

# **LARGE-SCALE DEMONSTRATION OF THE MERCAP™ TECHNOLOGY FOR MERCURY CONTROL**

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## **ABSTRACT**

The EPRI MerCAP™ (Mercury Control Adsorption Process) is being demonstrated at two coal-fired utilities under a DOE/NETL program. Gold-coated structures have been retrofitted in the existing pollution control equipment and mercury is removed from the flue gas as it flows past the rigid structure. With this process, mercury can be recovered and the substrates can be regenerated and used repeatedly. This technology does not affect by-product utilization.

This paper will describe results from the first ever full-scale installation and demonstration of the MerCAP™ technology. Results will show the mercury control performance of the technology for a unit equipped with a spray dryer absorber/baghouse (SDA/BH) pollution control arrangement. The performance of the technology for the same unit while burning North Dakota Lignite (NDL) and then Powder River Basin (PRB) fuels with extended testing totaling over 4000 hours of continuous operation will be presented. Additionally, results of multiple regeneration cycles, parametric evaluations, and economic analysis of the technology will be reported.

## **INTRODUCTION**

The current effort is funded primarily by the Department of Energy's National Energy Technology Laboratory (NETL) to obtain the necessary information to evaluate the ability of gold-based EPRI<sup>1</sup> Mercury Control Adsorption Process (MerCAP™) to control vapor-phase mercury in flue gas downstream of dry and wet scrubbers. MerCAP™ uses fixed structure sorbents located directly in a flue gas stream to adsorb mercury. When sorbent surfaces become saturated, they can be thermally regenerated and the mercury can be recovered. The MerCAP™ technology is targeted as the primary mercury control process on plants burning low-rank coals and as a polishing technology for plants with wet scrubbers or employing other mercury control technologies. This paper discusses the first phase of this large-scale demonstration, the application of MerCAP™ technology downstream of a SDA/BH combination treating ND L flue gas. The technology is retrofitted into a single compartment in the baghouse at Great River Energy's (GRE's) Stanton Station Unit 10. Each compartment treats 6 mega-watt (MWe) equivalence of flue gas. After 1735 hours of operation a fuel switch to PRB sub-bituminous coal occurred providing the unique opportunity to evaluate the MerCAP™ technology on a full-scale basis for a second fuel type on the same unit. At the completion of the six-months planned demonstration (early 2005), the second phase of this program will demonstrate the technology downstream of a wet scrubber at a boiler burning Eastern bituminous coal. Additional tests will be performed at both sites to evaluate the ability to thermally or chemically regenerate the gold-coated plates. These tests will be carried out using a smaller extractive pilot probe to evaluate the effects of multiple regeneration cycles on the sorbent performance.

The results of this demonstration will provide data required for assessing the feasibility and estimating the costs of a full-scale MerCAP™ system for flue gas mercury removal. It will provide information about optimal operating conditions for different flue gas conditions, the effectiveness of sorbent regeneration, and the ability of the gold sorbent to hold up to flue gas over an extended period. In addition, if successful, the novel approach of incorporating MerCAP™ structures in existing baghouse compartments will demonstrate a cost-effective means for achieving mercury control using existing baghouse technologies.

This paper covers the demonstration and results from the first test site, Great River Energy's Stanton Station Unit 10, Stanton, North Dakota.

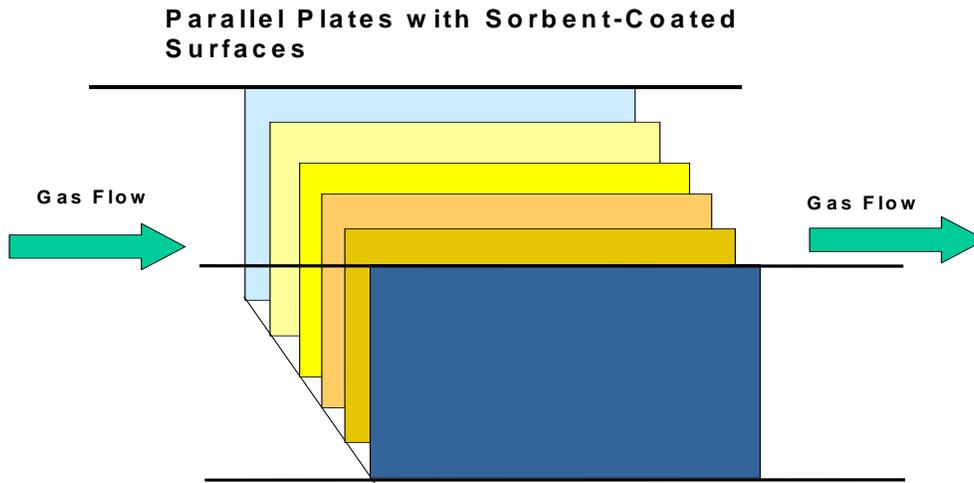
## **EXPERIMENTAL**

### **MerCAP™ Technology**

The general concept for MerCAP™ is to place fixed sorbent structures into a flue gas stream to adsorb mercury and then, as the sorbent surfaces becomes saturated, thermally regenerate the sorbent and recover the mercury. One example includes parallel gold-coated plates, depicted in Figure 1. Mercury forms an amalgam with the gold and is removed from the flue gas flowing past the plates. The current program is utilizing an electroplated layer of gold on a stainless steel screen (substrate). The captured mercury can be subsequently sequestered using a carbon canister or cryogenic trap during thermal regeneration of the substrates.

