

## **A Novel Process for Onsite Production of Mercury Sorbents**

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## **ABSTRACT**

Activated carbon injection (ACI) represents a promising method to achieve the mercury reductions mandated by the Clean Air Mercury Rule (CAMR). Although powder activated carbon (PAC) is available for this application, its cost is significant. To address this issue Praxair is developing a flexible process to produce coal-based PAC at lower cost. Praxair's process allows for activated carbon production on-site by using a portion of the plant's pulverized coal supply. Apogee Scientific evaluated a variety of Praxair's sorbents by using Electric Power Research Institute's Pollution Control Test system (PoCT) at two facilities burning PRB coal. Data from these facilities, We Energies' Pleasant Prairie Plant and Xcel Energy's Comanche Station, showed Praxair produced sorbents removed greater than 85 % of the mercury in the flue gas slip-stream. First comparisons to other in-flight sorbents indicate that Praxair's pilot-scale produced sorbents have comparable or considerably better mercury removal performance at significantly reduced costs. Additional data from the performance of sub-bituminous, bituminous and lignite coal-based sorbents are also discussed.

## **INTRODUCTION**

The detrimental health effects of mercury consumption on critical segments of the world's population are well known. One source of mercury in the environment is the combustion of mercury-containing fossil fuels, such as coal. In fact one study estimated that coal-fired power plants in the US alone emit 48 tons of mercury a year<sup>1</sup>. This fact has led the U.S. and Canadian governments to enact regulations to limit mercury emissions, with several individual states proposing stricter standards with earlier adoption dates. While air pollution control devices, such as SCR's and scrubbers, have shown a significant co-benefit of mercury reduction for bituminous flue gas streams, removal from sub-bituminous and lignite streams is more problematic. Activated carbon injection, particularly halogenated carbons, has been shown to be more effective for these coals, but can be costly.

Praxair has developed a novel process to produce powder activated carbon from the power plant's own coal source. This process uses a patented oxy-fuel burner to devolatilize and activate the coal to produce activated carbon. By simply changing processing conditions, and with simple addition of dopants, this process can produce a wide variety of carbons, allowing the customer to tailor the sorbent's properties to meet specific mercury capture needs. Mercury capture results from sorbents produced with this process and tested on slipstreams from two different boilers are discussed.

## PAC PRODUCTION PROCESS

The heart of the proprietary Praxair process is the patented hot oxygen burner (HOB), shown schematically in Figure 1. In this burner natural gas is used to combust a portion of an oxygen stream, producing a high temperature oxygen-rich stream which passes through a nozzle. Downstream of the hot oxygen nozzle the parent coal mixes with the hot oxygen and begins to burn. Devolatilization and activation take place in a reactor which leads to a particle separation step where the product is separated from the syngas stream. The syngas can then be ducted to the boiler to provide added fuel value. At several points in the process additives can be introduced to dope the product, or to control the product morphology. The composition of the hot oxidant mixture, the ratio of hot oxidant flow to coal flow, residence time in the mixing chamber and the use of optional additives determine the final mercury capture performance of the sorbents.

