NOVEL GAS CLEANING/ CONDITIONING FOR INTEGRATED GASIFICATION COMBINED CYCLE

VOLUME II – PROCESS DEVELOPMENT UNIT (PDU) TEST RESULTS

OPTIONAL PROGRAM FINAL REPORT

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DISCLAIMER

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ACRONYMS AND ABBREVIATIONS

BCB	Bethlehem Coke Breeze
Btu	British Thermal Unit
CF-R	Conditioning Filter-Reactor
CRS	GTI’s Chemical Research Services Department
DOE	Department of Energy
DSQ	Direct Spray Quench
EPA	Environmental Protection Agency
FFTF	Flex-Fuel Test Facility
FPD	Flame Photometric Detector
FT-IR	Fourier Transform Infrared Spectrometer
GC	Gas Chromatograph
GRE/CCS	Great River Energy Coal Creek Station
GRI	Gas Research Institute
GRI	Gas Research Institute
GTI	Gas Technology Institute
IC	Ion Chromatograph
IGCC	Integrated Gasification Combined Cycle
IMACC	Industrial Machine and Control Corporation
JM	Johnson Matthey
MAF	Moisture and Ash Free
MS	Mass Spectrometer
MW	Molecular Weight
NDIR	Non-Dispersive Infrared
NETL	National Energy Technology Laboratory
NGC	Novel Gas Cleaning
NGC-OPT1	Novel Gas Cleaning Optional Program Test Campaign #1
NGC-OPT2	Novel Gas Cleaning Optional Program Test Campaign #2
NGC-OPT3	Novel Gas Cleaning Optional Program Test Campaign #3
P&ID	Piping and Instrumentation Diagram
PDU	Process Demonstration Unit
PFD	Process Flow Diagram
PFPD	Pulsed Flame Photometric Detector
ppbv	Parts per billion by volume
ppmv	Parts per million by volume
ppmw	Parts per million by weight
PRDA	Program Research and Development Announcement
SCF	Standard Cubic Feet
SE&C	Sample Extraction and Conditioning
SGB	Sulfur Guard Bed
Siemens	Siemens Power Generation, Inc.
TC	Trim Cooler
TCD	Thermal Conductivity Detector
TDA	TDA Research, Inc.
TF-R	Test Filter-Reactor
UAB	University of Alabama at Birmingham

1. EXECUTIVE SUMMARY

Much of the hot gas cleanup research and development efforts have been conducted within the context of the Integrated Gasification Combined Cycle (IGCC), focusing predominantly on the development of regenerable metal oxide sorbents for the removal of reduced sulfur compounds (mainly hydrogen sulfide (H_2S) and carbonyl sulfide (COS)) at high temperature and pressure. The objective in this application is to reduce the H_2S concentration in the fuel gas to less than 20 ppmv to satisfy gas turbine requirements. In recent years there has been significant interest in extending the hot gas cleanup capabilities so that the cleaned fuel gas becomes suitable for a wide range of applications, including fuel cells and production of chemicals and transportation fuels, in addition to electric power generation via the IGCC technology. These applications require the removal to near-zero levels, of the sulfur-, nitrogen-, alkali-, and chlorine-containing gas emissions and fine particulate matter ($PM_{2.5}$) caused by fuel bound constituents that are naturally present in many forms in a variety of carbonaceous materials which are useful as feedstocks to gasification processes. When the IGCC system is applied to creating synthesis gas for production of liquid products (e.g., methanol, F-T liquids), these species can be poisonous to downstream processing units and may be contaminants in the high purity products. HCl in particular is a significant contaminant that causes severe deterioration to various fuel cell materials.

Commercial technology is available to clean coal-gasification hydrocarbon gases to the stringent levels required for these demanding applications. The prevalent commercial gas cleaning process, capable of achieving the very stringent gas cleaning requirements 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, particulates, 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 U.S. Department of Energy advanced, near-zero emission, efficient multi-production energy plants.

To address this need, the Siemens Power Generation, Inc. (Siemens) and the Gas Technology Institute (GTI) have been developing a novel process compatible with known gasifier systems that promises, in a pre-combustion treatment, to prepare carbonaceous feedstock-based fuel gases or syngases for use in power generation applications with gas turbines or with fuel cells, or for co-production of power with chemicals or transportation fuels. This Novel Gas Cleaning (NGC) Process can be applied as an add-on cleaning step following a near-commercial, state-of-the-art hot gas polishing system. The process can also be a stand-alone fuel gas cleanup system, depending on the carbonaceous fuel properties, the extent of in-gasifier cleaning (bulk sulfur removal), and the cleanup requirements of the intended application. This novel process specifically addresses sulfur, chloride, mercury, and particulate removal to meet the most stringent requirements (total sulfur (mainly H_2S and COS) < 60 ppbv, halide (mainly HCl) < 10 ppbv, Hg < 0.01 ppbv, and particulate < 0.1 ppmw). These are contaminant levels below detection limits of conventional measurement instrumentation. In addition, various options have been conceptualized to incorporate the removal of other contaminants, such as ammonia (NH_3), into the NGC Process.

Novel Gas Cleaning Process

A schematic flow diagram of the NGC Process configuration, for simultaneous control of particulate matter and sulfur and halide gaseous contaminants, is shown in Figure 1. It is a dry process that follows a hot, or warm, bulk desulfurization step. The process injects fine sulfur and halide sorbent particles into two stages of barrier filter-reactors integrated in series, coupling efficient particle capture with an effective entrained and filter cake reaction environment. The first stage injects inexpensive, fine sodium-based and zinc-based sorbents into the hot (371 to 593ºC; 700 to 1100ºF) fuel gas stream for reducing the concentration of the primary contaminants (H_2S and HCl) to about the 1-ppmv level. In the second stage, the fuel gas exiting from the first barrier filter-reactor is first cooled to 260 to 316ºC (500 to 600ºF), and then injected with highly reactive, fine particles of ZnO-containing materials for sulfur removal and Na_2CO_3- or Na_2O-containing materials for halide removal before entering a second barrier filter-reactor, where contaminant concentrations are further reduced to the required levels.

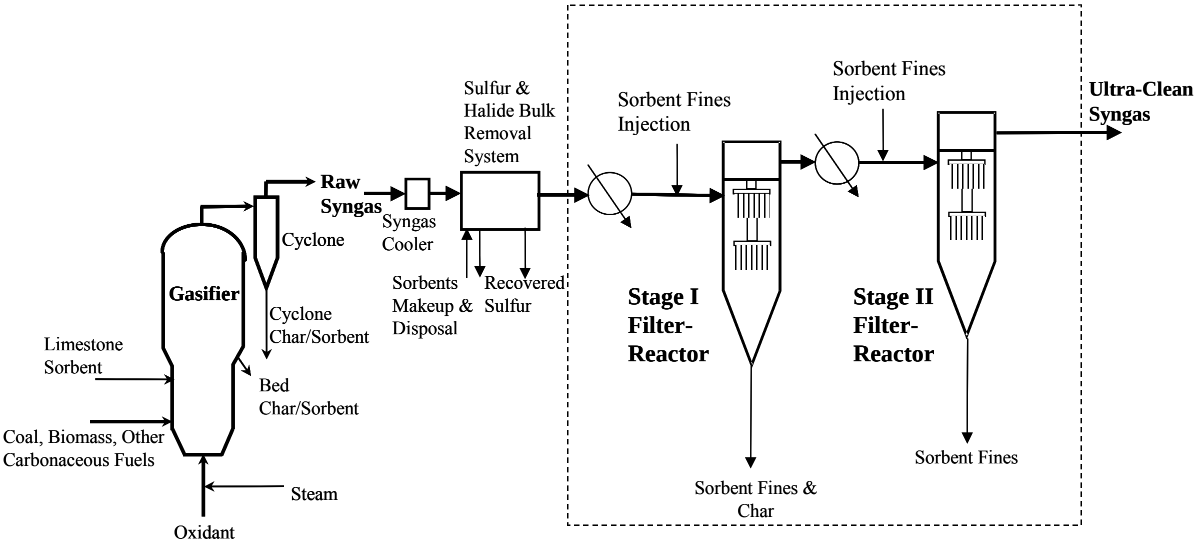

Figure 1 - Schematic Diagram of the Novel Gas Cleaning Process

The main basis for the NGC Process concept is that, in addition to filtration, barrier filters provide ideal environments for chemical reactions. Syngas contaminant (e.g., HCl, H_2S, COS, etc.) removal via fine sorbent particles injected into the syngas upstream of the barrier filter occurs both from the dilute, entrained sorbent particles and within the consolidated filter cake. The nature of the filter cake is modified by the low ash content of the fuel gas and the relatively high content of injected sorbent particles. The high permeability of the resulting filter cake, compared to the normally very low permeability of gasifier ashes, allows for higher face velocity design, resulting in a more compact vessel having lower cost than the typical fuel gas hot gas filter. Only a portion of the filter elements (about 5%) are pulse cleaned at any given time, so the loss in the contaminant removal performance of the barrier filter-reactor due to loss of filter cake contaminant removal capacity will be very small.

As described in Volume I the NGC Process concept has many merits and provides for a “one-box” solution to hot/warm syngas cleaning. For example, there is significant potential to incorporate, into the NGC Process, the capability to control mercury emissions to meet syngas mercury removal requirements for chemical synthesis applications (as low as 0.01 ppbv in the syngas, or > 99% removal) and for IGCC applications (< 0.45 kg of mercury per 1.06 trillion kJ (< 1 lb of mercury per trillion Btu), or about 90% removal). Mercury control can be accomplished through injection of an appropriate sorbent into the second stage of the NGC Process, or in a dedicated downstream packed-bed reactor operating at a lower temperature.

The overall Novel Gas Cleaning Process development program consisted of two phases: a Base Program phase and an Optional Program phase. The goal of the Base Program (completed in August 2001) was to provide the necessary data to verify the technical and economic feasibility of the NGC Process. GTI’s scope of work in this first phase was dedicated most heavily to the laboratory testing of selected candidate sorbent materials for removal of reduced sulfur species (primarily H_2S and COS) and halide species (primarily HCl) from simulated fuel gas mixtures. Experimental approaches were designed to closely simulate the gas/solid contact as well as the operating conditions in the NGC Process. Analytical techniques were developed for the measurement of sulfur and chloride species at trace levels to generate reaction conversion performance data. The most suitable desulfurization and dechlorination materials were identified and the optimum ranges of operating conditions determined for each stage of the NGC Process to achieve the target contaminant levels (H_2S < 60 ppbv and HCl < 10 ppbv) in the cleaned fuel gas with acceptable conversion rates (i.e., sorbent feed rates).

The Base Program provided for laboratory and conceptual exploration of the concept and derived an indication of its feasibility, leading to selection of the concept for further support. The second phase of the NGC Process development program (Optional Program) was exercised for conducting pilot-scale experiments and performing thorough economic, technical, and commercial feasibility analyses. The main goal of the Optional Program was to conduct a proof-of-principles demonstration of the integrated NGC Process on a GTI carbonaceous fuel gasifier producing raw fuel gases representative of commercial gasifier practice, to confirm technical and economic feasibility of the process. An important objective of the Optional Program was to verify, at the pilot-scale, the laboratory test results obtained in the Base Program with respect to operating temperatures for Stages I and II of the NGC Process, sorbent selections, sorbent/contaminant ratios, and ability of the process to accomplish very stringent contaminant levels in the syngas (i.e., particulates < 0.1 ppmw, total reduced sulfur compounds (H_2S, COS) < 60 ppbv, and total halides (mainly HCl) < 10 ppbv). In addition to particulates and sulfur and halide species, efforts were devoted in the Optional Program to evaluate the potential of incorporating mercury control into the NGC Process, with the objective of reducing mercury (mainly elemental mercury, Hg^0) concentration in the syngas to less than 0.01 ppbv, corresponding to mercury removal efficiencies > 99%.

Preparation of Pilot-Scale Facilities

The original plan was to refurbish an existing GTI gasifier to generate syngas via coal gasification for the NGC Process testing. Project schedule, however, coincided with GTI's decision to construct a new carbonaceous fuel gasification facility (Flex-Fuel Test Facility) with capability to process about 10 tons of coal per day. The overall Flex-Fuel Test Facility configuration includes the fluidized-bed gasifier, the NGC Process section, and the exhaust gas handling and cleanup section. Preparation of the NGC Process section was conducted in parallel with the Flex-Fuel Test Facility design and construction activities. This included designing a suitable process configuration and specifying, procuring, and installing the necessary pieces of equipment. The final NGC Process section layout, shown schematically in Figure 2, was determined after evaluation of several options and redirection of the program goals to focus on the more challenging aspects of the project, i.e., to achieve very stringent contaminant removal targets at the ppbv level. This part of the plant consists of two major sections: Conditioning and Testing. In the Conditioning section, the raw gasifier gas is treated to meet the requirements of the NGC Process Testing section (i.e., Stage II). The Conditioning section, however, did incorporate one of Siemens' barrier filters primarily to control syngas particulates, but also to remove the bulk of halides (i.e., HCl). Therefore, this first barrier-filter reactor represented Stage I in the NGC Process base configuration (i.e., Figure 1).

As shown in Figure 2, the NGC Process section consists of several major components:

<u>Conditioning Section</u>

- Direct Spray Water Quench (DSQ)
- Conditioning Filter-Reactor (CF-R)
- Conditioning halide sorbent feed system (Stage I halide sorbent)
- Conditioning char and spent sorbent handling system
- Pressure letdown valve
- Sulfur Guard Bed and associated bypass line and pre-heater
- Syngas Trim Cooler

Test Section

- Test Filter-Reactor, TF-R (for Stage II testing)
- Test sulfur, halide, and mercury sorbent feed systems (for Stage II testing)
- Test spent sorbent handling system

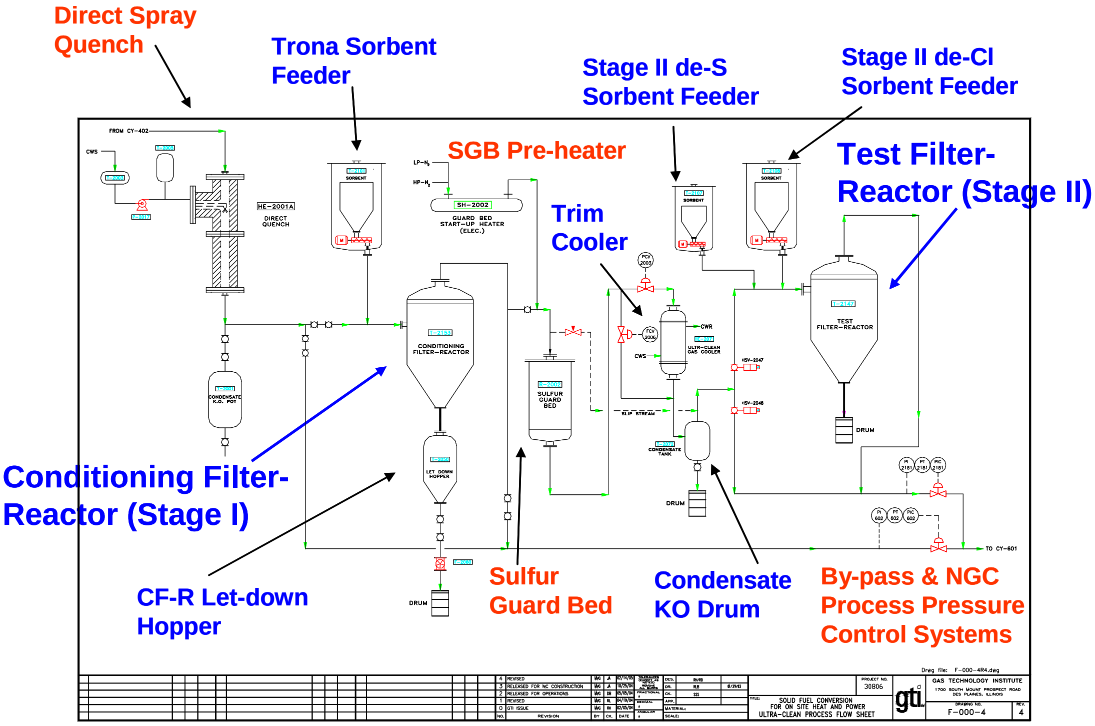

Figure 2 - P&ID for the Ultra-Clean Process Section in the Flex-Fuel Test Facility

To accomplish the NGC Process PDU test program goals, GTI, in collaboration with Siemens, developed a sampling and analysis protocol, as part of the Test Plan for the program, which defined the sampling locations, sample type (solid, gas, or liquid), sample description, purpose, number of samples, analyses to be performed, and measurement methods, during each PDU test campaign. Every effort was made to ensure that the state of the raw syngas was well defined before and after conditioning, and most importantly that performance of Stage II of the NGC Process could be properly assessed. Moreover, sufficient data would be collected to develop adequate material and energy balances for the gasifier to assess its efficiency in generating syngas from the test feedstock. The data generated would also permit characterization of process emissions for permitting activities and gasification and syngas cleanup byproduct materials for assessment of disposal options. Process samples included fuel feedstock, ash, raw syngas, fresh sorbent materials, spent sorbents, and condensed liquids, in addition to several gas samples throughout the NGC Process section.

To meet the very stringent requirements of the analytical work scope in the NGC Process PDU test program, one double-train and two single-train sample extraction and conditioning (SE&C) skids were designed and installed at three main sampling locations: Conditioning Filter-Reactor inlet (SE&C Skid #1), Conditioning Filter-Reactor outlet (SE&C Skid #2), and Test Filter-Reactor outlet (SE&C Skid #3). These three SE&C systems use the controlled condensation management approach, which incorporates filtration, gas cooling, condensate collection and removal, and drying. This process interface approach provides for separation of suspended particles, condensates, and gases. Particles and condensates are accumulated in the skid for post-test recovery and analysis. The gases, before and after drying stages, can be collected in sample canisters, passed through collection impingers (i.e., for HCl sampling) or absorption traps (i.e., carbon traps for mercury sampling, for example), or sent directly to analytical instruments for on-line measurements.

Two analytical stations were set up in the FFTF. The first station included four instruments: an Industrial Machine and Control Corporation (IMACC) Fourier-Transform Infrared Spectrometer (FT-IR), a Stanford Research Systems QMS300 Mass Spectrometer (MS), an Agilent 5890 gas chromatograph with flame photometric detector (GC/FPD), and a Varian micro gas chromatograph with thermal conductivity detector (μGC). The gas sampling system at this station was built to allow for the selection of samples from any of three sources from the process (i.e., CF-R inlet, CF-R outlet, and conditioned syngas) and direct the gas stream to one of the above four analyzers. In addition to supplying the on-line analyzers with representative syngas samples, the sampling system was used to extract sample gases to EPA Method 26 impingers, allowing for direct comparison of batch and FT-IR HCl measurements.

The second analytical station was set up in order to meet the analytical work scope requirements of the second test campaign during which critical measurements were made to assess the NGC Process Stage II performance for removal of multiple contaminants (H_2S, COS, HCl) to ppbv levels, and those of the third test campaign during which mercury removal via dry sorbent injection was investigated. This station included a Varian gas chromatograph featuring a built-in high performance sample concentrator, a sensitive pulsed flame photometric detector (PFPD) with a detection limit of 30 to 50 parts-per-trillion (ppt), and significant capability for speciated and total sulfur analyses. For on-line Hg analysis, a Tekran Mercury Vapour Analyzer 2537A was set up at the TF-R outlet that was much more sensitive than the off-line instrument, a Nippon WA-4 Mercury Analyzer (~ 0.01 $\mu g/m^3$ detection limit). To measure HCl at the ppmv and ppbv levels, glass impingers were setup at both analytical stations for chlorine sampling according to EPA Method 26, for subsequent analysis using an ion chromatograph instrument (Dionex ICS-1000).

The sampling systems were installed to measure reduced sulfur (H_2S and COS) and halide (HCl) compounds at various concentrations throughout the NGC Process section, ranging from hundreds of parts-per-million (ppmv) to very low concentrations at the parts-per-billion (ppbv) level. Extreme care was taken in the selection of construction materials for sampling to provide very low detection and to avoid contamination and loss of analyte. All sample transport lines from the various process interface points to the analytical stations were heat-traced and insulated to preserve gas sample integrity and to maintain gas temperatures above the instrument inlet conditions. Components of the SE&C skids at the G-13 and G-19 locations (tubing, fittings, valves, flow metering orifices, and Mott filters) and sample transport lines were coated with chemically-inert Silcosteel® and Sulfinert® coatings to minimize reactions and adsorption of gases on the surfaces. Sample canisters and valves were made from Sulfinert® materials. Low pressure and non-heated sampling lines and vessels were constructed of Teflon or borosilicate glass. Flexible silicone tubing was used to make low pressure connections between the coated steel or Teflon tubing and glass apparatus. The sampling methodology was validated throughout testing by purging sampling points with dry N_2 and reference gases containing certified concentrations of HCl and H_2S.

PDU Test Materials and Scope of Work

The pilot-scale test program comprised three one-month test campaigns. Table 1 lists the sorbents and operating conditions as well as the estimated, nominal stream flows and pressures for the Conditioning Filter-Reactor and the Test Filter-Reactor that would be applied in these three test campaigns. All of the sorbents are commercial, with the possible exception of the two mercury sorbents, which had been selected through a comprehensive laboratory test program and interactions with other R&D organizations. The Stage I and Stage II inlet temperatures are controlled process variables in the PDU test program. The syngas pressure is fixed in a given test campaign, and the syngas flow rate is set by the Flex-Fuel gasifier operating capacity. The inlet sulfur and halide contaminant levels are also controlled process variables, but with some uncertainty as to the levels of control that can be achieved in the process. The ranges of sorbent feed rates listed (moles of sorbent active component divided by the moles of the specific contaminant) reflect the expected range that might be required to achieve the targeted gas cleaning performance.

Pilot-scale testing materials stocks were determined based on estimates of NGC Process flows, test campaign durations, and other considerations. Test materials included a relatively low-sulfur carbonaceous feedstock (metallurgical coke (0.69% S, 800 ppmw Cl, 0.02 ppmw Hg), North Dakota Lignite (0.89% S, ~ 10 ppmw Cl, 0.06 ppmw Hg), and a high-ash coal from India (0.56% S, < 100 ppmw Cl, 0.14 ppmw Hg) that was available from a recent GTI project), trona (and nahcolite as an alternative material) for bulk HCl removal in the Conditioning Filter-Reactor, BASF's R5-12 catalyst or Süd -Chemie's G-72E catalyst as a ZnO sulfur guard bed material, Süd -Chemie's G-72E and G-92C catalysts as Stage II desulfurization and dechlorination sorbents, respectively. Except for trona and nahcolite, which were procured in fine form from a commercial supplier, all of the sorbents are sized (ground and sieved) to -325 mesh at GTI, with an estimated mass-mean diameter of 20 μm.

Table 1 - Conditioning Filter-Reactor and Test Filter-Reactor Nominal Test Conditions

Filter-Reactor	Conditioning	Test
Inlet temperature (°F)	830	550
Inlet pressure (psia)	277	215
Inlet syngas flow (lb/hr)	3439	3648
Filter Face velocity (ft/min)	2.7	3.1
Inlet total sulfur content (ppmv)	not applicable	1 – 5
Inlet halide content (ppmv)	150 – 500	1 – 5
Sulfur sorbent (-325 mesh)	None	G-72E
Halide sorbent (-325 mesh)	Trona	G-92C
Target sulfur outlet content (ppmv)	not applicable	0.06
Target halide outlet content (ppmv)	1 – 5	0.01
Sulfur and halide sorbent feed rates (mole/mole contaminant)	2 – 10	2 – 10
Mercury sorbents (-325 mesh)	None	GTI-Hg-S9 TDA's Hg Removal Sorbent
Mercury sorbent feed rate (sorbent-to-Hg^0 mass ratio)	None	1000 - 2000

Results and Discussion

NGC Test Campaign One (NGC-OPT1)

The primary objective of the Novel Gas Cleaning Optional Program Test Campaign 1 (NGC-OPT1) was to evaluate the performance of the Conditioning Filter-Reactor for combined particulate/halide removal from syngas derived from the gasification of a carbonaceous feedstock. This first test campaign was conducted primarily with metallurgical coke (Bethlehem Coke Breeze), whose chloride content (~ 800 ppmw) best suited the test objectives. In addition to the Flex-Fuel gasifier, the Direct Spray Quench system and the Conditioning Filter-Reactor and associated halide sorbent (trona) injection system and pulse control skid were successfully commissioned and tested during this test campaign.

Gasification of Bethlehem Coke Breeze and washed Indian coal was conducted successfully for ~ 62 hours. This campaign comprised four test segments with three representing steady-state testing periods involving operation with metallurgical coke without trona injection, metallurgical coke with trona injection, and Indian coal without trona injection. Trona was injected into the syngas immediately upstream of the CF-R vessel for ~ 18 hours. Pulsing cycles during operation with metallurgical coke were long (once every 2 to 4 hours), but increased to approximately 7-8 pulses per hour as the solids loading in the syngas increased significantly during operation with the high-ash Indian coal. In both cases, however, the filter pressure drop behavior was stable.

Using certified gas mixtures containing appropriate HCl and H_2S concentrations and spike-and-recovery techniques, the high-temperature process interface approach for syngas sample extraction and conditioning was validated at the CF-R inlet and outlet locations. Reproducibility of the impinger sampling/ion chromatograph chloride measurements was also demonstrated. The EPA Method 26 impinger/ion chromatograph batch HCl sampling and measurements and on-line FT-IR HCl analyses showed very good agreement. Both approaches were able to identify and quantify the effect of char on HCl concentrations in the raw syngas, leading to confirmation of the expected HCl concentration (106 ppmv was measured compared to an expected HCl concentration of ~ 111 ppmv).

Both time-averaged (batch) impinger measurements and on-line FT-IR analyses indicated that the HCl concentration in the CF-R product syngas slowly decreased as the trona injection rate was increased. The lowest HCl concentration in the CF-R outlet syngas was measured at 10.8 ppmv during trona injection, corresponding to ~ 90% HCl removal in the CF-R vessel. This lower than expected HCl removal performance could be due to several factors, including lower reaction temperature, high raw syngas steam content (equilibrium limitation), higher size distribution of the injected trona, lower face velocity (syngas flow rate). The influence of each of these parameters was examined and it appears likely that a large portion of the trona fed would not have deposited on the filter elements given the relatively large portion of large particles in the trona, and the low syngas velocity through the CF-R vessel. Because metallurgical coke was used in this test campaign, the syngas flow rate was limited to ~ 1800 lbs/hr, which corresponds to a face velocity of ~ 2 ft/min (a face velocity > 3 ft/min is desired). In addition, post-test analyses indicated the particle size distribution of the as-received Solvay T-200® trona was much coarser than the char. The volume moment mean diameter (i.e., mean diameter with respect to the mass of the particles) is about 13 μm and the median diameter, d(0.5), is about 8 μm for the char sample. The corresponding values for the bulk dechlorination material were significantly higher, 53.8 μm and 35.6 μm, respectively.

NGC Test Campaign Two (NGC-OPT2)

The primary objective of the NGC-OPT2 was to evaluate the performance of the Test Filter-Reactor (TF-R) for sulfur (H_2S and COS) and halide (HCl) removal (individually and simultaneously) to very stringent levels from syngas derived from the gasification of a carbonaceous feedstock. The washed Indian coal was selected as the primary feedstock for this test campaign, due to its chloride and sulfur content. After the test objectives were achieved, the coal feed was switched to North Dakota lignite to evaluate this fuel's suitability for the third test campaign focusing on mercury control. The entire Flex-Fuel Test Facility (gasification and NGC Process sections) was successfully operated throughout the NGC-OPT2A (week of March 21) and the NGC-OPT2B (week of March 28) test campaigns, including two Siemens barrier filters (CF-R and TF-R), Sulfur Guard Bed (SGB) and associated low-pressure nitrogen pre-heater and slipstream by-pass system, and Stage II sulfur (G-72E) and halide (G-92C) sorbent feeders. The low HCl content of the raw syngas (10 to 20 ppmv) made it possible to forego trona injection into the syngas upstream of Stage I and focus solely on the more challenging aspects of the process, i.e., achieving parts-per-billion (ppbv) levels in the ultra-cleaned Stage II product syngas. The Trim Cooler (located between the SGB and TF-R) was not utilized in these tests. In addition, G-92C halide sorbent was fed as a 50/50 physical mixture with nahcolite to improve its feeding as determined in prior commissioning tests.

The raw syngas, derived from the gasification of primarily washed Indian coal, was successfully conditioned to the temperatures and contaminant levels required at the inlet to the TF-R. Throughout testing, temperatures across the NGC Process section (Figure 2) were maintained at ~ 1450ºF at the secondary cyclone, ~ 1400ºF at the inlet to the Direct Spray Quench, ~ 700ºF at the inlet to the CF-R, ~ 650ºF at the outlet of the CF-R, ~ 650ºF at the SGB inlet, ~ 600ºF at the SGB outlet, ~ 600ºF at the TF-R inlet, and ~ 550ºF at the TF-R outlet. These conditions ensured operation of the SGB at optimal conditions for maximized utilization of the SGB catalyst and efficient sulfur removal. These conditions also ensured that contaminant removal reactions across the TF-R vessel were kept within the optimum temperature range (550°F to 575°F). The total sulfur concentration (H_2S and COS) at the inlet was regulated within a 1-5 ppmv range throughout testing by maintaining a regulated syngas slipstream that bypassed the SGB vessel. An on-line GC/FPD provided near-continuous H_2S and COS measurements. In addition, because of low levels of HCl in the raw syngas (about 20 ppmv) and some measured HCl removal in the CF-R vessel (through interaction with char and residual trona) and in the SGB vessel (a small amount of CaO in the SGB catalyst), it was not necessary to engage the trona sorbent feeder upstream of the CF-R for bulk HCl removal. The measured HCl concentration in the syngas at the G-14 location (TF-R inlet) consistently averaged ~ 2 ppmv. HCl measurements were made using both the on-line IMACC FT-IR instrument as well as the batch impinger sampling with ion chromatography analysis.

The second test campaign comprised several test segments, including halide removal by injection of finely-ground G-92C sorbent, sulfur removal via injection of the finely ground G-72E sorbent, combined removal of HCl and sulfur species (H_2S and COS) via simultaneous injection of both sorbents from two separate feeders (Figure 2), and other segments of interest. The gasification section was operated under steady state conditions throughout these test segments as demonstrated by stable gasifier output. Conditioning the syngas (at the TF-R inlet) and halide removal by injection of ground G-92C sorbent were the focus of the initial phase of the second test campaign. The halide sorbent feeder functioned very well with a 50/50 physical mixture of G-92C and nahcolite which was found to facilitate feeding in prior commissioning tests. During this week of testing, efforts concentrated on controlling HCl in the TF-R and monitoring sulfur species concentrations. It was clearly demonstrated that the injected material reached the filter elements (candles): ΔP across the filter increased steadily reaching ~ 150 in. H_2O by the time this test phase was completed. Initially, the G-92C/nahcolite mixture was injected at a higher rate than was necessary (~ 100 g/min) to “pre-coat” the candle surfaces with sorbent materials and expedite testing. Within 2.5 hours, ΔP across the TF-R reached ~ 75 in. H_2O. Sorbent injection was then continued at the test design rate of 20 g/min. The Test Filter-Reactor was not pulsed during testing.

Throughout testing, numerous samples were taken from a variety of locations and were analyzed using a wide array of instrumental methods. During the second test campaign approximately 55 impinger/ion chromatography analyses and 78 gas sample canisters involving the main four sampling points as well as validation runs were taken, in addition to data taken with online instruments. During halide sorbent injection, HCl concentrations were measured to be about 58, 61, and 52 ppbv. Each of these concentrations was measured from batch impinger samples that were obtained over a 2-hour sampling period. Taking into account the background HCl concentration that was estimated to range from 40 to 55 ppbv based on blank runs, these measurements would represent approximately 3-18, 6-21, and 0-12 ppbv HCl in the ultra-clean syngas.

At the conclusion of the HCl removal testing the Test Filter-Reactor was pulsed and the sulfur removal test segment was started with pre-coating the filter elements (candles) by feeding the finely-ground G-72E sorbent at the higher rate of 30 g/min, and when the filter ΔP reached ~ 75 in. H_2O, the feed rate was reduced to 5 g/min. As in the previous halide sorbent injection test completed in the prior week, ΔP across the second filter increased steadily. The total sulfur concentration (H_2S and COS) in the TF-R outlet was measured consistently at less than 50 ppbv, using batch samples. Semi-continuous online sulfur measurements (every 24 minutes) using the Varian CP-3800 PFPD gas chromatograph were quite stable, averaging ~ 20 ppbv, much lower than the 60 ppbv target. During this test segment the total sulfur (H_2S + COS) level was maintained in the 2-5 ppmv range at the TF-R inlet through increasing the amount of raw syngas that was bypassed around the SGB vessel.

Following the sulfur removal test segment, the Test Filter-Reactor was pulsed and readied for the next test segment: the combined removal of sulfur and halide species (H_2S, COS, HCl). A "pre-coating phase" was first performed with the G-92C/nahcolite mixture at 50 g/min and the G-72E sorbent at 20 g/min. Within an hour, ΔP across the TF-R increased to ~ 95 in. H_2O. Combined contaminant removal continued for approximately 5 hours, when ΔP across the TF-R reached 150 in. H_2O. However, instead of pulsing the TF-R, it was decided to stop sorbent injection and continue to measure contaminant concentrations at the inlet and outlet of the TF-R for an extended period of time. Furthermore, to develop additional insights into the nature, amount, and uniformity of the filter cake on the TF-R candles, the total sulfur concentration at the TF-R inlet was raised to ~ 25 ppmv. The total sulfur concentration in the TF-R outlet was monitored overnight. Throughout this period, the total sulfur concentration ranged between 20 and 40 ppbv, indicating the efficacy of the Test Filter-Reactor in removing sulfur and the NGC Process flexibility with respect to regulating the sulfur level at the Stage II inlet. Thus, it appears that sulfur levels at the TF-R inlet do not need to be maintained within a strict 1-5 ppmv range to achieve a desired output sulfur level of < 60 ppbv. Successful simultaneous removal of sulfur and halide species to ultra-clean levels was also demonstrated with syngas generated by gasifying lignite. The same cleaning efficiencies during this test (with lignite) were measured as were achieved with the washed Indian coal, showing that the NGC Process properly functions with two diverse fuels.

NGC Test Campaign Three (NGC-OPT3)

The primary objective of the third test campaign (NGC-OPT3) was to evaluate the performance of the Test Filter-Reactor for mercury removal to very stringent levels (> 90%) from syngas derived from the gasification of a carbonaceous feedstock. North Dakota lignite was used exclusively in this campaign given its suitable sulfur, chloride, and mercury content. Selection and laboratory evaluation of candidate mercury-removal sorbents had been completed earlier in the project, identifying two candidate sorbents with potential to capture mercury to levels below 0.01 ppb in the NGC Process configuration. During selected test periods, Stage II sulfur and halide sorbents were injected, simultaneously with the Hg sorbent, into the conditioned syngas upstream of the TF-R to assess their effects on the Hg sorbent performance. GTI demonstrated the capability to measure mercury at ppb levels in coal-derived syngas and obtain reasonable material balance. The results obtained also established evidence of a significant level of mercury capture (50-75%) with one of the two selected sorbents at the relatively high temperature of 572ºF (optimum NGC Process Stage II operating temperature for sulfur and halide removal). Additional testing is needed to evaluate mercury removal at lower temperatures (350 to 450ºF) using both selected sorbents.

Conclusions and Recommendations

Three test campaigns were successfully completed as proof-of-principle demonstration of the NGC Process "filter-reactor" concept configuration in full integration with GTI's Flex-Fuel Test Facility. Extensive efforts in these tests were devoted to designing, installing, and validating state-of-the-art gas sampling equipment and instruments to meet the very stringent analytical needs of the program, involving measurements of concentrations of various compounds ranging from hundreds of parts-per-million (ppmv) to very low concentrations at the parts-per-billion (ppbv) level. The test program clearly demonstrated the flexibility of the Flex-Fuel Test Facility (gasifier/NGC Process section) to efficiently produce syngas from three different feedstocks, to condition the resulting raw syngas to meet the requirements of the NGC Process Test section, and to ultra-clean the conditioned syngas to meet the very stringent cleaning requirements of chemical synthesis applications (i.e., total S < 50 ppbv, total halides < 10 ppbv, particulate < 0.1 ppmw).

Consistent with the significance of the data developed in the PDU test program and the recommendations of conceptual process evaluations, GTI highly recommends the NGC Process development work enter into a process optimization phase. Specifically, four additional test campaigns are proposed prior to undertaking further scale-up work and ultimately commercial-scale demonstration. The objectives of these tests are to:

- Optimize key process parameters:
    - sorbent feed rates
    - Sorbent sizes and size distributions
    - process operating temperatures
    - inlet contaminant levels
- Explore the envelope of these parameters both separately and in an integrated configuration
    - Develop the necessary data to extract quantitative design parameters for scaling up the bulk HCl removal performance (in the Stage I barrier filter-reactor simultaneously with ash), and the combined removal of sulfur and halide species to ppbv levels in the Stage II barrier filter-reactor.
    - Extract quantitative information (filter cake permeability, cake thickness, portion of ash reaching the filter elements, etc) from the pressure drop data (based on ash flow rate and size distribution to the CF-R and filter cake properties, such as density, re-entrainment rate, etc.)
- Conduct integrated testing to demonstrate NGC Process suitability for "futuristic" IGCC and methanol synthesis applications.

In addition to process optimization, the proposed campaigns will provide another opportunity to perform additional mercury removal testing (using both the lower temperature and higher temperature sorbents and potentially other promising Hg sorbents), further advancing the syngas mercury capture technology base. Other facets of the process will also be explored including bulk HCl removal at higher temperature, continuous removal of ash/spent halide sorbent fines from the CF-R, etc.

2. PROGRAM OBJECTIVES

The Novel Gas Cleaning Program consisted of two phases: a Base Program phase and an Optional Program phase. The goal of the Base Program (completed in August 2001) was to provide the necessary data to verify the technical and economic feasibility of the Novel Gas Cleaning (NGC) Process. The scope of work in this first phase was dedicated most heavily to the laboratory testing of selected candidate sorbent materials for removal of reduced sulfur species (primarily H_2S and COS) and halide species (primarily HCl) from simulated fuel gas mixtures. Experimental approaches were designed to closely simulate the gas/solid contact as well as the operating conditions in the NGC Process. Analytical techniques were developed for the measurement of sulfur and chloride species at trace levels to generate reaction conversion performance data. The most suitable desulfurization and dechlorination materials were identified and the optimum ranges of operating conditions determined for each stage of the NGC Process to achieve the target contaminant levels (H_2S < 60 ppbv and HCl < 10 ppbv) in the cleaned fuel gas with acceptable conversion rates (i.e., sorbent feed rates). Laboratory test results were reported in the Base Program Final Report.[1]

The main goal of the second phase of the Novel Gas Cleaning Program (Optional Program) was to conduct a proof-of-principles demonstration of the NGC Process on a GTI carbonaceous fuel gasifier producing raw fuel gases representative of commercial gasifier practice, to confirm technical and economic feasibility of the process. An important objective of the Optional Program is to verify, at the PDU scale, the laboratory test results obtained in the Base Program with respect to operating temperatures for Stages I and II of the NGC Process, sorbent selections, sorbent/contaminant ratios, and ability of the process to accomplish very stringent contaminant levels in the syngas (i.e., particulates < 0.1 ppmw, total reduced sulfur compounds (H_2S, COS) < 60 ppbv, and total halides (mainly HCl) < 10 ppbv). In addition to particulates and sulfur and halide species, efforts have also been devoted in the Optional Program to evaluate the potential of incorporating mercury control into the Novel Gas Cleaning Process, with the objective of reducing mercury (mainly elemental mercury, Hg^0) concentration in the syngas to less than 0.01 ppbv, corresponding to mercury removal efficiencies > 99%.

The Optional Program PDU test results, and the reaction rates and conversion factors extracted from the results, were used as the basis for an update of the commercial process performance and economics (Optional Program Final Report, Volume I). The fuel gas cleanup process technical and economic feasibility were estimated, and the areas of greatest performance and economic issues identified.

3. BACKGROUND

Much of the hot gas cleanup research and development efforts have been conducted within the context of the Integrated Gasification Combined Cycle (IGCC), focusing predominantly on the development of regenerable metal oxide sorbents for the removal of reduced sulfur compounds (mainly hydrogen sulfide (H_2S) and carbonyl sulfide (COS)) at high temperature and pressure. The objective in this application is to reduce the H_2S concentration in the fuel gas to less than 20 ppmv to satisfy gas turbine requirements. In recent years there has been significant interest in extending the hot gas cleanup capabilities so that the cleaned fuel gas becomes suitable for a wide range of applications, including fuel cells and production of chemicals and transportation fuels, in addition to electric power generation via the IGCC technology. These applications require the removal to near-zero levels, of the sulfur-, nitrogen-, alkali-, and chlorine-containing gas emissions and fine particulate matter ($PM_{2.5}$) caused by fuel bound constituents that are naturally present in many forms in a variety of carbonaceous materials which are useful as feedstocks to gasification processes. When the IGCC system is applied to creating synthesis gas for production of liquid products (e.g., methanol, F-T liquids), these species can be poisonous to downstream processing units and may be contaminants in the high purity products. HCl in particular is a significant contaminant that causes severe deterioration to various fuel cell materials.[2]

Commercial technology is available to clean coal-gasification hydrocarbon gases to the stringent levels required for these demanding applications. The prevalent commercial gas cleaning process, capable of achieving the very stringent gas cleaning requirements 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, particulates, and other contaminants, resulting in extensive water treatment requirements.

Three factors inherent in conventional, low-temperature fuel gas cleaning technologies result in lower power plant efficiencies and higher equipment costs:

- Nearly all of the water vapor in the fuel gas is condensed out, and is typically later replaced in a fuel gas humidification process, resulting in significant plant energy loss
- The low-temperature, sulfur absorption processes used remove a significant portion of the fuel gas CO_2 content along with the sulfur species, reducing the fuel gas mass flow and making sulfur recovery more energy intensive and expensive.

The process condensate streams generated require considerable processing to effectively remove contained contaminant salts and gases, increasing plant complexity and cost.

Several plant availability issues have been reported that relate to conventional, low temperature fuel gas cleaning:

- Volatile metal species in the cleaned fuel gas, in the form of iron and nickel carbonyls, are reported in some IGCC plants to result in deposition and corrosion in the gas turbine, and conventional fuel gas cleaning provides no protection from these metal carbonyls that are expected to form primarily at low temperatures within the fuel gas cleaning equipment.
- Particulate generated by fuel gas piping corrosion is reported in some IGCC power plants to reduce availability, resulting from gas turbine erosion and deposition, and has been dealt with in some IGCC power plants by adding a final fuel gas filter to protect the gas turbine from such particulate.
- The process condensate streams represent highly corrosive environments for process equipment and result in reduced power plant availability.

New, more economical technologies are needed for stringent gas cleaning duty if coal is to become competitive with cleaner fuel sources, such as natural gas, in U.S. Department of Energy advanced, near-zero emission, efficient multi-production energy plants.

To address this need, Siemens Power Generation, Inc. (Siemens) and the Gas Technology Institute (GTI) have been developing a novel process compatible with known gasifier systems that promises, in a pre-combustion treatment, to prepare carbonaceous feedstock-based fuel gases or syngases for use in power generation applications with gas turbines or with fuel cells, or for co-production of power with chemicals or transportation fuels. This process can be applied as an add-on cleaning step following a near-commercial, state-of-the-art hot gas polishing system (based on entrained-bed transport reactor technology, for example). The process can also be a stand-alone fuel gas cleanup system, depending on the carbonaceous fuel properties, the extent of in-gasifier cleaning, and the cleanup requirements of the intended application. This novel process specifically addresses sulfur, chloride, mercury, and particulate removal to meet the most stringent requirements (total sulfur (mainly H_2S and COS) < 60 ppbv, halide (mainly HCl) < 10 ppbv, Hg < 0.01 ppbv, and particulate < 0.1 ppmw). These are contaminant levels below detection limits of conventional measurement instrumentation. In addition, various options have been conceptualized to incorporate the removal of other contaminants, such as ammonia (NH_3), into the NGC Process. The NGC Process configurations, its barrier-filter reactor equipment, its performance goals, and its potential merits relative to commercial gas cleaning technologies were described in Volume I of this report.

4. LABORATORY SUPPORTING STUDIES

The Novel Gas Cleaning Process concept was previously described in detail.[3,4] The rationale for the technical approach adopted, laboratory simulation of the process and operating conditions, sorbent/material requirements and selection, and reactor design and testing procedures were also outlined. Laboratory gas sampling and measurement procedures using gas and ion chromatography techniques were described and their reliability and accuracy were demonstrated.[5,1] Incorporation of mercury removal into the process and laboratory selection of sorbents and test evidence of sorbent performance capabilities have also been addressed in a dedicated publication.[6] A brief summary of the Base Program work scope and findings is provided below, as well as a concise summary of the mercury-related work (i.e., laboratory component of Task 6).

4.1 Sulfur and Halide Removal

In the first development phase, laboratory testing at GTI focused on the identification of suitable sulfur and halide sorbents and operating conditions for Stage I and Stage II of the NGC Process. This small-scale laboratory testing was also performed to provide evidence of the capability of the process to reach its stringent gas cleaning goals under operating conditions closely simulating process requirements, and also to explore the sensitivity of the sorbent performance to the major process parameters. This work systematically evaluated suitable Cu-, Fe-, Mn-, and Zn-containing fines and Na-containing fines as desulfurization and dechlorination materials, respectively, for both stages of the NGC Process. The materials selected for both stages of the process, their chemical and physical characteristics, their desulfurization or dechlorination performance in a packed-bed reactor, and the performance of physical mixtures of leading desulfurization and dechlorination materials were previously discussed in detail.[5] Consistency of experimental data was also demonstrated based on product gas analyses using gas and ion chromatographs (i.e., breakthrough curves), chemical analyses of spent samples from different locations in the sorbent bed, and X-ray diffraction (XRD) analyses. Based on thermodynamic simulations and analyses, guidelines were developed to rationalize the experimental work and confirm or explain the results obtained.

Tests with individual sorbents, and mixtures of sulfur and halide sorbents were conducted in simulated coal syngas containing individually H_2S, HCl, or mixtures of these contaminants. These parametric tests were conducted at near-atmospheric pressure in a packed-bed reactor facility. The laboratory tests used a simulated coal-based syngas composition passing through thin packed beds of sorbents operated at face velocities representative of sorbent filter cakes in the NGC Process syngas polishing filter-reactors. Typical breakthrough data, such as shown in Figure 3, comparing HCl removal performance (efficiency and effective chloride capacity) of candidate Stage I dechlorination materials, were collected to measure the sorbent reaction performance. Sectional analysis of the packed bed sorbent reaction products to confirm the reaction mechanisms and conversions were included. The laboratory test procedures, equipment, and test results have been previously described.[5]

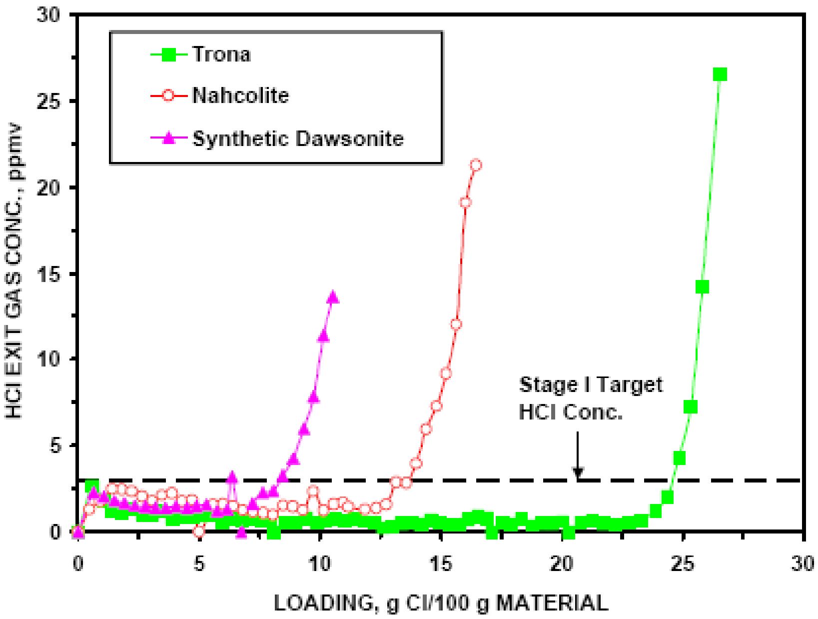

Figure 3 - Performance Comparison of Stage I Dechlorination Minerals

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

- Stage I temperature: 499ºC (930ºF),
- 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: 288ºC (550ºF),
- 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 an inexpensive, commercially available, natural mineral. The Stage II sorbents G-72E (zinc-based) and G-92C (sodium-based) are catalyst pellet materials that are commercially available through Süd-Chemie.

Uncertainties exist in making gas contaminant measurements as low as 60 ppbv for H_2S and 10 ppbv for HCl, and a critical element of the program was the development of reliable procedures and equipment to make these measurements. State-of-the-art equipment, sampling and measurement and operating procedures were utilized by GTI to minimize and account for contaminant losses and background contaminant levels. Ion Chromatography was successfully used to make HCl measurements down to 10 ppbv. Stage I sulfur species contents down to 1 ppmv were reliably measured by a gas chromatograph equipped with a flame photometric detector (FPD). The Stage II sulfur species were measured by a special gas chromatograph technique, but could only achieve a detection limit of 85 ppbv, compared to the target of 60 ppbv. This was considered acceptable for the Base Program laboratory screening and verification tests. GTI procured a trace sulfur system featuring the Varian 3800 Gas Chromatograph with built-in high performance sample concentrator and a sensitive pulsed flame photometric detector (PFPD). This system has a detection limit of 30 to 50 parts-per-trillion (pptv). It would be used for speciated and total sulfur analyses in the ultra-cleaned syngas during the testing campaigns planned in the Flex-Fuel Test Facility.

