NOVEL GAS CLEANING/ CONDITIONING FOR INTEGRATED GASIFICATION COMBINED CYCLE

BASE PROGRAM FINAL REPORT

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By

Richard A. Newby (SWPC), Program Manager
Eugene E. Smeltzer (SWPC)
Thomas E. Lippert (SWPC)
Rachid B. Slimane (GTI)
O. Mehmet Akpolat (GTI)
Keyur Pandya (GTI)
Francis S. Lau (GTI)
Javad Abbasian (GTI)
Brett E. Williams (GTI)
Dennis Leppin (GTI)

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National Energy Technology Laboratory

Prepared by
Siemens Westinghouse Power Corporation
Science & Technology Center
1310 Beulah Rd.
Pittsburgh, Pennsylvania 15235

&

Gas Technology Institute
1700 S. Mt. Prospect Rd.
Des Plaines, Illinois 60018

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ABSTRACT

Coal gasification can generate hydrocarbon gases that may be utilized for the synthesis of chemicals or liquid fuels, or for fuel cell power generation, if extensive, deep syngas cleaning is first conducted. Conventional gas cleaning technology for this duty is expensive and may limit the feasibility of coal usage for such applications. The Siemens Westinghouse Power Corporation has proposed a novel scheme for polishing sulfur, halide, and particulate from gases to meet very stringent cleaning requirements for chemical or liquid fuel synthesis, or for fuel cell power generation. This "Ultra-Clean" gas polishing process is a dry process, injecting fine sulfur and halide sorbent particles into two stages of filter-reactors to accomplish the gas polishing by dry sorbent chemisorption of the contaminants. Stage I can utilize either a barrier filter-reactor or a granular, moving bed filter-reactor, while Stage II must apply a barrier filter-reactor to meet the final, stringent particulate requirement. The sorbent materials for each stage, their feed rates, and the two stage temperatures must be specified to satisfy the gas cleaning requirements of any specific application. The Ultra-Clean gas polishing process has the potential for controlling sulfur species to less than 60 ppbv, halides to less than 10 ppbv, and particulate to less than 0.1 ppmw.

The Base Program experimental activities described in this report have been completed to identify candidate sorbents and suitable operating conditions for each of the two stages of the Ultra-Clean process. The laboratory process simulation testing has identified a set of zinc-based and sodium-based, -325 mesh sorbents for each of the two stages that yield the performance potential for meeting the most stringent gas cleaning requirements. With these selected sorbents, the selected Stage I temperature is 499°C (930°F) and the Stage II temperature is 288°C (550°F).

Conceptual commercial process evaluation of a novel gas cleaning process that utilizes the Ultra-Clean gas polishing process has been performed to devise potentially viable process details for two applications: a general chemical or liquid fuel synthesis application, and a solid oxide fuel cell power generation application. Commercial process performance and economics have been estimated for this novel gas cleaning process. The results indicate promising performance and economic potential compared to the conventional, Rectisol-based, gas cleaning technology. Sorbent maximum acceptable consumption criteria have been extracted from the commercial process evaluations and show that relatively high, once-through sorbent feed rates can be economically viable in the Ultra-Clean gas polishing process. The process can also incorporate ammonia removal and mercury removal. The next phase of the program will conduct integrated, bench-scale testing of the Ultra-Clean syngas polishing process on a sub-scale coal gasifier with coal capacity of about 9,000 kg/day (10 tons/day).

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1. INTRODUCTION

Currently, natural gas is the premium fuel for the synthesis of chemicals or liquid fuels, and for fuel cell power generation. The literature on these natural gas-based applications, showing their performance and cost advantages over coal-based processing, is extensive (Basye, L. and S. Swaminathan, 1997; Czuppon, T. A., S. A. Knea, and J. M. Rovner, 1990; Czuppon, T. A., S. A. Knez, and D. S. Newsome, " 1990; English, A. J. Rovner, J. Brown, and S. Davies, 1990; Steinberg, M. and Hsing C. Cheng, 1988). This cost advantage results from the high investment costs for coal handling, coal gasification, coal-gas cleaning, and coal gas conditioning compared to the respective costs for natural gas processing. The high capital cost of coal handling and gasification is currently being reduced through larger-scale experience and process optimizations. As natural gas prices increase relative to coal, coal is becoming a potentially more attractive fuel for these applications (West Virginia University and Union Carbide Technical Center, 1995).

Commercial technology is available to clean coal-gasification hydrocarbon gases to the stringent levels of contaminants required for applications such as the synthesis of chemicals or liquid fuels, and fuel cell power generation. The prevalent commercial gas cleaning process, capable of achieving the very stringent gas cleaning requirements (<60 ppbv total sulfur species, < 10 ppbv total halides, <0.1 ppmw particulate) for these types of applications, is based on the "Rectisol" gas desulfurization technology. The Rectisol process uses refrigerated methanol absorption of sulfur species and is expensive to build and operate, consuming extensive power. Commercial gas cleaning processes also apply wet, low-temperature removal of halides, particulate, and other contaminants, resulting in extensive water treatment requirements. New, cheaper technologies are needed for stringent gas cleaning duty if coal is to become competitive with cleaner fuel sources, such as natural gas, in DOE Vision 21, multi-production plants.

The Siemens Westinghouse Power Corporation (SWPC), working with the Gas Technology Institute (GTI), is conducting the early development of a new process for coal-gas polishing, the “Ultra-Clean" gas polishing process, to meet the needs of coal gasification-based co-production of electric power with chemical or liquid fuel products. Many gas contaminants must be controlled to very low levels to meet the downstream processing requirements for fuel cell power generation, chemical synthesis, or liquid fuel synthesis. Reduced sulfur species, halides, and particulate are the specific contaminants addressed by the SWPC Ultra-Clean gas polishing process, although the process can also incorporate the control of other contaminant species. It is the development objective of this gas polishing process to economically meet the most stringent cleanup requirements for sulfur species, halide species and particulate expected for these applications. These contaminant levels are below the detection limits of conventional measurement instrumentation.

A 56-month, two-phase program is being conducted, consisting of a Base Program (23-months) and an Optional Program (33-months). The Base Program has produced laboratory-scale sorbent performance and characterization test data used to select specific sorbents to be developed and demonstrated in the Optional Program. The Base Program has also produced process performance evaluations and economic studies, as well as a conceptual market evaluation. The Optional Program will conduct comprehensive, integrated, bench-scale proof-of-principle tests of sorbents and advanced gas-sorbent filter-reactors at a GTI coal gasifier test facility.

1.1 ULTRA-CLEAN GAS POLISHING PROCESS CONCEPT

Figure 1.1 illustrates the basic Ultra-Clean gas polishing process concept. A coal gasifier produces a high-temperature, raw hydrocarbon gas containing many types of contaminants including sulfur species, halide species, and particulate. This gas is cooled to the operating temperature of a high-temperature (371 - 538°C, 700 - 1000°F) "bulk" desulfurization process, where a substantial amount of the sulfur is removed using a dry, regenerative sulfur sorbent. Limited bulk desulfurization could also be conducted within some types of fluidized bed and transport coal gasifiers.

The Ultra-Clean gas polishing process follows the bulk gas desulfurization step. It has two sorbent injection cleanup stages in series, as is illustrated in Figure 1.1. The bulk-desulfurized gas is reduced in temperature to the operating temperature of the first stage. The first stage reduces the concentration of the primary contaminants (sulfur and halide species) to about the 1 ppmv level in either a barrier filter-reactor, or in a granular, moving bed filter-reactor (shown in the figure), by injecting appropriate sulfur and halide sorbent particles into the gas stream. The barrier filter, or moving bed filter provides an excellent environment for dilute gas-particle contacting and packed-bed gas-particle contacting through uniform sorbent filter cakes. The partially-cleaned Stage I gas is lowered further in temperature to the operating temperature of the second stage.

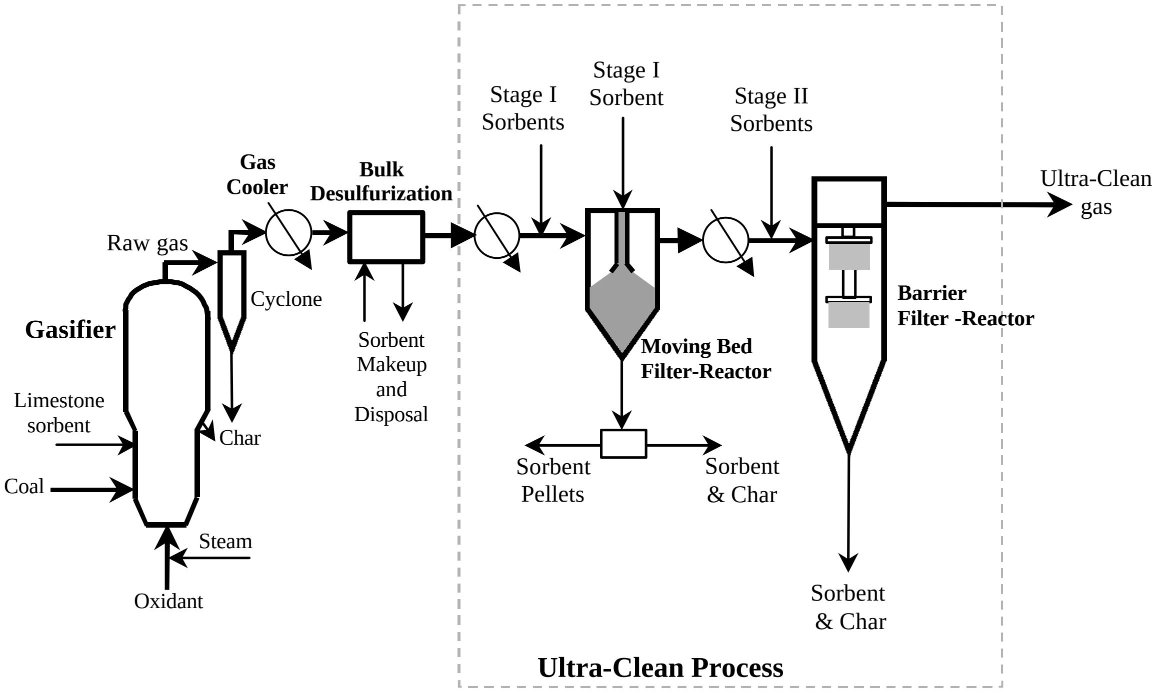


Figure 1.1 - Ultra-Clean Gas Polishing Concept

In Stage I, various dry halide sorbent materials (e.g., sodium-based) and various metal oxide-based, dry sulfur sorbent materials (e.g., zinc, copper, iron, and manganese-based) can be applied as fine particles (-325 mesh) injected into the gas stream. If desired, coarse sorbent pellets that also function as granular, moving-bed filter media can be used in Stage I.

In Stage II, a barrier filter-reactor must be used to reduce the particulate to the required level, and a second set of injected sorbents are used to reduce the sulfur and halide species. The Stage II barrier filter-reactor limits the penetration of particulate to less than 0.1 ppmw. Similar sorbent material types may be used in Stage II as in Stage I, but their particulate forms may differ from those in Stage I to promote better performance at the lower operating temperature of Stage II.

The Ultra-Clean gas polishing process is classified as a "dry" gas cleaning scheme using "once-through" sorbents. Process variations have also been identified that may provide potential improvements over this Base configuration. It is possible to incorporate the removal of other contaminants, such as ammonia and mercury, into Stage II of the process.

1.2 BASE PROGRAM OBJECTIVES AND SCOPE

The Base Program reviewed in this report was carried out to produce ground-work, laboratory test data and process evaluations for a conceptual feasibility assessment of this novel gas cleaning process. The GTI laboratory testing has focussed on the identification of suitable sulfur and halide sorbents and operating temperatures for Stage I and Stage II gas cleaning. This small-scale laboratory testing was also performed to provide evidence of the capability of the process to reach its stringent gas cleaning goals.

Process evaluations were performed in the Base Program to identify process alternatives, to devise process flow schemes, and to estimate process material & energy balances, process performance, and process costs. Comparisons have been made with the state-of-the-art conventional gas cleaning process, based on the Rectisol desulfurization technology, for a generalized chemical or liquid fuel synthesis application, and for a solid oxide fuel cell (SOFC) power generation application. The SOFC has been selected for evaluation over alternative fuel cell types because it has the highest thermal efficiency potential of the fuel cell technologies, and it has a unique set of gas cleaning requirements. While the work has focussed on sulfur, halide, and particulate control, considerations of ammonia, and mercury control have been included.

2. EXECUTIVE SUMMARY

Coal gasification can generate hydrocarbon gases that may be applied for the synthesis of chemicals or liquid fuels, or for fuel cell power generation, if extensive, deep gas cleaning is first performed. The conventional gas cleaning process for this duty, applying Rectisol desulfurization, a refrigerated, methanol-based absorbent technology, is expensive and may limit the feasibility of coal usage for such applications.

A novel gas cleaning scheme for polishing the sulfur, halide, and particulate content of syngases and fuel gases, so that they can satisfy very stringent gas cleaning requirements, has been proposed by the Siemens Westinghouse Power Corporation. The general "Ultra-Clean" gas polishing scheme is a dry process, injecting fine sulfur and halide sorbent particles into two stages of filter-reactors to accomplish the gas polishing by dry sorbent chemisorption of the contaminants. Stage I can utilize either a barrier filter-reactor, or a granular, moving bed filter-reactor, while Stage II must apply a barrier filter-reactor to meet the final, stringent particulate requirement. The temperature of each stage is controlled for optimum sulfur and halide removal with the selected sorbents.

The Base Program laboratory testing described in this report has been completed to identify candidate sorbents and suitable operating conditions for each of the two stages of the Ultra-Clean gas polishing process. Thermodynamics show that sodium-based sorbents are strong candidates for halide removal, with HCl being the main halide contaminant of interest in the program. Likewise, zinc, copper, iron, and manganese-based sorbent materials are strong thermodynamic candidates for sulfur removal, with H_2S being the major sulfur contaminant of interest in the program.

The laboratory testing has identified a specific set of zinc-based and sodium-based sorbents having the capability of meeting the process performance requirements for each Stage and has demonstrated this performance potential through laboratory test simulations. The sorbent characteristics and selected stage operating conditions are

- Stage I temperature: 499°C (930°F),
- Stage I sulfur sorbent type: IGTSS-362C (Zn/Ti mole ratio 1.5),
- Stage I halide sorbent type: trona ($Na_2CO_3 \bullet NaHCO_3 \bullet 2H_2O$),
- Stage I sorbents size distribution: -325 mesh, mass-mean diameter about 20 μm,
- Stage II temperature: 288°C (550°F)
- Stage II sulfur sorbent type: G-72E (70 wt% Zn),
- Stage II HCl sorbent type: G-92C (6.4 wt% Na),
- Stage II sorbents size distribution: -325 mesh, mass-mean diameter about 20 μm.

The Stage I sulfur sorbent, IGTSS-362C, is a manufactured, zinc-based sorbent previously developed by GTI in granular form for high-temperature H_2S removal. The Stage I halide sorbent, trona, is a cheap, commercially available, natural mineral. The Stage II sorbents G-72E (zinc-based) and G-92C (sodium-based) are commercial, Süd Chemie catalyst pellet materials.

The capability of these sorbents to achieve the required levels of gas cleaning has been substantiated in the laboratory test program under conditions that simulated a representative coal-based gas composition passing through thin packed beds of sorbents. Testing with individual sorbents, and mixtures of sulfur and halide sorbents were conducted in gases containing individually H_2S, HCl, or mixtures of these contaminants. These parametric tests were conducted at near-atmospheric pressure, with limited, additional tests to demonstrate sorbent performance under pressurized conditions being performed. Uncertainties exist in making gas contaminant measurements as low as 60 ppbv for H_2S and 10 ppbv for HCl, and GTI applied state-of-the-art equipment and procedures for making the measurements with minimum uncertainty in the test program. Test rig and sampling line equipment and operating procedures were designed to minimize both contaminant losses and background contaminant levels. Ion Chromatography was successfully used to make HCl measurements down to 10 ppbv, and the procedures are reviewed in appendix A. Stage I sulfur species contents down to 1 ppmv were reliably measured by a gas chromatograph equipped with a flame photometric detector. The Stage II sulfur species were measured by a special gas chromatograph technique reviewed in Appendix B, but could only achieve a detection limit of 85 ppbv, compared to the target of 60 ppbv. This was considered acceptable for the laboratory screening and verification tests.

Conceptual commercial process evaluations have been performed to devise potentially viable process scheme details for a novel gas cleaning process that utilizes the Ultra-Clean gas polishing process. The novel gas cleaning process consists of four, integrated process sections: a raw gasifier-gas cooling section, a bulk desulfurization section, a sulfur recovery section, and the Ultra-Clean gas polishing section. A base configuration and several alternative Ultra-Clean process configurations have been devised that require further, larger-scale testing to fully characterize and establish.

Commercial process performance and economics have been estimated for the state-of-the-art, Rectisol-based, conventional gas cleaning process and for the novel gas cleaning process for two applications: general synthesis of chemicals or liquid fuels, and SOFC power generation. Applying a conservative design basis for the evaluations, the novel gas cleaning process, using the Ultra-Clean gas polishing technology, shows extremely promising performance potential, environmental advantages, and economic potential compared to the conventional technology. The "dry" gas cleaning characteristic of the novel gas cleaning process minimizes waste water and condensate treatment requirements inherent with the conventional gas cleaning process. Several process options have been proposed to deal with the sorbent solid wastes generated in the novel gas cleaning process. The capital investment for the novel gas cleaning process is estimated to be at least 30% lower than that of the conventional gas cleaning process. The total cost-of-gas-cleaning, in dollars per unit mass of gas cleaned, is estimated to be at least 20% less than that of the conventional gas cleaning process.

The rates of sorbent consumption for the bulk desulfurization sorbent and the Ultra-Clean gas polishing sorbents, and the delivered prices of these sorbents, are the key parameters that influence the commercial cost feasibility of the novel gas cleaning process. These parameters are uncertain at this time, requiring further, larger-scale testing to establish, but the laboratory testing and other available data provides preliminary estimates for consumption rates and prices. Sorbent maximum acceptable consumption-and-price criteria, based on a 20% cost reduction relative to conventional technology, have been estimated and appear to be easily satisfied. The sorbent consumption rates of greatest concern are those for the bulk desulfurization sorbent and for the Stage I sulfur sorbent. While only particulate, sulfur and halide control were considered in the detailed process evaluations, process schemes have been proposed that allow ammonia and mercury gas cleaning to be included in the Ultra-Clean gas polishing process.

3. EXPERIMENTAL - LABORATORY SORBENT TESTING

Based on thermodynamic equilibrium considerations and available literature data, transition metal oxide-containing materials, such as oxides of zinc, copper, iron, and manganese, are the primary candidates for effective removal of sulfur (H_2S and COS) from coal gasification syngases. Materials containing sodium oxide/carbonate are the primary candidates for the effective removal of halides (primarily HCl) to the desired, stringent levels required of the Ultra-Clean gas polishing process.

A conceptual process flow diagram for the Ultra-Clean gas polishing process is shown in Figure 1.1. Approximate syngas and sorbent stream flows are listed in Table 3.1 to illustrate the expected characteristics of the process streams for a hypothetical, oxygen-blown gasifier, commercial application. A 907,000 kg (1,000 tons) coal/day gasification and integrated methanol plant is the basis for the rough estimates in Table 3.1. The plant coal is a 3 wt% sulfur, eastern bituminous coal. The flows are roughly equivalent to those that would represent an advanced, 150 MWe fuel cell plant. The general process concept includes the option for a Stage I granular, moving bed filter media that also functions as a sorbent for sulfur or halide removal. The experimental activities and process evaluations reported have excluded this option on the grounds that it is probably not as effective or economical as using powdered, injected sorbents and inert granular, moving bed filter media.

H_2S removal in the first stage of the process might be accomplished by using manufactured, zinc-, copper-, iron-, or manganese-based sorbents in powder form (-325 mesh) each at an appropriate Stage I temperature. In the Table 3.1 illustration, a manufactured, powdered, zinc-based sorbent is assumed for this duty, and an inert, pellet material is utilized as the Stage I granular, moving bed filter media. As shown in Table 3.1, the estimated, required feed rate in the first stage, for a zinc-based sorbent containing 25% zinc and achieving almost 50% conversion (with a zinc/total sulfur molar feed ratio of 2) is about 68 kg/hr. This sorbent feed rate is calculated from a simple material balance:

Sorbent Rate = (gas mass flow rate) / (gas molecular weight)
x (gas sulfur mole fraction) x (Zn/S molar feed ratio) x (Zn molecular weight)
/ (sorbent weight fraction Zn)

$$= (74{,}000 \text{ kg/hr}) \;/\; (19.9 \text{ kg/kg-mole}) \times (35 \times 10^{-6}) \times (2.0 \text{ moles/mole}) \times (65.4 \text{ kg/kg-mole}) \;/\; (0.25) = 68.1$$

where the gas molecular weight is estimated to be 19.9 kg/kg-mole. This sorbent flow represents only about 0.3% of the total inert pellet circulation rate of 24,000 kg/hr, where the inert pellet circulation rate is estimated as 25 times the total particulate flow rate to the granular, moving bed filter-reactor. The Stage I granular, moving bed filter considered in Figure 1.1 and in Table 3.1 might be equally-well replaced by a barrier filter.

Similar sorbents are candidates for Stage II sulfur removal at appropriate Stage II temperatures, and again a powdered, zinc-based sorbent is assumed in the table. H_2S removal in the second stage of the process is accomplished by injecting fine (–325 mesh), zinc-based powder into the syngas, upstream of the Stage II barrier filter. As shown in Table 3.1, the estimated required feed rate in the second stage for a zinc-based sorbent containing 75% zinc and achieving less than 20% conversion (with Zn/S molar ratio of 5) is only 3.2 kg/hr. This sorbent flow is estimated using the same material balance relationship presented above. Given the very low sorbent feed required for removal of H_2S in the second stage of the process, highly porous and reactive sorbents were considered in this program. Because of such low level of H_2S and the high surface area of the sorbents, adsorption can also be expected to play a significant role in retaining H_2S. The highly porous, once-through sorbents may be more prone to attrition, which would bring about a reduction of particle size accompanied by an increase in surface area, further improving sorbent utilization.

Removal of HCl from the syngas stream in the first stage of the Ultra-Clean gas polishing process is assumed 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 Table 3.1, the estimated required feed rate in the first stage for a sodium bicarbonate-based material containing 30% sodium (i.e., 70% purity), and achieving less than 50% conversion (with a Na/Cl molar feed ratio of 2) is only 143 kg/hr. The same relationship applied on Page 6 is used to make this estimate. 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., 70 kg/hr).

As shown in Table 3.1, removal of HCl from the syngas stream in the second stage of the Ultra-Clean gas polishing process is accomplished by injecting highly porous and reactive sodium-based sorbent into the syngas upstream of the barrier filter. 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 less than 20% conversion (with Na/Cl molar feed ratio of 5) is only 2.5 kg/hr, using the same relationship presented on Page 6.

Table 3.1 – Approximate Stream Flows in Ultra-Clean Gas Polishing Process (907,000 kg coal/day methanol plant or 150 MWe fuel cell plant)

	Stage I	Stage II
Gas Inlet		
total flow (kg/hr)	74,000	74,000
sulfur species (ppmv/ kg/hr)	35 / 4.2	2 / 0.2
halide species (ppmv/ kg/hr)	250 / 34	2.5 / 0.3
particulate (ppmw/ kg/hr)	10,000 / 740	340 / 25
Sulfur Sorbent Feed		
sorbent type	manufactured , zinc-based powder (25 wt% Zn)	manufactured, zinc-based powder (75 wt% Zn)
mass feed rate (kg/hr)	68	3.2
Halide Sorbent Feed		
sorbent type	natural, sodium-based powder (30 wt% Na)	manufactured, sodium-based powder (43 wt% Na)
mass feed rate (kg/hr)	143	2.5
Gas Outlet		
total flow (kg/hr)	74,000	74,000
sulfur species (ppmv/ kg/hr)	2/ 0.2	0.045 / 0.005
halide species (ppmv/ kg/hr)	2.5 / 0.3	0.008 / 0.0009
particulate (ppmw/ kg/hr)	340 / 25	0.1 / 0.009
GBF Media Rate (kg/hr)	24,000	----

GBF Solid Waste Rate (kg/hr)	790	----
Barrier Filter Waste Rate (kg/hr)	----	31

The laboratory test work conducted in this program was geared toward evaluating these sorbent materials in the context of both a moving bed filter-reactor and a barrier filter-reactor, to identify the best sorbent and the optimum operating conditions for removal of sulfur and halide species to the desired levels required of the Ultra-Clean gas polishing process. The sorbents evaluated in this program were all –325 mesh powder forms with mass-mean particle diameters of about 20 to 40 μm, similar in size to the ash/char particles contained in the syngas stream.

3.1 THERMODYNAMIC CONSIDERATIONS

The initial, principal criterion used for sorbent selection was based on thermodynamic equilibrium calculations to limit the choice of the active sorbent oxides to those that can meet the requirement of removing H_2S and HCl in Stage I to below 3 ppmv at the baseline temperature of 500°C and at 20 bar pressure. For Stage II, sorbent materials selection was based on the most stringent cleanup requirement, i.e., reducing H_2S and HCl concentrations to below 60 ppbv and 10 ppbv, respectively. Materials selection, based on thermodynamic guidelines, is discussed below for both process stages.

3.1.1 Syngas Simulation

The composition of the simulated syngas used for experimentation in this program, representative of oxygen-blown coal gasification, is presented in Table 3.2. It is intended to provide a representative, but simplified, gas test environment relative to a commercial syngas. The syngas nitrogen content used represents the nitrogen and argon contents of the oxidant stream, as well as nitrogen contributed by transport and purge sources. It was assumed that no HCl removal takes place prior to Stage I of the Ultra-Clean gas polishing process. Therefore, the inlet HCl concentration is assumed to be in the range 50-500 ppmv, with 350 ppmv taken as a baseline concentration. For H_2S, however, bulk removal is assumed to be accomplished in a high-temperature sulfur removal mode using a regenerable sorbent, such as zinc titanate, in an external reactor configuration such as a fluidized bed or a transport reactor. Therefore, the inlet H_2S concentration is assumed to range from 10 to 50 ppmv, with 35 ppmv taken as a baseline concentration.

Table 3.2 - Simulated Syngas Composition

Gas Component	Vol%
H_2	30
CO	35
H_2O	15
CO_2	10
CH_4	3
N_2	7
HCl	50 – 500 ppmv
H_2S	10 – 50 ppmv

The commercially available "HSC Chemistry" software package (Roine, 2000) was used for all thermodynamic simulations. The simplified, simulated syngas composition for oxygen-blown coal gasification, excluding HCl and H_2S, was equilibrated over the range of temperatures of interest to the Ultra-Clean gas polishing process (250 to 600°C), in increments of 50°C. Two cases were considered. In the first case, the 3 vol% CH_4 in the feed syngas, as well as the presence of CH_4 in the equilibrium syngas was taken into consideration. In the second case, CH_4 was not accounted for either in the feed syngas or as a stable component in the equilibrium gas composition. The 3% CH_4 was eliminated and the N_2 content was increased from 7% to 10%.

The equilibrium gas compositions of the two cases considered are shown in Figure 3.1 and Figure 3.2, respectively. As shown in Figure 3.1, when CH_4 is present, the equilibrium gas composition is dominated by CO_2 and CH_4, while the concentrations of the primary syngas components CO and H_2 are reduced substantially. This indicates a high degree of methanation according to the following reaction:

$$2\ CO + 2\ H_2\ =\ CH_4 + CO_2 \qquad (3.1)$$

When CH_4 is excluded from consideration, the syngas re-equilibrates, but the primary syngas components dominate almost throughout the entire temperature range considered. H_2 is seen to have the highest concentration, which then steadily declines as temperature increases. At the lower temperature end of the range considered, CO has the second highest concentration, but increases, approaching that of H_2. The H_2O concentration also steadily increases with increasing temperature.

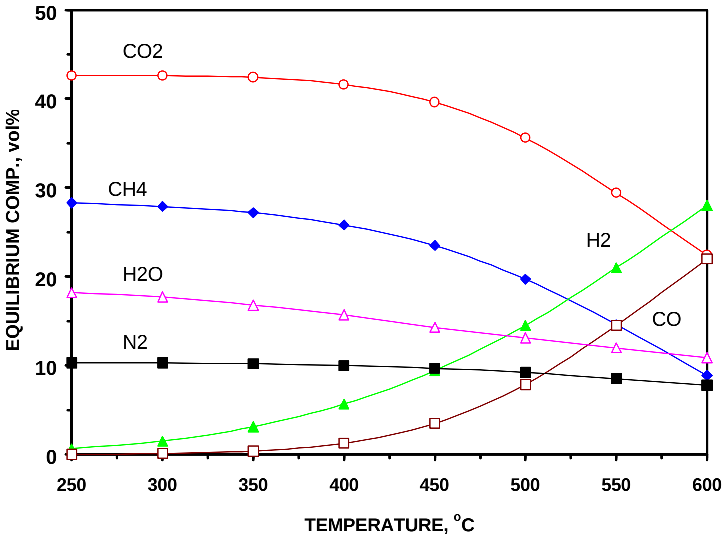


Figure 3.1 - Equilibrium Syngas Composition in the Presence of CH_4

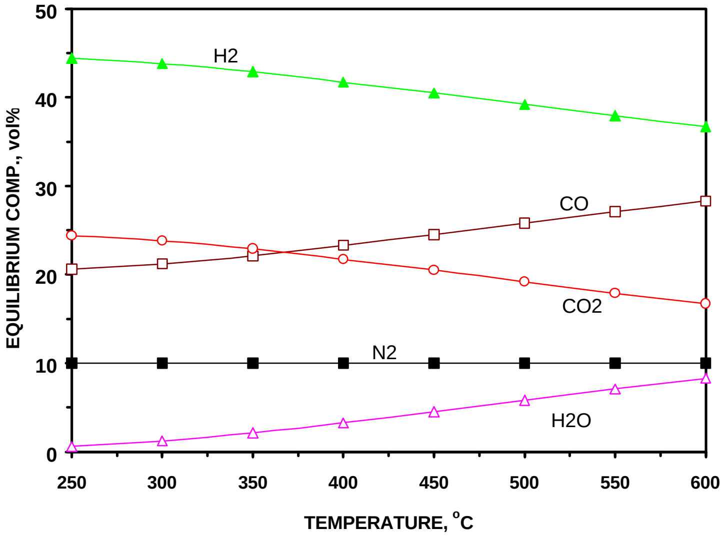


Figure 3.2 - Equilibrium Syngas Composition in the Absence of CH_4

These observations are consistent with the fact that the water gas shift reaction, as shown in equation (3.2), occurs to a lesser extent as temperature increases:

$$H_2O + CO = H_2 + CO_2 \tag{3.2}$$

The equilibrium gas composition of the simulated syngas, in the presence of CH_4, would not be representative of the actual syngas because of its artificially low CO and H_2 concentrations. Previous experimental work showed that methanation of a gasifier syngas occurs to a significantly lower extent than thermodynamic predictions and that the CH_4 concentration in the equilibrated syngas closely approximates that of the feed syngas. In addition, material balances involving steam showed that the water gas shift reaction dictates the equilibrium gas composition. Therefore, the equilibrium gas composition without CH_4 is taken in this analysis to represent a “true” equilibrium composition of the simulated syngas in the temperature range considered and was applied as the basis for sorbent equilibrium performance estimates.

3.1.2 Materials Selection for Chloride Removal in Stages I and II

Figure 3.3 shows the equilibrium HCl concentration following equilibration of the simulated syngas (with and without CH_4) with Na_2CO_3, the active dechlorination component of naturally occurring sodium-containing minerals, such as nahcolite or trona. At ambient pressure, the equilibrium HCl concentration is higher when CH_4 is present compared to when no CH_4 is present. This is consistent with the high H_2O and CO_2 concentrations in the syngas when CH_4 is present and the stoichiometry of the dechlorination reaction:

$$Na_2CO_3 + 2\,HCl = 2\,NaCl + CO_2 + H_2O \tag{3.3}$$

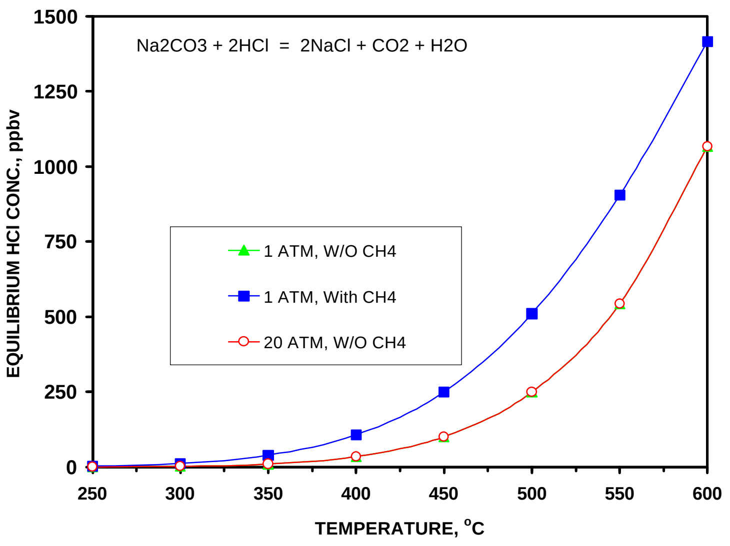


Figure 3.3 – HCl Concentration Following Equilibration with Na_2CO_3

Also, consistent with the stoichiometry of the dechlorination reaction (2 moles of HCl react to form 1 mole of CO_2 and 1 mole of H_2O, resulting no net change in the total number of moles), pressure does not have any effect on the extent of HCl removal. This was demonstrated in a previous related investigation (Krishnan and Gupta, 1999). Figure 3.3 clearly shows that the target of < 3 ppmv HCl in the cleaned gas can easily be achieved in Stage I, using inexpensive sodium-containing minerals, throughout the entire temperature range considered. Figure 3.4 displays the HCl concentration in the simulated syngas following equilibration with Na_2O, K_2CO_3, in addition to Na_2CO_3. As shown, Na_2O is highly efficient in removing HCl and virtually quantitative removal of HCl can be expected with Na_2O-containing materials. K_2CO_3 is also highly efficient.

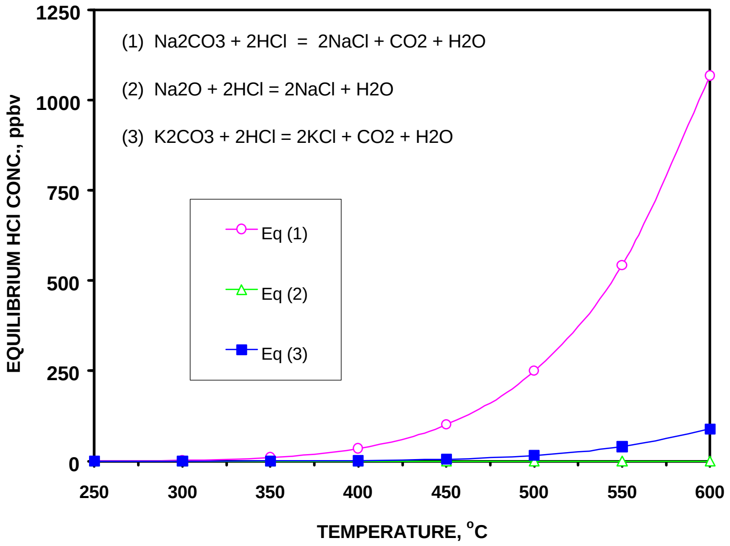


Figure 3.4 – HCl Concentration Following Equilibration with Na_2CO_3, Na_2O, and K_2CO_3

A closer representation of the equilibrium values of interest to Stage II is provided in Figure 3.5, where it is seen that the target concentration of 10 ppbv HCl in the cleaned gas can be achieved by Na_2O throughout the entire range considered. K_2CO_3 is also capable of achieving this target at temperatures up to about 475°C. For Na_2CO_3, however, the dechlorination temperature has to be limited to an upper value of 350°C to achieve the target HCl concentration. At 400°C (the baseline temperature for Stage II experiments), the equilibrium HCl concentration with Na_2CO_3 is about 36 ppbv.

Two predominance area diagrams for the Na-C-H-O system were constructed at 500°C and 300°C, and are superimposed as shown on Figure 3.6. The equilibrium compositions of the simulated syngas were then equilibrated at both temperatures, and are represented by the small circle and triangle indicated on Figure 3.6. As shown, both equilibrium compositions are well within the Na_2CO_3 stability region. Figure 3.6 shows that Na_2CO_3 is even more stable, with respect to Na_2O, as temperature is reduced. Therefore, because of the availability of CO_2 in the syngas and the high stability of the carbonate, Na_2O can be expected to undergo immediate conversion to Na_2CO_3 upon exposure to the syngas environment. Consequently, equilibrium HCl concentrations with Na_2O-containing materials can be expected to be dictated by the HCl/Na_2CO_3 equilibrium rather than by the HCl/Na_2O equilibrium.

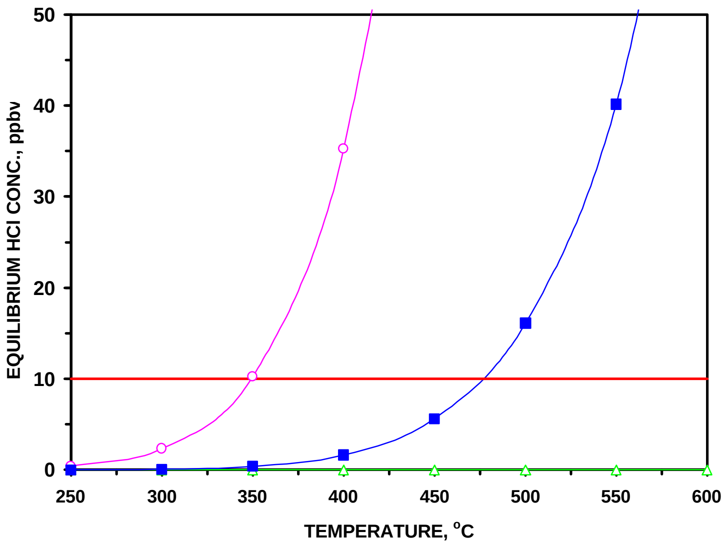


Figure 3.5 – HCl Concentration in Simulated Syngas Following Equilibration with Na_2CO_3, Na_2O, and K_2CO_3

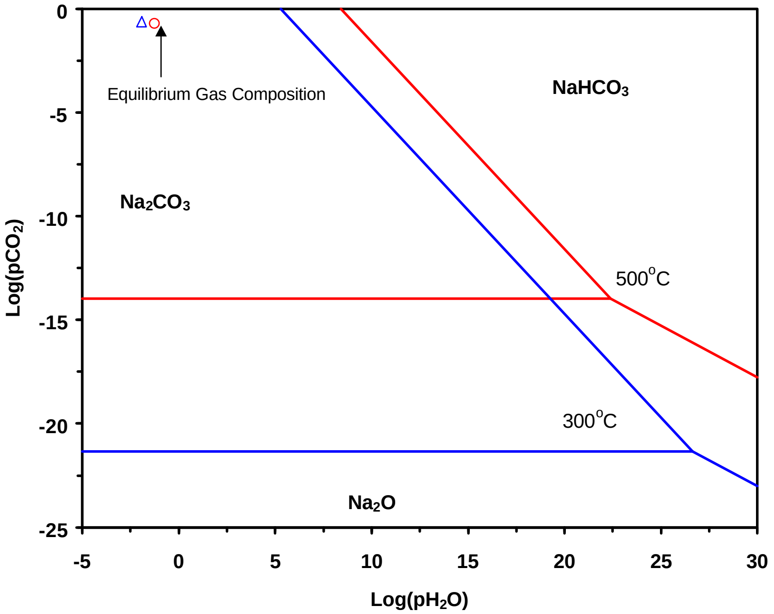


Figure 3.6 – Predominance Area Diagram for the Na-C-H-O System at 300 and 500°C

Based on thermodynamic predictions the concentration of the HCl contaminant in Stage II of the Ultra-Clean gas polishing process will be dictated by the Na_2CO_3/HCl equilibrium, regardless of whether the active component in the original, fresh dechlorination sorbent material is Na_2CO_3 (i.e., trona or nahcolite) or Na_2O (i.e., Katalco 59-3 or G-92C). Upon exposure to the simulated syngas environment, Na_2O will be immediately converted to the more stable Na_2CO_3. Therefore, from a thermodynamic standpoint, there appears to be no advantage to using especially manufactured materials (i.e., Katalco 59-3 or G-92C) unless they offer the potential of preventing or retarding the reaction of Na_2O with CO_2 to form Na_2CO_3, which would provide an opportunity for the extent of dechlorination to be governed by the more efficient Na_2O/HCl equilibrium. While this could be investigated experimentally and is believed to be highly unlikely, these especially manufactured materials may still offer an advantage if one considers reaction kinetics.

As demonstrated before, the target HCl concentration of 10 ppbv may only be achieved with Na_2CO_3 if the operating temperature is limited to 350°C. As dechlorination temperature is lowered, reaction kinetics experience an Arrhenius-type decrease, further reducing the utilization of the dechlorination sorbent material. At these lower temperatures, materials with high surface areas may yield reasonable conversions and accomplish HCl removal efficiencies below the target HCl concentration. Materials with lower surface areas, such as trona or nahcolite, may achieve conversions that are too limited to be considered practical.

3.1.3 Materials Selection for Sulfur Removal in Stages I and II

In a recent publication (Slimane and Abbasian, 2000), the principal investigator discussed in detail issues relating to the selection of suitable metal oxide-based sorbents for H_2S removal to meet IGCC requirements ($H_2S < 20$ ppmv). Taking into account several practical issues, in addition to thermodynamic constraints, sorbents based on the oxides of copper (Cu), iron (Fe), manganese (Mn), and zinc (Zn) were identified as suitable candidates in the moderate temperature range of 343 to 538°C (650 to 1000°F). Similar arguments can be made to identify these oxides as potentially suitable for accomplishing the goal of reducing H_2S concentration to < 3 ppmv in Stage I of the Ultra-Clean gas polishing process, and possibly for achieving the more stringent target of Stage II (total sulfur < 60 ppbv).

Figure 3.7 represents predominance area diagrams for Cu, Fe, Mn, and Zn oxides as a function of temperature and CO_2 to CO ratio in the gas phase. Each line in Figure 3.7 represents a boundary below which the lower oxide (or elemental metal) is stable. The equilibrium compositions of the syngas used in the experimental work are superimposed on Figure 3.7 as a dashed line.

Figure 3.7 is useful in predicting, among other things, the stable oxide form under prevailing syngas conditions, and therefore, the governing equilibrium reaction for desulfurization. It is seen that Cu, Fe_3O_4, MnO, and ZnO are the stable forms of the oxides considered in this study. The implications from this figure are as follows: For the Cu system, the stable form is elemental Cu, which is undesirable from the standpoint of desulfurization efficiency. Effective desulfurization may be achieved by combining copper oxide (CuO or Cu_2O) with a suitable inert oxide to significantly diminish its reduction rate in the syngas environment (Abbasian and Slimane, 1998). If that is realized, it is very desirable to develop a copper-based sorbent mainly because of its high sulfur removal efficiency (i.e., < 1 ppmv). Lower desulfurization temperatures favor the stability of copper-based sorbents against complete reduction, thus increasing the likelihood of developing effective sorbents based on this oxide. In a more recent investigation (Slimane and Abbasian, 2000), the development of effective copper-based sorbents for the moderate temperature range is described in detail.

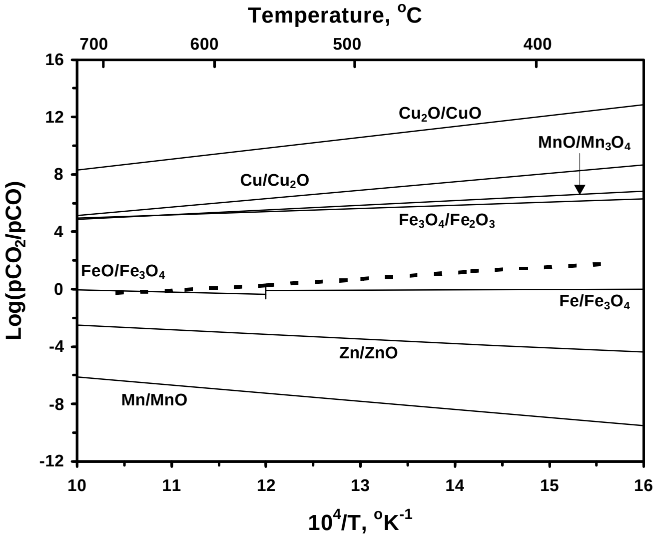


Figure 3.7 – Superimposed Stability Diagrams for Cu, Fe, Mn, and Zn Oxides as a Function of Temperature and CO_2 to CO Ratio

For the Fe system, the stable form of iron in the temperature range considered is either Fe or Fe_3O_4, depending on the reducing power of the syngas. At 500°C, the higher oxidation state of iron oxide (i.e., Fe_3O_4) is stable, which can be expected to result in more efficient H_2S removal. In addition, research (Focht et al., 1988) showed that Fe_3O_4 is significantly more reactive with H_2S than Fe. For the Mn system, MnO is the stable form of manganese both in very reducing atmospheres as well as in those that are only slightly reducing. For the Zn system, the stable form is ZnO throughout the entire temperature range considered.

Based on thermodynamics alone, only ZnO-containing materials can be expected to reduce the H_2S concentration to below the target level of 3 ppmv at the baseline temperature of 500°C (Figure 3.8). Fe- and Mn-based sorbents may be effective if the Stage I temperature were reduced to less than 400°C. As discussed above, there are ways to render CuO-containing materials capable of accomplishing this target, such as through compounding of CuO with an inert oxide (Al_2O_3, for example) such that complete reduction of CuO to the metallic form Cu is retarded and the material made more effective. This approach will require the manufacturing of the material. It was deemed quite reasonable in this program to acquire minerals containing Cu, Fe, Zn, or Mn to evaluate as potentially suitable sulfur removal candidates in Stage I of the Ultra-Clean gas polishing process. Because of the synergies that may exist, the target may be achieved with an inexpensive iron oxide-containing material that also contains minor quantities of more effective oxides. This is particularly the case with the iron oxide byproduct, as Stage I test results will show.

Figure 3.9 shows the H_2S concentration in equilibrium with ZnO and Na_2O. As shown, Na_2O is highly efficient for H_2S removal from reducing syngases. Based on the information provided in Figures 3.4, 3.5, and 3.9, Na_2O can be expected to act both as a dechlorination and a desulfurization material. However, because of the availability of CO_2 in the syngas and the high stability of the carbonate, Na_2O would undergo immediate conversion to Na_2CO_3 upon exposure to the syngas environment. Figure 3.6 shows that Na_2CO_3 is even more stable, with respect to Na_2O, as temperature is reduced. Therefore, equilibrium HCl concentrations with a Na_2O-containing material would probably be dictated by the HCl/Na_2CO_3 equilibrium rather than by the HCl/Na_2O equilibrium. In addition, as will be shown, Na_2CO_3 is not efficient for H_2S removal and a Na_2O-containing material may not be a viable desulfurization material in the Ultra-Clean gas polishing process.

As shown in Figure 3.9, ZnO is highly efficient for desulfurization; however, the equilibrium H_2S concentration at 400°C is about 97 ppbv, which exceeds the target H_2S concentration for Stage II of the Ultra-Clean gas polishing process of 60 ppbv. It may prove necessary to operate Stage II at temperatures $\leq$ 375°C to achieve this target H_2S level using a ZnO-containing material.

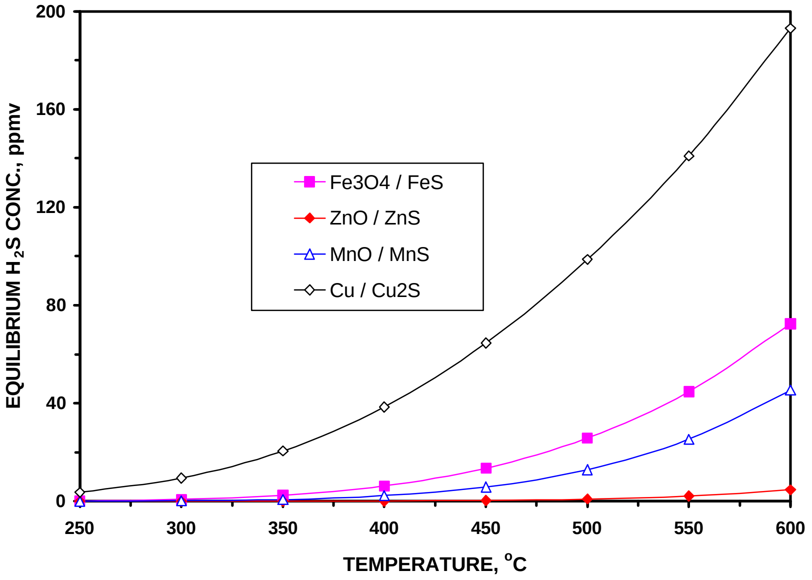


Figure 3.8 – Equilibrium H_2S Concentration for Fe, Cu, Mn, and Zn Oxides

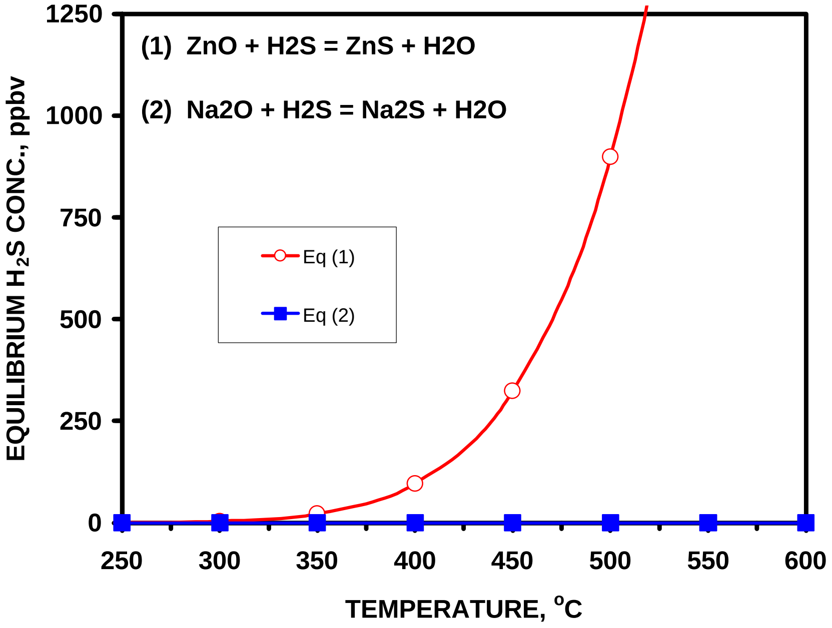


Figure 3.9 – Equilibrium H_2S Concentration for ZnO and Na_2O

3.2 MATERIALS SELECTION AND ACQUISITION

A list of all materials procured for evaluation in this program as well as their sources is provided in Table 3.3. The materials procured for HCl capture consist of nahcolite ($NaHCO_3$), trona ($Na_2CO_3 \bullet NaHCO_3 \bullet 2H_2O$), synthetic dawsonite or dihydroxyaluminum sodium carbonate ($NaAl(OH)_2CO_3$), Katalco 59-3, and G-92C. Nahcolite, trona, and dawsonite are naturally occurring minerals and were considered for the removal of HCl down to the 1 ppmv level in the first stage of the Ultra-Clean gas polishing process. Katalco 59-3 and G-92C are a dehalogenation catalyst and a heterogeneous catalyst for chloride removal. Both catalysts consist of sodium oxide (Na_2O) supported on an alumina (Al_2O_3) matrix. These latter two materials were selected on the basis of their high surface areas and, therefore, their potential suitability for the second stage of the Ultra-Clean gas polishing process, to reduce the total halide concentration to less than 10 ppbv. The dechlorination materials were ground and classified to a size range of – 325 mesh for use in the planned tests.

Table 3.3 –Sources of Procured Materials

Material	Source
HCl Sorbents	
Nahcolite	White River Nahcolite Minerals, Meeker, Colorado
Trona	FMC, Green River, Wyoming
Synthetic Dawsonite	Chattem Chemicals, Chattanooga, Tennessee
Katalco 59-3	Synetix (USA), Oakbrook Terrace, Illinois
G-92C	Süd Chemie (formerly United Catalysts, Inc., Louisville, Kentucky)
H_2S Sorbents	
Copper Concentrate	Highland Valley Copper, Logan Lake, British Columbia
EMP Filter Cake (Fe Ore)	Cliffs Mining Services Company, Ishpeming, Michigan
Brickox 6801 (Mn Ore)	The Prince Manufacturing Company, Quincy, Illinois
Iron Oxide Waste	Acme Steel Corporation, Chicago, Illinois
TSR-11	Süd Chemie formerly United Catalysts, Inc., Louisville, Kentucky)
G-72E	Süd Chemie (formerly United Catalysts, Inc., Louisville, Kentucky)
IGTSS-179	Developed at GTI under ICCI sponsorship
IGTSS-362C	Developed at GTI under NETL/DOE sponsorship
IGCC Ashes/Chars	
Gasifier Fly Ash	Sierra Pacific Power Company, Reno Nevada
TECo “Slag”	Tampa Electric Power Company, Reno, Nevada
GPGA	North Dakota Environmental Research Center

Samples from the ground materials were submitted for chemical analysis and the results obtained are summarized in Table 3.4. Moisture analysis on the sodium carbonate based minerals could not be performed because of carbonate decomposition during the drying step. As shown, trona has the highest Na content followed by nahcolite, synthetic dawsonite, Katalco 59-3, and G-92C, in this order.

Table 3.4 – Chemical Analyses of Materials for HCl Removal (As-Received Wt%)

	Nahcolite	Trona	Synthetic Dawsonite	Katalco 59-3	G-92C
Al			17.6	37.3	39.6
C	14.07	10.68	7.51		
H	1.38	1.84	2.52		
Na	26.9	35.6	13.5	9.98	6.41
Moisture	N/D	N/D	N/D	2.00	N/D

* N/D: Not Determined

As can be shown by a thermodynamic analysis, in the reducing syngas environment employed during testing in this program, the stable reactive components for nahcolite and trona can be expected to be either Na_2CO_3 or a combination of Na_2O and Na_2CO_3, depending on temperature. For synthetic dawsonite, Katalco 59-3, and G-92C, sodium aluminate ($NaAlO_2$ or $Na_2O{\bullet}Al_2O_3$) should be expected to be the stable reactive component. These observations are confirmed by previous experimental investigations (Krishnan et al., 1996; Krishnan and Gupta, 1999).

The materials selected and acquired for the removal of H_2S from the simulated syngas consist of a copper concentrate, an iron ore, a manganese ore, an iron oxide byproduct of iron/steelmaking operations in the Chicago area, two catalysts, and two regenerable metal oxide-based sorbents that have been developed at GTI. The chemical analyses of these materials are reported in Table 3.5. Close inspection of Table 3.5 reveals that the manganese ore, the EMP filter cake material, and the iron oxide byproduct may be suitable, in their as-received condition, for the first stage of the process, where the removal of H_2S down to the 1 ppmv level is sought. As can be expected, the high sulfur content of the copper concentrate is indicative of the existence of both copper and iron as sulfides. Therefore, the copper concentrate material required a pretreatment step (i.e., roasting), to drive off the sulfur prior to evaluation for sulfur capture.

TSR-11 and G-72E are heterogeneous catalysts manufactured by Süd Chemie (formerly United Catalysts, Inc., Louisville, Kentucky) in the form of 1/8-inch and 3/16-inch extrusions, respectively. TSR-11 consists of copper oxide (CuO) supported on alumina (Al_2O_3), while G-72E consists of zinc oxide (ZnO) supported on calcium aluminate ($CaAl_2O_4$). Both of these materials were selected on the basis of their high surface area and therefore, their potential suitability for use in the second stage of the Ultra-Clean gas polishing process to reduce the reduced sulfur species concentration to less than 60 ppbv.

IGTSS-179 is a regenerable copper-based sorbent that was developed at GTI under the sponsorship of the U.S. DOE and the Illinois Clean Coal Institute (ICCI). This sorbent was developed as highly reactive and attrition-resistant pellets ranging in size from 2 to 12 mm, based on reagent-grade oxides of copper, manganese, and alumina. Chemical analysis of this sorbent yielded 35.8% Cu, 11.3% Mn, and 17.9% Al, as shown in Table 3.5. The actual theoretical capacity of this sorbent for sulfur is about 9 g S/100 g sorbent; XRD (X-ray diffraction) analysis indicated Mn_2O_3 to be present in the sorbent as $MnAl_2O_4$, which is unreactive (Slimane and

Abbasian, 2000). Therefore, manganese oxide does not contribute to the desulfurization capacity of the IGTSS-179 sorbent. This sorbent was included for evaluation in Stage I both as a desulfurization agent and filtering medium in the granular, moving bed filter-reactor, as an alternative approach to the use of non-reactive pellets in conjunction with once-through minerals for H_2S removal.

Table 3.5 – Chemical Analyses of Materials for H_2S Removal (As-Received wt%)

	Brickox 6801 (Mn Ore)	Copper Concentrate	EMP Filter Cake (Fe Ore)	Iron Oxide Byproduct	TSR-11	G-72E	IGTSS-179	IGTSS-362C
Al	1.92			0.032	31.2	4.18	17.9	
Ba	0.41							
Ca	0.16			2.59		1.17		
Cu		40.7		0.10	21.2		35.8	
Fe	3.43	15.3	59.5	63.7				
Mg				0.63				
Mn	48.7			1.27			11.3	
Mo		< 0.03						
Si	1.87	3.91	2.31	0.36				
Na	0.34							
S		20.9						
Ti							0.54	34.7
Zn				0.86		69.8		27.4
Moisture	0.74	4.16	8.58		4.39			

The IGTSS-362C is a granular zinc titanate sorbent that has been developed also under the sponsorship of the DOE/NETL and ICCI. This sorbent was developed based on sol-gel processing that was found to produce sorbents that are substantially more effective than those produced by conventional techniques, such as co-precipitation or solid oxide mixing followed by granulation or spray drying (Slimane et al., 2001). This sol-gel sorbent exhibited a highly desirable combination of high chemical reactivity (desirable pore size distribution and high surface area), regenerability at lower temperature, and attrition resistance properties far exceeding the stringent requirement of the transport reactor application. This zinc titanate sorbent was included as potentially suitable for Stage II of the Ultra-Clean gas polishing process.

Physical characterization data are provided for the selected materials in Tables 3.6 and 3.7, considering the $<45\ \mu m$ and $> 45\ \mu m$ particle size cuts, respectively. These properties will be used to correlate materials performance.

Table 3.6 – Physical Characteristics of Selected Sorbent Materials (< 45 mm)*

	Hg Particle Density (g/cm^3)	Hg Bulk Density (g/cm^3)	Skeletal (He) Density (g/cm^3)	Hg Pore Volume (cm^3/g)	Porosity** (%)	Hg Surface Area (m^2/g)	Median Pore Diam. (Å)	Average Pore Diam. (Å)
Nahcolite	2.18	1.33	2.27	0.018	3.8	5.86	981	2110
Trona	1.16	0.85	2.38	0.444	51.4	21.50	N/D	1414
Katalco 59-3	1.47	0.90	2.72	0.314	46.0	78.89	172	374
G-92C	1.29	0.79	2.04	0.284	36.7	58.83	336	529
Iron Oxide Byproduct	1.35	0.87	4.37	0.513	69.1	12.10	N/D	3030
G-72E	2.28	1.51	4.83	0.232	52.8	47.75	223	382
IGTSS-362C	2.55	1.38	3.97	0.140	35.7	42.76	125	441
UCI-4169	2.19	1.38	3.14	0.138	30.3	0.71	8200	22567

* Corrected for inter-particle void.

** Calculated based on corrected values as $(1 - \rho_b/\rho_a)*100$, or equivalently as $\rho_b*(\text{Hg Pore Volume})*100$

Table 3.7 –Physical Characteristics of Selected Sorbent Materials (> 45 mm)

	BET N_2 Surface Area (m^2/g)	Hg Bulk Density	
		lbs/ft^3	g/cm^3
Nahcolite	9.69	59.6	0.95
Trona	8.65	76.1	1.22
Katalco 59-3	66.5	64.2	1.03
G-92C	165	53.2	0.85
Iron Oxide Byproduct	6.65	44.6	0.71
G-72E	40.3	89.2	1.43
IGTSS-362F	59.4	86.1	1.38

A selected sample of gasifier fly ash was obtained from the Sierra Pacific Power Company. This ash is designated as the Piñon Pine hot gas filter fines and contains about 56% carbon and 40% ash, in addition to minor amounts of sulfur, nitrogen, hydrogen, chlorine, and moisture, as indicated on Table 3.8. Size distribution of this material, as determined by the Coulter Counter technique, is presented in Figure 3.10. As shown, most of this material ranges in size between 2 and 10 μm.

Table 3.8 – Chemical Analyses of Selected Gasifier Fly Ash (Piñon Pine)

Component	Wt.%
C	55.77
Cl	0.017
H	0.46
N	0.38
S	1.37
Moisture	0.32
Ash	40.07

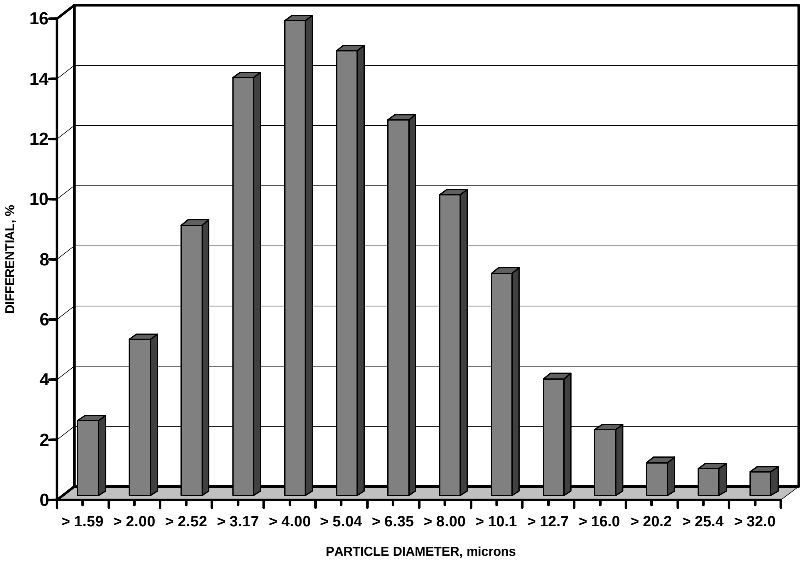


Figure 3.10 – Size Distribution of Selected Gasifier Fly Ash (Piñon Pine)

A 10-pound sample of gasifier fly ash was obtained from the North Dakota Environmental Research Center. This material, labeled as GPGA (Great Plaines Gasifier Ash), dates back to 1985. To assess its suitability for use in this program, a sample of this ash was exposed to the simulated syngas (less H_2S and HCl) at 500°C and the H_2S concentration in the reactor effluent was measured. As shown in Figure 3.11, H_2S evolved at a concentration of about 60 ppmv in the initial stages and slowly decreased to about 30 ppmv following 5 hours of testing.

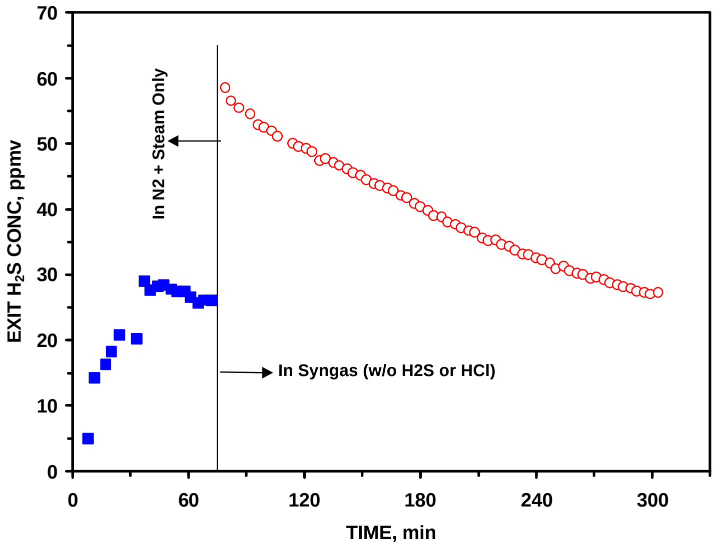


Figure 3.11 – H_2S Evolution from GPGA Ash Sample upon Exposure to Syngas

A large drum of ash sample, designated as "slag", was acquired from the Tampa Electric Company (TECo). This material was completely wetted and had a black "sand-like" appearance with a persistent ammonia-like odor. As suggested by TECo, this material was thoroughly washed prior to drying and classification. A sample was then submitted for chemical analysis, including Si, Al, Fe, Ca, K, Na, Cl, and sulfide and sulfate S. Because of its iron oxide, potassium oxide, and sodium oxide content, this material can be expected to contribute to the removal of both H_2S and HCl from the simulated syngas. Therefore, evaluation of the suitability of this material for use in this program also included quantification of its sulfur and chloride absorption capacity. The composition of this material, both according to the Material Safety Data Sheet (MSDS) provided and chemical analysis, is reported in Table 3.9.

Table 3.9 – Chemical Analysis of TECo "Slag" Sample

MSDS		Chemical Analysis	
Component	Wt %	Component	Wt %
Silica (SiO_2), amorphous	40-60%	Total Sulfur	1.76
Alumina (Al_2O_3)	15-35%	Sulfur	0.20
Ferric Oxide (Fe_2O_3)	5-25%	Chloride	0.02
Calcium Oxide (CaO)	1-10%	Aluminum	7.69
Potassium Oxide (K_2O)	1-5%	Calcium	2.06
Sodium Oxide (Na_2O)	1-5%	Iron	7.94
Balance	< 1%	Potassium	0.97
		Sodium	0.79
		Silicon	15.2
		Total Carbon	33.63

It should be noted that in the TECo operation, streams from a radiant syngas cooler directly following the gasifier, two parallel convective syngas coolers, and syngas particle scrubbers are combined into one slag + water stream, which is fed to a slag/water separation & slag handling unit. The wetted material received from TECo was taken from the fine slag portion. More information about this material is available in a paper by McDaniel et al., 1998.

To assess its suitability for use in this program, a sample of the TECo slag was exposed to the simulated syngas (less H_2S and HCl) at 500°C and the H_2S and HCl concentrations in the reactor effluent were measured. As shown in Figure 3.12, similar to the GPGA material, H_2S evolved at a concentration of about 60 ppmv in the initial stages and slowly decreased to about 30 ppmv following 4 hours of testing. Some HCl was also detected, but at concentrations lower than 5 ppmv. These results are explained by the presence of both sulfur and chloride (although to a much lower extent) as the source of H_2S and HCl emissions upon exposure to the reducing syngas environment. Following the reductive treatment, HCl and H_2S were introduced in the feed gas at concentrations of 350 and 50 ppmv respectively. The results obtained, also reported in Figure 3.13, indicate the TECo slag does not have a significant HCl or H_2S removal capability.

3.3 LABORATORY SIMULATION OF THE ULTRA-CLEAN GAS POLISHING PROCESS

A major portion of the gas cleaning in the Ultra-Clean gas polishing process is accomplished inside a moving-bed of granules mixed with entrapped sorbent particles, or within a filter cake of sorbent particles on the surface of the barrier filter elements. A portion of the contaminant removal also will take place in the dilute, entrained phase of the two filter-reactor vessels, but this is expected to be less significant. Accordingly, to closely simulate the moving-bed filter-reactor, the laboratory experiments for evaluation of the candidate sorbent materials were carried out in a packed bed reactor that includes sorbent fines, inert pellets (or sorbent pellets), and gasifier fly ash, as shown in Figure 3.13. Based on the flow rates of different solid streams shown in Table 3.1, the estimated pellet/total fines mass ratio is about 85, but because of much lower fraction of void space in the packed-bed test unit, the pellet/fines mass ratio in the test unit packed-bed test unit is about 2 times higher than is estimated for the actual process.

In the barrier filter-reactor, gas cleaning in the filter cake is simulated by a shallow bed of sorbent fines and fly ash, as shown in Figure 3.14. Based on the flow rates of different solid streams shown in Table 3.1, the filter cake should ideally consist of about 24 wt% H_2S sorbent, 50 wt% HCl sorbent, and 26 wt% ash. The filter cake is expected to have a 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 would be 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.

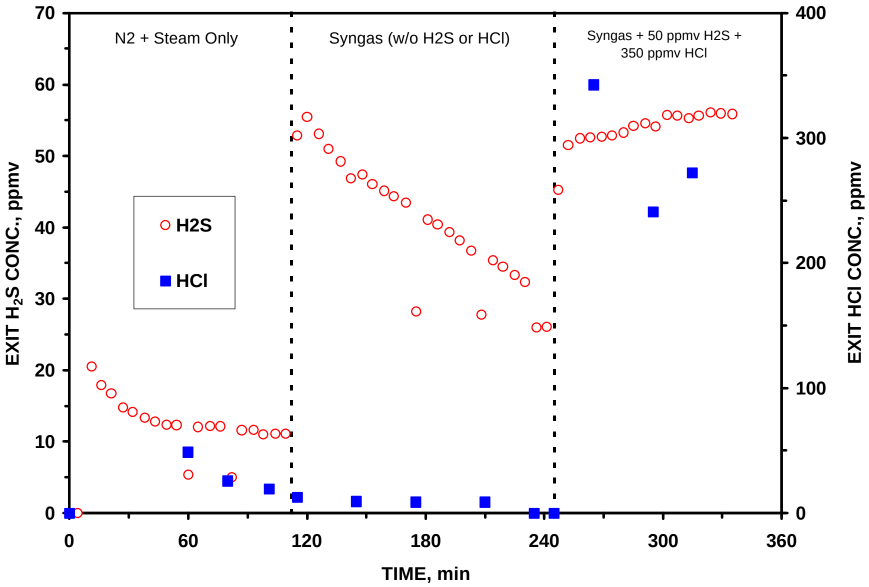


Figure 3.12 – H_2S and HCl Evolution from TECo Slag Sample upon Exposure to Syngas

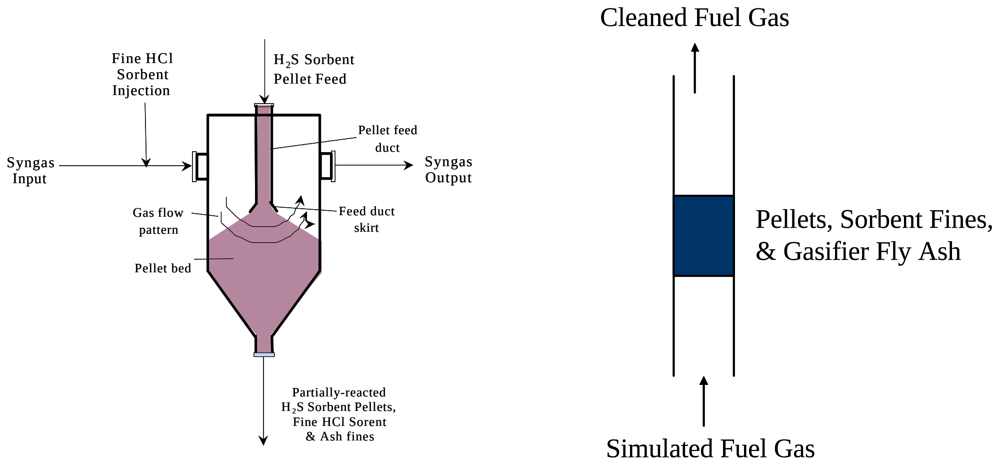


Figure 3.13 – Laboratory Simulation of Moving Bed Filter-Reactor

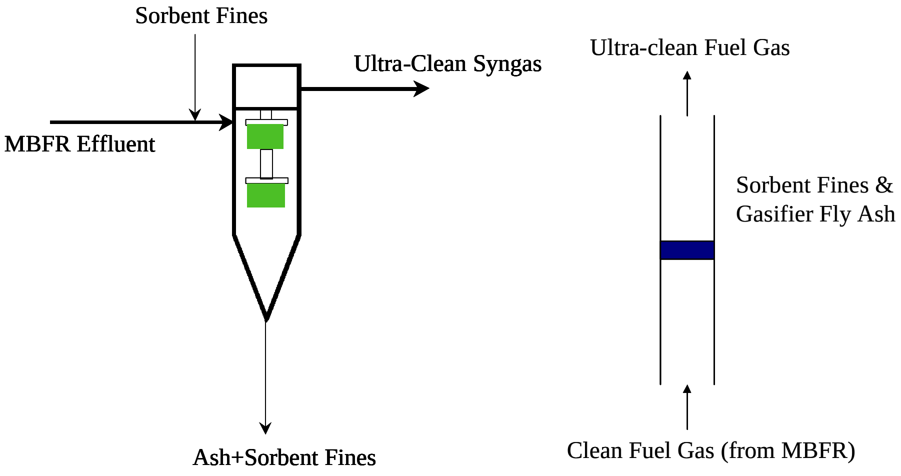


Figure 3.14 – Laboratory Simulation of Barrier Filter-Reactor

The laboratory experiments were conducted initially in an ambient pressure packed-bed reactor to identify promising desulfurization and dechlorination materials and their optimum ranges of operating conditions. A high-pressure/high-temperature reactor (HPHTR) unit was then to be used to quantify the effect of pressure on the performance of superior materials. The operating conditions including gas composition, gas residence time, reactor temperature and pressure, and sorbent bed height were selected to closely simulate those prevailing in the Ultra-Clean gas polishing process. The ranges of operating variables used in tests representing the first and second stages of the process are summarized in Table 3.10.

