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An update on DOE's Phase II and Phase III mercury control technology R&D program

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ABSTRACT

The U.S. Department of Energy's National Energy Technology Laboratory, under the Office of Fossil Energy's Innovations for Existing Plants Program, carried out a comprehensive Hg research and development program for coal-fired power generation facilities since the mid-1990s. Working collaboratively with the U.S. Environmental Protection Agency, the Electric Power Research Institute, power plant operators, state and local agencies, and a host of research organizations and academic institutions, the Program identified the major factors that affect mercury speciation and capture in coal combustion flue gas and funneled this knowledge into the development of a suite of mercury control technologies for the diverse fleet of U.S. coal-fired power plants. The high performance observed during full-scale field testing has given coal-fired power plant operators the confidence to begin deploying technology. As of March 2009, more than 130 full-scale activated carbon injection systems have been ordered by the U.S. coal-fired power generators. These contracts include both new and retrofit installations and represent over 55 GW of coal-based electric generating capacity.

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1. Introduction

Since first being identified for potential regulation in the 1990 Clean Air Act Amendments, there has been concern within the industry whether it would be possible to develop cost-effective emission control technologies for mercury (Hg) because of its low concentration and reactivity during coal combustion. However, while technical issues remain, the U.S. Department of Energy's National Energy Technology Laboratory (NETL) has been successful, through public-private partnership, in significantly improving both the cost and performance of Hg control technology.

Under the Office of Fossil Energy's Innovations for Existing Plants (IEP) Program, NETL carried out a comprehensive Hg research and development (R&D) program for coal-fired power generation facilities since the mid-1990s [1]. Working collaboratively with the U.S. Environmental Protection Agency (EPA), the Electric Power Research Institute (EPRI), the University of North Dakota Energy and Environmental Research Center, power plant operators, state and local agencies, and a host of research organizations and academic institutions, the IEP Program has fostered the development of reliable measurement techniques for the different chemical forms of Hg. And through sampling and data analysis, it identified the primary factors that affect Hg

speciation and capture in coal combustion flue gas, ultimately leading to the development of cost-effective Hg control technologies.

2. Theory

The trace amount of Hg present in coal is volatilized during combustion and converted to gaseous elemental mercury (Hg^0). Subsequent cooling of the flue gas and interaction of Hg^0 with other flue gas constituents, such as chlorine and unburned carbon, result in a portion of the Hg^0 being converted to gaseous oxidized forms of mercury (Hg^{2+}) and particulate-bound mercury (Hg_p). As a result, coal combustion flue gas contains varying percentages of Hg_p , Hg^{2+} , and Hg^0 and the exact speciation has a profound effect on the Hg capture efficiency of existing air pollution control device (APCD) configurations, which has been found to range from 0 to over 90% [2]. The Hg_p fraction is typically removed by a particulate control device such as an electrostatic precipitator (ESP) or a fabric filter (FF). The Hg^{2+} portion is water-soluble and therefore a relatively high percent can be captured in wet flue gas desulfurization (FGD) systems, while the Hg^0 fraction is generally not captured by existing APCD.

3. Experimental method

This knowledge was subsequently funneled into the development of a suite of Hg control technologies for the diverse fleet of U.S. coal-fired

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power plants. NETL initiated an R&D program in the mid-1990s directed at two general approaches for controlling Hg – (1) Hg-specific control technology such as sorbent injection and (2) Hg⁰ oxidation concepts that maximize co-benefit removal of Hg²⁺ in wet FGD systems. In 2000, following laboratory through pilot-scale development of these approaches, NETL launched a three-phase field testing program. This program called for the installation and full-scale and slip-stream testing of the most promising Hg control technologies at operating coal-fired power plants.

The initial field testing (Phase I) focused on untreated activated carbon injection (ACI) and improving the capture of Hg across wet FGD systems, while Phase II, which began in 2003, was expanded to include longer-term, full-scale field testing of chemically-treated ACI, sorbent enhancement additives (SEA), and sorbent-based technologies designed to preserve fly ash quality. Phase II also included evaluations of concepts, such as chemical additives and Hg⁰ oxidation catalysts, intent on enhancing FGD Hg capture. The goal of Phases I and II was to develop Hg control technologies (available for commercial demonstration by year-end 2007 for all coal ranks) that could achieve 50 to 70% Hg capture at costs 25 to 50% less than the baseline (1999) estimate of about \$60,000 per pound of Hg removed (\$/lb Hg removed).

Although 30-day long-term tests were conducted in Phase II, the test period was not sufficient to answer many fundamental questions about long-term consistency of Hg removal and reliability of the system when integrated with plant processes. To assess the potential balance-of-plant impacts associated with a continuously operating Hg-specific control technology for several months to years, NETL awarded nine new projects in 2006 to conduct Hg control tests of mature technologies at full-scale coal-fired units and novel concepts in the laboratory. The Phase III projects support the IEP Program's longer-term goal of developing advanced Hg control technologies (available for commercial demonstration by 2010) that could achieve at least 90% capture at costs 50 to 75% less than \$60,000/lb Hg removed¹.

