This is a Reproduction of a Presentation on

Advantages of Amended Silicates for Control of Mercury Emissions from Coal-Fired Power Plants

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Outline

- Negative Health Effects of Mercury Species
- The Mercury Cycle: Why Mercury Emissions From Power Plants Matters
- Leaching of Mercury From Fly Ash Adsorption vs Mercuric Sulfide
- Mercury Capture from Coal-Fired Power Plants by Configuration
 - Plants with Dry Scrubbers and Circulating Dry Scrubbers
 - Plants with Wet FGD Scrubbers
 - Capturing mercury in ESP or baghouse, before scrubber, or without scrubber
- Amended Silicates Improve Quality of Fly Ash for Use in Concrete
- Added Benefits of Amended Silicates
 - ESP Conditioning
 - No Halogens, No Corrosion
 - No Leaching of Any Metals
 - No Negative Impacts on Scrubbers or Waste Water
 - Not Flammable and Not Corrosive
- Amended Silicates for Removal of Organics from Waste Incinerators
 Potential use of ash from incinerators in concrete
 - Potential use of ash from incinerators in concrete
- Conclusions



Negative Impacts on Health from Eating Fish High in Methyl Mercury





- Methyl Mercury is a Strong Neurotoxin, <u>Bio-accumulating</u> in Our Bodies
 - Only <u>very small concentrations</u> are required to yield toxic effects



- Loss of peripheral vision
- Lack of coordination of movements
- Impairment of speech, hearing, and walking
- Muscle weakness
- Developmental impairment in children and unborn fetus, resulting in damage to cognitive thinking, memory, attention, language, fine motor skills, and vision
- Many other negative health impacts too many to list here
- Elemental Mercury and Other Inorganic Forms are Also Toxic
 - o But they *require much higher concentrations* in order to have health impacts
 - And, they *do not bio-accumulate* in fish, animals, or humans.
 - Health impacts include damage to cognitive abilities, mental disturbances, muscle weakness, tremors, emotional changes, headaches, etc.





The Mercury Cycle





Mercury Leaching Potential from Fly Ash

- U.S. Department of Energy Study on Leaching of Mercury from Fly Ash
 - Found that Mercury Leaches Slowly from ALL Fly Ash Samples
 - With or without Activated Carbon
 - Reference: China Workshop on Mercury Control from Coal Combustion, October 31-November 2, 2005, Beijing, China
 - Drinking Water Standards Are Not An Appropriate Comparison Mercury emitted from power plants does not pose a concern for drinking water, in an oxidized inorganic form at relatively low concentrations.
- The Problem is with <u>Any</u> of The Mercury <u>Ever</u> Reaching Water Ways
 - Specifically, the sediments in the shallows of lakes and oceans
 - Where it will be converted to <u>Methyl Mercury</u> and bio-accumulate in fish and other aquatic life
- Because Carbon (unburned or activated) Only Adsorbs Mercury, Eventually
 - o All the mercury will leach from the fly ash and will be released into the water ways
 - If all the mercury eventually leaches into water ways, the problem is worse, transferring a regional and global problem into a local problem



The Mercury Cycle



Elemental Mercury Hg^o is a Global Issue–may deposit anywhere in the world

Oxidized Mercury Hg⁺⁺ is a Regional Issue – i.e., not likely to travel far beyond the boarders of China



Reactive Capture vs Adsorption

Activated Carbon Only <u>Adsorbs</u> Mercury Species

$$\circ Rate = \frac{dC_{Hg}}{dt} = -k_A C_{Hg} (\bar{C}_m - \bar{C}) + k_D \bar{C}$$
Adsorption Desorption

- Hg Adsorption is a function of mercury concentration (C_{Hg}) in the fluid
- Hg Desorption is a function of mercury adsorbed (\bar{C}) on the carbon
- If the water passing through the fly-ash product is clean (C_{Hg} = 0.0), then the adsorption rate will be zero, and some of the adsorbed <u>mercury will begin to leach</u>
- Amended Silicates <u>Reactively Capture</u> Mercury
 - HgS is formed, which is the *most stable form* in the Environment

Reactive Capture

HgS formed on Amended Silicates <u>will not leach</u>

○ Amended Silicates: Rate =
$$\frac{dC_{Hg}}{dt} = -k_1 C_{Hg} C_{AS}$$

Multiple Challenges with Powdered Activated Carbon (PAC) and Brominated Powdered Activated Carbon (BPAC)

Activated Carbon (PAC & BPAC) for Hg Control

Only Adsorbs Mercury – It also Desorbs Mercury – All Hg will eventually leach

Mercury Must be Oxidized by a Halogen (Bromine, Chlorine, or Iodine) First

Limited to Low Sorbent Utilizations – i.e., Typically < 0.2%

FLAMMABLE and EXPLOSIVE – Silo Fires have been a problem in the U.S.

Often Requires Halogen Addition to Coal to Help Oxidize the Mercury – Corrosion!!!

