

Techniques for Mercury Control and Measurement in Gasification Systems

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Introduction

A major concern for power systems that use coal as an energy source is the air emissions from the plant. Although certain air emissions are currently regulated, the emergence of new regulations for other pollutants are on the horizon. Based on an earlier 1998 Report to Congress, the Environmental Protection Agency (EPA) in December 2000 announced its finding that regulation of mercury emissions from utility steam generating units is necessary and appropriate.¹ Emission standards will be proposed in December 2003 with promulgation following a year later. Additionally, the Clear Skies Initiative, proposed on February 14, 2002, would, if implemented, dramatically limit the emissions of mercury from coal-utilizing facilities.² The development of mercury emission regulations will have a direct impact on coal-using facilities, both conventional steam generating systems as well as integrated gasification combined cycle (IGCC) systems.

Gasification is an important strategy for increasing the utilization of abundant domestic coal reserves. The Department of Energy envisions increased use of gasification in the United States during the next twenty years. As such, the DOE Gasification Technologies Program will strive to approach a near-zero emissions goal with respect to pollutants. The mercury research detailed in this proposal addresses the Gas Cleaning and Conditioning program technology area.

For the advanced power generation systems, including IGCC, little research has been conducted with respect to mercury emissions. In a December 2001 draft report³ assembled by SAIC and in an EPA document⁴, the only total characterization of an advanced gasification technology was with Dow Chemical's Louisiana Gasification Technology Inc. in 1995. Although the mercury material closure was poor for the comprehensive study and significant advances in mercury sampling techniques have been made since the study, several important factors can be established. Almost all of the accounted mercury leaves the system with the combustion (flue) gas. Later, as part of the Information Collection Request (ICR), the Polk Power and the Wabash River IGCC units were characterized with respect to mercury air emissions (a full characterization of all streams was not conducted). The important conclusion was that nearly 60% of the mercury in the coal exited in the turbine combustion flue gas and most of the mercury was in the elemental form. From the information on these units, it can be hypothesized that a majority of mercury migrates through the system as elemental mercury in the present IGCC systems. It could be removed through a costly sorbent injection into the turbine exhaust gas. The remainder of the mercury is probably within one of the scrubbing systems needed

to clean the synthesis gas before further processing. It is anticipated that activated carbon treatment of these streams could remove the mercury, but this would be a costly application.

Benefits of a high temperature (500-700 °F) mercury removal⁵ in an IGCC application include: 1) the ability to utilize warm gas cleanup of hydrogen sulfide as compared to cooling the synthesis gas and then scrubbing the hydrogen sulfide, thus avoiding a loss in thermal energy efficiency; and 2) the capability of removing a vast majority of the coal-inlet mercury at one location as compared to the present IGCC systems where not all the mercury is accounted for.

Technical Challenges

Little information exists on the removal of mercury in gasification schemes within high temperature syngas streams. If a crude comparison of the research in flue gas streams can be drawn, typically, the adsorption of mercury on a sorbent improves as the temperature decreases. This is primarily true when the mechanism of removal is physical adsorption. However, other types of mechanisms could be advantageous at the higher temperatures. King et al.⁶ reports that amalgamation could be a technique for mercury control at higher temperatures.

Recent results from a pilot-scale gasifier suggest that all of the mercury in the coal ends up in the fuel gas.^{7,8} The data from a pilot-scale gasifier suggests that activated carbon and other carbon sorbents will be unsuited for mercury capture from syngas at temperatures greater than 400°F.^{7,8} Robust high temperature sorbents, as well as other techniques, are needed for mercury capture from syngas for continued development and proliferation of gasification technology in the United States. A recent report suggests that some sorbents will exhibit similar capacities in both flue and syngas streams.⁹ The in-house research effort at NETL has an extensive database of sorbent capacities in flue gas, nitrogen, argon, and oxygen-nitrogen mixtures at a wide variety of temperatures.¹⁰⁻¹⁸ Several promising sorbent candidates for mercury capture from high temperature syngas streams have already been identified. In addition, a photochemical method for mercury capture from flue gas that may prove highly effective in syngas has been developed.¹⁹⁻²⁵

Most of the available detectors for mercury are based upon the absorption or emission of 253.7-nm ultraviolet light.^{26,27} The measurement of mercury in the harsh syngas matrix has proven to be difficult.²⁸ Many of the prototype on-line continuous emissions monitors for mercury are based upon atomic absorption spectrophotometry (AAS) or atomic fluorescence spectrophotometry (AFS). Unless precautions, such as preconditioning the flue or fuel gas, are taken, photochemical quenching will interfere with the determination of mercury.²⁶⁻²⁸ Alternative methods are needed for on-line, continuous measurement of mercury in syngas for expansion of gasification technology in the United States. A promising sensor technology for mercury in high temperature syngas has been identified.¹⁹

Discussion and Results

Various sorbent materials were screened to obtain their performance with respect to mercury removal. In earlier work conducted by Granite et al.⁷, certain potential mercury sorbent materials were tested in oxidizing conditions, but also in inert conditions that would closely approximate the reducing conditions. Temperatures were chosen that simulated the conditions found in the ductwork of a coal-burning power utility, with 350 °F being the maximum. From this body of work, certain

sorbent compounds/composites performed better than others in the inert conditions with the elemental species as the form of mercury. The temperature of 350°F was the starting point for the sorbent screening.

