INEEL/CON-00-01332
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May 14, 2001

International Conference on Incineration and Thermal Treatment Technologies

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Removal of Mercury from the Off-Gas from Thermal Treatment of Radioactive Liquid Wastes

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ABSTRACT

Acidic, radioactive wastes with a high nitrate concentration, and containing mercury are currently being stored at the Idaho Nuclear Technology and Engineering Center (INTEC). In the past, these wastes were converted into a dry, granular solid by a high temperature fluidized-bed calcination process. In the future, the calcined solids may be immobilized by a vitrification process prior to disposal. It has been proposed that a vitrification facility be built to treat the acidic wastes, as well as the calcined solids. As was the case with the calcination process, NOx levels in the vitrification off-gas are expected to be high, and mercury emissions are expected to exceed the Maximum Control Technology (MACT) limits. Mitigation of mercury emissions by wet scrubbing, followed by adsorption onto activated carbon is being investigated.

Scoping tests with sulfur-impregnated activated carbon, KCl-impregnated activated carbon and non-impregnated activated carbon were conducted with a test gas containing1% NO_2, 28% H_2O, 4% O_2 and 67% N_2. Average removal efficiencies for Hg^o and $HgCl_2$ were 100 ± 2.5% and 99 ± 3.6% respectively, for sulfur-impregnated carbon. The KCl-impregnated carbon removed 99 ± 4.6% $HgCl_2$. The removal efficiency of the non-impregnated carbon was 99 ± 3.6% for $HgCl_2$. No short-term detrimental effects due to NO_2 and H_2O were observed. These results indicate that, placed downstream of a wet scrubber, an activated carbon adsorption bed has the potential of reducing mercury levels sufficiently to enable compliance with the MACT limit. Long-term exposure tests, and bed size optimization studies are planned for the future.

INTRODUCTION

The Idaho Nuclear Technology and Engineering Center (INTEC) is located at the Idaho National Engineering and Environmental Laboratory (INEEL) in southeastern Idaho. From 1982 to 2000 the New Waste Calcining Facility (NWCF) has employed a high temperature, fluidized bed calcination process to convert acidic radioactive wastes, generated by defense fuel reprocessing, to a granular solid for safe storage. The wastes currently being stored at INTEC contain mercury and high nitrate concentrations. Calciner off-gas measurements have indicated that mercury and other emissions exceeded the Maximum Achievable Control Technology (MACT) limits promulgated by the Environmental Protection Agency (EPA) for existing Hazardous Waste Combustors (HWC). As an alternative to upgrading the calcining facility to comply with the MACT rules, a new vitrification facility, which will immobilize both the acidic wastes and the calcined solids, has been proposed. It is anticipated that this facility will be required to be in compliance with the MACT rules. Thus, mitigation of mercury levels to below 45ug/dscm @7% O_2 will be required.

The off-gas from the vitrification process is expected to contain high levels of NO_x, H_2O and mercury. The mercury is likely to be in both the oxidized ($HgCl_2$ and HgO) and elemental (Hg^o) forms. It was estimated that the NWCF single-stage scrubber removed about 80% of the mercury in the off-gas. Thus, it may be possible to remove the required amount of mercury by using a multi-stage scrubber followed by a packed bed of activated carbon. Based on rough estimates of expected mercury concentrations in the off-gas, the required removal efficiency of the activated carbon could be as high as 99%.

The study described in this paper was initiated to support upgrading the NWCF so that future mercury emissions would be in compliance with the MACT rules. Thus, the high NO_2 concentration in the test gases used in the study were greater than what is expected in the vitrification off-gas. Concentrations of NO_2 and H_2O in the NWCF off-gas averaged 1.8%(wet) and 28% respectively. The off-gas from vitrification is expected to contain about 44% H_2O and a maximum of 1% NO_2.

The effect of high NO_2 and H_2O concentrations on the ability of activated carbon to remove mercury and mercury compounds has not been appreciably studied. Gray and Do measured high fractional uptakes of NO_2 by activated carbon at 100°C.[1] They also measured carbon weight losses due to reaction with 5000 ppmv NO_2 at temperatures greater than 150°C.[2] The formation of HNO_3 with resultant oxidation of the carbon was also a concern. Thus, studies have been conducted to determine the effects of high concentrations of NO_2 and H_2O on the adsoption of $HgCl_2$ and Hg^o by activated carbon.