Contaminates the Fly Ash so that it Cannot be Used in Concrete – Difficult to Treat

PAC & BPAC Skip Through ESPs - Increasing Particulate Release and Plant Opacity

PAC and BPAC are Poisoned by $SO_3 / H_2SO_4 - Often$ Requiring Hydrate Injection

However Hydrate/Trona Injection Capture Halides Which Increases BPAC Rate 3-4 Times

Combined with Halogen (Br or I) Injection, Contaminates Waste Water

BPAC Causes Severe Corrosion of Storage Silos, Including Structural Damage

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Multiple Benefits of Amended Silicates

Amended Silicates for Hg Control

Non-carbon, mineral based products

Reactively captures both Hg^o and Hg²⁺

Stabilizes all metals in the fly ash – reduces leaching

NOT FLAMMABLE NOT CORROSIVE

No Halogens in the Product – Does NOT need Halogens

Preserves fly ash sales – Eliminates liability of landfills

Improves ESP Performance by Lowering Mix Resistivity

Compatible with Hydrate/Trona Injection

Tolerant to SO₃ / H₂SO₄

Small Carbon Footprint

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Coal-Fired Power Plant Configurations in China

SCR, Spray Dryer, Baghouse



SCR, Circulating Dry Scrubber



Baghouse or ESP + Wet FGD



Plants Without a Scrubber



Mercury Removal by Plant Configuration

- Selective Catalytic Reduction (SCR) for deNOx also Catalytically Oxidizes Hg
- Dry Scrubbers and Circulating Dry Scrubbers are Effective Capturing Hg
 - However, they will need some help in order to meet low Hg-emission targets
 - Halogen addition to coal + activated-carbon injection, or Amended-Silicate injection
- Wet FGDs Can be Effective at Capturing Mercury, but the Mercury Must be Oxidized
 - Requires Halide injection on coal + Activated carbon injection
 - o Often also require re-emission prevention chemical in wet scrubber
 - And often additional injected chemicals, plus landfill of fly ash
 - OR, Amended Silicates *alone* will work continued fly-ash use in concrete
- In Order to Capture All of the Mercury in the ESP or Baghouse
 - A high rate of Powdered Activated Carbon (PAC) is needed, along with injection of halides on the coal, other additives, and landfill of fly ash
 - AS-ULTRA is a new Amended-Silicate product that was designed for such applications and can effectively reduce the mercury in the flue gas, while maintaining high-quality fly ash for use in concrete – no additives are needed



Advantages of Amended Silicates in Dry Scrubbers and CDS Systems

- Amended Silicates Capture Mercury by Direct Chemical Reaction
- Adsorption and Desorption are NOT Part of the Capture Process
- Longer Residence Times are Characteristic of Dry Scrubbers & CDS
 - With Particularly Long Solids Retention Times (on the order of minutes)
 - Amended Silicates Reach Very High Product Utilization, i.e., > 95%
 - Activated Carbon utilization is typically < 0.2%
 - Very Little Product is Needed to Achieve the Desired Mercury Control
- Amended Silicates are the Lowest Rate and Cost Option in the Market
 - For Spray-Dryer Absorbers (SDA), and
 - Circulating Dry Scrubbers (CDS)
- Amended Silicates are Also NOT Corrosive, Contain No Halogens, and are NOT Combustible or Explosive



Black Hills (U.S. Plant) – Process Flow Diagram





Wygen 1 – SDA / BH Approx. Avg Inj Rate of 60-80pph



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Dry Fork Station, U.S. – Circulating Dry Scrubber





Dry Fork Station U.S. Plant with CDS



Mechanism for Plants with Wet FGDs

- Product Catalytically Oxidizes Mercury in the Flue Gas
 - $\circ~$ Using the HCI inherent in the flue gas, derived from the coal
 - Amended Silicates do NOT contain any halides
- Amended Silicate Hg Oxidation Rate
 - o Is many times greater than its mercury capture rate
 - Therefore, very little product is required for mercury control
 - $\circ~$ Does NOT add anything to the flue gas or the Wet Scrubber
 - Does NOT encourage re-emission of mercury from the scrubber
- Multiple Tests at Plants with Wet FGDs
 - o A small rate of product injection achieved high mercury oxidation
 - $\circ~$ All the product was captured in the ESP, and
 - The mercury was captured in the scrubber



Unit 3 of Plant with Wet FGD – U.S. Plant



- Sells Fly Ash (UBC separation process on site)
- Eastern Bituminous Coal High Sulfur
- CaBr₂/Hydrated Lime/BPAC/Re-emission chemical CEM Could not sell fly ash even with concrete friendly PAC CEM Amended Silicates replaced all these additives Wet ID FGD Fan Hydrated Lime PAC Stack Injection Ports Injection Ports ESP Air Heater **Utility Saves** ~\$6 Million/year Air Heater for Unit 3 Alone ESP Boiler CEM

