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TECHNICAL REPORT
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Project Title:	Desulfurization of Hot Fuel Gas Produced from High-Chlorine Illinois Coals
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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 that can generate electricity with high thermal efficiency in either an integrated gasification combined cycle (IGCC) system or a molten carbonate 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 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 coal in these processes.

The work activity during the second quarter of this project involved the performance of the first block-set of experiments in the bench-scale fluidized bed. These experiments were designed to study the effect of HCl in the desulfurization of a medium-Btu fuel gas (simulating the product of the "Texaco" entrained-bed, oxygen-blown gasifier). Eleven single-cycle experiments were performed, at operating temperatures of 538, 650, and 750 °C, with HCl concentrations of 0, 200, and 1500 ppmv. While some HCl was adsorbed onto the sorbent at 538 °C, no significant HCl adsorption was detected at the higher temperatures. In addition to the 11 single cycle experiments, a 10-cycle sulfidation-regeneration sequence was performed at 650 °C with 1500 ppmv HCl in the simulated fuel gas. No adverse effects on the sorbent structure or its desulfurization capability were identified.

MASTER

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EXECUTIVE SUMMARY

It is vital to the industry of Illinois that new approaches be developed soon to increase the utilization of the abundant bituminous coal resources in the Illinois coal basin by processes that 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 been developed recently which remove both hydrogen sulfide (H_2S) and carbonyl sulfide (COS) at relatively high temperatures very efficiently.

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 HCl in the coal-gas product-stream from the gasifier. This HCl reacts with certain inorganic compounds, usually with undesirable results. In studying the fly ash deposited during the combustion of coal 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 coals (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 ppmv HCl in the gasifier effluent stream. Very little is known about how 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.

Almost all the gaseous chlorine exiting from the gasifier has been analyzed (or assumed to be) in the form of HCl. The alkali chloride (sodium, potassium, etc.) present in either the solid salt or as dissolved ions is reported to react with evolving hydrogen during the first devolatilization step in the coal-gasification reaction series. HCl either evolves from the coal-matrix with the pyrolysis gas, or the chloride may be trapped into the residual tars left behind in the secondary condensation reactions. The chloride species in these secondary hydrocarbon tars would then be released during the second-stage gasification reactions, probably also in the gaseous HCl form, since the reaction atmosphere is rich in hydrogen formed from the steam-carbon reaction, modulated by the water-gas shift (WGS) equilibrium.

This project, a cooperative effort between the Southern Illinois University at Carbondale (SIUC) and the Research Triangle Institute (RTI), is investigating the effect of HCl, in concentrations typical of a gasifier fed by high-chlorine Illinois coals, on the fluidizable zinc-titanate sorbents. These sorbents are being developed by RTI, under the sponsorship of the U.S. Department of Energy/Morgantown Energy Technology Center (DOE/METC), for H_2S and COS removal from hot coal gas in IGCC processes. The project's major objectives are to identify any deleterious changes in the sorbent caused by 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 includes the examination of HCl effects on each sorbent's chemical reactivity, its sulfur-adsorption capacity, its regeneration capability, and its attrition resistance. This objective is 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 multicycle tests are being conducted to determine the effect of HCl on the long-term chemical reactivity and mechanical durability of zinc-titanate sorbents.

During the first quarter of this project, the "Experimental Test Plan" was prepared and submitted to the Center for Research on Sulfur in Coal (CRSC). In this detailed test plan document, the equipment arrangement was described and the major operating conditions and experimental procedures were detailed for use in the initial two block-series of experiments. Also, during this time period, the existing reactor apparatus was modified for use in the corrosive HCl atmospheres and was operated in preliminary experiments to demonstrate reliability.

The work activity during the second quarter of this project involved the performance of the first block-series of experiments, this sub-study evaluating the effect of HCl in the desulfurization of a medium-Btu fuel gas (simulating the product gas from a "Texaco" entrained-bed, oxygen-blown gasifier). Two sorbents were examined, one with essentially pure zinc oxide with 2% to 3% TiO_2 in a suitable binder (labeled ZO-1) and a second sorbent (labeled ZT-4) containing ZnO and TiO_2 in a molar ratio of 1.5. Both of these sorbent formulations were prepared using RTI's proprietary granulation technique.

Eleven experiments were performed involving a single sulfidation reaction of the sorbent, followed by the oxidation-regeneration step. In these experiments, the two sorbents were sulfided at two temperatures (538 and 650 °C) and with three concentrations of HCl in the fuel-gas stream (0, 200, and 1500 ppmv). Following these single-cycle experiments, the ZT-4 sorbent was sulfided and regenerated in a 10-cycle sequence at 650 °C and with 1500 ppmv HCl in the fuel gas stream. Also a single cycle test was conducted with ZT-4 at 750 °C in Texaco gas containing 1500 ppm HCl.

Preliminary results indicated that excessive zinc vaporization occurred at the higher temperatures with the ZO-1 formulation as expected. Because of this, we do not plan to continue studying this sorbent in this project. Some HCl was adsorbed onto the sorbents during the sulfidation reactions at 538 °C; however, no significant HCl adsorption was identified at the higher temperatures. Evaluation of the collected quantitative analytical data is now under way to trace the fate of HCl during each of these sulfidation-regeneration reaction cycles.

A quick examination of the experimental data indicates that, when the sorbent is exposed to fuel gas containing 1500 ppmv HCl, significantly less HCl was retained in the solid sorbent at the higher temperatures than was absorbed into the sorbent at the lower temperature, 538 °C. However, when the fuel gas contained 200 ppmv HCl, excessive chloride retentions were observed at both 538 and 650 °C. The cause for this excessive chloride retention at moderate HCl concentrations is currently being investigated.

As expected, the ZT-4 zinc titanate sorbent consistently exhibited a prebreakthrough concentration of <20 ppmv despite 1500 ppmv of HCl in the coal gas, thus indicating that chloride does not affect the H_2S absorption by the sorbent. Higher sulfidation temperatures led to faster kinetics suggesting a reaction controlled mechanism for H_2S absorption. The X-ray diffraction (XRD) measurements of some single-cycle reacted samples indicated the presence of $TiCl_4$ phase in trace quantities.

