

# MERCURY EMISSION CONTROL TECHNOLOGIES FOR PPL MONTANA – COLSTRIP TESTING

Final Report

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## MERCURY EMISSION CONTROL TECHNOLOGIES FOR PPL MONTANA – COLSTRIP TESTING

### ABSTRACT

The Energy & Environmental Research Center (EERC) was asked by PPL Montana LLC (PPL) to provide assistance and develop an approach to identify cost-effective options for mercury control at its coal-fired power plants. The work conducted focused on baseline mercury level and speciation measurement, short-term parametric testing, and weeklong testing of mercury control technology at Colstrip Unit 3. Three techniques and various combinations of these techniques were identified as viable options for mercury control. The options included oxidizing agents or sorbent enhancement additives (SEAs) such as chlorine-based SEA1 and an EERC proprietary SEA2 with and without activated carbon injection.

Baseline mercury emissions from Colstrip Unit 3 are comparatively low relative to other Powder River Basin (PRB) coal-fired systems and were found to range from 5 to 6.5  $\mu\text{g}/\text{Nm}^3$  (2.9 to 3.8 lb/TBtu), with a rough value of approximately 80% being elemental upstream of the scrubber and higher than 95% being elemental at the outlet. Levels in the stack were also greater than 95% elemental. Baseline mercury removal across the scrubber is fairly variable but generally tends to be about 5% to 10%.

Parametric results of carbon injection alone yielded minimal reduction in Hg emissions. SEA1 injection resulted in 20% additional reduction over baseline with the maximum rate of 400 ppm (3 gal/min). Weeklong testing was conducted with the combination of SEA2 and carbon, with injection rates of 75 ppm (10.3 lb/hr) and 1.5 lb/MMacf (40 lb/hr), respectively. Reduction was found to be an additional 30% and, overall during the testing period, was measured to be 38% across the scrubber.

The novel additive injection method, known as novel SEA2, is several orders of magnitude safer and less expensive than current SEA2 injection methods. However, used in conjunction with this plant configuration, the technology did not demonstrate a significant level of mercury reduction. Near-future use of this technique at Colstrip is not seen.

All the additives injected resulted in some reduction in mercury emissions. However, the target reduction of 55% was not achieved. The primary reason for the lower removal rates is because of the lower levels of mercury in the flue gas stream and the lower capture level of fine particles by the scrubbers (relative to that for larger particles). The reaction and interaction of the SEA materials is with the finer fraction of the fly ash, because the SEA materials are vaporized during the combustion or reaction process and condense on the surfaces of entrained particles or form very small particles. Mercury will have a tendency to react and interact with the finer fraction of entrained ash and sorbent as a result of the higher surface areas of the finer particles. The ability to capture the finer fraction of fly ash is the key to controlling mercury.

Cost estimates for mercury removal based on the performance of each sorbent during this project are projected to be extremely high. When viewed on a dollar-per-pound-of-mercury removed basis activated carbon was projected to cost nearly \$1.2 million per pound of mercury removed. This value is roughly six times the cost of other sorbent-enhancing agents, which were projected to be closer to \$200,000 per pound of mercury removed.

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# MERCURY EMISSION CONTROL TECHNOLOGIES FOR PPL MONTANA – COLSTRIP TESTING

## EXECUTIVE SUMMARY

The Energy & Environmental Research Center (EERC) was requested by PPL Montana LLC (PPL) to provide assistance and develop an approach to identify cost-effective options for mercury control at its coal-fired power plants. The work conducted as part of the resulting project focused on conducting baseline mercury levels and speciation measurement, short-term parametric testing, and weeklong testing of mercury control technology at Colstrip Unit 3. Three techniques and various combinations of these techniques were identified as viable options for mercury control. The options included oxidizing agents or sorbent enhancement additives (SEAs), such as chlorine-based SEA1 and an EERC proprietary SEA2 with and without activated carbon injection. These control technologies have shown promise in testing with lignite and subbituminous coals.

Equipment was brought on-site on April 3, 2006, for testing across Unit 3 Scrubber 3-8. Testing was conducted from April 7 through May 8. Baseline mercury emissions from Colstrip Unit 3 are comparatively low relative to other Powder River Basin (PRB) coal-fired systems and were found to range from 5 to 6.5 ug/Nm<sup>3</sup> (2.9 to 3.8 lb/TBtu), with a rough value of approximately 80% being elemental upstream of the scrubber and higher than 95% being elemental at the outlet. Levels in the stack were also greater than 95% elemental. Baseline mercury removal across the scrubber is fairly variable but generally tends to be about 5% to 10%.

Parametric results of carbon injection alone yielded minimal reduction in Hg emissions. The best additional reduction, 9%, occurred with the highest rate, 3 lb/MMacf (81 lb/hr), but was not a significant increase over the middle rate of 2 lb/MMacf (54 lb/hr). SEA1 injection resulted in 20% additional reduction over baseline with the maximum rate of 400 ppm (3 gal/min). The measured result was not consistent when SEA1 was combined with activated carbon. This test yielded a smaller reduction of only 13% additional, resulting in an overall mercury reduction of 25%. SEA2 parametric testing was performed but was later rejected as inaccurate.

Weeklong testing was conducted with the combination of SEA2 and carbon with injection rates of 75 ppm (10.3 lb/hr) and 1.5 lb/MMacf (40 lb/hr) respectively. Reduction was found to be an additional 30% and, overall during the testing period, was measured to be 38% across the scrubber. This is an additional reduction of only 10% over SEA1.

The novel additive injection method, known as novel SEA2, is several orders of magnitude safer and less expensive than current SEA2 injection methods. However, used in conjunction with this plant configuration, the technology did not demonstrate a significant level of mercury reduction. Near-future use of this technique at Colstrip is not seen.

All the additives injected resulted in some reduction in mercury emissions. However, the target reduction of 55% was not achieved. The primary reason for the lower removal rates is



because of the lower levels of mercury in the flue gas stream and the lower capture level of fine particles by the scrubbers (relative to that for larger particles). The reaction and interaction of the SEA materials is with the finer fraction of the fly ash, because the SEA materials are vaporized during the combustion or reaction process and condense on the surfaces of entrained particles or form very small particles. Mercury will have a tendency to react and interact with the finer fraction of entrained ash and sorbent as a result of the higher surface areas of the finer particles. The ability to capture the finer fraction of fly ash is the key to controlling mercury.

The materials and injection methods explored during this testing did not provide the level of control exhibited when used with other air pollution control devices such as electrostatic precipitators (ESPs) and ESPs combined with wet scrubbers. The units at the Colstrip Steam Electric Station present a significant challenge for mercury reduction. The worst case was examined in this project, and projections have been made regarding the benefits across the rest of the unit. More information must be collected to verify the reaction of the entire system. Key findings indicate that when SEA or carbon is injected, mercury is reacting with the finer fractions of the fly ash and carbon based on the mercury captured on the filters. In addition, the shorter residence time for Scrubber 3-8 contributed to the removal efficiencies. Future testing must examine the feasibility of capturing mercury on coarser activated carbon particles and at increasing residence times. The use of coarser carbon materials will require added residence time and improved mixing with flue gas to achieve higher removal rates. Simple computer models were used in this report to generate the basic relationships between mercury removal, sorbent particle size, and residence time based on data acquired during testing. These models assumed a “perfect” sorbent and did not account for particle surface reactions. Before additional testing is conducted, it is recommended that advanced computer modeling be conducted to better determine the optimum size of sorbent particles, projected injection rates, and minimum required residence time. The modeling needs to take into account the physical layout of each scrubber duct for the unit to better quantify the overall mercury output to the stack. The data collected from this testing can be used as a benchmark guide for the advanced modeling. Once the sorbent characteristics and additive rates have been defined, testing should be considered. Two options for testing the impact of residence times include increasing the distance between the injection point and the scrubber on the duct work of Scrubber 3-8 and conducting injection testing across one of the scrubbers with longer duct work, such as Scrubber 3-5. Testing with Scrubber 3-8 would probably involve the installation of more ports upstream of the existing ports.

Cost estimates for mercury removal based on the performance of each sorbent during this project are projected to be extremely high. When viewed on a dollar-per-pound-of-mercury removed basis activated carbon was projected to cost nearly \$1.2 million per pound of mercury removed. This value is roughly six times the cost of other sorbent-enhancing agents, which were projected to be closer to \$200,000 per pound of mercury removed. Both costs are well above what has been projected by the U.S. Department of Energy to meet 90% control for locations utilizing a PRB coal such as Meramec Station, equipped with an ESP, where recent analysis has shown a projected cost of \$17,700 per pound of mercury removed.

# MERCURY EMISSION CONTROL TECHNOLOGIES FOR PPL MONTANA – COLSTRIP TESTING

## INTRODUCTION

### Mercury Control Challenge for Subbituminous Coals

Mercury emissions from utilities burning U.S. coals were determined under the U.S. Environmental Protection Agency's (EPA's) information collection request (ICR), which mandated Hg and chlorine analyses on coal shipped to units larger than 25 MWe during 1999 and emissions testing on 84 units selected to represent different categories of air pollution control devices (APCDs) and coal rank. As shown in Table 1, subbituminous coals from the western United States, on average, contain significantly lower concentrations of Hg, chlorine, and sulfur than bituminous coals from the eastern U.S., Appalachian, or interior regions.

Western subbituminous coal and lignite are also distinguished by their much higher alkaline-earth metal (i.e., magnesium and calcium) contents. Gulf Coast lignites resemble eastern bituminous coals in their high concentrations of Hg and iron but are similar to western coals in regard to low chlorine and high calcium contents. These compositional differences not only affect the quantities and chemical species of Hg emitted from a boiler but also the effectiveness of different control technologies to remove Hg from flue gas. As indicated by ICR data in Table 1, western coals contain about half as much Hg on a weight basis; however, the ICR data in Table 2 indicate that they emit almost twice as much Hg.

In general, currently installed electrostatic precipitators (ESPs), dry scrubbers, and wet scrubbers do not effectively control Hg emissions from subbituminous coal-fired power plants (1). The lack of Hg control is primarily attributable to the high proportions of  $\text{Hg}^0$  present in subbituminous coal combustion flue gases. In pulverized and cyclone subbituminous coal-fired units,  $\text{Hg}^0$  generally comprises >85% of the  $\text{Hg}_{\text{total}}$  emissions that average  $5.7 \text{ lb}/10^{12} \text{ Btu}$  (2).

In general, subbituminous coals are characterized by their relatively high oxygen, moisture, and alkali and alkaline-earth elemental concentrations and low chlorine contents. Based on the ICR data, Powder River Basin (PRB) coals produce as much as  $6 \text{ lb Hg}/10^{12} \text{ Btu}$  compared to  $8 \text{ lb Hg}/10^{12} \text{ Btu}$  for North Dakota lignites,  $6.5 \text{ lb Hg}/10^{12} \text{ Btu}$  for Illinois Basin bituminous coals,  $9.5 \text{ lb Hg}/10^{12} \text{ Btu}$  for Appalachian bituminous coals, and  $12.5 \text{ lb Hg}/10^{12} \text{ Btu}$  for Gulf Coast lignites (2). Coal composition has a major impact on the quantity and chemical form of Hg in the flue gas and, as a result, the effectiveness of APCDs to remove Hg from flue gas. Coals containing greater than about 200 ppm chlorine produce flue gases that are dominated by the more easily removable mercuric compounds ( $\text{Hg}^{2+}$ ), most likely mercuric chloride ( $\text{HgCl}_2$ ). Appalachian and Illinois Basin bituminous coals generally have >200 ppm chlorine. Conversely, low-chlorine (<50 ppm) subbituminous and lignite coal combustion flue gases contain predominantly  $\text{Hg}^0$ , which is substantially more difficult to remove than  $\text{Hg}^{2+}$  (3). Additionally, the abundance of calcium in subbituminous coal fly ashes may reduce the oxidizing effect of the already-low chlorine content by reactively scavenging chlorine species ( $\text{Cl}$ ,  $\text{HCl}$ , and  $\text{Cl}_2$ ) from the combustion flue gas.

**Table 1. Average Coal Compositions and Heating Values from a Select Group of ICR Data, on a dry basis**

Parameter	Eastern Appalachian	Western Subbituminous
Hg, ppm	0.126	0.068
Cl, ppm	1064	124
S, wt%	1.67	0.48
Ash, wt%	11.65	7.92
Ca, ppm	2700	14,000
HHV, <sup>a</sup> Btu/lb	12,900	9300
Moisture, wt%	2.5	19.4

<sup>a</sup> Higher heating value.

**Table 2. Mercury Emissions Based on ICR Data**

Parameter	Eastern Bituminous	Western Subbituminous
Coal Burned, % in United States	55	35
Uncontrolled Hg Emissions, lb/10 <sup>12</sup> Btu*	7	5.7
Av Hg Stack Emission, lb/10 <sup>12</sup> Btu*	2.6	4.6
Av Removal, %*	63	20
Particulate Hg Leaving Stack, lb/10 <sup>12</sup> Btu*	0.4	0
Hg <sup>2+</sup> Leaving Stack, lb/10 <sup>12</sup> Btu*	1.2	0.6
Hg <sup>0</sup> Leaving Stack, lb/10 <sup>12</sup> Btu*	1	4

\* Data presented are based on a total of 81 plants from the ICR sorted by coal region and categorized as eastern and western coals. Note, some plants did not supply adequate information as to the origin of their coal and were not considered.

### Mercury Control Options

Options for controlling Hg<sub>total</sub> emissions are being investigated that have the potential to attain >90% removal of Hg<sub>total</sub> from flue gas for selected configurations of boiler and air pollution control systems. ICR data and other test data of Hg<sub>total</sub> control for lignite and subbituminous coal-fired systems indicate that low Hg<sup>0</sup> reactivity poses technical and economic challenges and that innovative Hg<sup>0</sup> control technologies are needed for subbituminous coals. Hg<sub>total</sub> control strategies at subbituminous coal-fired power plants have primarily focused on enhancing existing control technologies, while investigating and developing new control technologies are secondary. The strategies include sorbent injection with and without sorbent enhancement additives (SEAs) upstream of an ESP or FF (fabric filter) and Hg<sup>0</sup> oxidation upstream of a wet or dry flue gas desulfurization (FGD) system.

### Activated Carbon Injection

Many potential Hg sorbents have been evaluated (1). These evaluations have demonstrated that the chemical speciation of Hg controls its capture mechanism and ultimate environmental fate. Activated carbon injection (ACI) is the most tested technology available for Hg<sub>total</sub> control. ACs have the potential to effectively adsorb Hg<sup>0</sup> and Hg<sup>2+</sup>, depending on the carbon characteristics and flue gas composition (1). Most AC research has been performed in fixed-bed reactors that simulate relatively long residence time (gas–solid contact times of minutes or hours)

and  $Hg_{total}$  capture by an FF filter cake (4–6). However, it is important to investigate short residence time (seconds) in-flight capture of  $Hg^0$  because most of the coal-burning boilers in the United States employ cold-side ESPs for controlling particulate matter emissions.

The projected annual cost for AC 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%  $Hg_{total}$  removal from a coal combustion flue gas containing  $10 \mu\text{g}/\text{Nm}^3$  of  $Hg_{total}$  (7). For subbituminous and lignite coals, >90% Hg control is not achievable with standard, nonchemically treated AC alone in power plants configured with an ESP only. More efficient carbon-based sorbents are required to enable lower carbon-to-mercury weight ratios to be used, thus reducing the costs.

Energy & Environmental Research Center (EERC) pilot-scale ESP and ESP-FF Hg removal efficiencies for Fort Union lignite and subbituminous coal combustion flue gases are compared in Figures 1 and 2 to those obtained at full-scale utility boilers while AC is injected into a bituminous coal combustion flue gas upstream of a TOXECON (pulse-jet FF) and into bituminous and PRB subbituminous coal combustion flue gases upstream of an ESP. As indicated in Figures 1 and 2, coal type (i.e., composition) was an important parameter that affected the  $Hg_{total}$  removal efficiency of a control device. During the pilot-scale lignite and utility-scale eastern bituminous coal tests,  $Hg_{total}$  removal efficiencies increased with increasing ACI rates. Conversely,  $Hg_{total}$  removal efficiencies were never greater than 70%, regardless of the ACI rate into the PRB subbituminous coal combustion flue gas. This limitation is probably caused by the low amount of acidic flue gas constituents, such as HCl, that promote Hg-AC reactivity.

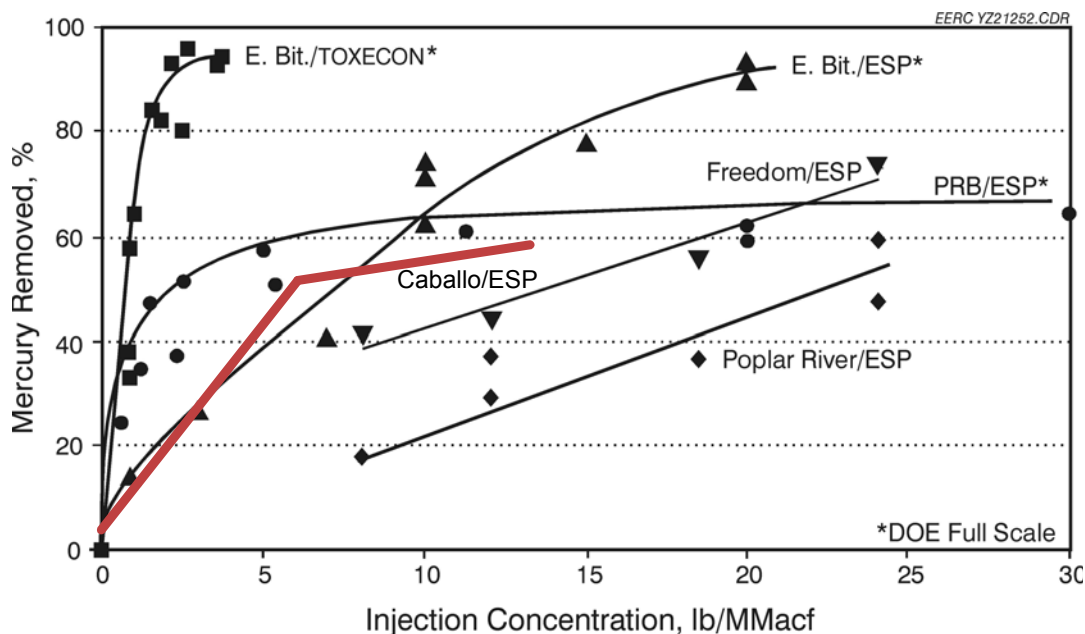


Figure 1. Pilot-scale ESP (7) and full-scale ESP (8)  $Hg_{total}$  removal efficiencies as a function of ACI rate.