AS-022 Injection Ports



New Amended Silicate Product for Capturing All Hg in ESP or BH

- For Plants Without a Scrubber, <u>Or For Capturing All Mercury Before Scrubber</u>
- Plants Configured with a Stand-Alone Cold-Side ESP Require All the Mercury to be Captured on the Powder Product and Collected in the ESP
 - Characteristic of very short residence times, i.e., several seconds at most
 - EES, Inc. has developed a separate product for these plants
- AS-ULTRA is the New Amended Silicate Product for Such Applications
- AS-ULTRA has a Very High Mercury Capture Rate
- AS-ULTRA Maintains All of the Other Benefits of Other Amended Silicate Products



Progress of the Product for Plants Without Scrubbers



Concrete Compatibility of Amended Silicates

- Amended Silicates Alumino-Silicate Clay Base Improves Fly Ash Quality
 - Foam Index same as no-carbon PRB fly ash
 - Strength Test Amended Silicates makes concrete stronger
 - Air Entrainment Only positive impacts on cement
 - Color No darkening improves brightness
- No Treatment of Fly Ash is Necessary to Make Fly Ash Suitable
- Wet FGD Plants in the United States have been Using the Amended-Silicate Product and Selling Ash for Two Years
- Many Other Independent Tests have Shown Fly Ash with Amended Silicates Passes All of the Concrete-Suitability Tests (both Class C & F)
- Fly-ash Trial Samples have been Analyzed by Separation Technologies, Ash Grove, Lafarge, Suwannee Cement, and National Cement





Amended Silicates Improve ESP Performance when Mixed in the Fly Ash



$$\Delta V_{ash} / R_{ash} = 1$$

 ΔV across ash layer depends on thickness and resistivity of ash.

Corona current carries charge to particles.

Particle capture is driven by electric field, which is Inversely proportional to R_{ash}.

Lower Ash Resistivity: More energy to electric field, which drives migration to plates.



Not Flammable, Not Corrosive, Stabilizes Metals

- Not Flammable or Explosive
 - Independent testing by Chilworth found
 - Amended Silicates are NOT flammable, and
 - Have an explosibility index $(K_{st} = 0)$ of zero
- Not Corrosive
 - Amended Silicates do NOT contain any halides
 - Amended Silicates do NOT contain any acids or other corrosive materials
- Fly Ash Collected During Injection of Amended Silicates
 - Was tested via EPA Methods 1311 (TCLP) and 1313 (Leachability as a function of pH)
 - Leaching of ALL metals was significantly less in the presence of amended silicates
- Most Environmentally Friendly Product on the Market

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AS-DIOX for Waste Incinerators

- Waste to Energy Plants Eliminate the Need to Landfill
 - Eliminates the need to landfill fly ash
 - Also provide a renewable source of electricity
 - Eliminates groundwater pollution as a result
 - <u>Combined with Amended Silicates for mercury control, may</u> <u>allow fly ash from incinerators to be used in concrete</u>
- AS-DIOX is Another Amended-Silicate Product
 - Destroys all toxic dioxins and furans from waste incinerators
 - Eliminates AC (which only adsorb dioxins & furans)
- AS-DIOX Benefit to Waste-to-Energy Plants
 - $\circ~$ Much less expensive than other technologies, including AC
 - Much more effective at eliminating these toxic pollutants

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AS-DIOX Bench Performance Results

Table 1. AS-DIOX Performance Compared with Alternative Effective Sorbent.

Dioxin Mitigation Product	% Dioxin/Furan Removed at 180 °C	% Dioxin/Furan Removed at 450 °C	Doses before Deactivation
AS-DIOX	100%	90%	> 30
Other Non-C Dioxin Sorbent	90%	5%	12
Activated Carbon	70%	0.0%	~25

For the environment, for safety, for your plant economics, AS-DIOX is the right choice.

AS-DIOX Combined with Amended Silicates for Hg control, may allow fly ash from incinerators to be used in concrete





Summary

- Mercury is Highly Toxic, Especially Methyl Mercury
 - Mercury from power plants is converted to methyl mercury in sediments under water
- Coal-Fired Power Plants Emit Mercury that Ultimately Gets in the Water Ways
 - The issue with mercury emitted from power plants is that it ends up in the fish we eat
 - PAC or other means of capturing mercury without sequestering it, makes problem worse
 - Amended Silicates reactively capture mercury in the stable form of HgS won't leach
- Mercury will Be Effectively Captured in the Existing Power Plants in China
 - They will need a little help as regulatory limits of mercury emissions are lowered
 - Activated carbon will leach the mercury and has other balance of plant issues
 - Halides injected to oxidize mercury will increase corrosion and contaminate the water discharge
- Amended Silicates Provide Solutions for All Power Plant Configurations
 - Effectively capturing or oxidizing the mercury as desired for each configuration
 - o Sequestering the mercury in the stable HgS form, where no leaching will occur
 - Amended Silicates are compatible with injection of other chemicals and processes
 - Amended Silicates do not corrode the duct work, air heaters, or cause other balance-of-plant issues
 - o Amended Silicates prevent leaching of mercury and reduce leaching of all other metals from the ash
 - o Amended Silicates condition ESPs, eliminate the need for landfills, and are tolerant to sulfuric acid
- Amended Silicates Improve the Quality of Fly-Ash for Use in Concrete