Table 3.10 – Ranges of Operating Variables

	First Stage	First Stage	Second Stage	Second Stage
Operating Parameter	Baseline	Range	Baseline	Range
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., μm	20 and 6,000 (If Needed)	20 and 6,000 (If Needed)	20	20
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	250-3000 ppmv	5-2000 ppmv	5-2000 ppmv
H_2S	35 ppmv – 2%	35 ppmv – 2%	5-2000 ppmv	5-2000 ppmv
COS	3-2000 ppmv	3-2000 ppmv	3-200 ppmv	3-200 ppmv
N_2	Balance	Balance	Balance	Balance

* Mass Ratio

Ambient Pressure Packed-Bed Reactor Unit

An existing ambient pressure packed-bed reactor system was significantly modified to accommodate the use of HCl in addition to H_2S, and to allow for careful handling and sampling of reactor off-gas. The schematic diagram of the overall experimental arrangement of this system is shown in Figure 3.15. The unit essentially consists of a quartz reactor shell and a quartz reactor insert that are externally heated by a three-zone electric furnace, equipment for feeding and measuring the flow rate of the gases, measuring and controlling the bed temperature, monitoring the reactor pressure and the pressure drop across the bed, off-gas sampling and analysis, and an automated data acquisition system.

The three-zone furnace is positioned with respect to the bed to accomplish gas preheating and careful control of the bed temperature. The reactor system is configured for flowing gas upward. Gas combinations for flows are produced via control of gases from pressurized gas cylinders through pre-calibrated electronic mass flow controllers, as shown in the diagram. The water content of simulated syngas is controlled by a metering pump acting on distilled water, which is discharged into a quartz tube. Hydrogen sulfide (H_2S) and carbonyl sulfide (COS) are obtained from a certified gas mixture of $H_2S/COS/H_2$. This mixture mixes with the other gases (CO_2, H_2, CO, CH_4, N_2) before the introduction of the complete mixture into the reactor. Hydrogen chloride (HCl) is obtained from a certified HCl/H_2 gas mixture and is introduced separately into the reactor to minimize corrosion problems.

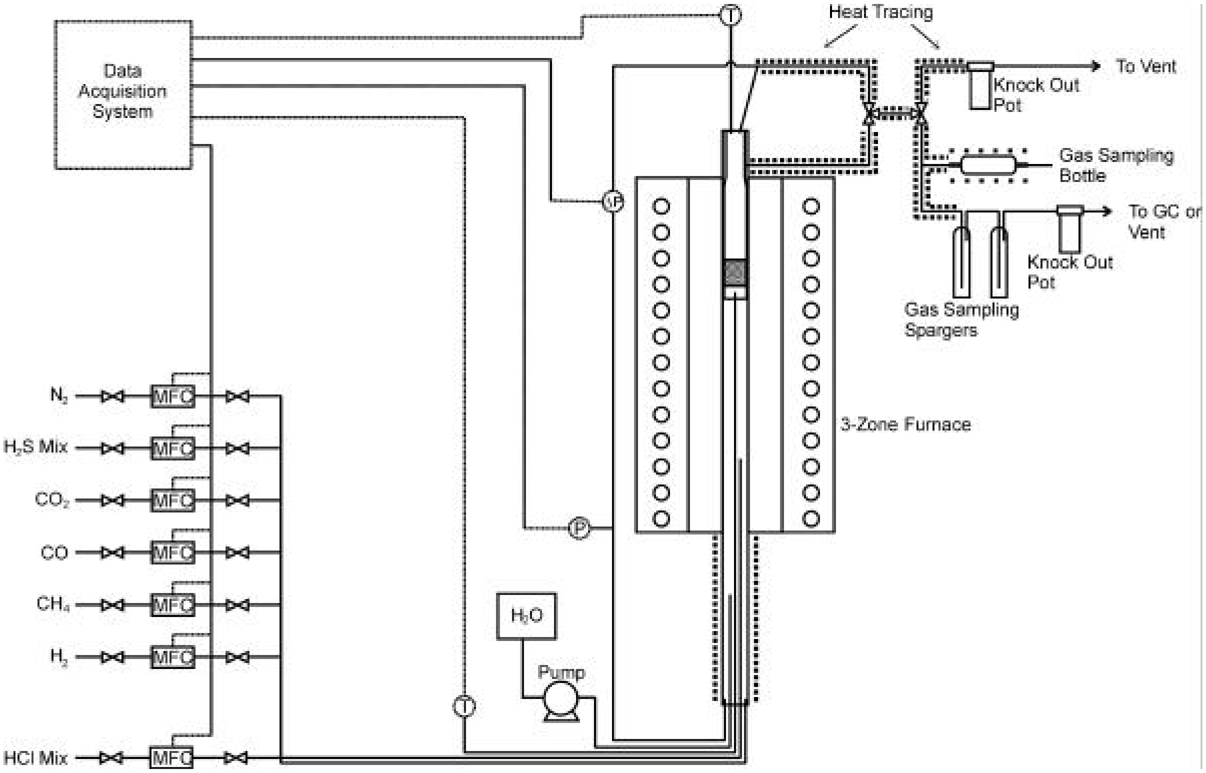


Figure 3.15 – Schematic Diagram of the Packed-Bed Reactor Unit

Water is introduced in the bottom portion of the 112 cm (44-inch) long by 5 cm (2-inch) I.D. quartz reactor shell containing 6 mm (¼ inch) diameter spherical deadburned alundum pellets to provide for better heat transfer characteristics. This part of the reactor shell is maintained at a temperature of at least 200°C to induce the vaporization of liquid water. The $CO_2/H_2/CO/CH_4/N_2/H_2S$ gas mixture is introduced in the lower zone of the furnace, while the HCl mixture is introduced just below the sorbent bed. A representative sample of the feed simulated syngas can be readily obtained through an outlet at the top of the reactor shell.

A number of reactor inserts have been especially designed to allow for maintaining a constant bed height and for easy replacement of bed materials between tests. Each insert has a 4.5 cm O.D. and a 4.2 cm I.D. sorbent bed cage of a predetermined height. The top of the cage is a fixed porous frit, while the bottom consists of a similar, but removable porous frit to allow for placement of sorbent bed materials (i.e., pellets, H_2S and HCl fine materials, and fly ash).

The reactor off-gas line and associated gas sampling lines are heat-traced to prevent condensation, which otherwise will interfere with the residual HCl content of the cleaned gas. In addition, to prevent any adsorption of residual HCl (or H_2S), the sampling lines are maintained at a minimum temperature of 200°C. These steps are critical for the accurate measurement of HCl in the cleaned gas via ion chromatography.

During each experiment, the reactor temperatures at different locations as well as the pressure drop across the bed were 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 were collected. These samples were 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 were determined to provide information on the level of contaminant loading across the bed.

Analytical Instrumentation for Measurement of HCl and H_2S Concentrations

Measurement of the HCl content of the feed as well as the cleaned gas streams will be carried out by dissolving HCl in a known quantity of a solvent (de-ionized water), and determining the chloride content of the solvent by Ion Chromatography. This method can be used for measurement of the HCl content of the reactor feed and exit gas streams over the entire range of interest in this program (i.e., 10 ppbv to 2 vol%), by using significantly different gas to solvent ratios.

A Dionex DX-320/IC20 chromatography system was acquired and used to perform ion chromatography (IC) analyses. This computer-operated 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.

Analytical work initially focused on establishing an ion chromatography method for the accurate measurement of chloride and sulfur both in the ppmv and the ppbv ranges. A number of liquid standards were used to calibrate the IC instrument, as shown in Figures 3.16 and 3.17. For the first stage of the Ultra-Clean gas polishing process, however, only HCl was measured with the IC instrument. The off-gas from the reactor was periodically bubbled through a two-sparger system in series to dissolve the HCl. Samples from the two spargers were then analyzed for chloride.

During the first stage of the process H_2S (and COS) was measured by a dedicated gas chromatograph equipped with a flame photometric detector (FPD). The GC-FPD unit has been in operation at GTI for several years and, prior to use, was calibrated for the 1 to 10 ppmv H_2S range. The H_2S concentration in the sub-ppmv range (.01-1 ppmv) was initially planned to be determined by the Dionex DX-320/IC20 chromatography system. A 5 mM KOH – 16 mM H_2O_2 was determined to be a suitable absorber solution for the dissolution and oxidation of all the residual H_2S in the syngas. H_2O_2 oxidizes H_2S into SO_4^-, which can be detected by the IC system.

Provision of High-Pressure Packed-Bed Reactor

A newly-reconstructed high-pressure/high-temperature reactor (HPHTR) is available at GTI to carry out material evaluation tests in a packed-bed or a fluid-bed mode of operation at a maximum temperature of 750^oC and a maximum pressure of 30 bar. The reactor vessel is a pressure-balance system, in which purge gases prevent corrosive gases from coming in contact with metal surfaces, such as the pressure-retaining vessel wall, which is made of 316 stainless steel. All reactor parts that come in contact with hot corrosive gases are constructed of quartz or ceramic material to prevent corrosion and loss of the reactive component in the gas mixture.

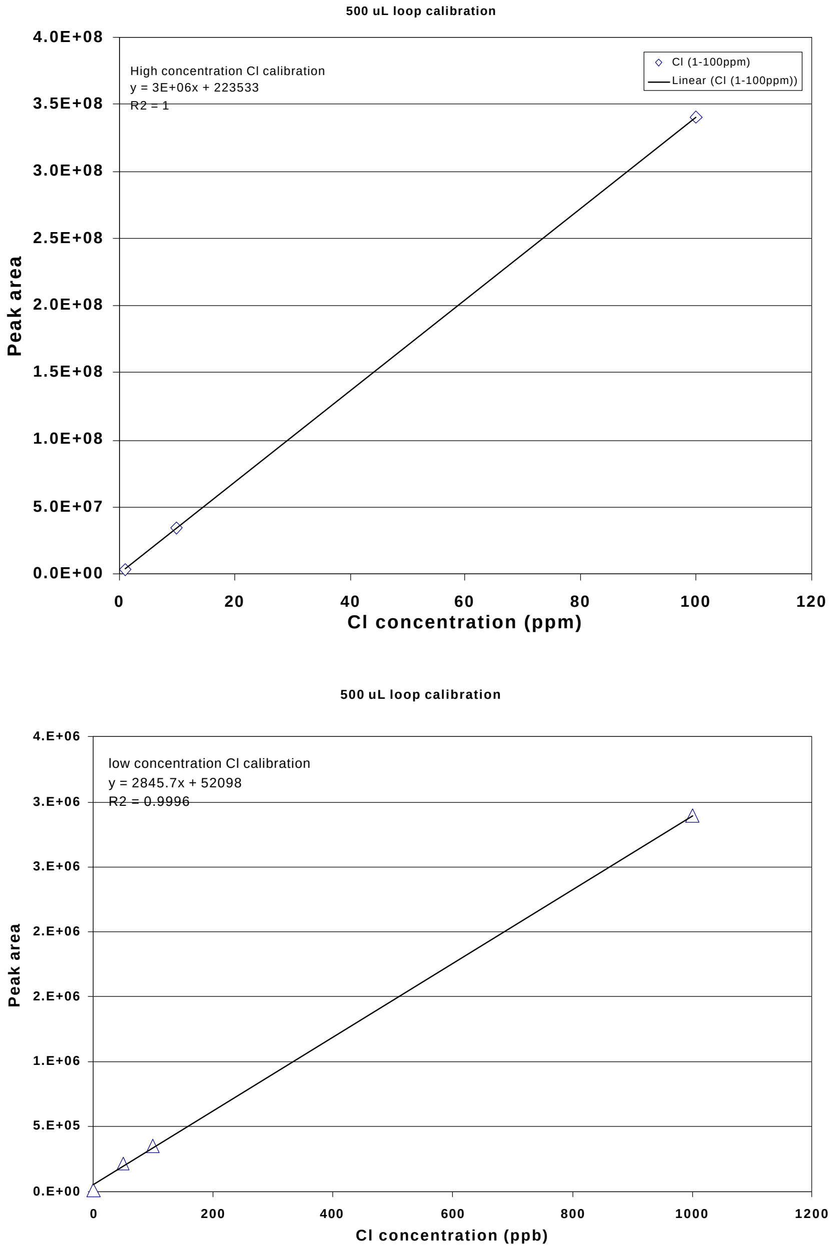


Figure 3.16 – Ion Chromatograph Calibration Curves for Chloride Measurement

This reactor system was designed specifically for use with hydrogen sulfide (H_2S) as the reactive component, with all parts of the reactor conveying cool corrosive feed gases being constructed of 316 stainless steel. Since hydrogen chloride (HCl) is reactive with stainless steel, even at low temperature and pressure, it was necessary to modify the system somewhat, by re-constructing any parts of the reactor that may come in contact with HCl out of Hastelloy C-276, with the exception of those parts made of quartz. Hastelloy C-276 is a nickel alloy known to have exceptional corrosion resistance to chloride-containing media.

A schematic diagram of the overall reactor arrangement is shown in Figure 3.18. The present reactor system consists of the following main components: (1) a pressure-retaining vessel,

(2) a quartz reactor insert, (3) a reactor heater assembly, (4) a feed gas and steam supply system, (5) process instrumentation and data acquisition, (6) an exit-gas heat-exchange and condensate-collection system, and (7) an exit gas sampling and analysis system.

The pressure retaining vessel houses the quartz reactor insert, the reactor assembly, metal liners, ceramic tubes, and thermowells. To be consistent with the testing done at low pressure, a new quartz reactor insert compatible with the high pressure reactor configuration, having an inner diameter of 4.2 cm and the capability to hold a bed height of up to 10 cm, was acquired. Similar to the original quartz reactor insert, the new insert was fabricated with a flange at the top of the reactor for ease of removal and replacement.

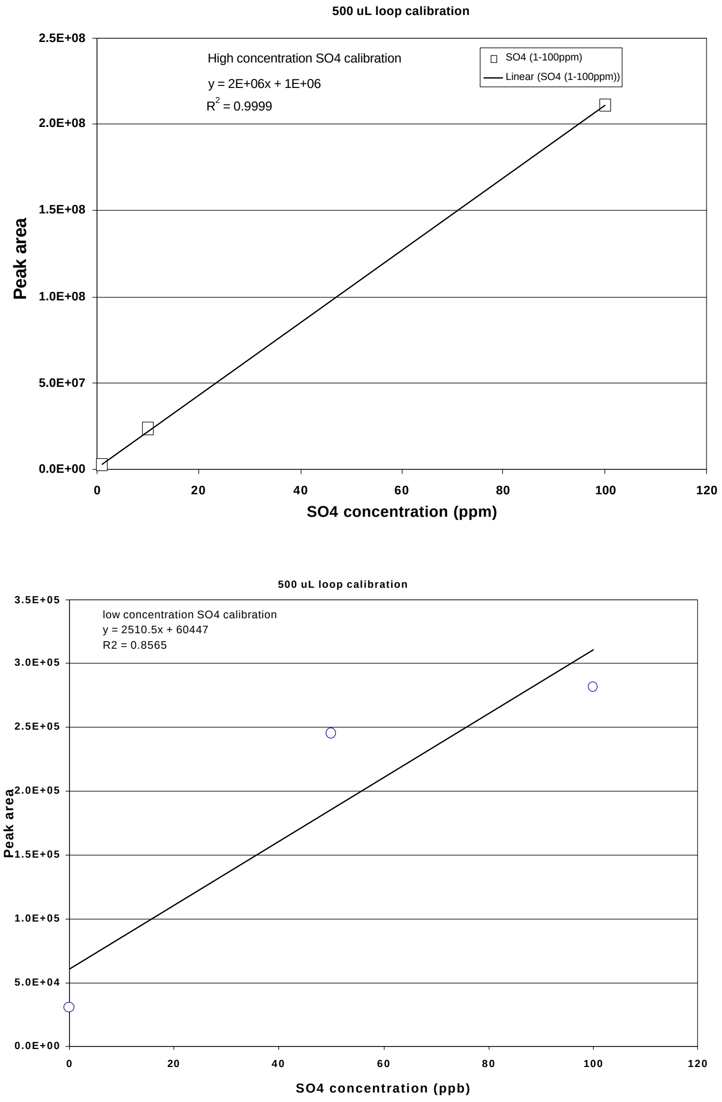


Figure 3.17 – Ion Chromatograph Calibration Curves for Sulfur Measurement

The reactor heater assembly consists of a three-zone furnace to heat the reactor to the operating temperature. Feed gases are supplied to the reaction vessel from compressed gas cylinders, while nitrogen gas is supplied from a tank of liquid nitrogen, using stainless steel tubing and mass flow controllers. Hastelloy C-276 tubing was added for the delivery of the HCl-H_2 gas mixture to the entry-point of the reactor system, where a quartz lance conveys both reactive gas mixtures, containing HCl and H_2S, to just below the frit of the quartz reactor insert holding the bed of sorbent material(s). Process instrumentation and data acquisition were modified to record the HCl gas mixture flow via a mass flow controller.

The reactor exit required modification in order to handle the presence of HCl in the effluent gas, since stainless steel tubing was previously used to convey the gas. Ability Engineering Technology, a local company who built the stainless steel flanges for the original reactor system, made a new top flange, as shown in Figure 3.19, with the following modifications. A plate of Hastelloy C-276 was welded to the face of the flange forming the seal to the reactor interior. A Hastelloy pipe, welded through the top flange and extending into the hot-zone of the reactor, will convey all of the exiting gas out of the reactor and into a ½” diameter Hastelloy tubing. A Hastelloy thermowell was also welded into the top flange, extending down into the reaction zone to just above the bed of sorbent material(s) being evaluated, providing the capability to monitor the gas temperature at the exit point of the bed.

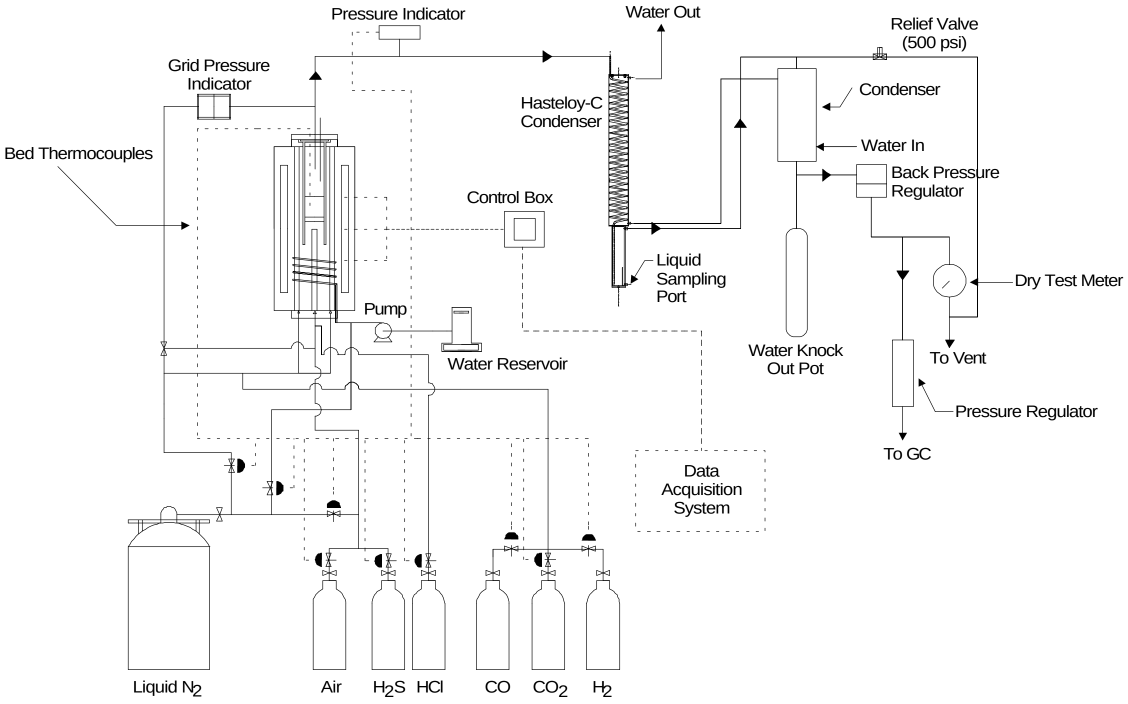


Figure 3.18 – Overall Arrangement of the High-Pressure High-Temperature Packed-/Fluidized-Bed Reactor System

The exit gas heat-exchange system and gas sampling and analysis system also required modification. The gas exiting the reactor through the Hastelloy tubing will be sent to a heat transfer coil made of Hastelloy having a loose helix shape to allow the condensing liquid to easily flow downwards and collect in a Hastelloy knockout-pot (Figure 3.20). The Hastelloy tubing extends vertically down into a volume of water contained in the bottom of the knockout-pot, to allow the water to absorb the HCl as the exit gas bubbles through it. The drain valve at the bottom of the knockout-pot allows this water to be sampled regularly and analyzed for its chloride content using the Dionex DX320/IC20 ion chromatograph. This heat-exchange and condensate-collection system was also constructed by Ability Engineering Technology. A slipstream of the non-condensable gas is then sent to an HP 5890 gas chromatograph, equipped with a flame photometric detector (FPD) and a thermal conductivity detector (TCD), for the determination of the H_2S (and COS) concentration in the exit gas.

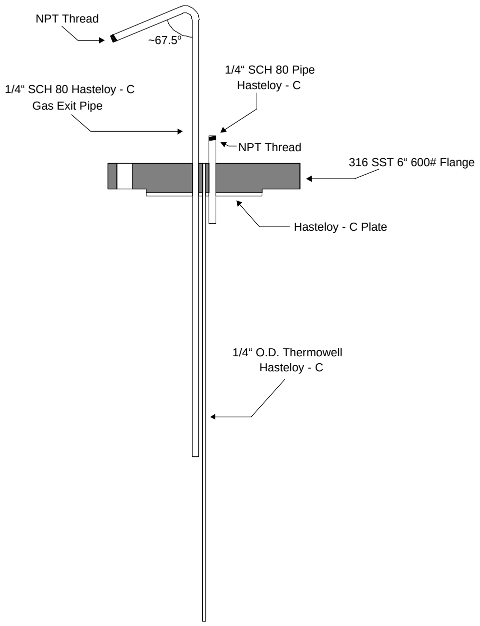


Figure 3.19 – Details of Newly-Designed Top Flange

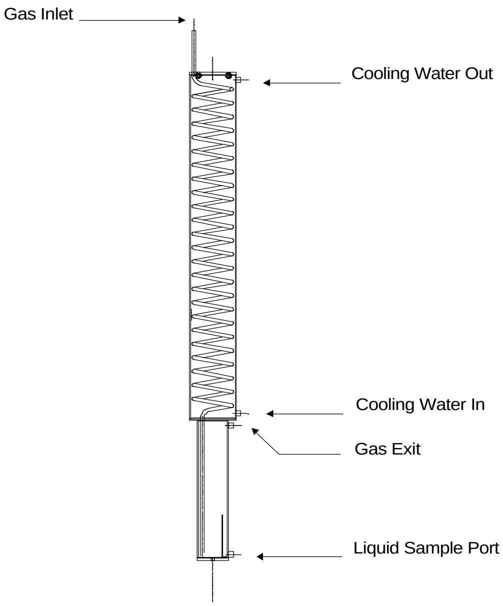


Figure 3.20 – Details of Exit Reactor Gas Cooling System and HCl Recovery

3.4 RESULTS AND DISCUSSION

3.4.1 Screening Tests of Stage I Dechlorination Materials

Naturally-occurring, sodium-containing minerals nahcolite and trona, as well as synthetic dawsonite were evaluated for their ability to remove HCl to meet Stage I target of < 3 ppmv HCl in the cleaned gas. Initially, nahcolite was expected to outperform trona and synthetic dawsonite. For these reasons, three scoping tests were carried out with nahcolite in the ambient-pressure, packed-bed reactor under the baseline operating conditions (i.e., 500°C, 5 cm/s gas velocity, 5-cm bed height). The purpose of these tests was to determine a suitable concentration of HCl in the feed gas such that the HCl concentration in the cleaned syngas is ≤ 3 ppmv and breakthrough (i.e., HCl concentration > 10 ppmv) is achieved within a reasonable time (i.e., < 8 hours). The contribution of the non-reactive pellets in the sorbent bed to HCl retention (via physical adsorption) was also assessed. Measurement of the HCl concentration of the inlet as well as exit gas streams was carried out by periodically bubbling the off-gas from the reactor through a sparger containing 100 cm^3 of de-ionized water. The chloride content of a sample from the sparger is then determined by the Dionex DX-320/IC20 ion chromatograph.

With 2000 ppmv HCl concentration in the feed gas, nahcolite, trona, and dawsonite were found to achieve effective capacities for chloride absorption of approximately 16.5, 26.5, and 10 g Cl/100 g of material (in as-received condition, i.e., non-calcined), respectively (Figure 3.21). Based on chemical analyses of fresh materials, these results translate into sodium (Na) conversions of about 40% for nahcolite, over 48% for trona, and 48% for synthetic dawsonite. The test with trona at 2000 ppmv HCl in the feed gas took so long that HCl concentration was raised to 2500 ppmv following about 17.5 hours of testing, to achieve breakthrough in a shorter time. Therefore, higher effective capacity for chloride absorption (and higher Na conversion) can be expected for trona.

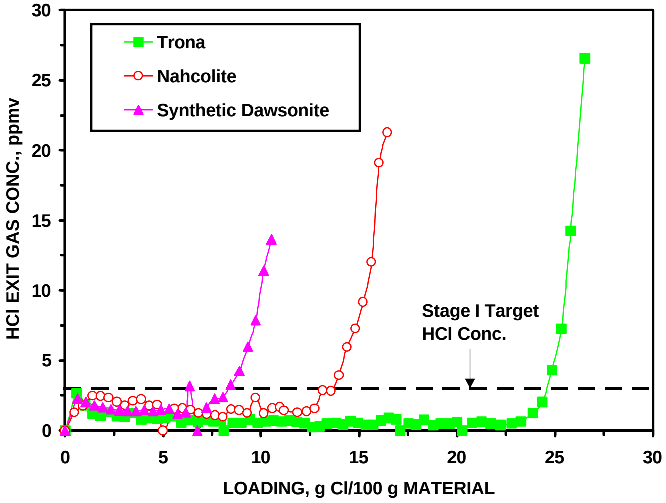


Figure 3.21 – Performance Comparison of Stage I Dechlorination Minerals

Because of the encouraging results obtained with trona, indicating this material to outperform nahcolite and synthetic dawsonite in terms both of efficiency and effective capacity for chloride removal, one additional test was carried out with trona at an inlet HCl concentration of 5000 ppmv in the feed gas. The purpose of this test was to achieve breakthrough within 8 hours. Even at this higher HCl concentration in the feed gas, trona performed well, achieving an effective capacity of 16.25 g Cl/100 g of as-received trona with a concentration of residual HCl in the cleaned gas of < 3 ppmv. This effective capacity corresponds to a conversion of approximately 30%. Time to breakthrough was about 6 hours.

The non-reactive pellets were found to make a somewhat sizeable contribution to chloride retention via physical adsorption that was equivalent to over an hour of testing. However, during an actual test, these pellets are entirely covered by highly reactive material and contaminant removal via chemical reaction should occur preferentially to contaminant removal via physical adsorption prior to breakthrough. Therefore, it was reasoned not to account for this contribution during data analysis.

A scoping test was carried out with trona to determine the HCl concentration in the effluent gas as a function of HCl concentration in the feed gas. This test was deemed necessary to provide guidelines for carrying out tests involving both trona and the selected desulfurization material. During this scoping test, HCl concentration in the reactor effluent was measured for different periods during which HCl concentration was raised from 1000 ppmv, to 2500, to 4000, and finally to 5000 ppmv. As indicated in Figure 3.22, the HCl concentration in the cleaned gas is well below the target HCl concentration of 1-3 ppmv, irrespective of the HCl concentration in the feed gas in the range investigated.

Prior to introducing HCl to the reactor, HCl concentration was closely followed as the feed gas was switched from N_2, to N_2 + steam, and to syngas (simulated syngas less HCl). Again, this procedure was needed to determine the contribution of reactor walls above the bed, sampling lines, and associated valves to residual HCl concentration in the effluent gas.

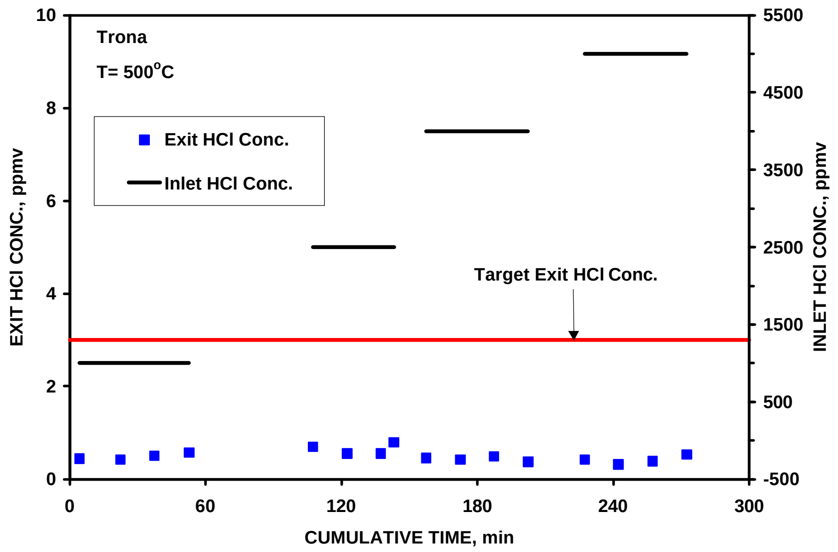


Figure 3.22 – Scoping Test with Trona

It should be pointed out that during reactor heat up in N_2, steam was seen to evolve from the sorbent bed and condense downstream before being swept away later with dry gas. As expected, this was an indication of trona undergoing calcination. In a separate test, it was shown that trona did in fact lose close to 30% of its weight upon calcination at high temperature. This is in agreement with the decomposition of trona according to the following reaction:

$$Na_2CO_3 \bullet NaHCO_3 \bullet 2H_2O \ = \ 3/2 \ Na_2CO_3 + 1/2 \ CO_2 + 5/2 \ H_2O \qquad (3.8)$$

Given the above consideration, a test was done with calcined trona to eliminate the effect of weight loss prior to testing, which would create void space in the sorbent bed and lead to a looser packing. This attempt was made to make trona evaluation comparable to the selected desulfurization material. Unfortunately, calcined trona could not be evaluated because of high pressure build up in the reactor of >28 kPa (4 psi), similar to the behavior exhibited by other materials, such as the EMP filter cake and the manganese ore, as discussed subsequently.

Reproducibility of the results from testing of the trona material was established with an inlet HCl concentration of 5000 ppmv. As shown in Figure 3.23, HCl concentrations well below the target concentration of 1-3 ppmv were achieved reproducibly in both tests at effective capacities for chloride absorption approximating 15.5 g Cl/100 g of trona. This corresponds to about 28% conversion of the sodium component of as-received trona. Based on previous testing, at lower HCl concentrations in the feed gas, this conversion can be expected to exceed 50%.

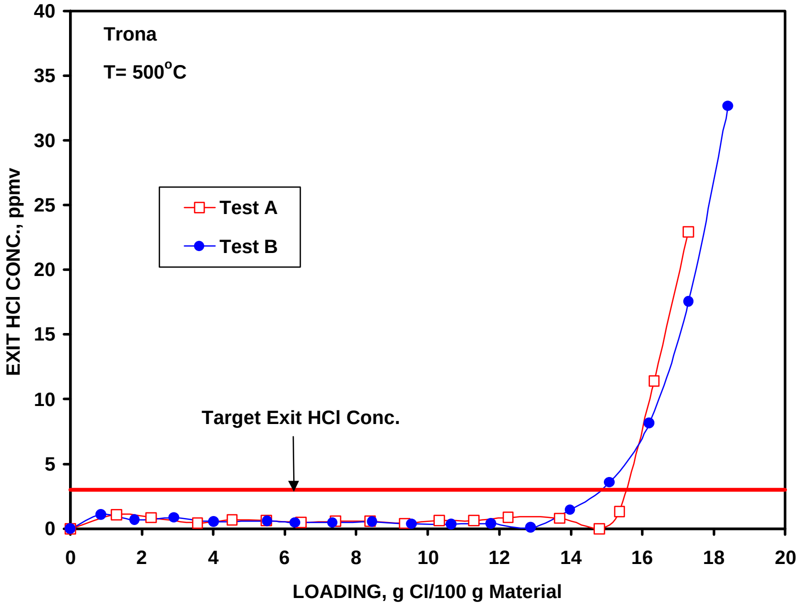


Figure 3.23 – Reproducibility of the Results from Testing of Trona

Similar to the scoping test procedure, during each of these reproducibility tests, the HCl concentration in the reactor effluent was closely followed first in N_2 only, then in N_2 + steam, and finally in syngas (simulated syngas less HCl), before HCl was introduced. This precaution was taken to eliminate any contribution to HCl in the reactor effluent that might be due to HCl desorption from reactor walls above the sorbent bed, sampling lines, and associated valves.

Occasionally, it was determined that these reactor system components accounted for 0.2-0.3 ppmv HCl in outlet gas, which was usually taken as a baseline concentration during data analysis. While this was not essential for the first stage of the Ultra-Clean gas polishing process, these steps were critical during the second stage of the process, where measurement of contaminant concentration in the ppbv range were needed. Some modifications to the reactor system were deemed necessary for accurate measurements of contaminant concentrations in the second stage.

Reacted samples from the dechlorination sorbent (trona) were also submitted for chemical analysis to confirm the effective capacity of trona for chloride absorption, as calculated based on the breakthrough curves (Test A, Figure 3.23). The results obtained are reported in Table 3.11, where the chloride content of the reacted material is seen to range from 41.8 wt% in the bottom portion (gas inlet), to 23.6 wt% in the middle portion, to 8.27 wt% in the top portion (gas outlet). These chloride assays correspond to conversions of 76%, 43%, and 15%, respectively, for the as-received trona. A rough estimate of the chloride loading gives an average of about 17.2 wt% Cl on as-received trona basis, which is consistent with the effective capacity calculated for trona based on the breakthrough curve.

Table 3.11 – Chemical Analysis of Reacted Trona

Element	Bed Location		
	Bottom	Middle	Top
Na	34.7	39.2	39.0
Cl	41.8	23.6	8.27

A fresh sample of trona was exposed to the simulated syngas (less HCl) for about the same period it takes to achieve breakthrough at an inlet HCl concentration of 5000 ppmv. Following this reductive treatment, the sorbent bed was divided into a bottom portion, a middle portion, and a top portion. A sample from the bottom portion (gas inlet), where the sorbent sample undergoes reduction to the highest extent, was submitted for XRD analysis to identify the form in which the reactive sodium-containing component is stable in the syngas environment. The XRD pattern for this reduced sample is shown in Figure 3.24, which identifies Na_2CO_3 as the only major stable reactive component, consistent with the thermodynamic analysis discussed earlier. XRD also identified SiO_2 as a minor phase and NaCl as a major phase. The phases Na_2CO_3, NaCl, and SiO_2 are denoted by 1, 2, and 3, respectively, in Figure 3.24. The presence of chloride in the reduced trona sample was also confirmed by chemical analysis, which revealed this sample contained 20.1 wt% Cl in addition to 38.9 wt% Na. This is the result of HCl desorbing from the alundum pellets that are used in the gas preheating section of the reactor inlet. This phenomenon is not present during tests involving HCl in the feed gas, as the alundum pellets are "saturated" and do not contribute to HCl removal.

The performance of trona, in a physical mixture with the GPGA material, was also evaluated. As shown in Figure 3.25, the effectiveness of trona for chloride absorption was not adversely affected by the ash material, as HCl concentration in the inlet gas was gradually raised from 350 to 1750 ppmv.

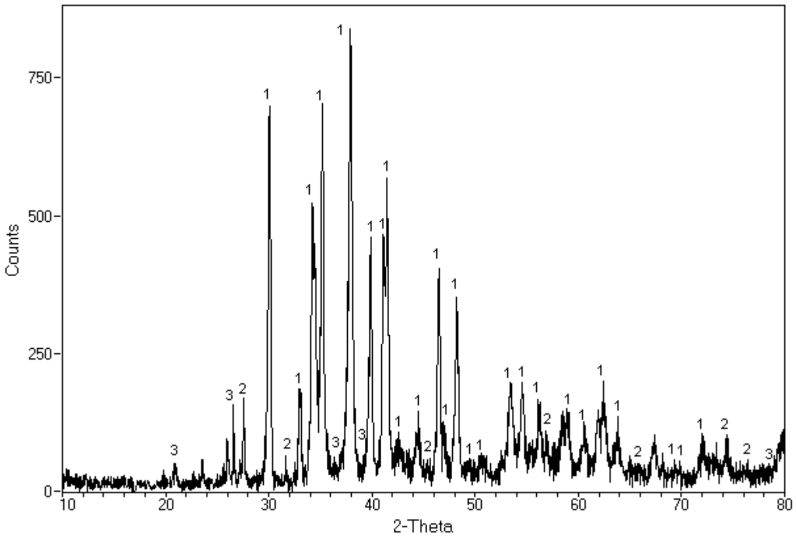


Figure 3.24 – XRD Pattern of Highly Reduced Trona Sample

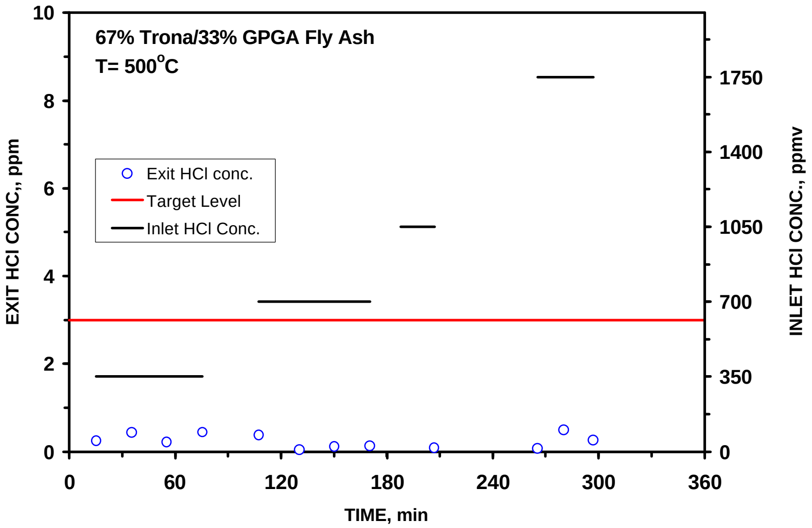


Figure 3.25 – Effect of GPGA Material on Trona Performance

3.4.2 Screening Tests of Stage I Desulfurization Materials

During these tests, H_2S was measured by a dedicated gas chromatograph equipped with a flame photometric detector (FPD). This GC-FPD unit was calibrated for the 1 to 10 ppmv H_2S range. Initial evaluation of the materials selected for H_2S removal in Stage I indicated that the goal of achieving the target H_2S concentration in the cleaned syngas of 1-3 ppmv could be accomplished with the iron oxide byproduct. With breakthrough arbitrarily defined at 10 ppmv H_2S in the exit gas, this material was found to achieve an effective capacity for sulfur absorption of about 12.5 g S/100 g sorbent. Regenerable pellets (4 to 5 mm in diameter) of the IGTSS-179 copper-based sorbent were also evaluated and were found to achieve the target H_2S concentration with an effective capacity for sulfur absorption of about 2 g S/100 g sorbent.

Unfortunately, because of high pressure build up in the reactor, two of the other selected materials for H_2S removal (i.e., EMP filter cake and manganese ore) could not be evaluated under the same experimental conditions (i.e., 5-cm bed height) used for the iron oxide byproduct. Given that in a granular, moving bed filter, reactor blockage would not be an issue, a different experimental arrangement was used to enable the evaluation and ranking of these materials in terms of their ability to remove H_2S. The sorbent bed height was reduced to 1 cm and the feed gas flow rate was reduced by 80%. In addition, a dry gas was used consisting simply of H_2S, H_2, and N_2. The iron oxide waste material was also evaluated under these conditions to be able to assess, by inference, the performance of the EMP filter cake and the manganese ore.

Figure 3.26 shows that the EMP filter cake achieved an effective capacity for sulfur removal of about 3.4 g S/100 g of material, significantly lower than the 12.7 g S/100 g of material effective capacity obtained with the iron oxide byproduct under the same conditions. This latter number is quite consistent with the result previously reported for the iron oxide waste (i.e., 12.5 g S/100 g of material). Therefore, the 1-cm sorbent bed was quite suitable for evaluation and ranking of the desulfurization minerals selected for Stage I of the Ultra-Clean gas polishing process. The results from the test with manganese ore indicated this material was not sufficiently effective to achieve Stage I H_2S target concentration in the cleaned gas of < 3 ppmv, as might be expected. The contribution of the non-reactive pellets to the retention of H_2S (via physical adsorption) was also assessed and was determined to be significantly less of a concern than in the case of HCl.

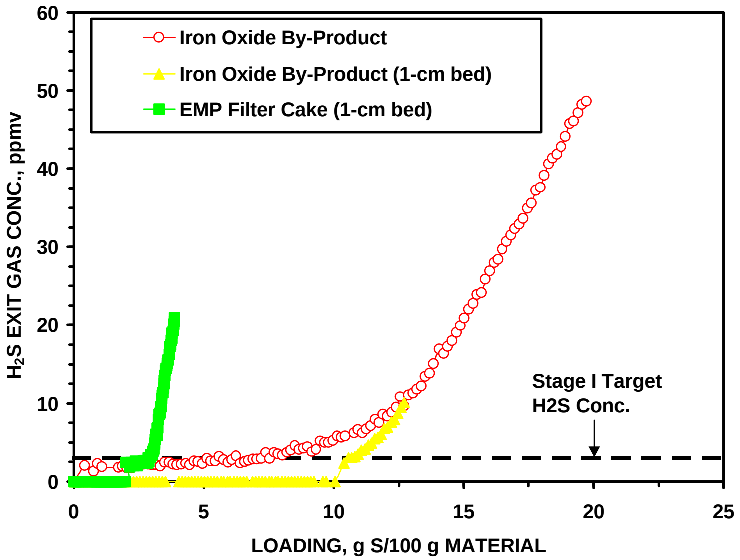


Figure 3.26 – Performance Comparison of Stage I Desulfurization Minerals

A sample of the copper concentrate material was roasted to drive off the 20.9% sulfur associated both with copper and iron. Reactor heat up to roasting temperature was carried out in an O_2-N_2 gas mixture to prevent evolution of elemental sulfur and subsequent condensation in off-gas lines. Roasting was initiated at 650°C. SO_2 in the roasting product gas was measured using a gas chromatograph equipped with a thermal conductivity detector (TCD). When SO_2 concentration was no longer detected, temperature was raised to 750°C and more SO_2 was determined to evolve, indicating incomplete removal of sulfur at 650°C. Temperature was not raised beyond 750°C not to sinter the copper concentrate material, which would adversely affect its reactivity with H_2S. At the conclusion of the roasting test, the material was taken out and was found to be highly agglomerated. In addition to the undesirable agglomeration tendencies of this material, the existence of residual sulfur in the roasted material was highly likely, which would require an additional pre-reduction treatment prior to evaluation. Unfortunately, such a treatment would lead to the complete reduction of copper oxide, which will not only increase its tendency to agglomerate, but also significantly reduce its efficiency for H_2S removal. Because of these issues, the copper concentrate material was dropped from any further consideration.

A scoping test involving the iron oxide by-product material was carried out to determine the concentration of residual H_2S in the cleaned gas as a function of H_2S concentration in the feed gas. As shown in Figure 3.27, during this scoping test, the initial inlet H_2S concentration was 250 ppmv. The outlet H_2S concentration was measured under these conditions for a period of 1 ½ hours before the inlet H_2S concentration was raised to 500 ppmv. This stepwise increase in the inlet H_2S concentration continued and covered 1000, 1500, and 2000 ppmv concentrations. As indicated in Figure 3.27, the target H_2S concentration of 1-3 ppmv in the cleaned gas was achieved throughout the 250-2000 ppmv H_2S concentration in the feed gas.

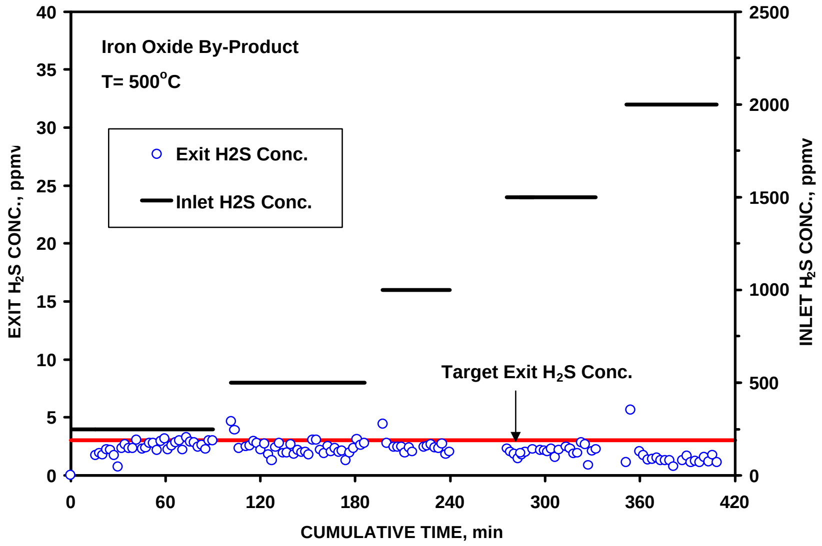


Figure 3.27 – Scoping Test With Iron Oxide By-Product Material

As indicated in Figure 3.28, reproducibility of the results from testing of the iron oxide by-product material was established with an inlet H_2S concentration of 2000 ppmv. The target H_2S concentration of 1-3 ppmv was achieved reproducibly in both tests at effective capacities for sulfur absorption approximating 10.5 g S/100 g of the iron oxide by-product material. In addition, at an inlet H_2S concentration of 2000 ppmv and breakthrough arbitrarily defined at 10 ppmv, this material was capable of achieving in both tests an effective capacity of about 12.5 g S/100 g of the iron oxide by-product, corresponding to approximately 34% conversion of the iron oxide component.

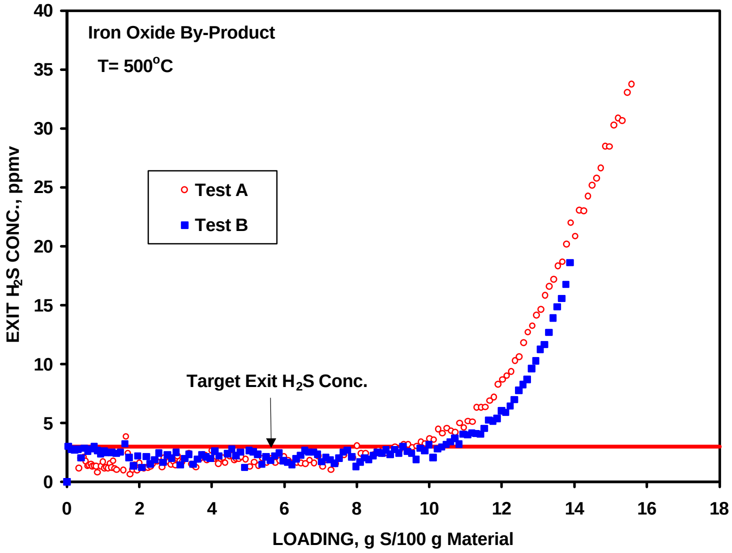


Figure 3.28 – Reproducibility of Results from Testing of the Iron Oxide By-Product

Similar to the scoping test procedure, during each of these reproducibility tests, the H_2S concentration in the reactor effluent was closely followed first in N_2 only, then in N_2 + steam, and finally in syngas (simulated syngas less H_2S), before H_2S was introduced. This precaution was taken to eliminate any contribution to H_2S in the reactor effluent that might be due to H_2S desorption from reactor walls above the sorbent bed, sampling lines, and associated valves. Occasionally, it was determined that these reactor system components accounted for 2-3 ppmv H_2S in outlet gas, which is usually taken as a baseline concentration during data analysis. While this is not essential for the first stage of the Ultra-Clean gas polishing process, these steps were critical during the second stage of the process, where measurement of contaminant concentration in the ppbv range was needed. Therefore, some modifications to the reactor system were deemed necessary for accurate measurements of contaminant concentrations in the second stage.

A fresh sample of the iron oxide by-product was exposed to the simulated syngas (less H_2S) for about the same period it takes to achieve breakthrough at an inlet H_2S concentration of 2000 ppmv. Following this reductive treatment, the sorbent bed was divided into a bottom portion, a middle portion, and a top portion. A sample from the bottom portion (gas inlet), where the sorbent undergoes reduction to the highest extent, was submitted for X-ray diffraction analysis (XRD) to identify the form in which the reactive iron oxide component is stable in the syngas environment. The pattern for this reduced sample is shown in Figure 3.29, clearly disclosing Fe_3O_4 as the only stable iron oxide.

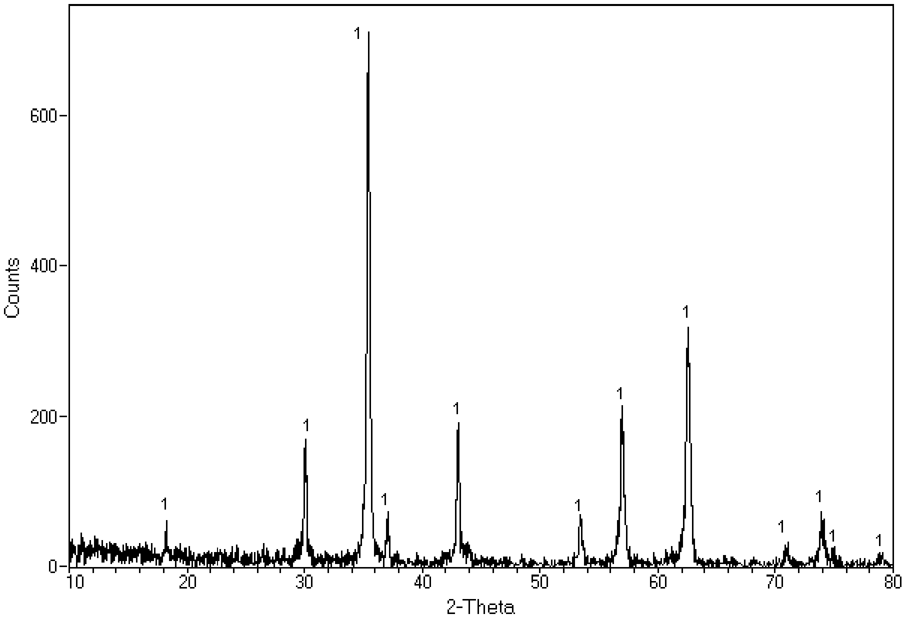


Figure 3.29 – XRD Pattern of Highly Reduced Iron Oxide By-Product Sample

Spent (i.e., sulfided) sorbent samples from the three different bed sections were also submitted for chemical analysis (Test B, Figure 3.28). The iron and sulfur analyses are reported in Table 3.12. Both the bottom and middle portions of the sorbent bed contain similar amounts of sulfur, indicating similar conversion. As would be expected in a packed-bed setting, the top portion of the sorbent bed (gas outlet) achieves the least sorbent conversion prior to breakthrough, as indicated by the 2.4 wt% sulfur. Based on the iron content of the iron oxide byproduct, the sulfur assays in the bottom and middle portions of the bed correspond to approximately 43% conversion. A rough estimate of the sulfur loading gives an average of about 11.3% S, which is consistent with the effective capacity of the iron oxide byproduct for sulfur absorption, as calculated based on the breakthrough curve.

Table 3.12 – Chemical Analysis (wt%) of Reacted Iron Oxide By-Product

Element	Bed Location		
	Bottom	Middle	Top
Fe	53.7	56.9	62.0
S	15.6	16.0	2.36

3.4.3 Combined Chloride/Sulfur Removal Tests Using Iron Oxide By-Product/Trona Mixtures

Based on the results obtained in the dechlorination and desulfurization screening tests, trona and the iron oxide byproduct were selected as once-through sorbent fines for Stage I of the Ultra-Clean gas polishing process, involving the moving bed filter-reactor (MBFR). Both of these materials were found to meet the criteria set for Stage I in terms of contaminant removal efficiency (i.e., HCl or H_2S concentration in cleaned gas < 3 ppmv) and pre-breakthrough conversion or effective capacity for contaminant absorption. Trona was found to outperform nahcolite and synthetic dawsonite, and the iron oxide by-product was found to be the only material that could be evaluated under the experimental conditions specified in the Test Plan. Additionally, in separate screening tests, this material was shown to outperform a manganese ore and an EMP filter cake material.

The mass balance around the MBFR (see Table 3.1) was then re-examined to determine if any significant changes are needed and to re-assess the validity of the original assumptions made. Again, the coal was assumed to be 3 wt% sulfur, eastern bituminous, and the resulting syngas H_2S content to the bulk desulfurizer was about 3,000 ppmv. This effort also provided some guidelines on conducting evaluation tests involving both HCl and H_2S using mixtures of trona and the iron oxide by-product material. As shown in Figure 3.30, trona and the iron oxide by-product are reasonably assumed to achieve 50% and 33% conversion, respectively. Based on the HCl and H_2S concentrations in the feed gas to the MBFR, the amount of trona needed is about 3.5 times the amount of the iron oxide by-product. Therefore, a suitable mixture of both sorbent fines should consist of about 78 wt.% trona and 22 wt.% iron oxide by-product.

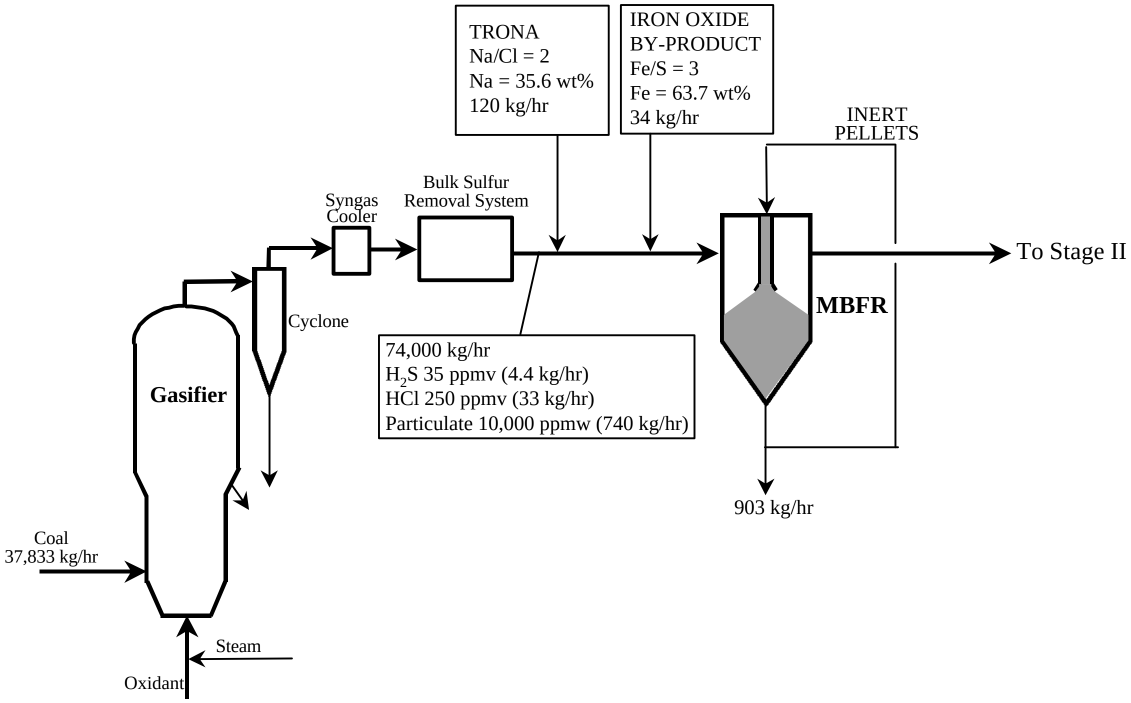


Figure 3.30 – Material Balance for the Moving Bed Filter-Reactor with Iron Oxide By-Product Sulfur Sorbent

In carrying out combined removal of HCl and H_2S, all thermodynamically possible reactions involved were taken into consideration. The reactions identified, along with their equilibrium constants at 500°C, are summarized in Table 3.13.

Table 3.13 – Possible Reactions Involving Trona and Iron Oxide By-Product with HCl and H_2S

Reaction		**K(at 500^{o}C)**
$Na_2O + H_2S = Na_2S + H_2O$	(3.7)	$6.238*10^{11}$
$Na_2CO_3 + H_2S = Na_2S + H_2O + CO_2$	(3.9)	$6.880*10^{-3}$
$Na_2O + 2HCl = 2NaCl + H_2O$	(3.4)	$1.628*10^{25}$
$Na_2CO_3 + 2HCl = 2NaCl + H_2O + CO_2$	(3.3)	$1.798*10^{11}$
$Fe_3O_4 + 3H_2S + H_2 = 3FeS + 4H_2O$	(3.10)	$1.755*10^{9}$
$Fe_3O_4 + H_2 + 6HCl = 3FeCl_2 + 4H_2O$	(3.11)	$2.710*10^{6}$

As indicated in Table 3.13, both Na_2CO_3 and Na_2O react with HCl to a great extent, with Na_2O being significantly more efficient for HCl removal. However, only Na_2O reacts with H_2S, with reaction of Na_2CO_3 with H_2S being very minor. The iron oxide component (reasonably assumed to be Fe_3O_4 under the experimental conditions, as indicated by XRD) of the iron oxide by-product material obviously reacts with H_2S, but can also potentially react with HCl, as shown by Reaction (3.11) in Table 3.13. As indicated earlier in Figure 3.6, Na_2CO_3 is the stable form of sodium in the syngas environment at 500°C; therefore, trona should not be expected to react with H_2S to any appreciable extent.

Based on the above considerations, a scoping test was devised and carried out for the combined removal of H_2S and HCl. The mixture of sorbent fines consisted of 32.4 wt.% iron oxide by-product and 67.6 wt.% trona. This scoping test consisted of two consecutive scoping tests with the first one involving only H_2S, and the second involving only HCl. The purpose was to determine whether the two materials, in the proportions in which they are mixed, could achieve the target contaminant concentrations in the cleaned gas of 1-3 ppmv. The scoping test involving H_2S only was carried out first because the dechlorination sorbent (trona) was not expected to react with H_2S, as explained above. Similar to previous scoping tests, H_2S concentration in reactor effluent was measured for different periods during which H_2S concentration in the feed gas was raised from 250 ppmv, to 500 ppmv, and finally to 700 ppmv. In the subsequent scoping test involving HCl only, HCl concentration in the feed gas was periodically raised from 1750 ppmv (7 x 250), to 2500 ppmv, to 4000 ppmv, and finally to 5000 ppmv.

The results obtained from the above two consecutive scoping tests are presented in Figure 3.31. As shown, the H_2S concentration in the reactor effluent did not meet the target of 1-3 ppmv, even with a H_2S concentration of 250 ppmv in the feed gas. However, the target 1-3 ppmv HCl in the cleaned gas was achieved throughout the entire concentration range investigated (1750-5000 ppmv). The HCl concentrations in the reactor effluent were similar to those obtained with trona alone. These results indicate trona is significantly more reactive than the iron oxide by-product material and that the possibility exists for using a lower amount of trona in the fine sorbent mixture. The target H_2S concentration may be obtained by increasing the amount of iron oxide by-product in the mixture, or possibly by lowering the H_2S concentration in the feed gas below 250 ppmv.

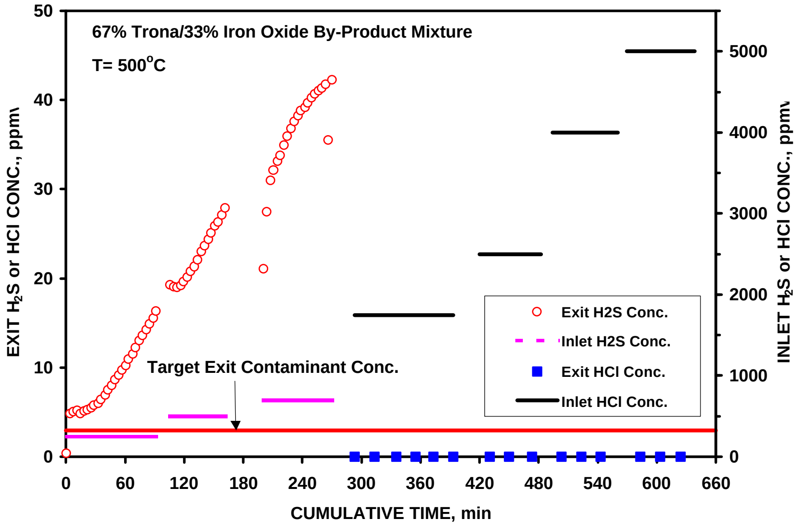


Figure 3.31 – Scoping Test Involving H_2S and HCl

To resolve the problem of not achieving the target 1-3 ppmv H_2S in reactor effluent when working with a combination of trona and the iron oxide byproduct, the following was attempted. First, the proportion of the iron oxide byproduct with respect to trona in the mixture was increased from 67%-33% to 50%-50% with both sorbent fines in the –325 mesh size range. Because of high-pressure build up, testing of this mixture could not continue. A mixture consisting of 60% trona and 40% iron oxide byproduct was then tried; however, the problem of high-pressure build up still persisted.

Second, the original sorbent mixture, which consisted of 33% iron oxide byproduct and 67% trona was then evaluated again, but with a reduced inlet H_2S concentration of 50 ppmv (250 ppmv was used earlier). Unfortunately, even with this reduced inlet H_2S concentration the desired 1-3 ppmv H_2S in the effluent gas could not be obtained.

Third, another 50% trona-50% iron oxide byproduct sorbent mixture was tried, but the size of each material was limited to the range of 44 to 75 µm (–270 + 325 mesh) in order to overcome the pressure build up problem. While this made testing possible, it did not achieve the 1-3 ppmv H_2S in the reactor effluent even with a 50 ppmv inlet H_2S concentration. Furthermore, this target was not achieved even when the flow rate of the feed gas was reduced so that the H_2S residence time in the sorbent mixture was the same as when the iron oxide byproduct was used alone.

It became evident it would not be possible to use a mixture consisting of trona and the iron oxide byproduct to achieve the target of 1-3 ppmv of H_2S and HCl in the reactor effluent. Obviously, iron oxide is not expected to reduce the H_2S concentration to this level even though Fe_3O_4 is the stable form of reactive component in the syngas environment. Apparently, there is a mechanism that makes this possible when the iron oxide byproduct is used by itself, but not when in a physical mixture with trona. Another explanation is the possible interference of HCl with the Fe_3O_4-H_2S reaction (see Reaction 3.11, Table 3.13).

3.4.4 Analysis of Iron Oxide By-Product/Trona Sorbent Mixture

As demonstrated by XRD, Fe_3O_4 is the stable form of iron oxide in the reducing syngas environment. Despite this fact, however, Fe_3O_4 cannot be expected to reduce the H_2S concentration to 1-3 ppmv. Experimental tests showed the iron oxide byproduct, by itself, to be capable of achieving this target concentration at an effective capacity of about 11 g S/100 g of material. However, this was not possible when the iron oxide byproduct was in a physical mixture with trona. It was hypothesized that there was a mechanism that makes the iron oxide byproduct efficient enough when used by itself, but not when in a physical mixture with trona. Another explanation was the possible interference of HCl with the Fe_3O_4-H_2S reaction. This latter possibility was not explained in detail because earlier testing showed that even in the absence of HCl, the trona/iron oxide byproduct mixture did not achieve the target H_2S concentration (see Figure 3.31). The following analytical/experimental work was done to clarify the situation.

The composition of the iron oxide byproduct is presented in Table 3.14. The elements whose oxides should be considered for potentially reacting with H_2S and/or HCl are: Ca, Cu, Fe, Mn, and Zn. Copper can be safely ignored since there is only 0.1%. Under our operating conditions, it would take about 10 minutes before all Cu is used up at an inlet HCl concentration of just 350 ppmv. Based on ΔG^o values for desulfurization reactions at 500°C, as shown in Table 3.15, the remaining oxides can be ranked in terms of thermodynamic efficiency for H_2S removal as follows: Zn > Ca > Mn > Fe. Similarly, these oxides can be ranked in terms of their thermodynamic efficiency for HCl removal as follows: Ca > Mn > Zn > Fe.

Table 3.14 – Chemical Composition of Iron Oxide By-Product

Element	Wt. %
Al	0.032
Ca	2.59
Cu	0.10
Fe	63.7
Mg	0.63
Mn	1.27
Si	0.36
Zn	0.86

Table 3.15 – Free Energies for Various Oxide/Chloride and Oxide/Sulfide Combinations

Oxide/Chloride Combination	ΔG^o, kCal/mol HCl	Oxide/Sulfide Combination	ΔG^o, kCal/mol H_2S
Fe_3O_4 / $FeCl_2$	-3.793	Fe_3O_4/FeS	-10.900
CaO / $CaCl_2$	-15.242	CaO/CaS	-14.571
ZnO / $ZnCl_2$	-4.309	ZnO/ZnS	-17.017
MnO / $MnCl_2$	-6.819	MnO/MnS	-12.937

By far, CaO is the most efficient oxide for HCl removal. A thermodynamic simulation using the HSC Chemistry software package was carried out to equilibrate the experimental syngas (35% CO, 30% H_2, 10% CO_2, 15% H_2O, 3% CH_4, 1000 ppmv HCl, balance N_2) with CaO in the temperature range of 350 to 600°C. The results obtained indicated that at 500°C, the equilibrium

HCl concentration is about 18 ppmv. The equilibrium concentration for Fe_3O_4 is well over 1000 ppmv. Therefore, any HCl removal that may take place with the iron oxide byproduct should be attributed to CaO only.

A scoping test (Test A) was carried out to evaluate the capability of the iron oxide byproduct for HCl removal. The simulated syngas contained 700 ppmv HCl, and no H_2S. Following HCl breakthrough, the same sorbent bed was evaluated for its effective capacity for sulfur absorption with an inlet H_2S concentration of 2000 ppmv, similar to previous desulfurization tests involving this material (see Figure 3.28) to obtain a meaningful comparison. The results from both tests are reported in Figure 3.32. As shown, the iron oxide byproduct was capable of reducing the HCl concentration to below the target value of 3 ppmv. The breakthrough time for HCl corresponds to an effective capacity of approximately 2.6 g Cl/100 g of material. Assuming HCl removal is due solely to reaction with CaO, this effective capacity corresponds to about 60% conversion of the CaO component in the iron oxide byproduct. The results also indicate that, following reaction with HCl, the iron oxide byproduct is still capable of reducing the H_2S concentration to below the target level of 3 ppmv. However, H_2S breakthrough was obtained after about 4 hours on stream, which corresponds to an effective capacity of approximately 5.5 g S/100 g of material. This value is about half the effective capacity reported earlier for the "fresh" iron oxide material (see Figure 3.28).

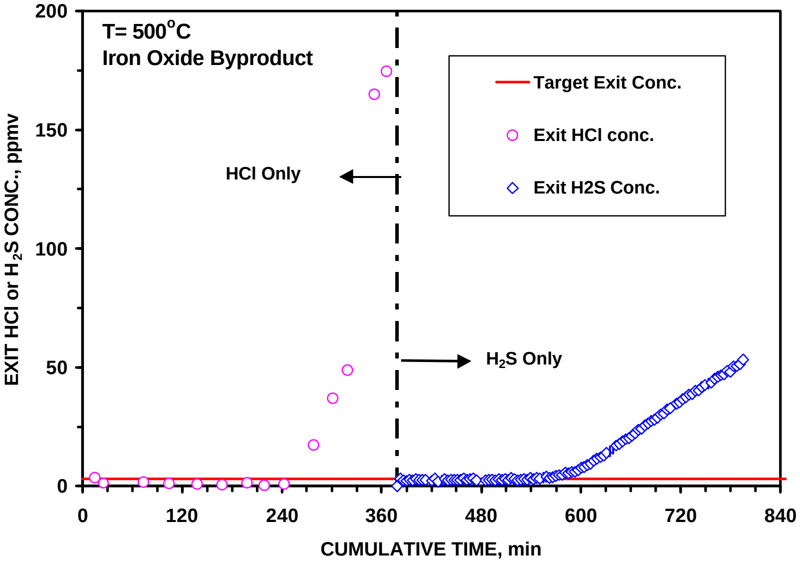


Figure 3.32 – Scoping Test A HCl and H_2S Breakthrough Curves

The above results hint to the likely possibility that CaO plays a role in achieving the previously reported effective capacity of 11 g S/100 g of iron oxide byproduct, at outlet H_2S concentrations in the range 1-3 ppmv. Following reaction with HCl, 60% of the CaO component was no longer available to participate in the desulfurization reaction, which caused the effective capacity of the iron oxide byproduct to decline by 50%. There is the possibility that the target H_2S concentration in the effluent gas is achieved as H_2S gradually reacts first with Fe_3O_4, then with CaO, and finally with ZnO, consistent with the proportions in which these oxides exist in the iron oxide byproduct. When CaO reacts with HCl to form $CaCl_2$, the CaO component does not play as significant of a role in this mechanism, which would explain the reduced effective capacity.