4.2 Mercury Removal

To incorporate mercury control into the NGC Process, GTI, in collaboration with Siemens, evaluated much of the prior and ongoing scientific and engineering studies on mercury removal in oxidizing as well as reducing gases, made many contacts with sorbent/catalyst manufacturers, and compiled a list of potential mercury sorbent materials for the syngas application. Candidate sorbents for meeting the stringent mercury removal requirements of commercial syngas applications include materials with potential to amalgamate with mercury (disposable as well as regenerable dispersed metal-based sorbents such as Ag, Au, Pt, Pd, Cu, etc.) and physical adsorbents, including chemically-promoted activated carbons, metal oxides, metal sulfides, halide salts, amended silicates, chlorinated sorbents, noble metals, fly ashes, zeolites, and calcium compounds.

On the basis of this assessment a primary list of sorbents (bulk and supported) was identified, comprising 15 materials based on the oxides of copper, manganese, molybdenum, and zinc, as well as mixed oxides, by-product materials, and activated carbons. The various sources for copper-based materials (bulk as well as supported sorbents) include a copper sulfide from a Canadian mine, Süd - Chemie, ALCOA, and previous GTI sulfur sorbent development programs. Mixed-oxide materials were obtained primarily from Johnson Matthey (MJ), and are marketed commercially as low-temperature shift conversion catalysts, or for sulfur and mercury removal at temperatures < 95ºC (203ºF). These consist of copper compounds (CuO and $Cu_2(CO_3)(OH)_2$), zinc oxide (ZnO), and alumina (Al_2O_3). To promote the performance of these mixed-oxide materials for mercury removal from hydrocarbon streams and fuel gases at elevated temperatures, "especially sulfided" versions of these materials were also procured from JM. Molybdenum- and manganese-based materials (MoO_3/TiO_2 and MnO/Al_2O_3) were obtained from the Millennium Inorganic Chemicals Co. in France and Chemetals in Baltimore, respectively. The "Norit Americas Darco FGD" activated carbon was selected to serve as a baseline sorbent in the laboratory portion of this work, and also as a potentially effective mercury sorbent at low temperature (38 to 121ºC; 100 to 250ºF) for chemicals synthesis applications. This material has been widely used in U.S. DOE-sponsored demonstration programs for flue gas mercury removal via sorbent injection. Finally, an additional sulfur-impregnated activated carbon was obtained from Calgon Corporation in the form of 4-mm extrudates containing 10-18% S, with reported effectiveness for mercury removal from natural gas, air, and by-product hydrogen streams.

GTI designed and constructed a totally enclosed reactor facility and procured a state-of-the-art gas-phase mercury analyzer (PS Analytical Sir Galahad II). Using the ″Norit Americas Darco FGD″ activated carbon material as a baseline sorbent, GTI validated the reactor system and associated mercury sampling and analysis procedures. All procured materials were evaluated systematically in stages, first using Hg^0-N_2 mixtures, and then using fuel gas mixtures simulating the Texaco gasifier gas composition. Promising candidates have also been subjected to parametric testing in the 38-288ºC (100-550ºF) temperature range, under a wide range of other key operating conditions. Over 60 screening/scoping tests were completed. A typical breakthrough curve, obtained with a promising formulation, is shown in Figure 4. This material, designated as GTI-Hg-S9, was found to exhibit acceptable mercury removal performance in the 149-204ºC (300-400ºF) temperature range, achieving effective mercury capacity of approximately 0.015 wt.%. GTI worked with JM (formerly Synetix) to produce about 12.5 kg (27.5 lb) of this material in the -325 mesh size range for pilot-scale testing in the Flex-Fuel Test Facility, where it would be injected into a coal-derived syngas upstream of the Stage II barrier filter-reactor in the NGC Process section. GTI also initiated efforts with JM to improve the performance of this material at the higher Stage II operating temperature.

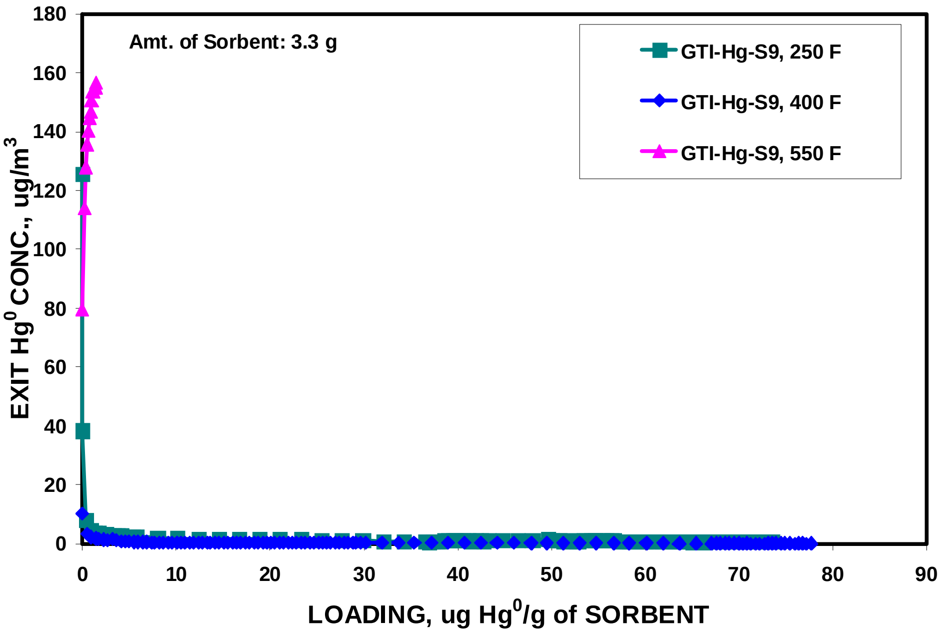

Figure 4 - Hg^0 Removal Performance of the GTI-Hg-S9 Mixed Oxide Sorbent at 121-288°C

To gain insight into the performance of these mercury sorbents, selected materials were subjected to chemical analysis and physical characterization, including XRD analysis. As indicated in Table 2, the GTI-Hg-S9 and GTI-Hg-S10 pre-sulfided mercury sorbents have high surface areas (45 and 38 m^2/g), about one order of magnitude higher than those of typical regenerable sulfur sorbents (such as the IGTSS-179 copper-based sorbent listed in Table 2) manufactured using granulation or spray drying techniques. However, these surface areas are well within reach using a proprietary sorbent manufacturing technique developed at GTI (see IGTSS-362 zinc titanate sorbent properties in Table 2). Accordingly, GTI expects that it may be quite feasible in a future effort to formulate effective mercury sorbents using its modified sol-gel based preparation technique.

Material balance estimations were previously made for both stages of the NGC Process, in conjunction with a gasification plant processing 909 tonnes/day (1000 tons/day) of coal. The flows are roughly equivalent to those that would represent an advanced, 150 MWe fuel cell plant. Figure 5 shows a “conservative-case scenario” where G-92C and G-72E, dechlorination and desulfurization materials, respectively, are each assumed to achieve only 20% conversion (i.e., Zn/S=5 and Na/Cl=5).

Table 2 - Physical and Chemical Characteristics of Selected Mercury and Sulfur Sorbents

Chemical & Physical Properties	GTI-Hg-S8	GTI-Hg-S9	GTI-Hg-S10	GTI-Hg-S11	IGTSS-179	IGTSS- 362
Aluminum, wt%	8.71	8.56	5.31	2.69	17.9	
Copper, wt%	34.5	32.4	26.4	38.5	35.8	
Zinc, wt%	20.4	19.9	13.8	7.11		30.2
Manganese, wt%					11.3	
Titanium, wt%					0.54	33.1
Carbon, wt%			5.95	4.63		
Hydrogen, wt%			2.0	1.14		
Sulfur, wt%	<0.01	14.3	16.7	<0.01		
Bulk density, g/cm^3	2.11	2.33	1.70	2.16	1.93	1.43
Particle (Hg) density (ρb), g/cm^3*	2.11	2.33	1.67	2.16	3.65	2.56
Skeletal density (ρa), g/ cm^3	4.16	3.48	2.93	3.47	4.17	4.17
BET Surface Area, m^2/g	88.2	71.1	35.2	30.4		47.2
Porosity, %**	49.16	32.85	42.94	37.70	12.5	38.7
Hg Surface Area, m^2/g	76.97	44.79	38.33	24.99	5.21	41.2

*Corrected for inter-particle void

**Calculated based on corrected values as (1 - ρb/ρa)*100, or equivalently as ρb*(Hg Pore Volume)*100

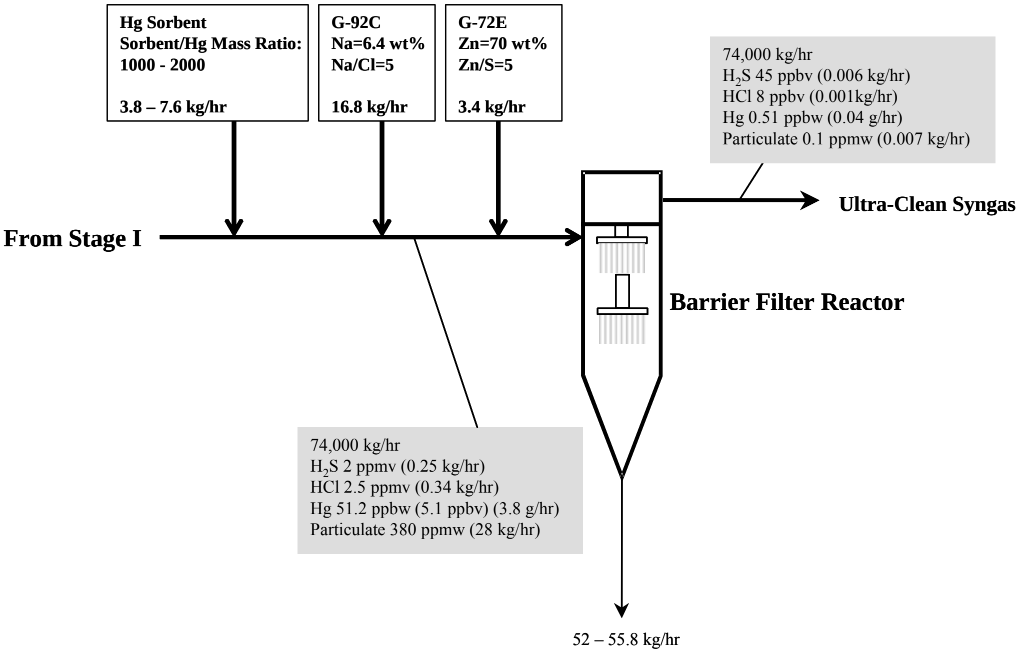

Figure 5 - Material Balance for Stage II Barrier Filter-Reactor in the Ultra-Clean Process with Additional Mercury Control (Chemical Synthesis Application, 550°F)

Mercury input to the Stage II Barrier Filter-Reactor of the NGC Process was based on a coal mercury content of approximately 100 ppbw (0.1 ppmw), the average level for different types of U.S. coals. A concentration of 100 ppbw in the coal is equivalent to 51.2 ppbw (5.1 ppbv) in the syngas. The mass balance around the Stage II Barrier Filter-Reactor is shown in Figure 5. Based on the estimate of 1000-2000 sorbent-to-Hg^0 mass ratio, approximately 3.8 to 7.6 kg of sorbent is needed to remove 99% of the mercury, as indicated. The mercury loading based on the mass balance can be calculated to be approximately 500-1000 µg Hg^0/g of sorbent (i.e., 0.05 to 0.1 wt% Hg retention capacity). This is quite reasonable considering that Eastman Chemical Co. has already demonstrated economic mercury removal from syngas at low temperature using activated carbon with effective capacity of about 0.4 wt.%.[7,8] Moreover, carbon-to-mercury weight ratios of 3,000:1 to 100,000:1 have been reported for mercury control in coal-fired utility flue gases via powdered activated carbon injection.[9]

For the promising GTI-Hg-S9 sorbent, according to the sorbent manufacturer (JM), the cost would be about \$10,000-\$15,000/m^3. This cost includes sorbent procurement from a JM facility in the U.S. and pretreatment (i.e., sulfidation) in a facility in the United Kingdom. The delivered cost for the sorbent would be about \$10 to \$15/kg (\$4.5 to \$6.8/lb), close to that of zinc titanate.

5. NGC PROCESS SECTION CONCEPTUAL DESIGN

Preparation of the NGC Process section was conducted in parallel with the Flex-Fuel Test Facility design and construction activities. This included designing a suitable process configuration and specifying, procuring, and installing the necessary pieces of equipment. The final NGC Process section layout, shown schematically in Figure 6, was determined after evaluation of several options and redirection of the program goals to focus on the more challenging aspects of the project, i.e., to achieve very stringent contaminant removal targets at the ppbv level. This part of the plant consists of two major sections: Conditioning and Testing. In the Conditioning section, the raw gasifier gas is treated to meet the requirements of the NGC Process Testing section (i.e., Stage II). The Conditioning section, however, does incorporate one of Siemens' barrier filters primarily to control syngas particulates, but also to remove the bulk of halides (i.e., HCl). Therefore, this first barrier-filter reactor represents Stage I in the NGC Process base configuration (i.e., Figure 1).

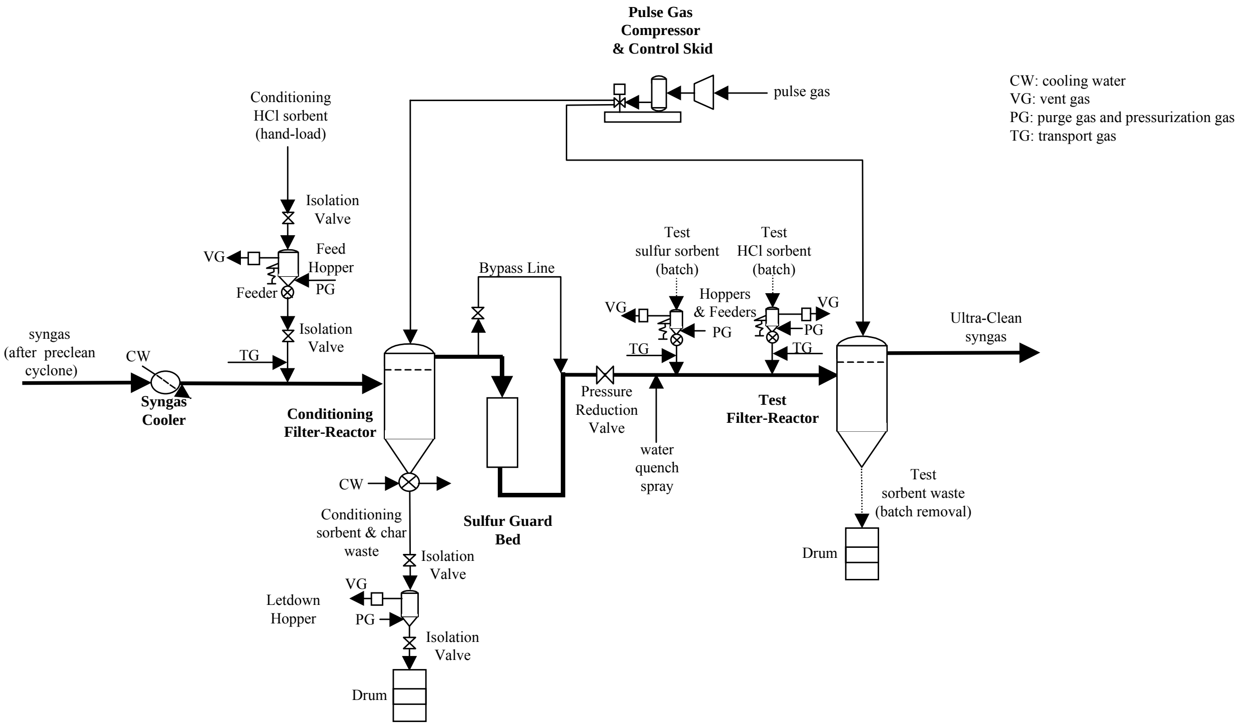

Figure 6 - Ultra-Clean Bench-Scale Test Facility Process Flow Diagram

An initial evaluation of the Novel Gas Cleaning Process pilot-scale test system was performed, providing for estimates of equipment duties and auxiliaries needs. A set of assumptions was used to allow the development of process material and energy balances and preliminary sizing of the equipment components. These assumptions were conservative to allow appropriate equipment design capacities to be selected.

5.1 Design Assumptions

5.1.1 Syngas Delivery Conditions

- Gasifier coal: Montana Coal (0.62 moisture-free wt% sulfur; 8.3 moisture-free ash)
- Gasifier: GTI air-blown fluid bed
- Gasifier desulfurization: none
- Inlet syngas composition at exit of secondary cyclone:

H_2	13.83 mole%
CH_4	2.21
CO	15.73
CO_2	10.5
H_2O	12.21
N_2	45.37
Sulfur (H_2S plus COS)	941 ppmv
Halides (HCl plus HBr)	100 - 500
Fuel nitrogen (NH_3 plus HCN)	1240 ppmv
Hg	2 ppbv (estimate)

- Syngas particulate content at secondary cyclone exit: 21,250 ppmw char (nominal GTI estimate) - 31,250 ppmw (maximum expected)
- Syngas temperature at secondary cyclone exit: 1634°F
- Syngas pressure at secondary cyclone exit: 285 psia
- Syngas flow rate at secondary cyclone exit: 3300 lb/hr for all tests

The H_2S and COS contents of the syngas are uncertain and are initial estimates, but the sulfur content of the syngas does not influence any of the test equipment designs other than the guard bed desulfurizer unit. The halide and particulate contents currently have very broad ranges of minimum and maximum expected values. Their estimated syngas contents may increase or decrease as the process estimates are improved. Other components listed above (NH_3, HCN) are included for future interest.

5.1.2 Test Conditions

- Syngas cooler outlet temperature: 830°F
- Halide removal in Conditioning Filter-Reactor using trona sorbent (maximum Stage II inlet halide of 5 ppmv; minimum of 1 ppmv)
- Guard Bed sulfur removal achieves > 99%, with bypass valve fully shut
- Maximum Stage II inlet H_2S + COS = 5 ppmv; minimum 1 ppmv
- Syngas pressure at Test Filter-Reactor inlet: 215 psia
- Test Filter-Reactor inlet temperature of 550°F (after sorbent injection)
- Target Stage II Test Filter-Reactor outlet H_2S + COS = 60 ppbv
- Target Stage II Test Filter-Reactor outlet halide = 10 ppbv

- Maximum test run duration in syngas:
  - Conditioning Filter-Reactor, 120 hr
  - Sulfur Guard Bed, 120 hr
  - Test Filter-Reactor, 96 hr
  - Number of test campaigns, 3

5.1.3 Sorbents

Conditioning halide sorbent: Trona (Na_2CO_3•$NaHCO_3$•$2H_2O$)
- 50 mol% H_2O
- 25 mol% sodium carbonate
- 25 mol% sodium bicarbonate
- maximum molar feed rate 10 times stoichiometric; minimum 2.0

Sulfur Guard Bed sorbent: BASF Catalyst R 5-12
- Approx. 95% highly activated ZnO extrudates
- sorbent utilization 50%

Stage II sulfur sorbent: G-72E
- 90.92 mol% ZnO
- 2.48 mol% CaO; 6.60 mol% Al_2O_3
- maximum molar feed rate 10 times stoichiometric; minimum 2.0

Stage II Halide sorbent: G-92C
- 15.96 mol% sodium oxide
- 84.04 mol% Al_2O_3
- maximum molar feed rate 10 times stoichiometric; minimum 2.0

5.1.4 Pressure Drops and Heat Losses

Estimates were included for component and piping pressure drops and heat losses. The following assumptions were made.

Refractory-lined pipe lengths for pressure drop estimates (3" ID, refractory-lined pipe):
- Secondary cyclone to syngas cooler inlet: 3 ft
- Syngas cooler to HCl conditioning sorbent injection point: 2 ft
- HCl conditioning sorbent injection point to Conditioning Filter-Reactor inlet: 5 ft
- Conditioning Filter-Reactor exit to Sulfur Guard Bed inlet: 5 ft with no insulation to promote syngas cooling
- Sulfur Guard Bed exit to Stage II Trim Cooler point: 5 ft
- Trim Cooler to sulfur sorbent and HCl sorbent injection points: 3 ft
- Sorbent injection points to Test Filter-Reactor: 5 ft

Component heat loss estimates:
- Ambient temperature 70°F
- Equivalent, overall insulated pipe estimated as a function of refractory thickness:
  - 1634°F: refractory thickness 4 in. and overall heat transfer coefficient of 2 Btu/hr ft^2°F
  - 550-950°F: refractory thickness 3 in. and overall heat transfer coefficient 1.5 Btu/hr ft^2 °F
  - Non-insulated pipe length overall heat transfer coefficient of 20 Btu/hr ft^2 °F
  - Filter-Reactor heat losses estimated as pipe 10 ft long with overall heat transfer coefficient of 4.5 at Stage II conditions

Component pressure drops:
- Syngas cooler heat exchanger gas-side pressure drop estimated to be 0.5 psi
- Filter-Reactors average pressure drop about 3% of inlet pressure (7 psi used)

- Sulfur Guard Bed pressure drop estimated to be 5 psi

5.1.5 Auxiliaries

- Pressurization gas rate: 1.1 times feed sorbent voidage flow, based on bulk voidage of 80%
- Solids transport gas rate: 3/8" tubing (20 gage) with gas velocity of 50 ft/s, results in 105 lb/hr transport gas rate per feed line
- Waste solids purge gas rate: 1.1 times waste solids voidage flow, based on bulk voidage of 80%; value fixed at maximum level
- Filter pulse gas rate: 0.1 lb of gas per pulse per candle; 14 candles in vessel; Conditioning Filter-Reactor pulse cleaned 6 times per hour, and Stage II Filter-Rector pulse cleaned 1time per hour
- Pulse gas supplied to test facility at 400 to 600 psia
- Pulse gas source nominal pressure 600 psi above operating pressure (900 psia)
- Pulse gas compressor adiabatic efficiency 75%
- Test facility nitrogen composition is 98 vol% N_2, 2 vol% O_2
- Cool waste solids from Conditioning Filter-Reactor to 250°F (if force cooling is needed)
- Cooling water and quench water available at 70°F; delta-temperature = 10°F

5.2 Computed Results

5.2.1 Filter-Reactor Conditions

Conditioning Filter-Reactor

Inlet temperature (°F): 830
Outlet pressure (psia): 277
Outlet temperature (°F): 770-808
Inlet gas flow (acfm): 107
Face velocity (ft/min): 2.7
Inlet dust load (ppmw): 27,500-42,000 (including trona)
Halide removal (%): 98.5 (min) - 98.9 (max)

Test Filter-Reactor

Inlet temperature (°F): 550 (after sorbent injection)
Outlet temperature (°F): 533
Inlet gas flow (acfm): 123
Face velocity (ft/min): 3.1
Inlet dust load (ppmw): 38 (min) - 690 (max)
Sulfur removal (%): 94.2 (min) - 97.7 (max)
Halide removal (%): 99.0 (min) - 99.8 (max)

5.2.2 Feed System Requirements

Conditioning halide sorbent feed system (trona -36 lb/ft^3 bulk density)

minimum feed rate (lb/hr; ft^3/hr): 2.0; 0.056
maximum feed rate (lb/hr; ft^3/hr): 34.4; 0.96
Total feed per test campaign (lb; ft^3): 40-4,128; 7-115
Total feed for program (3 test campaigns) (lb): 720 -12,384

Test halide sorbent feed system (G-92C - 36 lb/ft^3 bulk density)

minimum feed rate (lb/hr; ft^3/hr): 0.092; 0.0025
maximum feed rate (lb/hr; ft^3/hr): 2.3; 0.064
Total feed per test campaign (lb; ft^3): 8.8-221; 0.24-6.1
Total feed for program (3 test campaigns) (lb): 26 - 663

Test sulfur sorbent feed system (G-72E – 61 lb/ft^3 bulk density)

minimum feed rate (lb/hr; ft^3/hr):	0.04; 0.0007
maximum feed rate (lb/hr; ft^3/hr):	0.28; 0.0046
Total feed per test campaign (lb; ft^3):	3.8-26.9; 0.06-0.44
Total feed for program (3 test campaigns) (lb):	12 – 81

5.2.3 Sulfur Guard Bed

	At minimum flow conditions	At maximum flow conditions
Bypass (% of syngas flow)	0	0
Guard bed sulfur removal (%)	99.6	99
Outlet sulfur content (ppmv)	1	2.7
ZnO consumption (lb/hr)	6.2	6.2
Total ZnO consumed in run (lb)	744	744
Inlet temperature (°F)	734	720

Total BASF guard bed ZnO sorbent consumed in test program about 2150 lb.

5.2.4 Waste Handling System Requirements

Sorbent wastes bulk density assumed 30 lb/ft3; gasifier char bulk density assumed 20 lb/ft^3

Conditioning waste system

minimum rate (lb/hr; ft^3/hr):	69; 3.5
maximum rate (lb/hr; ft^3/hr):	125; 6.3
Total per test campaign (lb; ft^3):	8,280-15,000; 420-750
Total for program (3 test campaigns) (lb):	25,000 - 45,000

Test waste system

minimum rate (lb/hr; ft^3/hr):	0.14; 0.005
maximum rate (lb/hr; ft^3/hr):	2.5; 0.083
Total per test campaign (lb; ft^3):	13-243; 0.43-8.1
Total for program (3 test campaigns) (lb):	40 - 730

5.2.5 Axiliaries

Nitrogen

transport maximum (lb/hr):	315
pulse cleaning gas maximum (lb/hr):	15
purge gas maximum (lb/hr):	4
pressurization gas (lb/hr):	1
Total Nitrogen (lb/hr):	335

Cooling Water

syngas cooling (gpm):	185
waste solids cooling max (gpm):	1.8

Process Water

syngas quench max (gpm):	0.25

Electrical

Pulse gas compressor max (kW):	0.2
Screw conveyor max (kW):	0.85 (if used)

5.3 Conclusions

Conditioning HCl Sorbent (Trona) Feed System

This pressurization and feed system will use a batch, pressurization and feed hopper, with isolation valves, having a maximum storage capacity of about 144 lb, with a total bulk solids volume of 4 ft^3. Its design pressure is 300 psia. It will feed HCl sorbent (trona) to the Conditioning Filter-Reactor during testing. The feeder must control and measure the feed rate with 10% accuracy over a range of 2.0 to 35 lb/hr using a volumetric feeder to simplify construction. Basis for sizing is 36 lb/ft^3 measured bulk density. The refill time for this feed system ranges from a minimum of once every 10 hours to once per test campaign.

Conditioning Filter-Reactor

Drainage of the conditioning waste solids lock hopper must be accomplished periodically during conditioning filter vessel drainage shut-off. The maximum operating time that the Conditioning Filter-Reactor filter vessel can operate without vessel drainage is 5-9 hours. The new filter vessel, with design pressure of 300 psia, is used for this duty. The new filter vessel is nearly identical with the existing filter vessel, except that its hopper section storage capacity is enlarged (by about 10 ft^3) to store solids during the testing should drainage be interrupted.

Conditioning Waste Solids Handling System

A batch, 12-hour hopper, with isolation valves, will be used having a maximum capacity of 1500 lb, and a total volume of about 83 ft^3. Its design pressure is 300 psia. This hopper should be placed directly under the Conditioning Filter-Reactor so that the solids storage capacity is available without intermediate transport equipment. An existing water-cooled screw conveyor may be used for transport and solids cooling from this hopper, if it is found that it can handle the cooling duty (solids cooling from 800 to 150ºF, solids rate 828-1500 lb/hr (41-83 ft^3/hr), cooling load 140,000-254,000 Btu/hr, cooling water 13.9-25.2 gpm). GTI assumes one-hour drainage time. GTI recommended reducing the holding time for this hopper to 6 hours to reduce its size.

Sulfur Guard Bed

A bypass valve having an operating range of 0 to 17% of the full syngas flow during testing is needed to control the test system inlet syngas sulfur content. This bypass valve expected to be fully shut during the Stage II testing, and all of the syngas will pass through the guard bed. The guard bed should be sized to achieve at least 99 sulfur removal (H_2S and COS) at maximum sulfur flow rate.

Pressure Reduction Valve

This valve, located after the Sulfur Guard Bed, will reduce the syngas pressure from 285 psia (maximum) at 850ºF, to 215 psia at a maximum syngas flow rate of 3,323 lb/hr (105 acfm at inlet conditions).

Water Quench Spray

Process water will spray quench the syngas stream, at a maximum rate of 2 lb/hr, to cool the syngas to 550ºF, measured at a location following sorbent injection, but before the Test Filter-Reactor inlet nozzle. Indirect cooling and drying of the syngas may be incorporated in the future.

Test Sulfur Sorbent Feed System for Stage II

This existing pressurization and feed system is a batch, pressurization and feed hopper having a maximum capacity of about 60 lb and a total volume of about 1 ft^3, based on the Stage II maximum feed rate. It will contain many hours of sorbent for the Stage II testing and refill will not be needed (217 - 1428 hours feed capacity). Its design pressure is 300 psia. The feeder must be able to feed with 10% accuracy over the range of 0.04 to 0.3 lb/hr using a differential-weight feeder. Basis for volume is bulk density of 61 lb/ft^3. The pressure vessel dimensions are 39-inch OD with 63-inch height.

Test HCl Sorbent Feed System for Stage II

This pressurization and feed system will be a batch, pressurization and feed hopper having a capacity of 144 lb and a total volume of 4.0 ft^3. Its design pressure is 300 psia. The feeder mechanism must be able to feed with a 10% accuracy over the range of 0.09 - 2.3 lb/hr using a differential-weight feeder. Basis for volume is bulk density of 36 lb/ft^3. The sorbent capacity of this feeder vessel will be 156 - 4,000 hours, so refill will not be required. The vessel will have identical design to that of the trona feed vessel.

Test Filter-Reactor

The existing filter vessel will be used for this duty. The existing filter vessel has a sorbent storage capacity of 81-1,500 hours during Stage II testing.

Test Sorbent Waste Handling System

The Test Filter-Reactor and drain pipe will hold the entire Stage II test campaign waste accumulation without drainage. A separate depressurization vessel is not needed. Heat losses through the vessel wall following system turndown should be sufficient and cooling water is not needed. Care must be taken to avoid condensation within the waste solids before drainage occurs.

Pulse Gas Compressor and Control System

The existing system will be adapted to serve the pulse cleaning needs of both filter vessels, with the Conditioning Filter-Reactor being pulse cleaned several times per hour, and the Test Filter-Reactor being pulse cleaned infrequently (< 1 per hour).

6. PREPARATION OF PILOT-SCALE FACILITIES

The main goal of the second phase of the Novel Gas Cleaning Program (Optional Program) has been to conduct a proof-of-principles demonstration of the integrated NGC Process on a ~ 10-ton/day GTI coal gasifier to confirm technical and economic feasibility of the process. The original plan was to refurbish an existing GTI gasifier to generate syngas via coal gasification for the NGC Process testing. Project schedule, however, coincided with GTI's decision to construct a new carbonaceous fuel gasification facility (Flex-Fuel Test Facility) with capability to process about 10 tons of coal per day. Design and construction of the entire facility proceeded simultaneously.

6.1 Flex-Fuel Test Facility

GTI recently constructed a unique test platform to address the need for more thorough evaluation of gasification technology as well as other equipment and processes that can be used to convert various feedstocks into synthesis gas.

Built with the support of the natural gas industry and the State of Illinois, the state-of-the-art Henry R. Linden Flex-Fuel Test Facility (Figure 7 and Figure 8) evaluates innovative gasification processes and facilitates the commercialization of advanced gasification and downstream end-use technologies. The FFTF is designed to evaluate a variety of gasifier technologies in a versatile platform for testing all ranks of coal and other solid fuels, including biomass. The facility's flexible design allows testing of a variety of gasification, gas cleanup, and gas processing schemes independently or as integrated systems.

The term Flex-Fuel has been used in the designation of the facility to indicate its ability to process a variety of feedstocks, primarily solids such as coal and biomass, and for its adaptability as an

R&D unit. The gasifier unit was designed such that it can be modified to accommodate additional process configurations or equipment, such as solids filtration systems or high-temperature pollutant removal vessels. For example, the lower gasifier section can be removed and replaced to simulate a RENUGAS® type gasifier. Similarly, the upper section of the gasification reactor can be modified to incorporate a hydrogen-selective membrane for enhanced and direct hydrogen production from coal, an effort currently in progress at GTI.[10]

Innovative sampling and analytical systems were designed and implemented in the facility to enable detailed systems evaluations. Simultaneous on-line analyses of gas compositions from raw gas concentrations to ultra-clean levels allow for near real-time assessment of the performance of integrated gasification and gas conditioning systems. Comprehensive and accurate diagnostic capabilities make cost-effective testing of technologies and systems at the facility possible.

The heart of the Flex-Fuel facility is a U-GAS® type gasification reactor which uses heat and pressure to convert solid feedstocks such as coal and biomass into low to medium Btu-content gas. Following further processing, the produced fuel gas can then be used as fuel, purified to hydrogen, or used as feedstock for chemicals production. The Flex-Fuel gasifier is designed to operate at pressures up to 420 psig (30 bar) and temperatures up to 2000ºF (1093ºC), and can be used in conjunction with:

- Coal: 10 tons per day (tpd) with air, 20 tpd with oxygen
- Biomass: 20 tpd with air; 40 tpd with oxygen
- Downstream syngas clean-up and separation systems
- Advanced power conversion systems (fuel cells, small turbines, reciprocating engines)
- Coal to Synthetic Natural Gas (SNG)
- Syngas-to-Liquids conversion
- Hydrogen production
- CO_2 capture technology

The FFTF is intended for conducting research and validation of enabling technologies that have shown promise after laboratory and bench testing and need demonstration at a larger scale. These systems can be tested on either slipstreams from the gasifier or on the full gas stream on a dedicated basis or in conjunction with other users to reduce test costs. Novel gasification concepts can be tested at a variety of sizes in test campaigns typically conducted over a week period. Continuous long-duration testing is also possible.

Figure 7 – GTI's Newly-Commissioned Flex-Fuel Test Facility

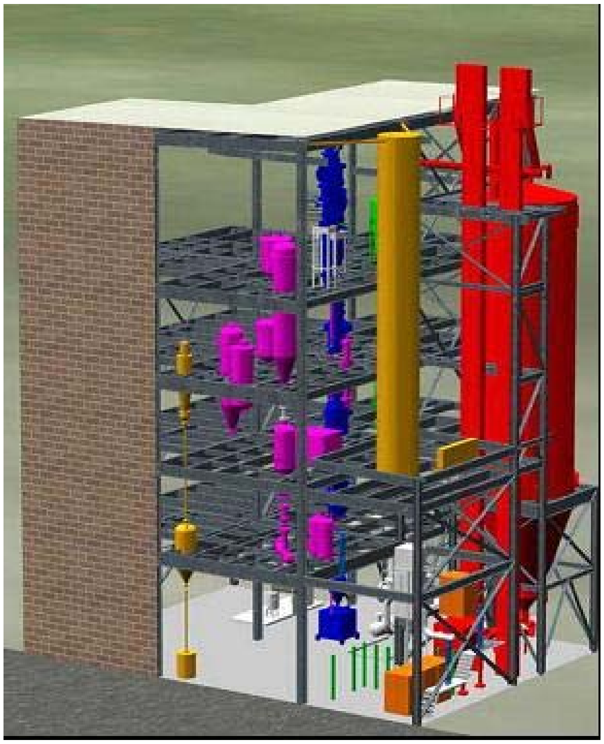

Figure 8 - Cutaway View of the FFTF Showing Solids Storage and Handling (Red), Gasification and Syngas (Blue), and NGC Process (Purple) Equipment

The FFTF includes an 11-inch (28 cm) diameter, adiabatic, single-stage fluidized-bed reactor system capable of gasifying 10 tons per day of coal in the air-blown mode at pressures up to 420 psig. This pilot plant facility includes equipment, process piping and controls for feed storage, transport and weighing, feed lock hopper pressurization and metering, air compression, fluidized bed gasification, ash and fines collection, depressurization, and weighing, and syngas cooling, cleaning, and flaring. Additional equipment, piping and controls provide utilities such as high pressure superheated steam, high-pressure nitrogen, demineralized high pressure quench water, process water, instrument air, and fire water.

The entire structure stands about 75 feet (~ 23 m) tall, with 5 decks of 1250 ft^2 (116 m^2) of process area per floor. The process area houses the various pressure vessels, reactors, piping and instrumentation necessary to run the facility. The facility is wholly contained (Figure 7) except for electricity, natural gas, and water. On the north side of the structure is the fuel storage silo, where feedstocks are held until transferred into the process unit. The facility was designed to process 10 tons (9 tonnes) of coal or 24 tons (21.8 tonnes) of biomass per day. All major equipment is shown in Figure 9. This Process Flow Diagram (PFD) shows the major flow streams for the storage and unloading of the coal; coal, air and steam feeding to the gasifier; and syngas to the flare. The NGC Process section, fully integrated into the Flex-Fuel Test Facility, is also shown.

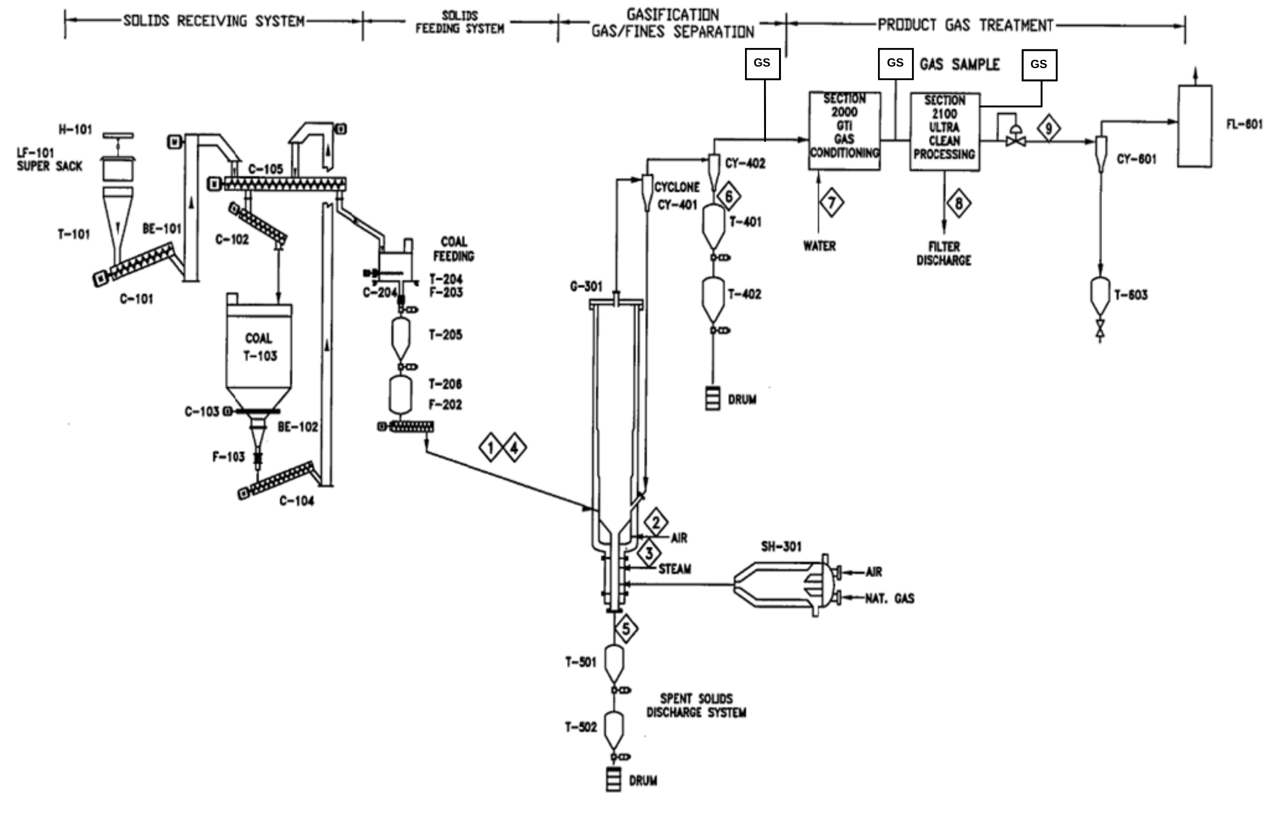

Figure 9 - Flex-Fuel Test Facility Process Flow Diagram

The FFTF solids receiving section receives feed materials from bulk storage bags, stores the feed in a storage silo, and transfers feed materials to the solids feeding section. Solid feed materials are dried and sized off-site and delivered to the plant by trucks in bulk storage bags and unloaded at the receiving area. The receiving area is enclosed with roof and retaining walls for weather. It is equipped with filtering ventilation for control of dust emission.

A forklift truck transfers coal to the loading hopper. The loading hopper is equipped with an open top and a conical bottom for top-fill and bottom-discharge operation. A screw feeder at the bottom of the loading hopper discharges the solids into a bucket elevator that conveys the solids into the storage silo.

The storage silo is an atmospheric cylindrical storage vessel designed for top fill and bottom discharge of fuel. The silo is sized to store a week's inventory of test fuel. It has a conical bottom with an apex angle of 60^o and is equipped with a bin activator assembly to allow use with biomass fuels. The silo is continuously purged with nitrogen to prevent oxidation of the fuel in the bin during storage.

Coal is discharged from the silo with a screw conveyer and bucket elevator. A second screw feeder transfers the coal from the bucket elevator to the weigh hopper. Coal can be delivered to the weigh hopper from either the storage silo or directly from the loading hopper. This allows coal switching without the need to empty the silo.

The weigh bin is equipped with load cells to continuously monitor and record coal feed batch weights as they enter the lockhopper system. At a set interval, the coal from the weigh bin is discharged into the lock hopper via rotary feeder. The lock hopper is equipped with quick open/close valves for cyclic pressurization and depressurization.

When the lock hopper is loaded and pressurized, the bottom lock hopper valve opens and coal is emptied into the coal feed hopper. When the lock hopper is emptied, it is depressurized to ambient condition; the cycle of coal loading to the lock hopper is repeated. The frequency of this cyclical loading/unloading operation of lock hopper is typically between 1 – 2 cycles per hour.

The coal from the feed hopper is continuously discharged to a pressurized variable speed metering feed screw to control feed rate and is then pneumatically conveyed with nitrogen into the gasifier.

When configured for fluidized-bed gasification the coal feed is processed (sized and dried) to the following specifications:

- 100% < ¼ - inch
- No more than 10% < 100 mesh
- No more than 5% surface moisture

For the NGC Process PDU testing, the FFTF was configured with a refractory-lined fluidized-bed gasifier based on GTI's U-GAS® coal gasifier design. In the fluid bed, coal reacts with steam and air to produce hydrogen (H_2), methane (CH_4), carbon monoxide (CO) and carbon dioxide (CO_2), which together with nitrogen (N_2) from the gasification air constitute the major elements of the gaseous fuel (syngas) product.

Syngas exits the top of gasifier, where the larger entrained particulates are captured in a cyclone and recycled to the gasifier through a dip leg to improve carbon conversion. The residual ash discharges from the bottom of the gasifier bed through the ash lock hopper system. The ash discharge rate is controlled by a terminal velocity mechanism having no moving parts. Adjusting the upward gas velocity through the ash discharge pipe controls the ash discharge rate. Ash is discharged to a surge hopper and then an ash lockhopper where the ash is depressurized. The ash is periodically discharged into a drum and the drum is weighed in order to monitor the ash discharge rate.

A start-up heater is used to preheat the refractory in the gasifier during start-up and then startup fuel is fed to the gasifier (typically metallurgical coke) to complete the heat-up process and ignition of the fluidized bed.

The FFTF is equipped with two refractory-lined cyclones in series downstream of the gasifier. The first (primary) cyclone separates the solids from the product gas exiting the gasifier freeboard. The separated fines in the cyclone dipleg are re-injected into the gasifier. The second (secondary) cyclone separates the residual fines from the gas exiting the primary cyclone. The fines removed in the secondary cyclone are discharged into a surge hopper and lockhopper, and subsequently into a collection drum, which is weighed to monitor the fines discharge rate.

The product gas exiting the cyclone is cooled to 650 to 850ºF (343 to 454ºC) by a direct-spray water quench prior to being routed to either the NGC Process system or directly to the flare. This is a "dry" quench with all water vaporized into the syngas stream. The syngas is then depressurized through a backpressure control valve station to near atmospheric pressure. A final cyclone captures any particulate left in the gas before the gas is combusted in a flare.

As indicated earlier, the overall Flex-Fuel Test Facility configuration (Figure 9) includes the gasification section, the NGC Process section, and the exhaust gas handling section. The NGC Process section is further divided into two major sections: Conditioning and Testing. In the Conditioning section, the raw syngas is first conditioned by bulk particulate, halide, and sulfur removal to produce a syngas having contaminant contents and temperature representative of inlet conditions to Stage II of the NGC Process. The Testing section is dedicated to assessing the most challenging aspects of the NGC Process performance, i.e., removal of reduced sulfur and halide species to ppbv levels. Detailed description of the NGC Process pilot-scale configuration is provided in the following report sections.

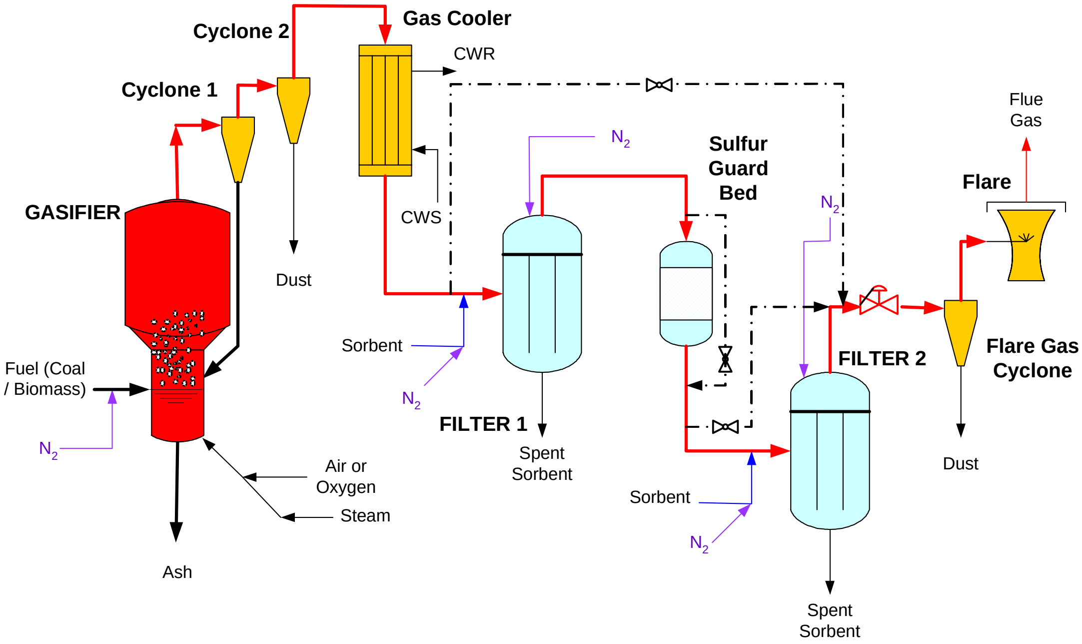

Figure 10 - Flex-Fuel Gasifier Facility Showing Ultra-Clean Process Section

6.2 Novel Gas Cleaning (NGC) Process Section

Preparation of the NGC Process pilot-scale test facility was carried out in parallel with the Flex-Fuel construction activities. This included designing, specifying, procuring, and installing various pieces of equipment for the NGC Process section, in concert with the requirements of the new gasification facility. The final NGC Process section layout was determined after evaluation of several options and redirection of the program goals to focus on the more challenging aspects of the project, i.e., to achieve very stringent contaminant removal targets at the ppbv level. This part of the plant consists of two major sections: Conditioning and Testing as shown in Figure 11, a piping and instrumentation diagram (P&ID) for the NGC Process section (a complete set of P&IDs is included in Appendix A of this report). In the Conditioning section, the raw gasifier gas is treated to meet the requirements of the NGC Process Testing section (i.e., Stage II). The Conditioning section, however, does incorporate one of Siemens barrier filters primarily to control syngas particulates, but also to remove the bulk of halides (i.e., HCl). Therefore, this first barrier-filter reactor represents Stage I in the NGC Process base configuration.

As shown in Figure 11, the NGC Process section consists of several major components:

Conditioning Section

- Direct Spray Water Quench (DSQ)
- Conditioning Filter-Reactor (CF-R)
- Conditioning halide sorbent feed system (Stage I halide sorbent)
- Conditioning char and spent sorbent handling system
- Pressure letdown valve
- Sulfur Guard Bed and associated bypass line and pre-heater
- Syngas Trim Cooler

Test Section

- Test Filter-Reactor, TF-R (for Stage II testing)
- Test sulfur, halide, and mercury sorbent feed systems (for Stage II testing)
- Test spent sorbent handling system

During a typical test, the gasifier is operated with coal in an air-blown mode to produce a syngas representative of commercial gasifier practice. Syngas off the Secondary Cyclone, at a temperature of about 1650ºF, is cooled to about 830ºF in the Direct Spray Quench tower. This stream is still relatively dirty, with a solids loading of about 2-3 wt%. Following flowrate measurement by an orifice flow meter and withdrawal of a gas sample for analysis, the syngas can be sent either towards the Conditioning Filter-Reactor inlet or bypassed towards the Tertiary Cyclone and then the Flex-Fuel Flare.

