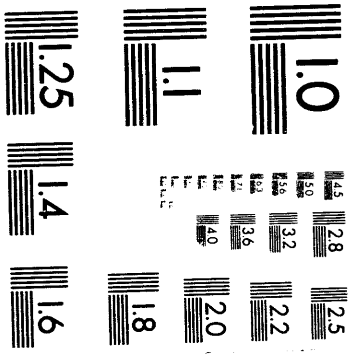
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DOE/PC/91334--T725

FINAL TECHNICAL REPORT
September 1, 1991, through August 31, 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

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 an integrated gasification combined cycle (IGCC) or in 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 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. In this project, simulated gasifier-product streams were contacted with the zinc titanate desulfurization sorbent in a bench-scale atmospheric fluidized-bed reactor at temperatures ranging from 538 to 750 °C (1000 to 1382 °F). The first set of experiments involved treating a medium-Btu fuel gas (simulating that of a "Texaco" oxygen-blown, entrained-bed gasifier) containing 1.4 percent H_2S and HCl concentrations of 0, 200, and 1500 ppmv. The second experimental set evaluated hot-gas desulfurization of a low-Btu fuel gas (simulating the product of the "U-Gas" air-blown gasifier), with HCl concentrations of 0, 200, and 800 ppmv. These operating conditions were typical of the gas-treatment requirements of gasifiers fueled by Illinois basin coals containing up to 0.6 percent chlorine.

The results of the experiments at 538 and 650 °C at all the HCl concentrations revealed no deleterious effects on the capability of the sorbent to remove H_2S from the fuel gas mixtures. In most cases, the presence of the HCl significantly enhanced the desulfurization reaction rate. Some zinc loss, however, was encountered in certain situations at 750 °C when low-steam operating conditions were present. Also of interest, a portion of the incoming HCl was removed from the gas stream and was retained permanently by the sorbent. This behavior was examined in more detail in a limited set of experiments aimed at identifying ways to modify the sorbent's composition so that the sorbent could act as a simultaneous desulfurization and dechlorination agent in the hot-gas cleanup process.

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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 systems 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 a combustion chamber of an IGCC system or in an MCFC vessel.

To realize the highest thermal efficiency for the overall conversion of coal to electricity, 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 this high temperature for the overall process to be thermally 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 in the 500 to 750 °C range.

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 a series of attrition-resistant, fluidizable zinc titanate sorbents at the Research Triangle Institute (RTI) offers excellent H_2S and COS removal efficiency, good sulfur absorption capacity, and excellent regenerability. In addition, these sorbents have 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 a much greater flexibility in designing alternative sub-systems for the continuous regeneration of the sorbent.

Unfortunately, some Illinois coals contain significant chlorine which primarily converts to 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 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 percent chlorine, by weight) in the typical present-day coal-gasification reactor designs ("Texaco," "U-Gas," "Lurgi," etc.) would produce from 100 to 1,400 ppmv HCl in the gasifier effluent stream. Very little is known about how the HCl will interact chemically with the zinc-based desulfurization sorbents at high temperatures and in the presence of the various fuel gas compositions that could be produced in the different present-day gasifier designs.

Almost all the gaseous chlorine exiting from the gasifier has been analyzed (or assumed to be) in the form of HCl, this form predominating because of the high hydrogen content in the gasifier effluent gas. A portion of the HCl may be scavenged by the alkaline species in the mineral slags which, after evolving from the coal matrix, would cling to the walls of the product gas main, or to any heat-transfer surfaces placed in the path of the gasifier product gas stream. The chlorine gas species, however, would still remain as HCl as long as the gas contains substantial hydrogen and is reducing in its reactive behavior.

This project, a cooperative effort between the Southern Illinois University at Carbondale (SIUC) and RTI, was aimed to investigate 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 systems. The major objective of this project was to identify any deleterious changes in the sorbent caused by the HCl, both in the absorptive operation and in the regeneration cycle, and to determine the fate of the chloride chemical-species.

Two zinc titanate sorbents were originally chosen for this examination, one with a high Zn-to-Ti ratio (designated as ZO-1) and the second (designated as ZT-4) with a Zn-to-Ti ratio found previously to perform optimum service in the hot coal-gas desulfurization process. The experimental evaluation during the project examined the HCl effects on each sorbent's chemical reactivity, sulfur-absorption capacity, regenerability and attrition resistance. These objectives were 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 HCl in the gas-stream. Also, a number of multicycle tests were 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). The equipment arrangement was described in this detailed test plan document. Details of the major operating conditions and experimental procedures to be used in the initial two block-sets of experiments were also discussed in the test plan. Also, during this time period, a bench-scale reactor system was designed, constructed, and tested 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-sets of experiments. This sub-study evaluated 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). During the examination of one of the sorbents, which contained essentially pure zinc oxide with only 2 to 3 percent TiO_2 in a suitable binder (labeled ZO-1), excessive zinc vaporization occurred at the higher temperatures. Because of this sorbent loss, this particular sorbent was not used in any experiments during the rest of the project.

Eleven experiments were performed involving a single sulfidation reaction of the sorbent (labeled ZT-4), which contained ZnO and TiO_2 in a molar ratio of 1.5. In these experiments, aliquots of the sorbent were sulfided at three temperatures (538, 650, and 750 °C) and with three concentrations of HCl in the fuel-gas stream (0, 200, and 1,500 ppmv). Following these single-cycle experiments, a sample of the ZT-4 sorbent was sulfided and regenerated in a 10-cycle sequence at 650 °C and with 1,500 ppmv HCl in the fuel gas stream. Critical review of the experimental data did not indicate any adverse effects of the multicycle reactions either on the sorbent physical structure or upon its desulfurization capability. In fact, the attrition resistance of the 10-cycle reacted material was significantly higher than that of the fresh sorbent. Furthermore, in all the experiments, the chloride material balance was consistently over 90 percent, indicating an excellent accuracy of analytical technique used for chloride analysis.

During the third quarter of the project, attention was directed at 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 developed by the Institute of Gas Technology in Chicago is now being marketed by Tampella Power of Finland. A second block-set of experiments was performed similar to those described above, except that the upper level of HCl in the fuel gas was established at 800 ppmv. This value was computed to be the potential concentration of HCl expected in the product stream of a "U-Gas" air-blown gasifier fed with an Illinois coal having a 0.6 percent chlorine content.

The series of the "U-Gas" experiments evaluating the desulfurization behavior of the sorbent at 538 and 650 °C revealed no harmful effects traceable to the presence of the HCl. However, excessive zinc vaporization occurred during the 750 °C experiments, which is attributed to the relatively low steam content of the incoming fuel-gas stream.

A 10-cycle set of sulfidation/regeneration at 650 °C and 800 ppmv HCl was completed with a coal gas composition simulating the U-Gas. The results indicated no harmful effects caused by the HCl. In fact, the data indicate that the presence of the HCl increased the H_2S-removal capability of the sorbent. This phenomenon is believed to be caused by the HCl reacting with the sorbent's internal pore structure and creating new reactive surface area.

The experimental work in the fourth and final quarter of this project was devoted to a set of experiments designed to probe some of the significant findings revealed during the performance of the two previous large experiment blocks. Several formulations of the zinc titanate sorbent were prepared, each with the same 1.5 Zn-to-Ti atomic ratio, but containing varying amounts of the bentonite binder. Experiments were conducted at 650 °C in a simulated U-Gas using these sorbent formulations in the presence of 800 ppmv of HCl to determine whether or not the sodium content of the bentonite is responsible for the permanent capture and retention of the chlorine by the sorbent.

These followup experiments indicated that sorbent formulation containing 10 percent bentonite exhibited a severe sorbent degradation most likely stemming from the evaporation of alkali chlorides that were formed by the reaction of HCl with various alkali species present in bentonite. These alkali chloride vapors condensed and deposited in a low-temperature region in the reactor forming a cloudy mist. The reacted sorbent appeared fairly fluffy, perhaps an indication of a loss in its mechanical strength. The sorbent formulations with 0 and 5 percent bentonite did not exhibit this phenomenon.

The following statements summarize the results of this study:

- The HCl in the coal-derived fuel gas does not have any long-term adverse effect on the sorbent's sulfur capture ability, its chemical reactivity, its regenerability, its resistance to attrition or any other of its structural properties.
- The presence of the HCl significantly enhanced the desulfurization efficiency of the sorbent.
- An increase in the sorbent's sulfidation temperature led to higher sulfur-retention capacities and reduced HCl retention by the sorbent. At higher temperatures (e.g., at 650 °C, some chloride was adsorbed on the sorbent surface and was subsequently released during regeneration.
- Some permanent HCl absorption on the sorbent was detected.
- The mechanism for permanent HCl absorption is believed to be a reaction between the Na_2O present in the binder portion of the sorbent.
- A sorbent formulation, composed of nearly pure ZnO, exhibited excessive zinc vaporization.

It is proposed that fillers containing increased concentrations of Na_2O be added to the formulation mix of the mixed-metal sorbent during its preparation. This could provide the modified sorbent with a capability to remove simultaneously both the HCl and the H_2S from the hot coal-gas stream during the hot-gas cleanup step. A further study would then have to be performed to evaluate the effect of this proposed sorbent-structure change on the sorbent's long-term sulfur capture efficacy, regenerability, and attrition resistance.

OBJECTIVES

The overall goal of this research has been to develop attrition-resistant regenerable sorbents to be used in desulfurizing the hot coal-derived gases generated in the integrated-gasification combined cycle (IGCC) and molten carbonate fuel cell (MCFC) power generation systems. The objective of this study was to evaluate the effects and the fate of hydrogen chloride (HCl) during hot-gas desulfurization, a corrosive gas-specie which could be present at levels as high as 1500 ppmv in the coal gas when high-chlorine Illinois coals are gasified. The performance (i.e., chemical reactivity, sulfur capacity, regenerability and attrition resistance) of zinc-based sorbents, specifically the fluidizable zinc titanate sorbents, was evaluated in a bench-scale fluidized-bed reactor using simulated coal gas with and without the HCl gas.

The specific objectives of the research during this 12-month contract were to:

- determine the most probable chemical structures, in addition to the HCl in the effluent gas, to which the chlorine in the coal will react, and to 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 absorption 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 the Southern Illinois University at Carbondale (SIUC) and the Research Triangle Institute (RTI), was designed to investigate the effect of HCl, in concentrations typical of a gasifier fed by high-chlorine Illinois coals, on the fluidizable zinc titanate sorbents. These sorbents have recently been developed by RTI, with 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.