A 10-cycle sulfidation-regeneration sequence was performed, exposing the ZT-4 sorbent to sulfidation at 650 °C with 1500 ppmv HCl in the simulated fuel gas. Some operational difficulties occurred when unexpectedly high corrosion in the HCl solution pump interfered with the pumping of the concentrated aqueous HCl solution into the reactor chamber. However, the multicycle reaction sequence was completed satisfactorily. Preliminary examinations of the experimental data have not identified any significant adverse effects of the multicycle reactions either on the sorbent physical structure or upon its desulfurization capability. The H_2S breakthrough behavior during 10 cycles of sulfidation regeneration remained essentially unchanged.

Post-test characterization of the 10-cycle reacted sorbent indicated no deleterious change either in attrition resistance or chemical reactivity. In fact, the attrition resistance of the sorbent on the reaction increased significantly. During the 10-cycle test, HCl was permanently absorbed into zinc titanate sorbent in the amount of about 300 ppm (by weight). The principal cause for this absorption is believed to be the reaction of HCl with the binder present in the sorbent. However, this needs to be further investigated.

During the third quarter of the project, attention will be directed to the capability of the ZT-4 sorbent in desulfurizing a low-Btu fuel gas simulating the product from the "U-Gas" air-blown coal gasifier. The "U-Gas" coal gasification system was developed by the Institute of Gas Technology (IGT) in Chicago and is now being marketed by Tampella, Inc., of Finland. A second block-set of experiments will be performed similar to those described above, except the upper level of HCl in the fuel gas will be about 800 ppmv. This value was computed as the potential concentration of HCl in the product stream of a "U-Gas" air-blown gasifier fed with an Illinois coal having a 0.6% chlorine content. Also in the third quarter, the search work of literature-review subtask will be enlarged to explore possible HCl removal techniques during the desulfurization step.

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OBJECTIVES

The overall goal of the research is to develop attrition-resistant regenerable sorbents for desulfurization of hot coal-derived gases for IGCC and MCFC power generation systems. The specific objectives of this investigation are to study the effects and the fate of HCl 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 either medium- or low-Btu fuel-gas products. 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 HCl gas.

The specific goals of the research during this 12-month contract period are to:

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

- 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;

- determine the material balances and chlorine distribution during the operation of a hot-gas desulfurization system;

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

- determine the extent of permanent chlorine retention by the zinc-titanate sorbent.

This project, a cooperative effort between SIUC and the RTI, is focused on the investigation of the effect of HCl, in concentrations typical of a gasifier fed by high-chlorine Illinois coals, on fluidizable zinc-titanate sorbents. These sorbents are being been developed by RTI, with the sponsorship of DOE/METC, for H_2S and COS removal from hot coal gas. The major objectives are to identify any deleterious changes in the sorbent caused by 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 among the most advanced power generation technologies with a projected coal-to-electricity thermal efficiency of 50% 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 1350 °F (538 to 732 °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 the 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 HCl. The chloride level of a medium-Btu fuel gas derived from Illinois coals can be as high as 1500 ppmv. HCl, 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 HCl on the performance of zinc-titanate sorbents must be addressed.

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

- How much HCl, if any, is removed by the zinc titanate in the adsorption cycle?
- If HCl is adsorbed, what is the form of chlorine when present in the sorbent?
- 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?
- 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?
- What are the forms of the chlorine compounds that come 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 present study is expected to 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 HCl 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 task is described below.

Task 1: 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.

Most of the chlorine found in the various coals have been attributed either to the presence of alkali-chloride salts retained in the coal's pore structure upon drying or the ionic bonding of the chloride ion, found in the brackish water in the coal seam, onto the acidic sites of the organic coal matrix. Estimates of the highest potential HCl concentrations in the product fuel gases were computed, based on literature-reported data from processing Illinois-basin coal in pilot plants, with the assumption that the Illinois feed coal could contain 0.6% (by wt.) chlorine. The medium-Btu fuel gas product from the "Texaco" oxygen-blown entrained-flow gasifier might contain as much as 1500 ppmv HCl if all the chlorine were evolved in the gaseous form. If a high-chlorine Illinois coal were processed in the air-blown IGT "U-Gas" gasifier (now marketed by Tampella, Inc.), the low-Btu fuel gas could contain as high as 800 ppm HCl.

Almost all the gaseous chlorine exiting the gasifier has been analyzed as (or assumed to be) in the form of HCl. The alkali-chloride (sodium, potassium, etc.) present in either the solid-salt or as dissolved ions is reported to react with evolving hydrogen during the first devolatilization step in the coal-gasification reaction series. HCl either evolves from the coal matrix with the pyrolysis gas or the chloride may be trapped into the residual tars left behind in the secondary condensation reactions. The chloride species in these secondary hydrocarbon tars would then be released during the second-stage gasification reactions, probably also in the gaseous HCl form, since the reaction atmosphere is rich in hydrogen formed from the steam-carbon reaction, modulated by the WGS equilibrium.

To date, very little deleterious effects have been reported while gasifying moderately high-chlorine coals. However, almost all the recent related literature describes gasifiers where the effluent coal gas is being water-scrubbed immediately after leaving the gasifier, to cool the gas along with removing condensable tars. Very few systems have heat-transfer tubes in the hot-gas stream immediately following the gasifier exit. Also, very few coal-gasifier systems have operated with even moderately high chlorine coals for prolonged time periods. Studies of fly-ash behavior in coal-fed boilers indicate that, probably, the vaporized alkali-species (i.e., sodium or potassium) condense and collect on the boiler tubes, with the gaseous HCl reacting with the alkali to form low-melting chloride salts which are active in the undesirable slagging and fouling behavior.

The search work of this literature-review sub-task has been enlarged to also explore possible removal techniques for HCl prior to, during, or following the desulfurization step. Also, information is being gathered regarding the potential chemical-sorbent treatment for other undesirable chemical species in the hot fuel-gas stream, for instance, the vaporized alkali species. The interim report summarizing these findings is now being drafted, with completion and distribution slated for early in the third quarter of this project.