The cooled syngas from the Direct Spray Quench system is directed to the lower section of the Conditioning Filter-Reactor vessel (Figure 12), which contains 14 filter elements or candles (Figure 13). Filter elements (60-cm I.D., 1.5-m long Schumacher Dia Schumalith, clay-bonded silicon carbide) are mounted seven (7) on each of two semi-cylindrical plenums. The bulk dechlorination sorbent, trona (or nahcolite as an alternative sorbent), is metered from a 4-ft^3 hopper into the syngas immediately upstream of the Conditioning Filter-Reactor, by a loss-in-weight feeding system (Figure 14, Figure 15) enclosed in a pressure vessel. Trona, in the form of very fine powder (~ 20 µm average particle size), is added at rates ranging from 2 to 35 lb/hr. The bulk halide sorbent is moved into the syngas stream by dilute-phase transport in nitrogen, which picks up the sorbent under the loss-in-weight mechanism. Periodically, the bulk halide removal sorbent addition can be stopped, the sorbent feeding vessel de-pressured, the sorbent supply in the hopper replenished, the sorbent feeding vessel re-sealed and re-pressured, and sorbent addition resumed.

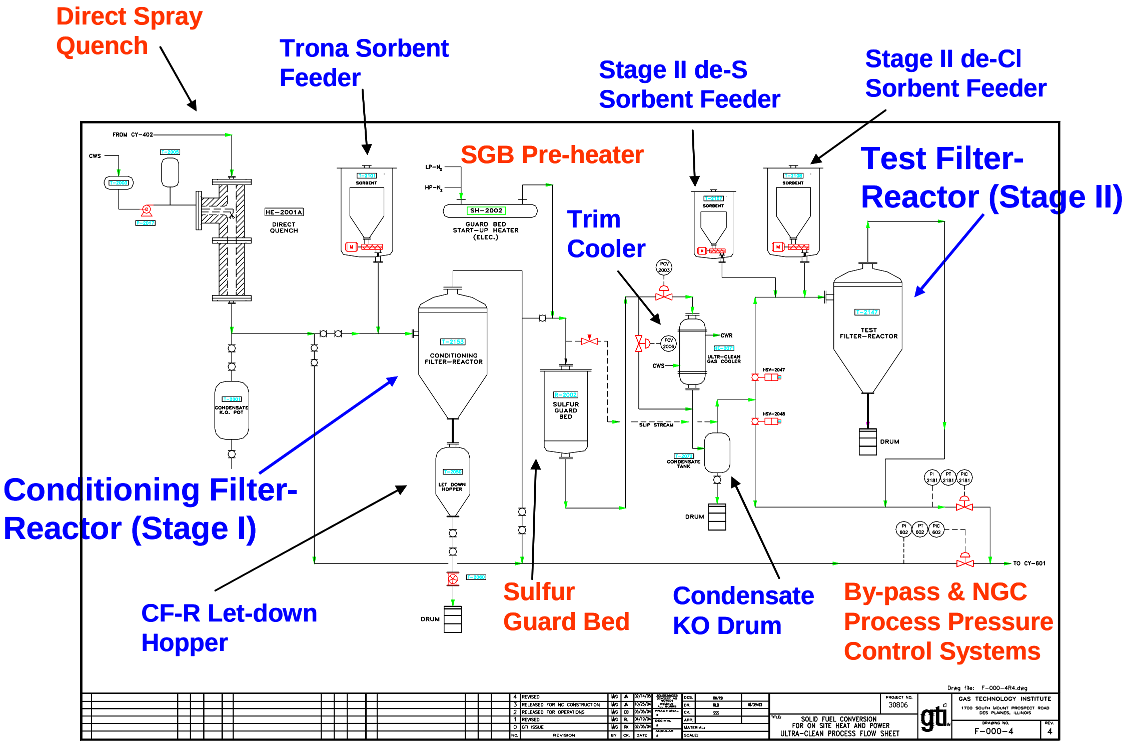

Figure 11 - P&ID for the Ultra-Clean Process Section in the Flex-Fuel Test Facility

Figure 12 – Loading of Candles into Filter Vessel

Figure 13 – Filter Elements (Candles)

In the Conditioning Filter-Reactor, essentially all the sorbent and the entrained solids from the Gasifier are captured on the surface of the filter elements (i.e., candles). Periodically, the solids captured on the filter elements are partially dislodged by pulses of regulated high-pressure nitrogen from a Pulse Control Skid (shared by both Conditioning and Test sections). The timing for these "blow-back" pulses can be determined by build-up of differential pressure across the filter elements, but may also be timed arbitrarily. Captured solids (entrained gasifier material and spent sorbent) flow from the bottom of the Conditioning Filter-Reactor into a Let-Down Hopper. The solids in this collection drum can be isolated from the Filter-Reactor by double block valves, de-pressured to the Vent System, and then unloaded through a Rotary Valve to a drum for post-test analysis and disposal.

The cleaned syngas exits the Conditioning Filter-Reactor from the top section. It can be split -- either to the Sulfur Guard Bed, or, under flow control, to bypass the Sulfur Guard Bed, which has been pre-heated to > 400ºF to avoid steam condensation and damaging the ZnO material in the SGB vessel. The objective is to provide a pre-determined level of sulfur compounds (1 to 5 ppmv), in the re-mixed syngas stream to the Test section of the NGC Process. Pressure is also reduced from about 285 psig (20.7 bar) to about 215 psig (15.8 bar) for the Testing section.

The re-mixed syngas, with the desired total sulfur and halide concentrations, enters the Syngas Trim Cooler at a reduced pressure of about 230 psig (16.9 bar). The syngas is cooled on the tube side of the cooler from an inlet temperature between 700 and 800ºF to an effluent range of 550 to 650ºF, as it flows vertically downward. On the shell side of the Syngas Trim Cooler, cooling water flow is controlled to give the desired syngas outlet temperature on the tube side. This stream is relatively clean, with very little (if any) solids loading. The cooled syngas is routed to a Condensate Tank, to allow liquids to drop out. The overhead syngas from the Condensate Tank can then be routed to either the Test Filter-Reactor or through a bypass towards the Tertiary Cyclone and then the Flex-Fuel Flare.

The cooled syngas out of the Syngas Trim Cooler is sent to the lower section of the Test Filter-Reactor. Two sorbents are injected into the conditioned syngas upstream of the Test Filter-Reactor: one for capture of reduced sulfur compounds and one for capture of halides (mostly HCl). The G-72E Stage II sulfur sorbent is metered into the syngas stream from a 1-ft^3 hopper, by a loss-in-weight feeding system enclosed in a pressure vessel (Figure 16). The sulfur sorbent, in the form of very fine powder (~ 20 µm average particle size), is injected at rates between 0.04 and 0.3 lb/hr (20-140 grams/hr). The sulfur sorbent is moved into the syngas stream by dilute-phase transport in nitrogen, which picks up the sorbent under the loss-in-weight mechanism. The G-92C Stage II halide sorbent is metered into the syngas stream from a 4-ft^3 hopper by a loss-in-weight feeding system enclosed in a pressure vessel. The halide sorbent, also in a very fine form, is added at injection rates between 0.1 and 2.3 lb/hr (45-1050 grams/hr). Periodically, the sulfur or HCl sorbent addition can be stopped, the feeding vessels de-pressured, the sorbent supply in the hopper replenished, the vessels re-sealed and re-pressured, and sorbent addition re-started.

In the Test Filter-Reactor essentially all the spent sorbents and any residual entrained solids from the Gasifier are captured on the surface of the filter candles. Periodically, these solids are partially dislodged by pulses of regulated high-pressure nitrogen from the Pulse Control Skid. These "blow-back" pulses can be accomplished automatically at timed intervals, or more frequently upon reaching a target differential pressure across the filter elements. Captured solids (mostly spent sorbents) are held in the bottom cone and lower cylinder of the Test Filter-Reactor vessel throughout the duration of a test campaign. At the conclusion of a test series, the Test Filter-Reactor is de-pressured to the Vent System, and the waste solids dropped through double block valves to a drum for analysis and proper disposal. The cleaned syngas exits the Test Filter-Reactor from the top section, flows towards pressure control valves and then the Tertiary Cyclone.

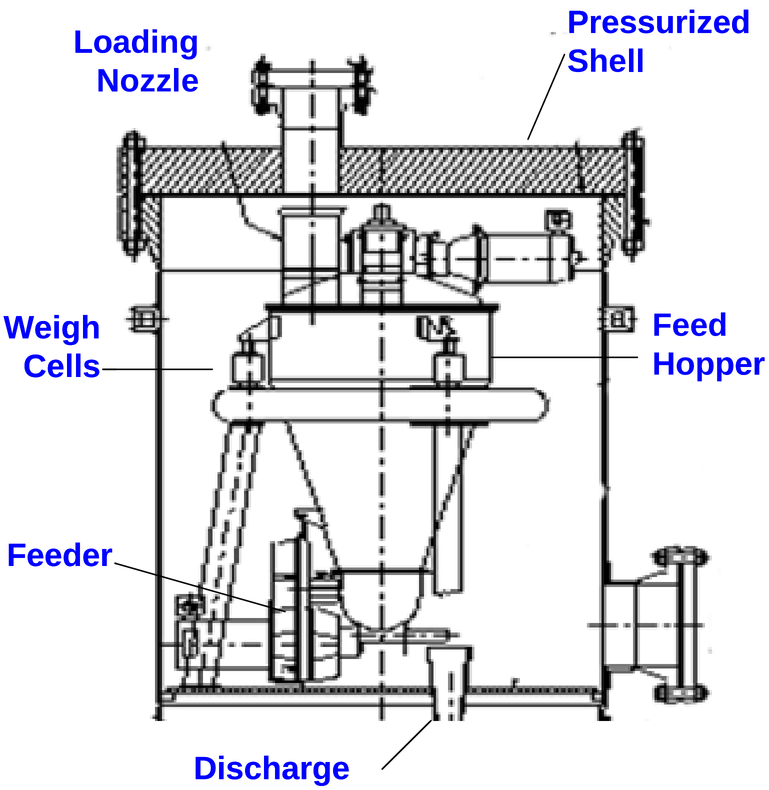

Figure 14- Schematic of Loss-in-Weight Fine Sorbent Feeding System

Figure 15 – Loss-in-Weight Fine Sorbent Feeder

Figure 16 – Stage II Fine Sorbent Feeding System Pressure Vessels

7. TEST PLAN

The Base Program identified the probable sorbents and operating conditions for the two stages of the Novel Gas Cleaning Process to achieve very stringent syngas cleaning levels of < 60 ppbv sulfur and < 10 ppbv halide. Table 3 lists the sorbents and operating conditions as well as the estimated, nominal stream flows and pressures for the Conditioning Filter-Reactor and the Test Filter-Reactor that would be applied in the three program test campaigns.

All of the sorbents are commercial, with the possible exception of the two mercury sorbents, which were selected through a comprehensive laboratory test program and interactions with other R&D organizations. Except for trona and nahcolite, which were procured in fine form from the commercial supplier, all of the sorbents are sized (ground and sieved) to -325 mesh at GTI, with an estimated mass-mean diameter of 20 μm. The Stage I and Stage II inlet temperatures are controlled process variables in the program. The syngas pressure is fixed in the test program, and the syngas flow rate is set by the Flex-Fuel gasifier operating capacity. The inlet sulfur and halide contaminant levels are also controlled process variables, but with some uncertainty as to the levels of control that can be achieved in the process. The ranges of sorbent feed rates listed (moles of sorbent active component divided by the moles of the specific contaminant) reflect the expected range that might be required to achieve the targeted gas cleaning performance.

Table 3 - Conditioning Filter-Reactor and Test Filter-Reactor Nominal Test Conditions

Filter-Reactor	Conditioning	Test
Inlet temperature (ºF)	830	550
Inlet pressure (psia)	277	215
Inlet syngas flow (lb/hr)	3439	3648
Filter Face velocity (ft/min)	2.7	3.1
Inlet total sulfur content (ppmv)	not applicable	1 – 5
Inlet halide content (ppmv)	150 - 500	1 – 5
Sulfur sorbent (-325 mesh)	none	G-72E
Halide sorbent (-325 mesh)	trona	G-92C
Target sulfur outlet content (ppmv)	not applicable	0.06
Target halide outlet content (ppmv)	1 - 5	0.01
Sulfur and halide sorbent feed rates (mole/mole contaminant)	2 - 10	2 – 10
Mercury sorbents (-325 mesh)	none	GTI-Hg-S9 TDA's Hg Removal Sorbent
Mercury sorbent feed rate (sorbent-to-Hg^0 mass ratio)	none	1000 - 2000

7.1 Conditioning Filter-Reactor Testing

The Conditioning Filter-Reactor testing objective is to collect data on the ability of the Conditioning Filter-Reactor to achieve the target performance level of 1-5 ppmv halide in the outlet gas and particulate less than 0.1 ppmw. The major test variables are:

- the halide sorbent feed rate, in the range of 2 to 10 molar feed ratio,
- the Conditioning Filter-Reactor inlet temperature, about 443ºC (830ºF),
- the Conditioning Filter-Reactor pulse cleaning frequency.

Secondary test variables are:

- the filter-reactor face velocity (which may be increased from its nominal value listed in Table 3 by removing selected filter elements),
- the sorbent type (nahcolite instead of trona, for example).

Both of the secondary variables are to be considered only if the filter-reactor does not meet its performance targets within the range of major test variables, or if the performance targets are achieved and additional test time remains.

Conditioning Filter-Reactor testing is the focus of the entire first test campaign, and the Test Filter-Reactor is isolated and not operated during this first test campaign. The consideration of the Conditioning Filter-Reactor is continued by monitoring its fixed operating conditions and performance over the remaining two test campaigns of the program. For purposes of sizing test equipment and identifying sorbent test quantities, it was assumed that each campaign would accumulate a maximum "operation period" of 5 days (120 hours) and a maximum "test time" of 4 days (96 hours).

The planned test matrix is shown in Table 4, and assumes that three full days of controlled test data are gathered. The first campaign would be held at nominal conditions of inlet temperature with variation over the full range of halide sorbent feed rates. The halide sorbent feed rates are shown to be varied initially, on each of the first two test days. On the third test day, the "optimum" halide sorbent feed rate is to be used.

Table 4 - Conditioning Filter-Reactor Representative Test Matrix

Campaign 1	Day 1	Day 2	Day 3
temperature (ºF)	830	830	830
halide sorbent rate (mole/mole)	0	5, 2, 10	optimum
pulse cleaning frequency (1/hr)	1 - 10	1 – 10	1 - 10
Campaign 2-3			
temperature (ºF)	830	830	830
halide sorbent rate (mole/mole)	optimum	Optimum	optimum
pulse cleaning frequency (1/hr)	1 - 10	1 – 10	1 - 10

Three day periods (24 hours each) of test running are assumed, with an initial period of each campaign (up to 2 days) being devoted to achieving steady gasifier and conditioning process operation at the desired conditions and confirmation of the controlled variables for the test campaign. The test conditions of subsequent campaigns 2 and 3 would be selected from the results of Test Campaign 1, and the Table 3 listed test conditions are those that would be selected if the process performance targets were achieved during Test Campaign 1. There would be a delay between each of the subsequent test campaigns 2 and 3 of several weeks used to analyze test data, maintain test facility equipment, select the subsequent test run conditions and modify test equipment as required. As stated above, the ability to modify the test sorbent type and/or the filter-reactor face velocity are also test options if dictated by the previous test results. The subsequent test campaign conditions might also be selected as the expected optimum conditions (as shown in Table 3) and held over several days to confirm steady, reliable behavior.

The key process measurements needed to conduct and monitor the test program are:

- Conditioning Filter-Reactor inlet and outlet syngas mass flow rate,
- Conditioning Filter-Reactor inlet and outlet syngas temperature,
- Conditioning Filter-Reactor halide sorbent mass flow rate,
- Conditioning Filter-Reactor inlet syngas sulfur (H_2S and COS) and halide (HCl, HBr, etc) contents,
- Conditioning Filter-Reactor outlet syngas sulfur (H_2S and COS) and halide (HCl, HBr, etc) contents.

Secondary measurements needed to assess the tests are:

- Conditioning Filter-Reactor inlet syngas major constituent composition (H_2, H_2O, CH_4, CO, CO_2, N_2),
- Conditioning Filter-Reactor inlet and outlet secondary contaminants (NH_3, HCN, Hg, particulate),
- Conditioning Filter-Reactor inlet pressure and pressure drop,
- Conditioning Filter-Reactor feed sorbent and collected waste sorbent particle size distributions and compositions,
- Conditioning Filter-Reactor collected waste sorbent accumulated mass.

The pulse cleaning frequency, pulse gas consumption rate, and pressure drop recovery of the Conditioning Filter-Reactor would also be recorded during the testing. Following each campaign, the Conditioning Filter-Reactor would be inspected, cleaned, and repaired as needed. The nature of the filter cakes accumulated on the filter elements, and the accumulation of char and sorbent within the filter-reactor vessels would also be noted.

The methods to be applied to make the process measurements are:

- Conditioning Filter-Reactor syngas mass flow rate: orifice meter continuous readout,
- Conditioning Filter-Reactor inlet and outlet syngas temperature: thermocouple continuous readouts,
- Conditioning Filter-Reactor halide sorbent mass flow rate: feed hopper continuous weight measurement,
- Conditioning Filter-Reactor inlet syngas sulfur (H_2S and COS) and halide (HCl, HBr, etc) contents: sulfur species by a gas chromatograph equipped with a flame photometric detector; halide species by periodic recovery into deionized water followed by liquid sample injection into an ion chromatograph,
- Conditioning Filter-Reactor outlet syngas sulfur (H_2S and COS) and halide (HCl, HBr, etc) contents: sulfur species by a gas chromatograph equipped with a flame photometric detector; halide species by periodic recovery into deionized water followed by liquid sample injection into an ion chromatograph,
- Conditioning Filter-Reactor inlet syngas major constituent composition (H_2, H_2O, CH_4, CO, CO_2, N_2): water condensed out and periodically weighed; dry gas analyzed by a gas chromatograph equipped with a thermal conductivity detector (TCD),
- Conditioning Filter-Reactor inlet and outlet secondary contaminants (NH_3, HCN, Hg, particulate): NH_3 by bubbling into an acid solution followed by electrode analysis or a calorimetric method; HCN by bubbling in sodium hydroxide solution followed by a calorimetric method; Hg by an on-line mercury analyzer (PS Analytical Sir Galahad II CEM Analyzer); particulate by periodic isokinetic syngas sampling,
- Conditioning Filter-Reactor inlet pressure and pressure drop: pressure transducer continuous readouts,
- Conditioning Filter-Reactor feed sorbent and collected waste sorbent particle size distributions and compositions: periodic sampling of feed sorbent supply and collected sorbent waste (about once every 24 hours),
- Conditioning Filter-Reactor collected waste sorbent accumulated mass: mass record of each lock hopper drainage.

Of course, during all of the Conditioning Filter-Reactor testing, the conditions and performance of the other components of the process must be monitored and controlled for the testing to be successful: the gasification process, the raw syngas cooler, the sulfur guard bed, the sorbent feed systems, the waste solids handling equipment, and the syngas exhaust treating system.

7.2 Test Filter-Reactor Testing

The Test Filter-Reactor testing would collect data on the ability of the Test Filter-Reactor to achieve the target performance levels of 60 ppbv sulfur and 10 ppbv halide in the outlet gas and 90 to 99% mercury removal. The major test variables are:

- the sulfur sorbent feed rate, over the range of 2 to 10 molar feed ratio,
- the halide sorbent feed rate, over the range of 2 to 10 molar feed ratio,
- the stage inlet temperature, over the range of 232 - 316ºC (450 - 600ºF),
- the Test Filter-Reactor pulse cleaning frequency,
- the mercury sorbent type.

Secondary test variables are

- the Test Filter-Reactor face velocity, which may be increased from its nominal value listed in Table 3 by removing selected filter elements,
- the sulfur or halide sorbent type.

Both of the secondary variables would only be considered if the filter-reactor does not meet its performance targets within the range of major test variables, or if the performance targets are achieved and additional test time remains.

Test Filter-Reactor testing would be conducted over the last 2 test campaigns of the three-campaign program. Each test campaign would accumulate a maximum "operation period" of 5 days (120 hours) and a maximum "test time" of 4 days (96 hours). The planned test matrix is shown in Table 5 and assumes three days of controlled test data are gathered in each test campaign. The first campaign (Test Campaign 2) would be devoted to Stage II sulfur and halide removal at representative inlet temperature with variation over the full range of sulfur and halide sorbent feed rates and Test Filter-Reactor pulse cleaning frequency. Test Campaign 3 would operate similarly, but at the lower range of temperatures for mercury removal. Three one-day periods (24 hours each) of testing are assumed, with an initial period of each test campaign (up to 2 days) being devoted to achieving steady gasifier and conditioning process operation at the desired conditions and confirmation of the controlled variables for the test campaign. Specifically, during this initial test period for each test campaign, the halide sorbent (trona) feed rate to the Conditioning Filter-Reactor must be established so that the inlet halide content of the conditioned syngas to the Test Filter-Reactor achieves its target of 1-5 ppmv halide, and the sulfur control achieved in the fixed guard bed must reach steady performance at its target value. The sulfur and halide sorbent feed rates are shown to be varied initially, on each of the first two test days, individually with the other set to zero flow rate. On the third test day, the "optimum" sulfur and halide sorbent feed rates are used.

Table 5 - Test Filter-Reactor Representative Test Matrix

Campaign 2 - Stage II Sulfur and Halide	Day 1	Day 2	Day 3
temperature (ºF)	550	550	550
sulfur sorbent rate (mole/mole)	5, 2, 10	0	optimum
halide sorbent rate (mole/mole)	0	5, 2, 10	optimum
pulse cleaning period (hr)	5 - 20	5 - 20	5 - 20
Campaign 3 - Mercury			

temperature (ºF)	300-450	300-450	300-450
mercury sorbent	1	2	best
mercury sorbent rate (lb/lb)	1000-2000	1000-2000	optimum
pulse cleaning period (hr)	5 - 50	5 - 50	5 - 50

There would be a delay between Test Campaigns 2 and 3 of several weeks used to analyze test data, maintain test facility equipment, select the subsequent test run conditions and modify test equipment as required. As stated above, the ability to modify the test sorbent type and/or the filter-reactor face velocity is also a test option if dictated by the previous test results.

The key process measurements needed to conduct and monitor the test program are:

- Test Filter-Reactor inlet and outlet syngas mass flow rate,
- Test Filter-Reactor inlet and outlet syngas temperature,
- Test Filter-Reactor sulfur sorbent mass flow rate,
- Test Filter-Reactor halide sorbent mass flow rate,
- Test Filter-Reactor inlet syngas sulfur (H_2S and COS) and halide (HCl, HBr, etc) contents,
- Test Filter-Reactor outlet syngas sulfur (H_2S and COS) and halide (HCl, HBr, etc) contents.

Secondary measurements needed to assess the tests are:

- Test Filter-Reactor inlet syngas major constituent composition (H2, H2O, CH4, CO, CO2, N2),
- Test Filter-Reactor inlet and outlet secondary contaminants (NH3, HCN, Hg, particulate),
- Test Filter-Reactor inlet pressure and Conditioning Filter-Reactor pressure drop,
- Test Filter-Reactor feed sorbent and collected waste sorbent particle size distributions and compositions,
- Test Filter-Reactor collected waste sorbent accumulated mass,
- The Conditioning Filter-Reactor conditions: halide sorbent (trona) feed rate, inlet and outlet temperature.

The pulse cleaning frequency, pulse gas consumption rate, and pressure drop recovery of the Test Filter-Reactor would be recorded during the testing. Following each test campaign, the Test Filter-Reactor would be inspected, cleaned, and repaired as needed. The nature of the filter cakes accumulated on the filter elements, and the accumulation of char and sorbent within the filter-reactor vessels would also be noted.

The methods to be applied to make the process measurements are:

- Test Filter-Reactor syngas mass flow rate: orifice meter continuous readout,
- Test Filter-Reactor inlet and outlet syngas temperature: thermocouple continuous readouts,
- Test Filter-Reactor sulfur sorbent mass flow rate: feed hopper continuous weight measurement,
- Test Filter-Reactor halide sorbent mass flow rate: feed hopper continuous weight measurement,
- Test Filter-Reactor inlet syngas sulfur (H_2S and COS) and halide (HCl, HBr, etc) contents: sulfur species by a gas chromatograph equipped with a flame photometric detector; halide species by periodic recovery into deionized water followed by liquid sample injection into an ion chromatograph,
- Test Filter-Reactor outlet syngas sulfur (H_2S and COS) and halide (HCl, HBr, etc) contents: sulfur species by a gas chromatography technique developed in Base Program (based on an ASTM procedure); halide species by continuous recovery into deionized water followed by continuous ion chromatography analysis,

- Test Filter-Reactor inlet syngas major constituent composition (H_2, H_2O, CH_4, CO, CO_2, N2): water condensed out and periodically weighed; dry gas analyzed by a gas chromatograph equipped with a thermal conductivity detector (TCD),
- Test Filter-Reactor inlet and outlet secondary contaminants (NH_3, HCN, Hg, particulate): NH_3 by bubbling into an acid solution followed by electrode analysis or a calorimetric method; HCN by bubbling in sodium hydroxide solution followed by a calorimetric method; Hg by an on-line mercury analyzer (PS Analytical Sir Galahad II CEM Analyzer); particulate by periodic isokinetic syngas sampling,
- Test Filter-Reactor inlet pressure and Conditioning Filter-Reactor pressure drop: pressure transducer continuous readouts,
- Test Filter-Reactor feed sorbent and collected waste sorbent particle size distributions and compositions: periodic sampling of feed sorbent supply and collected sorbent waste (once every 24 hours),
- Test Filter-Reactor collected waste sorbent accumulated mass: mass record of each lock hopper drainage.

Of course, during all of the Test Filter-Reactor testing, the conditions and performance of the other components of the process must be monitored and controlled for the testing to be successful: the gasification process, the raw syngas cooler, the Conditioning Filter-Reactor, the Sulfur Guard Bed, the second Indirect Syngas Cooler (Trim Cooler), the sorbent feed systems, the waste solids handling equipment, and the syngas exhaust treating system.

Further details on the scope of each testing campaign are provided in Table 6, Table 7, and Table 8. As can be seen in these tables, testing durations were estimated at 72 hours of continuous testing for the first test campaign and at 88 hours for each of the second and third test campaigns. These durations were estimated based on reasonable estimates of durations for the various test segments (or set points) to achieve program goals. The analytical scope of work was designed to meet program goals and includes “semi-continuous” measurements with “on-line” analytical instruments as well as time-integrated (batch) samples to be analyzed by GTI’s Chemical Services Research group to confirm “on-line” measurements and determine the concentrations of additional compounds of interest to the program.

The various process samples (defined in the following section of this report) include fuel feedstock, ash, raw syngas, fresh sorbent materials, spent sorbents, condensed liquids, and gas samples throughout the NGC Process section. These samples would be extracted using especially designed sampling and conditioning systems. These systems and the necessary analytical instruments and procedures are discussed in detail in the following report section.

Table 6 – First Test Campaign: Evaluate Performance of Conditioning Filter-Reactor (CF-R) for Combined Particulate/Halide Removal

Test Segment or Activity	Estimated Duration, hrs	Description
Gasifier start up & heating up of NGC Process conditioning section (CF-R product gas going directly to Flare Gas Cyclone (FGC))	24	
CF-R testing under first set point (SP#1) SS conditions	8	(no trona injection, 830F, 1-10 pulse cleaning frequency)
CF-R testing under second set point (SP#2) SS conditions	8	(inject trona at Na/Cl=5, 830F, 1-10 pulse cleaning frequency)
CF-R testing under third set point (SP#3) SS conditions	8	(inject trona at Na/Cl=2, 830F, 1-10 pulse cleaning frequency)
CF-R testing under fourth set point (SP#4) SS conditions	8	(inject trona at Na/Cl=10, 830F, 1-10 pulse cleaning frequency)
CF-R testing under fifth set point (SP#5) SS conditions	8	(inject trona at Na/Cl=optimum, 830F, 1-10 pulse cleaning frequency)
Shutdown	8	
	72	

ANALYTICAL WORK

Sampling Point	Purpose	No. of Batch Samples to be Taken	No. of Batch Samples to be Analyzed
G-7	Determine efficiency of primary & secondary cyclones	15	5
G-8	Determine complete syngas composition and concentrations of other species of interest: Bulk: H2, H2O, CH4, CO, CO2, N2 Minor: H2S, COS, HCl, particulate Other species of interest: TBD	15	5
G-13	Confirm semi-continuous HCl and particulate measurements in the CF-R product gas & determine fate of other species of interest	15	5
S-12	Confirm HCl removal & characterize particulate/spent trona waste for disposal	15	5
?	To satisfy environmental emissions requirements?		
S-1	Feedstock: How uniform is selected carbonaceous feedstock?	15	5 (may or may not be needed)
S-5	Gasifier ash: Characterize to satisfy disposal requirements	15	5
S-6	Dust from Secondary Cyclone: Charaterize to satisfy disposal requirements	15	5
S-21	Dust from Flare Gas Cyclone: Charaterize to satisfy disposal requirements	15	5
S-7C	Primary Cyclone return	15	5
S-7D	Bottom fluid-bed	15	5
S-7E	Middle fluid-bed	15	5
S-7F	Top fluid-bed	15	5

Table 7 – Second Test Campaign: Evaluate Performance of Test Filter-Reactor (TF-R) for Sulfur and Halide Removal (Separately and Together)

Note: Assumes CF-R is operating under optimum operating conditions (830ºF, 1-10 pulse cleaning frequency, and trona injected at Na/Cl optimum)

Test Segment or Activity	Estimated Duration, hrs	
Gasifier start up & heating up of CF-R & Sulfur Guard Bed (SGB) in NGC Process Conditioning section	24	
Establishment of conditioned syngas conditions & warming up of Test Filter-Reactor (TF-R)	8	
TF-R testing under first set point (SP#1) SS conditions	6	(sulfur sorbent injected at Zn/S=5, no halide sorbent injection, 550F, 5-20 pulse cleaning frequency)
TF-R testing under second set point (SP#2) SS conditions	6	(sulfur sorbent injected at Zn/S=2, no halide sorbent injection, 550F, 5-20 pulse cleaning frequency)
TF-R testing under third set point (SP#3) SS conditions	6	(sulfur sorbent injected at Zn/S=10, no halide sorbent injection, 550F, 5-20 pulse cleaning frequency)
TF-R testing under fourth set point (SP#4) SS conditions	6	(no sulfur sorbent injection, halide sorbent injected at Na/Cl=5, 550F, 5-20 pulse cleaning frequency)
TF-R testing under fifth set point (SP#5) SS conditions	6	(no sulfur sorbent injection, halide sorbent injected at Na/Cl=2, 550F, 5-20 pulse cleaning frequency)
TF-R testing under sixth set point (SP#6) SS conditions	6	(no sulfur sorbent injection, halide sorbent injected at Na/Cl=10, 550F, 5-20 pulse cleaning frequency)
TF-R testing under seventh set point (SP#7) SS conditions	12	(sulfur sorbent injected at Zn/S=optimum, halide sorbent injected at Na/Cl=optimum, 550F, 5-20 pulse cleaning frequency)
Shutdown	8	
	88	

ANALYTICAL WORK

Guidelines: No need to take batch samples up to and including G-13 (rely on semi-continuous measurements of species of direct interest to CF-R; or those that have impact on TF-R)
OR, take samples and store them, in case it becomes necessary to do some extra analyses for additional insight

Sampling Point	**Purpose**	**No. of Batch Samples to be Taken**	**Number of Batch Samples to be Analyzed**
G-14A	Assess desulfurization performance of SGB		
G-14B	Determine complete composition (bulk, minor, trace) of conditioned syngas (look particularly for COS since fate across SGB is not known) (conditioned syngas going directly to Flare Gas Cyclone (FGC))	3	1
G-14	Confirm semi-continuous S, HCl, and particulate in the TF-R inlet syngas & determine overall composition and concentrations of other species of interest	21	7
G-19	Confirm semi-continuous S, HCl, and particulate in the TF-R product gas & determine overall composition and concentrations of other species of interest	21	7
S-19	Confirm S and/or HCl removal & characterize particulate/spent sorbents waste for disposal	21	7
?	To satisfy environmental requirements?		
S-1	Feedstock: How uniform is selected carbonaceous feedstock?	21	7 (may or may not be needed)
S-5	Gasifier ash: Characterize to satisfy disposal requirements	21	7
S-6	Dust from Secondary Cyclone: Charaterize to satisfy disposal requirements	21	7
S-21	Dust from Flare Gas Cyclone: Charaterize to satisfy disposal requirements	21	7
S-7C	Primary Cyclone return	21	7
S-7D	Bottom fluid-bed	21	7
S-7E	Middle fluid-bed	21	7
S-7F	Top fluid-bed	21	7

Table 8 – Third Test Campaign: Evaluate Performance of Test Filter-Reactor (TF-R) for Mercury Removal (no Stage II Sulfur or Halide Sorbent to be Injected)

Note: Assumes CF-R is operating under optimum operating conditions (830F, 1-10 pulse cleaning frequency, and trona injected at Na/Cl optimum)

Test Segment or Activity	Estimated Duration, hrs	
Gasifier start up & heating up of CF-R & Sulfur Guard Bed (SGB) in NGC Process Conditioning section	24	
Establishment of conditioned syngas conditions & warming up of Test Filter-Reactor (TF-R)	8	
TF-R testing under first set point (SP#1) SS conditions	6	(lower-T mercury sorbent injected at sorbent/Hg=1000, 300F, 5-50 pulse cleaning frequency)
TF-R testing under second set point (SP#2) SS conditions	6	(lower-T mercury sorbent injected at sorbent/Hg=1500, 300F, 5-50 pulse cleaning frequency)
TF-R testing under third set point (SP#3) SS conditions	6	(lower-T mercury sorbent injected at sorbent/Hg=2000, 300F, 5-50 pulse cleaning frequency)
Load higher-T mercury sorbent	6	
TF-R testing under fourth set point (SP#4) SS conditions	6	(higher-T mercury sorbent injected at sorbent/Hg=1000, 450F, 5-50 pulse cleaning frequency)
TF-R testing under fifth set point (SP#5) SS conditions	6	(higher-T mercury sorbent injected at sorbent/Hg=1500, 450F, 5-50 pulse cleaning frequency)
TF-R testing under sixth set point (SP#6) SS conditions	6	(higher-T mercury sorbent injected at sorbent/Hg=2000, 450F, 5-50 pulse cleaning frequency)
TF-R testing under seventh set point (SP#7) SS conditions	6	(better mercury sorbent injected at sorbent/Hg=optimum, 300 or 450F, 5-50 pulse cleaning frequency)
Shutdown	8	
	88	

ANALYTICAL WORK

Guidelines: No need to take batch samples up to and including G-13 (rely on semi-continuous measurements of species of direct interest to CF-R; or those that have impact on TF-R) OR, take samples and store them, in case it becomes necessary to do some extra analyses for additional insight.

Put less emphasis on establishing S and HCl levels in conditioned syngas, and more of our resources on Hg analyses

do complete solids and liquids analyses for Hg to perform mass balance in the entire system

Sampling Point	Purpose	No. of Batch Samples to be Taken	No. of Batch Samples to be Analyzed
G-14A	Assess desulfurization performance of SGB		
G-14B	Determine complete composition (bulk, minor, trace) of conditioned syngas (look particularly for COS since fate across SGB is not known) (conditioned syngas going directly to Flare Gas Cyclone (FGC))	3	1
G-14	Confirm semi-continuous S, HCl, Hg, and particulate in the TF-R inlet syngas & determine overall composition and concentrations of other species of interest	21	7
G-19	Confirm semi-continuous S, HCl, Hg, and particulate in the TF-R product gas & determine overall composition and concentrations of other species of interest	21	7
S-19	Confirm Hg removal & characterize particulate/spent sorbent waste for disposal	21	7
?	To satisfy environmental requirements?		
S-1	Feedstock: How uniform is selected carbonaceous feedstock?	21	7 (may or may not be needed)
S-5	Gasifier ash: Characterize to satisfy disposal requirements	21	7
S-6	Dust from Secondary Cyclone: Charaterize to satisfy disposal requirements	21	7
S-21	Dust from Flare Gas Cyclone: Charaterize to satisfy disposal requirements	21	7
S-7C	Primary Cyclone return	21	7
S-7D	Bottom fluid-bed	21	7
S-7E	Middle fluid-bed	21	7
S-7F	Top fluid-bed	21	7

8. SAMPLE EXTRACTION & CONDITIONING SYSTEMS AND ANALYTICAL INSTRUMENTATION

An important objective of the Novel Gas Cleaning Optional Program is to verify, at the pilot-scale, the laboratory test results obtained in the Base Program with respect to operating temperatures for Stages I and II of the NGC Process, sorbent selections, sorbent/contaminant ratios, and ability of the process to accomplish very stringent contaminant levels in the syngas (i.e., particulates < 0.1 ppmw, total reduced sulfur compounds (H_2S and COS) < 60 ppbv, total halides (mainly HCl) < 10 ppbv, and mercury (mainly elemental mercury, Hg^0) < 0.01 ppbv. To accomplish these goals, GTI, in collaboration with Siemens, developed a sampling and analysis protocol, as part of the Test Plan for the program, which defined the sampling locations, sample type (solid, gas, or liquid), sample description, purpose, number of samples, analyses to be performed, and measurement methods, during each NGC program test campaign. Although the protocol was established as a general guideline that could be modified as needed based on the specific requirements for each test campaign, every effort was made to ensure that the scope of work allowed for development of the necessary data to accomplish Optional Program goals, that the state of the raw syngas was well defined before and after conditioning, and most importantly that performance of Stage II of the process could be properly assessed. Moreover, sufficient data would be collected to develop adequate material and energy balances for the gasifier to assess its efficiency in generating syngas from the test feedstock. The data generated would also permit characterization of process emissions for permitting activities and gasification and syngas cleanup byproduct materials for assessment of disposal options. As shown in Figure 17, process samples included fuel feedstock, ash, raw syngas, fresh sorbent materials, spent sorbents, and condensed liquids, in addition to several gas samples throughout the NGC Process section.

A list of the samples and their designations (solid = S, gas = G, liquid = L) is presented below. These sample locations are identified in Figure 17. Points listed without a S, G, or L designation are flow streams that can be calculated based on material balance considerations, but are not sampled. For each sampling point relevant to the NGC Process testing program, Table 9 provides temperature, pressure, and expected (estimated) concentrations of bulk gas constituents (i.e., H_2, CH_4, CO, CO_2, H_2O, N_2), major and minor contaminants (particulates, total sulfur (H_2S, COS), total halides (HCl, HBr), ammonia (NH_3), HCN), and trace contaminants (Hg).

Solid Samples: feedstocks, gasifier ash, gas particulates, fresh sorbents, spent sorbents

S-1	Carbonaceous feedstock (Bethlehem Coke Breeze, washed Indian coal, North Dakota lignite)
S-5	Gasifier ash
S-6	Dust from Secondary Cyclone
S-7C	Primary Cyclone dust recycled to Gasifier
S-9	Halide Sorbent (Trona) to Conditioning Filter-Reactor (CF-R)
S-12	Particulates/Spent Halide Sorbent (Trona) mix from CF-R
S-15A	UCP Stage II Sulfur Sorbent (Süd-Chemie's G-72E, finely ground) to Test Filter-Reactor (TF-R)
S-15B	UCP Stage II Halide Sorbent (Süd -Chemie's G-92C, finely ground) to TF-R
S-18	Spent UCP Stage II Sulfur and Halide Sorbents from TF-R (plus some particulates
S-21	Flare Cyclone dust
S-25	Sulfur Guard Bed Sorbent Material (Süd-Chemie's G-72E Catalyst, pellet form)
S-7D	Gasifier Lower Bed Sample
S-7E	Gasifier Middle Bed Sample
S-7F	Gasifier Upper Bed Sample

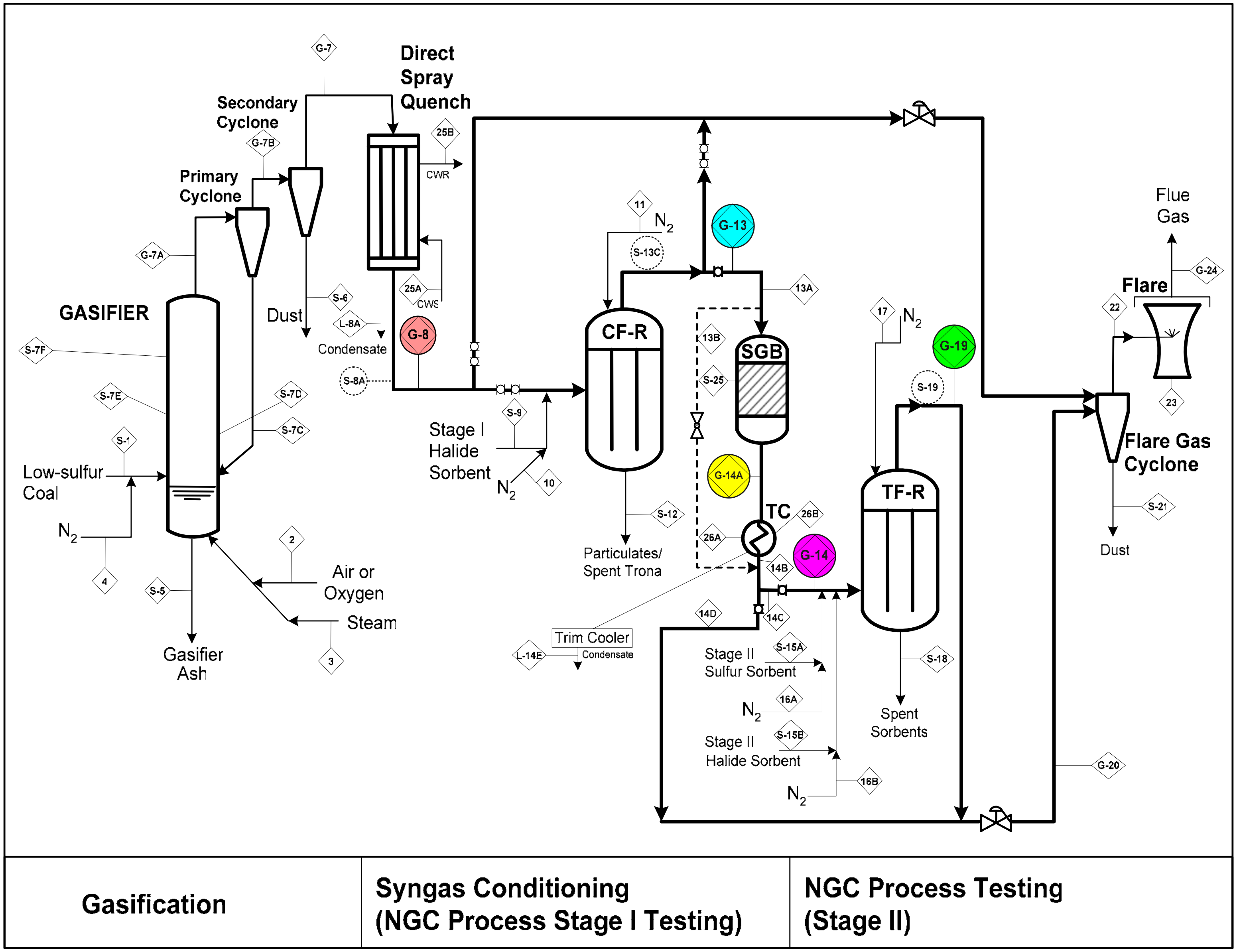

Figure 17 - Ultra-Clean Process Layout Showing Sampling Points for Solids, Liquids, and Gases

Gas Samples: Raw syngas and treated syngas at various stages in the UCP section

G-7A	Raw Syngas Exiting Gasifier
G-7B	Raw Syngas Exiting Primary Cyclone
G-7	Raw Syngas Exiting Secondary Cyclone
G-8	Partially-cooled raw syngas exiting Direct Spray Water Quench (DSQ) system
G-13	Partially-conditioned CF-R product syngas (essentially dust-free, dechlorinated to 1-5 ppmv HCl, but still containing all the raw syngas sulfur)
G-14A	Cooled de-Cl and de-S (desulfurized) Syngas from SGB (before blending with SGB By-pass)
G-14	Conditioned Syngas (de-Cl, de-S, T, P per UCP specifications) to TF-R: Cooled de-Cl and de-S Syngas from SGB and Trim Cooler (TC) (after blending with SGB By-pass and further cooling if necessary)
G-19	Ultra-Cleaned Syngas from TF-R
G-20	Depressurized, Cooled Raw Syngas or Ultra-Cleaned Syngas to Flare Cyclone
G-24	Flue Gas from Flare

Liquid Samples*:*

L-8A	Condensate from Direct Spray Quench system
L-14E	Condensate from Trim Cooler

Prior to this process demonstration unit (PDU) test program, existing analytical capability for the Flex-Fuel Test Facility included a double-train sample extraction and conditioning (SE&C) system (Figure 18, Figure 19), placed immediately after the Direct Spray Water Quench (i.e., at the G-8 sampling location) and a Rosemount CAT 200 on-line analyzer. As shown in Figure 19, in this conventional system partially-cooled raw syngas passes through a sintered metal filter (Mott™) while maintained at elevated temperature to remove particulate matter. Subsequently, particulate free sample gas is cooled and condensate removed. In the presence of condensable hydrocarbon vapors (tars and oils) this is best accomplished by rapid cooling to temperatures below the dew point of all significant condensable species in a configuration that drops them out in knockout pots. The SE&C system shown in Figure 18 uses water to quickly cool the sample gas to about 80°F followed by a second stage of cooling by expansion of high pressure nitrogen. Downstream of the knockout pots, traps, and coalescing filters, sample gas cylinders can then be readily filled as needed and clean sample gas is available for analyzers after pressure letdown.

The CAT 200 Rosemont online analyzer monitors carbon monoxide (CO), oxygen (O_2), methane (CH_4), and hydrogen (H_2) in the clean (particulate-free), dry syngas sample. It measures CH_4 and CO by NDIR, O_2 by a paramagnetic technique, and H_2 by a thermal conductivity detector (TCD). The analyzer was installed at the FFTF in late April 2004, and its performance is verified regularly by comparing output values to known standards and independent analyses on "grab" samples by GTI's in-house analytical laboratory. The CAT 200 analyzer was also connected to the DCS, allowing the instrument to be monitored from the FFTF Control Room.

The original plan for the analytical work in the NGC Process PDU tests was to install the required instruments (gas chromatographs, mercury analyzers, etc.) and impinger sets to obtain time-integrated (batch) samples at key points in the process (i.e., G-8, G-13, G-14, and G-19). At G-8, for example, these can be installed in parallel with the existing CAT 200 Rosemount analyzer for CO, O_2, CH_4, and H_2. However, accurate measurement of very low levels of sulfur and halide compounds, such as expected especially at G-19, requires the use of specially-prepared and inerted equipment, with Sulfinert™ or Silcosteel™ tubing and specialized fittings to minimize attachment of low levels of these compounds to surfaces.

Table 9 - Estimated Temperatures, Pressures, and Contaminant Concentrations at Various Sampling Points in the Novel Gas Cleaning Process Section

Sampling Point	**G-7**	**G-8**	**G-13**	**G-14A**	**G-14**	**G-19**
Temperature, °F	1634	830	800	800	550	533
Pressure, psia	285	285	235	235	215	215
Bulk Gas Constituents, vol%[a]						
H_2	13.77	13.77	13.77	13.77	13.77	13.77
CH_4	2.20	2.20	2.20	2.20	2.20	2.20
CO	15.67	15.67	15.67	15.67	15.67	15.67
CO_2	10.48	10.48	10.48	10.48	10.48	10.48
H_2O	12.17	12.17	12.17	12.17	12.17	12.17
N_2	45.50	45.50	45.50	45.50	45.50	45.50
Major & Minor Contaminants						
Particulates	21,250[b]	21,250	~ 0	~ 0	~ 0	~ 0
H_2S + COS (ppmv)	941[c]	941	941	< 10[d]	1-5	0.060
HCl + HBr (ppmv)	100-500[e]	100-500	1-5	1-5	1-5	0.010
NH_3 + HCN (ppmv)	1,240	1,240	TBD[f]	TBD	TBD	TBD
Trace Contaminants						
Hg (ppbv)	2[g]	TBD	TBD	TBD	TBD	TBD

The NGC PDU test program benefited greatly from a separate ongoing development effort at GTI for novel sample gas conditioning procedures that avoid condensation of species in the process gas. Part of the scope of the "Biomass Gasification Research" projects is development of a state of the art analytical suite to monitor syngas composition.[11,12] This new approach, as noted in Figure 18 and Figure 19 by the "Hot FT-IR Sample Line" bypasses the condensers of traditional gas sample extraction and conditioning systems and provides hot/warm samples directly to analyzers. This is described in more detail below.

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[a] Based on air-blown gasification (with no in-situ desulfurization) of a Montana coal (0.62 wt% S and 8.3% ash on a dry basis)

[b] 21,250 ppmw char (nominal GTI expected) – 31,250 ppmw (maximum expected)

[c] Total sulfur (CS_2 ignored); assuming $[H_2S] \approx 10[COS]$, about 855 ppmv H_2S and 86 ppmv COS can be expected

[d] Assuming > 99% sulfur removal by Sulfur Guard Bed (actual fate of COS in SGB not known for certain)

[e] Total halides (*estimate*); only HCl has been taken into consideration in the experimental work.