Recent work has shown that chemical desorption of the mercury from the gold-coated substrates is also a feasible regeneration technology.

**Figure 1. Parallel Plate Configuration of a Fixed Sorbent**



Results from modeling studies and field testing of MerCAP™ by EPRI<sup>2,3</sup> indicate this technology has the potential to remove >90% of the mercury in configurations that may be challenging for other technologies such as low-chlorine flue gas derived from lower rank coal. MerCAP™ is also an option as a polishing device downstream of other control devices to increase overall mercury removal across the system to >90%.

The MerCAP™ concept has been tested in actual flue gas since 1999, starting with evaluations of small gold-coated coupons and evolving to long-term tests of probes containing 10-ft substrates. These tests have shown that high (>80%) mercury removals can be achieved at various operating parameters and in different flue gas types. Tests have also indicated that gold-coated substrates can be thermally regenerated without degradation of the initial adsorption capacity. Recent tests conducted with an in-duct probe in ND L flue gas downstream of a spray dryer-baghouse configuration showed >80% mercury removal with a substrate configuration of 10-ft long gold-coated plates spaced 0.5 inches apart at a gas velocity of 40 ft/s. These results were consistent with mass transfer model predictions. Higher removals (>90%) should be achievable by increasing plate length, decreasing plate spacing, or reducing gas velocities. Results with a 140-acfm probe showed mercury removals of >70% for six months of continuous flue gas exposure in ND L-derived flue gas.

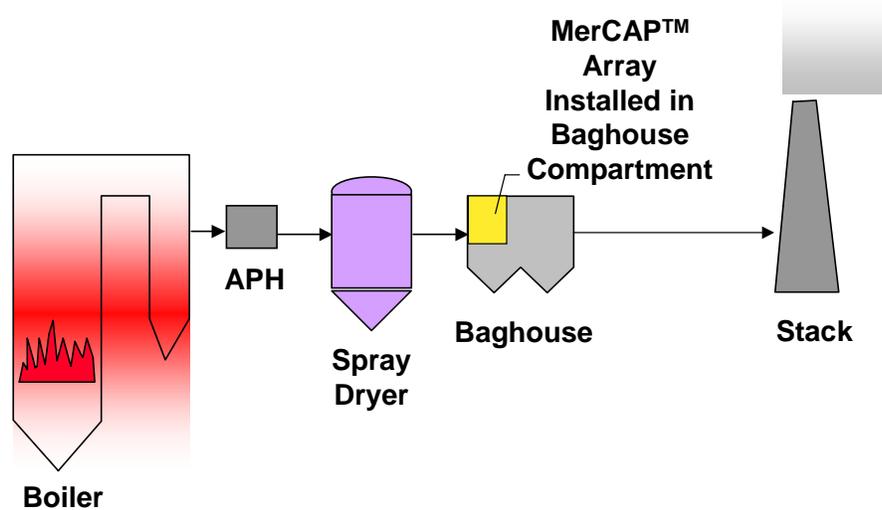
The most promising MerCAP™ results have been measured in ND L, PRB sub-bituminous, and Eastern bituminous gases that have been scrubbed via lime spray dryers, wet flue gas desulfurization units, or venturi-type wet scrubbers. The mercury removal results in unscrubbed gases downstream of ESP units have typically shown lower mercury removal rates (below 25%) and de-activation of the substrates. Several tests and analyses are continuing to better understand the flue gas chemistries that limit the technology in unscrubbed applications.

The modeling and field test efforts have refined the understanding of the relationship of plate length, spacing, substrate geometry, and flue gas parameters on the removal efficiency of the MerCAP™ technology. Ideally 10 to 15-foot long plates are required to achieve the 80%-90% removals in scrubbed low rank fuels. Plate spacings of ½-inch and 1-inch widths have been both modeled and field-tested. Tighter spacing provides greater surface area resulting in greater gas contact and better removals. However, this is at the cost of higher capital investments and increased pressure drop across the system. The 1-inch spacing was selected for this demonstration as removal rates of up to 70% have been achieved and pressure drops across the system are less than 1 inch of water (in H<sub>2</sub>O).

### Test Site 1 – GRE Stanton Station

The first test site for the full-scale installation and demonstration of the MerCAP™ technology is Unit 10 of Great River Energy’s Stanton Station, located near Stanton, North Dakota. Stanton Unit 10 is a tangential-fired boiler rated at 60 MW. The unit is equipped with a lime slurry spray dryer absorber and a reverse-gas baghouse. The MerCAP™ substrates were installed in a single baghouse compartment at the clear air plenum. This installation simulates a full-scale installation at 6-MW equivalent. Figure 2 schematically shows the gas path and the installation location of the MerCAP™ substrate array. Figure 3 shows a photograph of the MerCAP™ array installed in the baghouse compartment at Stanton Unit 10.

