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Using Coal Ash to Mitigate Alkali Silica Reactivity

For decades, the concrete construction industry has been plagued by the deleterious chemical reactions that can develop between the siliceous materials in concrete aggregate and the alkali hydroxides in cement. Known as alkali-silica reaction (ASR), this phenomenon can lead to premature and severe cracking. In recent years, this problem has worsened because natural aggregates not prone to ASR have been depleted in many locations. Concrete structures around the world are threatened by ASR, and the cost of rehabilitating these structures could well be in the hundreds of billions of dollars.

Using coal ash from power plants as a substitute for a portion of the portland cement in concrete is one simple and economical way of minimizing ASR-related damage. In particular, the reactive silica in power plant fly ash combines with the cement alkalis (that is, NaOH and KOH) more readily than the silica in aggregate. The resulting calcium-alkali-silica "gel" is nonexpansive, unlike the water-absorbing expansive gels produced by alkali-aggregate reactions. Alternatively, power plant boiler slag can be used in lieu of natural aggregates to reduce ASR-related degradation.

In virtually all cases, adding fly ash to concrete increases ASR resistance and improves the concrete's ultimate strength and durability while lowering costs. The optimal proportion of fly ash in the mix varies depending on the fly ash type (Class F or Class C), its soluble alkali content, fineness, and other factors. In some cases where very high concrete strength is required, a combination of fly ash and foundry "silica fume" are used to replace a fraction of the portland cement; these mixes are called ternary blends. Another type of ternary blend adds fly ash to a mixture of "slag cement" (a by-product of iron processing) and portland cement, producing an inexpensive concrete with good strength, workability, and ASR-resistance.

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Coal Ash 101

Like wood in a fireplace, coal burned in a power plant leaves behind ash. About 20% of power plant coal ash falls to the bottom of the furnace (and is hence called bottom ash), whereas about 80% is carried upward by the hot furnace exhaust gases (and is known as fly ash). Fly ash is captured in particulate collectors used by power plants to prevent pollution. Fly ash particles are very fine and are "pozzolanic," like natural volcanic ash, meaning they form cementitious compounds in the presence of calcium hydroxide ($Ca(OH)_2$) and water. These properties make fly ash an excellent concrete admixture.

Fly ash is categorized into two broad classes based on ASTM International (American Society for Testing and Materials) criteria for chemical composition, which correspond to the rank (type) of the coal source. Ashes from subbituminous and lignite coals are designated "Class C," and are sometimes called "high calcium." They may contain modest quantities of "free lime" (CaO), making then mildly cementitious when wetted even before exposure to calcium hydroxide. Ashes from bituminous and anthracite coals are designated "Class F," and are sometimes called "low calcium." They generally contain little or no free lime and only become cementitious after contact with calcium hydroxide and water.

Today, Class F is the primary type of fly ash used to mitigate ASR in concrete, although research by EPRI and others indicates that Class C ash can successfully control ASR in mix designs that replace a significant portion of portland cement (30% or more) with fly ash. Only Class C ash with a high soluble alkali sulfate content may be unsuitable.

Project managers using fly ash to mitigate ASR will want to assure its quality and impact on concrete performance. The four most common measures of fly ash quality are loss on ignition, fineness, chemical composition, and uniformity. These characteristics are influenced not only by the source coal, but also by various aspects of fuel preparation and combustion.

Loss on Ignition (LOI)

Standard LOI measurements approximate the quantity of unburned carbon (coal char) remaining in fly ash. Relatively high carbon content can inhibit the entrainment of air by concrete; trapped air is needed to permit crack-free expansion and contraction with temperature changes. As a result, standard C618 of ASTM International specifies a maximum carbon content of 6% (by weight) for fly ash used in concrete. By way of comparison, the Canadian standard allows up to 8% carbon for Class F fly ash. Historically, North American concrete mix designers have preferred fly ash with an LOI of 4% or less, but the use of air entrainment agents can compensate for the effects of ash carbon up to the ASTM 6% limit or higher.

