

Long-Term Performance of Sulfur-Impregnated, Granulated Activated Carbon (GAC) for Mercury Removal From NWCF Off-Gas

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SUMMARY

Radioactive, Sodium-Bearing Waste (SBW) from past nuclear fuel reprocessing is currently being stored at the Idaho Nuclear Technology and Engineering Center (INTEC). Calcination of the SBW in the New Waste Calcining Facility (NWCF), upgraded with off-gas treatment technology to comply with the Environmental Protection Agency (EPA) Maximum Achievable Control Technology (MACT) rules is being considered as a waste treatment option. Mercury is a volatile component of the SBW. Current flow sheets and off-gas monitoring results from past NWCF operations have indicated that future mercury emissions may exceed the proposed (MACT) limit of 45 ug/dscm (micrograms/dry standard cubic meter) normalized to 7% O₂ for existing Hazardous Waste Combustors (HWC) if modifications are not made.

The leading option being considered for the control of mercury emissions is the use of a fixed-bed of sulfur-impregnated granulated activated carbon (GAC) for removal of elemental and oxidized forms of mercury. Past laboratory-scale studies have indicated that Mersorb®, a sulfur-impregnated carbon manufactured by Nucon International, was highly effective (>99% removal) in removing both elemental mercury (Hg⁰) and mercuric chloride (HgCl₂), from simulated NWCF off-gas. In order to evaluate the possible effects of long-term exposure to off-gas components with regard to Hg⁰ removal efficiency, a test bed of Mersorb® was continually exposed to an NWCF off-gas simulant without mercury for 1000 hours. During this test the bed was periodically checked for elemental mercury removal efficiency. The off-gas simulant was composed of 70% H₂O, 2.4% CO₂, 4.4% O₂, 443 ppm NO, 428 ppm NO₂, 480 ppm N₂O, 29.5 ppm CO, 23.3 ppm SO₂ and 28.3 ppm HCl. The balance was nitrogen. A reference bed was simultaneously exposed to pure nitrogen for 1000 hours. Bed temperatures were maintained at 119-124°C. The linear velocity was 8.25cm/s and the residence time was 1s. The mercury removal efficiency was determined at 24,200,762 and 1000 hour. Simulant gas mercury concentrations were in the range of 2.46E+03 to 5.24E+04 ug/m³. With the exception of SO₂, removal of off-gas components was determined at 160 hours exposure time. Due to malfunctioning of the SO₂ chemical sensor, SO₂ removal was determined with a fresh carbon bed after the 1000 hours test was concluded.

The data indicated that there was no significant change in the Hg⁰ removal efficiency over the 1000- hour exposure time. Over the test period, the mean mercury removal efficiencies for the test and reference beds, were 100 ± 3.1% and 99.9 ± 3.0% respectively. Due to uncertainty levels for measurement of Hg⁰ concentrations, small changes in removal efficiency could not be determined with certainty. However, the intent of the test was to uncover possible large decreases in removal efficiency due to sulfur depletion, carbon degradation or pore blockage by off-gas components.

The effect of temperature on Hg⁰ removal efficiency was determined. Removal efficiencies for the test bed were as follows: 100°C, 99.2 ± 1.83%, 124°C, 100 ± 2.42%, 150°C, 100 ± 1.77%. Removal efficiencies for the reference bed were as follows: 100°C, 99.9 ± 0.910%, 124°C, 99.9 ± 2.04%, 150°C, 99.1 ± 1.0%. The small decreases in removal efficiency for the test bed when the temperature was decreased from 124°C to 100°C, and for the reference bed when the temperature was increased from 124°C to 150°C were reproducible, and appeared to be real effects. Therefore, the decreases are estimated to be significant despite the uncertainties associated with their measurement.

With the exception of SO₂, measurement of upstream and downstream concentrations of off-gas components for the test bed indicated no significant sorption of these gases at 124°C. Gas components removal efficiencies for the reference bed were not measured. The removal efficiencies of SO₂ from the test gas (off-gas simulant) and from dry N₂ were 98.7% and 10.8 % respectively. The high water vapor content of the test gas (70%) may have enhanced the sorption of SO₂ by formation of H₂SO₄.

A 178-hour breakthrough run with carbon that was exposed to calciner off-gas simulant for 1000 hours apparently failed to reach breakthrough. This may have been due to the oxidation of Hg⁰ by NO₂ resulting in oxidized forms of mercury which were not measurable by the analyzer that which measures only Hg⁰. In lieu of breakthrough capacity runs, two 39 hour runs were conducted to compare Hg⁰ loadings of carbon exposed to the calciner off-gas simulant with carbon exposed to dry N₂. Mercury loadings for these runs were much lower than expected. It was suspected that the method used to leach the mercury prior to analysis failed to dissolve all the mercury present in the carbon. The carbon from the 39 hour runs and the 178 hour run will be treated by microwave digestion which will destroy the carbon and thus release all the mercury. The analytical results will be reported in a future revision of this report.

