NOVEL GAS CLEANING/ CONDITIONING FOR INTEGRATED GASIFICATION COMBINED CYCLE

BASE PROGRAM

Test Plan
Topical Report

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By

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DISCLAIMER

PATENT STATUS

NOVEL GAS CLEANING/ CONDITIONING FOR INTEGRATED GASIFICATION COMBINED CYCLE

BASE PROGRAM

Program Objective

The objective of this program is to develop and evaluate novel sorbents for the Siemens Westinghouse Power Company's (SWPC's) "Ultra-Clean Gas Cleaning Process" for reducing to near-zero levels the sulfur- and chlorine-containing gas emissions and fine particulate matter ($PM_{2.5}$) caused by fuel bound constituents found in carbonaceous materials, which are processed in Integrated Gasification Combined Cycle (IGCC) technologies.

Background

Sulfur, nitrogen, alkali, and chlorine are naturally present in many forms in a variety of carbon-based materials, which are useful as feedstocks to gasification processes. In IGCC, these nitrogen, sulfur, alkali, and chlorine forms are converted during gasification to gaseous species - mainly ammonia (NH3), hydrogen cyanide (HCN), hydrogen sulfide (H_2S), carbonyl sulfide (COS), sodium/potassium macromolecules, and hydrogen chloride (HCl). The fine particulate matter is defined as that matter with an aerodynamic-equivalent diameter of 2.5 microns and smaller. This program only addresses the secondary $PM_{2.5}$ particles, which are formed in the atmosphere chiefly from gas-phase precursors such as SOx, NOx, and VOCs. Therefore, the primary $PM_{2.5}$ material which is directly emitted for example as fly ash, soot, dust, sea salt particles are not the subject of this program. The gaseous compounds pass directly through filtration and for nitrogen species, through desulfurization control devices. The alkali are known to be controlled by filtration processes, but at temperatures greater than 1250°F have been shown to escape physical separation devices, e.g., cyclone, barrier filters. When the IGCC system is applied to creating synthesis gas for production of liquid products (e.g., methanol, F-T liquids), these species can be both poisonous to downstream processing units and become contaminants in the desired high purity products. When employed for electric power generation, they are oxidized to SOx and NOx in gas turbines. These oxides are acid rain precursors and their emissions into the atmosphere are regulated by federal, state, and local laws.

SOx and NOx emissions are an unavoidable result of IGCC synthesis gas combustion. However, the amount of pollutants can be greatly reduced by using pre-combustion control processes. While sulfur control for IGCC technologies has received much attention and achieved certain successes over the past decades in relation to gas turbine systems, significant improvement (near three orders of magnitude) must be made to avoid poisonous effects on catalytic synthesis gas processing and to use directly in fuel cells technology. Additionally, for use where fuel cells are integrated, HCl becomes a significant actor to causing severe deterioration to various fuel cell materials.

Overall Program Description

The Siemens Westinghouse Power Corporation (SWPC), working with the Institute of Gas Technology (IGT), is developing an innovative process for hot syngas cleanup, the "Ultra-Clean Gas Cleanup Process," to meet the needs of advanced IGCC-based co-production of electric power and chemical or fuel products. It is the development objective of the Ultra-Clean Gas Cleanup System to meet the most stringent cleanup requirements expected in all of the applications (syngas H_2S content < 60 ppbv, HCl content < 10 ppbv, and particulate < 0.1 ppmw). These are contaminant levels below detection limits of conventional measurement instrumentation.

Description of the Ultra-Clean Gas Cleanup Process

A schematic diagram of the "Ultra-Clean Gas Cleanup Process" is illustrated in Figure 1. It has two cleanup stages, integrated in series, to reduce the concentration of the primary gaseous contaminants to about 1-3 ppmv level in a first stage, a moving-bed filter-reactor, and then to the required ppbv level within the second stage, a barrier filter-reactor.

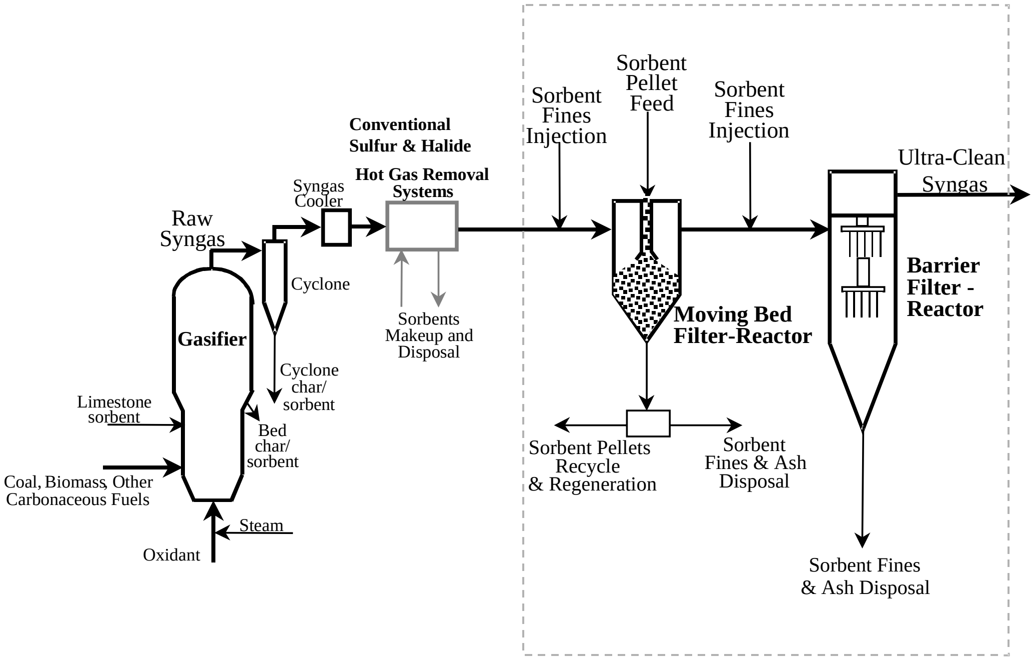

Figure 1. The Ultra-Clean Gas Cleanup Process

The first stage injects fine sorbent particles for halide and sulfur removal into the hot (700 to 1100°F) fuel gas stream, and if needed, it feeds sorbent pellets to a moving bed filter-reactor for sulfur removal. The moving bed filter-reactor performs thorough fuel gas desulfurization, halide removal, and particulate removal using the sorbent fines and pellets.

The moving bed filter-reactor conceptual design shown in Figure 2 is based on the existing Siemens Westinghouse Standleg Granular Bed Filter design (Yang et al., 1997), but uses a unique cross-flow configuration giving it greater flow capacity and better gas-sorbent contacting for reaction conversion. The pellets, having a mean diameter of about 1/4 inch, are fed at the top of the moving bed filter-reactor and flow down a rectangular duct, spreading to the diameter of the vessel according to their natural angle of repose. The base of the pellet feed duct is expanded as a short skirt section that spreads out the pellet flow and provides ample gas-pellet contact at the base where the lowest contact time exists. The pellets spread out to fill the lower vessel, again according to their natural angle of repose. The relatively shallow-packed bed flows downward into a conical section and drains from the vessel base.

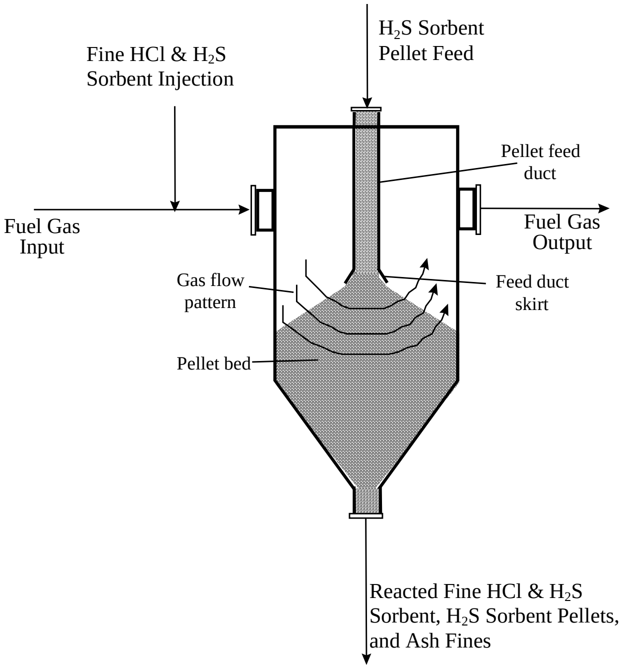

Figure 2. The Moving Bed Filter-Reactor.

Figure 3 shows the moving bed filter-reactor system diagram. The pellet flow through the bed is controlled by a rotary or screw feeder located at the base of the vessel. The ash, injected fine halide and sulfur sorbents, and attrited sulfur sorbent are easily separated from sulfur sorbent pellets by vibrational sieving. The separated sulfur sorbent pellets are recycled continually back to the feed hopper. Depending on the attrition rate of the sorbent pellets, a small portion of the sorbent pellet stream may be withdrawn from the unit, while equivalent amount of sorbent pellets is added to the moving bed filter-reactor feed hopper to make up for the lost sorbent and to maintain the desired sorbent capacity for H_2S removal in the moving bed filter-reactor. The pellet feed rate is controlled with respect to the sorbent pellet/ash weight ratio (20 to 50). If H_2S sorbent pellets are used, the pellet feed rate is also controlled with respect to the desired sorbent pellet sulfur capacity/total sulfur molar ratio (1.2 to 5 ratio).

