

*Concrete Compatibility of Fly Ash Containing  
Amended Silicates™ for Mercury Control*

**Environmental Energy Services (EES)**



## Executive Summary

Fly ash is used as a supplementary cementitious material in production of Portland cement concrete, which contributes to the properties of the hardened concrete through hydraulic and/pozzolan activity.

The use of PAC products of any type for mercury control at power plants contaminates the fly ash and subsequently the concrete into which it is mixed, often making the fly ash unsuitable for use in concrete, and always collecting the mercury in a form that will leach when it comes into contact with ground water.

Amended Silicates™ on the other hand, reactively capture mercury, forming an insoluble stable form of mercury that will not leach, and will not contaminate the fly ash, so that it remains available for use in concrete and for other beneficial purposes.

Multiple organizations in the cement and concrete industry have evaluated the suitability of fly ash containing spent Amended Silicates™ for use in concrete, including Lafarge, Suwannee Cement, Separation Technologies, Ash Grove, Boral Materials, Headwaters, and National Cement.

This white paper describes many of the results extracted from investigations performed by these organizations, which fully establish that the use of Amended Silicates™ for capturing mercury leaves the fly ash in a pristine condition for use in concrete.

The overall findings presented in this white paper on the compatibility of fly ash containing Amended Silicates™ for use in concrete are as follows:

- Amended Silicates™ evaluated as if it was a fly ash itself would be classified as both a C and F fly ash, based on the ASTM criteria for use of fly ash in concrete. Consequently, the addition of Amended Silicates™ for spent Amended Silicates™ collected with fly ash, does not change the classification of the neat fly ash, with regard to the ASTM classification.
- Amended Silicates™ do not contain any carbon, and do not contaminate fly ash, alter air entrainment in concrete, increase the foam index of the fly ash, or darken the fly ash or concrete into which it is mixed.
- Concrete made with fly ash containing activated carbon will continually leach mercury adsorbed on the carbon in the ash even after it has formed concrete blocks, foundations, and other structures used to construct buildings, bridges, and dams. Amended Silicates™ reactively capture and permanently sequester mercury as a mercuric sulfide (HgS), which will not leach from concrete structures.
- Fly ash containing spent Amended Silicates™, tested with different additives commonly used in concrete (specifically Pozzolite 210 and Polyheed 997), were found not to have any

observable interactions with the additives, and the behavior of the fly ash was observed to be the same, with or without spent Amended Silicates™ present.

- The presence of spent Amended Silicates™ in fly ash were observed not to impact the curing times or strength of the concrete into which the fly ash was mixed.
- Fly ash containing Amended Silicates™ has been evaluated by Headwaters and many other companies, expert in the concrete industry, and found that the fly ash easily passed all of the criteria for use in concrete.
- Among other things, the presence of spent Amended Silicates™ in fly ash was confirmed not to change the fly ash classification or to adversely impact its fineness or mineral composition.
- Finally, Amended Silicates™ have been used for years in coal-fired utility boilers for mercury control, allowing their fly ash to be sold and used to produce high-quality concrete, without any negative impacts or issues from the Amended Silicates™.

Environmental Energy Services (EES) is ready to work with any organization that feels they need to obtain more data on the impacts of Amended Silicates™ in fly ash and the associated use of that fly ash in concrete or for other beneficial uses.

Amended Silicates™ and KLeeNsrub™ (an organo-sulfide-based wet-scrubber additive used to prevent mercury emissions from wet FGD scrubbers) are the most effective and environmentally-friendly mercury-mitigation products available on the market today.

## Background for Fly Ash Compatibility with Concrete

As described in publications by the Portland Cement Association (PCA), fly ash is used as a supplementary cementitious material in production of Portland cement concrete, which contributes to the properties of the hardened concrete through hydraulic and pozzolanic activity. The pozzolanic activity of fine fly-ash powders allows them to chemically react with calcium hydroxide and moisture at ordinary temperatures to form compounds that have cementitious properties, and some fly ash, typically higher in calcium content than other ashes, possess cementitious attributes in and of themselves.

These properties and associated reactions when fly ash is used in concrete are beneficial, because they increase the quantity of the cementitious binder phase, thus improving the long-term strength, enhancing the durability, and reducing the permeability of the finished concrete product.

Nearly 15 million tons of fly ash was used in concrete and associated products in the United States in 2005.

Typical amounts of fly ash used in concrete range from 15 wt% to 25 wt%, but levels as high as 30 wt% to 60 wt% have been used for massive, structural applications, such as foundations and dams. The actual amount used depends on each specific application, chosen to maximize the technical, environmental, and economic benefit to the product, while minimizing impairment of the long-term performance of the finished product.<sup>1</sup>

## Benefits of Using Fly Ash in Concrete

There are many benefits of using fly ash in concrete, while using skill and understanding to implement the addition in such a way as maximize the benefits while avoiding deleterious impacts on the concrete, such as extreme cure times or loss of strength.

The following are a list of the many benefits that can be gained by the addition of fly ash into the concrete mix:

- Increased workability of fresh concrete.
- Increased cohesiveness and reduced segregation of concrete.
- Reduction in the heat of hydration.
- Increased long-term concrete strength.
- Reduced permeability and chloride resistance.
- Expansion of the concrete can be reduced or eliminated.
- Increased sulfate resistance.

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<sup>1</sup> Thomas, Michael, "Optimizing the Use of Fly Ash in Concrete", Concrete, Portland Cement Association, 2007.

In addition to these benefits, there are the economic and environmental benefits of not having to use as much cement in the mix and providing a beneficial use for the fly ash, rather than requiring the fly ash to be disposed of in a landfill.

### Fly Ash Type Classification

There are several differing specifications for fly ash. Table 1 below contains the ASTM specifications for two defined types (or Class) of fly ash, for use in concrete.

**Table 1.** ASTM Specification for Fly Ash use in concrete.

Class	ASTM C618 Description	Chemical Requirements
<b>F</b>	Fly ash normally produced from burning anthracite or bituminous coal that meets the applicable requirements for this class as given herein. This class of fly ash has pozzolanic properties.	$\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3 \geq 70\%$
<b>C</b>	Fly ash normally produced from lignite or sub-bituminous coal that meets the applicable requirements for this class as given herein. This class of fly ash, in addition to having pozzolanic properties, also has some cementitious properties. Note: Some Class C fly ashes may contain lime contents higher than 10%.	$\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3 \geq 50\%$

The Canadian specification, CSA A3001, is shown in Table 2.

**Table 2.** Canadian specification and classification of fly ash types for use in concrete.

Classification or Type	Chemical Requirement
<b>F</b>	< 8% CaO
<b>CI</b>	8 – 20% CaO
<b>CH</b>	> 20% CaO

The Class C fly ashes defined in the ASTM Specification are composed of lower rank coals that generally contain more calcium, and as such, they have some cementitious properties in and of themselves, in addition to pozzolanic properties.

The Canadian Specification is entirely based on calcium content.

If the calcium content of a fly ash is high enough, it may have enough cementitious capability to form a concrete of moderate strength, without the addition of cement or other additives.

### Amended Silicates™ and Fly Ash Containing Amended Silicates™ for Mercury Control

Amended Silicates™ are mostly composed of aluminosilicate clays, and would be classified as both a Class C and F fly ash for use in concrete, based on its composition.

In addition, Amended Silicates™ contain no carbon, so the addition of the small amount of Amended Silicates™ for mercury control (i.e., 2 wt% or less), will not change the classification of the fly ash it is collected with, and it will not change the salability of fly ash for use in concrete or other byproduct uses.

Concrete requires the addition of air-entraining admixtures to achieve a satisfactory air-void system. Higher doses of air-entrainment admixture are required as either the fly-ash content of the concrete increases (due to the unburned carbon in the fly ash) or the unburned carbon content of the fly ash increases.<sup>2</sup>

Powdered Activated Carbon (PAC), because it has a much higher adsorptive capacity than unburned carbon, injected for mercury control and collected with the fly ash, requires much more air-entrainment correction than does unburned carbon.

Furthermore, PAC collected with the fly ash creates other challenges as difficult to overcome, such as discoloring of the concrete that makes it unsuitable for many applications.

For these reasons, it is often not possible to separate the spent PAC from the fly ash or otherwise treat the fly ash sufficiently to obtain a fly-ash composition for use in concrete, and as a result, much of this fly ash contaminated with PAC must be landfilled at a substantial cost to the utilities.

### **Mercury Instability and Stability in Concrete when Using PAC vs Amended Silicates™**

Perhaps the most important difference between fly ash that contains spent PAC versus spent Amended Silicates™, is that the mercury on the spent PAC is not sequestered and will leach when exposed to water or air<sup>3</sup>, particularly when the gas or water is at least slowly flowing through the media or the ambient temperatures are elevated, while the mercury on the spent Amended Silicate™ particles is sequestered in the form of mercuric sulfide (HgS), the most stable form of mercury in the environment, and will not leach.

Hence, when using fly ash in concrete containing spent PAC, the concrete structures created therefrom will continually bleed mercury from the concrete structures, such as buildings and bridges until all the mercury is released into the environment.<sup>4</sup>

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<sup>2</sup> Gebler, S. and Klieger, P., "Effect of Fly Ash on the Air-Void Stability of Concrete", *Fly Ash, Silica Fume, Slag and Other Mineral By-Products in Concrete*, ACI SP-79, Vol. 1, American Concrete Institute, Farmington Hills, MI., 1983, pages 103-142.

<sup>3</sup> William W. Aljoe, Thomas J. Feeley III, James T. Murphy, Karl T. Schroeder, Lynn A. Brickett, and Candace L. Kairies, "Fate of Mercury in Coal Byproducts from DOE's Mercury Control Technology Field Testing Program and Related Projects", *China Workshop on Mercury Control from Coal Combustion*, October 31-November 2, 2005, Beijing, China.

<sup>4</sup> Wen Dua, Chao-yang Zhanga, Xiang-ming Konga, Yu-qun Zhuob, and Zhen-wu Zhuh, "Mercury Release from Fly Ashes and Hydrated Fly Ash Cement Pastes", *Atmospheric Environment* **178** (2018) 11–18.

When that happens, the impact of the leached mercury on the environment and human health through contamination of local water ways and ultimately bioaccumulation within aquatic life and the fish we eat, is *much more damaging than* if *no mercury-control* technologies were used at all to remove mercury from the flue gas, in which case the mercury would have been emitted from the stack and randomly distributed across the region (oxidized mercury) and around the world (elemental mercury).