**Figure 2. GRE Stanton Station Unit 10 Plant Schematic**



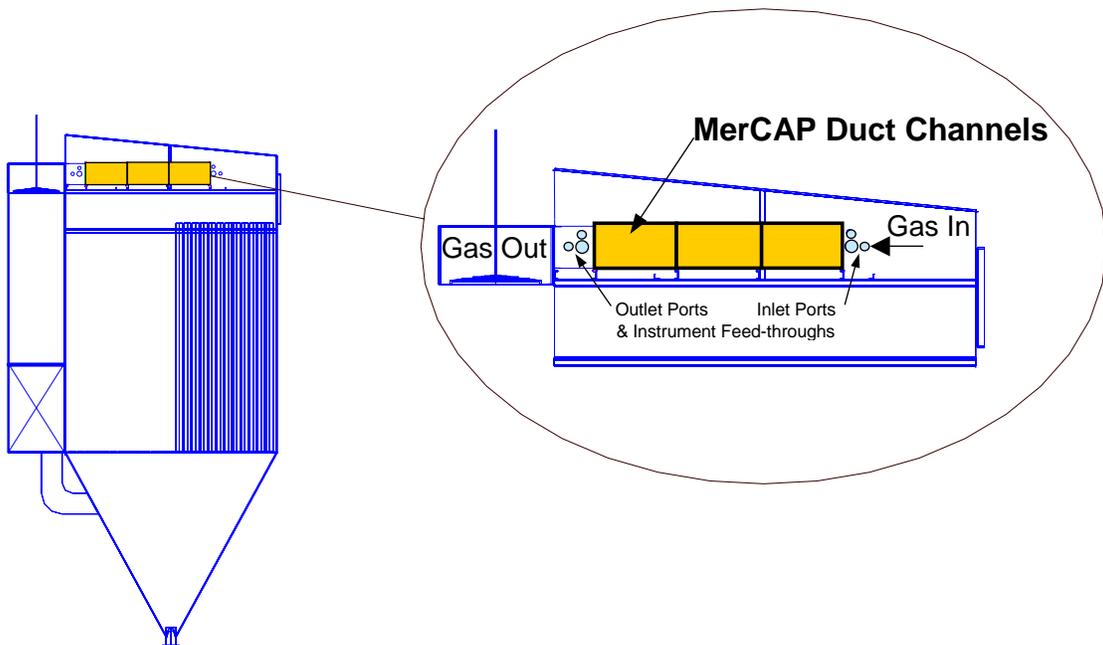
**Figure 3. MerCAP™ Substrate Array Installed at Stanton Unit 10**



### Sampling Systems

Apogee Scientific, Inc. installed permanent sampling systems for use with mercury semi-continuous emissions monitoring (SCEM) equipment to evaluate the mercury removal performance of the MerCAP™ array. Modified versions of commercially available QGIS™ sampling technology were used in the construction of the sampling systems. Figure 4 shows a schematic of the MerCAP™ installation and sampling locations.

**Figure 4. MerCAP™ Installation and Sampling Locations**



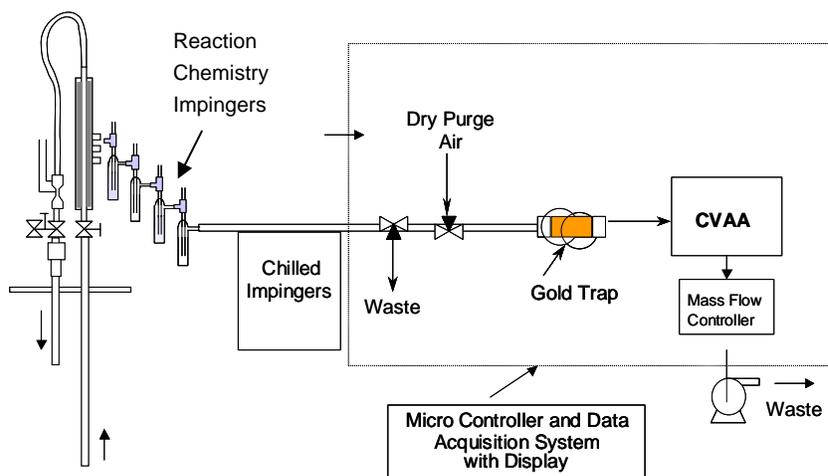
Inlet and outlet sampling arrays were designed to allow continuous extraction of flue gas from the each of the four duct inlets and outlets of the MerCAP™ array. These sampling arrays utilize bulkhead feed-throughs on the outer wall of the baghouse compartment so that

continuous samples of vapor-phase mercury concentrations (total and elemental) are available for analysis by a mercury SCEM. These sampling arrays were designed to provide high volume samples with short residence times, inertia particulate separation, and independent temperature control of the sample gas to minimize any bias of the mercury level in the sample systems. Additional sample ports at the inlet and outlet of the MerCAP™ array allow for Ontario Hydro method measurements and independent flow and velocity measurements.

### Mercury SCEM Equipment

One Apogee mercury SCEM was used during this program to monitor vapor-phase mercury concentrations in duct flue gas. The SCEM used is a research-oriented instrument that employs wet-chemistry impinger-based sample conditioning equipment. The mercury instrument consists of a commercially available cold vapor atomic absorbance (CVAA) spectrometer coupled with a gold amalgamation system (Au-CVAA). A sketch of the Apogee mercury SCEM is shown below in Figure 5. The SCEM was calibrated daily using elemental vapor-phase mercury (EM).

**Figure 5. Schematic of Apogee Mercury SCEM**



Although it is very difficult to transport non-EM in sampling lines, EM ( $\text{Hg}^0$ ) can be transported without significant problems. Since the Au-CVAAS measures mercury by using the distinct lines of the UV absorption characteristic of  $\text{Hg}^0$ , the non-elemental fraction is either converted to EM (for total mercury measurement) or removed (for measurement of the elemental fraction) near the sample extraction point. This minimizes any losses due to the sampling system.