INTRODUCTION AND BACKGROUND

Several IGCC and MCFC power systems employing hot-gas cleanup are now actively being developed to produce electric power from coal. These systems are two of the advanced power generation technologies with a projected coal-to-electricity thermal efficiency of 45 percent or better. One of the key components of each of these power systems is a hot-gas desulfurization system that 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 HTHP desulfurization processes, now under development, employ regenerable mixed-metal oxide sorbents for absorbing the H_2S and COS present in the coal gas, with zinc titanate currently being the leading sorbent candidate. The chemistry of H_2S and COS absorption by zinc titanate sorbents is described elsewhere (Gupta and Gangwal, 1992).

Some of Illinois coals, in addition to having a high sulfur content, also have a high chlorine content. During gasification, some of the chlorine present in the coal is scavenged by the coal-ash residue, but most is converted to gaseous HCl. The HCl content 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 evaluated before high-chlorine Illinois coals can be considered as a viable fuel for these processes.

This study deals with the determination of the effect of HCl on the sulfur capacity, chemical reactivity, regenerability and attrition resistance (mechanical strength) of the zinc titanate sorbent. Also, the fate of the HCl itself during the hot gas desulfurization system must be tracked to identify where and in what form the chlorine is removed from the process.

Knowledge regarding the behavior of chlorine during these hot-gas cleanup processes is of paramount importance for the commercialization of IGCC and MCFC power-generation technologies. Deficiencies in this state-of-knowledge must be addressed if Illinois coals with high chlorine concentrations are to be used as feed to these high efficiency and environmentally acceptable coal-conversion technologies of the future.

It is hoped that this study will aid in the future development of a promising class of sorbents that will remove H_2S and COS to high degrees from coal gas containing HCl, without the sorbents or other process conditions undergoing deleterious changes. Such development will result in enhanced, more economically attractive and efficient power generation systems for converting the large reserves of high-sulfur, high-chlorine containing Illinois coals into electricity.

EXPERIMENTAL PROCEDURES

The research work in this project was divided into five tasks 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 were:

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 was conducted at SIUC. This task was subdivided into two study segments. The first was a survey of recent literature references to catalog the existence and effects of chlorine compounds in gasifier fuel gas. The second study involved the thermodynamic/kinetic modeling of the behavior of chlorine chemical-species in a high-temperature desulfurization process system.

A comprehensive literature survey of recent literature references, including technical papers, government and industrial reports, and conference proceedings, was assembled to document reported or speculated potential behavior of chlorine chemical species in gasifier effluent-gas atmospheres. Of importance were 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.

A second portion of this task involved the assembling and correlating of the literature-reported thermodynamic and kinetic data that were 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. Of great concern were 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. The search work of this literature review was expanded to also explore possible removal techniques for HCl prior to, during, or following the desulfurization step.

Task 2: Experimental Test Plan

Under this task, a detailed "Experimental Test Plan" was prepared. This plan described the details of the major proposed bench-scale tests that were carried out during the course of the project. A preliminary version of the test plan was delivered to the Center for Research on Sulfur In Coal (CRSC) in mid-October 1991, 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 1991.

Task 3: Modifications in Existing Test Facility

Because hydrogen chloride is a highly corrosive gas that severely attacks stainless steel in the presence of steam, the previously used bench-scale test facility at RTI was extensively modified. The flow scheme of the bench-scale experimental reactor system is shown in Figure 1.

In place of the previous stainless steel reactor, a 1-in. (26 mm) I.D. quartz reactor system was designed and constructed. Housed in a three-zone furnace, the new reactor had an inside diameter of 26 mm, a 2-mm wall thickness, and a total length of 44 in. (112 cm). Teflon parts replaced those components exposed to the HCl at the lower (<200 °C) temperatures.

As shown in Figure 1, the dry coal gas (without steam) was introduced from a side arm in the reactor. The bottom section of the quartz reactor was tightly packed with quartz wool and acted as a preheater for the inlet coal gas and the incoming water solution. Originally, the HCl was introduced into the reactor chamber through a capillary as a dilute HCl-in-water solution, metered in using a spring pump. Severe corrosion problems in the pump seals led to a design change. The water was still metered in with a syringe pump, but the HCl was injected as a dry gas premixed with nitrogen from a pressurized cylinder. Much care was necessary to keep the HCl-gas delivery lines absolutely free of moisture, purging liberally and completely with bone-dry nitrogen before and after the test runs.

The system was operated in a bubbling fluidized-bed mode. A coarse porous quartz fit at the bottom of the reactor bed was used as the distributor for the simulated HCl-containing coal gas. All the original stainless steel lines in and out of the reactor were replaced by quartz lines in order to prevent corrosion. Approximately 15 in. of freeboard served as a cooling zone for the gas exiting the reactor. A special Inconel alloy thermocouple constantly monitored the sorbent-bed temperature.

The partially cooled (200 to 300 °C) product gas from the reactor was sent to a glass condenser in which all the water and HCl vapors were condensed and collected in a catch pot. A slipstream of the non-condensable gases was sent to a gas chromatograph (GC) system for analysis. The rest of the gas exiting the condenser was vented through a hood and a blower. A positive pressure of

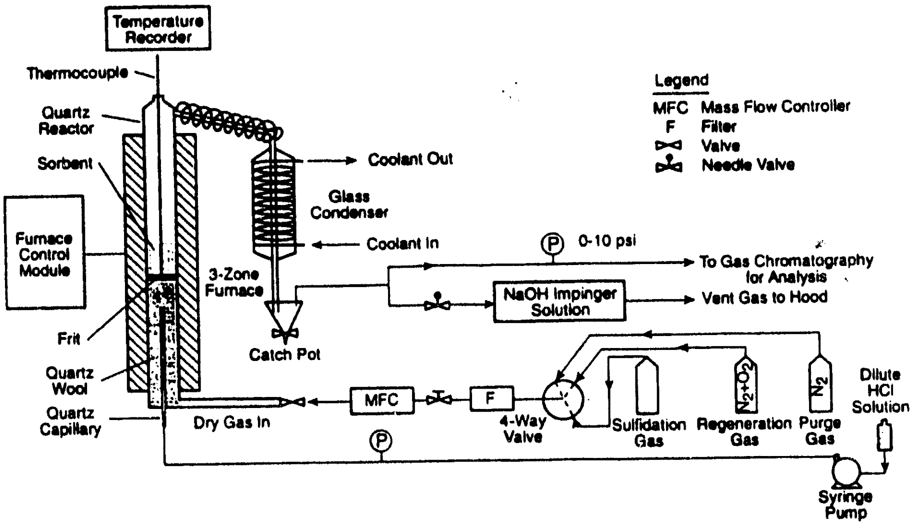


Figure 1. Bench-scale experimental test setup

approximately 5 psig was maintained using a pressure-regulating valve downstream of the GC analysis system to ensure the slipstream sample flow to the GCs.

The GC system, which was built with DOE/METC funds, consisted of two GCs, a Carle Series 400 AGC with a thermal conductivity detector (TCD) and a Varian Model 3300 with a flame photometric detector (FPD). Each GC was connected separately to Spectra Physics SP4270 integrators that continuously recorded the analyses of the gas streams. Multiple GC sampling valves and dual loops in the Varian FPD provide the capability of measuring H_2S and COS from 1,500 ppmv to less than 0.1 ppmv every 2 minutes. A Chromosil-310 column was used to separate these gaseous components at 50 °C. Prior to each experimental run, the Varian GC was calibrated using a standard gas sample. The concentrations of H_2S, SO_2, and the other bulk gases (H_2, CO_2, N_2, O_2, CH_4 and CO) were measured every 25 minutes with the Carle-TCD. A complete description of the GC system is given elsewhere (Gupta and Gangwal, 1992).

The dry gases required for sulfidation and regeneration of the sorbent were bought premixed in cylinders. A four-way valve, shown in Figure 1, was used to pass the appropriate gas through a pre-calibrated electronic mass flow controller into the bottom of the reactor bed. A nitrogen purge gas was used during the pre-run heating and the post-run cooling of the sorbent bed, and also during the switching between sulfidation and regeneration cycle steps.

After the reactor system was assembled, several startup experiments were performed to demonstrate the operability and reliability of the experimental equipment and all the analytical instruments.

Task 4: Bench-Scale Testing and Analysis

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

A typical bench run consisted of a number of sequential steps. A known weight of the sorbent, approximately 50 to 60 grams in the 100 to 300 µm particle size range, was charged to the reactor. The reactor was heated to the desired gas desulfurization temperature (538° to 750 °C), with a continuous stream of nitrogen passing through the sorbent bed.

The sulfidation of the sorbent (fuel gas desulfurization) was performed by continuously flowing the simulated coal gas through the fluidized bed. The simulated medium-Btu gas contained 1.4 percent

H_2S (14,000 ppmv), while the simulated low-Btu fuel gas contained 0.5 percent H_2S (5000 ppmv). The sorbent sulfidation continued until the H_2S concentration in the reactor exit gas reached 100 ppmv, which was arbitrarily defined as the breakthrough value.

Following the sulfidation, the reactor was switched to the sorbent regeneration mode and heated to the desired temperature under nitrogen flow. Generally, the initial regeneration temperature was set at a value from 50 to 150 °C higher than the sulfidation temperature. Once the desired temperature was attained, the flow of regeneration gas was started. The typical regeneration gas contained 2 to 5 percent O_2 in nitrogen. This regeneration reaction continued until the outlet SO_2 concentration dropped to less than 500 ppmv.

At both the end of the sorbent sulfidation and the end of the regeneration step, a sample of the sorbent was withdrawn and analyzed for its chloride content. Representative samples of the condensate and other gas-stream scrubbing solutions were 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 was 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 were performed primarily to obtain chloride and sulfur material balances. Additional tests were performed on the reacted sorbent to identify changes in chemical reactivity, surface area, particle size distribution, and Zn-to-Ti contents.

The effect of the following specific operating variables was investigated in order to determine the influence of the 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 were performed. The first set of experiments was conducted with a medium-Btu fuel gas, while the second set examined the effects of HCl when processing a low-Btu gas. The third set of experiments, during the last quarter of the project involved a closer examination of the sorptive behavior of a selected number of specially made solid sorbents in which the concentration of the filler, bentonite, was varied. This followup set of experiments was designed to evaluate if the bentonite filler was the active reagent in permanently removing the HCl from the hot fuel-gas stream, as the results from the two block-sets of experiments had implied.