To further confirm the above reasoning, a second test (Test B) was carried out on a fresh batch of iron oxide byproduct to evaluate its capability for simultaneous HCl and H_2S removal. HCl and H_2S were fed simultaneously at inlet concentrations of 700 ppmv and 2000 ppmv, respectively. The breakthrough curves obtained with HCl and H_2S are reported separately in Figures 3.33 and 3.34, respectively. The results obtained from Test A, as described above, are also shown in these figures for comparison purposes. As shown in Figure 3.33, the exit pre-breakthrough HCl concentration is slightly higher and breakthrough time is shorter for Test B compared to Test A. The same is true for H_2S, although to a lesser extent, as shown in Figure 3.34. These slight differences between the results of Tests A and B are likely due to the fact that HCl and H_2S are "competing" simultaneously for the same CaO component of the iron oxide byproduct. The results of Test B, however, clearly support the reasoning in the interpretation of Test A results.

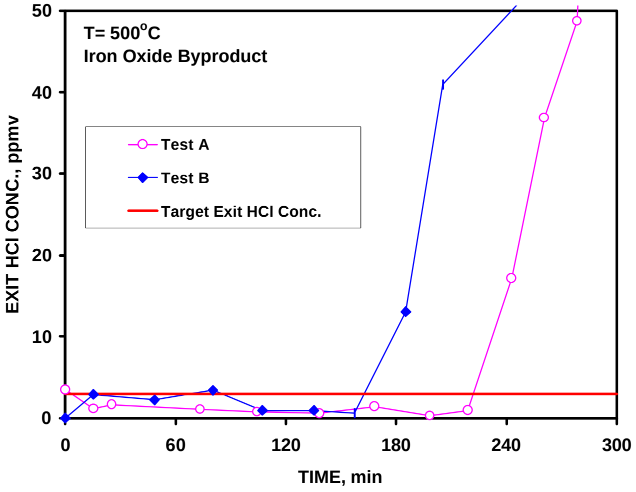


Figure 3.33 – HCl Breakthrough Curves from Tests A and B

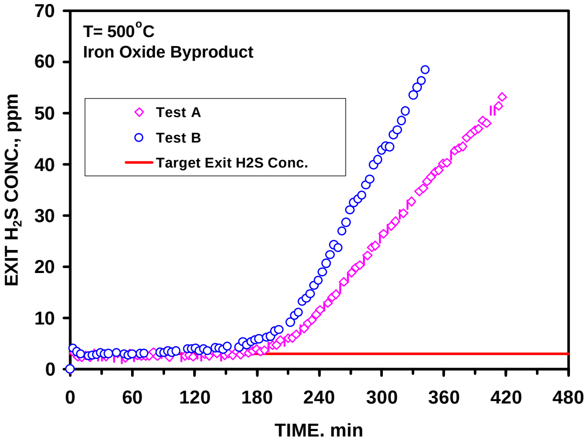


Figure 3.34 – H_2S Breakthrough Curves from Tests A and B

As indicated above, data were presented showing that even when the iron oxide byproduct was not exposed to HCl, the target H_2S concentration was not achieved when this sorbent is in a mixture with trona. This may be explained by the fact that there is only about 2.6% Ca in the iron oxide material. The H_2S gas "sees" even less of this material when it is dispersed in the physical mixture, and therefore, the CaO component does not play its role in the mechanism described above for reducing the H_2S concentration to below the target level of 3 ppmv.

3.4.5 Combined Chloride/Sulfur Removal Tests Using Zinc Titanate/Trona Mixtures

To validate the above reasoning, a different mixture was used that consisted of 67 wt% trona and 33 wt% of a GTI zinc titanate sorbent. Because of the high efficiency of ZnO and the high chemical reactivity of this material, no H_2S was detected in the reactor effluent as the inlet H_2S concentration was gradually raised from 50, to 150, and finally to 250 ppmv. Following this scoping test with H_2S only, HCl was introduced at the 1750 ppmv level (7 x H_2S concentration), while H_2S was maintained at the 250 ppmv. Based on the results obtained, it was confirmed neither HCl adversely affected the zinc titanate capability for H_2S removal, nor H_2S adversely affected the performance of trona for chloride removal.

The trona/zinc titanate sorbent mixture was selected for use during parametric testing. During the raw material selection and acquisition phase, it was not possible to find an inexpensive zinc mineral that did not also have objectionable elements such as lead. If an alternative zinc oxide-containing material were found, then its performance in combination with trona can be inferred from the results obtained with the trona/zinc titanate mixture.

Based on the above results, trona and a zinc oxide-containing material are recommended as suitable once-through sorbent fines for Stage I of the Ultra-Clean gas polishing process. The mass balance around the moving bed filter-reactor was determined based on the use of the GTI zinc titanate sorbent for sulfur capture, which has a nominal ZnO content of 40% by weight. This effort also provided some guidelines on conducting evaluation and parametric tests involving both HCl and H_2S using mixtures of trona and the zinc titanate sorbent. As shown in Figure 3.35, trona and the GTI zinc titanate sorbent are reasonably assumed to both achieve 50% conversion. Based on the HCl and H_2S concentrations in the feed gas to the Moving Bed Filter- Reactor, the amount of trona needed is slightly over 2.5 times the amount of the zinc titanate sorbent. Therefore, a suitable mixture of both sorbent fines should consist of about 72.5 wt.% trona and 27.5 wt.% zinc titanate sorbent.

A scoping test involving both HCl and H_2S was carried out using a sorbent mixture consisting of 67 wt% trona and 33 wt% GTI zinc titanate sorbent. For three periods of time ranging from 1 to 2 hours, inlet contaminant concentrations were changed from 50 ppmv H_2S and 350 ppmv HCl initially, to 100 ppmv H_2S and 700 ppmv HCl, and finally to 250 ppmv H_2S and 1750 ppmv HCl. The target 1-3 ppmv of contaminant concentration in the effluent gas was achieved for both H_2S and HCl during all three periods. It was deemed unnecessary to go beyond these inlet concentrations, as they would be sufficient to achieve breakthrough within reasonable time.

The above scoping test was followed by another test, the objective of which was to determine the effective capacities of trona and the zinc titanate sorbent for chloride and sulfur absorption, respectively. The test employed a sorbent mixture consisting of 67 wt% trona and 33 wt% zinc titanate and was carried out at the baseline operating conditions with inlet HCl and H_2S

concentrations of 1750 ppmv and 250 ppmv, respectively. Surprisingly, neither HCl nor H_2S broke through following about 13.5 hours of testing under these conditions. At this point, the inlet HCl and H_2S concentrations were raised to 5000 and 700 ppmv, respectively. It took an additional 3.5 hours of testing under these conditions before breakthrough was obtained.

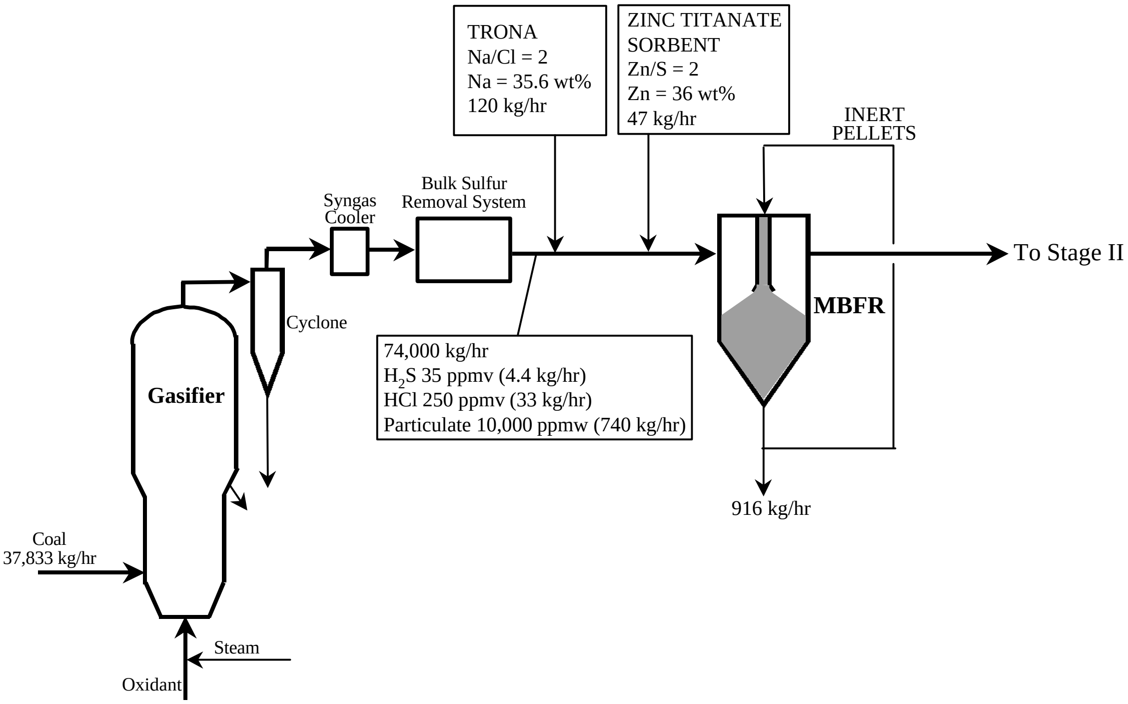


Figure 3.35 – Material Balance for the Moving Bed Filter-Reactor with Zinc Titanate Sulfur Sorbent

These testing periods correspond to a total chloride loading of 32.4 g Cl/100 g of trona and 8.4 g S/100 g of zinc titanate sorbent. These effective capacities account for about 58.5% conversion for trona and about 53% conversion for the zinc titanate sorbent. Therefore, the utilization of trona in this sorbent mixture is about twice the utilization achieved when trona was evaluated by itself under the same operating conditions (Tests A &B, Figure 3.23). The results obtained with the zinc titanate sorbent are consistent with previous tests conducted with this sorbent in a separate research program at GTI (Abbasian and Slimane, 1997). Based on the results obtained, 700 ppmv H_2S and 5000 ppmv HCl were selected as suitable inlet concentrations for subsequent testing involving the sorbent mixture.

The breakthrough curves from a test conducted under the conditions specified above are shown in Figure 3.36. Consistent with previous results, the target contaminant concentration of 1-3 ppmv in the effluent gas was achieved for both HCl and H_2S, even at the higher inlet concentrations of 5000 and 700 ppmv for HCl and H_2S, respectively. More surprising, however, are the pre-breakthrough times for both contaminants, which are about 8.4 hours for HCl and 8.3 hours for H_2S. These values correspond to effective capacities approximating 32.6 g Cl/100 g of trona and 8.2 g S/100 g of zinc titanate sorbent. In addition to being consistent with the results obtained in the previous test, these results also indicate that the utilization of trona and that of the zinc titanate sorbent in the bed mixture are not sensitive to the inlet contaminant concentrations.

The composition of the sorbent mixture (i.e., 67 wt% trona and 33 wt% zinc titanate) and the operating conditions used allowed the synchronization of HCl and H_2S breakthrough points.

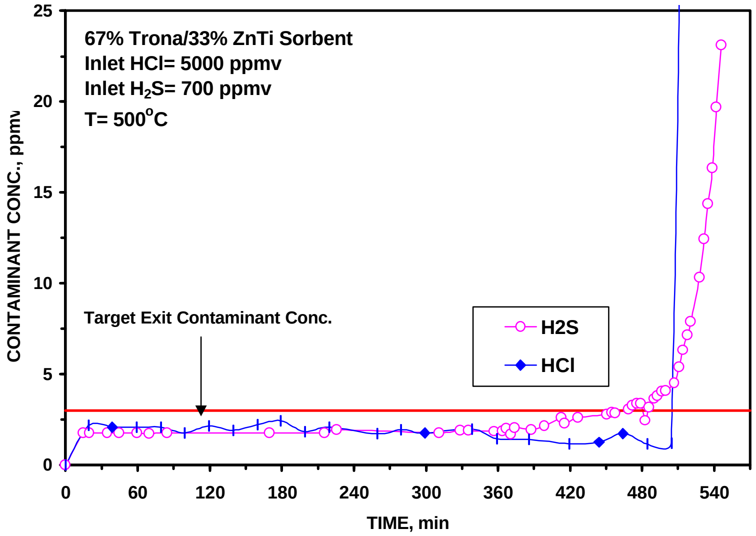


Figure 3.36 – HCl and H_2S Breakthrough Curves at 5 cm/s Gas Velocity

The effect of higher inlet gas velocity on the performance of the fine sorbent mixture is shown in Figure 3.37 for HCl and in Figure 3.38 for H_2S. As shown in Figure 3.37, at the higher gas velocity of 7 cm/s, HCl concentrations in the effluent reactor gas are slightly higher initially compared to those obtained at the baseline operating condition of 5 cm/s. However, at both gas velocities trona achieves similar effective capacities for chloride absorption. The same is true of the zinc titanate sorbent, as shown in Figure 3.38, except that at the higher gas velocity of 7 cm/s the H_2S pre-breakthrough concentrations are slightly higher, ranging from 3-6 ppmv.

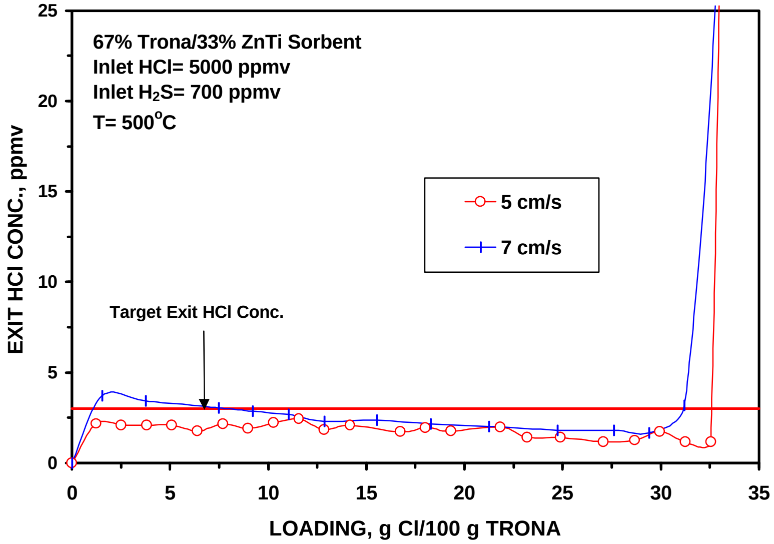


Figure 3.37 – HCl Breakthrough Curves at Two Gas Velocities

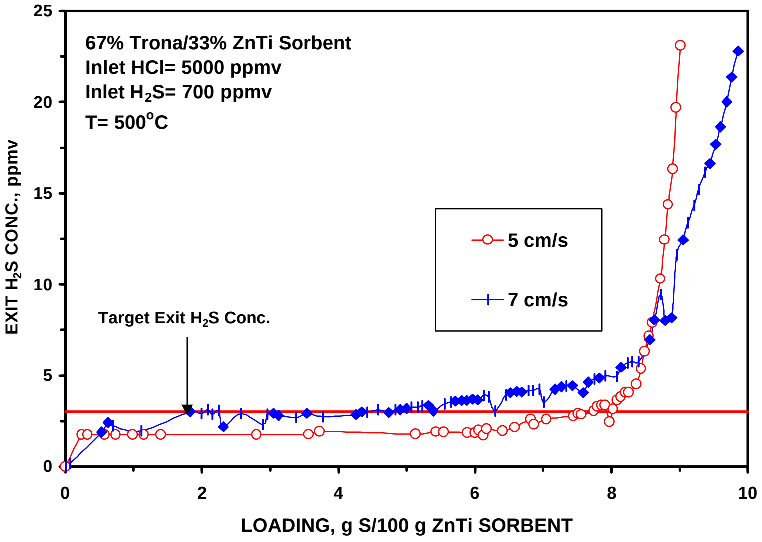


Figure 3.38 – H_2S Breakthrough Curves at Two Gas Velocities

The effect of temperature, in the range of 450 to 550°C, on the dechlorination and desulfurization performance of trona and the zinc titanate sorbent, respectively, is shown in Figures 3.39 and 3.40. As shown in Figure 3.39, at 500°C trona achieves the highest effective capacity for chloride absorption, with residual HCl concentrations < 3 ppmv. HCl concentrations in reactor effluent are lowest at 450°C and highest at 550°C, ranging from about 3-5 ppmv. At both temperatures, however, trona achieves similar effective capacities for chloride absorption.

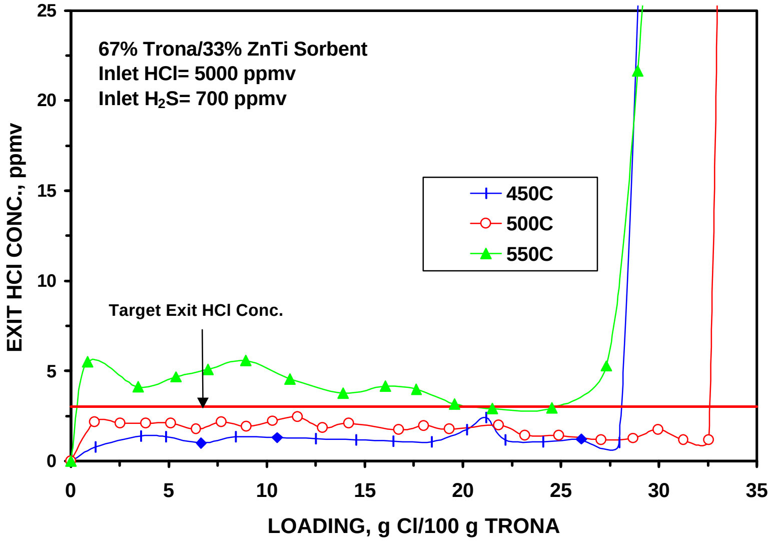


Figure 3.39 – Effect of Temperature on Efficiency and Effective Capacity of Trona for Chloride Absorption

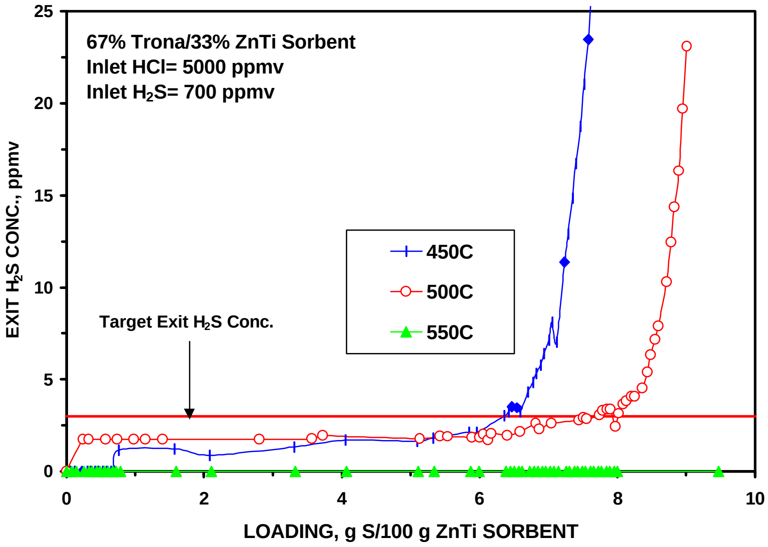


Figure 3.40 – Effect of Temperature on Efficiency and Effective Capacity of GTI's Zinc Titanate Sorbent for Sulfur Absorption

The zinc titanate sorbent exhibited different trends than trona at the three temperatures tested. As can be expected, at 450°C the zinc titanate sorbent is slightly more efficient (lower residual H_2S concentrations); however, its effective capacity for sulfur absorption is lower than that at 500°C. At the higher temperature of 550°C, virtually no H_2S was detected throughout the entire test, which was terminated when HCl breakthrough was obtained. The higher H_2S removal efficiency at the higher operating temperature is likely due to the availability of Na_2O from trona for reaction with H_2S. Na_2O is significantly more efficient than ZnO for H_2S removal. This would also explain the lower effective capacity of trona for chloride absorption at 550°C than at 500°C, as discussed above

Following breakthrough, the sorbent bed was divided into a bottom portion, a middle portion, and a top portion. Spent (i.e., sulfided and chlorinated) sorbent samples from the three different bed sections were submitted for chemical analysis to confirm the effective capacity of trona for chloride absorption and that of the zinc titanate sorbent for sulfur absorption, as calculated based on the breakthrough curves. The sodium, chloride, zinc, and sulfur analyses are reported in Table 3.16. Both the bottom and middle portions of the sorbent bed contain similar amounts of chloride and sulfur, indicating similar conversions for trona and the zinc titanate sorbent in both bed locations. As would be expected in a packed-bed setting, the top portion of the sorbent bed (gas outlet) achieves the least sorbent conversion prior to breakthrough. The chloride content of the reacted material ranges from 32.4 wt% in the bottom portion (gas inlet), to 31.4 wt% in the middle portion, to 22.4 wt% in the top portion (gas outlet). These chloride assays correspond to conversions of 59%, 57%, and 41%, respectively, for the as-received trona. A rough estimate of the chloride loading gives an average of about 32.0 wt% Cl on as-received trona basis, which is consistent with the effective capacity reported earlier for trona, based on gas analysis (i.e., breakthrough curve).

Table 3.16 – Chemical Analyses of Reacted Trona/Zinc Titanate Sorbent Mixture

Element	Bed Location		
	Bottom	Middle	Top
Na	20.4	20.9	21.5
Cl	32.4	31.4	22.4
Zn	13.0	12.9	13.6
S	4.99	4.39	2.36

The sulfur content of the reacted material ranges from 4.99 wt% in the bottom portion (gas inlet), to 4.39 wt% in the middle portion, to 2.36 wt% in the top portion (gas outlet). Based on the zinc oxide content, these sulfur assays correspond to conversions of approximately 40.6%, 35.7%, and 19.2%, respectively, for the zinc titanate sorbent. A rough estimate of the sulfur loading gives an average of about 8.4 wt% on fresh zinc titanate sorbent basis, which is consistent with the effective capacity of the zinc titanate sorbent, as calculated based on the breakthrough curve.

A sample from the bottom portion (gas inlet), where the sorbent undergoes conversion to the highest extent, was submitted for X-ray diffraction analysis (XRD) to identify the forms in which the various mixture components exist. The pattern for this reacted sample is shown in Figure 3.41, clearly disclosing the presence of NaCl (major phase), ZnS, ZnO, and TiO_2 (minor phases) as the only stable compounds. These phases are denoted by 3, 2, 1, and 4, respectively, in Figure 3.41. This further confirms the lack of any interaction between H_2S and the dechlorination sorbent, and HCl and the desulfurization sorbent, in agreement with thermodynamic predictions outlined in previous sections. Gas analysis (i.e., breakthrough) data, chemical analysis of reacted and fresh sorbent samples, and XRD information are completely in agreement, providing a high degree of confidence in the experimental data developed in this program

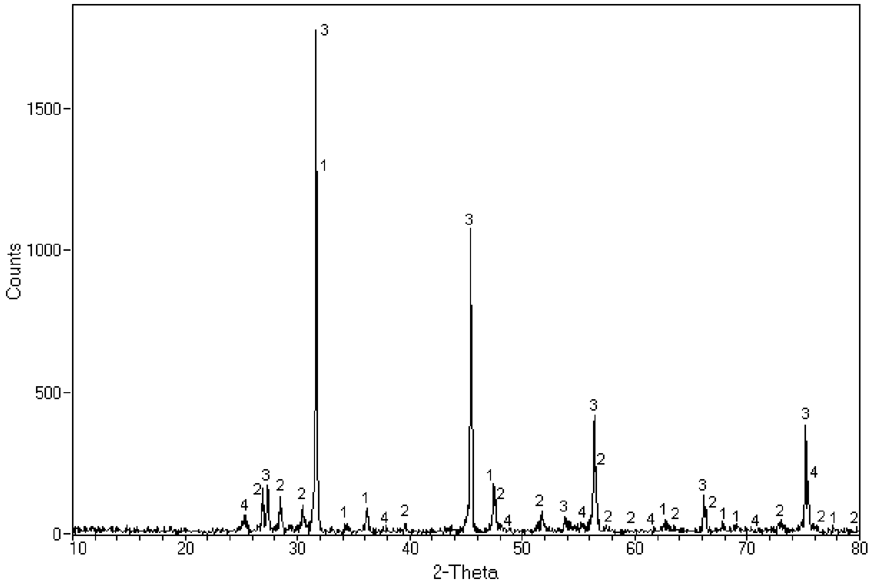


Figure 3.41 – XRD Pattern of Reacted Materials from a Trona/Zinc Titanate Sorbent Mixture

3.4.6 Preliminary Stage II HCl Removal Tests

Modifications of the ambient pressure reactor arrangement were made to accommodate tests in Stage II of the program. Alundum pellets in the reactor inlet section were replaced with quartz chips to eliminate any interference with contaminants. Some modifications were also made to the sample collection setup to provide for continuous sampling. The exit gas line from the reactor is fed directly to one port of a "y" glass adapter, which is connected to a spiral condenser for steam condensation. The output from the condenser is bubbled through deionized water for dissolution of all HCl from the gas. The accumulating chloride concentration was measured continuously by ion chromatography by circulating the deionized water through the IC. instrument sample port with a peristaltic pump. The waste line from the IC sampling port was connected to the second port of the "y" glass adapter. This allowed the water level in the HCl recovery container to remain constant and also rinsed any condensed water droplets on the walls of the condenser.

The exit gas was bubbled through 450 mL of deionized water (volume of absorbing solution was adjusted to account for steam condensation from the gas) and sampled every about 11 minutes. The cumulative Cl concentration was measured by ion chromatography. An "instantaneous" Cl concentration was then calculated based on the cumulative value. A scoping test was carried out at 400°C using a fresh batch of the G-92C material. During this test, both the feed gas flow rate and composition were varied. First, nitrogen was introduced into the reactor at 500 cc/min and the dissolved Cl concentration was measured to obtain a baseline concentration. Then a dry gas containing 4 ppmv HCl in a N_2-H_2 mixture was introduced at about 521 cc/min. After obtaining a steady measurement of the HCl concentration in the exit gas, the flow rate was raised to 996 cc/min and maintained for about 2 hours, then to 1840 cc/min and maintained for an additional period of about 2 hours. This latter total gas flow rate corresponds to the baseline operating condition of 5 cm/s gas velocity at 400°C. Steam was then added to the HCl-H_2-N_2 feed gas mixture. Finally, the inlet feed gas composition was adjusted to the baseline composition by adding CO and CO_2.

As shown in Figure 3.42, in N_2 at 500 cc/min, the average HCl concentration in the exit gas is about zero. When the feed gas consisted of 4 ppmv HCl in N_2-H_2, the steady state HCl concentration in the exit gas averaged about 25 ppbv, and about 22 ppbv at the higher flow rate of 996 cc/min of this same gas mixture. At the baseline gas flow rate of 1840 cc/min, the measured HCl concentration averaged about 44 ppbv. When steam was introduced in the feed gas, the exit HCl concentration increased to about 110 ppbv. Finally, when CO and CO_2 were introduced, bringing the overall feed gas composition closer to the baseline operating conditions, the HCl concentration remained steady at about 80 ppbv.

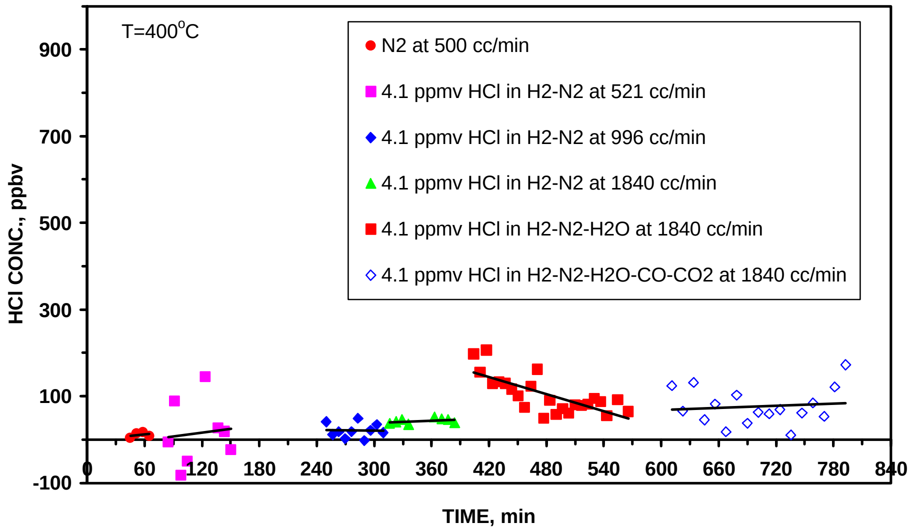


Figure 3.42 – Scoping Test with the G-92C Dechlorination Material

The high gas flow rate of 1840 cm^3/min, which corresponds to a gas velocity of 5 cm/s at the baseline temperature of 400°C, appears to be problematic. The 1-cm deep sorbent bed almost always developed a crack during testing, raising the possibility of channeling and misleadingly high HCl concentrations in the cleaned gas. It was reasoned that lower gas flow rates and/or higher bed heights should be examined to obtain a meaningful HCl concentration in equilibrium with the G-92C material. It should be noted, however, that the calculated HCl concentration in the gas is directly related to the Cl concentration in deionized water, but inversely related to the gas flow rate ($[HCl] \propto [Cl]/Q$). Therefore, HCl calculations tend to have a large standard deviation when the gas flow rate is low. This has nothing to do with the sensitivity of the equipment and the dissolved Cl concentration in liquid has a very low standard deviation. However, even a 0.5 ppb change in Cl concentration (in the liquid) results in a change of 60 ppbv in the calculated HCl concentration (in the gas) at 500 cc/min. The same 0.5 ppb Cl change at 1500 cc/min is equivalent to 20 ppbv HCl. The average of the calculated HCl concentration can, however, be used as a reliable estimate. Finally, these results suggest the G-92C material should be evaluated at temperatures < 400°C to achieve lower equilibrium HCl concentrations.

A scoping test was then carried out to establish that the HCl delivery system was the source of the measured HCl contamination, and not the sampling setup. Another objective was to make a preliminary determination of the HCl removal efficiency of the G-92C dechlorination sorbent at 300°C. A 1-cm bed height and a gas velocity of 5 cm/s were used. The exit HCl concentration was measured as the feed gas was changed from N_2, to N_2 + steam, to syngas (w/o HCl), and finally to a simulated syngas containing about 147 ppmv HCl. The results from this scoping test are reported in Figure 3.43. As shown, in N_2 at full flow (2160 cc/min), the exit HCl concentration was ~10 ppbv. When steam was introduced, this background HCl concentration increased to ~25 ppbv, but dropped down to ~5 ppbv when the syngas mixture (w/o HCl) was introduced. This establishes that the sorbent bed material can absorb any HCl desorbing from the gas delivery system, preventing any contamination. The results also indicate that a short pretreatment period with a N_2-steam mixture eliminates any contamination that would otherwise result from the quartz reactor parts, exit gas lines, and sampling apparatus downstream of the sorbent bed.

A more significant result is the measured exit HCl concentration when a simulated syngas containing about 147 ppmv HCl was introduced. These values remained constant at ~5 ppbv, establishing that the G-92C is capable of reducing the HCl concentration to below the target level of 10 ppbv at this lower temperature of 300°C, consistent with thermodynamic predictions.

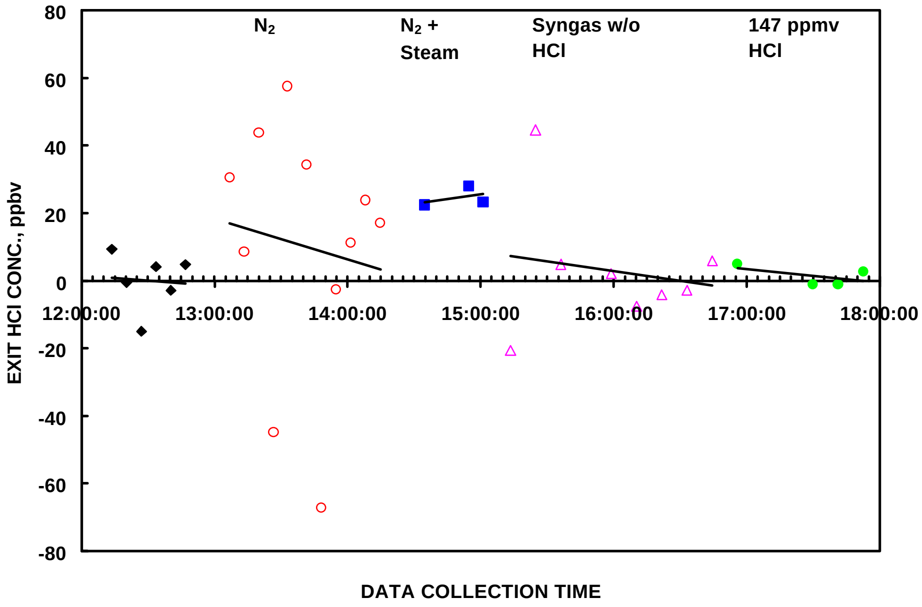


Figure 3.43 – Scoping Dechlorination Test with the G-92C Material

3.4.7 Priorities for Experimental Testing for Balance of Base Program

The experimental results obtained thus far into the program were assessed. Based on the results, the difficulties encountered, particularly with measurement of chloride and sulfur at trace levels using the IC instrument (see Appendix A and Appendix B), there was a consensus to address the issues identified in testing at ambient pressure, rather than doing high-pressure tests. An assessment of the progress made to-date identified the following as warranting further investigation to add to the technical quality of the Base Program.

Feed HCl as Liquid Rather Than Gas

Up to this point in the program, certified HCl-H_2 gaseous mixtures had been used as a source of HCl in the simulated syngas. There were some difficulties associated with this approach. First, mass flow controllers failed somewhat frequently because of HCl poisoning, leading to the interruption of several tests. Unexpectedly, this problem was encountered with special HCl MFCs more frequently than with regular N_2 MFCs. Second, the tendency of HCl to adsorb on feed lines, valves, heat exchange media, etc between the HCl-H_2 gas cylinder and the sorbent bed was identified to be somewhat problematic, leading to contamination. As pointed out earlier, because of the high inlet HCl concentration in Stage I experiments (about 5000 ppmv), contamination did not present a major concern.

The alternative approach suggested was to employ dilute hydrochloric acid solutions instead of distilled water as a source of both steam and HCl components in the simulated syngas stream. Three certified such solutions were obtained, with HCl concentrations of 0.02, 0.1, and 2.0 M. Through dilution of these standard solutions with distilled water, inlet HCl concentrations ranging from 10 ppbv HCl to 5000 ppmv HCl could be simulated.

HCl Issues – IC Instrument

The lowest certifiable HCl concentration in HCl-H_2 gas mixtures was about 9 ppmv. To produce gas mixtures containing HCl at the ppbv level, dilution of the HCl-H_2 mixture with N_2 was necessary. Unfortunately, because of contamination problems, as explained above, calibration of the IC instrument using the HCl-H_2 gas mixture did not provide results that could be considered sufficiently conclusive. It was deemed necessary the use the alternative approach described above for feeding HCl as a liquid rather than a gas to prevent any possible contamination, thereby further refining the calibration procedure. Distilled water, containing HCl at a predetermined concentration, would be pumped through a quartz tube extending through heat transfer media in the bottom portion of the reactor shell to just below the frit of the reactor cage containing the sorbent bed. This would ensure that, upon vaporization in the hot zone, the HCl-containing gas did not come into contact with the heat transfer media and no adsorption would take place. Using an empty reactor (i.e., no sorbent bed), nitrogen-steam mixtures, containing HCl at concentrations of 10 to 500 ppbv, would be generated and used to provide a more reliable calibration of the IC instrument for Stage II experiments.

H_2S Issues – IC Instrument

Earlier work established that the Dionex DX320/IC20 unit was capable of detecting SO_4^{--} in liquid standards at concentrations ranging from 10 ppb to 100 ppm levels. For this instrument to be useful for Stage II experiments, residual H_2S in ultra-cleaned effluent gases had to be first absorbed into a solution and then oxidized to SO_4^{--}. It was established that H_2S capture in a scavenger solution consisting of hydrogen peroxide and sodium hydroxide was virtually quantitative; however, H_2S oxidation was kinetically-limited, requiring at least ½ hour to complete. Preliminary analytical tests early in the program indicated that in the first 5 minutes two peaks typically appeared in the chromatogram, disclosing the presence of both SO_3^- and SO_4^{--}. As oxidation was allowed to occur to a greater extent, the SO_3^- peak area decreased while that of the SO_4^{--} increased. Following about 30 minutes, the SO_3^- peak disappeared and the SO_4^{--} peak remained constant at about 90-95% of the sample gas concentration (based on calibration with liquid standards). This indicated the possibility that about 5-10% of the H_2S in the feed gaseous stream was not captured during bubbling through the absorber solution.

Based on the above, using an approach similar to the continuous measurement of HCl might not be possible for H_2S. The need to allow at least 30 minutes for the oxidation of H_2S to SO_4^{--} limited the frequency of sampling. A different approach was suggested, where the effluent gas containing trace levels of H_2S would be periodically sampled for a predetermined period. This sample would then be set aside to allow for the oxidation of the captured H_2S to complete, prior to IC analysis.

A certified gas mixture containing about 0.5 ppmv H_2S in N_2 was obtained for these efforts. The extent of H_2S absorption as a function of H_2S concentration in the inlet gas would be evaluated. The make up of the scavenger solution would also be optimized. Various concentrations of the basic component (i.e., sodium hydroxide) and the oxidizer (i.e., hydrogen peroxide) would be evaluated. A strong oxidizing solution might produce peaks that would shadow the SO_4^{--} peak and prevent it from being measured. Therefore, the amount of the oxidizer in the scavenger solution would be optimized to provide acceptable oxidation of H_2S, while preventing any conflicts with the IC measurement method. In addition, the effect of other gaseous species (such as CO) on the detection method for H_2S measurement would be determined. In tests involving both HCl and H_2S, HCl would be removed upstream of the H_2S scavenger solution and therefore, the effect of the presence of HCl in the gas mixture on H_2S detection would not be considered. However, the extent of H_2S absorption in the HCl solution, if any, would be quantified.

Screening Tests for Stage II HCl Sorbents

G-92C, Katalco 59-3, and pre-calcined trona were recommended for consideration in screening tests aiming to reduce the HCl concentration from 1-3 ppmv to less than 10 ppbv. Consistent with thermodynamic predictions, preliminary experimental test results indicated the need to operate Stage II of the Ultra Clean Gas Cleanup Process at temperatures lower than 400°C, as originally planned. Preliminary results also suggested the feasibility of achieving the target HCl concentration of < 10 ppbv at a temperature ≈300°C.

Because of high-pressure build up in the quartz reactor, gas velocity in these tests was limited to about 3 cm/s. For this reason, sufficient quantities of these materials were ground and sieved in bigger and more limited size ranges, as follows < 44 µm, 44-75 µm, 75-90 µm, and > 90 µm, in preparation for their evaluation using the new approach of feeding HCl as a liquid, under the following operating conditions:

- Temperature: 350°C
- Gas velocity: 5 cm/s
- Inlet HCl concentration: could be as low as 5 ppmv, but should be selected to obtain breakthrough in reasonable time (i.e., < 8 hours), while achieving the target HCl concentration of < 10 ppbv in the cleaned gas

These screening tests would provide the information necessary to rank the candidate sorbent materials in terms of their HCl removal efficiency and effective capacity for chloride absorption. Pressure drop problems would be overcome by using bigger sorbent particles that are in a more limited size range. The effectiveness of the best dechlorination material would be evaluated in the 300-400°C temperature range.

Evaluation of Stage II H_2S Sorbent

G-72E was selected as a desulfurization sorbent for H_2S removal in Stage II down to the target level of < 60 ppbv. Similar to dechlorination materials, this sorbent would be evaluated at 350°C for its H_2S removal efficiency and sulfur absorption capacity. G-72E would also be tested at the temperature that would be determined to be optimum for HCl removal. If the target H_2S concentration in the ultra-cleaned gas was not achieved, lower operating temperatures would be considered. In addition, the efficiency of the G-72E sorbent for H_2S removal would be determined using a simulated dry syngas, to assess the potential for enhancement of sorbent efficiency through steam removal.

Parametric Tests on Best HCl Sorbent + G-72E

The best dechlorination material would be used in combination with the G-72E desulfurization sorbent to conduct a parametric study involving simultaneous removal of HCl and H_2S. The following would be determined:

- Effect of temperature: 300-400°C
- Effect of gas velocity: 3-8 cm/s
- Effect of inlet HCl and H_2S concentrations
- Effect of thickness of sorbent bed mixture

3.4.8 Feeding HCl as a Liquid Rather Than a Gas

To overcome operational and contamination issues associated with the use of certified $HCl\text{-}H_2$ gaseous mixtures as a source of HCl in the simulated syngas, an alternative approach was proposed, which promised to be very useful for Stage II tests at trace contaminant concentrations. This alternative approach employed dilute hydrochloric acid solutions instead of distilled water as a source of both steam and HCl components in the simulated syngas stream. Three certified such solutions were obtained, with molarities of 0.02, 0.1, and 2.0 M. Through dilution of these standard solutions with distilled water, it was calculated that inlet HCl concentrations ranging from 10 ppbv HCl to 5000 ppmv HCl could be simulated.

To ensure the viability of this new approach, it was necessary to verify that feeding HCl as a dilute hydrochloric acid solution was equivalent to feeding HCl as a $HCl\text{-}H_2$ gas mixture. An empty bed test was carried out in the existing reactor shell assembly to estimate the saturation time for the heat exchange media (quartz chips) and to determine the generated HCl concentration in the gas phase. First, only nitrogen was introduced at a total flowrate of 1186.3 cc/min to the reactor shell at 350°C. As shown in Figure 3.44, the measured background HCl concentration averaged about 2 ppmv. Then N_2 flow was reduced to 996.4 cc/min and a standard 0.02 M hydrochloric acid solution was introduced through the steam line. Monitoring of pump performance revealed that the hydrochloric acid solution was introduced at an average flowrate of about 8.6 cc/hr, corresponding to about 194.2 cc/min of steam. (Note: at the same setting, the pump delivered a steady flow of 8.6 cc/hr of deionized water; however, when a more concentrated HCl solution was used, the pump performance declined significantly). The total flow rate then became 1186.3 cc/min and the percentage of H_2O in this feed gas was about 16.4. It can be shown that the molarity of the hydrochloric acid solution, the percentage of steam in the feed gas, and the concentration of HCl generated in the gas phase are related by the following equation:

$$[\mathrm{HCl}],\ \mathrm{ppmv} = 180*(\%\mathrm{H_2O})*M \qquad (3.12)$$

where M designates molarity in moles of HCl per liter of solution. Therefore, the HCl concentration in the above feed gas could be estimated as 58.932 ppmv.

Following about 30 min of saturation time, the HCl exit gas concentration was measured at about 58.4 ppmv and remained somewhat constant at this value for over 40 minutes in the $HCl\text{-}H_2O\text{-}N_2$ environment, as indicated by the slope of the curve in Figure 3.44 corresponding to this time period. When the remaining components of the syngas (i.e., CO, CO_2, CH_4, and H_2) were added, the HCl concentration in the exit gas increased slightly to about 59.4 ppmv, likely because of a slight increase in the HCl background concentration. This explanation is consistent with the results obtained during the following two periods, which showed an increasing trend in the measured HCl concentration. As shown in Figure 3.44, when the syngas consisted again of just HCl, H_2O, and N_2 the measured HCl concentration averaged about 62.4 ppmv. In addition, the measured background HCl concentration in N_2 only at the end of this test averaged about 3.5 ppmv, almost double what it was in the beginning of the test.

The above results demonstrated that the alternative approach of feeding HCl as dilute hydrochloric acid solutions could be used reliably. Although these measured HCl concentrations departed slightly from the designed value of about 59 ppmv, this did not present a concern since the concentration of HCl in the feed gas during actual screening tests of Stage II dechlorination sorbents would likely range from 250-2000 ppmv. Therefore, the background HCl concentration would represent only a negligible fraction of the feed concentration. Furthermore, by rearranging the reactor shell assembly, it could be possible to prevent or minimize the background HCl concentration as the feed gas was prevented from coming into contact with the heat exchange media.

It should be pointed out that the results reported in Figure 3.44 were calculated based on the “cumulative” chloride concentration in the deionized water absorber solution, as measured periodically by the IC instrument. It can be shown that the slope of each curve represents the average HCl concentration in the exit gas during the corresponding time period. This method of reporting test results is essentially equivalent to the way the results were previously reported, where the “instantaneous” HCl concentration was given as a function of time.

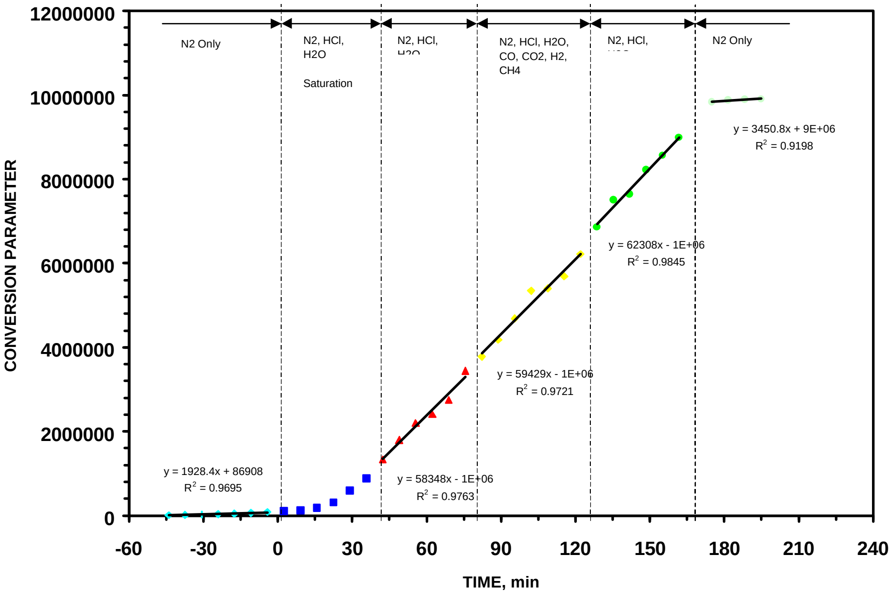


Figure 3.44 – Empty-Bed Scoping Test Results

3.4.9 Screening Tests for Stage II HCl Sorbents

A dechlorination test was carried out with the Katalco 59-3 material at 350°C and 5 cm/s gas velocity in the 1-cm bed height arrangement. To avoid high-pressure build up in the reactor, material for this test was classified to a particle size range of 75 to 90 µm. Because of mass flow meter limitation, the gas composition differed slightly from the baseline. H_2 and CO accounted for 24.2 and 40.8% instead of 30 and 35% of the total gas flow rate, respectively. The breakthrough curve from this test is shown in Figure 3.45.

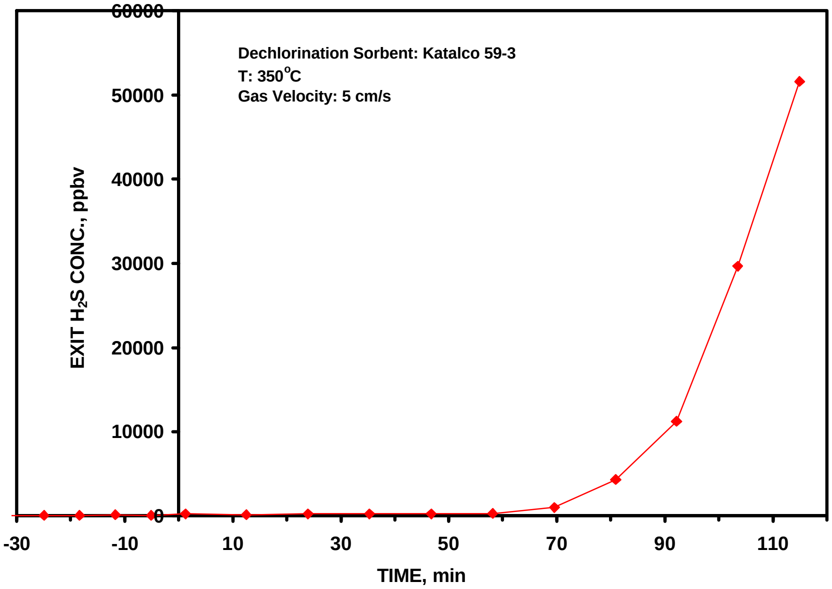


Figure 3.45 – HCl Breakthrough Curve for the Katalco 59-3 Sorbent at 350°C

To assess the efficiency of this material for HCl removal more readily, the results from this test are reported in Figure 3.46 using the alternative approach, as explained above. As indicated by the slopes of the two lines shown on Figure 3.46, the background HCl concentration averaged about 53.2 ppbv, while the pre-breakthrough value averaged about 229.9 ppbv. Therefore, the average pre-breakthrough HCl concentration can be estimated at 176.7 ppbv. It should be noted that a crack in the sorbent bed was observed at the conclusion of this test.

Pre-calcined trona, in the 75 to 90 µm size range, was also evaluated for its HCl removal capability in the 1-cm bed height arrangement. Because of its high theoretical chloride capacity, the main purpose of this test was to evaluate the HCl removal efficiency and not the effective capacity. Two temperatures were investigated, 350 and 300°C. The results obtained at both temperatures are reported in Figure 3.47. As shown, the background HCl concentration averaged about 31.6 ppbv. At 350°C and a 5 cm/s gas velocity, the measured HCl concentration in the cleaned gas averaged about 484.2 ppbv. Therefore, at 350°C, pre-calcined trona is capable of removing HCl down to about 452.6 ppbv. During the transition period from 350 to 300°C, the measured HCl concentration averaged about 178.3 ppbv. When temperature was stable at 300°C, the efficiency of pre-calcined trona for HCl removal improved significantly to about 37.6 ppbv (i.e., 69.2 – 31.6). Pre-calcined trona appears promising for achieving the target HCl concentration of 10 ppbv. It is worthwhile to investigate other ways to further reduce the HCl concentration in the cleaned gas, such as lowering the operating temperature, the HCl concentration in the inlet gas, or the gas velocity.

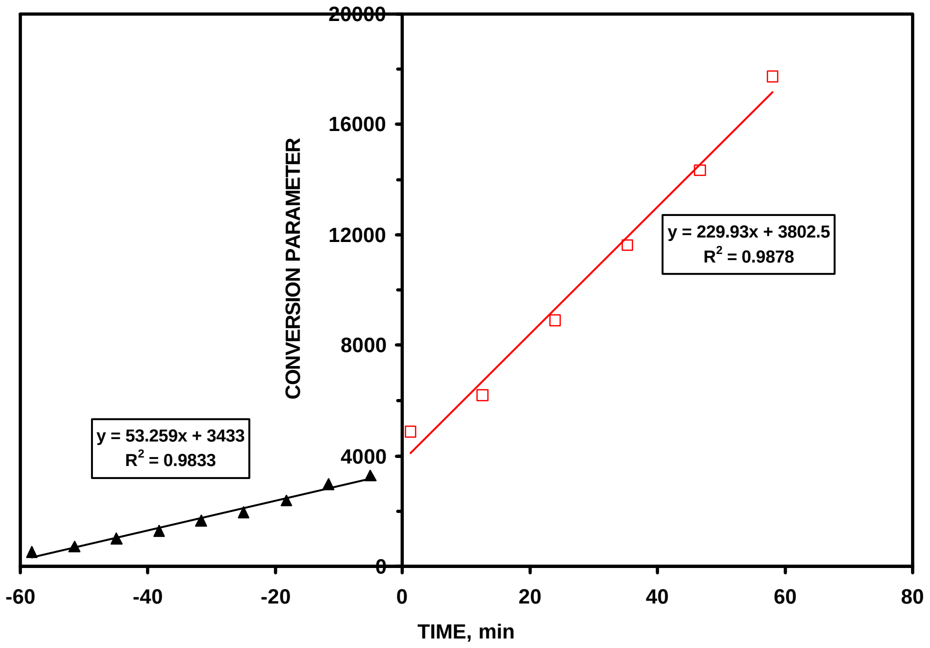


Figure 3.46 – HCl Pre-breakthrough Concentration with Katalco 59-3 at 350°C

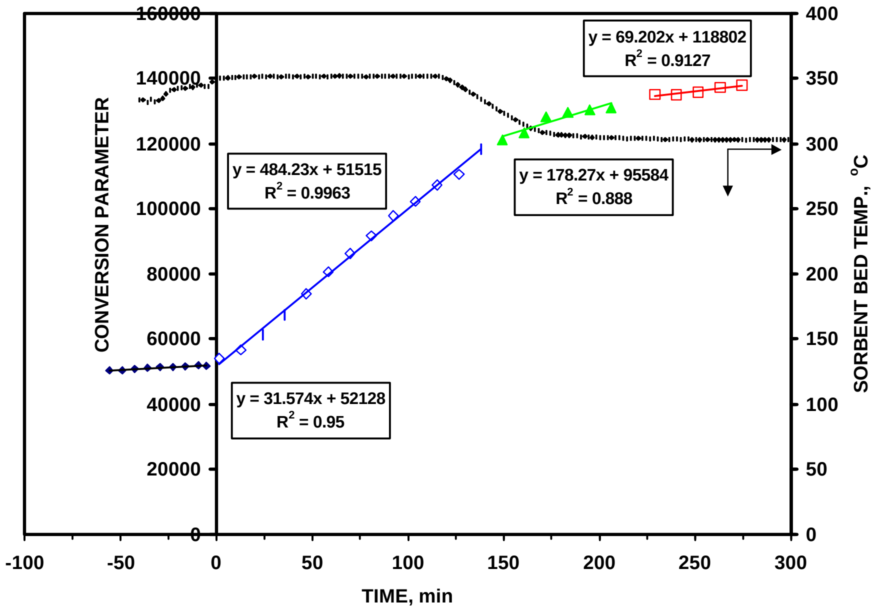


Figure 3.47 – Scoping Dechlorination Test with Pre-calcined Trona at 350 and 300°C

The profiles for reactor pressure and pressure drop across the sorbent bed are shown in Figure 3.48. Both appear stable throughout the testing period with no sudden changes. This provides a good indication that no channeling occurred during this test in the 1-cm bed arrangement, and that the exit HCl concentrations measured at 350 and 300°C could be considered reliable.

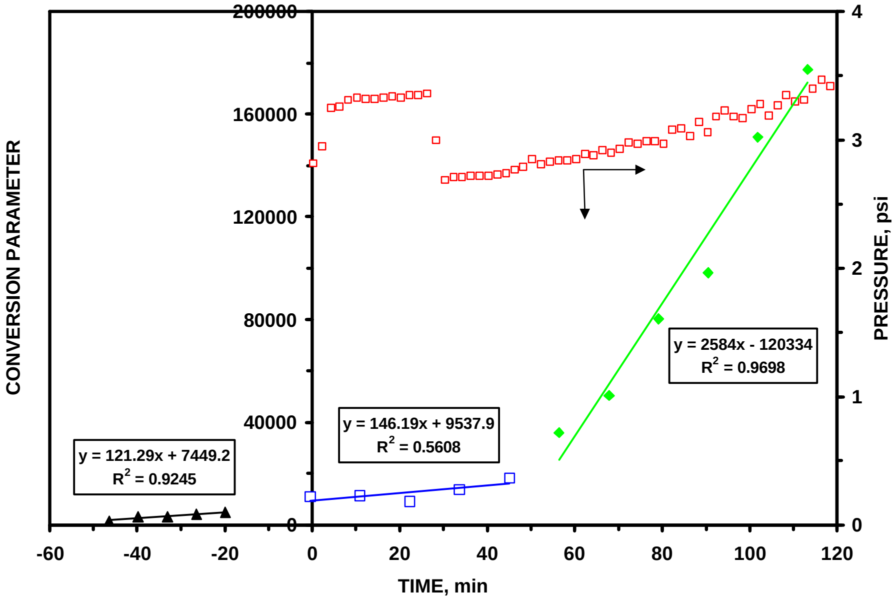


Figure 3.48 – Reactor Pressure and Pressure Drop Across Sorbent Bed During Dechlorination Test with Trona

The above test with pre-calcined trona was continued at 300°C until breakthrough was obtained. Preliminary calculations indicated that the cumulative amount of chloride loaded at 350°C, during the transition period, and at 300°C was about 4.5 g Cl/100 g of pre-calcined trona. The G-92C material, in the 75 to 90 µm size range, was also evaluated in the 1-cm bed height arrangement, but at a temperature of 300°C and a reduced gas velocity of 3 cm/s. The lower temperature was used to enhance the likelihood of achieving the target HCl concentration of 10 ppbv in the cleaned gas. The reduced gas velocity was used for the same purpose, and also to minimize the possibility of developing cracks or channels in the thin sorbent bed. The results obtained are reported on Figure 3.49. As shown, the background HCl concentration averaged about 121.3 ppbv. During testing, the measured HCl concentration averaged about 146.2 ppbv during the first 45 minutes. Therefore, G-92 appears to be capable of reducing HCl concentration down to about 25 ppbv at 300°C. As can be seen on Figure 3.49, there was a sudden rise in the measured HCl concentration to an average value of about 2.6 ppmv following about an hour of testing. This appears to be a direct result of the sudden drop in reactor pressure that preceded it, which might be explained by the development of channeling through the sorbent bed. Channeling appears to constitute a problem with this material even at the lower gas velocity of 3 cm/s.

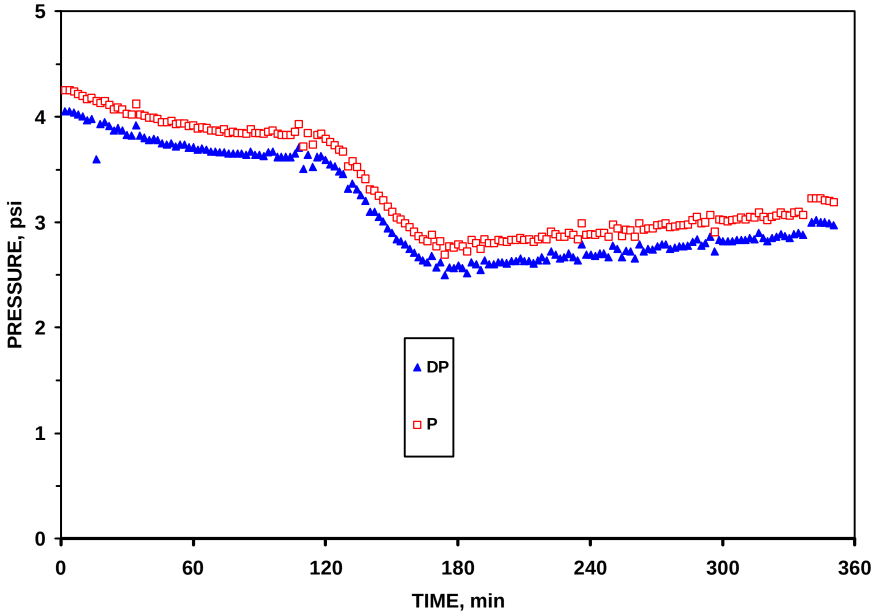


Figure 3.49 – HCl Breakthrough Curve with G-92C Sorbent at 300°C and 3 cm/s

A separate test was conducted with the G-92C material at 350°C and a 3 cm/s gas velocity. Although in this test also channeling was suspect, the results obtained (Figure 3.50) indicated this material was capable of removing HCl at 350°C down to about 108 ppbv.

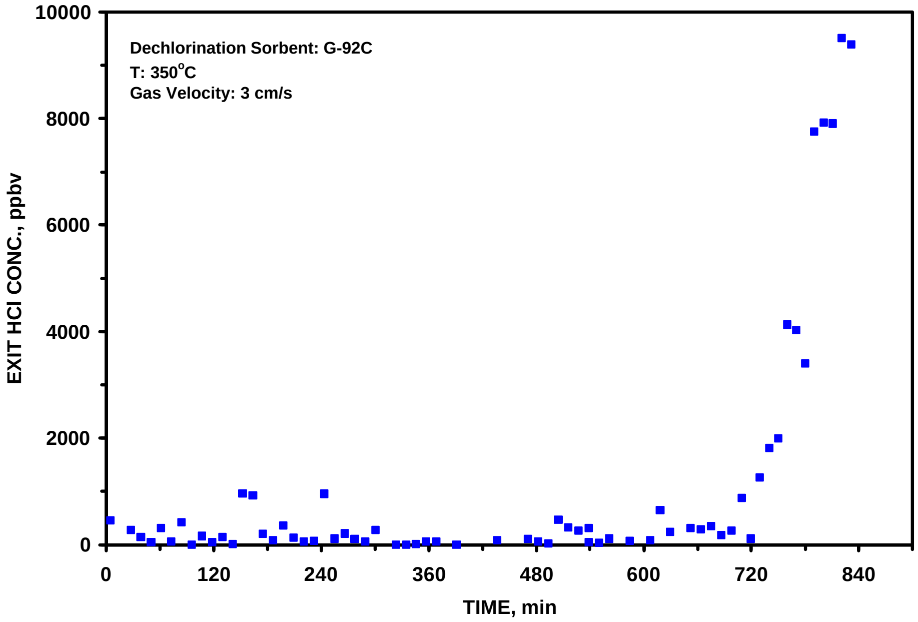


Figure 3.50 – HCl Breakthrough Curve with G-92C Sorbent at 350°C and 3 cm/s

In summary, based on the above test results, the three dechlorination sorbents selected for Stage II of the Ultra-Clean gas polishing process could be ranked in terms of their HCl removal efficiency as follows: G-92C > Katalco 59-3 > pre-calcined trona. At 350°C, the measured HCl concentrations in the cleaned gas are approximately 108, 176.7, and 452.6 ppbv for G-92C, Katalco 59-3, and pre-calcined trona, respectively. At 300°C, these values are reduced to about 25 ppbv for G-92C and 37.6 ppbv for pre-calcined trona. These values are quite consistent with the BET N_2 surface areas of 165, 66.5, and 8.65 m^2/g as reported in Table 3.7 for G-92C, Katalco 59-3, and trona, respectively.

These results were promising and it appeared the target HCl concentration of 10 ppbv could possibly be achieved through manipulation of operating conditions. It remained to be determined if the target HCl removal efficiency could be obtained with effective chloride capacities that could be considered sufficient for economic operation.

A scoping test was carried out using the G-92C dechlorination sorbent in the size range 250 to 355 µm, in a 5-cm bed height arrangement and using an inlet HCl concentration of 295 ppmv. Initially, temperature was held at 350°C, and then reduced to 325°C and the appropriate change in gas flow rate made to maintain a gas velocity of 5 cm/s. This overall scoping test was done over two days. The results obtained in Day 1 at 350°C are reported in Figure 3.51.

As shown, the measured background HCl concentration (i.e., in N_2 only) averaged about 68.2 ppbv, while the exit HCl concentration in the cleaned gas averaged about 133.2 ppbv. Therefore, the "net" exit HCl concentration can be estimated at about 65 ppbv. This value is lower than the measured concentration in the 1-cm bed height arrangement of 108 ppbv (which also uses finer sorbent material), and may be due to the possibility of channeling as explained earlier.

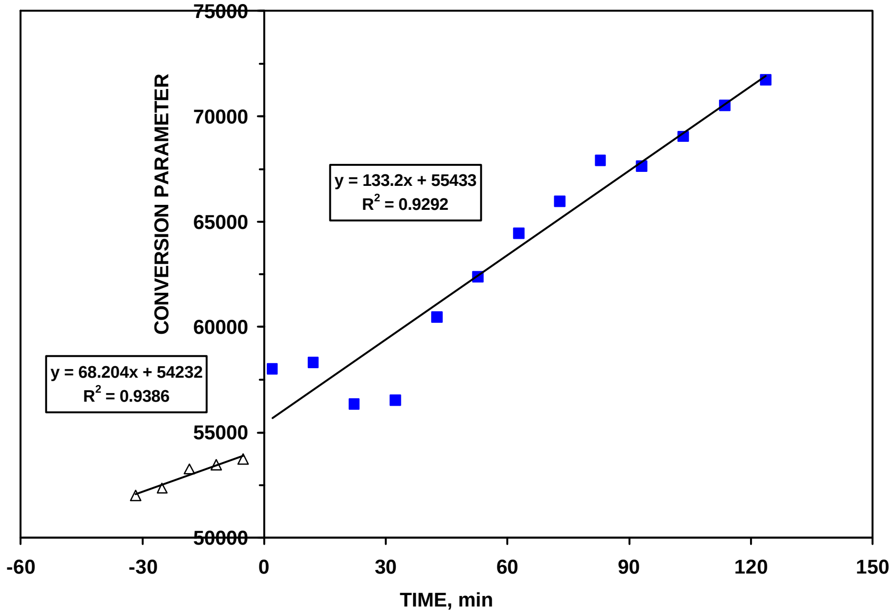


Figure 3.51 – HCl Pre-breakthrough Concentration with G-92C at 350°C

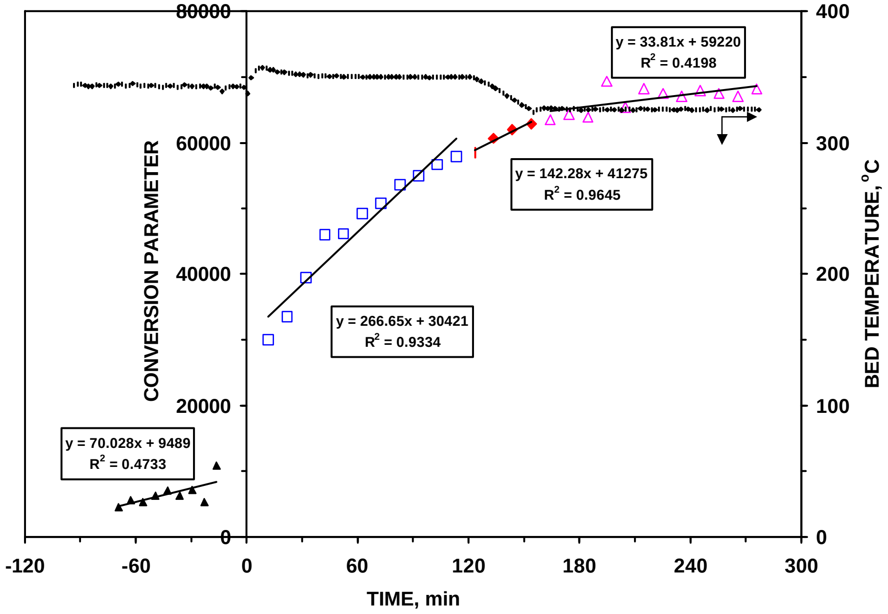


Figure 3.52 – HCl Pre-breakthrough Concentration with G-92C at 350°C and 325°C

During Day 2 (Figure 3.52), the measured background HCl concentration averaged about 70 ppbv, very close to the value obtained in the previous day. However, the measured HCl concentration in the exit gas averaged about 267, 142 and 34 ppbv at 350°C, during the transition period, and at 325°C, respectively. The average value obtained at 350°C differs significantly from the value obtained in the previous day, possibly due to the build up of contamination upstream of the sorbent bed as a result of prolonged exposure to HCl. These results also indicate that contamination is highest during the early stages, but soon starts to be less of a concern. When temperature was stable at 325°C, the measured HCl concentration of 34 ppbv is less than the background HCl concentration that was measured initially (i.e., about 70 ppbv). This clearly indicates the background HCl concentration drops steadily as testing progresses, making it very difficult to quantify the contribution it makes to the measured HCl concentration in the exit gas.

An additional scoping/reproducibility test was carried out with a fresh bed of the G-92C material, similar to the above test. To eliminate the problems associated with extending the test over a 2-day period, this test was completed in a single day. In addition, initially temperature was set at 300°C, then raised to 325°C, and then to 350°C, as shown in Figure 3.53. Similar to the above test, the measured background HCl concentration averaged about 72 ppbv. The HCl concentration in the exit gas averaged about 112.5, 84.5 and 69.5 ppbv at 300°C, 325°C and 350°C, respectively. Again, the measured HCl concentration in the late stages of the test was lower than the initial background concentration. At the conclusion of this test, the background concentration was measured and was found to average about 4.6 ppbv. If this value is used to estimate the exit HCl concentration at 350°C, then the exit HCl concentration could be estimated at 64.9 ppbv, which is quite consistent with the results of the above test. Similarly, the exit HCl concentration at 300°C could be estimated at about 40.4 ppbv, using the background HCl concentration measured initially. The exit HCl concentration is estimated at 46.1 ppbv, using the average of the initial and final background concentrations.

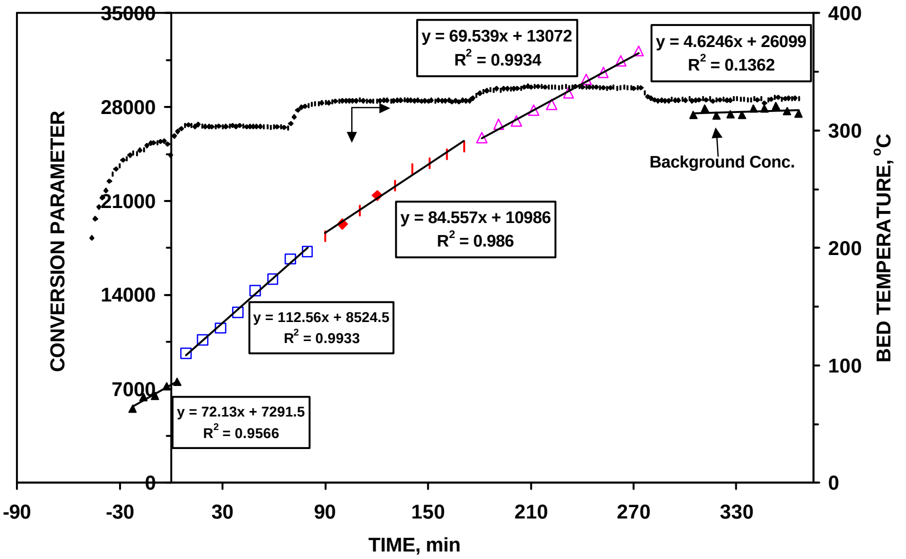


Figure 3.53 – Scoping/Reproducibility Test with G-92C at 300-325°C

A third test was carried out on the G-92C dechlorination sorbent to estimate its effective capacity for chloride absorption at 300°C. The inlet HCl concentration was kept at 270 ppmv at first, but later was increased to 1440 ppmv, and then finally to 5400 ppmv. The measured exit HCl concentration averaged about 10.1 ppbv for the first 3.5 hours, then increased to 90.5 ppbv for the remaining 1.8 hours of the first day. When testing of this material resumed during the second day, the measured exit concentration was 164.4 ppbv in the first hour, but decreased to an average value of about 39.9 ppbv during for the following 6 hours. Testing of this material continued until breakthrough was obtained. The calculated chloride capacity at breakthrough was estimated at over 6 g Cl/100 g of G-92C material, which can be considered surprisingly high.