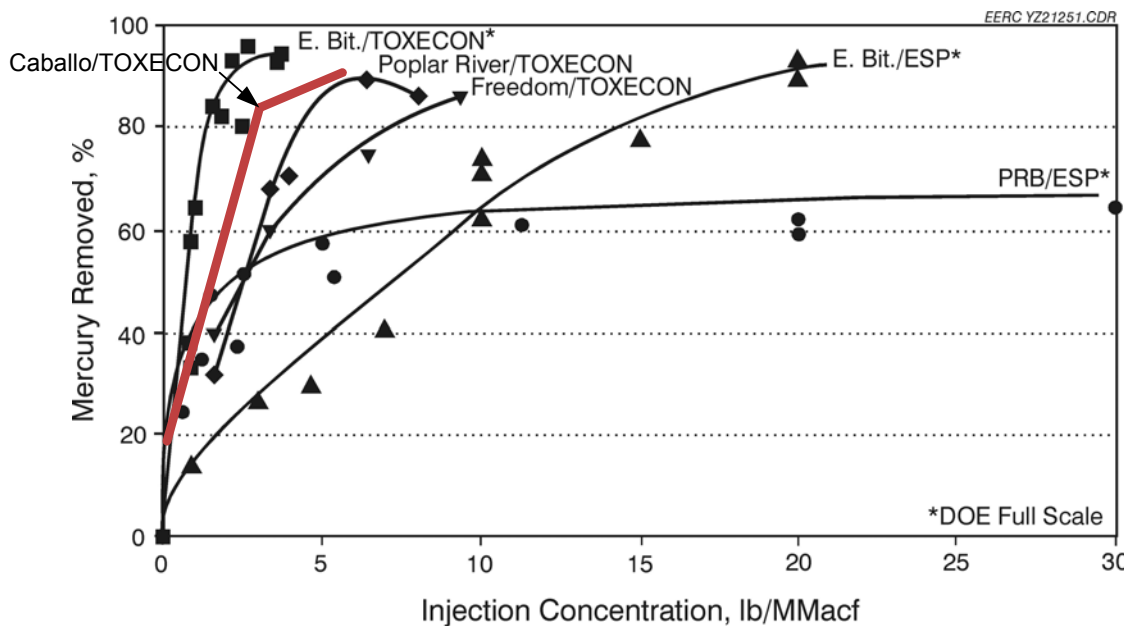


Figure 2. Pilot-scale ESP–FF (7) and full-scale TOXECON and ESP (8)  $Hg_{total}$  removal efficiencies as a function of ACI rate.

### $Hg^0$ Oxidation and Sorbent Enhancement Additives

$Hg^0$  oxidation technologies being investigated for lignite and subbituminous coals include catalysts, chemical additives, and cofiring fuels. The catalysts that have been tested include metal-impregnated, oxide-impregnated, noble metal, and selective catalytic reduction (SCR) catalysts for  $NO_x$  reduction. The chemical additives tested are generally halogen-containing salts. The cofired fuels tested contained oxidizing agents (9).

Mercury speciation sampling was conducted upstream and downstream of SCR catalysts at power plants firing bituminous and subbituminous coals (10). Test results indicated evidence of  $Hg^0$  oxidation across SCR catalysts when bituminous coals are fired. However, when subbituminous coal is fired, the results indicated limited  $Hg^0$  oxidation; more testing needs to be conducted on low-rank coals. The capability of SCR systems to promote  $Hg^0$  oxidation is coal-specific and probably related to the chlorine, sulfur, and calcium contents of the coal as well as temperature and specific operation of the SCR catalyst, including space velocity.

$Hg^0$  oxidation catalysts were very effective, with  $>80\%$  conversion of  $Hg^0$  to  $Hg^{2+}$  during testing on a North Dakota power plant flue gas slipstream for periods of  $\leq 6$  months (9). Tests were also conducted using iron oxides and chromium, with little success of oxidation. Zygarlicke and others (11) 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 (1).

Coal additives for  $Hg^0$  oxidation and sorbent enhancement have been tested at the EERC (12, 13). The additives to the coal are called SEAs. SEA1 is a  $CaCl_2$  solution added to the coal, and SEA2 is a proprietary additive. The results of the addition of SEA2 to North Dakota lignite coal at very low levels along with ACI upstream of a TOXECON, an *Advanced Hybrid*<sup>TM</sup> filter, and an ESP are illustrated in Figure 3. Baseline  $Hg$  emissions ranged from 9 to 12  $\mu g/Nm^3$ , with 80% to 90% of the  $Hg_{total}$  as  $Hg^0$ . Coal additives improved the  $Hg_{total}$  removal efficiencies of the TOXECON, *Advanced Hybrid*<sup>TM</sup> filter, and ESP devices to  $\geq 90\%$  removal. The  $Hg_{total}$  control efficiency obtained with the ESP significantly improved compared to the previous ESP results presented in Figure 3. The coal additive technology has shown potential to improve SDA–ESP and SDA–FF  $Hg_{total}$  control efficiency. In addition, novel methods for introduction of SEA2 with sorbent are being investigated.

### ESP-Only Testing

ACI and SEA addition upstream of an ESP were evaluated for controlling  $Hg_{total}$  emissions associated with North Dakota lignite combustion. The testing was performed using the EERC's particulate test combustor (PTC) equipped with an ESP. Test results are presented in Figure 4. DARCO FGD injection at 3.75 and 15 lb/MMacf reduced  $Hg_{total}$  emissions by 50% and 60%, respectively. The addition of SEA to the coal and ACI at 3.75 lb/MMacf reduced  $Hg_{total}$  emissions by  $>70\%$ .

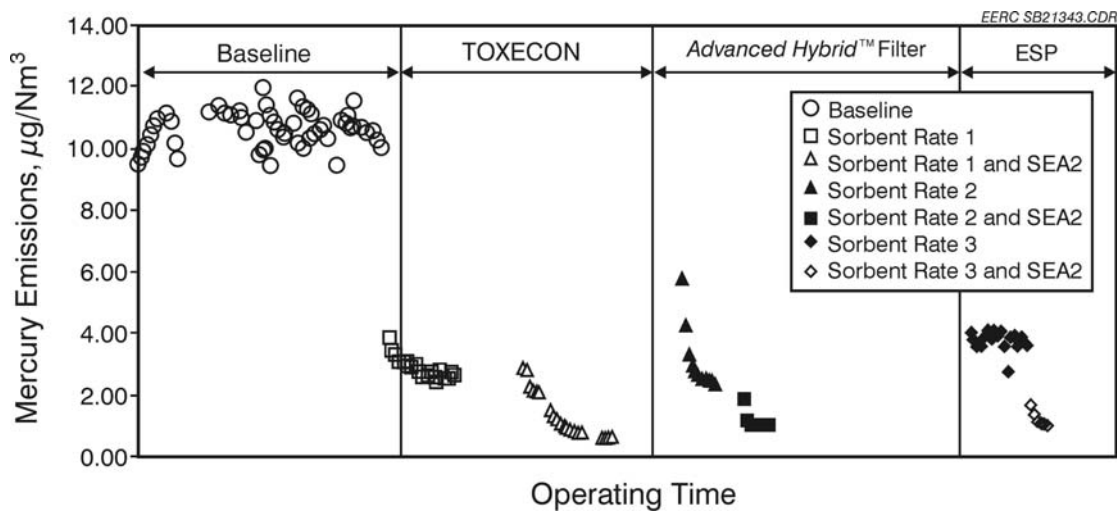


Figure 3. Mercury emissions for ACI combined with additives.

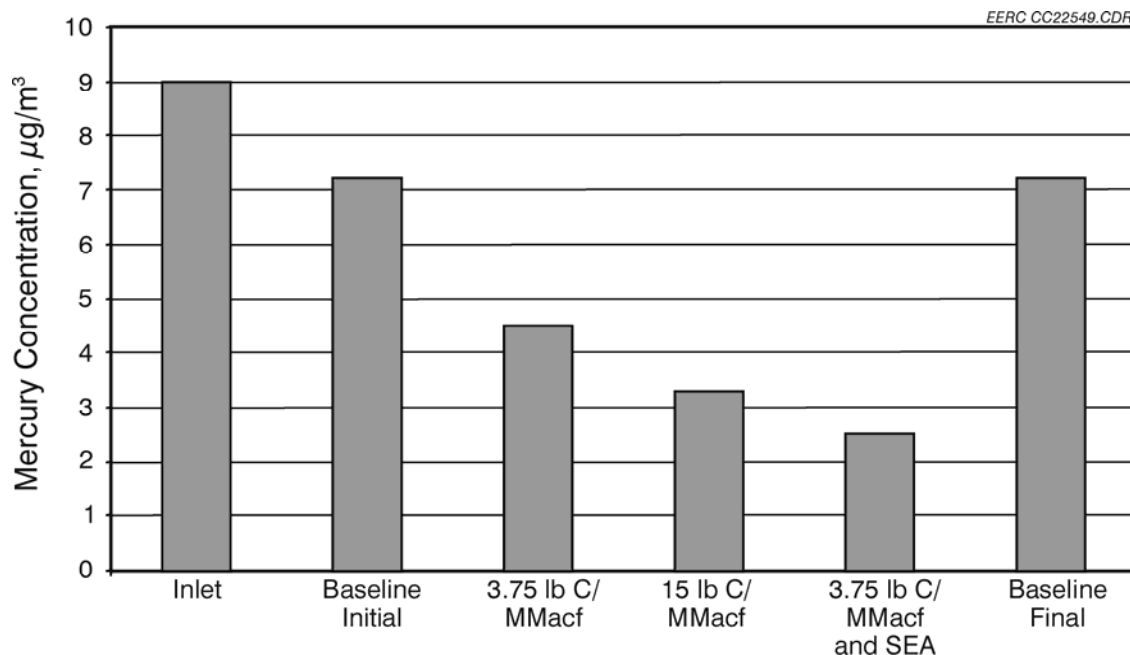


Figure 4. ESP inlet and outlet  $\text{Hg}_{\text{total}}$  concentrations as functions of ACI and SEA addition rates into North Dakota lignite combustion flue gases (12).

The addition of SEA1 alone and combined with ACI was tested for Caballo subbituminous coal ash, as shown in Figure 5. SEA1 alone had a negligible effect on ESP  $\text{Hg}_{\text{total}}$  removal. However, SEA1 addition used in conjunction with DARCO FGD injection resulted in higher  $\text{Hg}_{\text{total}}$  removals compared to those obtained with ACI alone. SEA1 addition at a rate of 2.9 lb/MMacf along with 4.8 lb/MMacf ACI resulted in nearly 60%  $\text{Hg}_{\text{total}}$  removal. Even though SEA1 addition alone reduced the proportion of  $\text{Hg}^0$ , it did not result in significant  $\text{Hg}_{\text{total}}$  removal. SEA1 addition combined with ACI resulted in substantial  $\text{Hg}_{\text{total}}$  removal. Increasing the addition rate of SEA1 above 2.9 lb/MMacf did not significantly increase  $\text{Hg}_{\text{total}}$  removal.

The effectiveness of SEA2 addition, SEA2 addition combined with DARCO FGD injection, and a 50:50 wt% SEA1 and SEA2 mixture addition combined with ACI to remove  $\text{Hg}_{\text{total}}$  and  $\text{Hg}^0$  from Caballo coal combustion flue gas is shown in Figure 6. SEA2 addition at 1.9 lb/MMacf reduced the ESP outlet  $\text{Hg}_{\text{total}}$  concentration by 70%. When SEA2 was added during ACI, ESP  $\text{Hg}_{\text{total}}$  capture increased moderately to >80%. The Hg speciation results in Figures 6 and 7 suggest that in addition to  $\text{Hg}^0$ , some  $\text{Hg}^{2+}$  exited the ESP during the SEA2 and SEA2–SEA1 addition and ACI tests. The addition of the SEA1–SEA2 mixture at 0.5 lb/MMacf combined with ACI at 2.9 lb/MMacf resulted in a slightly lower ESP  $\text{Hg}_{\text{total}}$  removal as compared to the SEA2 addition and ACI tests.

Figure 8 shows results obtained from the Phase II mercury control field tests conducted on several plants with various types of mercury control technologies. These technologies included ACI, enhanced carbon injection, and SEA combined with carbon. The best methods include SEA2 combined with activated carbon and enhanced carbons.

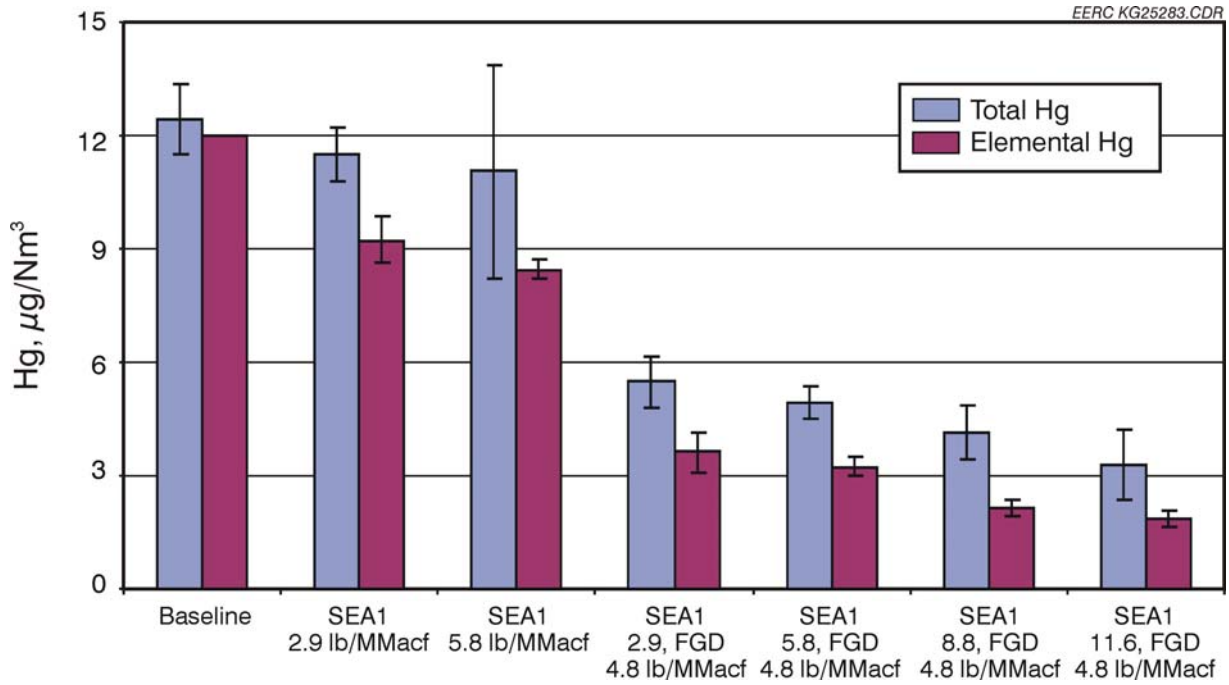


Figure 5. ESP outlet  $Hg_{total}$  and  $Hg^0$  concentrations during Caballo coal combustion and SEA1 additions alone and in combination with DARCO FGD injections (13).

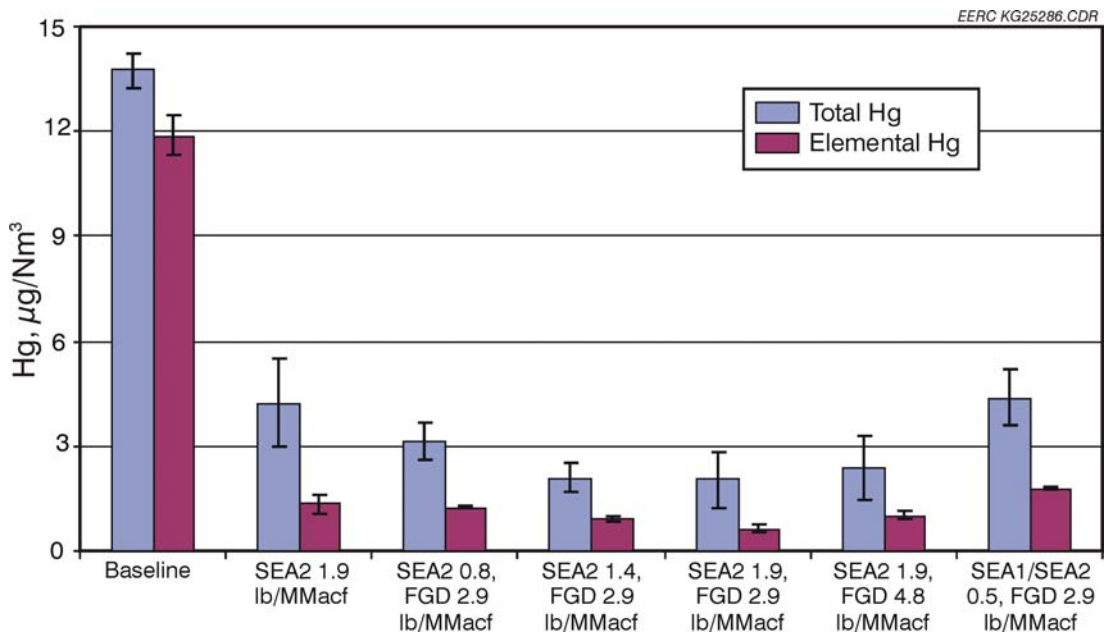


Figure 6. ESP outlet  $Hg_{total}$  and  $Hg^0$  concentrations during SEA2 addition, SEA2 addition and DARCO FGD injections, and SEA1 and SEA2 mixture addition combined with DARCO FGD injection into the Caballo coal combustion flue gas (13).



