DOE/PC/913

DOE/PC/91334--T1

DE92 007978

TECHNICAL REPORT
September 1 through November 30, 1991

Project Title: Desulfurization of Hot Fuel Gas Produced from High-Chlorine Illinois Coals

DE-FG22-91PC91334

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ABSTRACT

There is a primary need to increase the utilization of Illinois coal resources by developing new methods of converting the coal into electricity by highly efficient and environmentally acceptable systems. New coal gasification processes are now being developed which can generate electricity with high thermal efficiency either in a combined gas-turbine, steam-turbine cycle (IGCC) or in a fuel cell (MCFC). Both of these new coal-to-electricity pathways require that the coal-derived fuel gas be at a high temperature and be free of potential pollutants, such as sulfur compounds. Unfortunately, some high-sulfur Illinois coals also contain significant chlorine which converts into hydrogen chloride (HCl) in the coal-gas. This project investigates the effect of HCl, in concentrations typical of a gasifier fed by high-chlorine Illinois coals, on zinc-titanate sorbents that are currently being developed for H_2S and COS removal from hot coal-gas. This study is designed to identify any deleterious changes in the sorbent caused by the HCl, both in adsorptive operation and in the regeneration cycle, and will pave the way to modify the sorbent formulation or the process operating procedure to remove HCl along with the H_2S and COS from hot coal-gas. This will negate any harmful consequences of utilizing high-chlorine Illinois in these processes.

The work activity during the first quarter of this project involved the preparation and submittal to CRSC of the detailed Experimental Test Plan and the modification/startup of the reactor apparatus in which the experiments are to be performed. The Test Plan describes the equipment arrangement and the operating conditions selected for the initial two block-series of experiments, the first set studying the effect of HCl in the desulfurization of a medium-Btu fuel gas (simulating the product of the "Texaco" entrained-bed, oxygen-blown gasifier) and the second set studying the desulfurization of a low-Btu fuel gas (simulating the effluent from a "U-Gas" air-blown gasifier). The bench-scale fluidized bed has been modified to prevent potential HCl corrosion and startup experiments have proven the reactor system operable and capable of yielding reliable experimental results. The first of the planned experiments in the project are now being performed.

This project is funded by the U. S. Department of Energy (METC) and by the Illinois Department of Energy and Natural Resources as part of their cost-shared program.

EXECUTIVE SUMMARY

It is vital to the industry of this state that new approaches be developed soon to increase the utilization of the abundant bituminous coal resources in the Illinois coal basin by processes which are both thermally efficient and environmentally acceptable. Two of the most attractive techniques now being actively developed to cleanly convert coal into electricity are the integrated gasification combined cycle (IGCC) and the molten carbonate fuel cell (MCFC) power generation systems. In both of these innovative systems, the coal is gasified to form a fuel gas which must then be purified of particulate matter and undesirable gas-species, mainly sulfur compounds, before being oxidized in the IGCC combustion chamber or in the MCFC fuel cell vessel.

To realize the highest thermal efficiency for the overall coal-to-electricity conversion, both of these processes require that the temperature of this coal-derived fuel gas flowing from the gasifier be as high as possible. However, the coal-derived fuel gas contains reduced sulfur species which would have to be removed at high temperature for the overall process to be efficient. Solid regenerable sorbents of mixed-metal oxides have recently been developed which very efficiently remove both hydrogen sulfide (H_2S) and carbonyl sulfide (COS) at relatively high temperatures.

Zinc-based sorbents are currently the leading sorbent candidates. They have been extensively developed for fixed-bed operation. Fixed-bed systems, however, suffer many limitations including poor temperature control and unsteady state operation. The recent development of an attrition-resistant, fluidizable zinc-titanate sorbent at the Research Triangle Institute (RTI) offers excellent H_2S and COS removal efficiency, good sulfur absorption capacity, and excellent regenerability. This sorbent has high attrition resistance which offers the opportunity to conduct the hot-gas desulfurization in a bubbling or circulating fluidized bed reactor system, leading to much better gas-solid contact efficiency, better temperature control, and much greater flexibility in design-alternatives for continuous sorbent regeneration sub-systems.