### **Independent Evaluations of the Suitability of Fly Ash Containing Amended Silicates**

Multiple organizations in the cement and concrete industries have evaluated the suitability of fly ash containing spent Amended Silicates™ for use in concrete, including Lafarge, Suwannee Cement, Separation Technologies, Ash Grove, Boral Materials, Headwaters, and National Cement.

The following test descriptions, data, and findings were extracted from results of testing conducted by these independent, cement and concrete companies, as well as results obtained from similar testing elsewhere.

#### Description and Outcome of Investigation # 1:

Amended Silicates™ were mixed in concrete with the following characteristics:

- 355 kg/m<sup>3</sup> total cementitious
- Water/cement ratio of 0.45
- No supplementary cementitious materials
- Water reducer
- Air entraining admixture – BASF MicroAir and Grace Darex II

Fresh and hardened concrete properties measured were:

- Setting time
- Air content – on selected mixes, air stability over a 60-minute period was recorded
- Strength – on selected mixes

Rheology

- Admixture interactions using the Lafarge Automated Test

#### *Results of Air-Entrainment Investigations*

The objective of the effort was to determine the air-entraining-agent dosage requirement as a function of the concentration of Amended Silicates™ to achieve 5% to 7% air in fresh concrete, and also to determine the impact of Amended Silicate™ concentration on concrete air content (fresh concrete) at a constant air-entraining-agent dosage.



Table 3 below provides the Amended Silicate™ concentrations in the cement and concrete samples tested.

**Table 3.** Summary of mixes tested.

Cement	AEA	Company	Nature of AEA	Amended Silicate™ Concentration, (wt% of total mix)						
				0.00	0.05	0.10	0.30	0.50	0.75	1.00
GU	MicroAir	BASF	Synthetic Detergent based on tall oil, fatty acids, and polyethylene glycol	No Add	AS	AS	AS	AS	AS	AS
GU	DAREX	Grace Concrete Products	Mixture of Organic Acid Salts: tall oil, fatty acids, rosin, and sodium dodecylbenzenesulfonate	No Add	AS	AS	AS	AS	AS	AS

GU = General Use Cement, AEA = Air Entrainment Additive, AS = Amended Silicates™

The range of Amended Silicate™ concentrations investigated was intended to cover the potential addition rates of spent Amended Silicates™ in fly ash, after injection at a power plant or other industrial facility, for the purpose of mercury control at that facility.

At a power plant or other industrial facility, the maximum anticipated concentration of Amended Silicates™ in the fly ash would be 2 wt%, but would normally be much less. Even if the maximum anticipated concentration of 2 wt% was achieved, and as much as 25 wt% of the fly ash was used in making the concrete, that would still only amount to 0.5 wt% spent Amended Silicate™ material being added to the concrete.

In some cases, as much as 40 to 50 wt% fly ash may be used in making concrete, for large structural projects. Even in these rare cases, the concentration of Amended Silicate™ added to the concrete would not be more than 1.0 wt%.

For this test, the Amended Silicates™ were manually blended with the cement before being introduced in the concrete mixer.

### Air-Entrainment Test Results

Air is intentionally entrained in concrete (using air entraining admixtures) to protect the material from the damages caused by the repeated cycles of freezing and thawing. Concrete is a porous material that can be saturated. Upon freezing, the water in the pores undergoes a natural expansion while transitioning from a liquid state to a solid state. If there is no room to accommodate this expansion, internal pressures are generated that can cause cracking that will evolve with the repetition of freezing and thawing cycles. Air entrained bubbles in hardened concrete provide space for water expansion, thus protecting concrete against freezing damages. The vast majority of concrete produced in North America is air entrained.

Air entraining agents are surfactants that stabilize the air entrained by the mixing operations.



Sorbents, such as all versions of powdered activated carbon (PAC), strongly interfere with air entraining agents, thus reducing the ability to entrain air in concrete as well as increasing the sensitivity to repeated cycles of freezing and thawing.

Amended Silicates™ on the other hand, are not sorbents, do not contain any carbon, and possess chemical and physical properties that are substantially the same as the fly ash in which it is collected. Therefore, Amended Silicates™, which reactively capture mercury in the stable HgS form, rather than adsorb mercury as PAC does, do not interfere with the air-entraining agents or reduce the ability to entrain air in concrete, as will be shown in the following test results.

In order to protect concrete against repeated cycles of freezing and thawing, the concrete should have an adequate total air content. A fresh concrete air content of 5 to 7 % is usually targeted.

In order to determine the impact of Amended Silicate™ concentration on concrete air entrainment, the amount of AEA required to entrain 5 to 7 % air in the concrete was determined by measurements. Tables 2 and 3 and Figure 1 present the results.

As shown for the entire concentration range, the impact of the Amended Silicates™ on air entrainment was minimal. Up to 0.5 wt% Amended Silicates™ with Microair and 0.75 wt% Amended Silicates™ with Darex, there was no measurable impact on air requirement. For higher Amended Silicates™ concentrations, the impact remains small. The slope of the curves was not steep, which implies a low sensitivity to Amended Silicate™ dosage.

The sensitivity of air requirement to PAC dosage (contamination of fly ash by PAC, from attempts to control mercury at power plants) is probably the biggest challenge from a ready-mix perspective.

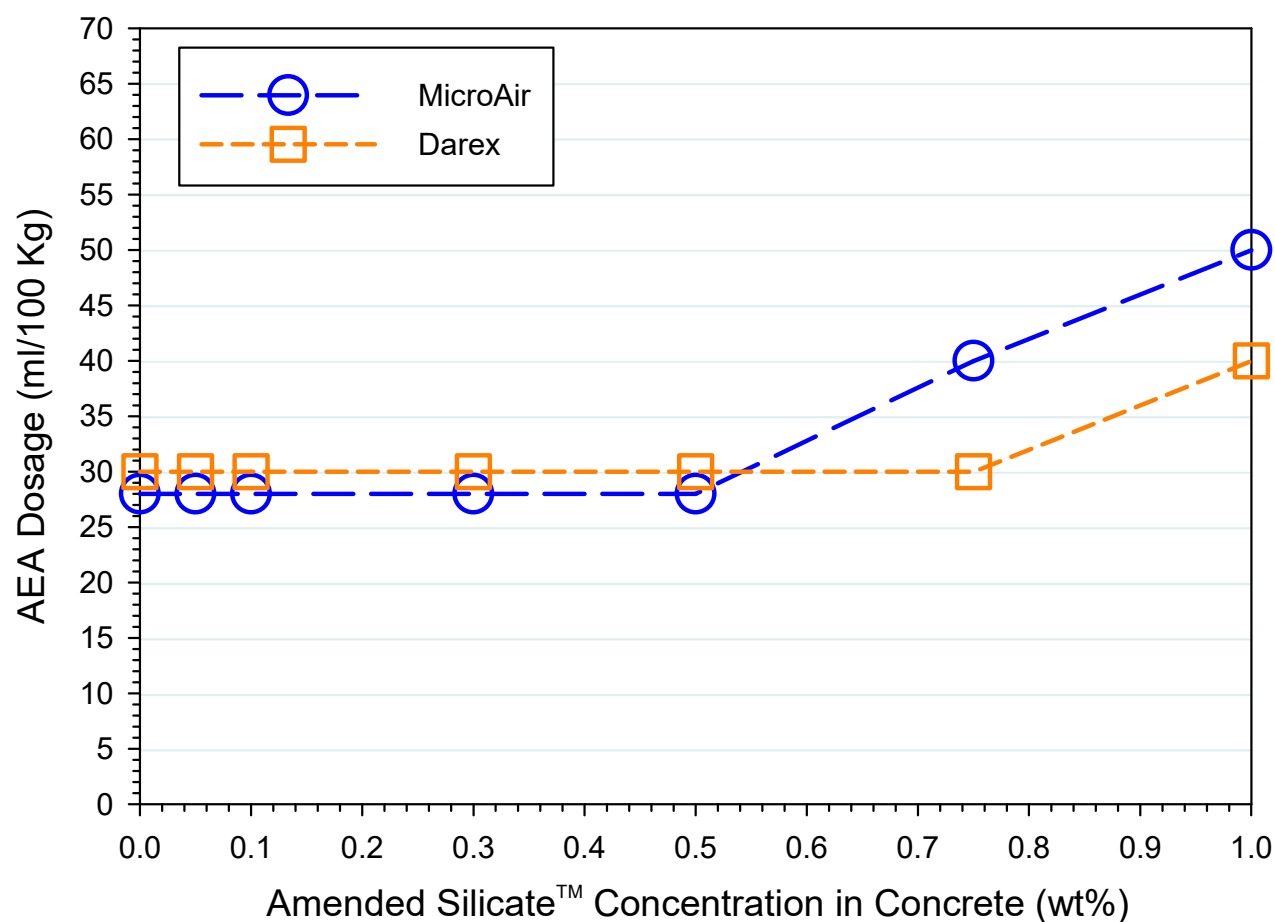
On the other hand, as shown in Tables 4 and 5, the air loss over a 60 minute period for the concrete mixes containing Amended Silicates™ is similar to the control mix, which indicates no specific impact on the air stability.

**Table 4.** Detailed Results at Constant Concrete Air Content with MicroAir.

Amended Silicates™	0.00 wt%	0.05 wt%	0.10 wt%	0.30 wt%	0.50 wt%	0.75 wt%	1.00 wt%
Cement	GU	GU	GU	GU	GU	GU	GU
AEA	MicroAir	MicroAir	MicroAir	MicroAir	MicroAir	MicroAir	MicroAir
AEA Dosage (ml/100 Kg)	28	28	28	28	28	40	50
Initial Air (%)	5.9	6.6	6.0	5.8	5.0	6.0	5.8
Air 30 min (%)	4.9	5.6	5.1	---	4.6	5.4	---
Air 60 min (%)	4.7	5.2	4.6	---	4.2	5.0	---
Air Loss (%)	1.2	1.4	1.4	---	0.8	1.0	---

**Table 5.** Detailed Results at Constant Concrete Air Content with Darex.

Amended Silicates™	0.00 wt%	0.05 wt%	0.10 wt%	0.30 wt%	0.50 wt%	0.75 wt%	1.00 wt%
Cement	GU	GU	GU	GU	GU	GU	GU
AEA	Darex	Darex	Darex	Darex	Darex	Darex	Darex
AEA Dosage (ml/100 Kg)	30	30	30	30	30	30	40
Initial Air (%)	7.1	6.0	6.1	6.0	5.8	5.1	5.6
Air 30 min (%)	5.9	4.8	5.2	---	5.1	4.5	---
Air 60 min (%)	5.4	4.2	4.8	---	4.7	4.3	---
Air Loss (%)	1.7	1.8	1.3	---	1.1	0.8	---


**Figure 1.** Impact of Amended Silicates™ on AEA requirement.

In order to determine the impact of Amended Silicate™ concentration in the concrete on air entrainment, the evolution of the concrete air content was examined at constant AEA dosage. The dosage of AEA throughout this series of tests correspond to the dosage required to entrain 5 to 7% air in a control mix that does not contain any Amended Silicates™.