The U.S. Environmental Protection agency (EPA) is currently developing regulations to limit mercury emissions from coal-fired power plants. To comply with the expected regulations, many plants may choose to inject activated carbon into boiler exhaust gases upstream of the particulate collection device to adsorb vaporous mercury. Thus, mercury-laden activated carbon would be captured along with fly ash. In some systems, activated carbon will be separated and recycled for added mercury removal, but even in those designs a portion of the activated carbon will become co-mingled with captured fly ash. By virtue of its high surface-area-to-volume ratio, activated carbon in fly ash could inhibit air entrainment in concrete. Researchers are investigating this potential issue to ensure that the majority of fly ash remains suitable for concrete applications.

Fineness

The fineness of fly ash is related to the operating condition of the power plant's coal pulverizers and the "grindability" of the coal itself. The commonly reported parameter is the percentage of fly ash retained on a No. 325 sieve. Generally speaking, the finer the ash, the more reactive and, therefore, the greater the ASR mitigation benefit.

Chemical Composition

The chemical composition of a particular fly ash relates directly to the source coal burned, and is useful for predicting hydration rates and other parameters of interest to concrete mix designers. Significant compositional variation among ashes from a given coal seam is uncommon. So once a data set is established, it is generally valid for all fly ash from the source. Further, ash producers and brokers generally keep reliable records on the source coal(s) for individual ash lots.

Uniformity

Uniformity of fly ash from shipment to shipment helps assure the production of consistent concrete products. If a significant variation in ash characteristics is anticipated for a given shipment, advance information enables mix designs and field procedures to be adjusted as appropriate.

Standard Specifications

U.S. specifications for concrete incorporating fly ash are produced and maintained by ASTM International, the American Association for State Highway and Transportation Officials (AASHTO), and ACI International (American Concrete Institute). Canadian specifications are maintained by the Canadian Standards Association (CSA, also known as Association Canadienne de Normalisation). In Europe, individual national standards have been the norm, but European Union members have been working on a common specification. Australia, South Africa, and several Asian countries also have national standards, although they are similar to those of ASTM International. Table 1 lists a sampling of relevant North American standards.

Table 1
Specifications for Incorporating Coal Ash in Concrete and Testing for ASR Susceptibility

Specification	Name
ASTM C618-03	Standard Specification for Coal Fly Ash and Raw or Calcined Natural Pozzolan for Use as a Mineral Admixture in Concrete
AASHTO M295	Use of Fly Ash in Portland Cement Concrete
ACI 232.2R-96 (references ASTM C618)	Use of Fly Ash in Concrete
ASTM C311-02	Standard Test Methods for Sampling and Testing Fly Ash or Natural Pozzolans for Use as a Mineral Admixture in Portland -Cement Concrete
ASTM C289-02	Standard Test Method for Potential Alkali - Silica Reactivity of Aggregates (Chemical Method)
ASTM C1260-01	Standard Test Method for Potential Alkali Reactivity of Aggregates (Mortar -Bar Method)
ASTM C227-97a	Standard Test Method for Potential Alkali Reactivity of Cement-Aggregate Combinations (Mortar-Bar Method)
ASTM C1293-01	Standard Test Method for Determination of Length Change of Concrete Due to Alkali - Silica Reaction
CSA A23.5-98	Supplementary Cementing Materials

Recycling coal combustion products to mitigate ASR offers substantial environmental benefits. Currently, U.S. power plants generate over 80 million tons of coal ash and boiler slag per year, of which only about a third is productively used; the remainder is typically sent to landfill. Greater fly ash and slag use in concrete can reduce landfill disposal requirements. Further, substituting fly ash for portland cement reduces CO_2 emissions (from cement manufacturing) in proportion to the cement replaced. For these reasons, many states encourage the use of coal ash in highway construction projects.