Following this strategy, during the 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. The second block-set of experiments was performed during the project's third quarter and was designed to evaluate the behavior of HCl on the desulfurization of 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 Power of Finland). Both of these gasifiers have been developed at nearly commercial scale and are ideally suited for gasifying the high-sulfur Illinois coals. The compositions of the two laboratory fuel-gas streams simulating these two gasifier products are shown in Table 1.

Two zinc titanate sorbents were originally chosen for this study, both sorbents prepared using RTI's proprietary granulation technique. The sorbent ZO-1 contained essentially pure ZnO with 2 to 3 percent TiO_2 and a suitable binder. This sorbent was selected to establish the role of TiO_2 in the

Table 1. Typical Compositions of Coal-Derived Fuel Gases

Gasifier Type	**Texaco**	**U-Gas**
Oxidant	Oxygen	Air
Fuel Gas	Medium-Btu	Low-Btu
(Volume %)		
H_2	28	13
CO	39	24
CO_2	13	5
H_2O	19	6
N_2	None	52
H_2S*	10,000 ppm	5000 ppm

*Based on 3.5% S in coal.

zinc titanate on chloride removal reactions; however, this sorbent proved chemically unstable at the higher desulfurization operating temperatures and its use was discontinued. The second sorbent evaluated was 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 (Gupta and Gangwal, 1992), this particular zinc titanate sorbent proved the most efficient in high-temperature coal gas desulfurization service.

The originally planned test matrices for each of the Set 1 (medium-Btu "Texaco" gas) and the Set 2 (low-Btu "U-Gas" gas) experiments were designed to examine the zinc titanate sorbents (ZO-1 and ZT-4, described above) at 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, was selected as zero, 200 ppmv and 1500 ppmv. The HCl concentrations for the low-Btu fuel-gas desulfurization were at zero, 200 and 800 ppmv. Experiments at the higher sulfidation temperature of 750 °C (1382 °F) were later added to probe the expected upper temperature limit of sorbent activity. After the completion of each set of single cycle tests, a 10-cycle test was 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 10-cycle test were determined based on the results of the foregoing single-cycle tests.

During the third set of experiments in the summer of 1992, batch quantities of three specially prepared solid sorbents were prepared using RTI's proprietary sorbent preparation method. The same ratio of Zn-to-Ti of 1.5 as in the test sorbent ZT-4 was maintained, but the concentration of the bentonite filler was varied from 0 to 10 percent. It was postulated that the permanent HCl sorption observed during the previous experiments was due to a reaction with the sodium present in the bentonite filler. This mini-set of experiments was designed to prove or disprove this hypothesis, and to probe the concept that adding additional filler and/or another sodium-compound to the Zn-titanate sorbent might allow the sorbent to dechlorinate the fuel gas simultaneously with the high-temperature desulfurization.

Task 5: Reporting

This task consisted 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, an oral presentation describing the project work and results was made to the technical staff of CRSC. A paper describing the results of the project was presented at the CRSC/Illinois Coal Development Board (ICDB) Contractors' Meeting in Urbana, Illinois, on August 4, 1992.

RESULTS AND DISCUSSION

ASSESSMENT OF CHLORINE BEHAVIOR IN COAL GASIFICATION SYSTEMS

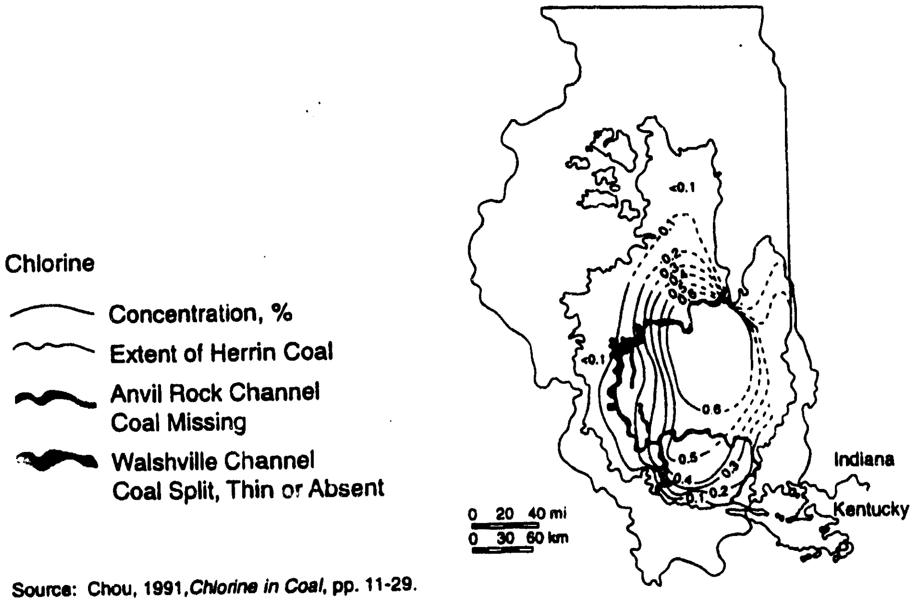
Occurrence of Chlorine in Illinois Coals

Since the beginning of the coal-conversion industry, the presence of chlorine and other trace elements in certain coals has been reported as causing significant deleterious effects to the utilization of these coals (Chou, 1991). Although sulfur was probably the major culprit, a high chlorine content also could have been a major contributor to the reported ultra-corrosive nature of the "sea coals" consumed in the London area in the Middle Ages (Schobert, 1987), the open burning of which led to the enactment of the first air pollution laws. As part of the development of modern boilers which utilized higher and higher combustion flame temperatures, the design engineers and operators began to direct their attention to which of the mineral species in the fuel coals were causing the efficiency-robbing fouling and slagging of the boiler tubes, as well as attempting to better understand the chemical mechanisms of these reactions (Bryers, 1983). Coals that were high in alkalies, sulfur, and chlorine were reported to cause the most difficulties (Gluskoter and Rees, 1964).

Although there is still much debate in the matter, most researchers believe that the majority of coal chlorine exists as chloride ions in the moisture water existing in the internal pore structure of the coal. Raask (1985, 1986) states that chloride salts are rarely found in coal because of the high solubility of sodium, calcium, and other trace metal chlorides in the coal strata waters. He also associates the "inherent" water content, and therefore the dissolved chloride species, with the porosity of the coals. He credits Skipsey (1975) with identifying the direct relationship of the distribution of chlorine content in the coals with the salinity of the associated mine waters. Skipsey (1975) attributes the low chlorine content of high-rank bituminous coals to their low internal porosity, while the lower-rank, more porous bituminous coals could contain over 1 percent chlorine.

A very thorough survey of the distribution of chlorine in Illinois coals was presented by Gluskoter and Rees (1964), with the distribution of other trace elements in Illinois coals examined by Ruch et al. (1974a, 1974b). Chlorine in Illinois Basin coals was found to range from less than 0.1 percent to nearly 0.6 percent. An updated version of Gluskoter and Rees's study which includes more recent data has appeared recently (Chou, 1991). Figure 2, taken from Chou's paper, shows an aerial distribution of chlorine concentration in the Herrin Coal, Illinois Basin, which is situated in much of Illinois and part of Indiana and Kentucky. The contour lines in this figure are drawn to indicate a general trend of increasing chlorine concentration in the seam toward the deep interior of the basin. The highest chlorine coals were found in the south-center portion of Illinois, in the Effingham-Shelby Counties region. These highest chlorine coals were directly associated with the depth of the coal seams, the coal being nearly 1000 ft deep in these regions. The localized depth of this high-chlorine portion of the Herrin (Illinois) No. 6 seam, in this case, was the result of post-formation buckling of the geological strata. Ruch and coworkers (1974b) found that sodium and chlorine had a strong positive correlation, with that correlation more predominant with the younger coals in the Illinois Basin than in the older seams. A recent paper by Bragg and coworkers (1991) at the U.S. Geological Survey attempted to describe the distribution of chlorine concentration in various coals in most regions of the United States.

In studies like those cited above (Bragg et al., 1991; Gluskoter and Rees, 1964; Chou, 1991), there is a potential bias problem built into statistical surveys of coal characteristic data. By nature, the largest number of samples were gathered from easily accessible sources, existing mine sites or core drillings of potential sites to be exploited in the near future. Relatively few samples were obtained from the deep coal seams, those coals possibly lying in brackish waters that could be high



Source: Chou, 1991,*Chlorine in Coal*, pp. 11-29.

Figure 2. Aerial view of distribution of chlorine concentration in Herrin No. 6 coal

in chlorine and other undesirable compounds. Out of the 143 samples examined from the Eastern Interior Coal Region, the maximum chlorine content that Bragg et al. (1991) reported contained only 0.268 percent chlorine as compared to 0.6 percent by Chou (1991). The present day mining operations are rapidly exploiting the low-chlorine coal reserves that still remain accessible to surface mining and medium-depth underground operations.

Most researchers have identified most of the chlorine as residing in the coal as in the ionic form, associated mainly with the inorganic mineral matter or weakly linked to organic cationic sites. It has been noted that washing the coal in a coal preparation plant often yields a product containing a higher chlorine value than the chlorine content of the unwashed coal. This has been attributed to the retention of the chlorine ion in the finer pore structure of the washed coal's organic-matrix during the dewatering portion of the coal preparation process, but may also be caused by high dissolved chloride salts in the coal-washing waters in the preparation plants.

Studies have been made to develop coal-cleaning processes to reduce the coal's chlorine content by hot-water leaching (Daybell and Gilham, 1959; Bettleheim and Hann, 1980; Chen et al., 1991). Over 60 percent of the chlorine can be removed by a combination of hot-water leaching and heat-treatment; however, the technique has not been shown, as yet, to be economically feasible.

A chlorine-leaching study of several lithotypes taken from a single channel sample of a Herrin (Illinois) No. 6 coal indicate that the chlorine leachability may be related to the pore-size distribution, with the finer pore-structure retaining the chloride ion (Demir et al, 1990). In this study, Demir and coworkers (1990) found that the chlorine was concentrated mainly in the vitrinite, with significantly lower concentrations in the roof partings and mineral matter. Sodium, on the other hand, was found mainly in the roof partings and the mineral matter, with a significant portion of the sodium adsorbed onto the surface of the clay minerals. It would seem that, although the coal was exposed to the brackish water, the various sites within the coal structure served to partition the various chemical species from the water; the chlorine was adsorbed to the pore walls of the carbon matrix, while the sodium tends to adhere to the inorganic mineral surfaces in the coal.