[f] To be determined for general interest only; filter-reactors may have catalytic activity for NH_3 destruction

[g] Estimate (2 ppbv)

Figure 18 - Main FFTF Sample Extraction and Conditioning Skid (Untreated Syngas)

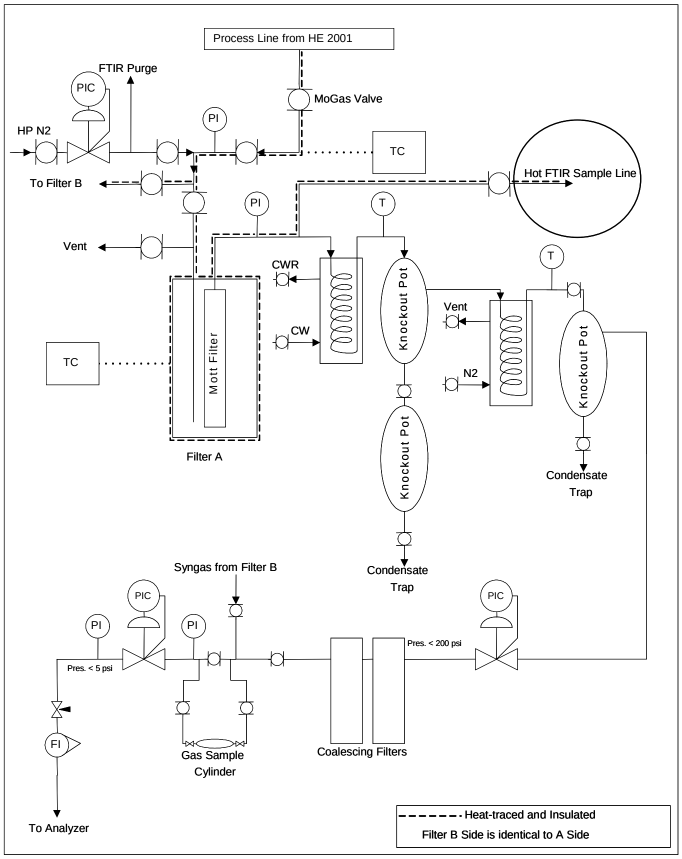

Figure 19 - Sample Conditioning System for Inlet of the Conditioning Filter-Reactor

To meet the requirements of the analytical work scope in the Optional Program, two additional single-train sample extraction and conditioning (SE&C) skids were designed and installed at sampling locations “G-13” (Conditioning Filter-Reactor product gas) and/or “G-14” (Conditioned syngas, inlet to Test Filter-Reactor) and at “G-19” (Test Filter-Reactor product gas – ultra-cleaned syngas). The two additional SE&C skids were installed in the FFTF during early March 2005. Figure 17 shows the process configuration on which the sampling interface systems were installed. In this figure, the gas sampling points are identified and the locations of sample extraction interfaces are highlighted (i.e., G-8, G-13, G-14, G-14A, and G-19). A Varian gas chromatograph system equipped with a pulsed flame photometric detector (PFPD), CP-Cil5 capillary columns, and a cryo-trap, was selected and procured as a suitable instrument for sulfur measurement at the ppbv level. This Trace Sulfur System (TSS) features a built-in high performance sample concentrator, a sensitive PFPD detector with a detection limit of 30 to 50 parts-per-trillion (ppt), and significant capability for speciated and total sulfur analyses. To measure HCl at the ppmv and ppbv levels, glass impingers were setup for chlorine sampling according to EPA Method 26, for subsequent analysis using an ion chromatograph instrument.

The three gas SE&C systems implemented for the PDU test program use the controlled condensation management approach, which incorporates filtration, gas cooling, condensate collection and removal, and drying. The controlled condensation management approach is depicted in Figure 22 (and previously in Figure 19). This process interface provides for separation of suspended particles, condensates, and gases. Particles and condensates are accumulated in the skid for post-test recovery and analysis. The gases, before and after drying stages, can be collected in sample canisters, passed through collection impingers (i.e., for HCl sampling) or absorption traps (i.e., carbon traps for mercury sampling, for example), or sent directly to analytical instruments for on-line measurements. Figure 21 shows a photograph of the controlled condensation SE&C Skid #2 (based on the design shown in Figure 20) for process gas samples from locations G-13, G-14, and G-14A. This photograph shows the system before heat tracing and insulation were completed. Figure 22 shows the same system after heat tracing and insulation were completed.

Two analytical stations were set up in two areas of the FFTF outside of the process area boundary because of Class I, Division II code restrictions on equipment in areas with potentially flammable, explosive gases. Sample lines of from 30 to 55 ft were needed from the various process interface points to accommodate this restriction. All sample lines were heat-traced and insulated to preserve gas sample integrity and to maintain gas temperatures above the instrument inlet conditions. Figure 23 shows the arrangement of components for the sample transport lines for the on-line analyses of gas composition.

A photo of the first analytical station, set up on the second floor of the FFTF, is shown in Figure 24. It includes four instruments:

- an Industrial Machine and Control Corporation (IMACC) Fourier-Transform Infrared Spectrometer (FT-IR)
- a Stanford Research Systems QMS300 Mass Spectrometer (MS)
- an Agilent 5890 gas chromatograph with flame photometric detector (GC/FPD)
- a Varian micro gas chromatograph with thermal conductivity detector (μGC)

The gas sampling system was built to allow for the selection of samples from any of three sources from the process (i.e., G-8, G-13, and G-14/G-14A) and direct the gas stream to one of the above four analyzers. In addition to supplying the on-line analyzers with representative syngas samples, the system shown in Figure 24 was used to extract sample gases to EPA reference method 26 impingers, allowing for direct comparison of batch and FT-IR HCl measurements. The sample network is illustrated in Figure 25. All lines are heat traced to maintain gas temperatures above the instrument inlet conditions.

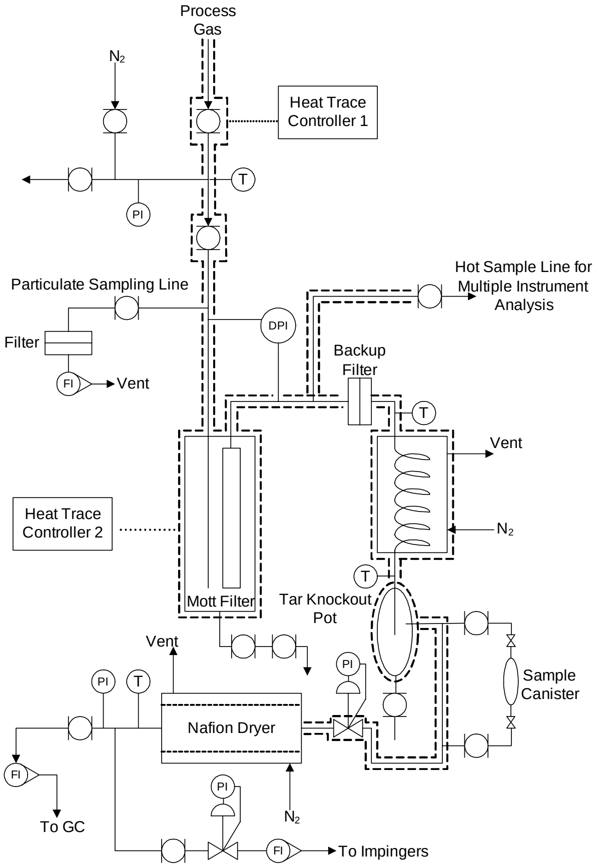

Figure 20 – Ultra-Clean Process Section Second Sample Extraction & Conditioning Skid (Placed Between Conditioning and Test Barrier Filter-Reactors)

Figure 21 - Photograph of the SE&C Skid #2 at the G-13/G-14 Locations (Before Insulation)

Figure 22 - Photograph of the SE&C Skid #2 at the G-13/G-14 Locations (After Insulation)

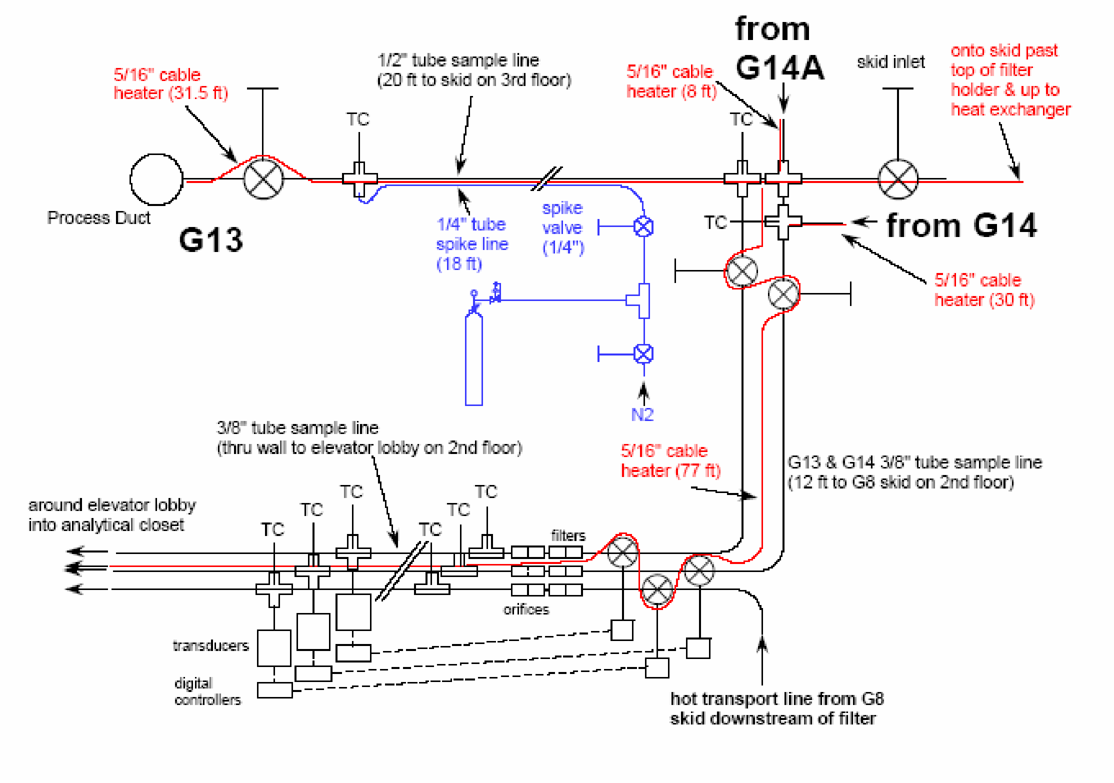

Figure 23 - Gas Sample Transport for On-line Analysis for Ultra-Clean Process in Flex-Fuel Test Facility

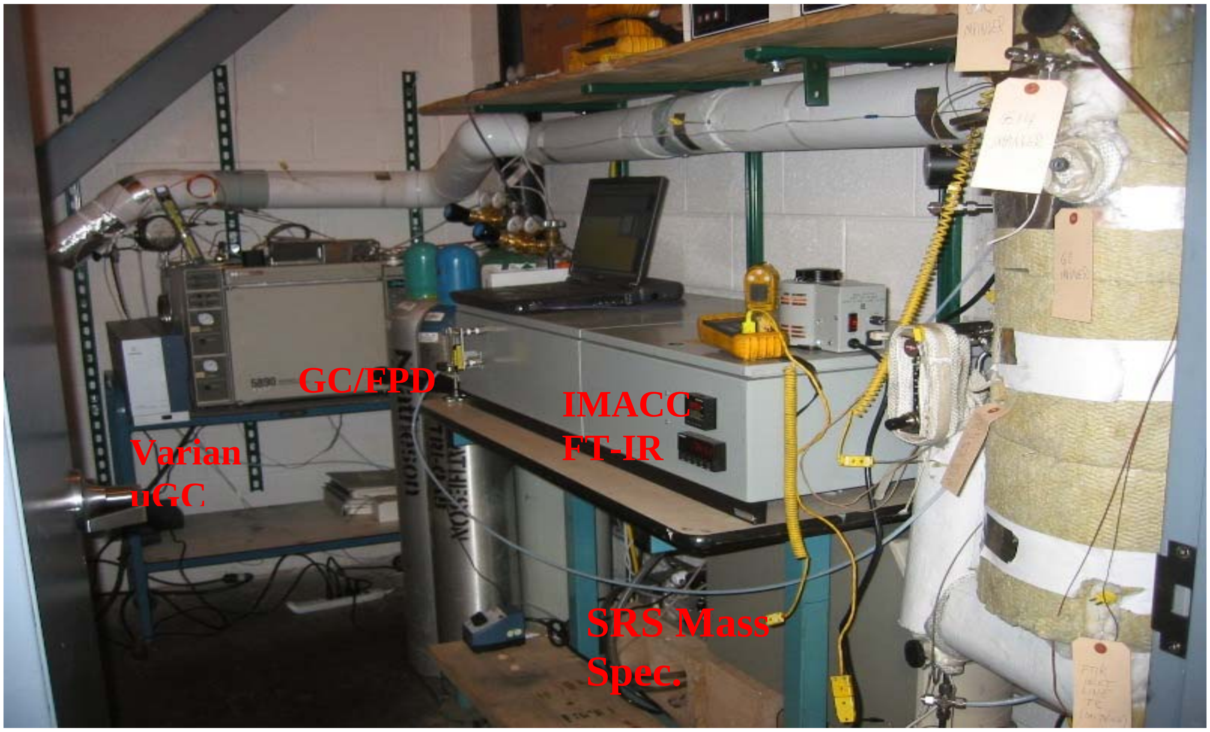

Figure 24 - Analytical Instruments Installed in the Second-Floor Gas Analysis Station in the Flex-Fuel Test Facility.

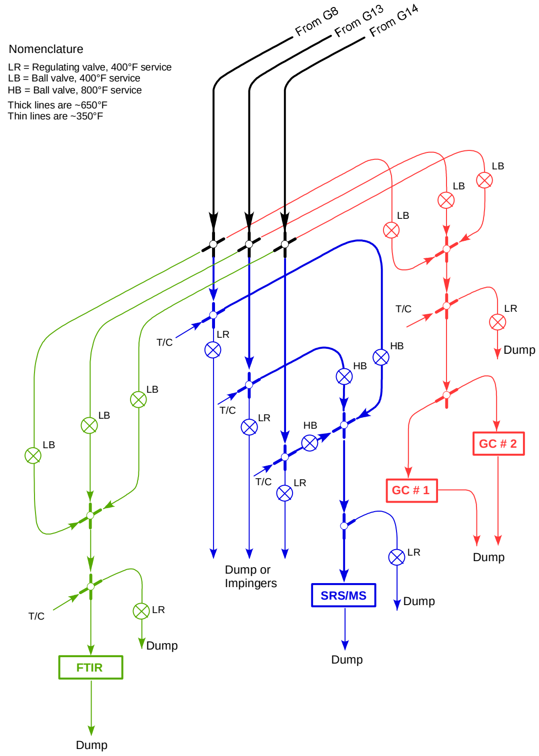

Figure 25 - Sample Switching Network for Multiple Analyzers

The sample transport lines from the raw syngas sample (G-8, before removal of suspended ash particles) used either of the two filters mounted on the main sample extraction & conditioning skid (i.e., SE&C Skid #1) at the G-8 location. The connection to this system is illustrated in Figure 26.

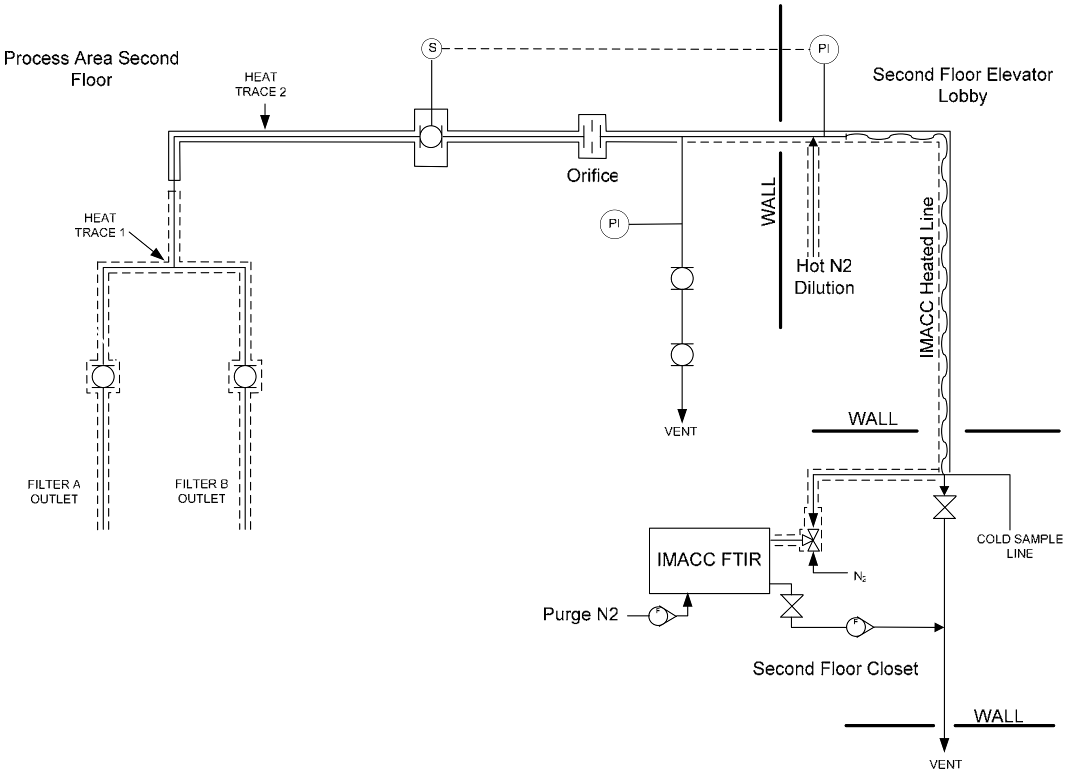

Figure 26 - Illustration of High-Temperature Process Interface for FT-IR Line at G-8.

A photograph of the second analytical station is shown in Figure 27. Close up views of the GC/PFPD installed at the station are presented in Figure 28. This station was set up on the fourth floor of the FFTF in order to meet the analytical work scope requirements of the second test campaign during which critical measurements were made to assess the NGC Process Stage II performance for removal of multiple contaminants (H_2S, COS, HCl) to ppbv levels, and those of the third test campaign during which mercury removal via dry sorbent injection upstream of the Test Filter-Reactor was investigated. A much simpler flow distribution arrangement was required for this station compared to the second floor gas analysis station. Because the only source of syngas being delivered to this station was from sampling location G-19 (i.e., Test Filter-Reactor product gas), no provisions for syngas source switching had to be made. Therefore at this analysis station, tees were installed in the sample line for sample to be withdrawn for impinger measurements, mass spectrometer measurements, and GC/PFPD measurements. Each of these analyzer streams included its own tee and regulating valve for an adjustable dump line to an outside vent. In addition, the excess flow through the line not entering any of the analyzer streams was also dumped to an outside vent. Although provision was made to install the SRS MS at the fourth floor station, the MS was used exclusively at the second floor station during the NGC Program PDU tests.

Figure 27 – Flex-Fuel Test Facility Fourth Floor Analytical Station

Figure 28 – Trace Sulfur Analysis GC/PFPD Installed at the FFTF Fourth Floor Analytical Station

Except for vent lines, all of the sample lines at each analysis station were heat traced and insulated. Silimar to the lines from G-8, G-13, and G-14/G-14A, the sample transport line from G-19 to the fourth floor analysis station included a manual and actuated ball valve, an in-line filter and orifice, and a pressure transducer to actuate the ball valve in the event excess pressure was detected within the sample line. A cable heater was used to heat trace this line, and the line was insulated. The initial portions of the G-19 sampling line are shown in Figure 29, before heat tracing and insulation were applied.

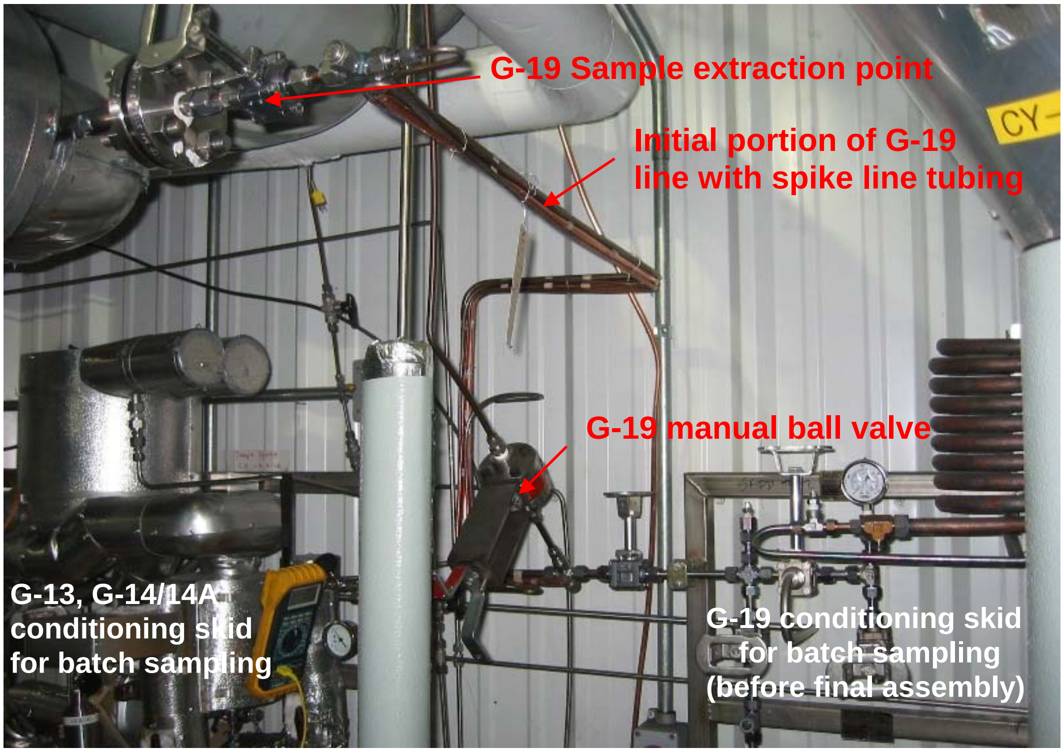

Figure 29 - Initial Sections of the G-19 Sample Location and Sampling Line

The sampling systems were installed to measure reduced sulfur (H_2S and COS) and halide (HCl) compounds at various concentrations throughout the NGC Process section, ranging from hundreds of parts-per-million (ppmv) to very low concentrations at the parts-per-billion (ppbv) level, as indicated earlier in Table 9. To provide very low-level detection, it was necessary to take extreme care in the selection of construction materials for sampling to avoid contamination and loss of analyte. The construction of an ultimate contamination- and corrosion-free sampling system was achieved with the use of clean materials with minimal active surfaces and suitable passivation. The product selected for heated and pressurized sampling lines was Silcosteel®-CR (Restek Corporation, Bellefonte, PA). Components of the SE&C skids at the G-13 and G-19 locations (tubing, fittings, valves, flow metering orifices, and Mott filters) were coated with chemically inert Silcosteel® and Sulfinert® (also from Restek Corporation) coatings to minimize reactions and adsorption of gases on the surfaces. Silcosteel®-CR was also used for the G-13, G-14, and G-19 sampling lines. The only exception was the G-8 sampling lines which were not coated. Sample canisters and valves were made from Sulfinert® materials. Low pressure and non-heated sampling lines and vessels were constructed of Teflon or borosilicate glass. Flexible silicone tubing was used to make low pressure connections between the coated steel or Teflon tubing and glass apparatus.

The Silcosteel®-CR treatment was developed specifically to protect equipment exposed to hydrochloric acid, nitric acid, sulfuric acid, or marine environments. A Silcosteel®-CR treatment upgrades the corrosion resistance of 300-grade stainless steels by greater than an order of magnitude. The Sulfinert® coating was developed for inertness to sulfur species. Both coating processes bond a very thin, flexible layer of glass to the stainless steel and prevent direct gas-metal interaction.

8.1 Hydrogen Chloride (HCl) Analysis

Hydrogen chloride (HCl) in a gaseous stream is measured by sparging raw or treated syngas streams through glass bubblers containing dilute sulfuric acid, and which are at all times immersed in a water/ice bath. HCl is quantitatively solubilized in the acidic solution and forms chloride ions. The chloride ions are measured using ion chromatography. A rotameter downstream of the bubblers controls the gas flow to around 1-L/minute. A dry test meter downstream of the rotameter measures the absolute gas volume. The method used is similar to EPA Method 26 (40CFR Part 60 promulgated test method).

Samples were collected using four spargers connected in series. The first sparger was empty, the second and third each contained 15-ml of the dilute sulfuric acid solution. The fourth sparger contained a fresh charge of indicating silica gel, 6-16 mesh. Later samples collected at the G-19 location used both sulfuric acid and plain deionized water. The use of deionized water was investigated in order to reduce carbonate ion interference and to provide the lowest possible detection limit. A schematic of the sampling system is shown below in Figure 30.

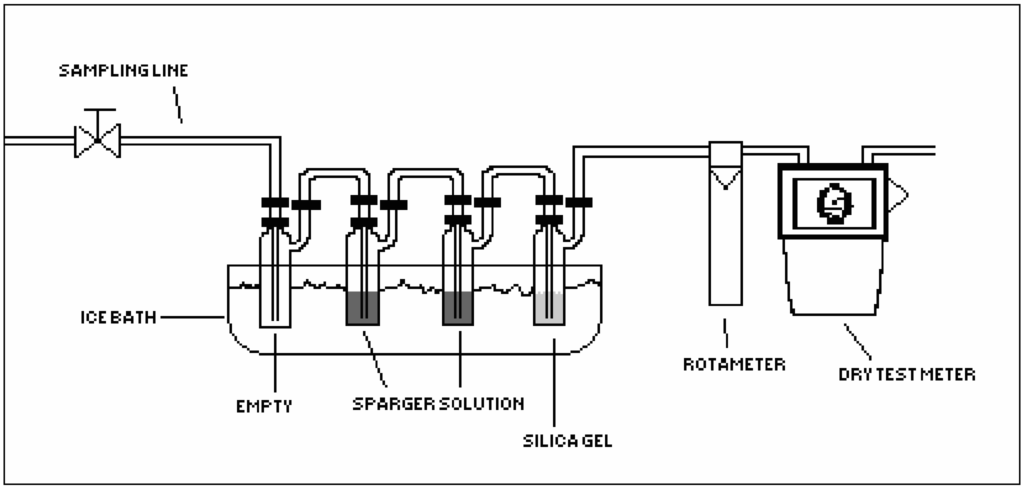

Figure 30 - Hydrogen Chloride (HCl) Sampling System

Possible interferents include other gaseous chlorine-containing species that could hydrolyze to chloride ions, such as ClO_2 or NH_4Cl, or particulate matter containing chlorine. High levels of carbonate ion, likely to be present in syngas, can potentially interfere with the ion chromatography analysis. Careful selection of eluent pH and column type, depending on sample location, was necessary to reduce its impact.

Type 3 deionized water was used for all solution preparation, dilutions, and washing. The gas washing bottles (spargers) were soaked in dilute nitric acid and rinsed several times using deionized water prior to use. The sulfuric acid solution was prepared from ACS grade concentrated sulfuric acid (2.8-ml diluted to 1-liter with deionized water). Chloride standards were prepared from 1000-mg/L chloride IC standards purchased from Spex Corporation. 100-ml Class A volumetric flasks and an Eppendorf variable volumetric pipet was used to prepare standards and samples. Very dilute standards were prepared by serial dilution of higher concentrations. An independent QC check was run to verify instrument response using a standard purchased from Dionex Corporation. All standard concentrations are certified and NIST-traceable. Unused samples were stored in 125-ml clear pre-cleaned I-Chem borosilicate glass bottles with Teflon sealed tops.

Samples were analyzed on a Dionex ICS-1000 isocratic ion chromatography system. A standard suppressed conductivity detector with a Dionex ASRS-Ultra background suppressor measured chloride responses. Dionex Chromeleon chromatography software was used for data acquisition, peak integration, and reporting. At least four levels of calibration were used for each analysis. The actual calibration concentrations depended on the expected analytical concentration in each sample. Reagent blanks were analyzed and while no chloride was found, an interfering peak was present in the initial Novel Gas Cleaning Optional Program test campaign (NGC-OPT1) runs. The interferent was identified as HSO_4-, present due to the pH of the eluent. The analytical method was changed to eliminate the interference for the critical NGC-OPT2 test campaign runs wherein a much lower concentration of HCl was expected. As the information in Table 10 shows, the specific column and eluent used in the analysis changed in order to continually improve the method as different sample types were analyzed.

Table 10 - Analytical Method Parameters for Chloride Analysis

Test Campaign	Date	Column	Eluent	Flow Rate, ml/min
NGC-OPT1	3/8/05-3/9/05	AS14	8mM/1mM carb/bicarb	1.0
NGC-OPT2A	3/24/05-3/29/05	AS10	40mM NaOH	1.2
NGC-OPT2B	3/30/05-3/31/05	AS17	2mM NaOH	1.0

The sampling methodology was validated by purging sampling points with dry nitrogen and reference gases containing a certified concentration of HCl (29.88 ppm HCl in N_2, 2.95 ppm HCl in N_2, and 0.578 ppm HCl in N_2). Validation data are provided in Table 11. The validation blanks for the NGC-OPT2A test were taken at the end of the test campaign and it is believed that the sample lines were not given sufficient time to purge out the remaining HCl. Because of this, additional validation blanks for the NGC-OPT2B test that followed were taken at the beginning of the test campaign. These blanks are more representative of true field blanks. Validation standards were not taken at the G-19 sampling point because it was feared that the high concentration of HCl in the reference gas would remain in the lines and slowly permeate into the test syngas, resulting in biased data. The satisfactory results at the G-13 location proved the inertness of the Silcosteel®-CR coated sampling lines. It should also be pointed out that replicate impinger measurements were made during the first test campaign (NGC-OPT1) using spargers run side-by-side. The reproducibility of the impinger sampling with ion chromatography chloride measurements was demonstrated. Duplicate analyses at G-13 resulted in concentrations of 10.9 and 10.8 ppmv HCl.

The following approach was developed to estimate the background HCl concentration at any point during the test. Before testing commenced, when the system was being purged with nitrogen, the average HCl concentration present in a “clean” sample line was defined as the sum of the average of the ‘true’ field blanks measured before HCl exposure in the NGC-OPT2B test (i.e., ~ 0.020 ppmv or 20 ppbv). Likewise, after testing concluded, when the system was being purged with nitrogen, the average HCl concentration present in the sample lines was defined as the sum of the average of the ‘true’ field blanks measured after HCl exposure in the NGC-OPT2B test (i.e., 57.3 ppbv). Then, because sample flow through these lines was maintained throughout testing, it is reasonable to assume that a 37.3 ppbv of HCl “burden” accumulated in a linear fashion and that during testing, the background concentration of HCl at any time t, C(t), can be determined from the following equation:

$$C(t) = 20 + [37.3/T]\bullet t$$

where T is the total time of syngas exposure (in hours) and t is the elapsed time, also in hours, from the start of testing to the time of interest.

Table 11 – Chloride Analysis Validation Data for the First and Second Test Campaigns

Date	Validation Point	Validation Type	Certified Result	Analytical Result, avg	Comment
NGC-OPT2A					
3/25/05	G-19	Blank	-----	40 ppbv	Post-test blank
3/25/05	G-14	Blank	-----	56 ppbv	Post-test blank
3/25/05	G-19	Blank	-----	76 ppbv	Post-test blank (N=2)
NGC-OPT2B					
3/29/05	G-14	Blank	-----	28 ppbv	Pre-test blank
3/29/05	G-19	Blank	-----	< 20 ppbv	Pre-test blank
3/29/05	G-19	Blank	-----	23 ppbv	Pre-test blank
3/29/05	G-19	Blank	-----	< 20 ppbv	Pre-test blank

8.2 Hydrogen Sulfide and Carbonyl Sulfide Analysis

Gas samples for laboratory analysis of H_2S and COS were collected at G-8, G-13, G-14, and G-19 to provide backup and confirmatory data for the on-line Varian PFPD GC measurements. Each Sulfinert® coated sampling canister used was cleaned by washing with high purity (chromatography grade) n-hexane and acetone, followed by baking at 70°C under vacuum with periodic air purges for at least 12 hours.

Gaseous H_2S and COS were measured in GTI's in-house analytical laboratory using a GC coupled with either a flame photometric detector (GC-FPD) or a pulsed flame photometric detector (PFPD), following ASTM D6228 and GTI SOP PP-108. This analysis determines sulfur species in gas samples at concentrations greater than 0.00005% by volume (0.05 ppmv or 50 ppbv). The GC-FPD system is an HP 5890 with a standard flame photometric detector. The GC-PFPD system is the S-Pro from OI Corporation (OIC), utilizing an Agilent 6890 GC with an OIC pulsed flame photometric detector. The S-Pro system also contains a fully integrated permeation system that continuously supplies quantitative gas standards for calibration and performance checks. The entire sample pathway of both GCs is Sulfinert® coated. The GC-FPD system uses a 60-meter, 0.53-mm i.d. Supelco SPB-1 column with a 1-meter pre-column. The GC-PFPD system uses a 60-meter, 0.32-mm i.d. Agilent/J&W DB-1 column.

Interferences are any co-eluting species that may quench the response of the sulfur signal. These are mainly the light gases such as methane, carbon monoxide, nitrogen, and carbon dioxide. These compounds must be adequately separated from the components of interest. The use of the PFPD system eliminates many of these common interferences by using emission time domain processing as well as wavelength filtering to improve sensitivity and selectivity. In the PFPD system photometric emissions from selected elements (e.g. carbon and sulfur) are characterized by different decay rates. By setting time gates, inter-element interferences are reduced or eliminated.

Each GC is conditioned daily by injections of a sulfur standard to passivate the system. Following this, a minimum of three (GC-FPD) or two (GC-PFPD) calibration checks are made at varying pressures for each component. The recovery for the consecutive calibration checks must be within ±10%. Final sulfur component quantitation is done by external calibration consisting of a minimum of four calibration points comprising a second order calibration curve for each component. Each calibration curve must have an $r^2 > 0.995$. The calibration check runs are then added to the calibration curve, and the curve is checked to ensure it maintains an $r^2 > 0.995$. All standard concentrations are certified and NIST-traceable. The actual injected pressure (in torr or mm Hg) is used to correct all sample and standard data to an equivalent pressure basis. Each injection loop and/or range setting has its own calibration curve to avoid any variances in loop size or inertness. The sample loop size for G-8, G-13/G-14, and G-19 samples was 15-µL, 100-µL, and 1-mL, respectively.

GTI's SOP requires that the GC column maintain adequate separation of components. Adjacent components analyzed at similar concentrations must maintain a valley point less than 5% of the height of the smaller peak. If the peak area for a given compound exceeds the highest calibration area by more than 10%, the sample will be reanalyzed either at a lower injection pressure, smaller injection volume, or adjusted detector range to obtain a peak area within the calibration range. The actual pressure that was injected is recorded.

The sampling methodology was validated during the NGC-OPT2 test campaign by purging sample points with dry nitrogen and reference gases containing a certified concentration of H_2S. Satisfactory results were obtained at G-13 and G-14, which proved the inertness of the Silcosteel®-CR coated sampling lines. Validation standards were not taken at G-19 because it was feared that the high concentration of H_2S in the reference gas would remain in the lines and slowly permeate into the test gas, resulting in biased data. Validation blanks taken at G-14 and G-19 consistently measured below the analytical method detection limit of 50 ppbv.

9. TEST MATERIALS

Pilot-scale testing materials stocks were determined based on estimates of Novel Gas Cleaning Process flows, test campaign durations, and other considerations such as cost and availability. Test materials included a relatively low-sulfur carbonaceous feedstock (metallurgical coke, Indian coal, and lignite), trona (and nahcolite as an alternative material) for bulk HCl removal in the Conditioning Filter-Reactor, BASF's R5-12 catalyst or Süd -Chemie's G-72E catalyst as a ZnO sulfur guard bed material, T-46 PROX-SVERS inert balls (92-95% alumina; 9.5, 19, and 38.1 mm (3/8, ¾, and 1-1/2 inch) in diameter) from Christy Companies in St. Louis, MO as support balls for the ZnO catalyst in the Sulfur Guard Bed, Süd -Chemie's G-72E and G-92C catalysts as Stage II desulfurization and dechlorination sorbents, respectively. These latter two materials are available commercially as 4.8 mm (3/16 in) extrudates and would require grinding to -325 mesh for injection into the syngas upstream of the Test Filter-Reactor. A suitable pulverizer was acquired for this purpose (LC-140 Fritsch Rotor-Speed Mill from the Gilson Company with an automatic vibrating feeder and a bag collection kit). The pulverizer made it possible for sorbent sizing to take place immediately before use, thus making sure sorbent properties were not adversely affected.

9.1 Carbonaceous Feedstocks

The proximate analysis, ultimate analysis, heating value, and size distribution properties are summarized in Table 12, Table 13, and Table 14, for the metallurgical coke (Bethlehem Coke Breeze), Indian coal, and lignite coal, respectively. These analyses were performed on equal-weight composite samples from several supersacks. Bethlehem Coke Breeze is typically used as a startup material for the Flex-Fuel gasifier, but was included in this PDU test program given its relatively high chloride content which made it a preferred candidate for the first test campaign focusing on HCl removal in the Conditioning Filter-Reactor. The washed Indian coal was available from a recent project completed at GTI.[13]

The lignite coal was procured specifically for this program. Saskatchewan lignite (Shand) was first gasified during the latter stages of the second test campaign, where its suitability was confirmed as the feedstock of choice for the third test campaign. The third test campaign, which focused on the evaluation of mercury capture with sorbents at relatively high temperatures, used lignite exclusively as the source of syngas and provided another opportunity to demonstrate efficient gasification of lignite in the fluidized bed gasifier. The properties (proximate analysis, ultimate analysis, mineral ash analysis, etc.) of the processed coal are shown in Table 14 and in Table 15 for the raw coal (i.e., prior to drying and sizing, as provided by Great River Energy).

Arrangements were made with the Green River Energy Coal Creek Station (GRE/CSS) to have about 100 tons of Saskatchewan lignite processed (crushed, screened, and dried) to meet the Flex-Fuel gasifier feed specifications. GRE's fluidized-bed drying process produced three streams: product, elutriates, and undercuts, with a surface moisture of ~ 0% and inherent moisture of ~ 20%. To preserve the quality of the lignite and more importantly the contaminant levels for the NGC PDU test program (especially mercury content), the product and elutriates fractions were blended and the undercuts re-crushed, screened, and stored in proper containers for additional blending, if necessary.

All three carbonaceous feedstocks have relatively low sulfur contents (0.56 to 0.89 wt.% S). Both the washed Indian coal and the North Dakota Lignite are suitable feedstocks for the second and third test campaigns. Each of these feedstocks contains very low chlorine so that trona injection in Stage I of the NGC Process could be foregone in these campaigns and focus could be directed primarily at the contaminant removal in Stage II of the process. Also, each feedstock contains sufficient mercury for the third test campaign.

Table 12 - Properties (Proximate Analysis, Ultimate Analysis, Screen Analysis, Heating Value, and Bulk Density) of Metallurgical Coke (Bethlehem Coke Breeze)

Bethlehem Coke Breeze

(Equal-weight composite of coke samples 051094-001, -002, -003, -004, & -005) from Feb. 2005 batch
Assays by SGS Minerals Services (through GTI CRS)

Proximate Analysis		(As Received)			
	Moisture, %	0.40			
	Volatile Matter, %	2.71			
	Ash (950C), %	13.57			
	Fixed Carbon, % (by difference)	83.32			
Ultimate Analysis		(Dry Basis)			
	Ash (950C), %	13.56			
	Carbon, %	82.42			
	Hydrogen, %	0.20			
	Nitrogen, %	1.11			
	Sulfur, %	0.69			
	Mercury, micro g/g	0.02			
	Chlorine, micro g/g	800			
	Oxygen, % (by difference)	1.98			
Heating Value		(Dry Basis)	**Fusion Temperature of Ash (ASTM D1857), deg.F**		
				Reducing	Oxidizing
	BTU/lb	12,320			
			Initial Deformation (I	2220	2,460
			Softening (ST)	2325	2,500
			Hemispherical (HT)	2340	2,540
			Fluid (FT)	2500	2,600

Table 13 - Properties (Proximate Analysis, Ultimate Analysis, Screen Analysis, Heating Value, and Bulk Density) of Washed Indian Coal

Indian Coal (Washed)

(Equal-weight composite of washed and screened Indian Coal from bags W2, W4, W6, W8, W10, W12, W14, & W16
Assays by SGS Minerals Services (through GTI CRS)

Proximate Analysis		(As Received)	(As Received) w/SO3 correction	(Dry basis w/SO3 correction
	Moisture, %	9.97	9.97	
	Volatile Matter, %	26.04	26.04	28.89
	Ash (750C), %	31.64	31.56	35.02
	Fixed Carbon, % (by difference)	32.45	32.53	36.09

Ultimate Analysis		(Dry Basis)
	Ash (750C), %	35.02
	Carbon, %	48.48
	Hydrogen, %	3.09
	Nitrogen, %	1.01
	Sulfur, %	0.56
	Mercury, micro g/g	0.14
	Chlorine, micro g/g	< 100
	Oxygen, % (by difference)	11.84

Heating Value		(Dry Basis)	**Fusion Temperature of Ash (ASTM D1857), F**	Reducing	Oxidizing
	BTU/lb	8,310			
			Initial Deformation (I	> 2,700	> 2,700
			Softening (ST)	> 2,700	> 2,700
			Hemispherical (HT)	> 2,700	> 2,700
			Fluid (FT)	> 2,700	> 2,700

Screen Analysis	Retained on	Wt. %
	6	5.0%
	12	13.1%
	20	18.1%
	40	20.2%
	60	15.0%
	80	9.3%
	100	4.9%
	140	6.9%
	200	3.9%
	230	1.1%
	270	0.8%
	325	0.5%
	PAN	1.2%
	Total	100.0%

Bulk Density	
	1.019 g/ml 63.6 lb/cu ft

Table 14 - Properties (Proximate Analysis, Ultimate Analysis, Screen Analysis, Heating Value, and Bulk Density) of Processed North Dakota Lignite

Lignite Coal (North Dakota)

(Equal-weight composite of samples LC #46, LC #51, LC # 66, and LC #70
Assays by GTI Chemical Research Services Department

Proximate Analysis		(As Received)	(As Received) w/SO3 correction	(Dry Basis) w/SO3 correction
	Moisture, %	18.62	18.62	
	Volatile Matter, %	35.49	35.49	43.61
	Ash (750C), %	11.54	10.27	12.62
	Fixed Carbon, % (by difference)	34.35	35.62	43.77

Ultimate Analysis		(Dry Basis)	
	Ash (750C), %	12.62	
	Carbon, %	60.38	
	Hydrogen, %	3.93	
	Nitrogen, %	0.92	
	Sulfur, %	0.89	
	Mercury, micro g/g	0.06	(0.000006) pct
	Chlorine, micro g/g	122	(0.0122) pct
	Oxygen, % (by difference)	21.25	

Heating Value		(Dry Basis)	**Fusion Temperature of Ash (ASTM D1857), F**	Reducing	Oxidizing
	BTU/lb	10,200			
			Initial Deformation (I	2,065	2,160
			Softening (ST)	2,080	2,185
			Hemispherical (HT)	2,105	2,210
			Fluid (FT)	2,120	2,240

Screen Analysis	Retained on	Wt. %
	6	9.0%
	12	23.8%
	20	26.3%
	40	21.5%
	60	11.6%
	80	4.5%
	100	1.3%
	140	1.0%
	200	0.4%
	230	0.1%
	270	0.1%
	325	0.1%
	PAN	0.3%
	Total	100.0%

Bulk Density	0.837 g/ml 52.3 lb/cu ft

Table 15 - Proximate, Ultimate, and Mineral Ash Analyses for Saskatchewan Lignites (Provided by Great River Energy)

Saskatchewan Lignites	**Boundary Dam**	**Poplar River**	**Shand**	
Proximate Analysis As Rec.				
Moisture, %	35.00	37.78	33.54	
Ash, %	9.47	13.11	13.46	
Volatile, %	24.82	24.74	24.39	
Fixed Carbon, %	30.71	24.36	28.61	1 j/g = 0.430 btu/lb
HHV, BTU/#	6,728	5,598	6,433	
HHV, j/g	15,676	13,044	14,988	
Sulfur, %	0.54	0.65	0.49	1 btu/lb = 2.33 j/g
MAF BTU/#	11,433	10,356	11,183	
MAF j/g	26,639	24,129	26,057	
Mercury, ppb	79	89	**93**	
Chlorine, ppm	10.2	11.4	**7.9**	
Ultimate Analysis As Rec.				
Moisture, %	35.00	37.78	33.54	
Carbon, %	41.70	35.84	39.58	
Hydrogen, %	2.61	2.26	2.57	
Nitrogen, %	0.79	0.48	0.67	
Sulfur, %	0.54	0.65	0.49	
Ash, %	9.47	13.11	13.46	
Oxygen, %	9.90	9.87	9.70	

						Boundary Dam	**Poplar River**	**Shand**
	Mineral Ash Analysis Dry	**Factor**				Elemental Concentrations. Ppm in coal		
SiO2	Silicon Dioxide, %	2.14	34.57	37.14	45.56	15299.38	22770.92	28659.97
Al2O3	Aluminum Oxide, %	1.89	15.25	21.75	20.21	7640.91	15096.45	14389.40
TiO2	Titanium Dioxide, %	1.67	0.50	0.63	0.88	282.75	493.58	706.59
FeO	Iron Oxide, %	1.29	5.02	5.46	3.61	3693.79	5562.94	3779.42
CaO	Calcium Oxide, %	1.40	15.53	14.62	9.34	10508.55	13705.02	8982.61
MgO	Magnesium Oxide, %	1.66	3.66	5.99	2.47	2092.03	4739.63	2003.71
K2O	Potassium Oxide, %	1.42	0.87	0.92	1.17	580.61	846.26	1107.32
Na2O	Sodium Oxide, %	1.35	3.70	0.30	5.36	2596.26	292.38	5355.53
SO3	Sulfur Trioxide, %	2.50	15.19	9.53	9.29	5752.50	5000	5000
P2O5	Phosphorus Pentoxide, %	2.29	0.49	0.04	0.29	203.94	25.30	171.22
SrO	Strontium Oxide, %	1.18	0.30	0.13	0.31	242.94	143.94	348.16
BaO	Barium Oxide, %	1.12	0.23	0.37	0.42	199.23	430.93	509.97
	Undetermined, %		4.68	3.12	1.09	50907.13	30892.63	28986.09

9.2 Sulfur and Halide Sorbent Materials

Table 16 provides the chemical analyses, measured BET N_2 surface area, and the theoretical sulfur or chloride capacity for the PDU test program sulfur and halide sorbents. For reference, the laboratory counterparts for the Stage I bulk HCl removal sorbents are also included. Details on the NGC Process sulfur and halide sorbents were provided in the Base Program final report.[1] For the laboratory work, the Stage I bulk HCl removal sorbents were obtained from FMC in Green River, Wyoming (trona) and from the White River Nahcolite Minerals (WRNM) in Meeker, Colorado (nahcolite). For the PDU test program, Solvay Minerals in Houston, Texas was selected as the commercial supplier for both materials. Chemical analyses in Table 16 indicate both Solvay trona and nahcolite materials contain slightly less sodium than their laboratory counterparts, leading to lower theoretical chloride capacities. According to the information provided by the supplier, the Solvay T-200® contained 97.5% Na_2CO_3•$NaHCO_3$•$2H_2O$ (i.e., 97.5% purity), 0.01% free moisture, 2.3% H_2O insoluble material, and 0.1% NaCl. The bulk density is 49.0 lbs/ft^3. The particle size distribution is as follows: 75% by weight $<$ 70 µm, 50% $<$ 50 µm, and 10% $<$ 6 µm. The Solvay sodium bicarbonate (nahcolite) contained $>$ 99.9% $NaHCO_3$. Its (loose) bulk density is 71.7 lbs/ft^3. The particle size distribution is as follows: 82.1% by weight $>$ 45 µm (+325 mesh), 26.8% $>$ 75 µm (+200 mesh), and 0.5% $>$ 150 µm (+100 mesh). Both commercial trona and nahcolite materials were deemed to have suitable size distributions for the PDU test program and no additional grinding or sieving was performed on the Solvay bulk HCl removal sorbents.

Appropriate quantities of the G-92C (Stage II dechlorination sorbent) and G-72E (Stage II desulfurization sorbent) were procured from Süd-Chemie as extrudates. Sufficient amounts of each material were finely ground using the Gilson LC-140 Fritsch Rotor-Speed Mill. Preparation of the Stage II materials for injection into the conditioned syngas stream was performed in two steps. In a first step, each batch was ground to pass a 100 mesh screen, and in a second step this fine material was ground further to pass a 325 mesh screen. Finely-ground materials were stored in proper containers until use.

Table 16 – Novel Gas Cleaning Process Sulfur and Halide Sorbents

	Chemical Analysis (wt. %)						**Theoretical Capacity (g Cl or S/100 g)**	**BET N_2 Surface Area (m^2/g)**
	Na	Zn	C	H	Al	Ca		
Trona (Na_2CO_3•$NaHCO_3$•$2H_2O$								
Solvay T-200®	31.63		6.92	1.81			48.8	
FMC (Green River, Wy)	35.6		10.68	1.84			54.9	8.65
Nahcolite ($NaHCO_3$)								
Solvay Sodium Bicarbonate	23.9		10.01	0.74			36.9	
WRNM (Meeker, CO)	26.9		14.07	1.38			41.5	9.69
G-92C (Na_2O/Al_2O_3) Süd-Chemie (Louisville, Ky) (two-stage grinding at GTI)	6.41				39.6		9.9	165
G-72E (ZnO/calcium aluminate) Süd-Chemie (Louisville, Ky) (two-stage grinding at GTI)		69.8			4.18	1.17	34.2	40.3

9.3 Mercury Sorbent Materials

Selection and laboratory evaluation of candidate mercury-removal sorbents was completed earlier in the project, identifying two candidate sorbents with potential to capture mercury to levels below 0.01 ppb in the NGC Process configuration. The first sorbent, intended as the lower temperature mercury removal sorbent, was acquired from Synetix/Johnson Matthey (JM) in a pre-sulfided form. This mixed metal oxide (CuO and ZnO) sorbent was designated as GTI-Hg-S9. Characterization work at GTI indicated the sorbent contained 32.4% Cu, 19.9% Zn, 14.3% S, and 8.56% Al, and had a BET nitrogen surface area of 71.1 m^2/g. The second sorbent was provided by TDA, as an improved version of an earlier mercury sorbent that was evaluated in the laboratory portion of this program under a non-disclosure agreement. TDA's mercury removal sorbent (also consisting of CuO, ZnO, and Al_2O_3 as the primary components in addition to some minor promoters) was provided as 150-250 µm powder and required some additional activation, as discussed below, prior to further grinding at GTI.