TEST EQUIPMENT AND PROCEDURE

The test apparatus used for the determination of mercury removal efficiencies is illustrated in Fig.1. Test gases contained either $HgCl_2$ or Hg^o. These vapors were generated by passing N_2 through either a packed bed of $HgCl_2$, or over a pool of Hg^o in a vessel whose temperature was controlled by a constant temperature bath. Downstream of the mixing chamber, the test gas was split to allow continuous measurement of mercury concentrations upstream and downstream of the carbon bed. The split test gas was passed through impingers containing 2 w/v % $SnCl_2$/5 w/v % NaOH, where the $HgCl_2$ was reduced to Hg^o, which was purged through the condensers and into the analyzer. The NaOH was used to remove NO_2 from the test gas in order to maintain reducing conditions in the impingers and to protect the mercury analyzer. The analyzer used was the PS Analytical Sir Gallahad mercury analyzer, which uses gold-coated sand to amalgamate Hg^o in the sample stream, followed by a heat/purge cycle to release the mercury for measurement by atomic fluorescence. The instrument alternated between sampling the test gas upstream and downstream of the carbon bed, using a computer-controlled five-minute sampling/measurement cycle.

The mercury 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 N_2 carrier gas by means of a sample port. The analyzer software calculated the mass of mercury injected, which was converted to a mercury concentration by using both the measured carrier gas flow rate and the time interval used for sampling.

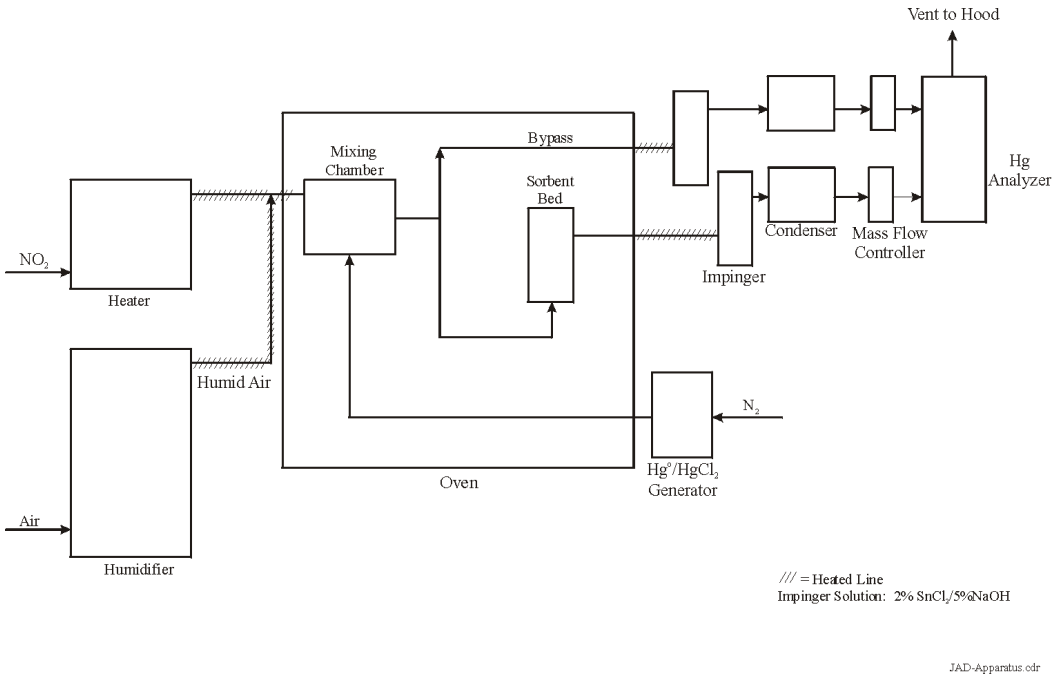

Figure 1. Apparatus for testing sorbents for removal of mercury from the off-gas from thermal treatment of acidic radioactive wastes.

Calibration plots for high and low range mercury concentration ranges were developed in order to measure $HgCl_2$ concentrations upstream and downstream of the carbon bed. Linear regression was used to fit Eq.1 to the calibration data.

$$s = mc + b \qquad \text{(Eq. 1)}$$

where,

s = signal
m = slope of linear regression line
c = Hg^o concentration, ug/dscm
b = y intercept

Instrument signals due to the detection of Hg^o in the test gas upstream and downstream of the carbon bed were averaged over the run time. Average mercury concentrations were calculated by inputting signal averages into Equation 1. Standard deviations of the measured mercury concentrations were calculated by propagating standard deviations of s, m and b through Equation 1. Mercury removal efficiencies were calculated by the following expression:

$$\% RE = ((C_1 - C_2) / C_1)100 \quad \text{(Eq. 2)}$$

where,

% RE = Removal Efficiency
C_1 = Average Hg^o Concentration upstream of carbon bed, ug/dscm
C_2 = Average Hg^o Concentration downstream of the carbon bed, ug/dscm

Standard deviations for removal efficiencies were calculated by propagating the standard deviations for measured mercury concentrations through Equation 2.