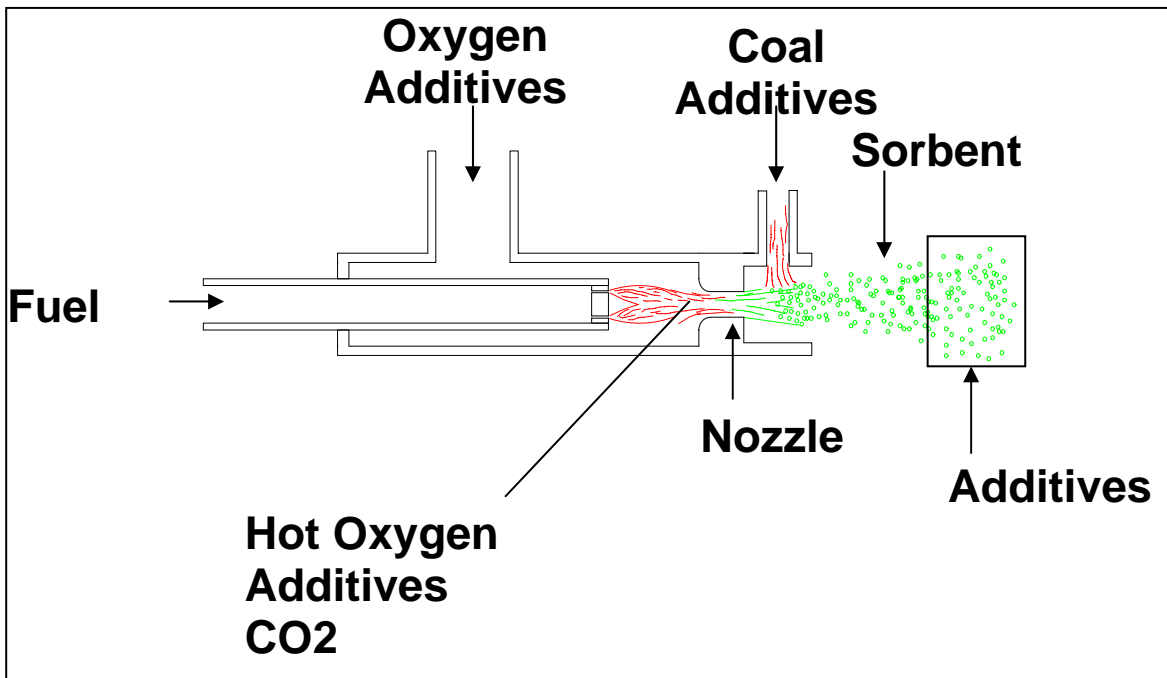


Figure 1. Schematic of hot oxygen burner

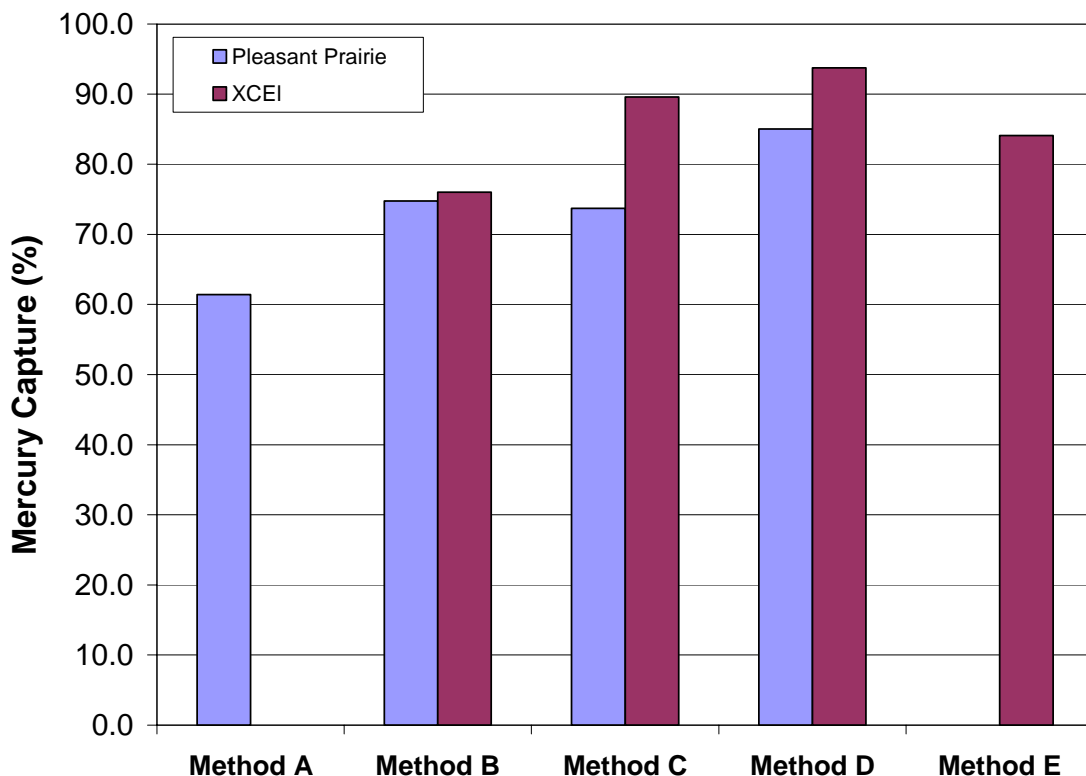
## **SLIP-STREAM TESTING**

A pilot-scale unit of the above process was used to generate a variety of sub-bituminous coal-based sorbents for this paper. A variety of hot oxidant mixtures, hot oxidant flow to coal flow ratios, mixing chamber residence times and additives were used to generate sorbents. To screen and determine performance, slip-stream tests were conducted by Apogee Scientific. Apogee evaluated the sorbents by using Electric Power Research Institute's Pollution Control Test system (PoCT) at We Energies' Pleasant Prairie Plant. The Pleasant Prairie Plant is a 605-MW unit that burns PRB coal and the PoCT is a residence time chamber used to simulate in-flight sorbent injection before the first field of an electrostatic precipitator (ESP)<sup>2</sup>. Residence times of two and four seconds and an injection rate of 6 lb per MMACF were used. The results are discussed in the next section.