Evolution of Chlorine in the Conversion Processes

Most of the studies involving the evolution of chlorine were involved with its reactions in coal-combustion in a mild to highly oxidative atmosphere. Raask (1985) presented a very detailed examination of the evolution reactions of coal chlorine, its volatilization and interactive behavior with volatile sulfur. Summarizing the conclusions of numerous previous investigators, he states that, below 1000 K, chlorine is given off as HCl before the evaporation of NaCl occurs, with some evolution identified at temperatures below 500 K and significant amounts in the 575 to 675 K range. No significant loss of alkalies occurred below 1100 K. Raask (1985) examined the thermodynamics and kinetics of the potential reactions of sulfur oxides and chlorides, since, in an oxidizing atmosphere, SO_2 tends to react with the NaCl forming sodium sulfate and evolving HCl. Among other workers studying the evolution of mineral matter from coal-conversion, Gluskoter and Rees (1964) reported a significant synergistic effect caused by combined interactions of sulfur and chlorine, as compared to the behavior during the devolatilization of chlorine from carbons that did not contain sulfur.

A study by Pinchin (1958) on the thermal decomposition products of some British coals reported that the carbonization of chlorinated coals produced only HCl with reduced amounts of volatile matter, but no chlorinated tar products. Kear and Menzies (1956) reported that the fraction of chlorine passing into the volatile products increases with increasing carbonization temperature, amounting to about 75 percent at 1000 °C.

As O'Brien (1987) noted in an examination of sulfur evolution during coal combustion and gasification, the amount and form of the inorganic gas species are affected by temperature as well as the reaction atmosphere and the path that the volatile species must take inside the gasifier before they reach the final effluent-exit port. For instance, in a countercurrent moving-bed coal-gasifier like the Lurgi-design, the high-temperature oxidizing reactions take place in the bottom zone where the mostly reacted carbon char, and its corresponding mineral matter, is oxidized with steam and oxygen. The gases, possibly containing the evolved trace elements then pass upward through the bed of gasifying solids in a steadily changing cooler and more-reducing atmosphere. In contrast, in the concurrent-downward entrained-bed design of the "Texaco" type, the hot oxidation zone is at the top portion of the gasifier where contact is made with the incoming fresh coal. The final reactions take place at the gasifier bottom where, presumably, the mineral matter in the char is exposed and reacted in a reducing atmosphere. A fluidized-bed gasifier, such as the Winkler design, offers a stirred-pot mixture of temperatures and mineral-reacting atmospheres depending on its operating conditions, such as dense-phase or dilute-phase, complicated by the possible addition of calcium sorbents.

Most researchers assume that the chlorine evolves from the coal matrix as gaseous HCl because of the usually high hydrogen and water content of the gasifying atmosphere. No references have been found describing chlorine evolution during the producer-gas generation of a low-hydrogen, dry coal.

Very few studies have experimentally linked the amount of chlorides evolving from a large-scale coal-gasification system utilizing a high-chlorine feed coal. In a small reactor unit pyrolyzing several United Kingdom coals, Herold et al. (1983) found that between 40 and 60 percent of the coal chlorine was removed by heating at 300 °C in helium for about 24 hours. Periods of isothermal first-evolution of HCl indicate that the release of HCl was controlled by a first-order step which may be either the release of HCl within the coal or a diffusion-controlled transport to the surface. This study involved a low-temperature carbonization in an inert atmosphere.

In an international conference held in 1989 on "Chlorine in Coal" (Stringer and Banerjee, 1991), sponsored by CRSC and the Electric Power Research Institute (EPRI), a number of studies reported the detrimental effect of chlorine on the corrosion of materials of construction. Bakker and Perkins (1991) pointed out that the product-gas from a coal-fired gasifier would contain as much as six times the ppmv concentration of HCl as would the combustion-gas from a coal-fired boiler, due to the different volume-quantity of product-gas produced.

A recent EPRI report prepared by Lockhead (Perkins et al., 1990) presents a detailed study of the interactions of chlorine with various slags on the syngas coolers of entrained slagging gasifiers. Considerable amounts of chloride are commonly found on the heat exchanger surfaces, particularly in syngas coolers which operate with a waterside temperature in the 300 to 500 °C range. These chloride deposits are believed to strongly accelerate aqueous corrosion (pitting, intergranular corrosion, stress corrosion, cracking) of the steel, particularly accelerated when the gasifier system undergoes low-temperature cycling and/or frequent downtimes. Perkins et al., (1990) described the HCl in the coal gas as reacting with the ferric/ferrous species of the deposited slags forming low-temperature melting $FeCl_2$ and $FeCl_3$ melts which cake the slag surface. Other chloride forms of NaCl and NH_4Cl have also been found in coal-gasifier slags, and $CaCl_2$ and KCl would also be expected if the feed-coal were high in these elements.

Regardless of the many reactions described in literature as happening within the structure of the gasifier and boiler slags matrices, the chlorine-containing gaseous reactant or product of the literature-cited reactions has always been implied to be HCl. Therefore, although the quantity of chlorine in the coal-gas stream which would reach the HTHP desulfurization process is unknown because of the scavenging actions of the slag, the gaseous form of the chlorine is still believed to be HCl.

Order-of-magnitude calculations on HCl evolution were made using the data from several literature reported mass balances of low-Btu (the Westinghouse Process) gas-production (Westinghouse, 1973), medium-Btu syngas (the Texaco "Cool-Water" Process) production (Rib, 1989), a Winkler fluidized-bed gasifier in Germany (Engelhard and Adhoch, 1989) and an early theoretical low-Btu theoretical study (Wen, 1973; Wen et al., 1974). If Illinois Basin coals with chlorine contents ranging from 0.1 to 0.6 percent were gasified, and if all the chlorine were converted to HCl gas, the effluent fuel-gas streams exiting the gasifier could contain as much as 1500 ppmv, depending on the type and composition of the fuel-gas product as can be seen from Figure 3. For example, a "Texaco-type" medium-Btu coal-gas could contain as high as 1500 ppmv, while the HCl-content in a low-Btu fuel gas like that produced in an air-blown "U-Gas" gasifier may reach 800 ppmv.

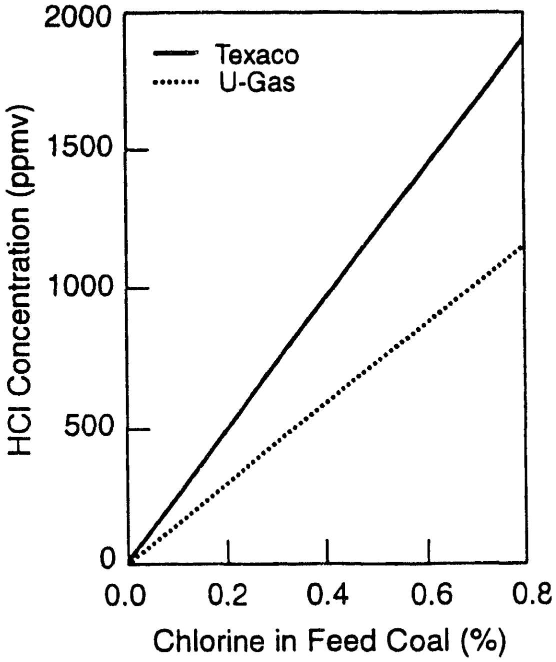


Figure 3. Potential HCl content of gasifier fuel gas

Removal of HCl from Hot Coal Gas

A number of studies have been reported in the literature describing the simultaneous removal of H_2S and HCl from hot coal gases. Metal oxides will probably not be able to remove HCl to ppb levels because of the unfavorable thermodynamics for such an occurrence. In fact, a systematic theoretical study of the potential for chloride to adsorb on various metal oxides was conducted by Physical Sciences, Inc., in the early 1980s under DOE/METC's sponsorship. This potential was evaluated using equilibrium thermodynamics to obtain the lower limits of chloride vapor pressures over the potential sorbents in contact with a gas having the appropriate gasifier composition. Results of this screening showed that the alkali carbonates are the only practical substances that can reduce the total chloride concentration in the coal gas to low ppmv levels at equilibrium and temperatures up to 800 K, and that above 800 K the chloride concentration cannot be reduced to low ppmv levels at equilibrium (Ham et al., 1983).

Based on the above study, Battelle Pacific Northwest Laboratories developed a solid-supported molten salt (SSMS) system for the removal of sulfur compounds and chlorides from coal gas. This system utilized porous lithium aluminate ceramic pellets loaded with a low-calcium salt as the sorbent. In this study, removal of H_2S, COS, and HCl to 1 ppm or less was demonstrated for multiple sorption cycles, and conditions for continued removal of H_2S to less than 1 ppm level were established. However, chloride adsorption by SSMS was so irreversible that regeneration of the spent sorbent was found to be impractical, thereby making the use of the supported sorbent economically unattractive. Also, a sulfate formation upon regeneration was identified to be a serious problem (Lyke and Sealock, 1983).

Studies were also conducted at the Institute of Gas Technology (IGT) to develop eutectic mixtures of molten alkali carbonates to reduce HCl to ppb levels. One molten carbonate had a chemical composition of 52 percent Li_2CO_3 and 48 percent Na_2CO_3. This eutectic mixture melted at 488 °C (910 °F). Although tests in a fixed-bed reactor showed that this compound reduced the HCl level of gas from 400 ppmv to less than 1 ppmv, it proved difficult to regenerate in practice because of the very high volumes of gas and very high temperatures required to reverse the reaction between HCl and molten carbonates. In addition to this, the high costs associated with the sorbent and disposal of spent sorbent in an environmentally acceptable manner led to poor process economics. Furthermore, the sorbent did not exhibit a high degree of reactivity for H_2S (Anderson et al., 1984). Hence, further process development efforts were terminated.

Process studies for chloride removal from hot gas streams were also carried out at SRI International under the sponsorship of DOE/METC. Thermodynamic calculations indicated and the experimental results of this study confirmed that sodium carbonate-based sorbents can reduce the level of HCl in coal gas to about 1 ppmv at 550 to 650 °C. SRI investigated three sorbents, Katalco Chloride Guard 59-3, shortite, and nahcolite, for removal of HCl from coal gas in the temperature range of 523 to 623 °C. All three sorbents reacted rapidly with the HCl vapor and were able to reduce the level of HCl in the simulated coal gas environment to about 1 ppm. The capacity for chloride uptake was found to be a function of both the porosity and the Na_2CO_3 content of the sorbents. The Katalco Chloride Guard, which is a synthetic sorbent commonly used for the removal of chloride from natural gas and light hydrocarbon feedstocks, exhibited a decline in capacity in the presence of steam and at higher temperatures. Both shortite and nahcolite, which are naturally occurring minerals, exhibited reasonable chloride removal performance. However, shortite exhibited a low capacity utilization because of its low porosity. The mineral nahcolite, after calcination, had a chloride capacity of 54 wt percent because of its sodium content and moderate porosity (Krishnan, 1986). Very few details are available for use of nahcolite for HCl removal in the presence of H_2S.