Toxicity Characteristics Leaching Procedure (TCLP) tests of carbon from the 178 hour run and the two 39 hour runs resulted in mercury concentrations which far exceeded the Land Disposal Restrictions (LDR) limit for direct disposal listed in 40CFR, Part 268.40. This was an indication that a significant amount of the sorbed mercury was in the oxidized state. If the mercury in the test gas were present solely as Hg⁰, then mercury in the carbon would have been present as HgS. Oxidized forms of mercury such as HgO, HgCl₂ and Hg(NO₃)₂ are more soluble than HgS by several orders of magnitude.

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Long-Term Performance of Sulfur-Impregnated, Granulated Activated Carbon (GAC) for Mercury Removal from NWCF Off-Gas

1. INTRODUCTION

From 1982 to 2000, the New Waste Calcining Facility (NWCF) at the Idaho Nuclear Technology and Engineering Center (INTEC) converted acidic, radioactive waste, generated by defense fuel reprocessing, into a granular solid for safe storage. The presence of mercury in the waste is due to its use as a catalyst for the dissolution of aluminum-clad fuel. Continued calcination of the Sodium-Bearing Waste (SBW) in the NWCF is being considered as a waste treatment option. The NWCF will be upgraded to comply with the Maximum Achievable Control Technology (MACT) off-gas emissions standards for Hazardous Waste Combustors (HWC) promulgated in February 2002.¹ The main component of the upgrade is a two-stage combustion unit designed to reduce NO_x, CO and hydrocarbon emissions. Due to the presence of mercury in the waste and its volatility, the high mercury levels expected in the off-gas are of major concern. Based on the latest mass balances, mercury levels could be as high as 24,000 ug/dscm normalized to 7% O₂ when processing WM-189, which has the highest mercury concentration.² The MACT standard for new HWC facilities is 45 ug/dscm normalized to 7% O₂.¹ If the target mercury effluent concentration is set at 20 ug/dscm normalized to 7% O₂, the target removal efficiency for the proposed granulated activated carbon (GAC) adsorption bed is 99.9%, as was recommended in the most recent engineering evaluation of GAC performance requirements.³ Previous short-term (5-30h) tests in support of past vitrification and calcination flowsheets, as well as the current flowsheet, have indicated that Mersorb®, a sulfur-impregnated GAC has the potential to meet the target removal efficiency for both elemental mercury (Hg⁰) and mercuric chloride (HgCl₂).^{4,5,6} A previous five-hour test with a test gas simulant based on the current flowsheet resulted in Hg⁰ removal efficiencies of 99.7% and 99.8% at temperatures of 90°C and 120°C respectively.⁶ Mersorb® was chosen because of the stability of the sulfur-impregnation at high temperatures (>200°C).⁷

While all previous tests have shown that high mercury removal efficiencies can be obtained in the presence of off-gas constituents such as HCl, SO₂, NO, NO₂, H₂O and CO, the long-term effects of these gases on removal efficiency, breakthrough capacity and sulfur content has not been determined for Mersorb® or, as a literature search revealed, for any other sulfur-impregnated carbon. The possible effects of oxidants include oxidation of sulfur and carbon by NO₂ or by H₂SO₃ and HNO₃ which may form on the carbon surface by interaction with H₂O. Adsorption of HCl and H₂O on active sites may block diffusion pathways and prevent Hg⁰ from reacting with the impregnated sulfur to form HgS. In short-term tests with sulfur-impregnated carbons, Wiu and Vidic⁸ measured a 25% decrease in Hg⁰ uptake at 140°C from a test gas containing 10% H₂O in N₂ compared with dry N₂. The effect of HCl on Hg⁰ uptake was not studied.

The removal of Hg⁰ by the GAC relies on the reaction with S to form HgS. The high temperature (600°C) sulfur impregnation process used in the production of Mersorb® allows sulfur adsorption into the micropores as well as the macropores of the carbon. Off-gas molecules competing with Hg⁰ for active sites migrate rapidly into the macropores of the carbon, but move more slowly into the smaller pores. Thus, pore blockage with a corresponding decrease in Hg⁰ removal efficiency may not have occurred during the short term tests, but may be exhibited over a longer period of time. Pore blockage and/or sulfur depletion will result in decreases in the mercury removal efficiency and breakthrough capacity, requiring more frequent bed changeout. Determination of possible declines in GAC performance over

time will aid in designing an adsorption bed which will accomplish the target mercury removal efficiency and which will be of sufficient size as to minimize bed changeout.

The purpose of this study was to determine if measurable declines in mercury removal efficiency and breakthrough capacity of Mersorb® will occur as a result of prolonged exposure to simulated calcination off-gas conditions. Additional objectives were to measure any significant sulfur depletion as a result of exposure to the test gases, to measure sorption of off-gas components and to determine mercury leachability from the carbon by the use of the Toxicity Characteristics Leaching Procedure (TCLP) test. The data can be used to establish performance acceptance criteria with regard to removal efficiency, breakthrough capacity, sulfur depletion, operating temperature, and mercury leachability.