4. Results and discussion

Over the past seven years, the IEP Program has managed full-scale field tests of Hg control technologies at nearly 50 U.S. coal-fired power plants. The flexibility of the IEP Program allowed NETL to quickly incorporate insights and lessons learned from its partners into the development of advanced Hg control technologies tailored to specific areas of need. For instance, a determination that chlorine released during coal combustion promotes Hg oxidation in flue gas led to field testing of technologies designed to provide a halogen “boost” for coals, such as subbituminous and lignite, that tend to contain low levels of chlorine. NETL has observed a step-change improvement in both the cost and performance of Hg control during full-scale field tests of chemically-treated ACI upstream of a particulate control device, and coal treatment with an aqueous calcium bromide (CaBr₂) solution at plants equipped with a wet FGD system.

4.1. Chemically-treated sorbent injection

The development, and subsequent field testing, of chemically-treated ACI represents a concerted effort to enhance Hg capture at units firing low-rank coal after Phase I results at We Energies' Powder River Basin (PRB) subbituminous coal-fired Pleasant Prairie Unit 2 showed total Hg removal via untreated ACI was limited to about 65% [3]. Fig. 1 provides a comparison of untreated and chemically-treated ACI performance at three of NETL's Phase II field testing sites: (1) Great River Energy's Stanton Station Unit 10 (Lignite/FF); (2) Basin

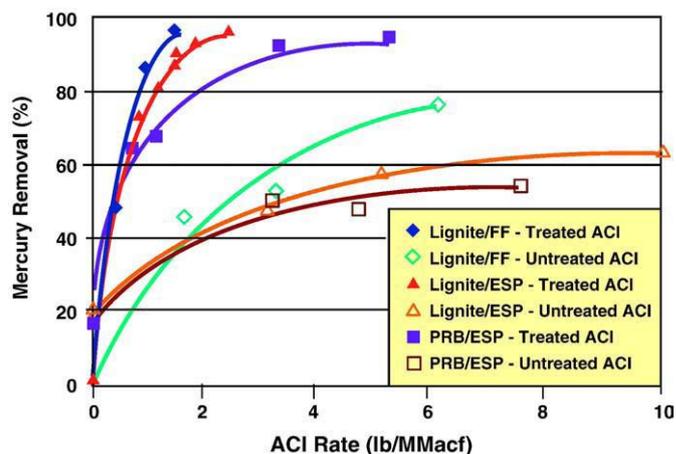


Fig. 1. Comparison of untreated and chemically-treated ACI performance at facilities burning lower-rank coals.

Electric's Leland Olds Station Unit 1 (Lignite/ESP); and (3) Stanton Station Unit 1 (PRB/ESP). These parametric data curves illustrate the improved Hg capture efficiency of chemically-treated sorbents at power plants burning lower-rank coals as high levels of Hg capture are attainable at relatively low injection rates. In fact, the treated sorbents achieved at least 90% total Hg capture at an injection rate of 3 lb per million actual cubic feet (lb/MMacf) of flue gas or less at these Phase II field testing sites.

An NETL economic analysis [4] released in May 2007 indicates that the high Hg capture efficiency of chemically-treated sorbents has drastically reduced the estimated cost of Hg control due to a reduction in the injection rate required to achieve a given level of control, which offsets the higher cost of these treated sorbents. As shown in Fig. 2, the 20-year levelized incremental cost of 90% ACI Hg control ranges from about \$30,000 to less than \$10,000/lb Hg removed for seven of NETL's Phase II field testing sites where chemically-treated ACI was evaluated. These results point to the fact that NETL has surpassed the Hg control cost goal set forth by the IEP Program.

4.2. Technical issues associated with sorbent injection

While the advent of chemically-treated ACI has yielded improvements in Hg control cost and performance, technical uncertainties remain. The following issues, if resolved, will further enhance the efficiency, economics, applicability, and reliability of sorbent-based Hg control technologies.

4.2.1. Fly ash impacts

The typical ACI system is located upstream of a particulate control device to enable simultaneous capture of the spent sorbent and fly ash. This Hg control strategy leads to commingling of the sorbent and fly ash that can prohibit certain fly ash recycling efforts. One of the highest-value reuse applications for fly ash is as a substitute for Portland cement in concrete production [5]. The utilization of fly ash in concrete production is particularly sensitive to carbon content as well as the surface area of the carbon present in the fly ash. Accordingly, NETL's Hg control technology portfolio includes alternative sorbent injection technologies designed to minimize fly ash carbon contamination caused by ACI upstream of a particulate control device.