Unfortunately, some Illinois coals contain significant chlorine which becomes hydrogen chloride (HCl) in the coal-gas product-stream from the gasifier. This HCl reacts with certain inorganic compounds, usually with undesirable results. In studying the flyash deposits from coal-combustion in boilers, investigators found that chlorides in the gas stream tended to react with the metallic oxides (zinc and ferric) in the slag deposits on the boiler-tubes, forming metal-chlorides which had lower melting temperatures than the oxides and were more chemically reactive. Based on mass-balance calculations, the gasification of the higher chlorine Illinois coal (containing 0.1% to 0.6% chlorine, by weight) in the typical present-day coal-gasification reactor designs ("Texaco", "U-Gas", "Lurgi", etc.) would produce from 100 to 1400 ppm HCl (by volume) in the gasifier effluent stream. Very little is known about how the HCl will interact chemically with the zinc-based sorbents at high temperatures and in the presence of the various fuel gas compositions that would be produced in the different gasifier designs.

This project, a cooperative effort between the Southern Illinois University at Carbondale (SIUC) and the Research Triangle Institute (RTI), will investigate the effect of HCl, in concentrations typical of a gasifier fed by high-chlo-

rine Illinois coals, on the fluidizable zinc-titanate sorbents. These sorbents are being developed by RTI, with the sponsorship of the US DOE/METC, for H_2S and COS removal from hot coal gas in the IGCC processes. The major objectives in this project will be to identify any deleterious changes in the sorbent caused by the HCl, both in the adsorptive operation and in the regeneration cycle, and to determine the fate of the chloride chemical-species.

Two zinc-titanate sorbents have been chosen for this examination, one with a high zinc/titanium (Zn/Ti) content ratio and the second with a Zn/Ti-ratio found previously to perform optimum service in the hot coal-gas desulfurization process. The experimental evaluation during the project will examine the HCl-effects on each sorbent's chemical reactivity, its sulfur-adsorption capacity, its regeneration capability and its attrition resistance. This objective will be accomplished by testing the two durable zinc-titanate sorbents in a bench-scale fluidized bed reactor with simulated hot coal-gas, at different temperatures, with and without several concentrations of HCl in the gas-stream. Also, a number of multi-cycle tests will be conducted to determine the effect of HCl on the long term chemical reactivity and mechanical durability of zinc-titanate sorbents.

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The bench-scale fluidized bed has been modified to prevent potential HCl corrosion, replacing the stainless steel reactor tube with a 26 mm, I.D. quartz tube and replacing most of the other components contacting the HCl stream with either glass or Teflon-coated fixtures. Startup experiments in the last week of October have proven the reactor system operable and capable of yielding reliable experimental results.

The first of the planned experiments in the project are now being performed. As stated above, the first block-set of experiments will evaluate the effect of HCl on the sorbent behavior in a simulated medium-Btu fuel gas. Most of the Second Quarter of the project will be devoted to the completion and evaluation of this experimental set.

OBJECTIVES

The overall goal of the research is to develop attrition-resistant regenerable sorbents for desulfurization of hot coal-derived gases for integrated-gasification combined cycle (IGCC) and molten carbonate fuel cell (MCFC) power generation systems. The specific objectives of this investigation are to study the effects and the fate of hydrogen chloride during hot-gas desulfurization, which can be present at levels up to 1500 ppmv in the coal gas when high-chlorine Illinois coals are converted to a medium-Btu fuel-gas product. The performance, (i.e., chemical reactivity, sulfur capacity, regenerability and attrition resistance) of zinc-based sorbents, specifically the zinc-titanate which is being developed for H_2S and COS removal from the hot coal gas for fluidized bed applications will be evaluated in a bench-scale fluidized bed reactor using simulated coal gas with and without the HCl gas.