2. TEST EQUIPMENT AND PROCEDURE

The test apparatus used for the determination of Hg^0 removal efficiencies is illustrated in Figure 1. The test gas mixture was produced by the use of commercial calibration gases. The test gas composition and estimates from the SBW flow sheet² are listed in Table 1. With the exception of N_2 and N_2O , all gases were measured by commercial instrumentation. CO_2 , SO_2 , O_2 , and HCl were measured by chemical sensors supplied by Nova Analytical. CO was measured with the Enviromax 3000T infra-red analyzer, also supplied by Nova. NO and NO_2 were measured with the Thermo-Environmental model 42C chemiluminescent analyzer. Water vapor content was determined by condensing the water vapor at 4°C , weighing the collected water and calculating the water vapor content using measured flow rates and the measured collection time. The water vapor content was also continuously monitored by means of a Vaisala humidity monitor. The flow rates of all gases were controlled by mass flow controllers having either up-to-date vendor calibrations or recent in-house calibrations.

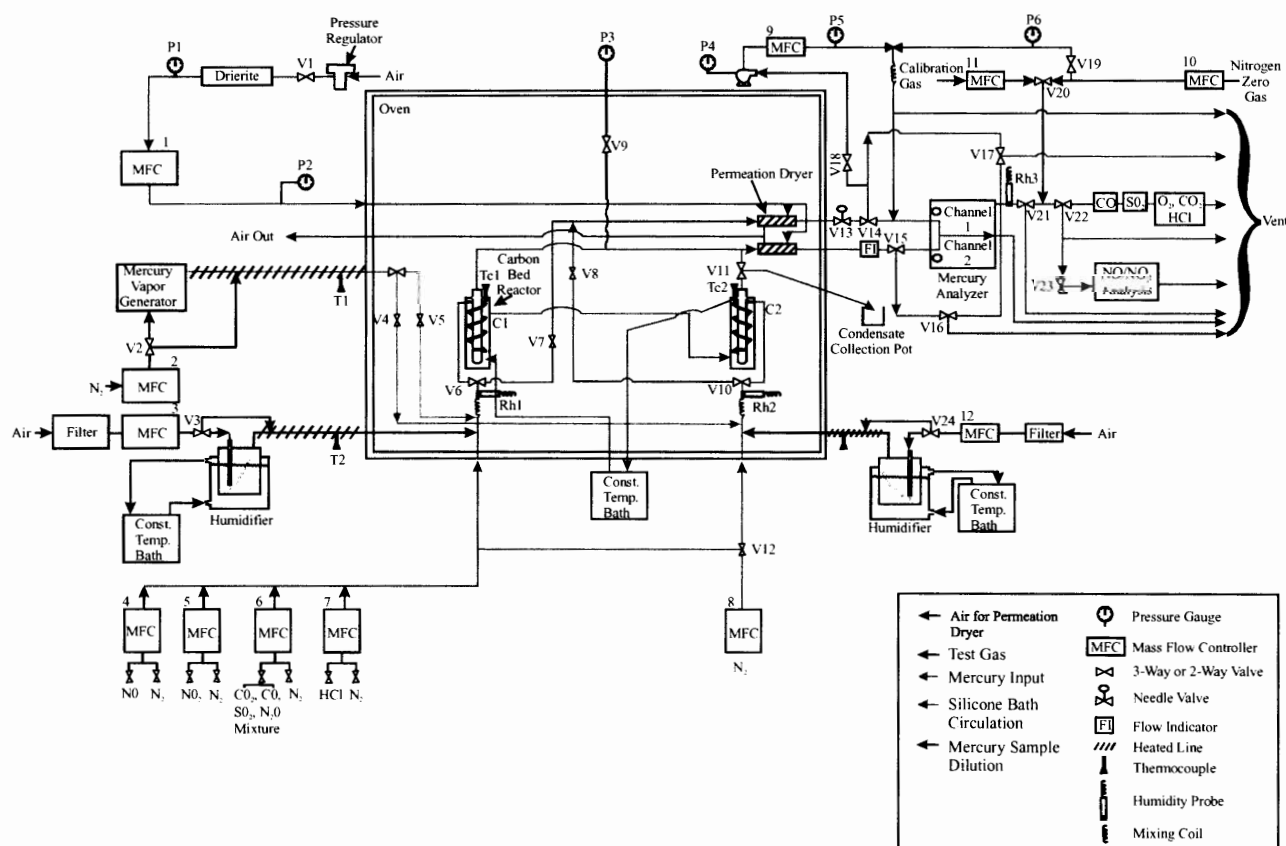


Figure 1. Long-Term GAC Performance Test Apparatus

Table 1. Test gas composition and estimates from SBW flow sheet

Component	Test Gas Composition	SBW Flow Sheet ²
N ₂	23%	23%
H ₂ O	70.0±1.3%	70%
CO ₂	2.4±0.1%	5.5%
O ₂	4.4±0.1%	1.25%
NO	443±4.6 ppm	970 ppm
CO	29.5±0.6 ppm	18 ppm
SO ₂	23.3±0.3 ppm	1.0 ppm
NO ₂	428 ± 3.5 ppm	13 ppm
HCl	28.3 ±1.3 ppm	12 ppm
N ₂ O	480 ppm	None listed
Hg	2.46E+03	3.85E+03