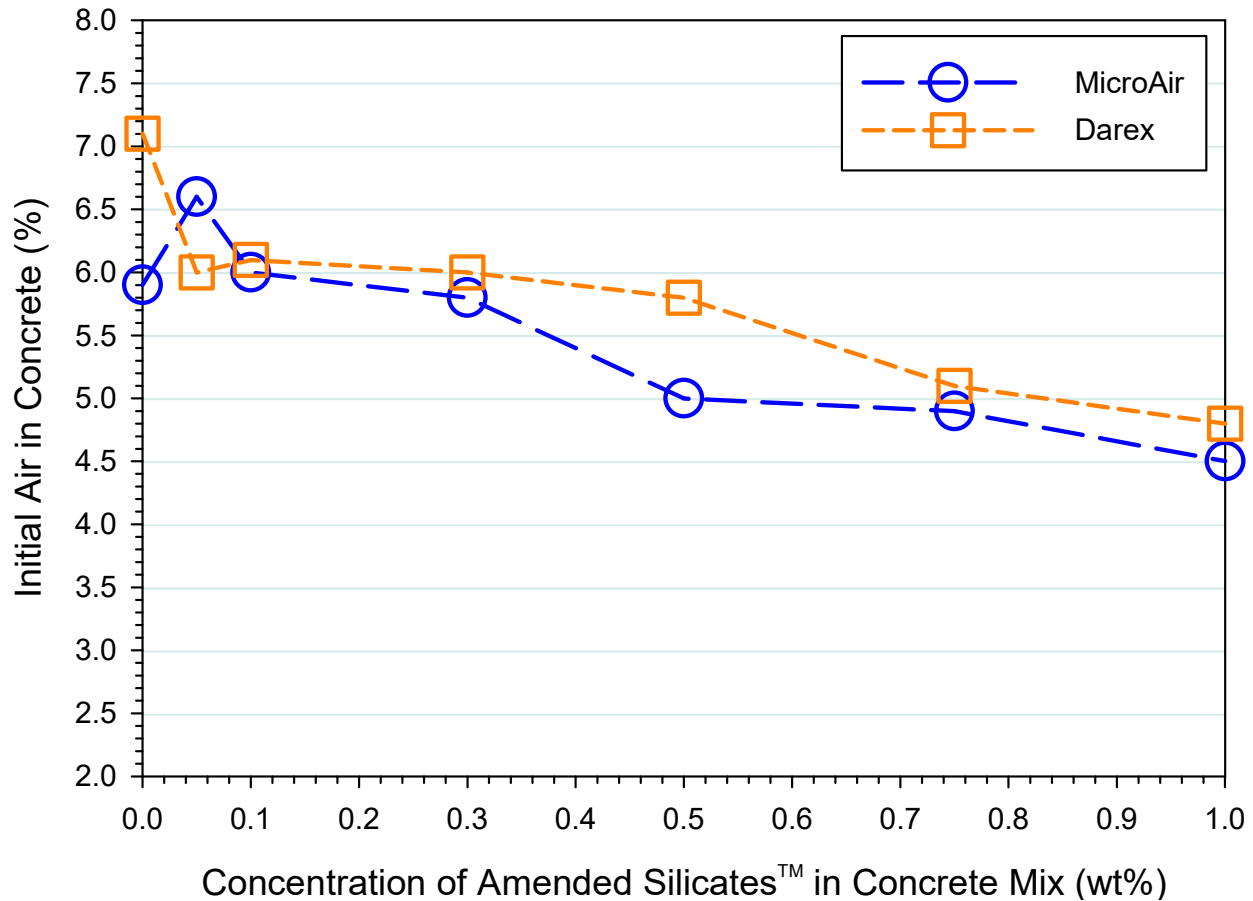
The results presented in Tables 6 and 7 and Figure 2, illustrate that an increase in the concentration of Amended Silicates™ has an almost imperceptible impact on air entrainment in concrete, starting at a sorbent dosage of 0.50% when tested with Microair and 0.75% when tested with Darex. Here again, the sensitivity of the concrete air content to the Amended Silicate™ concentration is small, and the initial-air decrease is very small.

**Table 6.** Detailed Results at Constant Air Entraining Agent Dosage – MicroAir.

Amended Silicates™	0.00 wt%	0.05 wt%	0.10 wt%	0.30 wt%	0.50 wt%	0.75 wt%	1.00 wt%
Cement	GU	GU	GU	GU	GU	GU	GU
AEA	MicroAir	MicroAir	MicroAir	MicroAir	MicroAir	MicroAir	MicroAir
AEA Dosage (ml/100 Kg)	28	28	28	28	28	40	50
Initial Air (%)	5.9	6.6	6.0	5.8	5.0	4.9	4.5
Air 30 min (%)	4.9	5.6	5.1	---	4.6	4.4	---
Air 60 min (%)	4.7	5.2	4.6	---	4.2	4.0	---
Air Loss (%)	1.2	1.4	1.4	---	0.8	0.9	---

**Table 7.** Detailed Results at Constant Air Entraining Agent Dosage – Darex.

Amended Silicates™	0.00 wt%	0.05 wt%	0.10 wt%	0.30 wt%	0.50 wt%	0.75 wt%	1.00 wt%
Cement	GU	GU	GU	GU	GU	GU	GU
AEA	Darex	Darex	Darex	Darex	Darex	Darex	Darex
AEA Dosage (ml/100 Kg)	30	30	30	30	30	30	40
Initial Air (%)	7.1	6.0	6.1	6.0	5.8	5.1	4.8
Air 30 min (%)	5.9	4.8	5.2	---	5.1	4.5	---
Air 60 min (%)	5.4	4.2	4.8	---	4.7	4.3	---
Air Loss (%)	1.7	1.8	1.3	---	1.1	0.8	---



**Figure 2.** Impact of Amended Silicate™ Concentration on Concrete Initial-Air Content.

*Impact of Amended Silicates on fresh and hardened concrete properties*

Table 8 presents results showing the impact of Amended Silicate™ concentration on fresh and hardened properties of concrete. As shown, the temperature was not impacted by the presence of Amended Silicates™. There seems to be a retardation effect with the microair admixture, while the setting times were not impacted when the Darex AEA was used. Although perhaps within the scatter and uncertainty associated with the strength test, the results indicate that Amended Silicates™ may cause a small drop in long-term strength when using the MicroAir AEA, while essentially no strength drop was observed with the Darex.

**Table 8.** Impact of Amended Silicates™ in fly ash on fresh and hardened concrete properties.

		Reference	Reference	Amended Silicates™	Amended Silicates™	Amended Silicates™	Amended Silicates™
	W.R.	210	ADVA 140	210	210	ADVA 140	ADVA 140
Parameters	Units	MicroAir	Darex	MicroAir	MicroAir	Darex	Darex
<b>MIX DESIGN</b>							
Water	Kg/m <sup>3</sup>	169	167	168	168	168	167
Cement GU	Kg/m <sup>3</sup>	359	355	358	357	358	355
Fine Aggregate	Kg/m <sup>3</sup>	745	737	744	740	742	736
Coarse Aggregate	Kg/m <sup>3</sup>	1062	1051	1060	1054	1058	1050
Water Reducer	ml/100Kg	180	200	180	180	200	200
AEA - MicroAir	ml/100Kg	28	30	30	42	28	38
Amended Silicates™	wt%	---	---	0.30	0.75	0.30	0.75
Unit Weight	Kg/m <sup>3</sup>	2308	2308	2308	2308	2308	2308
<b>PROPERTIES OF FRESH CONCRETE</b>							
Water/Cement Ratio	W/C	0.47	0.47	0.47	0.47	0.47	0.47
Temperature	°C/°F	21.5/70.7	21.5/70.7	23.0/73.4	23.0/73.4	22.5/72.5	22.0/71.6
Initial Air Content	%	5.9	7.1	5.3	5.6	5.3	6.0
30 min Air Content	%	4.9	5.9	---	---	---	---
60 min Air Content	%	4.7	5.4	---	---	---	---
Setting Time	hr.min	5.20	4.45	6.55	6.00	5.05	5.05
Setting Time repeat	hr.min	---	---	6.30	6.15	---	---
Unit Weight	Kg/m <sup>3</sup>	2335	2311	2360	2350	2342	2331
<b>PROPERTIES OF HARDENED CONCRETE</b>							
Compressive Strength	MPa	23.3	21.1	21.8	22.1	19.8	18.0
		35.3	32.9	35.8	34.4	34.8	32.7
		44.1	40.0	42.4	41.6	41.8	39.0