4.2.1.1. TOXECON™ configuration. The toxic emission control (TOXECON™) configuration, developed by EPRI, will not impact fly ash utilization since the ash is removed by an ESP upstream of the sorbent injection location, while the spent sorbent is captured by a downstream FF. TOXECON™ was selected for a first-of-a-kind commercial Hg control technology demonstration at We Energies'

¹ In Fiscal Year 2008, the IEP Program's focus was redirected to the research and development of advanced carbon dioxide capture and compression technologies for the existing fleet of coal-fired power plants.

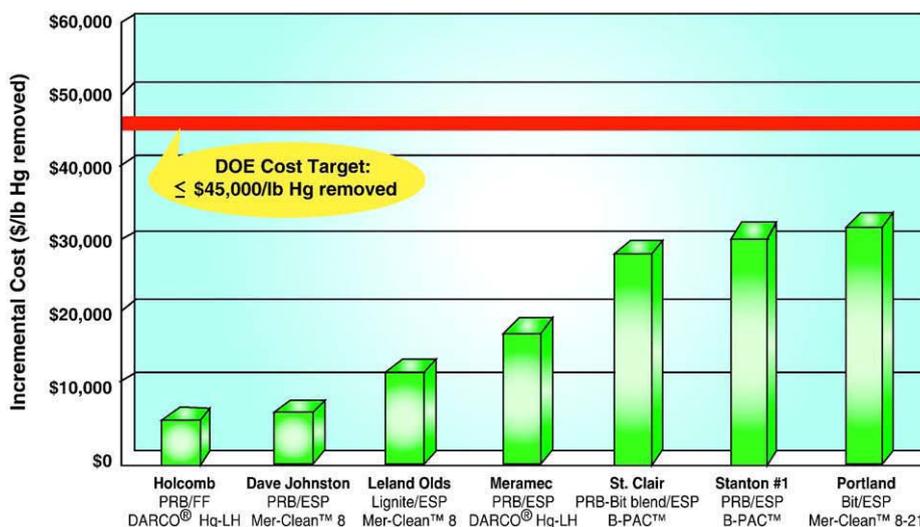


Fig. 2. 20-year levelized incremental cost of 90% Hg control with chemically-treated ACI.

Presque Isle Power Plant in Marquette, Michigan, under DOE's Clean Coal Power Initiative. Commercially operational since 2006, the TOXECON™ configuration maintained greater than 90% total Hg removal for 48 consecutive days with both untreated DARCO® Hg and brominated DARCO® Hg-LH sorbent injection at less than 3 lb/MMacf [6].

4.2.1.2. TOXECON II™ configuration. EPRI's TOXECON II™ technology injects sorbents directly into the downstream collecting field(s) of an ESP. Since the majority of fly ash (~90%) is collected in the upstream ESP fields, only a small portion of the total collected ash contains spent sorbent. During full-scale TOXECON II™ testing at Entergy's PRB-fired Independence Station Unit 1, DARCO® Hg-LH injection at 5.5 lb/MMacf achieved 90% total Hg removal [7]. A remaining concern with any Hg control strategy involving sorbent injection, particularly the TOXECON II™ configuration that limits ESP residence time, is the potential for increased particulate emissions that could trigger New Source Review requirements.

4.2.1.3. "Ash-friendly" sorbents. Activated carbon sorbents passivated during production could potentially allow coal-fired power generators to continue marketing fly ash commingled with the spent sorbent as a suitable replacement for Portland cement in concrete. Sorbent Technologies conducted a 30-day long-term evaluation of their brominated, "concrete-friendly" C-PAC™ sorbent at Midwest Generation's PRB-fired Crawford Station Unit 7 [8]. Total Hg removal averaged 81% with C-PAC™ injection upstream of the ESP at about 4.6 lb/MMacf.

More recently, a high-temperature version of C-PAC™ was tested at Midwest Generation's PRB-fired Will County Unit 3, which is equipped with a hot-side ESP [9]. During a six-day continuous test, Hg removal ranged from about 60 to 73% with C-PAC™ injection at 5 lb/MMacf. Most importantly, preliminary results indicate that fly ash collected during C-PAC™ injection at these sites remains suitable for reuse in concrete production.

During Phase III testing at Lower Colorado River Authority's PRB-fired Fayette Unit 3, ALSTOM evaluated three sorbents (eSorb™ 11, eSorb™ 13, and eSorb™ 18) designed by Envergen to preserve fly ash quality [10]. Results indicate that fly ash remains marketable with eSorb™ 13 at about 0.5 lb/MMacf (~85% ACI Hg capture).

4.2.2. Sulfur trioxide interference

Field testing has shown that sulfur trioxide (SO₃) in the flue gas, even at low concentrations, can impede the performance of ACI. It

appears that SO₃ competes with Hg for adsorption sites on the sorbent surface thereby limiting its performance [11].

