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Concrete-Friendly™ Powdered Active Carbon (C-PAC™) for Safely Removing Mercury from Flue Gas

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Primary Sponsor: Albemarle Corporation
With partial support from NSF and DOE

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The nominated technology is not eligible for the small business or the academic award.

The focus area: This technology is nominated for The Design of Greener Chemicals Award. The novel C-PAC composition features the following green principles:

1. Reduction of mercury emissions and safe sequestrations in concrete
2. Prevention of hazardous waste
3. Less hazardous chemical synthesis
4. Designing a safer chemical
5. Solvent-free process
6. Elimination of post treatment and resulting waste
7. No derivatization

Technology developed in the United States with partial support from NSF and DOE.

Abstract: The novel mercury sorbent, C-PAC, was developed from renewable carbon sources with greener manufacturing pathway. It removes large amounts of mercury from air, it is concrete-friendly, and eliminates the need for large amounts of landfill space.

Coal-fired power plants emit 45 tons of gaseous mercury to air and produce 65.5 million metric tons of fly ash annually. This fly ash has a composition similar to volcanic ash and is an excellent replacement for cement in concrete. Currently, it is used in about half of the concrete produced in U.S. Of the 65.5 million metric tons of fly ash generated in U.S. in 2008, more than 11.5MM tons were beneficially used in concrete and 16.0MM tons were used in structure fills, soil modification, and other applications. According to the EPA's 2008 report to congress, federal concrete projects used 5.3MM tons of fly ash in 2004 and 2005. This led to savings of about 25 billion megajouls of energy, 2.1 billion liters of water, and reduced CO_2 emissions by about 3.8MM tons.

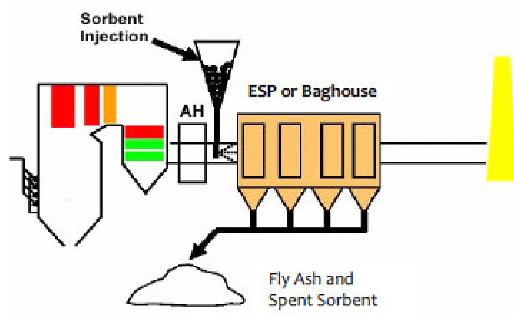
Powdered Activated Carbon Injection (ACI) technology significantly reduces mercury emissions by power plants. However, contamination with conventional mercury sorbents renders fly ash unsuitable for concrete and thus generates huge amounts of waste that has to be landfilled. More than 322MM cubic feet of landfill space would be needed to dispose 11.5MM tons of fly ash. These additional landfills would cost about $196 million to develop, fill, and maintain.

Albemarle, with partial funding from NSF, designed, synthesized, developed, and commercialized the novel Concrete-Friendly mercury sorbent, C-PAC, which efficiently captures mercury and preserves the quality of fly ash for concrete use. C-PAC was plant tested in 2006 with support from DOE and is currently used in several power plants across US. Here we provide data from the commercial use of C-PAC and its impact on saving landfill space, elimination of mercury from the air, and economic return.

1. Background: Coal fired power plants that supply half of U.S electric power, emit 45 tons of mercury each year. The fly ash generated after coal combustion is virtually identical in its composition to volcanic ash and is ideal for concrete use. According to the American Coal Ash Association, the US produced 65.6 million metric (MM) tons of fly ash in 2008. Replacing cement in concrete is the primary use of fly ash. About 11.5MM tons of fly ash went to concrete market in 2008[1]. According to United States EPA's 2008 Report to Congress[2], federal concrete projects used an estimated 5.3MM tons of coal fly ash in 2004 and 2005 combined. This substitution created a number of significant environmental benefits:

- Lowered energy consumption by approximately 25 billion megajoules
- Reduced water consumption by two billion liters
- Removed an equivalent emission of 3.8MM tons carbon dioxide from air
- Saved 148.4 million cubic feet of landfill space and reduced the need for 3,477 acre-feet of landfill space[3].