W.R. = Water Reducing additive

### *Impact of Amended Silicates™ on compatibility with other admixtures*

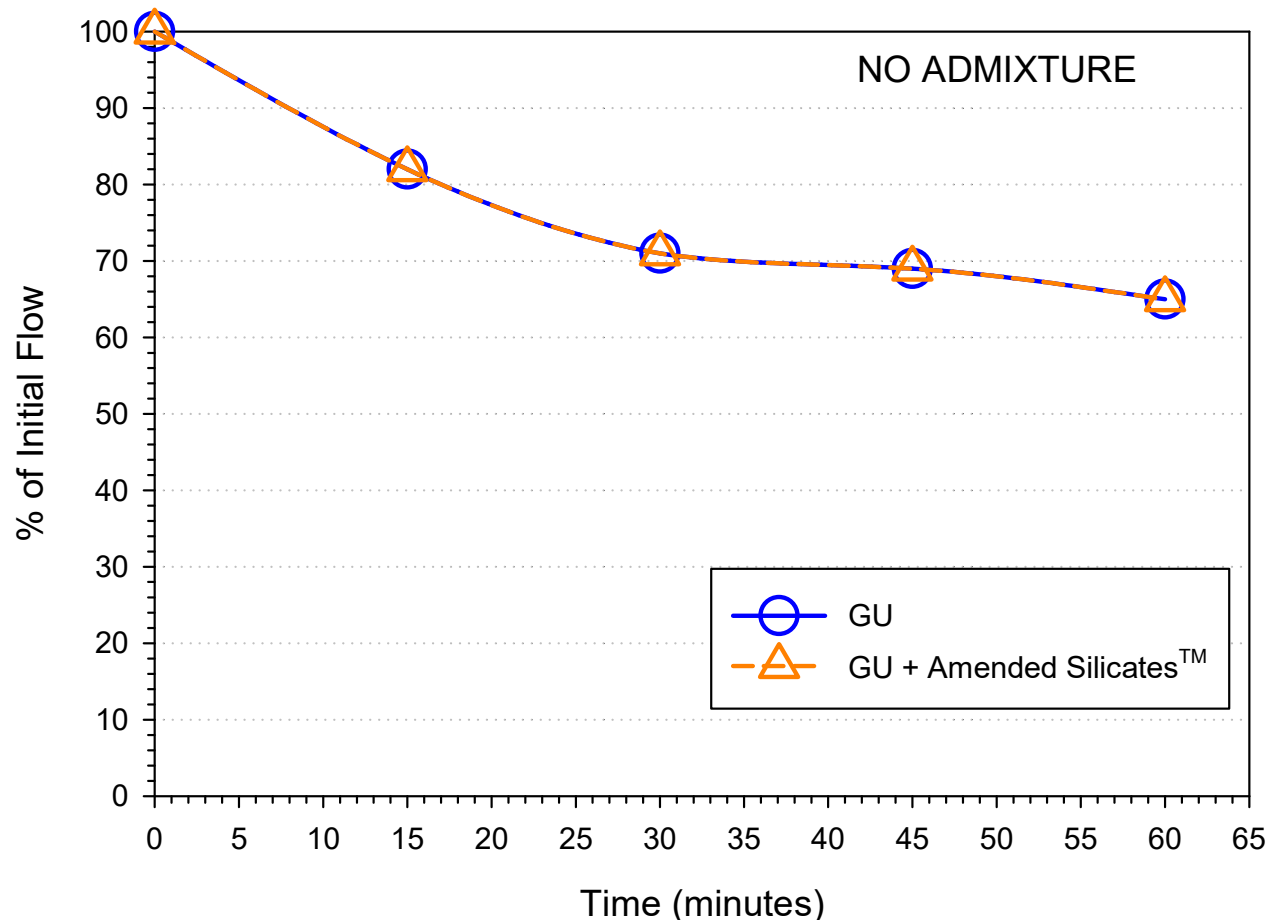
The potential interactions of Amended Silicates™ with other commonly used admixtures in the field was assessed using the Lafarge automated test, a 60-minute test designed for grouts, which was developed to highlight any potential compatibility problem between cements and admixtures.

The test consists of mixing a grout using a wearing blender, followed by a slump test with a mini cone that is lifted automatically to minimize operator variability, following which the spread of the grout is measured. The grout is maintained in continuous agitation between the spread measurements using a rotating cylinder. Results are reported as a percentage of initial spread. A drastic loss of spread highlights the potential for admixture incompatibility.

The Amended Silicates™ were tested with 2 different commonly used admixtures:

1. Pozzolith 210 – water reducer – glucose syrup based, and
2. Polyheed 997 – water reducer – lignosulfonate based

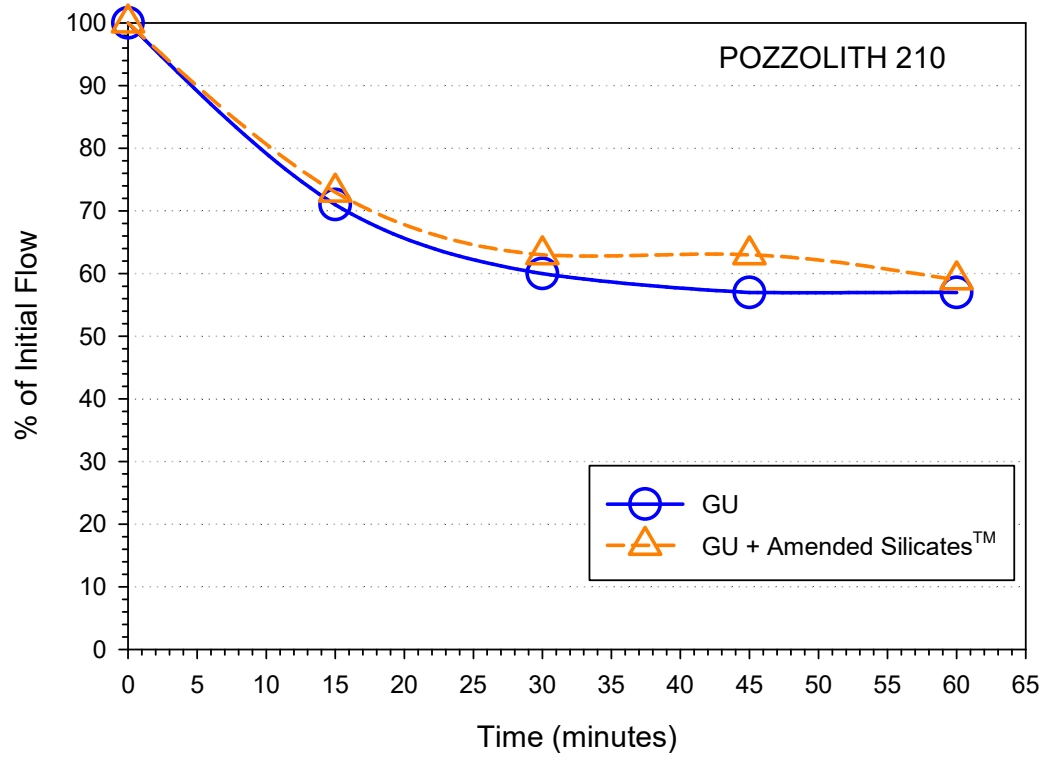
A high concentration of Amended Silicates™ (0.7%) was used to highlight any potential impact. Results are presented in Figures 3-5. The results indicate that there were no specific interactions with Pozzolith 210 and Polyheed 997 admixtures. The curves follow a similar pattern with or without Amended Silicates™. The gradual reduction in spread over time is expected.



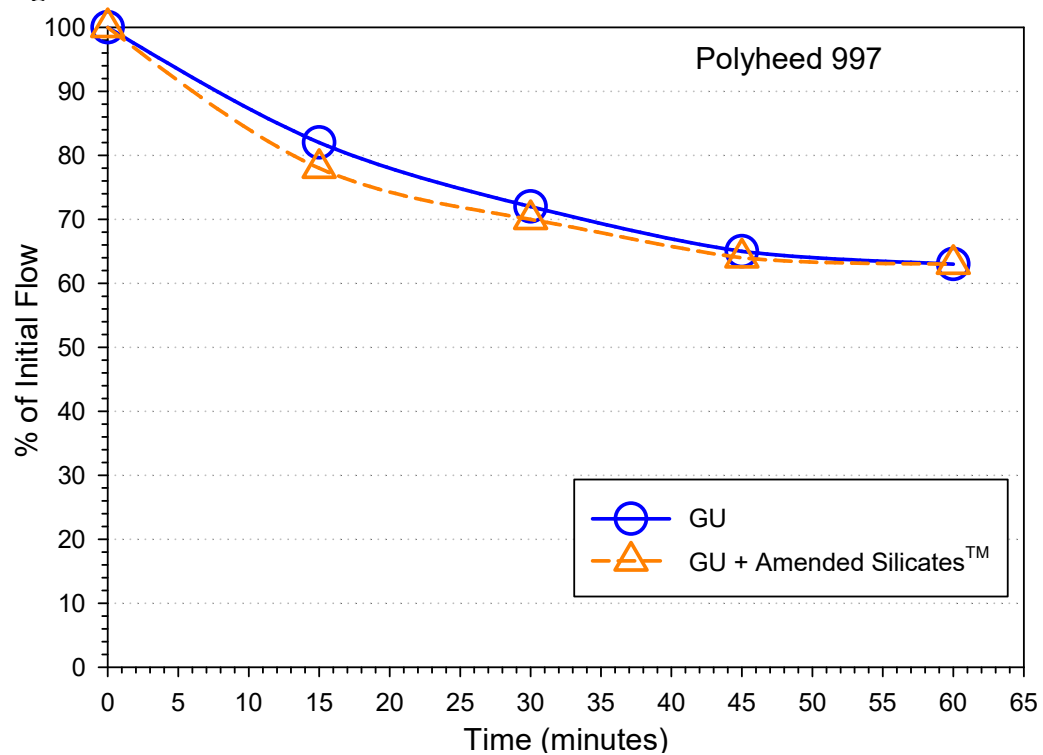
**Figure 3.** Initial flow vs time, without any additional admixture.

There are of course other admixtures that have not been tested, which may react differently with fly ash containing Amended Silicates™.

Environmental Energy Services (EES) will work with its clients and customers to obtain the information needed to ensure them that their fly ash will be salable for use in concrete and other purposes when using Amended Silicates™ for mercury control.



**Figure 4.** Initial flow vs time, with Pozzolath 200 admixture.



**Figure 5.** Initial flow vs time, with Polyheed 997 admixture.



## CONCLUSIONS FROM INVESTIGATION #1

Based on the test results described above, the following conclusions have been made:

- In the range of Amended Silicate™ concentrations tested, which is fairly high with respect to the concentrations expected to end up in the concrete, the required increase in AEA to maintain the necessary concrete air entrainment is fairly small.
- The air-retention properties of concrete are not impacted by the presence of Amended Silicates™.
- Setting time of the concrete was only slightly extended when tested with the MicroAir AEA, while no noticeable impact was measured when tested with Darex.
- The presence of Amended Silicates™ had little impact on the concrete strengths, but results differed slightly between AEA types.
- Results suggest a lack of any significant interactions between Amended Silicates™ in the fly ash and commonly used admixtures, although other specific superplasticizers, not specifically tested in this effort, may behave differently.