Sorbents were screened in a small laboratory scale reactor, as described by Granite et al.¹¹. Experiments were conducted with nitrogen as the carrier gas. On-line mercury measurements were not available, and total sorbent capacity was determined after a predesignated time on stream by analyzing the solid sorbent for mercury.

Most sorbents will display poor capacity for elemental mercury at elevated temperatures. Previous experience with sorbents in flue gas allowed for judicious selection of potential high temperature candidate sorbents. The capacities of several sorbents for elemental mercury with nitrogen at temperatures between 400°F-500°F were determined. Some of these results are summarized in Table 1 below:

| <u>Sorbent</u> | Table 1. Sorbent Capacities in Nitrogen | <u>Capacity (mg/g)</u> | <u>Temperature (°F)</u> |
|----------------------------------------------------------------|------------------------------------------------|-------------------------------|--------------------------------|
| Insul AC | | 0.06 | 400 |
| NM-S-AC | | 0.07 | 400 |
| Sorbent X | | 1.37 | 400 |
| MoS ₂ | | 0.50 | 400 |
| PbSe | | 0.00 | 400 |
| MnO ₂ -Al ₂ O ₃ | | 0.14 | 400 |
| Cr ₂ O ₃ -Al ₂ O ₃ | | 0.99 | 400 |
| NiO-Al ₂ O ₃ | | 0.03 | 400 |
| CuO-Al ₂ O ₃ | | 0.05 | 400 |
| Co ₂ O ₃ -Al ₂ O ₃ | | 2.00 | 400 |
| SiO ₂ | | 0.00 | 400 |
| Sorbent Y | | 2.11 | 400 |
| Sorbent Y | | 2.69 | 450 |
| Sorbent Y | | 2.90 | 500 |

Gas Composition: 270 ppb Hg in N₂

Flow-rate: 60 ml/min

Packed-bed reactor: 1/4 inch OD, 1/6 inch ID, quartz tube, 10 mg sorbent

Length of sorbent exposure to mercury in nitrogen: 350 min

Maximum capacity (100% mercury capture): 5.5 mg Hg/gram sorbent

The unpromoted activated carbon Insul AC exhibits a poor capacity for elemental mercury from nitrogen at 400°F. This was expected based upon our past experience with activated carbons. The sulfur promoted activated carbon NM-S-AC also displays a low capacity for elemental mercury from nitrogen at 400°F. Previous results from our lab have shown that sulfur impregnated carbons exhibit loss of sulfur promoter at elevated temperatures. Reed^{7,8} and Tascon⁹ have previously demonstrated that carbon exhibits poor capacity for mercury from fuel gas at 400°F.

Sorbent X, a treated carbon, shows a fair capacity for mercury. It can be speculated that a chemisorbed mercury species forms on the surface of this carbon when exposed to elemental mercury. Results suggest that the promoted sorbent could be utilized for high temperature IGCC application.

Several metal oxides (Co_2O_3 and Cr_2O_3) capture a significant fraction of mercury from nitrogen at 400°F. Cobalt and chromium oxides are active deep oxidation catalysts. Lattice oxygen serves as the oxidizing agent in a Mars-Maessen mechanism. Cobalt and chromium oxides can oxidize many hydrocarbons in the absence of gas-phase oxygen, suggesting that they could also capture mercury as mercuric oxide in the reducing environment of an IGCC system.

Molybdenum sulfide displays a small, but significant capacity for mercury from nitrogen at 400°F. Previous work with MoS_2 suggested mercury capture as mercuric sulfide.

Sorbent Y displays excellent capacity for mercury from nitrogen at temperatures between 400-500°F. It was discovered that this sorbent will indeed adsorb mercury from high temperature gas streams. Most sorbents display poor capacities for mercury at elevated temperatures above 300°F. This substance has the unusual property of having an increasing capacity for mercury with increasing temperature in the range 400-500°F in nitrogen. The sorbent removed 38% and 53% of the elemental mercury from nitrogen at temperatures of 400°F, 450°F, and 500°F. Testing with a simulated syngas will be the next step in this research.

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Disclaimer

Reference in this paper to any specific commercial product, process, or service is to facilitate understanding and does not imply its endorsement by the United States Department of Energy.

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