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 would be carried out during the project. A preliminary version of the test plan was delivered to CRSC in mid-October for their evaluation. The technical staff at CRSC approved the test plan and the bench-scale studies were initiated during the first week of November. Thus, Task 2 is considered complete.

Task 3: Modifications in Existing Test Facility

Because HCl 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. A detailed description of various modifications made to the reactor system was presented in the last quarterly report.

The original system installed to introduce HCl into the reactor as a dilute HCl solution through a capillary using a positive displacement pump offered a number of operational problems, mainly stemming from corrosion of stainless steel by the aqueous solution of HCl. The problem was resolved by using a high-pressure syringe pump typically used in high-pressure liquid chromatography (HPLC) systems. Unfortunately, HCl solution also induced a severe corrosion to this pump's reservoir as indicated by a number of macroscopic pits. The reservoir of this pump will be replaced by a specially designed barrel made for handling highly corrosive solutions.

This task is now complete.

Task 4: Bench-Scale Testing and Analysis

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

A typical bench run consists of the following steps. A known weight of the sorbent, approximately 50 to 60 g in the 100 to 300 μm particle size range, is charged to the reactor. The reactor is 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) is carried out by continuously flowing the simulated coal gas through the fluidized bed. The simulated medium-Btu gas contains approximately 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 continues until the H_2S concentration in the reactor exit gas reaches 500 ppmv, which is an arbitrarily defined breakthrough value.

Following the sulfidation, the reactor is switched to the sorbent regeneration mode [illegible] heated to the desired temperature under nitrogen flow. Generally, the initial regeneration temperature is around 740 °C. Once the desired temperature is attained, the flow of regeneration gas will be started. The typical regeneration gas contains 3% O_2 in nitrogen. Regeneration is 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 is withdrawn and analyzed for its chloride content. Representative samples of the condensate and other gas-stream scrubbing solutions are collected and analyzed to determine the chloride-ion material balance during both the sulfidation and the regeneration steps. At the end of the run, the total quantity of sorbent solids removed from the reactor is weighed to determine any loss due to elutriation and attrition.

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

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

- HCl concentration in the coal gas,
- Sulfidation gas composition,
- Sulfidation temperature, and
- Sorbent composition.

Three block-sets of experiments are planned. The first set of experiments was to 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, during this second quarter of the project, the first set of experiments was 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 to be performed during the project's third quarter, we plan to use a low-Btu gas simulating that being generated in the U-Gas air-blown gasifier (developed by IGT, 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% to 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, conducted at RTI with DOE/METC sponsorship, comparing several candidate sorbents with varying Zn/Ti ratios, this particular zinc-titanate sorbent 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 includes examinations of 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) as detailed in our "Experimental Test Plan" document and last quarterly report. For example, HCl concentrations for the medium-Btu gas study, Experiment Set 1, was selected as 0, 200, and 1500 ppmv. A higher sulfidation temperature of 750 °C (1382 °F) may also be selected to probe the expected upper limit of sorbent reactivity. After completion of the single-cycle tests, a 10-cycle test is also planned 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 10-cycle test will be determined based on the results of the foregoing 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 multicycle 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 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 Illinois Coal Development Board (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

The work activity during the second quarter of this project involved the performance of the first block-series of experiments, this sub-study evaluating the effect of HCl in the desulfurization of a medium-Btu fuel gas (simulating the product gas from a "Texaco" entrained-bed, oxygen-blown gasifier). The use of two sorbents was examined, one with essentially pure zinc oxide with 2% to 3% TiO_2 in a suitable binder (labeled ZO-1) and a second sorbent (labeled ZT-4) containing ZnO and TiO_2 present with a ratio of 1.5. Both of these sorbents were prepared using RTI's proprietary granulation technique.

Single-Cycle Tests

Eleven experiments were performed involving a single sulfidation reaction of the sorbent, followed by the oxidation-regeneration step. In these experiments, the two sorbents were separately sulfided at two temperatures (538 and 650 °C) and with three concentrations of HCl in the fuel-gas stream (0, 200, and 1500 ppmv). Also, one experiment was performed at 750 °C with 1500 ppmv of HCl in Texaco gas.

Table 1. Pertinent Test Conditions and Sorbent HCl Retention for Single Cycle Runs Made in Set 1

Run no.	Sorbent formulation	HCl concentration in feed gas (ppmv)	Temperature (°C)	HCl retention by sorbent* (% of feed)
1	ZT-4	-0-	650	-0-
2	ZT-4	-0-	538	-0-
3	ZO-1	-0-	650	-0-
4	ZO-1	-0-	538	-0-
5	ZT-4	1,500	650	2.57
6	ZT-4	1,500	538	11.37
7	ZO-1	1,500	650	8.82
8	ZO-1	1,500	538	14.35
9	ZT-4	1,500	750	2.26
10	ZT-4	200	538	69.16
11	ZT-4	200	650	18.38

$$* \text{ Chloride Retention} = \frac{\text{HCl Level of Sulfided Sorbent} \times \text{Amount of Sorbent}}{\text{HCl Level of Aqueous Feed} \times \text{Amount of Solution Pumped}} \times 100 .$$

Table 1 shows the pertinent test conditions for Runs 1 to 11. Also included in this table are percent chloride retentions by the sorbent. As expected, percent HCl retention decreased with an increase in temperature. For ZT-4 formulations in Texaco gas containing 1500 ppmv of HCl, the percent chloride retentions at 538, 650, and 750 °C were 11.37%, 2.57%, and 2.27%, respectively. A similar trend was observed for the ZO-1 formulation where percent chloride retentions observed were 14.35% and 8.82% at 538 and 650 °C temperatures, respectively. These observations are in direct agreement with the thermodynamic predictions. One interesting point to note here is that for Runs 10 and 11 in which the HCl level of coal gas was kept at 200 ppmv, the chloride retentions were high—18.38% and 69.16% at 650 and 538 °C temperatures, respectively. The cause for these unexpected amounts of HCl retention by sorbent is not clear and needs further investigation.