TDA provided a 10-kg batch of their mercury sorbent. Approximately 6.8 kg of this batch, in the form of weak pellets, was provided in a separate container. The remainder was provided separately in the form of stronger pellets. The chemical compositions of both materials are identical. TDA requested that we use the weak pellet batch first. In addition, TDA specified that their sorbent requires activated prior to use. According to the information provided, activation is typically carried out at 230ºC using hydrogen as the reducing gas. Typically, 2% hydrogen in an inert carrier gas is used, with total usage of 20 grams of hydrogen per kilogram of sorbent. Flow rates of activation gas for small quantities are usually 100 sccm/g for eight hours. This equates to 800 sLpm/kg divided by the desired number of hours of flow. Following activation, the sorbent is kept under an inert or reducing atmosphere until use. Ideally, it is preferable first to grind the sorbent to the required size (i.e., < 325 mesh), and then to activate the resulting sorbent fines. In this work, however, given the sorbent quantities involved, it was necessary to activate the TDA sorbent while still in pellet form, and then to finely grind the resulting activated sorbent. Every effort was made to minimize sorbent exposure to the atmosphere during this process.

10. NOVEL GAS CLEANING OPTIONAL PROGRAM TEST CAMPAIGN #1 (NGC-OPT1)

10.1 Objectives

The primary objective of the Novel Gas Cleaning Program Test Campaign 1 (NGC-OPT1) was to evaluate the performance of the Conditioning Filter-Reactor (CF-R, T-2153) for combined particulate/halide (mainly HCl) removal from syngas derived from the gasification of a carbonaceous feedstock. This was accomplished through a series of test segments that were designed to:

1. set the Flex-Fuel gasifier operating conditions for producing syngas from the test feedstocks (Bethlehem Coke Breeze and washed Indian coal) at 200 to 225 psig pressure, preferably with a face velocity of at least 3 ft/min in the T-2153 CF-R; this corresponds to approximately 2,700 lbs/hr of syngas.
2. determine the operating conditions for the Direct Spray Water Quench (DSQ) system, the CF-R (including pulsing), and the sorbent (trona) injection system to achieve 1 to 5 ppmv of HCl and ~ < 0.1 ppmw particulate content in the T-2153 CF-R product syngas, at an operating temperature of at least 830ºF (preferably).
3. confirm the effectiveness of "conventional" syngas Sample Extraction & Conditioning (SE&C) systems at sample points G-8 (CF-R inlet) and G-13 (CF-R outlet), using two carbonaceous feedstocks with different chlorine contents (~ 800 ppmw for Bethlehem Coke Breeze and ~ 135 ppmw for washed Indian Coal), with and without sorbent injection for HCl capture.

4. provide “cold” and “hot/warm” slipstream samples from G-8 and G-13 for comprehensive, continuous, sensitive, and accurate measurements by personnel from the GTI Birmingham Office, as part of their project scope to develop an analytical suite as a key enabling technology for gasification systems integration.

10.2 Process Flow Diagram for NGC-OPT1

For this test series in the Flex-Fuel Test Facility (FFTF), the syngas flow in the NGC Conditioning Section was as shown in Figure 31.

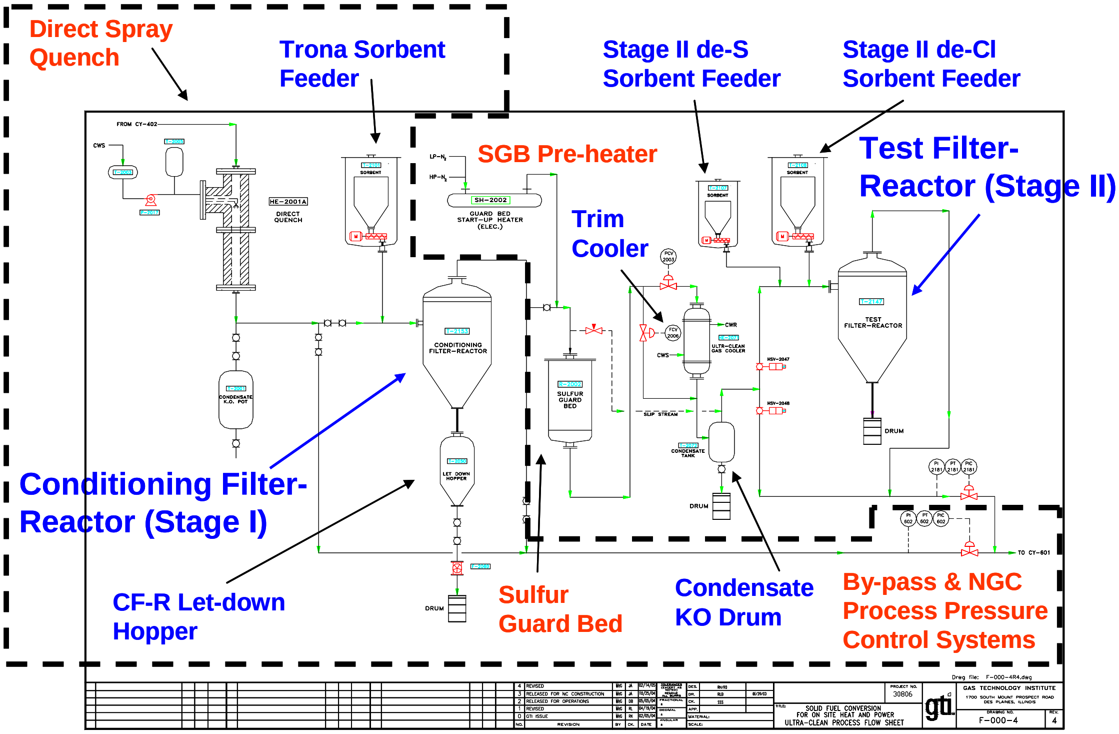

Figure 31 – Flow Diagram of NGC Process Section in the Flex-Fuel Test Facility (area delineated by dashed lines indicates equipment used in NGC-OPT1)

Raw syngas from the Secondary Cyclone (CY-401) was partially cooled in the DSQ system (HE-2001A) and was then directed to the T-2153 CF-R vessel. After passing through the filter elements or candles in the CF-R vessel, the syngas was routed through the Pressure Let-Down station (PIC-602), then to the Tertiary Cyclone (CY-601), and finally to the Flare (FL-601). As indicated above, the Conditioning Section also comprises a Sulfur Guard Bed (SGB) and a second Indirect Syngas Cooler (Trim Cooler) for bulk sulfur removal and temperature reduction of the CF-R product gas to meet the requirements of the inlet syngas to the Test Section. It was acceptable to by-pass the SGB in this test since the relatively low sulfur contents of the test feedstocks (0.69% for Bethlehem Coke Breeze and 0.55% for washed Indian coal) allowed operation while still meeting the EPA sulfur emissions requirements.

After pulsing cycles were established with the nitrogen blow-back system on the T-2153 CF-R vessel, HCl removal sorbent, trona (or nahcolite as an alternative sorbent, if necessary), was injected into the syngas stream, immediately before entering the T-2153 CF-R, through the T-2101 Sorbent Injection system. The latter combines a loss-in-weight solids feeder with dilute-phase flow in nitrogen to convey the sorbent into the syngas.

Representative samples of the syngas were extracted, conditioned (de-dusted, cooled, and de-pressured), and analyzed with suitable instruments at two main locations:

- G-8: Partially-cooled raw syngas (between DSQ and CF-R)
- G-13: Partially-conditioned T-2153 CF-R product syngas (essentially dust-free, dechlorinated to 1-5 ppmv HCl, but still containing all the raw syngas sulfur).

Other analytical work was also performed on various samples to estimate CF-R particulate leakage (at S-13C), to characterize gasifier performance and efficiency in generating syngas from the test feedstock, to characterize process emissions for permitting activities, and to assess disposal options for the gasification and syngas cleanup byproduct materials. Process samples included fuel feedstock, ash, dust, raw syngas, fresh sorbent materials, spent sorbents, and condensed liquids, in addition to several gas samples throughout the NGC Process section. Additional details are provided in the following sections.

10.3 NGC-OPT1 Sequence / Chronology

During the NGC-OPT1 campaign, the following sequence was followed to accomplish test objectives:

1. System Heat up with Start-Up Heater (SH-201): Direct flue gas from Gasifier through DSQ, through T-2153 CF-R vessel, to pressure control valve(s), PCV-602.
2. Initiate solids feeding with metallurgical coke (Bethlehem Coke Breeze), for second-stage gasifier heating, for establishing a fluidized-bed of solids within the gasifier, and ultimately for establishing steady-state (SS) gasifier operation at 200-225 psig pressure.
    - 2.1. Adjust Gasifier operating parameters to achieve target gasifier pressure and target syngas flowrate (and face velocity for filter candles).
    - 2.2. Establish CF-R operating temperature at ~ 830ºF or higher.
        - 2.2.1. Adjust DSQ system set point to achieve target T-2153 syngas outlet temperature
        - 2.2.2. TIC-2022 set point likely between ~ 900 and 950ºF
        - 2.2.3. TIC-2022 may be limited by thermal expansion of process piping
    - 2.3. Verify SE&C skid viability at the G-8 and G-13 sampling locations via spike-and-recovery methods (HCl ~ 7.7 ppmv; H_2S ~ 535 ppmv (and COS ~ 65 ppmv)). Impinger samples and FT-IR (FT-IR has a nominal detection limit for HCl in the range of ~ 1 to 5 ppmv)
3. When a reasonable rate of syngas generation from the Gasifier has been established, continue operating at SS conditions to verify/establish the following:
    - 3.1. Measure HCl (and H_2S & COS) levels in the raw syngas (at G-8) and establish variability
        - 3.1.1. Impinger samples and FT-IR at G-8 with syngas. (Important to establish range of variation in HCl using FT-IR in order to evaluate removal effectiveness with this instrument at G-13 (see below).)
        - 3.1.2. With G-8 hot-gas sample line to FT-IR inlet, monitor HCl concentration during pulsing on T-2153 to determine if nitrogen pulse affects measurement.
        - 3.1.3. Monitor raw gas composition at G-8 with mass spectrometer and GC/FPD/TCD. Determine spike duration requirements and recoveries for GC system (with H_2S and COS spike).
    - 3.2. Establish preferred conditions for CF-R pulsing frequency in the 1-10 range to handle dust loading from the metallurgical coke.

3.2.1. Observe pressure-drop increase on the T-2153 CF-R and adjust pulsing as needed to give consistent "clean" differential pressure for filter candles.

3.2.2. Fine-tune Pulsing on the T-2153 CF-R to achieve cleaning at minimal nitrogen use

3.2.3. Pulsing of the T-2153 filter with the fast-acting valve

3.2.4. Pressure of Blow-Back system nitrogen in T-2304 Accumulator: starting point ~ twice process pressure (i.e., 400 to 450 psig)

3.2.5. Length of pulsing time with fast-acting valve: 0.2 to 0.3 sec

3.3. Measure HCl levels with impingers and FT-IR (and H_2S & COS) in the raw syngas and CF-R product syngas (at G-8 and G-13) and establish that, with no trona sorbent being injected, inlet and outlet syngas halide (and sulfur) contaminant concentrations are essentially the same.

4. When preferred test conditions are satisfied as described under 3 above:

4.1. Prepare to start trona injection into the syngas stream upstream of the CF-R vessel

4.1.1. Set Transport Nitrogen rate (as controlled by differential pressure) required for adequate conveying of sorbent into process syngas.

4.1.2. Start with ~ 50 ft/sec injection velocity (22 scfm nitrogen rate), yielding approximately 5 psi differential pressure.

4.1.3. (Might study minimum pressure differential required for protecting sorbent-weighing system from gasifier cycles / upsets)

4.2. Initiate bulk HCl removal sorbent (trona) injection at the maximum rate of Na/Cl=10 based on the syngas HCl content at G-8

Trona (Solvay T-200®): Chemical formula: $Na_2CO_3 \bullet NaHCO_3 \bullet 2H_2O$
Purity: 97.5%
Bulk density: 49.0 lbs/ft^3
Size distribution: 75% < 70 μm, 50% < 28 μm, 10% < 6 μm

$$\boxed{\text{Trona Injection Rate (grams/min)} = [(453.6)*(226)/[(3)*(60)*(10\^{}6)]] * [[HCl]_o*Q_m/MW_{sg}] * R}$$

- $[HCl]_o$ = Measured HCl concentration in raw syngas (at G-8), ppmv
- Q_m = Raw, partially-cooled syngas, lbs/hr
- MW_{sg} = Molecular weight of raw, partially cooled syngas, lbs/lb-mole
- R = Na to Cl molar ratio

Example: Raw syngas at 3000 lbs/hr with an average MW of 25 and containing about 75 ppmv HCl, the trona injection rate required for a sodium-to-chlorine (Na/Cl) ratio of 10 is about 51.3 g/min (52.6 g/min for 97.5% purity for the Solvay T-200® trona material).

4.2.1. While allowing the system to stabilize (i.e., a somewhat constant fly ash/trona mixture composition of the filter cake), continue to measure HCl with impingers (and H_2S & COS) levels in the CF-R inlet and outlet syngas (at G-8 and G-13 sampling locations).

4.2.2. Monitor filtered syngas composition at G-13 with GC/FPD/TCD.

4.2.3. Attach G-13 hot-gas sample line to FT-IR inlet to monitor HCl concentrations. Monitor HCl concentration during pulsing on T-2153 to determine how pulsing affects HCl removal. (Re-plumb FT-IR to sample from G-8 inlet after this test (1-2 hrs)).

4.2.4. If the CF-R product syngas HCl content (i.e., at G-13) is < 5 ppmv, continue operating at Na/Cl=10 for six (6) hours, which should result in at least 4-6 consistent samples. Note: If we do not achieve < 5 ppmv at G-13 with Na/Cl=10, then examine the HCl sorbent fines/total fines ratio and adjust (increase) sorbent injection rate to achieve 0.1 to 0.4.

4.2.5. Transition to a lower sorbent injection rate (i.e., Na/Cl=5) and measure effect of lower sorbent rate on HCl in syngas with impingers at G-8 and G-13 (3-4 hours or about 3 consistent samples).

4.2.6. Attach G-13 hot-gas sample line to FT-IR inlet to monitor HCl concentrations. Monitor HCl concentration during pulsing on T-2153 to determine how pulsing affects HCl removal. Leave FT-IR sampling from G-13.

4.2.7. Shut off HCl sorbent injection and Transport Nitrogen; allow system to stabilize (pulse clean manually to accelerate sorbent removal) and measure HCl in syngas with impingers at G-8 and G-13 (3 hours or 3 consistent samples)

4.2.8. Measure (estimate) particulate leakage (at S-13)

4.3. Transition from Bethlehem Coke Breeze to washed Indian coal feeding to Gasifier

4.3.1. Re-plumb FT-IR to sample from G-8 inlet.

4.3.2. Continue to operate gasifier at 200-225 psig; measure HCl and (H_2S and COS) at inlet (G-8) and outlet (G-13), with no trona sorbent injection (see note below); (3-4 hours or about 3 consistent samples).

4.3.3. Adjust Gasifier operating parameters to achieve new target gasifier pressure (300 psig

4.3.4. Adjust Gasifier bed-ash to target level; achieve high-carbon conversion

4.3.5. Adjust CF-R pulsing frequency as necessary

4.3.6. Collect samples in the Gasification Section for material and energy balances

4.3.7. Measure HCl and (H_2S & COS) at inlet (G-8) and outlet (G-13). Note: with the HCl content of the raw syngas expected to be ~ 10 ppmv, no trona injection should be performed. The measurements taken would serve as another check on the viability of our SE&C skids and measurement instruments.

GC system samples to be collected from both G-8 and G-13 hot-gas sample lines.

10.4 Results and Discussion - NGC-OPT1

Gasifier and Conditioning Filter-Reactor Operations

This first test campaign concentrated on the performance of the Conditioning Filter-Reactor filtration and HCl removal. The salient characteristics of the gasification section (Flex-Fuel gasifier and Direct Spray Quench system) and the Conditioning Filter-Reactor of the NGC Process section are summarized in Table 17 and Table 18. Gasification of Bethlehem Coke Breeze was conducted successfully for ~ 53 hours, from about 12:00 noon on March 8 through 17:00 on March 10, at which time the feed to the gasifier was switched to washed Indian coal. Testing with washed Indian coal extended for ~ 9 hours, until about 02:00 on March 11 when the NGC-OPT1 test campaign was terminated. This test campaign has been divided into four (4) test segments as described in Table 17. Test segments 2, 3, and 4 represent, respectively, steady-state testing periods during operation with metallurgical coke without trona injection, metallurgical coke with trona injection, and Indian coal without trona injection. The bulk HCl removal sorbent (trona) was injected through the T-2101 Sorbent Injection System from about 23:00 on March 9 until about 17:00 on March 10, i.e., third test segment (1-TS3). Trona was injected into the syngas immediately upstream of the T-2153 CF-R vessel. As a precaution, trona injection during this campaign was shut off during pulsing of the T-2153 filter vessel.

Table 17 - Test Segments in the NGC-OPT1 Test Campaign (March 7-11, 2005)

Overall	
Start	3/8/2005 at ~ 12:00
End	3/11/2005 at ~ 02:00
Duration, hr	62
Start-up and Establishing Steady State with Metallurgical Coke (1-TS1)	
Start	3/8/2005 at ~ 12:00
End	3/8/2005 at ~ 18:00
Duration, hr	~ 6
Operating at Steady State with Met Coke (1-TS2)	
Start	3/8/2005 at ~ 18:00
End	3/9/2005 at ~ 23:00
Duration, hr	~ 29
Trona Sorbent Injection (1-TS3)	
Start	3/9/2005 at ~ 23:00
End	3/10/2005 at ~ 17:00
Duration, hr	~ 18
Transition to Washed Indian Coal (1-TS4)	
Start	3/10/2005 at ~ 17:00
End	3/11/2005 at ~ 02:00
Duration, hr	~ 9
Terminate NGC-OPT1	3/11/2005 at ~ 02:00

Throughout testing, the syngas temperature at the outlet of the Direct Spray Quench system was maintained consistently above 800ºF (Table 18). The process conditions for the Conditioning Filter-Reactor were relatively constant for ~ 47 hours, from about 18:00 hours on March 8 through the end of the gasification of metallurgical coke at 17:00 on March 10. The solids loading in the syngas was relatively low, and the pulsing cycles were relatively long (once every 2 to 4 hours). As the gasifier feed was switched from metallurgical coke to washed Indian coal, the syngas flow rate increased considerably, as did the solids loading in the syngas. The frequency of pulsing had to be increased to approximately 7-8 pulses per hour.

Table 18 - Gasification and NGC Process Sections Operating Conditions during the NGC-OPT1 Test Campaign

	Met Coke	Indian coal (washed)
Start	3/8/2005 at ~ 18:00	3/10/2005 at ~ 17:00
End	3/10/2005 at ~ 17:00	3/11/2005 at ~ 02:00
Duration, hr	47	9
Gasifier		
Pressure, psig	205	210
Bed Temp., ºF	1800 – 1875	1625 – 1725

Outlet Temp., ºF	1675 – 1725	1600 – 1625
Bed Height, ft	8 – 11	6 - 9
Syngas Temp. at Secondary Cyclone, ºF	1400 - 1450	1425 - 1450
Direct Spray Quench (DSQ)		
DSQ Inlet Temp., ºF	1400 - 1450	1425 - 1450
DSQ Outlet Temp., ºF	800 - 875	800
Quench Rate, lb/hr	0 - 150	275 - 325
Syngas Flowrate, lbs/hr	1800 - 2000	2300 - 2700
Pressure, psig	200	200
Conditioning Filter-Reactor (CF-R)		
CF-R Inlet Temp., ºF	710 - 750	> 750
CF-R Outlet Temp., ºF	670 - 690	690 - 710
Pressure, psig	200	200
Pulsing Frequency, times/hr	0.3 – 0.5	7 - 8

Temperature drop and pressure drop behaviors, and key process parameters (inlet syngas temperature, syngas mass flowrate, and operating face velocity) for the CF-R vessel are reported in Figure 32 and Figure 33 for the NGC-OPT1 campaign. The figures shown cover the entire test duration, and on each figure the various test segments are delineated consistent with the information provided in Table 17. The Flex-Fuel gasifier pressure was brought up to ~ 200 psig after initiating the gasification of Bethlehem Coke Breeze (during test segment 1-TS2). The inlet temperature for the syngas to the CF-R was maintained consistently above 800ºF throughout testing. Process conditions were relatively constant for the CF-R vessel, during each of the three test segments shown on the figures. The syngas mass flowrate at the CF-R inlet was quite stable, averaging ~ 2,740 lbs/hr, which corresponds to approximately 2.18 ft/min operating face velocity. Both the syngas flowrate and face velocity increased during the final test segment of the NGC-OPT1 campaign, when the gasifier feed was switched from metallurgical coke to the more reactive washed Indian coal.

As shown in Figure 32, during metallurgical coke operation (i.e., test segment 1-TS2) the pulse cleaning frequency was low and the filter pressure drop behavior was relatively stable, with about 89 minutes between pulse cleaning events due to the relatively low gas flow rate and the low metallurgical coke ash content. The baseline pressure drop was 25-30 inches of water (in wg), and the peak pressure drop was about 50 in wg, with the pressure recovery on cleaning being about 20 in wg. The gas temperature drop experienced across the filter vessel was 175 to 250°F. This large temperature drop is due to the small vessel size and the low syngas flow rate through the vessel.

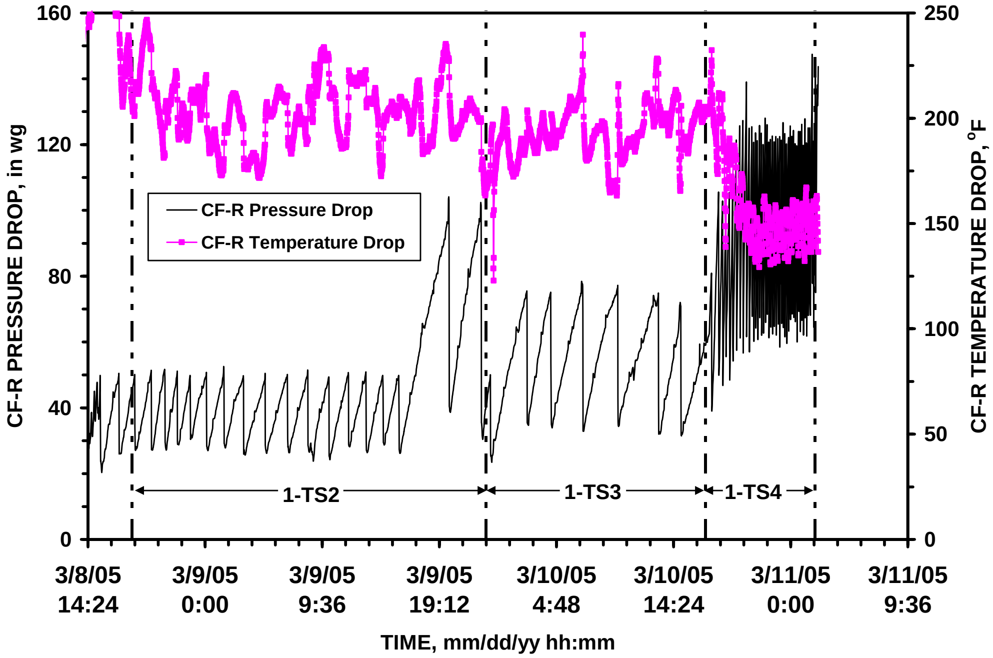

Figure 32 – Test Campaign #1 Conditioning Filter-Reactor Pressure and Temperature Drop

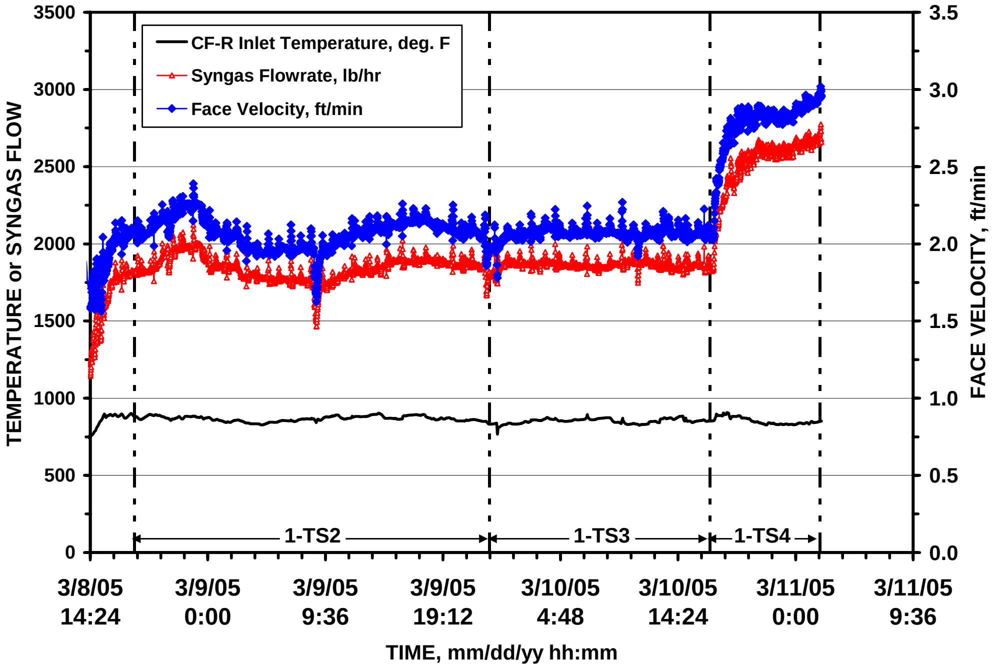

Figure 33 – Conditioning Filter-Reactor Inlet Syngas Temperature, Mass Flowrate, and Face Velocity during Test Campaign #1

When trona feeding was included in the operation (i.e., 1-TS3), the pulse cleaning frequency was reduced further to about 154 minutes between pulse cleanings (this is an operating parameter selection), resulting in a pressure drop recovery of about 40 in wg. The baseline pressure drop was about 36 in wg, and the peak pressure drop was about 71-77 in wg. The gas temperature drop experienced across the filter vessel was 173 to 225°F. It does not appear that the injected Trona resulted in much additional filter pressure drop.

During the final period of operation with washed Indian coal without Trona injection (i.e., 1-TS4), the pulse cleaning frequency was much higher and the filter pressure drop behavior was a little less stable, with about 10 minutes between pulse cleaning events due to the high Indian coal ash content. The baseline pressure drop was 47-83 in wg, increasing slowly with time. The peak pressure drop was about 106-159 in wg, with the pressure recovery on cleaning being about 50-60 in wg. The gas temperature drop experienced across the filter vessel was lower at 130 to 160°F due to the increased mass flow of Indian coal ash.

Bulk HCl Removal

The high-temperature process interface approach for syngas sample extraction and conditioning (illustrated in Figure 19 and in Figure 20) was validated at G-8 (CF-R inlet) and at G-13 (CF-R outlet) process locations. For the process conditions encountered, the sample gas was maintained at temperatures above 400ºF, the pressure of the gas was reduced from 200 psig to 1-2 psig, and no dilution was required to prevent condensation into the FT-IR or mass spectrometer on-line instruments. A Nafion® dryer was used on the sample syngas stream ahead of the gas chromatographs to protect the columns from water in the sample gas.

Using a certified 7.7 ppmv HCl-N_2 gas mixture and spike-and-recovery techniques, EPA Method 26 impingers were used to collect samples from the high-temperature process interface sample lines from a tee at the inlet to the on-line instruments. Concentrations of HCl measured (using ion chromatography) 8.1, 7.7, and 6.8 ppmv HCl from these spike samples, yielding an average 100% recovery (see sample ID #'s 051119-038, -039, and -040 in Table 19 below, which provides a summary of all impinger/ion chromatography analyses made during the NGC-OPT1 test campaign). Reproducibility of the impinger sampling/ion chromatograph chloride measurements was demonstrated. Duplicate (simultaneous) impinger samples from the second SE&C Skid at the G-13 location measured 10.9 and 10.8 ppmv HCl (see sample ID #'s 051119-129 and -130 in Table 19).

The syngas HCl content at the Conditioning Filter-Reactor inlet, as measured at the G-8 sampling location, is displayed in Figure 34 as a function of time over the total test campaign duration. At first glance it appears that the inlet HCl content was quite variable over the test period using metallurgical coke, ranging from 10 to 105 ppmv. These variations, however, have been determined to be caused by char interferences of the first sample extraction and conditioning skid. As noted earlier, the SE&C Skid #1 comprises two gas trains each containing one Mott filter (A and B). During data collection from the beginning of the NGC-OPT1 until about 13:15 on 3/10/2005, Filter A was being used to remove char from the syngas slipstream. As char collected on the filter surface, the measured HCl concentration gradually decreased as, apparently, HCl was being removed through reaction (adsorption and/or chemisorption) with the char. A post-test sample from Filter A on the SE&C Skid #1 (at G-8) was analyzed for chloride and determined to contain about 0.014 % Cl (and 0.56% S).

To confirm the expected HCl concentration in the product raw syngas, the char-laden syngas slipstream at G-8 was directed through Filter B, the Mott filter housing of which had previously been thoroughly cleaned. As shown in Figure 34, immediately after switching, the measured HCl concentration increased from approximately 27 ppmv to 106 ppmv (see sample ID # 051119-132 in Table 19 taken within 30 minutes of filter switching). This value closely confirmed the expected HCl concentration in the product raw syngas, shown as a horizontal solid line in Figure 34. At a coke feed rate of approximately

372 lb/hr, a coke feed assaying about 800 µg Cl/g (i.e., 0.08 wt. % Cl or 800 ppmw Cl, Table 12), a product syngas mass flowrate of about 1,853.24 lb/hr, and an average MW of 24.6 for the product syngas, the HCl concentration in the wet syngas (after the DSQ system) was expected to contain about 111.3 ppmv HCl during the operating period from 18:00 on 3/8/2005 to 17:00 on 3/10/2005. Therefore, the inlet HCl concentration is considered to be about 111 ppmv for the purpose of estimating HCl removal efficiency in the CF-R. The washed Indian coal (~ 596 lb/hr coal feed to gasifier, ~ 2,509 lb/hr of syngas, and 100-140 ppmw Cl, Table 13) should generate about 16-23 ppmv HCl in the syngas, sufficiently low to forego trona injection upstream of the CF-R vessel.

Table 19 - Summary of Impinger/Ion Chromatography Analyses during the NGC-OPT1 Test Campaign

Ref	Lab Sample ID	Sample Point	Date	Time Period	Average Time (min)	Test Segment	Measured HCl, ppmv
1	051119-022	G-8 Validation Test #1		-	-		1.7
2	051119-023	G-8 Validation Test #2		-	-		3.5
3	051119-038	G-13 Validation Test #1		-	-		8.1
4	051119-039	G-13 Validation Test #2		-	-		7.7
5	051119-040	G-13 Validation Test #3		-	-		6.8
6	051119-045	G-13	3/9/2005	04:29 - 04:58	29	1-TS2	15.9
7	051119-046	G-13	3/9/2005	05:20 - 05:59	39	1-TS2	8.9
8	051119-047	G-13	3/9/2005	06:02 - 06:39	37	1-TS2	7.9
9	051119-054	G-8	3/9/2005	06:57 - 07:31	34	1-TS2	38.5
10	051119-055	G-8	3/9/2005	07:36 - 08:09	33	1-TS2	54.2
11	051119-057	G-8	3/9/2005	08:14 - 08:45	31	1-TS2	77.4
12	051119-058	G-8	3/9/2005	10:14 - 10:47	33	1-TS2	67.1
13	051119-064	G-13	3/9/2005	10:56 - 11:27	31	1-TS2	10.6
14	051119-065	G-13	3/9/2005	11:34 - 12:07	33	1-TS2	20.9
15	051119-066	G-13	3/9/2005	12:14 - 12:43	29	1-TS2	22.2
16	051119-069	G-13	3/9/2005	12:54 - 13:24	30	1-TS2	27.0
17	051119-071	G-13	3/9/2005	14:48 - 15:19	31	1-TS2	18.3
18	051119-072	G-13	3/9/2005	15:24 - 16:00	36	1-TS2	21.5
19	051119-073	G-8	3/9/2005	16:34 - 17:04	30	1-TS2	20.0
20	051119-081	G-8	3/9/2005	17:24 - 17:54	30	1-TS2	11.7
21	051119-089	G-8	3/9/2005	22:19 - 22:51	32	1-TS2	88.4
22	051119-090	G-8	3/9-10/05	23:45 - 00:20	35	1-TS3	35.4
23	051119-097	G-13	3/10/2005	00:54 - 01:34	40	1-TS3	12.4
24	051119-098	G-8	3/10/2005	01:40 - 02:12	32	1-TS3	30.4
25	051119-099	G-13	3/10/2005	02:20 - 02:43	23	1-TS3	45.8
26	051119-105	G-8	3/10/2005	03:07 - 03:30	23	1-TS3	12.7
27	051119-106	G-13	3/10/2005	03:38 - 04:10	32	1-TS3	41.0
28	051119-111	G-8	3/10/2005	04:15 - 04:46	31	1-TS3	13.9
29	051119-112	G-13	3/10/2005	05:15 - 05:41	26	1-TS3	33.9
30	051119-113	G-8	3/10/2005	05:48 - 06:17	29	1-TS3	41.3
31	051119-114	G-13	3/10/2005	06:22 - 06:45	23	1-TS3	14.5
32	051119-115	G-13	3/10/2005	07:03 - 07:27	24	1-TS3	19.6
33	051119-118	G-8	3/10/2005	07:34 - 07:59	25	1-TS3	38.3
34	051119-119	G-13	3/10/2005	08:04 - 08:30	26	1-TS3	17.4
35	051119-121	G-8	3/10/2005	08:50 - 09:28	38	1-TS3	13.2
36	051119-128	G-13	3/10/2005	10:32 - 11:05	33	1-TS3	18.5
37	051119-129	G-13 (A, DTM-1)	3/10/2005	11:26 - 11:56	30	1-TS3	10.9
38	051119-130	G-13 (B, DTM-2)	3/10/2005	11:20 - 11:56	36	1-TS3	10.8
39	051119-131	G-8	3/10/2005	12:33 - 13:00	27	1-TS3	20.4
40	051119-132	G-8	3/10/2005	13:44 - 14:13	29	1-TS3	106
41	051119-143	G-8	3/10/2005	16:17 - 16:47	30	1-TS3	69.9
42	051119-146	G-13	3/10/2005	16:56 - 17:25	29	1-TS4	18.7
43	051119-147	G-13	3/10/2005	17:37 - 17:56	19	1-TS4	10.6
44	051119-148	G-13	3/10/2005	18:02 - 18:17	15	1-TS4	11.8
45	051119-163	G-8	3/10/2005	19:38 - 20:08	30	1-TS4	14.7
46	051119-164	G-13	3/10/2005	20:15 - 20:47	32	1-TS4	13.6
47	051119-165	G-13	3/10/2005	21:50 - 22:13	23	1-TS4	9.4
48	051119-166	G-8	3/10/2005	23:02 - 23:27	25	1-TS4	9.2
49	051119-178	G-13	3/11/2005	00:00 - 00:27	27	1-TS4	7.5
50	051119-179	G-8	3/11/2005	01:00 - 01:25	25	1-TS4	5.1
51	051119-180	G-13	3/11/2005	02:01 - 02:22	21	1-TS4	9.8
						1-TS4	
52	051119-190	Impinger Field Blank	3/11/2005	10:30			< 1.0

The EPA Method 26 impinger/ion chromatograph batch HCl sampling and measurements and on-line FT-IR HCl analyses showed very good agreement. Both approaches were able to identify and quantify the effect of char on HCl concentrations in the syngas. The FT-IR measurements, superimposed on the batch measurements in Figure 35, also showed a marked drop in HCl levels and clearly indicated char was a significant factor in this reduction. The data indicated a very rapid and significant response to char. As shown in Figure 35, immediately on switching from Filter A to Filter B, the on-line FT-IR measured HCl > 100 ppmv. The peak value of HCl measured was consistent with the maximum HCl concentration expected in the process gas based on an analysis of chloride content in the fuel, as discussed above.

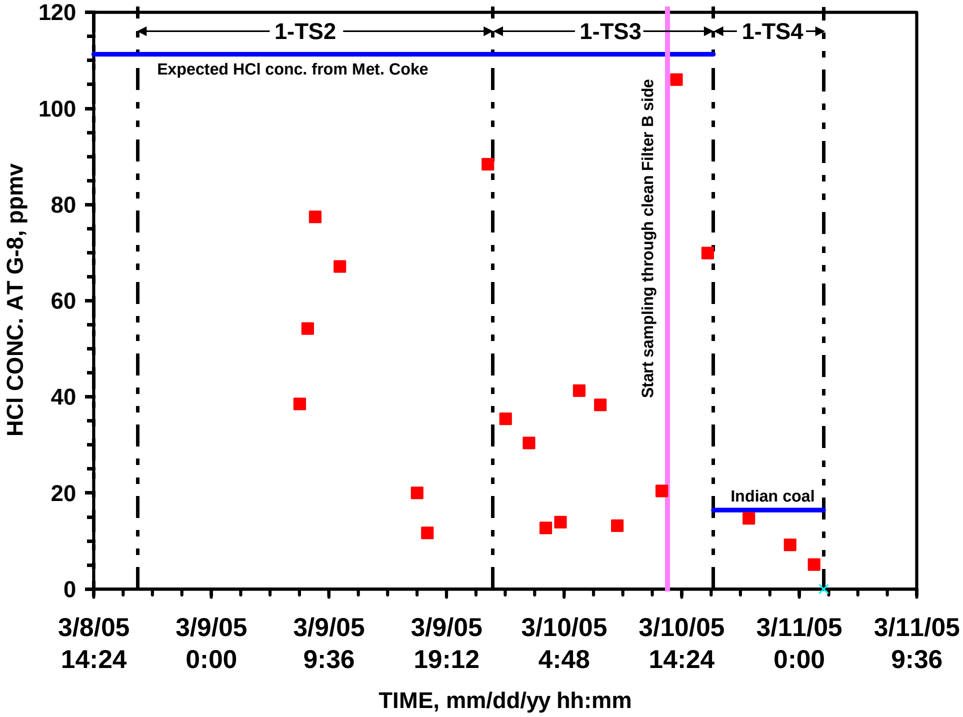

Figure 34 - Effect of Char on EPA Method 26 HCl Measurements When Switching from a Filter with Char (A Side) to a Cleaned Filter (B Side) on SE&C Skid #1

Prior to initiating trona injection, several HCl concentration measurements in the CF-R outlet syngas (i.e., at the G-13 sampling location) were made, to verify that the outlet HCl concentration was close to the inlet value. The highest HCl concentration measured was about 30 ppmv, before it was decided to proceed to the next test segment. It appeared some HCl removal was taking place in the CF-R vessel. This might be due to residual amounts of trona from pre-test sorbent feeder (T-2101) commissioning tests at pressure. Further evaluation of baseline results is required (particularly to determine whether any HCl is removed in the CF-R vessel by coke/coal char).

Figure 36 shows the measured HCl concentrations in the CF-R outlet syngas (i.e., at the G-13 sampling location) during trona injection (i.e., 1-TS3 test segment) as a function of test time and trona sorbent feed rate. Both time-averaged (batch) impinger measurements and on-line FT-IR analyses are shown. These measurements show good agreement and indicate that the HCl concentration slowly decreased during the trona injection test period. There appears to be a relationship between the trona feed rate and the HCl concentration in the CF-R product syngas: HCl concentration was further reduced as the trona feed rate was increased. The lowest HCl concentration in the CF-R outlet syngas was measured at 10.8 ppmv during trona injection (see sample ID # 051119-130 in Table 19). This represents about 90.3% HCl removal in the CF-R vessel.

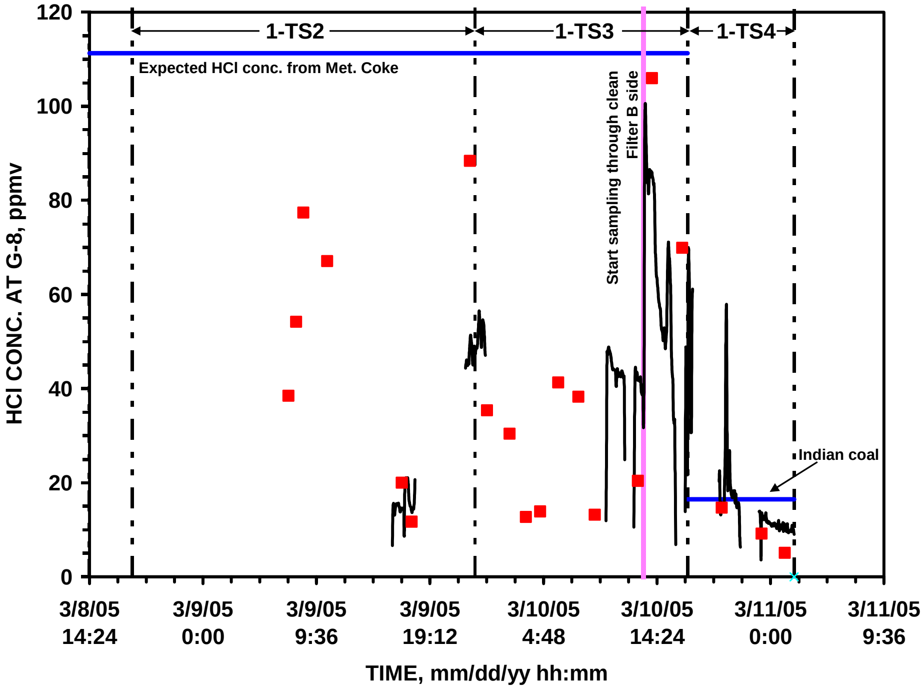

Figure 35 - Measured HCl Concentration in the Raw Syngas at Sampling Location G-8 (SE&C Skid #1)

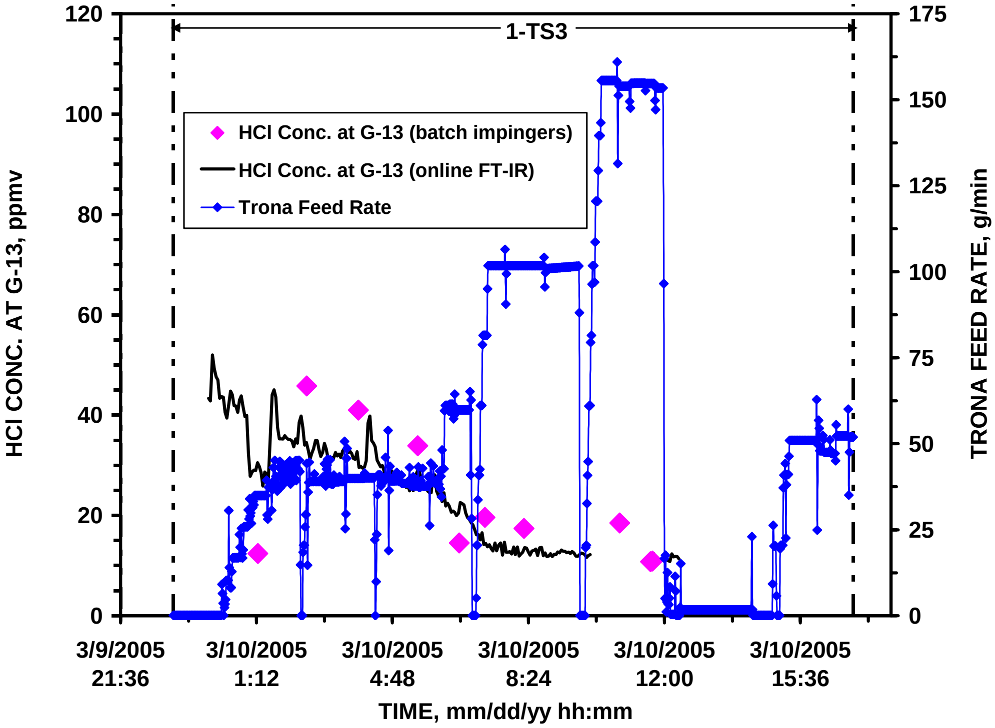

Figure 36 - Measured HCl Concentration in the CF-R Product Syngas at Sampling Location G-13 (SE&C Skid #2)

The trona feed rates shown in Figure 36 correspond to Na-to-Cl molar ratios (i.e., active sorbent component to contaminant) ranging from 5 to 30. These values are much higher than had been estimated in the Base Program (i.e., a Na-to-Cl molar ratio of 5 or less had been estimated to be sufficient to impart the desired HCl removal efficiency in the CF-R vessel). Several factors can cause this less than desired HCl removal performance. First, the temperature of the CF-R vessel (~ 800ºF or 427ºC) is lower than the optimum CF-R operating temperature of 932ºF (500ºC), which could have adversely affected the trona reactivity. Second, the water content of the raw syngas at the CF-R inlet (i.e., after the DSQ system) could have been too high leading to thermodynamic limitations. Third, the size distribution of the injected trona could be higher than desired, especially that, because metallurgical coke (much less reactive than coal) was used in this test campaign, the syngas flow rate was limited to about 1800 lbs/hr, which corresponds to a face velocity of about 2 ft/min (a face velocity > 3 ft/min was desired, as stated earlier).

A sample of the trona material used (Solvay T-200® sodium sesquicarbonate) was submitted for chemical and size distribution analyses to properly compare its performance with the results obtained in the Base Program with a naturally-occurring trona mineral from FMC in Green River, Wyoming. As shown in Table 16, the Solvay T-200® material assayed 31.6 Na compared to 35.6% for the FMC material used in the Base Program. This slight difference can be expected to lead to a lower effective capacity for the former material, but is not sufficiently significant to cause major reduction in performance. Similarly, although lower than the optimum temperature at which sorbent to contaminant ratios were estimated, the NGC-OPT1 operating temperature was not significantly lower than the lowest temperature investigated in the Base Program (i.e., 842ºF or 450ºC). At this lower temperature, trona was found to be more efficient in HCl removal (and at only slightly lower effective capacity) than was obtained at 500ºC. Therefore, neither the nature of the bulk dechlorination material used nor the operating temperature of the CF-R filter-reactor could be expected to significantly influence the results obtained.

The steam content of the partially-cooled raw syngas at the CF-R inlet (i.e., at G-8) was estimated to range from 30 to 35 vol%, based on online measurements by the TF-IR instrument. To examine equilibrium limitations in the CF-R filter-reactor vessel, the estimated raw syngas composition was equilibrated with the trona active dechlorination component (i.e., Na_2CO_3) in the temperature range from 482ºF (250ºC) to 1202ºF (650ºC) with the steam content varied between 0 and 40 vol%. The results are summarized in Figure 37 and clearly indicate the equilibrium HCl concentration in the CF-R product syngas should be below 1 ppmv and therefore no equilibrium limitations exist under the operating conditions of the CF-R filter-reactor vessel.

The particle size distribution of the as-received Solvay T-200® is shown in Figure 38. For comparison, the Filter A char sample size distribution was also determined, as shown in Figure 39. The volume moment mean diameter (i.e., mean diameter with respect to the mass of the particles) is about 13 μm and the median diameter, d(0.5), is about 8 μm for the char sample. The corresponding values for the bulk dechlorination material were significantly higher, 53.8 μm and 35.6 μm, respectively. It appears likely that a large portion (at least half) of the trona fed would not have deposited on the filter elements given the relatively large portion of large particles in the trona, and the low syngas velocity through the Conditioning Filter-Reactor.

Figure 40 displays both the HCl concentration in the CF-R product syngas, as measured by the online FT-IR instrument at the G-13 sampling location, and the Conditioning Filter-Reactor pressure drop. As indicated earlier, during the trona injection test segment pulsing events took place every about 2 ½ hours. During the initial stages of the 1-TS3 segment, pulsing appears to have caused spikes in the measured HCl concentration. It should be noted the measured HCl concentration was influenced by the char accumulating on the Mott filter in the SE&C Skid #1, and so these spikes would not correspond to the inlet HCl value. The data shown in Figure 40 suggest these spikes appear to have diminished (or even eliminated) as more trona was fed. This trend supports the above analysis indicating that perhaps only a small portion of the trona injected reached the CF-R filter elements. The HCl concentration spikes might have been eliminated once sufficient amounts of the very fine portions of trona accumulated on the candles.) Figure 41 shows a picture of the CF-R candles after completion of the first test campaign.