Figure 1. ASR Damage to Concrete Mixture Using a Reactive Aggregate with Portland Cement (Courtesy of Thomas, *et al.*, University of Toronto)

Table 2
Virginia Department of Transportation Specification for Concrete Resistant to ASR

Material	Maximum Portland Cementalkali Content, % Na_2O eq
Portland cement only	0.45
Cement with min. 15% Class F fly ash	0.60
Cement with min. 20% Class F fly ash	0.68
Cement with min. 25% Class F fly ash	0.75
Cement with min. 30% Class F fly ash	0.83
Cement with min. 25% ground slag	0.60
Cement with min. 35% ground slag	0.90
Cement with min. 50% ground slag	1.00

Regulations Governing Use of Fly Ash and Boiler Slag for ASR Control

California and New Mexico require highway construction projects to use concrete mix designs that replace 20% of cement with Class F fly ash. Other states—including New Jersey, Pennsylvania, and Virginia—have developed guidelines for using fly ash as an ASR retardant. Guidelines vary from state to state, although most identify Class F fly as an approved ASR-mitigating additive.

Table 2 shows the ASR-resistant concrete specification from the Virginia Department of Transportation. This table shows that without the use of fly ash or boiler slag, concrete designers must buy more expensive low-alkali cement to curb ASR. The greater the percentage of fly ash or boiler slag blended into a cement mix, the more flexibility designers have in selecting cement sources.

Mix Designs with Fly Ash

For construction project managers, ASR control options consist of (1) selective quarrying for non-reactive aggregates, (2) diluting reactive aggregates with non-reactive ones, (3) using low-alkali cements, and (4) adding supplementary cementing materials such as fly ash. Given the lack of low-alkali cements in many places and the increasing cost of non-reactive aggregates, using fly ash as a partial cement substitute is normally the most cost-effective approach.

Because the severity of ASR depends on numerous factors—including the reactivity of aggregate, the alkali content of the cementing materials, and available moisture—there is no single "recipe" for ASR-resistant concrete. Bridges and other critical structures constantly exposed to weather may need much greater ASR resistance than less exposed structures or roadways in arid climates. In general, however, the greater the portion of Class F fly ash in a mix design, the greater the ASR resistance of the resulting concrete.

The ASR mitigation benefits of Class C fly ash are less well known. A few Midwestern states have decreased their recommended usage rates for Class C ashes because of concerns that their higher calcium content (alkalinity) would not adequately mitigate ASR. There may be an impression that Class C ash could actually exacerbate ASR, which research has shown is almost never the case.

According to recent EPRI studies, both Class F and Class C fly ash are effective at mitigating ASR in concrete when used as substitutes for portland cement. The major difference between the two ash types is that a greater portion of cement must be replaced with Class C ash to provide the same effect as using Class F ash in a mix design with a smaller ash-to-cement ratio. Each concrete mix design, however, is unique, and the ASR-mitigating effects of fly ash depend on the chemical composition of the selected fly ash, aggregate reactivity, and the alkali content of the portland cement used in the mix.

Class F Mixtures

Expert opinion varies on exactly how much Class F fly ash is necessary for an ASR reduction effect. Different studies indicate that ASR reduction benefits begin at cement replacement levels of 15% to 30%, depending on the reactivity of the aggregate and other factors. As illustrated in Figure 2, once the replacement threshold has been reached, the reduction in expansive reactions for a given cement alkali level is dramatic. Additionally, the greater the proportion of cement replaced with Class F ash, the greater the ASR reduction.

High-Volume Fly Ash Mixes

High-volume fly ash concretes, in which 50% or more of portland cement is replaced by Class F fly ash, may be particularly useful for minimizing ASR. At present, high-volume fly ash mixtures are not explicitly used for this purpose. This is, to a certain extent, because ACI International's code 318 (that is, building code requirements for structural concrete) specifies a maximum fly ash replacement volume of 25% for concrete exposed to deicing chemicals. It appears that sometimes engineers may believe this restriction applies for all applications. High-volume fly ash concretes are, in fact, appropriate for many applications where durability and ASR resistance are critical and high early strength is not required.