For total vapor-phase mercury (TVM) measurements, all non-elemental vapor-phase mercury in the flue gas must be converted to EM. A reduction solution of stannous chloride in hydrochloric acid is used to convert  $\text{Hg}^{2+}$  to  $\text{Hg}^0$ . The solution is mixed as prescribed in the draft Ontario Hydro Method for Manual Mercury Measurements. To measure elemental

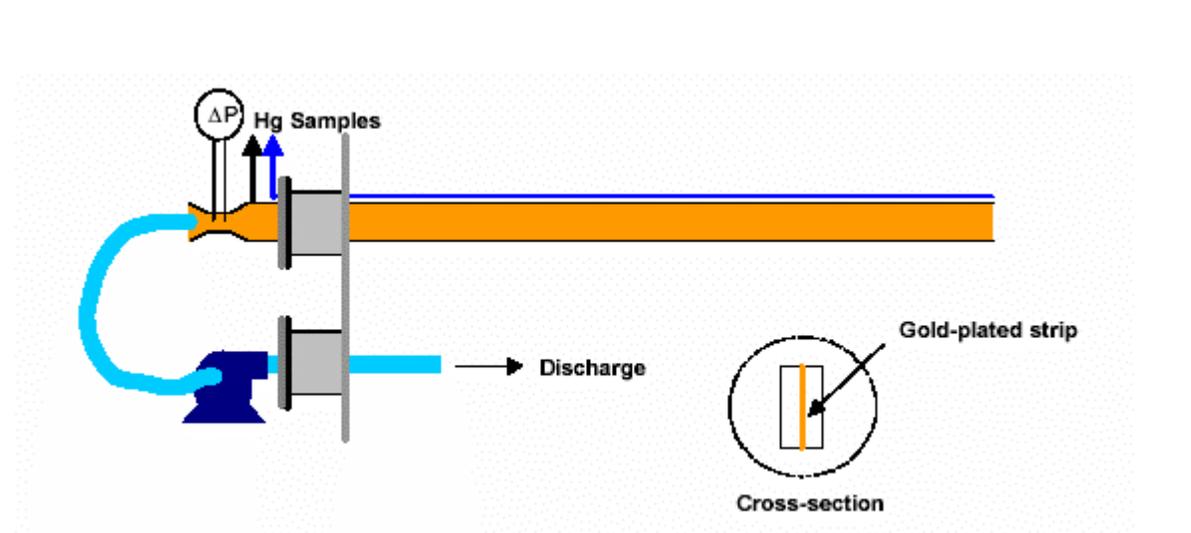
mercury, an impinger of potassium chloride (KCl) solution mixed as prescribed by the draft Ontario Hydro Method replaces the stannous chloride solution to capture oxidized mercury. The oxidized fraction of the vapor-phase mercury concentration (OVM or  $\text{Hg}^{2+}$ ) is computed by difference. The impinger solutions are continuously refreshed to assure continuous exposure of the sample gas to active chemicals.

### Substrate Regeneration and Pretreatment

As part of the scope of this program MerCAP™ substrates were regenerated thermally and chemically to verify and investigate the long-term effects that repeated regeneration and use cycles would have on the substrates.

A small pilot-scale probe used to test MerCAP™ arrays, referred to as a Mini-MerCAP™ Probe, was used to repeatedly test regeneration cycles on a single sorbent structure array. After exposure to flue gas from Stanton Unit 10 the MerCAP™ substrate was removed from service and heated in an oven to a temperature in excess of 850°F for a period of several hours. Mercury emissions from the oven were captured using a carbon trap and the amount of mercury desorbed was quantified by later analysis. The MerCAP™ substrate was then returned to service to determine if any performance degradation occurred as a result of the regeneration process. Figure 6 shows a schematic of the Mini-MerCAP™ Probe used to expose the MerCAP™ substrate for the purpose of regeneration cycle evaluations.

**Figure 6. Mini-MerCAP™ Probe**



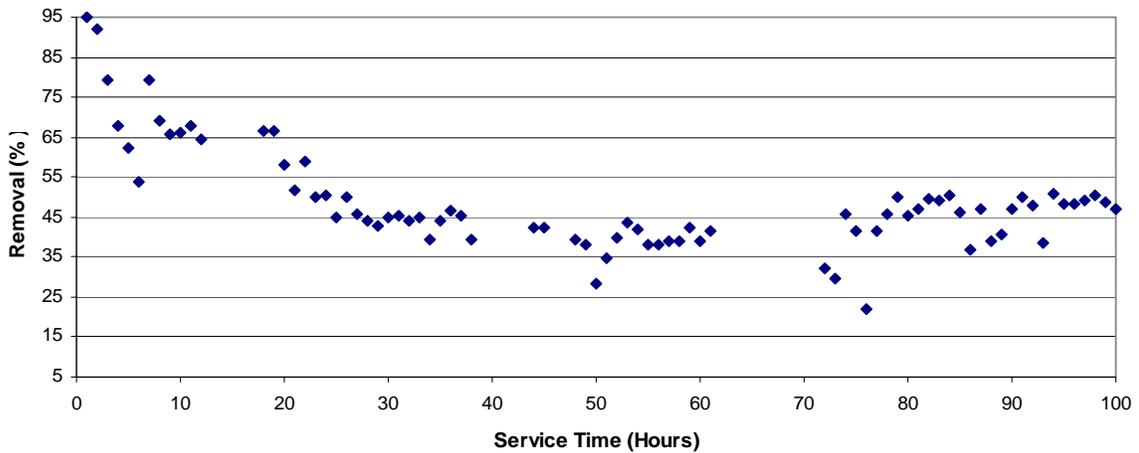
In addition a chemical rinse process was tested as both a regeneration method and a substrate pre-treatment method.

