# COMPARISON OF SORBENTS AND FURNACE ADDITIVES FOR MERCURY CONTROL IN LOW-RANK FUEL COMBUSTION SYSTEMS

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## Introduction

North Dakota lignite-fired power plants have shown a limited ability to control mercury emissions in currently installed electrostatic precipitators (ESPs), dry scrubbers, and wet scrubbers (1). This low level of control can be attributed to the high proportions of $Hg^0$ present in the flue gas. Speciation of mercury in flue gases analyzed as part of the EPA information collection request (ICR) for Hg data showed that $Hg^0$ ranged from 56% to 96% and the oxidized Hg ranged from 4% to 44%. The Hg emitted from power plants firing North Dakota lignites ranged from 45% to 91% of the total Hg, with the emitted Hg being greater than 85% elemental. The average emitted from North Dakota power plants was 6.7 lb/TBtu (1, 2).

The composition of a coal has a major impact on the quantity and form of Hg in the flue gas and, as a result, on the ability of air pollution control devices (APCDs) to remove Hg from flue gas. In general, North Dakota lignite coals are unique because of a highly variable ash content, ash that is rich in alkali and alkaline-earth elements, with high oxygen levels, high-moisture levels, and low chlorine content. Experimental results indicate that low-chlorine (<50-ppm) coal combustion flue gases (typical of North Dakota lignite) contain predominantly $Hg^0$, which is substantially more difficult to remove than $Hg^{2+}$ (3). The generally high calcium contents of lignite coals may reduce the oxidizing effect of the already low chlorine content by reactively scavenging chlorine species (Cl, HCl, and $Cl_2$) from the combustion flue gas. The level of chlorine in flue gases of recently tested North Dakota and Saskatchewan lignites ranged from 2.6 to 3.4 ppmv, with chlorine contents ranging from 11 to 18 ppmw in the coal on a dry basis, respectively.

The technologies utilized for the control of Hg will ultimately depend upon the EPA-mandated emission limits. The strategies include sorbent injection with and without enhancements upstream of an ESP or fabric filter (FF) and Hg oxidation upstream of a wet or dry flue gas desulfurization system (FGD). The new technologies being investigated include Hg capture using the Energy & Environmental Research Center's (EERC) advanced hybrid particulate collector (AHPC) or the *Advanced Hybrid*™ gold-coated materials, baghouse inserts, and carbon beds (4).

Sorbent injection for removing Hg involves adsorption of Hg species by a solid sorbent injected upstream of a particulate control device such as a FF (baghouse) or ESP. Many potential Hg sorbents have been evaluated (4). These evaluations have demonstrated that the chemical speciation of Hg controls its capture mechanism and ultimate environmental fate. Activated carbon injection is the most mature technology available for Hg control. Activated carbons have the potential to effectively sorb $Hg^0$ and $Hg^{2+}$ but depend upon the carbon characteristics and flue gas composition (4). The projected annual cost for activated carbon adsorption of Hg in a duct injection system is significant. Carbon-to-mercury weight ratios of 3000:18,000 (lb carbon injected/lb Hg) in flue gas have been estimated to achieve 90% Hg removal from a coal combustion flue gas containing 10 $\mu g/Nm^3$ of Hg (5).

Mercury oxidation technologies being investigated for Fort Union lignites include catalysts, chemical agents, and cofiring materials. The catalysts that have been tested include a selective catalytic reduction (SCR) catalyst for $NO_x$ reduction, noble metal-impregnated catalysts, and oxide-impregnated catalysts. The chemical agents include chlorine-containing salts and cofiring fuels that contain oxidizing agents (6).

Mercury oxidation catalysts have shown high potential to oxidize $Hg^0$. Results in testing a slipstream at a North Dakota power plant indicated over 80% conversion to oxidized Hg for periods of up to 6 months (6). Tests were also conducted using iron oxides and chromium, with little success of oxidation. Galbreath and others (7) have conducted short-term pilot-scale testing with maghemite ($\gamma$-$Fe_2O_3$) additions and were able to transform about 30% of the $Hg^0$ in North Dakota lignite combustion flue gases to $Hg^{2+}$ and/or Hg(p) and, with an injection of a small amount of HCl (100 ppmv), nearly all of the $Hg^0$ to $Hg^{2+}$. Theoretically, the use of chloride compounds to oxidize $Hg^0$ to $Hg^{2+}$ makes sense. The evidence includes chemical kinetic modeling of bench-scale test results indicating that the introduction of chloride compounds into the high-temperature furnace region will most likely result in the production of atomic chlorine and/or molecular chlorine, which are generally thought to be the dominant $Hg^0$ reactants in coal combustion flue gases (4).

The overall purpose of this research is to develop advanced, innovative Hg control technologies to reduce Hg emissions by 50% to 90% in flue gases typically found in North Dakota lignite-fired power plants at costs of one-half to three-fourths of current estimated costs. The specific objectives are focused on determining the feasibility of the following technologies: Hg oxidation for increased Hg capture in dry scrubbers and the use of Hg adsorbents with a baghouse.

## Experimental

The pilot-scale evaluations of sorbent injection and sorbent-enhancement agents (SEA) were performed using the EERC's particulate test combustor (PTC) equipped with several particulate control options to evaluate Hg sorbent effectiveness in coal combustion flue gases. Initial tests included a comparison of particulate control technologies with the same sorbents and SEAs. The second phase of the research is focused on evaluating various sorbents and SEAs for Hg control effectiveness in conjunction with the ESP-only configuration.