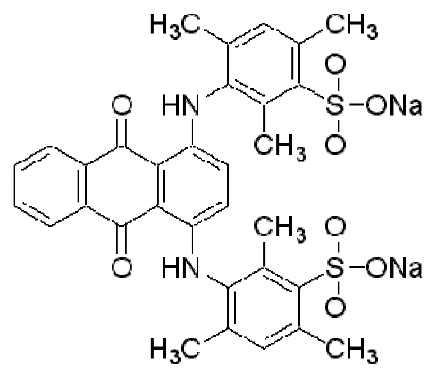
While the United States EPA is developing new federal regulation on mercury emission based on Maximum Achievable Control Technology (MACT), 20 states have started controlling their own mercury emissions by up to 70-90%[4]. For the majority of the coal-fired power plants, the leading technology to comply with the new mercury regulations is the Active Carbon Injection (ACI)[5]. It injects powdered activated carbon (PAC) based mercury sorbent into the flue gas to capture mercury. The carbon sorbent is injected in front of the plant's existing particulate control devices, either Electrostatic Precipitator (ESP) or Fabric Filter (FF) baghouse, as shown in the figure above. Currently, 150 ACI systems have been installed by the coal-fired power plants across the country[6]. However, PAC sorbent changes the composition of the fly ash and makes it incompatible with concrete and it has to landfilled[7]. Therefore, there was an urgent need to develop Concrete-Friendly mercury sorbent that would allow the fly ash to recycle into concrete. The other challenge was to produce PAC sorbent from renewable feedstock like coconut shells and waste wood to make it CO_2 neutral. To address these challenges, with partial funding from NSF, Albemarle Corporation successfully developed Concrete-Friendly sorbent, C-PAC.



2. The technology: PAC sorbent is produced by treating a carbonaceous substrate with an effective amount of a bromine-containing gas as disclosed in US 6,953,494[8]. These sorbents effectively remove mercury from the flue gas, but at the same time, ***they deleteriously interact with the Air Entraining Admixtures (AEA) in the concrete slurry and as such make the fly ash useless for concrete production and it has to be landfilled***. The presence of bromine enhances gas-phase mercury species capture [elemental (Hg^0) and oxidized mercury (HgX_2)] by brominated activated carbon (PAC-Br) as described below:

$$\text{PAC-Br(s)} + Hg^0(g) \rightarrow \text{PAC-HgBr (s)}$$
$$\text{PAC-Br(s)} + HgX_2(g) \rightarrow \text{PAC-HgBr(s)} (+ X_2) \quad X=Br \text{ or } Cl$$
$$\text{PAC-Br(s)} + HgX_2(g) \rightarrow \text{PAC-HgXBr(s)} (+ X) \quad X=Br \text{ or } Cl$$

Unlike conventional PAC-Br sorbents, C-PAC prevents Air Entraining Admixture (AEA) adsorption that is the critical factor for concrete compatibility. It is produced by careful selection of carbon feedstock, tailored microstructure, proper surface chemistry and a greener manufacturing process (WO 2008/064360[9]). The key to development of C-PAC is careful monitoring of the extent of its acid blue 80 (AB80) (CAS 4474-24-2; see the figure to the right) adsorption or Acid Blue Index (ABI). Through numerous theoretical and experimental investigations a criterion for ABI was established. Subsequently the PAC manufacturing process was modified to develop products with the specified ABI[9]. In summary the C-PAC product:

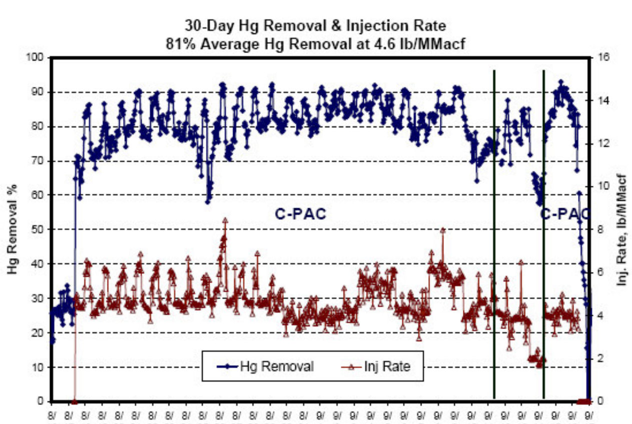


- Safely sequesters mercury from waste gas streams
- Exhibits little interference with the AEA compounds in concrete slurry
- Can be made in traditional commercial equipment and with methods that apply to existing activated carbon production
- Is made from renewable carbon sources and are concrete-friendly
- Is more effective (20-30%) than competing materials in mercury removal from flue gas.