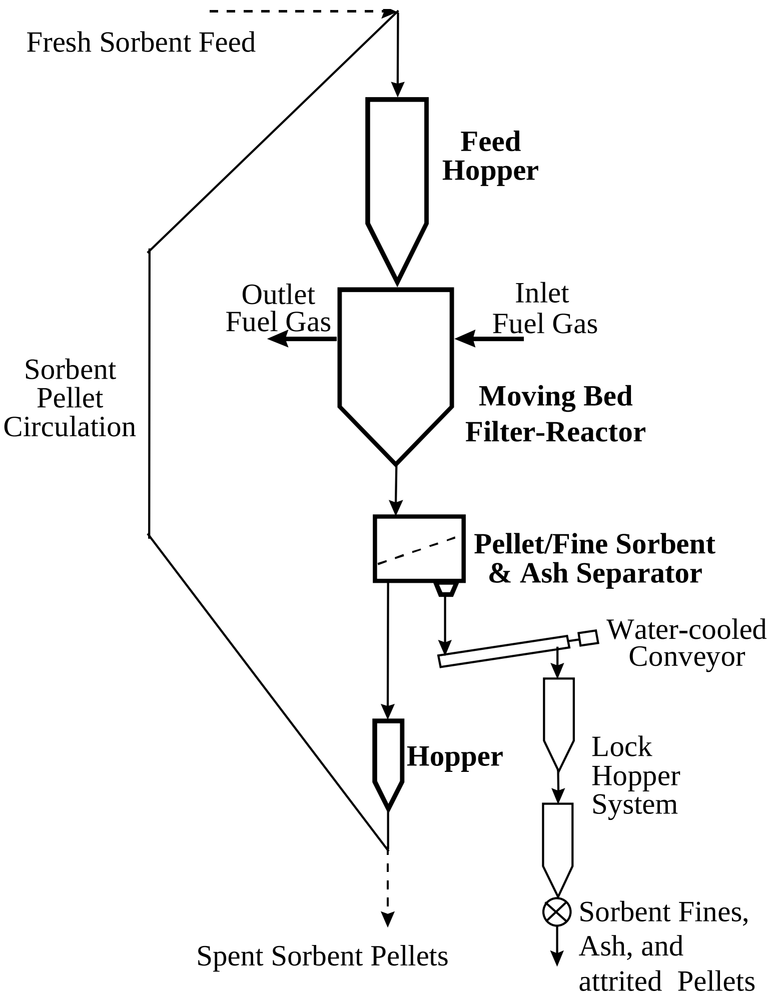

Figure 3. The Moving Bed Filter-Reactor System

In the second stage, the fuel gas exiting from the moving bed filter-reactor is further injected with highly reactive, fine particles of sorbents for sulfur and halide removal before entering a barrier filter-reactor for final particulate removal. The barrier filter-reactor conceptual design is pictured in Figure 4. The barrier filter-reactor is identical in almost all of its features to the Siemens Westinghouse commercial hot gas filter design used in coal-based IGCC and proposed for biomass IGCC applications (Lippert et al., 1998). Final sulfur removal with the injected sorbent particles occurs both from the dilute, entrained sorbent particles and within the consolidated filter cake particles. The nature of the filter cake is modified by the addition of injected sorbent particles. The high permeability of the resulting filter cake, compared to the normally very low permeability of gasifier ashes, allows for higher face velocity design and a resulting more compact vessel having lower cost than the typical fuel gas hot gas filter.

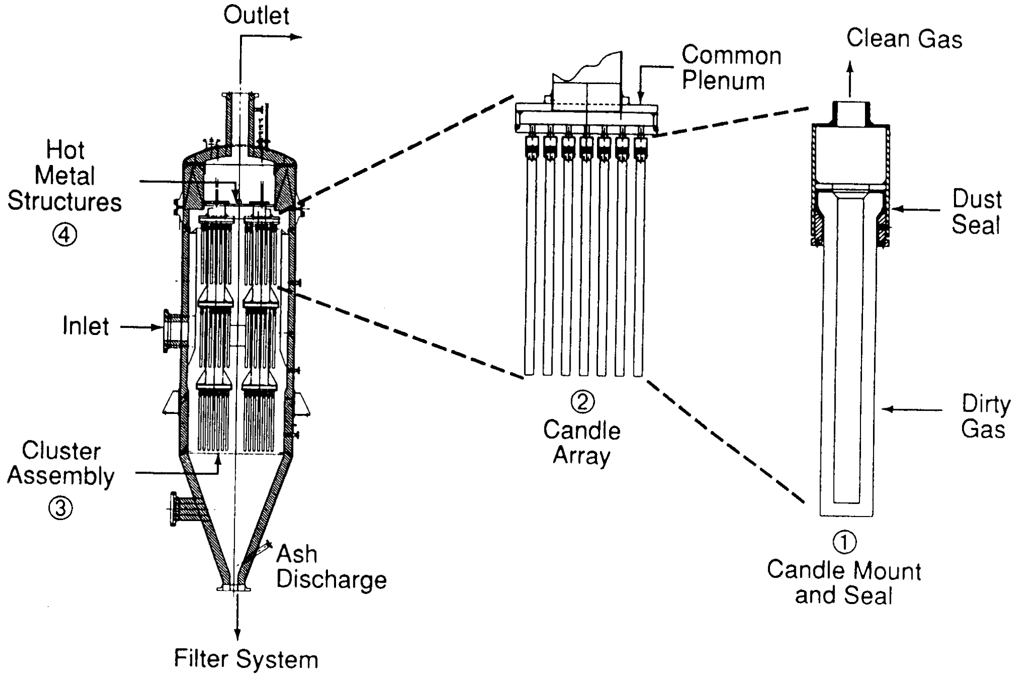

Figure 4. The Barrier Filter-Reactor Design Concept.

The overall program consists of two programs. The Base Program will provide for laboratory exploration of the concept and derive an indication of its feasibility. If the concept is selected for further support, the Optional Program will be exercised for verifying bench-scale experiments and performing thorough economic, technical and commercial feasibility analyses. The work is divided into the following five (5) tasks:

Base Program

Task 1 - NEPA Documentation
Task 2- Technical and Economical Feasibility Studies

Optional Program

Task 3 - NEPA Documentation
Task 4 - Bench-Scale Evaluation
Task 5 - Data Analysis

BASE PROGRAM TEST PLAN

The Base Program will select initial key process parameters and produce initial laboratory-scale data and conceptual design feasibility evidence that the process goals can be economically achieved. The Base Program scope of work is dedicated most heavily to the laboratory testing of candidate advanced sorbents for reduced-sulfur species removal (primarily H_2S) and halide species removal (primarily HCl). The laboratory sorbent testing will focus on the ability of the candidate sorbents to achieve very low contaminant levels (H_2S < 60 ppbv and HCl < 10 ppbv) with acceptable conversion rates. The candidate sorbent particle sizes considered are in two ranges, fine sorbent particles for gas injection (-325 mesh), and if needed, sorbent pellets for use in the moving bed filter-reactor (1/4 inch). This report describes the test plan for selection of candidate sorbent materials and evaluation of the sorbents in the laboratory–scale units to provide the necessary data to verify the technical and economical feasibility of the Ultra-Clean Gas Cleanup Process.

The particulate removal performance of each of the two stages of the Ultra-Clean Gas Cleanup process are relatively well understood since significant development programs have been completed by SWPC for both the granular bed filter and the ceramic barrier filter technologies. For this reason, no testing of the particulate removal performance of the process is included in the Base Program, although characteristics of the sorbent-ash mixtures that may be important to particulate removal will be observed and recorded during the test program.

The laboratory-scale tests in the Base Program will be carried out at the Fundamental Research Laboratories at IGT. The scope of work in the Base Program is geared toward evaluation of both desulfurization and dechlorination sorbents to identify suitable materials and the optimum ranges of operating conditions to achieve the required levels of contaminants (i.e., H_2S < 60 ppbv and HCl <10 ppbv) in the cleaned fuel gas. The experiments will be designed to provide the necessary data for the optimum design of the Ultra-Clean Gas Cleanup Process by closely simulating the gas/solid contact as well as the operating conditions in the process. The experimental data to be collected in the Base Program will include:

- Sorption efficiency (i.e., Pre-breakthrough concentration of H_2S and HCl)
- Sorption capacity
- Effects of operating variables (i.e., T, P, Space Velocity, Sorbent Concentration, etc.)
- Integrated H_2S and HCl removal

A detailed description of the Base Program test plan is described below.

Sorbent Requirements and Selection

Based on thermodynamic equilibrium considerations, as well as available literature data, transition metal oxide-based sorbents such as zinc, copper, iron, or manganese will be the primary candidates for removal of H_2S, while sodium-based sorbents will be the primary candidates for removal of HCl to the desired level in the Ultra-Clean Gas Cleanup Process.

The process flow diagram for the Ultra-Clean Gas Cleanup Process in an IGCC-based plant integrated with 1000 ton/day methanol plant, which is equivalent to stream flow rate for a 180 MWe fuel cell plants is shown in Figure 5. H_2S removal in the first stage of the process will be accomplished by using zinc-, copper-, iron-, or manganese-based sorbents in either powder or pellet forms.

In general, if the total cost of all the sorbents in the Ultra-Clean Gas Cleanup Process is limited to less than 1% of the value of the plant product (methanol or electricity), the total sorbents cost for a 180 MWe plant should be lower than $100/hr.

Comparison of the cost of transition metal oxide based sorbent powders (i.e., $250/ton) and the manufactured sorbent pellets cost (i.e., $3.75/lb) indicates that assuming similar effective sulfur capacities and neglecting the regeneration and disposal costs, sorbent pellets must be regenerated 30 times to become an economically viable alternative to once-through mineral sorbent powders.

As shown in Figure 5, if sorbent pellets are used, the estimated required feed rate in the first stage for a zinc-based sorbent containing 25% zinc and achieving 50% conversion (i.e., zinc/total sulfur molar ratio of 2) is about 150 lb/hr, which represents about 0.3% of the total sorbent pellet circulation rate (i.e., 52000lb/hr). Therefore, based on the assumption of 30 sulfidation/regeneration cycles, the attrition rate of sorbent pellets must be lower than 0.01% per pass (or cycle).

Given the stringent requirement of the regenerable sorbent pellets and the low requirement for the fresh sorbent feed rate, the primary focus of the work in the Base Program will be on the evaluation of <u>once-through</u> sorbents. If the effective sulfur capacity of the fine sorbent powders is shown to be too low, regenerable sorbent pellets will also be evaluated.

As discussed earlier and shown in Figure 5, removal of HCl from the fuel gas stream in the first stage of the Ultra-Clean Gas Cleanup Process is accomplished by injecting sodium-based minerals. Based on earlier studies (Anderson et al., 1988, Krishnan et al., 1996), sodium-based minerals such as nahcolite are capable of removing HCl to about 1 ppmv. As shown in Figure 5, the estimated required feed rate in the first stage for a sodium bicarbonate-based material containing 30% sodium (i.e., 70% purity), and achieving only 50% conversion (i.e., Na/Cl molar ratio of 2) is only 300 lb/hr. By using a more reactive material with higher active sodium concentration, the estimated required sorbent feed rate may be reduced by as much as 50% (i.e., 150 lb/hr).