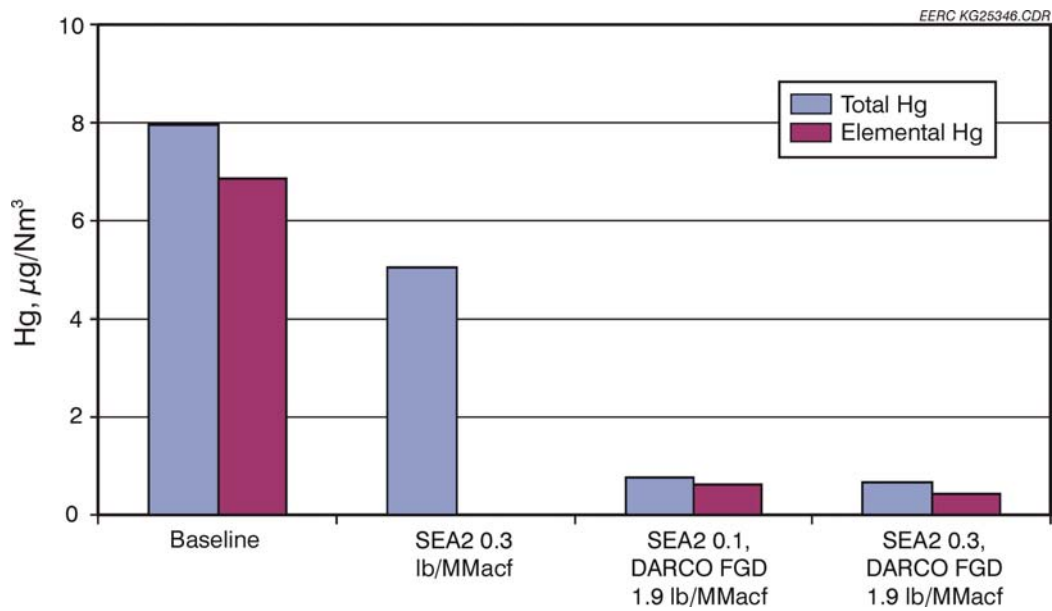


Figure 7. SDA–FF outlet  $Hg_{total}$  and  $Hg^0$  concentrations during baseline Caballo coal testing and SEA2 addition at 0.3 lb/MMacf and SEA2 additions at 0.1 and 0.3 lb/MMacf combined with DARCO FGD injection at 1.9 lb/MMacf into Caballo coal combustion flue gas (13).

### Dry and Wet Scrubber Testing

Pilot- and full-scale testing has been conducted on dry and wet scrubbers. The results of pilot-scale dry scrubbing tests were conducted using SEA1 and SEA2 and were combined with the use of carbon. The results of testing conducted with SEA1 and ACI are shown in Figure 9. In the baseline Caballo coal testing, the SDA–FF removed about 27% of the  $Hg_{total}$ . SEA1 addition at 1.9 and 2.9 lb/MMacf did not significantly improve  $Hg_{total}$  capture in the SDA–FF. In combination with 1.9 lb/MMacf ACI, SEA1 additions of 1.9 and 2.9 lb/MMacf resulted in 67% and 80%  $Hg_{total}$  removals.

Figure 7 indicates the effects of adding SEA2 alone or combined with injecting DARCO FGD into the Caballo coal combustion flue gas on SDA–FF outlet  $Hg_{total}$  concentrations and  $Hg_{total}$  removal efficiencies, respectively. SEA2 addition alone resulted in slightly over 40%  $Hg_{total}$  removal, which is comparable to the SDA–ESP  $Hg_{total}$  removals achieved with SEA2 addition. SEA2 addition at 0.1 lb/MMacf combined with ACI at 1.9 lb/MMacf enhanced SDA–FF  $Hg_{total}$  removal to approximately 90%. Increasing the SEA2 addition to 0.3 lb/MMacf combined with ACI at 1.9 lb/MMacf did not significantly affect SDA–FF  $Hg_{total}$  removal. Similar to the SDA–ESP results, SEA2 addition was very effective at enhancing  $Hg_{total}$  removal in the SDA–FF.

The results of recent testing conducted as part of the U.S. Department of Energy (DOE) Phase II program for subbituminous and lignite-fired systems equipped with SDA–FF are illustrated in Figure 10. Based on these results, the most effective methods for mercury control are SEA combined with ACI and enhanced ACI.

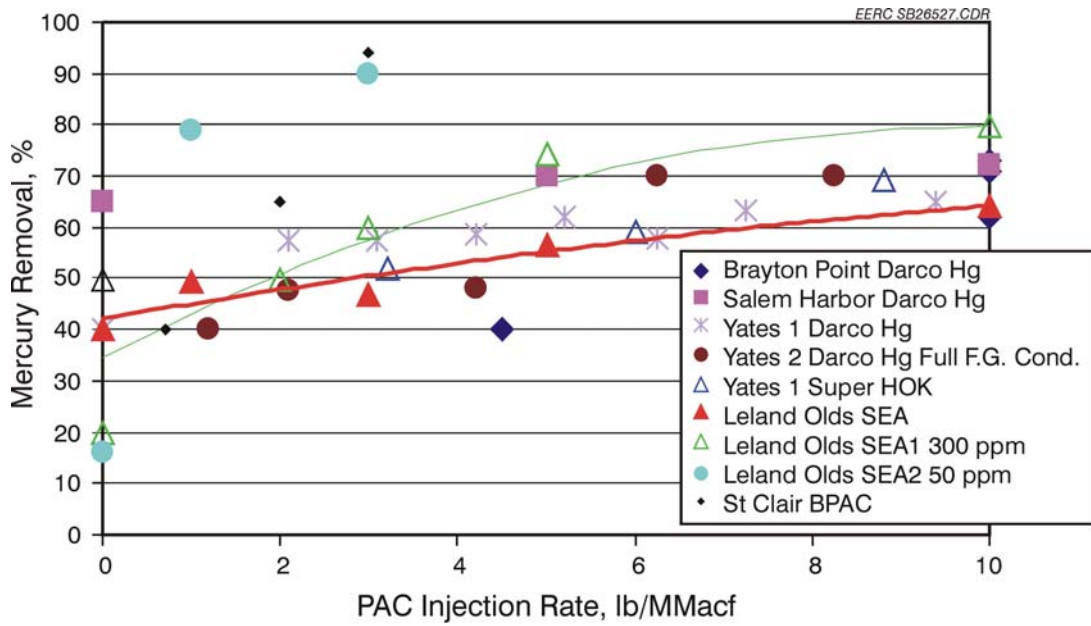


Figure 8.  $Hg_{total}$  removal percentages across the ESP during full-scale testing supported by DOE.

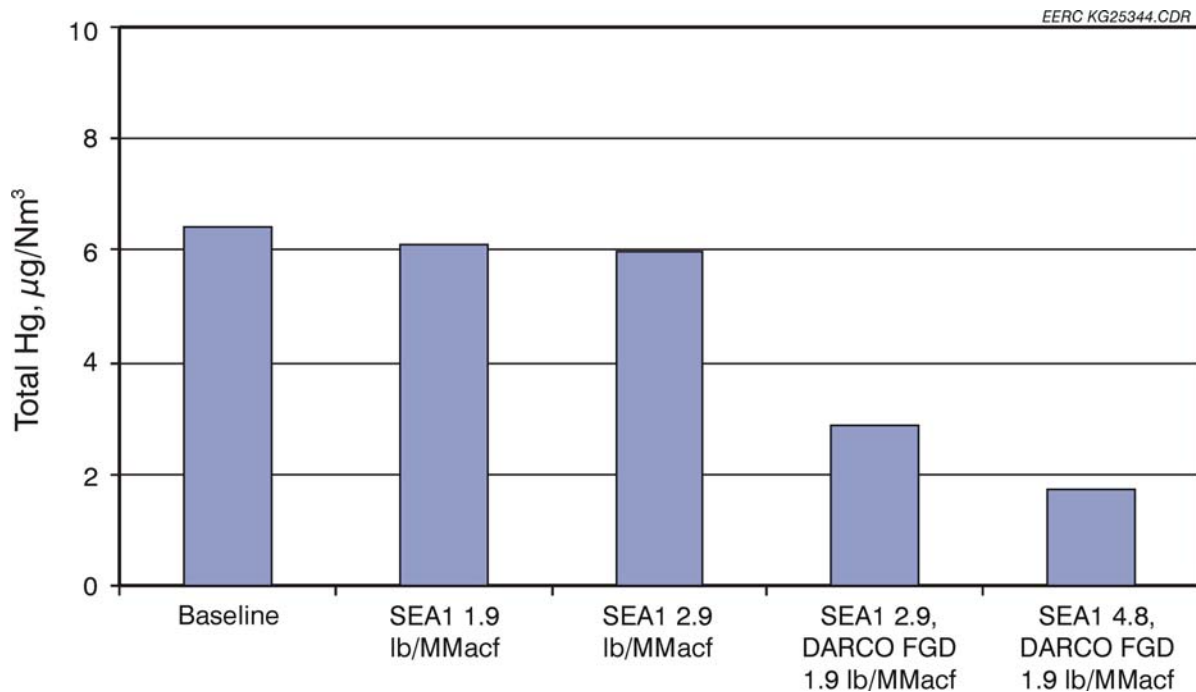


Figure 9. SDA–FF outlet  $Hg_{total}$  concentrations during baseline Caballo coal testing conditions and additions of SEA1 at 1.9 and 2.9 lb/MMacf and additions of SEA1 at 2.9 and 4.8 lb/MMacf combined with DARCO FGD injection at 1.9 lb/MMacf into Caballo coal combustion flue gas (13).

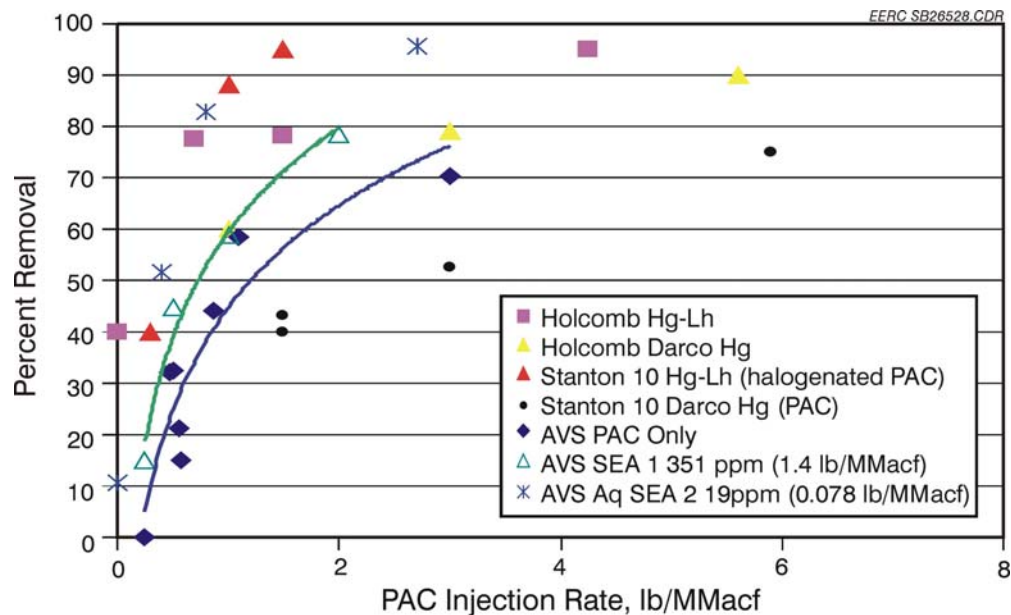


Figure 10. Percent removal achieved in Phase II DOE field testing with SDA–FF using sorbents and SEA.

Testing of mercury removal for wet FGD systems has been conducted as part of the DOE Phase II efforts. The EERC recently completed testing at Minnkota Power’s Milton R. Young (MRY) Unit 2. MRY Unit 2 is a cyclone-fired boiler equipped with an ESP wet scrubber. The testing was aimed at determining the feasibility of mercury oxidation combined with capture using the ESP FGD systems. The mercury removal attained with the addition of SEA1, SEA2, and  $MgCl_2$  across both the ESP and FGD is shown in Figure 11. The  $CaCl_2$  and  $MgCl_2$  show similar results. The SEA2 shows appreciably higher removal rates with the addition of much smaller quantities. However, the goal of 55% removal was not achieved using up to 75 ppm addition of SEA2. Surprisingly, nearly all of the mercury removal occurred in the ESP, with little removal occurring in the FGD. It appears that what mercury is oxidized is removed in the ESP, with the remaining mercury in elemental form, which passes through the FGD unit. The SEA1 was not particularly effective in oxidizing and removing mercury, with stack continuous mercury monitor (CMM) measurements indicating only 16% removal at 500 ppm SEA1 (ppm halogen on a dry coal basis). The Ontario Hydro (OH) method measurements indicate a similar removal at the same SEA1 concentration based on stack OH method total mercury measurements relative to baseline.

The SEA2 shows appreciably higher removal rates with addition of much smaller quantities. However, the ability to reach the goal of 55% removal was not achieved using up to 75 ppm addition of SEA2 which resulted in only 44% removal, as shown in Figure 12. The response time after injection of SEA2 to the boiler was almost instantaneous, as illustrated in Figure 12.

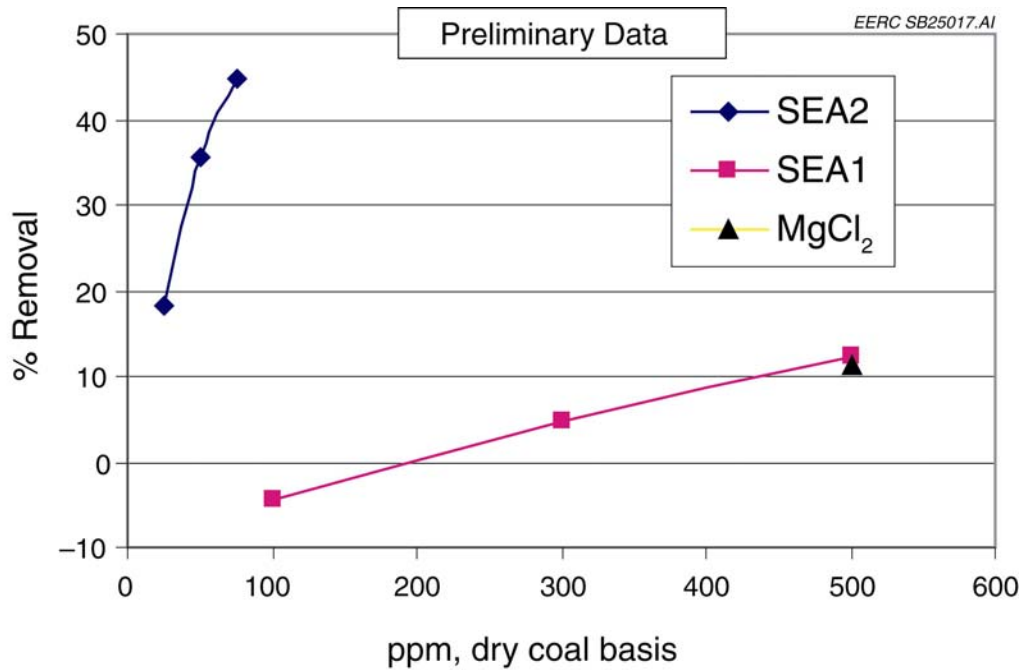


Figure 11. Mercury reduction across ESP and FGD using SEA only (14).

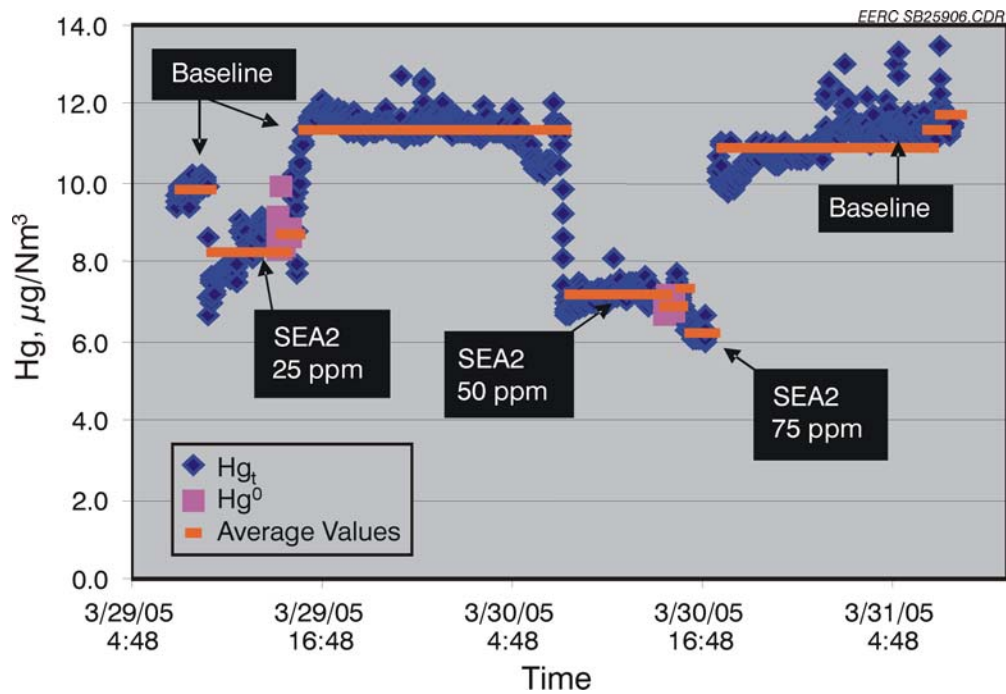


Figure 12. Mercury stack measurements downstream of an ESP and wet FGD conducted during the injection of SEA2 at MRY Station (14).

SEA with the addition of small amounts of carbon has been shown to enhance the oxidation of mercury as well as its capture (7). The results obtained at the MRY Station during parametric testing are shown in Figure 13. The results with powdered activated carbon (PAC) only show removals up to 35% with the addition of 1 lb/MMacf. The addition of SEA1 showed some improvement at lower PAC addition rates, but showed no significant improvement at higher PAC addition rates. The improvement in capture using SEA1 with carbon was not as significant as the results obtained in other field-demonstrated activities. The reason is likely the high sodium content of the North Dakota lignite and the ash partitioning during the cyclone combustion process. The results obtained with the combination of SEA2 and PAC showed much better removal than observed with SEA2 alone.