## RESULTS AND DISCUSSION

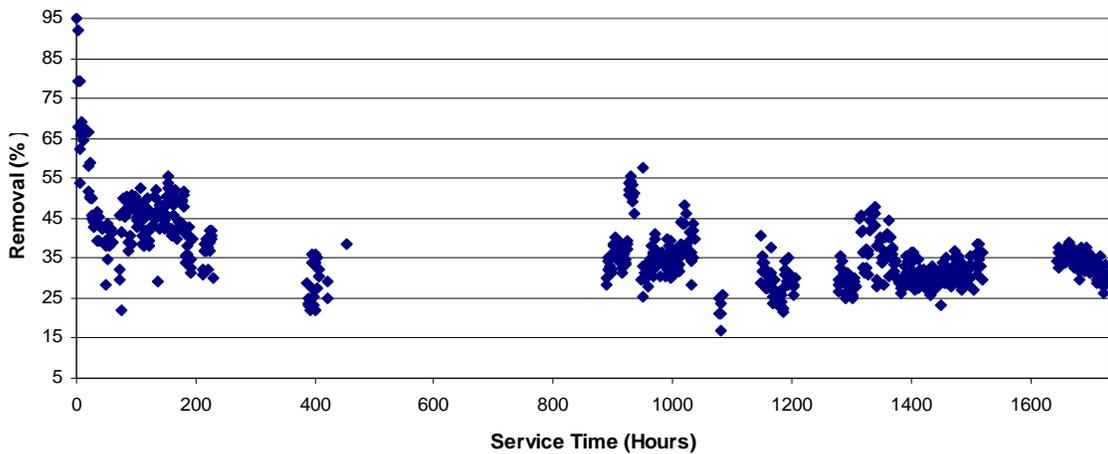
### MerCAP™ Performance – North Dakota Lignite Conditions

The MerCAP™ substrate array was installed at Stanton Unit 10 when the unit was still fueled by NDL. The initial performance of the system was monitored via mercury SCEM measurements and was to be verified by Ontario Hydro measurements. Unexpected difficulties resulting from the design of the sampling system made the Ontario Hydro measurements difficult to perform and the data therefore suspect. Figure 7 shows the mercury removal performance of the MerCAP™ array for the first hundred hours of operation and Figure 8 shows the performance of the array for the entire duration of testing under North Dakota Lignite conditions.

**Figure 7. MerCAP™ Performance – First 100 Hours of Operation**



**Figure 8. MerCAP™ Performance – North Dakota Lignite Conditions**

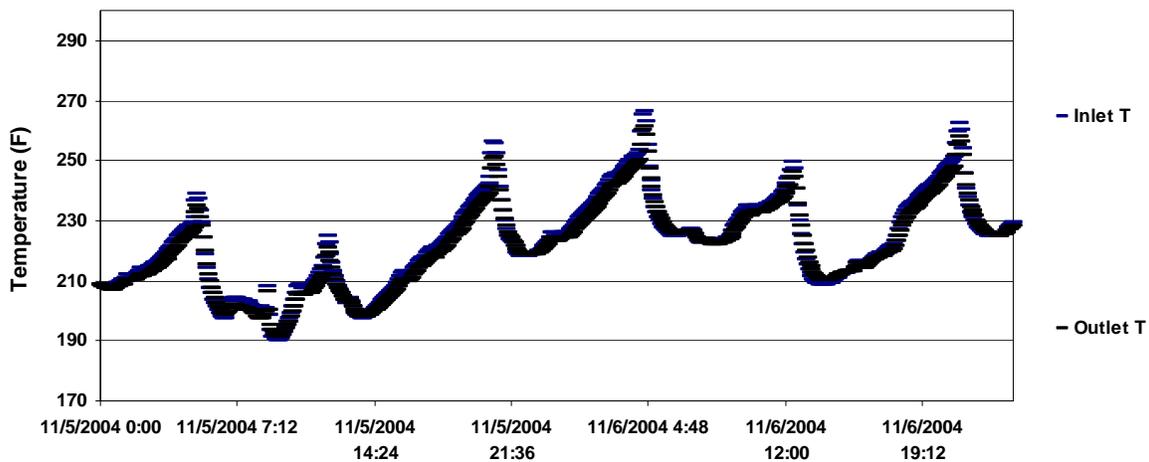


Initial performance of the array was quite good, achieving mercury capture in excess of 90%, however, as has been observed in previous testing the performance of the array began to drop shortly after installation. Removal performance stabilized at approximately 45% mercury removal after 20 hours of operation and remained fairly stable past 100 hours of operation. During the next set and subsequent performance evaluations the performance of the array was observed to have stabilized at approximately 35% mercury removal. Figure 8 shows the mercury removal performance of the array out to 1735 hours of continuous operation. At that point removals of between 30 and 40% were being observed.

### MerCAP™ Performance – Powder River Basin Conditions

At approximately 1735 hours the host unit switched fuels from NDL to a PRB Sub-bituminous fuel. The resulting changes in plant operation had a significant effect on the performance of the MerCAP™ array. Overall gas temperatures increased from an average of 180°F while burning NDL to well over 220°F. In addition wide temperature variations were seen at the test location of the MerCAP™ array. These temperature variations were observed to affect the mercury removal performance of the array. Figure 9 shows a trace of gas temperature recorded at the test location under PRB conditions. As unit operations stabilized the operating temperature of the unit stabilized with fewer temperature spikes occurring. Gas temperatures were still higher than when the unit burned NDL fuel and the performance of the MerCAP™ array continued to be affected.