A dechlorination test with pre-calcined trona was carried out to breakthrough, at 300°C, in the 5-cm bed arrangement (Figure 3.54). Based on the results obtained, pre-calcined trona is estimated to have an effective capacity of about 4.5 g Cl/100 g of material.

A test was carried out to breakthrough on the selected G-92C dechlorination sorbent to determine its effective chloride absorption capacity at 300°C. To avoid channeling, a 5-cm bed height was used. Based on the nominal inlet HCl concentration of ~ 500 ppmv and a gas velocity of about 5 cm/s, the effective capacity of the G-92C material under these operating conditions was estimated at about 9.7 g Cl/100 g of G-92C (as-received). This estimated value was surprisingly high because it corresponds to approximately 100% conversion of the active component of the G-92C sorbent (Na_2O). This material contains about 6.41 Na and accordingly its theoretical chloride capacity can be calculated as 9.89 g Cl/100 g of G-92C.

Three reacted samples from the above test, taken from the top, middle, and bottom portions of the sorbent bed, were analyzed for their chloride content. The results obtained are reported in Table 3.17. Based on these results and the mass of each portion, the average chloride content of the reacted sorbent bed was estimated at about 7.4% Cl. The discrepancy between the estimated value based on reactor exit gas analyses and chemical analysis of reacted samples can be attributed to a number of reasons. The inlet HCl concentration may be lower than the nominal value of 500 ppmv because of pump underperformance when using dilute HCl-H_2O liquid solutions. Separate testing of the G-92C sorbent showed this material loses about 8.8% of its weight in a H_2O-N_2 gas atmosphere at 300°C.

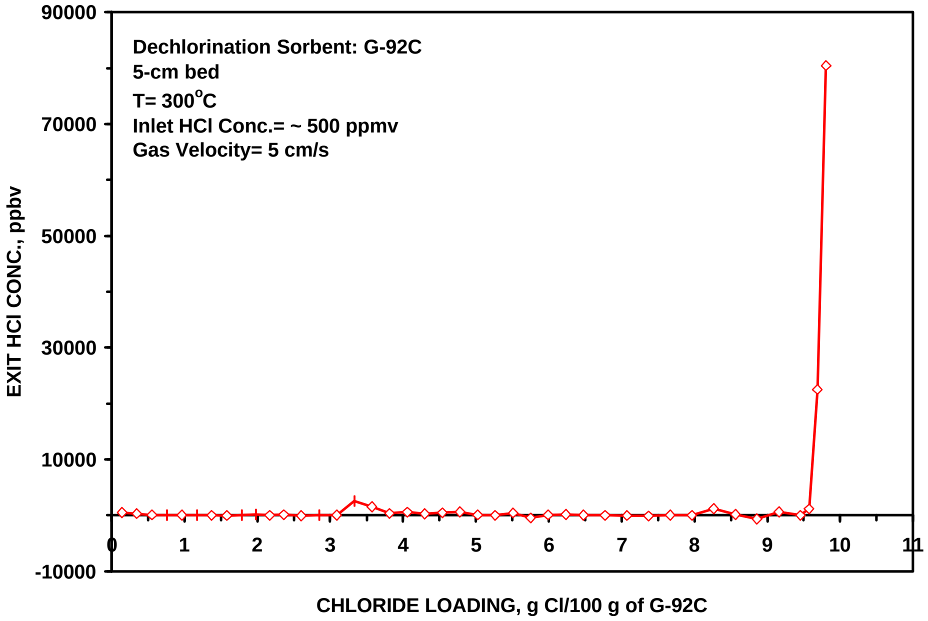


Figure 3.54 – HCl Breakthrough Curve

Table 3.17 – Chemical Analysis of Reacted Samples

Sample	Chloride Content, wt.%
Bottom (gas inlet section)	8.40
Middle	7.96
Top (gas outlet section)	5.96

The results from the above test are also shown in Figure 3.55, where the “conversion parameter” is plotted as a function of testing time. As indicated, with just N_2 flowing through the reactor, the measured HCl concentration averaged about 24 ppbv (background concentration). Two stable levels of HCl concentrations were measured during actual HCl removal testing. During the first 3 hours, the measured HCl concentration averaged about 36 ppbv (60-24), which is slightly higher than the value of 25 ppbv previously obtained with the G-92C sorbent, possibly because of the higher particle size used in this test (90 to 150 µm versus < 44 µm). The second level of “equilibrium” averaged about 108 ppbv, possibly because of the diminishing existence of sodium as Na_2O as it is converted to Na_2CO_3 upon reaction with CO_2 in the simulated syngas environment.

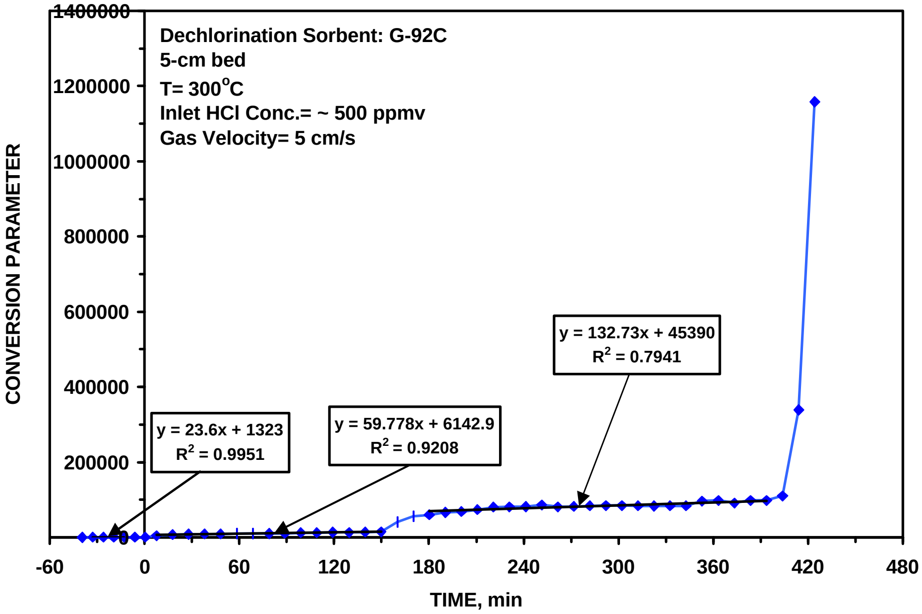


Figure 3.55 – HCl Removal Efficiency

3.4.10 Evaluation of Stage II H_2S Sorbents

After establishing a suitable measurement technique for trace level H_2S, one sulfur sorbent material, readily available in the 355-850 µm size range, was evaluated. This material is known as Zingard^{TM} 1000 Sulfur Absorber and was obtained, probably over 10 years ago, from the New Jersey Zinc Company. Because of the potential difficulties (both relating to high pressure build up and erroneous exit H_2S concentrations due to channeling in the 1-cm bed height arrangement) of evaluating the selected G-72E sulfur sorbent in the –325 mesh size range, this alternative material was evaluated in the indicated size range using a 5-cm sorbent bed height. This material was evaluated for its H_2S removal efficiency at 350°C, in 3 different gas atmospheres, as summarized in Table 3.18. The purpose of varying the gas composition in this manner was to determine if the presence of steam in the gas would affect the equilibrium to an extent such that removal of H_2S to the required level could not be obtained. In each case, the sorbent was at least one hour on stream with frequent GC analysis being carried out. During all 3 test periods, no H_2S was detected by the GC, indicating that the H_2S concentration in the ultra-cleaned gas is lower than 85 ppbv (on a wet basis), which is as indicated above the detection limit for the analytical technique developed (see Appendix B for issues relating to H_2S measurement at trace levels).

An additional scoping test was carried out with this sulfur sorbent at 350°C, where the inlet H_2S concentration was gradually increased from 247.1 ppmv (dry simple gas, wet simple gas, then syngas) to 496.9, 993.8, and finally 1990.6. Each inlet H_2S concentration was maintained for a period exceeding one hour and the H_2S concentration in the exit gas measured with the GC. In each of these cases, no H_2S was detected; therefore, the H_2S concentration in the exit gas was below the 85 ppbv detection limit of the analytical technique.

Table 3.18 – Different Gas Atmospheres for Evaluation of Desulfurization Sorbent

	Dry Simple Gas	Wet Simple Gas	Simulated Syngas
H_2S	250 ppmv	250 ppmv	250 ppmv
H_2	26%	26%	20%
H_2O		16%	16%
CO			40%
CO_2			10%
CH_4			3%
N_2	Balance	Balance	Balance

A reproducibility test was also carried out on the Zingard^{TM} 1000 Sulfur Absorber material. In addition, this test was continued until breakthrough was achieved (see Figure 3.56) by increasing the inlet H_2S concentration first to 4966 ppmv, and then to 19800 ppmv (≈ 2 vol%). Based on these results, the effective capacity of this material at 350°C is estimated at about 10 g S/100 g of sulfur sorbent.

A scoping test, similar to the one described above for the Zingard^{TM} 1000 Sulfur Absorber, was also carried out using the G-72E sulfur sorbent. Similar results were obtained with this material, i.e., no H_2S was detected in the exit gas as the inlet H_2S concentration was periodically increased from about 250 to 2000 ppmv. In addition, its effective sulfur absorption capacity was estimated at 10 g S/100 g of G-72E.

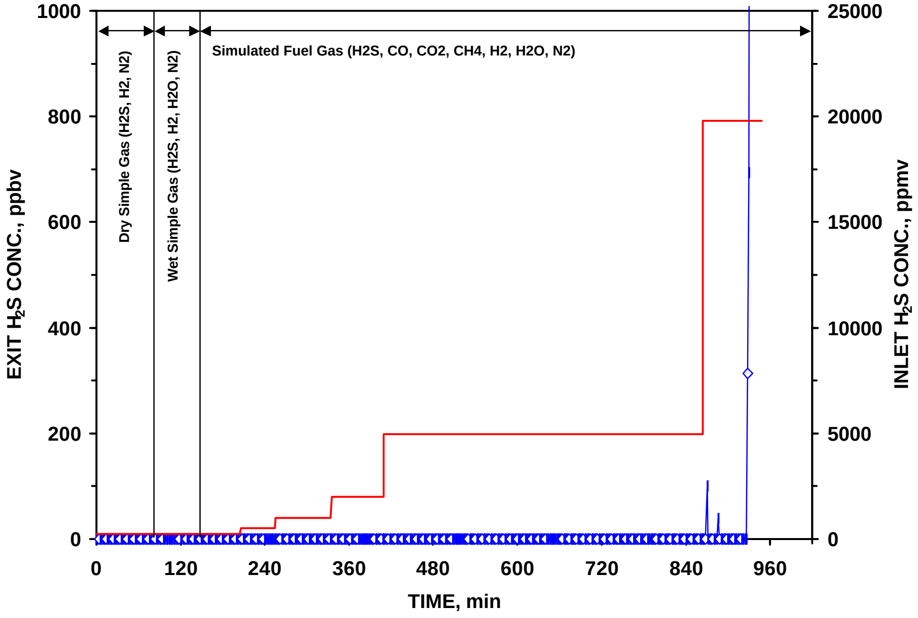


Figure 3.56 – Scoping/Loading Test with Zingard 1000 Sulfur Absorber at 300°C

3.4.11 Combined Chloride/Sulfur Removal Tests Using G-72E/G-92C Sorbents

Appropriate physical mixtures of the selected dechlorination sorbent (G-92C) and the sulfur sorbent (G-72E) were used and their effectiveness for simultaneous removal of H_2S and HCl were determined. Based on thermodynamic analysis and Stage I test results, the Na_2O active component in the G-92C dechlorination sorbent was expected to undergo immediate transformation to the more stable compound Na_2CO_3 upon reaction with CO_2 in the simulated syngas. This Na_2CO_3 would then react with HCl. It was regarded important to determine whether the existence of H_2S in the syngas would interfere with this mechanism.

A test was carried out at 300°C using a sorbent mixture consisting of 50% G-92C and 50% G-72E under Stage II operating conditions (1-cm bed height and a 5 cm/s gas velocity). The inlet concentrations for HCl and H_2S were about 500 ppmv. The results are reported in Figure 3.57. Surprisingly, the G-92C material maintained a very high effective capacity for chloride removal despite using a thin sorbent bed (1-cm bed height) and despite being in a physical mixture with the G-72E desulfurization sorbent. The effective capacity for chloride removal achieved in this test was about 12 g Cl/ 100 g of G-92C (at an arbitrary 3 ppmv breakthrough point), and actually exceeds the theoretical capacity of the G-92C material, which can be attributed to the contribution of the G-72E material to chloride removal because of its calcium content (G-72E contains about 1.2% Ca).

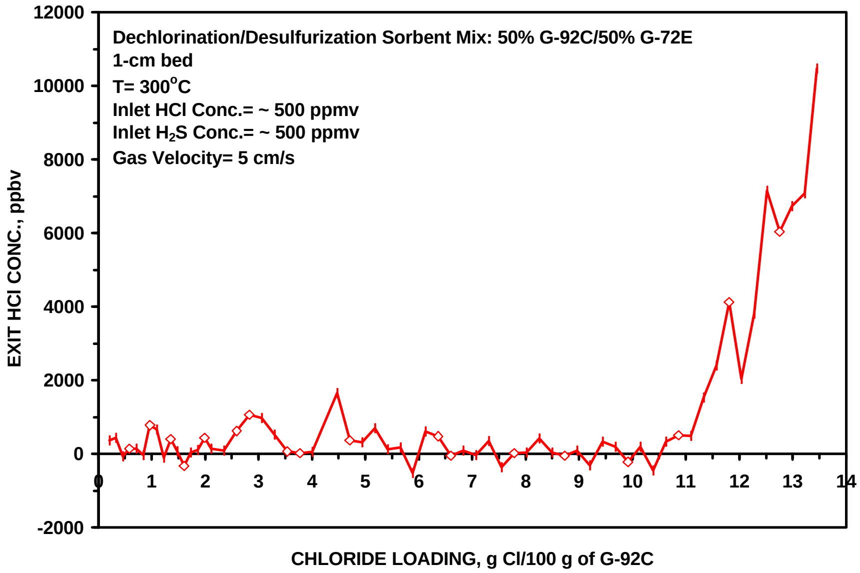


Figure 3.57 – HCl Breakthrough Curve in Simultaneous HCl/H_2S Removal Test

Although surprising in the 1-cm bed arrangement, these results are quite consistent with similar observations made during Stage I testing. These results suggest that possibly conversion of Na_2O to Na_2CO_3 is immediate upon sorbent exposure to the syngas containing CO_2. This prevents Na_2O from reacting with H_2S. There is also the possibility that Na_2O reacts more readily with HCl than H_2S, preventing any undesirable sorbent/contaminant interactions.

The H_2S breakthrough curve from the above test is shown in Figure 3.58. As indicated, the G-72E sorbent also achieves a high effective capacity for sulfur absorption approximating 10 g S/100 g of material under these conditions.

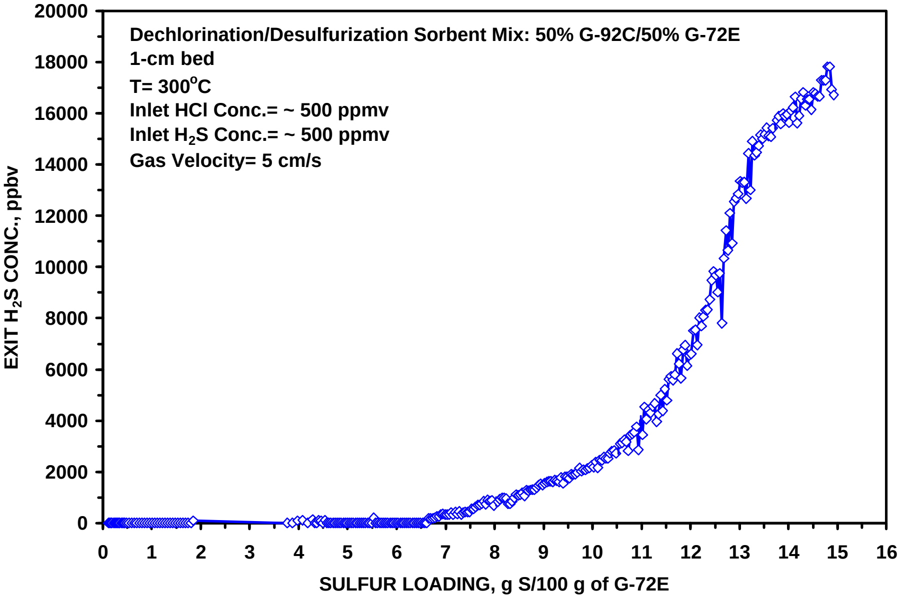


Figure 3.58 – H_2S Breakthrough Curve in Simultaneous HCl/H_2S Removal

The HCl removal efficiency of the sorbent mixture in the 1-cm bed arrangement is reported in Figure 3.59. As shown, the background HCl concentration was measured at about 72 ppbv. During the initial stages of the actual HCl removal test, the measured HCl concentration was much higher (about 200 ppbv) than obtained with the G-92C material alone in the sorbent bed (~ 25 ppbv). However, during the last 5 hours of this test, the measured HCl concentration

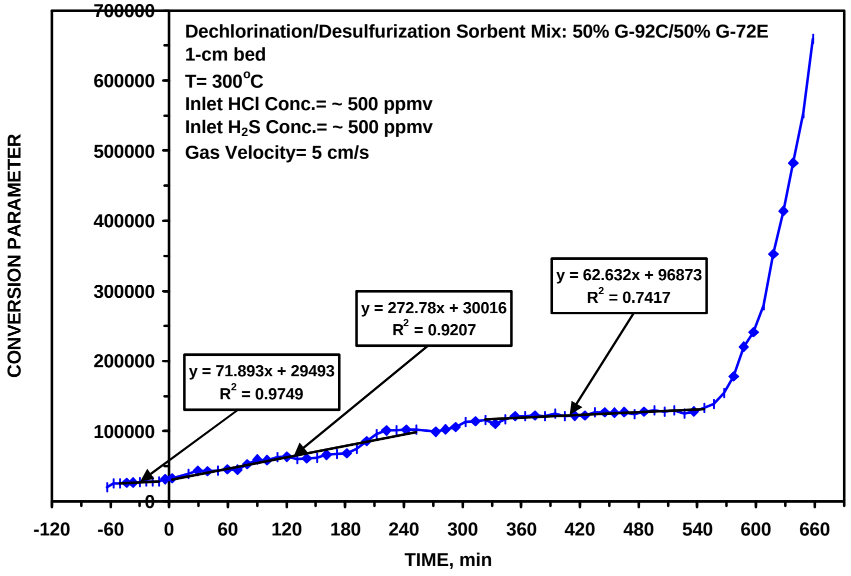


Figure 3.59 – HCl Removal Efficiency in Simultaneous HCl/H_2S Removal Test

averaged about 63 ppbv. Because this value is lower than the initial background HCl concentration and because this latter changes (tends to decrease with time) during the course of an experiment, the actual HCl in the exit gas may very well be around the expected value of 25 ppbv. Although not reported, similar observations can be made based on the results obtained with H_2S.

When the proportion of the G-92C material in the sorbent mixture was reduced to 40% and that of the G-72E sorbent increased to 60%, the effective capacity for chloride absorption was reduced as shown in Figure 3.60, further supporting the interpretations made above about the results reported in Figures 3.55 and 3.57, and particularly the lack of any undesirable interactions between the dechlorination/desulfurization sorbents and the HCl and H_2S contaminants.

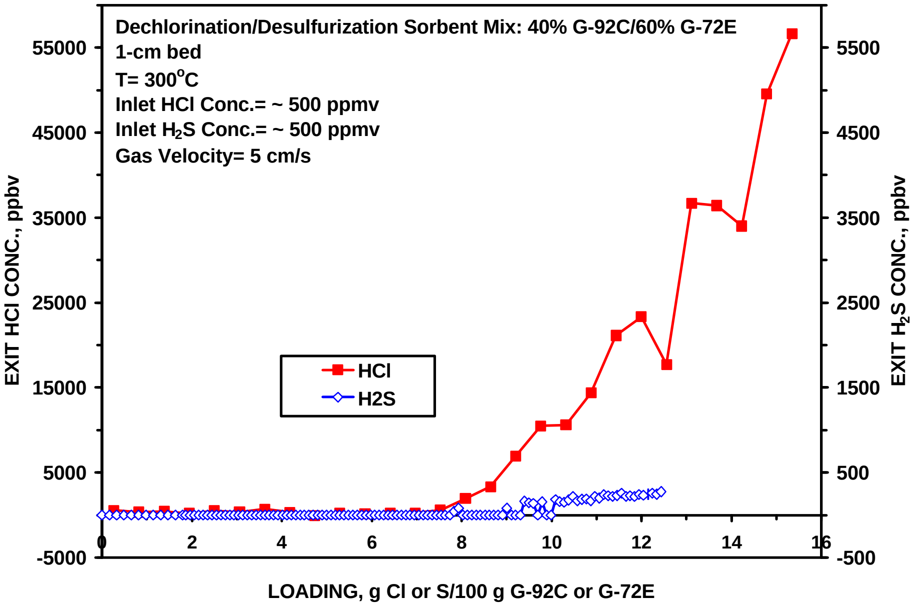


Figure 3.60 – HCl and H_2S Breakthrough Curves

Reproducibility of Stage II testing was established using a 50% G-92C/50% G-72E sorbent mixture in a 5-cm bed height arrangement (to avoid channeling). The results from two identical tests are superimposed in Figure 3.61, where it is clearly seen that the results were very reproducible. In both cases, the effective capacity for chloride absorption was very high, exceeding 21 g Cl/100 g of G-92C. This higher capacity is due to a greater contribution of the desulfurization G-72E sorbent to HCl removal than in previous cases, where the inlet HCl concentration was limited to ~ 500 ppbv. In these reproducibility tests, the inlet HCl concentration was ~ 5000 ppbv, which is higher than the equilibrium HCl value for $ZnO/ZnCl_2$ (estimated roughly at about 1000 ppmv).

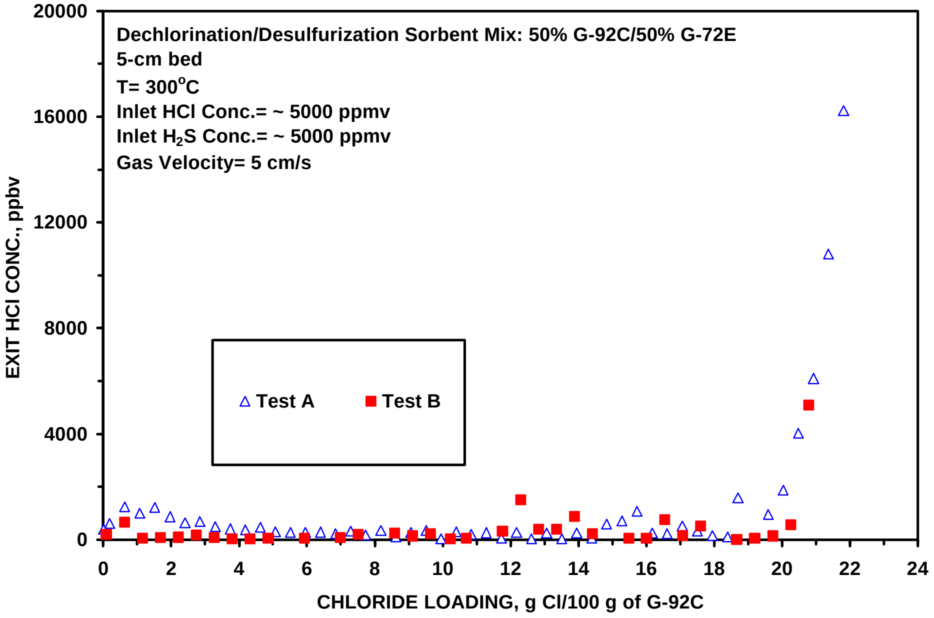


Figure 3.61 – Stage II Chloride Removal Reproducibility

Because of the high effective capacities achieved with the G-92C/G-72E sorbent mixture at 300°C, lower operating temperatures were investigated. The main objective was to determine if higher HCl removal efficiencies can be accomplished to meet the ultimate target of 10 ppbv. A scoping test was carried out using the 50%-50% sorbent mixture in the 5-cm bed height arrangement. Again, the inlet HCl and H_2S concentrations were ~ 5000 ppmv. During this test, temperature was maintained initially at 250°C for a few hours, before it was raised to 275°C and the test continued to breakthrough. The cumulative effective capacity of the sorbent mixture for chloride absorption is shown in Figure 3.62, and is estimated at about 20 g Cl/100 g of G-92C.

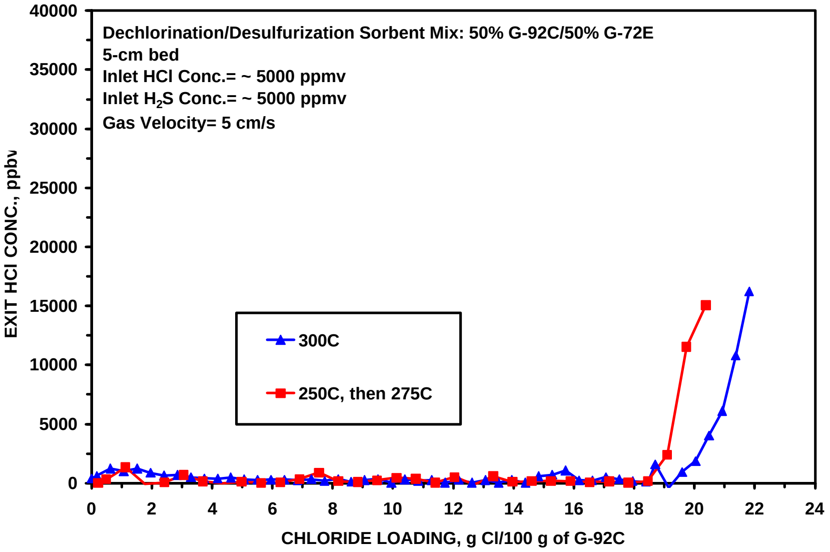


Figure 3.62 – Effect of Temperature on Sorbent Effective Capacity

The effective capacity does not appear to be sensitive to temperature in the range 250-300°C. Although not shown separately, the HCl removal efficiency was estimated at about 240 ppbv at 250°C and 140 ppbv at 275°C. This trend strongly suggests 300°C may be optimum for operating Stage II of the Ultra-Clean gas polishing process to achieve the highest sorbent utilization and the lowest possible contaminant concentrations in the ultra-cleaned gas.

3.5 Comments On Effect Of Reactor Pressure

According to the previous sections, desulfurization (H_2S removal) and dechlorination (HCl removal) occur according to reactions (3.6) and (3.3):

$$ZnO + H_2S = ZnS + H_2O \tag{3.6}$$

$$Na_2CO_3 + 2HCl = 2NaCl + CO_2 + H_2O \tag{3.3}$$

Because in both heterogeneous reactions, equal volumes of gas appear on both sides of the equations, the net change in the total number of moles of gaseous species is nil. As a result, reactor pressure changes have no effect on the position of equilibrium.

Extensive experimental work at GTI (and elsewhere) confirmed this observation for desulfurization of coal-derived fuel gases using zinc titanates. For example, GTI researchers carried out a major study involving several zinc titanate sorbents for hot gas fluidized-bed desulfurization application under the sponsorship of Tampella Power, Inc. (Lau et al., 1994). This study was designed to identify the most promising commercially available sorbent for pilot plant testing, and to provide experimental data that could be directly used in the design of a hot gas cleanup system in Finland. Several zinc titanate sorbents were tested in the high-pressure/high-temperature reactor (HPTR) unit. The results obtained indicated the reactor pressure did not significantly affect the performance of the zinc titanate sorbents (Konttinen and Mojtahedi, 1993).

In another extensive study by Krishnan and Gupta (1999) for the development of disposable sorbents for chloride removal from high temperature coal-derived gases, pressure was shown to have only a minor effect on the reactivity of dechlorination sorbents similar to the ones employed in this investigation. Dechlorination test results obtained at 150 psig indicated the sorbent achieved an effective chloride removal capacity that was similar to ambient pressure test results. In addition, although there was a greater degree of data scatter at high pressure, the pre-breakthrough residual HCl concentrations showed levels that, on the average, were similar to those obtained at ambient pressure.

Because the desulfurization and dechlorination sorbents used in the present investigation are quite similar to the materials in the above two studies, reactor pressure can be expected to have little, if any, effect on the performance of the sorbents as determined at ambient pressure. It was intended to conduct one desulfurization/dechlorination test at high pressure to confirm Stage I and Stage II test results obtained at ambient pressure. Unfortunately, due to operational problems and time constraints, it was not possible to complete these tests on time for inclusion in this report. These tests will be carried out during the Optional Program.

3.6 Recommendations

3.6.1 Recommendations for Stage I Operating Conditions

Based on testing results, trona and a zinc oxide-containing material (such as a bulk zinc titanate sorbent or any other cheaper ZnO-containing material) are recommended as suitable once-through sorbent fines for Stage I of the Ultra-Clean Gas Polishing Process. Trona has the highest Na content and is the least expensive among the materials selected for Stage I. Stage I should be operated at a temperature of about 500°C. This temperature was determined to be optimum with respect to HCl removal efficiency and effective capacity for chloride absorption for the as-received trona material. Moreover, operating Stage I at 500°C would also be desirable for the sulfur sorbent to achieve acceptable conversion for H_2S removal. Under these conditions, the chloride and sulfur sorbents can reasonably be assumed to achieve at least 50% conversion.

The mass balance around the Moving-Bed Filter Reactor, shown earlier in Figure 3.35 and reproduced in Figure 3.63 , was determined based on the use of a GTI zinc titanate sorbent (IGTSS-362C) for sulfur capture, which has a nominal ZnO content of 40% by weight. Based on the HCl and H_2S concentrations in the feed gas to the MBFR, the feed rates of trona and the GTI zinc titanate sorbent are calculated as 120 and 47 kg/hr, respectively. It should be noted that 40% ZnO by weight corresponds to a ZnO to TiO_2 molar ratio of about 0.65 in the GTI zinc titanate sorbent. Other GTI zinc titanate formulations from this class of sorbents were shown to maintain a good desulfurization performance even when the molar ratio of ZnO to TiO_2 were to be increased to 1. This value has in fact been shown to be optimum with respect to the effective capacity of the sorbent and its ability to resist attrition as required by the stringent transport reactor application.

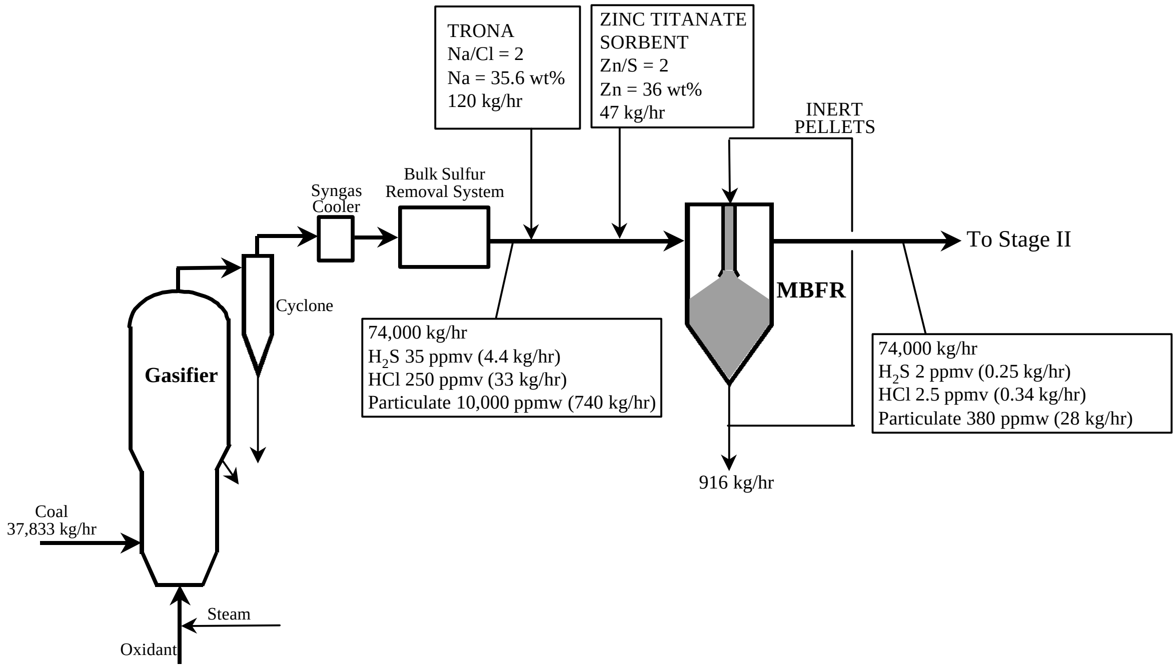


Figure 3.63 – Material Balance for the Stage I Moving Bed Filter-Reactor (500°C)

For a typical zinc titanate sorbent, prepared by conventional techniques such as solid oxide mixing or co-precipitation, followed by granulation, extrusion, or spray drying, extensive work

(Woods et al., 1990) showed that the optimum ZnO to TiO_2 molar ratio is 1.5. This would correspond to a sorbent containing about 48.6% Zn. If such a sorbent were used in Stage I, then the sulfur sorbent feed rate would be reduced to about 34 kg/hr.

3.6.2 Recommendations for Stage II Operating Conditions

Two candidate materials were considered for the removal of H_2S down to the ppbv level in Stage II: G-72E and a Zingard^{TM} 1000 Sulfur Absorber. G-72E contains about 70% Zn. This material was shown to reduce H_2S concentration to < 85 ppbv (on a wet basis) at temperatures ≤ 350°C. H_2S concentrations below 85 ppbv cannot be detected by our analytical technique. However, this concentration can arguably be considered to satisfy the H_2S criterion for the chemical synthesis application (i.e., < 60 ppbv). In the Optional Program, H_2S will be measured by either modifying the sampling technique to achieve the detection limit reported by Bruner et al (i.e., 50 ppbv), or by looking into the use of a chemilumoinescence detector coupled with a gas chromatograph. These approaches are discussed in Appendix B.

The choice of a dechlorination sorbent for Stage II should be made between 2 candidates: trona (as-received or pre-calcined) and G-92C, depending on the application. To satisfy gas-cleaning requirements for the fuel cell application (i.e., total sulfur < 100 ppbv and HCl < 1 ppmv), Stage II is recommended to operate at 350°C, using trona and G-72E for chloride and sulfur control, respectively. The required feed rates are as indicated in Figure 3.64, where trona is assumed to achieve 33% conversion and G-72E 50% conversion. It may even be possible to accomplish the HCl concentration limit in Stage I and eliminate any need for further chloride control in Stage II.

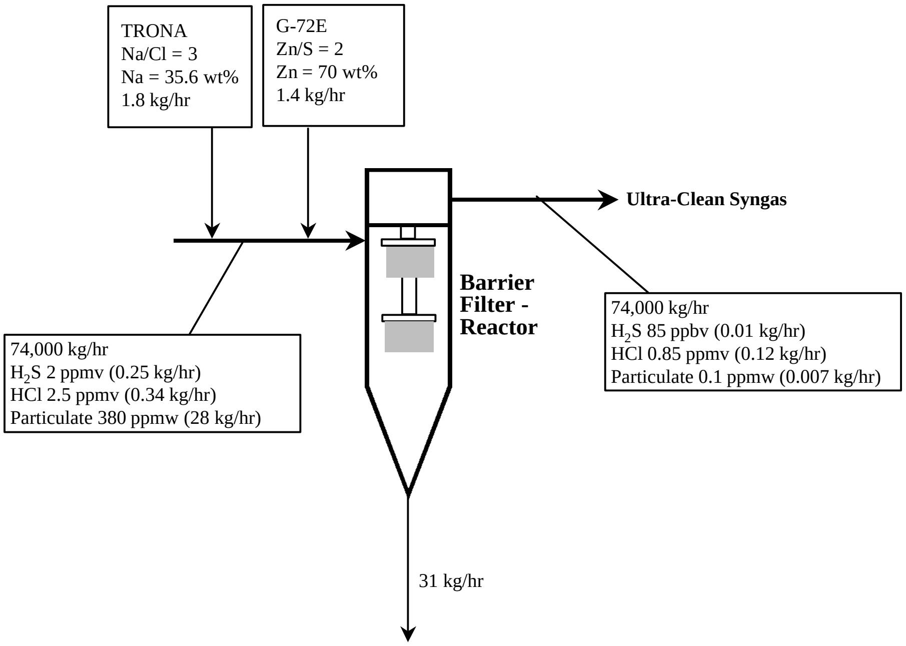


Figure 3.64 – Material Balance for the Barrier Filter Reactor – Fuel Cell Application (350°C)

To satisfy gas-cleaning requirements for the more stringent chemical synthesis application, then an operating temperature of about 300°C is recommended for Stage II. At this temperature, G-92C is more likely than trona to accomplish the target HCl concentration of < 10 ppbv. Also, operating Stage II at this lower temperature may be desirable to maintain the physical properties of this manufactured sorbent to accomplish acceptable conversion. The mass balance around the Barrier Filter Reactor is shown for two cases below. Figure 3.65 shows a "conservative-case scenario" where G-92C and G-72E are each assumed to achieve only 20% conversion. In this case, because of the low Na content of the chloride sorbent (6.4% Na), 17 kg/hour will be needed. Figure 3.66 shows a "still realistic scenario" where G-92C and G-72E are assumed to achieve 50% conversion. In this case, the feed rate of the chloride sorbent is reduced to about 7 kg/hour. It should be noted that process evaluation results obtained by SWPC have clearly indicated that the overall process economics is not sensitive to the costs of Stage II materials, primarily because of the small flow rates involved.

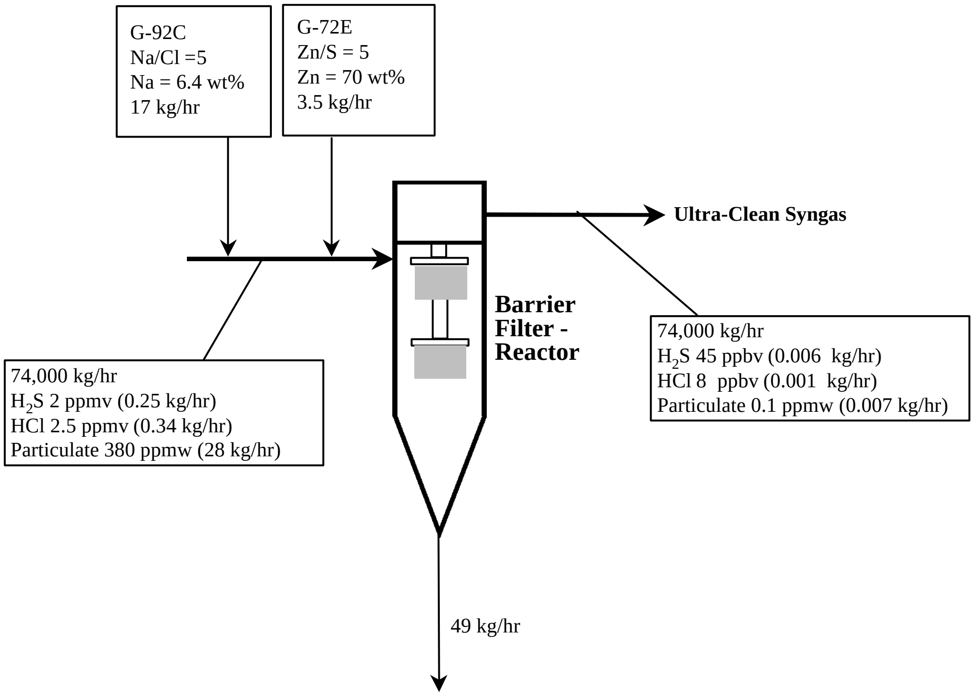


Figure 3.65 – Material Balance for Stage II Barrier Filter Reactor with 20% Sorbent Conversion – Chemical Synthesis Application (300°C)

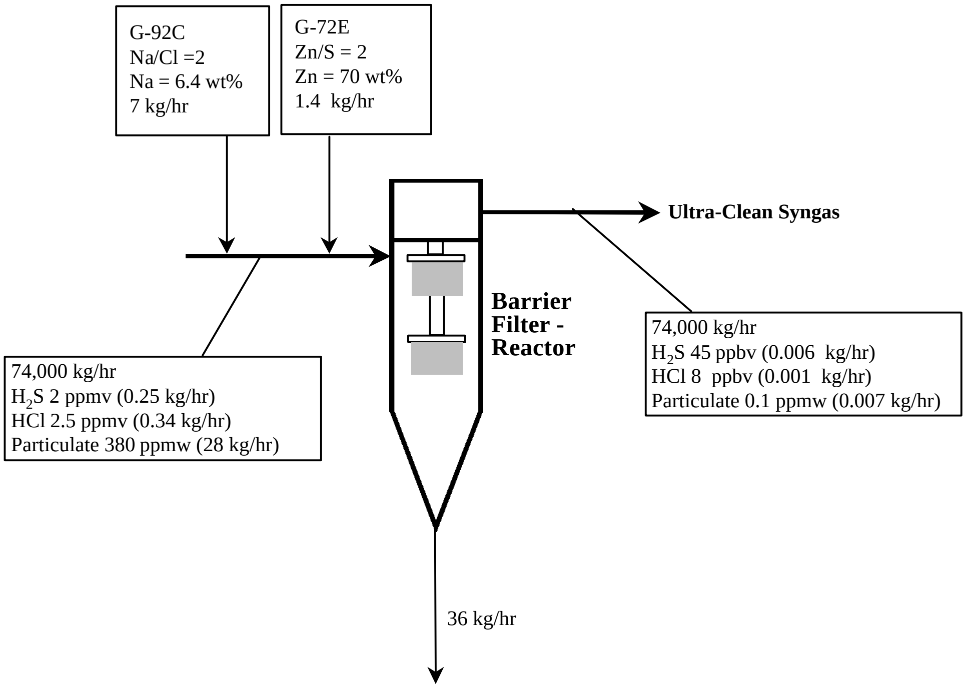


Figure 3.66 – Material Balance for Stage II Barrier Filter Reactor with 50% Sorbent Conversion – Chemical Synthesis Application (300°C)

4. CONCEPTUAL PROCESS EVALUATION

The objective of this conceptual evaluation is to generate a comparison of performance and cost between the state-of-the-art, conventional gas cleaning technology (based on Rectisol desulfurization) and a novel gas cleaning process that utilizes the "Ultra-Clean" gas polishing technology. This comparison provides the basis to judge the potential commercial merits of the Ultra-Clean gas polishing technology. A generalized synthesis of chemicals or liquid fuels application, and a solid oxide fuel cell (SOFC) power generation application are considered in this study because of their future commercial importance and their differences in processing conditions and gas cleaning requirements.

A comprehensive procedure was followed to determine the potential performance and economic merits of the novel gas cleaning process:

- Select the process evaluation basis:
    - coal-type,
    - gasifier-type,
    - estimated raw gas delivery conditions to the cleanup process,
    - estimated raw gas composition,
    - raw gas flow capacity for each application,
    - gas cleaning requirements for each application,
    - gas cleanup process scope and boundaries,
    - major process component technologies applied in the cleanup systems,
    - import-stream supply conditions,
    - export-stream requirements,
    - economic premises.
- compile design basis information for the Ultra-Clean process (sorbent types, operating conditions, feed rates) from the GTI laboratory sorbent testing and other key sources,
- devise a suitable novel and conventional gas cleanup process scheme and process flow diagram for each application, and identify alternative novel gas cleaning schemes,
- estimate material & energy balances for the novel and conventional gas cleanup processes for the two applications,
- specify and conceptually design major, conventional process equipment (e.g., solids feeding and handling equipment, heat exchangers, pumps and compressors, absorption and stripping columns, sorbent storage and disposal equipment),
- prepare conceptual designs of the unique process equipment (e.g., granular, moving bed filter-reactor system, and barrier filter-reactor system),
- estimate the cost of major process equipment using general cost algorithms and apply factored estimation procedures for the total investment cost and operating cost for the gas cleaning processes,
- compare the novel gas cleaning process performance and cost to that of the conventional gas cleaning process for the two applications, and identify additional feasibility and assessment factors,

- extract sorbent and reactor performance goals/targets from the evaluations, these to be used in subsequent development activities,
- conduct a conceptual market-potential evaluation.

The proposed success criteria for the novel gas cleanup process for the chemical synthesis and SOFC applications are based on the most stringent of the gas cleaning requirements for these applications and was used to assess the conceptual process evaluation results. The novel gas cleaning process must show the potential to:

- Satisfy application gas cleaning requirements for sulfur species, halide species, and particulate,
- Provide economic advantage of greater than 20% over the conventional, state-of-the-art gas cleaning technology (based on Rectisol desulfurization).

Section 4.1 presents the details of the basis for the evaluation, considering all the items listed above. Section 4.2 describes the state-of-the-art, conventional syngas cleaning process selected for the chemical synthesis application. It includes process flow diagrams, material & energy balances, overall performance results, and process economics. The conventional fuel gas cleaning process for the SOFC power generation application is described in Section 4.3. Two alternative SOFC fuel gas cleaning approaches are considered, a high-pressure fuel gas cleaning scheme and a low-pressure fuel gas cleaning scheme.

The novel syngas cleaning technology for the chemical synthesis application is described in Section 4.4. It provides process flow diagrams, material & energy balances, overall performance results, and process economics for novel gas cleaning process using a base Ultra-Clean process and two alternative Ultra-Clean process schemes. The novel fuel gas cleaning process for the SOFC power generation application is described in Section 4.5. As with the conventional fuel gas cleaning process, two alternative SOFC fuel gas cleaning approaches are considered using the novel fuel gas cleaning technology, a high-pressure fuel gas cleaning scheme and a low-pressure fuel gas cleaning scheme.

A conceptual market study for the novel gas cleaning technology is presented in Section 4.6 and this is followed in Section 4.7 with an evaluation of the process results and comparisons of the conventional and novel gas cleaning technologies.

4.1 EVALUATION BASIS

The basis for the conceptual process evaluation is defined in detail in Sections 4.1.1 through 4.1.7. Additional evaluation assumptions, such as the process and project contingencies will be identified in the economic evaluation sections for each application.

4.1.1 Applications

Coal gasification can generate a raw hydrocarbon gas that may be utilized for several applications. Examples are "syngas" utilization for chemical or liquid fuel synthesis:

- hydrogen,
- carbon monoxide,

- methanol,
- ammonia,
- Fischer-Tropsch liquid fuels,
- oxygenated synfuels,
- oxoalcohols,
- Iron ore reductant,

and "fuel gas" production for power generation:
- gas turbine, combined-cycles power generation,
- fuel cell power generation.

Several synthesis products, as well as power and steam can be generated in parallel in the same plant, sharing common feed materials, auxiliaries, facilities and processes. The basic synthesis products listed above may also be processed further at the same plant site to generate a variety of other chemical and liquid fuel commodities, and the integration of the "total" plant with the gas cleaning and conditioning processes can result in the sharing and co-utilization of many side-streams, processes and utilities, such as power and steam. Likewise, the power generation applications could be stand-alone power plants or an internal power generation unit as part of a larger co-production plant.

Two application types are considered in this evaluation because of their current levels of interest, their differing operating conditions, and their differing gas cleaning requirements: a general chemical or liquid fuel synthesis application, and a solid oxide fuel cell (SOFC) power generation application. The gas being cleaned is designated "syngas" for the chemical or liquid fuel synthesis application, and is "fuel gas" for the SOFC application.

The general, chemical or liquid fuel synthesis case has stringent specifications for particulate, total sulfur, halides, ammonia and HCN. Mercury may also be a contaminant (catalyst poison) in some synthesis applications, and it may become an emission regulated component for coal-fueled plants. The conventional syngas cleaning process can satisfy all of these requirements, if a special cleaning contactor for low-temperature mercury is added. The novel syngas cleaning process evaluated in this report only specifically considers particulate, sulfur and halides, but the potential capability for adding ammonia, and mercury controls is discussed.

The chemical or liquid fuel synthesis, syngas cleaning process simulation and evaluation considers a generalized, coal-syngas cleaning situation that requires stringent gas cleaning performance, but is not coupled to any specific synthesis application. An example of a chemical synthesis application where the general, syngas cleanup process could apply is methanol synthesis. Since syngas cleaning for this application, and many other applications that require stringent syngas cleaning, will be configured similarly, it is expected that a valid comparison of conventional syngas cleaning with the novel syngas cleaning process can be made without reference to a particular synthesis application.

The SOFC power generation case has relatively stringent fuel gas cleaning specifications for particulate and sulfur, a much less stringent requirement for HCl, very limited ammonia cleaning required, and no removal of HCN required. Mercury would probably become an emission regulated contaminant in the future for such an application. In the SOFC application case, the novel fuel gas cleaning process can conceptually meet all of the fuel gas specifications with injected sulfur and halide sorbents, and the potential capability of adding mercury control is also addressed.

4.1.2 Process Evaluation Boundaries

A general, Vision 21, co-production plant configuration is illustrated in Figure 4.1. The plant is separated into eight major processing sections, and the three sections enclosed in the shaded box comprise the process boundaries of the "gas cleaning process" evaluated in this report. The boundaries have been chosen so that the evaluation will be relatively insensitive to the actual application and so that equivalent gas cleaning functions are characterized for the conventional and novel gas cleaning technologies. The figure also indicates the variety of major import and export streams for the gas cleaning process that are considered in the evaluation.

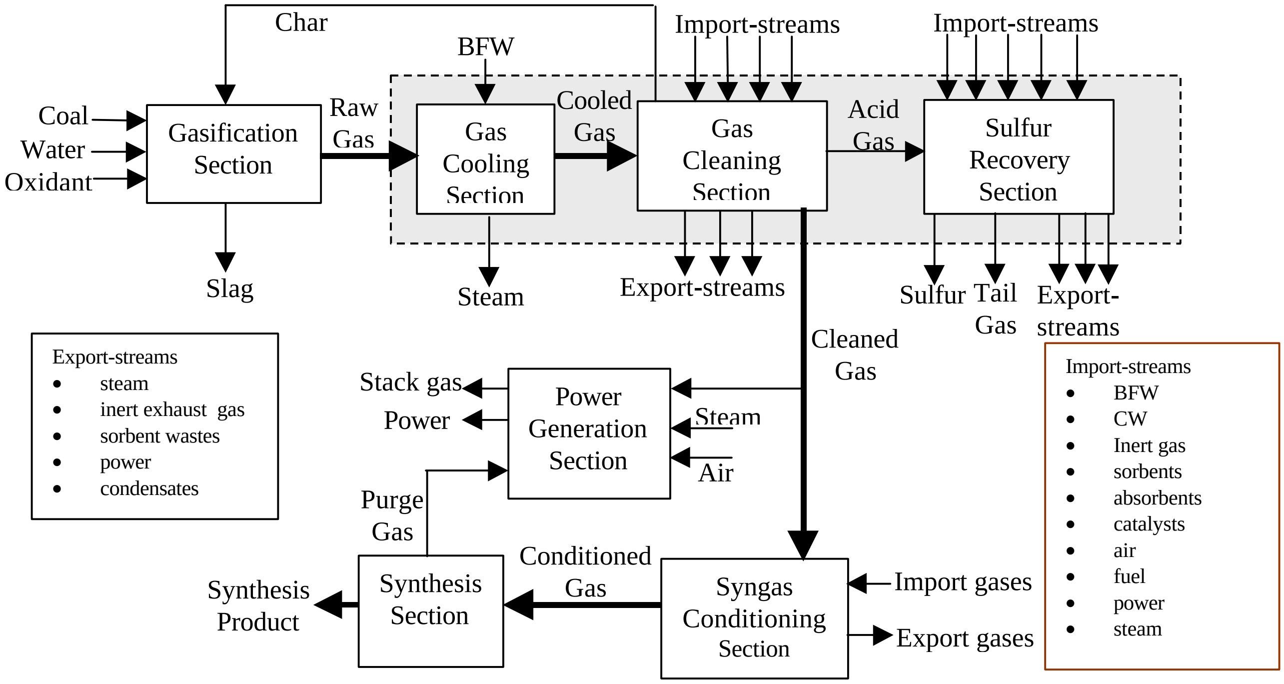


Figure 4.1 – Vision 21 Co-production Plant and Gas Cleaning Process Boundaries

In the figure, an oxygen-blown, coal gasifier generates a hot, raw hydrocarbon gas containing contaminants far exceeding the gas requirements for synthesis applications or SOFC operation. This raw gas enters the gas cooling section where the raw gas is cooled sufficiently for the gas cleaning functions that follow. Power steam and process steam are generated in the gas cooler. The gas cleaning process removes the contaminants (e.g., particulate, sulfur and halide species) to the degree required. Acid gas produced in the cleaning section is sent to a sulfur recovery process that generates elemental sulfur, steam and a tail gas stream. Other sulfur recovery options such as sulfuric acid are available but are not considered here. Char removed from the syngas cleaning section is recycled to the gasifier. Possible import and export streams are noted on the figure.

The cleaned gas exits the cleaning section and enters the syngas conditioning section where the major constituent proportions in the syngas (H_2, CO, CO_2, H_2O, N_2) are adjusted to satisfy the synthesis reaction needs. The conditioned syngas passes to the synthesis section to produce the process synthesis product. Purge gases from the synthesis section and/ or the cleaned gas, and steam from the gas cleanup processing may be utilized for power generation.

Significant water processing will be required in the gas cleaning process, more in the conventional process than in the novel gas cleaning process. A water treatment system integrated with the entire plant is assumed to exist and is not considered as a specific part of the gas cleaning process to be evaluated.

Other import and export streams for the gas cleaning process are either supplied by the total-plant or utilized by the total-plant. Their consumption or production is accounted for as cost-streams in the cost evaluation and their associated processing (for example, compression or heating) within the gas cleaning process is included in the evaluation.

There are many conventional gas cleaning process configurations and gas cleaning technologies that have been proposed and /or applied for the gas cleaning functions that are considered here. The configuration and technologies most representative of conventional, state-of-the-art practice, and having the appropriate cleaning capabilities have been selected and represented in this evaluation.

4.1.3 Gas Cleaning Requirements

Two major types of gas cleaning requirements exist -- those relating to the gas contaminant "cleaning", and those relating to the gas conditioning. "Cleaning" means the removal of species from the gas that poison or foul some reactor step(s) in the synthesis plant, or are poisons for the eventual application of the synthesized product. "Conditioning" means the transformation of the major gas species composition in the gas to make the gas acceptable for their synthesis reaction steps (for example, the adjustment of the H_2/ CO molar ratio in the gas, or the removal of CO_2, water vapor, and hydrocarbons from the gas).

The cleaned and conditioned syngas must be provided to the synthesis reactor process at the appropriate pressure and temperature. The pressure and temperature requirements depend on the specific product being synthesized. The contaminant cleaning requirements are product and process specific, and higher contaminant levels may be acceptable if the process economics allow higher corrosion and poisoning rates, or poorer quality products. The focus of this evaluation is on very stringent gas cleaning requirements for particulate, sulfur components, and halide components. The specific gas cleaning requirements for chemical or liquid fuel synthesis and SOFC power generation are listed in Table 4.1. It is assumed that the barrier filter technology applied in the novel gas cleaning process will reliably achieve the particulate control requirement, and this is substantiated by recent pilot testing where detailed particle sampling has been reported (Southern Co., 1998). While mercury control was not specifically addressed in this program, consideration of the potential to control mercury in the Ultra-Clean process was included.

Table 4.1 – Gas Cleaning Requirements

Application	Requirements
Chemical or Liquid Fuel Synthesis	Particulate < 0.1 ppmw Total sulfur < 60 ppbv Total halides < 10 ppbv $NH_3 < 10$ ppmv HCN < 10 ppbv
SOFC power generation	Particulate < 0.1 ppmw $H_2S < 100$ ppbv HCl < 1 ppmv $NH_3 < 5000$ ppmv

4.1.4 Specific Evaluation Basis

The specific characteristics of the process evaluation basis are outlined in Table 4.2. The Texaco gasifier is a coal-slurry fed, oxygen-blown, entrained gasifier that generates a very hot, slag-bearing, medium heating-value raw gas. The Texaco gasifier has been selected because it is one of the most widely used gasifiers today and represents the current state-of-the-art gasification technology.

A 907,000 kg/day (1,000 ton/day) coal feed rate is a representative capacity for many types of synthesis processes and is equivalent to the coal feed rate for an approximately 132 MWe IGCC power plant, assuming a plant heat rate of about 8333 kJ/kWh (7900 Btu/kWh). The selected gasifier pressure of 4137 kPa (600 psia) is also representative of a pressure level that would be applied for many synthesis operations, where, in most applications, the conditioned syngas must be cooled and compressed before going to a very high-pressure syngas reactor. The raw syngas rate of 81,140 kg/hr (178,800 lb/hr) is equivalent to 2,221,796 Nm^3/day (3,455,429 sft^3/hr), or 238.3 MW_t.

The SOFC power generation application might utilize the same gas rate (81,140 kg/hr) as the chemical synthesis plant and at the same high pressure (4137 kPa), being part of a larger co-production plant. Alternatively, a stand-alone SOFC plant having a power island, power generation capacity of, for example, 100 MWe, might operate the fuel gas production and cleaning processes at the SOFC power island pressure. Both of these situations, "high-pressure" SOFC gas cleaning (4137 kPa) and "low-pressure" SOFC gas cleaning (1034 kPa), are considered in the evaluation.

Many configurations for the gas cooling section have been proposed, ranging from gas quench to heat recovery with superheated steam generation, and selection of the best option is dependent on the plant configuration and economics. In the current evaluation, it is assumed that the maximum production of superheated, HP-steam is desired.

Collected char is recycled to the gasifier to maximize carbon utilization and to place plant solid waste into a single slag stream, which is a typical design philosophy. Other solid wastes generated in the gas cleaning process could be recycled to the gasifier, but are treated as disposal products in the evaluation to maintain a conservative basis. The desired final form for the captured sulfur is as elemental sulfur meeting purity requirements for by-product sale. In this evaluation, the sulfur is collected as a contaminated condensate, and the equipment required for final sulfur by-product preparation is not included in the study. This has little impact on the results since the is a relatively small cost, and both the conventional and novel processes have similar elemental sulfur rates.

The capacity of the plant is suitable for a single gasifier and gas processing train, and no parallel train, over-capacity is designed into the plant. Excess design capacity is incorporated into all process equipment, and 100% excess capacity is included in all of the solids handling equipment (storage, feeding, pressurization, transportation).

The assumed import-stream compositions and conditions, and the export-stream requirements are also listed in Table 4.2. Import and export streams are considered commodities that are assigned costs or values in the evaluation. They are supplied by the greater-plant at the specified conditions and must be compressed to the required use conditions by the gas cleaning process. The equipment cost and power consumption of their compression to the required use-pressures is included in the cost and performance evaluations.

4.1.5 Raw Gas Conditions and Composition

The nature of the raw hydrocarbon gas generated (its major components composition, content of contaminants, and temperature) is primarily a function of the coal properties, the type of gasifier used, and the oxidant composition used (air, oxygen-enriched air, or oxygen -- 90-99% purity). Many other factors have secondary effects on the raw gas conditions and composition, including the coal feed method (dry or water slurry), the use of in-gasifier sulfur removal, and the use of in-gasifier tar cracking. Other fuels similar to coal, with high contaminant contents, such as petroleum wastes (petroleum coke, oil residuals), biomass, industrial wastes, etc. will produce similar raw gases that may be processed similarly to coal-gases.

Several types of gasifiers produce gases that can be applied for the above product applications. They are primarily:

- Entrained, oxygen-blown gasifiers (single stage and two-stage; slurry and dry coal feed),
- Fluidized bed (oxygen-blown and air-blown) gasifiers,
- Moving bed, oxygen-blown gasifiers.

In most cases, the use of an oxygen-blown gasifier provides economic benefits compared to air-blown gas cleaning and conditioning. Other types of gasifiers are also under development and are not specifically considered here since they would produce gases similar to one or more of the commercial gasifier types:

- transport gasifier,
- catalytic fluid bed gasifiers,
- fluidized bed, air-blown carbonizers.

The raw gas composition has been estimated from Texaco gasifier reports and thermodynamic predictions, and is listed in Table 4.3. The contaminants of interest (sulfur species, hydrogen chloride, hydrogen cyanide, ammonia, particulate) are included in the estimated raw gas composition. The estimated HCl content is at the high end of the likely range of HCl contents, and for many coals, it will be much lower. The ammonia and HCN estimates are very uncertain and are probably higher than actual. The particulate (char) in the raw gas has an estimated size distribution such that a conventional, high-efficiency cyclone will result in about 10 wt% penetration of particulate, those particles being primarily < 10 µm in diameter.

Table 4.2 – Process Evaluation Basis

Gas Generation	Coal type	Pittsburgh #8 - 3 wt% sulfur, 29,070 kJ/kg (12,500 Btu/lb) LHV
	Gasifier type	Oxygen-blown, Texaco, entrained gasifier
Chemical Synthesis capacity	Raw syngas rate	81,140 kg/hr (178,880 lb/hr)
	Raw syngas conditions	1371°C/ 4137 kPa (2500°F/ 600 psia)
High-Pressure SOFC gas cleaning capacity	Power island capacity	148 MWe
	Raw fuel gas rate	81,140 kg/hr (178,880 lb/hr)
	Raw fuel gas conditions	1371°C/ 4137 kPa (2500°F/ 600 psia)
Low-Pressure SOFC gas cleaning capacity	Power island capacity	100 MWe
	Raw fuel gas rate	54,886 kg/hr (121,000 lb/hr)
	Raw fuel gas conditions	1371°C/ 1034kPa (2500°F/ 150 psia)
Overall process configurations	Raw gas cooling configuration	Maximum superheated steam production
	Ash/Char disposition	Recycle to gasifier
	Sulfur product form	Elemental sulfur
	Excess design capacity	20% equipment excess design capacity; 100% excess design capacity for solids handling systems
	Number of parallel trains	Single train
Import-stream conditions	Air	16°C, 99.3 kPa (60°F, 14.4 psia)
	Natural gas	16°C, 2068 kPa (60°F, 300 psia)
	Raw water	24°C (75°F)
	Cooling water (CW)	29°C (85°F)
	Boiler feed water (BFW)	82°C (180°F)
	Sorbent feed streams	16°C, 99.3 kPa (60°F, 14.4 psia)
	Inert gas for fluffing, transport, pulse gas, etc.	16°C, 1379 kPa (60°F, 200 psia)
Import-stream compositions	Air (vol%)	nitrogen 77.23, oxygen 20.72, carbon dioxide 0.03, water, 1.01, argon 1.01
	Auxiliary fuel (natural gas) (vol%)	methane, 100
	Inert gas (vol%)	nitrogen, 100
	Raw water	contains NaCl ($1.6x10^{-3}$ mole%), $CaCO_3$ (0.0158 mole%)
Export-Stream Conditions and Compositions	Char and solid waste	Cooled to <121°C (250°F), reduced to atm. pressure
	LP-steam	154°C, 517 kPa (310°F, 75 psia)
	IP-steam	253°C, 4240 kPa (488°F, 615 psia)
	HP-stream	510°C, 10,446 kPa (950°F, 1515 psia)

	Tail gas	SO_2 content < 100 ppmv

Table 4.3 – Texaco Gasifier Raw Gas Conditions and Composition

Temperature, °C (°F)	1371 (2500)
Pressure, kPa (psia)	4137 (600)
Mass flow, kg/hr (lb/hr)	81,140 (178,800)
Molar flow CO + H_2, kg-mole/hr	3,253.6
Composition	
hydrogen (mole%)	33.11
methane (mole%)	0.16
nitrogen (mole%)	0.75
argon (mole%)	0.67
carbon monoxide (mole%)	45.67
carbon dioxide (mole%)	7.67
water (mole%)	11.29
hydrogen sulfide (mole%)	0.32
carbonyl sulfide (ppmv)	192
hydrogen chloride (ppmv)	505
hydrogen cyanide (ppmv)	30
ammonia (ppmv)	999
char (ppmw)	5931

4.1.6 Equipment Sizing and Specification

Equipment and process sub-systems have been sized and specified using standard sizing criteria and design factor estimates. For example:

- heat transfer coefficients, with fouling,
- heat exchanger pressure drops,
- heat exchanger minimum temperature approaches,
- reactor operating temperatures and pressure drops,
- reactor equilibrium temperature approaches,
- reactor residence times,
- compressor types and efficiencies,
- pump types and efficiencies,
- absorber and stripper column contacting efficiencies and pressure drops.

The ChemCad simulation package (by Chemstations, Inc., Houston TX) used in the process evaluation includes facilities for the design and specification of many of the equipment components and does rigorous design of heat exchangers, and absorption and stripping columns. Barrier filters, barrier filter-reactors, and granular, moving bed filter-reactors have been sized and designed using SWPC proprietary design codes. Heat recovery designs have accounted for appropriate materials of construction, reliability and maintenance.

Solids handling equipment are particularly important for the novel gas cleaning technology. Equipment for on-site storage, transport, pressurization, and feeding of sorbents have been sized using typical specifications for vessel storage and holding times, transport gas requirements, and vent gas cleaning. Likewise, equipment for waste solids cooling, depressurization, transport and storage have been designed by similar criteria. All solids handling equipment has been designed using a 100% excess capacity factor.

4.1.7 Economic Criteria

An "EPRI TAG" cost analysis was performed to generate the total capital requirement, the annual operating cost for the process, and the overall cost-of-gas-cleaning (EPRI, 1986). The economic premises applied are listed in Table 4.4.

Table 4.4 – Economic Assumptions

Cost year				end-1999	
Project life, years				30	
Book life, years				30	
Tax life, years				20	
Federal and state income tax rate, %				38.0	
Investment Tax Credit, %				0.0	
Inflation rate, % per year				3.0	
Real escalation rates (over inflation)					
Fuel, % per year				0.7	
Operating & Maintenance, % per year				0.0	
Interest during construction					
Plant construction period (years)				2	
Construction interest rate (%)				12.5	
Other factors					
Gas cleaning process land charged, hectares				0	
Plant capacity factor (%)				80	
Financial structure					
Type of Security	% of Total	Current dollar basis		Constant dollar basis	
		Cost, %	Return, %	Cost, %	Return, %
Debt	50	11.0	5.5	4.6	2.3
Preferred Stock	15	11.5	1.7	5.2	0.8
Common Stock	35	15.2	5.3	8.7	3.0
Discount rate (cost of capital)			12.5		6.1

A factored cost evaluation of the gas cleaning processes has been performed, sizing all of the major equipment, using generalized equipment cost correlations and other available cost data to estimate the purchase price of each major equipment component, and applying "installation factors" to each item to estimate the installed equipment cost for the entire process. In some cases, for very expensive process components, vendor budgetary cost inputs have been solicited. Barrier filters, barrier filter-reactors, and granular, moving bed filter-reactors have been costed using SWPC internal cost data and correlations.

Process and project contingencies have been assigned for the conventional and novel gas cleaning processes that reflect the state of the technologies involved and the quality of the process evaluations. The Total Capital Requirement (TCR) is estimated from the values of the installed major equipment costs, using the assumptions and procedure outlined in Table 4.5. The economic premises result in "levelizing factors" based on the 10th year of operation that account for the transient value of money, and the "cost-of-gas-cleaning" is determined on the basis of "current" dollars and "constant" dollars. The current-dollar basis accounts for the inflated value of money over the time period of consideration, and the constant-dollar basis uses the starting value of money (end-1999).

Table 4.5 – Total Capital Requirement Calculation Procedure

Cost Item	Procedure
Process Plant Cost (PPC)	Sum of installed major equipment
General Plant Facilities (GPF)	0.2 * PPC
Engineering Fees (EF)	0.11 * PPC
Process Contingency (PRC)	Sum of process sections installed costs times Process Contingency values
Project Contingency (PJC)	(PPC + GPF) * Project Contingency fraction
Total Plant Cost (TPC)	PPC + GPF + EF + PRC + PJC
Adjustment for Interest & Inflation (IDC)	0.04612 * TPC
Total Plant Investment (TPI)	TPC + IDC
Prepaid Royalties (PR)	0.005 * PPC
Initial Catalyst & Chemical Inventory (ICI)	Separate tabulation
Startup Costs (SCST)	Separate tabulation
Working Capital (WC)	Separate tabulation
Land	0
Total Capital Requirement (TCR)	TPI + PR + ICI + SCST + WC + Land

The levelizing factors are:

- capital carrying charge (10th year): 0.175 (current $) and 0.103 (constant $)
- fuel (10th year): 1.187 (current $) and 1.036 (constant $)
- operating & maintenance (10th year): 1.148 (current $) and 1.000 (constant $)

Process commodity costs and values have been assigned to the various import stream catalysts, chemicals, and fuels consumed or export streams produced by the process:

- fuel (natural gas): 3.8 $/GJ (4 $/ MBtu)
- Claus catalyst: 1.1 $/kg (1000 $/ ton)
- ZnO pellets for conventional guard bed: 4.4 $/kg (4,000 $/ ton)
- raw water: 0.00022 $/kg (0.2 $/ ton)
- methanol: 0.66 $/kg (600 $/ton)
- power: $0.05 / kW-hr
- HP-steam: 3.3 $/GJ (3.5 $/ MBtu)
- IP-steam: 2.13 $/GJ (2.25 $/ MBtu)
- LP-steam: 1.18 $/GJ (1.25 $/ MBtu)

- cooling water: 0.237 $/GJ (0.25 $/ MBtu)
- ash/sorbent waste disposal: 0.022 $/kg (20 $/ ton)
- inert gas (nitrogen generated at the site): 0.00276 $/kg (2.5 $/ton)
- bulk desulfurization sorbent: 8.8 $/kg (8,000 $/ ton)
- Stage I sulfur sorbent: 8.8 $/kg (8,000 $/ ton)
- Stage II sulfur sorbent: 8.8 $/kg (8,000 $/ ton)
- Stage I HCl sorbent: 0.066 $/kg (60 $/ ton)
- Stage II HCl sorbent: 2.2 $/kg (2,000 $/ ton)
- sulfur by-product value: 0.061 $/kg (55 $/ton)

No cost has been associated with the process waste water and condensate streams generated in these gas cleaning processes and exported to the plant water treatment system. The five sorbent costs listed above represent maximum expected, delivered prices for these sorbent materials in the future as mature, commercial commodities. Some of the chemicals above, such as methanol and sulfur, have very unstable costs, but they play a relatively small part in the gas cleaning process costs.

4.2 CONVENTIONAL SYNGAS CLEANING FOR SYNTHESIS APPLICATIONS

The overall, simplified process schematic for the conventional, state-of-the-art, syngas cleaning process, with process boundaries as defined in Figure 4.1, is shown in Figure 4.2. Here, the conventional syngas cleaning process is separated into five major process sections: the syngas cooling section, the precleaning section, the desulfurization section, the sulfur recovery section, and the refrigeration system.