Reaction of Chloride with Hot-Gas Desulfurization Sorbents

Chlorides in a sulfur-laden hot fuel gas do interfere with the sorbent chemical behavior, Gangwal et al. (1988) noted that the presence of HCl in the feed gas significantly decreased the H_2S-absorbing capacity of the zinc ferrite sorbent after the second regeneration cycle.

A limited number of recent studies conducted at DOE/METC with zinc ferrite sorbents in a fixed-bed reactor purported that the presence of HCl (average 112 ppmv) in coal gas had little deleterious short-term effect on the desulfurization performance of zinc ferrite sorbent (Jain and Grindley, 1991). Later, data taken on long-term activity and mechanical strength of zinc ferrite sorbents at DOE/METC showed a 65 percent decrease in the breakthrough time over 10 cycles of sulfidation-regeneration (Grindley, 1990). Limited thermogravimetric analysis (TGA) studies conducted at RTI for Texaco (Gangwal et al., 1990) revealed that chloride was adsorbed on the zinc titanate sorbent surface and was subsequently released during regeneration with very little accumulation of chlorides on the sorbent (~100 to 200 ppm). This finding was in agreement with Grindley's results (Grindley, 1990).

The emphasis of the studies described above was on zinc ferrite sorbents. Since applicability of zinc ferrite sorbents is limited to 550 °C and low severity reducing gases (Gupta and Gangwal, 1991), it becomes necessary to determine the effect of chloride on the zinc titanate sorbents. The study reported here, therefore, primarily deals with the effect of chloride on the performance of zinc titanate sorbents.

ZINC TITANATE SORBENT BEHAVIOR IN MEDIUM-BTU FUEL GAS

The work activity during the second quarter of this project involved the performance of the first block-series of experiments. This sub-study evaluated 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 percent TiO_2 in a suitable binder (labeled ZO-1) and 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 regeneration step. In these experiments, the two sorbents were separately sulfided at three temperatures (538, 650, and 750 °C) and with three concentrations of HCl in the fuel-gas stream (0, 200, and 1,500 ppmv).

Table 2 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 1,500 ppmv of HCl, the percent chloride retentions at 538, 650, and 750 °C were 11.3, 2.57, and 2.27 percent, respectively. A similar trend was observed for the ZO-1 formulation where percent chloride retentions observed were 14.35 and 8.82 percent at 538 and 650 °C temperatures, respectively.

Figure 4 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, indicating that sulfidation reaction is predominantly kinetically controlled. Furthermore, operating the reactor at higher temperatures (>650 °C) would reduce the reactor vessel size significantly due to the faster kinetics.

The effect of HCl level in coal gas is compared in Figure 5 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 enhanced the desulfurization efficiency of the ZT-4 formulation. Reasons for this enhancement are discussed later.

Table 2. Test Conditions and Chloride Retentions During 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

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

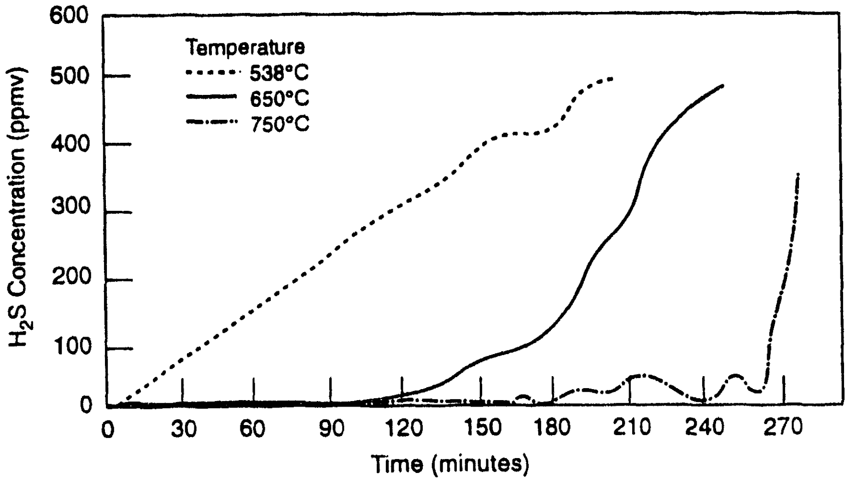


Figure 4. H_2S breakthrough curves at various temperatures. (ZT-4 in Texaco Gas containing 1500 ppm HCl)

Preliminary results indicated that excessive zinc vaporization occurred when the low Ti/Zn sorbent (ZO-1) was exposed to the higher temperatures. Because of this, we did not continue extensive study of this sorbent during the rest of this project.

10-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 high corrosion interfered with the pumping of the concentrated aqueous-HCl solution into the reactor chamber.

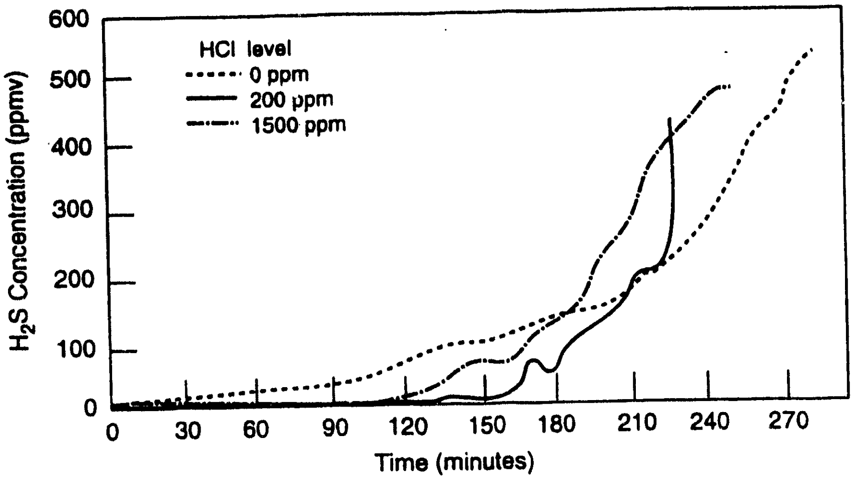


Figure 5. H_2S breakthrough curves at various HCl levels.
(ZT-4 in Texaco Gas at 650 °C)

Figure 6 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 were encountered during Cycle 2 which are believed to be primarily responsible for a rather early breakthrough shown in Figure 6. Nevertheless, during all 10 cycles, the prebreakthrough H_2S level was consistently below 20 ppmv. This indicates that the presence of 1,500 ppmv of HCl does not affect the long-term chemical reactivity of the sorbent.

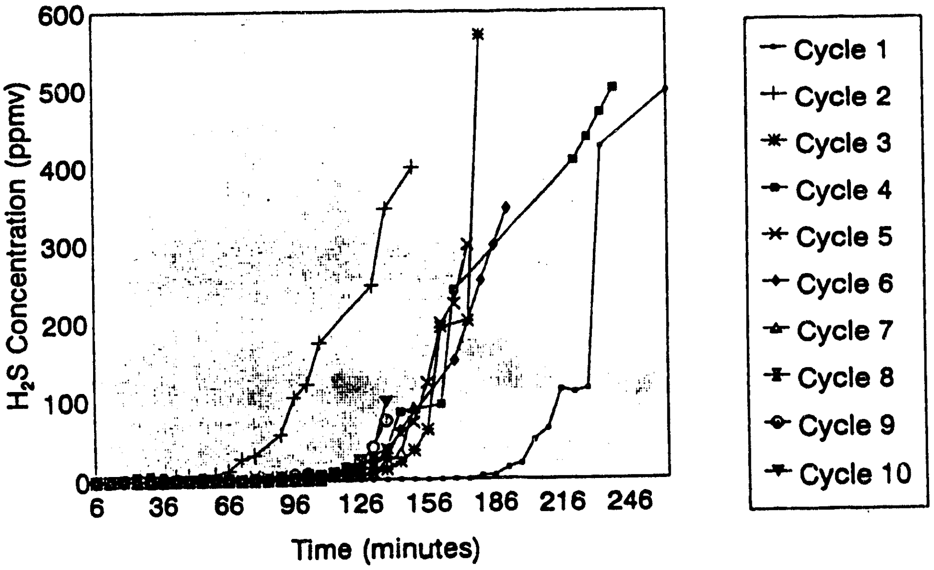


Figure 6. Breakthrough behavior of ZT-4 during 10-cycle testing in Texaco gas; 1500 ppm HCl; 650 °C

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.

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 3. The particle and pore size distribution remained unchanged. X-ray diffraction (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 percent loss due to attrition for the reacted material as opposed to 32.2 percent 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.

Table 3. 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[e]
XRD phases[d]	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)

ZINC TITANATE SORBENT BEHAVIOR IN LOW-BTU FUEL GAS

Following the successful completion of first block-series of experiments with Texaco gas, the work activity during the third quarter of this project involved the performance of the second block-series of experiments. This sub-study evaluated the effect of HCl in the desulfurization of a low-Btu fuel gas (simulating the product gas from a "U-Gas" fluidized-bed, air-blown gasifier).

Single-Cycle Tests

Nine experiments were performed involving a single sulfidation reaction of the sorbent, followed by the regeneration step. In these experiments, batches of the sorbent were sulfided at three temperatures (538, 650, and 750 °C) and with three concentrations of HCl in the fuel-gas stream (0, 200, and 800 ppmv).

The series of experiments evaluating the desulfurization behavior of the sorbent at 538 and 650 °C revealed no harmful effects traceable to the presence of the HCl. However, excessive zinc vaporization occurred during the 750 °C experiments, which is attributed to the relatively low steam content of the incoming fuel-gas stream. The low steam in coal gas made it highly reducing, which in turn led to instability in the zinc/zinc oxide/zinc sulfide solids reactions, a chemical equilibrium effect of the bulk gas composition.

Figures 7 and 8 show the H_2S breakthrough curves at 538 and 650 °C, respectively, for three levels of HCl in coal gas, i.e., 0, 200, and 800 ppm. As can be seen from these figures, the sorbency of zinc titanate is significantly enhanced due to the presence of HCl in the coal gas at both temperatures. Higher concentrations of HCl led to significantly better H_2S removal efficiencies at both these temperatures. The dimensionless time (t^*) in Figures 7 and 8 is defined as the ratio of actual time to the total time that will be required to convert all the ZnO in the sorbent into ZnS. Hence,

$$t^* = \frac{\text{Actual time}}{\text{Mol of ZnO in the reactor/Molar inlet flow rate of } H_2S} .$$

According to the above definition, at $t^*=1$, all the ZnO will convert to ZnS. However, in practice, t^* varies between 0.3 and 0.6. Thus, t^* is a direct measure of the sorbent utilization.

