

# Regenerable Sorbent Development for Sulfur, Chloride, and Ammonia Removal from Coal-Derived Synthesis Gas

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## Abstract

A large number of components in coal form corrosive and toxic compounds during coal gasification processes. DOE's NETL aims to reduce contaminants to parts per billion in order to utilize gasification gas streams in fuel cell applications. Even more stringent requirements are expected if the fuel is to be utilized in chemical production applications.

Regenerable hydrogen sulfide removal sorbents have been developed at NETL. These sorbents can remove the hydrogen sulfide to ppb range at 316 °C and at 20 atmospheres. The sorbent can be regenerated with oxygen. Reactivity and physical durability of the sorbent did not change during the multi-cycle tests. The sorbent development work has been extended to include the removal of other major impurities, such as HCl and NH<sub>3</sub>.

The sorbents for HCl removal that are available today are not regenerable. Regenerable HCl removal sorbents have been developed at NETL. These sorbents can remove HCl to ppb range at 300 °C to 500 °C. The sorbent can be regenerated with oxygen. Results of TGA and bench-scale flow reactor tests with both regenerable and non-regenerable HCl removal sorbents will be discussed in the paper. Bench-scale reactor tests were also conducted with NH<sub>3</sub> removal sorbents. The results indicated that the sorbents have a high removal capacity and good regenerability during the multi-cycle tests.

Future emphasis of the NETL coal gasification/cleanup program is to develop multi-functional sorbents to remove multiple impurities in order to minimize the steps involved in the cleanup systems. To accomplish this goal, a regenerable sorbent capable of removing both HCl and H<sub>2</sub>S was developed. The results of the TGA conducted with the sorbent to evaluate the feasibility of both H<sub>2</sub>S and HCl sorption will be discussed in this paper.

## Keywords

Gas clean up, coal gasification, multi pollutant controls

## INTRODUCTION

A large number of components in coal form corrosive and toxic compounds during gasification processes. The U.S. Department of Energy's National Energy Technology Laboratory (DOE/NETL) aims to reduce contaminants to parts per billion to utilize gasification gas streams in fuel cell applications. Even more stringent requirements are expected if the fuel is to be utilized in chemical production applications.

A regenerable desulfurization sorbent was developed at NETL to remove sulfur levels to the ppb range. Both Research Triangle Institute and NETL conducted successful multi-cycle high-pressure bench-scale tests at 316 °C and 20 atm with simulated coal gas to demonstrate the ppb-level sulfur

removal efficiency of the sorbent.<sup>1 2</sup> Sorbent regeneration was conducted at 649 °C, and it retained the ppb-level sulfur removal efficiency after regeneration. The sorbent also showed good performance when it was tested at Southern Company power system's development facility at Wilsonville, Alabama, with real coal gas. This sorbent could be used as either a bulk sulfur removal sorbent or in the polishing sorbent after the bulk sulfur removal.

Hydrogen chloride (HCl) is one of the impurities that must be removed to less than 1 ppm from the coal gas. Non-regenerable sorbents are commercially available for HCl removal. A regenerable HCl sorbent has been developed at NETL to remove HCl levels to the ppb range. A successful 5-cycle test was conducted at 400 °C and 1.4 atm with simulated coal gas to demonstrate the sorbent's ppb-level HCl removal efficiency. The sorbent maintained HCl removal efficiency in ppb range during the multi-cycle test. Sorbent regeneration was conducted at 700 °C. Commercial non-regenerable sorbents were also tested at NETL, and the results of both regenerable and non-regenerable sorbents will be discussed in this paper.

Ammonia (NH<sub>3</sub>) is another major impurity present in the coal gas stream. NH<sub>3</sub> levels have to be reduced to less than 50 ppmv. Various zeolites and alkali earth metal chlorides were tested at 315 °C and at 20 atm for NH<sub>3</sub> sorption, and regenerations were performed at 350 °C and 500 °C.

Multi-functional sorbent development is important for the coal gasification program to decrease the number of steps involved in the cleanup process. The multi-functional sorbent developed for both HCl and hydrogen sulfide (H<sub>2</sub>S) sorption showed good sorption capacity for sulfur and chloride removal during the TGA tests conducted at 400 °C. The sorbent was regenerable at 700 °C. The results indicated that the sorbent can potentially be utilized as a multi-functional sorbent for coal gasification cleanup systems.