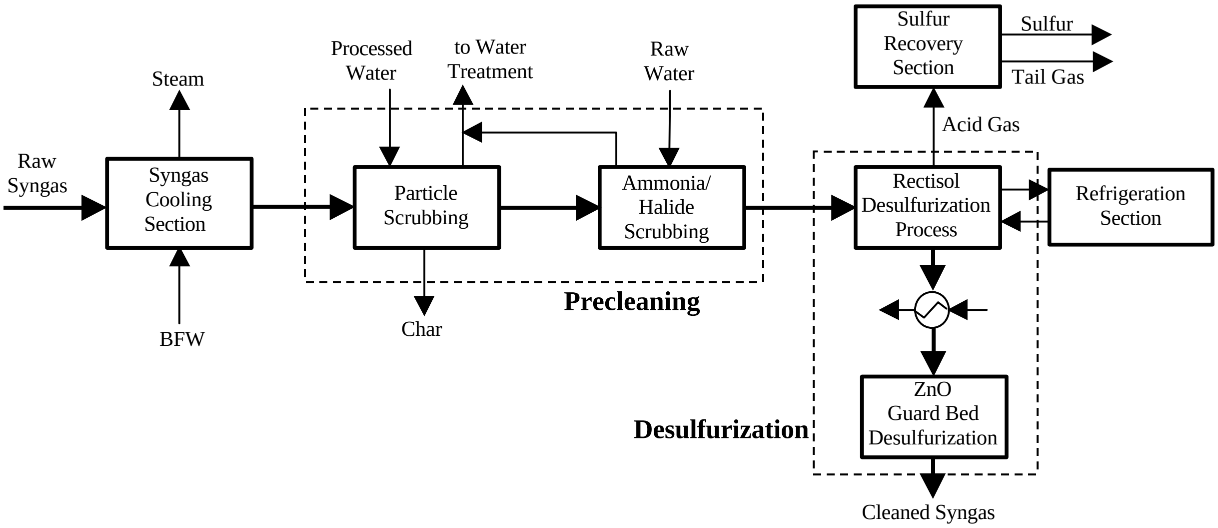


Figure 4.2 – Conventional Syngas Cleaning Schematic

In the syngas cooling section, the raw syngas from the gasifier, at 1371°C (2500°F), is cooled to an acceptable temperature for low-temperature cleanup of about 149°C (300°F) while generating superheated steam. In the precleaning section, recycled process water is used to scrub particulate from the cooled syngas. The char captured is recycled to the gasifier coal-slurry feed system. The next step applies raw water to scrub ammonia and halides from the syngas to meet the stringent syngas requirement. The waste water is processed in a water treatment plant.

The precleaned syngas is then piped to the desulfurization section where it is treated in a Rectisol process to remove H_2S and COS to very low content. The Rectisol process also removes a large portion of the syngas CO_2 content. The Rectisol desulfurization process has performance characteristics ideal for this cleaning function (Biansca et al., 1987). The Rectisol process is a low-temperature absorption process having the capability to achieve very low H_2S and COS levels in the syngas and is the typical choice for methanol synthesis plants. The Eastman, Kingsport coal gasification plant applies the Rectisol desulfurization process for methanol synthesis, acetic anhydride synthesis and other synthesis products (Tijm et al., 1999). This is followed by syngas reheat and additional desulfurization in a zinc oxide guard bed system to satisfy the syngas sulfur content requirement.

The acid gas from the Rectisol process, consisting of dilute H_2S in primarily CO_2, is treated in the sulfur recovery section to remove sulfur in the form of elemental sulfur. The Rectisol process also requires a refrigeration system, which is treated as a separate process section because it is very expensive and consumes significant power.

The integration of the processing steps requires heat interchange between several process streams. Heat exchange equipment represents a dominant cost class in the conventional process. Steam generation and utilization throughout the conventional process must be carefully integrated.

4.2.1 Process Description

The detailed process diagrams for the conventional process are placed on three major process flow diagrams: 1) syngas cooling and syngas precleaning, 2) syngas desulfurization (Rectisol desulfurization and ZnO final desulfurization), and 3) sulfur recovery. The refrigeration section process diagram is not shown. These three process diagrams are shown in Figures 4.3 through 4.5. The process flow diagrams show the major process streams, identified by stream numbers in boxes, and the major process equipment, identified by bold numbers in circles. The three diagrams number the process streams and equipment consecutively. Several references have been applied to develop these process flow diagrams and are listed in the Bibliography Section (Section 7) of this report. The actual process diagrams analyzed using the ChemCad simulator have a total of 125 process streams and 68 process unit operations. The diagrams in Figure 4.3 and 4.5 identify a reduced number of streams and equipment components.

Syngas Cooling and Syngas Precleaning Section

Figure 4.3 shows the process diagram for this section of the conventional process. The raw syngas is first cooled to an acceptable temperature for the low-temperature precleaning functions, and superheated steam is raised. Since the raw syngas enters at a very high temperature and contains slag droplets, the syngas cooler design must accommodate this environment with special features. The raw syngas first passes into the radiant evaporator (Item 1), with its low velocity, water-walled radiant zone that evaporates water through refractory-lined heat transfer tubes. The radiant zone cools the syngas down to the level where the slag can solidify, about 815°C (1500°F), before the syngas enters the convective zone of the evaporator. The syngas then passes through the steam superheater (Item 3), followed by the feedwater heater (Item 4). The syngas cooler requires water-cooled tubesheets in the evaporator and superheater, and sootblowers are placed at several locations. Syngas velocities in each of the heat exchangers.

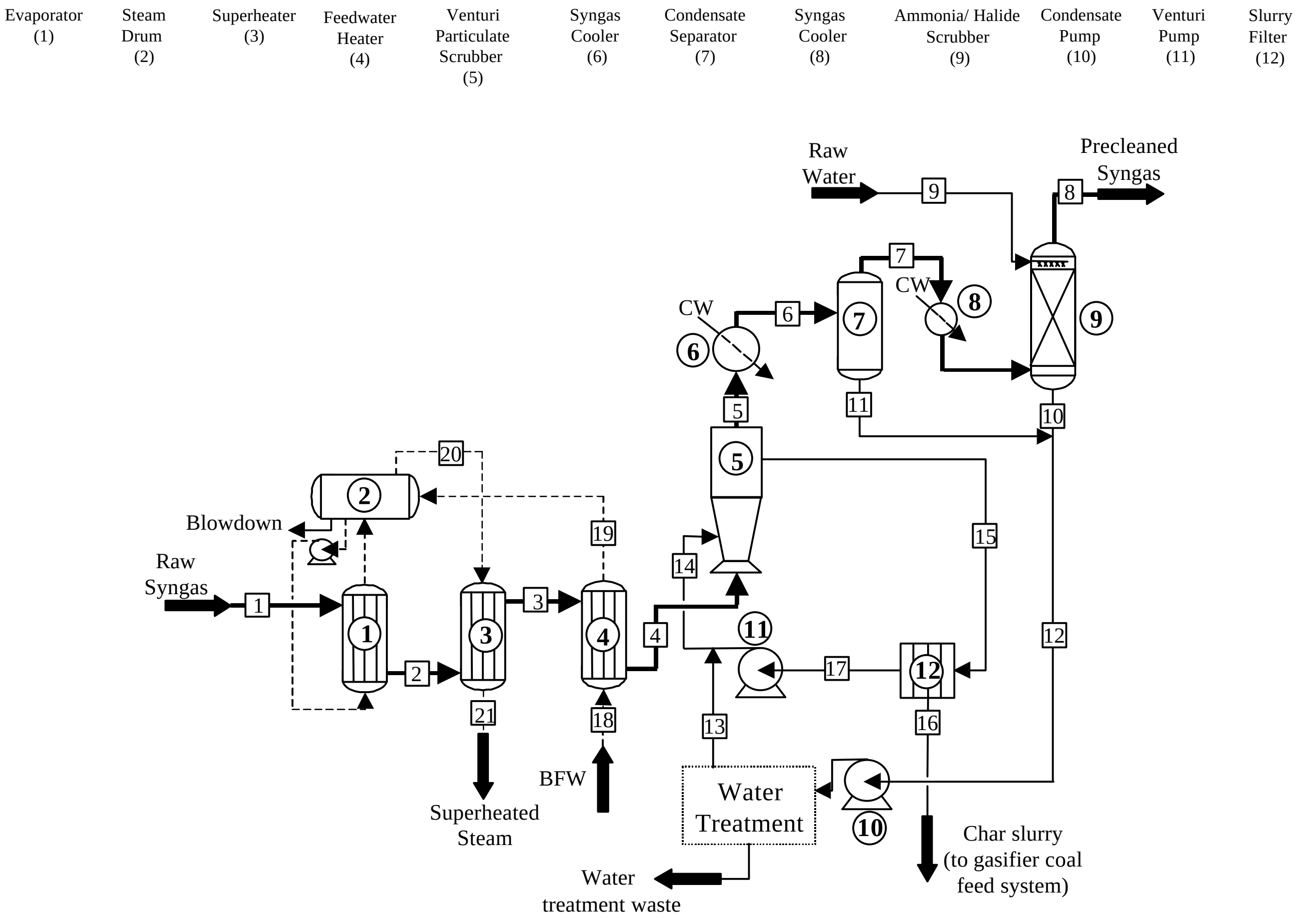


Figure 4.3 - Conventional Syngas Cleaning - Syngas Cooling and Preclean Sections

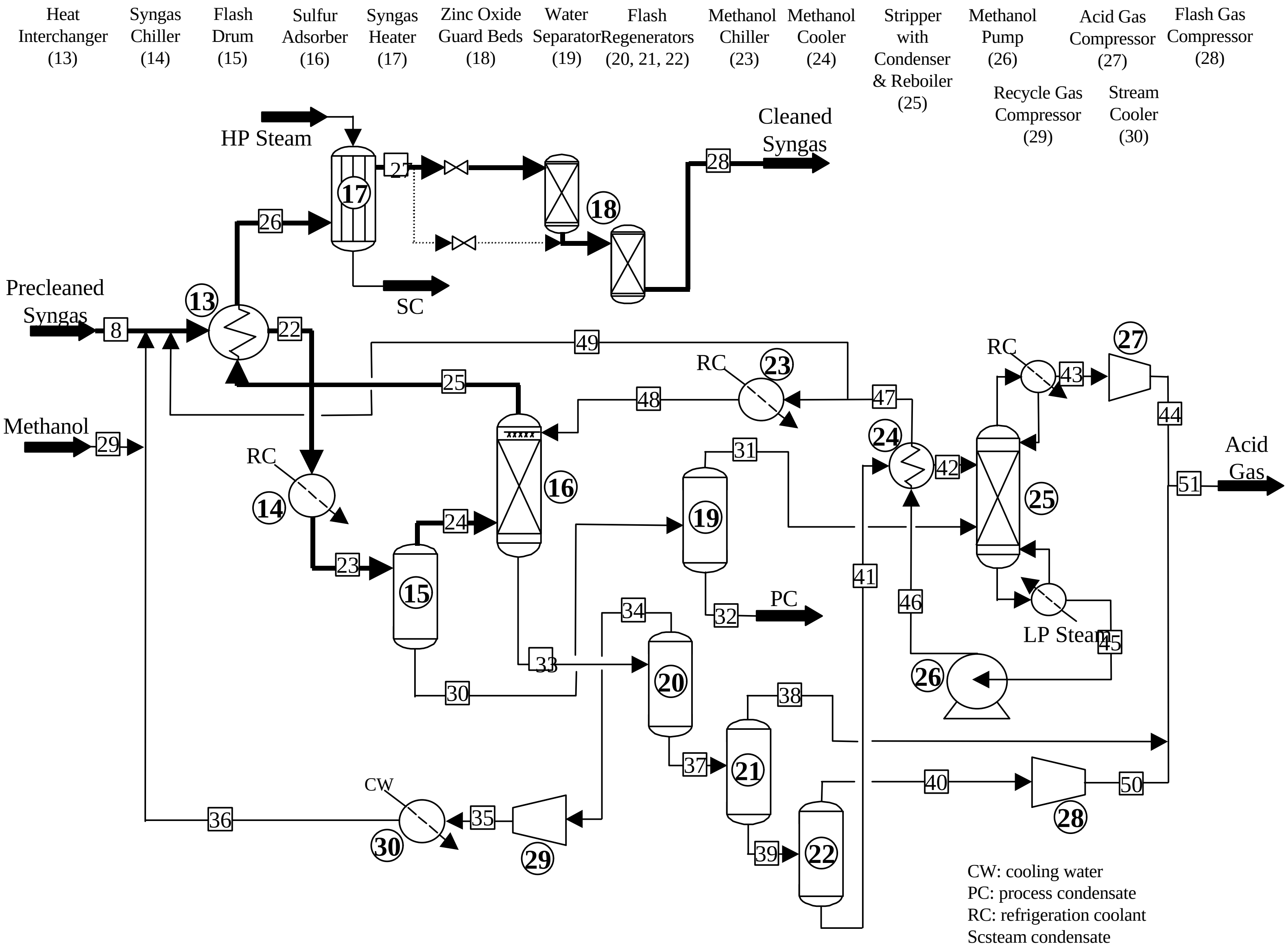
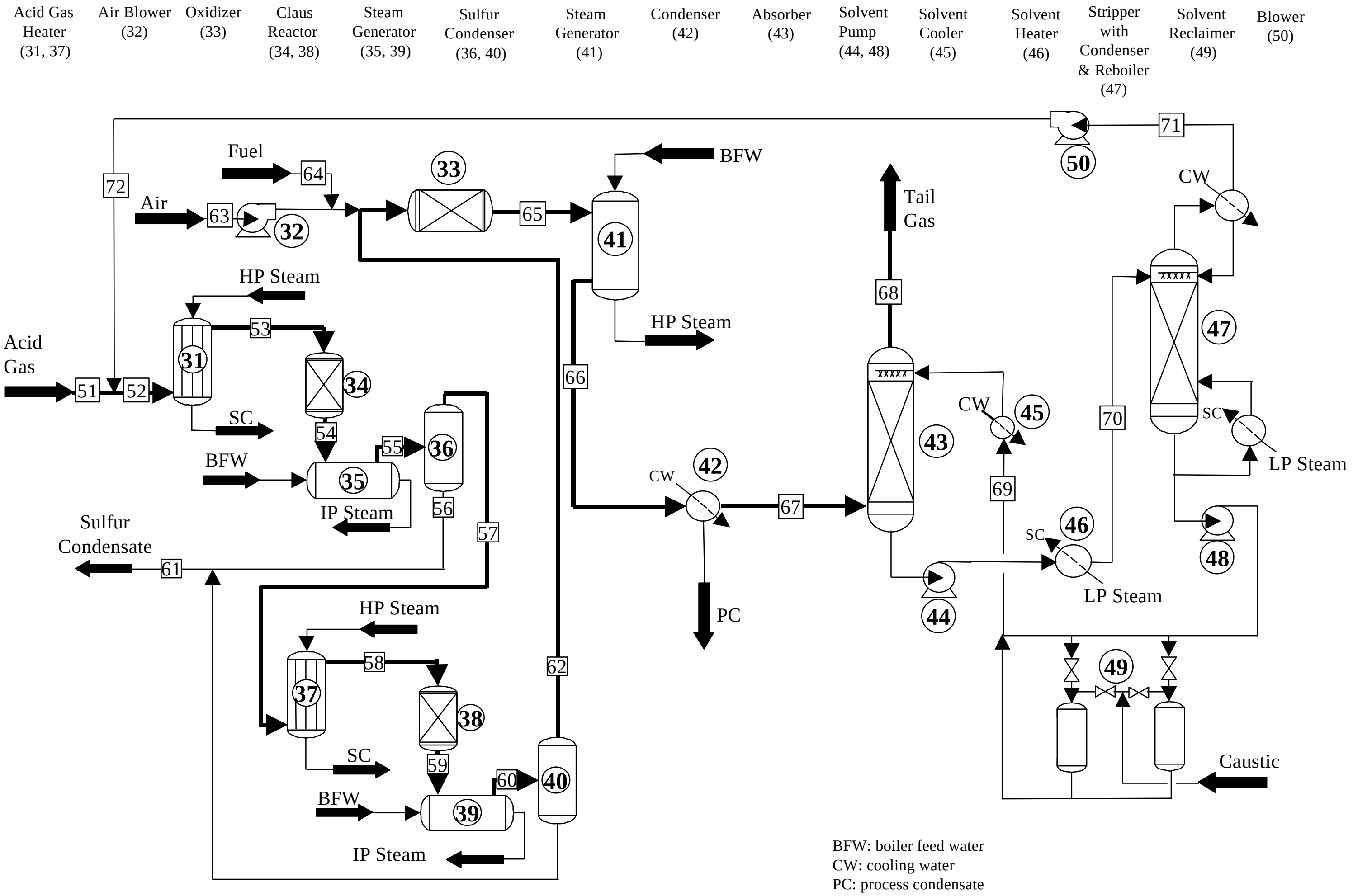


Figure 4.4 - Conventional Syngas Cleaning - Desulfurization Section



BFW: boiler feed water
CW: cooling water
PC: process condensate
SC: steam condensate

Figure 4.5 - Conventional Syngas Cleaning - Sulfur Recovery Section

must be selected for acceptable heat transfer coefficients, materials erosion, deposition and pressure drops. Heat transfer estimates must account for the fouled-nature of the heat transfer surfaces. Maintenance costs are high and refractory replacement is required on an annual basis when operating with high-sulfur coals

The cooled, raw syngas is then passed to the precleaning section of the process where it is subjected to wet particle removal in a venturi scrubber (Item 5). The venturi slurry is filtered (Item 12) to remove char that is recycled to the gasifier, and the filtered water is reinjected (Item 11) into the venturi scrubber. It is assumed that the venturi scrubber will meet the particulate removal requirement, but the other wet processing steps that follow may be contaminated with particulate and will contribute to the overall particulate control. The wet char removed is recycled to the gasifier through the coal slurry feed system.

The syngas is then further cooled (Item 6) to about 38°C (100°F), and the process condensate is separated (Item 7) and applied for the particle scrubbing operation. After further cooling (Item 8), the syngas is contacted with raw water in a packed scrubbing tower (Item 9) to removal ammonia and halides to the required syngas cleaning level, and the contaminated scrubbing water is again used in the venturi scrubber. The packed column for ammonia and halide removal (Item 9) is about 12.2 m (40 ft) tall and 1 m (3.25 ft) in diameter. It operates at about 80% of flooding with 50 mm packing, having a 96% voidage. Its internal pressure drop is about 21 kPa (3 psi). It uses stainless-steel materials of construction and its design pressure is 4480 kPa (650 psia).

A water treatment process is shown in the diagram, but it has not been included in the material & energy balances or in the process costing. There are many water treatment needs in the entire plant and a central water treatment facility would be used.

The precleaned syngas (Stream 8) conditions and composition are listed in Table 4.6. The molar flow of CO and H_2, the basic synthesis building blocks, are also listed. Ammonia and HCl are both removed very effectively by the water scrubbing.

Table 4.6 – Precleaned Syngas Conditions and Composition

Temperature, °C (°F)	39 (103)
Pressure, kPa (psia)	3647 (529)
Mass flow, kg/hr (lb/hr)	72,186 (159,140)
Molar flow CO + H_2, kg-mole/hr	3,253.6
Composition	
hydrogen (mole%)	37.39
methane (mole%)	0.18
nitrogen (mole%)	0.85
argon (mole%)	0.76
carbon monoxide (mole%)	51.58
carbon dioxide (mole%)	8.62
water (mole%)	0.24
hydrogen sulfide (mole%)	0.36
carbonyl sulfide (ppmv)	165
hydrogen chloride (ppbv)	7
hydrogen cyanide (ppmv)	23
ammonia (ppbv)	15

char (ppmw)	0

Rectisol Desulfurization and ZnO Guard Bed Desulfurization Section

Figure 4.4 shows the Rectisol desulfurization process section. The precleaned syngas (Stream 8) entering the process is first mixed with recycled offgas (Stream 36) from the first stage of three flash strippers, and with makeup methanol (Stream 29). The syngas is then mixed with methanol solvent from the methanol stripper (Item 25), before being chilled to about -48°C (-55°F) across a process heat interchanger (Item 13) and using a refrigeration cooler (Item 14). The methanol, a physical solvent, removes H_2S, COS, and CO_2 very effectively. The mixture (Stream 23) enters a phase separator (Items 15), and then a methanol adsorption tower (Item 16) operating at about -73°C (-100°F) to remove H_2S and COS to very low level (about 400 ppbv).

The absorption tower (Item 16) is a thirty-three-stage, bubble cap tower, having a total height of 23 m (76 ft) and diameter of 2 m (6.4 ft). It operates at about 70% of flooding and has a design pressure of 4480 kPa (650 psia). It generates the cleaned syngas stream (Stream 25) that is treated for final desulfurization in the ZnO guard bed system. The refrigeration system is a multistage, cascading, vapor compression system using trifluoromethane as the refrigerant.

The methanol solvent (Stream 33) then passes through a series of three flash strippers (Item 20, 21, 22), and then through a 22-stage, solvent stripping tower (Item 25). The stripping column uses bubble cap trays, and is 16.5 m (54 ft) tall and 2.1 m (7 ft) in diameter. Its condenser duty is about 4.1 GJ/hr (3.9 MBtu/hr) and its reboiler duty is about 17.1 GJ/hr (16.2 MBtu/hr). The vessel design pressure is 345 kPa (50 psia).

The stream generated (Stream 43) consisting primary of CO_2 with about 4.0 vol% H_2S. The purified methanol (Stream 45) is recycled to the adsorber after intercooling with the stripper inlet solvent stream (Item 24), and refrigeration cooling to -73°C (-100°F) (Item 23). The stripper acid gas (Stream 43) is compressed (Item 27) and passed to the sulfur recovery process. There are alternative process schemes for the Rectisol process that can reduce the CO_2 content mixed with the H_2S acid gas, and thus make the sulfur recovery process simpler, but these are much more complex and costly.

Superheated steam is utilized to heat the cleaned syngas (Stream 26) to about 371°C (700°F) (Item 17). The ZnO desulfurizing system (Item 18) consists of a pair of guard beds (fixed bed reactors) that are operated at about 371°C (700°F) in parallel, periodically disposing of the spent ZnO sorbent, without regeneration, from one bed while the other bed is in operation. An average of about 0.34 kg/hr (0.75 lb/hr) of ZnO is consumed in these batch reactors. The cleaned syngas (Stream 28) is then be utilized in the plant synthesis application, probably requiring further cooling and compression.

The cleaned syngas (Stream 28) conditions and composition are shown in Table 4.7. The cleaned syngas is nearly bone-dry and has very low CO_2 content. The cleaned syngas meets all of the requirements on its contaminant content, except for hydrogen cyanide, which is at about 91 ppbv as compared to its 10 ppbv requirement. A small amount of the raw syngas CO and H_2 are lost in the desulfurization process.

The acid gas (Stream 51) conditions and composition are shown in Table 4.8. The acid gas is relatively dilute in H_2S and COS content. It also has high CO_2 and low water vapor content.

Table 4.7 – Cleaned Syngas Conditions and Composition

Temperature, °C (°F)	371 (700)
Pressure, kPa (psia)	3275 (475)
Mass flow, kg/hr (lb/hr)	57,579 (126,938)
Molar flow CO + H_2, kg-mole/hr	3,250.7
Composition	
hydrogen (mole%)	41.24
methane (mole%)	0.19
nitrogen (mole%)	0.94
argon (mole%)	0.82
carbon monoxide (mole%)	56.81
carbon dioxide (ppmv)	7.30
water (ppmv)	0.32
hydrogen sulfide (ppbv)	54.80
carbonyl sulfide (ppbv)	4.50
hydrogen chloride (ppbv)	0.0
hydrogen cyanide (ppbv)	91.4
ammonia (ppbv)	0.0
methanol (ppmv)	1.0
char (ppmw)	0

Table 4.8 – Acid Gas Conditions and Composition

Temperature, °C (°F)	11 (52)
Pressure, kPa (psia)	183 (26.5)
Mass flow, kg/hr (lb/hr)	14,519 (32,008)
Composition	
hydrogen (mole%)	0.02
methane (mole%)	0.04
nitrogen (mole%)	0.01
argon (mole%)	0.11
carbon monoxide (mole%)	0.75
carbon dioxide (mole%)	94.30
water (mole%)	0.0
hydrogen sulfide (mole%)	3.95
carbonyl sulfide (mole%)	0.18
hydrogen chloride (ppmv)	0
hydrogen cyanide (ppmv)	313
ammonia (ppmv)	0.22
methanol (ppmv)	0.61

Sulfur Recovery Section

Figure 4.5 shows a process to convert the acid gas sulfur constituents into elemental sulfur. Because of the small H_2S content of the gas, a modified Claus plant is required, based on the Union Carbide Alkanolamine process (Lorton, 1980). The acid gas (Stream 51) is first mixed with a concentrated SO_2 stream (Stream 72) from the amine stripper (Item 47). This mixture is heated by superheated steam (Item 31), and the mixture (Stream 53) passes through two stages of catalytic Claus reactors (Items 34 and 38), generating elemental sulfur vapor.

The Claus reactor off-gas is cooled (Items 35 and 39), generating steam, and the sulfur vapor is condensed and removed (Items 36 and 40) from the offgas, producing a sulfur by-product (Stream 61). Air (Stream 63) and fuel (Stream 64) combustion product (Item 32) is used to burn the off-gas (Stream 62), converting it into an oxidizing gas (Stream 65) and converting the excess sulfur and H_2S into SO_2. The oxidized gas is cooled (Item 41) and this is following by water removal (Item 42). The gas is scrubbed with triethanolamine solution in a 31-stage, bubble-cap tray, absorber column (Item 43), removing SO_2 from the gas. The column is 22 m (72 ft) tall and has a diameter of 12.5 ft. Its design pressure is 50 psia. The tail gas is exhausted (Stream 68).

The triethanolamine solvent is regenerated in a pair of parallel, 6-stage, bubble- cap tray, stripper columns (Item 47) and the concentrated SO_2 stream (Stream 71) produced is re-circulated to be mixed with the inlet acid gas. Each stripper column is 6.1 m (20 ft) tall and has a diameter of 4.1 m (13.5 ft). The reflux ratio is 1.48. The total condenser duty is 1.24 GJ/hr (1.18 MBtu/hr) and the total reboiler duty is 302.5 GJ/hr (286.7 MBtu/hr). A solvent reclaimer (Item 49) is also required to purify the continual accumulation of contaminant in the solvent, using a caustic feed (Na_2CO_3) and generating a waste sludge.

The conditions and composition of the tail gas (Stream 68) is shown in Table 4.9. Further cleanup of the tail gas may be required depending on the site emissions requirements since it contains significant SO_2, NH_3, NOx and CO. It was assumed in the evaluation that local environmental restrictions dictate a maximum tail gas SO_2 content of about 100 ppmv.

Table 4.9 – Tail Gas Conditions and Composition

Temperature, °C (°F)	32 (90)
Pressure, kPa (psia)	120.7 (17.5)
Mass flow, kg/hr (lb/hr)	33,565.5 (73,998.0)
Composition	
nitrogen (mole%)	55.23
oxygen (mole%)	3.04
argon (mole%)	0.76
carbon dioxide (mole%)	37.73
water (mole%)	3.24
sulfur dioxide (ppmv)	107
carbon monoxide (ppmv)	3
hydrogen cyanide (ppbv)	0.4
triethanolamine (ppbv)	2.4

4.2.2 Process Material & Energy Balances and Overall Performance

Process simulation was performed using the ChemCad simulator. Tabulations of process stream conditions and compositions are shown for each of the three process flow diagrams (Figures 4.3, 4.4, 4.5) in Tables 4.10, 4.11, and 4.12. Each tabulation provides the molar and mass flows, the temperature, pressure, and vapor mole fraction, and the composition for each of the numbered streams in the Figures. Note that the stream values in these tables are reported in English Engineering units only.

Table 4.10 – Process Streams for Conventional Syngas Cleaning - Syngas Cooling and Precleaning Sections (Figure 4.3)

Stream No.	1	2	3	4	5	6	7	8	9	10
Stream Name	Raw Syngas			Cool Raw Syngas		Particle-free Syngas		Precleaned Syngas	Raw Water	Scrubber Effluent
Molar flow (lb-mole/hr)	6,159.4	6,159.4	6,159.4	6,159.4	9,034.6	9,034.6	8,098.9	8,060.9	55.5	93.5
Mass flow (lb/h)	121,000.0	121,000.0	121,000.0	121,000.0	176,850.0	176,850.0	159,970.0	159,140.0	1,000.0	1,825.5
Temp (°F)	2500	1584	1130	325	287	140	133	103	75	98
Pressure (psia)	150.0	148.7	144.8	144.8	555.8	545.8	545.8	528.8	528.8	535.8
Vapor mole fraction	1	1	1	1	1	0.8947	1	1	0	0
Component mole fractions										
Hydrogen	0.3311	0.3311	0.3311	0.3311	0.3336	0.3336	0.3722	0.3739		
Methane	0.0016	0.0016	0.0016	0.0016	0.0016	0.0016	0.0018	0.0018		
Nitrogen	0.0075	0.0075	0.0075	0.0075	0.0076	0.0076	0.0085	0.0085		
Carbon Monoxide	0.4567	0.4567	0.4567	0.4567	0.4603	0.4603	0.5134	0.5158		0.0003
Carbon Dioxide	0.0767	0.0767	0.0767	0.0767	0.0773	0.0773	0.0862	0.0862		0.0282
Hydrogen Sulfide	3.22E-03	3.22E-03	3.22E-03	3.22E-03	3.24E-03	3.24E-03	3.60E-03	3.61E-03		7.19E-04
Water	0.1129	0.1129	0.1129	0.1129	0.1080	0.1080	0.0053	0.0024	0.9998	0.8511
Argon	6.70E-03	6.70E-03	6.70E-03	6.70E-03	6.75E-03	6.75E-03	7.53E-03	7.56E-03		6.17E-06
Hydrogen Chloride	5.05E-04	5.05E-04	5.05E-04	5.05E-04	4.92E-04	4.92E-04	5.08E-04	7.09E-09		4.40E-02
Hydrogen Cyanide	3.03E-05	3.03E-05	3.03E-05	3.03E-05	2.93E-05	2.93E-05	2.66E-05	2.34E-05		2.93E-04
Carbonyl Sulfide	1.92E-04	1.92E-04	1.92E-04	1.92E-04	1.78E-04	1.78E-04	1.68E-04	1.65E-04		3.44E-04
Ammonia	9.99E-04	9.99E-04	9.99E-04	9.99E-04	9.20E-04	9.20E-04	8.63E-04	1.53E-08		7.48E-02
Char	1.94E-03	1.94E-03	1.94E-03	1.94E-03	0.0000			0.0000		
Sodium Chloride								1.59E-15	1.60E-05	9.49E-06
Calcium Carbonate								1.57E-14	1.58E-04	9.37E-05

Table 4.10 (Cont.) – Process Streams for Conventional Syngas Cleaning - Syngas Cooling and Precleaning Sections

Stream No.	11	12	13	14	15	16	17	18	19	20	21
Stream Name	Process Condensate	Recycle Condensate	Treated Water	Venturi Water	Recycle Water	Char Slurry	Char-free Water	BFW	Preheated Water	Sat. Steam	HP-Steam
Molar flow (lb-mole/hr)	935.7	1,029.2	1,002.6	268,170.0	268,240.0	1,069.4	267,170.0	4,752.7	4,752.7	4,752.7	4,752.7
Mass flow (lb/h)	16,888.0	18,714.0	18,071.0	4,833,800.0	4,835,700.0	20,018.0	4,815,700.0	85,619.0	85,619.0	85,619.0	85,619.0
Temp (°F)	133	135	136	290	287	287	287	180	585	610	950
Pressure (psia)	545.8	535.8	565.0	565.0	555.8	535.8	535.8	1575.0	1550.0	1535.0	1515.0
Vapor mole fraction	0	0	0	0	0	0	0	0	0	1	1
Component mole fractions											
Hydrogen	0.0001	0.0002		0.0001	0.0001	0.0001	0.0001				
Methane											
Nitrogen											
Carbon Monoxide	0.0002	0.0002		0.0002	0.0002	0.0002	0.0002				
Carbon Dioxide	0.0006	0.0031	0.0003								
Hydrogen Sulfide	1.24E-04	1.78E-04		5.53E-05	5.55E-05	5.46E-05	5.55E-05				
Water	0.9968	0.9836	0.9996	0.9985	0.9984	0.9820	0.9985	1.0000	1.0000	1.0000	1.0000
Argon	5.05E-06	5.15E-06		8.09E-06	8.12E-06	7.99E-06	8.12E-06				
Hydrogen Chloride	3.52E-04	4.32E-03	4.43E-05	1.89E-04	1.90E-04	1.87E-04	1.90E-04				
Hydrogen Cyanide	5.20E-05	7.39E-05	7.58E-07	1.17E-05	1.17E-05	1.15E-05	1.17E-05				
Carbonyl Sulfide	2.69E-04	2.76E-04	2.84E-06	1.29E-04	1.30E-04	1.28E-04	1.30E-04				
Ammonia	1.41E-03	8.07E-03	8.29E-05	8.16E-04	8.19E-04	8.05E-04	8.19E-04				
Char		0.0000		6.59E-08	6.59E-05	1.65E-02	6.62E-08				
Sodium Chloride		8.62E-07									
Calcium Carbonate		8.51E-06									

Table 4.11 – Process Streams for Conventional Syngas Cleaning - Desulfurization Section (Figure 4.4)

Stream No.	8	22	23	24	25	26	27	28	29	30
Stream Name	Precleaned Syngas	Precooled Syngas	Cooled Syngas		Desulfurized Syngas	Reheated Syngas	Heated Syngas	Final Cleaned Syngas	Makeup Methanol	
Molar flow (lb-mole/hr)	8,060.9	8,088.6	8,088.6	8,040.1	7,309.4	7,309.4	5,228.9	5,228.9	4.6	48.6
Mass flow (lb/h)	159,140.3	160,006.8	160,006.8	158,672.0	126,937.6	126,937.6	98,319.2	98,319.2	145.9	1,334.9
Temp (°F)	103	-83	-83	-83	-100	87	700	700	70	-83
Pressure (psia)	528.8	518.8	518.8	518.8	510.8	500.8	120.0	117.9	600.0	518.8
Vapor mole fraction	0.9995	0.994	0.994	1	1	1	1	1	0	0
Component mole fractions										
Hydrogen	0.3739	0.3727	0.3727	0.3750	0.4124	0.4124	0.3899	0.3899		
Methane	0.0018	0.0018	0.0018	0.0018	0.0019	0.0019	0.0019	0.0019		
Nitrogen	0.0085	0.0085	0.0085	0.0085	0.0094	0.0094	0.0089	0.0089		
Carbon Monoxide	0.5158	0.5144	0.5144	0.5175	0.5681	0.5681	0.5378	0.5378		0.0001
Carbon Dioxide	0.0862	0.0860	0.0860	0.0860	0.0000	0.0000	0.0536	0.0536		0.0737
Hydrogen Sulfide	3.61E-03	3.60E-03	3.60E-03	3.45E-03	3.78E-07	3.78E-07	2.45E-07	6.13E-08		0.0273
Water	0.0024	0.0023	0.0023							0.3910
Argon	7.56E-03	7.54E-03	7.54E-03	7.59E-03	8.23E-03	8.23E-03	7.87E-03	7.87E-03		1.85E-05
Hydrogen Chloride	7.09E-09	7.07E-09	7.07E-09	7.04E-09	1.43E-13	1.43E-13	2.52E-07	2.52E-07		1.24E-08
Hydrogen Cyanide	2.34E-05	2.40E-05	2.40E-05	9.64E-06	9.14E-08	9.14E-08	1.11E-06	1.11E-06		2.40E-03
Carbonyl Sulfide	1.65E-04	1.64E-04	1.64E-04	1.63E-04	2.92E-08	2.92E-08	1.55E-07	3.87E-08		2.95E-04
Ammonia	1.53E-08	1.53E-08	1.53E-08	9.16E-09	5.41E-11	5.41E-11	9.83E-07	9.83E-07		1.03E-06
Methanol		3.03E-03	3.03E-03	2.40E-06	9.77E-07	9.77E-07	1.11E-05	1.11E-05	1.0000	0.5051

Table 4.11 (Cont.) – Process Streams for Conventional Syngas Cleaning - Desulfurization Section

Stream No.	31	32	33	34	35	36	37	38	39	40
Stream Name		Process Condensate	Rich Solvent	Solvent Flash Gas	Compressed Flash Gas	Recycled Flash Gas	Flashed Solvent			
Molar flow (lb-mole/hr)	29.6	19.0	10,506.2	3.2	3.2	3.2	10,503.0	4.8	10,498.2	5.6
Mass flow (lb/h)	992.8	342.1	344,937.0	79.9	79.9	79.9	344,857.1	146.2	344,711.0	212.4
Temp (°F)	-83	-83	-72	-72	195	100	-72	-72	-72	-73
Pressure (psia)	513.8	513.8	518.8	250.0	530.0	522.0	250.0	80.0	80.0	20.0
Vapor mole fraction	0	0	0	1	1	1	0	1	0	1
Component mole fractions										
Hydrogen			0.0001	0.1638	0.1638	0.1638		0.0259		0.0012
Methane				0.0035	0.0035	0.0035		0.0086		0.0190
Nitrogen				0.0122	0.0122	0.0122		0.0119		0.0045
Carbon Monoxide	0.0001		0.0008	0.7472	0.7472	0.7472	0.0005	0.7572	0.0002	0.3019
Carbon Dioxide	0.1211		0.0658	0.0581	0.0581	0.0581	0.0658	0.1603	0.0658	0.6060
Hydrogen Sulfide	0.0449		2.65E-03	3.44E-04	3.44E-04	3.44E-04	2.65E-03	9.44E-04	2.65E-03	3.58E-03
Water	0.0000	1.0000	0.0001							
Argon	3.03E-05		8.28E-05	0.0148	0.0148	0.0148	7.83E-05	0.0351	6.21E-05	0.0635
Hydrogen Chloride	2.04E-08		5.38E-09	2.79E-09	2.79E-09	2.79E-09	5.39E-09	7.74E-09	5.38E-09	2.94E-08
Hydrogen Cyanide	3.94E-03		2.62E-04	4.06E-07	4.06E-07	4.06E-07	2.62E-04	9.73E-07	2.62E-04	3.47E-06
Carbonyl Sulfide	4.84E-04		1.25E-04	2.95E-05	2.95E-05	2.95E-05	1.25E-04	7.78E-05	1.25E-04	2.90E-04
Ammonia	1.69E-06		2.14E-08	3.67E-10	3.67E-10	3.67E-10	2.14E-08	9.96E-10	2.14E-08	3.75E-09
Methanol	0.8294		0.9301	1.05E-05	1.05E-05	1.05E-05	0.9304	2.52E-05	0.9308	8.98E-05

Table 4.11 (Cont.) – Process Streams for Conventional Syngas Cleaning - Desulfurization Section

Stream No.	41	42	43	44	45	46	47	48	49	50	51
Stream Name		Heated	Stripper	Compressed	Lean		Cooled	Chilled	Feed Stream	Compressed	Acid Gas
		Solvent	Gas	Gas	Solvent		Solvent	Solvent	Methanol	Flash Gas	
Molar flow (lb-mole/hr)	10,492.6	10,492.6	726.7	726.7	9,795.5	9,795.5	9,795.5	9,775.5	20.0	5.6	737.1
Mass flow (lb/h)	344,498.5	344,498.4	31,649.9	31,649.9	313,843.3	313,843.3	313,843.3	313,202.6	640.8	212.4	32,008.4
Temp (°F)	-73	100	2	54	172	176	-28	-100	-28	-28	52.4
Pressure (psia)	20.0	19.6	19.6	27.0	24.1	532.0	521.0	511.0	521.0	27.0	26.5
Vapor mole fraction	0	0.07611	1	1	0	0	0	0	0	1	1
Component mole fractions											
Hydrogen										0.0012	0.0002
Methane			0.0002	0.0002						0.0190	0.0004
Nitrogen										0.0045	0.0001
Carbon Monoxide			0.0003	0.0003						0.3019	0.0075
Carbon Dioxide	0.0655	0.0655	0.9508	0.9508						0.6060	0.9430
Hydrogen Sulfide	2.65E-03	2.65E-03	0.0400	0.0400	1.00E-05	1.00E-05	1.00E-05	1.00E-05	1.00E-05	3.58E-03	0.0395
Water	0.0001	0.0001			0.0001	0.0001	0.0001	0.0001	0.0001	0.0000	3.81E-07
Argon	2.85E-05	2.85E-05	4.13E-04	4.13E-04	5.53E-23	5.53E-23	5.53E-23	5.53E-23	5.53E-23	0.0635	1.12E-03
Hydrogen Chloride	5.37E-09	5.37E-09	7.84E-08	7.84E-08	2.43E-16	2.43E-16	2.43E-16	2.43E-16	2.43E-16	2.94E-08	7.76E-08
Hydrogen Cyanide	2.62E-04	2.62E-04	3.18E-04	3.18E-04	2.73E-04	2.73E-04	2.73E-04	2.73E-04	2.73E-04	3.47E-06	3.13E-04
Carbonyl Sulfide	1.25E-04	1.25E-04	1.82E-03	1.82E-03	3.01E-07	3.01E-07	3.01E-07	3.01E-07	3.01E-07	2.90E-04	1.80E-03
Ammonia	2.14E-08	2.14E-08	2.25E-07	2.25E-07	1.55E-08	1.55E-08	1.55E-08	1.55E-08	1.55E-08	3.75E-09	2.21E-07
Methanol	0.9313	0.9313	6.21E-03	6.21E-03	0.9996	0.9996	0.9996	0.9996	0.9996	8.98E-05	6.13E-03

Table 4.12 – Process Streams for Conventional Syngas Cleaning - Sulfur Recovery Section (Figure 4.5)

Stream No.	51	52	53	54	55	56	57	58	59	60	61
Stream Name	Acid Gas		Heated Acid Gas	Claus Off Gas	Cooled Claus Gas	Sulfur Condensate					Sulfur Condensate
Molar flow lb-mole/hr)	737.1	778.9	778.9	792.2	792.2	20.3	771.9	771.9	778.5	778.5	30.5
Mass flow (lb/h)	32,008.4	34,141.8	34,141.8	34,141.7	34,141.7	648.3	33,493.4	33,493.4	33,493.4	33,493.4	973.6
Temp (°F)	52	61	650	696	285	285	285	600	623	260	277
Pressure (psia)	26.5	26.5	26	25.3	24.8	24.8	24.8	24.4	23.7	23.3	23.3
Vapor mole fraction	1	1	1	1	0.9744	0	1	1	1	0.9869	0.000171
Component mole fractions											
Hydrogen	1.79E-04	1.70E-04	1.70E-04	1.67E-04	1.67E-04	2.80E-09	1.71E-04	1.71E-04	1.70E-04	1.70E-04	2.72E-09
Methane	3.88E-04	3.67E-04	3.67E-04	3.61E-04	3.61E-04	1.09E-08	3.71E-04	3.71E-04	3.67E-04	3.67E-04	1.04E-08
Nitrogen	1.15E-04	7.73E-04	7.73E-04	7.60E-04	7.60E-04	9.55E-09	7.80E-04	7.80E-04	7.73E-04	7.73E-04	9.09E-09
Oxygen		7.31E-05	7.31E-05	7.18E-05	7.18E-05	1.13E-09	7.37E-05	7.37E-05	7.31E-05	7.31E-05	1.10E-09
Carbon Monoxide	7.50E-03	7.10E-03	7.10E-03	6.98E-03	6.98E-03	1.08E-07	7.17E-03	7.17E-03	7.10E-03	7.10E-03	1.05E-07
Carbon Dioxide	0.9430	0.9118	0.9118	0.8965	0.8965	8.27E-03	0.9198	0.9198	0.9120	0.9120	7.30E-03
Hydrogen Sulfide	0.0395	0.0374	0.0374	0.0200	0.0200	2.76E-06	0.0205	0.0205	0.0118	0.0118	2.51E-06
Sulfur Dioxide		0.0274	0.0274	0.0186	0.0186	2.64E-06	0.0191	0.0191	0.0147	0.0147	3.12E-06
Water	3.81E-07	6.11E-03	6.11E-03	0.0228	0.0228	0.0105	0.0231	0.0231	0.0314	0.0314	0.0139
Argon	1.12E-03	1.08E-03	1.08E-03	1.06E-03	1.06E-03	5.74E-08	1.09E-03	1.09E-03	1.08E-03	1.08E-03	5.32E-08
Hydrogen Chloride	7.76E-08	7.34E-08	7.34E-08	7.22E-08	7.22E-08	2.82E-06	3.73E-11	3.73E-11	3.70E-11	3.70E-11	1.88E-06
Hydrogen Cyanide	3.13E-04	2.97E-04	2.97E-04	2.92E-04	2.92E-04	1.98E-05	2.99E-04	2.99E-04	2.96E-04	2.96E-04	2.13E-05
Carbonyl Sulfide	1.80E-03	1.70E-03	1.70E-03	1.68E-03	1.68E-03	2.69E-05	1.72E-03	1.72E-03	1.70E-03	1.70E-03	2.83E-05
Ammonia	2.21E-07	2.10E-07	2.10E-07	2.06E-07	2.06E-07	5.44E-06	6.86E-08	6.86E-08	6.80E-08	6.80E-08	4.82E-06
Sulfur		4.05E-22	4.05E-22	0.0251	0.0251	0.9803	8.99E-05	8.99E-05	0.0128	0.0128	0.9778
Methanol	6.13E-03	5.80E-03	5.80E-03	5.70E-03	5.70E-03	8.99E-04	5.83E-03	5.83E-03	5.78E-03	5.78E-03	1.00E-03
Triethanolamine		2.54E-14	2.54E-14	2.50E-14	2.50E-14	9.70E-13	2.16E-16	2.16E-16	2.14E-16	2.14E-16	6.50E-13

Table 4.12 (Cont.) – Process Streams for Conventional Syngas Cleaning - Sulfur Recovery Section

Stream No.	62	63	64	65	66	67	68	69	70	71	72
Stream Name		Air	Fuel	Oxidized Gas		Cooled Gas	Tail Gas	Lean Solvent	Rich Solvent	Recycle SO2	Pressurized Recycle Gas
Molar flow (lb-mole/hr)	768.3	1,559.0	115.3	2,436.8	2,436.8	2,231.6	2,180.2	67,813.2	67,864.6	41.8	41.8
Mass flow (lb/h)	33,168.1	45,000.0	1,850.0	80,022.7	80,022.7	76,310.7	73,998.0	2,980,690.5	2,983,003.3	2,133.3	2,133.3
Temp (°F)	260	60	60	2105	300	95	90	229	100	120	202
Pressure (psia)	23.3	14.4	30	22.3	21.9	21.5	17.5	36.5	35.5	15	26.5
Vapor mole fraction	1	1	1	1	1	1	1	0	0	1	1
Component mole fractions											
Hydrogen	1.72E-04			3.79E-07	3.79E-07	4.14E-07	4.24E-07	1.00E-21	7.59E-12	1.24E-08	1.24E-08
Methane	3.72E-04		1.0000	9.05E-22	9.05E-22	9.88E-22	3.53E-22	3.53E-22	3.73E-22	3.53E-22	3.53E-22
Nitrogen	7.83E-04	0.7723		0.4944	0.4944	0.5398	0.5523	5.50E-25	7.62E-06	0.0124	0.0124
Oxygen	7.41E-05	0.2072		0.0272	0.0272	0.0296	0.0303	5.69E-25	8.39E-07	1.36E-03	1.36E-03
Carbon Monoxide	7.20E-03			2.57E-06	2.57E-06	2.81E-06	2.87E-06	5.47E-21	5.78E-11	9.43E-08	9.43E-08
Carbon Dioxide	0.9240	3.00E-04		0.3438	0.3438	0.3754	0.3773	4.67E-10	2.22E-04	0.3605	0.3605
Hydrogen Sulfide	0.0120			6.43E-16	6.43E-16	7.02E-16	2.02E-12	3.80E-10	3.80E-10	6.68E-14	6.68E-14
Sulfur Dioxide	0.0149			9.04E-03	9.04E-03	9.73E-03	1.07E-04	1.00E-08	3.16E-04	0.5115	0.5115
Water	0.0315	0.0101		0.1188	0.1188	0.0380	0.0324	0.8023	0.8019	0.1139	0.1139
Argon	1.09E-03	0.0101		6.81E-03	6.81E-03	7.43E-03	7.60E-03	7.68E-24	2.45E-07	3.99E-04	3.99E-04
Hydrogen Chloride	3.75E-11										
Hydrogen Cyanide	3.00E-04			9.65E-09	9.65E-09	1.04E-08	4.07E-10	6.21E-10	9.48E-10	3.05E-11	3.05E-11
Carbonyl Sulfide	1.73E-03			5.70E-13	5.70E-13	6.17E-13	2.11E-15	1.68E-16	2.04E-14	3.24E-11	3.24E-11
Ammonia	2.12E-08			1.00E-04	1.00E-04	9.15E-11	1.12E-15	1.09E-09	1.09E-09	4.66E-16	4.66E-16
Sulfur	4.14E-05			5.64E-12	5.64E-12	1.08E-18	1.56E-23	1.08E-15	1.08E-15	7.56E-21	7.56E-21
Methanol	5.84E-03			9.05E-22	9.05E-22	9.88E-22	3.39E-10	8.37E-10	8.26E-10	1.82E-08	1.82E-08
Triethanolamine	1.50E-18						2.35E-09	1.98E-01	1.98E-01	4.74E-13	4.74E-13

The conventional syngas cleaning process performance is summarized in Table 4.13. Mass flow rates for all significant input and output streams are listed, showing a total mass balance across the process boundaries. The total syngas pressure drop across the conventional cleaning process is estimated to be 125 psi. Net steam productions (HP, IP, and LP-steam), power consumption, and fuel consumption are also listed for comparison with the novel gas cleaning process and for operating cost estimates.

Table 4.13 – Conventional Syngas Cleaning Process Performance

INPUTS	
Material	**kg/hr (lb/hr)**
Raw syngas	81,140 (178,880)
Raw water	4,536 (1,000)
Air	20,412 (45,000)
Fuel	839 (1,850)
Chemicals	
Methanol	66 (146)
ZnO	0.34 (0.75)
Caustic	0
Total	102,911 (226,877)
Heat Energy	**GJ/hr (MBtu/hr)**
Fuel	42.0 (39.8)
Power Use	**kW**
Pump power	535
Compressor power	355
Refrigeration power	4607
Total power	5497
OUTPUTS	
Material	**kg/hr (lb/hr)**
Cleaned syngas	57,579 (126,938)
Char (dry)	481 (1,061)
Waste water	10,843 (23,904)
Sulfur condensate	442 (974)
Tail gas	33,565 (73,998)
Total	102,910 (226,875)
Heat Energy	**GJ/hr (MBtu/hr)**
Net HP-steam production	178.7 (169.4)
Net IP-stream product	6.9 (6.5)
Net LP-stream product	-341.1 (-323.6)
Net cooling water used	367.5 (348.3)
Sulfur Removal Performance	
Total Process sulfur removal eff (%):	99.24
Sulfur byproduct, kg/hr (lb/hr):	433.2 (955.1)
Sulfur byproduct efficiency (%):	95.84

The cleaned syngas flow rate is about 71% of the raw syngas feed rate due primarily to the removal of CO_2 and water vapor in the process. The H_2/CO mole ratio in the cleaned syngas is about 0.73. The precleaning section removes a small amount of sulfur (2.13% of the inlet sulfur to this section) through the water contacting operations, while the desulfurization section removes about 99.99% of its input sulfur. The guard bed removes about 85.43%, and the sulfur recovery section removes about 99.23%. The overall process removal is 99.24%, and about 95.84% of the raw syngas input sulfur is converted into byproduct sulfur.

4.2.3 Process Economics

Equipment costs are broken down into the separate contributions of the five major process sections in Table 4.14. The refrigeration section and the sulfur recovery section have the highest equipment costs. In the syngas precleaning section, heat exchange equipment accounts for 39% of the equipment cost, and flash drums and absorption towers account for 27%, the two dominant cost classes. In the syngas desulfurization section, heat exchange equipment accounts for 49% of the equipment cost, and flash drums and absorption and stripping towers account for 38%, the two dominant cost classes. In the sulfur recovery section, heat exchange equipment accounts for 49% of the equipment cost, and flash drums and absorption and stripping towers account for 35%, the two dominant cost classes in that section.

Table 4.14 – Conventional Syngas Cleaning - Major Equipment Costs

Process Section	Purchased cost (k$)	Installed cost (k$)
Syngas cooling	1,099	2,073
Syngas precleaning	769	1,643
Syngas desulfurization	2,714	5,314
Sulfur recovery	3,541	7,063
Refrigeration	4,206	6,309
Total	12,329	22,402

The total capital requirement is calculated in Table 4.15. The table lists at the top the installed equipment cost of each of the Process Sections, and these are summed to give the Process Plant Cost. The table lists the assumed process and project contingencies, based on the guidelines set in the EPRI TAG Manual. The process contingencies are small for the conventional syngas cleaning process sections, reflecting their state of development. The largest contingencies are assumed for the sulfur recovery and the refrigeration sections because of their greater design uncertainty. Additional economic assumptions are indicated in the table.

For perspective, the total capital requirement determined in Table 4.15 is equivalent to about 277 $/kW (= $36,588,000 / 132,000 kW) if this conventional syngas cleaning process were applied to an equivalent 132 MWe IGCC power plant. This relatively high cost results from the stringent nature of the syngas cleaning requirements.

The initial catalyst and chemical inventory, startup cost, and working capital, representing other capital items utilized in Table 4.15, are estimated in Table 4.16. Here, the startup cost is the highest contributor. Note that Tables 4.16 and 4.17 use only English Engineering Units.

The annual operating cost is estimated in Table 4.17. The cost of fuel represents about 20% of the total annual operating cost. Makeup methanol adds about 6% to the annual operating cost. About 35% of the operating cost results from power consumption, and 52% from LP-steam use. Significant cost credit is obtained for HP-steam generation, but the sulfur by-product credit provides only about a 3% reduction in operating cost.

Table 4.15 – Conventional Syngas Cleaning - Capital Requirement

Process Section	Process Contingency, %	Cost, k$ w/o Contingency
Syngas Cooling	10	3,670
Precleaning	10	1,535
Desulfurization	10	9,971
Sulfur Recovery	15	2,447
Refrigeration	15	5,272
Subtotal, Process Plant Cost		**22,402**
General Plant Facilities		2,800
Engineering Fees		2,464
Process Contingency		2,909
Project Contingency (10%)		2,520
Total Plant Cost (TPC)		**33,095**
Adjustment for Interest and Inflation		1,526
Total Plant Investment (TPI)		**34,622**
Prepaid Royalties		114
Initial Catalyst and Chemical Inventory		50
Startup Costs		1,204
Spare Parts		165
Working Capital		435
Total Capital Requirement (TCR)		**36,588**

Table 4.16 – Conventional Syngas Cleaning - Other Capital Items

	Quantity		Unit Price, $		Cost, k$
Initial Catalyst Inventory					
Claus catalyst	1,000	lb.	0.5	/lb.	1
ZnO sorbent	9,500	lb.	2	/lb.	19
Initial Chemicals Inventory					
Methanol	100,000	lb.	0.3	/lb.	30
Total Catalyst and Chemical Inventory					**50**
Startup costs					
Plant modifications, 2% of TPI					692
Operating costs					482
Fuel					29
Total Startup Costs					**1,204**
Working capital					
Fuel & Consumables inventory: 60 days supply					295
By-Product inventory: 30 days supply					19
Direct expenses: 30 days					122
Total Working Capital					**$435**

Table 4.17 – Conventional Syngas Cleaning - Annual Operating Cost

Cost Item	Quantity		Unit Price, $		Annual Cost, k$
Fuel (natural gas)	955.2	MBtu/day	4	/MBtu	1,116
Consumable Materials					
Claus catalyst	0.0005	ton/day	1000	/ton	0
ZnO pellets	0.009	ton/day	4000	/ton	11
Methanol	1.752	ton/day	600	/ton	307
Power	131,928	kW-hr/day	0.05	/kW-hr	1,926
Raw water	12	ton/day	0.2	/ton	1
HP-steam	-4065.6	MBtu/day	3.5	/MBtu	(4,155)
IP-steam	-156	MBtu/day	2.25	/MBtu	(102)
LP-steam	7766.4	MBtu/day	1.25	/MBtu	2,835
Cooling water	8359	MBtu/day	0.25	/MBtu	610
Sorbent Disposal Costs	0.01	ton/day	20	/ton	0
Plant Labor					
Operating Labor	2	Men/shift	35	/hr.	612
Supervision & Clerical					342
Maintenance Costs					1,324
Insurance & Local Taxes					662
Royalties					11
Other Operating Costs					114
Total Operating Costs					5,612
By-Product Sulfur Credit	11.4	ton/day	55	/ton	183
Net Annual Operating Costs					5,429

The total, levelized cost-of-syngas-cleaning, based on the tenth year of operation, is shown in Table 4.18. The syngas cleaning cost-unit is dollars per 1000-kg (per 1000-pounds) of raw syngas cleaned. The results are determined for both a "current" dollar basis and a "constant" dollar basis. This syngas cleaning cost is the "bottom-line" and provides the basis for comparison with the novel gas cleaning process. The cost-of-syngas-cleaning is split fairly evenly between capital charges and O&M costs. Variations in the cost of fuel (natural gas), methanol, or power could have significant impact on the cost-of-syngas-cleaning. The current-dollar basis weighs the capital requirements more that the constant-dollar basis does.

Table 4.18 – Conventional Syngas Cleaning - Cost-of-Syngas-Cleaning

	Current-$ basis $/ 1000-kg ($/ 1000-lb)	**Constant-$ basis $/ 1000-kg ($/ 1000-lb)**
Capital charges	11.27 (5.11)	6.61 (3.00)
Fuel costs	2.34 (1.06)	2.03 (0.92)
Operating & maintenance	8.71 (3.95)	7.58 (3.44)
Total	22.32 (10.12)	16.22 (7.37)

4.3 CONVENTIONAL FUEL GAS CLEANING FOR SOFC

The SOFC fuel gas requires slightly less stringent cleaning than the synthesis syngas, but the sectional process diagrams are identical for both of these applications. The SOFC power plant, a combined SOFC-gas turbine cycle, requires a fuel gas having a lower pressure than the syngas pressure for the synthesis application, a pressure of about 811 kPa (8-atmospheres) at the inlet to the SOFC power island. While the SOFC technology for such a large-scale power plant is several years away, the consideration of the coal-based, raw fuel gas cleaning development needs is critical to its eventual commercialization.

4.3.1 Process Alternatives

Two approaches for SOFC fuel gas cleaning are considered and are illustrated in Figure 4.6, a high-pressure (HP) approach and a low-pressure (LP) approach. First, in the HP-SOFC fuel gas cleaning approach, the fuel gas cleaning system is operated at an elevated pressure to reduce fuel gas generation and cleaning equipment sizes and costs. The cleaned fuel gas is then expanded to the required pressure for the SOFC power island. A 4137 kPa (600 psia) raw fuel gas inlet is assumed in the evaluation, the same as was used for the chemical or liquid fuel synthesis application. For the evaluation, the same raw fuel gas feed rate, 81,140 kg/hr (178,880 lb/hr), as was used for the chemical or liquid fuel synthesis application. The only significant change is to incorporate the cost and power generation of an expander-generator expanding the cleaned fuel gas product. The SOFC power island would produce about 148 MWe of power in this case, assuming a power island efficiency of about 60%.

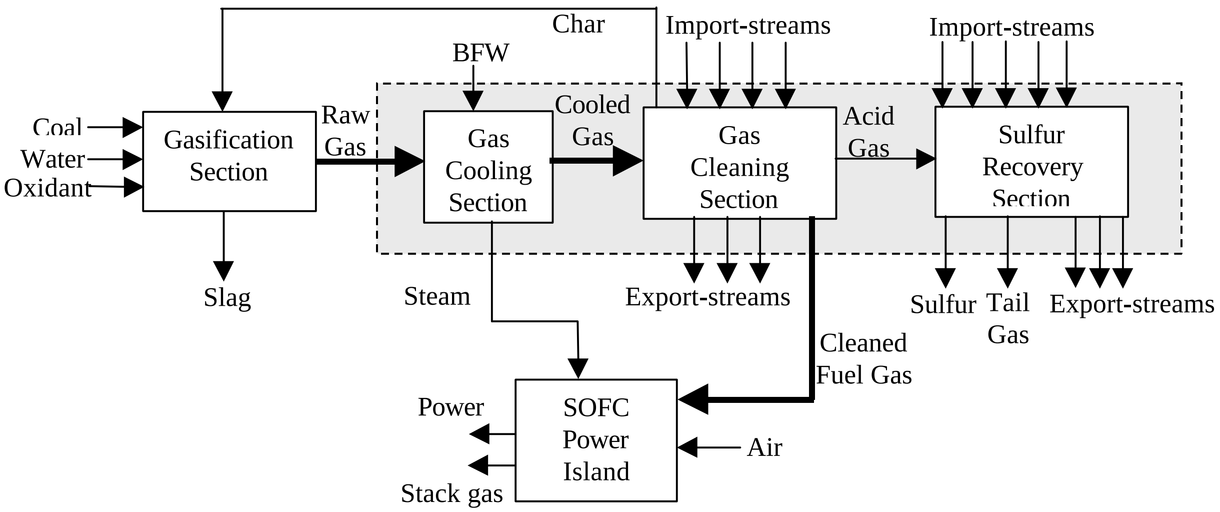
Secondly, in the LP-SOFC fuel gas cleaning approach, the fuel gas cleaning system is operated at a lower pressure, using the same sectional process diagrams as the HP-SOFC application, to provide the fuel gas directly to the SOFC power island at its required pressure. The process evaluation selects a nominal power island generating capacity of 100 MWe in this case, requiring a raw fuel gas rate from the gasifier of about 54,886 (121,000 lb/hr), assuming a power island efficiency of 60% (LHV).

4.3.2 Process Descriptions

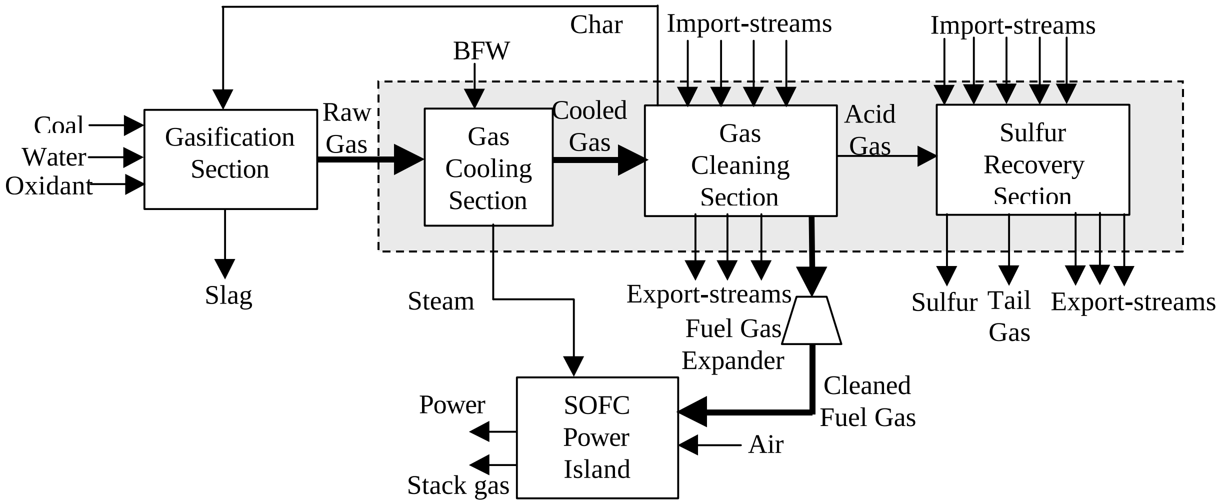
The process descriptions are identical to those presented for conventional syngas cleaning for the chemical synthesis application. The only alteration for the HP-SOFC fuel gas cleaning is that an expansion turbine and electric generator are placed at the high-pressure, cleaned fuel gas, expanding the fuel gas to the SOFC power island inlet pressure, and generating electric power. The LP-SOFC gas cleaning process has a raw fuel gas inlet pressure of 150 psia, but the process configuration is identical to that for the conventional chemical or liquid fuel synthesis gas cleaning process. Of course, the process equipment and stream conditions change significantly in the LP-SOFC application.

4.3.3 Process Material & Energy Balances and Overall Performance

The performance of both the conventional high-pressure (HP) SOFC and the conventional LP-SOFC fuel gas cleaning processes are described in this section. Detailed process stream tabulations are not presented since they are so similar to those presented in Section 4.2 for the conventional syngas cleaning process.



Low-Pressure SOFC Gas Cleaning



High-Pressure SOFC Gas Cleaning

Figure 4.6 – SOFC Fuel Gas Cleaning Alternative Approaches

Conventional HP-SOFC Fuel Gas Cleaning

The process equipment and the stream conditions and compositions for the HP-SOFC conventional gas cleaning process are nearly identical to those listed and described in Section 4.2 for the conventional chemical or liquid fuel synthesis application. A 4.88 MWe gas turbine expander and electric generator are added after the desulfurization section to reduce the cleaned fuel gas pressure down from 3,275 kPa (475 psia) to that needed for the SOFC power island, 811 kPa (117.6 psia).

The performance results are shown in Table 4.19 and are identical to those shown for the chemical synthesis application with conventional syngas cleaning, except for the power generated by the fuel gas expansion.

Table 4.19 – Conventional HP-SOFC Gas Cleaning Process Performance

INPUTS	
Material	**kg/hr (lb/hr)**
Raw syngas	81,140 (178,880)
Raw water	4,536 (1,000)
Air	20,412 (45,000)
Fuel	839 (1,850)
Chemicals	
Methanol	66 (146)
ZnO	0.34 (0.75)
Caustic	0
Total	102,911 (226,877)
Heat Energy	**GJ/hr (MBtu/hr)**
Fuel	42.0 (39.8)
Power Use	**kW**
Pump power	535
Compressor power	355
Refrigeration power	4607
Expansion power	-4881
Total power	616
OUTPUTS	
Material	**kg/hr (lb/hr)**
Cleaned syngas	57,579 (126,938)
Char (dry)	481 (1,061)
Waste water	10,843 (23,904)
Sulfur condensate	442 (974)
Tail gas	33,565 (73,998)
Total	102,910 (226,875)
Heat Energy	**GJ/hr (MBtu/hr)**
Net HP-steam production	178.7 (169.4)
Net IP-stream product	6.9 (6.5)
Net LP-stream product	-341.1 (-323.6)
Net cooling water used	367.5 (348.3)
Sulfur Removal Performance	
Total Process sulfur removal eff (%):	99.24
Sulfur byproduct, kg/hr (lb/hr):	433.2 (955.1)
Sulfur byproduct efficiency (%):	95.84

Significant power is generated from the fuel gas expansion relative to the process power consumption such that the process net power consumption is relatively small. The cleaned fuel gas mass flow rate is about 70% of the raw fuel gas rate. This reduction in mass flow rate reduces the gas expansion power capacity and will also influence the performance of the SOFC power island.

The HP-SOFC cleaned fuel gas conditions and composition are shown in Table 4.20. Note that even though it is not required for the SOFC application, the conventional fuel gas cleaning process reduces the ammonia content and the HCl content in the fuel gas to very low values. The fuel gas composition is identical to that presented for the conventional syngas cleaning application except that the H_2S and COS content is slightly larger for the SOFC fuel gas. The guard beds capture 75.93% of the inlet gas sulfur to that section of the plant, as compared to 85.43% in the chemical or liquid fuel synthesis application. The fuel gas heating value (cold, lower heating value) is also listing in the table. All other import and export streams are identical to those in the conventional syngas cleaning application.

Table 4.20 – Conventional HP-SOFC Fuel Gas Cleaning - Cleaned Fuel Gas

Temperature, °C (°F)	195 (383)
Pressure, kPa (psia)	814 (118)
Mass flow, kg/hr (lb/hr)	57,579.1 (126,938.0)
Heating value, GJ/kg-mole (Btu/lb-mole)	262,095 (112,700)
Composition	
hydrogen (mole%)	41.24
methane (mole%)	0.19
nitrogen (mole%)	0.94
argon (mole%)	0.82
carbon monoxide (mole%)	56.81
carbon dioxide (ppmv)	7.30
water (ppmv)	0.29
hydrogen sulfide (ppbv)	90.8
carbonyl sulfide (ppbv)	7.3
hydrogen chloride (ppbv)	0.0
hydrogen cyanide (ppbv)	91.4
ammonia (ppbv)	0.0
methanol (ppbv)	977

Conventional LP-SOFC Fuel Gas Cleaning

Operation of the conventional fuel gas cleaning process at lower pressures changes the equipment designs and the process material & energy balances for the process. Some of the differences in the behavior at the lower pressure are reflected in Table 4.21, showing the overall performance for the LP-SOFC gas cleaning process.

The major equipment is significantly different at the lower pressures. The column for ammonia and halide removal in the precleaning section (Item 9 in Figure 4.3) is selected as a 9-stage sieve column. It is about 8.5 m (28 ft) tall and 2 m (6.5 ft) in diameter. It operates at about 70% of flooding. It uses stainless-steel materials of construction and its design pressure is 1034 kPa (150 psia).

The absorption tower in the desulfurization section (Item 16 in Figure 4.4) is a thirty-three-stage, bubble-cap tower, having a total height of 23 m (76 ft) and diameter of 2 m (6.4 ft). It operates at about 70% of flooding and has a design pressure of 1034 kPa (150 psia). The stripping column in the desulfurization section (Item 25) uses 22 stages of bubble-cap trays, and is 16.5 m (54 ft) tall and 1.7 m (5.5 ft) in diameter. Its condenser duty is about 1.3 GJ/hr (1.2 MBtu/hr) and its reboiler duty is about 7.2 GJ/hr (6.8 MBtu/hr). The vessel design pressure is 345 kPa (50 psia).

Table 4.21 – Conventional LP-SOFC Gas Cleaning Process Performance

INPUTS	
Material	**kg/hr (lb/hr)**
Raw syngas	54.886 (121,000)
Raw water	118 (260)
Air	8,165 (18,000)
Fuel	302 (665)
Chemicals	
Methanol	19.8 (43.7)
ZnO	0.34 (0.75)
Caustic	0
Total	63,490 (139.969)
Heat Energy	**GJ/hr (MBtu/hr)**
Fuel	15.1 (14.3)
Power Use	**kW**
Pump power	114
Compressor power	143
Refrigeration power	2671
Total power	2928
OUTPUTS	
Material	**kg/hr (lb/hr)**
Cleaned syngas	44,597 (98,319)
Char (dry)	326 (718)
Waste water	6,662 (14,686)
Sulfur condensate	303 (667)
Tail gas	11,604 (25,582)
Total	63,491 (139,972)
Heat Energy	**GJ/hr (MBtu/hr)**
Net HP-steam production	132.3 (125.4)
Net IP-stream product	2.6 (2.5)
Net LP-stream product	-145.7 (-138.1)
Net cooling water used	164.8 (156.2)
Sulfur Removal Performance	
Total Process sulfur removal eff (%):	99.64
Sulfur byproduct, kg/hr (lb/hr):	286.9 (632.6)
Sulfur byproduct efficiency (%):	95.84

The triethanolamine scrubber in the sulfur recovery section (Item 43 in Figure 4.5) is a 31-stage, bubble-cap tray, absorber column. The column is 22 m (72 ft) tall and has a diameter of 2.6 m (8.5 ft). Its design pressure is 50 psia. The triethanolamine solvent is regenerated in a single, 6-stage, bubble-cap tray, stripper column (Item 47). The stripper column is 7.3 m (24 ft) tall and has a diameter of 3.8 m (12.5 ft). The reflux ratio is 0.62. The condenser duty is 0.65 GJ/hr (0.62 MBtu/hr) and the reboiler duty is 129.6 GJ/hr (122.8 MBtu/hr).