## **EFFECT OF PROCESSING METHODS**

One of the biggest benefits of the Praxair PAC production process is the ability to easily change processing conditions and processing methods. For example, the process can easily be used to produce undoped powder activated carbon. For doped carbons the additive can be introduced at several points in the process, allowing maximum flexibility. For highly demanding applications the process can be modified further to allow a second processing step. To illustrate this flexibility several methods were used to produce activated carbon. Figure 2 shows optimized mercury capture data for each method. All of the methods used the same PRB coal as the feedstock. Method A was production of a simple undoped activated carbon. This sample showed approximately 61% removal in the PoCT at P4. For comparison the standard undoped Norit FGD achieved 56% capture, indicating that the undoped PAC from the hot oxygen process is as effective, if not better, than the standard PAC. For Methods B and C the HOB-based carbon was doped with a halide using two different strategies. The data at Pleasant Prairie suggests these methods were comparable for mercury capture (although Method C is easier to implement). At Xcel's Comanche station the capture with Method C was substantially higher, but this is likely related to optimized processing conditions not the method itself. Method D involved post processing the doped carbon. As can be seen from the data this method provides the best mercury capture. However, the additional processing step adds incrementally to the cost, so the method would be used by those plants with the most stringent capture requirements. Finally Method E, which was only evaluated at Comanche station, involved injection of a second processing additive to the process producing doped carbon. This method was less effective than the basic doping process.

Development efforts are ongoing to optimize the production method to maximize mercury capture and minimize production costs. A number of additional variables are being considered, including some that will simplify Method D, and will be reported as data becomes available.



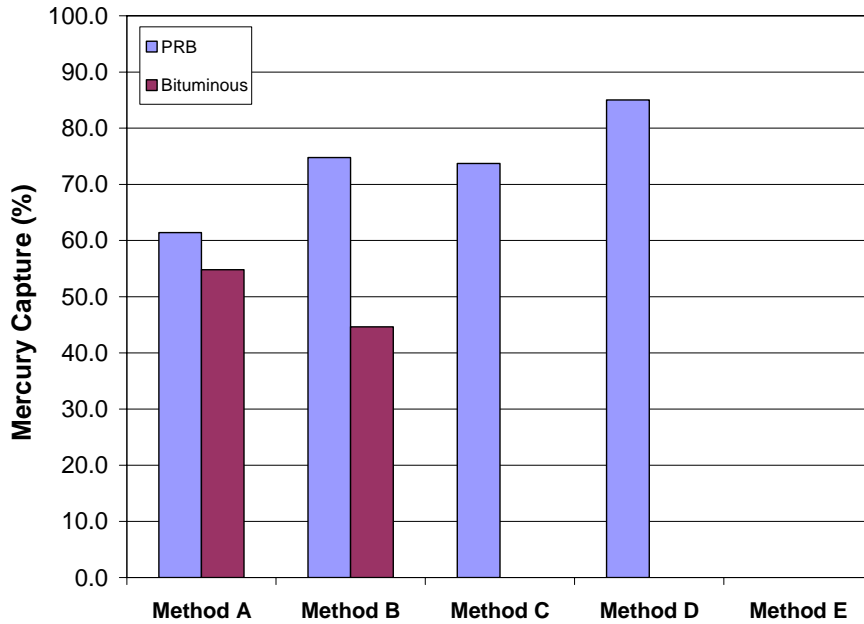
**Figure 2. Effect of production methods on mercury capture**