## **EXPERIMENTAL**

### **Thermogravimetric Analysis of HCl Removal Sorbent and Multi-Functional Sorbent Tests**

Sorbent was tested in a thermogravimetric analyzer (TGA). The sorbent was placed in the TGA and heated to the reaction temperature (315 °C, 400 °C, and 500 °C) under nitrogen (N<sub>2</sub>) at 90 cc/min. A gas consisting of 0.1 vol. % HCl, 39 vol. % hydrogen (H<sub>2</sub>), and N<sub>2</sub> was then introduced to the sample for 8 hours. After the chlorination cycle was completed, the sample was heated to 700 °C and air was introduced for 275 minutes. Solid samples were collected at various stages of the reaction and chlorine analysis was conducted on the solid sample using wet chemical methods. The samples were also analyzed using scanning electron microscopy/energy dispersive analysis (SEM/EDS) and X-ray photoelectron spectroscopy (XPS). Similar TGA tests were conducted with the multi-functional sorbent. The sorbent was tested for both HCl uptake (utilizing a gas consisting of 0.1 vol. % HCl, 39 vol. % H<sub>2</sub>, and N<sub>2</sub>) and sulfur uptake (utilizing a gas consisting of 0.94 vol. % H<sub>2</sub>S in N<sub>2</sub>).

### **Bench-Scale Flow Reactor Tests with HCl Removal Sorbent and the NH<sub>3</sub> Removal Sorbents**

Both regenerable and non-regenerable sorbents were tested in a 2-inch diameter bench-scale quartz flow reactor. Components of the reactor were made with a special alloy material to avoid reaction with HCl. A continuous flow ion mobility spectrometry detector system was utilized to measure HCl

and chlorine, and the detector was calibrated to measure HCl levels to less than 500 ppb-level detection.

The sorbent bed had a depth of 6 inches, a weight of 245.8 g; and it was heated to 315 °C, 400 °C, and 500 °C and pressurized to 25 psig. The simulated integrated gasification combined cycle (IGCC) gas mix utilized for chlorination cycles contained 18 vol. % N<sub>2</sub>, 13 vol. % CO<sub>2</sub>, 38 vol. % CO<sub>2</sub>, and 30.8 vol. % H<sub>2</sub>, mixed with HCl. The sorbent was exposed to the gas mix with 150 ppmv HCl at a space velocity of 2,000 hr<sup>-1</sup>. During the 1-cycle tests, both the non-regenerable and the regenerable sorbents were exposed to a gas mix with 150 ppm HCl for 4 hours at 315 °C. The HCl concentration was then increased to 3000 ppm.

The test conditions utilizing five-cycle tests were similar to those of the one-cycle tests. However, during the first 4 cycles, 150 ppm HCl was introduced for 8 hours, and the sorbent was regenerated. For cycle 5, after exposing the sorbent for 150 ppm of HCl for 8 hours, the HCl concentration was increased to 3000 ppm, and the reaction with HCl was continued for an additional 4 hours. Regeneration started at 500 °C, at 25 psig, with 3 vol. % oxygen in N<sub>2</sub> and a space velocity of 2,000 h<sup>-1</sup>.

The NH<sub>3</sub> removal tests were conducted with the sorbent utilizing 1 vol. % NH<sub>3</sub> in N<sub>2</sub> at a gas space velocity of 20,000 hr<sup>-1</sup> and at 20 atm. The absorption tests were conducted at 315 °C and regenerations were conducted at both 350 °C and 500 °C. A mass spectrometer was utilized to measure the NH<sub>3</sub> concentration.

## RESULTS

### TGA Tests of Regenerable HCl Removal Sorbent and the Multi-Functional Sorbent

TGA was conducted at 315 °C, 400 °C, and 500 °C. Chloride analysis was conducted on solid samples obtained after some chlorination cycles and some regeneration cycles. Chloride was detected on samples obtained after chlorination cycles but chloride was not detected for samples obtained after regenerations at all three temperatures. The HCl uptake appeared to increase with increasing number of cycles, which indicated that the reactivity improved with as the number of cycles increased. The chloride data obtained by total chlorine analysis utilizing wet chemical methods, SEM analysis, and XPS analysis were very consistent. The data confirmed that the sorbent is regenerable. The best HCl uptake was obtained at 400 °C. The amount of chloride present in the solid after the tenth chlorination cycle was higher than what was obtained with the G-92C non-regenerable sorbent, which is commercially available from Sud Chemie.