Ternary Blends

Where silica fume, a very fine material high in reactive SiO_2 , is used in concrete for high strength, adding Class F fly ash to create a "ternary blend" can significantly reduce ASR susceptibility without diminishing high concrete performance. The effects of silica fume and fly ash are complementary, with the silica fume improving the early-age performance of concrete and the fly ash continuously refining the properties of the concrete as it ages. In terms of durability, such blends are vastly superior to conventional portland cement-based concrete, and they have been shown to offer greater chloride resistance. In some cases, price differences between the individual components may allow ternary blends to compete with high-strength concrete using conventional portland cement on the basis of material costs.

In a similar manner, using fly ash to replace a portion of portland cement in low-cost blends containing iron industry slag cement can improve concrete properties while further reducing mix costs. These ternary blends provide better workability, early strength, and overall strength than concrete produced with slag and portland cement. Moreover, the addition of fly ash reduces concrete permeability, helping to limit moisture intrusions that can promote ASR reactions.

Most often, mix designers use Class F fly ash in ternary blends because it is relatively coarser than Class C ash and can better ameliorate potential problems with silica fume, which reacts very quickly, causing partial setting that makes the concrete difficult to pump. By adding Class F ash, which increases concrete setting time, highway engineers can create a concrete with a longer period of workability. According to EPRI research, the addition of just 20% fly ash in structural concrete can make a significant difference, increasing the time to initial setting by about 1.5–2 hours and the time to final setting by 3.5–4 hours. A 40% fly ash substitution further increases initial and final setting times by about another 2 hours.

Class C Mixtures

Use of Powder River Basin (PRB) coals by North American power producers has increased to the point where 40% of all fly ash produced is high-calcium Class C