During Phase II field testing at AEP's high-sulfur (3–4%) bituminous-fired Conesville Station Unit 6, total Hg removal was limited to approximately 30% with chemically-treated ACI at 12 lb/MMacf [12]. Consequently, a long-term field test was not conducted at this unit; instead, NETL funding was used to evaluate the impact of SO₃ flue gas conditioning (FGC) on ACI performance at AmerenUE's PRB-fired Labadie Station Unit 2 [13]. As shown in Fig. 3, turning the SO₃ FGC system off at Labadie increased total Hg removal from about 50 to 80% with DARCO® Hg-LH injection at 8 lb/MMacf. Greater than 90% Hg removal was observed with no SO₃ injection and DARCO® Hg-LH injection upstream of the air preheater (APH) at about 5 lb/MMacf. The performance of brominated B-PAC™ was also impacted by SO₃ FGC at Progress Energy's Lee Station Unit 1 [14]. With B-PAC™ injection at 8 lb/MMacf, Hg capture increased from 32 to 82% when SO₃ FGC was idled.

One possible solution to the SO₃ issue is dual injection of Hg sorbents and alkaline materials. This approach was explored during a Phase III field test at Public Service of New Hampshire Company's Merrimack Station Unit 2, which utilizes a cyclone-fired boiler to burn a blend of bituminous coals (~1% sulfur) and is equipped with a selective catalytic reduction (SCR) system followed by two ESPs in series [15]. During parametric testing, several Hg sorbents were

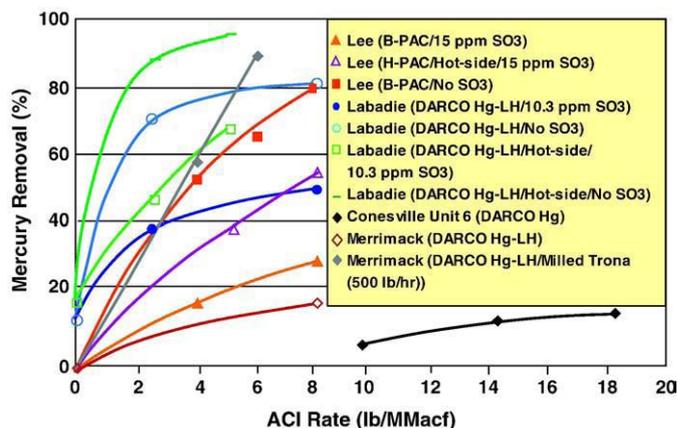


Fig. 3. Impact of flue gas SO₃ on ACI performance.

evaluated both with and without the injection of magnesium oxide (MgO) or sodium sesquicarbonate (trona) — two potential SO₃ mitigation additives. Results indicate that trona injection enhanced ACI performance to a greater degree than MgO; however, the sodium content of trona may limit fly ash recycling opportunities.

Without SO₃ mitigation, Hg removal was limited to about 22% with chemically-treated ACI at 8 lb/MMacf. During a continuous injection test completed in March 2008, 50% Hg removal was achieved with trona injection upstream of the air preheater at 500 lb/hr and DARCO® Hg-LH injection between the two ESPs at about 4 lb/MMacf.

4.3. Enhancing FGD Hg capture

Oxidation of flue gas Hg⁰ followed by absorption of Hg²⁺ across a wet FGD system has the potential to be a reliable and cost-effective Hg control strategy for some coal-fired power plants. During a two-week trial conducted at Luminant Power's Monticello Station, which burns a blend of PRB and Texas lignite coals, total Hg capture averaged 86% with a CaBr₂ injection rate of 113 parts per million (ppm) Br in the coal [16]. Greater than 90% total Hg capture was observed during a short-term test with a CaBr₂ injection rate of 330 ppm Br in the coal.

5. Technology commercialization

Although the Federal regulatory structure for Hg emissions from coal-fired power plants is once again uncertain following the vacatur of EPA's Clean Air Mercury Rule on February 8, 2008 [17], NETL's field testing program has successfully brought Hg control technologies to the point of commercial-deployment readiness. As of March 2009, more than 130 full-scale ACI systems, a signature technology of the IEP Program, have been ordered by the U.S. coal-fired power generators [18]. These contracts represent over 55 gigawatts (GW) of coal-fired electric generating capacity. This includes approximately 43 GW of existing capacity (~13% of the total U.S. coal-fired capacity) that will be retrofit with ACI systems to control Hg emissions. The ACI systems have the potential to remove more than 90% of the Hg in most applications, at a cost that can dip below \$10,000/lb Hg removed. Although the results achieved during NETL's field tests met or exceeded program goals, site-specific Hg characterization and testing may be required to evaluate alternative methods and their Hg capture efficiency on individual power plant generating units.

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