**Figure 9. Gas Temperatures at MerCAP™ Array Under PRB Conditions**



The temperature variations seen as a result of the fuel source switch had significant impact on the mercury removal performance of the MerCAP™ array. At points where temperature spiked upwards very quickly, mercury concentrations at the outlet of the array were seen to increase to levels in excess of those at the inlet to the array. As temperatures would drop the mercury removal performance of the array would improve, however, the overall elevated temperature reduced the mercury removal performance of the array. Figure 10 shows the mercury SCEM data from the same time period as Figure 9. The variations in outlet mercury concentrations correlate very closely with the temperature variations seen in Figure 9.

**Figure 10. Mercury SCEM Data from MerCAP™ Array Under PRB Conditions**

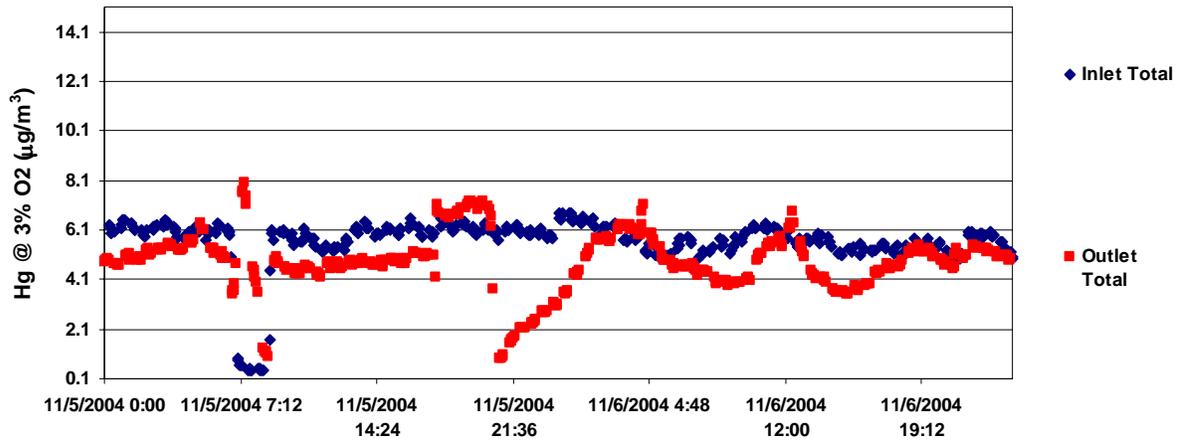
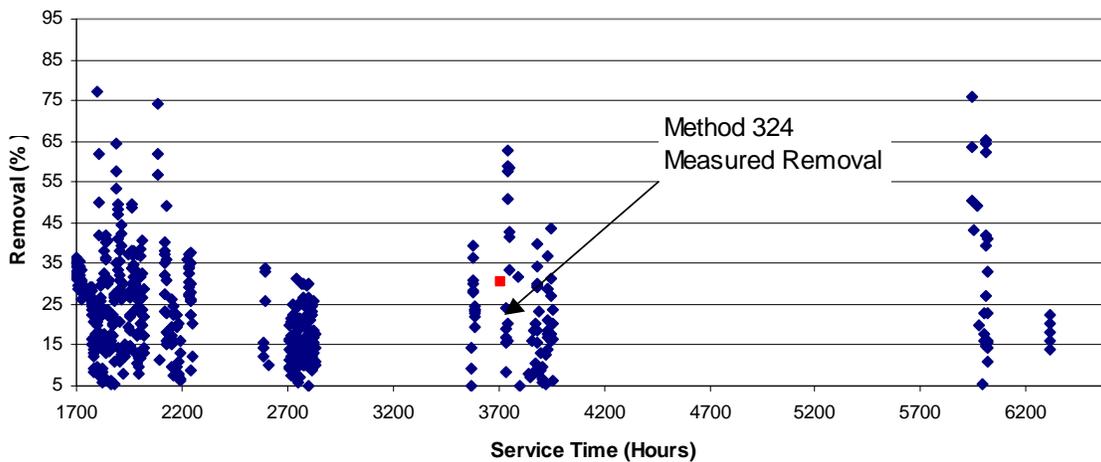


Figure 11 shows the mercury removal performance of the array from the point at which the fuel switch occurred through the end of the testing and evaluation period at Stanton Unit 10.

**Figure 11. Mercury Removal Performance of the MerCAP™ Array – PRB Conditions**



The mercury removal performance of the array continued to vary throughout the remainder of the test program, mainly as a function of the gas temperature. However, scrubber parameters, specifically, lime slurry injection rate, were also seen to have an effect on the performance of the array and are still under investigation. The removal performance, as measured by the mercury SCEM, was verified by a series of Method 324 measurements shown in Figure 11, above.

### **Substrate Regeneration and Pre-treatment**

Under this program testing of the effects of repeated regeneration and use cycles of a single MerCAP™ substrate were conducted by regenerating a single substrate array six times. Thermal and chemical regeneration methods were both tested. The multiple regeneration cycles simulate an estimated six years of performance and use. Table 1 details the results of the multiple regeneration cycles conducted under this program.