The activated carbon was not pretreated prior to use. The carbon particle size used was 1-2 mm. Bed dimensions were 1cm. x 11.5 cm. The flow rate was 94 dscc/min and the superficial linear velocity was 4.3 cm /s. The residence time was 2.7s, and the carbon bed temperature was 80°C. The activated carbons used were Nusorb®, a non-impregnated carbon, Mersorb®, a sulfur-impregnated carbon and a KCl-impregnated carbon. All activated carbons are products of Nucon International.

RESULTS AND DISCUSSION

Calibration plots for high and low mercury concentration ranges are illustrated in Fig. 2 and Fig. 3 respectively. Good fits of the calibration data to Eq.1 were obtained. The use of high and low range calibrations resulted in acceptable standard deviations for measured Hg^o concentrations, which resulted in acceptable standard deviations for calculated mercury removal efficiencies.

Table1lists the results of tests conducted to determine mercury removal efficiencies for activated carbon. The results indicate that all the activated carbons tested had high removal efficiencies for $HgCl_2$, and that Mersorb® had a high removal efficiency for Hg^o. The residence time was relatively short (2.7s) considering that a 10s residence time is usually recommended for full scale operations. The high removal efficiencies obtained with the short residence time were probably due to the fact that a packed bed of carbon having a 1-2mm particle size has a larger surface area available for contact with the test gas than one made up of 3mm particles, which is the size usually recommended for large adsorption beds. Future tests with larger carbon beds will determine whether pressure drops are acceptable with the smaller particle size.

There were no apparent short-term effects of NO_2 and H_2O on mercury removal efficiency. Possible long-term effects include oxidation of the carbon to CO_2, and oxidation of the sulfur to SO_2. These reactions are thermodynamically favorable. These effects will be investigated in future long-term breakthrough runs.

During test 4, it was estimated that at least 46% of the Hg^o was oxidized by the NO_2, and that an unknown fraction of the oxidized mercury was not measured by the analyzer. The fraction of the oxidized Hg^o that was not measured by the analyzer may have been HgO in particulate form that did not dissolve in the impinger solution, and/or adhered to the walls of the apparatus.

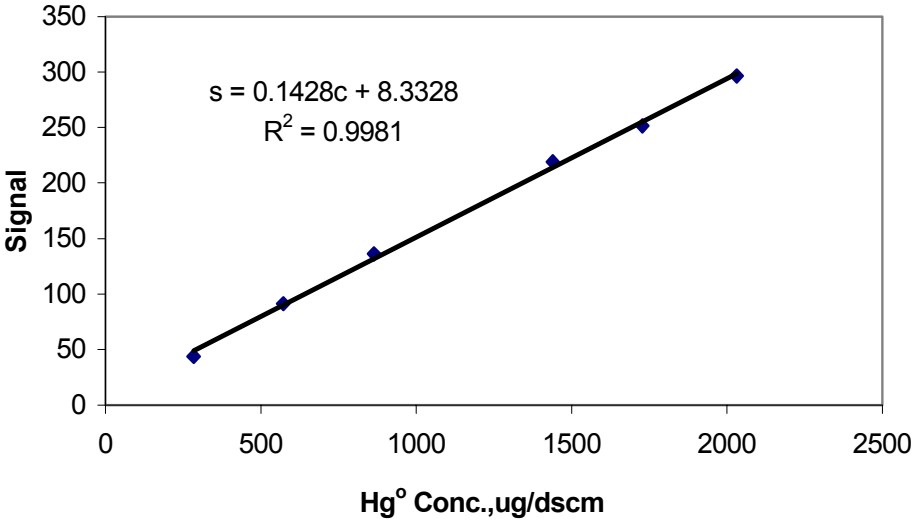

Figure 2. High-range calibration plot for PSA mercury analyzer.