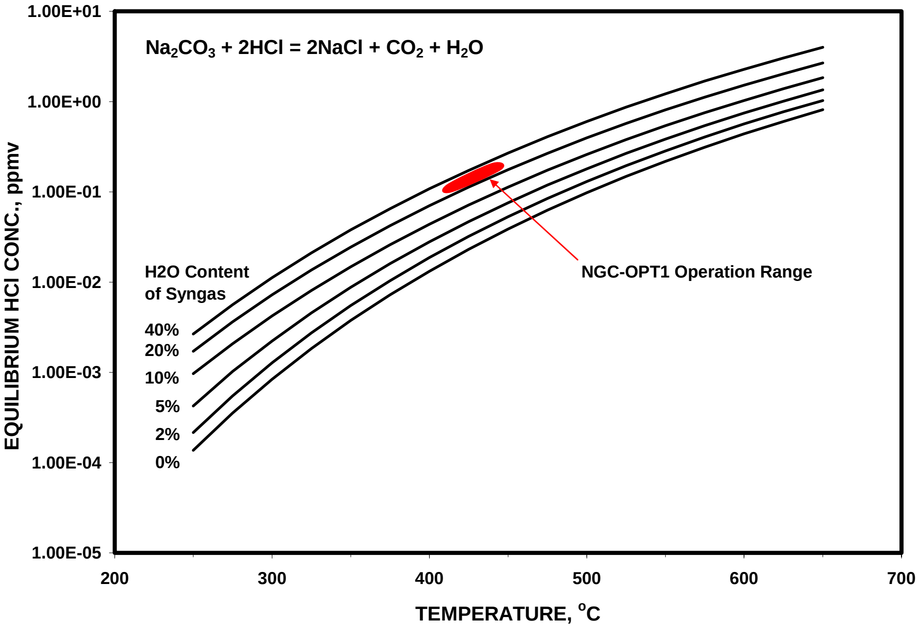

Figure 37 – Predicted Equilibrium HCl Concentration in the CF-R Product Syngas

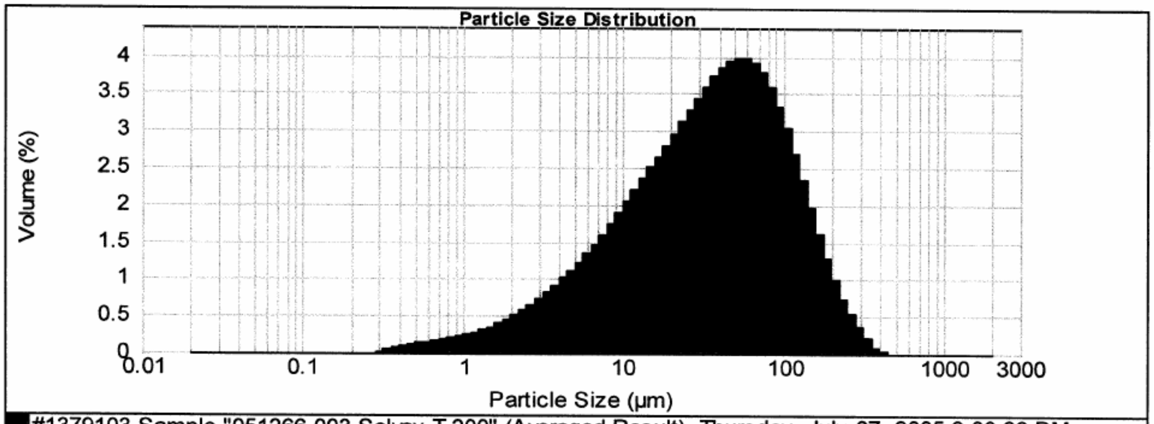

Figure 38 - Particle Size Distribution of the As-received Solvay T-200 Trona (Stage I Bulk Halide Sorbent)

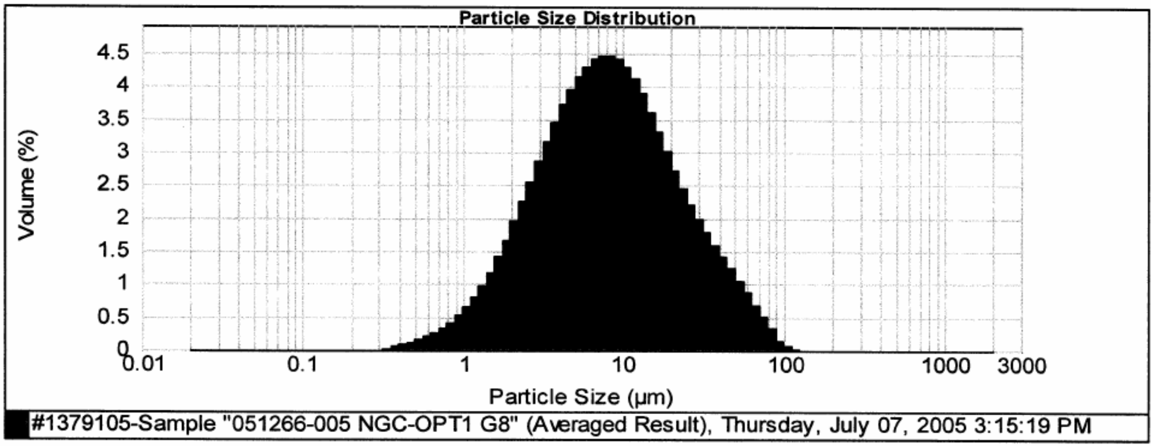

Figure 39 - Particle Size Distribution of the Syngas Ash Sample (Collected from Filter A on the SE&C Skid #1 at the G-8 Sampling Location)

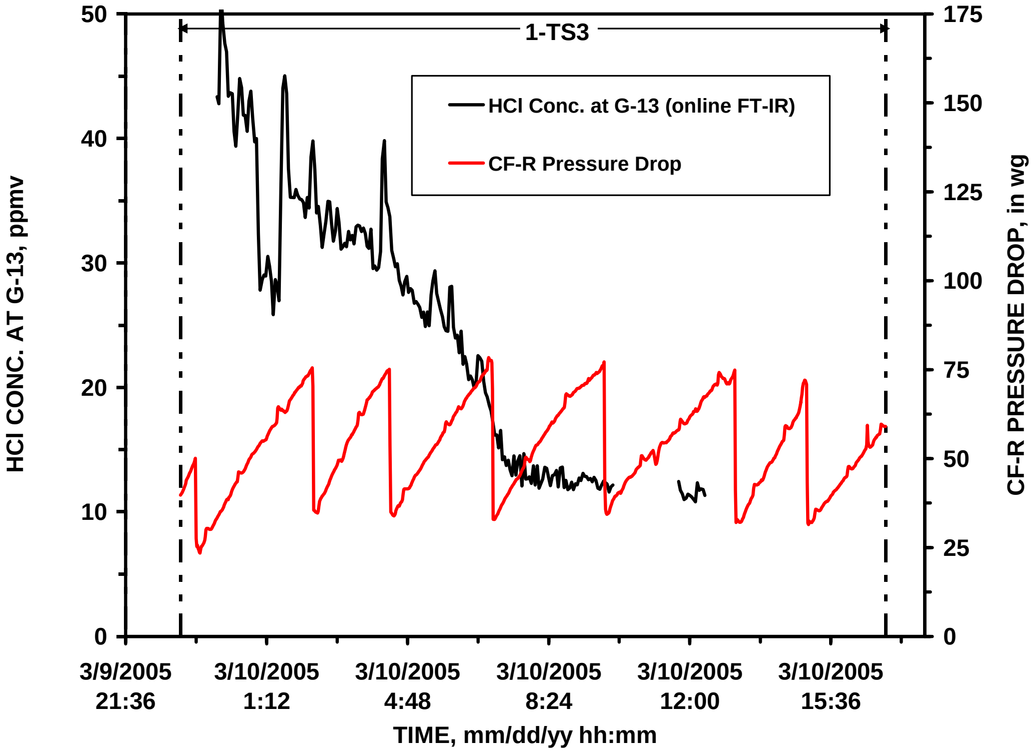

Figure 40 - Measured HCl Concentration in the CF-R Product Syngas and CF-R Pressure Drop during Trona Injection

Figure 41 – CF-R Candles (Post-Test)

Sulfur-Related Analytical Measurements

The results from the gas chromatography analyses of the “dry” gas samples collected at the G-8 (CF-R inlet) and G-13 (CF-R outlet) sampling locations are summarized in Table 20. These results include the raw syngas bulk composition (i.e., H_2, CO_2, N_2, CO, CH_4) and total sulfur (H_2S and COS) analyses.

The H_2S and COS measurements from the SE&C Skid #1 (dry sample) were evaluated. The metallurgical coke feed rate during the NGC-OPT1 test campaign varied between 336 and 350 lb/hr. The raw syngas (wet) flow rate was about 1850 lb/hr on the average (Table 18). The coke assayed 0.69% S. Assuming all coke sulfur is released during gasification, then the wet syngas would contain approximately 960 to 1,000 ppmv H_2S. Assuming 32.5% H_2O, the dry syngas sample might contain 1,422 to 1,482 ppmv. Coke conversion, however, was limited to < 50%. Therefore, it was possible to have 550 to 700 ppmv S as we measured (“grab” samples at G-8 by GTI CRS Lab, Table 20).

To confirm these estimates, selected samples from the T-502 vessel (S-5, Gasifier bottom ash) and the T-402 vessel (S-6, Secondary Cyclone fines) from samples taken between 04:00 and 17:20 on 3/9/2005 were analyzed for sulfur. During this test period, the total sulfur (H_2S + COS) concentration in the dried syngas sample at G-8, as determined by GTI’s CRS Lab, averaged ~ 660 ppmv, very close to the above estimate based on the coke sulfur content, operating conditions, carbon conversion, etc. The selected S-5 samples assayed 0.51% S. The selected S-6 samples assayed 0.56% S. Based on material balance considerations, the syngas H_2S content was estimated to range from 500 to 650 ppmv. These analyses confirmed that the total sulfur released in the product gas correlated very well with coke conversion, and provided additional validation of our sampling and GC measurements.

Semi-continuous total sulfur (H_2S and COS) measurements using the HP 5890 GC with flame photometric detector (FPD) at the G-13 location (CF-R outlet) showed that COS concentration in the syngas was affected when trona was being injected. COS concentration decreased from the baseline level of about 65 ppmv to about 20 ppmv during trona injection. As shown in Figure 42, the COS level in the presence of trona was insensitive to the trona feed rate over the range from 40 to 150 g/min. This GC, with 15-minute cycle time, performed very well following transients on the time scale of the NGC Process. Results of sulfur measurements on batch samples corroborate this interesting observation, as can be seen in Table 20.

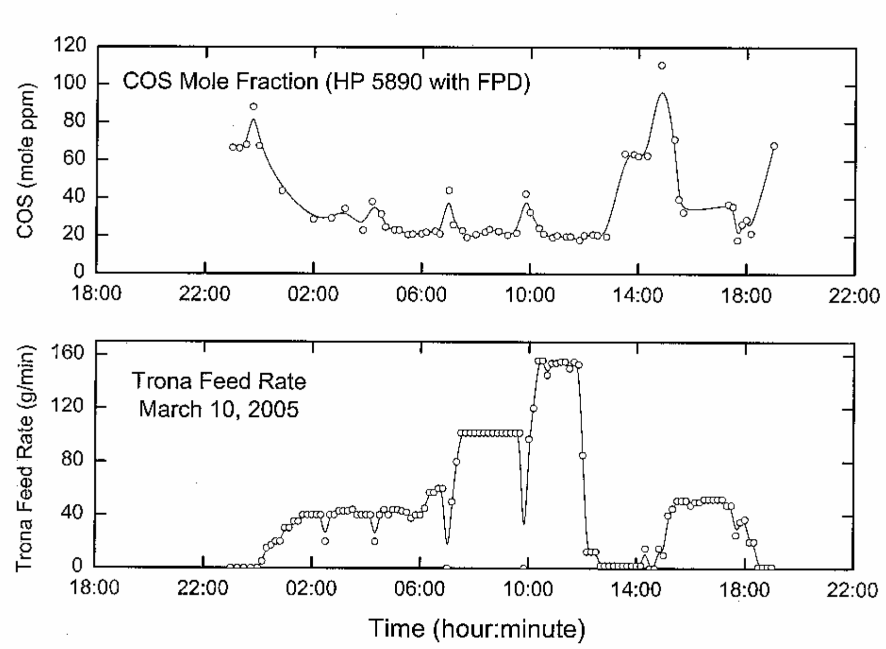

Figure 42 - Relationship between Trona Feed Rate and COS Concentration in the CF-R Outlet Syngas (Analysis by Prof. Peter Walsh, UAB)

During the NGC-OPT1 test campaign, some modifications were made to the SE&C Skid #2 (G-13). The original plan (see Figure 20) included maintaining the process gas at about 800ºF as it passed through the Mott filter, and then reducing its temperature to just above 400ºF in a heat traced heat exchanger with N_2 as the cooling medium. Tar from the syngas sample would be removed in a knockout pot below the heat exchanger. A grab sample would then be taken in a Silcosteel®-coated sample cylinder, in a similar arrangement to the SE&C Skid #1 (Figure 19), although this sample would contain steam. The canister is, however, not heated, and steam would later condense out in the cylinder. Pressure is reduced to about 40 psi before the gas goes through a Nafion dryer to perform warm temperature drying (presumably without affecting HCl). One sample of the dried gas is then sent to a GC and another (following further pressure reduction) to a set of impingers for HCl removal. Results from measurements with this approach are shown in Figure 43. The shaded region in Figure 43 covers sample results that were compromised by the condensation of water in the sample canisters. Laboratory analyses of H_2S were erratic when liquid water from the samples was trapped in the GC sample column. However, excluding the compromised data, the results show a level of H_2S in the process syngas that provides a good material balance for sulfur from the fuel and the unspent carbon in the gasification process, as discussed earlier.

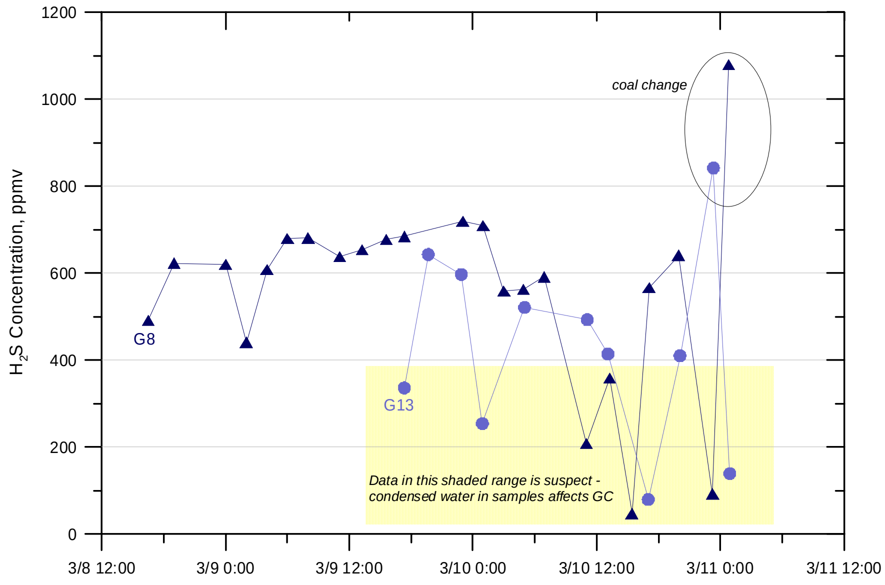

Figure 43 - Laboratory H_2S Measurements from Sample Cylinders Collected at the SE&C Skids #1 and #2

The SE&C Skid #2 was modified significantly to deliberately condense the water from the process syngas by using cold water to chill the process gas to below laboratory temperatures. The "Hot Sample Line for Multiple Instrument Analysis" (Figure 20) was relocated upstream of the Mott filter. This hot line, which extends all the way into the Flex-Fuel second floor analytical station, was also used for providing samples to the sulfur GCs as well as the set of HCl impingers. Based on the sulfur analyses ("grab" samples) at the G-13 location, additional modifications to the SE&C Skid #2 were necessary for the NGC-OPT2 campaign to eliminate any water from the grab sample, which appears to be physically interfering with the GC measurements. The temperature controller on the heat exchanger was turned off and water (rather than nitrogen) was used as the cooling medium to control temperature to < 40ºF, similar to the SE&C Skid #1. Similar modifications were also made to the SE&C Skid #3 at the G-19 location (ultra-clean syngas).

Table 20 - Summary of Batch Sample Gas Analyses during the NGC-OPT1 Test Campaign

Ref	Lab Sample ID	Sample Point	Date	Time	Test Segment	H2	CO2	O2/Ar	N2	CO	CH4	Ethane	Ethene	H2S	COS
1	051119-010	G8	3/8/2005	16:30	1-TS1	5.5%	15.1%	0.81%	71.9%	6.48%	0.197%			492	108
2	051119-014	G8	3/8/2005	19:00	1-TS2	5.9%	14.4%	0.77%	71.8%	6.81%	0.213%			623	80
3	051119-029	G8	3/9/2005	0:00	1-TS2	5.6%	14.0%	0.74%	73.4%	6.07%	0.190%			620	74
4	051119-035	G8	3/9/2005	2:00	1-TS2	5.5%	14.2%	0.75%	73.6%	5.72%	0.190%			441	81
5	051119-044	G8	3/9/2005	4:00	1-TS2	5.2%	14.4%	0.75%	74.4%	5.02%	0.189%			608	65
6	051119-053	G8	3/9/2005	6:00	1-TS2	5.2%	14.4%	0.75%	74.5%	4.95%	0.193%			680	62
7	051119-056	G8	3/9/2005	8:00	1-TS2	5.1%	14.5%	0.75%	74.6%	4.81%	0.199%			681	58
8	051119-059	G8	3/9/2005	11:05	1-TS2	5.3%	14.5%	0.75%	74.2%	5.01%	0.195%			638	60
9	051119-070	G8	3/9/2005	13:15	1-TS2	5.5%	14.3%	0.75%	73.5%	5.61%	0.199%			654	65
10	051119-074	G8	3/9/2005	15:35	1-TS2	5.7%	14.3%	0.75%	73.0%	6.07%	0.202%			678	69
11	051119-075	G8	3/9/2005	17:20	1-TS2	5.9%	14.2%	0.75%	72.5%	6.43%	0.203%			685	69
12	051119-076	G13	3/9/2005	17:20	1-TS2	5.7%	13.8%	0.73%	73.0%	6.49%	0.199%			336	36
13	051119-082	G13	3/9/2005	19:40	1-TS2	5.5%	13.4%	0.72%	73.8%	6.32%	0.195%			643	34
14	051119-091	G13	3/9/2005	22:50	1-TS2	5.4%	13.9%	0.73%	73.9%	5.70%	0.208%			597	40
15	051119-092	G8	3/9/2005	23:00	1-TS2	5.7%	14.4%	0.74%	73.5%	5.29%	0.223%			719	60
16	051119-095	G8	3/10/2005	1:00	1-TS3	5.8%	14.2%	0.74%	73.1%	5.88%	0.213%			709	63
17	051119-096	G13	3/10/2005	0:55	1-TS3	5.2%	13.3%	0.70%	75.2%	5.44%	0.198%			254	32
18	051119-103	G13	3/10/2005	2:55	1-TS3	5.2%	12.9%	0.69%	75.3%	5.77%	0.193%			N/m	15
19	051119-104	G8	3/10/2005	3:00	1-TS3	5.9%	14.1%	0.74%	72.7%	6.32%	0.214%			559	65
20	051119-109	G8	3/10/2005	4:55	1-TS3	6.2%	13.9%	0.73%	72.3%	6.54%	0.223%			563	70
21	051119-110	G13	3/10/2005	5:00	1-TS3	5.5%	12.8%	0.69%	74.6%	6.12%	0.202%			521	16
22	051119-116	G8	3/10/2005	6:55	1-TS3	6.2%	13.7%	0.73%	72.1%	6.95%	0.221%			592	67
23	051119-117	G13	3/10/2005	7:00	1-TS3	5.6%	12.6%	0.68%	74.5%	6.47%	0.202%			N/m	N/m
24	051119-120	G13	3/10/2005	9:20	1-TS3	5.3%	12.7%	0.68%	75.0%	6.13%	0.199%			M/m	N/m
25	051119-126	G8	3/10/2005	11:00	1-TS3	5.9%	13.8%	0.73%	72.9%	6.41%	0.203%			208	58
26	051119-127	G13	3/10/2005	11:05	1-TS3	5.3%	12.7%	0.69%	74.9%	6.08%	0.193%			493	14
27	051119-133	G13	3/10/2005	13:05	1-TS3	5.3%	12.6%	0.69%	74.9%	6.22%	0.186%			414	12
28	051119-134	G8	3/10/2005	13:15	1-TS3	5.8%	13.8%	0.73%	73.1%	6.39%	0.198%			359	59
29	051119-141	G13	3/10/2005	15:20	1-TS3	4.9%	13.6%	0.72%	75.5%	5.18%	0.186%			N/m	51
30	051119-142	G8	3/10/2005	15:25	1-TS3	5.2%	14.3%	0.74%	74.3%	5.30%	0.194%			47	59
31	051119-144	G13	3/10/2005	17:00	1-TS3	4.8%	13.1%	0.70%	76.0%	5.21%	0.184%			79	18
32	051119-145	G8	3/10/2005	17:05	1-TS4	5.4%	14.2%	0.74%	73.9%	5.54%	0.201%			567	63
33	051119-161	G8	3/10/2005	19:55	1-TS4	5.4%	14.1%	0.75%	73.9%	5.53%	0.197%			641	65
34	051119-162	G13	3/10/2005	20:05	1-TS4	9.2%	13.4%	0.71%	67.6%	7.44%	1.559%			410	23
35	051119-170	G8	3/10/2005	23:15	1-TS4	9.9%	12.9%	0.72%	65.8%	8.68%	1.934%	0.003%	0.004%	92	54
36	051119-171	G13	3/10/2005	23:20	1-TS4	9.8%	12.8%	0.71%	65.8%	8.79%	1.939%	0.002%	0.004%	842	24
37	051119-176	G8	3/11/2005	0:50	1-TS4	9.8%	12.8%	0.71%	65.8%	8.84%	1.822%	0.002%	0.003%	1080	56
38	051119-177	G13	3/11/2005	0:55	1-TS4	9.7%	12.6%	0.72%	66.1%	8.97%	1.822%	0.002%	0.003%	139	25

11. NOVEL GAS CLEANING OPTIONAL PROGRAM TEST CAMPAIGN #2 (NGC-OPT2)

The second test campaign, NGC-OPT2, was performed as two separate campaigns, requiring two gasifier start-up periods in two different weeks (week of March 21 and week of March 28). Because of slight differences in gasification and NGC Process sections operating conditions, this test is treated as two separate tests, NGC-OPT2A and NGC-OPT2B.

11.1 Objectives

The primary objective of the NGC-OPT2 was to evaluate the performance of the Test Filter-Reactor (TF-R) for sulfur (H_2S and COS) and halide (HCl) removal (individually and simultaneously) to very stringent levels from syngas derived from the gasification of a carbonaceous feedstock. The Conditioning Filter-Reactor (CF-R) is to be operated under optimum operating conditions (830ºF, 1-10 pulse cleaning frequency, and trona injected at optimum Na-to-Cl ratio when it is necessary to control HCl levels in the CF-R outlet). This was accomplished through a series of test segments, which were designed to:

1. set the Flex-Fuel gasifier operating conditions for producing syngas from the test feedstock (washed Indian coal) at 300 psig pressure, preferably with a syngas flow rate at the secondary cyclone exit of at least 3,300 lb/hr.
2. determine the operating conditions for the entire NGC Process "Conditioning" section to consistently result in a syngas with the target characteristics at the TF-R inlet: 1-5 ppmv total sulfur (H_2S + COS), 1-5 ppmv halide (HCl), ~ < 0.1 ppmw particulate content, a temperature of 600 to 650ºF (316 to 343ºC), a pressure of ~ 200 psig, and a flow rate equivalent to a face velocity of at least 3 ft/min. The "Conditioning" section includes the Direct Spray Water Quench (DSQ) system for partial cooling of the raw syngas, the CF-R (including pulsing) vessel for particulate control, the Sorbent (Trona) Injection system for bulk HCl removal, a Sulfur Guard Bed (and associated pre-heater and slipstream syngas by-pass) for total sulfur control within the desired range at the TF-R inlet, and a Trim Cooler (indirect heat exchanger) for temperature control.
3. operate the TF-R to confirm the feasibility of removing total reduced sulfur compounds (H_2S and COS) and halide (mainly HCl) to < 60 ppbv and to < 10 ppbv, respectively, via selected dry, fine sorbent injection into the "conditioned" syngas upstream of the TF-R vessel. The key TF-R operating parameters include sorbent-to-contaminant ratio (i.e., sorbent feed rate), temperature, and pressure (i.e., face velocity).
4. confirm the effectiveness of "conventional" syngas Sample Extraction & Conditioning (SE&C) systems at Sample Points G-8 (CF-R inlet), G-13 (CF-R outlet), G-14 (conditioned syngas), and G-19 (ultra-cleaned syngas) with contaminant concentrations ranging from pp<u>m</u>v to pp<u>b</u>v levels.
5. provide "cold" and "hot/warm" slipstream samples from G-8, G-13, G-14, and G-19 for comprehensive, continuous, sensitive, and accurate measurements by personnel from the GTI Birmingham Office, as part of their project scope to develop an analytical suite as a key enabling technology for gasification systems integration.

11.2 Process Flow Diagram for NGC-OPT2

For this test series in the Flex-Fuel Test Facility (FFTF), the syngas was directed through the entire NGC Process section (Figure 6), which includes a "Conditioning" section and a "Test" section.

Syngas from the Secondary Cyclone (CY-401) is partially cooled in the DSQ system (HE-2001A) and then flows to the T-2153 CF-R. After passing through the filter elements or candles in the CF-R vessel, the syngas is initially routed through the Pressure Let-Down station (PIC-602) to the Tertiary Cyclone (CY-601) and finally to the Flare (FL-601). During the Heat-Up period, after the Sulfur Guard Bed (R-2002) has been heated, the process gas flow is lined up from the T-2153 CF-R vessel through the Sulfur Guard Bed, the PCV-2006 pressure control valve, and the PIC-2181 pressure let-down valve to the Tertiary Cyclone (CY-601) and the Flare (FL-601). The T-2147 Test Filter-Reactor is bypassed, until the desired conditions are achieved in the "Conditioning" section of the NGC Process. After pulsing cycles are established with the nitrogen blow-back system on the T-2153 CF-R vessel, when it is necessary to control the HCl level in the CF-R outlet, trona (or nahcolite as an alternative halide sorbent), can be injected into the syngas stream, immediately before entering the T-2153 CF-R vessel, through the T-2101 Sorbent Injection system. The latter combines a loss-in-weight solids feeder with dilute-phase flow in nitrogen to convey the sorbent into the syngas.

Representative samples of the syngas are extracted, conditioned (de-dusted, cooled, and de-pressured), and analyzed with suitable instruments at two main locations:

- G-8: Partially-cooled raw syngas (between DSQ and CF-R)
- G-13: Partially-conditioned T-2153 CF-R product syngas (essentially dust-free, dechlorinated to 1-5 ppmv HCl, but still containing all the raw syngas sulfur).

As indicated above, the "Conditioning" section also comprises a Sulfur Guard Bed (SGB) and a Trim Cooler (indirect heat exchanger) for bulk sulfur removal and temperature reduction of the CF-R product gas to meet the requirements of the inlet syngas to the "Test" section. Once conditioned, the syngas stream is then introduced into the TF-R vessel for additional deep cleaning via selected dry, fine sorbents that are injected separately into the syngas immediately upstream of the TF-R vessel. Representative samples of the syngas are extracted, conditioned (de-dusted, cooled, and de-pressured), and analyzed with suitable instruments at two additional locations:

- G-14: Conditioned syngas (TF-R inlet)
- G-19: Ultra-cleaned syngas (TF-R outlet)

Other analytical work is also be performed on various samples to estimate CF-R particulate leakage (at S-13C), to characterize gasifier performance and efficiency in generating syngas from the test feedstock, to characterize process emissions for permitting activities, and to assess disposal options for the gasification and syngas cleanup byproduct materials. As shown in Figure 17, process samples include fuel feedstock, ash, dust, raw syngas, fresh sorbent materials, spent sorbents, and condensed liquids, in addition to several gas samples throughout the NGC Process section.

11.3 Run Sequence / Chronology

During the NGC-OPT2 campaign, the following sequence was followed to accomplish test objectives:

1. Conduct normal pressure testing to check for leaks throughout the Gasification and NGC Process "Conditioning" and "Test" sections.
    - 1.1. Gasifier pressure at 300 psig by PIC-2003; NGC Process "Test" section at 200 psig by PIC-2181
    - 1.2. Simulate / Practice: Cutting from T-2153 only into R-2002 etc. at 300 psig, By-passing T-2147 HSV-2047/HSV-2048
        - 1.2.1. Cutting from T-2153 only into R-2002 etc. while gasifying at 300 psig
        - 1.2.2. Cutting into T-2147 at 200 psig from by-pass mode, with HSV-2047/HSV-2049 system
2. Commission "Test" section Sorbent Feeders
    - 2.1. Establish N_2 flow rate versus differential pressure relationship for T-2107
    - 2.2. With injection N_2 at 15 scfm (FI-2107), verify ground, dried G-72E feeding at 3 g/min for WI-2107 (Stage II sulfur sorbent feeder)

2.3. Establish N_2 flow rate versus differential pressure relationship for T-2108
2.4. With injection N_2 at 15 scfm (FI-2108), verify G-92C (or alternative sorbent/sorbent combination) feeding at 20 g/min for WI-2108 (Stage II halide sorbent feeder)

3. Verify SE&C skid viability at the G-8, G-13, G-14, and G-19 locations via spike-and-recovery methods (several HCl and S standards are available: 30 ppmv HCl/N_2, 3 ppmv HCl/N_2, 0.5 ppmv HCl/N_2, 1200 ppmv H_2S/N_2, 0.5 ppmv H_2S/N_2). Impinger samples and analyzers. [Note: This is a major effort, and will need to be repeated during the test program to assure chemical stability and integrity of sampling systems.]

4. Heat up Gasification section and NGC Process "Conditioning" <u>and</u> "Test" sections
   4.1. Initiate pre-heating of Sulfur Guard Bed vessel (R-2002) with SH-2002 and LP nitrogen (up to 500°F)
      4.1.1. Heat-up gas to be routed through HE-2071 Bypass / T-2147 / PCV-2181 (Open 100%)
   4.2. Route Start-up Heater (SH-301) Flue Gas through HE-2001A initially, bypassing T-2153 and remainder of NGC Process section.
   4.3. When R-2002 temperature reaches 400°F, initiate heat up of gasifier with SH-301
   4.4. When SH-301 reaches Hi-Fire, route Flue Gas through T-2153 and remainder of NGC Process "Conditioning" section (everything except T-2147 TF-R vessel)

5. Calibrate Rosemount analyzer at the G-8 location (SE&C Skid #1); put it on line.

6. Initiate second stage of heat up with metallurgical coke (Bethlehem Coke Breeze)
   6.1. Pressurize gasifier to 50 psig

7. Establish gasification with washed Indian coal
   7.1. Switch feed from metallurgical coke to washed Indian coal
   7.2. Establish gasifier bed level
   7.3. Increase gasifier pressure in stages to 200 psig, with PIC-602 system. Increase gasifier pressure in stages from 200 psig to 300 psig, with PIC-2006 system
   7.4. Adjust Gasifier operating parameters to achieve target gasifier pressure (300 psig) and target syngas flowrate (>3,300 lb/hr) – operate gasifier at less than optimum carbon conversion to ensure long, uninterrupted operating durations for gasifier and the continuous generation of a suitable raw syngas for the NGC Process section for cleaning.

8. Establish preferred CF-R operating conditions (inlet temperature, outlet temperature)
   8.1. Observe pressure-drop increase on the T-2153 CF-R vessel and adjust pulsing as needed to give consistent "clean" differential pressure for filter candles
   8.2. Establish preferred conditions for CF-R pulsing frequency in the 1-10 range to handle dust loading from the washed Indian coal feedstock.
   8.3. Fine-tune pulsing on the T-2153 CF-R vessel to achieve cleaning at minimal nitrogen use
   8.4. Pulsing of the T-2153 filter with the fast-acting valves
   8.5. Pressure of Blow-Back system nitrogen in T-2304 Accumulator: starting point ~ twice process pressure (i.e., 400 to 450 psig)
   8.6. Length of pulsing time with fast-acting valves: 0.2 to 0.3 sec
   8.7. Note: An optimum temperature for the SGB is in the range 675 to 700ºF (this should be a consideration in the operation of the CF-R; given that no HCl removal via trona injection is to be performed in this test, we have some flexibility to reduce the CF-R outlet temperature, if necessary, to match the desired SGB inlet temperature)

9. When reasonable syngas delivery conditions have been established, continue operating with washed Indian coal at "steady-state" conditions to verify/establish the following:

9.1. Measure HCl and total sulfur (H_2S & COS) levels in the raw syngas (at G-8) and establish their variability (Note: HCl impinger measurements will require a clean Mott filter on SE&C Skid #1).

9.1.1. Monitor raw gas composition at G-8 with mass spectrometer and GC/FPD/TCD. With G-13 hot-gas sample line to FT-IR inlet, monitor HCl concentration during pulsing on T-2153 to determine if nitrogen pulse affects measurement (can this be used to assess char contribution to HCl removal?).

9.2. Measure HCl levels with FT-IR and total sulfur (H_2S & COS) in the raw syngas and CF-R product syngas (at G-8 and G-13)

9.2.1. Throughout above test periods, monitor temperatures at the SGB inlet, SGB outlet, TC (Trim Cooler) inlet, TC outlet. Also, monitor syngas flow rate (FI-2005), quench temperature (TI-2022), etc.

9.3. If syngas temperature from T-2071 is too high, divert some syngas through HE-2071

9.3.1. Initiate CWS through HE-2071 (Open Min Flow Bypass)
9.3.2. Put TIC-2071 in Auto for 550°F
9.3.3. Monitor CWR from HE-2071, to assure TI-2073 on CWR is less than 180°F
9.3.4. With TIC-2006 in Manual, adjust process bypass around HE-2071 to give 600-650°F inlet to NGC Process "Test" section (TI-2073)

10. When preferred "Conditioning" section operating parameters are satisfied as described above:

10.1. Establish syngas flow through T-2147 and establish process conditions for sorbent testing

10.1.1. Check pressure on T-2147 -- should be 200 psig by back-pressuring
10.1.2. Gradually open HSV-2047 and close HSV-2048, to establish syngas flow through T-2147 to PCV-2181

10.2. Set conditions for sorbent testing

10.2.1. Allow TF-R vessel to heat up (and achieve desired TF-R outlet temperature of ~ 550ºF)
10.2.2. Face velocity in T-2147 at Min of 3 ft/min (syngas rate at approx 3800 lb/hr

10.3. Continue to operate NGC "Conditioning" section under optimum conditions to ensure TF-R desired inlet conditions for long, uninterrupted testing durations

<u>Test Filter-Reactor</u>

Inlet temperature (°F):	600 to 650ºF (after sorbent injection)
Outlet temperature (°F):	~ 550ºF
Inlet gas flow (acfm):	> 123
Face velocity (ft/min):	> 3
Inlet Total Sulfur (ppmv):	1-5

10.3.1. Make frequent H_2S (and COS) measurements, using online FPD GC.
10.3.2. If H_2S level too low, open Slipstream Bypass (FCV-2012) incrementally to give 1-5 ppmv H_2S

10.4. Prepare to start operating the Stage II Halide Sorbent Feeder (T-2108) for deep HCl removal in the TF-R

10.4.1. Set Transport Nitrogen rate (as controlled by differential pressure) required for adequate conveying of the fine G-92C sorbent into the "conditioned" process syngas
10.4.2. Start with ~ 50 ft/sec injection velocity (15 scfm nitrogen rate (for 200 psig)), yielding approximately 30 in-H_2O differential pressure.

10.4.3. Pre-coat filter candles with G-92C sorbent fines; feed G-92C in combination with nahcolite (50/50 mix by weight) at maximum feeding rate (about 100 g/min)

10.4.4. Reduce the Stage II halide sorbent (G-92C) injection rate to correspond to the maximum rate of Na/Cl=10 based on the syngas HCl content at G-14

G-92C (Süd-Chemie):	Chemical formula: Na_2O supported on Al_2O_3
	Chemical analysis: 6.41% Na, 39.6% Al
	Approx. formula: 0.256 Na_2O•0.744 Al_2O_3
	Bulk density: 45 lbs/cu ft (for 3/16-inch extrudates)
	Size distribution: ground at GTI to -325 mesh

$$\boxed{\text{G-92C Injection Rate (grams/min)} = [(453.6)*(91.73)/[(0.512)*(60)*(10\^{}6)]] * [[HCl]_o*Q_m/MW_{sg}] * R_{Cl}}$$

- $[HCl]_o$ = Measured HCl concentration in conditioned syngas (at G-14), ppmv
- Q_c = Conditioned syngas, lbs/hr
- MW_{sg} = Molecular weight of conditioned syngas, lb/lb-mole
- R_{Cl} = Na to Cl molar ratio

Example: Raw syngas at 3,300 lbs/hr with an average MW of 25 and containing about 5 ppmv HCl, the G-92C sorbent injection required for a Na/Cl ratio of 10 is ~ 8.9 g/min.

10.4.5. While allowing the system to stabilize (i.e., a somewhat constant fly ash/trona mixture composition of the filter cake), continue to measure total sulfur (H_2S + COS) concentration and HCl levels with impingers in the TF-R inlet and outlet syngas (G-14 and G-19).

10.4.6. Monitor TF-R outlet gas composition at G-19 with GC/FPD/TCD/PFPD.

10.4.7. Attach G-19 hot-gas sample line to FT-IR inlet to monitor HCl concentrations.

10.4.8. If the TF-R product syngas HCl content (i.e., at G-19) is < 10 ppbv, continue operating at Na/Cl=10 for six (6) hours, which should result in at least 4-6 consistent samples. Note: If we do not achieve < 10 ppbv at G-19 with Na/Cl=10, then consider operating TF-R at a higher temperature or at a lower pressure (to increase face velocity)

10.4.9. Transition to a lower sorbent injection rate (i.e., Na/Cl=5) and measure effect of lower sorbent rate on HCl concentration in syngas with impingers at G-19 (3-4 hours or about 3 consistent samples).

10.4.10.Attach G-19 hot-gas sample line to FT-IR inlet to monitor HCl concentrations. Continue to monitor HCl concentration at G-14 (using FT-IR and/or impingers) and at G-19 (using impingers).

10.4.11.Shut off Stage II halide sorbent injection and Transport Nitrogen; allow system to stabilize (pulse clean manually to accelerate sorbent removal) and measure HCl in syngas with impingers at G-14 and G-19 (3 hours or 3 consistent samples)

10.5. Prepare to start operating the Stage II Sulfur Sorbent Feeder (T-2107) for deep sulfur removal in the TF-R

10.5.1. Set Transport Nitrogen rate (as controlled by differential pressure) required for adequate conveying of the fine G-72E sorbent into the “conditioned” process syngas

10.5.2. Start with ~ 50 ft/sec injection velocity (15 scfm (for 200 psig) nitrogen rate), yielding approximately 60 in-H_2O differential pressure.

10.5.3. Pre-coat filter candles with G-72E sorbent fines; feed G-72E at maximum feeding rate (about 20 g/min, WI-2107)

10.5.4. Reduce the Stage II sulfur sorbent (G-72E) injection rate to correspond to the maximum rate of Zn/S=10 based on the syngas total sulfur (H_2S + COS) content at G-14

G-72E (Süd-Chemie):	Chemical formula: ZnO supported on $CaAl_2O_4$
	Chemical analysis: 4.18% Al, 1.17% Ca, 69.8% Zn
	Approx. Formula: 0.928 ZnO•0.072 $CaAl_2O_4$
	Bulk density: 78 lb/cu ft (for 3/16-inch extrudates)
	Size distribution: ground at GTI to -325 mesh

G-72E Injection Rate (grams/min) = $[(453.6)*(86.9)/[(0.928)*(60)*(10^6)]] * [[S]_o*Q_c/MW_{sg}] * R_S$

- $[S]_o$ = Measured total sulfur (H_2S + COS) concentration in conditioned syngas (at G-14), ppmv
- Q_c = Conditioned syngas, lb/hr
- MW_{sg} = Molecular weight of conditioned syngas, lbs/lb-mole
- R_S = Zn-to-S molar ratio

Example: Raw syngas at 3,300 lbs/hr with an average MW of 25 and containing about 5 ppmv total S (H_2S & COS), the G-72E sorbent injection required for a Zn/S ratio of 10 is ~ 4.7 g/min.

10.5.5. While allowing the system to stabilize (i.e., a somewhat constant ash/sorbent mixture composition of the filter cake), continue to measure total sulfur (H_2S + COS) concentration and HCl levels with impingers in the TF-R inlet and outlet syngas (G-14 and G-19).

10.5.6. Monitor TF-R outlet gas composition at G-19 with GC/FPD/TCD/PFPD.

10.5.7. Attach G-14 hot-gas sample line to FT-IR inlet to monitor HCl concentrations.

10.5.8. If the TF-R product syngas total S (H_2S & COS) content (i.e., at G-19) is < 60 ppbv, continue operating at Zn/S=10 for six (6) hours, which should result in at least 4-6 consistent samples. Note: If we do not achieve < 60 ppbv at G-19 with Zn/S=10, then we will consider other measures in consultation with Siemens (Dr. Newby) (operating at a higher temperature or at lower pressure (e.g., 100 psig) to increase face velocity)

10.5.9. Transition to a lower sorbent injection rate (i.e., Zn/S=5) and measure effect of lower sorbent rate on total S in syngas with PFPD GC and "grab" gas samples at G-19 (3-4 hours or about 3 consistent samples).

10.5.10. Attach G-19 hot-gas sample line to FT-IR inlet to monitor HCl concentrations. HCl sampling with impingers at both G-14 and G-19.

10.5.11.Shut off Stage II sulfur sorbent injection and Transport Nitrogen; allow system to stabilize (pulse clean manually to accelerate sorbent removal) and measure total S in syngas with PFPD and "grab" samples at G-14 and G-19 (3 hours or 3 consistent samples)

10.6. Prepare to start operating both the Stage II Sulfur and Halide Sorbent Feeders (T-2107 & T-2108) for simultaneous deep removal of total S (H_2S & COS) and HCl in the TF-R

10.6.1. Set Transport Nitrogen rate (as controlled by differential pressure) required for adequate conveying of the fine G-72E and G-92C sorbents into the "conditioned" process syngas

10.6.2. Start with ~ 50 ft/sec injection velocity (15 scfm nitrogen rate), yielding approximately 60 in-H_2O differential pressure.

10.6.3. Pre-coat filter candles with G-72E and G-92C sorbent fines; feed both G-72E and G-92C at maximum feeding rates

10.6.4. Reduce the Stage II sulfur and halide sorbents (G-72E and G-92C) injection rates to correspond to the maximum rates of Zn/S= 10 and Na/Cl=10 based on the syngas total S and HCl contents at G-14

10.6.5. While allowing the system to stabilize (i.e., a somewhat constant fly ash/sorbent mixture composition of the filter cake), continue to measure total sulfur (H_2S + COS) concentration and HCl levels with impingers in the TF-R inlet and outlet syngas (G-14 and G-19).

10.6.6. Monitor TF-R outlet gas composition at G-19 with GC/FPD/TCD/PFPD.

10.6.7. If the TF-R product syngas (i.e., at G-19) total S content is < 60 ppbv and the HCl content is < 10 ppbv, continue operating at Zn/S=10 and Na/Cl=10 for six (6) hours, which should result in at least 4-6 consistent samples. Note: If we do not achieve < 10 ppbv HCl at G-19 with Na/Cl=10, then consider changing TF-R operating temperature or pressure (lower pressure to increase face velocity.)

10.6.8. Transition to lower sorbent injection rates (i.e., Zn/S=5 and Na/Cl=5) and measure effect of lower sorbent rates on total S and HCl concentrations in syngas with impingers and PFPD GC at G-19 (3-4 hours or about 3 consistent samples).

10.6.9. Shut off Stage II halide and sulfur sorbent injection and Transport Nitrogen; allow system to stabilize (pulse clean manually to accelerate sorbent removal) and measure HCl in syngas with impingers at G-14 and G-19 and total S concentration at both locations using PFPD GC (3 hours or 3 consistent samples)

11. Adjust Flex-Fuel gasifier operating conditions to optimize carbon conversion of the washed Indian coal feedstock

11.1.1. Discontinue sending syngas through SGB, TC, and TF-R

11.1.2. Route raw syngas through DSQ, through T-2153 CF-R, to pressure control valve(s), PCV-602, to Flare.

11.1.3. Continue to operate the T-2153 CF-R (pulsing with no trona sorbent injection)

11.1.4. Adjust Gasifier bed-ash to target level; achieve high-carbon conversion

11.1.5. Adjust CF-R pulsing frequency as necessary

11.1.6. Collect samples in the Gasification section more frequently for material and energy balances

11.1.7. Measure HCl and (H_2S & COS) at inlet (G-8) and outlet (G-13). Note: with the HCl content of the raw syngas expected to be ~ 10 ppmv, no trona injection should be performed. The measurements taken will serve to relate contaminant concentrations in the raw syngas with the extent of carbon conversion.

11.1.8. GC system samples to be collected from both G-8 and G-13 hot-gas sample lines.

11.4 Results and Discussion - NGC-OPT2

The Flex-Fuel Test Facility (gasification and Novel Gas Cleaning Process sections) was successfully operated throughout the NGC-OPT2A (week of March 21) and the NGC-OPT2B (week of March 28) test campaigns, including two Siemens' barrier filters (Conditioning Filter-Reactor, CF-R, and Test Filter-Reactor, TF-R), Sulfur Guard Bed, SGB (and associated low-pressure nitrogen pre-heater and slipstream by-pass system), and Stage II sulfur (G-72E) and halide (G-92C) sorbent feeders. The Trim

Cooler (located between the SGB and TF-R) was not utilized in these tests. In addition, finely-ground G-92C halide sorbent was fed as a 50:50 physical mixture with nahcolite to improve its feeding as determined in prior commissioning tests.

Because the raw syngas stream contains steam, it was necessary to heat up the SGB catalyst bed (Süd-Chemie's G-72E catalyst) in the NGC Process "Conditioning" section above the syngas dew point to avoid water condensation, which otherwise would severely damage the catalyst's desulfurization performance. Accordingly, during the NGC-OPT2A and NGC-OPT2B campaigns the raw syngas was initially routed from the DSQ system (HE-2001-A) through the CF-R vessel (T-2153), and then bypassed directly to the PCV-602 pressure let-down system. Simultaneously, low-pressure nitrogen was fed through the Nitrogen Pre-Heater (SH-2002) into the SGB vessel (R-2002), which had been isolated from the front-end of the NGC Process section (Figure 2 and Figure 31). The hot nitrogen exiting the SGB vessel was then routed around the Trim Cooler (HE-2071) through the Test Filter-Reactor (T-2147), and then through the PCV-2181 pressure let-down system. This made it possible to also pre-heat the TF-R vessel before directing the conditioned syngas stream into it.

Once the "Conditioning" section reached steady state and the TF-R brought to a sufficiently high temperature, the partially-cooled and essentially particulate-free syngas stream exiting the CF-R was sent through the SGB vessel, then bypassed through the PCV-2006, around the Trim Cooler, to the Condensate Knock-Out Tank (T-2072), and then to the TF-R. Pressure in the "Conditioning" section was controlled by the PCV-2003 pressure let-down system, and pressure in the "Test" section was controlled by the PCV-2181 pressure let-down system. In order to optimize the performance of the Stage II desulfurization and dechlorination sorbents in the "Test" section of the NGC Process, the temperature in the TF-R should be in the 550°F to 575°F range. Since no trona injection was necessary in the "Conditioning" section, the operating temperature for the CF-R vessel was determined primarily by the requirements of the SGB vessel. Therefore, the temperature strategy adopted involved (1) avoiding the complications of operating the HE-2071 cooler, with bypass, and (2) setting the inlet temperature to the CF-R vessel so that, with ambient heat losses from the intervening vessels and piping, the operating temperature of the TF-R vessel would be in the optimal range for sulfur and halide removal to the targeted ppbv levels.

During the second test campaign, raw syngas, derived from the gasification of washed Indian coal (0.56% S, < 100 µg/g Cl, 0.14 µg/g Hg) and North Dakota lignite (0.89% S, ~ 122 µg/g Cl, 0.06 µg/g Hg), was successfully conditioned to the temperatures (Table 21) and contaminant levels required at the inlet to the TF-R. Throughout testing, temperatures across the NGC Process section were maintained at ~ 1450ºF at the secondary cyclone, ~ 1400ºF at the inlet to the Direct Spray Water Quench, ~ 700ºF at the inlet to the CF-R, ~ 650ºF at the outlet of the CF-R, ~ 650ºF at the SGB inlet, ~ 600ºF at the SGB outlet, ~ 600ºF at the TF-R inlet, and ~ 550ºF at the TF-R outlet. These conditions ensured that the SGB was operated at optimal conditions for maximized utilization of the SGB catalyst and efficient sulfur removal. These conditions also ensured that contaminant removal reactions across the TF-R vessel were kept within the optimum temperature range (550°F to 575°F). The total sulfur concentration (H_2S and COS) at the inlet was regulated within a 1-5 ppmv range throughout testing by maintaining a regulated syngas slipstream that bypassed the SGB vessel. An on-line GC/FPD provided near-continuous H_2S and COS measurements (every 3 minutes). As indicated above, there was no need to engage the Trim Cooler for this test campaign. In addition, because of low levels of HCl in the raw syngas (~ 20 ppmv) and some measured HCl removal in the CF-R vessel (through interaction with char and residual trona) and in the SGB vessel (a small amount of CaO in the SGB catalyst), it was not necessary to engage the trona sorbent feeder upstream of the CF-R for bulk HCl removal. The measured HCl concentration in the syngas at the G-14 location (TF-R inlet) consistently averaged ~ 2 ppmv. HCl measurements were made using both an on-line IMACC FT-IR instrument as well as by batch impinger sampling with ion chromatography (IC) analysis. Results from both test campaigns are discussed in more detail below.