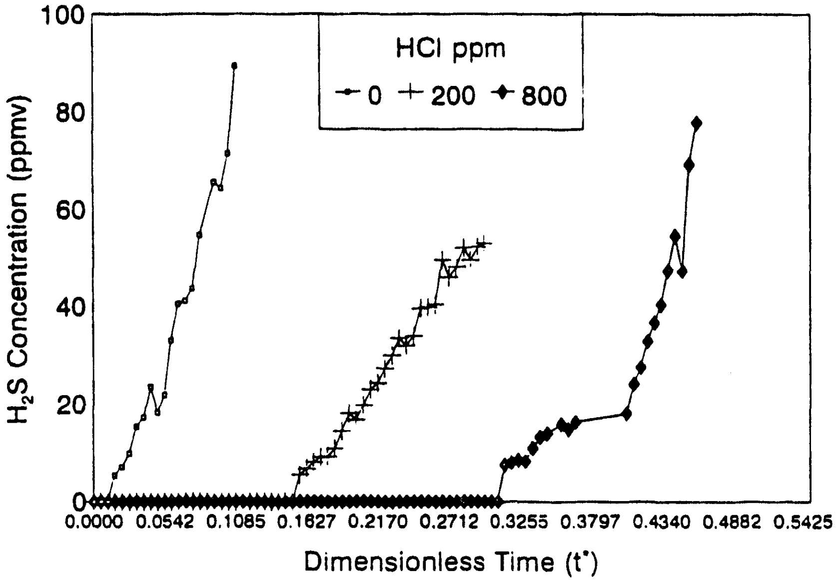


Figure 7. H_2S breakthrough curves for U-gas system (Inlet gas temperature = 538 °C)

A comparison of breakthrough behaviors at 538 and 650 °C for two HCl concentration cases, namely 200 and 800 ppm, indicated a significantly higher reactivity at 650 °C as compared to 538 °C, indicating a kinetic control of the sulfidation reaction.

Chloride Material Balance

During each single-cycle test, five samples were collected for chloride analysis. These samples included sulfided sorbent, regenerated sorbent, condensate sample after sulfidation, impinger solution samples after each sulfidation and each regeneration. These samples were analyzed for chloride using an ion chromatograph.

Table 4 shows the HCl distribution as determined by chloride material balance in sorbent, condensate, and impinger. As can be seen, greater than 90 percent material balance is obtained for the Runs 4, 5, and 6, whereas for Run No. 7, only 61.1 percent of HCl (relative to total amount fed) could only be accounted for. The reasons for the poor material balance for this run are not obvious.

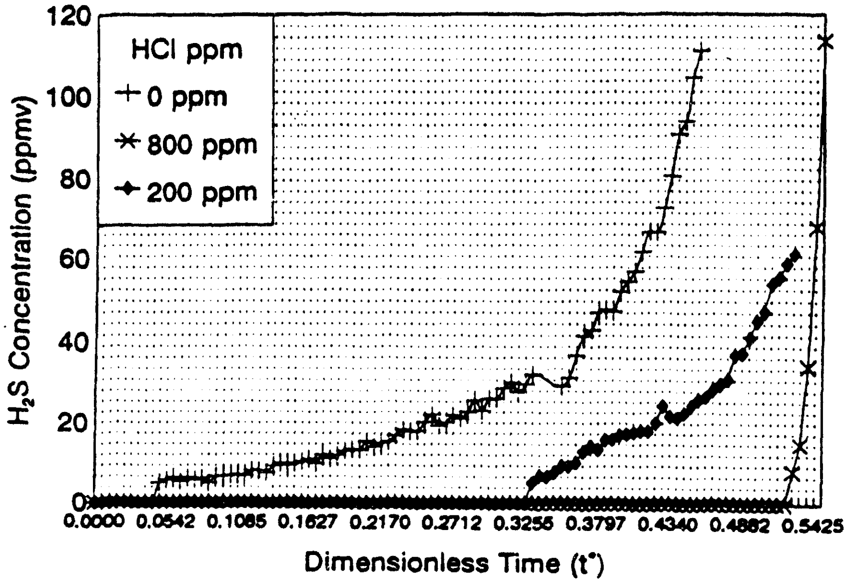


Figure 8. H_2S breakthrough curves for U-gas system (Inlet gas temperature = 650 °C)

TABLE 4. HCl DISTRIBUTION FOR U-GAS RUNS

			HCl Content (ppmv)		HCl Distribution (% of Feed)			
Run No.	Temp (°C)	HCl Content of Feed (ppmv)	Sulfided Sorbent	Regenerated Sorbent	Sorbent	Condensate	Impinger	Total
4	538	200	734	571	22.1	72.3	3.3	97.7
5	650	200	303	356	5.2	82.4	6.1	93.7
6	538	800	1053	289	5.1	76.6	11.1	92.8
7	650	800	323	304	2.0	50.8	8.3	61.1

A number of interesting observations can be made from the data reported in Table 4. It is clear that at 538 °C, some of the HCl reacts with ZnO to form $ZnCl_2$ which converts back to ZnO during subsequent regeneration, giving rise to HCl. At 650 °C, however, the absorption of HCl by the sorbent appears to be permanent in a concentration of about 300 ppmw and very little, if any, HCl absorption takes place via $ZnCl_2$ formation. These observations are in direct agreement with thermodynamic predictions as will be discussed later.

10-Cycle Test

Following the completion of nine single-cycle tests as described above, a 10-cycle test was performed with U-Gas at 650 °C with 800 ppmv of HCl in the gas to determine any deleterious effect of HCl on the long-term chemical reactivity of the sorbent. A number of problems were encountered during this run. Severe plugging of reactor lines and GC sampling system by the zinc vapors that evolved during a 750 °C run (described earlier) offered a number of operational problems. As a result, the GC sampling valves and the back pressure regulator were replaced.

Figure 9 shows the breakthrough curves for cycles 1 to 10. As can be seen, the breakthrough sulfur capacity during the first cycle is higher than the other nine cycles. The prebreakthrough HCl level was consistently below 10 ppm in all the 10 cycles.

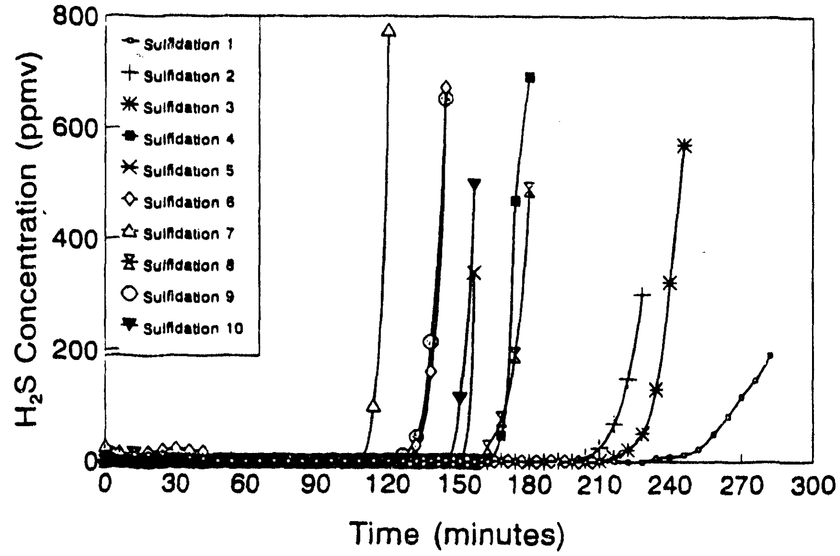


Figure 9. Breakthrough curves for ZT-5
(U-sulfidation gas at 650 °C)

During this 10-cycle test, after each regeneration, a small sorbent sample was withdrawn from the reactor for chloride analysis. Figure 10 shows the chloride content of the regenerated sample as a function of cycle number. As can be seen, the average chloride content of the sorbent during each

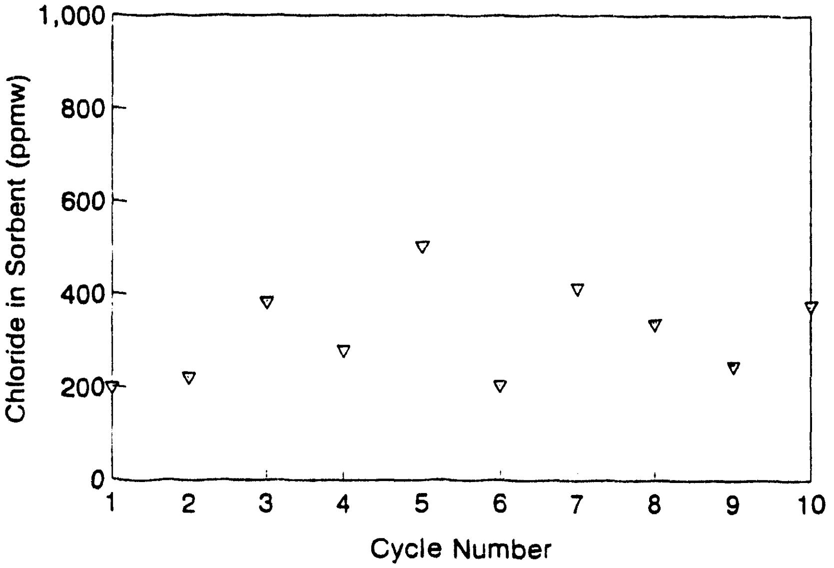


Figure 10. Chloride retention during 10 cycles
(U-gas; 650 °C; 800 ppmv HCl in fuel gas)

of the 10 cycles remains around 300 ppmw. XRD analysis of 10-cycle regenerated sample did not indicate any presence of $ZnCl_2$. Therefore, it is believed that this chloride absorption is due to the formation of alkali chlorides. The bentonite binder used during the sorbent preparation is a source of alkali in the sorbent. Preliminary estimates of chloride absorption by sorbent via reaction of Na indicate that up to 650 ppmv of chloride can be retained just by NaCl formation. Thus, it is strongly believed that at 650 °C, the primary mechanism of chloride retention by the sorbent is reaction between sodium oxide and HCl. NaCl will not convert to Na_2O during regeneration because of the absence of steam as discussed later.