### Description and Outcome of Investigation # 2:

A direct comparison between spent Amended Silicates™ and Powdered Activated Carbon (PAC) was made, to determine their relative impact on concrete, from using fly ash in the mix.

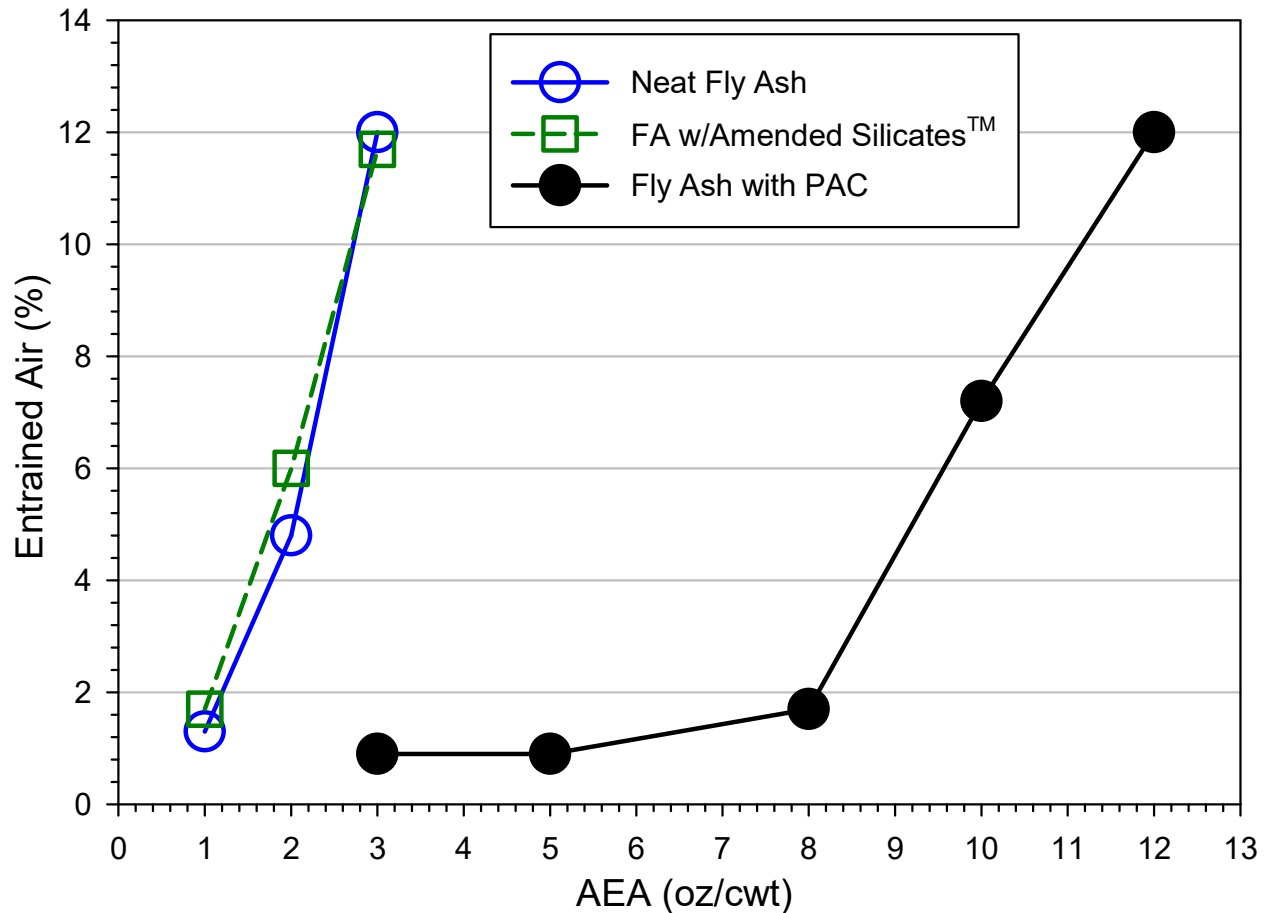
Fly ash samples were collected from a full-scale power plant. Samples were collected while injecting PAC to mitigate mercury emissions at the power plant. Samples were also collected at the same power plant while injecting Amended Silicates™ to mitigate mercury emissions.

These fly-ash samples, some containing spent PAC and others contain spent Amended Silicates™, were then tested for their concrete compatibility.

Figure 6 shows a comparison between fly ash containing spent PAC and fly ash containing spent Amended Silicates™ on the required addition of AEA and the associated entrained air within the concrete. As shown, the difference between the concrete produced using the neat fly ash and that produced using the fly ash containing Amended Silicates™ was negligible.

The fly ash containing spent PAC, on the other hand, required much more AEA in order to entrain the air needed in the concrete.

The impact of PAC on fly ash is often so great that it cannot be used in concrete or for other purposes, and must be landfilled. Although there are methods to remove PAC from fly ash or treat the fly ash with PAC in it, in order to make it compatible for use in concrete, these methods are often not capable of dealing with the concentration of PAC in the fly ash, and the fly ash must nevertheless be disposed of in a landfill.



**Figure 6.** Fly Ash Compatibility compared for Amended Silicates™ and PAC.

The foam index value is a measurement of the relative degree to which fly ash will adsorb surfactants such as air-entraining agents used in the production of concrete. While the unburned carbon content of fly ash is an important factor contributing to the foam index value, the adsorption capacity of the carbon is also a major influence, independent of the absolute concentration of carbon in the fly ash.

The use of conventional PAC for mercury control is known to greatly increase the foam index of fly ash, due to its high adsorption capacity, typically rendering the fly ash unsuitable for concrete production.

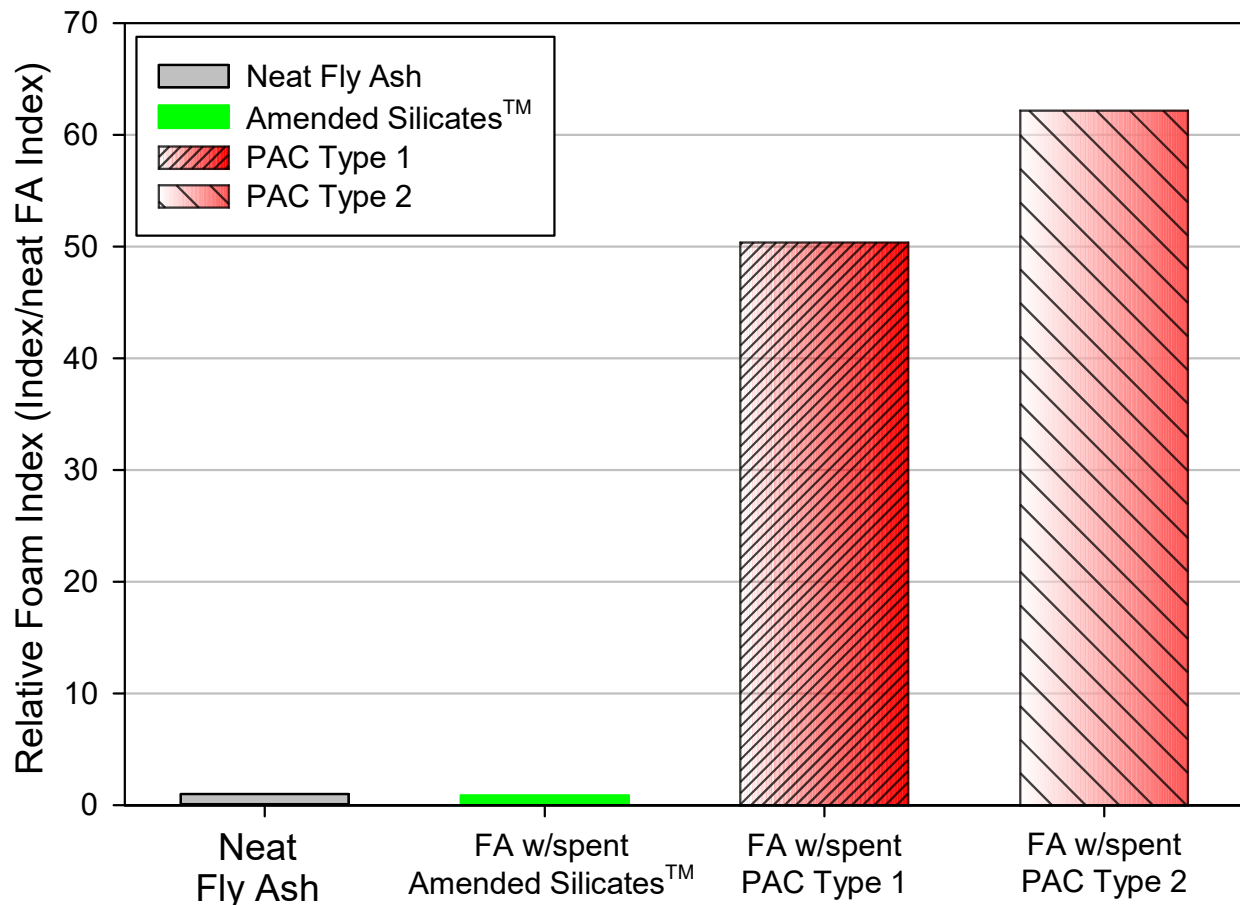
There isn't any one standard method for determining the foam index, and each cement and concrete company uses their own method. Consequently, the absolute values of foam index are not always comparable with other measured foam index.

In order to address this discrepancy, relative foam indexes have been calculated from the measured foam index, setting the neat fly ash foam index to 1.0, by dividing it by itself. The

relative foam index for the other samples were obtained by dividing their measured foam index by the measured foam index of the neat fly ash measured by the same method.

Figure 7 compares the relative foam index of neat Powder River Basin (PRB) fly ash with that of fly ash collected during injection of Amended Silicates™ and fly ash collected with different types of PAC injected for mercury control.

The relative foam index of the PRB fly ash containing spent Amended Silicates™ is very similar to and actually slightly less than that of the neat fly ash, while the relative foam index of fly ash containing spent PAC is over 50 times higher than that of the neat fly ash.