The specific goals of the research during the twelve month contract period are:

(i) to determine the most probable chemical structures, in addition to the HCl in the effluent gas, to which the chlorine will react in the coal-gasifier and in the effluent streams, and to correlate this distribution of compounds with the chlorine content of the variety of parent coals and gasifier operating conditions;

(ii) to understand the effect of varying concentrations of HCl in coal gas on the chemical reactivity, regenerability, sulfur adsorption capacity and attrition resistance of zinc-titanate sorbents in a fluidized bed reactor;

(iii) to determine the material balances and chlorine distribution during the operation of a hot gas desulfurization system;

(iv) to determine how the presence of HCl in coal gas affects the kinetics of H_2S absorption by the zinc-titanate sorbents; and

(v) to determine the extent of permanent chlorine retention by the zinc-titanate sorbent.

This project, a cooperative effort between the Southern Illinois University at Carbondale (SIUC) and the Research Triangle Institute (RTI), will investigate the effect of HCl, in concentrations typical of a gasifier fed by high-chlorine Illinois coals, on fluidizable zinc-titanate sorbents. These sorbents have recently been developed by RTI, with the sponsorship of the US DOE/METC, for H_2S and COS removal from hot coal gas. The major objectives will be to identify any deleterious changes in the sorbent caused by the HCl, both in the adsorptive operation and in the regeneration cycle, and to determine the fate of the chloride chemical-specie.

INTRODUCTION AND BACKGROUND

Several IGCC and MCFC power systems employing hot gas cleanup are now actively being developed to produce electric power from coal. Both of these systems are two of the most advanced power generation technologies with a projected coal-to-electricity thermal efficiency of 50 percent or better. One of the key components of each of these two power systems is a hot gas desulfurization system which would operate under high-temperature, high-pressure (HTHP) conditions, typically at 1000° to 1200°F (538° to 649°C) and up to 300 psig (2.17 MPa). Most of these desulfurization processes, now under development, employ regenerable mixed-metal oxide sorbents for adsorbing the H_2S and COS present in the coal gas, with zinc-titanate currently being the leading sorbent candidate.

Some of Illinois coals, in addition to having a high sulfur content, also have a high chlorine content. During gasification, the chlorine present in the coal is converted to hydrogen chloride. The chloride level of a medium-Btu fuel gas derived from Illinois coals can be as high as 1500 ppmv. Hydrogen chloride, if present in sufficiently high levels, might cause serious damage to the desulfurization sorbents. For example, the zinc-titanate might chemically react to form molten zinc chloride which has a significant vapor pressure at 1000°F. Therefore, the effect of hydrogen chloride on the performance of zinc-titanate sorbents must be addressed.

The proposed study deals with the determination of the effect of hydrogen chloride on the sulfur capacity, chemical reactivity, regenerability and attrition resistance (mechanical strength) of the sorbent. Also, the fate of the HCl itself in the hot gas desulfurization system is not known. Several specific questions to be addressed include:

(i) How much HCl, if any, is removed by the zinc-titanate in the adsorption cycle?

(ii) If the HCl is adsorbed, what is the form of chlorine when present in the sorbent?

(iii) Zinc chloride being volatile, does the titanium component of the sorbent help to stabilize it in the sorbent matrix during adsorption, or will the formed zinc chloride vaporize back into the gas stream?

(iv) Does retained chloride stay with the sorbent during the regeneration step, or is it removed from the sorbent with the SO_2-laden regeneration gases?

(v) What are the forms of the chlorine compounds that comes off the sorbent during regeneration, depending on whether the regeneration gas consists of an air-steam mixture as opposed to an air-nitrogen mixture?

These questions are of paramount importance for the commercialization of IGCC and MCFC power-generation technologies and must be addressed if Illinois coals with high chlorine concentrations are to be used as feed to these high efficiency and environmentally acceptable future coal-conversion technologies.