THERMODYNAMIC ANALYSIS OF CHLORIDE RETENTION

Presence of HCl in coal gas may lead to the following chemical reaction:

$$ZnO + 2HCl \rightarrow ZnCl_2 + H_2O \ . \tag{1}$$

Since $ZnCl_2$ in the 500 to 750 °C temperature range is liquid and therefore has significant vapor pressure, it will tend to escape from the sorbent. However, the thermodynamics of the above reaction is not very favorable. Estimates of the equilibrium HCl concentration as a function of steam content in the simulated U-Gas composition for two cases, 800 and 200 ppm HCl in the inlet gas, were made. For the 5 percent steam case used in this study, the extent of HCl removal possible is fairly low. For example, at 900 K (623 °C), the equilibrium HCl level is 681 ppm for a feed gas containing 800 ppm HCl.

It is hypothesized that the $ZnCl_2$ formed by Reaction (1) subsequently reacts with H_2S via the following reaction:

$$ZnCl_2 + H_2S \xrightarrow{K} ZnS + 2HCl \ . \tag{2}$$

The Gibbs force energy (ΔG) and equilibrium constant (K) values for Reaction (2) at various temperatures are listed in Table 5. The thermochemical data needed to estimate ΔG are directly taken from Knacke et al. (1991).

Table 5. Gibbs Free Energy and K Value for Reaction (2)

Temperature (K)	ΔG (J/mol)	Equilibrium Constant (K)
800	-63,996	15,837
900	-59,968	3,134
1000	-56,051	870
1100	-52,238	309

The relatively high equilibrium constant values as shown in Table 5 will force Reaction (2) to go to completion almost instantaneously, thus allowing more $ZnCl_2$ formation by Reaction (1). Since formation of $ZnCl_2$ is more favorable at 538 °C than at 650 °C, the reaction of H_2S with $ZnCl_2$ at 538 °C will be more pronounced as compared to 650 °C. This can be clearly seen in Figure 7 which shows the effect of HCl concentration on the H_2S breakthrough behavior at 538 °C. $ZnCl_2$ being in the liquid phase in the temperature range of 500 to 750 °C is more accessible to H_2S to react than ZnO which is a solid. A surface layer of $ZnCl_2$ is always present for H_2S to react. This mechanism, therefore, explains the enhancement in the breakthrough capacity of the sorbent.

Thus, higher levels of HCl in the coal gas lead to higher $ZnCl_2$ concentrations and hence to more rapid removal of H_2S via Reaction (2).

On the other hand, the thermodynamics of HCl reaction with sodium oxide which may be present in the sorbent through bentonite is extremely favorable. The reaction

$$Na_2O + 2HCl \overset{K}{\rightarrow} 2NaCl\ (s) + H_2O\ . \tag{3}$$

almost goes to completion. The equilibrium constant values calculated using the thermochemical data of Knacke et al. (1991) for Reaction (3) are shown in Table 6. Based on the K values shown in Table 6, Reaction (3) is almost irreversible. Also, the value of K decreases with an increase in temperature, indicating higher HCl absorption at lower temperatures. This is seen experimentally as indicated by data reported in Tables 2 and 4. Thus, the sodium oxide containing materials have a potential to remove HCl down to very low levels. After all, use of nahcolite, a sodium carbonate mineral, for HCl removal is based on this principle.

Table 6. Equilibrium Constants for Reaction (3)

Temp (K)	800	900	1000	1100
K	6.7×10^{24}	3.1×10^{21}	7×10^{18}	5.5×10^{16}

The next issue that needs to be addressed is what happens with NaCl formed in the sorbent during regeneration. Technically, regeneration of NaCl is possible in the presence of SO_2 under strong oxidizing conditions via the following reaction:

$$NaCl + SO_2 + \frac{1}{2}O_2 + H_2O \rightarrow Na_2SO_4 + 2HCl\ . \tag{4}$$

Sodium chloride can thus be converted into sodium sulfate in the presence of SO_2, O_2, and steam, and HCl is evolved in the regenerator off-gas. Sodium sulfate is readily reduced by H_2 present in coal gas into Na_2O.

$$Na_2SO_4 + 4H_2 \rightarrow Na_2O + H_2S + 3H_2O\ . \tag{5}$$

No data are available on the kinetics of Reactions (4) and (5) and it may be true that these reactions are slow and no significant regeneration takes place. In that case, NaCl will remain in the sorbent structure.

REACTION OF HCl WITH FILLER PORTION OF THE SORBENT

Following the successful completion of first two block-series of experiments with medium- and low-Btu fuel gases, the experimental work in the fourth and final quarter of this project was devoted to several mini-sets of experiments designed to probe some of the significant findings revealed in the earlier part of this project. For instance, the role of sodium in the zinc titanate sorbent as an HCl scavenger was investigated.

As discussed earlier, three zinc titanate sorbent formulations were prepared using RTI's proprietary granulation technique. The same Zn-to-Ti ratio (1.5) as in the test sorbent ZT-4 was maintained, but the concentration of the bentonite filler was varied from 0 to 10 percent. The sorbent formulations that were prepared had a bentonite content, of 0, 5, and 10 percent. These three sorbents were tested in our bench unit with U-Gas containing 800 ppm HCl at 650 °C using the test procedures described earlier. During this testing, it was observed that the sorbent formulation containing 10 percent bentonite lost its mechanical strength and appeared like a fluffy material. Also the reactor walls were coated with a white cloudy substance in low temperature regions. It is believed that reaction of HCl with bentonite formed NaCl which might have destroyed the sorbent structure due to its appreciable vapor pressure at 760 °C, at which regeneration took place. Furthermore, silica present in bentonite might have reacted with HCl to form a silica-chloride complex (e.g., $SiCl_4$). The formulations with 0 and 5 percent bentonite showed no degradation in their structure. Therefore, it appears that an upper limit exists on how much bentonite can be added in the sorbent for desulfurizing fuel gas from high chlorine coals principally because of the instability of silica at high temperatures.

CONCLUSIONS

The project tasks, as originally proposed, have been completed on schedule. In addition to a literature survey concerning the behavior of chlorine in coal-gasification systems, the major work activity centered on bench-scale experimentation in a fluidized-bed reactor system. In these experiments, hot gas-mixtures (538 to 750 °C) simulating the products from coal-fed gasifier processes and containing H_2S and HCl, were contacted with a zinc titanate sorbent which is currently one of the most promising near-commercial candidates as a hot-gas desulfurizing agent.

The specific objectives of this study were to determine the effect of HCl concentrations on the physical performance of the sorbent and to determine the effect of the HCl on the rate of the H_2S removal. It was found desirable to conduct a material balance of the chloride in the various streams entering and leaving the hot-gas desulfurization system, and to determine if and how much chloride is permanently retained by the solid sorbent following the regeneration step.

During the first quarter of this project, the "Experimental Test Plan" was prepared and submitted to CRSC. The equipment arrangement was described in this detailed test plan document. Details of the major operating conditions and experimental procedures to be used in the initial two block-sets of experiments were also discussed in the test plan. Also, during this time period, a bench-scale reactor system was designed, constructed and tested 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-sets of experiments. This sub-study evaluated 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). During the examination of one of the sorbents, which contained essentially pure zinc oxide with only 2 to 3 percent TiO_2 in a suitable binder (labeled ZO-1), excessive zinc vaporization occurred at the higher temperatures. Because of this sorbent loss, this particular sorbent was not used in any experiments during the rest of the project.

Eleven experiments were performed involving a single sulfidation reaction of the sorbent (labeled ZT-4), which contained ZnO and TiO_2 in a molar ratio of 1.5. In these experiments, aliquots of the sorbent were sulfided at three temperatures (538, 650, and 750 °C) and with three concentrations of HCl in the fuel-gas stream (0, 200, and 1,500 ppmv). Following these single-cycle experiments, a sample of the ZT-4 sorbent was sulfided and regenerated in a 10-cycle sequence at 650 °C and with 1,500 ppmv HCl in the fuel gas stream. Critical review of the experimental data did not indicate any adverse effects of the multicycle reactions either on the sorbent physical structure or upon its desulfurization capability. In fact, the attrition resistance of the 10-cycle reacted material was significantly higher than that of the fresh sorbent. Furthermore, in all the experiments, the chloride material balance was consistently over 90 percent, indicating an excellent accuracy of analytical technique used for chloride analysis.

During the third quarter of the project, attention was directed at 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 developed by the Institute of Gas Technology in Chicago is now being marketed by Tampella Power of Finland. A second block-set of experiments was performed similar to those described above, except that the upper level of HCl in the fuel gas was established at 800 ppmv. This value was computed to be the potential concentration of HCl expected in the product stream of a "U-Gas" air-blown gasifier fed with an Illinois coal having a 0.6 percent chlorine content.

The series of the "U-Gas" experiments evaluating the desulfurization behavior of the sorbent at 538 and 650 °C revealed no harmful effects traceable to the presence of the HCl. However, excessive zinc vaporization occurred during the 750 °C experiments, which is attributed to the relatively low steam content of the incoming fuel-gas stream.

A 10-cycle set of sulfidation/regeneration at 650 °C and 800 ppmv HCl was completed with a coal gas composition simulating the U-Gas. The results indicated no harmful effects caused by the HCl. In fact, the data indicate that the presence of the HCl increased the H_2S-removal capability of the sorbent. This phenomenon is believed to be caused by the HCl reacting with the sorbent's internal pore structure and creating new reactive surface area.

The experimental work in the fourth and final quarter of this project was devoted to a set of experiments designed to probe some of the significant findings revealed during the performance of the two previous large experiment blocks. Several formulations of the zinc titanate sorbent were prepared, each with the same 1.5 Zn-to-Ti atomic ratio, but containing varying amounts of the bentonite binder. Experiments were conducted at 650 °C in a simulated U-Gas using these sorbent formulations in the presence of 800 ppmv of HCl to determine whether or not the sodium content of the bentonite is responsible for the permanent capture and retention of the chlorine by the sorbent.

These followup experiments indicated that sorbent formulation containing 10 percent bentonite exhibited a severe sorbent degradation most likely stemming from the evaporation of alkali chlorides that were formed by the reaction of HCl with various alkali species present in bentonite. These alkali chloride vapors condensed and deposited in a low-temperature region in the reactor forming a cloudy mist. The reacted sorbent appeared fairly fluffy, perhaps an indication of a loss in its mechanical strength. The sorbent formulations with 0 and 5 percent bentonite did not exhibit this phenomenon.