The work planned in this program will be geared toward evaluating these sorbent minerals in the context of the moving bed filter reactor, to identify the best sorbent and the optimum operating conditions for removal of HCl to the desired level in the first stage of the Ultra-Clean Gas Cleanup Process. The minerals to be evaluated in this program will be in the –325 mesh powder form with particle diameters of about 20 to 40 microns that are similar to those of the ash in the fuel gas stream.

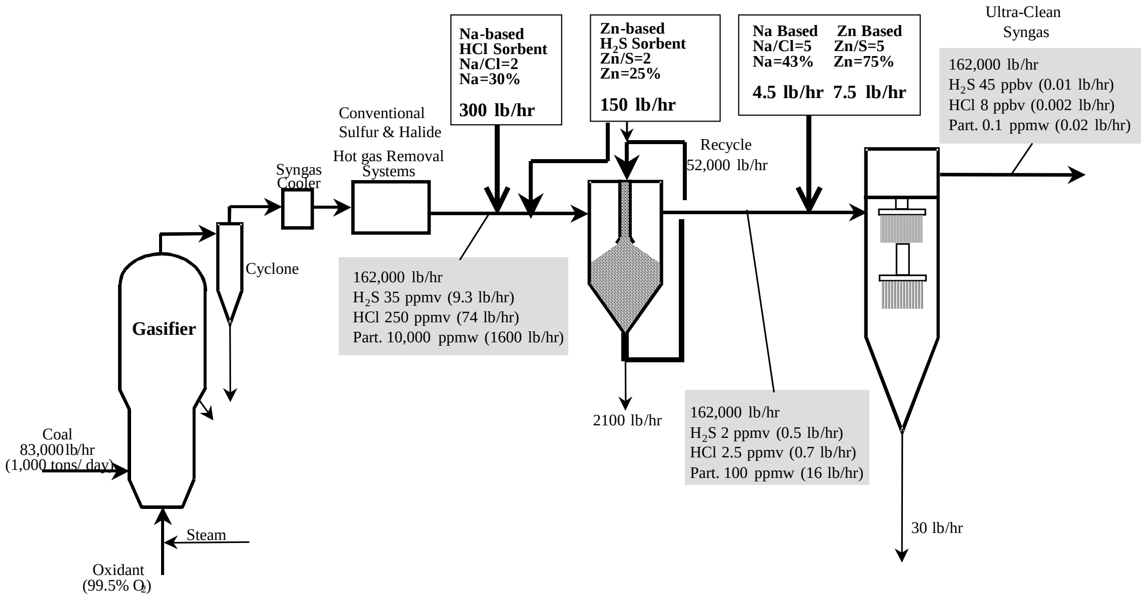

Figure 5. Representative Process Flows in Ultra-Clean Gas Cleaning Process (IGGC -1000 t/d Methanol Plant or 180 MWe Fuel Cell Plant)

H_2S removal in the second stage of the process will be accomplished by injecting fine zinc-based –325 mesh (i.e., < 40 microns) powders into the fuel gas, upstream of the barrier filter. As shown in Figure 5, the estimated required feed rate in the second stage for a zinc-based sorbent containing 75% zinc and achieving only 20% conversion (i.e., Zn/S molar ratio of 5) is only 7.5 lb/hr. Given the very low sorbent feed required for removal of H_2S in the second stage of the process, highly porous and reactive sorbents will be developed in this program. Because of such low level of H_2S, adsorption is also expected to play a major role in retaining H_2S. Therefore, the work planned in this program will focus on development of high surface area sorbents. The highly porous <u>once-through</u> sorbents are expected to be prone to excessive attrition, which will further improve sorbent utilization through reduction of sorbent particle size and increasing surface area of the sorbent. In general, 3 to 4 different zinc-based sorbent materials will be evaluated for removal of H_2S in the second stage of the process.

As shown in Figure 5, removal of HCl from the fuel gas stream in the second stage of the Ultra-Clean Gas Cleanup Process is accomplished by injecting highly porous and reactive sodium-based sorbents into the fuel gas upstream of the barrier filter. In general, 3 to 4 different materials will be evaluated for removal of HCl in the second stage of the process. As shown in Figure 5, the estimated required feed rate in the second stage for a highly porous sodium bicarbonate-based material containing 43% sodium (i.e., 98% purity), and achieving only 20% conversion (i.e., Na/Cl molar ratio of 5) is only 4.5 lb/hr.

Laboratory Simulation of the Process

Because a major portion of the gas cleaning in the Ultra-Clean Gas Cleaning Process is accomplished inside the moving-bed and at the surface of the barrier filter elements, the laboratory experiments planned in this program are designed to simulate the gas/solids contact inside the respective reactor vessels. Therefore, although a fraction of the cleaning process takes place in the dilute entrained phase upstream of the two filter-reactor vessels, simulation of gas cleaning in the dilute phase will only be pursued, if the desired level of cleaning is shown to be unachievable in the dense phases inside the filter-reactors.

To closely simulate the moving bed filter reactor, the laboratory experiments planned for evaluation of the candidate sorbent materials will be carried out in a packed bed reactor that includes sorbent fines, inert Pellets (and if needed sorbent Pellets), and fly ash (see Figure 6). Although, based on the flow rates of different solid streams shown in Figure 5 (base case), the pellet/total fines ratios is 27, because of much lower fraction of void space in the packed-bed, the pellet/fines ratio in the packed-bed will be about 5 times lower than that of the actual process. The operating conditions including bed height, gas composition, gas residence time, and reactor temperature in the laboratory experiments will be similar to those in the actual process.

Figure 7 shows the laboratory simulation of gas cleaning in the barrier filter-reactor. The gas cleaning in the filter cake is simulated by a shallow bed of sorbent fines and fly ash. Based on the flow rates of different solid streams shown in Figure 5 (i.e., base case), the filter cake consists of about 25% H_2S sorbent, 15% HCl sorbent, and 60% ash. The filter cake is expected to have uniform composition with a cake thickness of about 3-10 mm. In the laboratory experiments planned for this program, the composition of the filter cake is closely simulated by thoroughly mixing the sorbents and the ash. The packing density of the cake is simulated by maintaining similar superficial gas velocity (i.e., face velocity) in the barrier filter-reactor.

As indicated earlier, the laboratory-scale tests in the Base Program are carried out at the Fundamental Research Laboratories at IGT. The laboratory experiments will be conducted in the ambient pressure packed-bed reactor as well as the high-pressure/high-temperature reactor (HPTR) unit. The schematic diagrams of the reactor systems to be used in this project are shown in Figures 8 and 9, respectively. The detailed descriptions of the experimental procedures involving these units are provided below.

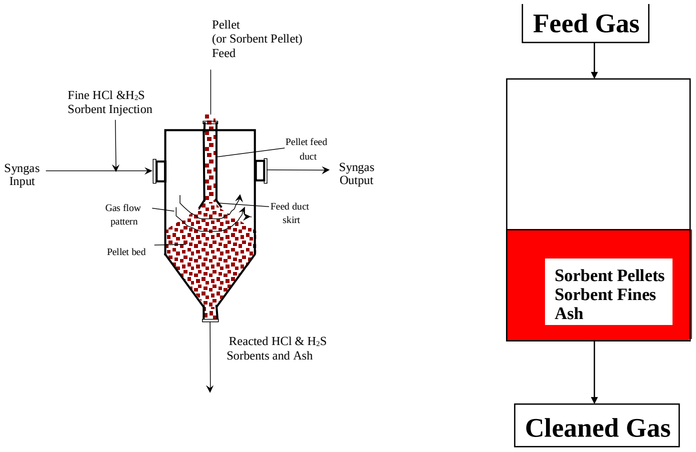

Figure 6. Laboratory Simulation of Gas Cleaning in Moving-Bed Filter-Reactor

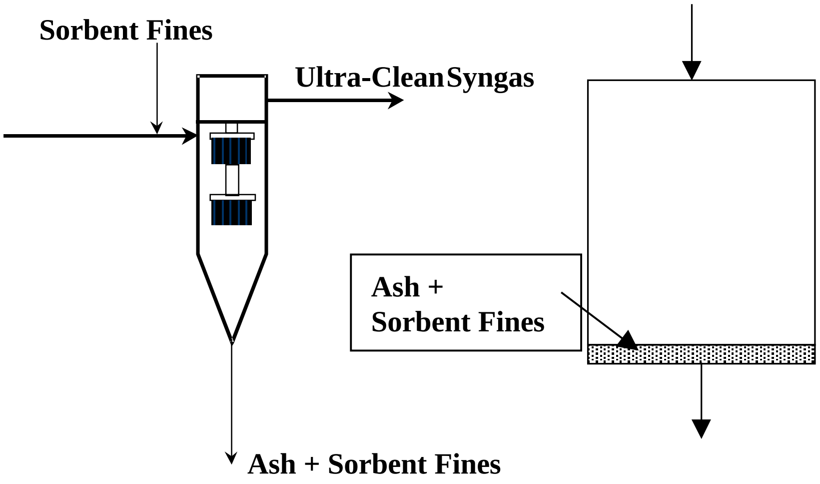

Figure 7. Laboratory Simulation of Gas Cleaning in Barrier Filter-Reactor

Laboratory-Scale Facilities

Ambient Pressure Packed-Bed Reactor Unit

The schematic diagram of the ambient-pressure packed-bed reactor to be used in this program is shown in Figure 8. The unit essentially consists of a quartz reactor that is externally heated by two electric furnaces, equipment for feeding and measuring the flow rate of the gases, measuring and controlling the bed temperature, and monitoring the reactor pressure.

For the packed-bed operation, the reactor system is configured for flowing gas either upward or downwards for both desulfurization and dechlorination reactions. Although, different reactors with diameters ranging from .5 to 7.5 cm can be used in this unit, a reactor diameter of 4.5 cm will be used in all the tests in this program. A quartz frit near the middle reactor is used to support the sorbent bed. Temperature is recorded as a function of time using a computerized data acquisition system. Teflon^R tubing is used to convey contaminants-containing exit gas at temperatures < 200°C.