Water vapor was introduced by passing air through a water column whose temperature was controlled by a constant temperature bath. Mercury vapor was introduced by passing N₂ over a pool of Hg⁰ in a vessel whose temperature was controlled by a constant temperature bath. Water vapor was "removed upstream" of the gas and mercury analyzers by means of a shell and tube Perma-Pure® drier manufactured by the Perma-Pure corporation.

The GAC, supplied by Nucon International, consisted of 1.5 mm diameter rods impregnated with 12- 13wt% sulfur. This material was placed in two small jacketed fixed-bed reactors inside a temperature-controlled oven. The temperature of the reactors was controlled by the circulation of silicone oil from a constant temperature bath. One carbon bed (test bed) was exposed to a test gas whose composition simulated calciner off-gas, while the other bed (reference bed) was exposed to dry N₂. Each bed was separated into an upper and lower bed by glass wool. This allowed for a long enough total bed length (8cm) to allow for a 1s residence time, while providing a smaller amount of carbon (lower bed) to maximize the effects of gas components. The lower beds were used to determine possible sulfur depletion, to estimate breakthrough capacity and to load Hg⁰ for TCLP testing. The breakthrough time was defined as the elapsed run time at which the removal efficiency fell below a steady state value. The breakthrough capacity was defined as the weight of sorbed Hg⁰ at the breakthrough time divided by the weight of carbon.

Both the test gas and the N₂ streams were split upstream of their respective GAC beds to allow for mercury and gas measurements upstream and downstream of the beds. The GAC beds were exposed to their respective gases (without Hg⁰) for approximately 1000 hours. Mercury removal efficiencies were measured at 24, 200, 760 and 1000 hours. Gas concentrations upstream and downstream of the test bed were measured at 160 hours. During the final removal efficiency tests after 1000 hours exposure, the carbon bed temperature was adjusted from 124°C to 150°C and then to 100°C to determine the effect of temperature on removal efficiency.

Mercury removal efficiencies after 24 and 200 hours exposure time were measured with the the PS Analytical (PSA) Sir Gallahad mercury analyzer which has a 2 channel system for measuring Hg⁰ concentrations upstream and downstream of the carbon bed with a 5 minute cycle time between each measurement. The analyzer measured the concentration of mercury in the test gas by pumping a measured sample volume of the gas through a bed of gold-coated sand for a specified time interval. The Hg⁰ formed an amalgam with the gold. The gold-coated sand was then heated and purged with N₂ to release the mercury into an atomic fluorescence cell for measurement. The mass of mercury measured was converted to a concentration by dividing by the measured sample volume. The analyzer was calibrated using a mercury vapor injection system supplied by the vendor. This system consisted of a vessel

containing liquid mercury from which measured volumes of mercury-saturated air, at a measured temperature were withdrawn by hypodermic syringe and injected into an N₂ carrier gas by means of a sample port. The analyzer software calculated the mass of mercury injected for each injection and developed a calibration curve relating the mass of mercury injected to the signal obtained.

Due to software problems and electronic malfunctions, the PSA analyzer became inoperable after the 200 hour removal efficiency measurements. All remaining Hg⁰ measurements were made with the Tekran Model 2537A Mercury Vapor Analyzer manufactured by Tekran Inc. This instrument is a single channel analyzer. Thus, determining Hg⁰ removal efficiencies required obtaining Hg⁰ measurements by manually switching between gas streams upstream and downstream of the carbon beds. The main components of the Tekran 2537A Mercury Vapor Analyzer include the sample pump, pure gold amalgamation traps, and the atomic fluorescence detection cell containing a mercury vapor lamp and photomultiplier tube. Mercury measurement involves withdrawal of a precise volume of sample gas by means of a pump and a mass flow controller which precisely controls the sample flow rate at a predetermined setpoint for a specific predetermined period of time. The sample gas flows through one of the two pure gold amalgamation traps and the mercury in the sample gas forms an amalgam with the gold. The analyzer contains dual gold cartridges to allow for continuous sampling of the process. The gold cartridge is then purged with Ultra-High Purity (UHP) argon to purge any residual sample gas. Following the purge, the gold cartridge is heated to release the amalgamated mercury, which is carried by the argon into the atomic fluorescence detection cell. In the detection cell, a mercury vapor lamp emits a beam of light at a wavelength of 253.7 nm, causing the mercury vapor in the sample to fluoresce. The photomultiplier tube is positioned at a right angle to the optical path of the mercury vapor lamp, and measures the intensity of the fluorescence produced by the mercury vapor in the sample. The measured intensity is directly proportional to the mass of mercury vapor in the sample.