The proposed study will aid in the future development of a promising class of sorbents which will remove H_2S and COS to high degrees from coal gas containing hydrogen chloride without undergoing deleterious changes. Such development will result in enhanced, more economically attractive and efficient power generation systems for converting high-sulfur, high-chlorine containing Illinois coals into electricity.

EXPERIMENTAL PROCEDURES

The research work has been divided into five tasks, all directed at gaining a better understanding of the effects and the fate of HCl in the desulfurization of hot coal-derived fuel gases. These tasks are:

Task 1. Assessment of Forms of Chloride Compounds in Coal Gas
Task 2. Experimental Test Plan
Task 3. Modifications in Existing Test Facility
Task 4. Bench-Scale Testing and Analysis
Task 5. Reporting

Each of these tasks is described below.

<u>Task 1</u>: Assessment of Forms of Chlorine Compounds in Coal Gas

The work on this task is being conducted at SIUC. This task is subdivided into two sub-tasks. The first study is a survey of recent literature references to catalog the existence and effects of chlorine compounds in gasifier fuel gas. The second study involves the thermodynamic/kinetic modeling of the behavior of chlorine chemical-species in a high-temperature desulfurizing process system.

A comprehensive literature survey of recent literature references including technical papers, government and industrial reports, conference proceedings, etc., is being assembled to document reported or speculated potential behavior of chlorine chemical species in gasifier effluent-gas atmospheres. Of importance are the reported compositions of the feed-fuel and the product gas stream, the temperature and the chlorine content of the gas, and any comments about operational problems or other observations attributable to the presence of the chlorine.

The second sub-task in Task 1 involves the assembling and correlating of the literature-reported thermodynamic and kinetic data which are applicable to modeling the behavior of diatomic chlorine, hydrogen chloride and other chlorine species when in contact with the metallic and other active compounds involved in the hot-gas desulfurization system. This involves potential interactions of the chlorine compounds in the coal gas with sulfur, zinc, titanium, carbon monoxide, carbon dioxide, hydrogen and steam, in both reducing and oxidizing atmospheres.

Using the gathered data, detailed thermodynamic/kinetic models will be developed to aid in interpreting the experimental results of Task 4, as described later. Behavior models will be developed for both the sorbent sulfidation (gas desulfurization) cycle and the sorbent regeneration cycle.

In addition, a thermodynamic study will be conducted of the potential reactions of the hot gaseous chlorine species with solid compounds with which the HCl-containing gas could contact in the gasifier system; the gasifier refractory, the coal-char mineral matter, the construction material of the hot-gas particulate cleanup system, etc. The results of this examination might reveal possible scavengers of the HCl, which could eliminate or reduce any detrimental effects to zinc-titanate sorbent.

Task 2: Experimental Test Plan

Under this task, a detailed Experimental Test Plan was prepared. As stated above, this plan described the details of the proposed bench-scale tests which will be carried out during the project. A preliminary version of the test plan was delivered to the Center for Research on Sulfur in Coal (CRSC) in mid-October for their evaluation. The technical staff at CRSC approved of the test plan and the bench-scale studies was initiated during the first week of November. Thus, Task 2 is considered complete.

Task 3: Modifications in Existing Test Facility

Because hydrogen chloride is a highly corrosive gas which severely attacks stainless steel in the presence of steam, the present bench-scale test facility at RTI was modified.

In place of the older stainless steel reactor, a 26mm-I.D. quartz reactor system was designed and constructed. Figure 1 shows the schematic of this test setup. Housed in a three-zone furnace, the reactor has an inside diameter of 26 mm, a 2-mm wall thickness and a total length of 44 inches (112 cm). Teflon parts replaced those components exposed to the HCl at the lower (less than 200°C) temperatures. The system operates in a bubbling fluidized bed mode. A coarse porous quartz frit at the bottom of the reactor bed is used as the distributor for the simulated HCl-containing coal gas. All the original stainless steel lines in and out of the reactor has been replaced by quartz lines in order to prevent corrosion.