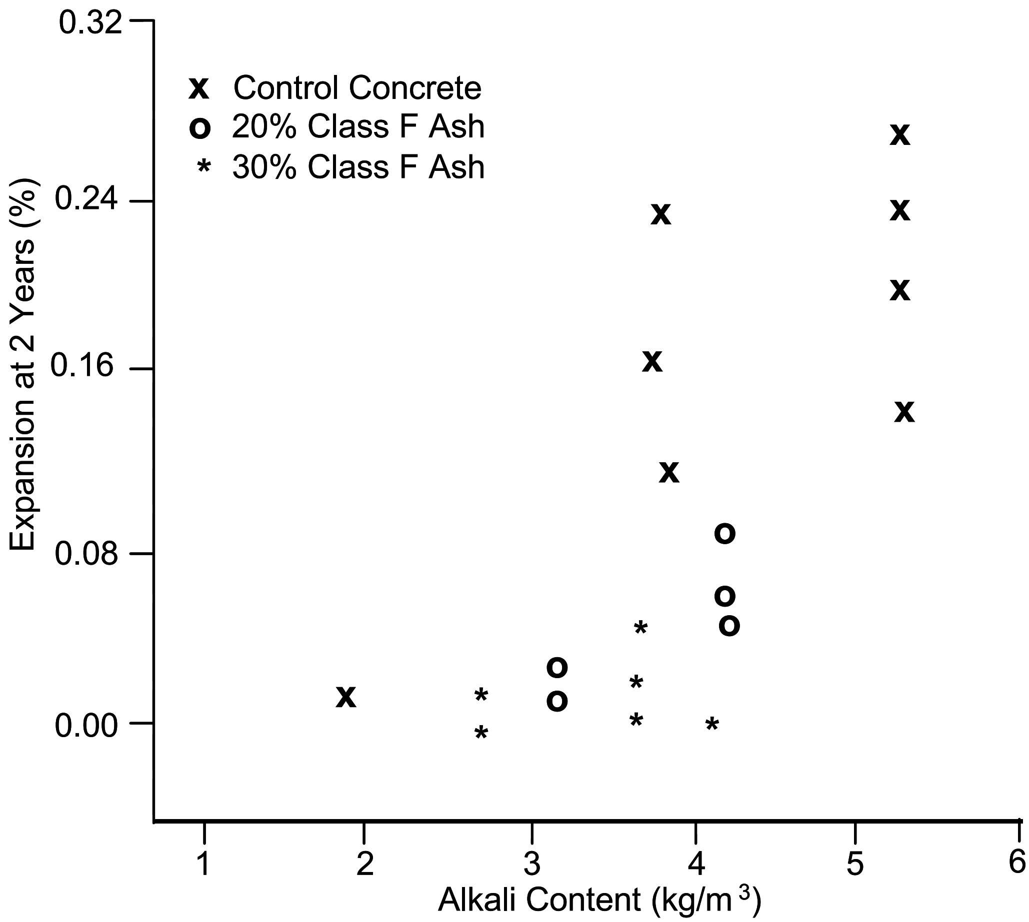

Figure 2. Effect of Substituting Class F Fly Ash for Portland Cement on ASR Expansion in Concrete Prism Tests (Courtesy of CANMET (abbreviated))