SEA1 in combination with PAC injection resulted in improved mercury removal, as shown in Figure 13. At the highest rates tested of 300 ppm SEA1 with 1.00 lb/MMacf PAC, the removal was 35% based on stack CMM measurements. However, this is significantly lower than the goal of 55% removal. Again, nearly all of the mercury removal occurred across the ESP, with primarily  $Hg^0$  exiting the ESP.

PAC alone performed nearly as well as when injected in combination with SEA1, achieving approximately 35% removal at a rate of 1.00 lb/MMacf; at 1.80 lb/MMacf, there was 53% mercury removal, which was near the 55% goal. The objectives of the project, however, precluded the use of PAC at such a high rate.

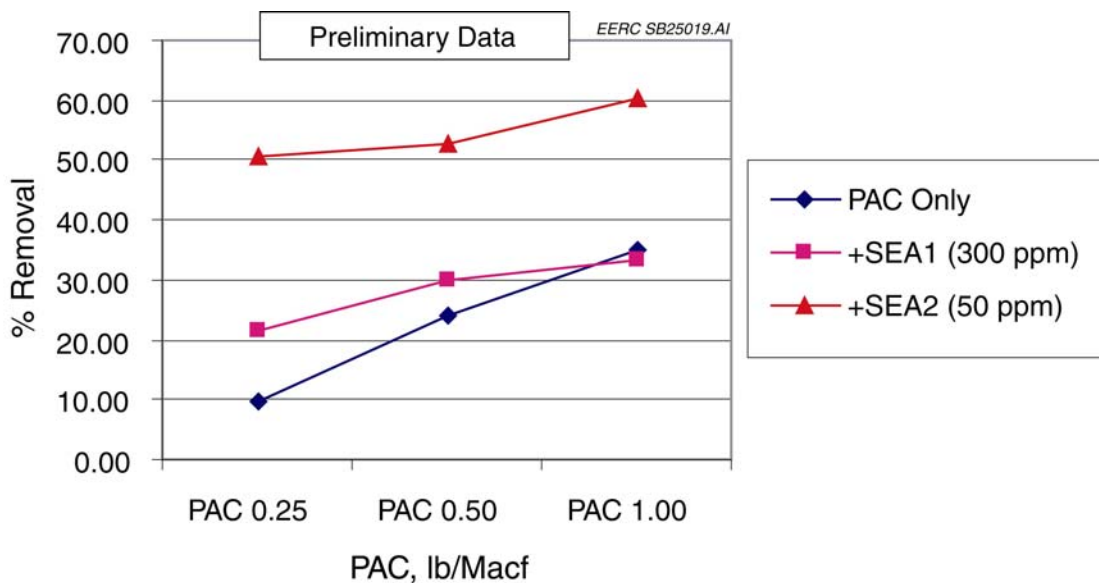


Figure 13. Mercury reduction with SEA or PAC at the MRY Station (14).

The removal rates attained at the MRY site were not as high as anticipated. The primary reason for the lower removal rates for mercury is likely due to a combination of coal characteristics and boiler type. The coal fired during the course of testing was a high-sodium lignite. During combustion in the cyclone-fired boiler, a significant amount of the sodium is vaporized and subsequently condenses upon gas cooling to form very reactive, small particles. These small particles likely reacted with the SEA materials that were injected, decreasing their potential to oxidize mercury.

A second method of delivering SEA2 (Technique 2) was developed as an alternative to the addition of SEA2 to the boiler as part of an effort conducted by the EERC and Babcock & Wilcox Company (B&W). Technique 2 minimizes any impact of SEA2 injection in the boiler and limits the reaction of SEA2 with other ash components in the boiler, convective pass, and air heater. Feasibility testing of Technique 2 for SEA2 injection has been conducted at two sites with promising results. The first site was Antelope Valley Station (AVS), with injection occurring upstream of an SDA–FF system (15). The results are shown in Figure 14. The results indicate that with low levels of injection of PAC and SEA2, removal efficiencies of 90% mercury reduction can be obtained. Further testing was conducted at Hawthorn Unit 5 on July 11–26, 2005, with the results shown in Table 3. The removal efficiencies (including baseline) for Technique 2 SEA2 injection, combined with ACI, ranged from 76% to 94% with varying levels of SEA2 and PAC addition.

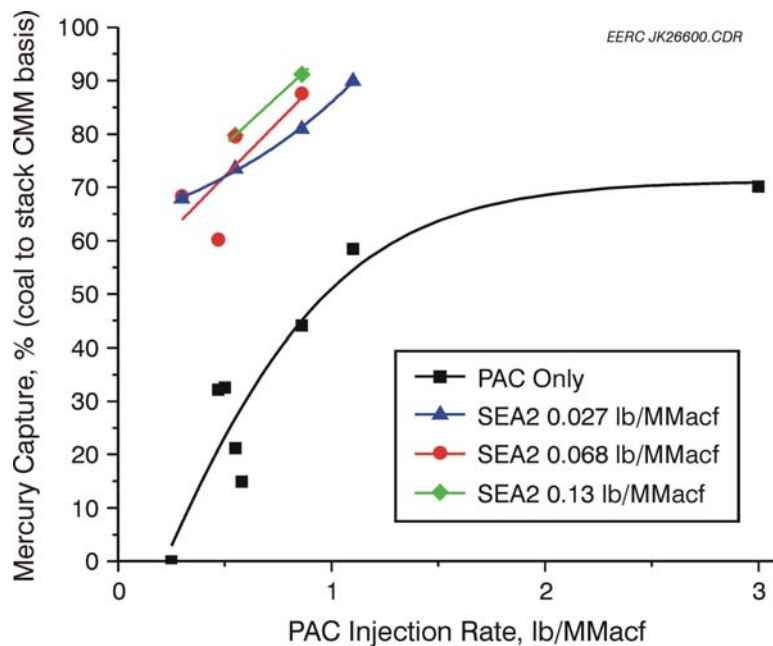


Figure 14. Results of mercury capture testing at AVS SDA–FF using Technique 2 SEA2 injection with activated carbon.

**Table 3. Results of Parametric Tests at Hawthorn Unit 5 (total Hg) Using Technique 2 SEA2 Injection**

Test No.	Hg Control Technology	SDA Inlet, $\mu\text{g/dscm}$	FF Inlet, $\mu\text{g/dscm}$	Stack, $\mu\text{g/dscm}$	Total Mercury Removal, %
7	0.025 lb/lb (SEA2), 1 lb/MMacf (PAC)	9.1	3.8	1.1	88
8	0.05 lb/lb (SEA2), 0.5 lb/MMacf (PAC)	9.4	5.7	2.3	76
9	0.075 lb/lb (SEA2) 0.5 lb/MMacf (PAC)	9.2	5.1	1.7	82
10	0.0125 lb/lb (SEA2) 2 lb/MMacf (PAC)	10	4.2	0.6	94

Technique 2 for injection of SEA2 is a major change in the technical approach in the use of SEA2 injection over past methods. Technique 2 offers several advantages over injection of SEA2 to the boiler or adding it to the coal. The advantages include 1) use of much lower levels of SEA2 to achieve the required sorbent enhancement and mercury oxidation; 2) minimizing potential impact on the boiler, convective pass, and air preheater; and 3) minimizing the potential for sorption of the SEA2 by high-alkali and alkaline-earth ash components.

Technique 2 shows significant potential for very high mercury removal rates, greater than 90% in an SDA–FF application. Technique 2 also provides technical and cost advantages over the use of treated carbons. Since the additive amount is determined on-site, it can be tailored to provide only the amount needed for given coals and conditions and can be varied as these change.

### Novel SEA2 Injection

Recently, testing was conducted at the pilot scale using a novel SEA2 injection method. Table 4 summarizes pilot-scale testing using the EERC PTC equipped with an ESP. The coal fired was a subbituminous coal that produced flue gas where mercury was primarily in the elemental form. The results show significant enhancements in mercury removal efficiencies with the use of the novel SEA2 method. Novel SEA2 shares the same versatility as Technique 2 with the added benefits of increased safety and much lower chemical cost.

**Table 4. Results of Parametric Tests Using Novel SEA2 with Carbon**

Sorbent	Injection Rate, lb/MMacf (carbon)	Hg Removal Within ESP, %
DARCO-Hg (activated carbon)	2.6	52
DARCO-Hg-LH (enhanced activated carbon)	2.6	59
Novel SEA2-AC-1	2.6	79
Novel SEA2-AC-2	2.6	88

PPL Montana LLC (PPL) requested the EERC's assistance in developing a strategy to successfully meet the Hg control requirements for its coal-fired power production assets in Montana. PPL Montana owns and operates the Corette Station in Billings and is part owner and the operator of the Colstrip Station which consists of four units. PPL is aggressively pursuing developing the information it will require to meet its obligations for Hg control requirements resulting from either the federal Clean Air Mercury Rule or a Montana-specific rule. The work covered in this report is critical to allow PPL to take prudent first steps in accomplishing that goal.

EERC personnel met with representatives of PPL in December 2005 to discuss mercury control options that had potential for the Colstrip Station. The EERC, working with PPL Montana, developed an approach to identify cost-effective options for mercury control at its coal-fired power plants. The overall approach involved the following steps:

- Establish baseline mercury levels and speciation
- Conduct short-term parametric testing
- Analyze, assess, and propose recommendations for long-term tests
- Conduct long-term 6- to 12-month tests
- Analyze and assess test results
- Perform economic evaluations
- Identify the best options for control

The work conducted as part of this project focused on conducting baseline mercury levels and speciation measurement, short-term parametric testing, and weeklong testing of a mercury control technology at Colstrip Unit 3. This activity will be followed by more testing focused on longer-term performance, balance-of-plant impacts, and possibly other technologies.

The mercury control technologies utilized involved the use of oxidizing agents or SEAs alone or in combination with ACI. These processes have shown promise in testing conducted with lignite and subbituminous coals. Additional testing is required at Colstrip because of its unique particulate and sulfur scrubber system. Mercury control technologies using this system with a subbituminous coal have not been tested in the past.

## **EXPERIMENTAL**

The Colstrip generating station located in Colstrip, Montana, consists of four units. Units 1 and 2 have a design capacity of 330 MW, and Units 3 and 4 have a design capacity of 805 MW. Sampling was conducted on Unit 3. Unit 3 has a tangentially fired boiler equipped with a wet FGD system comprising eight independent scrubber units (seven working/one standby). Inlet ducts to the scrubbers are of lengths from tens of feet to hundreds of feet.

Based on the mercury speciation data, past pilot- and full-scale experience, plant configuration, and discussions with Colstrip plant personnel, three techniques and various combinations of these techniques were identified as viable options for mercury control. The options included oxidizing agents such as chlorine-based SEA1 and an EERC proprietary SEA2



with and without ACI. Injecting SEA1 into the coal feed allows the chloride ions to dissociate at high temperature in the boiler, producing free chloride ions. The chloride ions or radicals react with elemental mercury to produce oxidized mercury species. The resulting oxidized mercury species are more effectively captured in the wet scrubbers. Activated carbon injected upstream of the wet scrubber can be effective in absorbing  $\text{Hg}^0$  and  $\text{Hg}^{2+}$ , depending on gas conditions. SEA2 injected upstream of the wet scrubber can oxidize mercury, which will then be captured by the wet scrubber as well as enhance the surface of the carbon.

CMM data of  $\text{Hg}^0$  and  $\text{Hg}_{\text{total}}$  concentrations were collected at the FGD inlet, FGD outlet, and stack using Tekran Model 2537A analyzers. OH method samples were collected at the same locations to verify the CMM data. In conjunction with the mercury measurements, six coal samples, along with samples of bottom ash, fly ash, and scrubber slurry, were taken throughout the testing period. Each sample was submitted for detailed characterization and mercury analysis.

The Tekran Model 2537A, a gold amalgamation and cold-vapor atomic fluorescence spectroscopy (CVAFS)-based Hg vapor analyzer, is used in conjunction with a PS Analytical S235C400 wet-chemistry conversion unit. CVAFS systems can only measure elemental mercury. The S235C400 uses two separate liquid flow paths, one to continuously reduce  $\text{Hg}^{2+}$  to  $\text{Hg}^0$ , resulting in a total gas-phase Hg sample, and the other to continuously scrub out  $\text{Hg}^{2+}$ , resulting in an  $\text{Hg}^0$  sample. The S235C400 also uses a Peltier thermoelectric cooler module to cool and dry the sample gases prior to analysis. The Tekran instrument traps the Hg vapor from the conditioned sample onto a cartridge containing an ultrapure gold sorbent. The amalgamated Hg is then thermally desorbed and detected using AFS. A dual-cartridge design allows alternate sampling and desorption, resulting in continuous measurement of the sample stream. Model 2537A allows two methods of calibration: manual injection or automatic permeation source. Permeation source calibration was used to calibrate the instrument daily. Manual injection calibration on both cartridges was performed for verification. The Tekran instrument can measure either  $\text{Hg}_{\text{total}}$  or  $\text{Hg}^0$ , with one analysis point being obtained approximately every 2.5 minutes. The system is designed only to measure the mercury concentration in the vapor phase, so the contribution of particulate-bound mercury was not measured. Because of the high ash load at the FGD inlet, an inertial separation probe was utilized for CMM sampling at that location.

For verification of the CMM measurements in the flue gas, ASTM International Method D6784-02 (Standard Test Method for Elemental, Oxidized, Particle-Bound, and Total Mercury in Flue Gas Generated from Coal-Fired Stationary Sources – Ontario Hydro Method) was used. Samples were withdrawn from the flue gas stream isokinetically through a probe/filter system, maintained at 120°C or the flue gas temperature, whichever was greater, followed by a series of impinger solutions in an ice bath. Particle-bound mercury was collected on a quartz filter in the front half of the sampling train.  $\text{Hg}^{2+}$  was collected in impingers containing a chilled aqueous potassium chloride solution.  $\text{Hg}^0$  was collected in subsequent impingers (one impinger containing a chilled aqueous acidic solution of hydrogen peroxide and three impingers containing chilled aqueous acidic solutions of potassium permanganate). Samples were recovered and sent to the lab for analysis. Results were initially reported as  $\mu\text{g}/\text{L}$  and then converted to  $\mu\text{g}/\text{dscm}$ .

In order to test the feasibility of ACI/SEA2 injection to capture mercury, a single scrubber was selected for testing instead of treating all seven working scrubber units. Also scrubber units are turned on and off depending on load conditions. Scrubber 3-8 was selected to serve as the test scrubber for the project because it has the shortest duct length, providing a “worst case” for mercury removal. Removal efficiencies are highly affected by residence time, and this location would provide the shortest residence time and therefore the lowest removal.

At the 3-8 FGD inlet, the CMM sampling probe was inserted using existing ports located on the duct (between Levels 7 and 8 of the scrubber building). The injection lance was inserted 3 feet downstream of this port. The sorbent injection lance consists of 1.5-inch-i.d. stainless steel tube 15 feet long. The tube was inserted to cover the entire 12.5-ft-i.d. length of the duct. Two sets of ten, 1/8-inch holes were drilled along each side of the tube to allow for injection of material tangentially to the gas flow. The ten holes were distributed equally along the 12.5-foot length of the duct. The distance from injection lance to the entrance of the scrubber was approximately 15 feet. Based on a duct gas flow rate of 75 ft/sec, the residence time would be approximately 0.2 seconds. The outlet CMM probe was inserted into existing ports located at Level 3 of the scrubber building. The stack CMM was placed in the equipment room located approximately at the 400-foot level of the stack and used existing ports.

The location of the injection skid for SEA1 was located on the floor level of the Unit 3 boiler building. Injection skids for AC and SEA2 were located outdoors on the northeast corner of the Unit 3 scrubber building. The novel SEA2 skid was placed on the northeast corner of the Unit 3 scrubber building, on the roof at Level 5.

Novel SEA2 shares the same versatility as Technique 2 but requires a completely new hardware delivery system. In the development of the hardware field testing evaluation and modification to the system is a must. To aid in this development PPL Montana LLC agreed to allow the system to be setup and run for three days at their facility in Colstrip, Montana.

Because of the challenges of Hg removal at this facility it was intended to use this opportunity to advance the method, not necessarily promote it as the best option. Parametric testing was conducted with two activated carbon rates: 1) a minimal rate, which was the lowest injection rate that could be maintained with the PAC injection skid, equal to 0.25 lb/MMacf, and 2) a PAC injection rate of 1.5 lb/MMacf, a rate used during the weeklong testing of SEA2 Technique 2.

## **RESULTS AND DISCUSSION**

The baseline and parametric test plans are shown in Table 5. Once the CMMs were fully operational and verified using the OH method, the parametric testing commenced. The parametric testing rates were selected based on two criteria. The first was the addition of a material that did not impact plant operation. Plant personnel provided input for overall rates of material addition in order to minimize impacts. The second was to add a level sufficient to where measurable impacts could be made.

Table 5 summarizes the testing that occurred on Unit 3. The first two days were reserved for gathering baseline data. The monitors were collecting data throughout the entire test schedule; therefore, baseline data were also being collected at night after the daily parametric testing was completed. Two days of delay were experienced during parametric testing. SEA1 was scheduled to be tested on April 9. After a few hours of injection, the mill became plugged and testing was halted. The plugging was due to the SEA1 injection location, and the injection location was relocated to inject directly into the boiler. This was not completed until late on April 11. Because of these problems, April 10 was used for initial testing of ACI. On April 12, SEA1 parametric testing was rerun and completed, along with subsequent scheduled testing on subsequent days. Plant output was held as constant as possible during testing. However, energy dispatch needs and the market dictated load changes that could not always be avoided. These changes do affect the equilibrium of the unit and will introduce variability into the data.