The C-PAC technology meets the following principles of Green Chemistry:

1. Prevention of hazardous waste
2. Less hazardous chemical synthesis
3. Designing a safer chemical
4. Solvent-free process
5. Elimination of post treatment and resulting waste
6. New metric for in-process assessment of product (ABI)

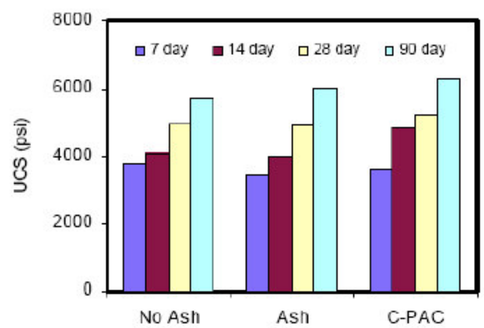
The first full-scale plant trial of C-PAC was carried out at Midwest Generation's Crawford Station Unit 7 in Chicago in the summer of 2006 with the support from Department of Energy[10,1]. The Crawford Unit 7 fires Powder River Basin (PRB) coal and most of the plant's fly ash is sold for concrete use. During the month-long continuous test, C-PAC was injected at an average rate of 4.6 pounds of sorbent per million actual cubic feet of flue gas (lb/MMacf). An average total mercury removal rate of over 80% was achieved, as indicated in the figure on the left. C-PAC was further tested by more than 14 full-scale power plants with various configurations and the value and capacity of C- PAC for removing mercury was confirmed[11-14].



In collaboration with two major fly ash marketers in the US (Headwater Resources and Lafarge), we examined the concrete compatibility of the fly ash generated at Midwest Generation's Crawford Station[15]. The results of these studies are summarized below.

Air content of fresh concrete: The performance of C-PAC was compared with a non-sorbent control and an alternative commercial PAC. To make concrete with 6 vol% voids, about twice the amount of AEA additives was needed for C-PAC, while approximately ten times the amount of AEA was needed for the alternative PAC. Even though somewhat more AEA was required in the C-PAC concrete than in the non-sorbent control to achieve the same air content, the dosage still satisfied the contractor specifications. Furthermore, we found that the properties of fly ash with C-PAC were very consistent, even more consistent than the control fly ash. The added cost of more AEA is negligible relative to the benefits of utilizing the fly ash in concrete production and eliminating the cost and environmental impact of the landfill.

Unconfined compressive strength (UCS): Compressive strength is the capacity of the concrete to withstand axially directed compressive forces. Concretes produced with fly ash containing C-PAC met the target compressive strength of 4000 psi at 14 days. In fact, it appears that the C-PAC also improves early strength relative to the control as shown in the figure on the right.



Stability of mercury in fly ash and concrete: To assess the effect of C-PAC on the stability of the mercury in fly ash and concrete, we followed EPA's Toxic Characteristic Leaching Procedure (TCLP) and Synthetic Groundwater Leaching Procedure (SGLP). The fly ash collected during the Crawford mercury emission control trial was tested and the results are summarized in Table 1.

Table 1. Mercury Leaching Test Results of the Blank and ACI Fly Ashes

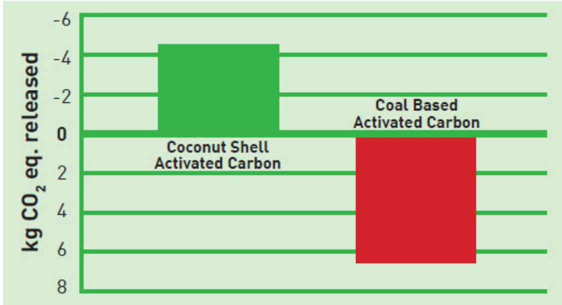
Fly Ash	**Hg Content** ppb	**Hg Content in Leachate, ng/l**		
		DI Water	Acetic Acid	Sodium Carbonate
Blank extraction solution		11	13	25
Baseline fly ash without mercury sorbent	39	15	9	34
Fly ash with C-PAC	2004	22	5	14

The fly ash samples containing the mercury sorbent generally exhibited a lower rate of mercury release even though it contained as much as two orders of magnitude more mercury. In all cases except for distilled water, the mercury leachate concentration from the long-term fly ash samples was below that of the bland extraction solution.