The dry gases required for desulfurization and dechlorination sorbents are obtained from pressurized cylinders. The gases are passed through pre-calibrated electronic mass flow controllers which are set to give the desired mixture composition prior to entering the reactor. A syringe pump is used to introduce water through capillary tubing into the reactor.

This unit will be used for the initial evaluation of the sorbents. As indicated earlier in this test plan, to simulate the moving-bed filter-reactor, the tests will be conducted using a packed-bed consisting of pellets and sorbent fines as well as fine ash particulates. The gas/solid contact at the filter cake (in the barrier filter-reactor) will be simulated by employing shallow bed of fine powders (i.e., 3-10 mm) as the sorbent bed.

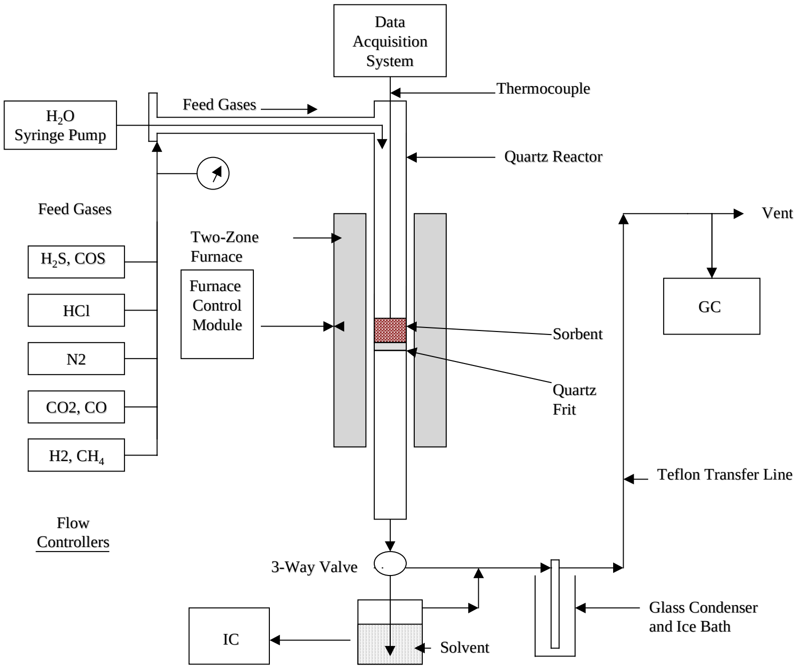

Figure 8. Schematic Diagram of the Packed-Bed Reactor Unit

During the experiments, the reactor temperature at different locations as well as the pressure drop across the bed will be measured and recorded by the automated data acquisition system. Samples of the reacted sorbents from the top, the middle, and the bottom of sorbent bed will be collected. These samples will be examined to determine the extent of particle-particle interaction (if any) during the test. The chemical compositions of a selected number of the collected samples will determined to provide information on the level of contaminant loading across the bed.

HCl Concentration Measurement. Because of the highly reactive nature of HCl, measurement of HCl content of the gas stream should be carried out by dissolving HCl in a known quantity of a solvent (e.g., carbonate), and determining the HCl content of the solvent. This method which has successfully been used by many researchers can be used for measurement of the HCl content of the reactor feed and exit streams over the entire range of interest in this program (i.e., 10 ppbv to 2%), by using significantly different gas to solvent ratios. The HCl content of the solvent will be determined by Ion Chromatography. Ion chromatographs are routinely used at IGT for determination of the chemical composition of various solid and liquid materials. An IGT resident chemist with over 10 years of Ion Chromatography experience will be involved in the early stages of the program to establish the sampling and measurement techniques for determination of the HCl content of the gas streams.

A Dionex DX-320/IC20 chromatography system will be used to perform ion chromatography (IC) and high performance liquid chromatography (HPLC) analyses. This DX 320 system consists of an Ion Chromatograph, a Chromatography Oven, and an Eluent Generator. The Ion Chromatograph performs isocratic ion analyses using conductivity detection. The Ion Chromatograph electronics provide sensitive, accurate detection and quantification of ionic analytes in liquid and ion chromatography. This is especially useful for analytes that lack UV chromophores and cannot be determined with adequate sensitivity by UV absorbance.

H_2S Concentration Measurement. The H_2S content of the feed and reactor exit gas streams at concentrations above 1 ppmv are determined by a dedicated gas chromatograph. A Flame Photometric Detector (FPD) will be used for the 1-500 ppmv range, while a Thermal Conductivity Detector (TCD) is utilized for measurement of H_2S concentrations above 500 ppmv. The GC-FPD/TCD unit has been used successfully by IGT's Fundamental Research team over the last 15 years for determination of H_2S concentrations above 1 ppmv level.

The H_2S concentrations in the sub-ppmv range (.01-1 ppmv) will be determined by the Dionex DX-320/IC20 Chromatography system. As indicated earlier, this method provides the necessary flexibility and accuracy to determine the concentration of sulfur species over the entire range of interest in this program (i.e., 50 ppbv to 2%), by using significantly different gas to solvent ratios. Therefore, the IC unit may also be used for measurements of the H2S content of the gas above 1ppmv levels)

IGT's researchers have been involved in the development of measurement techniques for determination of very low levels of sulfur species (e.g., 10 ppbv to 10 ppmv) for natural gas odorization for over two decades, and developed an instrument based on GC-FPD technology (Chao, et al. 1994). Based on IGT's past experience, it is believed that FPD is probably the most common detector for sulfur measurement with a detection limit better than 100 ppbv with a good accuracy and precision of approximately 5%. The detection range can be extended to 10-100 ppbv levels depending on the sample size and selection of GC column. Various commercially available capillary columns such as J&W DB-5, GS-Q, and Supelco SPB-1 can be selected to achieve the desired level of separation. Given the availability of the GC-FPD unit at the Fundamental Research Laboratories and IGT's past experience, the GC-FPD unit may be used as an alternative method for H_2S measurement in the sub-ppmv range.

Among other commercially available sulfur-specific detectors, the H_2S rateometric detector (HRD), which is based on lead acetate tape, and sulfur chemiluminescence detector (SCD), which is based on light output from chemilininescence reactions, also appear to be suitable for H_2S measurement in the sub-ppmv range. However, based on IGT's past experience, operational difficulties associated with these detectors make them less desirable. It should be noted that a GC-SCD unit is currently available at IGT, that if necessary, can be used in this program.

Although it is desirable to conduct all the experiments at the elevated pressure prevailing in the process, because of the time and budget limitations, initially, all the tests will be conducted in the ambient pressure unit to identify promising sorbents and the optimum ranges of operating conditions. The high-pressure tests will be conducted toward the end of the program to quantify the effect of pressure on the performance of the sorbents.

High Pressure/High Temperature Reactor (HPTR)

A schematic diagram of the high-pressure high-temperature reactor (HPTR) is given in Figure 9. The unit is suitable for packed-bed mode of operation and is designed for operation at a maximum temperature of 750°C at a pressure of 30 bar. The reactor is capable of handling corrosive gas mixtures including hydrogen sulfide (H_2S) and hydrogen chloride (HCl). The unit has been constructed of stainless steel for the outer shell to withstand the static pressure. Ceramic materials are used for the wetter internal section of the reactor to prevent corrosion of the unit during use of corrosive gases such as HCl and H_2S. A ceramic tube directs the corrosive gas mixture to the reactor. All of the hot wetted parts are made of quartz materials. Surrounding the ceramic tube is an electrical furnace with three zones. The reactant gases (dry) are supplied by a commercial supplier in compressed gas cylinders. The flow rates are controlled by mass flow controllers. The gas mixture is preheated inside the ceramic tube before reaching the sorbent bed.

The downstream gas processing section consists of: 1) a heat exchanger to cool the gas stream, 2) a water knockout-vessel to collect water during absorption, 3) a dome loaded, back-pressure regulator with a Teflon diagram to let-down the pressure of the effluent gas, and 4) a separate gas-sampling line to monitor the effluent gas for H_2S and HCl. To prevent corrosion and to determine the correct content of the corrosive gases in the gas stream, the gas sampling line is made from Teflon-lined stainless steel and polyethylene tubing.

This unit will be used for the final evaluation of the sorbents. Similar to the ambient pressure unit, to simulate the moving-bed filter reactor, the tests will be conducted using a packed-bed consisting of pellets and sorbent fines as well as fine ash particulates. The gas/solid contact at the filter cake will be simulated by employing shallow bed of fine powders as the sorbent bed. The H_2S and HCl contents of the feed and reactor exit gas streams are determined by a dedicated gas chromatograph equipped with Flame Photometric Detector (FPD) and by Ion Chromatography (IC), as described above.

Support Facilities and Equipment

In addition to the facilities and equipment at the Fundamental Research Laboratories, described above, the Chemical Research Services (CRS) department with state-of-the-art equipment will be used for analysis of the physical and chemical properties of the materials produced in this program. The wide range of resources at IGT's Technical Information Center will also be utilized to obtain information on past as well ongoing research activities in the subject areas related to this project.