**Table 5. Test Summary for Unit 3**

Date	SEA1	ACI	SEA2 Injection	Description
April 7	None	None	None	Baseline
April 8	None	None	None	Baseline
April 10	None	27 lb/hr 54 lb/hr 81 lb/hr	None	Three rates of activated carbon alone
April 12	150 ppm 300 ppm 400 ppm	None	None	Three rates of SEA1 alone
April 13	400 ppm	54 lb/hr	None	One rate of SEA1 and ACI combined
April 14	None	7 lb/hr	25 ppm 75 ppm 100 ppm	Three rates of SEA2 with one rate of ACI for all tests
April 15	None	27 lb/hr 40 lb/hr 54 lb/hr	75 ppm	Three rates of ACI with one rate of SEA2 for all tests
April 29 – May 5	None	54 lb/hr	75 ppm	Weeklong test
May 6–8	None	54 lb/hr	2.2 lb/hr 4.4 lb/hr 6.6 lb/hr	Novel SEA2 parametric testing, three rates of SEA2 with one rate of ACI for all tests

Further delays were experienced at the conclusion of the parametric testing. Delays due to a chemical vendor supply shortage for SEA2 caused testing to be halted from April 17 through April 23. Unfortunately, a tube leak caused the unit to be shut down from April 24 through April 27. The unit was brought back online on April 28, and testing resumed on April 29.

Injection of SEA1 to the boiler was based on parts per million addition on a coal basis, 150 ppm a solution injection rate of 1.06 gal/min, 300 ppm equal to a rate of 2.11 gal/min, and 400 ppm equivalent to 2.82 gal/min. The ACI injection rates were based on gas flow through the duct. 27 lb/hr, 54 lb/hr, and 81 lb/hr equivalent to 1 lb/MMacf, 2 lb/MMacf, and 3 lb/MMacf, respectively. SEA2 was based on fuel equivalent across the one scrubber. This is equates to 3.4 lb/hr for 25 ppm, 10.3 lb/hr for 75 ppm, and 13.7 lb/hr for 100 ppm SEA2.

Table 6 contains the Unit 3 coal analysis data for six coal samples obtained throughout the testing period. It is seen from the table that the coal samples are consistent in proximate and ultimate data. The composition of the coal is consistent with a northern PRB subbituminous coal. The key component in the coal that influences the degree of oxidation of the mercury is Cl content. Based on Table 6, the chlorine content of the coal samples is extremely low at less than 6 ppm. In addition, the level of mercury is below the average for subbituminous coals fired in the United States. The average level based on ICR data is 5.7 lb/TBtu.

The results of all the mercury testing are summarized in Table 7. The baseline data showed some variability in the mercury measurements at the Scrubber 3-8 inlet. The average total mercury content was  $5.6 \mu\text{g}/\text{Nm}^3$  (3.3 lb/TBtu), with greater than 80% elemental upstream of the scrubber and higher than 95% elemental at the outlet. Levels in the stack are also greater than 95% elemental. Because of fluctuation of these values and the use of multiple scrubbers, it is difficult to identify a definite trend of mercury from one scrubber outlet to the stack. Based on the data collected during these tests, reemission of mercury captured in the scrubber has not been detected.

Baseline mercury removal across the scrubber is fairly variable but generally tends to be about 5% to 10%, but was measured to be as high as 16% and as low as 2%. Figure 15 compares baseline OH and CMM measurements with the calculated level of mercury in the flue gas based on coal. This roughly correlates with the increase of elemental mercury across the scrubber. As expected, the scrubber is removing oxidized mercury, leaving mostly elemental mercury to travel to the stack.

### **Parametric Testing**

Parametric testing was conducted over 9 days to generate data on the effectiveness of SEA alone and in combination with AC. Injection rates were maintained for a short duration, and so several rates and combinations were tested in the course of the same day. The selected injection rates were maintained until the FGD outlet CMM showed that the mercury levels had reached

**Table 6. Coal Proximate, Ultimate, Chlorine, and Mercury Analysis**

Data Sampled	4/7/2006	4/10/2006	4/12/2006	4/14/2006	5/1/2006	5/3/2006
Basis	As received	As received	As received	As received	As received	As received
Proximate, wt%						
Moisture	27.10	27.40	27.40	27.50	28.20	27.80
Volatile	25.55	26.41	26.12	26.14	25.72	25.45
Fixed Carbon (ind.)	36.27	36.68	36.69	36.58	35.93	35.86
Ash	11.08	9.51	9.80	9.78	10.14	10.89
Total	100	100	100.01	100	99.99	100
Ultimate, wt%						
H	6.10	6.24	6.19	6.23	6.20	6.17
C	45.02	46.26	45.67	46.12	45.06	44.85
N	0.86	0.89	0.88	0.87	0.88	0.86
S	0.54	0.64	0.67	0.76	0.51	0.64
O (ind.)	36.39	36.47	36.80	36.24	37.20	36.60
Ash	11.08	9.51	9.80	9.78	10.14	10.89
Total	99.99	100.01	100.01	100	99.99	100.01
Heating Value, Btu/lb	7947	8201	8187	8180	8127	8048
Chlorine Content, µg/g (dry basis)	<6	<6	<6	<6	<6	<6
Mercury Content, µg/g (dry basis)	0.0383	0.0411	0.0393	0.0424	0.0342	0.0384
Hg, lb/TBtu	3.51	3.64	3.49	3.76	3.02	3.44

**Table 7. Mercury Measurement Summary, mercury concentrations on a dry basis, 3% O<sub>2</sub>**

Test Run	Total Hg Concentration						Elemental Hg Concentration			% Elemental Hg			% Additional Removal	% Removal Across Scrubber
	FGD Inlet		FGD Outlet		Stack		FGD Inlet	FGD Outlet	Stack	FGD Inlet	FGD Outlet	Stack		
	µg/Nm <sup>3</sup>	lb/TBtu	µg/Nm <sup>3</sup>	lb/TBtu	µg/Nm <sup>3</sup>	lb/TBtu	µg/Nm <sup>3</sup>	µg/Nm <sup>3</sup>	µg/Nm <sup>3</sup>					
<b>Beginning Baseline</b>	5.6	3.3	4.8	2.8	5.3	3.1	5.0	4.8	5.0	88	100	94	-	14
OH Results	5.1	3.0	5.1	3.0	5.1	3.0	3.7	5.1	5.1	62	100	100	-	0
<b>PAC Only</b>														
Baseline Before	5.6	3.3	5.3	3.1	5.2	3.1	5.1	5.3	5.2	90	100	100	-	5
1 lb/MMacf (27 lb/hr)	5.7	3.4	5.2	3.1	5.5	3.2	5.4	5.1	5.5	94	98	100	2	9
2 lbs/MMacf (54 lb/hr)	5.9	3.5	5.0	3.0	5.4	3.2	5.2	5.0	5.3	87	100	98	6	15
3 lbs/MMacf (81 lb/hr)	5.6	3.3	4.8	2.8	5.4	3.2	5.1	4.8	5.4	90	100	100	9	14
Baseline After	6.0	3.5	5.2	3.1	5.5	3.2	5.4	5.1	5.3	89	98	96	-	13
<b>SEA1 Only</b>														
Baseline Before	5.6	3.3	5.4	3.2	5.4	3.2	4.8	5.2	5.2	83	96	96	-	4
150 ppm (1 gal/min)	6.5	3.8	5.6	3.3	5.5	3.2	4.7	5.6	5.5	62	100	100	0	14
300 ppm (2 gal/min)	6.3	3.7	5.4	3.1	5.4	3.1	5.3	5.3	5.2	81	98	96	0	14
400 ppm (3 gal/min)	6.9	4.0	4.3	2.5	4.9	2.9	5.7	4.2	4.7	79	98	96	20	38
OH (during 400 ppm test)	5.4	3.1	4.7	2.7	5.1	3.0	3.7	4.6	4.8	54	98	94	13	13
Baseline After	6.1	3.6	5.5	3.2	5.5	3.2	5.3	5.4	5.4	85	98	98	-	10
<b>SEA1 + PAC</b>														
Baseline Before	6.8	4.0	6.2	3.6	6.4	3.7	6.1	6.2	6.4	89	100	100	-	9
400 ppm, 2 lb/MMacf PAC	6.3	3.7	4.7	2.7	5.5	3.2	5.7	4.7	5.5	89	100	100	13	25
Baseline After	6.2	3.6	5.4	3.1	5.7	3.3	5.5	5.3	5.7	87	98	100	-	13

Continued . . .

**Table 7. Mercury Measurement Summary, mercury concentrations are on a dry basis, 3% O<sub>2</sub> (continued)**

Test Run	Total Hg Concentration						Elemental Hg Concentration			% Elemental Hg			% Additional Removal	% Removal Across Scrubber
	FGD Inlet		FGD Outlet		Stack		FGD Inlet	FGD Outlet	Stack	FGD Inlet	FGD Outlet	Stack		
	µg/Nm <sup>3</sup>	lb/TBtu	µg/Nm <sup>3</sup>	lb/TBtu	µg/Nm <sup>3</sup>	lb/TBtu	µg/Nm <sup>3</sup>	µg/Nm <sup>3</sup>	µg/Nm <sup>3</sup>					
<b>Weeklong – SEA2 + PAC</b>														
Baseline Before	5.8	3.4	5.4	3.1	5.5	3.2	5.4	-	5.5	93	-	100	-	7
75 ppm, 1.5 lb/mm <sup>3</sup> PAC	6.1	3.6	3.8	2.2	5.4	3.1	5.7	-	5.4	93	-	100	30	38
OH	4.9	2.9	3.5	2.0	4.1	2.3	4.1	2.4	3.9	80	54	95	35	29
<b>Novel SEA2</b>														
<i>Day 1</i>														
Baseline Before	5.1	3.0	4.8	2.8	5.2	3.0	4.8	4.7	5.2	94	98	100	-	6
13 ppm (2.2 lb/hr)	5.5	3.2	4.9	2.9	5.5	3.2	4.8	4.9	5.5	85	100	100	0	11
38 ppm (6.6 lb/hr)	5.3	3.1	5.0	2.9	5.6	3.3	4.8	5.0	5.6	90	100	100	0	6
51 ppm (8.8 lb/hr)	5.4	3.1	5.1	3.0	5.7	3.3	5.3	5.0	5.6	98	98	98	0	6
13 ppm, 1.5 lb/MM <sup>3</sup> PAC	5.3	3.1	4.5	2.6	5.4	3.1	4.7	4.5	5.3	87	100	98	6	15
<i>Day 2</i>														
13 ppm, 1.5 lb/MM <sup>3</sup> PAC	5.5	3.2	4.4	2.6	5.2	3.0	5.2	4.3	5.2	94	98	100	2	20
25 ppm, 1.5 lb/MM <sup>3</sup> PAC	5.4	3.1	4.3	2.5	5.0	2.9	4.8	4.3	4.9	88	100	98	4	20
38 ppm, 1.5 lb/MM <sup>3</sup> PAC	5.2	3.0	4.2	2.4	4.7	2.7	4.8	4.2	4.7	92	100	100	7	19
Baseline After	5.2	3.0	4.5	2.6	4.8	2.8	5.1	4.6	4.8	98	100	100	-	13
<i>Day 3</i>														
Baseline Before	6.1	3.6	5.2	3.0	5.3	3.1	5.6	5.2	5.3	91	100	100	-	15
PAC only, 1.5 lb/MM <sup>3</sup> PAC	5.9	3.4	4.7	2.7	-	-	5.4	4.7	-	91	100	-	10	20
13 ppm, 1.5 lb/MM <sup>3</sup> PAC	6.4	3.7	5.3	3.1	5.7	3.3	5.9	5.3	5.7	92	100	100	0	17
25 ppm, 1.5 lb/MM <sup>3</sup> PAC	6.6	3.8	5.4	3.1	5.7	3.3	6.0	5.4	5.7	90	100	100	0	18
OH (during 25 ppm test)	7.4	4.3	6.1	3.6	-	-	6.9	5.8	-	93	100	-	0	18

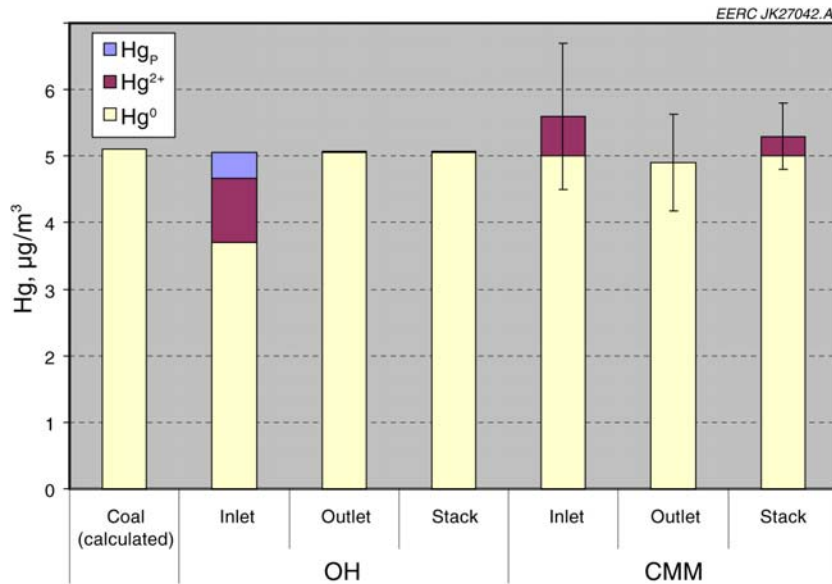


Figure 15. Results of baseline measurements comparing OH and CMM data with the flue gas Hg content calculated from coal Hg content.

steady-state conditions. The SEA and/or AC injection rates during the time OH sampling took place were maintained for 2 hours past the point at which steady-state conditions had been established.

Parametric results of carbon injection alone yielded minimal reduction in Hg emissions. The best additional reduction, 9%, occurred with the highest rate, 3 lb/MMacf, but was not a significant increase over the middle rate of 2 lb/MMacf. Further increases in reduction would have occurred with increases in the rate of carbon injection; however, the benefit of increased carbon would be minimal, making it impractical to do so.

SEA1 injection did result in additional reduction, but again, significant results were not observed until the maximum rate of 400 ppm was used. Injection produced an additional 20% reduction across the scrubber and, during the injection period, resulted in a total mercury reduction of 38%. The measured result was not consistent when SEA1 was combined with activated carbon. This test yielded a smaller reduction of only 13% additional, resulting in an overall mercury reduction of 25%.

Challenges to measuring mercury at the scrubber outlet were discovered during SEA2 testing. This resulted in the rejection of SEA2 parametric testing. The discussion of this challenge is included in Appendix A.

The vendor supplying the SEA2 additive experienced difficulties in maintaining the constant supply of additive needed to conduct a 7-day test. It was therefore agreed that testing



should be halted until the supply flow could be reestablished with the vendor. Testing was delayed for 7 days.

### **Weeklong Testing**

It was decided that the weeklong test would be conducted with the combination of SEA2 and AC. AC combined with SEA2 produces an active material that when injected into a flue gas typical of a PRB coal provides the ability to oxidize mercury and creates a site on the carbon for reaction and bonding.

The summary of results of weeklong testing is listed in Table 7. A different sampling probe was found to be necessary to accurately measure the mercury leaving the scrubber outlet. The probe does not filter the sampled gas stream before chemical conversion but rather brings the conversion chemicals directly to the probe tip, removing the filtering step. Unfortunately, the process does not allow for the measurement of elemental mercury but only total mercury in the gas stream.

Speciation was obtained through OH sampling. Reduction of mercury using SEA2 in combination with activated carbon was found to be only an additional 30% across the scrubber. This is an additional reduction of only 10% over SEA1.

It appears that the reaction and interaction of the SEA materials is with the finer fraction of the fly ash, because the SEA materials are vaporized during the reaction process and condense on the surfaces of entrained particles or form very small particles. Mercury will have a tendency to react and interact with the finer fraction of entrained ash and sorbent as a result of the higher surface area of finer particles. Because of the configuration of the scrubber system, the ability to control finer particles is limited as indicated by the higher opacity values at the plant.

Table 7 also includes calculated rates in lb Hg/TBtu. Value calculations were based on the analyses of collected coal samples and plant-provided coal feed rates in conjunction with CMM data. During weeklong testing, mercury output was reduced from 3.6 lb/TBtu to 2.2 lb/TBtu. 3.6 lb/TBtu lies on the upper end of FGD inlet values calculated during testing.

### **Novel SEA2 Injection Technique**

The results of the parametric tests can be seen in Table 7. Benefits were measured that were only slightly better than AC alone. During testing, several challenges were discovered with the operation of the system, many of which could be corrected during field testing and a few that could not. Examination of the hardware at the conclusion of the field work revealed that much of the sorbent material was not being introduced to the AC feed but was being contained within the delivery skid. The small feed rates used did not cause plugging in the skid so this discovery was not made during field testing. This helps to explain the poor performance of the system in that a much lower rate of sorbent was being introduced to the flue gas than was expected. The nature of the containment, however, makes it impossible to ascertain the actual injection rates.

The results of the testing at Colstrip using the novel SEA2 method allowed for further improvements to be made to the hardware on the injection skid, increasing its potential for commercial application. Further field testing of the method is under way.

### **Method 26a Testing**

The emission of total halogen as a result of the addition of SEA was determined using EPA Method 26a extractive sampling at the scrubber outlet. This method utilizes a sampling train similar to the one used for the OH method. Samples were withdrawn from the flue gas stream isokinetically through a probe/filter system maintained at 120°C or the flue gas temperature, whichever was greater, followed by a series of impinger solutions in an ice bath. A quartz filter was used in the front half of the sampling train to capture any particulate matter in the gas stream. Hydrogen halides were collected in impingers containing a chilled aqueous sulfuric acid solution. Halogens were collected in subsequent impingers containing aqueous sodium hydroxide solution. Samples were recovered and sent to the lab for analysis. The Method 26a testing did not detect any bromine in the gas stream at the outlet, and chlorine levels did not rise beyond baseline levels. This demonstrates bromine introduced into the gas stream by the additive was neutralized by the scrubber slurry. Independent sampling was conducted by Maxim Technologies, Billings, Montana for halogen exposure risk to PPL Montana employees at the request of PPL Montana. Their testing also indicated that no halogens could be detected. The Maxim Technologies report can be found in Appendix B.

### **Ash and Slurry Results**

The results of ash and slurry testing are shown in Tables 8 and 9. The chemical compositions of the bottom and fly ash were fairly consistent. A slight increase in chlorine content was noted in the bottom ash sampled after SEA1 injections. Scrubber slurry samples taken after the start of SEA2 injection clearly show the effects of the additive to the system with both highly elevated bromine and a significant increase in carbon content. Curious and worth further study is the trend of increasing chlorine content in the slurry with increasing injection duration of bromine. The levels measured were significantly higher than with chlorine injection from the use of SEA1. The effect does not appear to be an artifact from analysis but perhaps from secondary reactions occurring within the scrubber.