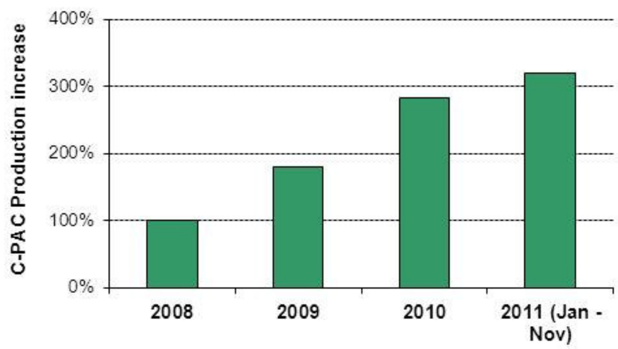
Stability of mercury in fly ash was also confirmed by others. In a 2008 report[5], the Department of Energy researchers concluded that "not only have the ACI mercury control technologies demonstrated capture of Hg that would otherwise be released into the environment, but the mercury has generally been shown to be retained in the control technology by-products under conditions of laboratory leaching tests. For some of these materials, the tests performed in this study show these control technology ashes, in spite of their higher mercury content, to be environmentally more stable with respect to mercury release than the corresponding baseline ashes of lower mercury content." This further confirms that mercury would be safely sequestrated in concrete by C-PAC.

Other properties of concrete with C-PAC laden fly ash including air stability, air voids distribution, and setting time were also investigated and it was confirmed that C-PAC mercury sorbents at appropriate dosage levels do not deleteriously affect any of the important properties of concrete.

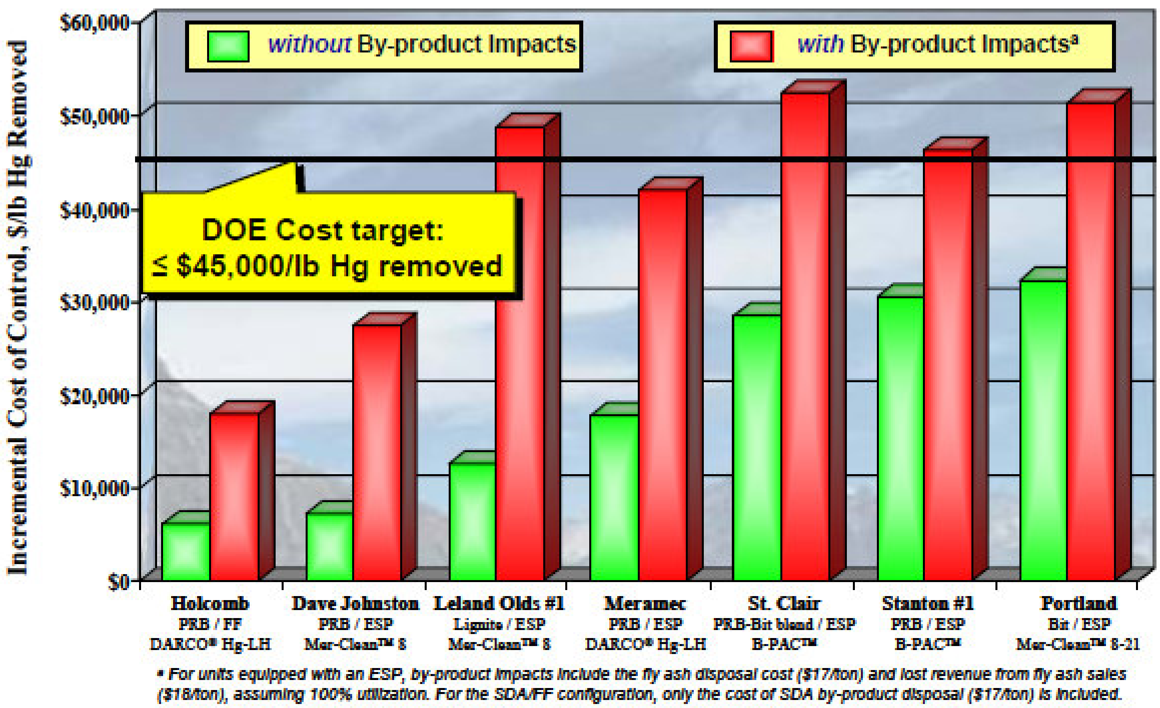
C-PAC from renewable carbon sources: Most activated carbon has been made from fossil fuels such as anthracite, bituminous coal, or lignite. Recently, we were able to successfully produce C-PAC from the activated carbon made from renewable feedstocks such as coconut shells and waste wood chips from paper industry. Such C-PAC not only removes mercury from flue gas, but also has the added advantage of fixing CO_2 into solid carbon form, which further offset the carbon footprint of mercury emission control. The production of 1 ton of standard coal based activated carbon releases about 6 tons of CO_2[16]. However, the production of activated carbon from renewable feedstocks actually instead fixes the CO_2 that would have been released into the atmosphere if they decayed naturally. Production of one ton of activated carbon from coconut shell fixes about 4 tons of CO_2 from the atmosphere, as shown in the chart to the right[16].