Table 21 - Gasification and NGC Process Sections Operating Conditions during the NGC-OPT2 Test Campaign

	NGC-OPT2A		NGC-OPT2B		
	Met Coke	Indian coal (washed)	Met Coke	Indian coal (washed)	Lignite
Start	3/23/2005 at ~ 13:30	3/23/2005 at ~ 21:00	3/29/2005 at ~ 10:30	3/29/2005 at ~ 16:30	3/31/2005 at ~ 05:30
End	3/23/2005 at ~ 21:00	3/25/2005 at ~ 05:00	3/29/2005 at ~ 16:30	3/31/2005 at ~ 05:30	3/31/2005 at ~ 15:00
Duration, hr	7.5	32	6	37	9.5
Gasifier					
Pressure, psig	50 – 200	200 – 255	50 – 125	125 – 250	250
Bed Temp., ºF	1750 – 1825	1625 – 1725	1750 – 1825	1675 – 1775	1550 – 1625
Outlet Temp., ºF	1775 – 1850	1600 – 1625	1775 – 1850	1725 – 1775	1550 – 1625
Bed Height, ft	10 - 6	6 - 8	5 - 12	12 - 10	3 - 8
Syngas Temp. at Secondary Cyclone, ºF	-	1400 - 1475	-	1400 - 1525	1500 - 1350
Direct Spray Quench (DSQ)					
DSQ Inlet Temp., ºF		1200 – 1475		1425 - 1525	1500 – 1350
DSQ Outlet Temp., ºF	-	800 – 650	-	725 - 750	725
Syngas Flowrate, lbs/hr	-	2500 – 2900	-	2300 - 2900	2700 – 3000
Pressure, psig	-	200 - 250	-	125 - 250	250
Conditioning Filter-Reactor (CF-R)					
CF-R Inlet Temp., ºF	-	700 – 710	-	725 - 750	725
CF-R Outlet Temp., ºF	-	650 - 670	-	675 - 700	675
Sulfur Guard Bed (SGB)					
SGB Inlet Temp., ºF	-	600 - 630	-	600 - 630	600 - 630
SGB Outlet Temp., ºF	-	600 – 630	-	600 - 630	600 - 630
Trim Cooler	N/A	N/A	N/A	N/A	N/A
Test Filter-Reactor (TF-R)					
TF-R Inlet Temp., ºF		600 – 630		650 - 675	625 – 650
TF-R Outlet Temp., ºF		540 - 560		575 - 600	575

11.4.1 NGC-OPT2A

Conditioning the raw syngas (at G-14, TF-R inlet) and deep halide removal by injection of finely-ground G-92C sorbent (in combination with nahcolite) were the focus of the initial phase of the second test campaign (NGC-OPT2A). This campaign occurred during the week of March 21 and comprised the test segments shown in Table 22. As indicated, gasification of metallurgical coke (Bethlehem Coke Breeze, for second-stage heating up of the gasifier) and then washed Indian coal occurred over ~ 39 hours, from ~ 13:30 on 3/23/2005 through 05:00 on 3/25/2005. The period on washed Indian coal, during which NGC Process Stage II testing was performed, began at ~ 21:00 on 3/23/2005 and continued for 32 hours, until the test was terminated at ~ 05:00 on 3/25/2005. The gasification section was operated under steady state conditions throughout most of these test segments as demonstrated by the stable gasifier output shown in Figure 44. In this figure the hydrogen (H_2), carbon monoxide (CO), and methane (CH_4) concentrations in the raw, dry product syngas are given, as measured by the Rosemount CAT 200 online analyzer at the G-8 sampling location (CF-R inlet).

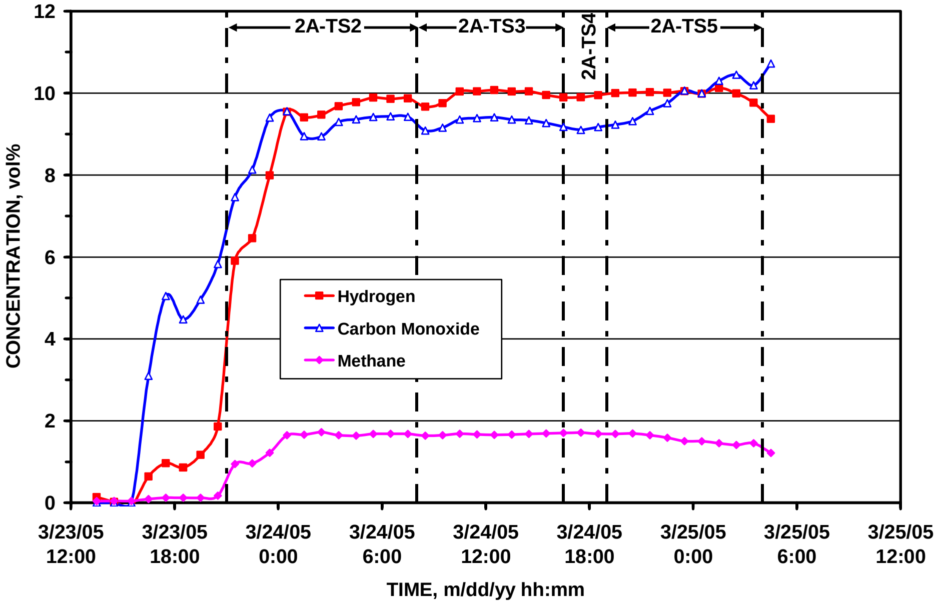

Figure 44 - H_2, CO, and CH_4 in the Raw Gasifier Product Syngas at G-8 during the NGC-OPT2A Test Campaign

Table 22 - Test Segments in the NGC-OPT2 Test Campaign (March 21-25 & 28-31, 2005)

NGC-OPT2A		NGC-OPT2B	
	Indian coal (washed)		Indian coal (washed)
Overall		**Overall**	
Start	3/23/2005 at ~ 21:00	Start	3/29/2005 at ~ 16:30
End	3/25/2005 at ~ 05:00	End	3/31/2005 at ~ 05:30
Duration, hr	32	Duration, hr	37
Establishing Steady State with Indian coal (2A-TS2)		**Sulfur sorbent injection (including TF-R “pre-coating”); 2B-TS3**	
Start	3/23/2005 at ~ 21:00	Start	3/30/2005 at ~ 01:00
End	3/24/2005 at ~ 08:00	End	3/30/2005 at ~ 09:30
Duration, hr	11	Duration, hr	~ 8.5
		Pulse TF-R	3/30/2005 at ~ 11:00
Establishing Preferred Conditions in NGC Process Section (2A-TS3)		**Simultaneous sulfur and halide sorbent injection (including TF-R “pre-coating”); 2B-TS5**	
Start	3/24/2005 at ~ 08:00	Start	3/30/2005 at ~ 13:30
End	3/24/2005 at ~ 16:30	End	3/30/2005 at ~ 18:30
Duration, hr	8.5	Duration, hr	~ 5
TF-R “pre-coating” with halide sorbent mix (2A-TS4)			
Start	3/24/2005 at ~ 16:30	**Breakthrough testing of accumulated filter cake (from above test segment); 2B-TS6**	
End	3/24/2005 at ~ 19:00	Start	3/30/2005 at ~ 18:30
Duration, hr	~ 2.5	End	3/31/2005 at ~ 05:00
		Duration, hr	~ 10.5
Halide sorbent injection (2A-TS5)			
Start	3/24/2005 at ~ 19:00	**Transition to lignite (2B-TS7)**	
End	3/25/2005 at ~ 04:00	Start	3/31/2005 at ~ 05:30
Duration, hr	~ 9	End	3/31/2005 at ~ 15:00
		Duration, hr	~ 9.5
Terminate NGC-OPT2A	3/25/2005 at ~ 05:00		
		Pulse TF-R	3/31/2005 at ~ 10:30
		Simultaneous sulfur and halide sorbent injection (including TF-R “pre-coating”); 2B-TS8	
		Start	3/31/2005 at ~ 12:15
		End	3/31/2005 at ~ 14:20
		Duration, hr	~ 2

11.4.1.1 Gasifier and Filter-Reactor Operations

Temperature drop and pressure drop behaviors, and key process parameters (inlet syngas temperature, syngas mass flowrate, and operating face velocity) for the CF-R and TF-R vessels are reported in Figure 45 through Figure 48 for the NGC-OPT2A campaign. The figures shown cover the entire test duration, and on each figure the various test segments are delineated consistent with the information provided in Table 22. The Flex-Fuel gasifier pressure was brought up to ~ 250 psig after initiating the gasification of washed Indian coal (during test segment 2A-TS2). The inlet temperature for the syngas to the CF-R was also reduced from over 800ºF to ~ 600ºF and then raised back to ~ 650ºF during this test segment. From about 08:00 on 3/24/2005 through the end of the gasification of Indian coal at 05:00 on 3/25/2005 the process conditions were relatively constant for the CF-R vessel.

The syngas mass flowrate at the CF-R inlet was quite stable, averaging ~ 2,740 lbs/hr, which corresponds to approximately 2.18 ft/min operating face velocity. The increase in syngas flowrate and face velocity shown on Figure 47 during the final test segment of the NGC-OPT2A campaign marks the beginning of our efforts to improve gasifier performance (i.e., increase carbon conversion). The solids loading in the syngas was moderate, and the time between pulses varied from about 22 minutes to 18-19 minutes at the end of the campaign. As shown in Figure 45, the differential pressure (PDI-2153) was allowed to increase to about 75 in wg before pulsing was initiated. After pulsing the differential pressure was about 20 in wg, indicating very effective pulsing with the fast-acting valves. The syngas temperature drop across the CF-R vessel appears to be in the range of 40 to 50ºF, especially during steady state operating periods. This temperature drop is significantly lower than the one previously reported for the first test campaign (NGC-OPT1). This is due to the fact that the thermocouple on the syngas outlet from the CF-R vessel, TE-2155, was re-positioned during final preparations for this second test campaign. This new location is believed to indicate the actual syngas temperature more accurately than in previous tests involving this filter.

Figure 46 shows the measured temperature and pressure drop behavior for the TF-R vessel. Figure 48 shows the measured inlet syngas temperature and mass flowrate, and the calculated operating face velocity for the TF-R vessel. The syngas temperature at the TF-R inlet was reduced from over 745ºF (at ~ 03:30 on 3/24/2005) and maintained at approximately 620ºF throughout the 2A-TS3, 2A-TS4, and 2A-TS5 test segments. Temperature drop across the TF-R vessel ranged from ~ 65 to 75ºF. Therefore, the TF-R was operated at a temperature approximating 550ºF. The syngas mass flowrate at the TF-R inlet was stable, averaging ~ 2,480 lbs/hr, which corresponds to approximately 2.24 ft/min operating face velocity. During the 2A-TS4 test segment, when "pre-coating" of the TF-R candles was performed, the operating face velocity was ~ 2.5 ft/min, but steadily increased to slightly over 3 ft/min by the time sorbent injection was completed during the 2A-TS5 test segment.

The pressure drop behavior depicted in Figure 46 for the TF-R vessel is distinctly different from the pressure drop behavior for the CF-R vessel (Figure 45). Throughout the NGC-OPT2A campaign the TF-R was intentionally not pulsed (nor did it require pulsing). Prior to initiating sorbent injection during the 2A-TS4 test segment, i.e., from the time the test began to about 16:30 on 3/24/2005, the TF-R pressure drop was very stable at about 17 in wg. This is a very positive result because it clearly demonstrated there was no particulate leakage through the CF-R and that the syngas stream at the TF-R inlet was essentially particulate-free. During the candles "pre-coating" phase, i.e., 2A-TS4 test segment, which was performed for about 2.5 hours, the TF-R pressure drop increased steadily reaching about 80 in wg. This is also a very positive result because it clearly indicated that a portion of the fine sorbent mixture (finely-ground G-92C in combination with nahcolite) being injected was reaching the filter elements and uniformly depositing on their surfaces. As shown on Figure 46, when the sorbent feed rate was reduced to the test design rate during the 2A-TS5 test segment, the TF-R pressure drop continued to increase, but at a lower rate than in the previous test segment when the fine sorbent mixture was being injected at a much higher rate.

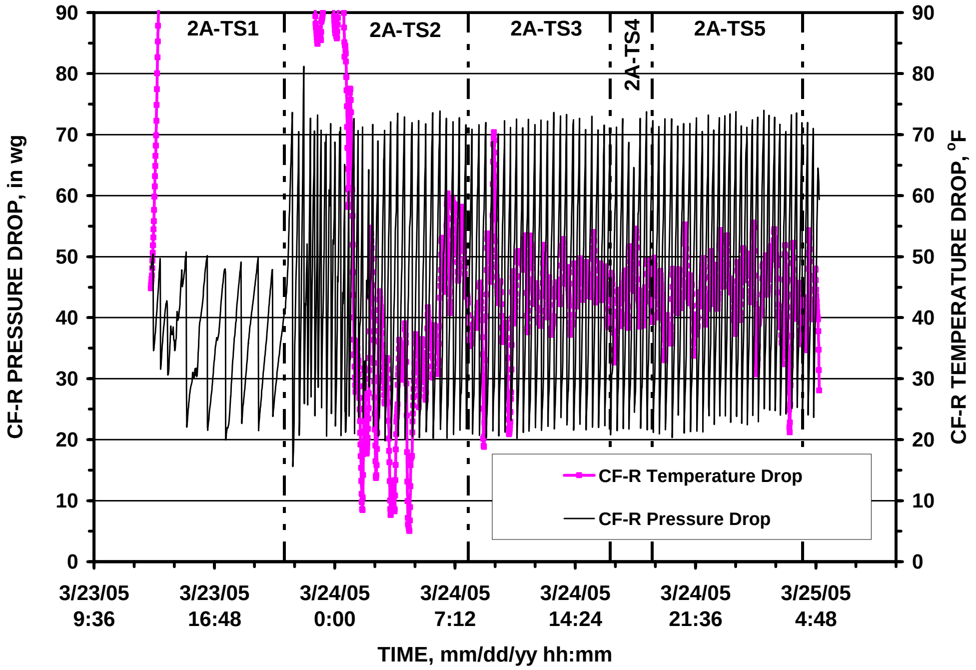

Figure 45 – Temperature and Pressure Drop Behavior of the Conditioning Filter-Reactor during the NGC-OPT2A Campaign

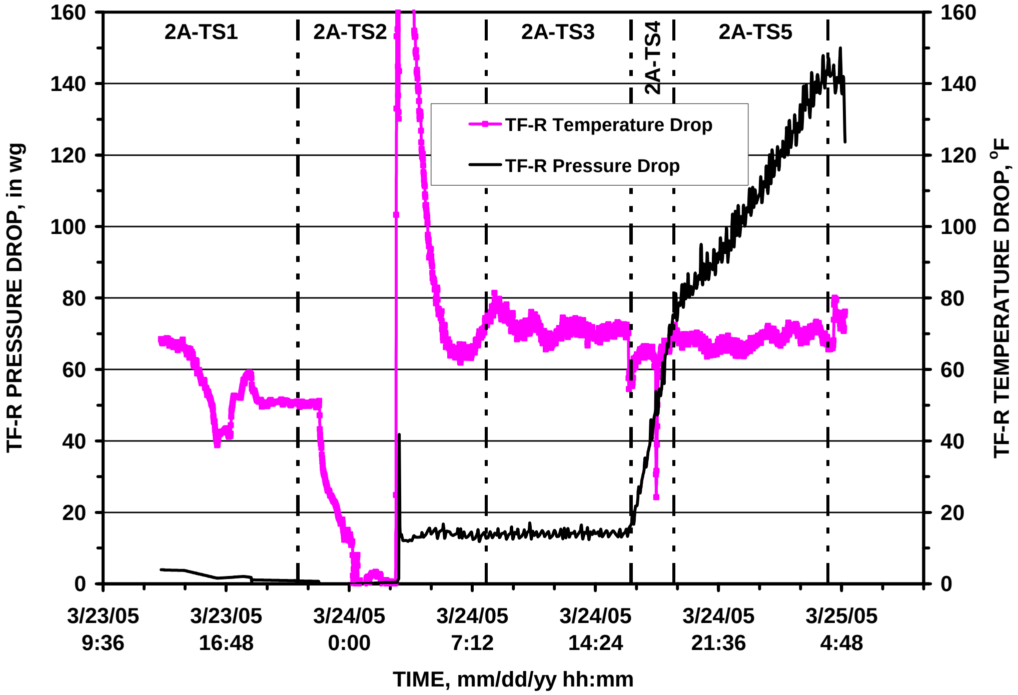

Figure 46 - Temperature and Pressure Drop Behavior of the Test Filter-Reactor during the NGC-OPT2A Campaign

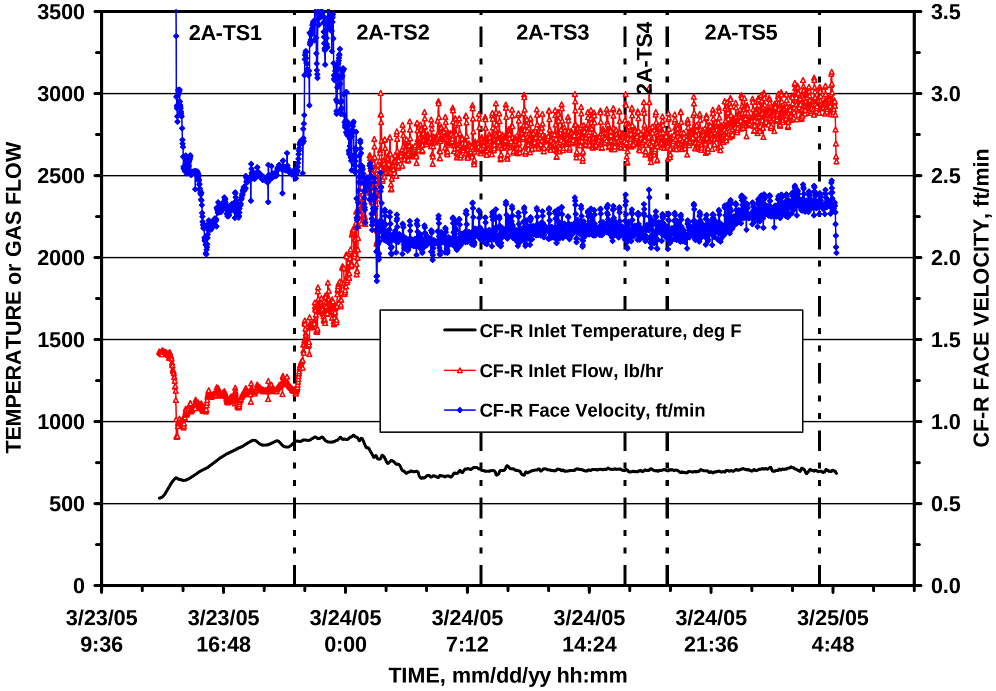

Figure 47 – Temperature, Syngas Flowrate, and Face Velocity at the Conditioning Filter-Reactor Inlet during the NGC-OPT2A Campaign

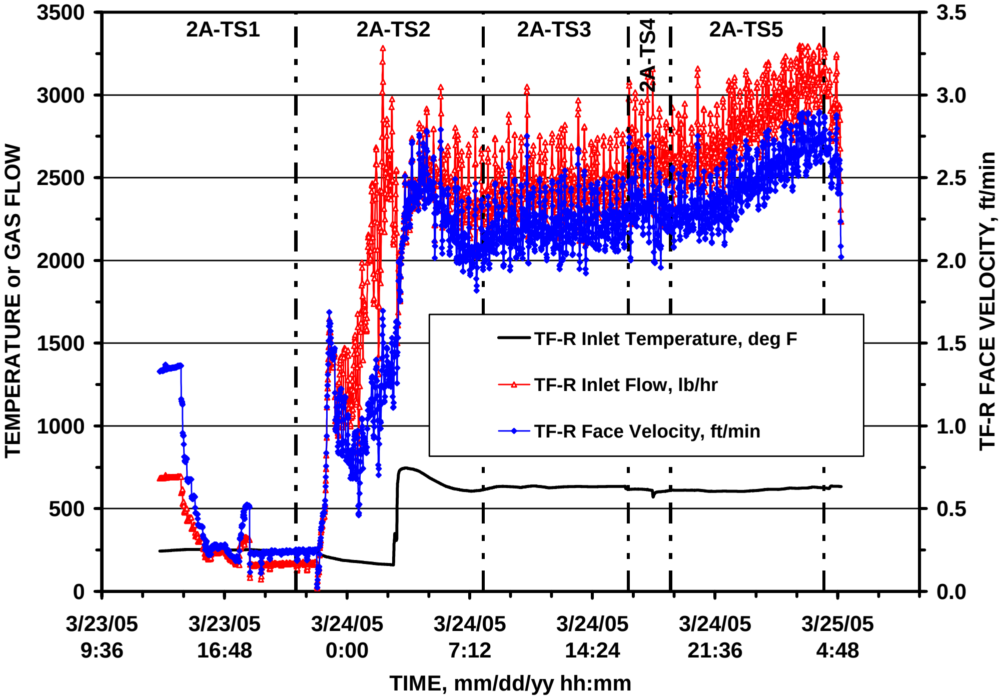

Figure 48 - Temperature, Syngas Flowrate, and Face Velocity at the Test Filter-Reactor Inlet during the NGC-OPT2A Campaign

11.4.1.2 Deep HCl Removal

(During the one-week NGC-OPT2A campaign, efforts concentrated on controlling hydrogen chloride (HCl) in the TF-R and monitoring sulfur species concentrations throughout the NGC Process section. The fine, dry sorbent, a 50:50 physical mixture of nahcolite and finely-ground G-92-C, was injected from the T-2108 system into the conditioned syngas just upstream of the TF-R vessel. Commissioning tests with the preferred sorbent alone, i.e., G-92C, indicated the finely-ground material could not be injected consistently and without frequent intervention in the existing W-2108 K-Tron system. However, commissioning tests determined that nahcolite facilitated feeding of the finely-ground G-92C material.

Stage II halide sorbent injection was initiated at ~ 16:30 on 3/24/2005 and performed for ~ 12 hours during test segments 2A-TS4 and 2A-TS5, as indicated earlier in Table 22. Initially, the finely-ground G-92C/nahcolite mixture was injected at a much higher rate than was necessary (~ 100 g/min) to “pre-coat” the candle surfaces with sorbent materials and expedite testing. This test segment (2A-TS4) was continued for 2.5 hours, until the differential pressure (ΔP) across the TF-R reached ~ 75 in wg. Subsequently, the Stage II halide sorbent feed rate was reduced to the test design rate of 20 g/min and sorbent injection continued for the duration of the 2A-TS5 test segment. As shown in Figure 49, ΔP across the filter increased steadily reaching ~ 150 in wg by the time this test phase was completed. This level of pressure drop was considered safe and the TF-R was conveniently not pulsed during this test campaign.

The results reported on Figure 49 clearly demonstrated that the injected material (or at least portions of it) reached the candles and uniformly deposited on their surfaces. The Stage II halide sorbent feed rate data does show some variability in the instantaneous rates, but the average rates (as determined from manual recordings of the K-Tron net weights at intervals of 30 to 60 minutes) were very close to the set points investigated (100 g/min and 20 g/min). Therefore, the T-2108 halide sorbent feeder functioned very well with the 50:50 mixture of the two materials.

Throughout testing, numerous samples were taken from a variety of locations and were analyzed using a wide array of instrumental methods. During Stage II halide sorbent injection, HCl concentrations were measured to be about 58, 61, and 52 ppbv (see Table 23, Lab Sample IDs 051143-074, -081, and 086). Table 23 provides a summary of all impinger/gas chromatography analyses made during the NGC-OPT2A test campaign at the G-8 (CF-R inlet), G-13 (CF-R outlet), G-14 (conditioned syngas at the TF-R inlet), and G-19 (ultra-cleaned syngas at the TF-R outlet) sampling locations. As indicated, each concentration at the G-19 location was measured from batch impinger samples that were obtained over a 2-hour sampling period. Using the approach described earlier for estimating the background HCl concentration and taking into account the total duration of syngas exposure during the NGC-OPT2B campaign, the time at which each sampling activity was performed, and whether or not test periods on metallurgical coke were considered, the background HCl concentration was estimated to range from ~ 40 to 55 ppbv. Therefore, the measurements made during the NGC-OPT2A campaign would represent approximately 3-18, 6-21, and 0-12 ppbv HCl in the ultra-clean syngas, as shown graphically in Figure 50. These HCl levels in the NGC Process Stage II product syngas are reasonably close to the desired output target of < 10 ppbv.

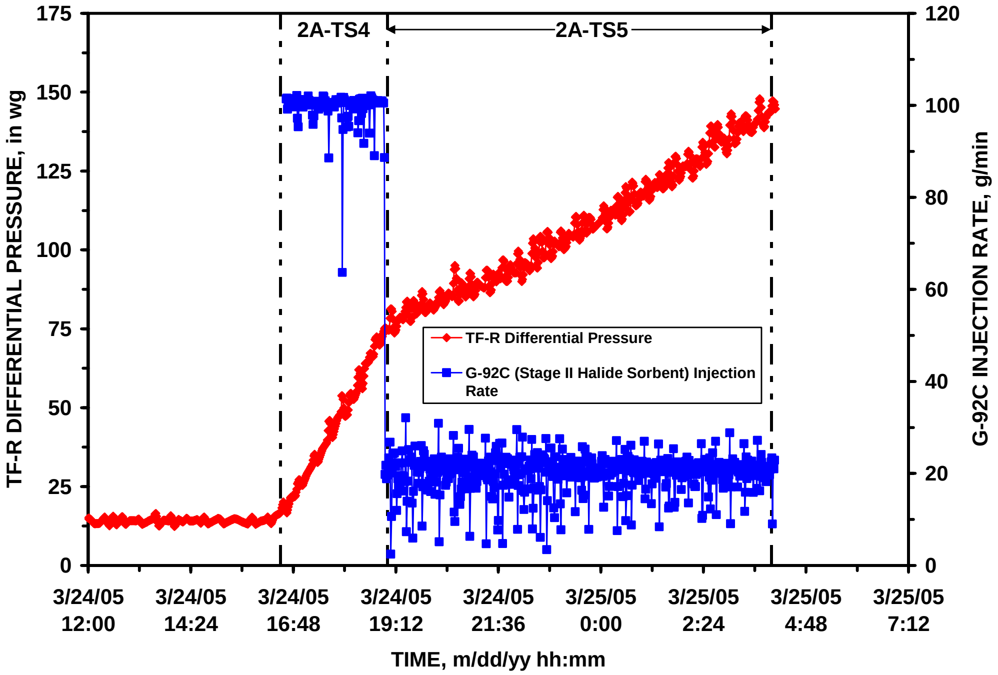

Figure 49 - Test Filter-Reactor Differential Pressure during Stage II Halide Sorbent Injection (NGC-OPT2A)

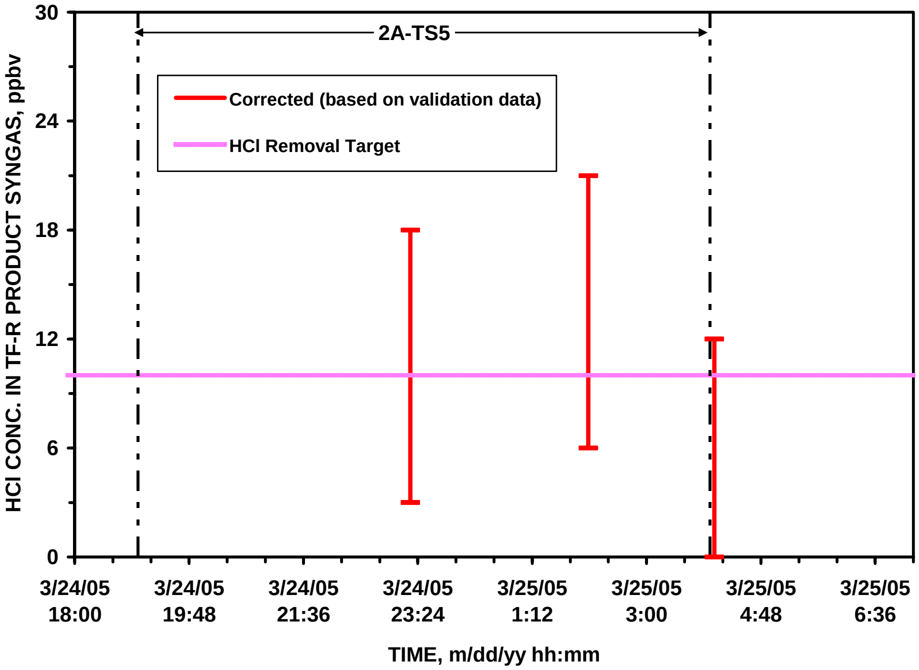

Figure 50 - Measured HCl Concentrations in the TF-R Product Syngas

The COS species was determined to be partially removed by the SGB material (see Table 24 and Table 26). It was also conclusively observed that the water-gas-shift reaction was taking place in the SGB vessel (a decrease in CO concentration accompanied by an increase in CO_2 and H_2 concentrations). For example, at the G-13 sampling point (upstream of SGB), gas analysis indicated 9.6% CO, 12.3% CO_2, and 10% H_2 at ~ 11:45 on 3/24/05 (Lab Sample ID# 051143-041 in Table 24). At the G-14 sampling point (downstream of SGB), gas analysis indicated 6.21% CO, 15.4% CO_2, and 12.9% H_2 at ~ 13:55 on 3/24/05 (Lab Sample ID# 051143-047 in Table 24). This is illustrated graphically in Figure 51.

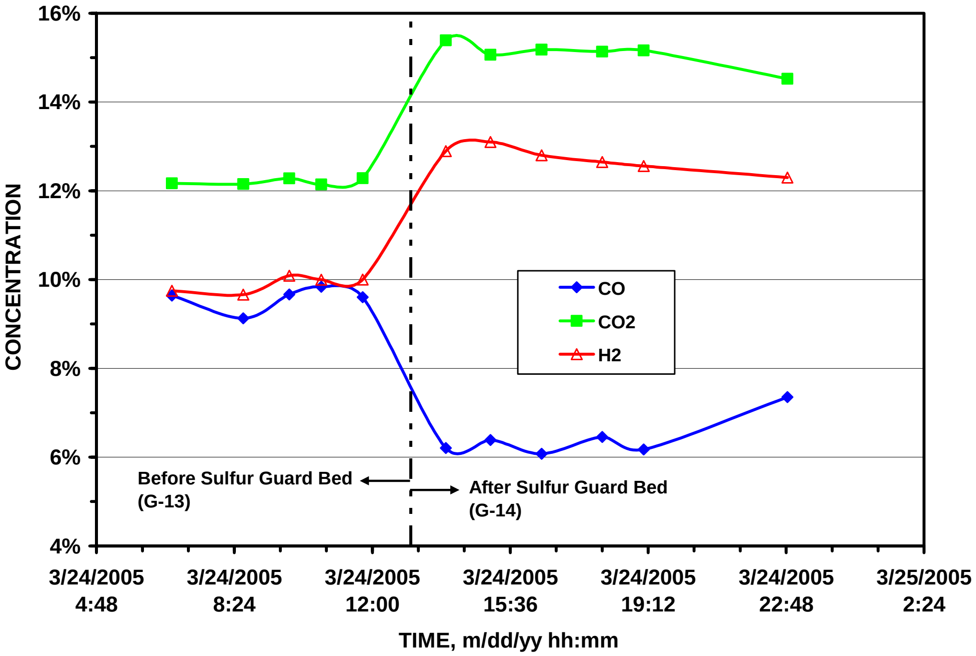

Figure 51 – CO, CO_2, and H_2 Concentrations in the Syngas Upstream and Downstream of the Sulfur Guard Bed

Table 23 - Summary of Impinger/Ion Chromatography Analyses during the NGC-OPT2A Test Campaign

Ref	Lab Sample ID	Sample Point	Date	Time Period	Average Time (min)	Test Segment	Measured HCl, ppmv
1	051143-006	G-14 Validation Test #1	03/24/05	00:16-00:51	35	2A-TS2	0.6
2	051143-007	G-14 Validation Test #2	03/24/05	00:56-01:24	30	2A-TS2	0.3
3	051143-016	G-8	3/24/2005	04:34-05:07	31	2A-TS2	<0.1
4	051143-017	G-13	3/24/2005	04:36-05:26	50	2A-TS2	4.2
5	051143-022	G-8	3/24/2005	05:59-06:31	32	2A-TS2	1.1
6	051143-023	G-13	3/24/2005	06:01-06:43	42	2A-TS2	2.3
7	051143-024	G-8	3/24/2005	07:19-07:51	32	2A-TS2	1.6
8	051143-025	G-13	3/24/2005	07:21-08:32	71	2A-TS3	1.8
9	051143-032	G-8	3/24/2005	09:39-10:05	26	2A-TS3	1.2
10	051143-037	G-8	3/24/2005	10:19-10:49	30	2A-TS3	1.3
11	051143-042	G-14	3/24/2005	10:34-11:04	30	2A-TS3	0.54
12	051143-043	G-14	3/24/2005	11:48-12:24	36	2A-TS3	0.35
13	051143-044	G-13	3/24/2005	12:30-13:09	39	2A-TS3	12.1
14	051143-045	G-13	3/24/2005	13:31-14:13	42	2A-TS3	14.4
15	051143-046	G-14	3/24/2005	13:32-14:13	41	2A-TS3	0.33
16	051143-051	G-13	3/24/2005	14:37-15:14	37	2A-TS3	14.2
17	051143-052	G-14	3/24/2005	14:37-15:14	37	2A-TS3	0.31
18	051143-056	G-14	3/24/2005	17:15-17:58	38	2A-TS4	0.37
19	051143-061	G-14	3/24/2005	18:04-19:04	60	2A-TS4	0.26
20	051143-064	G-14	3/24/2005	19:29-20:36	67	2A-TS5	0.27
21	051143-065	G-19	3/24/2005	20:13-22:17	64	2A-TS5	
22	051143-066	G-14	3/24/2005	21:42-22:44	62	2A-TS5	0.15
23	051143-074	G-19	03/24-03/25	22:20-00:13	53	2A-TS5	0.058
24	051143-075	G-14	03/24-03/25	23:18-00:27	69	2A-TS5	0.16
25	051143-080	G-14	3/25/2005	01:01-02:06	65	2A-TS5	0.11
26	051143-081	G-19	3/25/2005	01:05-03:05	120	2A-TS5	0.061
27	051143-083	G-14	3/25/2005	02:49-03:54	65	2A-TS5	0.095
28	051143-086	G-19	3/25/2005	03:09-04:58	109	2A-TS5	0.052
29	051143-087	G-14	3/25/2005	04:05-05:02	57		0.19
30	051143-088	G-14	3/25/2005	09:48-10:59	71		0.16
31	051143-089	G-19	3/25/2005	09:43-11:55	132		0.040
32	051143-090	G-14	3/25/2005	11:03-12:05	62		0.056
33	051143-099	G-19	3/25/2005	11:58-14:00	122		0.076

Table 24 - Summary of Batch Sample Gas Analyses during the NGC-OPT2A Test Campaign

Ref	Lab Sample ID	Sample Point	Date	Time	Test Segment	H2	CO2	O2/Ar	N2	CO	CH4	Hexane Plus	H2S (ppmv)	COS (ppmv)
1	051143-003	G-14 H2S Validation	3/23/2005	21:36	2A-TS2								1220	
2	051143-010	G-8	3/24/2005	2:10	2A-TS2	9.6%	12.4%	0.72%	65.9%	9.75%	1.556%	0.015%	959	83.5
3	051143-013	G-8	3/24/2005	3:40	2A-TS2	9.7%	12.3%	0.71%	65.9%	9.56%	1.731%	0.015%	300	70.9
4	051143-014	G-13 H2S Validation	3/24/2005	2:45	2A-TS2								195	
5	051143-015	G-13 H2S Validation	3/24/2005	3:30	2A-TS2								449	
6	051143-020	G-8	3/24/2005	6:35	2A-TS2	9.8%	12.2%	0.70%	65.6%	9.63%	1.840%	0.020%	1041	68.7
7	051143-021	G-13	3/24/2005	6:46	2A-TS2	9.7%	12.2%	0.70%	65.9%	9.64%	1.763%	0.017%	167	52.9
8	051143-028	G-8	3/24/2005	7:55	2A-TS2	9.8%	12.3%	0.70%	65.7%	9.53%	1.808%	0.015%	992	57
9	051143-029	G-13	3/24/2005	8:38	2A-TS3	9.7%	12.2%	0.69%	66.5%	9.13%	1.795%	0.016%	814	57.5
10	051143-030	G-13	3/24/2005	9:50	2A-TS3	10.1%	12.3%	0.70%	65.4%	9.66%	1.854%	0.020%	322	47
11	051143-031	G-8	3/24/2005	10:10	2A-TS3	10.0%	12.3%	0.70%	65.5%	9.62%	1.786%	0.015%	583	74
12	051143-038	G-13	3/24/2005	10:40	2A-TS3	10.0%	12.1%	0.70%	65.5%	9.84%	1.746%	0.017%	569	51
13	051143-039	G-8	3/24/2005	11:00	2A-TS3	10.0%	12.2%	0.70%	65.6%	9.54%	1.798%	0.016%	646	70
14	051143-040	G-8	3/24/2005	11:55	2A-TS3	10.0%	12.2%	0.70%	65.6%	9.58%	1.768%	0.016%	854	68
15	051143-041	G-13	3/24/2005	11:45	2A-TS3	10.0%	12.3%	0.70%	65.6%	9.60%	1.759%	0.015%	700	52
16	051143-047	G-14	3/24/2005	13:55	2A-TS3	12.9%	15.4%	0.68%	63.1%	6.21%	1.718%	0.016%	6.52	0.08
17	051143-050	G-14	3/24/2005	15:05	2A-TS3	13.1%	15.1%	0.67%	63.0%	6.39%	1.747%	0.019%	1	0.05
18	051143-055	G-14	3/24/2005	16:25	2A-TS3	12.8%	15.2%	0.67%	63.5%	6.07%	1.728%	0.017%	1.09	0.06
19	051143-059	G-14	3/24/2005	18:00	2A-TS4	12.6%	15.1%	0.68%	63.3%	6.45%	1.735%	0.017%	122	3.5
20	051143-060	G-14	3/24/2005	19:05	2A-TS4	12.6%	15.2%	0.68%	63.6%	6.18%	1.782%	0.016%	1.7	0.23
21	051143-067	G-8	3/24/2005	22:33	2A-TS5	10.0%	12.3%	0.71%	65.3%	9.87%	1.750%	0.015%	1025	63.5
22	051143-068	G-14	3/24/2005	22:50	2A-TS5	12.3%	14.5%	0.69%	63.6%	7.35%	1.496%	0.010%	0.93	0.13
23	051143-071	G-14	3/25/2005	0:25	2A-TS5	12.4%	14.5%	0.68%	63.9%	7.05%	1.431%	0.009%	0.29	0.13
24	051143-076	G-14	3/25/2005	2:40	2A-TS5	13.0%	14.9%	0.69%	62.841%	7.139%	1.454%	0.010%	0.69	0.12
25	051143-077	G-8	3/25/2005	3:00	2A-TS5	10.0%	11.8%	0.72%	65.0%	10.91%	1.461%	0.010%	992	69.4
26	051143-082	G-14	3/25/2005	4:00	2A-TS5	12.4%	14.7%	0.69%	63.5%	7.17%	1.536%	0.011%	0.14	0.1

11.4.2 NGC-OPT2B

The NGC-OPT2 test campaign was resumed on March 28, 2005 to accomplish the two remaining objectives: deep sulfur removal via injection of the finely-ground G-72E sorbent, followed by combined removal of HCl and sulfur species (H_2S and COS) via simultaneous injection of both Stage II sorbents from two separate feeders. This one-week campaign comprised the test segments shown in Table 22. As indicated, gasification of metallurgical coke (Bethlehem Coke Breeze, for second-stage heating up of the gasifier), washed Indian coal, and then North Dakota lignite occurred over ~ 53 hours, from ~ 10:30 on 3/29/2005 to ~ 15:00 on 3/31/2005. The period on washed Indian coal, during which most of the NGC Process Stage II testing was performed, began at ~ 16:30 on 3/29/2005 and continued for ~ 37 hours, at which time lignite coal feeding was initiated. Testing with North Dakota lignite continued for ~ 10 hours, until the NGC-OPT2B campaign was terminated voluntarily at ~ 15:00 on 3/31/2005. The main goal of the testing with lignite was to confirm suitability of this feedstock for the third test campaign, focusing on mercury removal. However, deep sulfur and halide species removal was also evaluated during testing with lignite coal to confirm viability of the NGC Process with diverse carbonaceous feedstocks.

The gasification section was operated under steady state conditions throughout the NGC-OPT2B test segments as demonstrated by the stable gasifier output shown in Figure 52. In this figure the H_2, CO, and CH_4 concentrations in the raw, dry product syngas are given, as measured by the Rosemount CAT 200 online analyzer at the G-8 sampling location (CF-R inlet).

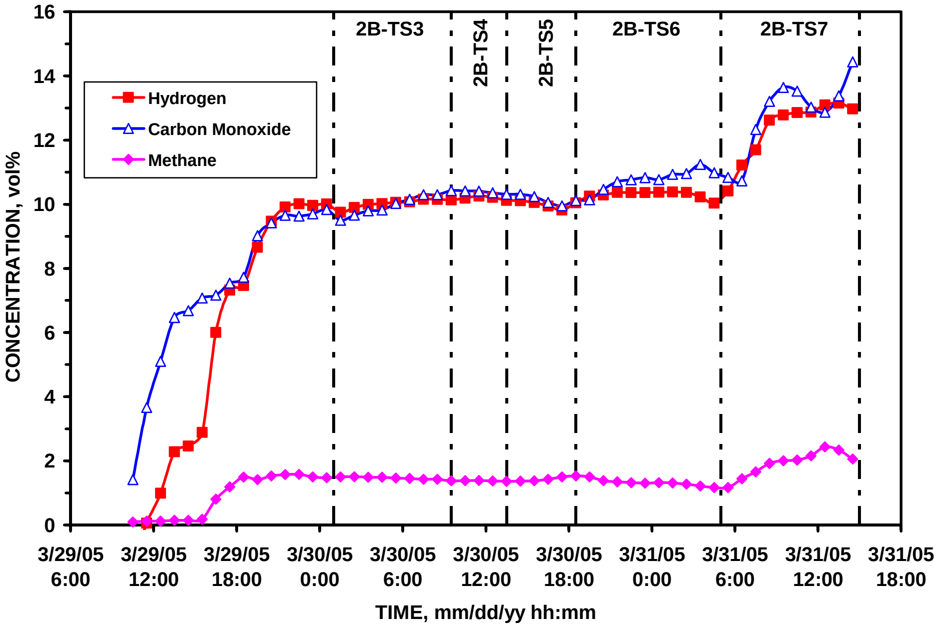

Figure 52 - H_2, CO, and CH_4 in the Raw Gasifier Product Syngas at G-8 (CF-R Inlet) during NGC-OPT2B

11.4.2.1 Gasifier and Filter-Reactor Operations

Temperature drop and pressure drop behaviors, and key process parameters (inlet syngas temperature, syngas mass flowrate, and operating face velocity) for the CF-R and TF-R vessels are reported in Figure 53 through Figure 56 for the NGC-OPT2B campaign. The figures shown cover the entire test duration, and on each figure the various test segments are delineated consistent with the information provided in Table 22. The Flex-Fuel gasifier pressure was brought up to ~ 250 psig after initiating the gasification of washed Indian coal (during test segment 2B-TS2). The inlet temperature for the syngas to the CF-R was also reduced from over 875ºF (at ~ 15:00 on 3/29/2005) to ~ 725ºF (at ~ 07:00 on 3/30/2005) and maintained at approximately this level for the remainder of this campaign. Figure 53 shows there were three distinct periods during which process conditions were relatively constant for the CF-R vessel: from ~ 19:00 on 3/29/2005 to 18:30 on 3/30/2005, from 18:30 on 3/30/2005 to 05:30 on 3/31/2005, and from 05:30 on 3/31/2005 to 15:00 on 3/31/2005 when the NGC-OPT2B campaign was terminated.

The Flex-Fuel gasifier performance (carbon conversion) was improved gradually over the NGC-OPT2B campaign, and accordingly, the syngas mass flowrate at the CF-R inlet increased steadily, as shown in Figure 55. The syngas mass flowrate increased from ~ 2,500 lbs/hr during the 2B-TS2 test segment, when the preferred operating conditions for the gasifier were initially achieved, to slightly over 3,000 lbs/hr at the end of the 2B-TS6 test segment (i.e., end of operations with washed Indian coal). These syngas mass flowrates correspond to approximately 2 ft/min and 2.5 ft/min face velocity, respectively. During the transition from washed Indian coal to North Dakota lignite, the syngas mass flowrate and face velocity trends experienced a reduction, but eventually regained their previous values.

The solids loading in the syngas was moderate, and the time between pulses varied from about 15 to 18 minutes at the end of the campaign. As shown in Figure 53, the differential pressure (PDI-2153) was allowed to increase to about 60 in wg before pulsing was initiated. After pulsing the differential pressure was slightly over 20 in wg during operations with washed Indian coal up to ~ 18:30 on 3/30/2005, and between 25 and 30 in wg during the 2B-TS6 (washed Indian coal) and 2B-TS7 (North Dakota lignite) test segments. CF-R pulsing was performed effectively throughout the NGC-OPT2B campaign. The syngas temperature drop across the CF-R vessel initially varied between 40 and 60ºF, but appears to have stabilized in the 40 to 50ºF range, once the syngas temperature at the CF-R inlet was controlled to ~ 725ºF. This temperature drop is quite similar to the one previously reported for the first phase of this test campaign (NGC-OPT2A).

Figure 54 shows the measured temperature and pressure drop behavior for the TF-R vessel. Figure 56 shows the measured inlet syngas temperature and mass flowrate, and the calculated operating face velocity for the TF-R vessel. The syngas temperature at the TF-R inlet was reduced from ~ 725ºF (at ~ 05:00 on 3/30/2005) and maintained at approximately 639ºF, 672ºF, and 642ºF throughout the 2B-TS5, 2B-TS6, and 2B-TS7 test segments. Temperature drop across the TF-R vessel ranged from ~ 65 to 75ºF. Therefore, the TF-R was operated at a temperature approximating 550ºF. The syngas mass flowrate at the TF-R inlet and the face velocity, shown in Figure 56, exhibit similar trends to their counterparts at the CF-R inlet, shown in Figure 55. The syngas mass flow rate increased steadily over the test period, from about 2,500 lbs/hr to over 3,250 lbs/hr. Correspondingly, the TF-R face velocity increased from about 2 ft/min to over 3.2 ft/min.