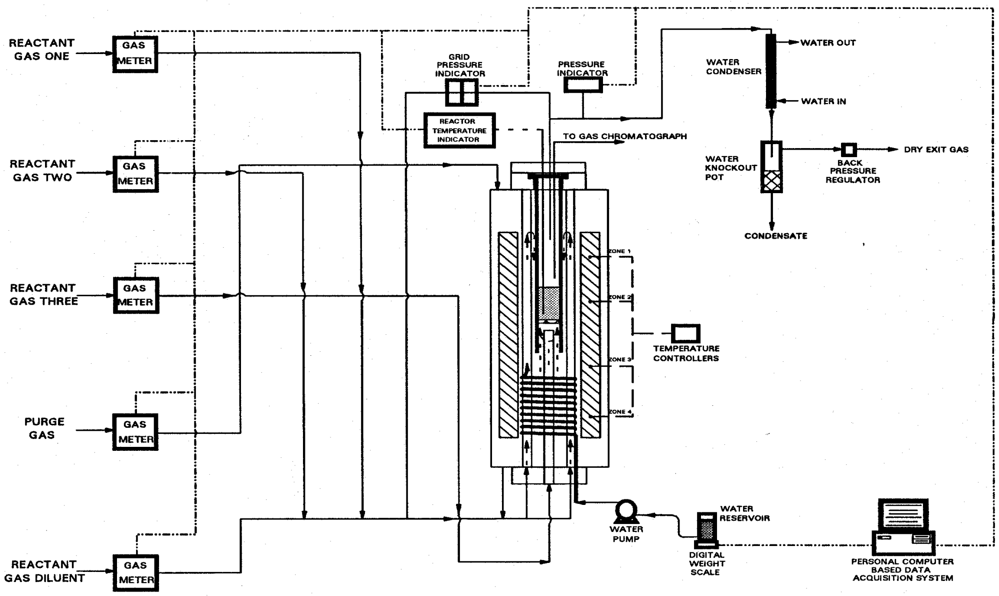

Figure 9. Schematic Diagram of the High Pressure /High Temperature Reactor (HPTR)

Sorbent Preparation

Based on earlier work at IGT (abbasian et al., 1997), inexpensive minerals or by-product powders from metal processing operations which contain oxides of iron, zinc, copper, and manganese are capable of removing H_2S to about 1 ppmv. Therefore, suitability of injecting -325 mesh (20-40 microns) mineral powders containing transition metal oxides, upstream of the moving bed filter reactor for removal of H_2S in the first stage of the Ultra-Clean Gas Cleanup Process will be investigated in this program. Up to four (4) different metal oxide-containing powders will be evaluated for H_2S removal in the first stage of the process. Non-reactive pellets, such as dead-burnt dolomite (or limestone) will be used in conjunction with these minerals, as bed filtering media.

As indicated earlier, the primary focus of the work in the Base Program will be on the evaluation of once-through sorbents. If the effective sulfur capacity of the fine sorbent powders is shown to be too low, regenerable sorbent pellets will also be evaluated for the moving bed application. Based on the results of evaluation of numerous desulfurization sorbents developed at IGT in an earlier NETL sponsored research program (Abbasian et al., 1998a and 1998b), a number of sorbent formulations are believed to be suitable candidates for moving bed filter reactor application in this program. Although these sorbents were originally developed for fluid bed application, the sorbent preparation technique can be readily modified to produce the required sorbent pellets for the moving bed filter reactor application.

The candidate sorbent pellets that will be selected for the moving bed filter reactor evaluation in this program will be spherical with an average pellet diameter of about 1/4 inch (i.e., 6 mm). Based on the results of sorbent evaluation in the high temperature moving bed reactor in earlier NETL sponsored Clean Coal Technology IGCC demonstration program at Tampa Electric, to prevent excessive attrition losses, the sorbents to be evaluated in this program will have crush strength higher than 7 lbf/pellet.

As indicated earlier, removal of HCl in the first stage of the Ultra-Clean Gas Cleanup Process will be accomplished by injection of sodium-based minerals such as nahcolite, trona, and dawsonite upstream of the moving bed filter reactor. Based on earlier NETL sponsored programs (Anderson et al., 1988, Krishnan et al., 1996) these inexpensive minerals are capable of removing HCl to about 1 ppmv. The minerals to be evaluated in this program will be in the –325 mesh powder form with particle diameters of about 20 to 40 microns that are similar to those of the ash in the fuel gas stream.

In the second stage of the process, because of the very low level of H_2S and HCl in both the feed and the reactor effluent, highly reactive sorbents are needed to reduce the concentration of the contaminants to the required ppbv levels. Therefore, development of sorbents for the second stage of the process will focus on preparation of highly porous sorbents with high surface areas. The highly porous once-through sorbents are expected to be prone to excessive attrition, which will further improve sorbent utilization through reduction of sorbent particle size and increasing surface area of the sorbent.

In general, sorbents to be prepared for application in the second stage of the process will be in powder form with particle diameters of about 20 to 40 microns (–325 mesh) that are similar to those of the ash in the fuel gas stream. The sorbents to be evaluated for H_2S removal in the second stage of the process will include up to four (4) highly porous and high surface area zinc-based sorbents that will be prepared by co-precipitation or sol-gel processing (e.g., aerogel). Commercially available zinc guard sorbents may also be evaluated in this program. Preparation of sorbents for removal of HCl in the second stage of the process will be geared toward development of up to four (4) highly porous and reactive sodium-based sorbents.

Operating Conditions

As indicated earlier, the operating variables in the laboratory-scale tests will be selected to closely simulate those prevailing in the Ultra-Clean Gas Cleaning Process. The ranges of operating variables to be used in tests representing the first and the second stages of the process are given in Table 1.

Table 1. Ranges of Operating Variables

	First Stage	First Stage	Second Stage	Second Stage
Operating Parameter	Baseline	Range of Parameter	Baseline	Range of Parameter
Temperature, °C	500	450 - 550	400	350 - 450
Pressure, bar	1	1, 20	1	1, 20
Sorbent Bed Dia, mm	45	45	45	45
Sorbent Bed Height, mm	50	50	3-10(TBD)	3-10(TBD)
H_2S Sorbent Dia., mm	0.02 and 6 (if needed)	0.02 and 6 (if needed)	0.02	0.02
HCl Sorbent Dia., µm	20	20	20	20
Total Fines/ Pellet*	0.15	0.15	N/A	N/A
HCl Sorbent Fines/Total Fines*	0.2	0.1- 0.4	0.15	0.07-0.3
H_2S Sorbent Fines/Total Fines*	0.2	0.1- 0.4	0.25	0.1-0.5
Superficial Gas Velocity, cm/s	5	3-10	5	3-10
Gas Composition				
CO	35%	35%	35%	35%
H_2	30%	30%	30%	30%
CO_2	10%	10%	10%	10%
H_2O	15%	15%	15%	15%
CH_4	3%	3%	3%	3%
HCl	250-3000 ppmv (TBD)	250-3000 ppmv (TBD))	5-2000 ppmv (TBD)	5-2000 ppmv (TBD)
H_2S	35 ppmv – 2% (TBD)	35 ppmv – 2% (TBD)	5-2000 ppmv (TBD)	5-2000 ppmv (TBD)
COS	3-2000 ppmv (TBD)	3-2000 ppmv (TBD)	3-200ppmv (TBD)	3-200 ppmv (TBD)
N_2	Balance	Balance	Balance	Balance

* Mass Ratio

Table 2. Tentative General Test Matrix

Tests Category	# of Tests	Operating Conditions
1.1 - Blank	4	Baseline condition
1.2 – Inert Bed	4	Baseline condition, separate and combined sorbent/pollutants
2.1 – 1st Stage HCl Sorbent Screening	4	Baseline condition with 4 sorbents
2.2 – 1st Stage H_2S Sorbent Screening	4	Baseline condition with 4 sorbents
2.3 – 2nd Stage HCl Sorbent Screening	4	Baseline condition with 4 sorbents
2.4 – 2nd Stage H_2S Sorbent Screening	4	Baseline condition with 4 sorbents
3.1 - 1st Stage HCl and H_2S Combined	4	Baseline condition with 4 sorbent combinations
3.2 – 1st Stage Parametric Studies	8	2 Temperatures, 2 levels of concentrations, 2 gas velocities, 2 bed heights
3.3 – 2nd Stage HCl and H_2S Combined	4	Baseline condition with 4 sorbent combinations
3.4 – 2nd Stage Parametric Studies	8	2 Temperatures, 2 levels of concentrations, 2 gas velocities, 2 bed heights
4.1 – 1st Stage High P Parametric Studies	8	2 Temperatures, 2 levels of concentrations, 2 gas velocities, 2 bed heights
4.2 – 2nd Stage High P Parametric Studies	8	2 Temperatures, 2 levels of concentrations, 2 gas velocities, 2 bed heights

1. Preliminary Ambient Pressure Tests

1.1 Blank Tests

The objective of this series of tests is to demonstrate the reliability and the accuracy of the sampling and measurement techniques for determination of concentration of contaminants.

Given the very low level of H_2S and HCl in both the feed and the reactor effluent streams, demonstration of the reliability and the accuracy of the sampling and measurement techniques to be used for determination of concentration of contaminants is the most important issue to be addressed in the early stages of the Base Program.

A series of tests will be conducted with empty reactor, where gas mixtures with known compositions (supplied from certified gas cylinders) will flow through the reactor.

Different sampling techniques will be used to collect samples of the reactor effluent and analyzed by the gas chromatograph and ion chromatograph. The issues to be addressed in this series of tests will include:

- calibration of measurement equipment
- determination of optimum sample size
- development of sample line preconditioning techniques

1.2 Inert Bed Tests

The objective of this series of tests is to determine the HCl and H_2S sorption (i.e., absorption or adsorption) capacities of the inert pellets (e.g., dead burnt limestone or dolomite, gravel, etc.,) and ash materials to be used in this program.

As indicated earlier, to closely simulate the moving bed filter reactor, the laboratory experiments planned for evaluation of the candidate sorbent materials will be carried out in a packed bed reactor that includes sorbent (or inert) pellets, fly ash, and sorbent fines, while the gas cleaning in the filter cake is simulated by a shallow bed of sorbent fines and fly ash.

This series of tests will be conducted with inert pellets and ash to simulate the moving bed filter, and with a shallow bed of ash for barrier-filter tests. These tests will be conducted at the baseline operating conditions presented in Table 1. The sorption capacity of the bed materials for H_2S and HCl will be determined separately and together, by using feed gas mixtures containing one or both contaminants (i.e., H_2S and HCl).

The experimental data to be collected in these tests will include a complete set of the test operating conditions and the contaminants concentrations in the reactor feed and effluent stream as a function of reaction time, until the desired breakthrough concentration of about 10 ppmv is achieved. As indicated earlier, during the experiments, the reactor temperature at different locations as well as the pressure drop across the bed will be measured and recorded by the automated data acquisition system. The H_2S and HCl content of the reactor feed and exit streams will be determined by the Gas Chromatograph and the Ion Chromatograph. Samples of the bed materials from the top, the middle, and the bottom of bed will be collected. These samples will be examined to determine the extent of particle-particle interaction (if any) during the test. The chemical compositions of a selected number of the collected samples will be determined to provide information on the level of contaminant loading across the bed.