A system was installed to introduce the HCl into the reactor as a dilute HCl solution through a capillary using a positive displacement pump. A special alloy thermocouple made of Inconel constantly monitors the temperature within the sorbent bed.

The partially cooled (200°-300°C) gas from the reactor is sent to a glass condenser in which all the water and HCl vapors are condensed and collected in a catch pot. A slipstream of the non-condensable gases is sent to a gas chromatography (GC) system for analysis.

The dry gases required for sulfidation and regeneration of the sorbent are bought premixed and available in cylinders. A four way valve is used to pass the appropriate gas through a pre-calibrated electronic mass flow controller into the bottom of the reactor bed. A purge gas, such as nitrogen, is being

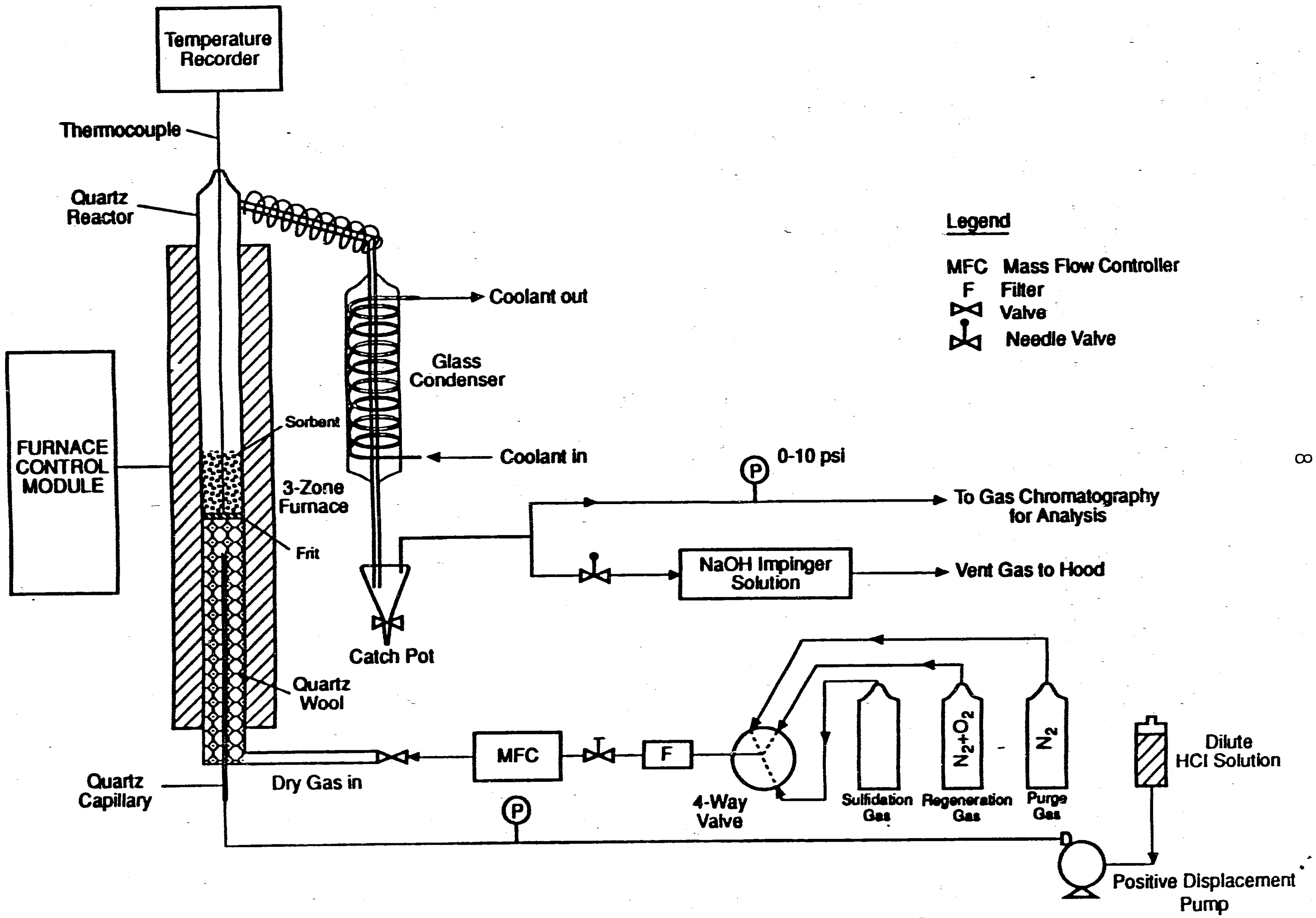

Figure 1. Bench-scale Experimental Test Setup

used during the heating and cooling of the sorbent bed and during the switching between sulfidation and regeneration cycle-steps.

The reactor system has been assembled and a number of startup experiments have been performed to demonstrate the operability and reliability of the experimental equipment and all the accessory apparatus and analytical instruments. The work of this task is essentially complete.

Task 4: Bench-Scale Testing and Analysis

Carefully controlled experiments will be conducted in the modified test setup described under Task 3. All the experiments for this project will be carried out at nearly atmospheric pressure, with a 2 psig positive pressure maintained to assure sufficient sample flow to the GC gas-analysis system.

A typical bench run will consist of the following steps. A known weight of the sorbent, approximately 50 to 60 grams in the 100 to 300 μm particle size range, will be charged to the reactor. The reactor will be heated to the desired gas desulfurization temperature (538° or 650°C) with a continuous passage of nitrogen through the sorbent bed.

The sulfidation of the sorbent (fuel gas desulfurization) will be carried out by continuously flowing the simulated coal gas through the fluidized bed. The simulated medium-Btu gas contains 1.4% H_2S (14,000 ppmv), while the simulated low-Btu fuel gas will contain 0.5% H_2S (5000 ppmv). The sorbent sulfidation cycle-step will continue until the H_2S concentration in the reactor exit gas reaches 100 ppmv, which is an arbitrarily defined breakthrough value.