### **Ash Loading**

As part of the OH sampling method, isokinetic particulate sampling was conducted in a method analogous to EPA Method 5. The dust-loading values are calculated during sampling, and values were calculated from baseline, SEA1, and SEA2 testing from all three locations. The results are presented in Table 10. The addition of SEA and PAC did not appear to increase the particulate emissions.

**Table 8. Ash Sample Analyses**

	Bottom Ash						Fly Ash					
	April 7	April 10	April 12	April 14	May 1 SEA 2 +	May 3 SEA 2 +	April 7	April 10	April 12	April 14	May 1 SEA 2 +	May 3 SEA 2 +
	Baseline Oxide, wt%	PAC Oxide, wt%	SEA 1 Oxide, wt%	SEA 2 Oxide, wt%	PAC Oxide, wt%	PAC Oxide, wt%	Baseline Oxide, wt%	PAC Oxide, wt%	SEA 1 Oxide, wt%	SEA 2 Oxide, wt%	PAC Oxide, wt%	PAC Oxide, wt%
SiO <sub>2</sub>	52.50	51.10	51.50	25.70	52.10	52.00	51.40	49.00	47.50	48.80	49.30	49.10
Al <sub>2</sub> O <sub>3</sub>	18.30	17.70	17.90	9.00	20.10	20.30	21.50	22.50	22.70	22.50	23.20	24.60
Fe <sub>2</sub> O <sub>3</sub>	7.70	10.76	11.60	21.09	7.70	7.08	2.22	2.56	2.99	2.37	2.16	2.31
TiO <sub>2</sub>	0.87	0.88	0.89	0.32	0.91	0.92	0.96	1.00	1.02	0.95	0.98	0.97
P <sub>2</sub> O <sub>5</sub>	0.31	0.32	0.32	0.20	0.45	0.46	0.49	0.55	0.63	0.75	0.79	0.78
CaO	14.30	13.70	12.40	4.80	13.10	13.80	14.30	15.00	15.60	14.40	14.60	13.90
MgO	3.13	2.93	2.93	1.47	2.84	2.90	4.20	4.33	4.54	3.71	4.07	4.05
Na <sub>2</sub> O	0.27	0.24	0.27	0.33	0.32	0.40	0.76	0.80	0.96	2.35	1.05	0.72
K <sub>2</sub> O	0.79	0.76	0.65	0.46	0.67	0.68	1.56	1.38	1.06	1.35	1.33	1.18
SO <sub>3</sub>	0.37	0.07	0.08	36.30	0.52	0.25	1.32	1.59	1.56	1.36	1.22	1.05
BaO	1.03	1.10	1.14	0.33	0.88	0.81	0.79	0.78	0.91	0.94	0.71	0.75
SrO	0.38	0.37	0.35	0.10	0.42	0.43	0.47	0.54	0.56	0.56	0.59	0.57
	<b>µg/g</b>	<b>µg/g</b>	<b>µg/g</b>	<b>µg/g</b>	<b>µg/g</b>	<b>µg/g</b>	<b>µg/g</b>	<b>µg/g</b>	<b>µg/g</b>	<b>µg/g</b>	<b>µg/g</b>	<b>µg/g</b>
Br	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5
Cl	13	6	26	13	12	18	<5	<5	<5	<5	<5	<5
Hg	0.0342	<0.0009	0.011	0.108	0.011	0.0841	0.02	0.0058	0.004	<0.003	0.004	0.004
	<b>wt%</b>	<b>wt%</b>	<b>wt%</b>	<b>wt%</b>	<b>wt%</b>	<b>wt%</b>	<b>wt%</b>	<b>wt%</b>	<b>wt%</b>	<b>wt%</b>	<b>wt%</b>	<b>wt%</b>
C	0.44	0.06	0.23	0.35	0.08	0.12	0.11	0.08	0.06	0.04	0.08	0.12
H	0.07	ND*	0.04	0.06	0.02	0.02	ND	ND	ND	ND	ND	0.02
N	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND

\* Not detected.

**Table 9. Slurry Analyses**

	April 7 Baseline		April 10 PAC		April 12 SEA 1		April 14 SEA 2		May 1 SEA 2 + PAC		May 3 SEA 2 + PAC	
	Solid Oxide, wt%	Liquid	Solid Oxide, wt%	Liquid	Solid Oxide, wt%	Liquid	Solid Oxide, wt%	Liquid	Solid Oxide, wt%	Liquid	Solid Oxide, wt%	Liquid
SiO <sub>2</sub>	37.50		33.40		26.40		31.90		34.90		34.80	
Al <sub>2</sub> O <sub>3</sub>	15.10		14.30		11.70		13.80		15.70		16.60	
Fe <sub>2</sub> O <sub>3</sub>	1.75		1.79		1.87		1.89		1.99		1.72	
TiO <sub>2</sub>	0.73		0.71		0.61		0.64		0.73		0.74	
P <sub>2</sub> O <sub>5</sub>	0.35		0.37		0.35		0.44		0.48		0.52	
CaO	17.60		20.20		21.50		19.90		18.30		18.10	
MgO	3.22		2.98		5.58		3.48		2.81		3.08	
Na <sub>2</sub> O	0.70		0.74		1.36		1.54		0.81		0.91	
K <sub>2</sub> O	1.12		0.87		0.70		0.95		0.87		0.79	
SO <sub>3</sub>	21.01		23.87		28.85		24.53		22.54		21.90	
BaO	0.50		0.42		0.47		0.48		0.44		0.43	
SrO	0.32		0.35		0.30		0.33		0.40		0.41	
Cl	0.07		0.08		0.29		0.11		0.06		0.08	
	<b>µg/g</b>	<b>µg/g</b>	<b>µg/g</b>	<b>µg/g</b>	<b>µg/g</b>	<b>µg/g</b>	<b>µg/g</b>	<b>µg/g</b>	<b>µg/g</b>	<b>µg/g</b>	<b>µg/g</b>	<b>µg/g</b>
Br		30		30		26		74		140		305
Cl		706		773		795		772		822		1000
Hg	0.0097	0.012	0.012	0.06	0.019	0.01	0.014	<0.01	0.0654	0.01	0.0993	0.024
	<b>wt%</b>		<b>wt%</b>		<b>wt%</b>		<b>wt%</b>		<b>wt%</b>		<b>wt%</b>	
C	0.1		0.26		0.29		0.19		0.34		0.46	
H	0.88		0.86		0.99		0.82		0.84		0.8	
N	ND*		ND		ND		ND		ND		ND	

\* <sup>1</sup> Not detected.

**Table 10. Dust-Loading Results from the FGD Inlet, FGD Outlet, and Stack, grains/scf**

	Inlet	Outlet	Stack
Baseline	4.4312	0.0133	0.0133
SEA 1 + PAC	4.3347	0.0120	0.0069
SEA 2 + PAC	4.7914	0.0133	0.0088

## MATERIAL COSTS

Material costs were estimated for the use of SEA1, SEA2, and carbon based on the testing performed using an economic model developed at the EERC. Inputs and assumptions made in the model are given in Table 11. Model output was based solely on the performance seen across Scrubber 3-8 and do not reflect the costs associated with treating the entire unit. They do provide a good comparison between additives. Additive cost was based on market values at the time of testing. These costs, especially the cost of SEA2, are strongly market driven and can change quickly. The costs associated with retrofitting a plant, permitting, and Hg emissions monitoring were not included. All costs are based on 2004 U.S. dollars ( $\pm 20\%$ ).

Figures 16 and 17 show the results of the economic modeling. Figure 17 focuses on the annual costs projected to run, operate, and maintain a system to inject the various additives that were tested and at the rates of injection used during testing. The annual costs take into account the purchase of equipment and sorbent(s), operation, maintenance, etc. The annual costs are

**Table 11. Hg Control Cost Analysis Assumptions**

Parameter	Assumption
Output	110 MW net (single scrubber)
Capacity Factor	85%
Flue Gas Hg <sub>total</sub> Concentration	Calculated from coal composition
Heat Rate	10,009 Btu/kWh
Discount Rate <sup>1</sup>	6.5%
Plant Life <sup>1</sup>	20 years
Carbon Cost	\$0.58/lb
SEA1 Cost	\$0.30/lb
SEA 2 Cost	\$2.05/lb
Operation Labor	\$50/hr
Maintenance Labor	\$27/hr
Overhead Rate	20%
Depreciation	5%
Insurance	1.5%
Escalation Rate	3.5%/yr

<sup>1</sup> Discount rate and plant life were used to calculate a capital recovery factor.

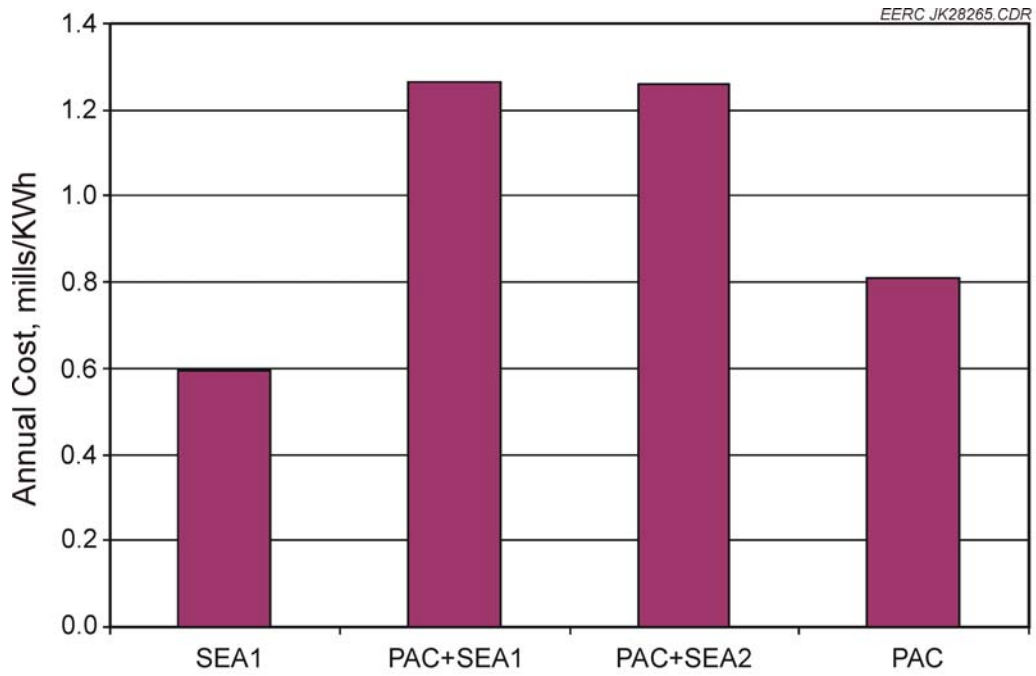


Figure 16. Annual cost associated with the various additives tested.

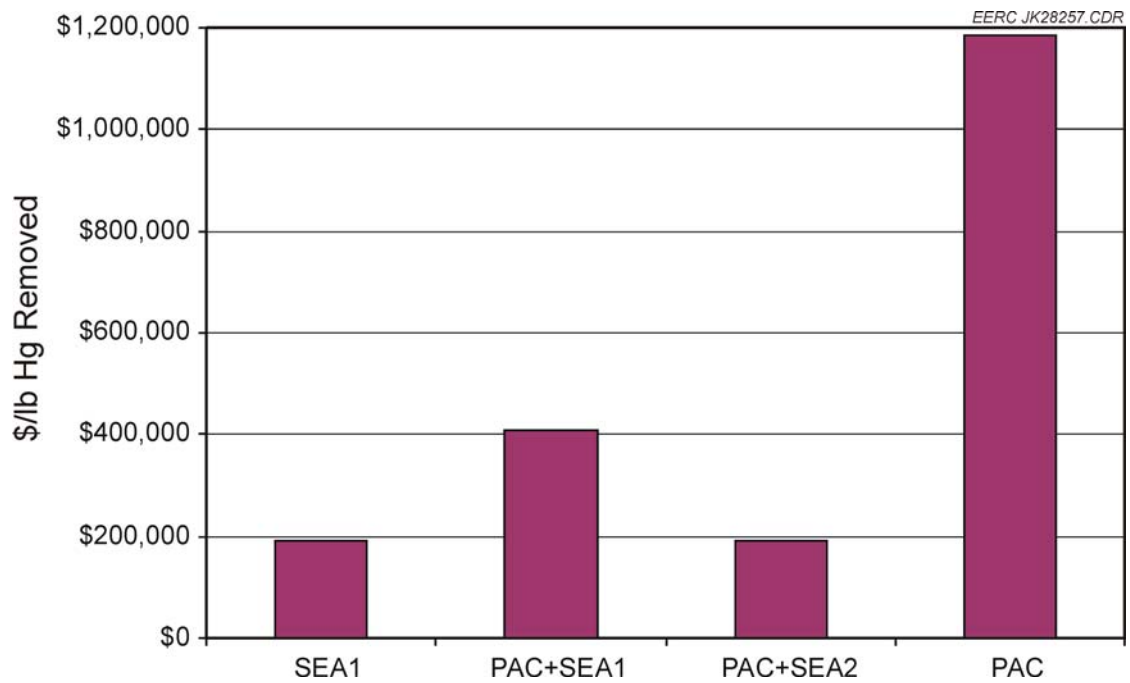


Figure 17. Cost per pound of mercury removed based on the various additives tested.

much higher for the combined systems of SEA and PAC because of the high cost of equipment and installation. Figure 17 shows the relationship of sorbent costs per pound of mercury removed. For each sorbent, the calculation is made from the amount of mercury removal seen during testing. For example, although the annual costs of operating and maintaining a PAC system are low, as shown in Figure 16, the cost per pound of mercury removed is very high because of the poor performance of the activated carbon as measured across Scrubber 3-8.

DOE (16) provided initial cost estimates for achieving 90% Hg emission control using ACI to range from \$25,000 to \$70,000/lb Hg removed. More recently, DOE concluded that at Meramec Station, a plant using PRB coal and equipped with an ESP, the cost for 90% removal was projected to be \$17,700/lb Hg removed, without by-product impacts (17). It is important to keep in mind that the starting data for these figures were generated from testing across one scrubber which indicated a low benefit in regard to sorbent injection. This low performance projected much higher cost estimates than those proposed by DOE. If sorbent performance could be improved, these costs would drop dramatically. As the projections now stand, the cost estimates would be incredibly high for meeting 90% removal.

## **RESIDENCE TIME**

As an aid to help in the understanding of the issue of residence time and the effect of fine particles, models were created to show relative mercury removal. Figures 18, 19, and 20 show the relative mercury removal with three sorbent particle sizes at sorbent loadings of 1, 2.5, and 5 lb/MMacf and an initial mercury concentration of  $6\mu\text{g}/\text{m}^3$ . The model assumes all sorbent particles are of a single size for each curve. Further, the removal is based on the rate of Hg diffusion to the sorbent particle surface, and no account is taken of reactions on the particle surface or of the form of Hg, in effect treating the sorbent as a “perfect” sorbent, capturing all Hg arriving at the surface. The results should be taken only as an indication of the relative ability to remove Hg as a function of particle size and sorbent loading and not as “absolute” removal rates for actual sorbent injection.

Additionally, Figure 21 shows relative mercury removal using a model that uses a sorbent size distribution. This provides a somewhat closer approximation to actual sorbent injection. The model used sorbent size distribution consisting of 170 particle-size bins from  $0.01\ \mu\text{m}$  to  $34\ \mu\text{m}$ . This distribution is based on aerodynamic particle sizing of a typical commercial sorbent. Like the first model, removal is based on the rate of Hg diffusion to the sorbent particle surface, and no account is taken of reactions on the particle surface or of the form of Hg, in effect treating the sorbent as a “perfect” sorbent, capturing all Hg arriving at the surface. The sorbent size distribution was truncated as several minimum particle sizes, i.e., there are no particles smaller than the minimum size. Figure 22 shows the relative mercury removal based on a minimum particle size of  $10\ \mu\text{m}$ . This is to represent the ability of the scrubber to completely remove the carbon from the gas stream.

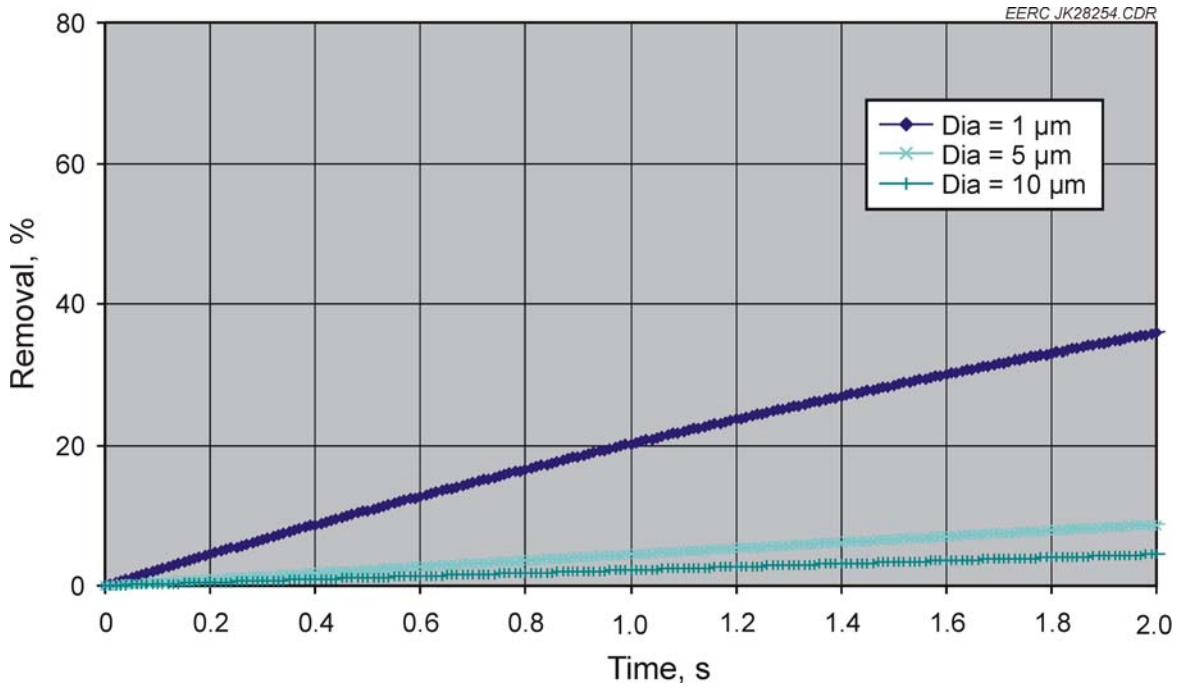


Figure 18. Single particle-size diffusion model with a sorbent load of 1 lb/MMacf.