Figure 1 compares the breakthrough behavior of ZT-4 at three temperatures, 538, 650, and 750 °C, in Texaco gas containing 1500 ppmv of HCl. Except for the 538 °C run, the pre-breakthrough HCl concentration is consistently below 20 ppmv. As expected, the sulfur capacity of the sorbent increased with an increase in the temperature, indicting that sulfidation reaction is predominantly kinetically controlled. Furthermore, operating the reactor at higher temperatures (>650 °C) will reduce the reactor vessel size significantly due to the faster kinetics.

The effect of HCl level in coal gas is compared in Figure 2 where the H_2S breakthrough behavior of ZT-4 at 650 °C in Texaco gas containing three levels of HCl is shown. As can be seen, the presence of HCl in coal gas does not appear to affect the breakthrough behavior. This is primarily because of the unfavorable thermodynamics of the reaction between ZnO and HCl at 650 °C.

Figure 3 compares the H_2S breakthrough curves for ZT-4 and ZO-1 formulations at 650 °C in Texaco gas containing 1500 ppm of HCl. Essentially, as can be seen, both formulations exhibit similar breakthrough behaviors, except for the fact that the H_2S-retention capacity of the ZO-1 sorbent fails suddenly after about 150 minutes of exposure, while a gradual increase in H_2S concentration is observed for the ZT-4 formulation even after 240 minutes.

Excessive zinc vaporization was observed when the high Zn/Ti sorbent (ZO-1) was exposed to the higher temperatures. Because of this, we do not plan to continue extensive study of this sorbent during the rest of this project.

Ten-Cycle Test

Following the 11 single-cycle experiments, a 10-cycle sulfidation-regeneration sequence was performed. During this experiment, the sulfidations of the sorbent took place at 650 °C with 1500 ppmv HCl in the simulated fuel gas. Some difficulties occurred when unexpectedly

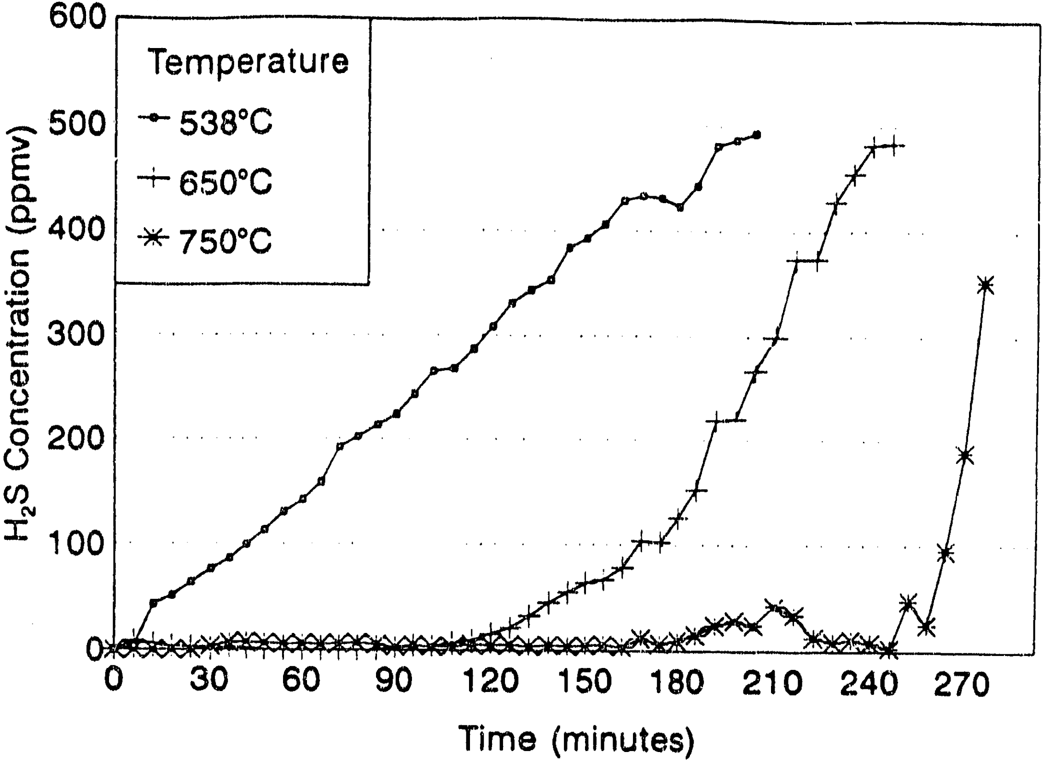


Figure 1. H$_2$S breakthrough curves at various temperatures. (ZT-4 in Texaco gas containing 1500 ppm HCl)