Table 4.22 lists the cleaned fuel gas conditions and composition. The cleaned fuel gas composition differs slightly from the cleaned fuel gas composition for the HP-SOFC gas cleaning process, with the differences being greatest for the contaminant species. These differences result from the process lower pressure of operation. The estimated H_2S/COS molar ratios are much different, 1.58 for the LP-SOFC application, and 12.4 for the HP-SOFC application. Also, predicted ammonia, methanol, HCN, and HCl are all higher for the LP-SOFC application. While the cleaned fuel gas flow rate for the HP-SOFC fuel gas cleaning process is 71% of the raw fuel gas flow, it is 81% of the raw fuel gas flow rate for the LP-SOFC fuel gas cleaning process, and this is due to a much reduced CO_2 removal from the raw fuel gas at the lower pressure. For the same reason, the acid gas generated and fed to the sulfur recovery process has a much higher H_2S content (about 10 vol%) than in the HP-SOFC case.

Table 4.22 – Conventional LP-SOFC - Cleaned Fuel Gas

Temperature, °C (°F)	371 (700)
Pressure, kPa (psia)	812.9 (117.9)
Mass flow, kg/hr (lb/hr)	44,597.5 (98,319.1)
Heating value, GJ/kg-mole (Btu/lb-mole)	247,909 (106,600)
Composition	
hydrogen (mole%)	38.99
methane (mole%)	0.19
nitrogen (mole%)	0.89
argon (mole%)	0.79
carbon Monoxide (mole%)	53.78
carbon Dioxide (mole%)	5.36
water (ppmv)	0.02
hydrogen Sulfide (ppbv)	61.3
carbonyl Sulfide (ppbv)	38.7
hydrogen Chloride (ppbv)	253
hydrogen Cyanide (ppbv)	1113
ammonia (ppbv)	983
methanol (ppbv)	11,115

Table 4.23 shows the tail gas conditions and composition. The differences in the tail gas compositions between the HP-SOFC and the LP-SOFC fuel gas cleaning processes are significant. The mass flow rate of tail gas is about 41% of the raw fuel gas mass flow rate in the HP-SOFC application, while it is only about 21% of the raw fuel gas mass flow rate in the LP-SOFC application.

4.3.4 Process Economics

The economics of both the conventional HP-SOFC and the conventional LP-SOFC fuel gas cleaning processes are described in this section.

Table 4.23 – Conventional LP-SOFC Fuel Gas Cleaning - Tail Gas

Temperature, °C (°F)	32 (90)
Pressure, kPa (psia)	120.7 (17.5)
Mass flow, kg/hr (lb/hr)	11,603.9 (25,581.7)
Composition	
nitrogen (mole%)	61.69
oxygen (mole%)	4.15
argon (mole%)	0.82
carbon Dioxide (mole%)	30.08
water (mole%)	3.24
sulfur Dioxide (ppmv)	97
carbon Monoxide (ppmv)	2
hydrogen Cyanide (ppbv)	1
triethanolamine (ppbv)	2

Conventional HP-SOFC Fuel Gas Cleaning

The economic evaluation results for the conventional HP-SOFC fuel gas cleaning process are shown in Tables 4.24 through 4.27. The process section costs shown in Table 4.24 are identical to those for the conventional chemical or liquid fuel synthesis application, except that the cost of the turbine expander and electric generator has been added to the cost of the desulfurization section. This increases the total capital requirement for the fuel gas cleaning system by about 7%. The total capital requirement is equivalent to 264 $/kW (=$39,114,000 / 148,000 kW) based on the power island generating capacity.

Table 4.24 – Conventional HP-SOFC Fuel Gas Cleaning - Capital Requirement

Plant Section	Process Contingency, %	Cost, k$ w/o Contingency
Syngas Cooler Section	10	2,073
Precleaning Section	10	1,643
Desulfurization Section	10	7,038
Sulfur Recovery Section	15	7,063
Refrigeration System	15	6,309
Subtotal, Process Plant Cost		**24,126**
General Plant Facilities		3,016
Engineering		2,654
Fees		
Process Contingency (Using contingencies listed above)		3,081
Project Contingency (10%)		2,714
Total Plant Cost (TPC)		**35,591**
Adjustment for Interest and Inflation		1,641
Total Plant Investment (TPI)		**37,232**
Prepaid Royalties		121
Initial Catalyst and Chemical Inventory		50
Startup Costs		1,094
Spare Parts		178
Working Capital		440

Total Capital Requirement (TCR)	**39,114**

The annual operating cost items, Table 4.25, are identical to those for the conventional chemical or liquid fuel synthesis application, except that the turbine expander and electric generator have greatly reduced the annual power cost for the plant. The result is an annual operating cost that is about 72% of the annual operating cost for the conventional chemical or liquid fuel synthesis application.

The initial catalyst and chemical inventory cost, startup cost and working capital requirement, Table 4.26, are nearly identical to those for the conventional chemical or liquid fuel synthesis application.

Table 4.25 – Conventional HP-SOFC Fuel Gas Cleaning - Annual Operating Costs

Cost Item	Quantity		Unit Price, $		Annual Cost, k$
Fuel (natural gas)	955.2	MBtu/day	4	/MBtu	1,116
Consumable Materials					
Claus catalyst	0.0005	ton/day	1000	/ton	0
ZnO pellets	0.009	ton/day	4000	/ton	11
Methanol	1.752	ton/day	600	/ton	307
Power	14784	kW-hr/day	0.05	/kW-hr	216
Raw water	12	ton/day	0.2	/ton	1
HP-steam	-4065.6	MBtu/day	3.5	/MBtu	(4,155)
IP-steam	-156	MBtu/day	2.25	/MBtu	(102)
LP-steam	7766.4	MBtu/day	1.25	/MBtu	2,835
Cooling water	8359	MBtu/day	0.25	/MBtu	610
Sorbent Disposal Costs	0.01	ton/day	20	/ton	0
Plant Labor					
Operating Labor	2	Men/shift	35	/hr.	612
Supervision & Clerical					354
Maintenance Costs					1,424
Insurance & Local Taxes					712
Royalties					11
Other Operating Costs					118
Total Operating Costs					**4,068**
By-Product Sulfur Credit	11.4	ton/day	55	/ton	183
Net Annual Operating Costs					**3,885**

The levelized cost-of-fuel-gas-cleaning, Table 4.27, shows an almost 14% reduction over the conventional chemical synthesis application. This reduction is due entirely to the reduced power cost in the HP-SOFC conventional fuel gas cleaning process.

Table 4.26 – Conventional HP-SOFC Fuel Gas Cleaning - Other Capital Items

		Quantity		Unit $ Price		Cost, k$
Initial Catalyst Inventory						
	Claus	1,000	lb.	0.5	/lb.	1
	ZnO	9,500	lb.	2	/lb.	19
Initial Chemicals Inventory						
	Methanol	100,000	lb.	0.3	/lb.	30
	Total Catalyst and Chemical Inventory					**50**
Startup costs						
Plant modifications,		2	% TPI			745
Operating costs						320
Fuel						29
	Total Startup Costs					**1,094**
Working capital						
Fuel & Consumables inv,		60	days supply			295
By-Product inventory,		30	days supply			19
Direct expenses,		30	days			126
	Total Working Capital					**440**

Table 4.27 – Conventional HP-SOFC - Cost-of-Fuel-Gas-Cleaning

	Current-$ basis $/1000-kg ($/ 1000-lb)	**Constant-$ basis $/1000-kg ($/ 1000-lb)**
Capital charges	12.06 (5.47)	7.08 (3.21)
Fuel costs	2.34 (1.06)	2.03 (0.92)
Operating & maintenance	5.60 (2.54)	4.87 (2.21)
Total	19.97 (9.06)	13.98 (6.34)

Conventional LP-SOFC Fuel Gas Cleaning

The economic results for the conventional LP-SOFC fuel gas cleaning process are shown in Tables 4.28 through 4.31. Table 4.28 shows that the refrigeration section and the sulfur recovery section have the highest equipment costs, as was the case for the conventional HP-SOFC fuel gas cleaning process.

In the syngas precleaning section, heat exchange equipment accounts for 47% of the equipment cost, and flash drums and absorption towers account for 24%, the two dominant cost classes. In the syngas desulfurization section, heat exchange equipment accounts for 25% of the equipment cost, and flash drums and absorption and stripping towers account for 59%, the two dominant cost classes. In the sulfur recovery section, heat exchange equipment accounts for 35% of the equipment cost, and flash drums and absorption and stripping towers account for 39%, the two dominant cost classes in that section. The total capital requirement is equivalent to 223 $/kW (= $22,304,000 / 100,000 kW) based on the power island generating capacity. This is significantly less than the 264 $/kW estimated for the HP-SOFC application.

Table 4.28 – Conventional LP-SOFC Fuel Gas Cleaning - Capital Requirement

Plant Section	Process Contingency, %	Cost, k$ w/o Contingency
Syngas Cooler Section	10	1,442
Precleaning Section	10	1,243
Desulfurization Section	10	3006
Sulfur Recovery Section	15	3,567
Refrigeration System	15	4,426
Subtotal, Process Plant Cost		**13,684**
General Plant Facilities		1,711
Engineering Fees		1,505
Process Contingency (Using contingencies listed above)		1,768
Project Contingency (10%)		1,539
Total Plant Cost (TPC)		**20,207**
Adjustment for Interest and Inflation		932
Total Plant Investment (TPI)		**21,139**
Prepaid Royalties		68
Initial Catalyst and Chemical Inventory		49
Startup Costs		730
Spare Parts		101
Working Capital		216
Total Capital Requirement (TCR)		**22,304**

Table 4.29 shows an operating cost breakdown for conventional LP-SOFC fuel gas cleaning similar to that for the conventional HP-SOFC fuel gas cleaning process.

Table 4.29 – LP-SOFC Conventional Fuel Gas - Annual Operating Cost

Cost Item	Quantity		Unit Price, $		Annual Cost, k$
Fuel (natural gas)	343.2	MBtu/day	4	/MBtu	401
Consumable Materials					
Claus catalyst	0.0003	ton/day	1000	/ton	0
ZnO pellets	0.009	ton/day	4000	/ton	11
Methanol	0.52	ton/day	600	/ton	91
Power	70296	kW-hr/day	0.05	/kW-hr	1,026
Raw water	3.12	ton/day	0.2	/ton	0
HP-steam	-3009.6	MBtu/day	3.5	/MBtu	(3,076)
IP-steam	-60	MBtu/day	2.25	/MBtu	(39)
LP-steam	3314.4	MBtu/day	1.25	/MBtu	1,210
Cooling water	3748.8	MBtu/day	0.25	/MBtu	274
Sorbent Disposal Costs	0.01	ton/day	20	/ton	0
Plant Labor					
Operating Labor	2	Men/shift	35	/hr.	612
Supervision & Clerical					280
Maintenance Costs					808
Insurance & Local Taxes					404
Royalties					4
Other Operating Costs					93
Total Operating Costs					**3,126**
By-Product Sulfur Credit	7.6	ton/day	55	/ton	122
Net Annual Operating Costs					**3,003**

The conventional LP-SOFC fuel gas cleaning initial catalyst and chemical cost, startup costs, and working capital requirement are shown in Table 4.30.

Table 4.31 shows the breakdown for the levelized cost of fuel gas cleaning for the conventional LP-SOFC fuel gas cleaning process. Its lower capital investment, compared to HP-SOFC fuel gas cleaning, is offset by its higher operating and maintenance cost. The total cost-of-fuel-gas-cleaning is only 1% lower than that for the conventional HP-SOFC fuel gas cleaning process. This relatively small difference implies that either the conventional LP or the HP-SOFC fuel gas cleaning process could be used, depending on the cost impacts on the other sections of the power plant (e.g., the gasifier and coal feed system costs). As in the conventional syngas cleaning process, cost variations in power, fuel and methanol could significantly influence the cost-of-fuel gas-cleaning.

Table 4.30 – Conventional LP-SOFC Fuel Gas Cleaning - Other Capital Items

	Quantity		Unit $ Price		Cost, k$
Initial Catalyst Inventory					
Claus	250	lb.	0.5	/lb.	0
ZnO	9500	lb.	2	/lb.	19
Initial Chemicals Inventory					
Methanol	100,000	lb.	0.3	/lb.	30
Total Catalyst and Chemical Inventory					**49**
Startup costs					
Plant modifications,	2	% TPI			423
Operating costs					297
Fuel					10
Total Startup Costs					**730**
Working capital					
Fuel & Consumables inv,	60	days supply			103
By-Product inventory,	30	days supply			13
Direct expenses,	30	days			100
Total Working Capital					**216**

Table 4.31 – Conventional LP-SOFC - Cost-of-Fuel-Gas-Cleaning

	Current-$ basis $/1000-kg ($/ 1000-lb)	**Constant-$ basis $/1000-kg ($/ 1000-lb)**
Capital charges	10.16 (4.61)	5.97 (2.71)
Fuel costs	1.23 (0.56)	1.08 (0.49)
Operating & maintenance	7.76 (3.52)	6.76 (3.07)
Total	19.16 (8.69)	13.82 (6.27)

4.4 NOVEL SYNGAS CLEANING FOR SYNTHESIS APPLICATIONS

The Ultra-Clean gas polishing process is a conceptual process, untested except at laboratory scale. The major equipment components of the Ultra-Clean gas polishing process, barrier filters and sorbent handling and feeding equipment, have reached a mature status and have been demonstrated at large scales, but the use of barrier filters as chemical reactors has seen only limited testing (Newby et al., 1995). Candidate sorbents have been identified, but their contaminant removal performance and rates of consumption in the Ultra-Clean process, and their costs are uncertain. Three Ultra-Clean process configurations have been conceived, providing differing levels of contaminant removal performance potential. The objective of this section is to estimate the performance and cost of the three configurations. The cost sensitivity of these three process configurations is also determined.

4.4.1 Process Alternatives

The novel syngas cleaning process overall configuration is illustrated in Figure 4.7. The novel syngas cleaning process consists of four major process sections:

- syngas cooling
- bulk desulfurization,
- sulfur recovery,
- Ultra-Clean gas polishing.

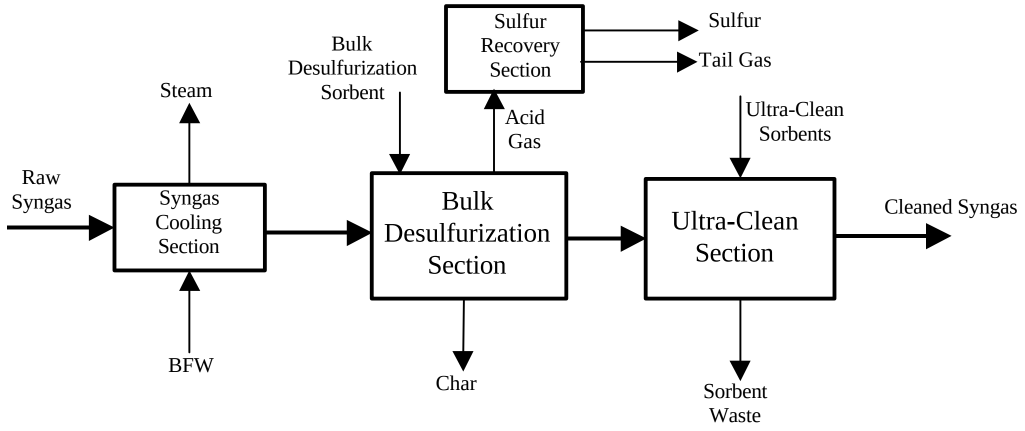


Figure 4.7 – Novel Syngas Cleaning Process Overall Configuration

The syngas cooling equipment reduces the raw syngas temperature to the temperature of the bulk desulfurization section and generates HP-steam, representing a fully commercial technology for use with the Texaco gasifier. Process design configurations have been proposed in this evaluation for the bulk desulfurization section and the sulfur recovery section based on information available on commercial and developing technologies. Bulk desulfurization is a developing process technology under DOE sponsorship for many years and is nearing demonstration status, although it still has several development issues (Parsons Power Group, 1997). A variety of bulk desulfurization sorbents can be used over a range of temperatures from 370 to 540°C (700 to 1000°F), and bulk sorbent regeneration is an economic necessity. Bulk sorbent attrition and deactivation represent major issues (Abbasian et al., 1997). Sulfur recovery for this application is based on commercial configurations, but is a more complex process than is typical of sulfur recovery because the acid gas is a low-concentration SO_2 gas. The Ultra-Clean gas polishing section is the key conceptual section in the novel syngas cleaning process, and is the main subject of the evaluation.

Three alternatives are considered for the Ultra-Clean section of the novel syngas cleaning process because of uncertainties in performance and cost potential. These alternatives are illustrated in Figures 4.8 through 4.10. The Base Ultra-Clean section for syngas cleaning, Figure 4.8, consists of two stages of barrier filter-reactors. They are separated by a syngas cooler for Stage II temperature control. The Stage I temperature is selected as the highest temperature for achieving total sulfur and HCl in the 1 ppmv concentration range using the selected Stage I sorbents. The Stage II temperature is reduced to an optimum for HCl and sulfur removal to the final cleaning requirement with the selected sorbents. The Stage II temperature selection requires a tradeoff between reaction kinetics and thermodynamic limitations.

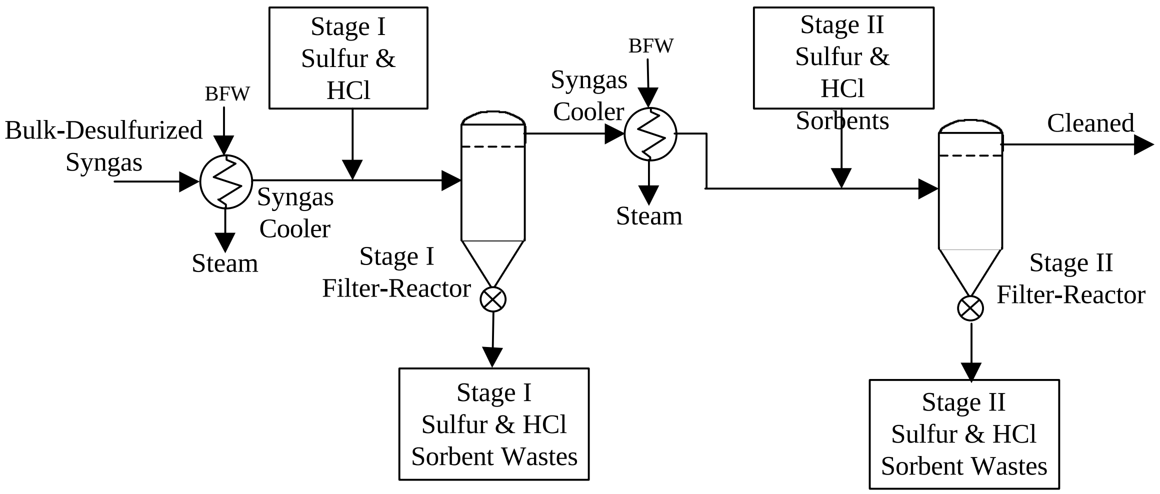


Figure 4.8 – Base Ultra-Clean Section for Syngas Polishing

There are three possibilities for dealing with the sorbent wastes streams: 1) they might be disposed of in a landfill, 2) they might be recycled to the gasifier to be incorporated into the plant slag, or 3) they might be regenerated for reuse in the process. Specifically, the waste sorbents collected in Stage II can be disposed of in a landfill since they represent a very small mass flow of waste and their cost of purchase and disposal should be very small. They also can be recycled to the gasifier to be incorporated into the gasifier slag since their content of sulfur and HCl is so small as to have no impact on the raw syngas contaminant contents if the contaminants are released back into the syngas in the gasifier. Regeneration of the Stage II sorbents would not be appropriate.

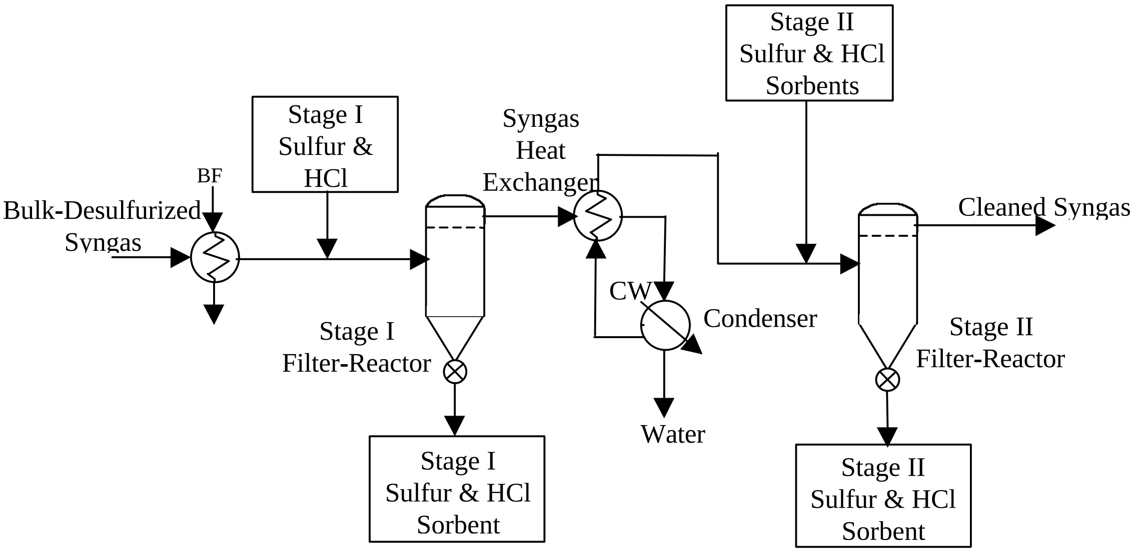


Figure 4.9 – Ultra-Clean Section with Drying for Syngas Polishing

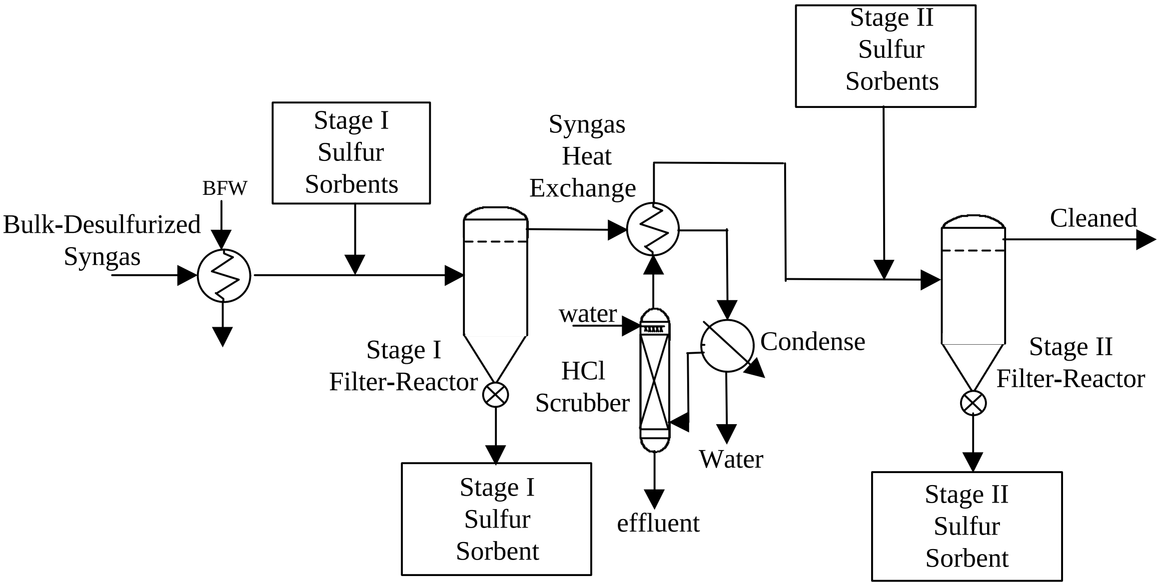


Figure 4.10 – Ultra-Clean Section with HCl Scrubbing for Syngas Polishing

Likewise, the Stage I sorbent waste can be disposed in a landfill, but recycling the waste to the gasifier would only be possible if the HCl sorbent could be separated from the sulfur sorbent, since the HCl sorbent would release a very large HCl content back into the raw syngas. The same is true of cycling the Stage I sorbent waste to the bulk desulfurization section regenerator for regeneration -- this can only be done if the HCl sorbent is first separated from the sulfur sorbent.

Since there is significant water vapor in the bulk desulfurized syngas, and this water vapor may hinder the performance of the Stage II syngas cleaning, the first alternative, Figure 4.9, dries the syngas after Stage I by condensation. The Stage II temperature may then be set at a higher level for optimum performance in the dry syngas and/or the rate of Stage II sorbent consumption might be reduced. This configuration does not greatly modify the nature of the waste sorbents or their disposition from the Base Ultra-Clean configuration.

The second alternative, Figure 4.10, accomplishes both syngas drying and HCl removal by syngas cooling and water scrubbing of HCl following Stage I. In this alternative, no HCl sorbent is required in either stage, greatly simplifying the sorbent feed equipment and providing the potential for simplified sulfur sorbent reuse. Here, the Stage I sulfur sorbent can be directly recycled to the bulk desulfurizer section regenerator, or can be disposed of in the gasifier. The optimum Stage II temperature is expected to be the same as in the first process alternative. In this alternative, other contaminants such as ammonia might also be effectively removed in the water scrubber, if it is designed for this duty. This alternative, of course, generates a particulate-free, waste water stream for treatment in the plant. It would be possible to include mercury control in the Stage II zone by incorporating appropriate sorbent injection or fixed bed system.

All three of these alternative Ultra-Clean syngas cleaning sections are considered for the chemical or liquid fuel synthesis application to identify their relative benefits and issues.

4.4.2 Process Descriptions

Preliminary evaluation has indicated that there might be significant capital cost advantage for the novel syngas cleaning process over the conventional syngas cleaning process. This allows the more expensive, but more effective, barrier filter technology to be applied to separate char from the syngas prior to the bulk desulfurization process, and even to separate the two stages in the Ultra-Clean gas polishing section so that the sorbents for each stage can be segregated. This overall process principle is followed in the description below, understanding that it will make the novel syngas cleaning process more expensive but more effective than the cheaper option of using a cyclone before the bulk desulfurization process, and a moving bed filter-reactor in Stage I of the Ultra-Clean section.

The specific assumptions made for the novel gas cleaning bulk desulfurizer section and Ultra-Clean gas polishing section are listed in Table 4.32. The Table indicates the selected stage sorbents and the expected maximum sorbent feed rates needed for the Ultra-Clean section. There is significant uncertainty as to the sorbent feed rates that will be required in Stages I and II. The highest-temperature sulfur sorbent type, zinc-based, is selected for the evaluation. As Table 4.32 indicates, it is expected that some bulk desulfurization sorbent, a zinc titanate material, will be lost from the transport desulfurizer and the entrained regenerator by attrition, decrepitation, and elutriation, this loss mechanism being faster than sorbent deactivation mechanisms. The assumed bulk desulfurization loss rate is about 0.03% of the desulfurizer cyclone inlet solids mass rate. This loss factor is later treated as an economic parameter.

There is no data on the source and characteristics of the sorbent elutriated from the transport desulfurizer and entrained regenerator. It is assumed in the evaluation that this elutriated sorbent has a mass-mean particle size of about 10 microns, and has the same sulfur content as the bulk sorbent streams exiting the transport desulfurizer and the entrained regenerator. In this case, this elutriated sorbent might be sufficient in quantity to provide all of the Ultra-Clean section Stage I desulfurization needs, with an unreacted ZnO-to-sulfur molar ratio of about 2.8. On-the-other-hand, the elutriated sorbent could be highly sulfided and unreactive material. Because of this great uncertainty, a Stage I, zinc titanate sorbent feed is also applied, adding a Zn-to-sulfur molar feed ratio of 2.0 to bring the total ZnO/S molar ratio going to the Stage I barrier filter-reactor up to 4.8.

Trona is the selected Stage I HCl sorbent and is assumed to be fed at a sodium-to-HCl molar ratio of about 4.0 to meet the Stage I HCl removal target. The Stage II temperature is reduced to 288°C (550°F), and a zinc-based sorbent developed by GTI, G-72E, is used for Stage II desulfurization. In the two, dry syngas process alternatives, the Stage II temperature is assumed to be higher, at 348°C (650°F), providing better reaction kinetics. The Stage II HCl sorbent is a sodium oxide-based sorbent developed by GTI, G-92C, having less than 7 wt% sodium content, and fed at a sodium-to-HCl mole ratio of about 5.0. These are expected to be conservatively-high estimates of the sorbent feed rates.

Table 4.32 – Novel Gas Cleaning Sorbent Conditions for Syngas Cleaning

Bulk Desulfurizer Section	
Bulk sorbent type	zinc titanate (Zn/Ti mole ratio 1.5)
Desulfurizer contactor type	transport reactor
Desulfurizer gas inlet temperature	510°C (950°F)
Regenerator contactor type	entrained bed
Regenerator temperature	732°C (1350°F)
Bulk sorbent makeup rate	Zn/S molar ratio 0.024 (100 lb/hr in chemical synthesis case)
Mechanism of bulk sorbent loss	Attrition and elutriation
Ultra-Clean Section	
Stage I temperature	499°C (930°F)
Stage I sulfur sorbent type	zinc titanate (Zn/Ti mole ratio 1.5)
Stage I sulfur sorbent feed rate	ZnO/S molar ratio 2.8 from elutriated sorbent; fresh sorbent fed to increase ZnO/S to 4.8
Stage I HCl sorbent type	Trona ($Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O$)
Stage I HCl sorbent feed rate	Na/HCl molar ratio 4.0
Stage I sorbents size distribution	-325 mesh, mass-mean diameter of 20 μm
Stage II temperature	288°C (550°F) - 343°C (650°F) in dry syngas
Stage II sulfur sorbent type	G-72E (70 wt% Zn)
Stage II sulfur sorbent feed rate	Zn/S molar ratio 5.0
Stage II HCl sorbent type	G-92C (6.4 wt% Na)
Stage II HCl sorbent feed rate	Na/HCl molar ratio 5.0
Stage II sorbents size distribution	-325 mesh, mass-mean diameter of 20 μm

Syngas Cooling and Bulk Desulfurization Sections

The integrated syngas cooler and bulk desulfurizer sections are shown in Figure 4.11. Major equipment components are identified by circled, bold numbers, and process stream are identified by boxed numbers. The syngas cooler (items 1, 2, 3 and 4) cools the raw syngas down to the temperature of the bulk desulfurizer, about 510°C (950°F) in the evaluation case. The description of the syngas cooler equipment is the same as that provided for the conventional syngas cleaning process (Section 4.2.1). Because the syngas cooling temperature in the novel syngas cleaning process is higher than it is in the conventional process, less high-pressure steam is generated than in the conventional process.

The objective of the bulk desulfurization section is to reduce the syngas sulfur content down to 20 to 50 ppmv and to remove most of the char particulate from the syngas. In the evaluation case, the char is completely removed by a primary barrier filter and the total sulfur content is reduced to 25 ppmv. Information on the design of the bulk desulfurizer has been taken from many sources (e.g., Sierra Pacific Power Company, 1994).

The cooled, raw syngas (Stream 4) enters the primary barrier filter (Item 5) where all of the char in the syngas is removed. This refractory-lined barrier filter vessel holds 240 standard ceramic filter candles, each 1.5 m in length and 60 mm in diameter, arranged on three parallel clusters. Each cluster has 2 plenums and each plenum is independently pulse cleaned. The filter operating face velocity is 0.0305 m/s (6.0 ft/min) and the inlet char loading is about 6,000 ppmw. The filter pressure vessel has an outer diameter of 2.4 m (7.8 ft) and an overall height of 11 m (36 ft). Its total weight with the internals installed is about 68,000 kg (75 tons). The primary barrier filter is pulse cleaned at a nominal frequency of about 2.3 times per hour and uses about 54 kg/hr (120 lb/hr) of pulse gas (nitrogen). The barrier filter system includes a water-cooled screw conveyor to smoothly withdraw the char from the filter hopper, a pulse gas compressor and a pulse gas control skid that provides pulse gas to periodically clean the char from the filter elements. The pulse gas, and all other inert gas utilized in the syngas cleaning process, is assumed to be nitrogen provided by the plant at a pressure of 1379 kPa (200 psia). The captured char is cooled (Item 6) and is pneumatically transported back to the gasifier coal feed system (Stream 6).

It should be noted that the Stage I HCl removal could be completed within the primary barrier filter by injecting the HCl sorbent, trona, into the primary barrier filter. This would 1) protect the bulk desulfurization sorbent from HCl interactions, if this is a concern, and 2) separate the Stage I HCl sorbent from the Stage I sulfur sorbent. The separation would allow the Stage I waste sulfur sorbent to be either regenerated in the bulk desulfurizer regenerator, or transported to the gasifier to be disposed of in the gasifier slag. Alternatively, the Stage I HCl sorbent could be injected directly into the transport desulfurizer to remove HCl within the desulfurizer and protect the zinc-based sorbent.

The particle-free syngas (Steam 5) enters the transport desulfurizer (Item 7) where it is contacted by circulating zinc-based sorbent particles, and regenerated sorbent particles (Stream 10) from the entrained regenerator reactor (Item 8). Well known chemical reactors occur between the gaseous sulfur species (H_2S and COS) and the sorbent particles, sulfiding the sorbent zinc constituent. Fluffing gas and stripping gas (Stream 7), assumed to be nitrogen provided by the plant, are distributed to several locations in the transport desulfurizer and regenerator. The refractory-lined transport desulfurizer operates at a nominal velocity of 9 m/s (30 ft/s). It has an outer diameter of about 0.76 m (2.5 ft) and is about 18 m (60 ft) tall, including its integral cyclone section. The entrained regenerator is a refractory-lined pressure vessel operating at about 6 m/s (20 ft/s) velocity. Its outer diameter is about 0.46 m (1.5 ft) and its overall height is about 10.7 m (35 ft). An inert gas compressor system is provided with this process section that compresses all of the inert gas needed in the novel syngas cleaning process up to 4482 kPa (650 psia). The desulfurized syngas (Stream 8) exits the bulk desulfurization section at about 547°C (1017°F).

Sorbent is circulated between the transport desulfurizer and the entrained regenerator (Streams 9 and 10) through refractory-lined ducts at about 23,150 kg/hr (51,000 lb/hr), while the estimated internal solids circulation rate in the transport desulfurizer is about 13,300 kg/hr (294,000 lb/hr). Air (Stream 11) is compressed (Item 9) and preheated in a fired heater (Item 10) to 593°C (1100°F). The heated air (Stream 12) enters the entrained regenerator and reacts with the sulfided sorbent, converting the zinc sulfide back to zinc oxide and releasing the sulfur primarily as SO_2. The SO_2-rich regenerator gas (Stream 13) contains about 14.8 vol% SO_2, less than 0.1 vol% O_2, and entrained sorbent particles.

The regenerator offgas passes through a barrier filter (Item 11) at a temperature of 736°C (1357°F) to capture all of the entrained sorbent particles and exits from the bulk desulfurization section. The regenerator barrier filter pulse gas control skid utilizes pulse gas provided by the primary barrier filter compressor (Item 5). A small portion of the bulk-desulfurized syngas (about 1.5%) is drawn off (Steam 14), and is cleaned of particulate in a barrier filter (Item 12) to be used as a reducing gas for the sulfur recovery process section. The Item 12, desulfurizer barrier filter shares the Item 11 pulse control skid. The captured sorbent particles from the two barrier filters (Items 11 and 12) are combined and pressurized (part of Item 12) to be pneumatically fed and combined with the bulk-desulfurized syngas (Stream 15). Both of these barrier filters are very small, each holding only 8 standard ceramic candles. They are both refractory-lined pressure vessels, about 0.6 m (2 ft) in diameter and 3.7 m (12 ft) tall. The regenerator barrier filter operates at about 0.028 m/s (5.5 ft/min) face velocity and is pulse cleaned once every 12 minutes. The desulfurizer barrier filter operates at about 0.015 m/s (3 ft/min) face velocity and is pulse cleaned about once every 2 hours.

It is assumed that most of the bulk sulfur sorbent losses occur from attrition of the sorbent particles, and a fresh sorbent feed system (Item 13) is used to replace the lost sorbent (Steam 16). The base case makeup sorbent rate is 45 kg/hr (100 lb/hr). Since the sorbent is relatively expensive and its rate of loss is uncertain, it is later treated as an economic parameter to investigate its impact.

Also noted on the diagram are locations of streams for cooling water, fluffing gas, pulse gas, pressurization gas, stripping gas, transport gas, and vent gas. Estimates of each of these flows has been made and included in the process evaluation.

Sulfur Recovery Section

While it would be much simpler and more economical for the regenerator acid gas to be converted to sulfuric acid rather than elemental sulfur, it was decided as part of the evaluation basis that the conventional and novel gas cleaning processes should both generate sulfur by-product in the same form to make their comparisons more direct. Figure 4.12 shows the process flow diagram for the novel syngas cleaning sulfur recovery process.

The same general configuration and technologies are applied for the novel syngas cleaning sulfur recovery process as was used for the conventional case, but there are four significant differences in the sulfur recovery process configuration. First, the novel sulfur recovery process requires a thermal reducing reactor (Item 14) to combine reducing gas (Stream 14) with the regenerator acid gas (Stream 13) to convert it to a primarily H_2S gas (Stream 17). Secondly, the regenerator acid gas is at a high pressure condition and it is expanded (Item 15) to reduce its pressure to the sulfur recovery pressure and to generate power. Thirdly, the acid gas contains significant water vapor compared to the acid gas in the conventional process, and water is condensed from the acid gas at several points (Items 18, 22, and 27) to improve the Claus reactor performance. Finally, the acid gas in the novel gas cleaning case is warm and the amount of HP-steam heating needed is reduced compared to the conventional case, sulfur recovery process. The fact that the sulfur content of the acid gas in the novel syngas cleaning case is much higher than it is in the conventional syngas cleaning case is an advantage for the novel gas cleaning process.

Base Ultra-Clean Section

Figure 4.13 shows the Base Ultra-Clean syngas polishing section process flow diagram. The bulk-desulfurized syngas (Stream 8) is cooled (Item 44) to the Stage I temperature of 499°C (930°F). Here it is mixed with Stage I sulfur and HCl sorbents (Streams 46 and 47), pressurized and fed in parallel systems (Items 45 and 46). In the Base case evaluation, it is assumed that the primary sulfur sorbent material contained in the bulk-desulfurized syngas might be sufficient for effective Stage I sulfur removal, but fresh Stage I, zinc-based sorbent is also fed because of the uncertainty in the reactivity of the elutriated sorbent. The HCl sorbent is Trona, a cheap, highly available sodium-based sorbent.

The syngas and entrained sorbents enter the Stage I barrier filter-reactor (Item 47) where they are well mixed and circulated within the vessel for almost 5 seconds before the sorbent particles uniformly deposit on the barrier filter elements. The syngas passes through the sorbent filter cake and is effectively desulfurized down to about the 1 ppmv level and dechlorinated down to about the 2.5 ppmv level. The gas-sorbent average contact time in the Stage I filter cake is about 0.25 seconds and the sorbent will reside in the filter cake for about one-half hour before being removed by pulse cleaning. Significant entrained sorbent-gas reaction is expected, as well as even greater reaction conversion within the filter cake. The total, unreacted-sorbent, zinc-to-sulfur molar feed ratio is about 4.8 in Stage I, consisting of elutriated bulk-desulfurization sorbent and fresh sorbent fed to Stage I. The sodium-to-HCl molar ratio in Stage I is about 4.0.

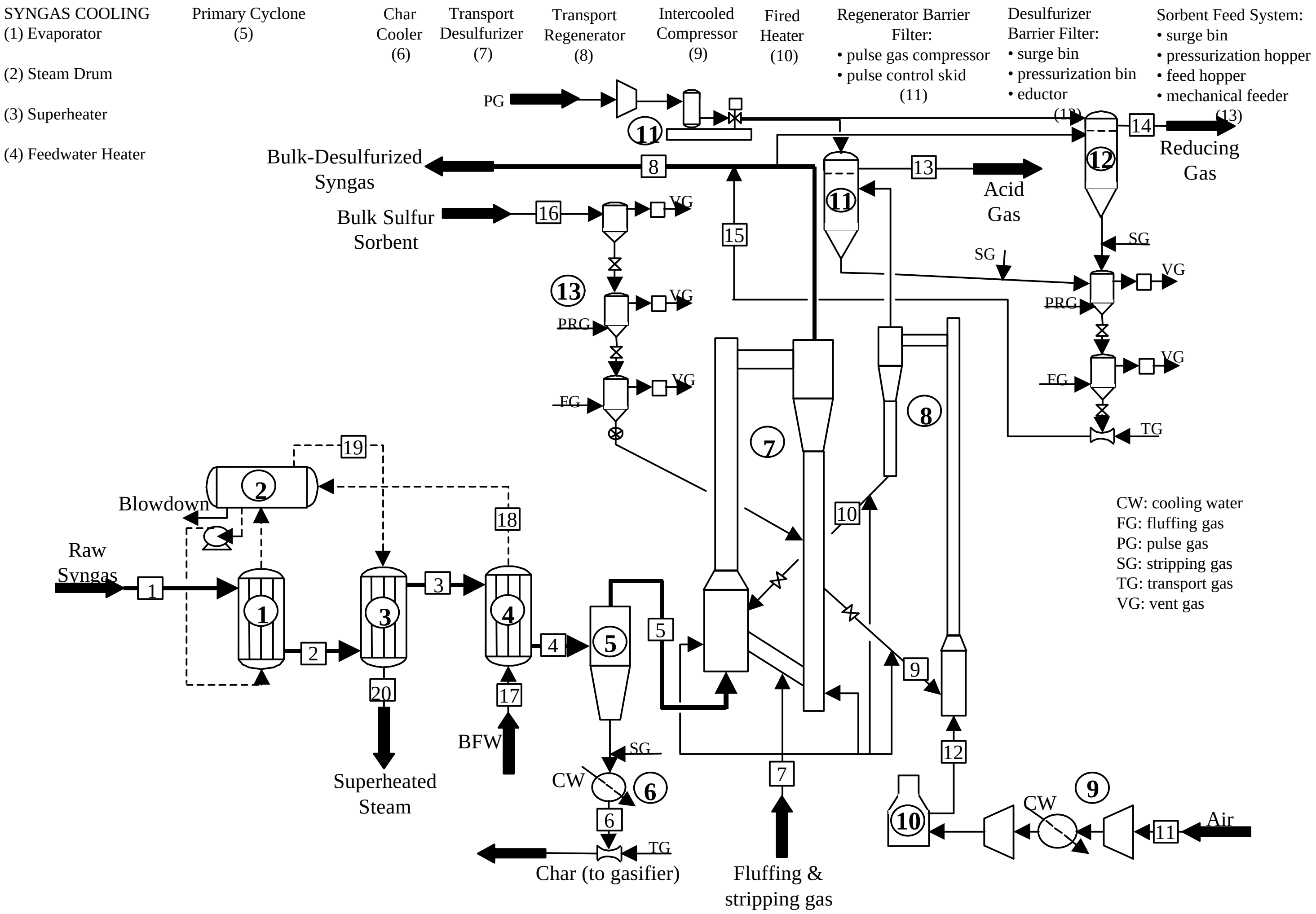


Figure 4.11 - Syngas Cooler and Bulk Desulfurization Sections

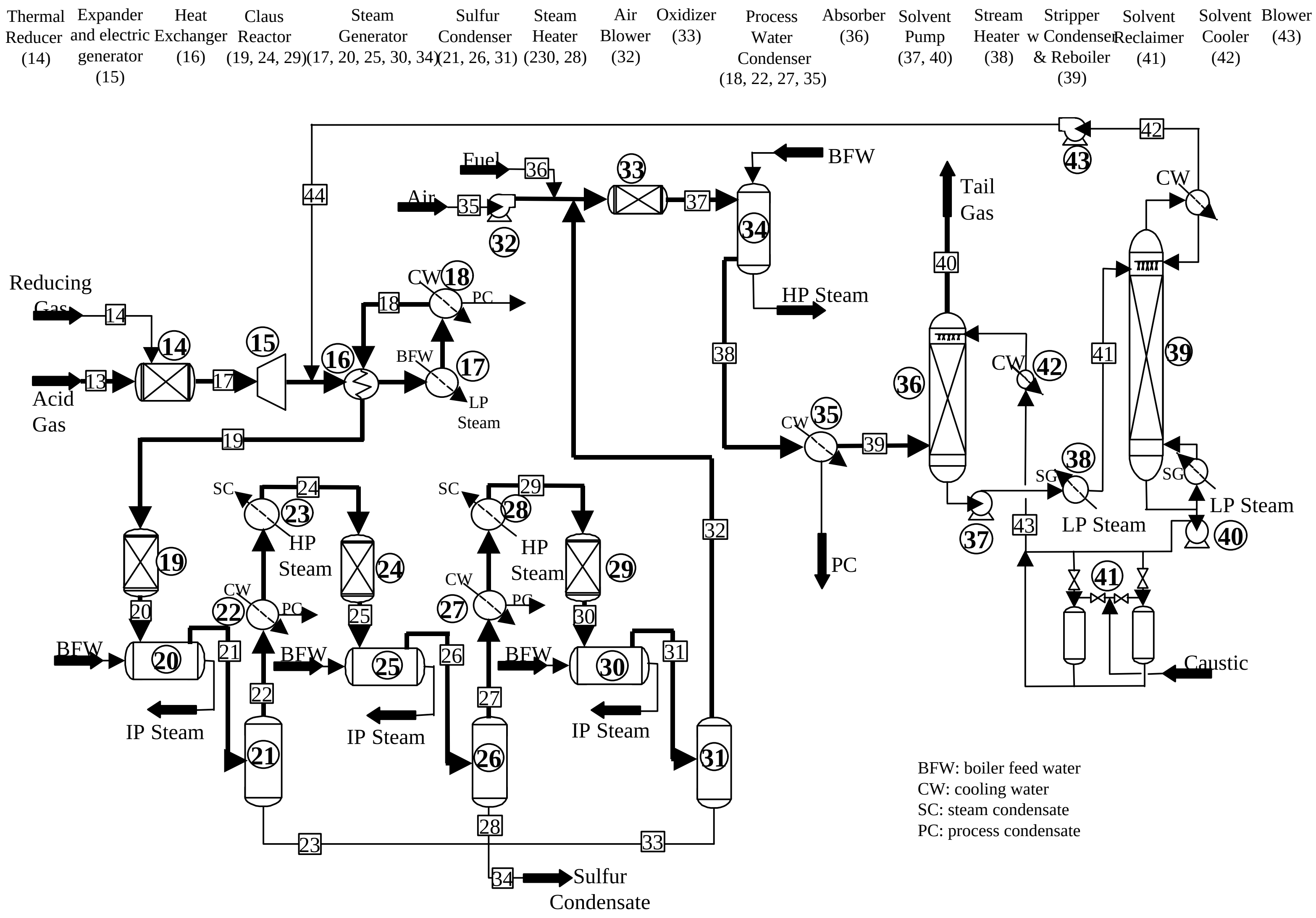


Figure 4.12 - Novel Syngas Cleaning - Sulfur Recovery Section

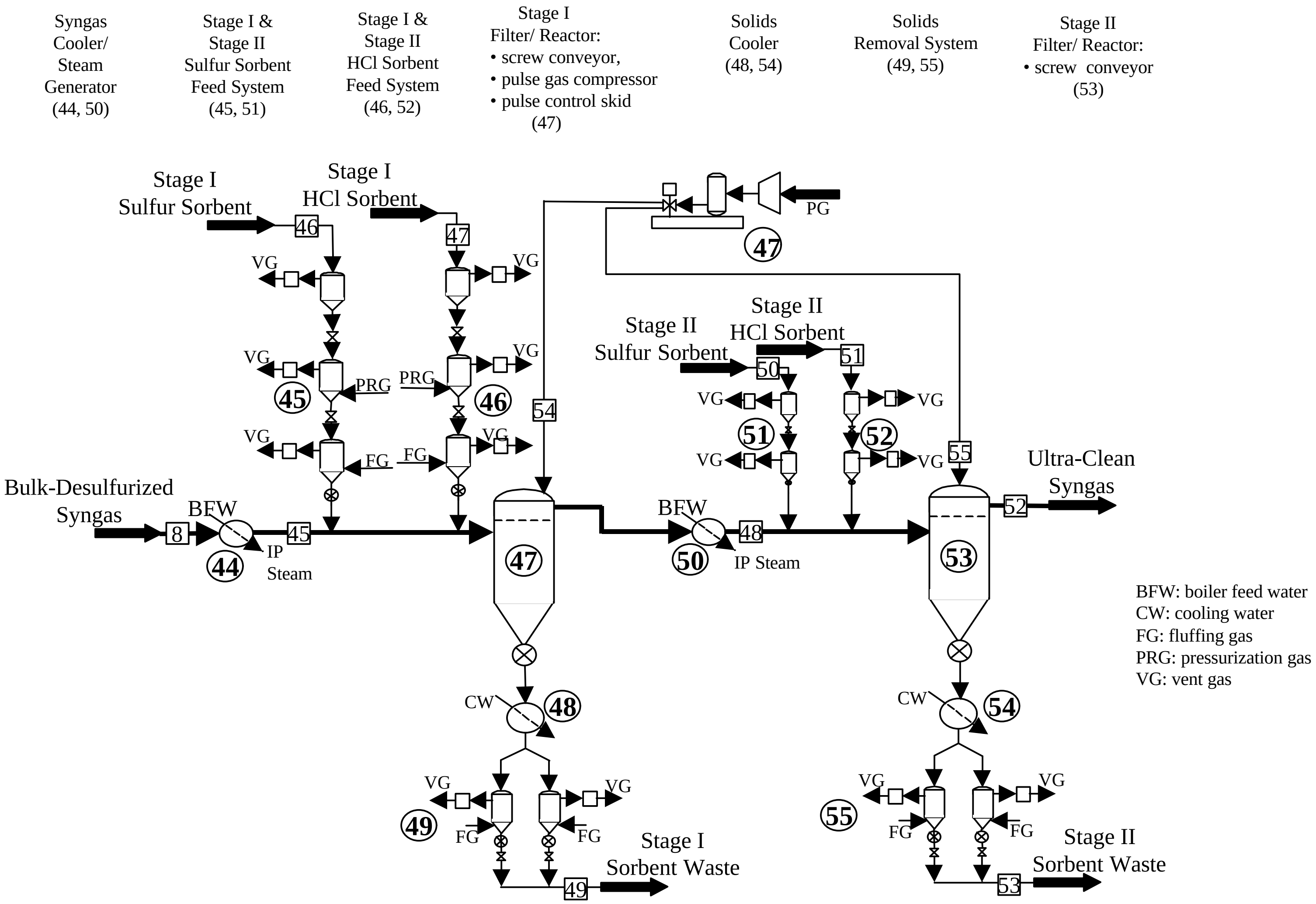


Figure 4.13 - Novel Syngas Cleaning - Ultra-Clean Base Section

The Stage I barrier filter-reactor includes a screw conveyor, pulse gas compressor and pulse gas control skid. The Stage I barrier filter is a refractory-lined vessel holding 187 standard ceramic candles in a single cluster of 4 to 8 plenums. It operates at a face velocity of 0.4 m/s (8.1 ft/min) and the inlet sorbent loading is about 7,240 ppmw. It is pulse cleaned every 30 minutes, with a pulse gas consumption of about 23 kg/hr (50 lb/hr). The pressure vessel is 1.8 m (5.8 ft) in diameter, 13.7 m (45 ft) tall, and weighs about 56,000 kg (62 tons) with the internals installed.

The Stage I sorbent waste is cooled (Item 48) and depressurized (Item 49) and transported to a storage vessel. The Stage I sulfur sorbent waste might be injected into the bulk desulfurizer regenerator if the sulfur sorbent can be separated from the HCl sorbent waste, it might be injected into the gasifier to be incorporated into the plant slag, or it might be disposed of by a waste contractor. The cost of waste disposal is included in the process economic analysis, and other feasible options could result in cost reductions.

The Stage I syngas is cooled (Item 50) to the Stage II temperature, 288°C (550°F) in the Base case. It is mixed with Stage II sorbents (Items 51 and 52), these sorbents again being zinc-based and sodium-based, but differing in their components, manufacturing and possibly particle size from the Stage I sorbents. They are fed at zinc-to-sulfur molar feed ratios and sodium-to-HCl molar ratios of about 5.0, conservatively-high values because of the uncertainty in the sorbent feed requirements. The syngas and entrained sorbents enter the Stage II barrier filter-reactor (Item 53) where they are well mixed and circulated within the vessel for almost 6 seconds before the sorbent particles uniformly deposit on the barrier filter elements. The syngas passes through the sorbent filter cake and is effectively desulfurized and dechlorinated down to about the required levels. The gas-sorbent average contact time in the Stage I filter cake is about 0.35 seconds and the sorbent particles will reside on the filter cake for 10 to 20 hours before pulse cleaning. The pulse cleaning equipment is shared with the Stage I barrier filter-reactor (Item 47).

The Stage II barrier filter is a refractory-lined vessel holding 155 standard ceramic candles in a single cluster of 4 to 8 plenums. It operates at a face velocity of 0.038 m/s (7.4 ft/min) and the inlet sorbent loading is about 265 ppmw. It is pulse cleaned every 10 to 20 hours, with an average pulse gas consumption of about 0.5 kg/hr (1 lb/hr). The pressure vessel is 1.7 m (5.6 ft) in diameter, 13.7 m (45 ft) tall, and weighs about 50,000 kg (55 tons) with the internals installed.

Since the Stage II sorbent feed rates are assumed to be in high excess, the sorbent waste removed from the barrier filter-reactor could be boosted in pressure and recirculated to the Stage II filter-reactor inlet for added conversion and improved performance. Stage II waste sorbents (Stream 53) are cooled (Item 54) and depressurized (Item 55). They may be fed to the gasifier for incorporation into the plant slag, or disposed of by a contract vendor. The final syngas product (Stream 52) is withdrawn for further processing in the chemical synthesis plant.

Both of the barrier filters in the Ultra-Clean system are pulse cleaned on a "uniform" basis, meaning that individual plenums are pulse cleaned separately on a uniform schedule rather than cleaning all of the filter plenums over a short time period. This results in a smaller difference between the trigger and baseline pressure drop and a much smaller difference in gas flow between the just-cleaned plenum and the other uncleaned plenums.

For example, in the evaluation case designed with 4 plenums, a Stage I barrier filter plenum would be pulse cleaned every 7.5 minutes, and the average trigger pressure drop would be about 49.6 kPa (7.2 psi) with an average baseline pressure drop of 41.4 kPa (6.0 psi). The Stage I barrier filter-reactor behavior is illustrated in Figures 4.14 through 4.16, showing the transient pressure drop profile, the individual plenum face velocity variation, and the individual plenum filter cake thickness variation with time, respectively.

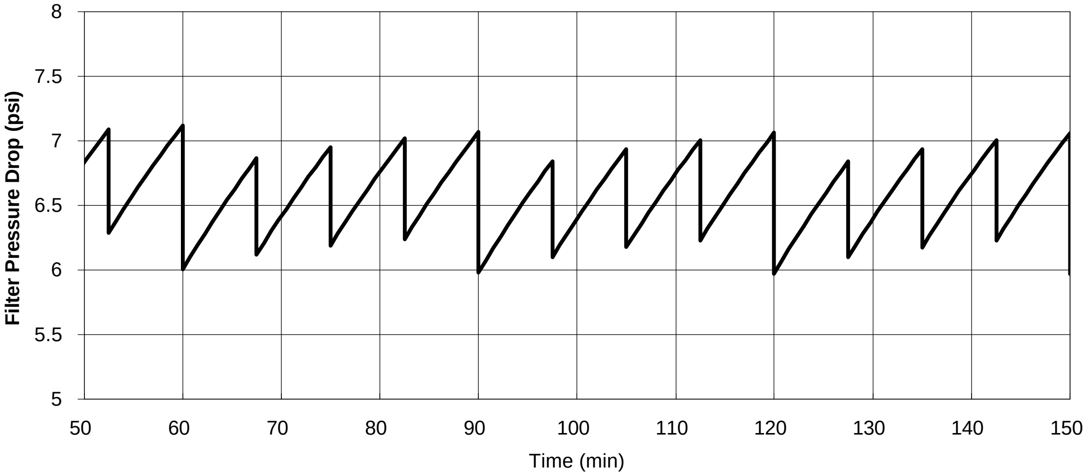


Figure 4.14 - Stage I Barrier Filter-Reactor Pressure Drop Transient Profile

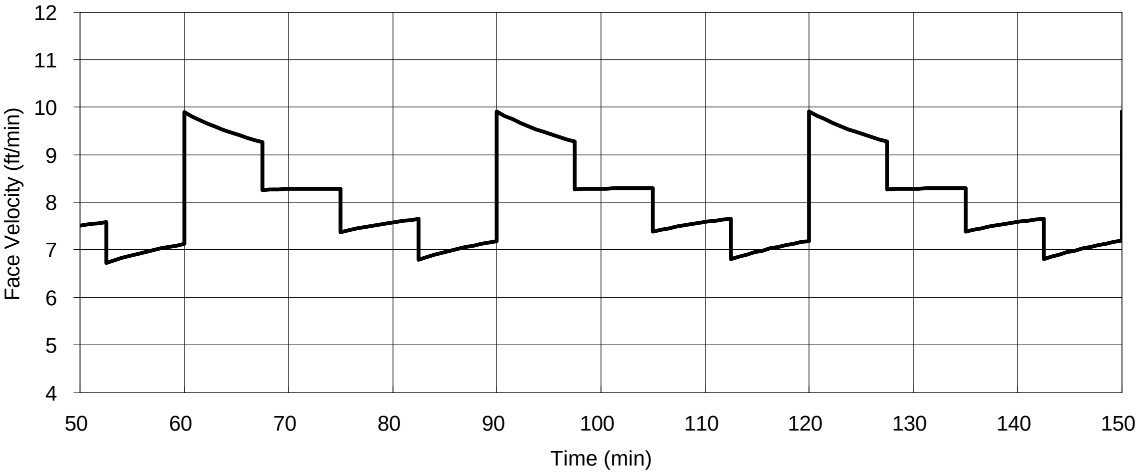


Figure 4.15 - Stage I Barrier Filter-Reactor Plenum Face Velocity

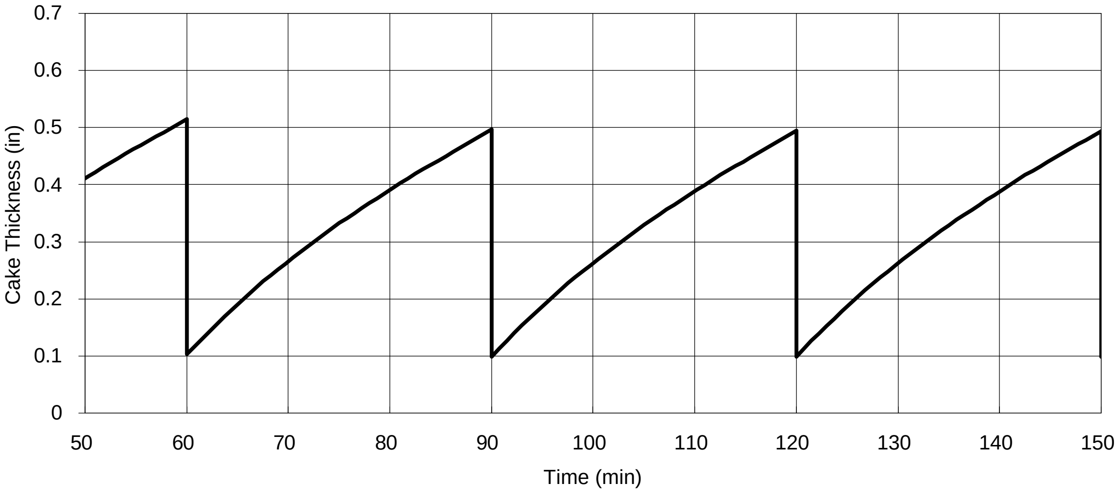


Figure 4.16 - Stage I Barrier Filter-Reactor Plenum Filter Cake Thickness

This set of pulse cleaning conditions result in a maximum increased gas flow through the just-cleaned plenum of only about 20% above the average flow, which continuously decreases until the next plenum is again pulse cleaned. The overall loss in cleaning capacity during a pulse event would be negligible because 1) there is a degree of entrained sorbent-gas cleaning that always occurs, and 2) the resulting higher gas rate to the just-cleaned filter plenum is accompanied by an equally increased flow of sorbent particles that react effectively with the gas contaminants as soon as they are deposited on the filter surface, and 3) the over-design of the barrier filter cleaning system capacity allows for short transient variations. The use of more plenums in the barrier filter-reactor, or increased pulse cleaning frequency would reduce the degree of nonuniformity in gas flow to the plenums due to pulse cleaning. The pulse cleaning effect would be even smaller for the Stage II barrier filter system, where the trigger pressure drop is about 51.0 kPa (7.4 psi) and the baseline is 45.5 kPa (6.6 psi).

Ultra-Clean Section with Syngas Drying

Figure 4.17 shows the process flow diagram for the Ultra-Clean section with syngas drying. The only changes from the base Ultra-Clean section are the addition of the syngas heat exchanger (Item 50) and the syngas condenser (Items 51 and 52). For the evaluation, the Stage II operating temperature was selected as 343°C (650°F) and the sorbent feed rates were assumed to be the same as in the Base Ultra-Clean syngas polishing section.

Ultra-Clean Section with HCl Scrubbing

Figure 4.18 shows the process flow diagram for the Ultra-Clean section with HCl scrubbing. The changes from the base Ultra-Clean section process are the removal of the Stage I and Stage II HCl sorbent handling and feed systems, the addition of the syngas heat exchanger (Item 49) and the syngas condenser (Items 50 and 51), and the HCl water scrubber (Item 52). For the evaluation, the Stage II operating temperature was selected as 343°C (650°F) and sulfur sorbent feed rates were assumed to be the same as in the Base Ultra-Clean section. Here, the Stage

I and Stage II waste sulfur sorbents are uncontaminated by HCl sorbent wastes and might be more easily regenerated by circulation to the bulk desulfurization section regenerator, or transported to the gasifier for disposal. This process alternative provides the potential to operate Stage I regeneratively with minimum Stage I sulfur sorbent makeup. Little, though, can be done about the bulk desulfurizer section sorbent losses. This attrited sorbent can be cycled to the bulk desulfurization section regenerator, but makeup for the degraded bulk desulfurization sorbent must also be fed to the transport desulfurizer.

4.4.3 Process Material & Energy Balances and Overall Performance

Material & energy balance results in the form of process stream flows, conditions and compositions are listed for each of the three process sections in Tables 4.33 through 4.37. Each of the numbered streams in each process diagram has been characterized and is reported. The actual process simulator process flow diagrams have 157 process streams and 81 equipment components, but the number of streams and components have been reduced for the report presentation.

The overall performance of the novel syngas cleaning process for each of the three alternative process arrangements of the Ultra-Clean section is summarized in Table 4.38. This tabulation lists mass flows of all of the major input and output streams, the heat energy input and outputs, and the power consumption. The sulfur removal performance is also characterized. The cleaned syngas composition for each novel chemical synthesis process alternative are listed in Table 4.39. Table 4.40 lists the sulfur recovery process tail gas composition, which is identical for all of the process alternatives.

The performance results for the three novel syngas cleaning alternatives are identical except for HCl sorbent feed rate, the power consumption, cleaned syngas flow rate, the waste water rate, the inert exhaust gas rate, the solid waste rate, the IP-steam production rate, and the cooling water consumption rate. The advantage of the drying and HCl scrubbing schemes over the Base scheme may be in their greater desulfurization and HCl removal capabilities in light of the uncertainty that currently exists. The alternative with HCl scrubbing will allow effective ammonia removal in the water scrubber.

All three of the Ultra-Clean section alternatives might incorporate mercury removal in Stage II by mercury sorbent injection or packed bed contactor systems using activated carbon or coke, activated alumina, zeolites, or advanced higher-temperature sorbents.