Calibration of the Tekran analyzer was performed by automatic injection from an internal calibration source. The internal calibration apparatus consisted of a Teflon permeation tube with a known Hg⁰ permeation rate that is regulated in a temperature-controlled oven. The argon carrier gas flows through the permeation tube and carries a known quantity of elemental mercury through the sample train to the detector cell. The quantity of mercury may be adjusted by changing the sampling time and sample flow rate. An alternate method of calibration involves injection of a known quantity of mercury into the carrier gas with a gas-tight syringe. Since the peak area vs. Hg⁰ concentration correlation is linear over any given range of mercury concentrations, only a zero and span are necessary for proper calibration of the analyzer.

The linear concentration ranges of the PSA and Tekran analyzers are approximately 0-1000 ug/m³ and 0-50 ug/m³ respectively. Therefore, use of the Tekran analyzer required air dilution of the test gas upstream and downstream of the carbon beds in order to assure that the measured Hg⁰ concentration was within the linear range of the Tekran instrument. The upstream and downstream dilution points were upstream of the Perma-Pure drier and downstream of the flow indicator, respectively. Diluent flow rates were controlled by mass flow controllers. Due to corrosive effects of the acid gases, the mass flow indicator (FI) downstream of the carbon beds was replaced by a rotameter after the 200 hour Hg⁰ removal efficiency determination. Also, a rotameter was added downstream of the upstream dilution point in order to measure total flow for dilution calculations. Both rotameters were calibrated using standard bubble-meter techniques.

Mercury and sulfur analyses of the carbon were performed by leaching with aqua regia (3HCl: 1HNO₃) followed by cold vapor and Inductively-Coupled Plasma (ICP) techniques respectively. Mercury Toxicity Characteristics Leaching Procedure (TCLP) tests involved leaching the carbon for 18 hours in 0.56% acetic acid followed by cold vapor analysis of the leachate.

3. DATA ANALYSIS

Removal efficiencies for Hg^0 and gaseous components of the test gas were determined as follows:

$$\% \text{ RE} = ((C_1 - C_2) / C_1) 100 \quad \text{Equation 1}$$

where,

$\% \text{ RE}$ = Percent removal efficiency

C_1 = Mean Hg^0 or gas concentration upstream of the carbon bed, ug/m^3

C_2 = Mean Hg^0 or gas concentration downstream of the carbon bed, ug/m^3

Several measurements of upstream and downstream concentrations were made. The uncertainty in the removal efficiency was determined as follows:

$$\% \text{ RE}_{\text{max}} = ((C_1 + s_{C1}) - (C_2 - s_{C2})) / (C_1 - s_{C1}) \times 100 \quad \text{Equation 2}$$

$$\% \text{ RE}_{\text{min}} = ((C_1 - s_{C1}) - (C_2 + s_{C2})) / (C_1 + s_{C1}) \times 100 \quad \text{Equation 3}$$

$$U_{\% \text{ RE}} = (\% \text{ RE}_{\text{max}} - \% \text{ RE}_{\text{min}}) / 2 \quad \text{Equation 4}$$

where,

s_{C1} = Standard deviation of C_1 measurements

s_{C2} = Standard deviation of C_2 measurements

$U_{\% \text{ RE}}$ = Uncertainty expressed as $\pm \% \text{ RE}$

Standard deviations for a set of measurements were determined using the Excel® descriptive statistics program. The standard deviations were used in Equations 2 and 3 to calculate a maximum and minimum value for the removal efficiency. The span between the maximum and minimum removal efficiencies was divided by 2 in order to obtain the uncertainty in the calculated removal efficiency. This method has been well documented.⁹

4. RESULTS AND DISCUSSION

The removal efficiencies for Hg^0 over the 1000 hour exposure period are listed in Table 2. There was no measurable decline in removal efficiency of the test bed, which was exposed to a calciner off-gas simulant, compared to the reference bed which was exposed to dry N_2 . Removal efficiencies after the 1000 hour test period for the test and reference beds were $100.0 \pm 2.4\%$ and $99.9 \pm 2.0\%$ respectively. Mean removal efficiencies over the test period were $100 \pm 3.1\%$ for the test bed and $99.9 \pm 3.0\%$ for the reference bed. The data indicate that Mersorb® has the potential for achieving the target removal efficiency (99.9%) for a wide range of Hg^0 concentrations. Input Hg^0 concentrations ranged from $2.46\text{E}+03 \text{ ug/m}^3$ to $5.24\text{E}+04 \text{ ug/m}^3$.