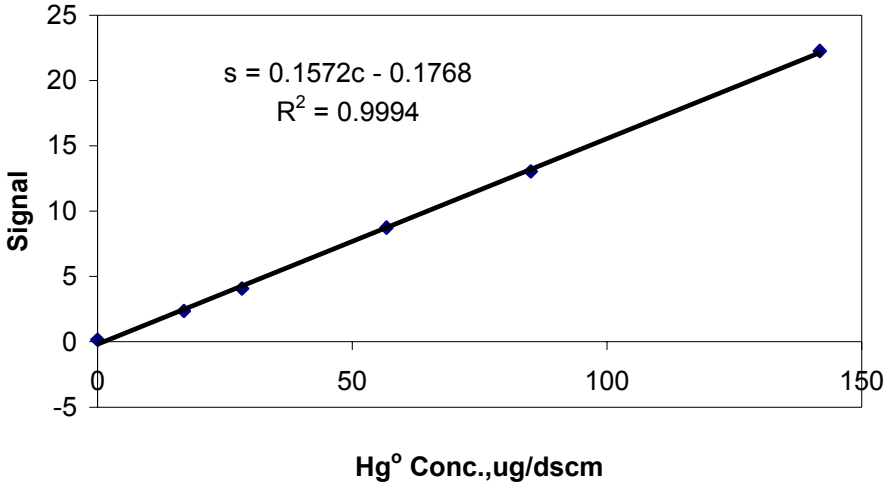

Figure 3. Low-range calibration plot for PSA mercury analyzer.

Table I. Mercury and Mercuric Chloride Removal Efficiencies of Activated Carbon.

Test #	Run Designation	Run Time Hours	Carbon Type	Average Mercury Input Conc. µg/dscm	NO_2 Ppm	H_2O Vol.%	Superficial Linear Velocity M/s	Residence Time s	Removal Efficiency %
1	HGCL N12880-2	10	Nusorb	$HgCl_2$ 1100	10,000	28	4.25	2.7	99 ± 3.6%*
2	HGCLM12880-2	5	Mersorb	$HgCl_2$ 1500	10,000	28	4.25	2.7	99 ± 3.6%
3	HGCL K12880-3	5	K-Nusorb	$HgCl_2$ 1200	10,000	28	4.25	2.7	99 ± 4.6%
4	HGM12880-1	5	Mersorb	Hg^o 3300	10,000	28	4.25	2.7	100 ± 2.5%

*Uncertainty expressed as 1 standard deviation

NOTES:
1. Nusorb® = non-impregnated carbon. Mersorb® = sulfur-impregnated carbon. K-Nusorb® = KCl-impregnated carbon
2. Carbon bed temperature: 80°C
3. Particle size: 1-2 mm
4. Flow rate: 94 dscc/min
5. Bed dimensions: 1 cm. x 11.5 cm

CONCLUSIONS AND FUTURE STUDIES

Without appropriate mitigation, the proposed thermal treatment of mercury-containing acidic radioactive wastes by vitrification is expected to result in mercury emissions that will exceed the MACT limits. Removal of elemental mercury and mercury compounds from vitrification off-gas by wet scrubbing followed by adsorption by activated carbon is being investigated. Short-term tests with a simulated off-gas containing high NO_2 and high H_2O levels have indicated that high removal efficiencies (99%) for $HgCl_2$ can been obtained with non-impregnated activated carbons, and with carbons impregnated with S and KCl. A sulfur-impregnated activated carbon removed 99% of Hg^o from the same simulated off-gas. Thus, these carbons, in combination with upstream wet scrubbing, have the potential to reduce mercury levels sufficiently to enable compliance with the MACT limits. The removal of oxidized forms of mercury other than $HgCl_2$, such as HgO, has not been investigated. In the form of a particulate, it is likely that HgO will be dissolved in the acidic wet scrubber, and/or removed by High Efficiency Particulate Air (HEPA) filters.

High removal efficiencies of $HgCl_2$ and Hg^o may be possible with relatively short (3s) residence times using a carbon particle size of 1-2 mm. Pressure drop considerations will dictate whether the use of small carbon particle sizes is feasible.

Long-term effects of NO_2 and H_2O on removal efficiencies of $HgCl_2$ and Hg^o will be conducted on the bench scale with selected activated carbons. Studies with a larger test bed will be conducted in order to optimize superficial linear velocity and residence time to provide data for design of a pilot adsorption unit. The larger test bed will be used to determine the breakthrough capacity, defined as the mercury loading on the bed when the effluent mercury concentration reaches the MACT limit. Verification of the effectiveness of a carbon adsorption unit in reducing mercury concentrations to below the MACT limit can only be conclusively demonstrated by measuring mercury concentrations in the off-gas of a fully integrated vitrification pilot plant.

ACKNOWLEDGMENTS

The authors wish to acknowledge the support and assistance of Dr. Warren Corns of PS Analytical.

This work was funded by the Department of Energy under contract number DE-AC07-99ID13727.

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