Steam Generator, Syngas Cooler (44)

Stage I & Stage II Sulfur Sorbent Feed System (45, 53)

Stage I & Stage II HCl Sorbent Feed System (46, 54)

Stage I Filter/ Reactor:
- screw conveyor,
- pulse gas compressor
- pulse control skid

(47)

Solids Cooler (48, 56)

Solids Removal System (49, 57)

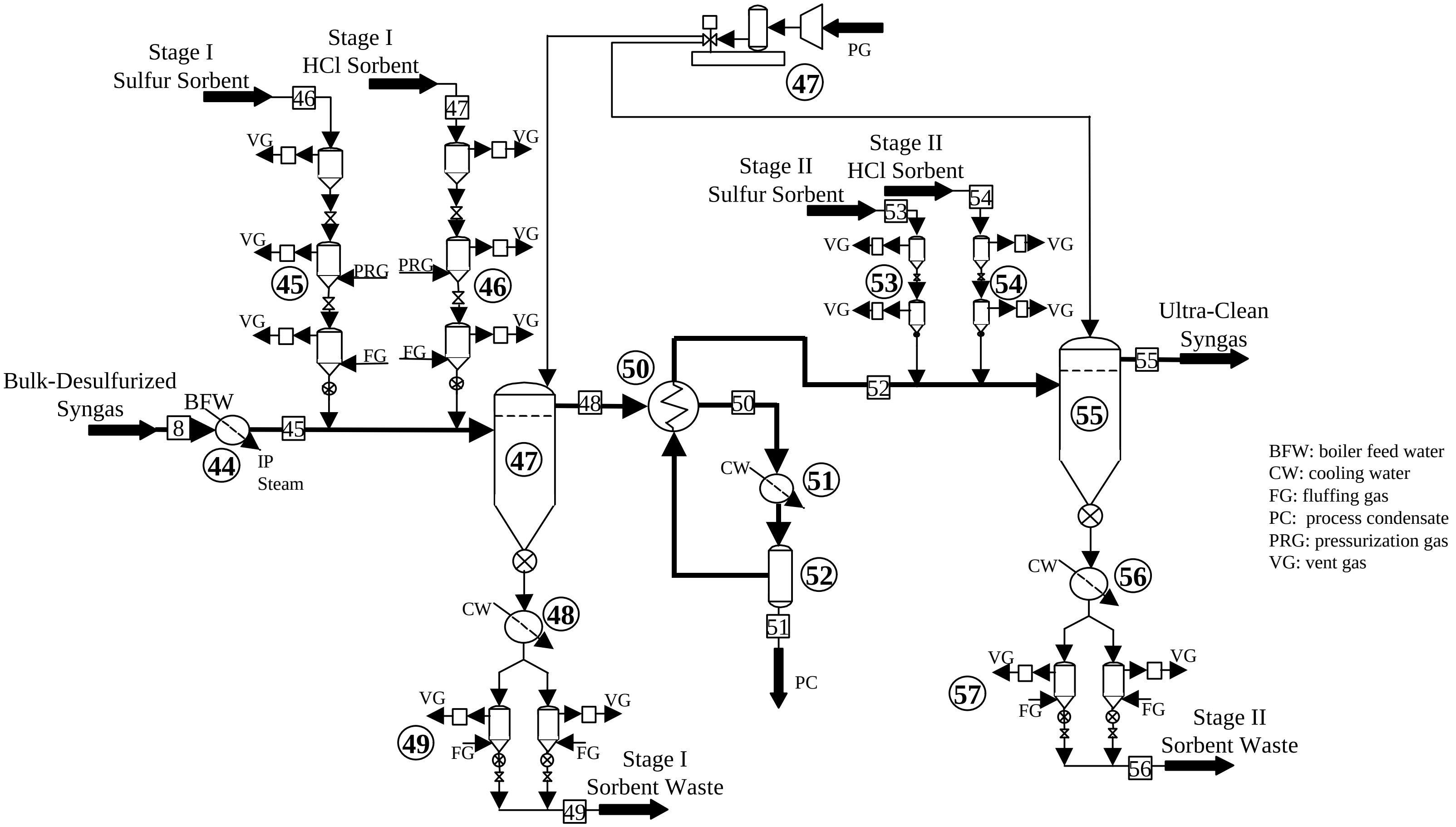
Syngas Heat Exchanger (50)

Syngas Cooler (51)

Water Separation Tank (52)

Stage II Filter/ Reactor:
- screw conveyor

(55)



BFW: boiler feed water
CW: cooling water
FG: fluffing gas
PC: process condensate
PRG: pressurization gas
VG: vent gas

Figure 4.17 - Novel Syngas Cleaning - Ultra-Clean Section with Drying

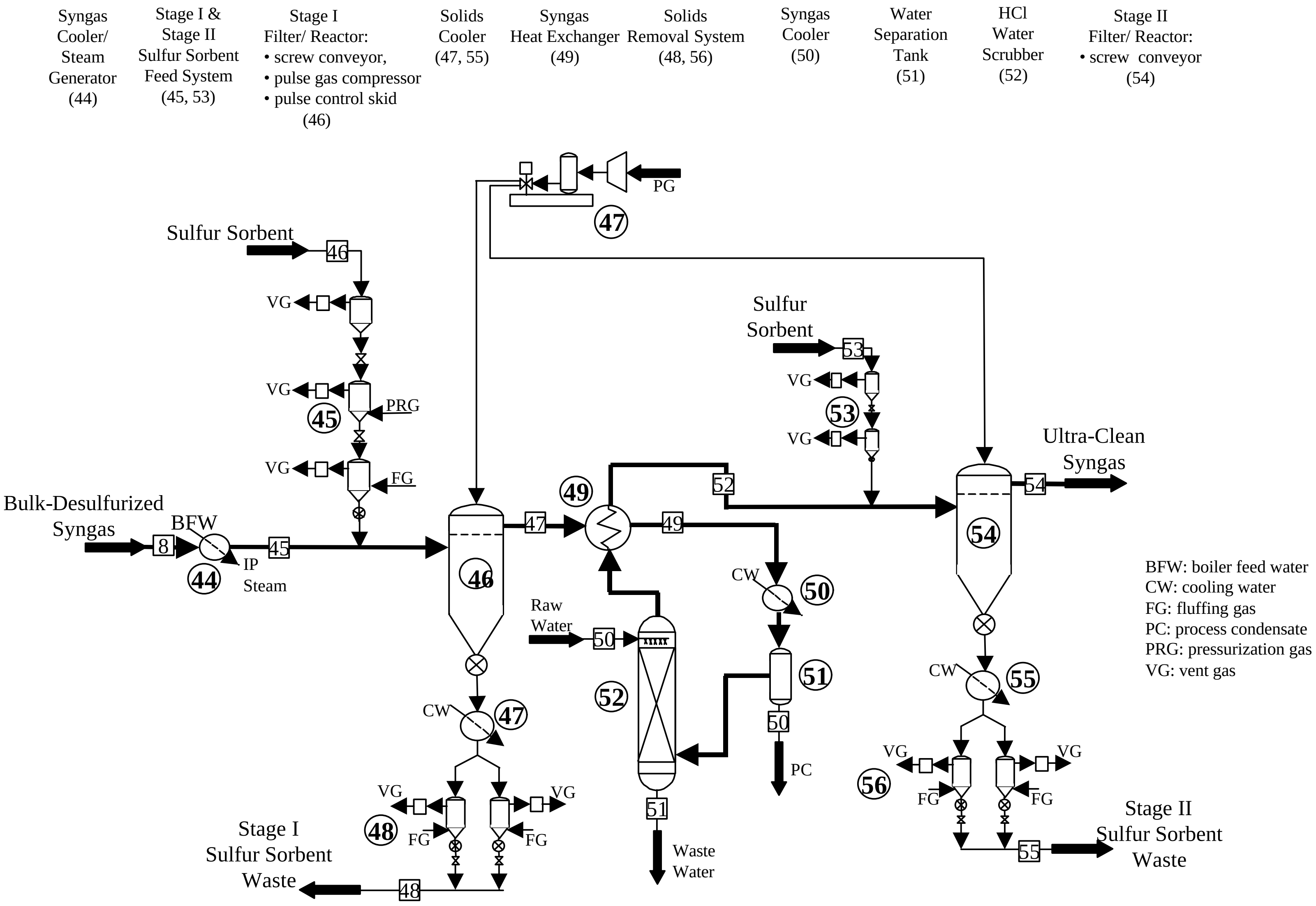


Figure 4.18 - Novel Syngas Cleaning - Ultra-Clean Section with HCl Scrubbing

Table 4.33 - Process Streams for Novel Syngas Cleaning - Bulk Desulfurization Section (Figure 4.11)

Stream No.	1	2	3	4	5	6	7	8	9	10
Stream Name	Raw Syngas				Particle-free Syngas	Char	Fluffing & Stripping Gas	Bulk-desulfur Syngas	Sorbent to Regenerator	Sorbent to Desulfurizer
Molar flow (lb-mole/hr)	9,106	9,106	9,106	9,106	9,088	18	250	9,199	632	632
Mass flow (lb/h)	178,880	178,880	178,880	178,880	177,820	1,061	7,000	181,660	51,884	51,377
Temperature (°F)	2500	1834	1510	952	952	952	120	1017	1017	1357
Pressure (psia)	600.0	595.0	580.0	565.0	559.5	559.5	650.0	544.0	544.0	545.0
Vapor mole fraction	1	1	1	1	1	0	1	1	0	0
Component mole fractions										
Hydrogen	0.3311	0.3311	0.3311	0.3311	0.3317			0.3228		
Methane	0.0016	0.0016	0.0016	0.0016	0.0016			0.0015		
Nitrogen	0.0075	0.0075	0.0075	0.0075	0.0075		1.0000	0.0341		
Oxygen										
Carbon Monoxide	0.4567	0.4567	0.4567	0.4567	0.4576			0.4453		
Carbon Dioxide	0.0767	0.0767	0.0767	0.0767	0.0768			0.0749		
Hydrogen Sulfide	3.22E-03	3.22E-03	3.22E-03	3.22E-03	3.23E-03			2.36E-05		
Sulfur Dioxide										
Water	0.1129	0.1129	0.1129	0.1129	0.1131			0.1132		
Argon	6.70E-03	6.70E-03	6.70E-03	6.70E-03	6.71E-03			6.53E-03		
Hydrogen Chloride	5.05E-04	5.05E-04	5.05E-04	5.05E-04	5.06E-04			4.92E-04		
Hydrogen Cyanide	3.03E-05	3.03E-05	3.03E-05	3.03E-05	3.04E-05			2.95E-05		
Carbonyl Sulfide	1.92E-04	1.92E-04	1.92E-04	1.92E-04	1.92E-04			1.41E-06		
Ammonia	9.99E-04	9.99E-04	9.99E-04	9.99E-04	1.00E-03			9.74E-04		
Zinc Oxide								7.06E-05	0.5189	0.5676
Titanium Dioxide								5.37E-05	0.4000	0.4000
ZnS								1.00E-05	0.0811	0.0324
Char	1.94E-03	1.94E-03	1.94E-03	1.94E-03		1.0000				

Table 4.33 (Cont.) - Process Streams for Novel Syngas Cleaning - Bulk Desulfurization Section

Stream No.	11	12	13	14	15	16	17	18	19	20
Stream Name	Air	Heated Air	Acid Gas	Reducing Gas	Collected Sorbents	Makeup Sorbent	BFW	Preheated Water	Saturated Steam	HP-steam
Molar flow (lb-mole/hr)	223	223	208	140	0	1	5,168	5,168	5,168	5,168
Mass flow (lb/h)	6,450	6,450	6,944	2,763	14	100	93,100	93,100	93,100	93,100
Temperature (°F)	60	1100	1357	1017	1333	60	180	585	610	950
Pressure (psia)	14.4	570.0	537.0	536.0	545.0	600.0	1575.0	1550.0	1535.0	1515.0
Vapor mole fraction	1	1	1	1	0	0	0	0	1	1
Component mole fractions										
Hydrogen				0.3228						
Methane				0.0015						
Nitrogen	0.7723	0.7723	0.8294	0.0341						
Oxygen	0.2072	0.2072	0.0008							
Carbon Monoxide			0.0000	0.4453						
Carbon Dioxide	0.0003	0.0003	0.0003	0.0749						
Hydrogen Sulfide			0.0000	2.36E-05						
Sulfur Dioxide			0.1478							
Water	0.0101	0.0101	0.0108	0.1132			1.0000	1.0000	1.0000	1.0000
Argon	0.0101	0.0101	0.0108	6.53E-03						
Hydrogen Chloride				4.92E-04						
Hydrogen Cyanide				2.95E-05						
Carbonyl Sulfide				1.41E-06						
Ammonia				9.74E-04						
Zinc Oxide					0.5631	0.6000				
Titanium Dioxide					0.4000	0.4000				
ZnS					0.0369					
Char										

Table 4.34 - Process Streams for Novel Syngas Cleaning - Sulfur Recovery Section (Figure 4.12)

Stream No.	17	18	19	20	21	22	23	24	25	26
Stream Name	Sulfur Gas		Dried Acid gas				Sulfur Condensate			
Molar flow (lb-mole/hr)	321	323	323	331	331	318	13	310	317	317
Mass flow (lb/h)	9,707	10,691	10,691	10,691	10,691	10,266	425	10,126	10,126	10,126
Temperature (°F)	2316	100	650	745	285	285	285	650	726	260
Pressure (psia)	524.0	25.1	24.6	23.9	23.4	23.4	23.4	22.6	21.9	21.5
Vapor mole fraction	1	1	1	1	0.9595	1	0	1	1	0.9675
Component mole fractions										
Hydrogen	0.0135	0.0134	0.0134	0.0131	0.0131	0.0136	2.10E-07	0.0140	0.0137	0.0137
Methane	7.85E-09	7.80E-09	7.80E-09	7.59E-09	7.59E-09	7.91E-09	2.20E-13	8.11E-09	7.94E-09	7.94E-09
Nitrogen	0.5532	0.5505	0.5505	0.5361	0.5361	0.5587	6.46E-06	0.5726	0.5607	0.5607
Oxygen	4.26E-11	1.09E-04	1.09E-04	1.07E-04	1.07E-04	1.11E-04	1.60E-09	1.14E-04	1.11E-04	1.11E-04
Carbon Monoxide	0.0639	0.0635	0.0635	0.0618	0.0618	0.0644	9.20E-07	0.0660	0.0647	0.0647
Carbon Dioxide	0.1641	0.1699	0.1699	0.1655	0.1655	0.1724	1.39E-03	0.1767	0.1730	0.1730
Hydrogen Sulfide	0.0866	0.0860	0.0860	0.0575	0.0575	0.0599	7.83E-06	0.0614	0.0393	0.0393
Sulfur Dioxide	9.39E-03	0.0689	0.0689	0.0540	0.0540	0.0563	7.33E-06	0.0576	0.0460	0.0460
Water	0.0987	0.0376	0.0376	0.0629	0.0629	0.0643	0.0282	0.0412	0.0612	0.0612
Argon	9.89E-03	9.86E-03	9.86E-03	9.60E-03	9.60E-03	1.00E-02	4.98E-07	1.03E-02	1.00E-02	1.00E-02
Hydrogen Chloride	2.15E-04	1.23E-09	1.16E-09	1.13E-09	1.13E-09	1.15E-09	5.82E-10	2.06E-12	2.01E-12	2.01E-12
Hydrogen Cyanide	1.29E-05	1.43E-04	1.43E-04	1.39E-04	1.39E-04	1.45E-04	8.88E-06	1.48E-04	1.45E-04	1.45E-04
Carbonyl Sulfide	6.14E-07	6.04E-07	6.04E-07	5.89E-07	5.89E-07	6.13E-07	9.04E-09	6.27E-07	6.14E-07	6.14E-07
Ammonia	4.25E-04	2.20E-09	1.74E-09	1.70E-09	1.70E-09	4.83E-10	3.04E-08	4.83E-10	4.73E-10	4.73E-10
Sulfur	4.03E-06	7.88E-13	7.88E-13	0.0394	0.0394	9.44E-05	0.9703	7.63E-11	0.0313	0.0313
Triethanolamine		1.45E-19	1.45E-19	1.41E-19	1.41E-19	4.07E-22	3.47E-18	1.43E-28	1.40E-28	1.40E-28

Table 4.34 (Cont.) - Process Streams for Novel Syngas Cleaning - Sulfur Recovery Section

Stream No.	27	28	29	30	31	32	33	34	35
Stream Name		Sulfur Condensate					Sulfur Condensate	Total Sulfur	Air
Molar flow (lb-mole/hr)	307	10	301	306	306	298	8	31	520
Mass flow (lb/h)	9,801	325	9,702	9,702	9,702	9,456	246	996	15,000
Temperature (°F)	260	260	650	711	285	285	285	277	60
Pressure (psia)	21.5	21.5	20.6	20.1	19.6	19.6	19.6	19.6	14.4
Vapor mole fraction	1	0	1	1	0.9747	1	0	2.29E-06	1
Component mole fractions									
Hydrogen	0.0141	1.95E-07	0.0144	0.0142	0.0142	0.0145	1.87E-07	1.99E-07	
Methane	8.21E-09	1.94E-13	8.36E-09	8.22E-09	8.22E-09	8.43E-09	1.96E-13	2.05E-13	
Nitrogen	0.5795	5.57E-06	0.5900	0.5803	0.5803	0.5953	5.76E-06	6.00E-06	0.7723
Oxygen	1.15E-04	1.51E-09	1.17E-04	1.15E-04	1.15E-04	1.18E-04	1.43E-09	1.53E-09	0.2072
Carbon Monoxide	0.0668	8.34E-07	0.0680	0.0669	0.0669	0.0687	8.21E-07	8.67E-07	
Carbon Dioxide	0.1788	9.17E-04	0.1820	0.1790	0.1790	0.1836	1.26E-03	1.20E-03	3.00E-04
Hydrogen Sulfide	0.0406	6.59E-06	0.0413	0.0241	0.0241	0.0247	2.70E-06	6.16E-06	
Sulfur Dioxide	0.0475	2.69E-05	0.0484	0.0393	0.0393	0.0403	1.39E-06	1.23E-05	
Water	0.0620	0.0377	0.0450	0.0608	0.0608	0.0618	0.0227	0.0300	0.0101
Argon	1.04E-02	3.92E-07	1.06E-02	1.04E-02	1.04E-02	1.07E-02	4.45E-07	4.50E-07	1.01E-02
Hydrogen Chloride	2.08E-12	1.96E-16	2.12E-12	2.08E-12	2.08E-12	2.14E-12	1.84E-16	2.48E-10	
Hydrogen Cyanide	1.49E-04	1.09E-05	1.51E-04	1.49E-04	1.49E-04	1.53E-04	7.91E-06	9.29E-06	
Carbonyl Sulfide	6.34E-07	1.06E-08	6.44E-07	6.34E-07	6.34E-07	6.50E-07	8.03E-09	9.29E-09	
Ammonia	4.89E-10	9.46E-12	4.89E-10	4.81E-10	4.81E-10	4.94E-10	7.24E-12	1.30E-08	
Sulfur	4.44E-05	0.9614		0.0248	0.0248	1.13E-04	0.9760	0.9688	
Triethanolamine	1.44E-28	3.14E-25	3.86E-30	3.80E-30	3.80E-30	3.90E-30	2.71E-21	1.48E-18	

Table 4.34 (Cont.) - Process Streams for Novel Syngas Cleaning - Sulfur Recovery Section

Stream No.	36	37	38	39	40	41	42	43	44
Stream Name	Fuel	Oxidized Gas			Tail Gas	Rich Solvent	Recycle SO2	Lean Solvent	
Molar flow (lb-mole/hr)	25	827	827	777	744	31,198	33	31,165	33
Mass flow (lb/h)	405	24,861	24,861	23,955	22,409	1,353,300	1,549	1,351,700	1,549
Temperature (°F)	60	2098	300	95	90	100	162	229	257
Pressure (psia)	30.0	18.6	18.2	17.8	17.1	29.6	15.0	26.5	26.5
Vapor mole fraction	1	1	1	1	1	0	1	0	1
Component mole fractions									
Hydrogen		2.78E-07	2.78E-07	2.96E-07	3.09E-07	5.00E-12	4.71E-09	3.20E-20	4.71E-09
Methane	1.0000	2.67E-21	2.67E-21	2.84E-21	5.60E-22	6.17E-22	6.17E-22	6.17E-22	6.17E-22
Nitrogen		0.7000	0.7000	0.7452	0.7777	9.69E-06	9.13E-03	2.61E-14	9.13E-03
Oxygen		0.0408	0.0408	0.0434	0.0453	1.13E-06	1.07E-03	7.13E-15	1.07E-03
Carbon Monoxide		7.58E-07	7.58E-07	8.07E-07	8.42E-07	1.53E-11	1.44E-08	7.76E-20	1.44E-08
Carbon Dioxide		0.1217	0.1217	0.1296	0.1323	7.11E-05	0.0670	5.34E-10	0.0670
Hydrogen Sulfide		1.92E-16	1.92E-16	1.40E-16	3.70E-12	6.78E-10	1.15E-13	6.79E-10	1.15E-13
Sulfur Dioxide		0.0235	0.0235	0.0250	7.18E-05	7.25E-04	0.5847	1.04E-04	0.5847
Water		0.1038	0.1038	0.0460	0.0333	0.8060	0.3365	0.8065	0.3365
Argon		1.02E-02	1.02E-02	1.08E-02	1.13E-02	3.30E-07	3.11E-04	1.07E-14	3.11E-04
Hydrogen Chloride		7.71E-13	7.71E-13	3.46E-10	7.86E-14	1.76E-10	3.98E-16	1.76E-10	3.98E-16
Hydrogen Cyanide		5.50E-05	5.50E-05	5.79E-05	7.12E-07	1.56E-06	1.30E-03	1.83E-07	1.30E-03
Carbonyl Sulfide		3.51E-17	3.51E-17	3.71E-17	7.42E-19	9.65E-19	8.55E-16	5.77E-20	8.55E-16
Ammonia					7.19E-10	1.03E-04	2.09E-12	1.03E-04	2.09E-12
Sulfur		2.26E-15	2.26E-15	4.71E-22	7.68E-22	5.24E-14		5.25E-14	
Triethanolamine					2.32E-09	0.1931	8.30E-12	0.1933	8.30E-12

Table 4.35 - Process Streams for Novel Syngas Cleaning - Ultra-Clean Base Section (Figure 4.13)

Stream No.	8	45	46	47	48	49	50	51	52	53	54	55
Stream Name	Bulk-Desulf Syngas		Sulfur Sorbent	HCl Sorbent		Stage I Waste	Sulfur Sorbent	HCl Sorbent	Ultra-Clean Gas	Stage II Waste	Pulse gas	Pulse Gas
Molar flow (lb-mole/hr)	9,199	9,199	0.766	24.2	9,218	13.3	0.055	0.676	9,218	0.743	1.428	0.071
Mass flow (lb/h)	181,660	181,660	61.845	1,368	181,980	1,153	4.29	43.2	181,980	47.8	40.000	2.000
Temperature (°F)	1017	930	60	60	550	250	60	60	550	250	120	120
Pressure (psia)	544.0	536.0	600.0	600.0	518.0	521.0	550.0	550.0	507.5	502.5	1200.0	1200.0
Vapor mole fraction	1	1	0	0	1	1	0	0	1	0	1	1
Component mole fractions												
Hydrogen	0.3228	0.3228			0.3221				0.3221			
Methane	1.55E-03	1.55E-03			1.54E-03				1.54E-03			
Nitrogen	0.0341	0.0341			0.0342				0.0342		1.0000	1.0000
Carbon Monoxide	0.4453	0.4453			0.4444				0.4444			
Carbon Dioxide	0.0749	0.0749			0.0754				0.0754			
Hydrogen Sulfide	2.36E-05	2.36E-05			9.41E-07				5.64E-08			
Water	0.1132	0.1132		0.5000	0.1149				0.1149			
Argon	6.53E-03	6.53E-03			6.52E-03				6.52E-03			
Hydrogen Chloride	4.92E-04	4.92E-04			2.46E-06				9.83E-09			
Hydrogen Cyanide	2.95E-05	2.95E-05			2.95E-05				2.95E-05			
Carbonyl Sulfide	1.41E-06	1.41E-06			5.62E-08				3.38E-09			
Ammonia	9.74E-04	9.74E-04			9.72E-04				9.72E-04			
Zinc Oxide	7.06E-05	7.06E-05	0.6045			0.0627	0.8712			0.06354		
Titanium Dioxide	5.37E-05	5.37E-05	0.3955			0.0555						
ZnS	1.00E-05	1.00E-05				0.0264				0.01762		
Sodium Carbonate				0.2500		0.627		0.1388		0.10055		
Na Bicarbonate				0.2500								
Inert Carrier							0.1288	0.8612		0.7907		
Sodium Chloride						0.2284				0.02759		

Table 4.36 - Process Streams for Novel Syngas Cleaning - Ultra-Clean Section with Drying (Figure 4.17)

Stream No.	8	45	48	50	51	52	55
Stream Name	Bulk-Desulf Syngas				Process Condensate		Ultra-Clean Syngas
Molar flow (lb-mole/hr)	9,199	9,199	9,218	9,218	990	8,228	8,228
Mass flow (lb/h)	181,660	181,660	181,980	181,978	17,842	164,136	164,140
Temperature (°F)	1017	930	915	487	150	650	650
Pressure (psia)	540.0	532.0	515.0	507.0	500.0	492.0	475.0
Vapor mole fraction	1	1	1	1	0	1	1
Component mole fractions							
Hydrogen	0.3228	0.3228	0.3221	0.3221	1.27E-04	0.3609	0.3609
Methane	1.55E-03	1.55E-03	1.54E-03	1.54E-03	9.04E-07	1.73E-03	1.73E-03
Nitrogen	0.0341	0.0341	0.0342	0.0342	8.54E-06	0.0383	0.0383
Carbon Monoxide	0.4453	0.4453	0.4444	0.4444	1.63E-04	0.4978	0.4978
Carbon Dioxide	0.0749	0.0749	0.0754	0.0754	4.06E-04	0.0844	0.0844
Hydrogen Sulfide	2.36E-05	2.36E-05	9.41E-07	9.41E-07	2.94E-08	1.05E-06	5.67E-08
Water	0.1132	0.1132	0.1149	0.1149	0.9981	8.63E-03	8.63E-03
Argon	6.53E-03	6.53E-03	6.52E-03	6.52E-03	4.38E-06	7.30E-03	7.30E-03
Hydrogen Chloride	4.92E-04	4.92E-04	2.46E-06	2.46E-06	1.53E-06	2.57E-06	9.76E-09
Hydrogen Cyanide	2.95E-05	2.95E-05	2.95E-05	2.95E-05	4.10E-05	2.81E-05	2.81E-05
Carbonyl Sulfide	1.41E-06	1.41E-06	5.62E-08	5.62E-08	7.12E-08	5.44E-08	2.94E-09
Ammonia	9.74E-04	9.74E-04	9.72E-04	9.72E-04	1.19E-03	9.46E-04	9.46E-04
Zinc Oxide	7.06E-05	7.06E-05					
Titanium Dioxide	5.37E-05	5.37E-05					
ZnS	1.00E-05	1.00E-05					
Sodium Carbonate							
Na Bicarbonate							
Inert carrier							
Sodium Chloride							

*** Streams 46, 47, 49, 53, 54, and 56 are identical with the associated sorbent and waste streams in Table 4.36**

Table 4.37 - Process Streams for Novel Syngas Cleaning - Ultra-Clean Section with HCl Scrubbing (Figure 4.18)

Stream No.	8	45	47	48	49	50	51	52	54	55
Stream Name	Bulk-Desulf Syngas			Sulfur Sorbent Waste		Process Condensate	Waste Water		Ultra-Clean Syngas	Sulfur Sorbent Waste
Molar flow (lb-mole/hr)	9,199	9,199	9,199	2.002	9,199	1,018	57	8,169	8,169	0.055
Mass flow (lb/h)	181,660	181,660	181,600	166.7	181,597	18,358	1,160	162,879	162,881	4.43
Temperature (°F)	1017	930	930	250	470	113	117	650	640	250
Pressure (psia)	540.0	532.0	515.0	510.0	507.0	500.0	500.0	490.0	476.0	471.0
Vapor mole fraction	1	1	1	1	1	0	5.65E-06	1	1	1
Component mole fractions										
Hydrogen	0.3228	0.3228	0.3228		0.3228	1.42E-04	1.53E-04	0.3635	0.3635	
Methane	1.55E-03	1.55E-03	1.55E-03		1.55E-03	1.06E-06	1.13E-06	1.74E-03	1.74E-03	
Nitrogen	0.0341	0.0341	0.0343		0.0343	1.04E-05	1.11E-05	0.0386	0.0386	
Carbon Monoxide	0.4453	0.4453	0.4453		0.4453	1.99E-04	2.12E-04	0.5014	0.5014	
Carbon Dioxide	0.0749	0.0749	0.0749		0.0749	8.01E-04	0.0409	0.0840	0.0840	
Hydrogen Sulfide	2.36E-05	2.36E-05	9.42E-07		9.42E-07	4.02E-08	2.34E-07	1.05E-06	5.48E-08	
Water	0.1132	0.1132	0.1132		0.1132	0.9967	0.7587	3.48E-03	3.48E-03	
Argon	6.53E-03	6.53E-03	6.53E-03		6.53E-03	4.82E-06	5.18E-06	7.35E-03	7.35E-03	
Hydrogen Chloride	4.92E-04	4.92E-04	4.92E-04		4.92E-04	3.52E-04	0.0730	3.20E-09	3.20E-09	
Hydrogen Cyanide	2.95E-05	2.95E-05	2.95E-05		2.95E-05	6.18E-05	2.80E-04	2.36E-05	2.36E-05	
Carbonyl Sulfide	1.41E-06	1.41E-06	5.63E-08		5.63E-08	9.27E-08	8.20E-08	5.13E-08	2.67E-09	
Ammonia	9.74E-04	9.74E-04	9.74E-04		9.74E-04	1.71E-03	0.1265	3.64E-08	3.64E-08	
Zinc Oxide	7.06E-05	7.06E-05		0.4437						0.6778
Titanium Dioxide	5.37E-05	5.37E-05		0.4000						
ZnS	1.00E-05	1.00E-05		0.1563						0.1553
Sodium Carbonate										
Na Bicarbonate										
Inert Carrier										0.1669
Sodium Chloride							1.24E-05			

*** Streams 46 and 53 are identical to the associated streams in Table 4.36**

Table 4.38 - Performance of Novel Syngas Cleaning Alternatives

INPUTS	Base	with Drying	with HCl Scrub
Material	**kg/hr (lb/hr)**	**kg/hr (lb/hr)**	**kg/hr (lb/hr)**
Raw syngas	81,140 (178,880)	81,140 (178,880)	81,140 (178,880)
Inert gas (nitrogen)	3,350 (7,385)	3,350 (7,385)	3,297 (7,268)
Air	9,730 (21,450)	9,752 (21,450)	9,752 (21,450)
Fuel	184(405)	184(405)	184(405)
Raw water	0	0	800
Chemicals			
Bulk desulfurizer sorbent	45 (100)	45 (100)	45 (100)
Stage I sulfur sorbent	28 (62)	28 (62)	28 (62)
Stage I HCl sorbent	621 (1,368)	621 (1,368)	0
Stage II sulfur sorbent	2 (4)	2 (4)	2 (4)
Stage II HCl sorbent	21 (43)	21 (43)	0
Caustic	0	0	0
Total	95,119 (209,697)	95,119 (209,697)	94,788 (208,969)
Heat Energy	**GJ/hr (MBtu/hr)**	**GJ/hr (MBtu/hr)**	**GJ/hr (MBtu/hr)**
Fuel	10.24 (9.71)	10.24 (9.71)	10.24 (9.71)
Power Use	**kW**	**kW**	**kW**
Pump power	32	32	32
Compressor power	684	684	682
Solids handling power	2	2	0.2
Expander	-1023	-1023	-1023
Total power	-305	-305	-309
OUTPUTS			
Material	**kg/hr (lb/hr)**	**kg/hr (lb/hr)**	**kg/hr (lb/hr)**
Cleaned syngas	82,546 (181,980)	74,453 (164,137)	73,883 (162,881)
Char (dry)	481 (1,061)	481 (1,061)	481 (1,061)
Waste water	776 (1,710)	8,869 (19,552)	9,629 (21,228)
Sulfur condensate	452 (996)	452 (996)	452 (996)
Tail gas	10,165 (22,409)	10,165 (22,409)	10,165 (22,409)
Inert exhaust gas	152 (335)	152 (335)	101 (223)
Solid waste	545 (1,201)	545 (1,201)	78(171)
Total	95,116 (209,692)	95,116 (209,691)	94,788 (208,969)
Heat Energy	**GJ/hr (MBtu/hr)**	**GJ/hr (MBtu/hr)**	**GJ/hr (MBtu/hr)**
Net HP-steam production	139.3 (132.0)	139.3 (132.0)	139.3 (132.0)
Net IP-stream production	38.3 (36.3)	3.8 (3.6)	3.8 (3.6)
Net LP-stream production	-190.7 (-180.8)	-190.7 (-180.8)	-190.7 (-180.8)
Net cooling water used	216.5 (205.2)	266.5 (252.6)	2665.3 (251.5)
Sulfur Removal Performance			
Total Process sulfur removal eff (%):	99.83	99.83	99.83
Sulfur byproduct, kg/hr (lb/hr):	443.2 (977.1)	443.2 (977.1)	443.2 (977.1)
Sulfur byproduct efficiency (%):	98.05	98.05	98.05

The total syngas pressure drop across the novel syngas cleaning process using the Base Ultra-Clean process is estimated to be 641 kPa (93 psi), a reduction in pressure drop of about 220 kPa (32 psi) over the conventional process. Net steam productions (HP, IP, and LP-steam) and cooling water use are also in the favor of the novel syngas cleaning process (Table 4.38 versus

Table 4.13). Power consumption, and fuel consumption are both considerably lower than in the conventional syngas cleaning process. The cleaned syngas flow rate is slightly larger than the raw syngas flow rate due primarily to inert gas injection sources.

The cleaned syngas conditions and compositions listed in Table 4.39 differ in many aspects for each of the three alternatives, but none of these differences is considered to be substantial. The HCl scrubbing option also inherently reduces the syngas ammonia content, but it is still above the syngas cleaning requirement.

The cleaned syngas composition is comparable to that for the conventional syngas cleaning process, but the higher CO_2 and nitrogen contents in the novel cleaned syngas results in slightly higher molecular weight and lower heating value (Table 4.39 versus Table 4.7). The novel cleaned syngas has a slightly higher molar content of CO and H_2. Of course, the novel cleaned syngas has a much higher content of ammonia and HCN than in the conventional syngas cleaning process.

Table 4.39 - Novel Syngas Cleaning Alternatives - Cleaned Syngas

	Base	**with Drying**	**with HCl Scrub**
Temperature, °C (°F)	288 (550)	343 (650)	338 (640)
Pressure, kPa (psia)	3499.1 (507.5)	3275 (475)	3282 (476)
Mass flow, kg/hr (lb/hr)	82,545.9 (181,979.6)	74,452.7 (164,137.4)	73,882.8 (162,881.0)
Molar flow CO + H_2 (kg-mole/hr)	3,204.8	3,204.7	3,204.6
Heating value, GJ/kg-mole (Btu/lb-mole)	200,095 (86,040)	260,032 (98,650)	230,979 (99,320)
Composition			
hydrogen (mole%)	32.21	36.09	36.35
methane (mole%)	0.15	0.17	0.17
nitrogen (mole%)	3.42	3.83	3.85
argon (mole%)	0.65	0.73	0.74
carbon monoxide (mole%)	44.44	49.78	50.14
carbon dioxide (mole%)	7.54	8.44	8.40
water (mole%)	11.49	0.86	0.35
hydrogen sulfide (ppbv)	56.4	56.7	54.8
carbonyl sulfide (ppbv)	3.4	2.9	2.7
hydrogen chloride (ppbv)	9.8	9.8	3.2
hydrogen cyanide (ppbv)	29,484	29,094	23,613
ammonia (ppmv)	972	946	364

The tail gas mass flow rate (Table 4.40) is much smaller than in the conventional syngas cleaning process and also contains a much smaller SO_2 and CO_2 release to the environment (Table 4.40 versus Table 4.9). This results because the acid gas fed to the sulfur recovery section has a higher sulfur content and is thus more easily converted to elemental sulfur.

Table 4.40 - Novel Syngas Cleaning with Ultra-Clean Base Section - Tail Gas

Temperature, °C (°F)	32 (90)
Pressure, kPa (psia)	117.9 (17.1)
Mass flow, kg/hr (lb/hr)	10,164.5 (22,408.6)
Composition	
nitrogen (mole%)	77.77
oxygen (mole%)	4.53
argon (mole%)	1.13
carbon dioxide (mole%)	13.23
water (mole%)	3.33
sulfur dioxide (ppmv)	72
carbon monoxide (ppmv)	1
hydrogen cyanide (ppbv)	712
triethanolamine (ppbv)	2.3

4.4.4 Process Economics

The process economics for the novel chemical synthesis process with the three Ultra-Clean section variations are detailed in Tables 4.41 through 4.46. Individual tables are shown for the total capital requirement, other capital items, the annual operating cost, and the levelized cost-of-syngas-cleaning.

The total capital requirement tabulations in Table 4.41 compare the three alternatives and list the installed equipment costs of each section of the process. The process contingencies and project contingency are applied along with several other cost factors to estimate this total capital requirement. In the bulk desulfurization section, heat exchange equipment accounts for less than 1% of the equipment cost, and the two dominant cost classes are the barrier filter systems (56%) and the desulfurizer and regenerator system (15%). In the sulfur recovery section, heat exchange equipment accounts for 33% of the equipment cost, and flash drums and absorption and stripping towers account for 37%, the two dominant cost classes. In the Base Ultra-Clean section, the barrier filter-reactor systems accounts for 56% of the equipment cost, and the sorbent handling and feed, and sorbent waste handling equipment account for 41%, the two dominant cost classes in that section. These are also the two dominant cost classes for the alternative Ultra-Clean section configurations, though the sorbent and waste solids equipment is reduced to 19% of the total equipment cost for the Ultra-Clean section with HCl scrubbing. The total capital requirement for novel syngas cleaning using the Base Ultra-Clean section is equivalent to about 183 $/kW (= $24,177,000 / 132,000 kW) for the equivalent power plant application, considerably less than the 277 $/kW for the conventional syngas cleaning process (see Table 4.15).

The "other capital items" utilized within Table 4.41 are estimated in Table 4.42 only for the Ultra-Clean Base section. The other two alternatives have "other capital items" quite similar to these.

Table 4.41 - Novel Syngas Cleaning Alternatives - Capital Requirement

Plant Section	Process Contingency, %	Base Cost, k$ w/o Contingency	with Drying Cost, k$	HCl Scrub Cost, k$
Syngas Cooler Section	10	1026	1,026	1,026
Bulk Desulfurization Section	20	3675	3,675	3,675
Ultra-Clean Section	25	4256	5,092	4,632
Sulfur Recovery Section	15	4453	4,453	4,453
Subtotal, Process Plant Cost		**13,410**	**14,246**	**13,786**
General Plant Facilities		1,676	1,781	1,623
Engineering Fees		1,475	1,567	1,516
Process Contingency		2,570	2,779	2,664
Project Contingency, 10% Proc Plt & Gen Plt Fac		1,509	1,603	1,551
Total Plant Cost (TPC)		**20,640**	**21,975**	**21,240**
Adjustment for Interest and Inflation		952	1,013	980
Total Plant Investment (TPI)		**21,591**	**22,988**	**22,220**
Prepaid Royalties		67	71	69
Initial Catalyst and Chemical Inventory		552	552	520
Startup Costs		699	640	640
Spare Parts		110	106	106
Working Capital		1,202	1,077	1,077
Total Capital Requirement (TCR)		**24,177**	**25,622**	**24,632**

Table 4.42 - Novel Chemical Synthesis with Ultra-Clean Base Section – Other Capital Items

	Quantity		Unit $ Price		Cost, k$
Initial Catalyst Inventory					
Claus	400	lb.	0.5	/lb.	0
Sulfur sorbent 1	25,000	lb.	4	/lb.	100
Sulfur sorbent 2	3,000	lb.	4	/lb.	12
Bulk desulf sorbent	100,000	lb.	4	/lb.	400
Initial Chemicals Inventory					
HCl sorbent 1	500,000	lb.	0.03	/lb.	15
HCl sorbent 2	25,000	lb.	1	/lb.	25
Total Catalyst and Chemical Inventory					**552**
Startup costs					
Plant modifications,	2	% TPI			432
Operating costs					225
Fuel					7
Total Startup Costs					**663**
Working capital					
Fuel & Consumables inv,	60	days supply			1080
By-Product inventory,	30	days supply			19
Direct expenses,	30	days			101
Total Working Capital					**1,200**

It is possible to reduce the capital investment for the novel gas cleaning system significantly by taking a less conservative approach and using a cyclone in place of the bulk desulfurization section's primary barrier filter. Other options for capital cost reduction are to reduce the over-capacity of the design and to produce sulfuric acid rather than elemental sulfur. None of these modifications are needed to make the novel syngas cleaning process economically attractive because it has significantly lower investment cost using the conservative basis.

The annual operating cost tabulations in Tables 4.43, 4.44, and 4.45 list the consumable materials used in the three process alternatives and their unit costs to get annual cost burdens. Other cost factors for labor and maintenance, etc. are also applied to estimate the total annual operating cost. The annual operating cost is highest for the novel gas cleaning process using the Ultra-Cleaning process with drying. The annual operating costs are nearly the same for the novel gas cleaning processes with the Base Ultra-Clean section and with HCl scrubbing. Here, the reduced sorbent costs for the Ultra-Clean section with HCl scrubbing are countered by higher cost for less IP-steam production.

Table 4.43 - Novel Syngas Cleaning with Ultra-Clean Base Section - Annual Operating Cost

Cost Item	Quantity		Unit $ Price		Annual Cost, k$
Fuel Type: Natural Gas	233	MBtu/D	4	/MBtu	272
Consumable Materials					
Claus Catalyst	0.0005	ton/day	1000	/ton	0
Bulk desulf sorbent	1.2	ton/day	8000	/ton	2,803
Sulfur sorbent 1	0.744	ton/day	8000	/ton	1,738
Sulfur sorbent 2	0.052	ton/day	8000	/ton	121
HCl sorbent 1	16.42	ton/day	60	/ton	288
HCl sorbent 2	0.519	ton/day	2000	/ton	303
Inert gas	88.56	ton/day	2.5	/ton	65
Power	-7320	kW-hr/day	0.05	/kW-hr	(107)
HP Steam	-3168	MBtu/day	3.5	/MBtu	(3,238)
IL Steam	-871	MBtu/day	2.25	/MBtu	(572)
LP Steam	4339	MBtu/day	1.25	/MBtu	1,584
Cooling water	4925	MBtu/day	0.25	/MBtu	360
Ash/Sorbent Disposal Costs	14.41	ton/day	20	/ton	84
Plant Labor					
Oper Labor (incl benef)	2	Men/shift	35	/hr.	612
Supervision & Clerical					283
Maintenance Costs					826
Insurance & Local Taxes					413
Royalties					3
Other Operating Costs					94
Total Operating Costs					**5,930**
By-Product Sulfur Credits	11.67	ton/day	55	/ton	187
Net Operating Costs					**5,743**

Table 4.44 - Novel Syngas Cleaning with Ultra-Clean Section with Drying - Annual Operating Cost

Cost Item	Quantity		Unit $ Price		Annual Cost, k$
Fuel Type: Natural Gas	233	MBtu/D	4	/MBtu	272
Consumable Materials					
Claus Catalyst	0.0005	ton/day	1000	/ton	0
Bulk desulf sorbent	1.2	ton/day	8000	/ton	2,803
Sulfur sorbent 1	0.744	ton/day	8000	/ton	1,738
Sulfur sorbent 2	0.052	ton/day	8000	/ton	121
HCl sorbent 1	16.42	ton/day	60	/ton	288
HCl sorbent 2	0.519	ton/day	2000	/ton	303
Inert Gas	88.62	ton/day	2.5	/ton	
Power	-7320	kW-hr/day	0.05	/kW-hr	(107)
HP Steam	-3168	MBtu/day	3.5	/MBtu	(3,238)
IL Steam	-86	MBtu/day	2.25	/MBtu	(57)
LP Steam	4339	MBtu/day	1.25	/MBtu	1,584
Cooling water	6062	MBtu/day	0.25	/MBtu	443
Ash/Sorbent Disposal Costs	14.41	ton/day	20	/ton	84
Plant Labor					
Oper Labor (incl benef)	2	Men/shift	35	/hr.	612
Supervision & Clerical					289
Maintenance Costs					879
Insurance & Local Taxes					440
Royalties					3
Other Operating Costs					96
Total Operating Costs					**6,553**
By-Product Sulfur Credits	11.67	ton/day	55	/ton	187
Net Operating Costs					**6,366**

Finally, the "cost-of-syngas-cleaning", the bottom-line cost that represents the overall cost of cleaning the syngas, in dollars per 1000 kg (per 1000 lb) of raw syngas feed, is broken down between capital charges, fuel cost and operating and maintenance for the three alternatives in Table 4.46. The constant-dollar basis is the only basis utilized in the table. The cost-of-syngas-cleaning is highest for the novel gas cleaning process using the Ultra-Cleaning process with drying, due to its higher investment (Table 4.41) and operating cost (Table 4.44). The cost-of-syngas-cleaning are nearly the same for the novel gas cleaning processes with the Base Ultra-Clean section and with HCl scrubbing.

Since the sorbent feed rates and costs applied in the novel gas cleaning cost estimates represent the maximum expected values, it is enlightening to consider the sensitivity of the process costs to the sorbent feed rates and sorbent costs assumed. It is possible that the sorbent feed rates utilized in the evaluation, including that of the bulk desulfurization sorbent, might be cut in half and still achieve the syngas cleaning requirements. It is also possible that the sorbent delivered prices for the fabricated Stage I and II sulfur sorbent and the Stage II HCl sorbent

Table 4.45 - Novel Syngas Cleaning using Ultra-Clean Section with HCl Scrubbing - Annual Operating Cost

Cost Item	Quantity		Unit $ Price		Annual Cost, k$
Fuel Type: Natural Gas	233	MBtu/day	4	/MBtu	272
Consumable Materials					
Claus Catalyst	0.0005	ton/day	1000	/ton	0
Bulk desulf sorbent	1.2	ton/day	8000	/ton	2,803
Sulfur sorbent 1	0.744	ton/day	8000	/ton	1,738
Sulfur sorbent 2	0.048	ton/day	8000	/ton	112
HCl sorbent 1	0	ton/day	60	/ton	0
HCl sorbent 2	0	ton/day	2000	/ton	0
Inert Gas	87.22	ton/day	2.5	/ton	64
Power	-7416	kW-hr/day	0.05	/kW-hr	(108)
HP Steam	-3168	MBtu/day	3.5	/MBtu	(3,238)
IL Steam	-86.4	MBtu/day	2.25	/MBtu	(57)
LP Steam	4339	MBtu/day	1.25	/MBtu	1,584
Cooling water	6036	MBtu/day	0.25	/MBtu	441
Raw water	9.6	ton/day	0.2	/ton	1
Ash/Sorbent Disposal Costs	2.052	ton/day	20	/ton	12
Plant Labor					
Oper Labor (incl benef)	2	Men/shift	35	/hr.	612
Supervision & Clerical					285
Maintenance Costs					850
Insurance & Local Taxes					425
Royalties					3
Other Operating Costs					95
	Total Operating Costs				**5,892**
By-Product Sulfur Credits	11.67	ton/day	55	/ton	187
	Net Operating Costs				**5,705**

Table 4.46 - Novel Syngas Cleaning Alternatives - Cost-of-Syngas-Cleaning

	Base Constant-$ basis $/1000-kg ($/ 1000-lb)	**with Drying Constant-$ basis $/1000-kg ($/ 1000-lb)**	**with HCl Scrub Constant-$ basis $/1000-kg ($/ 1000-lb)**
Capital charges	4.39 (1.99)	4.63 (2.10)	4.45 (2.02)
Fuel costs	0.49 (0.22)	0.49 (0.22)	0.49 (0.22)
Operating & maintenance	9.61 (4.36)	10.71 (4.86)	9.55 (4.33)
Total	14.48 (6.57)	15.85 (7.19)	14.51 (6.58)

might be reduced 50% when mature technology is commercialized and used extensively -- the trona price is not likely to drop substantially and is fixed at its initial cost.

These two reduction factors have been applied and the results are listed in Table 4.47. In the case of the HCl scrubbing alternative, the reduced costs and reduced feed rates case assumes that the Stage I sulfur sorbent is utilized regeneratively by feeding the captured Stage I sorbent to the bulk desulfurizer regenerator, resulting in a sorbent makeup rate that is 10% of the maximum sorbent rate. There is a capital requirement reduction due to reduced solids handling capital costs, as well as reductions in the annual operating cost and the cost-of-syngas-cleaning. The annual operating cost in all three Ultra-Clean configurations drops by more than 60% and the cost-of-syngas-cleaning is reduced by more than 45%.

Table 4.47 - Novel Syngas Cleaning Cost Sensitivity

Novel Syngas Cleaning Case and sorbent assumptions	Capital Requirement, k$	Annual Operating Cost, k$	Cost-of-syngas-cleaning, $/1000 kg raw syngas (constant-$ basis)
Base - maximum sorbent costs and feed rates	24,177	5,743	14.48
Base - reduced costs and feed rates by 50%	22,935	1,833	7.39
Drying - maximum sorbent costs and feed rates	25,622	6,366	15.85
Drying - reduced costs and feed rates by 50%	24,380	2,455	8.75
HCl scrubbing - maximum costs and feed rates	24,632	5,705	14.51
HCl scrubbing - reduced costs and feed rates by 50%	23,444	1,861	7.54

4.5 NOVEL FUEL GAS CLEANING FOR SOFC POWER GENERATION

The SOFC fuel gas requires less stringent cleaning than the synthesis syngas, but the sectional process flow diagrams for novel gas cleaning are similar for both of these applications. The SOFC power island, a pressurized SOFC combined with a gas turbine bottoming cycle, requires a fuel gas having a lower pressure than the syngas pressure for the chemical synthesis application, a pressure of about 811 kPa (8-atmospheres) at the inlet to the SOFC power island. While the SOFC technology for a large-scale power plant is several years away from commercial demonstration, the consideration of the development needs of the coal-based, raw fuel gas cleaning process is critical to its eventual success.

4.5.1 Process Alternatives

The two approaches for SOFC fuel gas cleaning considered for conventional SOFC fuel gas cleaning, Section 4.3, are considered here. First, the fuel gas cleaning system is operated at an elevated pressure to reduce fuel gas generation equipment sizes and costs, and the cleaned fuel gas is expanded to the required pressure for the SOFC power island -- this option is designated "High-Pressure (HP) SOFC fuel gas cleaning". A 4137 kPa (600 psia) raw fuel gas inlet is assumed in the evaluation, the same as was used for the chemical synthesis application. This yields a power generation capacity of about 148 MWe.

Secondly, the fuel gas cleaning system is operated at a lower pressure to provide the fuel gas directly to the SOFC power island at its required pressure -- designated "Low-Pressure (LP) SOFC fuel gas cleaning". The process evaluation assumes a nominal power island generating capacity of

100 MWe, requiring a raw fuel gas rate from the gasifier of about 54,886 kg/hr (121,000 lb/hr), assuming a power island efficiency of 60% (LHV). These two novel gas cleaning process alternatives are illustrated in Figure 4.6.

4.5.2 Process Descriptions

The process descriptions for the HP-SOFC fuel gas cleaning application are identical to those for the novel syngas cleaning, chemical or liquid fuel synthesis application. The only alteration for the HP-SOFC gas cleaning is that an expansion turbine and electric generator is placed at the high-pressure, cleaned fuel gas, expanding the fuel gas to the SOFC power island inlet pressure and generating electric power. The HP-SOFC fuel gas cleaning process sectional diagrams are identical to Figures 4.11, 4.12, and 4.13.

The LP-SOFC fuel gas cleaning process has a raw fuel gas inlet pressure of 1034 kPa (150 psia), and the process configuration is modified slightly compared to that for the novel chemical or liquid fuel synthesis syngas cleaning process to improve process economics. The costs of the barrier filters used in the novel chemical or liquid fuel synthesis application are sensitive to the fuel gas volumetric flow, increasing significantly as the volumetric flow increases. The lower operating pressure of the LP-SOFC application calls for two changes in the process equipment used: (1) the primary barrier filter used in the bulk desulfurization section is replaced by a much lower-cost, high-efficiency cyclone; (2) the Stage I barrier filter-reactor used in the Ultra-Clean section is replaced by a cheaper granular, moving bed filter-reactor. The sulfur recovery system remains unchanged. The use of the high-efficiency cyclone in the bulk desulfurization section means that some gasifier char will pass through the transport desulfurizer, having uncertain impacts on the performance of that unit, and some char will also enter the Ultra-Clean section. The use of the granular, moving bed filter-reactor in the Ultra-Clean section means that Stage II will be exposed to some char as well as to some Stage I sulfur and HCl sorbent products.

Figure 4.19 shows the novel LP-SOFC bulk desulfurization section process flow diagram. Its description is similar to that for Figure 4.11, except for the noted modification with the high-efficiency cyclone replacing the primary barrier filter system. Figure 4.20 shows the novel LP-SOFC Ultra-Clean section process flow diagram, again modified as indicated above, with the granular, moving bed filter-reactor system replacing the Stage I barrier filter-reactor.

The granular, moving bed filter-reactor system consists of a SWPC granular, moving bed filter vessel, using a cheap bed media such as dead-burned dolomite, having a particle diameter range of 3.2 to 6.4 mm (1/8 inch to 1/4 inch) (Newby et al., 1996). The granular, moving bed filter vessel is a refractory-lined pressure vessel, about 3 m (10 ft) in diameter and 10.7 m (35 ft) tall. The bed media flows very slowly downward by gravity and collects about 90% of the injected Stage I sorbents, as well as char and bulk desulfurization sorbent. The injected sorbent particles are well-mixed with the fuel gas in the inlet region of the granular, moving bed filter-reactor, and are accumulated within the granular bed. The sorbent particles react with the sulfur and halide contaminants, reducing them to about the 1ppmv level. The average superficial gas velocity through the granular bed section is about 1.2 m/s (4 ft/s), providing about two to three seconds of gas-sorbent contact time in the bed.

The bed media, flowing with a rate of about 9,390 kg/hr (20,700 lb/hr), and captured fine particles, having a flow rate of about 454 kg/hr (1,000 lb/hr), drain from the bottom of the granular, moving bed filter. A screw conveyor controls the rate of media flow through the filter-reactor. The drained solids pass to a mechanical particle sieve-separator that separates greater than 90%

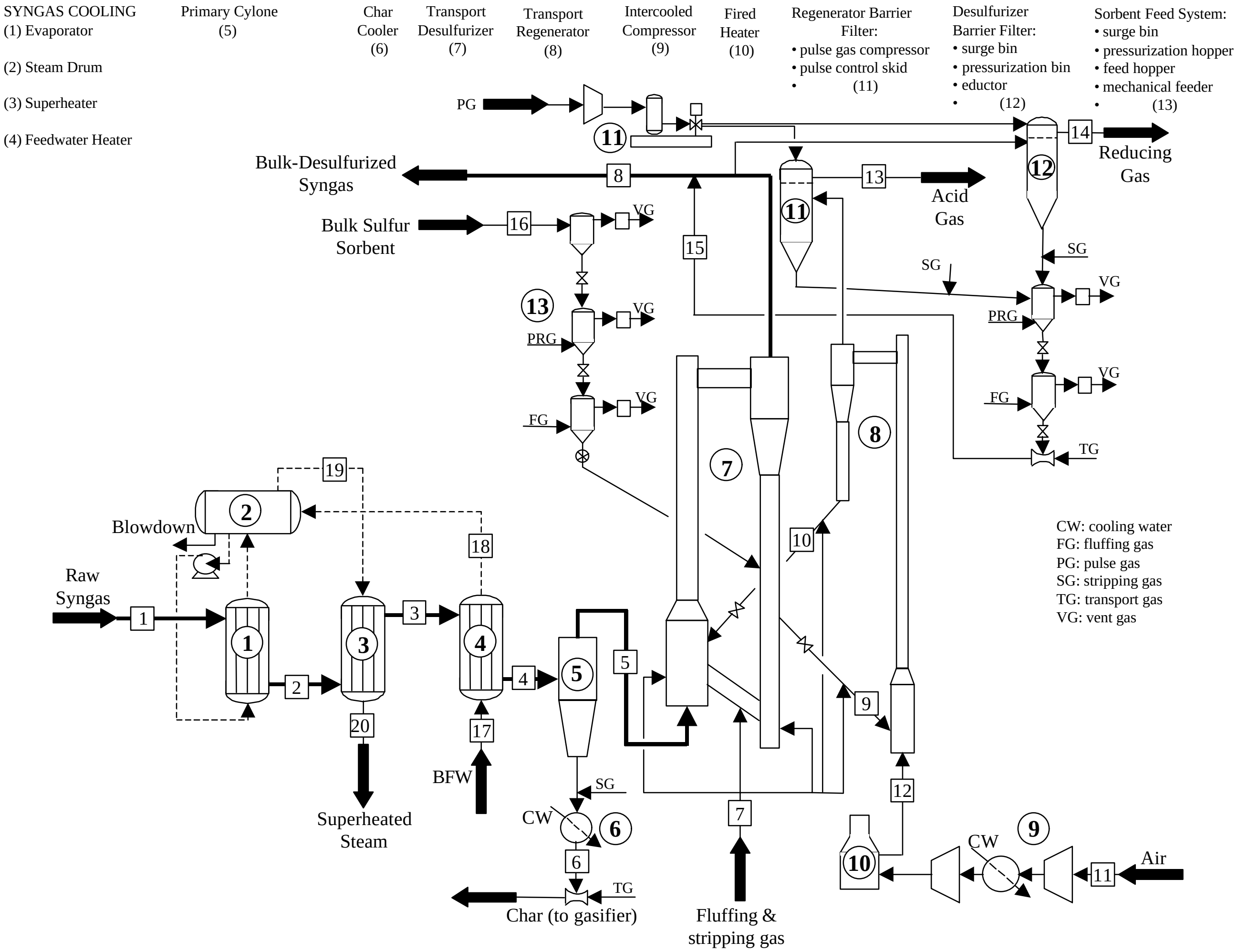


Figure 4.19 - Novel LP-SOFC Bulk Desulfurization Section

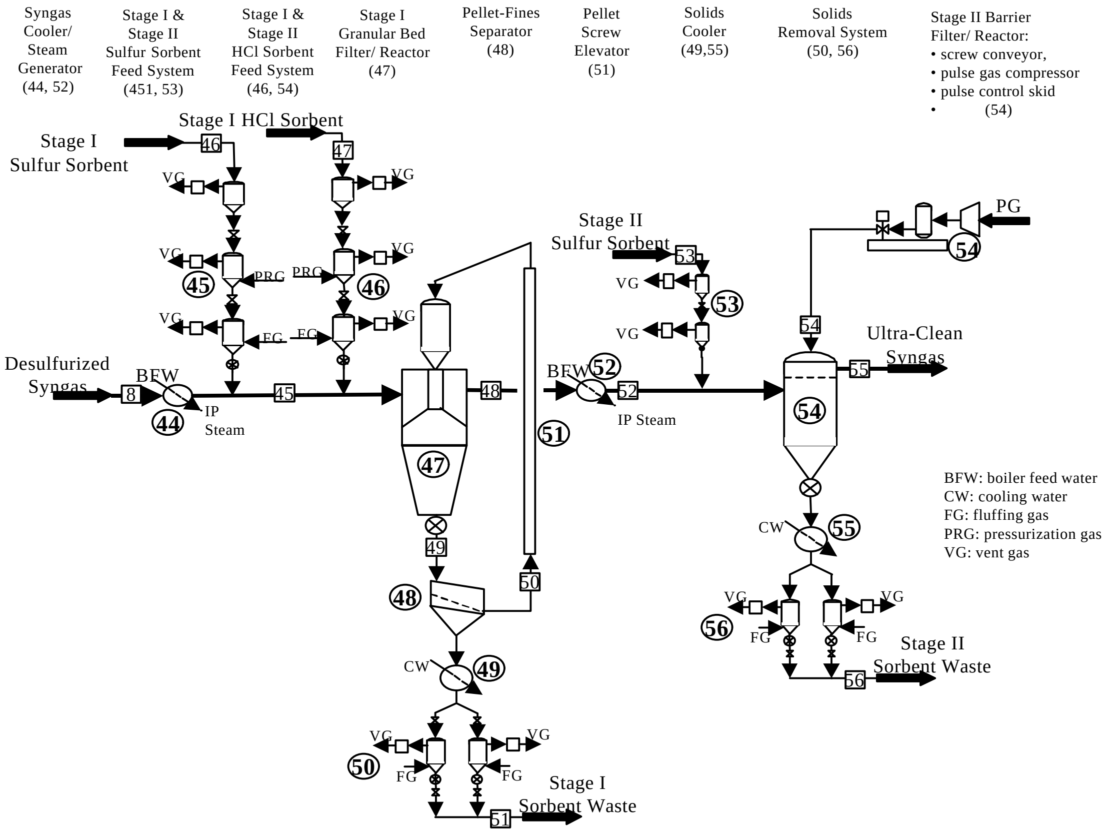


Figure 4.20 - Novel LP-SOFC Fuel Gas Cleaning Ultra-Clean Section

of the fine particles from the bed media. The bed media particles are then circulated back to the top of the granular, moving bed filter using screw conveyor sections that are water cooled with only minimal cooling of the bed media resulting. A fresh feed system to provide very small makeup of bed media is included.

Note that all of the HCl removal is completed in Stage I for the SOFC application. Process alternatives for fuel gas drying and HCl scrubbing are not considered appropriate for the SOFC application because of the less stringent gas cleaning requirement, but they could be used if needed. Figure 4.12 is representative for the novel SOFC sulfur recovery section. Table 4.48 lists the specific sorbent assumptions applied for the novel SOFC fuel gas cleaning process evaluation. The same assumptions are applied for both the HP and the LP-SOFC processes.

Table 4.48 - Novel SOFC Fuel Gas Cleaning Assumed Sorbent Conditions

Bulk Desulfurizer Section	
Bulk sorbent type	zinc titanate (Zn/Ti mole ratio 1.5)
Desulfurizer contactor type	transport reactor
Desulfurizer gas inlet temperature	510°C (950°F)
Regenerator contactor type	entrained bed
Regenerator temperature	732°C (1350°F)
Bulk sorbent makeup rate	Zn/S molar ratio 0.024 (100 lb/hr in chemical synthesis case)
Ultra-Clean Section	
Stage I temperature	499°C (930°F)
Stage I sulfur sorbent type	zinc titanate (Zn/Ti mole ratio 1.5)
Stage I sulfur sorbent feed rate	ZnO/S molar ratio 3.3 from elutriated sorbent; fresh sorbent fed to increase ZnO/S to 5.3
Stage I HCl sorbent type	Trona (Na_2CO_3·$NaHCO_3$·$2H_2O$)
Stage I HCl sorbent feed rate	Na/HCl molar ratio 5.0
Stage II temperature	343°C (650°F)
Stage II sulfur sorbent type	G-72E (70 wt% Zn)
Stage II sulfur sorbent feed rate	Zn/S molar ratio 5.0
Stage II HCl sorbent type	None
Stage II HCl sorbent feed rate	None

4.5.3 Process Material & Energy Balances and Overall Performance

High-Pressure SOFC Fuel Gas Cleaning

The material & energy balances for the novel HP-SOFC fuel gas cleaning process are identical to those listed and described in Section 4.3, Tables 4.34 and 4.35, for the novel chemical or liquid fuel synthesis application. The Ultra-Clean section flows, shown in Table 4.36 for the novel chemical or liquid fuel synthesis application, are modified slightly to account for less stringent cleaning requirements with the novel HP-SOFC application.

A gas expander and electric generator are added to reduce the cleaned syngas pressure down to that needed for the SOFC power island. The overall performance results are shown for novel HP-SOFC fuel gas cleaning in Table 4.49. Significant power is generated by the fuel gas expansion turbine-generator relative to the process power consumption.

Table 4.49 - Novel HP-SOFC Fuel Gas Cleaning Overall Performance

INPUTS	
Material	**kg/hr (lb/hr)**
Raw fuel gas	81,140 (178,880)
Inert gas (nitrogen)	3,358 (7,404)
Air	9,752 (21,450)
Raw water	800
Chemicals	
Bulk desulfurizer sorbent	45 (100)
Stage I sulfur sorbent	28 (62)
Stage I HCl sorbent	7,580 (1,671)
Stage II sulfur sorbent	2 (5)
Stage II HCl sorbent	0
Caustic	0
Total	95,246 (209,977)
Heat Energy	**GJ/hr (MBtu/hr)**
Fuel	10.24 (9.71)
Power Use	**kW**
Pump power	32
Compressor power	684
Solids handling power	3
Expander	-7197
Total power	-6478
OUTPUTS	
Material	**kg/hr (lb/hr)**
Cleaned fuel gas	82,587 (182,070)
Char (dry)	481 (1,061)
Waste water	776 (1,710)
Sulfur condensate	452 (996)
Tail gas	10,165 (22,409)
Inert exhaust gas	163 (359)
Solid waste	622 (1,371)
Total	95,245 (209,976)
Heat Energy	**GJ/hr (MBtu/hr)**
Net HP-steam production	139.3 (132.0)
Net IP-stream product	30.6 (29.0)
Net LP-stream product	-190.7 (-180.8)
Net cooling water used	265.6 (205.3)
Sulfur Removal Performance	
Total Process sulfur removal eff (%):	99.82
Sulfur byproduct, kg/hr (lb/hr):	443.2 (977.1)
Sulfur byproduct efficiency (%):	98.05

The HP-SOFC cleaned fuel gas conditions and composition are shown in Table 4.50. The cleaned fuel gas temperature is reduced to 176°C (348°F) by the expansion. The HP-SOFC tail gas conditions and composition are shown in Table 4.51, and is similar to that for the novel chemical or liquid fuel synthesis application.

Table 4.50 - Novel HP-SOFC - Cleaned Fuel Gas Conditions and Composition

Temperature, °C (°F)	176 (348)
Pressure, kPa (psia)	814 (118)
Mass flow, kg/hr (lb/hr)	82,586.8 (182,069.7)
Molar flow CO + H_2, kg-mole/hr	3,204.8
Heating value, GJ/kg-mole (Btu/lb-mole)	200,002 (86,000)
Composition	
hydrogen (mole%)	32.20
methane (mole%)	0.15
nitrogen (mole%)	3.42
argon (mole%)	0.65
carbon monoxide (mole%)	44.42
carbon dioxide (mole%)	7.54
water (mole%)	11.52
hydrogen sulfide (ppbv)	94.0
carbonyl sulfide (ppbv)	5.6
hydrogen chloride (ppbv)	982.4
hydrogen cyanide (ppbv)	29,471
ammonia (ppmv)	972

Table 4.51- Novel HP-SOFC Tail Gas Conditions and Composition

Temperature, °C (°F)	32 (90)
Pressure, kPa (psia)	117.9 (17.1)
Mass flow, kg/hr (lb/hr)	10,164.5 (22,408.6)
Composition	
nitrogen (mole%)	77.77
oxygen (mole%)	4.53
argon (mole%)	1.13
carbon dioxide (mole%)	13.23
water (mole%)	3.33
sulfur dioxide (ppmv)	72
carbon monoxide (ppmv)	1
hydrogen cyanide (ppbv)	712
triethanolamine (ppbv)	2.3

Low-Pressure SOFC Fuel Gas Cleaning

Operation of the novel gas cleaning process at lower pressures changes the details of the material & energy balances for the process. These differences are reflected in Table 4.52, showing the overall performance results for the novel LP-SOFC fuel gas cleaning process. Table 4.53 shows the cleaned fuel gas conditions and composition and Table 4.54 shows the tail gas conditions and composition.

Table 4.52 - Novel LP-SOFC Fuel gas Cleaning Process Performance

INPUTS	
Material	**kg/hr (lb/hr)**
Raw fuel gas	54,886 (121,000)
Inert gas (nitrogen)	2,127 (4,689)
Air	6,289 (13,865)
Granular bed filter media	3 (7)
Fuel	116(255)
Chemicals	
Bulk desulfurizer sorbent	30 (67)
Stage I sulfur sorbent	19 (42)
Stage I HCl sorbent	513 (1,130)
Stage II sulfur sorbent	2 (3)
Stage II HCl sorbent	0
Caustic	0
Total	64,062 (141,231)
Heat Energy	**GJ/hr (MBtu/hr)**
Fuel	6.80 (6.45)
Power Use	**kW**
Pump power	18
Compressor power	232
Solids handling power	64
Expander	-418
Total power	-104
OUTPUTS	
Material	**kg/hr (lb/hr)**
Cleaned fuel gas	55,835 (123,093)
Char (dry)	293 (646)
Waste water	508 (1,121)
Sulfur condensate	305 (673)
Tail gas	6,593 (14,534)
Inert exhaust gas	72 (159)
Solid waste	503 (1,109)
Total	64,069 (141,245)
Heat Energy	**GJ/hr (MBtu/hr)**
Net HP-steam production	94.0 (89.1)
Net IP-stream product	22.7 (21.5)
Net LP-stream product	-84.0 (-79.6)
Net cooling water used	87.6 (83.0)
Sulfur Removal Performance	
Total Process sulfur removal eff (%):	99.85
Sulfur byproduct, kg/hr (lb/hr):	299.7 (660.8)
Sulfur byproduct efficiency (%):	98.03

Table 4.53 - Novel LP-SOFC - Cleaned Fuel Gas Conditions and Composition

Temperature, °C (°F)	343 (650)
Pressure, kPa (psia)	834 (121)
Mass flow, kg/hr (lb/hr)	55,834.9 (123,092.8)
Molar flow CO + H_2, kg-mole/hr	2,167.7
Heating value, GJ/kg-mole (Btu/lb-mole)	200,071 (86,030)
Composition	
hydrogen (mole%)	32.21
methane (mole%)	0.15
nitrogen (mole%)	3.39
argon (mole%)	0.65
carbon monoxide (mole%)	44.44
carbon dioxide (mole%)	7.54
water (mole%)	11.52
hydrogen sulfide (ppbv)	94.0
carbonyl sulfide (ppbv)	5.6
hydrogen chloride (ppbv)	982.7
hydrogen cyanide (ppbv)	29,480
ammonia (ppmv)	972

Table 4.54 - Novel LP-SOFC - Tail Gas Conditions and Composition

Temperature, °C (°F)	32 (90)
Pressure, kPa (psia)	117.9 (17.1)
Mass flow, kg/hr (lb/hr)	6,592.8 (14,534.3)
Composition	
nitrogen (mole%)	77.65
oxygen (mole%)	4.23
argon (mole%)	1.14
carbon dioxide (mole%)	13.61
water (mole%)	3.37
sulfur dioxide (ppmv)	63
carbon monoxide (ppmv)	1
hydrogen cyanide (ppbv)	109
triethanolamine (ppbv)	2.2

4.5.4 Process Economics

The novel HP-SOFC fuel gas cleaning process plant section costs (installed equipment costs) are listed at the top of Table 4.55. The Ultra-Clean section has the highest cost of the four sections due to its inclusion of the fuel gas expander and electric generator. The other sections have the same equipment costs as in the novel syngas cleaning process. The table calculates the total capital requirement, equivalent to about 185 \$/kW (= \$27,421,000 / 148,000 kW). The HP-SOFC power island has a nominal generating capacity of 148 MWe.

Table 4.55 - Novel HP-SOFC Fuel Gas Cleaning - Capital Requirement

Plant Section	Process Contingency, %	Cost, k$ w/o Contingency
Syngas Cooler Section	10	1,026
Primary Desulfurization Section	20	3,675
Ultra-Clean Section	25	6,320
Sulfur Recovery Section	15	4,453
Subtotal, Process Plant Cost		**15,474**
General Plant Facilities		1,934
Engineering Fees		1,702
Process Contingency (Using contingencies listed above)		3,086
Project Contingency (10%)		1,741
Total Plant Cost (TPC)		**23,937**
Adjustment for Interest and Inflation		1,104
Total Plant Investment (TPI)		**25,041**
Prepaid Royalties		77
Initial Catalyst and Chemical Inventory		527
Startup Costs		499
Spare Parts		120
Working Capital		1,157
Total Capital Requirement (TCR)		**27,421**

The annual operating cost of the novel HP-SOFC gas cleaning process is shown in Table 4.56. The operating cost benefits significantly from the electric power generated by fuel gas expansion. Likewise, the cost-of-fuel-gas-cleaning, shown in Table 4.57 benefits from the value of the electricity generated by fuel gas expansion.

Novel LP-SOFC fuel gas cleaning, Table 4.58, has a slightly higher total capital requirement than in novel HP-SOFC, at about 191 $/kW (= $19,065,000 / 100,000 kW). The LP-SOFC power island has a nominal generating capacity of 100 MWe. The annual operating cost (Table 4.59) and cost-of-fuel-gas-cleaning (Table 4.60) are substantially higher than the HP-SOFC fuel gas cleaning process.

Since the sorbent feed rates and costs applied in the novel SOFC fuel gas cleaning cost estimates represent the maximum expected values, it is enlightening to consider the sensitivity of the process costs to the sorbent feed rates and sorbent costs, exactly as was done for the novel syngas cleaning process. It is possible that the sorbent feed rates utilized in the evaluation, including that of the bulk desulfurization sorbent, might be cut in half and still achieve the syngas cleaning requirements. It is also possible that the sorbent delivered prices for the fabricated Stage I and II sulfur sorbent and the Stage II HCl sorbent might be reduced 50% when mature technology is commercialized and used extensively. The trona price is not likely to drop substantially and is fixed at its initial cost.

These two reduction factors have been applied and the results are listed in Table 4.61. There is a capital requirement reduction due to reduced solids handling capital costs, as well as reductions in the annual operating cost and the cost-of-fuel-gas-cleaning. The annual operating costs in both novel SOFC configurations drop by more than 70% and the cost-of-syngas-cleaning is reduced by more than 50%.

Table 4.56 - Novel HP-SOFC Fuel Gas Cleaning - Annual Operating Cost

Cost Item	Quantity		Unit $ Price		Annual Cost, k$
Fuel Type: Natural Gas	233	MBtu/D	4	/MBtu	272
Consumable Materials					
Claus Catalyst	0.0005	ton/day	1000	/ton	0
Bulk desulf sorbent	1.2	ton/day	8000	/ton	2,803
Sulfur sorbent 1	0.744	ton/day	8000	/ton	1,738
Sulfur sorbent 2	0.054	ton/day	8000	/ton	126
HCl sorbent 1	20.05	ton/day	60	/ton	351
HCl sorbent 2	0	ton/day	2000	/ton	0
Inert Gas	88.85	ton/day	2.5	/ton	65
Power	-155472	kW-hr/D	0.05	/kW-hr	(2,270)
HP Steam	-3168	MBtu/day	3.5	/MBtu	(3,238)
IL Steam	-610	MBtu/day	2.25	/MBtu	(401)
LP Steam	4339	MBtu/day	1.25	/MBtu	1,584
Cooling water	4927	MBtu/day	0.25	/MBtu	360
Ash/Sorbent Disposal Costs	16.46	ton/day	20	/ton	96
Plant Labor					
Oper Labor (incl benef)	2	Men/shift	35	/hr.	612
Supervision & Clerical					298
Maintenance Costs					957
Insurance & Local Taxes					479
Royalties					3
Other Operating Costs					99
Total Operating Costs					**3,935**
By-Product Sulfur Credit	11.67	ton/day	55	/ton	187
Net Operating Costs					**3,748**

Table 4.57- Novel HP-SOFC Fuel gas Cleaning - Cost-of-Fuel-Gas-Cleaning (fuel gas flow = 81,140 kg/hr)

	Current-$ basis $/1000-kg ($/ 1000-lb)	**Constant-$ basis $/1000-kg ($/ 1000-lb)**
Capital charges	8.44 (3.83)	4.96 (2.25)
Fuel costs	0.57 (0.26)	0.49 (0.22)
Operating & maintenance	7.01 (3.18)	6.11 (2.77)
Total	16.03 (7.27)	11.57 (5.25)

Table 4.58 - Novel LP-SOFC Fuel Gas Cleaning - Capital Requirement

Plant Section	Process Contingency, %	Cost, k$ w/o Contingency
Syngas Cooler Section	10	776
Primary Desulfurization Section	20	1,851
Ultra-Clean Section	30	5,020
Sulfur Recovery Section	15	2,845
Subtotal, Process Plant Cost		**10,492**
General Plant Facilities		1,312
Engineering Fees		1,154
Process Contingency (Using contingencies listed above)		2,381
Project Contingency (10%)		1,180
Total Plant Cost (TPC)		**16,519**
Adjustment for Interest and Inflation		762
Total Plant Investment (TPI)		**17,280**
Prepaid Royalties		52
Initial Catalyst and Chemical Inventory		327
Startup Costs		523
Spare Parts		83
Working Capital		799
Total Capital Requirement (TCR)		**19,065**

Table 4.59 - Novel LP-SOFC Fuel Gas Cleaning - Annual Operating Cost

Cost Item	Quantity		Unit $ Price		Annual Cost, k$
Fuel Type: Natural Gas	155	MBtu/day	4	/MBtu	$181
Consumable Materials					
Claus Catalyst	0.0004	ton/day	1000	/ton	0
Bulk desulf sorbent	0.804	ton/day	8000	/ton	1,878
Sulfur sorbent 1	0.502	ton/day	8000	/ton	1,173
Sulfur sorbent 2	0.035	ton/day	8000	/ton	82
HCl sorbent 1	13.56	ton/day	60	/ton	238
HCl sorbent 2	0	ton/day	2000	/ton	0
Inert Gas	58.3	ton/day	2.5	/ton	
Power	-2496	kW-hr/day	0.05	/kW-hr	(36)
HP Steam	-2138	MBtu/day	3.5	/MBtu	(2,185)
IL Steam	-516	MBtu/day	2.25	/MBtu	(339)
LP Steam	1910	MBtu/day	1.25	/MBtu	697
Cooling water	1992	MBtu/day	0.25	/MBtu	145
Ash/Sorbent Disposal Costs	12.23	ton/day	20	/ton	71
Plant Labor					
Oper Labor (incl benef)	2	Men/shift	35	/hr.	612
Supervision & Clerical					263
Maintenance Costs					661
Insurance & Local Taxes					330
Royalties					2
Other Operating Costs					88
Total Operating Costs					**3,860**
By-Product Sulfur Credit	7.93	ton/day	55	/ton	127

Net Operating Costs	3,732

Table 4.60- Novel LP-SOFC Fuel Gas Cleaning - Cost-of-Fuel-Gas-Cleaning (fuel gas flow = 54,886 kg/hr)

	Current-$ basis $/1000-kg ($/ 1000-lb)	**Constant-$ basis $/1000-kg ($/ 1000-lb)**
Capital charges	8.69 (3.94)	5.09 (2.31)
Fuel costs	0.55 (0.25)	0.49 (0.22)
Operating & maintenance	10.60 (4.81)	9.24 (4.19)
Total	19.84 (9.00)	14.81 (6.72)

Table 4.61 - Novel SOFC Fuel Gas Cleaning Cost Sensitivity

Novel SOFC Fuel Gas Cleaning Case and sorbent assumptions	Capital Requirement, k$	Annual Operating Cost, k$	Cost-of-syngas-cleaning, $/1000 kg of Syngas (constant-$ basis)
HP-SOFC - maximum sorbent costs and feed rates (Tables 4.55, 4.56, 4.57)	27,421	3,748	11.57
HP-SOFC - reduced costs and feed rates by 50%	26,259	24	4.81
LP-SOFC - maximum sorbent costs and feed rates (Tables 4.58, 4.59, 4.60)	19,065	3,732	14.81
LP-SOFC - reduced costs and feed rates by 50%	18,306	1,228	8.11

4.6 CONCEPTUAL MARKET EVALUATION

Chemical or Liquid Fuel Synthesis Applications

A conceptual market evaluation for the novel syngas cleaning process, for chemical or liquid fuel synthesis, has been based on the novel syngas cleaning process total capital requirement range as reported in Table 4.41. The estimated total capital requirement is $24.2 to 25.6 million depending on the specific configuration of the novel syngas cleaning plant selected. This includes costs for the syngas cooler section, the bulk desulfurization section, the Ultra-Clean processing section, and the sulfur recovery section. Although the Ultra-Clean gas polishing section is the focus of this technology study, the full complement of integrated equipment is required to prepare syngas for the synthesis process. The technology development of the Ultra-Clean gas polishing section impacts the full list of equipment.