The pressure drop behavior depicted in Figure 54 for the TF-R vessel is distinctly different from the pressure drop behavior for the CF-R vessel (Figure 53). Prior to initiating sorbent injection during the 2B-TS3 test segment, the TF-R candles were pulsed to remove the accumulated G-92C/nahcolite sorbent mixture from the previous campaign (NGC-OPT2A). As shown on Figure 54, from ~ 19:00 on 3/29/2005 to ~ 01:00 on 3/30/2005, the TF-R pressure drop was very stable at about 32 in wg. This is a very positive result because it clearly demonstrated there was no particulate leakage through the CF-R and that the syngas stream at the TF-R inlet was essentially particulate-free. During the candles "pre-coating" phase, which was performed for about 1.5 hours within the 2B-TS3 test segment, the TF-R pressure drop increased steadily reaching about 95 in wg. This is also a very positive result because it clearly indicated that a portion of the fine sorbent mixture (finely-ground G-72E) being injected was reaching the filter elements and uniformly depositing on their surfaces. As shown on Figure 54, when the sorbent feed rate was reduced to the test design rate during the 2B-TS3 test segment, the TF-R pressure drop continued to increase, but at a lower rate. Figure 54 reveals that the ΔP was recovered back to about 30 in wg

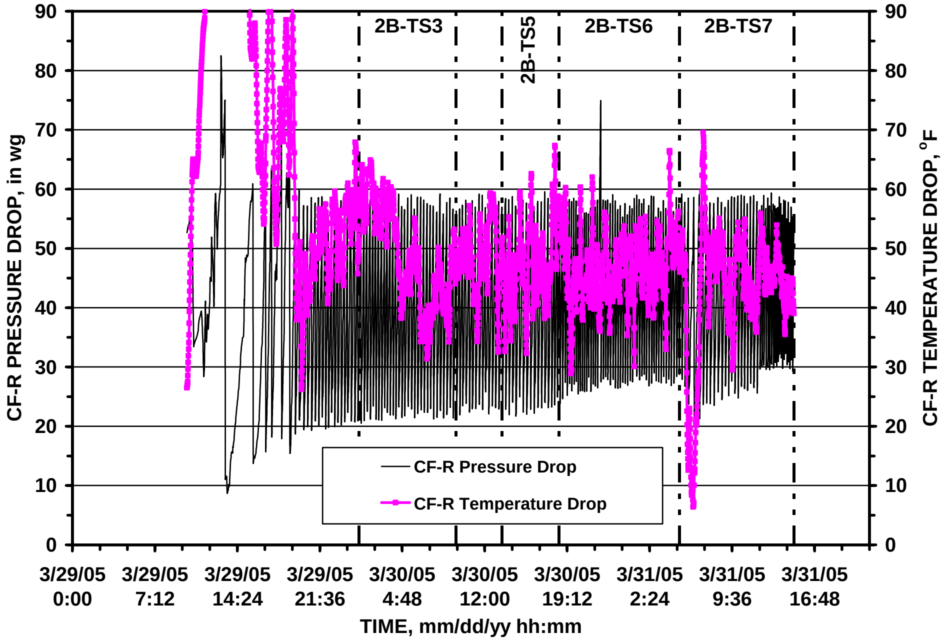

Figure 53 - Temperature and Pressure Drop Behavior of the Conditioning Filter-Reactor during the NGC-OPT2B Campaign

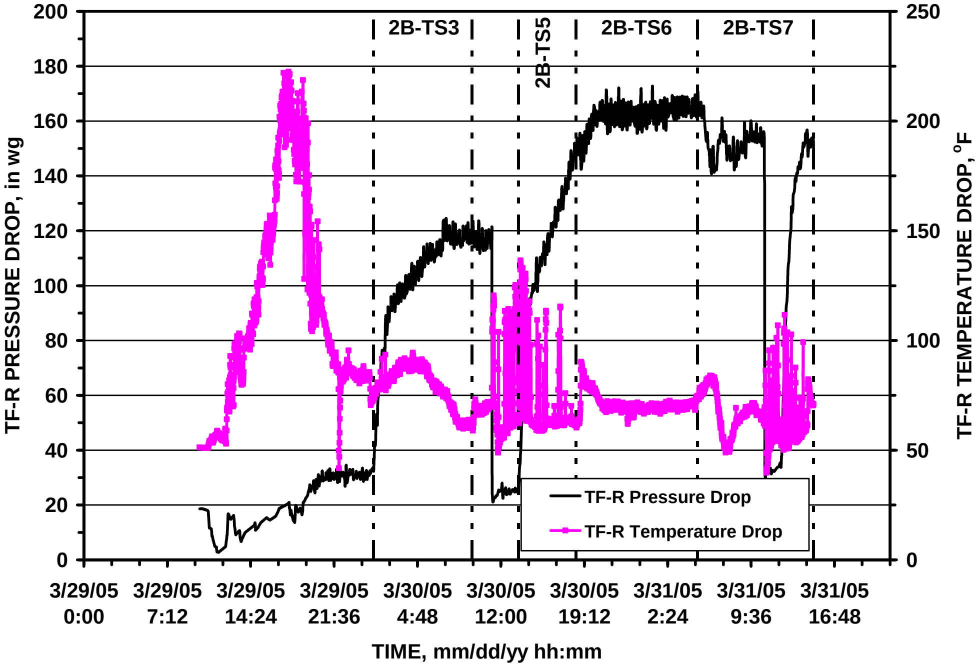

Figure 54 - Temperature and Pressure Drop Behavior of the Test Filter-Reactor during the NGC-OPT2B Campaign

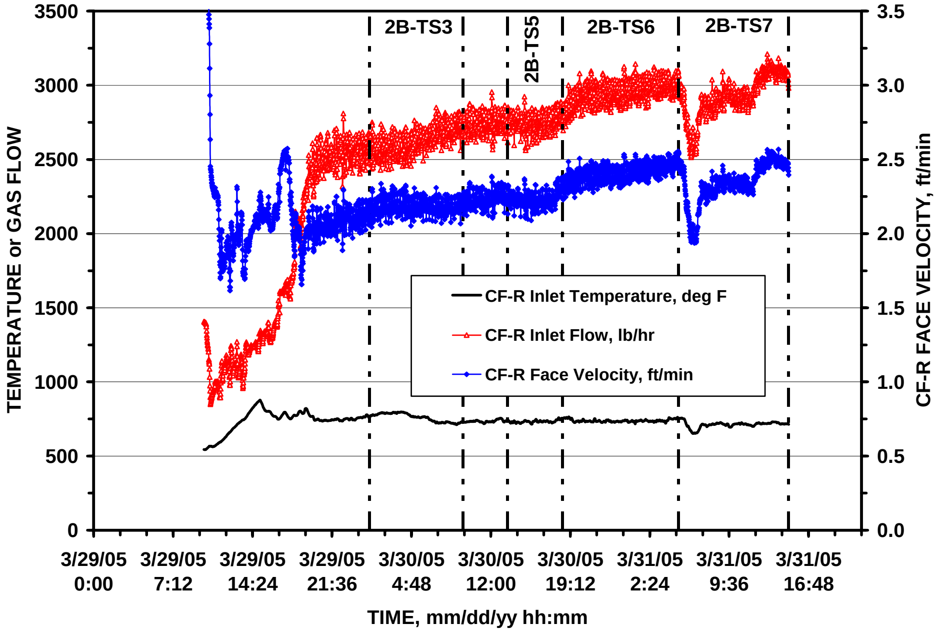

Figure 55 - Temperature, Syngas Flowrate, and Face Velocity at the Conditioning Filter-Reactor Inlet during the NGC-OPT2B Campaign

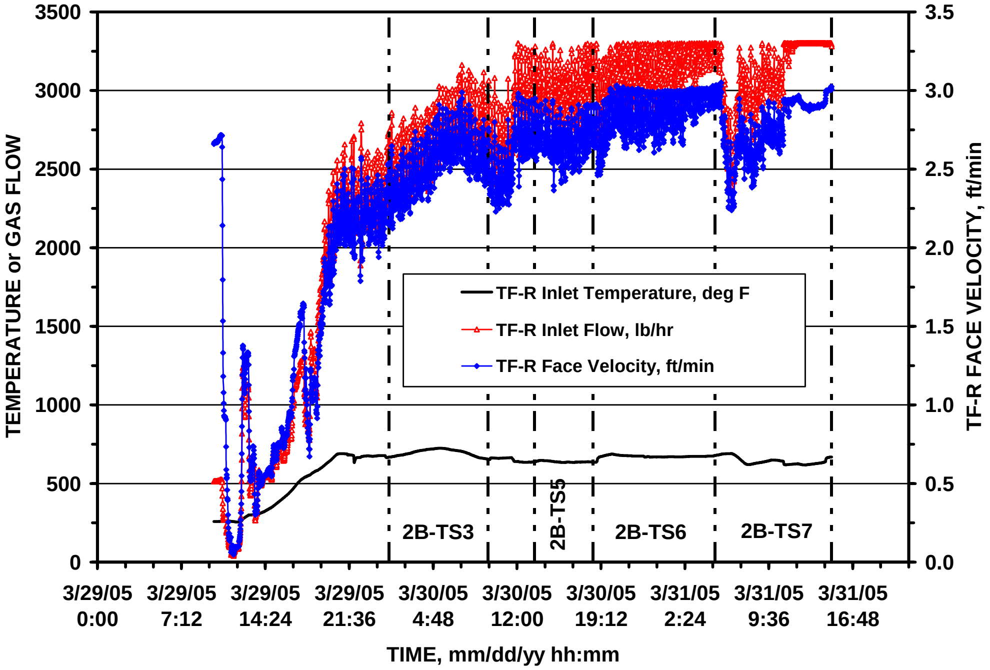

Figure 56 - Temperature, Syngas Flowrate, and Face Velocity at the Test Filter-Reactor Inlet during the NGC-OPT2B Campaign

following pulsing of the TF-R elements at ~ 11:00 on 3/30/2005 once the 2B-TS3 test segment objectives were achieved. This figure also shows the TF-R pressure drop behavior during the remaining test segments, including sorbent injection for simultaneous sulfur and HCl control, breakthrough testing of accumulated filter cake, and sorbent injection during operation with lignite coal. Details on these test segments are provided below, in connection with presentation and discussion of the measured cleaning efficiencies via dry sorbent injection.

11.4.2.2 Deep Sulfur Removal

Once the gasification and NGC Process sections operating conditions were established, the Test Filter-Reactor was pulsed. The H_2S concentration in the conditioned syngas at the TF-R inlet (i.e., G-14 sampling location) was increased to the target level of 1 to 5 ppmv, by opening up a slight flow in the slip-stream bypass around the R-2002 SGB vessel through the FCV-2012 system. The sulfur removal test segment (2B-TS3) was then started at ~ 01:00 on 3/30/2005 with pre-coating the filter elements (candles) by feeding the finely-ground G-72E sorbent, using the T-2107 Stage II Sulfur Sorbent Feeder, at the higher rate of 30 g/min. The pressure differential (ΔP) across the TF-R vessel, initially at ~ 30 in wg, began to increase significantly, and after 1.5 hours the TF-R ΔP reached ~ 95 in wg. The Stage II sulfur sorbent feed rate was then reduced to 5 g/min. As in the previous halide sorbent injection test completed in the prior week, ΔP across the TF-R continued to increase steadily, but at a slower rate than during the "pre-coating" phase. At the conclusion of the 2B-TS3 test segment, when sorbent injection was terminated, the TF-R ΔP stabilized and did not increase any further.

During this campaign, the total sulfur (H_2S + COS) level was maintained at ~ 2-5 ppmv at the TF-R inlet (G-14) through regulating the amount of raw syngas that was bypassed around the SGB vessel. Figure 57 reports the H_2S concentration in the conditioned syngas at the G-14 sampling location, as measured by the on-line GC/FPD (located in the FFTF second floor analytical station), during the Stage II sulfur sorbent injection test segment (2B-TS3). As shown, the H_2S concentration was maintained in the 2-5 ppmv range throughout this test segment. Figure 57 also shows that the total sulfur concentration measured at the TF-R product gas (i.e., G-19 sampling location), using batch samples collected at the SE&C Skid #3 was consistently below the 50 ppbv detection limit of GTI Analytical Laboratory's instrument. In Figure 57, the numerous total sulfur determinations made are shown arbitrarily at the 25 ppbv level.

Figure 57 shows that total sulfur concentration in the ultra-cleaned syngas measured below 50 ppbv also throughout the 2B-TS5 test segment, during which simultaneous control of sulfur and halide species was performed via dry sorbent injection of the finely-ground G-92C and G-72E sorbents (from two separate feeders).

11.4.2.3 Simultaneous Sulfur and Halide Species Removal

Following the sulfur removal test segment (2B-TS3), the Test Filter-Reactor was pulsed at ~ 11:00 on 3/30/2005 (to dislodge the accumulated filter cake of essentially Stage II sulfur sorbent) and readied for the next test segment: the combined removal of sulfur and halide species (H_2S, COS, HCl). A ″pre-coating″ phase was first performed with the G-92C/nahcolite mixture (from the T-2108 Stage II Halide Sorbent Feeder) at 50 g/min and the G-72E sorbent (from the T-2107 Stage II Sulfur Sorbent Feeder) at 20 g/min. The pressure differential on the T-2147 TF-R began to increase significantly and within an hour, ΔP across the TF-R increased to ~ 95 in wg. As the sorbent injection rates were reduced at ~ 14:30 to the test target rates of about 10 g/min for the Stage II sulfur sorbent and 20 g/min for the Stage II halide sorbent (in combination with nahcolite), the rate of increase in the TF-R pressure differential decreased. Combined sulfur and halide contaminant removal continued for approximately 5 hours, when ΔP across the TF-R reached 150 in wg. When sorbent injection was terminated at ~ 18:30, the pressure differential stabilized and did not increase any further.

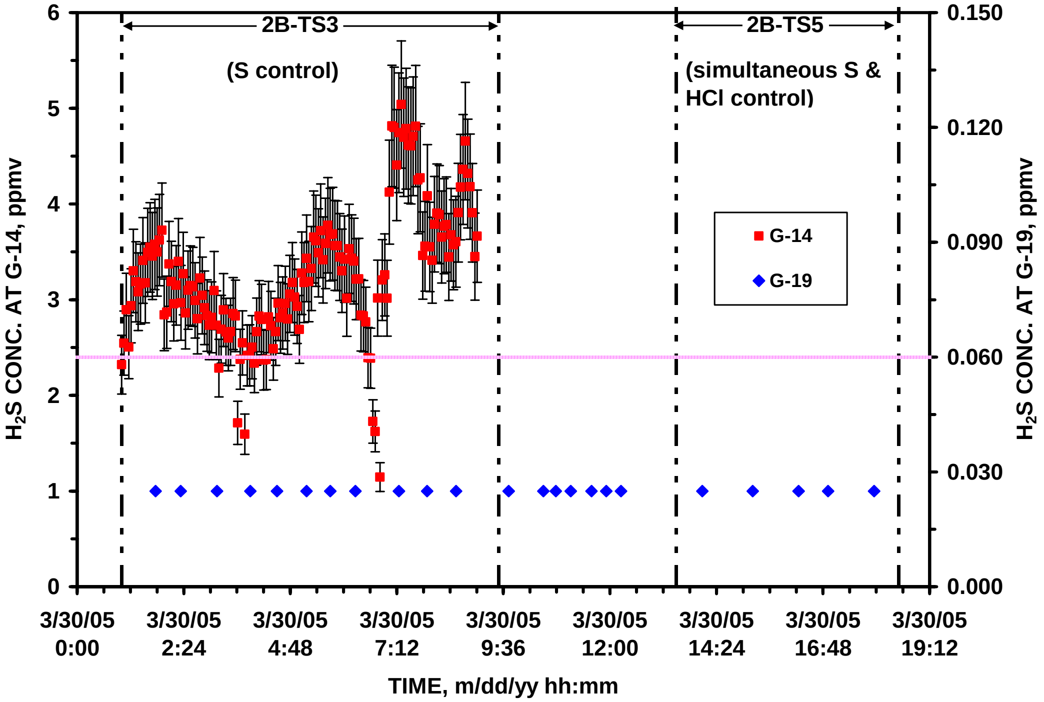

Figure 57 – Measured H_2S Concentration at the Test Filter-Reactor Inlet (Conditioned Syngas at G-14) and Outlet (Ultra-cleaned Syngas at G-19)

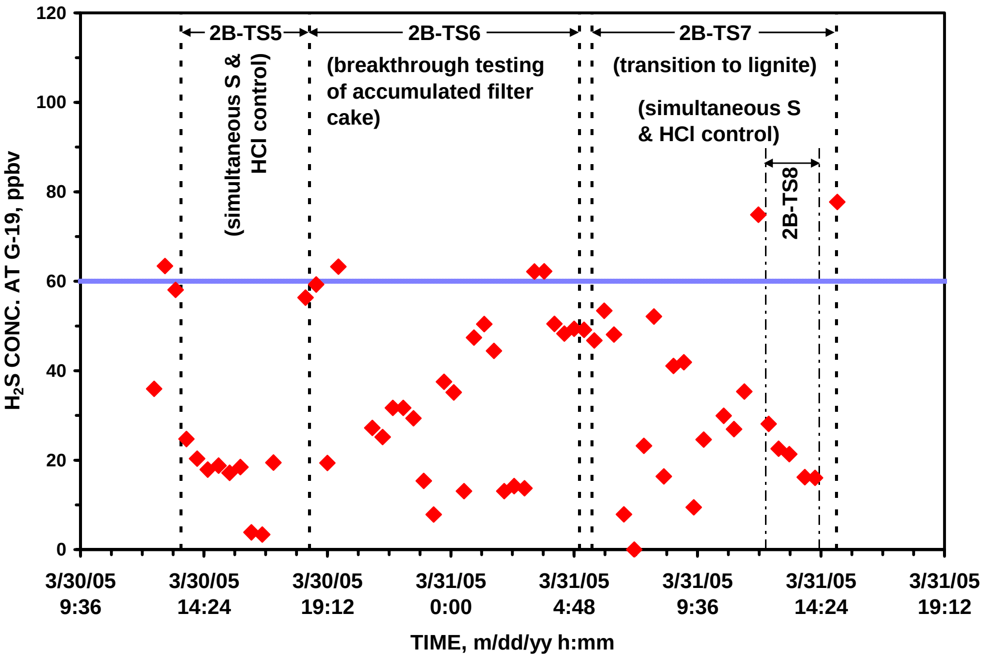

Figure 58 - H_2S Concentration in the Ultra-Clean Syngas at the Test Filter-Reactor Outlet

As indicated earlier, the total sulfur concentration (H_2S and COS) in the TF-R outlet (at G-19) was measured consistently at less than 50 ppbv, using batch samples. In addition, as shown in Figure 58, semi-continuous online sulfur measurements (every 24 minutes) using the Varian CP-3800 PFPD gas chromatograph were quite stable, averaging ~ 20 ppbv, well within our desired output level of < 60 ppbv.

11.4.2.4 “Breakthrough” Testing of Accumulated Filter Cake

At the conclusion of the 2B-TS5 (simultaneous removal of sulfur and halide species) test segment, with sorbent injection being stopped, very low contaminant concentrations continued to be measured in the TF-R outlet (G-19 sampling location). Therefore, instead of pulsing the TF-R, it was decided to continue to monitor contaminant concentrations at the inlet and outlet of the TF-R for an extended period of time, to evaluate the effectiveness of the accumulated filter cake for continued removal of sulfur and halide species to the desired output levels. Gasifier operations were continued with washed Indian coal. With H2S breakthrough still not detected after more than 4 hours of such operation, the total sulfur concentration at G-14 (the TF-R inlet) was raised (by increasing the flowrate through the slipstream bypass around the SGB vessel) to ~ 25 pp<u>m</u>v, as shown in Figure 59. To develop additional insights into the nature, amount, uniformity, etc. of the filter cake on the TF-R candles, this “breakthrough” testing of accumulated filter cake (i.e., 2B-TS6 test segment on Figure 59) continued overnight. The outlet total sulfur concentration was monitored overnight, and as shown in Figure 58, throughout this period, the total sulfur concentration ranged between 20 and 40 ppbv, indicating the efficacy of the Test Filter-Reactor in removing sulfur and the flexibility of the NGC Process with respect to regulating the sulfur level at the Stage II inlet. Thus, it appears that sulfur levels at the TF-R inlet do not need to be maintained within a strict 1-5 ppmv range to achieve a desired output sulfur level of < 60 ppbv.

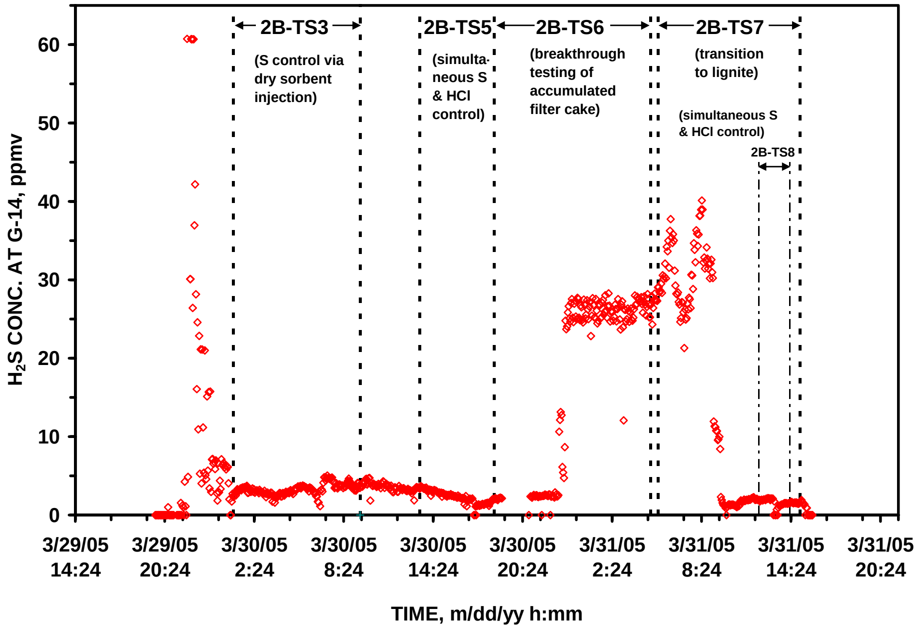

Figure 59 - H_2S Concentration in the Conditioned Syngas at the Test Filter-Reactor Inlet during the NGC-OPT2B Test Campaign

11.4.2.5 NGC Process Stage II Testing with Lignite-Derived Syngas

At approximately 06:30 on 3/31/05, we transitioned into lignite as a feedstock from washed Indian coal. Once stable operating conditions were established, the TF-R vessel was pulsed at ~ 10:30 on 3/31/05, to dislodge the TF-R filter cake (G-72E/G-92C/nahcolite mixture). More sorbent quantities were added into the two Stage II sorbent feeders and combined sulfur and halide removal via sorbent injection was performed. As sorbent injection from both the T-2107 and T-2108 systems was commenced at ~ 12:13 on 3/31/05, the pressure differential began to increase significantly on the TF-R. Initially, the rate of sorbent addition was 30 g/min for the Stage II sulfur sorbent (from the T-2107 system) and 50 g/min for the Stage II halide sorbent (in combination with nahcolite, from the T-2108 system). At ~ 12:26, the rate of the sulfur sorbent addition was decreased to 25 g/min, and at ~ 12:59 the set-point was further reduced to 20 g/min, and then to 15 g/min at ~ 13:08. As the sorbent injection rates were reduced at ~ 13:14 from the "pre-coat" rates to the test target rates (10 g/min for T-2107 and 20 g/min for T-2108), the rate of increase in the T-2147 pressure differential decreased. When sorbent injection was terminated at about ~ 14:20, the pressure differential stabilized and did not increase any further. As shown in Figure 58 and Table 26, the same cleaning efficiencies were measured during this test (with lignite) as were achieved with the washed Indian coal, showing that the NGC Process properly functions with two diverse fuels.

The particle size distribution (PSD) of the Stage II halide sorbent (i.e., finely-ground G-92C) is shown in Figure 60 and that for the Stage II sulfur sorbent (i.e., finely-ground G-72E) is shown in Figure 61. The volume moment mean diameter (i.e., mean diameter with respect to the mass of the particles) is about 13.5 μm and the median diameter, d(0.5), is about 8.2 μm for the dechlorination sorbent. The corresponding values for the desulfurization sorbent were lower, 6.5 μm and 3.5 μm, respectively. Size distributions for the Stage II sorbents are similar or lower than that for the char sample. The corresponding values for the Solvay sodium bicarbonate material (nahcolite), which was used to facilitate feeding of the finely-ground G-92C material, are about 64 μm and 60 μm, respectively.

The fine particle sizes of the Stage II sulfur and halide sorbents used appear to have worked very well. Additional work is needed to optimize Stage II sorbent particle sizes and size distributions to determine optimum size ranges to facilitate sorbent feeding and entrainment, and to result in a filter cake with optimum properties. Smaller sorbent particles may result in higher filter cake pressure drops and lower filter cake permeability, leading to either limited filter face velocities or more frequent pulse cleaning. Smaller sorbent particles may also result in difficulties in sorbent feeding, since they may not be free-flowing and may agglomerate and/or easily bridge feed hoppers. They may also result in filter cake "sintering" in some cases. The optimum mean diameter of the sorbent particles should probably be no less than 10 μm and could be as large as 20 μm.

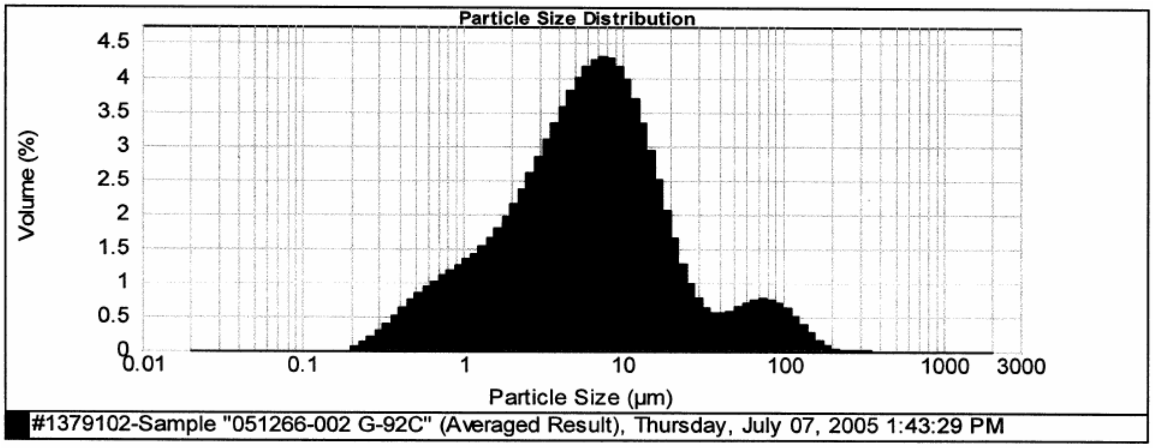

Figure 60 - Particle Size Distribution of the Finely-Ground G-92C Stage II Halide Sorbent

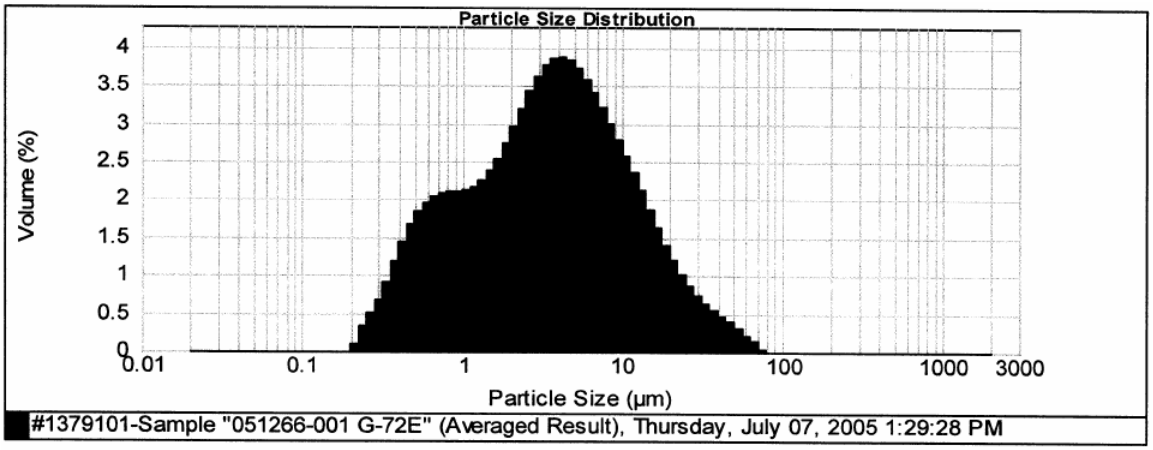

Figure 61 - Particle Size Distribution of the Finely-Ground G-72E Stage II Sulfur Sorbent

Table 25 - Summary of Impinger/Ion Chromatography Analyses during the NGC-OPT2B Test Campaign

Ref	Lab Sample ID	Sample Point	Date	Time Period	Average Time (min)	Test Segment	Measured HCl, ppmv
34	051143-100	G-14 Blank #1	3/29/2005	14:55-16:48	113	2B-TS2	0.028
35	051143-101	G-19 Blank # 1	3/29/2005	15:00-17:47	167	2B-TS2	< 0.020
36	051143-106	G-19 Blank # 2	3/29/2005	17:52-20:31	159	2B-TS2	0.023
37	051143-112	G-19 Blank # 3	3/29/2005	21:15-23:11	116	2B-TS2	< 0.020
38	051143-132	G-19	3/30/2005	00:52-03:48	176	2B-TS3	0.036
39	051143-141	G-19	3/30/2005	03:53-06:06	133	2B-TS3	0.066
40	051143-142	G-14	3/30/2005	03:48-06:38	170	2B-TS3	0.130
41	051143-148	G-19	3/30/2005	07:02-10:04	182	2B-TS3	0.048
42	051143-152	G-14	3/30/2005	07:06-09:43	157	2B-TS3	0.079
43	051143-163	G-14	3/30/2005	10:10-13:08	178	2B-TS4	0.049
44	051143-164	G-19	3/30/2005	10:15-13:13	178	2B-TS4	0.033
45	051143-180	G-14	3/30/2005	14:02-16:40	158	2B-TS5	0.060
46	051143-181	G-19	3/30/2005	14:06-15:56	164	2B-TS5	0.100
47	051143-186	G-19	3/30/2005	16:04-17:55	111	2B-TS5	0.059
48	051143-195	G-19	3/30/2005	18:00-20:11	131	2B-TS5	0.065
49	051143-196	G-14	3/30/2005	18:06-20:42	156	2B-TS5	0.034
50	051143-201	G-19	3/30/2005	20:28-22:38		2B-TS6	0.076
51	051143-209	G-19	3/31/2005	23:49-01:??		2B-TS6	0.041
52	051143-214	G-19	3/31/2005	02:23-04:26		2B-TS6	0.035
53	051143-233	G-13	3/31/2005	11:38-13:20		2B-TS7	2.030
54	051143-237	G-19	3/31/2005	12:50-14:00		2B-TS7	0.029
55	051143-238	G-8	3/31/2005	13:30-14:00		2B-TS7	0.250

Table 26 - Summary of Batch Sample Gas Analyses during the NGC-OPT2B Test Campaign

Ref	Lab Sample ID	Sample Point	Date	Time	Test Segment	H2	CO2	O2/Ar	N2	CO	CH4	Hexane Plus	H2S (ppmv)	COS (ppmv)
27	051143-109	G-8	3/29/2005	21:01	2B-TS2								977	81.2
28	051143-110	G-14	3/29/2005	22:00	2B-TS2								54.0	10.3
29	051143-111	G-14	3/29/2005	23:20	2B-TS2								<0.10	0.15
30	051143-115	G-8	3/30/2005	0:17	2B-TS2									
31	051143-116	G-14	3/30/2005	0:47	2B-TS2								<0.10	0.05
32	051143-117	G-19 Blank	3/30/2005	0:05	2B-TS2								< 0.050	< 0.050
33	051143-118	G-19	3/30/2005	0:43	2B-TS2	14.3%	16.7%	0.66%	62.4%	4.32%	1.527%	0.011%	4.63	<0.050
34	051143-121	G-14	3/30/2005	1:53	2B-TS3								<0.10	<0.050
35	051143-122	G-19	3/30/2005	1:46	2B-TS3	14.3%	17.1%	0.66%	62.9%	3.55%	1.474%	0.009%	< 0.050	< 0.050
36	051143-123	G-19	3/30/2005	2:20	2B-TS3								< 0.050	< 0.050
37	051143-124	G-8	3/30/2005	3:16	2B-TS3								923	75.5
38	051143-125	G-19	3/30/2005	3:09	2B-TS3	15.1%	17.6%	0.64%	62.2%	2.90%	1.465%	0.008%	< 0.050	< 0.050
39	051143-126	G-14	3/30/2005	3:12	2B-TS3								<0.10	8.65
40	051143-129	G-19	3/30/2005	3:54	2B-TS3	15.3%	18.0%	0.64%	62.1%	2.61%	1.433%	0.008%	< 0.050	< 0.050
41	051143-130	G-14	3/30/2005	4:12	2B-TS3								<0.10	<0.050
42	051143-131	G-19	3/30/2005	4:30	2B-TS3								< 0.050	< 0.050
43	051143-133	G-19	3/30/2005	5:10	2B-TS3	15.6%	18.0%	0.65%	61.5%	2.86%	1.37%	0.007%	0.23	< 0.050
44	051143-134	G-14	3/30/2005	5:19	2B-TS3								<0.10	0.1
45	051143-135	G-19	3/30/2005	5:42	2B-TS3								0.03*	< 0.050
46	051143-136	G-8	3/30/2005	6:25	2B-TS3								928	75.3
47	051143-137	G-14	3/30/2005	6:20	2B-TS3								<0.10	<0.050
48	051143-138	G-19	3/30/2005	6:16	2B-TS3	14.8%	17.3%	0.65%	62.3%	3.54%	1.42%	0.009%	< 0.050	< 0.050
49	051143-143	G-14	3/30/2005	7:20	2B-TS3								<0.10	<0.050
50	051143-144	G-19	3/30/2005	7:15	2B-TS3	14.3%	16.5%	0.7%	62.4%	4.7%	1.4%	0.007%	< 0.050	< 0.050
51	051143-145	G-19	3/30/2005	7:53	2B-TS3	13.6%	15.7%	0.7%	63.0%	5.6%	1.4%	0.007%	< 0.050	< 0.050
52	051143-146	G-14	3/30/2005	8:20	2B-TS3								<0.10	<0.050
53	051143-147	G-19	3/30/2005	8:32	2B-TS3	13.4%	15.5%	0.67%	63.1%	5.81%	1.42%	0.006%	< 0.050	< 0.050
54	051143-149	G-14	3/30/2005	9:30	2B-TS3								<0.10	<0.050
55	051143-150	G-19	3/30/2005	9:43	2B-TS4	13.4%	15.7%	0.69%	62.2%	6.61%	1.46%	0.0076%	0.27	<0.050
56	051143-151	G-8	3/30/2005	9:55	2B-TS4								918	74.1
57	051143-157	G-19	3/30/2005	10:30	2B-TS4	13.5%	15.7%	0.69%	62.3%	6.34%	1.42%	0.008%	<0.050	<0.050
58	051143-158	G-19	3/30/2005	10:47	2B-TS4								<0.050	<0.050
59	051143-159	G-19	3/30/2005	11:07	2B-TS4								<0.050	<0.050
60	051143-160	G-19	3/30/2005	11:35	2B-TS4	12.9%	14.8%	0.64%	64.4%	5.85%	1.39%	0.008%	<0.050	<0.050
61	051143-161	G-19	3/30/2005	11:55	2B-TS4								<0.050	<0.050
62	051143-162	G-19	3/30/2005	12:15	2B-TS4	12.5%	14.3%	0.64%	65.3%	5.97%	1.28%	0.005%	<0.050	<0.050
63	051143-165	G-19	3/30/2005	14:05	2B-TS5	12.9%	14.9%	0.64%	64.7%	5.64%	1.31%	0.006%	<0.050	<0.050
64	051143-166	G-8	3/30/2005	14:15	2B-TS5								910	72.9
65	051143-167	G-14	3/30/2005	14:20	2B-TS5								<0.10	0.05
66	051143-176	G-19	3/30/2005	15:13	2B-TS5	12.3%	14.3%	0.64%	65.4%	6.08%	1.29%	0.005%	<0.050	<0.050
67	051143-177	G-14	3/30/2005	15:20	2B-TS5								<0.10	0.05
68	051143-178	G-19	3/30/2005	16:15	2B-TS5	12.3%	14.4%	0.64%	65.4%	6.04%	1.28%	0.006%	<0.050	<0.050
69	051143-179	G-14	3/30/2005	16:18	2B-TS5								<0.10	0.05
70	051143-182	G-19	3/30/2005	16:55	2B-TS5	12.4%	14.2%	0.63%	65.8%	5.63%	1.40%	0.006%	<0.050	<0.050
71	051143-183	G-14	3/30/2005	16:57	2B-TS5								<0.10	0.01*
72	051143-184	G-14	3/30/2005	17:55	2B-TS5								<0.10	0.02*
73	051143-185	G-19	3/30/2005	17:57	2B-TS5	12.2%	14.2%	0.63%	65.5%	6.09%	1.46%	0.008%	<0.050	<0.050
74	051143-204	G-8	3/31/2005	0:20	2B-TS6	10.5%	12.1%	0.73%	63.9%	11.3%	1.41%	0.005%	903	70.8
75	051143-215	G-8	3/31/2005	4:35	2B-TS6	10.4%	12.5%	0.75%	63.4%	11.5%	1.37%	0.008%	1070	115
76	051143-234	G-14	3/31/2005	11:35	2B-TS7								<0.10	<0.05
77	051143-235	G-8	3/31/2005	11:55	2B-TS7	12.7%	12.7%	0.66%	58.0%	13.6%	2.33%	0.019%	1030	53.4
78	051143-236	G-19	3/31/2005	12:53	2B-TS7/8								<0.050	0.04*

11.4.3 FTIR Measurements

Selected results obtained with the FTIR instrument (installed in the FFTF second floor analytical station) are presented graphically in Figure 62 through Figure 64 for the NGC-OPT2A campaign and in Figure 65 through Figure 67 for the NGC-OPT2B campaign. Throughout these campaigns, the FTIR instrument took samples from any of the three sampling points G-8 (CF-R inlet), G-13 (CF-R outlet), or G-14 (conditioned syngas at the TF-R inlet). At any of these sampling locations the FTIR provided online measurements of the concentrations of a number of gaseous species, including CO_2, CO, H_2O, CH_4, NH_3, HCl, etc.

Figure 62 shows the measured HCl concentration at G-8, G-13, and G-14 throughout the NGC-OPT2A campaign. The FTIR measured concentrations are generally consistent with the concentrations measured via impingers/ion chromatography (Table 23). Because of char interference with sampling at the SE&C Skid #1, the measured HCl concentrations at the G-13 (~ 11 ppmv on the average) sampling location are higher than those at G-8 (ranging from about 3 to 8 ppmv). The measured HCl concentrations in the conditioned syngas at the G-14 location were well within the 1 to 5 ppmv range, with an average of ~ 2.7 ppmv. The fluctuations shown in the measured HCl concentration at G-13 during the 2A-TS3 testing period were caused by operating difficulties. At about 13:00 on 3/24/05 the FT-IR inlet/outlet heater was found to be off and was turned back on. This explains the preceding HCl concentration fall and subsequent rise (to ~ 30 ppmv) when the heater was back on.

Figure 63 shows the measured NH_3 concentration at G-8, G-13, and G-14 throughout the NGC-OPT2A campaign. The raw syngas derived from the gasification of the washed Indian coal appears to contain about 1000 ppmv NH_3. During most of the NGC-OPT2A campaign, the measured NH_3 concentration averaged about 1000 ppmv at G-8, 1034 at G-13, and 1117 at G-14. As gasifier performance improved during the 2A-TS5 testing period, the measured NH_3 concentration showed a declining trend. The NH_3 concentration at G-13 averaged about 953 ppmv and that at G-14 about 842 ppmv.

Figure 64 reports the measured H_2O concentration at G-8, G-13, and G-14 throughout the NGC-OPT2A campaign. The measured CO concentration is also superimposed on this figure. Both species concentrations appear stable during the various measurement periods. The measured H_2O concentration averaged about 36.6 vol% at G-8, about 37.1 vol% at G-13, and about 34.4 vol% at G-14. The measured CO concentration (in the wet syngas) averaged about 12.6 vol% at G-8, 12.9 vol% at G-13, and 9.8 vol% at G-14. The reduced CO concentration in the conditioned syngas stream at G-14 was due to the water-gas shift reaction taking place within the SGB vessel, as explained earlier. These measured values can be converted to a dry syngas basis and compared to results obtained with batch samples to assess the accuracy of the FTIR instrument.

Figure 65 through Figure 67 for the NGC-OPT2B campaign can be interpreted similarly. Compared to the NGC-OPT2A campaign with washed Indian coal, lower HCl concentrations were measured (Figure 65), reflecting the lower chloride content of lignite. However, the HCl concentration in the conditioned syngas was maintained within the desired 1 to 5 ppmv range. The raw syngas (at G-8) steam content averaged about 36.3 vol% during operations with washed Indian coal and about 30.4 vol% during operations with lignite. The measured H_2O concentrations averaged about 35.3 vol% at G-13 and about 32.2 vol% at G-14, with both series of measurements taken during operations with Indian coal. These differences relate to differences in operating temperature and heat losses associated with the gasifier during operations with Indian coal and lignite. The data shown in Figure 66 indicate that the measured NH_3 concentration during operations with Indian coal were slightly lower than those made during the NGC-OPT2A campaign and that significantly higher NH_3 concentrations (~ 3000 to 3350 ppmv compared to ~ 1000 ppmv) were measured during operations with lignite.

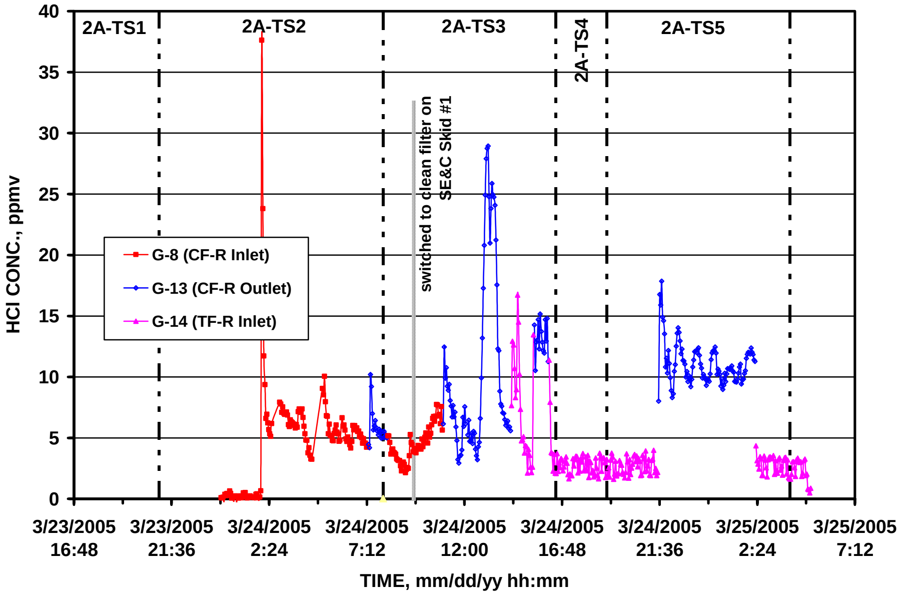

Figure 62 – FTIR Measured HCl Concentration in the NGC Process Section during the NGC-OPT2A Campaign

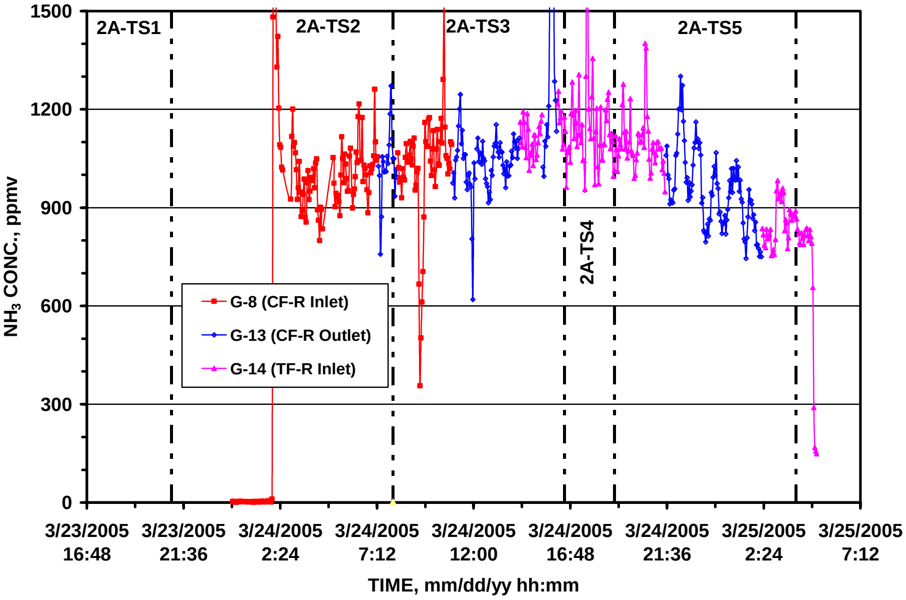

Figure 63 - FTIR Measured NH_3 Concentration in the NGC Process Section during the NGC-OPT2A Campaign

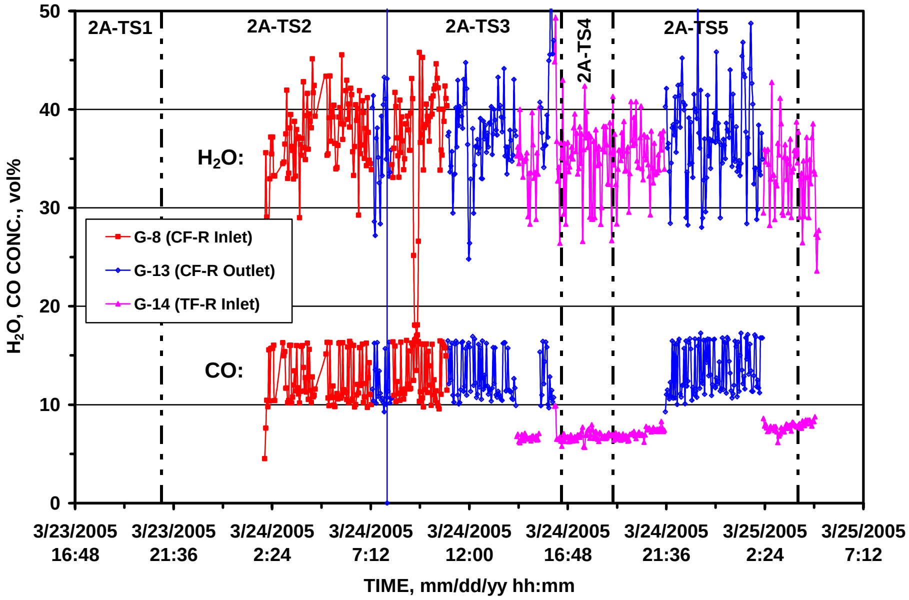

Figure 64 - FTIR Measured H_2O and CO Concentrations in the NGC Process Section during the NGC-OPT2A Campaign

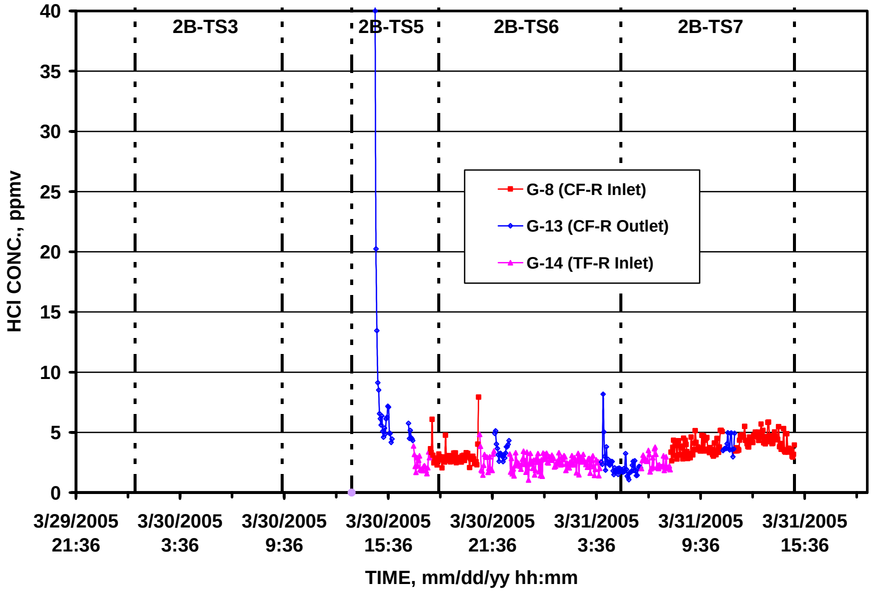

Figure 65 - FTIR Measured HCl Concentration in the NGC Process Section during the NGC-OPT2B Campaign

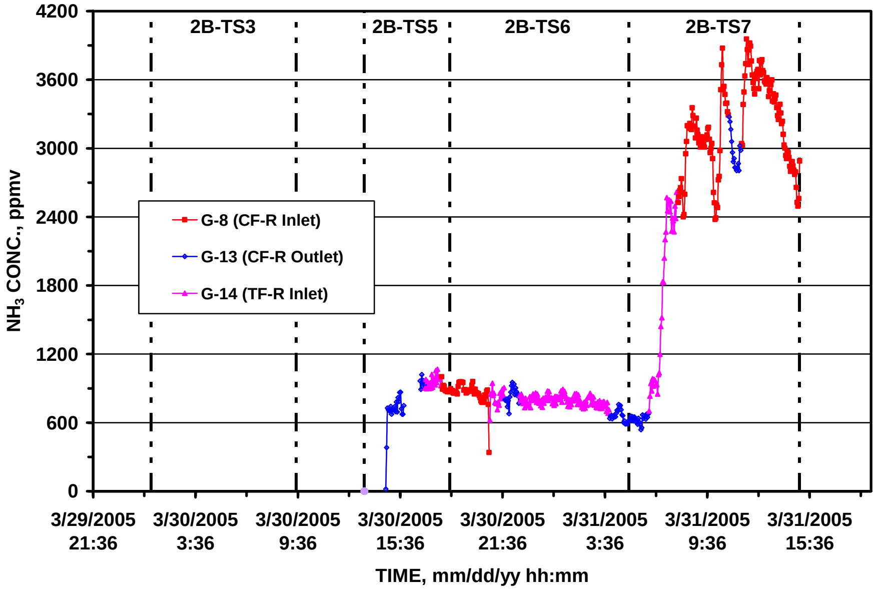

Figure 66 - FTIR Measured NH_3 Concentration in the NGC Process Section during the NGC-OPT2B Campaign

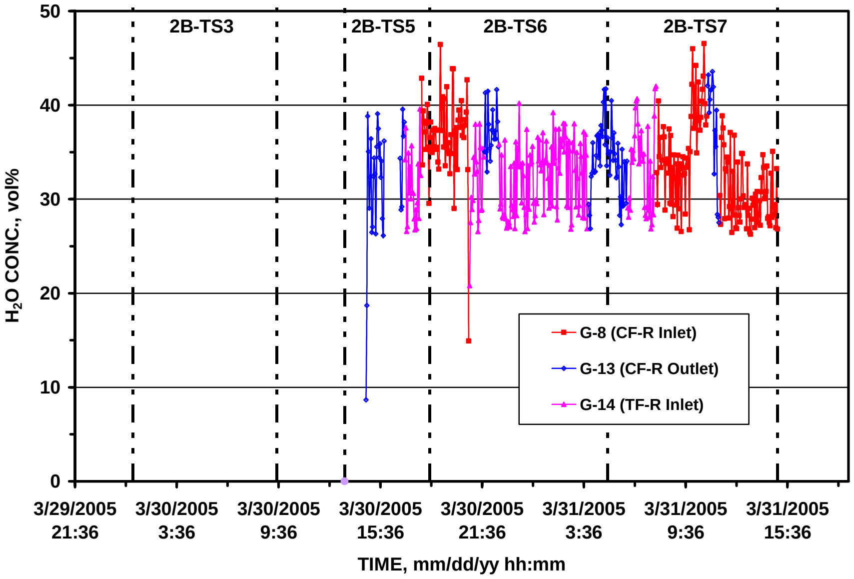

Figure 67 - FTIR Measured H_2O Concentration in the NGC Process Section during the NGC-OPT2B Campaign