Following the sulfidation, the reactor will be switched to the sorbent regeneration mode and heated to the desired temperature under nitrogen flow. Generally, the initial regeneration temperature is 50° to 150°C higher than the sulfidation temperature. Once the desired temperature is attained, the flow of regeneration gas will be started. The typical regeneration gas will contain 3% O_2 in nitrogen. Regeneration will be carried out until the outlet SO_2 concentration drops to less than 500 ppmv.

At both the end of the sorbent sulfidation and the end of the regeneration step, a sorbent sample will be withdrawn and analyzed for its chlorine content. Representative samples of the condensate and other gas-stream scrubbing solutions will be collected and analyzed to determine the chlorine-ion material balance during both the sulfidation and the regeneration steps. At the end of the run, the total quantity of sorbent solids will be removed from the reactor and weighed to determine any loss due to elutriation and attrition.

Post-test characterization tests of the sorbent solids and condensate-liquid samples will be performed primarily to obtain chlorine and sulfur material balances. Additional tests will be performed on the reacted sorbent to identify changes in chemical reactivity, surface area, particle size distribution and Zn-to-Ti contents.

The following variables will be investigated in order to determine the effect of chloride on the performance of the zinc-titanate sorbents in hot-gas desulfurization service.

1. HCl Concentration in the Coal Gas
2. Sulfidation Gas Composition
3. Sulfidation Temperature
4. Sorbent Composition

Three (3) block-sets of experiments are planned. The first set of experiments will be conducted with a medium-Btu fuel gas, while the second set will be with a low-Btu gas. The third set of experiments will involve a closer examination of specific operating conditions where mechanism changes, sorbent activity failure, or other unexpected phenomena have occurred, as identified during the first two experiment sets. Also, if time permits, the long-term detrimental effects of chlorine on the performance of the zinc-titanate sorbents will be examined in greater detail.