**Figure 7.** Relative foam index of PRB fly ash, with and without Amended Silicates™ and PAC.

## CONCLUSIONS FROM INVESTIGATION #2

Based on the test results described above, the following conclusions have been made:

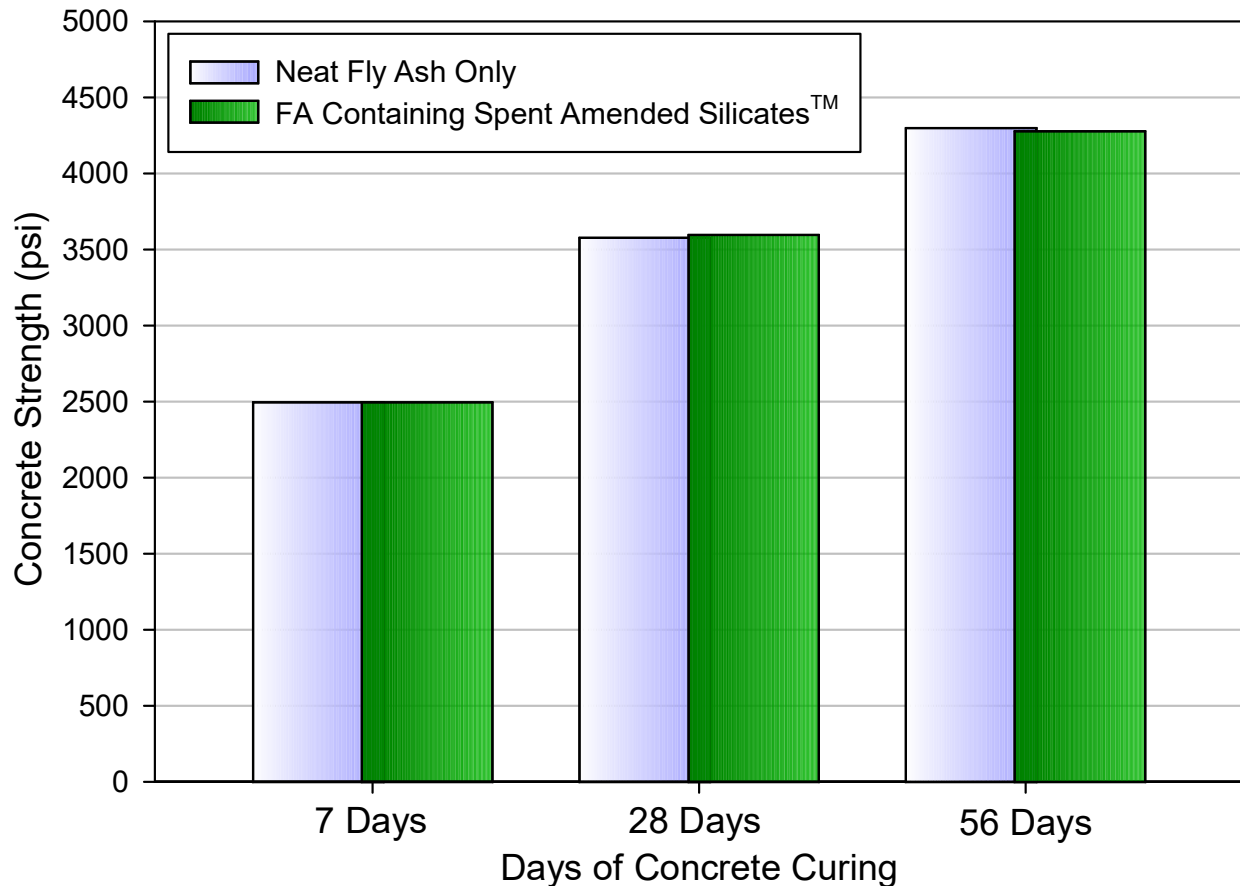
- Fly ash foam index is essentially unaffected by the presence of spent Amended Silicates™.

- Unlike Amended Silicates™, PAC was shown to increase the fly ash foam index by more than 50 times.
- Consistent with the conclusions regarding the impact of Amended Silicates™ and PAC on fly ash foam index, the entrained air in the concrete was essentially the same, with and without Amended Silicates™, while the presence of PAC required much more AEA in order to entrain the necessary air in the concrete.

#### Description and Outcome of Investigation # 3:

An independent investigation of concrete strength was performed using fly ash from a full-scale power plant, with and without spent Amended Silicates™, collected during times of Amended Silicate™ injection for mercury control at the power plant.

Figure 8 shows the resulting concrete strength measurements after 7, 28, and 56 days curing time. As observed, the strength measurements of the concrete made with fly ash with and without spent Amended Silicates™ contained therein were essentially identical.



**Figure 8.** Concrete Strength, made using fly ash with and without spent Amended Silicates™.

### CONCLUSIONS FROM INVESTIGATION #3

Based on the test results described above, the following conclusions have been made:

- The use of Amended Silicates™ for mercury control, will result in some amount of spent Amended Silicates™ being collected with the fly ash.
- The use of such fly ash, containing spent Amended Silicates™, does not have any deleterious impact on the strength of the fly ash at any stage of the curing process.

### Description and Outcome of Investigation # 4:

In order to specifically examine the impact of Amended Silicates™ in fly ash on the foam index, Sorbent Technologies, using their specific protocol and method for determining foam index, prepared multiple samples of fly ash (using a single starting fly ash type) with different added concentrations of Amended Silicates™.

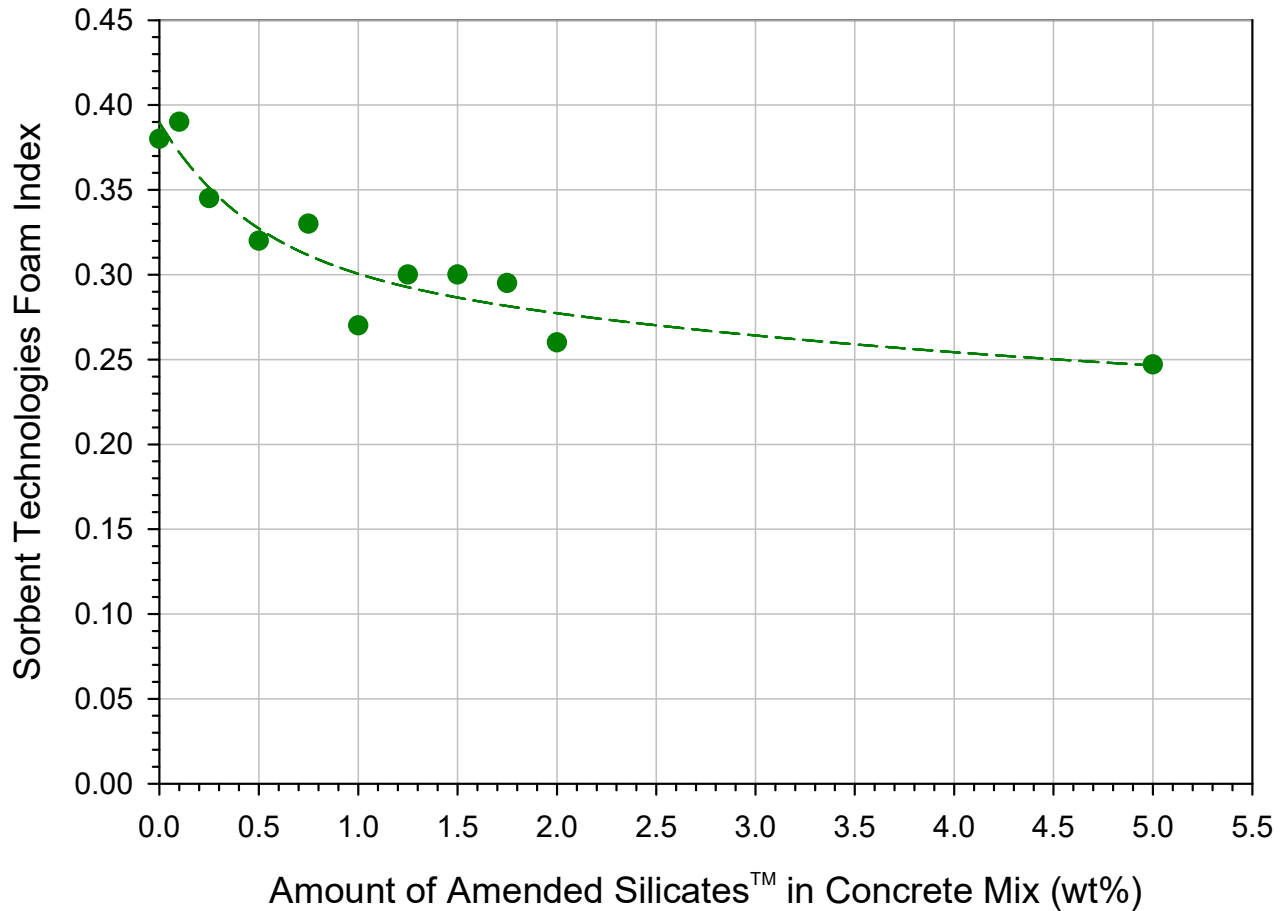
The neat fly ash used was a typical fly ash used in concrete, obtained from Cinergy's Miami Fort, Unit 6 boiler.

As shown in Figure 9, the foam index slightly decreased with increasing addition of Amended Silicates™. This decrease is quite possibly due to a dilution effect, as Amended Silicates™ do not contain any carbon.

Unlike the previous comparison above, with fly ash taken from a power plant, which contained spent Amended Silicates™, this investigation used fresh Amended Silicate™ powder to add to each sample of fly ash. The main difference between the fresh Amended Silicates™ and the spent Amended Silicates™ is that the minor surface coating of metal sulfides on the surface of the particles will be somewhat oxidized after passing through the boiler duct and collecting in the ESP or baghouse.