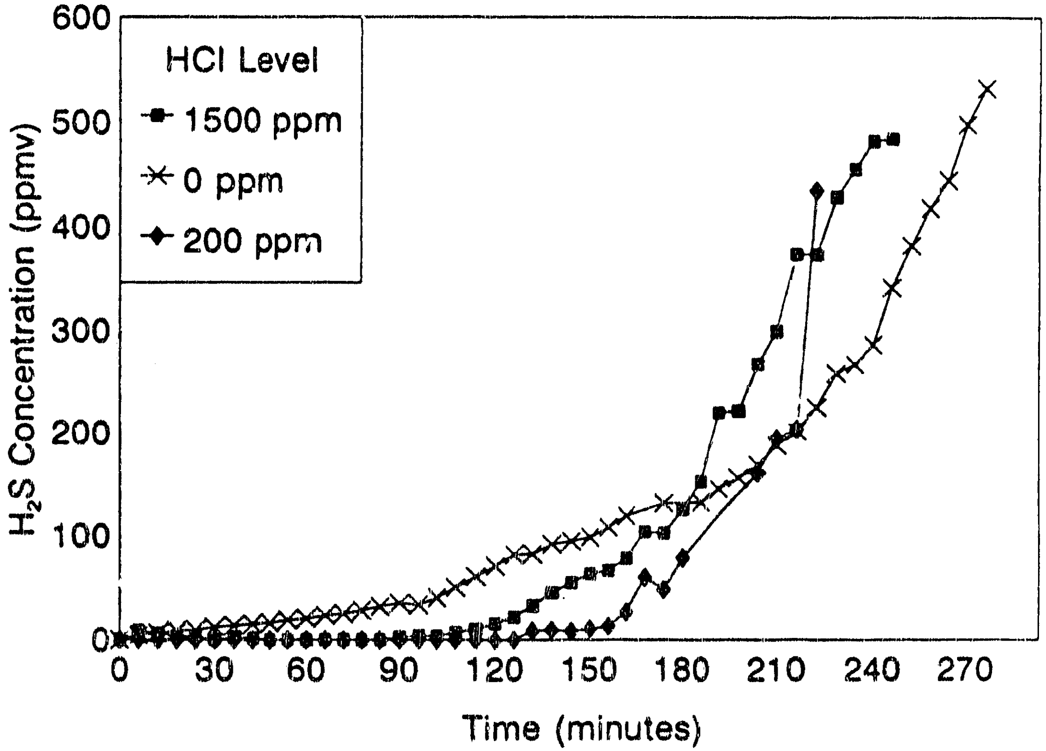


Figure 2. H$_2$S breakthrough curves at various HCl levels. (ZT-4 in Texaco gas at 650 °C)

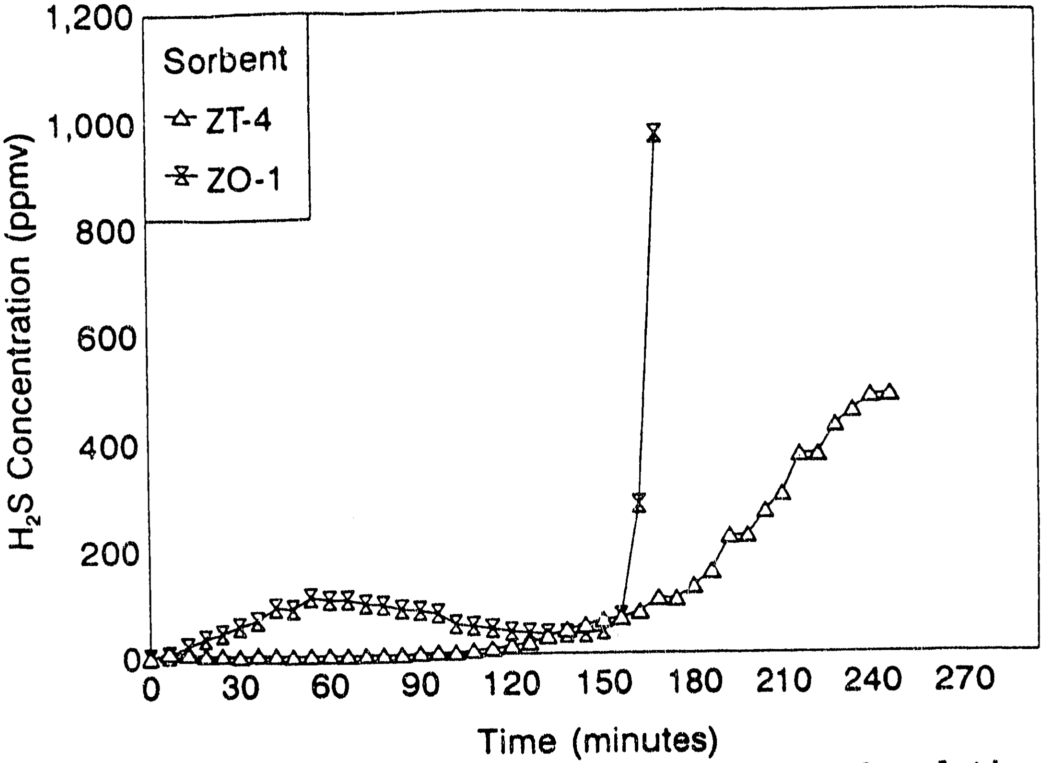


Figure 3. H_2S breakthrough curves for ZT-4 and ZO-1 formulations. (Texaco gas containing 1500 ppm HCl at 650 °C)

high corrosion interfered with the pumping of the concentrated aqueous HCl solution into the reactor chamber. Bubbles formed in the liquid flow stream which frequently interrupted steam and HCl feed flow to the reactor.

Figure 4 shows H_2S breakthrough curves for cycles 1 to 10. As can be seen, the breakthrough sulfur capacity during the first cycle is slightly higher than the other nine cycles. Unfortunately, a number of unexpected problems including irregular operation of pump, plugging of the porous distributor plate to the reactor, etc., were encountered during Cycle 2 which are believed to be primarily responsible for a rather early breakthrough shown in Figure 4. Nevertheless, during all 10 cycles, the prebreakthrough H_2S level was consistently below 20 ppmv. This indicates that the presence of 1500 ppmv of HCl does not affect the breakthrough behavior.

Regarding the fate of chloride, 367 ppmw of chloride were detected in the 10-cycle regenerated material. The chloride level of the sorbent after the first cycle was 359 ppm. Based on these data, it appears that at 650 °C, 350 to 370 ppmw of chloride are permanently absorbed by the sorbent. The primary cause of this absorption is believed to be the reaction between HCl and the clay binder present in the sorbent. This hypothesis, however, needs to be verified.