2. Sorbent Screening Tests at Ambient Pressure

The objective of this series of tests is to rank the potential candidate sorbents and to determine the effects of operating parameters on the performance of the sorbents.

2.1. Sorbent Screening for HCl Removal in Moving-Bed Filter Reactor

The objective of this series of tests is to identify and rank the potential candidate sorbents for removal of HCl in the first stage of the process.

This series of tests will be carried out in the packed bed reactor consisting of both pellets and fines (sorbent and ash) at the baseline condition presented in Table 1. Because the relatively high concentration of HCl in the feed gas may result in absorption of HCl by the zinc- or copper-based sorbents, the pellets in this series of tests will consist of inert materials such as low surface area alumina or dead-burnt dolomite (or limestone). Up to four (4) different sodium-based minerals such as nahcolite, trona, and dawsonite will be evaluated in these tests. Based on earlier NETL sponsored programs (Anderson et al., 1988, Krishnan et al., 1996) these inexpensive minerals are expected to be capable of removing HCl to about 1 ppmv. The minerals to be evaluated in this program will be in the –325 mesh powder form with particle diameters of about 20 to 40 microns that are similar to those of the ash in the fuel gas stream.

As indicated in Table 1, at the initial baseline operating conditions, the tests will be conducted in the 4.5-cm ID packed bed reactor at 500 °C with sorbent bed height set at 5 cm and the gas residence time at about 1 second. The HCl content of the feed gas in these baseline tests will be 1500 ppmv without H_2S (or COS). At this operating condition, using a sodium-based mineral sorbent containing 70% sodium bicarbonate and an ash to sorbent ratio of 4 to 1, the estimated theoretical HCl breakthrough time will be about 6.5 hours. Assuming a sorbent conversion of 50% (i.e., Na/Cl=2), the estimated HCl breakthrough time will be reduced to about 3.25 hours.

The experimental data to be collected in these tests will include a complete set of the test operating conditions and the HCl concentrations in the reactor feed and effluent streams as a function of reaction time, until the desired breakthrough concentration of about 10 ppmv is achieved. While the pre-breakthrough concentration of HCl represents the HCl removal efficiency of the tested sorbent, the overall breakthrough time provides a measure of the effective sorbent capacity. Therefore the selection of the best sorbent for further evaluation will be based on both the pre-breakthrough concentration and the effective sorbent capacity.

As indicated earlier, during the experiments, the reactor temperature at different locations as well as the pressure drop across the bed will be measured and recorded by the automated data acquisition system. The HCl content of the reactor feed and exit will be determined by the Ion Chromatograph. Samples of the reacted sorbents from the top, the middle, and the bottom of sorbent bed will be collected. These samples will be examined to determine the extent of particle-particle interaction (if any) during the test. The chemical compositions of a selected number of the collected samples will determined to provide information on the level of contaminant loading across the bed.

If none of the candidate sorbents can achieve the desired level of contaninant removal (i.e., $HCl_{out} < 3$ ppmv) and the desired level of loading (i.e., Cl/sorbent > 20%), the baseline condition will be modified by reducing the HCl content of the feed gas, and if necessary, by increasing the gas residence time or the sorbent content of the bed to achieve the desired level of cleaning.

Sorbent Ranking Criteria. Following the completion of the sorbent screening tests for HCl removal in the first stage, the promising sorbent materials will be identified and ranked for further evaluation. Ranking of the sorbents will be based on the pre-breakthrough concentration, the effective sorbent capacity, as well as the projected sorbent costs. In general, all sorbents that will meet the pre-breakthrough target of 3 ppmv and an effective sorbent capacity of 20%, will be considered suitable for further evaluation.

2.2. Sorbent Screening for H_2S Removal in Moving-Bed Filter Reactor

The objective of this series of tests is to identify and rank the potential candidate sorbents for removal of H_2S in the first stage of the process. The sorbents to be evaluated in this series of tests will be in powder and pellet (both bulk and supported) forms.

2.2.a. Screening Tests for Sorbents in Powder Form. As indicated earlier, based on earlier work at IGT (Abbasian et al., 1998), inexpensive minerals or by-product powders from metal processing opertations, which contain oxides of iron, zinc, copper, and manganese, are capable of removing H_2S to about 1 ppmv. Up to four (4) different metal oxide containing powders will be evaluated in these tests. The minerals to be evaluated in this program will be in the –325 mesh powder form with particle diameters of about 20 to 40 microns that are similar to those of the ash in the fuel gas stream.

This series of tests will be carried out in the packed bed reactor consisting of both pellets and fines (sorbent and ash) at the baseline condition presented in Table 1. The pellets in this series of tests will consist of inert materials such as low surface area alumina or dead-burnt dolomite (or limestone).

As indicated in Table 1, at the initial baseline operating conditions, the tests will be conducted in the 4.5-cm ID packed bed reactor at 500 °C with sorbent bed height set at 5 cm and the gas residence time at about 1 second. The H_2S content of the feed gas in these baseline tests will be 250 ppmv H_2S and 25 ppmv COS without HCl. At this operating condition, using a zinc-based mineral sorbent containing 25% zinc, and an ash to sorbent ratio of 4 to 1, the estimated theoretical H_2S breakthrough time will be about 10 hours. Assuming a sorbent conversion of 50% (i.e., Zn/S=2), the estimated H_2S breakthrough time will be reduced to about 5 hours.

The experimental data to be collected in these tests will include a complete set of the test operating conditions and the H_2S concentrations in the reactor feed and effluent streams as a function of reaction time, until the desired breakthrough concentration of about 10 ppmv is achieved. While the pre-breakthrough concentration of H_2S represents the H_2S removal efficiency of the tested sorbent, the overall breakthrough time provides a measure of the effective sorbent capacity. Therefore, selection of the best sorbent for further evaluation will be based on both the pre-breakthrough concentration and the effective sorbent capacity.

Similar to the tests described in the previous section, during the experiments, the reactor temperature at different locations as well as the pressure drop across the bed will be measured and recorded by the automated data acquisition system. The H_2S content of the reactor feed and exit gases will be determined by the dedicated gas chromatograph equipped with Flame Photometric Detector (FPD) for concentrations above 1 ppmv, and by the Ion Chromatograph (IC) for concentration in the sub-ppmv range. Samples of the reacted sorbents from the top, the middle, and the bottom of sorbent bed will be collected. These samples will be examined to determine the extent of particle-particle interaction (if any) during the test. The chemical compositions of a selected number of the collected samples will be determined to provide information on the level of contaminant loading across the bed.

If none of the candidate sorbents can achieve the desired level of contaminant removal (i.e., $H_2S_{out} < 3$ ppmv) and the desired level of loading (i.e., S/sorbent > 6%), the baseline condition will be modified by reducing the H_2S content of the feed gas, and if necessary, by increasing the gas residence time or the sorbent content of the bed to achieve the desired level of cleaning.

Sorbent Ranking Criteria. Following the completion of the sorbent screening tests for H_2S removal in the first stage, the promising sorbent materials will be identified and ranked for further evaluation. Ranking of the sorbents will be based on the pre-breakthrough concentration, the effective sorbent capacity, as well as the projected sorbent costs. In general, all sorbents that will meet the pre-breakthrough target of 3 ppmv and a sorbent capacity of 6%, will be considered suitable for further evaluation.

2.2.b. Screening Tests for Sorbents in Pellet Form. As indicated earlier, given the stringent requirement of the regenerable sorbent pellets and the low requirement for the fresh sorbent feed rate, the primary focus of the work in the Base Program will be on the evaluation of once-through sorbents. However, if the effective sulfur capacity of the fine sorbent powders is shown to be too low, regenerable sorbent pellets will also be evaluated.

The candidate sorbent pellets that will be selected for the moving bed filter reactor evaluation in this program will be spherical with an average pellet diameter of about 1/4 inch (i.e., 6 mm). Up to three (3) different sorbents in pellet form may be evaluated in this series of tests. This series of tests will be carried out in the packed bed reactor consisting of both pellets and fine (sorbent and ash) at the baseline condition presented in Table 1.

Similar to the tests described in the previous section, evaluation of the candidate sorbents for removal of H_2S in the first stage of the process will be carried out in the 4.5-cm ID packed bed reactor. As indicated in Table 1, at the initial baseline operating conditions, the tests will be conducted at 500 °C with sorbent pellet/ash bed height set at 5 cm and the gas residence time at about 1second. The H_2S content of the feed gas in these baseline tests will be 1% without HCl. At this operating condition, using a zinc-based sorbent containing 25% zinc, the estimated theoretical H_2S breakthrough time will be about 9 hours. Assuming a sorbent conversion of 50% (i.e., Zn/S = 2), the estimated H_2S breakthrough time will be reduced to about 4.5 hours. The experimental data to be collected in these tests will be similar to those described in section 2.2.a.

If none of the candidate sorbents can achieve the desired level of contaminant removal (i.e., H_2S_{out}< 3 ppmv) and the desired level of loading (i.e., S/sorbent > 6% for bulk sorbent or > 3% for supported sorbent), the baseline condition will be modified by reducing the H_2S content of the feed gas, and if necessary, by increasing the gas residence time to achieve the desired level of cleaning.

2.3. Sorbent Screening for HCl Removal in Barrier-Filter Reactor

The objective of this series of tests is to identify and rank the potential candidate sorbents for removal of HCl in the second stage of the process.

This series of tests will be carried out in the packed bed reactor with a shallow bed of fines, consisting of the coal ash and HCl sorbent fines at the baseline operating condition presented in Table 2. Because of the very low level of HCl in both the feed and the barrier filter reactor effluent, highly reactive sorbents will be used to reduce the concentration of HCl to the required ppbv level. Therefore, up to four (4) highly porous and high surface area sodium-based sorbent fines with particle diameters of about 20 to 40 microns (–325 mesh) will be evaluated for HCl removal in the second stage of the process. These sorbents are expected to be prone to excessive attrition, which will further improve sorbent utilization through reduction of sorbent particle size and increasing surface area of the sorbent.