Quantified demand for syngas cleaning processes is derived from recent forecasts of world-wide syngas capacity increases as reported jointly by SFA Pacific (Simbeck, 1999), the Gasification Technologies Council (GTC, 2001) and the U.S. Department of Energy (DOE, 2000). The studies report that, in the period 1999-2005, new gasifiers totaling 40 million Nm^3/day of syngas capacity will be commissioned to support production of chemicals. This capacity was also expressed as 5,000 MWt.

The baseline design Ultra-Clean syngas polishing section would process 2,221,796 Nm^3/day of syngas or 283.3 MW_t. Were this immediately planned capacity to be met with Ultra-Clean processing technology, 18 plants of the base design scale would be required. The total capital cost of those syngas cleaning systems would be about $450 million in end-1999 dollars (18 plants at $25 million each), and would represent a cost savings to industry of more than $200 million. The planned capacity described in the reports may be derived from a mix of coal or petroleum residual feedstocks. It is expected that the same degree of syngas cleanup would be required regardless of the planned feedstock.

The Ultra-Clean syngas polishing system will not be available in time to satisfy the capacity additions described in the reports. However, it can be reasonably assumed that the current plan for capacity additions can be extrapolated going forward. This suggests a market for novel syngas cleaning with Ultra-Clean syngas polishing systems of $75 million/yr for chemical and fuels production. It is planned to further evaluate this market potential concurrent with the next phase of bench scale testing of the Ultra-Clean syngas polishing process.

SOFC Power Generation Applications

The market for Ultra-Clean fuel gas polishing systems for Vision 21, SOFC based central power generation systems will not materialize before 2010. An SOFC production infrastructure is just now becoming commercial. Planned SOFC production capacity additions will not be enough to satisfy anticipated demand for natural gas-fueled distributed generation before 2010. By 2010 it is expected that fuel cell production capacity will be as much as 7 GWe/yr (Merrill Lynch, 2001) and applications in combined-cycle central generation plants will become feasible.

The novel fuel gas cleaning process, utilizing the Ultra-Clean fuel gas polishing system configured for SOFC power generation, would require a capital investment of about $185/kWe for HP-SOFC (Table 4.55). Thus each GWe of SOFC based power plant capacity would require $190 million in capital for novel fuel gas cleaning process equipment.

An estimate is made here of the relative cost-of-electricity between a natural gas-fueled SOFC power plant and a coal-fueled SOFC plant using the novel gas cleaning process. The following assumptions are applied:

- coal-based SOFC plant efficiency of 60%,
- natural gas-based, SOFC plant efficiency of 70% ,
- natural gas fuel cost of $4.7/ GJ ($5 / MBtu),
- coal fuel cost $1.2/GJ ($1.25 / MBtu),
- capital cost premium (over natural gas) for the high-pressure, coal handling and gasification section, $400/kWe (estimated from available IGCC plant cost data),
- premium (over natural gas) for the novel fuel gas cleaning process, $185/kWe.
- capital charges (current dollar basis) of 12.5%,
- differential O&M costs, estimated from HP-SOFC O&M cost in Table 4.57 and available cost data for IGCC and natural gas-fired SOFC,
- plant capacity factor, 80%, resulting in about 7,000 hours per year operation.

These assumptions mean that for equal coal and natural gas fuel energy inputs of 888 GJ/hr (842 MBtu/hr), the natural gas-fueled SOFC power plant will generate 173 MWe, and the coal-fueled SOFC power plant will generate 148 MWe. The coal-fueled SOFC power plant will produce cheaper electricity than the natural gas-fueled SOFC power plant under these assumptions, as is shown in Table 4.62. Coal will be competitive at natural gas prices greater than $4.2/GJ ($4.4 / MBtu).

Table 4.62 - Cost-of-Electricity Differential Breakdown Between Coal and Natural Gas SOFC Power Plants (current $)

Differential capital investment, (Coal - NG) $k	= (400 $/kW + 185 $/kW) x 148,000 kW	86,600
Differential power, MWe (Coal - NG)	= 173 MWe - 148 MWe	-25
Differential capital charges, mills/kWh (Coal - NG)	= (400 $/kW + 185 $/kW) x 1000 mills/$ X 0.125 / 7,000 hr	10.4
Differential fuel costs, mills/kWh (Coal - NG)	$= (1.25\ \$/10^{6}\ \text{Btu}^{-1}\ \text{x}\ 3412\ \text{Btu/kWh} / 0.6 - 5\ \$/10^{6}\ \text{Btu}^{-1}\ \text{x}\ 3412\ \text{Btu/kWh} / 0.7)\ \text{x}\ 1000\ \text{mills}/\$$	-17.3
Differential O&M costs, mills/kWh (Coal - NG)	estimated (see assumptions, p. 167)	4.1
Total Differential, mills/kWh (Coal - NG)	= 10.4 - 17.3 + 4.1	-2.8

4.7 RESULTS AND DISCUSSION

The conceptual process evaluations have been conducted to produce evidence that addresses the question: does the novel gas cleaning process, utilizing the Ultra-Clean gas polishing technology, have the potential to be sufficiently superior to the conventional gas cleaning technology to merit further development? The process evaluations indicate that this potential economic superiority is highly likely, but it is sensitive to the sorbent consumption rates, and the sorbent prices, needed to meet the gas cleaning requirements.

The conceptual process evaluations have identified potentially viable process flow schemes for the novel gas cleaning system for two applications, general chemical or liquid fuel synthesis, and SOFC power generation. Three process alternatives for chemical or liquid fuel synthesis were evaluated, novel gas cleaning using the Base Ultra-Clean section, novel gas cleaning using the Ultra-Clean section with drying, and novel gas cleaning using the Ultra-Clean section with HCl scrubbing. The Base Ultra-Clean section and the Ultra-Clean section with HCl scrubbing result in almost identical cost-of-syngas-cleaning. The Ultra-Clean section with drying has higher estimated cost-of-syngas-cleaning due to its higher capital investment, but has potentially improved performance. Two process alternatives for novel SOFC power generation fuel gas cleaning were evaluated: high-pressure gas cleaning and low-pressure gas cleaning. The high-pressure, fuel gas cleaning alternative has inherently lower capital cost and lower cost-of-fuel gas-cleaning than the low-pressure SOFC fuel gas cleaning process.

The following sorbents have been selected for all of the novel gas cleaning process alternatives, based on the test work completed:

- Bulk sorbent: zinc titanate (Zn/Ti mole ratio 1.5)
- Stage I sulfur sorbent: zinc titanate (Zn/Ti mole ratio 1.5)
- Stage I HCl sorbent: Trona
- Stage II sulfur sorbent: G-72E (70 wt% Zn)
- Stage II HCl sorbent: G-92C (6.4 wt% Na)

The novel gas cleaning process has the potential to achieve acceptable sulfur, halide and particulate content in the cleaned gas for the SOFC power generation application, satisfying all of the SOFC gas cleaning requirements:

- particulate < 0.1 ppmw,
- H_2S < 100 ppbv,
- HCl < 1 ppmv,
- NH_3 < 5000 ppmv.

For the general chemical or liquid fuel synthesis application, the novel gas cleaning process only addresses sulfur, halides and particulate, but does not deal with ammonia or HCN, typical contaminants for some synthesis applications:

- particulate < 0.1 ppmw,
- total sulfur < 60 ppbv,
- total halides < 10 ppbv,
- NH_3 < 10 ppmv,
- HCN < 10 ppbv.

The novel gas cleaning process alternative that utilizes HCl scrubbing does result in considerable ammonia removal and this can be extended to the level required for ammonia cleaning with little additional cost.

The control of mercury and arsenic may be required in some synthesis applications, and these components might be subject to future emissions control regulations from all coal-fueled plants. In coal gasification syngas, mercury will exist primarily as elemental mercury and arsenic may exist in several forms. Significant arsenic will probably be removed in the primary barrier filter, but mercury removal through char reactions in the primary barrier filter will be limited. Mercury might be easily controlled within the Ultra-Clean section using well known sorbents (activated carbon impregnated with sulfur, activated cokes, activated aluminas or zeolites) injected into the Stage II gas or using a packed bed reactor placed in Stage II (Bingham, 1990). While only limited testing has been conducted in reducing gases, a variety of other sorbents, operable at higher temperatures, might also be used in Stage II of the Ultra-Clean section (Granite et al., 1998; Nelson, 2000). Activated coke is used commercially in waste-to-energy plants to remove mercury and other trace components, SO_2 and NOx at normal flue gas temperatures. Activated carbon beds, operating at 0°C (32°F) are in commercial use for removing H_2S and halogens from dried fuel gas, produced by waste-water biogas cleaning, to fuel a phosphoric-acid fuel cell power generation system (Theron, 2000). Such options should be much cheaper than controlling mercury, or arsenic at the plant stack because of the much higher partial-pressures of the contaminants in the high-pressure syngas. Some of these sorbent options will also provide additional Stage II sulfur and halogen removal.

Tables 4.63, 4.64, and 4.65 list the major factors for comparison between the novel gas cleaning processes and the conventional processes for the two applications. Each table lists key process factors, environmental factors and economic factors.

Table 4.63 - Synthesis Syngas Cleaning Process Comparisons
Raw syngas rate 81,140 kg/hr (178,880 lb/hr), inlet pressure 4,137 kPa (600 psia)

	Conventional (Rectisol)	Novel		
		Base case	with Drying	with HCl scrub
Process Factors				
Total syngas pressure drop (% of inlet)	20.8	15.4	20.8	20.7
Clean syngas temperature °C (°F)	371 (700)	288 (550)	347 (650)	338 (640)
Raw syngas molar CO+H_2 flow loss (%)	0.088	1.50	1.50	1.50
Cleaned syngas H_2O mole%	3.2×10^{-5}	11.49	0.86	0.35
Cleaned syngas CO_2 mole%	7.3×10^{-4}	7.54	8.44	8.40
Environmental Factors				
Tail gas/Raw syngas mass ratio (%)	41.4	12.5	12.5	12.5
Tail gas SO_2 release, kg/hr (lb/hr)	6.8 (15.0)	1.5 (3.4)	1.5 (3.4)	1.5 (3.4)
Tail gas CO_2 release, kg/hr (lb/hr)	16,421 (36,202)	1,965 (4,333)	1,965 (4,333)	1,965 (4,333)
Maximum solid waste, kg/hr (lb/hr)	0	545 (1,201)	545 (1,201)	78 (171)
Waste water, kg/hr (lb/hr)	10,843 (23,904)	776 (1,710)	8,869 (19,55)	9,629 (21,228)
Economic Factors				
Total Capital Requirement (k$)	36,588	22.935-24,177	24,380-25,622	23,444-24,532
Annual Operating Cost (k$)	5,429	1,833-5,743	2,455-6,366	1,861-5,705
Cost of Syngas Cleaning (constant $), $ / 1000 kg raw syngas	16.22	7.39 - 14.48	8.75 - 15.85	7.54 - 14.51

Table 4.64 - High-Pressure SOFC Fuel Gas Cleaning Process Comparisons
Raw fuel gas rate 81,140 kg/hr (178,880 lb/hr), inlet pressure 4,137 kPa (600 psia)

	Conventional (Rectisol)	Novel
Process Factors		
Total fuel gas pressure drop (% of inlet)	20.8	15.4
Clean fuel gas heating value, GJ/kg-mole (Btu/lb-mole)	262,095 (112,700)	200,002 (86,000)
Clean-to-Raw fuel gas mass ratio (%)	71.0	101.8
Clean fuel gas temperature, °C (°F)	195 (383)	176 (348)
Clean fuel gas H_2 mole%	41.24	32.30
Environmental Factors		
Tail gas/Raw fuel gas mass ratio (%)	41.4	12.5
Tail gas SO_2 release, kg/hr (lb/hr)	6.8 (15.0)	1.5 (3.4)
Tail gas CO_2 release, kg/hr (lb/hr)	16,421 (36,202)	1,965 (4,333)
Maximum solid waste, kg/hr (lb/hr)	0	622 (1,371)

Waste water, kg/hr (lb/hr)	10,843 (23,904)	776 (1,710)
Economic Factors		
Total Capital Requirement (k$)	39,114	26,259 - 27,421
Annual Operating Cost (k$)	3,885	24 - 3,748
Cost of Fuel Gas Cleaning, $ / 1000 kg raw fuel gas	13.95 (6.34)	4.81 - 11.57

Table 4.65 – Low Pressure SOFC Fuel Gas Cleaning Process Comparisons
Raw fuel gas rate 54,886 (121,000 lb/hr), inlet pressure 1034 kPa (150 psia)

	Conventional (Rectisol)	Novel
Process Factors		
Total fuel gas pressure drop (% of inlet)	21.4	19.3
Clean fuel gas heating value, GJ/kg-mole (Btu/lb-mole)	247,909 (106,600)	200,071 (86,030)
Clean-to-Raw fuel gas mass ratio (%)	81.3	101.7
Clean fuel gas temperature, °C (°F)	371 (700)	343 (650)
Clean fuel gas H_2 mole%	38.99	32.21
Environmental Factors		
Tail gas/Raw fuel gas mass ratio (%)	21.1	12.0
Tail gas SO_2 release, kg/hr (lb/hr)	2.2 (4. 8)	0.9 (1.9)
Tail gas CO_2 release, kg/hr (lb/hr)	4,688 (10,336)	1,309 (2,886)
Maximum solid waste, kg/hr (lb/hr)	0	462 (1,019)
Waste water, kg/hr (lb/hr)	6,662 (14,686)	508 (1,121)
Economic Factors		
Total Capital Requirement (k$)	22,304	18,306 - 19,065
Annual Operating Cost (k$)	3,003	1,228 - 3,732
Cost of Fuel Gas Cleaning (constant $) $ / 1000 kg raw fuel gas	13.82 (6.27)	8.11 - 14.81

The total pressure drop across the gas cleaning systems listed in Table 4.63 is 35% lower for the novel gas cleaning Base Case process than for the conventional syngas cleaning process, and this may be a significant advantage for the novel syngas cleaning process for chemical or liquid fuel synthesis. This reduced pressure drop may also provide some advantage for the SOFC power generation application, especially for the LP-SOFC fuel gas cleaning case (Table 4.65). The evaluation conducted in this report does not account for this potential cost reduction factor.

The final, cleaned gas temperature listed in Tables 4.63 through 4.65 is comparable-to-lower for the novel gas cleaning process relative to the conventional process. This temperature may influence downstream processing of the cleaned syngas, but does not produce a major cost differential between the novel and conventional processes.

The valuable components in the syngas for chemical synthesis (Table 4.63) are CO and H_2, and a small amount of these are lost in the conventional gas cleaning operations (less than 0.1%) by absorption in the solvents and condensates. The novel gas cleaning process, though, looses about 1.5% of the CO and H_2 for the reduction of the regenerator offgas to permit sulfur recovery. The hydrogen content and the heating value of the cleaned fuel gas for SOFC is indicated in Tables 4.64 and 4.65, and both are about 20% lower for the novel fuel gas cleaning than for the conventional fuel gas cleaning process. This is due primarily to the higher CO_2 content of the fuel gas in the novel fuel gas cleaning cases. The hydrogen content and heating value of the fuel gas may influence the design and behavior of the SOFC system, but is not considered to be a critical factor.

The novel gas cleaning process, as indicated in Table 4.63 through 4.65, does not remove CO_2 from the gas, while the conventional gas cleaning process removes almost all of the CO_2 and water vapor from the gas. In the novel syngas cleaning process alternatives with drying and with HCl scrubbing, most of the water is removed from the syngas. This difference in behavior may be important to the specific synthesis application addressed in the plant. In SOFC power generation, it may be advantageous to overall power plant performance to maintain the CO_2 and water vapor in the gas because these components moderate the combustion temperature of the fuel gas and add about 25 to 40% more mass flow through the power generation equipment.

The novel gas cleaning process has some environmental advantages over the conventional gas cleaning process with respect to the tail gas flow and its contaminants (SO_2 and CO_2) released, and the waste water processing required, as is indicated in Tables 4.63 through 4.65. The tail gas mass flow rate is 2 -3 times as much in the conventional process as it is in the novel gas cleaning process, and the conventional process emits about four times as much SO_2 and eight times as much CO_2. The novel gas cleaning process, though, generates solid waste streams, some of which can be combined with the gasifier slag ash/slag as an inert product. The total solid waste generated is less than 1% of the total coal as rate in the plants. No cost for water treatment has been included in the economics, and this may be an important factor, especially for the SOFC power generation application where the typical plant will not have water treatment facilities. The novel gas cleaning processes do generate some waste water, but these waste water streams are lower in contaminants and coal ash than those generated in the conventional gas cleaning process, making water treatment simpler and cheaper. Only in the novel syngas cleaning process alternatives with drying or HCl scrubbing (Table 4.63) do the waste water streams approach the waste water rates of the conventional process.

Even with the conservative assumptions made, the capital investment for the novel gas cleaning process is expected to be much less than that of the conventional gas cleaning process. The novel gas cleaning process generally uses less power and fuel than the conventional gas cleaning process, so it has lower annual cost of operation. The cost-of-gas-cleaning for the novel gas cleaning process is very sensitive to the rate of the sorbent consumption in the process, and the prices of the sorbents. The bulk desulfurization sorbent and the Stage I sulfur sorbent are the key sorbents with respect to cost impact.

The ranges in the economic factors listed in each of the tables (Tables 4.63 through 4.65) relate to assumed ranges of the sorbent feed rates and their prices. The high values for the total capital requirement, annual operating cost and cost of syngas cleaning are those of the conservative design case. The low values in the tables represent reducing the conservative design feed rates of the Ultra-Clean section sorbents and the bulk-desulfurization sorbent by 50%, and reducing the price of the sorbents by 50% (except for the trona, which retains its nominal design price).

The cost-of-gas-cleaning shows very little sensitivity to feed rate and delivered price of the Stage I HCl sorbent, or the Stage II sulfur and HCl sorbents. The cost is most sensitive to the feed rates and delivered price of the bulk desulfurization sorbent and the Stage I sulfur sorbent.

Criteria for sorbent testing performance evaluation are estimated here, based on cost-of-gas-cleaning having greater than 20% advantage over the conventional gas cleaning processes for both the synthesis and the SOFC power generation applications. The guidelines are stated in terms of the maximum value of the sorbent-to-contaminant molar feed ratio (Ms/Mc), times the sorbent price in dollars per unit mass (Cs), that results in 20% cost advantage for the novel gas cleaning process.

In the case of the bulk desulfurization sorbent, the Ms quantity is the total molar makeup feed rate of fresh sorbent to the bulk desulfurizer. Mc is the contaminant (total sulfur or HCl) molar flow rate to the Ultra-Clean Stage I section of the novel gas cleaning process. For the Stage II sorbents, Ms is the sorbent molar feed rate to Stage II and Mc is the contaminant molar flow rate to Stage II. The sorbent prices should represent the commercially mature prices of these sorbents. The values of these factors used in the process evaluations were:

- Bulk desulfurization sorbent (Zn-based): (Ms/Mc) x Cs ($/kg) = 14.1 to 28.2
- Stage I sulfur sorbent (Zn-based): (Ms/Mc) x Cs ($/kg) = 8.8 to 17.6
- Stage I HCl sorbent (trona): (Ms/Mc) x Cs ($/kg) = 0.13to 0.26
- Stage II sulfur sorbent (Zn-based): (Ms/Mc) x Cs ($/kg) = 22 to 44
- Stage II HCl sorbent (NaO-based): (Ms/Mc) x Cs ($/kg) = 5.5 to 11.0
-

The results of an evaluation of the competing process cost estimates has been used to generate target criteria for bench-scale tests. In generating these target criteria, the sorbent feed rates for the design of the feed systems and the waste solids handling systems has been fixed at the conservatively high values. Table 4.66 lists the estimated maximum acceptable molar feed rate ratio (Ms/ Mc) times the sorbent price ($/mass) for each application and process alternative. The most sensitive sorbert group is the bulk desulfurization sorbent plus the Stage I sulfur sorbent. These are combined because the bulk desulfurization sorbent will contribute to Stage I sulfur removal and the two sorbent sources will have similar prices. The ranges in the factor in Table 4.66 for the combined sorbents (column 1) represent the range obtained when utilizing both the current-dollar basis and the constant-dollar basis for the process cost comparisons.

The Stage I HCl sorbent is shown separately because it has the largest flow rate of the sorbents, but it has a relatively low cost. Finally, the Stage II HCl sorbent plus the Stage II sulfur sorbent are considered, being the least sensitive sorbents with respect to cost due to the relatively low sulfur and HCl flow rates in Stage II. If reasonable commercial prices for the sorbents can be established, then the maximum acceptable sorbent feed rates can be projected from Table 4.66. Based on this Table, it is clear that very large sorbent molar feed rations may be applied in Stage II of the Ultra-Clean process, and for the Stage I HCl sorbent. Even the Stage I sulfur sorbent feed rate can be substantial if the bulk desulfurization sorbent losses can be limited.

Table 4.66 – Maximum Acceptable Sorbent Feed Rate Criteria for 20% Cost Advantage over Conventional Gas Cleaning

	Bulk Desulfurization Sorbent + Stage I Sulfur Sorbent (Ms/Mc) x $/kg	Stage I HCl Sorbent (Trona) (Ms/Mc) x $/kg	Stage II Sulfur Sorbent + Stage II HCl Sorbent (Ms/Mc) x $/kg
Chemical Synthesis Application			
Ultra-Clean Base Section	37.3-38.8	0.66	110
Ultra-Clean with Drying	29.1-29.5	0.66	110

Ultra-Clean with HCl Scrubbing	37.3-38.6	----	220
SOFC Power Generation Application			
HP Gas Cleaning	43.7-45.6	0.66	110
LP Gas Cleaning	19.8-24.3	0.66	110

5. CONCLUSIONS AND RECOMMENDATIONS

The Base Program for the conceptual evaluation of the novel gas cleaning process has entailed two parallel efforts: laboratory testing to identify candidate sorbents for sulfur and halide removal and the appropriate stage operating conditions, and commercial process performance and cost estimates to assess conceptual process feasibility. Both of these efforts have accomplished their objectives. The major conclusions drawn from this work are listed below.

Laboratory Testing

- The following sorbents have been selected for all of the novel gas cleaning process alternatives, based on the test work completed:
  - Bulk sorbent: zinc titanate (Zn/Ti mole ratio 1.5)
  - Stage I sulfur sorbent: zinc titanate (Zn/Ti mole ratio 1.5)
  - Stage I HCl sorbent: Trona
  - Stage II sulfur sorbent: G-72E (70 wt% Zn)
  - Stage II HCl sorbent: G-92C (6.4 wt% Na)
- The optimum stage temperatures for the selected sorbents, when the bulk desulfurization is conducted at about 538°C (1000°F) using a zinc-based sorbent, have been estimated as
  - Stage I: 499°C (930°F)
  - Stage II: 288°C (550°F)
- The laboratory testing has focussed on the most stringent gas cleaning requirements for industrial applications (sulfur species less than 60 ppbv, halides less than 10 ppbv, and particulate less than 0.1 ppmw), and has generated laboratory-scale evidence that these requirements can be achieved by the Ultra-Clean gas polishing process.
- Alternatively, lower-temperature (371- 427°C, 700 - 800°F), non-zinc-based sorbents, such as iron, copper, or manganese-based sorbents, might also be used for bulk desulfurization and for Stage I desulfurization.

Process Evaluation

Performance

- The novel gas cleaning process utilizing the Ultra-Clean gas polishing process is primarily a dry cleanup technology and results in little process water/ condensate treatment requirement. The novel gas cleaning process waste water rate is less than 10% of that of the conventional gas cleaning process, and the waste water generated is relatively contaminant free compared to the highly contaminated waste water from the conventional process.
- It does, though, generate solid waste, but in quantities that are very small, being less than 1% of the conventional plant slag rate.
- For general chemical or liquid fuel synthesis applications, two process alternatives (Drying and HCl Scrubbing) have been identified that have varying degrees of performance improvement potential over the Base process configuration -- these can be applied for SOFC power generation applications also. The waste water rate for these alternatives is comparable to that

of the conventional gas cleaning process, but the waste water generated is relatively contaminant free compared to the highly contaminated waste water from the conventional process.

- The Stage I sulfur sorbent solid waste might be sent to the bulk desulfurization section regenerator for reuse, if it can be separated from the Stage I HCl sorbent, and this would result in even greater advantage over the conventional gas cleaning process. Testing and solid waste characterization needs to be performed to assess the separation potential.
- Options have been identified to separate the Stage I HCl sorbent from the Stage I sulfur sorbent (HCl sorbent fed into primary barrier filter), including an option that requires no HCl sorbent use (HCl scrubbing option). Testing is needed to determine if these options are needed and to quantify their potential performance merits.
- It is highly likely that the small stream of Stage II sorbent solid wastes (solid waste less than 25 kg/hr having sulfur and chloride content of less than 0.2 kg/hr) can be sent to the gasifier for disposal as part of the gasifier slag.
- The Stage II sorbents drained from the barrier filter might be recycled to the Stage II barrier filter inlet to increase the quality of gas-particle contacting and the extent of reaction conversion. Testing is needed to determine the potential merits of sorbent recycling.

Process Applicability

- The process development and evaluation has concentrated on particulate, sulfur and halide removal.
- For SOFC power generation applications, the novel gas cleaning process can meet all of the SOFC fuel gas cleaning requirements ($H_2S < 100$ ppbv, $HCl < 1$ ppmv, particulate < 0.1 ppmw).
- The general chemical or liquid fuel synthesis application also requires efficient ammonia removal. An option has been identified to perform ammonia removal (Stage II scrubbing), but has not been completely assessed.
- Mercury removal may be needed in some synthesis applications, and may become an emissions control requirement for all coal-based plants. Options have been identified to perform mercury removal within the Ultra-Clean gas polishing process (Stage II sorbent injection), but have not been assessed.
- The conceptual market evaluation shows that there is ample market potential, estimated at $75 million per year for syngas cleaning equipment, for the chemical or liquid fuel synthesis applications to merit continued development.
- The near-term market for large-scale SOFC power generation is limited by SOFC production capacity and economics.
- The process evaluations have focussed on the most stringent gas cleaning requirements for industrial applications and have applied very conservative process and economic assumptions, resulting in large cost margins that account for the uncertainties in the novel gas cleaning process performance.
- The evaluation was based on an entrained, oxygen-blown, slagging gasifier representative of Texaco technology. Other gasifier types (e.g., Shell and E-Gas entrained gasifiers; air-blown;

fluid bed or transport gasifier, non-slagging) could utilize the same novel gas cleaning process with similar advantages over the conventional gas cleaning process.

- Cooling of the raw gasifier gas down to the temperature of novel gas cleaning was assumed to be by efficient heat recovery to generate high-pressure steam. Other raw gas cooling approaches, such as water quench, should also not influence the nature of the merits of the novel gas cleaning process evaluated.
- The novel gas cleaning process was simulated to contain a transport reactor, zinc titanate-based, bulk desulfurization process that precedes the Ultra-Clean section. Alternative bulk gas cleaning technologies, and sorbents operated at lower temperatures could also be used and should result in similar or greater advantages for the novel gas cleaning process.

<u>Process Economics</u>

- For chemical synthesis applications, the novel syngas cleaning process Total Capital Requirement is estimated to be about 34% lower than the conventional syngas cleaning process Total Capital Requirement. Based on the equivalent power plant generating capacity, the Total Capital Requirements are 183 $/kW and 277 $/kW for the novel and conventional syngas cleaning processes, respectively.
- For SOFC power generation applications, the novel fuel gas cleaning process Total Capital Requirement is estimated to be about 185 $/kW for high-pressure cleaning, and 191 $/kW for low-pressure cleaning. This is about 30% lower than the conventional syngas cleaning process Total Capital Requirement using high-pressure cleaning and about 14% lower than the conventional syngas cleaning process Total Capital Requirement using low-pressure cleaning.
- The novel gas cleaning process utilizing the Ultra-Clean gas polishing process has high potential for performance advantages, and a potential cost-of-gas-cleaning margin of at least 20%, relative to conventional gas cleaning technology for both chemical or liquid fuel synthesis applications, and for SOFC power generation applications.
- Sorbent maximum consumption criteria targets have been determined in the evaluation, to be used for bench-scale testing success criteria.
- The most sensitive parameter in the novel gas cleaning process cost is the sorbent feed rate multiplied times the sorbent price for the combined bulk desulfurization sorbent and the Stage I sulfur sorbent.
- The Stage I HCl sorbent and the Stage II sulfur and HCl sorbents can be applied at very high sorbent-to-contaminant molar feed ratios and still maintain favorable process economics.
- Stage I HCl sorbent disposal, the largest solid waste stream, should not be an environmental or economic issue.
- For SOFC power generation applications, the most favorable economics occur for the high-pressure gas cleaning configuration, and this is expected to provide the most favorable overall power plant economics as well.
- The evaluation required elemental sulfur recovery rather than sulfuric acid or other sulfur products. Alternative sulfur products, for example sulfuric acid, might produce additional, significant cost advantages for the novel gas cleaning process.

Development Needs

- The barrier filter technology applied in the Ultra-Clean gas polishing process for filter-reactor gas cleaning is already well established, and ready for commercial demonstration as a barrier filter. The remaining performance characterization needed is the performance of this system as a sorbent-gas reactor at the required level of removal performance. All other components of the Ultra-Clean process are fully commercial.
- Bulk desulfurization sorbent elutriated from the bulk desulfurizer might assist in Stage I desulfurization, but its properties and reactivity are unknown.
- Integrated, small-scale proof-of-principles testing of overall performance of the Ultra-Clean technology is needed.
- Continued development of bulk desulfurization and sulfur recovery technologies are also needed.

The positive conclusions that have resulted from the Base Program lead to the following recommendation:

- The development effort for the Ultra-Clean process should proceed to bench-scale testing integrated with a sub-scale coal gasification plant.
- The Base Ultra-Clean gas polishing process for syngas cleaning should be the focus of the testing, to confirm the selections of the sulfur and HCl sorbents, the associated stage operating conditions, and the overall syngas cleaning performance.
- The bench-scale testing should also focus on confirmation that the sorbent consumption criteria targets proposed in the Base Program can be satisfied.
- The bench-scale testing should produce sufficient process data to allow upgraded process evaluations and cost estimates for the full-scale, novel gas cleaning process using the Ultra-Clean process. Continued evaluation and incorporation of advances made in gasifier performance, bulk desulfurization process development, and sulfur recovery need to be included so that the integrated novel gas cleaning process performance and economics can be refined.
- Ultra-Clean polishing process variations, such as Stage II syngas drying, HCl scrubbing, and the inclusion of ammonia and mercury removal need to be further evaluated in the Optional Program.

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8. ACRONYMS AND ABBREVIATIONS

BFW: boiler feed water
CW: cooling water
DOE: U.S. Department of Energy
EF: engineering fees
EPRI: Electric Power Research Institute
FG: fluffing gas
FPD: flame photometric detector
GC: gas chromatograph
GPF: general plant facilities
GPGA: Great Plains gasifier ash
GTI: Gas Technology Institute
HP: high pressure
HTHPR: high-temperature, high-pressure reactor
IC: ion chromatography
ICCI: Illinois Clean Coal Institute
ICI: initial catalysts & chemicals inventory
IDC: interest during construction
IGCC: integrated gasification combined cycle
IP: intermediate pressure
LHV: lower heating value
LP: low pressure
MBFR: moving bed filter-reactor
Mc: molar flow rate of contaminant
Ms: molar feed rate of sorbent
PC: process condensate
PG: pulse gas
PJC: project contingency
PPC: process plant cost
PRC: process contingency
PR: prepaid royalties
PRG: pressurization gas
SC: steam condensate
SCD: sulfur chemiluminescence detector
SCST: startup costs
SG: stripping gas
SOFC: solid oxide fuel cell
SWPC: Siemens Westinghouse Power Corporation
TAG: technical assessment guide
TCD: thermal conductivity detector
TCR: total capital requirement
TECo: Tampa Electric Company
TG: transport gas
TPC: total plant cost
TPI: total plant investment
VG: vent gas
WC: working capital

XRD: X-ray diffraction

APPENDIX A – TRACE LEVEL HCl GAS SAMPLING TECHNIQUES AND METHODS

Analytical tests were carried out, as described below, to demonstrate that trace levels of chloride can be measured accurately by the DX-320/IC20 ion chromatography instrument. This work was deemed essential to reliably assess the efficiency and effective capacity of selected dechlorination materials for HCl removal to levels lower than 10 ppbv.

First, liquid calibration solutions were sampled to determine the detection limits of the ion chromatography system. These standards were prepared from commercially available 1000-ppm chloride standard solutions immediately before injection. Concentration levels of 10 ppb and 52 ppb were prepared. Before sampling these standard solutions, high purity deionized water (protocol water from Fisher, 18-MΩ conductivity) was sampled to measure the background concentration, which was then subtracted from every sample including the liquid standards.

Five consecutive runs were made for each measurement. During the analysis a peristaltic pump circulated the liquid sample to be injected between the IC sampling port and the sample container. This simulated the continuous sampling technique planned for use during actual Stage II experiments. A sequence was setup to carry out 5 consecutive runs at 6.5-minute intervals, and average results from these runs were used in calculations.

From the replicates for blank runs (Figures A1 and A2), which were made before as well as in-between runs, it is seen that the reproducibility of the ion chromatography measurements is excellent, indicating high precision for the instrument. The peak area deviation is less than 1.5%. Data from in-between tests are essentially similar to those before the tests, indicating that there is no residual chloride that might adversely affect the sensitivity of the IC unit. It should also be pointed out that these new calibration data are quite in agreement with previous calibration data that were collected early in this program using similar liquid standards (Figure 3.16).

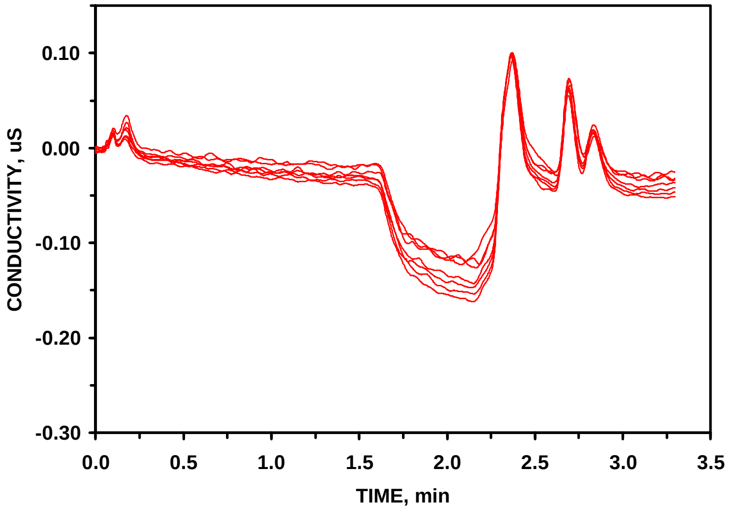


Figure A1 – Blanks (Before Tests)

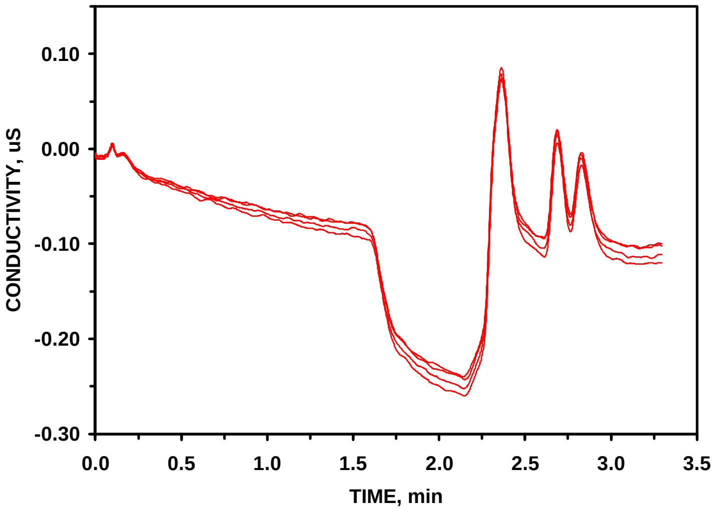


Figure A2 – Blanks (In-Between Tests)

The results obtained with the 52 ppb and 10 ppb Cl standard liquid solutions are reported in Figures A3 and A4, respectively. Both sets of measurements exhibit excellent reproducibility. A calibration curve was extracted from these data and is shown in Figure A5. The linear equation shown is considered valid in the 0-100 ppb Cl range. The detection limit for accurate and precise Cl measurement in liquid is around 1 ppb, which is close to the concentration corresponding to the peak area obtained with blank samples.

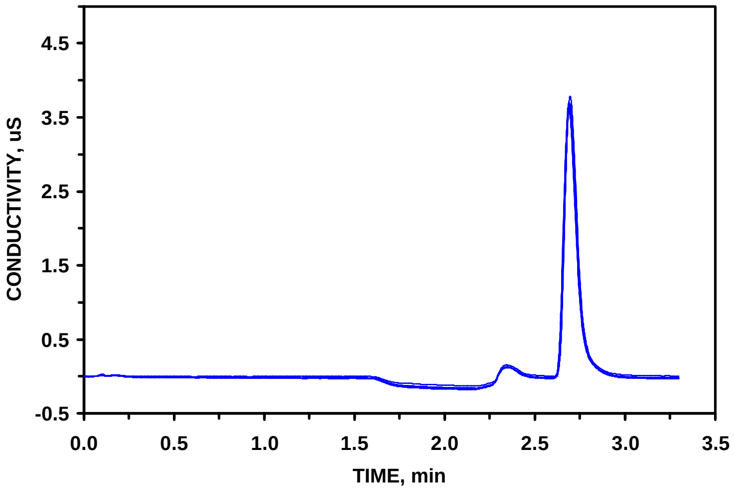


Figure A3 – IC Chromatograms for the 52-ppb Cl Standard Solution

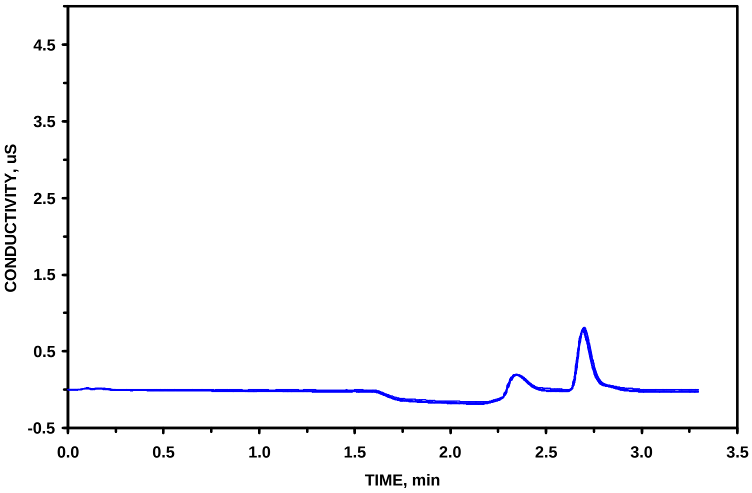


Figure A4 – IC Chromatograms for the 10-ppb Cl Standard Solution

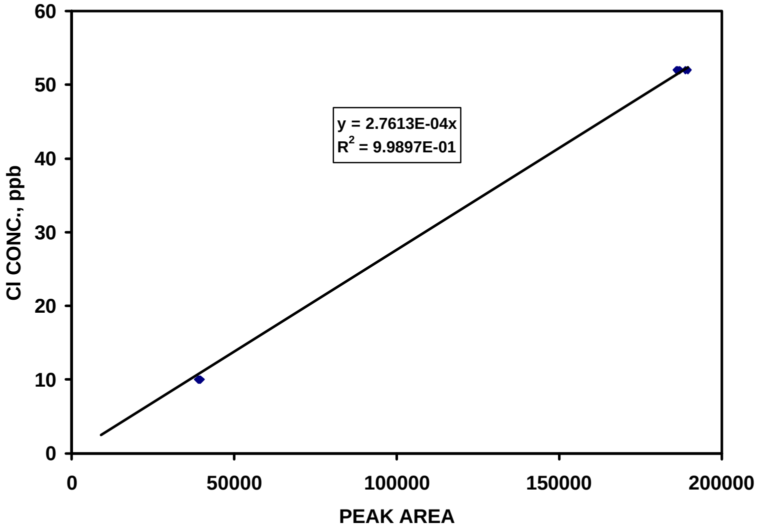


Figure A5 – IC Calibration Curve for Chloride Determination in Liquid Solutions

The corresponding HCl concentration in the gas phase can be calculated using the following equation:

$$[HCl]=([Cl]*V*RT/P)/(35.5*Q*t) \tag{A1}$$

where V is the volume of the liquid, R is the gas constant, T is the absolute temperature, P is the total pressure, Q is the total gas flow rate, and t is the bubbling time.

Following IC analysis using the prepared liquid standards, work focused on dissolving HCl from HCl-containing gas. The main purpose is to determine if HCl, at trace concentrations in the gas phase, can be quantitatively dissolved in water. This, however, will only be critical during initial periods of actual experiments because of the use of a continuous system during which the cumulative dissolved HCl is measured. In this continuous approach Cl gradually builds up in the absorbing liquid solution (deionized water), further increasing the precision of the IC measurement.

Two approaches were followed in measuring trace chloride levels in the simulated exit gas. Based on the fact that a high concentration HCl gas that is bubbled in a large amount of water for a short period of time gives the same dissolved HCl concentration in water as a low concentration gas bubbled for a long period of time, two tests were done. First an 8.2 ppmv HCl gas (a certified 8.2 ppmv HCl in H_2) was bubbled at 180 cc/min through 261.5 mL of deionized water for 1 minute (Test A). The theoretical Cl concentration in the liquid was calculated to be 8.25 ppb. The HCl dissolved in water was analyzed with ion chromatography and a chloride peak area of 655037 points was measured (Figure A6). The second test was done at sampling settings (total gas flow rate, volume of deionized water, duration of bubbling) that have been typically used during HCl analysis in Stage I of the Ultra-Clean gas polishing process. 8.2 ppmv HCl gas was diluted to 82 ppbv with nitrogen and bubbled through 111.5 mL of deionized water at 1600 cc/min for 5 minutes (Test B1). The theoretical Cl concentration for this sample was calculated as 8.59 ppb. The dissolved HCl gas was then analyzed by ion chromatography and a chloride peak area of 547835 points was measured (Figure A7).

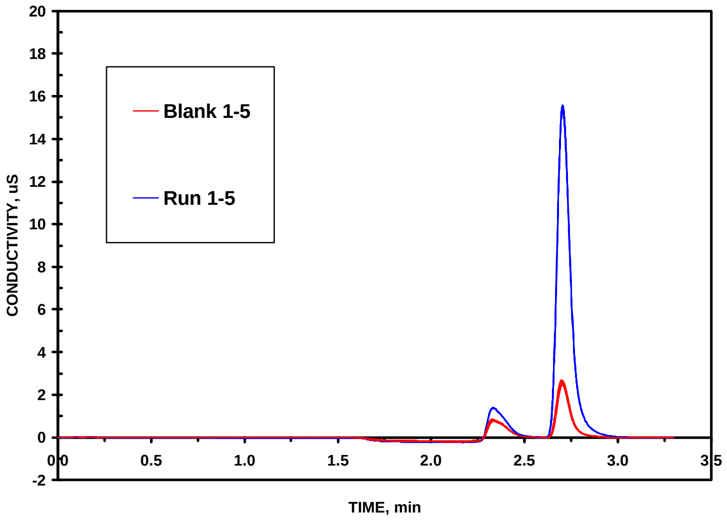


Figure A6 – Five Replicates of Sample and Blank Runs for Test A

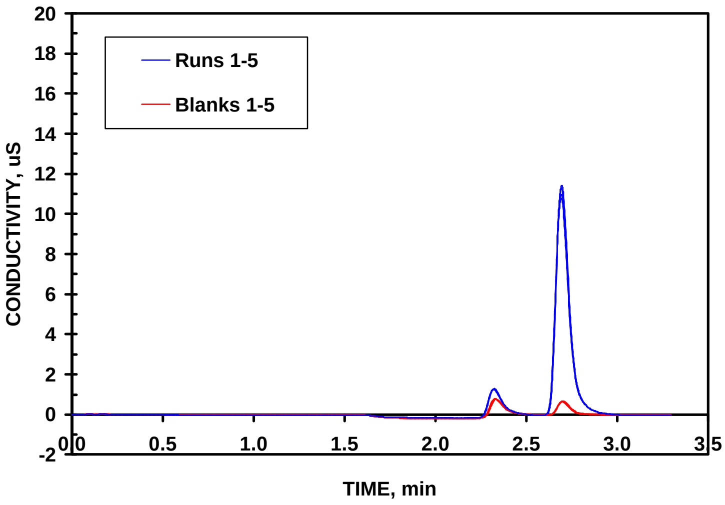


Figure A7 – Five Replicates of Sample and Blank Runs for Test B1

To determine the detection limit of this method a third test was done. 8.2 ppm HCl gas was diluted to 82 ppb with nitrogen and bubbled through 261.5 mL of deionized water at 1600 cc/min for only 1 minute. The theoretical Cl concentration in the liquid was calculated as 0.733 ppb, which would correspond to about 6.3 ppbv HCl concentration in the gas. The dissolved HCl gas was analyzed and the peak area was measured as 23739 points (Figure A8).

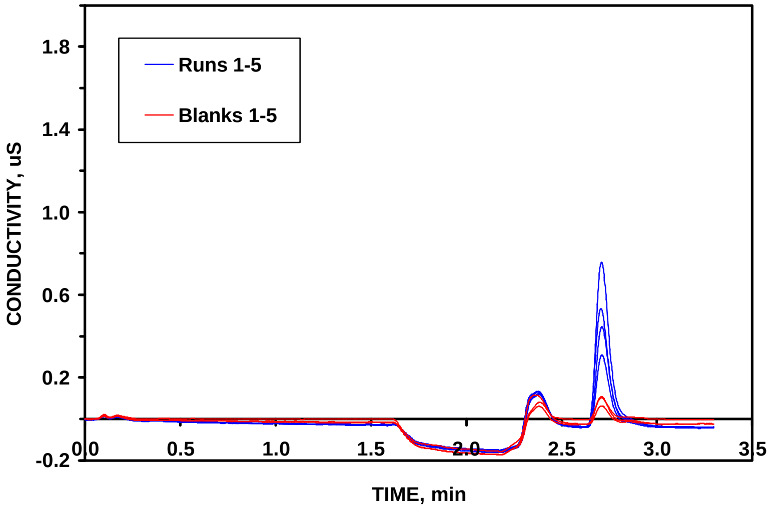


Figure A8 – Five Replicates of Sample and Blank

The results from the above 3 sets of tests are summarized in Table A1, which shows the calculated Cl concentration in the liquid, the average peak area from each set of 5 runs, and the measured Cl concentration based on the calibration curve developed above (Figure A5). The data show that the measured Cl concentration in the liquid is significantly higher than the calculated Cl concentration.

Table A1 – Summary of the Results

Test	Cl Peak Area (Sample – Blank)	Calculated Cl Concentration in Liquid (ppb)	Measured Concentration in Liquid (ppb)
A	655037	8.25	180.87
B1	547835	8.59	151.27
B2	23739	0.733	6.55

In a separate test, a simulated syngas containing 400 ppbv HCl in H_2 and N_2 was fed to an empty reactor where it was allowed to mix before exiting and directly bubbled through deionized water. This experiment was carried out for about 2 hours and the cumulative Cl concentration in the liquid was periodically measured. As shown in Figure A9, during the initial phase the measured Cl concentration is much higher than expected, but then stabilizes within 10 ppbv of the estimated 400 ppbv in the inlet gas. The results obtained during the initial "transient" period are consistent with the results reported in Table A1. It is likely that following gas switching from the vent into the liquid absorber solution, there exists a transient period where gas flow rate is much higher than desired, leading to significantly higher HCl measurements. This is probably due to pressure buildup after mass flow controllers and before the sampling valve. Other possible contributors to these erroneous measurements include minute differences in time keeping and contamination from valves and other equipment.

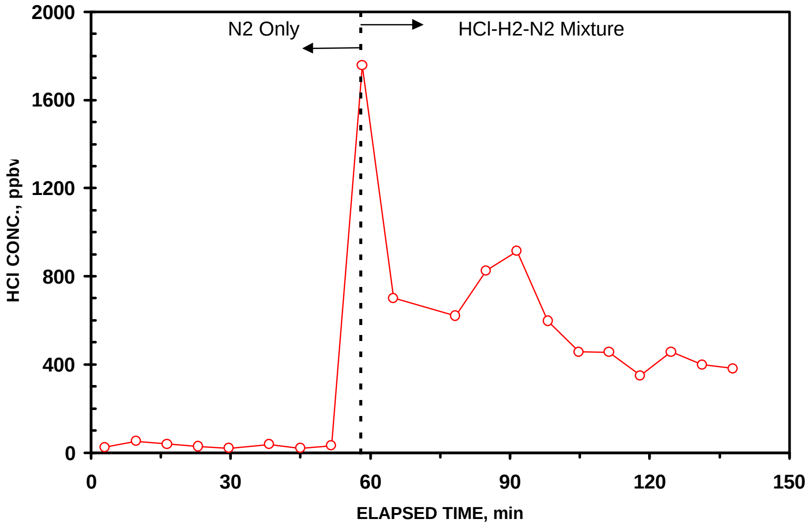


Figure A9 – Measured HCl Concentration in a 400 ppbv HCl in H_2-N_2 Mixture

These limitations prevented the verification of the accuracy of the IC instrument using the approach of dissolving a known HCl gas concentration in a given volume of liquid solution. In actual Stage II experiments, when the gas is continuously bubbled through liquid, these problems related to gas switching would not be encountered. The IC detection limit will then correspond to the detection limit of Cl measurement in liquid samples (i.e., 1 ppb). Nevertheless, it remained important to develop a suitable technique to establish the detection limit of the IC instrument using calibration gases where trace HCl gas concentrations at 5-20 ppbv could be measured. These tests can verify HCl concentration calculations based on IC unit calibration using liquid standards. The best way to accomplish this is to directly bubble a calibration gas containing trace amounts of HCl. However, it is not possible to obtain a stable certified HCl-H_2 gas mixture containing lower than about 10 ppmv HCl.

Several tests were carried out to calibrate the Ion Chromatograph instrument for the measurement of HCl in the ppbv range, using pre-mixed gases containing trace levels of HCl. Another objective of these tests was to determine the capability for complete recovery of HCl in a liquid absorber solution (i.e., Protocol deionized water) from a gas containing trace levels of HCl. As explained above, a certified standard gas mixture containing HCl at lower than about 8.2 ppmv HCl in H_2 could not be obtained because of stability issues. Therefore, the 8.2 ppmv HCl-H_2 gas mixture was diluted with N_2 to produce a gas mixture containing around 200 ppbv HCl. This is not a trivial operation for two reasons. First, at such high dilution level (1/40) and using a simple T connector the gas mix is not homogenous. Second, contamination of HCl delivery lines is quite significant. The problem that became apparent is that even after a single test with HCl, there is sufficient residual HCl in the lines to affect the results of a subsequent test. For example, when a simulated feed gas containing approximately 231.7 ppbv HCl in H_2 and N_2 was used, the lowest HCl concentration that was measured was ~300 ppbv despite the extra precautions that were taken. These precautions included using a completely brand new Teflon gas line, Teflon fittings, and prolonged purging with N_2 before the experiment. The additional ~70 ppbv that was measured is reasoned to be desorbing from a check valve that had previously come into contact with HCl. The results from this test are reported in Figure A10. As shown, the background exit HCl concentration was ~20 ppbv with only N_2 flowing through the sampling apparatus both before and after the test involving HCl.

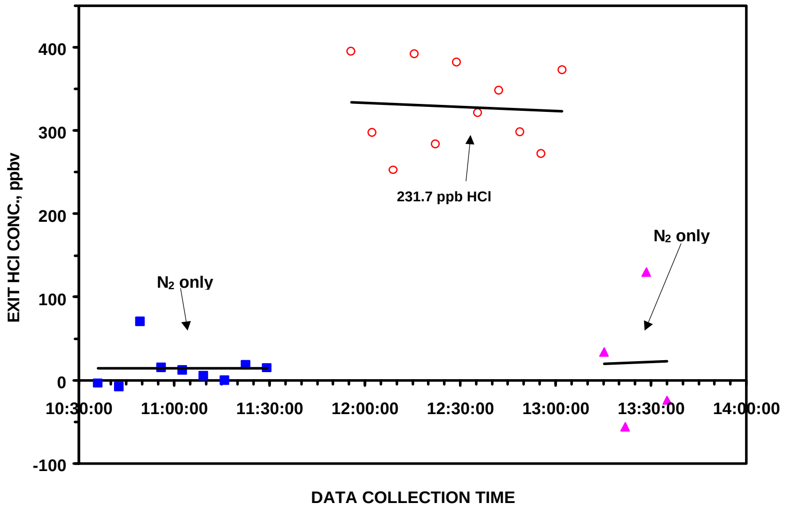


Figure A10 – Measurement of HCl at Trace Levels

The approach of feeding HCl as a liquid rather than a gas was also utilized to overcome the limitations of using certified HCl-H_2 gas mixtures, thereby further refining the calibration procedure of the IC instrument. Distilled water, containing HCl at a predetermined concentration, is pumped through a quartz tube extending through heat transfer media in the bottom portion of the reactor shell to just below the frit of the reactor cage containing the sorbent bed. This ensures that, upon vaporization in the hot zone, the HCl-containing gas does not come into contact with the heat transfer media and no adsorption takes place. Using an empty reactor (i.e., no sorbent bed), nitrogen-steam mixtures, containing HCl at concentrations of 10 to 500 ppbv, can be generated and used to provide a more reliable calibration of the IC instrument for Stage II experiments.

The results from two separate tests carried out with simulated HCl-H_2O-N_2 gas mixtures containing about 120 ppbv HCl are presented in Figure A11 and Figure A12. In both cases, the standard 0.02M hydrochloric acid solution was diluted to generate the desired HCl concentration in the gas phase. Figure A11 shows the results that were obtained when contamination was virtually suppressed due to the use of fresh (i.e., no prior exposure to HCl) heat exchange media. As indicated by the slope of the trend line shown in Figure A12, the measured HCl concentration in the exit gas averaged about 121.3 ppbv, well within the experimental error. These results clearly indicate that (i) our sampling technique is capable of quantitative removal of HCl from the exit gas even at trace levels and (ii) the Dionex DX/IC20 ion chromatograph instrument can be used reliably for chloride measurement in the ppbv range, as was previously demonstrated with standard chloride liquid solutions (Figure A5).

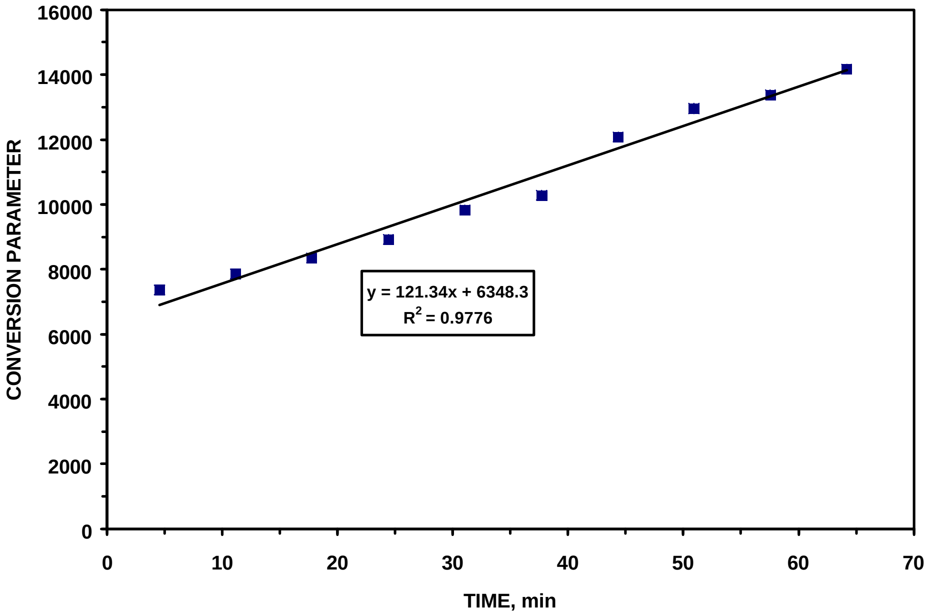


Figure A11 – Measured HCl Exit Gas Concentration (No Contamination)

Figure A12 shows the results obtained when some contamination exists. As shown, the measured HCl concentration in the exit gas is on the average about 33 ppbv higher than expected. Again, by rearranging the reactor shell assembly, it may be possible to eliminate or minimize the background HCl concentration as the feed gas is prevented from coming into contact with the heat exchange media.

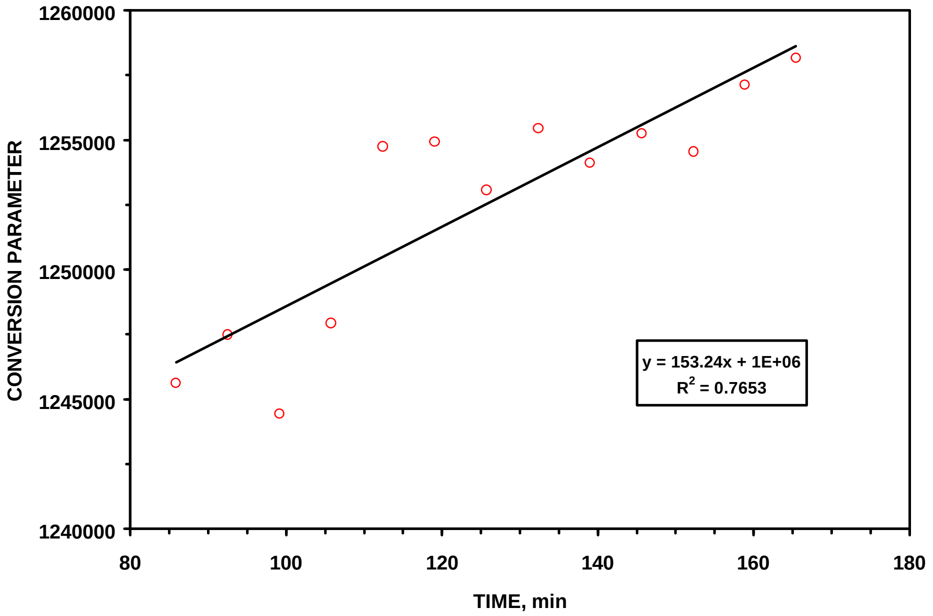


Figure A12 – Measured HCl Exit Gas Concentration (Some Contamination)

APPENDIX B – TRACE LEVEL H_2S GAS SAMPLING TECHNIQUES AND METHODS

Earlier work established that the Dionex DX320/IC20 ion chromatography unit was capable of detecting SO_4^{--} in liquid standards at concentrations ranging from 10 ppb to 100 ppm levels. For this instrument to be useful for Stage II experiments, residual H_2S in ultra-cleaned effluent gases has to be first absorbed into a solution and then oxidized to SO_4^{--}. We established that H_2S capture in a suitable scavenger solution was virtually quantitative; however, H_2S oxidation was kinetically-limited, requiring at least ½ hour to complete and longer times may be needed if conversions exceeding 75-80% are desired.

Based on the above, using an approach similar to the continuous sampling and measurement of HCl may not work for H_2S. The need to allow at least 30 minutes for the oxidation of H_2S limits the frequency of sampling and analysis. An alternative approach was developed to measure H_2S at trace level concentrations in the exit ultra-cleaned gas and consisted of trapping a sample of the effluent gas in a 1-liter glass sampling bottle, periodically throughout testing. This gas sample is then injected with a pre-determined amount of absorber solution and set aside to allow for the oxidation of the captured H_2S to proceed, prior to IC analysis. The absorber solution contains a basic component (i.e., sodium hydroxide), for the capture of H_2S, and an oxidizer (hydrogen peroxide), for the oxidation of H_2S into SO_4^{--}.

Various issues relating to this approach were identified for further investigation. First, the make up of the absorber solution should be optimized. Various concentrations of sodium hydroxide and hydrogen peroxide in the absorber solution should be evaluated. A strong oxidizing solution may produce peaks that will shadow the SO_4^{--} peak and prevent it from being measured. Therefore, the amount of the oxidizer in the absorber solution will be optimized to provide acceptable oxidation of H_2S, while preventing any conflicts with the IC measurement method. Second, the effect of other gaseous species (such as CO) on the detection method for H_2S measurement should also be determined. Third, in tests involving both HCl and H_2S, HCl will be removed upstream of the H_2S absorber solution and therefore, the effect of the presence of HCl in the gas mixture on H_2S detection need not be considered. However, the extent of H_2S absorption in the HCl solution, if any, may need to be quantified. Fourth, the extent of H_2S absorption as a function of H_2S concentration in the inlet gas should be evaluated.

A certified gas mixture containing about 0.5 ppmv H_2S in N_2 was ordered for these efforts; the mixture received contained 0.8 ppmv H_2S. To make a quick assessment of this approach, three sets of tests were conducted initially. First, the effectiveness of absorber solution for H_2S capture and oxidation to SO_4^{--} was investigated as a function of H_2S concentration in the inlet gas. The certified gas mixture was diluted with N_2 to produce H_2S-N_2 mixtures containing approximately 360 ppbv, 219 ppbv, and 118 ppbv. The diluted mixture was then sent directly through a 1-liter glass gas-sampling bottle and collected against atmospheric pressure. The gas samples were subsequently injected with 10 mL of the absorber solution, and set aside for 20 minutes before the resulting liquid was injected into the IC for analysis. The results obtained are summarized in Table B1. Based on the measured SO_4^{--} concentration in liquid samples, the corresponding H_2S concentration in the gas phase can be calculated. This value is reported in Table B1 as a percentage of the inlet concentration. As indicated, as the H_2S concentration in the inlet gas is reduced, the measured value within the allowed 20-min period is also reduced significantly.

Table B1 – Effect of Inlet H_2S Concentration on Effectiveness of Absorber Solution

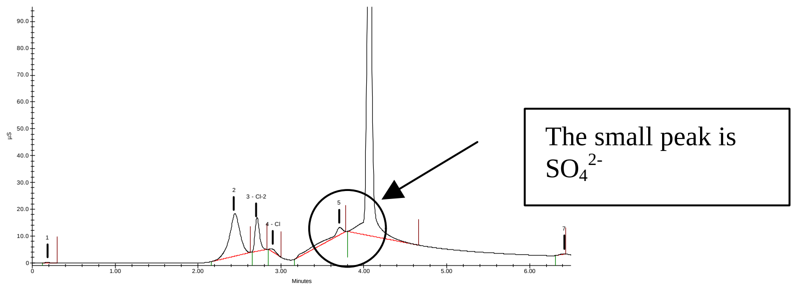
H_2S Concentration (ppbv)	Percent Conversion at 20 minutes
800	76.3
360	60.5
219	58.1
118	23.8

As can be expected, the effectiveness of the absorber solution for H_2S capture from the H_2S-N_2 mixture and subsequent oxidation improves as longer times are allowed for the oxidation to occur. About 80% of the inlet H_2S can be accounted for if one hour is allowed. This is, however, not the case when the inlet gas contains CO, CO_2, and CH_4. As reflected by the low numbers in Table B2, H_2S is essentially immeasurable with this technique in the presence of the additional gaseous components. The absorber solution is likely to be effective in the presence of these components.

Table B2 – Absorber Solution Effectiveness as a Function of Gas Composition and Time

Gas Composition	20 min.	40 min.	60 min.
H_2S in N_2	62.1	67.5	80.1
H_2S in N_2 + CO + CO_2 + CH_4	0.10	0.12	0.13

The poor results obtained can be explained by the likely interference of the gaseous species with the detection of H_2S. In an oxidizing solvent, any dissolved CO and CO_2 readily oxidize to CO_3^{2-} creating a peak that shadows the SO_4^{--} peak, as illustrated in Figure B1 below, and a shift in the SO_4^{--} peak retention time from 3.5 to 3.7 minutes. The concentration of SO_4^{--} in the mixture is low enough to have its peak nearly completely swallowed by the carbonate peak and as seen in the following chromatograms the SO_4^{--} peak is barely visible making it impossible to integrate accurately (compare with a typical peak for SO_4^{--} in a standard liquid, Figure B2).



The small peak is SO_4^{2-}

Figure B1 – Chromatogram for 219 ppbv H_2S in N_2, CO, CO_2, and CH_4

It should be noted that in all three sets of tests, an absorber solution containing low concentrations of sodium hydroxide (5 mM) and hydrogen peroxide (16 mM) was used. Although these concentrations are low, this absorber solution was previously shown to be effective for H_2S measurement at the ppmv level.

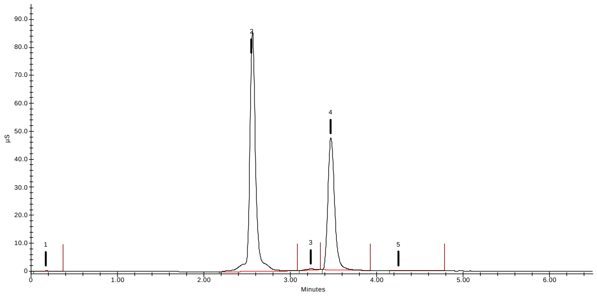


Figure B2 – 1 ppm HCl and SO_4^{--} Liquid Calibration Standard

A literature search was conducted on H_2S detection techniques. It appears that most of the current work being carried out on trace level H_2S analysis involves the use of a Sulfur Chemiluminescence Detector (SCD) coupled with a gas chromatograph (GC). Interestingly, however, two articles by Bruner et. al. in 1972 and 1974 reported on the successful measurement of H_2S and other sulfur compounds at trace levels in air. This work involved the use of a glass column with a special packing material, which is commonly used for hydrocarbons, and a FPD detector. A column, identical to Bruner's, was obtained from Supelco. A Varian GC, that has been dedicated for trace level sulfur analysis, was fitted with this new column, and calibration tests were conducted. Following careful experimentation with GC settings, a detection limit of 99.2 ppbv for H_2S was established. At this concentration level the H_2S peak was about to disappear (~2 times the noise); however the software was still capable of integrating it. Bruner et al. reported a detection limit of 50 ppbv for H_2S in air; however, this lower limit was achieved using sampling and delivery techniques that we determined our experimental arrangement could not accommodate.

Using the 0.8 ppmv H_2S in N_2 certified gas mixture, and other H_2S-N_2 mixtures containing approximately 504, 370, 255, and 150 ppbv H_2S, a calibration curve was developed, as shown in Figure B3. For practical purposes, this GC setup can be used reliably to evaluate Stage II sulfur sorbent materials. Our arbitrary breakthrough point will be in the ppmv range, and if H_2S cannot be detected prior to breakthrough, then we can safely assume the concentration to be less than 100 ppbv. Given that we have about 15% steam in the exit gas, then this concentration would correspond to about 85 ppbv on a wet basis. This is not too far from the target of 60 ppbv.

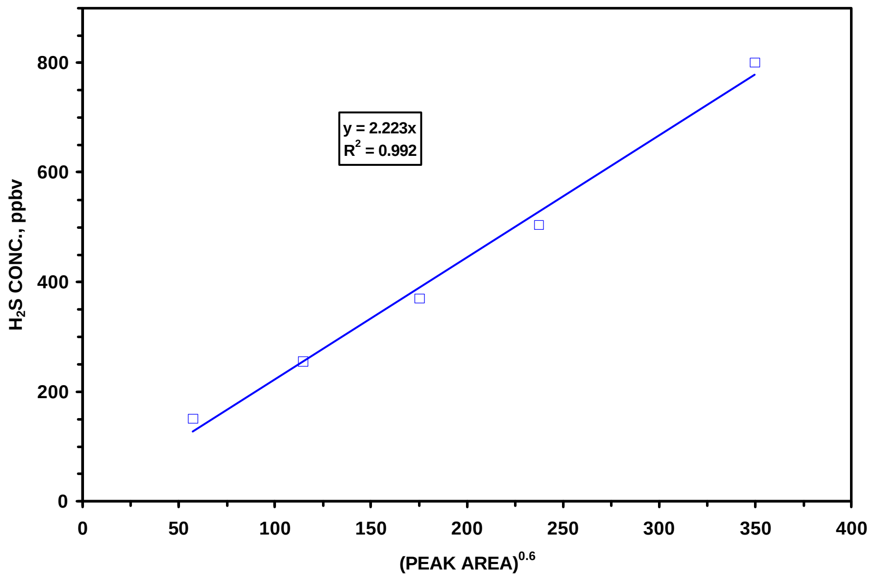


Figure B3 – GC Calibration Curve for H_2S Measurement at Trace Level