C-PAC commercialization: Albemarle has been producing thousands of tons of C-PAC made from renewable feedstocks. Since 2008 this product has been sold to power plants for reducing mercury emissions. The figure to the right illustrates the steady increase in C-PAC production from 2008 to present. Fly ash collected from these power plants with the greener C-PAC is being sold and reused in the concrete production today.



3. Environmental & Economic Benefits of C-PAC Technology: The US Department of Energy reported the huge economic impact of the loss of fly ash sales on the mercury control techniques[5]. As shown in the below figure, 20-year levelized cost estimates for the incremental cost of Hg control ($/lb Hg removal) were calculated for 90% ACI Hg removal at seven field testing sites. The average cost to dispose fly ash is $17/ton, and the average fly ash sale price is about $18/ton, the incremental cost of 90% mercury emission control ranges from much less than $10,000 to about $30,000/lb Hg removed, when fly ash impacts are excluded (e.g. use of C-PAC). For comparison, the cost of Hg removal ranges from about $18,000 to over $50,000/lb Hg removed with fly ash impact (use of conventional PAC).



4- CONCLUSIONS:

1. C-PAC was developed and fully commercialized with partial support from NSF and DOE. It is produced by a proprietary greener process that features:
    a. Use of catalytic amount of bromine for activation
    b. Elimination of post treatment of product with ozone, nitric acid, or other strong oxidizing agents
    c. Activation by air instead of carbon dioxide or steam
2. Renewable feedstocks are used successfully in producing the commercial product.
3. C-PAC retains fly ash integrity and renders it suitable for cement manufacture. This eliminates the need for land filling the mercury contaminated fly ash. Specifically, by recycling 11.5MM tons of fly ash, according to EPA we save 322 million cubic feet of landfill space and reduce the need for 7,544 acre-feet of landfill space.
4. By using C-PAC, industry can save $195.5 million that is needed to develop, fill, and maintain such landfill; and also generate fly ash sale revenue of $207 million.
5. The use of fly ash in cement production saves an equivalent of 632.5 million gallons of fossil fuels and so reduces 11.5MM tons of CO_2 emissions from cement production plants.
6. Furthermore, use of C-PAC eliminates the need for mining virgin materials for production of 11.5MM tons of cement, including 19.5MM tons of limestone. This translates to reduction of fossil fuel usage and it reduces the need for more mining.
7. Data shows that mercury is safely sequestered in concrete much more effectively when compared to other technologies.
8. By making C-PAC from renewable feedstock, a thousand tons of atmospheric CO_2 is being sequestrated.

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