TGA analysis of the multi-functional sorbent conducted at 400 °C showed chloride uptake of about 4 wt % after the HCl exposures and sulfur uptake of about 9 wt % after H<sub>2</sub>S exposures. The amount of chloride and sulfur retained in the sample after the regeneration with oxygen at 700 °C was significantly lower than that observed after the sorption cycles. This indicated that the sorbent can be utilized for both H<sub>2</sub>S and HCl sorption and that it is regenerable.

### Bench-Scale Flow Reactor Tests with HCl Sorbents

Four non-regenerable commercial sorbents from Sud Chemie, trade names G-132, C125-1-01, C28-1-01, and G-92C, were tested at 315 °C. Two of the sorbents, G-132 and C28-1-01,

showed highly exothermic reactions with reducing gas in the gas mixture and were not suitable for IGCC applications. G-92C and C125-1-01 sorbents showed less than 500 ppb HCl removal efficiency during the tests. Even when the HCl concentration was increased to 3000 ppm for 2 hours, the HCl concentration was less than 500 ppb with a 6-inch reactor bed.

The regenerable sorbent developed at NETL was tested for five cycles. The outlet concentration of HCl during a typical absorption cycle during the 5-cycle test when the inlet concentration of HCl was 150 ppmv is shown in Figure 1. The HCl removal efficiency was less than 1 ppm (less than 500 ppb a major portion of the time) during all the cycles, but occasional HCl spikes were observed. The reason for the HCl spikes was not clear but may be due to the HCl retained on the unit from prolonged use of the reactor unit during previous runs.

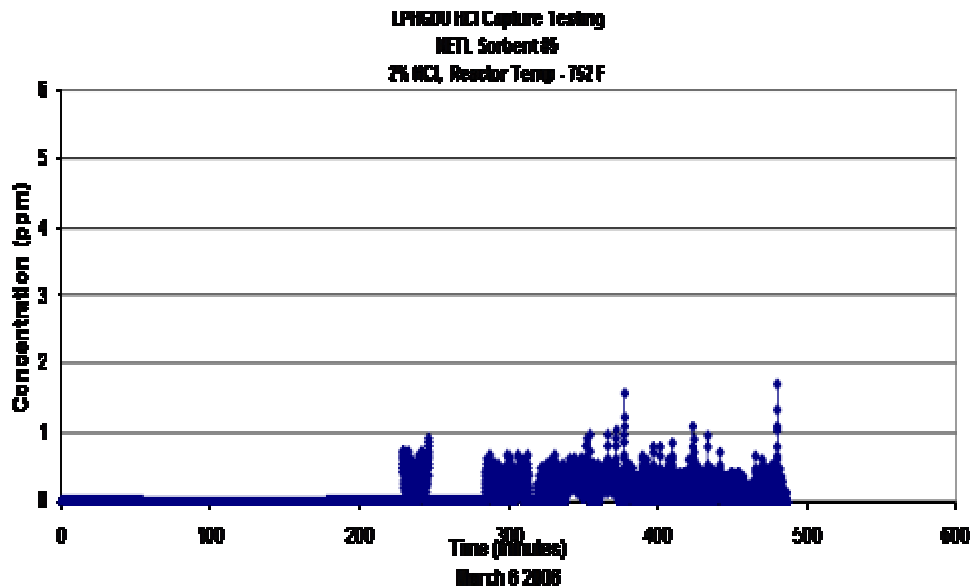


FIGURE 1: Concentration of HCl as a function of time during the 5-cycle test at 400 °C (inlet concentration of HCl -150 ppm).

After each cycle during the five-cycle test, regeneration was performed with oxygen. The initial regeneration temperature was 500 °C, but the temperature of the reactor bed increased to about 700 °C. The oxidative regeneration was started at 1.0 vol. % of oxygen and increased to 3 vol. % by the end of the regeneration cycle. Total regeneration time was approximately 180 minutes. Oxygen was fully consumed during regeneration cycle. Chlorine was detected during regeneration as shown in Figure 2. This confirmed the TGA results that the sorbent is regenerable. The temperature during regeneration increased due to exothermic reaction. The sorbent performed well during the five-cycle test and was able to remove the HCl from 150 ppm to less than 1.5 ppm during the tests. In the majority of the cycles, the removal efficiency was less than 500 ppb.