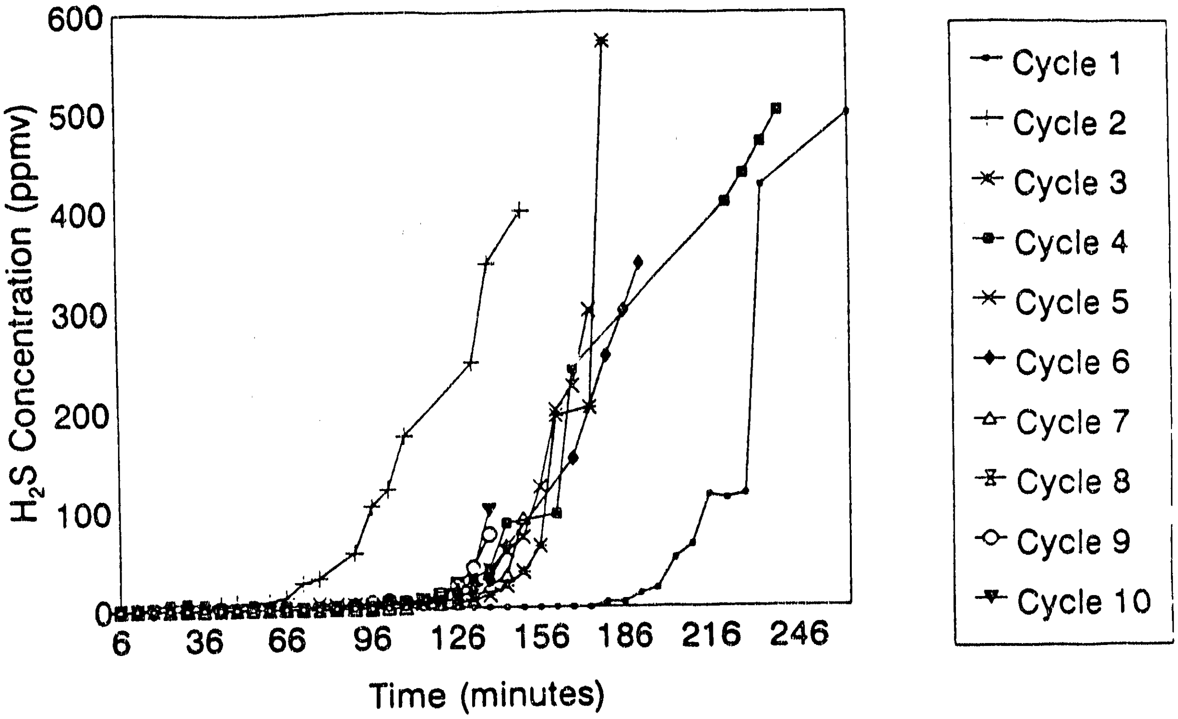


Figure 4. **H_2S breakthrough curves (run #12).**
(Texaco gas containing 1500 ppm HCl at 650 °C)

No deleterious effect of HCl during 10 cycles of sulfidation-regeneration on the physical and chemical properties of the sorbent was observed as is evident from Table 2. The particle and pore size distribution remained unchanged. XRD patterns taken on the reacted samples indicated some traces of $TiCl_4$ in undetectably small amounts. The attrition resistance of the sorbent significantly increased after cycling as indicated by 14.20% loss due to attrition for the reacted material as opposed to 32.2% for the fresh material. This indicates that the presence of chloride does not deteriorate either the mechanical strength or the chemical reactivity of the zinc-titanate sorbents.

During the third quarter of the project, attention will be directed to the capability of the ZT-4 sorbent in desulfurizing a low-Btu fuel gas simulating the product from the U-Gas air-blown coal-gasifier. The U-Gas Coal Gasification System was developed by IGT in Chicago and is now being marketed by Tampella, Inc., of Finland. A second block-set of experiments will be performed similar to those described above, except the upper level of HCl in the fuel gas will about 800 ppmv. This value was computed as the highest probable concentration of HCl in the product stream of a "U-Gas" air-blown gasifier fed with an Illinois coal having a 0.6% chlorine content.

Table 2. Properties of Sorbent Before and After Test

	Fresh	10-cycle regenerated
Average particle size (μm)[a]	176.0	175.4
BET surface area (m^2/g)	3.53	2.76
Pore size distribution		
Mercury pore volume (cc/g)	0.2200	0.2186
Median pore diameter (Å)	2157	2436
Attrition resistance[b]		
5-h loss (%)	32.20	14.20
Zn/Ti ratio (atomic)[c]	1.52	1.51[d]
XRD phases[e]	A mixture of Zn_2TiO_4 and $Zn_2Ti_3O_8$	A mixture of Zn_2TiO_4 and $Zn_2Ti_3O_8$ and traces of $TiCl_4$
TGA reactivity[f]	100%	91%
Chloride level (ppmw)	-0-	367

[a] Harmonic mean.

[b] Measured in a 3-hole attrition tester

[c] Measured using inductively coupled plasma (ICP) technique

[d] XRD phases

[e] Chemical analysis is being repeated.

[f] Chemical reactivity in a thermogravimetric reactor (TGR) (expressed in terms of percent conversion in 120 minutes)

CONCLUSIONS

The work activity during the second quarter of this project involved the performance of the first block-series of experiments, this sub-study evaluating the effect of HCl in the desulfurization of a medium-Btu fuel gas (simulating the product gas from a "Texaco" entrained-bed, oxygen-blown gasifier). Two sorbents were examined, one with essentially pure zinc oxide with 2% to 3% TiO_2 in a suitable binder (labeled ZO-1) and a second sorbent (labeled ZT-4) containing ZnO and TiO_2 in a molar ratio of 1.5. Both of these sorbent formulations were prepared using RTI's proprietary granulation technique.

Eleven experiments were performed involving a single sulfidation reaction of the sorbent, followed by the oxidation-regeneration step. In these experiments, the two sorbents were sulfided at two temperatures (538 and 650 °C) and with three concentrations of HCl in the fuel-gas stream (0, 200, and 1500 ppmv). Following these single-cycle experiments, the ZT-4 sorbent was sulfided and regenerated in a 10-cycle sequence at 650 °C and with 1500 ppmv HCl in the fuel gas stream. Also a single cycle test was conducted with ZT-4 at 750 °C in Texaco gas containing 1500 ppm HCl.

Preliminary results indicated that excessive zinc vaporization occurred with the ZO-1 formulation at the higher temperatures as would be expected. Because of this, we do not plan to continue studying this sorbent in this project. Some HCl was adsorbed onto the sorbents during the sulfidation reactions at 538 °C; however, no significant HCl adsorption was identified at the higher temperatures. Evaluation of the collected quantitative analytical data is now under way to trace the fate of HCl during each of these sulfidation-regeneration reaction cycles.

