 0.25 N NaOH solution at 80° C

Days	% Expansion		Mean Expansion (%)
	M22	M24	
0	0	0	0
4	0.005	0.010	0.008
7	-0.01	-0.008	-0.009
14	0.005	0.009	0.007
21	0.025	0.021	0.023
28	0.004	0.010	0.007

Mixture	High Alkali cement + 58% Class F Fly Ash
Testing Condition	Mortar bars immersed in 0.5 N NaOH solution at 80° C

Days	% Expansion		Mean Expansion (%)
	M26	M27	
0	0	0	0
4	0.002	0.002	0.002
7	0.002	0.002	0.002
14	0.003	0.0035	0.003
21	0.004	0.004	0.004
28	0.009	0.010	0.010

Mixture	Low Alkali cement only – Control Mix
Testing Condition	Mortar bars immersed in 1.0 N NaOH solution at 80° C

Days	% Expansion		Mean Expansion (%)
	M29	M30	
0	0	0	0
4	0.030	0.026	0.028
7	0.119	0.113	0.116
14	0.211	0.205	0.208
21	0.333	0.335	0.334
28	0.405	0.407	0.406

Mixture	Low Alkali cement only – Control mix
Testing Condition	Mortar bars immersed in 0.5 N NaOH solution at 80° C

Days	% Expansion			Mean Expansion (%)
	M31	M32	M33	
0	0	0	0	0
4	0.003	0.001	-0.007	-0.001
7	0.018	0.018	0.022	0.019
14	0.055	0.047	0.049	0.050
21	0.249	0.244	0.234	0.242
28	0.381	0.379	0.362	0.374

Mixture	Low Alkali cement only – Control mix
Testing Condition	Mortar bars immersed in 0.25 N NaOH solution at 80° C

Days	% Expansion			Mean Expansion (%)
	M34	M35	M36	
0	0	0	0	0
4	0.001	-0.001	0.002	0.001
7	0.002	-0.001	0.004	0.002
14	0.018	0.016	0.022	0.019
21	-0.002	0.004	0.001	0.001
28	0	0.006	0.004	0.003

Mixture	High Alkali cement + 58% Class F Fly Ash
Testing Condition	Mortar bars immersed in 0.25 N NaOH solution at 80° C

Days	% Expansion		Mean Expansion (%)
	M37	M39	
0	0	0	0
4	-0.005	-0.002	-0.004
7	-0.009	-0.007	-0.008
14	0.014	0.012	0.013
21	-0.006	-0.003	-0.005
28	-0.004	0.003	-0.001