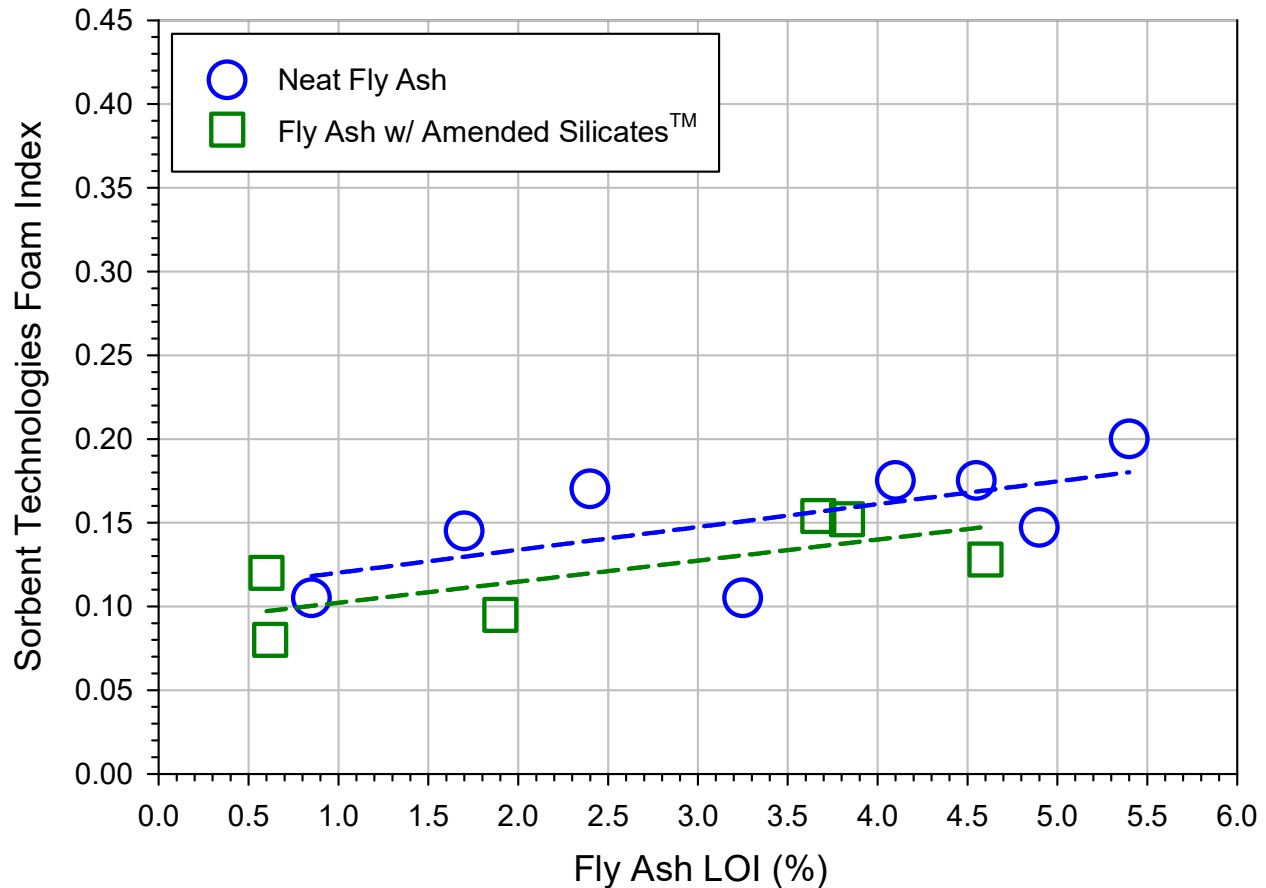
For the purposes of the present study, the concentration of Amended Silicates™ was extended out to 5 wt%, thus observing an extended range and potential impact on the foam index.

In practice however, the concentration of spent Amended Silicates™ would not be expected to ever surpass 2 wt%, and would most often be less than 0.5 wt%.



**Figure 9.** Foam Index vs Amended Silicate™ concentration in the fly ash.

In order to confirm that the impact of Amended Silicates™ on the foam index of fly ash was consistent, regardless of the loss on ignition (LOI) or unburned carbon (UBC) content of the fly ash, the foam index as a function of LOI was compared for the neat fly ash from Miami Fort Station and the same fly ash containing Amended Silicates™. As shown, the foam index of the neat fly ash increased slightly with increasing LOI, while that for the fly ash containing Amended Silicates™ also increased slightly with increasing LOI, illustrating that the fly-ash foam index relationship to LOI and UBC would not change when Amended Silicates™ were present.



**Figure 10.** Foam Index vs LOI for fly ash with and without Amended Silicates™ present.

#### CONCLUSIONS FROM INVESTIGATION #4

Based on the test results described above, the following conclusions have been made:

- Although spent Amended Silicates™ that collect with the fly ash in electrostatic precipitators and baghouses are a bit more surface oxidized, the behavior of fresh Amended Silicates™ in fly ash was determined to be similar to that of spent Amended Silicates™ collected with the fly ash at power plants.
- Increasing wt% of Amended Silicates™ decreased the overall foam index of fly ash.
- The presence of Amended Silicates™ in the fly ash did not change the relationship between the fly-ash foam index and its LOI or UBC content.
- Unlike other additives for mercury control, Amended Silicates™ not only effectively capture mercury, they also help increase the fly-ash suitability for beneficial use and help improve other balance-of-plant considerations.



### Description and Outcome of Investigation # 5:

The nature of the fly ash itself (dependent upon the coal fired and the plant configuration) at each power plant is a more significant factor in determining the suitability of the ash for use in making concrete than the small amounts of additives included therein.

Nevertheless, as some additives, such as PAC, can completely contaminate a fly ash so that it is not possible to use the fly ash in concrete or for other beneficial purposes, this investigation shows specific data for one power plant where Amended Silicates™ have been injected to control mercury, and the fly ash containing the spent Amended Silicates™ has been analyzed for suitable use in making concrete.

This document presents the testing of fly ash for concrete compatibility from a full-scale power plant injecting Amended Silicates™ product for mercury control. The test results were generated by using applicable ASTM methods and protocols, and meet the requirement of ASTM C618 for Class C fly ash, which is consistent with the analysis of the fly ash without injection of Amended Silicates™.

In part because of it is primarily composed of aluminosilicate clays and doesn't contain any carbon, Amended Silicates™ do not adversely impact the salability of fly ash as a pozzolan material. This feature has been confirmed by Headwaters Resources, an experienced fly ash marketer, and other users and manufacturers of cement and concrete, through numerous tests of power plant fly ash that contained spent Amended Silicate™ products.

The fly-ash samples used in this investigation were taken at various intervals during the full-scale testing of a 400MW power plant running at full load, burning PRB coal with a cold-side electrostatic precipitator (CS-ESP) particulate-collection system. Amended Silicates™ were injected at 150 lbs/hr during this testing sequence, delivering MATS compliant mercury removal at this rate.

Headwaters Resources tested the fly ash samples for concrete compatibility in addition to the required site-specific ASTM C-618 tests. Samples were analyzed for the full ASTM C-618 tests at their off-site lab.

The results of their analyses of the samples are shown in Tables 9 through 11.

**Table 9.** ASTM C618 / AASHTO M295 Ash Analysis Containing Spent Amended Silicates™.

Sample Type:	Random	Report Date:	2/3/2012
Sample Date:	12/6/2011	MTRF ID:	2425 WR
Sample ID:	Unit 5 Trial 369 MW		
<b>CHEMICAL ANALYSIS</b>			
	ASTM / ASSHTO Limits		
	Wt %	Class F	Class C
Silicon Dioxide (SiO <sub>2</sub> )	40.8		
Aluminum Oxide (Al <sub>2</sub> O <sub>3</sub> )	19.99		
Iron Oxide (Fe <sub>2</sub> O <sub>3</sub> )	6.16		
Sum of Constituents	66.95	70.0 % min	50.0 % min
Sulfur Trioxide (SO <sub>3</sub> )	1.03	5.0 % max	5.0 % max
Calcium Oxide (CaO)	21.56		
Moisture	0.05	3.0 % max	3.0 % max
Loss on Ignition (LOI)	0.77	6.0 % max	6.0 % max
		5.0 % max	5.0 % max
Available Alkalies, as Na <sub>2</sub> O	1.26	not required	not required
		1.5 % max	1.5 % max
<b>PHYSICAL ANALYSIS</b>			
Fineness, % retained on #325 Mesh	26.39	34 % max	34 % max
Strength Activity Index -	7-day or 28-day requirement		
7 day, % of control	93	75 % min	75 % min
28 day, % of control	94	75 % min	75 % min
Water Requirement, % Control	94	105 % max	105 % max
Autoclave Soundness, %	0.01	0.8 % max	0.8 % max
Density (g/cc)	2.67		

**Table 10.** ASTM C618 / AASHTO M295 Ash Analysis Containing Spent Amended Silicates™.

Sample Type:	Random	Report Date:	2/3/2012
Sample Date:	12/7/2011	MTRF ID:	2426 WR
Sample ID:	Unit 5 Trial 371 MW		
<b>CHEMICAL ANALYSIS</b>			
		ASTM / ASSHTO Limits	
	Wt %	Class F	Class C
Silicon Dioxide (SiO <sub>2</sub> )	40.87		
Aluminum Oxide (Al <sub>2</sub> O <sub>3</sub> )	21.10		
Iron Oxide (Fe <sub>2</sub> O <sub>3</sub> )	5.76		
Sum of Constituents	67.73	70.0 % min	50.0 % min
Sulfur Trioxide (SO <sub>3</sub> )	1.04	5.0 % max	5.0 % max
Calcium Oxide (CaO)	20.57		
Moisture	0.07	3.0 % max	3.0 % max
Loss on Ignition (LOI)	1.08	6.0 % max	6.0 % max
		5.0 % max	5.0 % max
Available Alkalies, as Na <sub>2</sub> O	1.23	not required	not required
		1.5 % max	1.5 % max
<b>PHYSICAL ANALYSIS</b>			
Fineness, % retained on #325 Mesh	26.26	34 % max	34 % max
Strength Activity Index -	7-day or 28-day requirement		
7 day, % of control	88	75 % min	75 % min
28 day, % of control	97	75 % min	75 % min
Water Requirement, % Control	97	105 % max	105 % max
Autoclave Soundness, %	0.03	0.8 % max	0.8 % max
Density (g/cc)	2.59		