**Table 1. Regeneration Cycle Details**

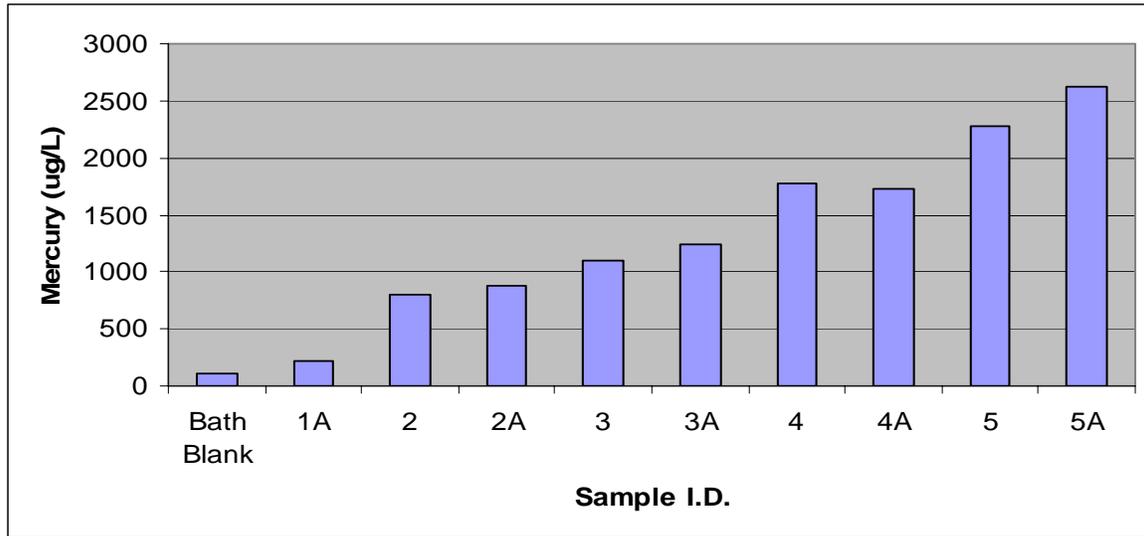
<b>Cycle #</b>	<b>Date of Regen</b>	<b>Hg Removal Before Regen (%)</b>	<b>Mass of Hg Desorbed (mg)</b>	<b>Hg Removal After Regen (%)</b>	<b>Regeneration Method</b>
1	07/26/04	0 - 5	Not Measured	Initially >90, Then 35 - 45	Chemical
2	2/1/05	10 - 15	4.9	15 - 20	Thermal
3	2/2/05	15 - 20	11.4	30 - 35	Thermal
4	2/3/05	30 - 35	0.4	35 - 40	Thermal
5	4/29/05	Not Measured	4.5	Not Measured	Thermal
6					Thermal

The MerCAP™ substrates installed in ducts 2 and 3 of the baghouse compartment were non-acid treated when initially installed in November 2004. Removal performance of these substrates lagged that which was measured on the acid-treated substrates in duct 1. The gold substrates of ducts 2 and 3 were removed from service on January 18, 2005 and shipped to Denver for acid treating/cleaning.

The acid treatment used is a Type VI passivation technique. This is a bath consisting of a 30% nitric acid in water held at room temperature. The treated material is immersed in the bath for a 30-minute soak time and then rinsed with distilled water. In the case of the MerCAP™ gold substrates, any contaminants in the gold or at the surface of the gold coating layer should be dissolved in the solution leaving a pure gold layer. The electroplated gold substrate has a high corrosion resistance to the acid bath, yet mercury or mercuric compounds that have formed on the surface or amalgamated into the gold structure are dissolved into the bath solution.

A fresh bath was prepared to clean the MerCAP™ substrates removed from ducts 2 and 3. Liquid samples for analytical analysis were taken from the bath prior to use, and at nine intervals between cleaning of the 10 MerCAP™ modules. Thus the mercury concentration in the baths was expected to increase as more modules were washed. These samples were subjected to ICP Mass Spectroscopy for evaluating a suite of elements, including gold, and mercury. The results of the bath analysis for mercury content are shown in Figure 12 below. Mercury concentrations in the bath increased as expected with the final concentration peaking at 2630 micrograms per liter (µg/L).

**Figure 12. Chemical Regeneration Bath Mercury Concentrations**



The final bath concentration and the bath volume were used to determine the total mercury removed from the plates by the cleaning process. A total of 0.8 grams of mercury were removed via the chemical regeneration process. A simple estimate of the total mercury captured in the two duct sections was calculated based on time of operation (61 days), average mercury inlet concentration ( $4 \text{ ug/m}^3$ ) and average gas flow treated ( $170 \text{ sm}^3/\text{minute}$ ) and the average removal rate over the period (15%). The estimate indicated the MerCAP™ arrays should have captured approximately 9 grams of mercury during their time in service. The order of magnitude difference in the estimated captured versus recovered mercury is being further investigated. There was no attempt to determine the effect of soak time of the MerCAP™ modules in the acid bath on mercury removal, so it is unclear if additional treatment time would have improved the closure of the estimated versus recovered mercury. Additionally there was no attempt to hermetically seal the modules when they were removed from service and transported to the processors.