A quick examination of the experimental data indicates that, when the sorbent is exposed to fuel gas containing 1500 ppmv HCl, significantly less HCl was retained in the solid sorbent at the higher temperatures than was absorbed into the sorbent at the lower temperature, 538 °C. However, when the fuel gas contained 200 ppmv HCl, excessive chloride retentions were at both 538 and 650 °C. The cause for this excessive chloride retentions at moderate HCl concentrations is currently being investigated.

As expected, the ZT-4 zinc titanate sorbent consistently exhibited a prebreakthrough concentration of <20 ppmv despite 1500 ppmv of HCl in the coal-gas, thus indicating that chloride does not affect the H_2S absorption by the sorbent. Higher sulfidation temperatures led to faster kinetics suggesting a reaction controlled mechanism for H_2S absorption. The XRD measurements of some single cycle reacted samples indicated the presence of $TiCl_4$ phase in trace quantities.

A 10-cycle sulfidation-regeneration sequence was performed, exposing the ZT-4 sorbent to sulfidation at 650 °C with 1500 ppmv HCl in the simulated fuel gas. Some operational difficulties occurred when unexpectedly high corrosion interfered with the pumping of the concentrated aqueous HCl solution into the reactor chamber. However, the multicycle reaction sequence was completed satisfactorily. Preliminary examinations of the experimental data have not identified any significant adverse effects of the multicycle reactions either on the sorbent physical structure or upon its desulfurization capability. The H_2S breakthrough behavior during 10 cycles of sulfidation-regeneration remained essentially unchanged. Post-test characterization of the 10 cycle reacted sorbent indicated no deleterious change either in attrition resistance or chemical reactivity. In fact, the attrition resistance of the sorbent on the reaction increased significantly. During the 10-cycle test, HCl was permanently absorbed into zinc titanate sorbent in the amount of about 300 ppm (by weight). The principal cause for this absorption is believed to be the reaction of HCl with the binder present in the sorbent. However, this needs to be further investigated.

During the third quarter of the project, attention will be directed to the capability of the ZT-4 sorbent in desulfurizing a low-Btu fuel gas simulating the product from the "U-Gas" air-blown coal gasifier. The "U-Gas" Coal Gasification System was developed by IGT in Chicago, and is now being marketed by Tampella, Inc., of Finland. A second block-set of experiments will be performed similar to those described above, except the upper level of HCl in the fuel gas will be about 800 ppmv. This value was computed as the potential concentration of HCl in the product stream of a "U-Gas" air-blown gasifier fed with an Illinois coal having a 0.6% chlorine content. Also in the third quarter, the search work of literature-review subtask will be enlarged to explore possible HCl removal techniques during the desulfurization step.

PROJECT MANAGEMENT REPORT
December 1, 1991, through February 29, 1992

Project Title:	Desulfurization of Hot Fuel Gas Produced from High-Chlorine Illinois Coals
Principal Investigator:	William S. O'Brien Southern Illinois University at Carbondale
Co-Principal Investigator:	Raghubir P. Gupta Research Triangle Institute
Project Manager:	Frank I. Honea, CRSC

COMMENTS

The Project Tasks are on schedule as originally proposed. The work activity during the second quarter of this project involved the performance of 12 experiments in the bench-scale fluidized-bed reactor, this block-set of experiments representing the first of the planned experiments in the project (Task 4). This sub-study involved the evaluation of the effect of HCl on zinc-titanate sorbent reactivity during the desulfurization of a medium-Btu fuel gas (simulating the project gas from a "Texaco" entrained-bed, oxygen-blown gasifier). Eleven of these experiments examined the effects of temperature and Cl concentration of the sorbent activities in single sulfudation-regeneration cycle reactions. The final twelfth experiment involved exposing one of the sorbents to a 10-cycle sequence of sulfidation and regeneration reactions.

Some operation difficulties occurred when unexpectedly high corrosion interfered with the pumping of the concentrated aqueous-HCl solution into the reactor chamber during this twelfth multicycle experiment. However, the planned 10-cycle sequence was completed and the objectives of the experiment were accomplished in spite of these operational problems.

In the next quarterly report, the second block-set of experiments, examining the desulfurization of a HCl-containing low-Btu fuel gas, will be discussed. This fuel gas would be typical of the product of an air-blown coal gasifier converting Illinois coal.

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.