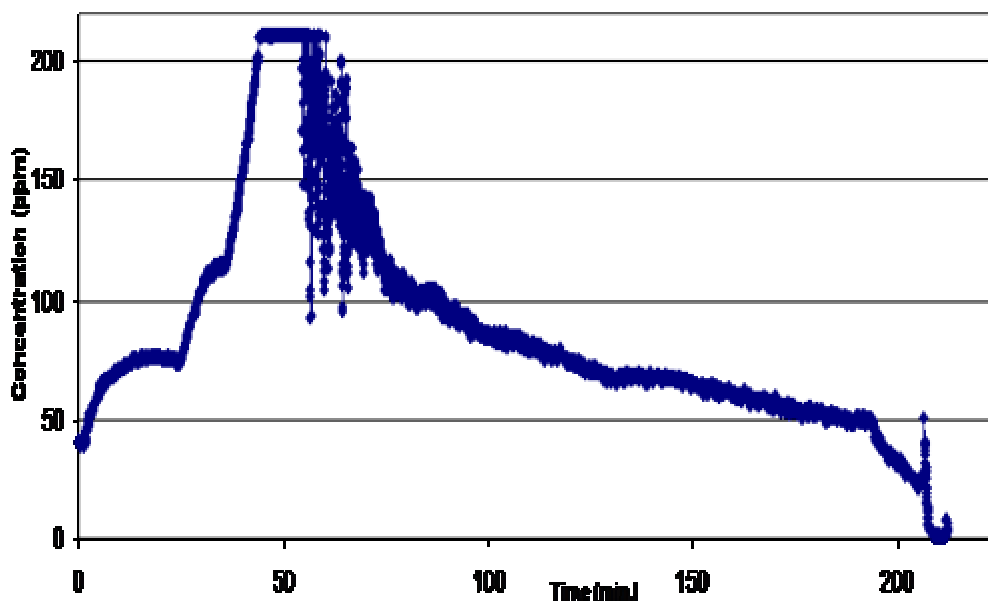


FIGURE 2: Chlorine concentration as a function of time during sorbent regeneration.

### Bench-Scale Flow Reactor Tests with NH<sub>3</sub> Removal Sorbents

Zeolites 4A, 13X, Z10-08, Z10-10, HZSM 5, and 5A were tested for NH<sub>3</sub> sorption. The zeolite 5A exhibited the highest NH<sub>3</sub> capture capacity while zeolite 10-08 showed the lowest capacity. The capacity of zeolite 5A did not change after regenerating at 350 °C but a decrease in capacity was observed after regenerating at 500 °C. Zeolite 4A showed the highest decrease in capacity after regenerating at 500 °C. Zeolite Z10-10 appeared to be stable, even after regenerating at 500 °C. The sorbents consisting of 25 percent MgCl<sub>2</sub>•6H<sub>2</sub>O/Al<sub>2</sub>O<sub>3</sub>, 25 percent CaCl<sub>2</sub>•6H<sub>2</sub>O/Al<sub>2</sub>O<sub>3</sub>, and 25 percent BaCl<sub>2</sub>•6H<sub>2</sub>O/Al<sub>2</sub>O<sub>3</sub> were also tested at 315 °C for NH<sub>3</sub> capture. Of the chlorides tested, magnesium chloride showed the highest capture capacity. There was a decrease in capacity after first regeneration but capacity appeared to be stable even after regenerating at 500 °C. Barium chloride showed the lowest capacity for NH<sub>3</sub> capture.

### CONCLUSIONS

NETL developed (commercially available at Sud Chemie) ZnO-based sulfur removal sorbent could be utilized for H<sub>2</sub>S removal in the ppb range at 315 °C and at 20 atm, and the sorbent is regenerable. A regenerable HCl removal sorbent was developed at NETL. The total HCl effluent concentration of synthesis gas can be reduced to less than 1 ppmv at 400 °C and at 25 psig during repeated cycles utilizing the sorbent developed at NETL. The multi-functional sorbent removed both HCl and H<sub>2</sub>S at 400 °C and was regenerable with oxygen. Zeolite 5A showed high capacity for NH<sub>3</sub> removal at 315 °C but zeolite 10-10 showed better stability after regenerating at 500 °C. Magnesium chloride also showed good capacity for NH<sub>3</sub> removal at 315 °C.

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## **References**

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