The PTC is a 550,000-Btu/hr (580-MJ/hr) pc-fired unit designed to generate fly ash and flue gas chemistry representative of that produced in a full-scale utility boiler. Coal is introduced to the primary air stream via a screw feeder and ejector. An electric air preheater is used for precise control of the combustion air temperature. The PTC instrumentation permits system temperatures, pressures, flow rates, flue gas constituent concentrations, and baghouse- or ESP-operating data to be monitored continuously and recorded on a data logger. Two PSA Sir Galahad atomic fluorescence-based continuous mercury monitors (CMMs) were located upstream of the sorbent injection point and at the particulate control device outlet to monitor Hg vapor concentrations continuously throughout the tests. Wet chemistry samples were collected using ASTM Method D6784 (Ontario Hydro Method) to verify CMM measurement and performance of the sorbents with SEA injection.

Freedom coal with a mean Hg content of 0.05 $\mu g/g$ was combusted at the nominal rate of 80 lb/hr. Based on the CMM data, the total Hg vapor concentration ($Hg_{gas}$) upstream of sorbent injection varied from 7.0 to 9.2 $\mu g/m^3$. The mean flue gas stream Hg level was 7.6 ± 0.5 $\mu g/m^3$ in dry flue gas, 3% $O_2$. The mean elemental Hg vapor content ($Hg^0$) was about 6.8 $\mu g/m^3$.

Two forms of Hg removal were evaluated—sorbent injection only and sorbent injection with SEAs. SEAs were added to the coal prior to introduction to the furnace. Sorbents were injected upstream of the ESP using a dual-screw K-Tron feeder. The feeder was calibrated prior to the start of sorbent injection. In addition, the weight of sorbent added during a day was divided by the time of injection to provide a mean feed rate. Average feed rates ranged from 3.75 to 15 lb C/MMacf.

**Results and Discussion**

The results of the addition of materials with coal at very low levels along with the activated carbon injection (Norit DARCO FGD®) upstream of an ESP–FF (TOXECON™), *Advanced Hybrid*™ filter, and ESP only are illustrated in Figure 1. The first part of the figure shows the baseline data for Hg emissions ranging from 9 to 12 μg/Nm$^3$, with 80% to 90% of the Hg in the elemental form. The second case is activated carbon injection alone and with the addition of SEA 2, showing a reduction in Hg emissions to 90% removal. The third case is the *Advanced Hybrid*™ filter alone and with the addition of SEA 2, which produced nearly 90% control efficiency. The final ESP-only case also indicated up to 90% control. The control efficiency for the ESP-only case showed significant potential improvement over past results obtained with the ESP only. All three configurations performed significantly better in Hg control with the combination of sorbent injection and SEAs added to the feed coal.

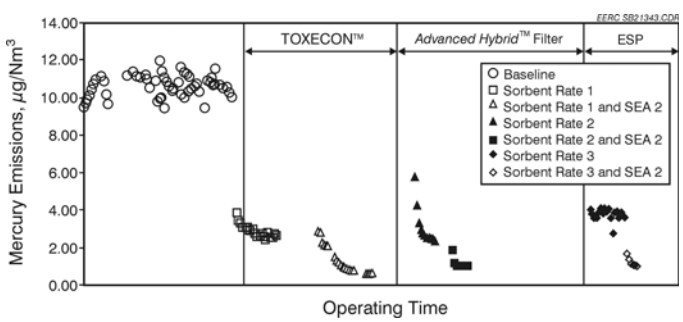


**Figure 1.** Mercury emissions for activated carbon injection combined with an SEA additive using various particulate control devices.

The second phase of testing included activated carbon sorbent injection and SEA upstream of an ESP for control of Hg emissions from North Dakota lignite. The testing was conducted using the EERC PTC equipped with an ESP only. The results of the first tests are illustrated in Figure 2. Figure 2 shows the inlet total Hg level at 9 μg/m$^3$ and baseline outlet (initial and final) at 7.2 μg/m$^3$. Norit DARCO FGD® activated carbon was injected at 3.75 and 15 lb C/MMacf, resulting in 50% to 60% Hg reduction. The addition of SEA with the coal and injection of 3.75 lb C/MMacf resulted in a reduction of over 70% of the Hg emissions.

**Conclusions**

The comparison tests show that Hg emissions from lignite-fired combustion systems can be reduced significantly using a variety of particulate control devices. Two different ESP–baghouse combinations and the ESP-only configuration were capable of controlling up to 90% of the gaseous Hg emissions when activated carbon sorbent injection was combined with Hg oxidant addition to the coal. This is particularly significant in the case of the ESP-only configuration, as many of the lignite-burning units are currently equipped with this configuration. This technology also has the potential to improve dry FGD baghouse control efficiency. While the

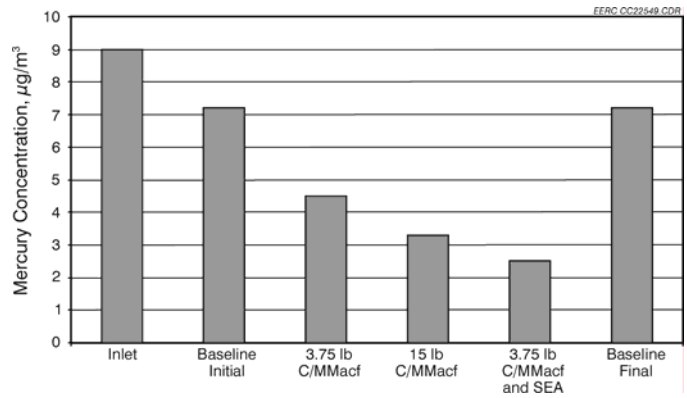


**Figure 2.** ESP mercury concentrations as a function of sorbent and SEA additive for a North Dakota lignite.

results to date demonstrate effective Hg removal across the ESP, optimization of sorbents and SEA types and the addition ratios is essentially to develop the most cost-effective plan for controlling Hg emissions.

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