The amount of gold measured in the regeneration bath was also monitored to determine if the chemical regeneration process would significantly damage or remove the gold coating. The gold concentration measured in the final bath was a mass of 0.6 grams. The gold electroplated onto the 10 MerCAP™ modules that were cleaned in the bath had a net mass of gold on them of 1800 grams (64 ounces). The loss or damage to the gold coating due to acid washing is less 0.1% by weight, suggesting that the chemical regeneration process could be utilized on the same set of MerCAP™ plates repeatedly with minimal damage or degradation.

### **Parametric Evaluations**

During the course of the program there was an opportunity to evaluate design variables and their effect on the mercury removal performance of the array. Two variables were chosen to be evaluated, substrate pretreatment and substrate plate spacing.

Using the different duct sections that are part of the design of the MerCAP™ array to house differently configured substrate arrays the design variables were tested. Table 2 summarizes the results of these parametric evaluations.

**Table 2. Substrate Summary**

Duct Section	Substrate	Plate Spacing	Install Date	Hours in Service	Average Hg Removal	Measured Outlet Oxidized Hg
Duct 1	Acid Treated	1-Inch	8/22/04	5,308	30 – 35%	35 – 40%
Duct 2	Non-Acid Treated	1-Inch	11/18/04	1,035 1,470	15 – 18% 10%	20%
Duct 2	Post Acid Treatment	1-Inch	1/25/05	Reinstalled after regen	52%	N/A
Duct 3	Non-Acid Treated	½-Inch	11/18/04	1,035 1,470	25 – 30% 12%	20 – 25%
Duct 3	Post Acid Treatment	½-Inch	1/25/05	Reinstalled after regen	58%	N/A
Duct 4	Empty/Baseline	N/A	N/A	N/A	0%	15%

Pre-treating the substrates with an acid wash was shown to increase the overall performance of the array. Seen in the removal performance difference between duct section 1 and section 2. Mercury removal was a factor of two better for the substrate treated with an acid wash than those without. Eventually the substrates in sections 2 and 3 were removed and subjected to an acid wash and then returned to service.

To test the effect of plate spacing two substrate arrays were constructed with different plate spacing arrangements. The two arrays were installed in the MerCAP™ array and evaluated. Duct section 2 housed a 1-inch spaced array and section 3 housed a ½-inch spaced array. The effect of reducing plate spacing, which also increases the overall surface area of the array, seemed to have little effect on the mercury removal performance, a difference of 25-30% versus 15-18% before acid wash and 58% versus 52% after acid wash. This suggests that the limiting factor of the substrate array performance may be in the flue gas itself.

### **Balance of Plant Effects**

Two of the ten host baghouse compartments are monitored with a data acquisition system. Baghouse compartment 1, housing the MerCAP™ Arrays, and compartment 6 (no arrays) are mirror images of each other at the inlet end of the Stanton Station Unit 10 baghouse. The tube sheet differential pressure drop (pressure drop across the filter bags) is monitored in both compartments to determine the overall impact of the MerCAP™ Array on the baghouse compartment. Additionally, the pressure drop specifically across the MerCAP™ Array is monitored within compartment 1.

As a result of the MerCAP™ Array installed in compartment 1, an average increase in the differential pressure of 1.5 inches of water (in-H<sub>2</sub>O) has been recorded compared to the adjacent compartment 6. Prior to installation of the MerCAP™ substrates, the physical duct structures installed in the top of compartment 1 to house the MerCAP™ Array resulted in

0.15 inches of water of the total reported pressure increase. These duct sections force the gas exiting the baghouse filters to pass through the MerCAP™ substrates prior to exiting the compartment. The MerCAP™ ducts have fairly severe entrance and exit planes. Severe changes in entrance and exit areas are often associated with increased flow resistance. A permanently installed MerCAP™ system could be more thoroughly engineered to minimize these entrance and exit losses.

### **Economic Analysis**

The data gathered from the test program will provide information needed to refine cost estimates for using MerCAP™ technology for controlling mercury in flue gas. EPRI models based upon current pilot-scale data will be refined by incorporating data from the full-scale baghouse compartment and pilot mist eliminator demonstrations. Data pertaining to attainable mercury removal efficiencies will be correlated to other performance aspects, such as pressure drop, estimated sorbent lifetimes, and installation costs. The results obtained during the long-term performance tests, Mini- MerCAP™ regeneration tests, and post-test gold surface analyses should provide data necessary for better predicting MerCAP™ sorbent lifetime. All of the test program data will be compiled to provide an analysis of the economic merits of MerCAP™ technology for use downstream of baghouses.

### **CONCLUSIONS**

The application of the MerCAP™ technology as a viable and economical means of controlling the mercury emission from coal-fired utility boilers is being demonstrated and evaluated for the first time on a full-scale baghouse compartment. The demonstration is focused on applying the technology to low rank fuels with high elemental mercury fractions that have proven difficult for other control technologies.

The program to date has demonstrated that MerCAP™ technology can be applied to a scrubbed flue gas stream to remove appreciable fractions of vapor-phase mercury. The effects of scrubber operations and temperature on the technology are still being evaluated, however, it is clear that the technology has higher mercury capture performance at lower gas temperatures. The effect that PRB fuel has on the technology could not be accurately compared to the NDL fuel due to significant changes in plant operations as a result of the fuel change. However, previous tests at sites burning PRB fuel have shown the technology to be viable.

The program to date has demonstrated that the MerCAP™ substrates can reliably be regenerated, both chemically and thermally, without a negative impact on mercury removal performance. The regeneration results to date show that the MerCAP™ substrates return to initial removal performance values following thorough regeneration.

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