**Table 11.** ASTM C618 / AASHTO M295 Ash Analysis Containing Spent Amended Silicates™.

Sample Type:	Random	Report Date:	2/3/2012
Sample Date:	12/8/2011	MTRF ID:	2426 WR
Sample ID:	Unit 5 Trial 399 MW		
<b>CHEMICAL ANALYSIS</b>			
		ASTM / ASSHTO Limits	
	Wt %	Class F	Class C
Silicon Dioxide (SiO <sub>2</sub> )	41.25		
Aluminum Oxide (Al <sub>2</sub> O <sub>3</sub> )	20.89		
Iron Oxide (Fe <sub>2</sub> O <sub>3</sub> )	5.74		
Sum of Constituents	67.88	70.0 % min	50.0 % min
Sulfur Trioxide (SO <sub>3</sub> )	0.89	5.0 % max	5.0 % max
Calcium Oxide (CaO)	20.92		
Moisture	0.05	3.0 % max	3.0 % max
Loss on Ignition (LOI)	0.79	6.0 % max	6.0 % max
		5.0 % max	5.0 % max
Available Alkalies, as Na <sub>2</sub> O	1.13	not required	not required
		1.5 % max	1.5 % max
<b>PHYSICAL ANALYSIS</b>			
Fineness, % retained on #325 Mesh	28.64	34 % max	34 % max
Strength Activity Index -	7-day or 28-day requirement		
7 day, % of control	92	75 % min	75 % min
28 day, % of control	103	75 % min	75 % min
Water Requirement, % Control	97	105 % max	105 % max
Autoclave Soundness, %	-0.01	0.8 % max	0.8 % max
Density (g/cc)	2.58		

## CONCLUSIONS FROM INVESTIGATION #5

Based on the test results described above, the following conclusions have been made:

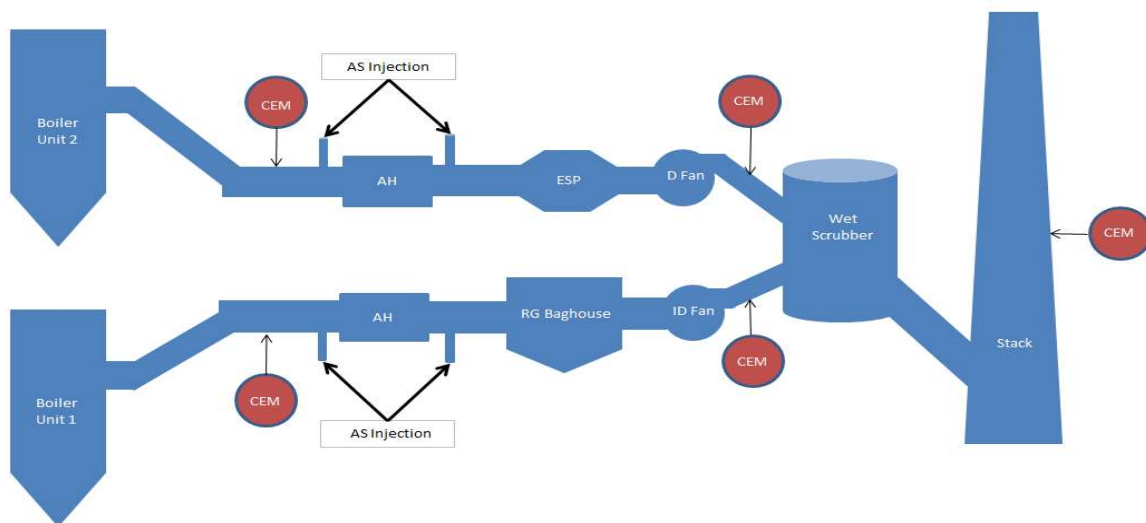
- As stated within the Headwaters report, the fly ash from this plant, which contained the Amended Silicates™ reagent, met the requirements of ASTM C618 for Class C fly ash.
- Also stated within the Headwaters report, the fly ash from this plant, which contained the Amended Silicates™ reagent, met the requirements of AASHTO M295 for Class C fly ash.
- Although not explicitly shown in the tables above, the fly-ash analysis was not substantially different than the neat fly ash analysis. This will be the case at all power plants using Amended Silicates™ for mercury control.

### Additional Evidence of the Concrete Compatibility of Fly Ash Containing Amended Silicates™:

In addition to the evidence provided in the descriptions of the 5 independent investigations above, fly ash containing spent Amended Silicates™ from full-scale power plants has been used to make concrete for many years, and the fly ash quality has never suffered from the use of the Amended Silicates™ for mercury control.

One particular power plant in the Eastern United States has used Amended silicates™ to control mercury in three large coal-fired units for a number of years, and they have been continually able to sell their fly ash for use in making concrete.

Figure 11 below shows the configuration of Units 1 & 2 at this power plant, which share a common scrubber. The combined capacity of Units 1 & 2 is approximately 670 MW.



**Figure 11.** Configuration of Units 1 & 2 at a U.S. power plant using Amended Silicates™ for mercury control, and selling their fly ash for use in concrete.

Figure 12 below shows the configuration of Unit 3 at the same power plant. Unit 3 alone is a 750 MW Unit. The combined capacity of all three units is greater than 1400 MW.

Prior to using Amended Silicates™, this U.S. power plant had to employ multiple technologies in order to meet their mercury regulatory limits, including the following:

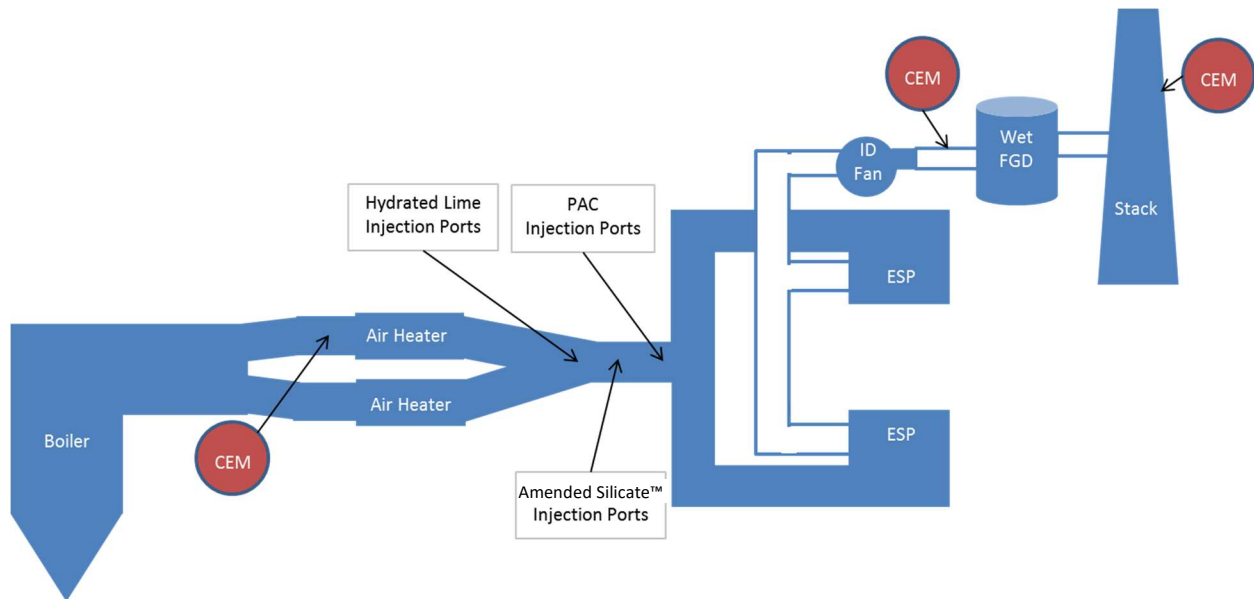
- A high injection rate of brominated Powdered Activated Carbon (BPAC) in order to absorb some of the mercury from the flue gas.
- Calcium Bromide injection on the coal, to aid in oxidizing the mercury, so that it could be more effectively captured by the BPAC and in the wet FGD scrubber.

- Injection of approximately 2000 lbs/hr of lime products in order to scavenge the SO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub> from the flue gas, in an effort to prevent the BPAC from being poisoned before it could capture any mercury.
- Scrubber re-emission additives to prevent mercury from emitting from the wet scrubber once it had been captured.

Although the utility has gone through multiple iterations of different types of control technologies and operational strategies, as they have dealt with vast differences in coal types burned at the plant, Amended Silicates™ alone was capable of replacing all of these additives, and thus controlling the mercury emission without help from any other additives.

At the Utility's discretion, Amended Silicates™ was used for years at the plant in conjunction with coal additives and scrubber re-emission additives to control the mercury emissions. Since the plant began using Amended Silicates™ to control their mercury emission instead of activated carbon, they have been able to sell all of their fly ash for use in concrete.

Interestingly, even though the plant employs a carbon/ash separation process on site, they were not able to correct the contamination of the fly ash by the PAC, even concrete-friendly PAC, to the point where they could sell it for any beneficial use, and were consequently still required to landfill their fly ash.



**Figure 12.** Configuration of ~750 MW Unit 3 at a U.S. power plant using Amended Silicates™ for mercury control and selling their fly ash for use in concrete.

This is one major example of a large full-scale utility boiler using Amended Silicates™ to control their mercury that has been able to sell their fly ash for use in concrete, without any setbacks or fly-ash quality degradation issues.

Without the Amended Silicate™ product, the Utility was forced to use large amounts of activated carbon, which prevented it from selling any of its fly ash.

## OVERALL CONCLUSIONS FROM ALL INVESTIGATIONS AND FINDINGS

The overall finding presented in this white paper on the compatibility of fly ash containing Amended Silicates™ for use in concrete are as follows:

- Amended Silicates™ evaluated as if it was a fly ash itself would be classified as both a C and F fly ash, based on the ASTM criteria for use of fly ash in concrete. Consequently, the addition of Amended Silicates™ for spent Amended Silicates™ collected with fly ash, does not change the classification of the neat fly ash, with regard to the ASTM classification.
- Amended Silicates™ do not contain any carbon, and do not contaminate fly ash, alter air entrainment in concrete, increase the foam index of the fly ash, or darken the fly ash or concrete into which it is mixed.
- Fly ash containing spent Amended Silicates™, tested with different additives commonly used in concrete (specifically Pozzolith 210 and Polyheed 997), were found not to have any observable interactions with the additives, and the behavior of the fly ash was observed to be the same, with or without spent Amended Silicates™ present.
- The presence of spent Amended Silicates™ in fly ash were observed not to impact the curing times or strength of the concrete in which the fly ash was mixed.
- Fly ash containing Amended Silicates™ has been evaluated by Headwaters and many other companies, expert in the concrete industry. These evaluations found and concluded that the fly ash easily passed all of the criteria for use in concrete.
- Among other things, the presence of spent Amended Silicates™ in fly ash was confirmed not to change the fly ash classification or to adversely impact its fineness or mineral composition.
- Finally, Amended Silicates™ have been used for years in coal-fired utility boilers for mercury control, allowing their fly ash to be sold and used to produce high-quality concrete, without any negative impacts or issues from the Amended Silicates™.