### **EFFECT OF COAL TYPE**

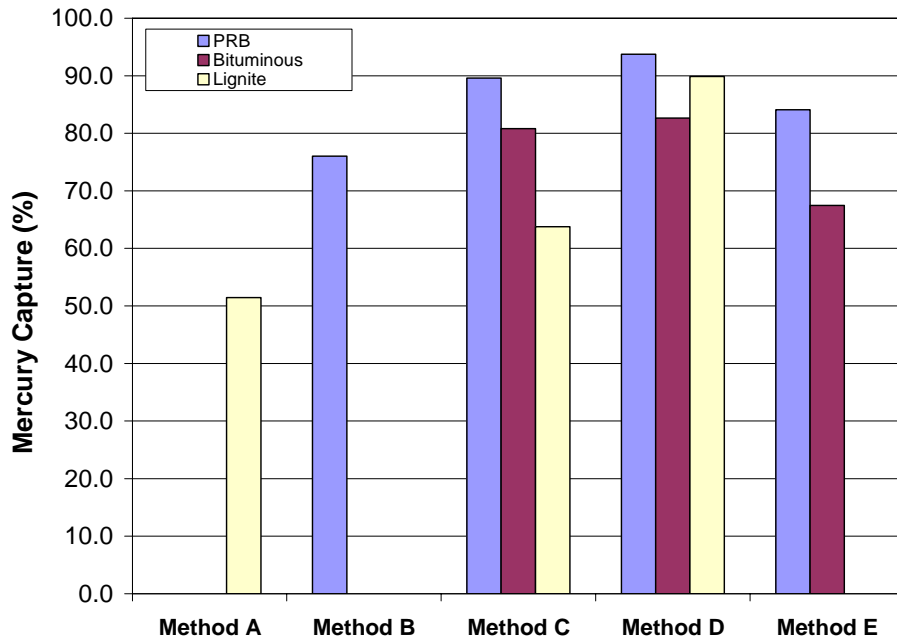
Another parameter of key interest to potential customers is the ability of the HOB process to produce high quality PAC with the coal available at the plant site. To address this issue Praxair used three different feedstock coals to produce PAC for evaluation at Pleasant Prairie and Comanche. The bulk of the development effort has focused on a sub-bituminous coal from the Powder River basin, since it's been demonstrated that plants firing these fuels have more difficulty in capturing mercury with conventional PAC. Plants firing bituminous coals are more likely to get significant mercury capture with a non-doped activated carbon. Several experiments were performed with a western bituminous coal to demonstrate that bituminous coals can be used to produce both doped and non-doped activated carbons. Finally limited testing was also done on a lignite coal.

Figure 3 shows the effect of coal type for samples evaluated at Pleasant Prairie. At that time only limited work had been done to optimize the doping strategies with the bituminous coal, and no work had been done on the lignite coal. First, undoped carbon from both coals yielded similar mercury capture to the standard undoped FGD carbon. Figure 4 shows similar data for samples evaluated at Comanche. In all cases the doped and undoped carbons produced from the bituminous coals were slightly less effective at capturing mercury from the PRB flue gas than

those made from the PRB coal. Preliminary data from lignite coal-derived activated carbon suggests that the second processing step (Method D) yields a much larger improvement in mercury capture than the other two coals. Although there may be coal-related reasons for this improvement, it is more likely the differences are due to unoptimized processing conditions for method C.



**Figure 3. Selected mercury capture data from Pleasant Prairie**



**Figure 4. Selected mercury capture data from Comanche Station**

## **EFFECT OF PRODUCT STORAGE**

Although onsite production of PAC with the HOB enables a plant to essentially produce the carbon as they need it, degradation of the product during long term storage may be an issue. To evaluate whether degradation is an issue for HOB produced carbons a doped carbon sample, made from the PRB coal using Method C, was evaluated at Comanche Station on July 1, 2005. The sample was tested again at Comanche on December 14, 2005. The measured capture was essentially identical between the two tests. During the approximately 5 months between tests the sample was stored at room temperature in a closed, but not purged, semi-transparent plastic bottle. Although the sample did not experience extreme temperature excursions, it was stored under air similar to what would be expected for product storage in a silo. The fact mercury capture was almost identical even after over 5 months in storage suggests the carbon does not suffer degradation during storage.

## **CONCLUSIONS**

Although development efforts continue to optimize the HOB process for PAC production, the results to date indicate the process is effective. Doped coal-based activated carbons produced with this process are able to achieve 85-94% capture of mercury from PRB flue gas streams. Different processing methods can be used, typically with the same processing equipment, to produce different quality carbons – allowing plant owners to incrementally improve mercury capture as required. Finally, evaluation of the same sample for mercury capture during test runs approximately 5 months apart indicate that the Praxair produced PAC is stable during long term storage.

## **REFERENCES**

- [1] US Environmental Protection Agency, <http://www.epa.gov/air/mercuryrule/>, March 15, 2005.
- [2] Ley, T., Ebner, T., Fisher, K., Slye, R., Patton, R., Chang, R. “Assessment of Low-Cost Novel Sorbents for Coal-Fired Power Plant Mercury Control”, Mercury Control Technology R&D Program Review Meeting, August 12-13, 2003.