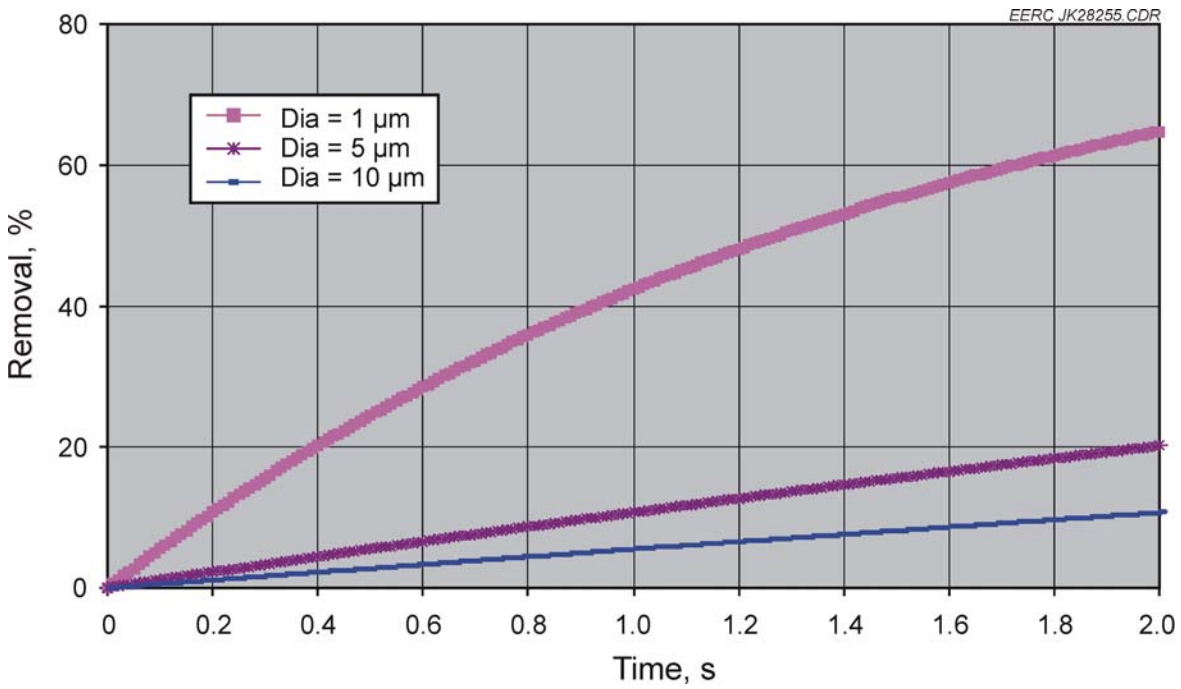


Figure 19. Single particle-size diffusion model with a sorbent load of 2.5 lb/MMacf.



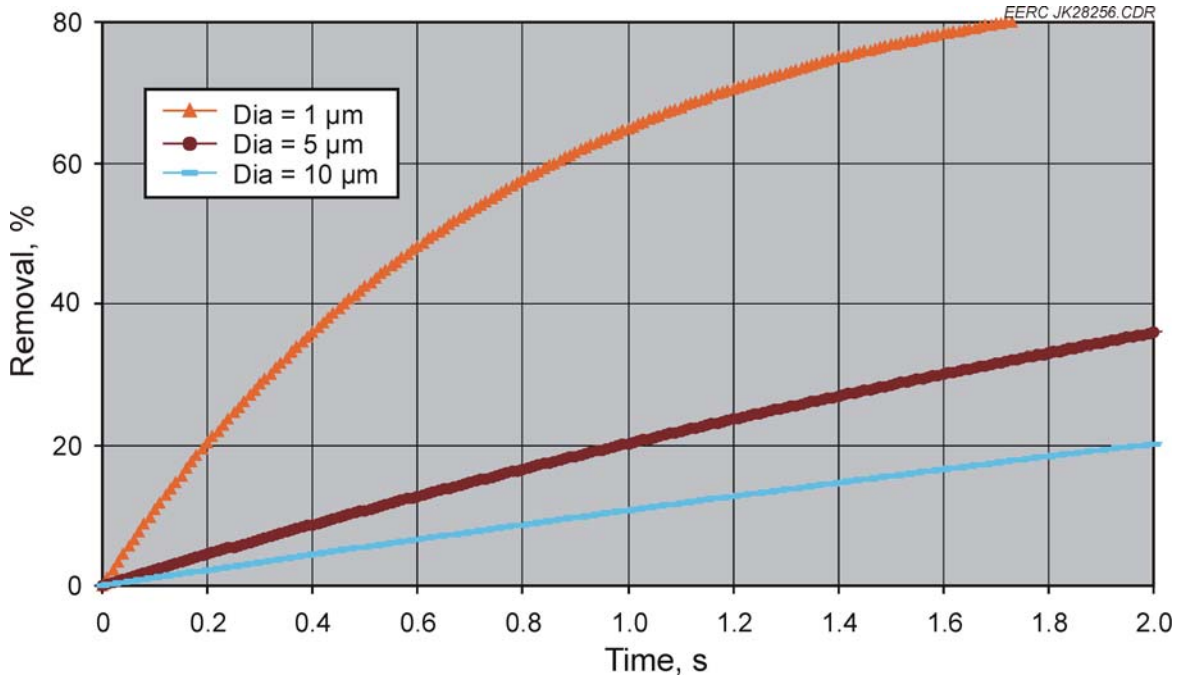


Figure 20. Single particle-size diffusion model with a sorbent load of 5 lb/MMacf.

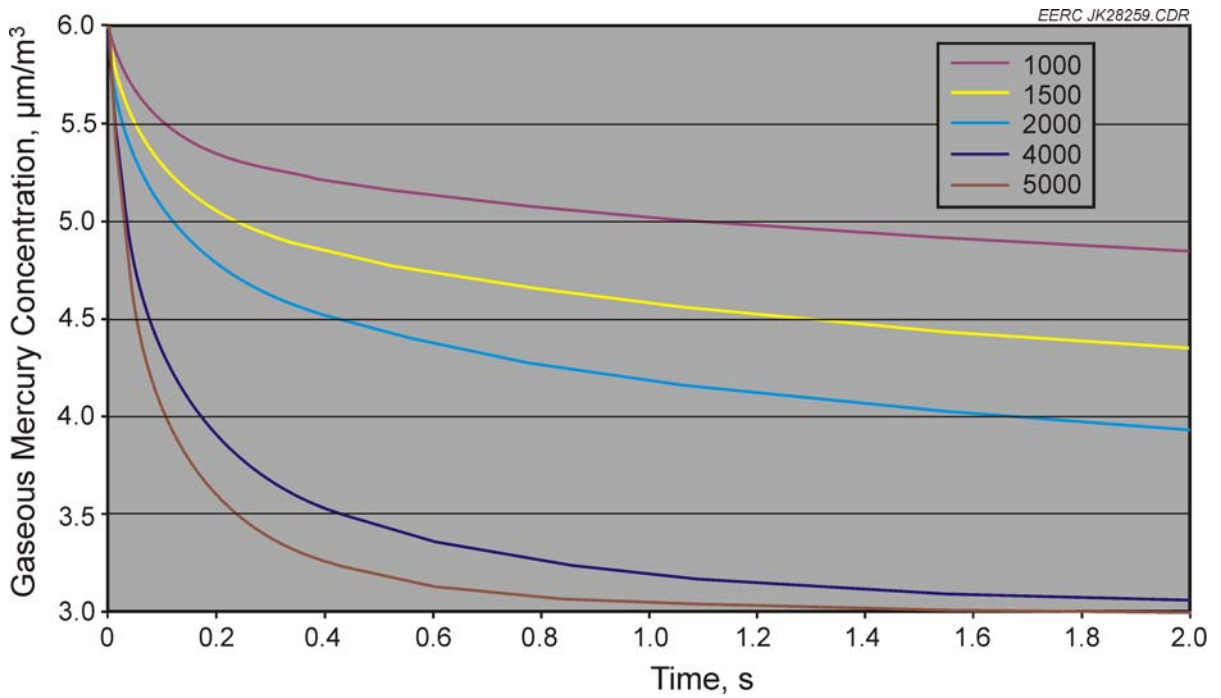


Figure 21. Mercury capture for different sorbent-to-Hg ratios.

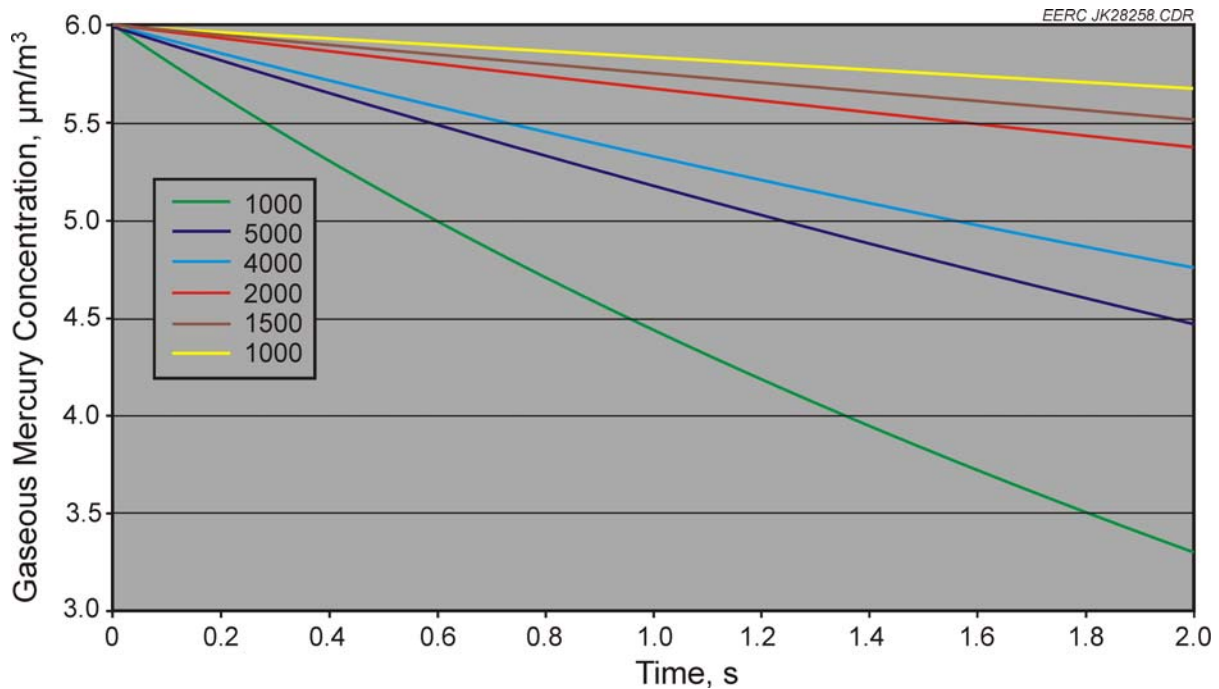


Figure 22. Mercury capture for different sorbent-to-Hg ratios where the minimum sorbent particle size is 10  $\mu\text{m}$ .

The single particle-size curves show well the relationship between residence time and particle size. The shift with higher loading is quite pronounced, as is seen with the effects on the smaller particle size. The most demonstrative of the effects is seen in the comparison between Figures 21 and 22. They clearly show the relationship of the finer fraction and Hg removal. Based on Figure 21, an increase of residence time from 1 to 2 seconds shows the potential for increased Hg removal by approximately 20%.

The results of this modeling highlight the potential benefits of more advanced modeling of Unit 3. It would prove beneficial to model the effects of sorbent particle size, residence time, potential particle surface reactions, and effects of injection rates against parameters such as sorbent type and scrubber efficiency before future testing is conducted. This information would serve as an invaluable guide for informed decision making when designing a test plan.

## CONCLUSIONS

Baseline mercury emissions from Colstrip Unit 3 are comparatively low relative to other PRB coal-fired systems and were found to range from 5 to 6.5  $\mu\text{g}/\text{Nm}^3$  (2.9 to 3.8 lb/TBtu), with a rough value of approximately 80% being in elemental form. At these lower ranges it is more difficult to attain high mercury removal percentages because of the challenges in containing the mercury, which is more diluted in the flue gas. In addition, stack mercury emissions are more than 95% elemental mercury and were measured to be on the order of 5 to 5.5  $\mu\text{g}/\text{Nm}^3$  (2.9 to 3.2 lb/TBtu). Baseline scrubber mercury removal percentages based on Scrubber 3-8 were found

to range from 5% to 10% of the mercury entering it. No evidence of Hg reemission from the scrubber was found, but more testing is required to determine if reemission is a concern because it could not be positively determined from the data collected during testing.

All the additives injected resulted in some reduction in mercury emissions. However, the target reduction of 55% was not achieved. The primary reason for the lower removal rates is because of the lower levels of mercury in the flue gas stream and the lower capture level of fine particles by the scrubbers (relative to that for larger particles). The reaction and interaction of the SEA materials is with the finer fraction of the fly ash because the SEA materials are vaporized during the combustion or reaction process and condense on the surfaces of entrained particles or form very small particles. Mercury will have a tendency to react and interact with the finer fraction of entrained ash and sorbent because of the higher surface areas of the finer particles. The ability to capture the finer fraction of fly ash is the key to controlling mercury. More discussion can be found in Appendix A.

AC produced minimal reduction of only approximately 9%, with injection of carbon at levels of 3 lb/MMacf. Higher reduction can be achieved, but the rates of carbon injection appear to be too high to be practical. SEA1 addition was twice as effective at reducing mercury emissions over AC alone, resulting in a removal rate of 20% with an injection rate of 400 ppm. Only slightly better removal was obtained with SEA2 injected upstream of the scrubber, resulting in a reduction in mercury emissions by up to 30% when injecting at a rate of 75 ppm. SEA2 combined with carbon demonstrated an overall reduction of 38% across the scrubber. This is equivalent to lowering the emission rates to as low as 2.2 lb/TBtu across the scrubber.

The novel SEA2 additive injection method is several orders of magnitude safer and less expensive than current SEA2 injection methods. However, used in conjunction with this plant configuration, the technology did not demonstrate a significant level of mercury reduction. Near-future use of this technique at Colstrip is not seen.

The testing of additives across Scrubber 3-8 presented the worst case for mercury reduction for this plant configuration. The short distance between injection point and scrubber only provides for fractions of a second of residence time for the additives to react and mix with the gas stream as opposed to 1 to 2 seconds for the scrubbers with much longer duct runs.

## **RECOMMENDATIONS**

The materials and injection methods explored during this testing did not provide the level of control exhibited when used with other air pollution control devices such as ESPs and ESPs combined with wet scrubbers. The units at the Colstrip Steam Electric Station present a significant challenge for mercury reduction. The worst case was examined in this project, and projections have been made regarding the benefits across the rest of the unit. More information must be collected to verify the reaction of the entire system. Key findings indicate that when SEA or carbon is injected, mercury is reacting with the finer fractions of the fly ash and carbon based on the mercury captured on the filters. In addition, the shorter residence time for Scrubber 3-8 contributed to the removal efficiencies. Future testing must examine the feasibility

of capturing mercury on coarser AC particles and increasing residence times. The use of coarser carbon materials will require added residence time and improved mixing with flue gas to achieve higher removal rates. Simple computer models were used in this report to generate the basic relationships between mercury removal, sorbent particle size, and residence time based on data acquired during testing. These models assumed a “perfect” sorbent and did not account for particle surface reactions. Before additional testing is conducted, it is recommended that advanced computer modeling be conducted to better determine the optimum size of sorbent particles, projected injection rates, and minimum required residence time. The modeling needs to take into account the physical layout of each scrubber duct for the unit to better quantify the overall mercury output to the stack. The data collected from this testing can be used as a benchmark guide for the advanced modeling. Once the sorbent characteristics and additive rates have been defined testing should be considered. Two options for testing the impact of residence times include increasing the distance between the injection point and the scrubber on the duct work of Scrubber 3-8 or conducting injection testing across one of the scrubbers with longer duct work such as Scrubber 3-5. Testing with Scrubber 3-8 would probably involve the installation of more ports upstream of the existing ports. This could easily provide an additional 30 to 50 feet of duct work for increased residence time, allowing reactions to take place. Testing of a scrubber such as 3-5 could use the existing ports and provide well over 100 feet of duct work for additive–gas reaction.

Although Unit 4 is a sister unit to Unit 3, testing should be considered for this unit to ensure that similar results can be obtained on that unit as well. Units 1 and 2 are of different manufacture and design, and testing should also be conducted on them independently to determine what technology would provide the best options for reduction.

SEA2 with carbon provided the best option for mercury reduction across Scrubber 3-8. Once the sorbent characteristics (particle size), residence time, and SEA addition rate have been optimized, longer-term testing should be carried out. In the short period of time this testing took place, a vital obstacle was identified for monitoring mercury emissions during sorbent injection with this plant configuration. What are not fully known are the longer-term effects these additives may have on the physical equipment of the plant. Lifetime reduction of alloys, scrubber components, and supplemental equipment are not known and should be investigated before a large capital expense is undertaken.

Secondly, it is recommended that evaluation of baghouse technology performance be considered for the Colstrip Steam Electric Station. The cost of a baghouse retrofit at Colstrip would be very high and, therefore, would only be necessary if other options have been explored and proven ineffective at achieving the desired goals and if such a retrofit proves to be the only technology able to achieve future emission limitations. The use of fabric filters not only has the potential to enhance the overall reduction of mercury emissions but also greatly reduce the opacity that is currently measured. Mercury reductions of over 80% are probable.