Following this strategy, the first set of experiments will be conducted with a medium-Btu fuel gas simulating the product from the Texaco entrained-bed, oxygen-blown gasifier. In the second block-set of experiments, we plan to use a low-Btu gas simulating that being generated in the U-Gas air-blown gasifier (developed by the Institute of Gas Technology, Chicago, and now marketed by Tampella, Inc., of Finland). Both of these gasifiers are being developed at nearly commercial scale and are ideally suited for gasifying the high-sulfur Illinois coals.

Two zinc-titanate sorbents have been chosen for this examination. The sorbent ZO-1 contains essentially pure ZnO with 2-3% TiO_2 and a suitable binder. It was prepared using RTI's proprietary granulation technique. The purpose of using this formulation is to establish the role of TiO_2 in the zinc-titanate on chloride removal. The second sorbent to be evaluated is ZT-4, which contains ZnO and TiO_2 in a molar ratio of 1.5. In previous studies comparing several candidate sorbents with varying Zn/Ti-ratios, the zinc-titanate sorbent with this particular molar ratio proved the most efficient in high-temperature coal gas desulfurization service.

The test matrix for each of the Set 1 (medium-Btu "Texaco" gas) and the Set 2 (low-Btu "U-Gas" gas) experiments will examine each of the sorbents (ZO-1 and ZT-4, described above) and two sulfidation temperatures, 538°C (1000°F) and 650°C (1202°F) and at three HCl concentrations (zero, medium and high). For example, the HCl concentrations for the medium-Btu gas study, Experiment Set 1, will be zero, 200 ppmv and 1500 ppmv. After completion of the single cycle tests, a ten-cycle test will be made to determine the long-term effect of HCl on the chemical reactivity and the attrition resistance of the zinc-titanate sorbents. The conditions for this ten-cycle test will be determined based on the results of the foregoing 12 single-cycle tests.

During the third set of experiments, selected sub-sets of experiments will be conducted to better define the reaction behavior of the sorbents in "critical" operating conditions. A closer examination of the effect of varying HCl concentrations in specific temperature ranges would be a candidate possibility. Also, varying the regeneration conditions might warrant more detailed examination, as would the need for additional multi-cycle evaluations. The specific objectives of these in-depth examinations will be identified during the course of performing and evaluating the outcomes of the first two experimental block-sets.

Task 5: Reporting

This task consists of the preparation and submittal of the quarterly and final technical and business management reports to the Center for Research on Sulfur in Coal (CRSC). In addition to the submission of the written reports, oral presentations describing the project work and results will be made to the technical staff of the CRSC and ICDB, and to the appropriate members of the Illinois Department of Energy and Natural Resources, including the presentation of a paper at the CRSC/ICDB Contractors' Meeting in Urbana, Illinois, in July 1992.

RESULTS AND DISCUSSION

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The first of the planned experiments in the project are now being performed. As stated above, the first block-set of experiments will evaluate the effect of HCl on the sorbent behavior in a simulated medium-Btu fuel gas. Most of the Second Quarter of the project will be involved with the completion and evaluation of this experimental set.

CONCLUSIONS

The work activity during the first quarter of this project involved the preparation and submittal to CRSC of the detailed Experimental Test Plan and the modification/startup of the reactor apparatus in which the experiments are to be performed. The Test Plan describes the equipment arrangement and the operating conditions selected for the initial two block-series of experiments, the first set studying the effect of HCl in the desulfurization of a medium-Btu fuel gas (simulating the product of the "Texaco" gasifier) and the second set studying the desulfurization of a low-Btu fuel gas (simulating the effluent from a "U-Gas" gasifier).

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