As indicated in Table 1, at the initial baseline operating conditions, the tests will be conducted in the 4.5-cm ID packed bed reactor at 400 °C with sorbent bed consisting of about 15% HCl sorbent and 85% ash. The maximum sorbent height in these tests will be set at 10 mm and the superficial gas velocity will be 5 cm/s resulting in a gas residence time of about 0.2 second. The HCl content of the feed gas in these baseline tests will be 1000 ppmv without H_2S (or COS). At this operating condition, using a sodium-based sorbent containing 98% sodium bicarbonate, the estimated theoretical HCl breakthrough time will be about 6hours. Assuming a sorbent conversion of 25% (i.e., Na/Cl=4), the estimated HCl breakthrough time will be reduced to about 1.5 hours.

The experimental data to be collected in these tests will include a complete set of the test operating conditions and the HCl concentration in the reactor feed and effluent stream as a function of reaction time, until the desired breakthrough concentration of about 1 ppmv is achieved. As indicated earlier, during the experiments, the reactor temperature at different locations as well as the pressure drop across the bed will be measured and recorded by the automated data acquisition system. The HCl content of the reactor feed and exit gases will be determined by the Ion Chromatograph. Samples of the reacted sorbents from the sorbent bed will be collected. These samples will be examined to determine the extent of particle-particle interaction (if any) during the test. The chemical compositions of a selected number of the collected samples will be determined to provide information on the level of contaminant loading in the bed.

If none of the candidate sorbents can achieve the desired level of contaminant removal (i.e., HCl_{out}<10 ppbv) and the desired level of loading (i.e., Cl/sorbent > 15%), the baseline condition will be modified by reducing the HCl content of the feed gas, and if necessary, by increasing the gas residence time or the sorbent content of the bed to achieve the desired level of cleaning.

Sorbent Ranking Criteria. Following the completion of the sorbent screening tests for HCl removal in the second stage, the promising sorbent materials will be identified and ranked for further evaluation. Ranking of the sorbents will be based on the pre-breakthrough concentration, the effective sorbent capacity, as well as the projected sorbent costs. In general, all sorbents that will meet the pre-breakthrough target of 10 ppbv and a sorbent capacity of 15%, will be considered suitable for further evaluation.

2.4. Sorbent Screening for H_2S Removal in Barrier-Filter Reactor

The objective of this series of tests is to identify and rank the potential candidate sorbents for removal of H_2S in the second stage of the process.

This series of tests will be carried out in the packed bed reactor with a shallow bed of fines, consisting of the coal ash and H_2S sorbent fines at the baseline operating condition presented in Table 1. Because of the very low level of H_2S in both the feed and the barrier filter reactor effluent, highly reactive sorbents will be used to reduce the concentration of H_2S to the required ppbv levels. Therefore, up to four (4) highly porous and high surface area zinc-based sorbent fines with particle diameters of about 20 to 40 microns (–325 mesh) will be evaluated for H_2S removal in the second stage of the process. These sorbents are expected to be prone to excessive attrition, which will further improve sorbent utilization through reduction of sorbent particle size and increasing surface area of the sorbent.

As indicated in Table 1, at the initial baseline operating conditions, the tests will be conducted in the 5-cm ID packed bed reactor at 400 °C with sorbent bed consisting of about 25% H_2S sorbent and 75% ash. The maximum sorbent height in these tests will be set at 10 mm and the superficial gas velocity will be 5 cm/s resulting in a gas residence time of about 0.2 second. The H_2S content of the feed gas in these baseline tests will be 1000 ppmv with 100 ppmv of COS without HCl. At this operating condition, using a zinc-based sorbent containing 75% zinc oxide, the estimated theoretical H_2S

breakthrough time will be about 5.5 hours. Assuming a sorbent conversion of 20% (i.e., Zn/S=5), the estimated H_2S breakthrough time will be reduced to about 1.1 hours.

The experimental data to be collected in these tests will include a complete set of the test operating conditions and the H_2S concentrations in the reactor feed and effluent streams as a function of reaction time, until the desired breakthrough concentration of about 1 ppmv is achieved. As indicated earlier, during the experiments, the reactor temperature at different locations as well as the pressure drop across the bed will be measured and recorded by the automated data acquisition system. The H_2S content will be determined by the GC Chromatograph for the feed stream and by the Ion Chromatograph for the reactor effluent stream. Samples of the reacted sorbents from the sorbent bed will be collected. These samples will be examined to determine the extent of particle-particle interaction (if any) during the test. The chemical compositions of a selected number of the collected samples will be determined to provide information on the level of contaminant loading in the bed.

If none of the candidate sorbents can achieve the desired level of contaminant removal (i.e., $H_2S_{out}< 60$ ppbv) and the desired level of loading (i.e., S/sorbent > 6%), the baseline condition will be modified by reducing the H_2S content of the feed gas, and if necessary, by increasing the gas residence time or the sorbent content of the bed to achieve the desired level of cleaning.

Sorbent Ranking Criteria. Following the completion of the sorbent screening tests for H_2S removal in the second stage, the promising sorbent materials will be identified and ranked for further evaluation. Ranking of the sorbents will be based on the pre-breakthrough concentration, the effective sorbent capacity, as well as the projected sorbent costs. In general, all sorbents that will meet the pre-breakthrough target of 60 ppbv and a sorbent capacity of 6%, will be considered suitable for further evaluation.

3. Parametric Studies at Ambient Pressure

The objective of this series of tests is to determine the performance of the selected sorbents (mixed HCl and H_2S sorbents) for simultaneous removal of HCl and H_2S, and to determine the effects of various operating parameters on the performances of the moving-bed and the barrier-filter reactors.

As indicated earlier, based on the results of the ambient pressure sorbent screening tests, all potential sorbents for H_2S and HCl removal will be identified and ranked. The baseline operating condition for the ambient pressure tests will also be determined. However, because the high concentrations of HCl in the feed gas may result in absorption of HCl by the zinc- or copper-based sorbent pellets, determination of the performance of the sorbents for combined removal of HCl and H_2S is required. Furthermore, combined removal of HCl and H_2S using both types of sorbents will provide additional data on possible interaction between H_2S and HCl sorbents.

3.1. Baseline Tests for HCl and H_2S Removal in Moving-Bed Filter Reactor

The objective of this series of tests is to evaluate the performance of a selected number of combined H_2S and HCl sorbents for simultaneous removal of H_2S and HCl in the first stage of the process. The H_2S sorbents will be in both pellet (both bulk and supported) and powder forms and the HCl sorbent will be in powder form.

This series of tests will be carried out in the packed bed reactor consisting of pellets, sorbent fines, and ash at the baseline condition presented in Table 1. Initially, the two (2) highest ranked H_2S and HCl sorbents will be selected for these tests.

When H_2S sorbent fines are used, the tests will be conducted with inert pellets and fines consisting of ash, H_2S and HCl sorbents. However, if H_2S sorbent pellets are used, the tests will be conducted with sorbent pellets and fines consisting of ash and HCl sorbents, whereas, The baseline tests will be conducted at 500 °C with a bed height of 5 cm, and the gas residence time of about 1 second.

Based on the results of the sorbent screening tests (section 2.1 and 2.2) the H_2S, COS, and HCl content of the feed gas in the initial baseline test as well as the HCl sorbent content of the fines will be selected such that the breakthrough time for both HCl and H_2S will be about 8 hours.

The experimental procedure and data to be collected in these tests will be similar to those described in previous sections. Comparison of the observed pre-breakthrough concentrations and breakthrough times for both HCl and H_2S with those obtained in the screening tests will determine the extent of interactions between the sorbent and contaminants. Samples of the reacted sorbents from the top, the middle, and the bottom of sorbent bed will be collected. The chemical compositions of the collected samples will provide information to determine the level of contaminant loading and cross interaction between H_2S sorbent and HCl (if any). If it is shown that there are significant cross interactions between the sorbents and the contaminants, the baseline condition will be revised by changing the feed composition, the sorbent bed composition, and/or the sorbents to achieve the desired breakthrough times for both HCl and H_2S, and sorbent conversions for both sorbents.

Sorbent Ranking Criteria. Following the completion of the baseline tests for simultaneous H_2S and HCl removal in the first stage, the most promising sorbent materials will be identified and ranked for further evaluation. Ranking of the sorbents will be based on the pre-breakthrough concentration, the effective sorbent capacity, as well as the projected sorbent costs. In general, all sorbents that will meet the pre-breakthrough target of 3 ppmv and a sorbent capacity of 6% for H_2S and 20% for HCl, will be considered suitable for further evaluation.

3.2. Ambient Pressure Parametric Studies for Moving-Bed Filter Reactor

The objective of this series of tests is to determine the effects of operation parameters on the performance of the selected sorbents for moving bed filter reactor application.

Following the completion of the baseline tests and determination of the baseline operating condition, the effects of reactor temperature, gas residence time (or superficial gas velocity), and sorbent concentration in the bed on the performance of the selected sorbents will be determined in a series of tests conducted over the range of operating parameters expected in the process.

This series of tests will be carried out in the packed bed reactor consisting of pellets, sorbent fines, and ash at the operating conditions presented in Table 1. Initially, the two (2) highest ranked H_2S and HCl sorbents will be selected for these tests.

When H_2S sorbent fines are used, the tests will be conducted with inert pellets and fines consisting of ash, H_2S and HCl sorbents. However, if H_2S sorbent pellets are used, the tests will be conducted with sorbent pellets and fines consisting of ash and HCl sorbents, whereas, The sorbent bed height and the feed gas composition will be similar to those used in the baseline tests described in the previous section.

The effect of temperature on the performance of the selected sorbents will be determined by conducting tests at 450 and 550 °C. The effect of gas residence time on the performance of the selected sorbents will be determined at half and twice the baseline gas residence time determined in the baseline tests described above. The fraction of the sorbent fines to be used in these parametric studies will also be selected at about half and twice that in the baseline tests.

The experimental procedure and data to be collected in these tests will be similar to those described in previous sections. Samples of the reacted sorbents from the top, the middle, and the bottom of sorbent bed will be collected. These samples will be examined to determine the extent of particle-particle interaction (if any) during the test. The chemical compositions of the collected samples will provide information to determine the level of contaminant loading and cross interaction between H_2S sorbent and HCl (if any).

3.3. Baseline Tests for HCl and H_2S Removal in Barrier Filter Reactor

The objective of this series of tests is to evaluate the performance of a selected number of sorbent materials for simultaneous removal of H_2S and HCl in the second stage of the process.