Table 2. Elemental mercury removal efficiencies during the 1000 hour exposure time

Test #	Run	Carbon Bed	Bed Temp. °C	Exposure Time, h	$C^a_1, \text{ug/m}^3$	$C^b_2, \text{ug/m}^3$	Removal Efficiency, %
1	HgInt1.24psa	test bed	120	24	$5.24\text{E}+04 \pm 1.42\text{E}+03$	$6.84\text{E}+01 \pm 8.24\text{E}-01$	100.2 ± 5.4
2	HgInt1.200psa	test bed	120	200	$2.46\text{E}+03 \pm 2.48\text{E}+01$	$1.90\text{E}+00 \pm 1.39\text{E}-01$	99.9 ± 2.0
3	HgInt1.762wtek	test bed	124	762	$8.51\text{E}+03 \pm 1.05\text{E}+02$	$3.26\text{E}+01 \pm 2.39\text{E}+00$	99.7 ± 2.5
4	HgInt1.762dtek	ref. bed	124	762	$1.14\text{E}+04 \pm 2.23\text{E}+02$	$2.99\text{E}+01 \pm 8.31\text{E}-01$	99.8 ± 3.9
5	HgInt1.1000wtek	test bed	124	1000	$9.94\text{E}+03 \pm 1.20\text{E}+02$	$2.75\text{E}+00 \pm 1.57\text{E}-01$	100.0 ± 2.4
6	HgInt1.1000dtek	ref. bed	124	1000	$1.45\text{E}+04 \pm 1.48\text{E}+02$	$1.22\text{E}+01 \pm 2.77\text{E}-01$	99.9 ± 2.0
7	HgInt1.150wtek	test bed	150	1000	$9.05\text{E}+03 \pm 8.01\text{E}+01$	$1.85\text{E}+00 \pm 2.08\text{E}-01$	100.0 ± 1.8
8	HgInt1.100wtek	test bed	100	1000	$9.05\text{E}+03 \pm 8.01\text{E}+01$	$7.18\text{E}+01 \pm 6.20\text{E}+00$	99.2 ± 1.8
9	HgInt1.150dtek	ref. bed	150	1000	$1.51\text{E}+04 \pm 6.9\text{E}+01$	$1.34\text{E}+02 \pm 1.40\text{E}+01$	99.1 ± 1.0
10	HgInt1.100dtek	ref. bed	100	1000	$1.51\text{E}+04 \pm 6.9\text{E}+01$	$1.36\text{E}+01 \pm 4.83\text{E}-01$	99.9 ± 0.90

- a. Mean of mercury concentrations upstream of carbon bed
- b. Mean of mercury concentrations downstream of carbon bed

- NOTES:
1. Bed Dimensions: 1cm x 8cm
 2. Flow Rate Through Carbon Beds: 38cc/min
 3. Empty Bed Linear Velocity: 8:25cm/s
 4. Residence Time: 0.99s
 5. Carbon Bed Weights: Test Bed, 3.3093g, Reference Bed, 3.2081g
 6. Gas Composition: Test Bed, Calciner Off-Gas Simulant (See Table 1), Reference Bed N_2
 7. Carbon Particle Size: 1.5mm

During the 1000 hour removal efficiency tests on the test and reference beds, the carbon bed temperature was increased from 124°C to 150°C , and then decreased to 100°C in order to determine the effect of temperature on Hg^0 removal efficiency. These tests are listed as tests 5-10 in Table 2. Increasing the temperature of the test bed from 124°C to 150°C had no effect on the removal efficiency (compare tests 5&7), while decreasing the temperature from 124°C to 100°C resulted in a decrease in removal efficiency from $100 \pm 2.4\%$ to $99.2 \pm 1.8\%$ (compare tests 5&8). Although the decrease was small and within experimental error, the effect was measurable and reproducible, and therefore is considered a real effect. The decrease in removal efficiency may be due to some competition for reactive sites provided by the sorption of water at the lower temperature. The opposite effect occurred with the

reference bed. When the temperature was increased from 124°C to 150°C, the removal efficiency declined from $99.9 \pm 2.0\%$ to $99.1 \pm 1.0\%$ (compare tests 6&9), while decreasing the temperature from 124°C to 100°C had no effect on the removal efficiency (compare tests 6&10). This effect could not be explained.

The removal efficiencies determined for the test gas components are listed in Table 3. These determinations were made 160 hours after the start of the 1000-hour test. With the exception of SO₂, there was no significant sorption of test gas components. Negative removal efficiencies are the result of downstream gas concentrations being higher than upstream concentrations. However, slight differences in upstream and downstream concentrations were not significant as the standard deviations of the measurements indicate. A small decrease in the NO concentration was accompanied by a similarly small increase in the NO₂ concentration. This may have been due to the reaction of NO with O₂ to form NO₂. This reaction may have occurred on the surface of the carbon. Possible increases in NO₂ levels due to this reaction should be investigated during pilot tests.