To explore further the benefits of a baghouse, the EERC does have a portable, trailer-mounted slipstream baghouse that could be brought on-site for testing of filter technology. This system would allow for the flexibility to examine multiple air-to-cloth ratios and multiple technologies simultaneously without a major disruption to the operation of the unit.

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## **APPENDIX A**

# **SAMPLING CHALLENGE AT THE SCRUBBER VESSEL 3-8 OUTLET DURING SEA2 INJECTION**

## **SAMPLING CHALLENGE AT THE SCRUBBER VESSEL 3-8 OUTLET DURING SEA2 INJECTION**

An issue was identified with the sampling and measurement methods at the scrubber outlet. Because of the unfortunate timing combination of suspended testing due to SEA availability immediately followed by an unscheduled unit shutdown for repairs, the problem was not immediately identified until weeklong testing had begun. Parametric testing indicated greater than 55% additional mercury removal across the scrubber. Parametric testing results are shown in Table A-1. This was a much greater reduction than was observed for SEA1, so it was chosen as the method for the weeklong test.

Results obtained during the first part of the test week indicated that the SEA2 and activated carbon combination was greatly reducing the mercury across the scrubber. However, it was found that the sampling probe assembly was causing exaggerated levels of removal. The gas-sampling probe utilizes a filter to remove particulate matter from the gas stream before the gas is analyzed by the CMM. Carbon and fine particulate matter not removed by the scrubber were collecting on the filter and providing additional mercury capture from the sampling gas stream, in effect acting as a fixed bed. Once this was discovered, the probe was immediately removed, and a replacement probe that minimizes the impact of solid material from the sample line was sent to the site.

Evidence of the capture of mercury by the CMM is given in Table A-1. Filters removed from the sampling probes during routine maintenance of the CMMs were analyzed after the completion of field testing for carbon and mercury content and compared against a blank filter. Exposure time for all filters was 8 hours, and filter changes at each site were performed during the same time interval. Before problems were suspected with the sampling method, filters were not kept and therefore analysis of the filters from parametric testing could not be conducted. The table shows that although carbon content was only slightly elevated, mercury content was increased over 100 fold. Because the carbon that passes through the scrubber is extremely fine, a small carbon content increase in the filter analysis would relate to a large increase in the quantity of carbon particles on the filter. The stack filters analyzed from the same time period had a mercury content that was practically identical to the blank. It must be remembered that the gas stream analyzed at the stack location is being diluted with gas coming from scrubbers not receiving sorbent. With this dilution, the mercury content of the gas at the stack is higher than the treated gas being analyzed at the Scrubber 3-8 outlet and has a lower carbon concentration. The lower carbon concentration at the stack gives evidence of the lack of CMM measurement difficulties at the stack and reinforces the fine particulate effect at the scrubber outlet.



**Table A-1. Results of CMM Filter Analyses**

Filter Location	Carbon Content, total C, $\mu\text{g}$	Mercury Content, total Hg, $\mu\text{g}$
Blank	1.91	<0.002
Scrubber Outlet Filter 1	3.40	0.166
Scrubber Outlet Filter 2	4.29	0.169
Stack Filter 1	2.59	0.008
Stack Filter 2	2.42	0.004

The second probe operates without a filter, bringing the mercury conversion solutions directly to the probe tip and then sending them straight to the CMM to be analyzed. Unfortunately, the process does not allow for the measurement of elemental mercury but only total mercury in the gas stream. Speciation was obtained through OH sampling. Values obtained with the second probe showed a much smaller reduction and compared well with the OH results. The data obtained from both the probes are shown in Table A-2 as First Probe and Second Probe. True reduction using SEA2 in combination with carbon was found to be only an additional 30% and overall during the testing period was measured to be 38% across the scrubber. This is an additional reduction of only 10% over SEA1.

The reaction and interaction of the SEA materials is with the finer fraction of the fly ash, because the SEA materials are vaporized during the reaction process and condense on the surfaces of entrained particles or form very small particles. This produced a greatly exaggerated degree of mercury reduction as measured by the CMM. This is shown in the results of the OH sampling presented in Figure A-1. During SEA2 injection, there is a marked increase in mercury oxidation. Mercury will have a tendency to react and interact with the finer fraction of entrained ash and sorbent as a result of the higher surface area of the finer particles. It is believed that this shift, along with higher availability of oxidized mercury, and in combination with the particulate fines collecting on the probe filter, was causing the effect seen on the first probe. The ability to capture the finer fraction of fly ash is the key to controlling mercury. However, because of the configuration of the scrubber system, the ability to control finer particles is limited as indicated by the higher opacity values at the plant.

Mercury measurement using the first probe indicated that the reduction was as high as 88%. In effect this is showing that it is possible for a combination of wet scrubber and fixed bed to reduce mercury emissions 88%. Based on this testing it could be possible for the combination to result in less than 0.3 lb/TBtu of mercury emission from the unit if the smaller size fraction of particles can be controlled.

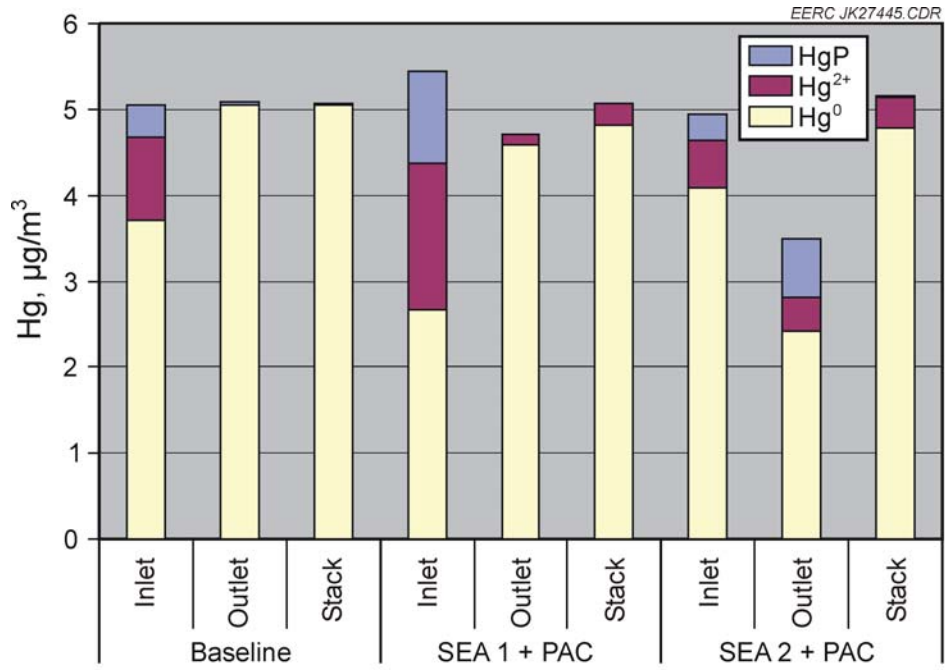


Figure A-1. Results of OH sampling.

**Table A-2. Results of the SEA2 Parametric Testing and Weeklong Testing (mercury concentrations on a dry basis, 3% O<sub>2</sub>)**

Test Run	Total Hg Concentration						Elemental Hg Concentration			% Elemental Hg				
	FGD Inlet		FGD Outlet		Stack		FGD Inlet	FGD Outlet	Stack	FGD Inlet	FGD Outlet	Stack	% Additional Removal	% Removal Across Scrubber
	µg/Nm <sup>3</sup>	lb/TBtu	µg/Nm <sup>3</sup>	lb/TBtu	µg/Nm <sup>3</sup>	lb/TBtu	µg/Nm <sup>3</sup>	µg/Nm <sup>3</sup>	µg/Nm <sup>3</sup>					
<b>SEA2 + Minimal PAC</b>														
Baseline Before	5.6	3.3	4.7	2.8	5.2	3.1	5.0	4.6	5.1	88	98	98	-	16
25 ppm (3.4 lb/hr)	5.6	3.3	3.6	2.1	4.8	2.8	4.6	3.3	4.7	78	91	98	23	36
75 ppm (10.3 lb/hr)	5.3	3.1	2.0	1.2	5.1	3.0	5.0	1.6	5.1	94	75	100	57	62
100 ppm (13.7 lb/hr)	5.5	3.3	2.4	1.4	5.1	3.0	5.0	2.4	5.0	90	100	98	49	56
Baseline After	5.5	3.3	5.0	3.0	5.1	3.0	5.2	5.0	5.1	94	100	100	-	9
<hr/>														
Baseline Before	5.0	2.9	4.9	2.9	-	-	4.5	4.8	-	89	98	-	-	2
First Probe (with filter)	5.1	3.0	0.6	0.3	4.8	2.8	4.7	0.4	4.8	91	50	100	88	88
Baseline Before	5.8	3.4	5.4	3.1	5.5	3.2	5.4	-	5.5	93	-	100	-	7
75 ppm, 1.5 lb/mmacf PAC	6.1	3.6	3.8	2.2	5.4	3.1	5.7	-	5.4	93	-	100	30	38
OH	4.9	2.9	3.5	2.0	4.1	2.3	4.1	2.4	3.9	80	54	95	35	29
<hr/>														
<b>SEA2 + PAC</b>														
Baseline Before	5.5	3.3	5.2	3.1	5.3	3.1	5.2	5.2	5.3	94	100	100	-	5
75 ppm, 1 lb/MMacf PAC	5.8	3.4	2.6	1.5	5.4	3.2	5.5	2.8	5.4	95	107	100	50	55
75 ppm, 1.5 lb/MMacf PAC	6.2	3.7	2.3	1.4	5.7	3.4	5.7	2.2	5.7	91	95	100	56	63
75 ppm, 2 lb/MMacf PAC	5.7	3.4	2.2	1.3	5.3	3.1	5.3	1.7	5.3	92	71	100	58	61
After Baseline	6.3	3.7	5.8	3.4	5.7	3.4	6.0	5.7	5.6	95	98	98	-	8

**APPENDIX B**

**AIR-SAMPLING RESULTS, SCRUBBER  
VESSEL 3-8, MAY 3, 2006**

June 6, 2006

Mr. Bill Neumiller  
PPL Montana, LLC  
P.O. Box 38  
Colstrip, Montana 59323

**SUBJECT: Industrial Hygiene Air Sample Results for Mercury and Bromine  
Colstrip Plant Facility  
Colstrip, Montana  
Maxim Project No. 6550944.200**

Dear Mr. Neumiller:

Enclosed are the industrial hygiene air sample results for mercury and bromine collected at the PPL Colstrip Plant Facility located in Colstrip, Montana on April 3, 2006. The industrial hygiene monitoring took place in the 3-8 vessel and on a PPL employee working in the 3-8 vessel.

#### **Air Sampling Methodology**

Employee and area exposure to mercury and bromine were assessed by collecting air samples on April 3, 2006. The samples were collected from breathing zone height on a PPL employee and in the area of operations in the 3-8 vessel. Air quality samples were collected using low-volume air sampling pumps and the sampling media described below. All samples were capped immediately following collection. Pump flow was calibrated at the start and end of the sampling period using a DryCal<sup>®</sup> primary air flow calibration meter. The sample durations were between eight and ten hours. Accordingly, exposure levels were calculated for an eight hour time-weighted average.

Samples were submitted to DataChem Laboratories in Salt Lake City, Utah for analyses of mercury and bromine. All samples were analyzed in general accordance with analytical methods published by the National Institute for Occupational Safety and Health (NIOSH).

#### **Air Sampling Results**

Sample results from the April 3, 2006 sampling event are presented on Table 1. Results of laboratory analyses, daily site specific data, and OSHA PELs obtained from the September 2005 *NIOSH Pocket Guide to Chemical Hazards* are also presented in Table 1. Copies of the laboratory analytical reports are contained in Attachment A.

Review of Table 1 indicates that no detectable concentrations of mercury or bromine were present in samples collected. Consequently, exposure levels were well below applicable OSHA PELs.

**TABLE 1**  
**LABORATORY ANALYTICAL RESULTS**  
**MERCURY ANALYSIS**  
**APRIL 3, 2006**

Sample Number	Sample Type	Sample Location	Concentration in Air (mg/m <sup>3</sup> )	
			Test Result	OSHA PEL*
1	Bromine	Personnel – Jared means	<0.0023	0.7
2	Mercury	Personnel – Jared means	<0.00023	0.01
3	Bromine	Area- Inside 3-8 Vessel	<0.0024	0.7
4	Mercury	Area- Inside 3-8 Vessel	<0.00015	0.01
B	Bromine	Field Blank	ND	N/A
B	Mercury	Field Blank	ND	N/A

\*:NIOSH Pocket Guide to Chemical Hazards, September, 2005.

ND: Not Detected

N/A: Not Applicable

We appreciate the opportunity to provide this service to PPL Montana, and look forward to providing environmental and engineering services to you on future projects. If you should have any questions or need any additional information, please feel free to contact us in our Billings, Montana office at (406) 248-9161.

Sincerely,

**Maxim Technologies**

A DIVISION OF TETRA TECH, INC.



Ryan C. Behrends  
Environmental Scientist

RCB/rr

Enclosure

n:\typing\Env-fac\6550944\PPL May 3 IH sampling report

6/12/06  
Per Bill. Neumiller  
wording "inside  
vessel 3-8" or similar  
will be changed.



**ATTACHMENT A**  
**LABORATORY ANALYTICAL REPORTS**

**RECEIVED**  
 MAY 24 2006  
**RECEIVED**

Date MAY 12 2006  
 Laboratory Group Name 06I-2183-01  
 Account No. 07003

Maxim Technologies, Inc.  
 Attention: Roger Herman  
 618 South 25th Street  
 Billings, MT 59101

FAX (406) 248-9282  
 Telephone (406) 248-9161  
 E-mail rbehrend@maximusa.com

**Sampling Collection and Shipment**

Sampling Site PPL-Colstrip Date of Collection May 03, 2006  
 Date Samples Received at Laboratory May 05, 2006

**Analysis**

Method of Analysis NMAM 6011mod  
 Date(s) of Analysis May 11, 2006

**Analytical Results**

Field Sample Number	Laboratory Number	Sample Type	Bromide ug/sample	Bromide mg/m <sup>3</sup>	Air Volume Liters					
1	06I17609	FILTER	ND	<0.0023	213.75					
3	06I17610	FILTER	ND	<0.0024	208.544					
B	06I17611	FILTER	ND	**	**					
Reporting Limit			0.5							

† See comment on last page.  
 ND Parameter not detected above LOD.  
 NR Parameter not requested.  
 NA Parameter not applicable.  
 \*\* See comment on last page.  
 ( ) Parameter between LOD and LOQ.

*Thomas T McKay*  
 Analyst: Thomas T McKay  
*Don Wickman*  
 Reviewer: Don Wickman



# CHAIN OF CUSTODY RECORD

# MAXIM

TECHNOLOGIES INC

600 South 25th Street  
Billings, Montana 59101  
Phone (406) 248-9161 • Fax (406) 248-9282

Contact Name: Roger Armin  
Report to (Firm or Agency): Maxim  
Address: Billy's  
Sampler Signature: Matthew Olsen

OTI-48-J

Project or Site Name: PP-Cooktop

Project Number: \_\_\_\_\_  
Sampler Name (Printed): Matthew Olsen

DATE COLLECTED	TIME COLLECTED	SAMPLE LOCATION OR DESCRIPTION	COMP OR GRAB	SAMPLE MATRIX	NO. OF CONTAINERS	ANALYSIS REQUIRED		NOTES	LAB NUMBER
						609	118		
5/3/06	10-1625	1- Jarol Means		Air	1	X		Volume (L) 213.75	OUT FLOW
	10-1533	2- Jarol Means			1	X		42.591	
	10S-1632	3- 3-8 Vessel			1	X		208.544	10
	10S-1638	4- 1			1	X		66.91	
	N/A	B- Blank			1	X			
	N/A	B- Blank			1	X			
Relinquished by: <u>Matthew Olsen</u>									
Relinquished by: <u>Keads</u>									
Relinquished by: _____									
Relinquished by: <u>For 24-We</u>									
Date: 5/4/6						Time: 820		Received by: <u>FEDEX</u>	
Date: 5/4/6						Time: 420		Received by: <u>FEDEX</u>	
Date: 5/5/6						Time: 945		Received by: <u>ANNY DALYALS</u>	
Date: <u>5/24/06</u>						Time: _____		Received by: <u>For 24-We</u>	

Remarks:  
6009 = Mercury  
6011 = Bromine



1173  
Booker

# CHAIN OF CUSTODY RECORD

# MAXIM TECHNOLOGIES INC

610 South 25th Street  
Billings, Montana 59101  
Phone (406) 248-9161 • Fax (406) 248-9282

Contact Name: Roger Harmon  
Report to (Firm or Agency): Maxim  
Address: Billy's  
Address: 21830

Project or Site Name: PL-Cooking

Project Number: 1173  
Sampler Name (Printed): Matt Olson

Sampler Signature: [Signature]

DATE COLLECTED	TIME COLLECTED	SAMPLE LOCATION OR DESCRIPTION	COMP OR GRAB	SAMPLE MATRIX	NO. OF CONTAINERS	ANALYSIS REQUIRED										NOTES	LAB NUMBER	
5/3/06	10-1625	1- Jarol Means		Air	1												Volume (L) 213.75	
	10-1533	2- Jarol Means			1	X											42.591	00117012
	1015-1638	3- 3-8 Vessel			1	X											208.544	13
	1015-1638	4- 1			1	X											66.91	
	N/A	B- Blank			1	X												
	N/A	B- Blank			1	X												14
Relinquished by: <u>[Signature]</u>						Date	5/4/06	Time	8:20	Received by:	<u>[Signature]</u>	Remarks: 6009 = Mercury 6011 = Bromine						
Relinquished by: <u>[Signature]</u>						Date	5/4/06	Time	9:20	Received by:	<u>[Signature]</u>							
Relinquished by: <u>[Signature]</u>						Date	5/5/06	Time	9:45	Received by:	<u>[Signature]</u>							
Relinquished by: <u>[Signature]</u>						Date	5/24/06	Time		Received by:	<u>[Signature]</u>							

CA