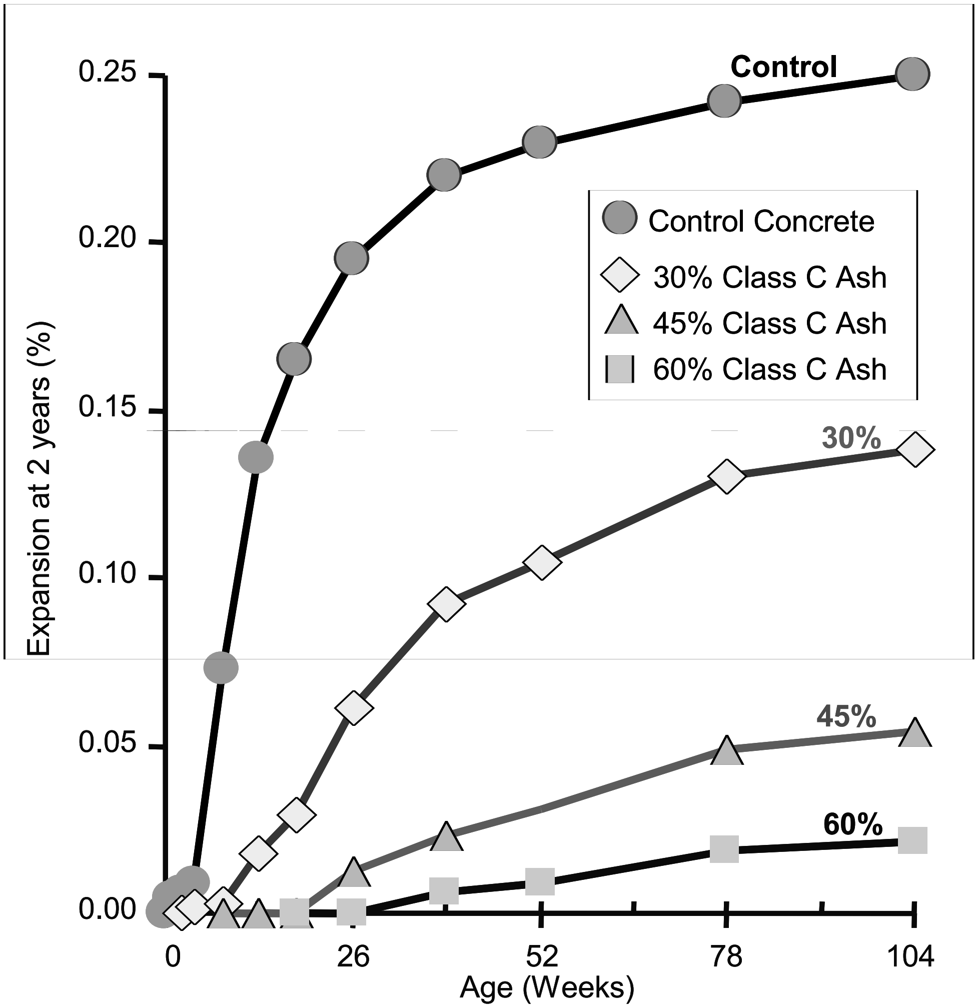

Figure 3. Effect of Substituting Class C Fly Ash for Portland Cement on ASR Expansion in Laboratory Specimens (Courtesy of Thomas, *et al.*, University of Toronto)
Note: Class C Fly Ash includes 28% CaO and 1.7% Na_2O eq

ash. In many locations, Class C ash is the only type of fly ash available within reasonable transportation distance. Because the use of Class C fly ash at similar replacement levels to Class F ash has not been as effective in mitigating ASR, some potential purchasers may have concluded that Class C ash is simply ineffective for ASR control.

Recent EPRI work suggests that this is not the case. A number of short-term studies show that replacing portland cement with Class C ash at volumetric rates of 30–50% is effective in controlling ASR. As shown in Figure 3, the greater the proportion of Class C fly ash used in a mix, the greater the ASR control benefit.

EPRI is currently working with the Canada Centre for Mineral and Energy Technology (CANMET) to evaluate the long-term effectiveness of several high-calcium ashes in reducing ASR in concrete using natural aggregates of different reactivity levels. If results meet expectations, this study should encourage state highway departments and other organizations to reconsider greater use of Class C fly ash for ASR control, thereby boosting the recycling rate for this prevalent coal combustion product.

How EPRI Can Help

EPRI provides a comprehensive array of products and services that help construction project managers develop cost-effective mix designs using fly ash and boiler slag for optimal ASR control. These include the development of new concrete blends, detailed technical reports assessing the performance of a wide spectrum of ash-based concrete blends, guidelines for tailoring concrete blends to meet specific engineering criteria, and a library of case studies outlining how U.S. highway departments, other government agencies, and private organizations have used fly ash to address construction challenges. In addition, EPRI's knowledgeable staff includes industry-leading civil engineers who can provide assistance on project-specific issues.

For more information, contact Dean Golden at 650.855.2516 or dgolden@epri.com. For copies of the reports listed below, see epri.com or call the EPRI Orders and Conference Center, 925.934.4212.

EPRI References

1998 Summary of Consortium on Alkali-Aggregate Reactivity in Concrete, Report TR-112453, March 1999.

CANMET/Industry Research Consortium on Alkali-Aggregate Reactivity, Report TR-109132, November 1997.

Concrete Applications of Coal Ash: Highway Structures and Pavement, Resource Paper 1004696, September 2002.

Development of Ternary Blends for High Performance Concrete, Report 1004077, November 2002.

The Role of High Calcium Fly Ashes in Controlling Alkali-Silica Reactions in Concrete, Report 1004407, November 2002.

Use of High Carbon Fly Ash as a Component of Raw Mix for Cement Manufacture, Report TR-110808, May 1998.

Evaluation of the Effectiveness of High-Calcium Fly Ashes in Reducing Expansion due to Alkali-Silica Reaction (ASR) in Concrete, Report 1004853, December 2003.

Other Resources

ACI International (www.aci-int.org)

American Association of State Highway and Transportation Officials (www.aashto.org)

American Coal Ash Association (www.acaa-usa.org)

ASTM International (www.astm.org)

Canadian Standards Association (www.csa-intl.org/onlinestore)

Federal Highway Administration (www.fhwa.dot.gov)

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