Table 3. Removal of test gas components by the test bed

Components	Upstream Concentration, ppm	Downstream Concentration, ppm	Removal Efficiency, %
CO	29.5 \pm 0.6	30.4 \pm 0.1	-3.24 \pm 2.25
CO ₂	2.40 \pm 0.10	2.40 \pm 0.10	-28.3 \pm 2.25
O ₂	4.40 \pm 0.10	4.40 \pm 0.10	0.85 \pm 2.26
HCl	28.3 \pm 1.3	27.4 \pm 0.8	1.61 \pm 7.45
NO	443.0 \pm 4.6	4.31 \pm 3.8	2.50 \pm 1.91
NO ₂	428.0 \pm 3.5	436.5 \pm .9	-0.92 \pm 1.71
SO ₂	23.3 \pm 0.3	1.0 \pm 0	98.7 \pm 2.3
SO ₂ (dry N ₂)	47.4	42.3	10.8

- NOTES:
1. Bed Dimensions: 1cm x 8cm
 2. Flow Rate Through Bed: 389cc/min
 3. Empty Bed Linear Velocity : 8.25cm/s
 4. Residence Time: 0.99s
 5. Carbon Bed Weight: 3.3093g
 6. Gas composition: calciner off-gas simulant (see table 1) except for last SO₂ test which was conducted with dry N₂ as listed.

Gas removal efficiencies for all gases except SO₂ were determined at 160 hours after the start of the 1000 hour test. SO₂ removal efficiency was determined with fresh carbon after termination of the 1000 hour test.

Due to problems with the SO₂ chemical sensor, the removal efficiency could not be determined during the 1000-hour test. The SO₂ removal efficiency was determined later with fresh carbon. The data indicate that the removal efficiency was high ($98.7 \pm 2.3\%$) in the calciner off-gas simulant and low (10.8 %) in dry N₂. Since the water content of the off-gas simulant was high (70%), this may have been due to the formation of H₂SO₄ which may have sorbed more strongly on the carbon surface. If a significant amount of SO₂ was sorbed on the carbon during the 1000 hour test, apparently this had no effect on the Hg⁰ removal efficiency.

Subsequent to the 1000-hour exposure test, carbon samples were submitted for sulfur analysis. As indicated in Table 4, there was no significant difference in sulfur content between the test and reference beds. The average values obtained for the test (8.48 ± 0.27 wt.%) and reference (8.39 ± 0.35 wt.%) beds

were low compared to the vendor estimate of 12-13 wt.%. It is possible that the preparation method employed, which involves boiling point digestions in concentrated HNO₃, 30% H₂O₂ and concentrated HCl failed to release all the impregnated sulfur, or that some sulfur was released as SO₂. It is not likely that the reference bed would lose sulfur due to exposure to dry N₂ at 124°C since the sulfur impregnation is performed at 600°C. Subsequent to development of a microwave digestion method, which will destroy the carbon and release all the sulfur, these samples will be resubmitted for analysis. The results will be reported in a future revision of this report.

Table 4. Sulfur content (wt%) of carbon beds after 1000 hours exposure test

Test Bed	Reference Bed
8.27	8.72
8.39	8.03
8.79	8.42
Mean 8.48 ±0.27	Mean 8.39 ±0.35

- Note: 1. Bed Dimensions: 1cm X 8 cm
 2. Flow Rate Through Carbon Beds: 389cc/min
 3. Empty Bed Linear Velocity: 8:25 cm/s
 4. Residence Time: 0.99
 5. Carbon bed weights: test bed, 3.3093g, reference bed, 3.2081g
 6. Gas composition: test bed, calciner off-gas simulant, reference bed, dry N₂
 7. Carbon particle size: 1.5mm
 8. Bed temperature: 120-124°C

A 178-hour breakthrough capacity test with carbon from the test bed exposed to the calciner off-gas simulant failed to reach breakthrough. The test gas for this run was calciner off-gas simulant. The initial Hg⁰ concentration upstream of the carbon bed at 5 hours after the start of the run was 5.43 E+04 ug/m³. The concentration measured at 176 hours near the end of the run was 3.56E+03, a decrease of 93.4%. This was probably the result of conversion of Hg⁰ to an oxidized form of Hg by NO₂. It is likely that a large amount of the oxidized Hg was sorbed on surfaces of the test apparatus. Thus, a reliable measurement of the input Hg⁰ concentration was not obtained. A total mercury analysis of the carbon bed from this run (run Hg178) and TCLP results are listed in Table 5. The samples were first subjected to the TCLP procedure and then leached twice in aqua regia (3HCl:1HNO₃) at 90°C. The two leaches were separately analyzed for mercury and the results combined to determine the wt.% mercury. The result from the second leach was nearly the same as the first leach indicating that the leaching procedure failed to remove all the mercury. Thus, the mercury content determined by analysis of the carbon was much lower than the estimated loading for two reasons: (1) oxidation of Hg⁰ with subsequent deposition before reaching the carbon bed, and (2) insufficient release of mercury during preparation of the samples. The TCLP results were high (5.7E+02 mg/L) compared to the Land Disposal Restrictions (LDR) requirement of less than 0.025 mg/L.¹⁰ As indicated in Table 5, 5.6% of the estimated mercury loading was released by the TCLP leach. Both the TCLP results and the high percentage of mercury leached are probably the result of deposition of oxidized forms of mercury on the carbon.