The following statements summarize the results of this study:

- The HCl in the coal-derived fuel gas does not have any long-term adverse effect on the sorbent's sulfur capture ability, its chemical reactivity, its regenerability, its resistance to attrition or any other of its structural properties.
- The presence of the HCl significantly enhanced the desulfurization efficiency of the sorbent.
- An increase in the sorbent's sulfidation temperature led to higher sulfur-retention capacities and reduced HCl retention by the sorbent. At higher temperatures (e.g., at 650 °C) some chloride was adsorbed on the sorbent surface and was subsequently released during regeneration.
- Some permanent HCl absorption on the sorbent was detected.
- The mechanism for permanent HCl absorption is believed to be a reaction between the Na_2O present in the binder portion of the sorbent.
- A sorbent formulation, composed of nearly pure ZnO, exhibited excessive zinc vaporization.

It is proposed that fillers containing increased concentrations of Na_2O be added to the formulation mix of the mixed-metal sorbent during its preparation. This could provide the modified sorbent with a capability to remove simultaneously both the HCl and the H_2S from the hot coal-gas stream during the hot-gas cleanup step. A further study would then have to be performed to evaluate the effect of this proposed sorbent-structure change on the sorbent's long-term sulfur capture efficacy, regenerability, and attrition resistance.

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FINAL PROJECT MANAGEMENT REPORT
September 1, 1991, through August 31, 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, as originally proposed, have been completed on schedule. The literature survey and chlorine-behavior study (Task 1) continued throughout the year and has been summarized in the project's Final Technical Report. The work activity during the first quarter of the project was devoted to preparing a Project Test Plan (Task 2) and to modifying the bench-scale fluidized-bed reactor system, previously constructed at RTI, to perform in the highly corrosive HCl environment (Task 3).

The work activity during the second and third quarters involved the performance of 22 experiments in the bench-scale fluidized-bed reactor, this work representing the two major block-sets of planned experiments in the project (Task 4). The first sub-study consisted of 12 experiments designed to evaluate of the effect of HCl on zinc titanate sorbent activity during the desulfurization of a medium-Btu fuel gas (simulating the product gas from a "Texaco" entrained-bed, oxygen-blown gasifier). The second set of 10 experiments was designed to examine the effect of HCl on zinc titanate sorbent activity during the desulfurization of a low-Btu fuel gas (simulating the product gas from a "U-Gas" fluidized-bed, air-blown gasifier). All of the experiments, except two, examined the effects of temperature and HCl concentration on the sorbent activities in a single sulfidation-regeneration cycle of reactions. The last experiment in each of the two sub-sets involved exposing the zinc titanate sorbent to the respective coal gas ("Texaco" or "U-Gas") in a 10-cycle succession of sulfidation and regeneration reactions.

In the final quarter of this 1-year project, a set of experiments was performed in which three special sorbents were prepared and reacted in the bench-scale fluidized bed reactor system. Each of these zinc titanate sorbent contained the same 1.5 atomic ratio of Zn-to-Ti as in the test sorbent, ZT-4, but each contained a different portion of the filler bentonite. This experimental mini-set was designed to explore the possible permanent removal of the HCl from the fuel gas into the sorbent, thus providing a combined high-temperature dechlorination and desulfurization process.

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

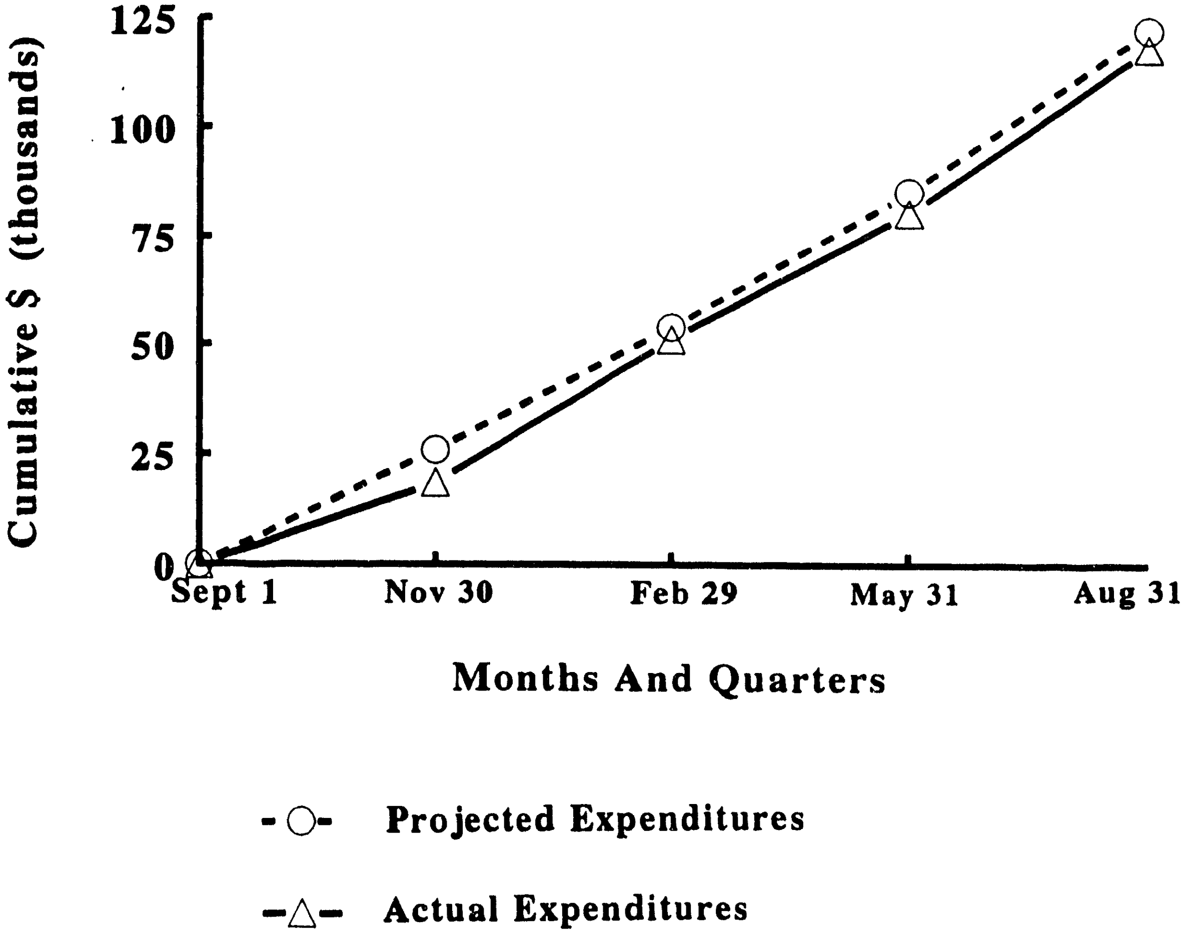
Quarter*	Types Of Cost	Direct Labor	Materials and Supplies	Travel	Major Equipment	Other Direct Costs	Indirect Costs	Total
Sept. 1, 1991 to Nov. 30, 1991	Projected	2,700	0	1,000	0	20,000	2,370	26,070
	Estimated Actual	2,460	0	930	0	13,392	1,679	18,464
Sept. 1, 1991 to Feb. 29, 1992	Projected **	5,400	373	1,300	0	40,327	6,540	53,940
	Estimated Actual	4,940	373	930	0	40,335	4,658	51,236
Sept. 1, 1991 to May 31, 1992	Projected **	14,568	700	2,000	0	59,700	7,697	84,665
	Estimated Actual							
Sept. 1, 1991 to Aug. 31, 1992	Projected **	23,830	1,000	3,000	0	83,378	11,121	122,329
	Estimated Actual	22,230	910	1,093	0	83,250	10.748	118,231

*Cumulative by quarter

**Proposed Budget Adjustment In March 1992

COSTS BY QUARTER

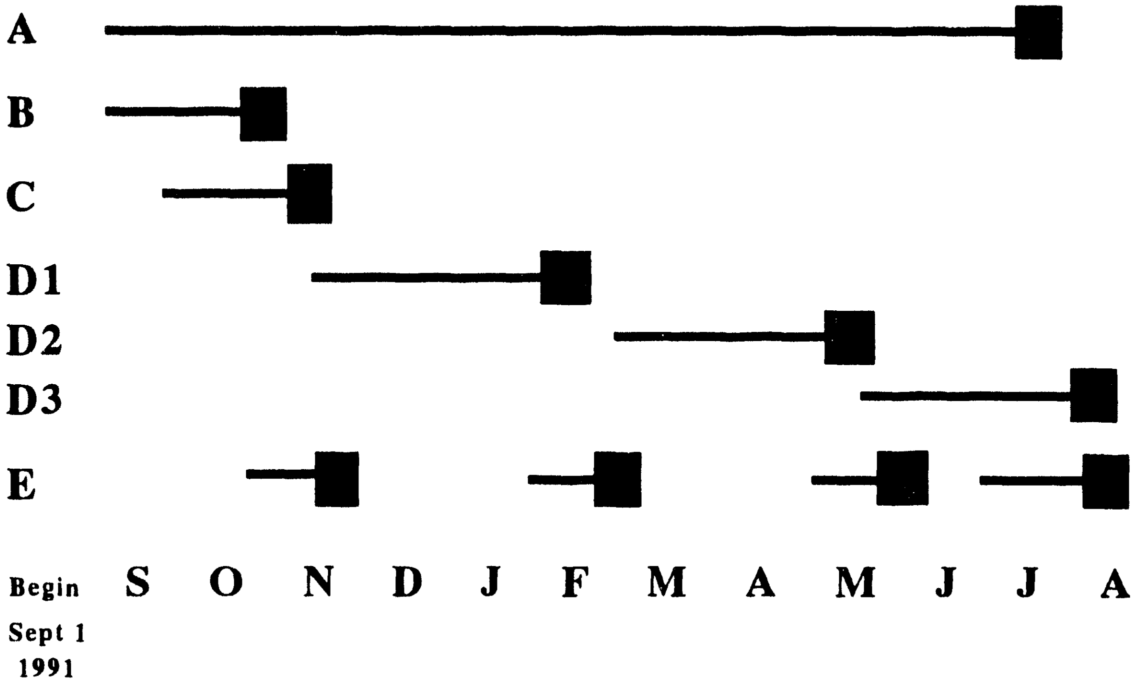
Desulfurization Of Hot Fuel Gas Produced From High-Chlorine Illinois Coals



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)

DATE
FILMED
3/1/94

END