This series of tests will be carried out in the packed bed reactor consisting of H_2S and HCl sorbent fines and ash at the baseline condition at 400 °C with a bed height of 10 mm. Initially, the two (2) highest ranked sorbents for each contaminant will be selected for these tests, and the gas residence time at about 0.2 second.

Based on the results of the sorbent screening tests (section 2.3 and 2.4) the H_2S, COS, and HCl content of the feed gas in the initial baseline test as well as the HCl sorbent content of the fines will be selected in such a way that the breakthrough time for both HCl and H_2S will be about 8 hours.

The experimental procedure and data to be collected in these tests will be similar to those described in previous sections. Comparison of the observed pre-breakthrough concentrations and breakthrough times for both HCl and H_2S with those obtained in the screening tests, will determine the extent of interactions between the sorbents and contaminants. Samples of the reacted sorbents from the top, the middle, and the bottom of sorbent bed will be collected. The chemical compositions of the collected samples will provide information to determine the level of contaminant loading and cross interaction between H_2S sorbent and HCl (if any). If it is shown that there are significant cross interactions between the sorbents and the contaminants, the baseline condition will be revised by changing the feed composition, the sorbent bed composition, and/or the sorbents to achieve the desired breakthrough times for both HCl and H_2S, and sorbent conversions for both sorbents.

Sorbent Ranking Criteria. Following the completion of the baseline tests for simultaneous H_2S and HCl removal in the second stage, the most promising sorbent materials will be identified and ranked for further evaluation. Ranking of the sorbents will be based on the pre-breakthrough concentration, the effective sorbent capacity, as well as the projected sorbent costs. In general, all sorbents that will meet the pre-breakthrough target of 10 ppbv for HCl and 60 ppbv for H_2S, and sorbent capacity of 4% for H_2S and 10% for HCl, will be considered suitable for further evaluation.

3.4. Ambient Pressure Parametric Studies for Barrier Filter Reactor

The objective of this series of tests is to determine the effects of operation parameters on the performance of the selected sorbents for barrier filter reactor application.

Following the completion of the baseline tests and determination of the baseline operating condition, the effects of reactor temperature, gas residence time (or superficial gas velocity), sorbent bed height, and sorbent concentration in the bed on the performance of the selected sorbents will be determined in a series of tests conducted over the range of operating parameters expected in the process.

This series of tests will be carried out in the packed bed reactor similar to tests described in the previous section. The sorbent bed height and the feed gas composition will be similar to those used in the baseline tests described in the previous section. Initially, the two (2) highest ranked sorbents for each contaminant (i.e., H_2S and HCl) will be selected for these tests.

The effect of temperature on the performance of the selected sorbent will be determined by conducting tests at 350 and 450 °C. The effect of gas residence time on the performance of the selected sorbents will be determined at half and twice the baseline gas residence time determined in the baseline tests described above. The fraction of the sorbent fines to be used in these parametric studies will also be selected at about half and twice that in the baseline tests.

Because the thickness of the filter cake is usually about only a few millimeters, to better simulate contaminant removal in the process, it is desirable to use a sorbent bed height that is as close as possible to the thickness of the filter cake. However, as the bed height is decreased, obtaining accurate and reproducible data becomes more challenging. Furthermore, to simulate the actual process it is desirable to use the lowest possible levels of H_2S and HCl in the feed gas. To achieve similar breakthrough time using lower concentrations of contaminants without changing the face velocity, it is necessary to reduce the bed height. Therefore, new experimental techniques and reactor arrangements will be investigated to determine the minimum bed height that will result in generation of accurate and reproducible data.

The experimental procedure and data to be collected in these tests will be similar to those described in previous sections. Samples of the reacted sorbents from the top, the middle, and the bottom of sorbent bed will be collected. These samples will be examined to determine the extent of particle-particle interaction (if any) during the test. The chemical compositions of the collected samples will provide information to determine the level of contaminant loading and cross interaction between H_2S sorbent and HCl (if any).

4. Parametric Studies at High Pressure

The objective of this series of tests is to verify the technical feasibility of the Ultra-Clean Gas Cleanup Process, identify the “best” sorbents for different stages of the process, and determine the optimum process operating conditions.

As described earlier, the results of the ambient pressure tests will identify the “most promising” sorbents for H_2S and HCl removal in both stages of the process and provide additional information on the reactivities and sorption capacities of the sorbents, sorbents interactions, and the effects of operating parameters on the performance of the sorbents. While the ambient pressure tests are needed to narrow down the choices of the sorbents and the optimum ranges of the operating parameters, to closely simulate the process, the effect of pressure on the performance of the sorbents must be determined by conducting the tests at the elevated pressure prevailing in the process.

The effects of pressure on the performance of the sorbents can be quite significant. The reactor pressure can affect both the thermodynamic equilibria (i.e., the minimum achievable concentrations of the contaminants) and the rate of chemical reactions involved in the process. Given the much higher flow rate of feed gases required for high pressure operation (at constant superficial gas velocity) concentration of the H_2S and HCl in the feed gases can be reduced to closely simulate the feed gas composition in the process, without significantly increasing the breakthrough time in the experiment.

All high pressure tests will be conducted in packed bed consisting of both H_2S and HCl sorbents as well as ash. The feed gas will consist of a simulated coal gas containing H_2S, COS, and HCl. The sorbents to be evaluated at high pressure will be selected based on the results of ambient pressure parametric tests described above.

4.1. High Pressure Tests for HCl and H_2S Removal in Moving-Bed Filter Reactor

The objective of this series of tests is to evaluate the performance of a selected number of combined H_2S and HCl sorbents for simultaneous removal of H_2S and HCl in the first stage of the process at an elevated pressure over the range of operating conditions expected in the Ultra-Clean Gas Cleanup Process. The H_2S sorbents will be in both pellet (both bulk and supported) and powder forms and the HCl sorbent will be in powder form.

Initially, a series of baseline tests will be carried out in the packed bed reactor consisting of pellets, sorbent fines, and ash at the baseline condition presented in Table 1. Two (2) highest ranked H_2S and HCl sorbents will be selected for each stage of the process and used in these tests.

When H_2S sorbent fines are used, the tests will be conducted with inert pellets and fines consisting of ash, H_2S and HCl sorbents, whereas, when H_2S sorbent pellets are used, the tests will be conducted with sorbent pellets and fines consisting of ash and HCl sorbents. The baseline tests will be conducted at 500 °C and 20 bar pressure, with a bed height of 5 cm, and a gas residence time of about 1 seconds.

Based on the results of the ambient pressure parametric tests (section 3.1) the H_2S, COS, and HCl content of the feed gas in the initial baseline test as well as the HCl and the H_2S sorbents content of the fines will be selected in such a way that the breakthrough time for both HCl and H_2S will be about 8 hours.

Following the completion of the baseline tests and determination of the baseline operating condition for high pressure operation, the effects of reactor temperature, gas residence time (or superficial gas velocity), and sorbent concentration in the bed on the performance of the selected sorbents will be determined in a series of tests conducted over the range of operating parameters expected in the process.

The effect of temperature on the performance of the selected sorbent will be determined by conducting tests at 450 and 550 °C. The effect of gas residence time on the performance of the selected sorbents will be determined at half and twice the baseline gas residence time determined in the baseline tests described above. The fraction of the sorbent fines to be used in these parametric studies will also be selected at about half and twice that in the baseline tests.

The experimental procedure and data to be collected in these tests will be similar to those described in previous sections. Samples of the reacted sorbents from the top, the middle, and the bottom of sorbent bed will be collected. The chemical compositions of the collected samples will provide information to determine the level of contaminant loading and cross interaction between H_2S sorbent and HCl (if any).

Best Sorbent Selection Criteria. Following the completion of the high pressure tests for simultaneous H_2S and HCl removal in the first stage, the "best" sorbent will be identified based on the pre-breakthrough concentration, the effective sorbent capacity, the effectiveness of the sorbent over the range of operating condition, as well as the projected sorbent cost.

4.2. High Pressure Tests for HCl and H_2S Removal in Barrier Filter Reactor

The objective of this series of tests is to evaluate the performance of a selected number of combined H_2S and HCl sorbents for simultaneous removal of H_2S and HCl in the second stage of the process at an elevated pressure over the range of operating conditions expected in the Ultra-Clean Gas Cleanup Process.

Initially, a series of baseline tests will be carried out in the packed bed reactor consisting of H_2S and HCl sorbent fines and ash at the baseline condition presented in Table 1. Two (2) highest ranked sorbents for each contaminant will be selected for each stage of the process used for these tests. These tests will be conducted at 400 °C and 20 bar using the minimum sorbent bed height determined from the parametric studies conducted at ambient pressure (section 3.4).

Based on the results of the ambient pressure parametric tests (section 3.4) the H_2S, COS, and HCl content of the feed gas in the initial baseline test as well as the HCl and the H_2S sorbents content of the fines will be selected in such a way that the breakthrough time for both HCl and H_2S will be about 8 hours.

Following the completion of the baseline tests and determination of the baseline operating condition for high pressure operation, the effects of reactor temperature, gas residence time (or superficial gas velocity), and sorbent concentration in the bed on the performance of the selected sorbents will be determined in a series of tests conducted over the range of operating parameters expected in the process.

The effect of temperature on the performance of the selected sorbent will be determined by conducting tests at 350 and 450 °C. The effect of gas residence time on the performance of the selected sorbents will be determined at half and twice the baseline gas residence time determined in the baseline tests described above. The fraction of the sorbent fines to be used in these parametric studies will also be selected at about half and twice that in the baseline tests.

The experimental procedure and data to be collected in these tests will be similar to those described in previous sections. Samples of the reacted sorbents from the top, the middle, and the bottom of sorbent bed will be collected. The chemical compositions of the collected samples will provide information to determine the level of contaminant loading and cross interaction between H_2S sorbent and HCl (if any).

Best Sorbent Selection Criteria. Following the completion of the high pressure tests for simultaneous H_2S and HCl removal in the second stage, the "best" sorbent will be identified based on the pre-breakthrough concentration, the effective sorbent capacity, the effectiveness of the sorbent over the range of operating condition, as well as the projected sorbent cost.

Schedule

The laboratory testing in the Base Program will be initiated following the approval of the submitted test plan, with an estimated start date of April 1, 2000, and is estimated to take 12 months to complete.

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