Table 5. Mercury loading and TCLP results for samples of the test and reference carbon beds.

Run	Bed Type	Run Time, h	Hg ⁰ Input Conc., ug/m ³	Bed Size, i.d.x l,cm	Residence Time, s	Estimated Mercury Loading, wt. %	Mercury Analysis, wt. %	TCLP, mg/L	% Mercury Leached
Hg178	test	178	5.43E+04	1 x 1.2	0.15	25.0	7.22	5.7E+02	5.6
Hg39w	test	39	5.65E+04	1 x 0.6	0.08	13.6	4.57	6.3E+02	7.5
Hg39d	ref.	39	5.54E+04	1 x 0.6	0.08	8.85	3.53	1.67E+00	0.038

- NOTES:
1. Runs Hg178 and Hg39w were conducted with samples of carbon from the test bed which was exposed to the calciner off-gas simulant for 1000 hours. The test gas used for the Hg⁰ loading was calciner off-gas simulant.
 2. Run Hg39d was conducted with samples of carbon from the reference bed which was exposed to dry N₂ for 1000 hours. The test gas for the Hg⁰ loading was dry N₂.
 3. Land Disposal Restrictions require that the TCLP be less than 0.025 mg/L.¹⁰

Test results from run Hg39w, which was conducted with carbon from the test bed, were similar to those from Hg178 for the same reasons as mentioned above. The % mercury leached and the TCLP results were high. The test results from run Hg39d, which was conducted in dry N₂, were very different than those from run Hg39w. Mercury concentrations from the TCLP leach test were lower by a factor of 2.65 E-03 and the percent mercury leached was a factor of 5.07 E-03 lower. This indicates that the mercury in the carbon from run Hg39d may have been predominantly present at HgS which would not be expected to dissolve in the 0.56% acetic acid used in the TCLP test. Although the TCLP leach result for Hg39d was low (1.67 E+00) mg/L, it was 67 times higher than the LDR requirement (0.025 mg/L) for determination of toxicity. It is very possible that oxidized mercury, deposited on tubing surfaces from previous tests was released and deposited on the carbon during this run. Oxidized forms such as HgCl₂, HgO and Hg(NO₃)₂ would have leached more readily than HgS. The TCLP test was used as a convenient method of determining the leachability of the sorbed mercury. The data should be considered when evaluating disposal options for the GAC.

In all likelihood, the aqua regia leach method used to release mercury from the carbon samples failed to dissolve all the sorbed mercury. As was the case with the sulfur analysis mentioned above, the carbon samples will be subjected to microwave destruction of the carbon prior to analysis in order to release the remaining mercury. The total mercury from these analyses will provide a conservative estimate of the breakthrough capacity. The results will be reported in a future revision of this report.

5. CONCLUSIONS AND RECOMMENDATIONS

Long-term performance tests have indicated that Mersorb®, a sulfur-impregnated activated carbon, has the potential for fulfilling the requirement of 99.9% removal of Hg^0 from NWCF off-gas in order to comply with the proposed MACT emission limit of 45ug/dscm normalized to 7% O_2 . The high removal efficiency should be sustainable for long periods at the design bed temperature of 120°C even under conditions of high water content (70%) and high NO_2 (430 ppm). Since a reduction in removal efficiency was observed at 100°C, the temperature should not be allowed to fall below the design temperature. A temperature excursion to 150°C should not have an impact on mercury removal efficiency. At concentration levels predicted by mass balances, long-term exposure of the GAC to the off-gas components studied in these tests should have no significant effect on the Hg^0 removal efficiency or the sulfur content of the GAC. The GAC is likely to sorb significant amounts of SO_2 , possibly as H_2SO_4 . However, it was demonstrated that sorbed SO_2 had no significant effect on Hg^0 removal efficiency.

Oxidized forms of mercury such as HgO and HgCl_2 which may be present downstream of the staged combustor will sorb on the GAC. Due to the leachability of these compounds, as defined by the TCLP tests, their presence may impact direct disposal of the GAC. It is not the intention of the authors to discuss the regulatory aspects of GAC disposal except to suggest that the reported TCLP results should be considered when evaluating GAC disposal options. TCLP tests should be conducted on GAC used in future SBW thermal treatment pilot tests.

Linear velocities and residence times used in the small-scale tests were not intended to be representative of those used in pilot or full-scale systems. In order to provide data to support design of a pilot-sized GAC bed for calciner pilot tests, it is recommended that tests be conducted with a laboratory scale-up test reactor. The scale-up reactor tests would provide data on optimum linear velocity and residence time, pressure drop vs. carbon particle size and breakthrough capacity. A 3.8cm i.d. x 81cm, fixed-bed, multi-stage reactor has been constructed for this purpose and will be available for future tests.

6. REFERENCES

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