EXPENDITURES

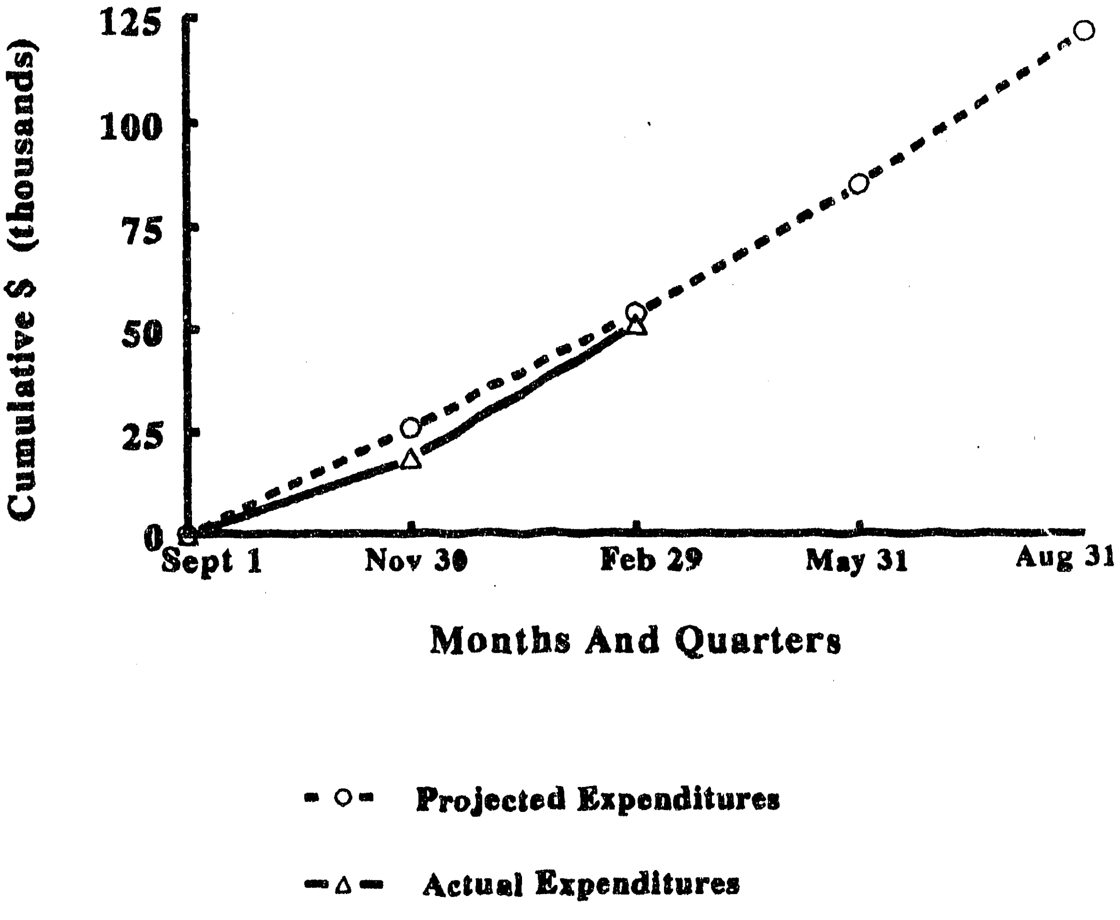
Projected and Estimated Actual Expenditures by Quarter

Quarter *	ypes Of Cost	Direct Labor	Materials and Supplies	Travel	Major Equipment	Other Direct Costs	Indirect Costs	Total
Sept. 1, 1991 to Nov. 30, 1991	Projected	2,700	0	1,000	0	20,000	2,370	26,070
	Estimated Actual	2,460	0	930	0	13,392	1,679	18,464
Sept. 1, 1991 to Feb. 29, 1992	Projected	5,400	0	2,000	0	40,000	6,540	53,940
	Estimated Actual	4,940	0	930	0	40,708	4,658	51,236
Sept. 1, 1991 to May 31, 1992	Projected	14,568	0	3,000	0	60,000	7,757	85,325
	Estimated Actual							
Sept. 1, 1991 to Aug. 31, 1992	Projected	23,830	0	3,700	0	83,678	11,121	122,329
	Estimated Actual							

*Cumulative by quarter

COSTS BY QUARTER

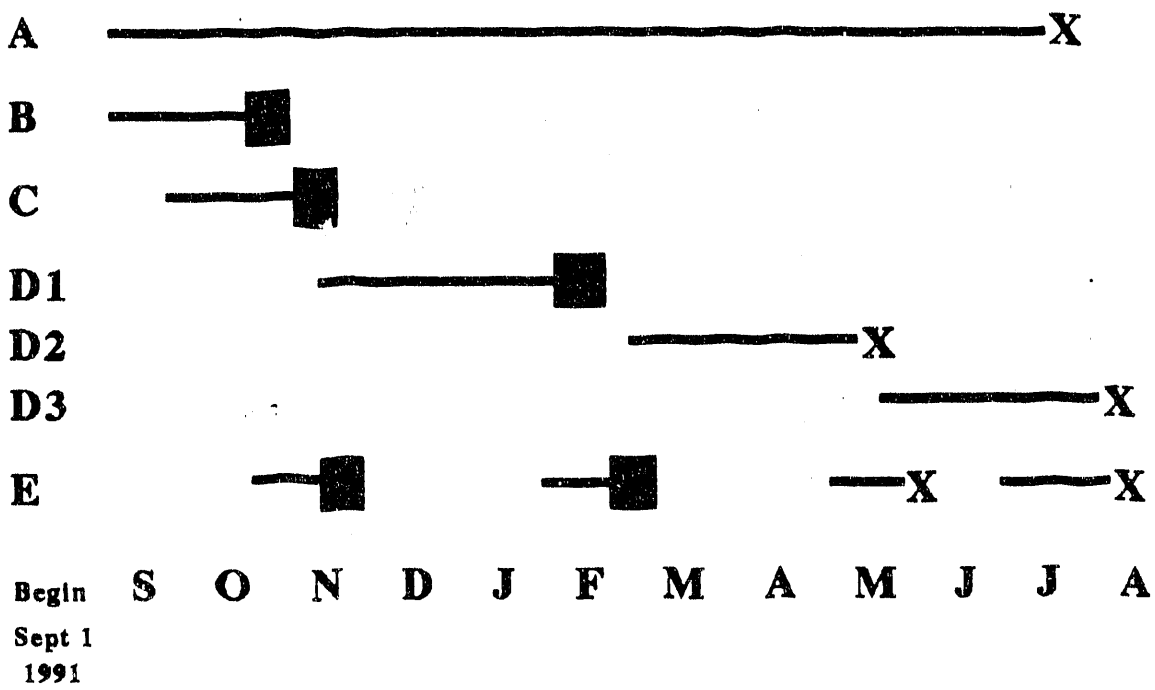
Desulfurization Of Hot Fuel Gas Produced From High-Chorine Illinois Coal



Total CRSC Award: $122,329

PROJECT MILESTONES

Desulfurization Of Hot Fuel Gas Produced From High-Chlorine Illinois Coals



Project Milestones:

A. Assessment: Chlorine Behavior In Coal Gas (Task 1)

B. Development Of Experimental Test Plan (Task 2)

C. Modifications In Existing Test Facility (Task 3)

D. Bench-Scale Testing And Analysis (Task 4)
  D1. Experiment Set 1: Medium-Btu (Texaco) Fuel Gas
  D2. Experiment Set 2: Low-Btu (U-Gas) Fuel Gas
  D3. Experiment Set 3: Followup Detailed Mini-Tests

E. Report Preparation And Submittal (Task 5)

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10/1/92