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RTI Warm Syngas Cleanup Operational Testing at Tampa Electric Company's Polk 1 IGCC Site

Final Scientific/Technical Report

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1. Executive Summary

The Department of Energy National Energy Technology Laboratory's (DOE/NETL's) cooperative agreement DE-FE0000489 (Recovery Act: High Temperature Syngas Cleanup Technology Scale-up and Demonstration Project) was an incredibly successful project on many different levels. The project was engineered and constructed on schedule and under budget and the process and sorbent performances were shown to duplicate previous lab, bench, and pilot plant results. However, an annual outage at the host site that was planned to last 6 weeks, but lasted closer to 5 months, and some corrosion and operability issues with auxiliary equipment during the scheduled operations phase of the project significantly limited the total operating time for the system. Although the data collected during this limited operating time supported existing bench- and pilot-scale test results, these results were not sufficient to fully enable the overall objective of mitigating the technical risks associated with the scale up and integration of RTI's Warm Gas Desulfurization Process (WDP) and carbon capture technologies, and to support subsequent commercial-scale demonstration. In this project (DE-FE-0026622), the overall objective was to complete 1,000 hours operation of the fully integrated 50 MW_e pre-commercial system (including 90% carbon capture) and 3,000 hours of WDP operation effectively enabling the mitigation of technical risks for scale up for subsequent commercial-scale demonstration.

RTI's WDP is a unique desulfurization process that utilizes dual transport-bed reactors and a proprietary attrition-resistant sorbent to selectively remove sulfur from coal-derived syngas at temperatures as high as 600°C and over a wide range of pressures (20-80 bar). In previous bench-, pilot-, and pre-commercial-scale testing, total sulfur removal for WDP, which includes both H_2S and COS, was $\geq$99.9%.

In a previous project with funding from DOE/NETL (cooperative agreement DE-FE0012066), RTI utilized Nexant to conduct techno-economic analyses to assess the benefits of RTI's WDP technology for power generation and chemical production both with >90+% carbon capture. The results from these independent assessments showed RTI's WDP technology enabled substantial reductions in CAPEX (20-50%) and in OPEX (up to 50+%) for the entire syngas cleanup block (WDP, water gas shift, low temperature gas cooling, carbon capture and sulfur recovery) compared to conventional technologies such as Selexol™ and Rectisol®, while providing improvement in overall process efficiencies and reduction in sulfur and CO_2 emissions. The first of two key observations made based on these assessments was that syngas was clean enough for chemical production, which has conventionally required a Rectisol® system, could be achieved with the integration of WDP and an activated amine process at a fraction of the CAPEX and OPEX typically associated with a Rectisol® system. The second was that the sulfur selective removal of WDP enabled it to be efficiently coupled with almost any commercial carbon dioxide removal process to achieve CAPEX and OPEX reductions versus conventional acid gas removal processes. The attractiveness of this technology that provides a combination of improvements including reductions in CAPEX and OPEX, overall process efficiency, and lower sulfur and CO_2 emissions and is versatile and compatible with other commercial carbon capture technologies should effectively drive its commercial implementation. Consequently, RTI's WDP represents a game-changing technology for syngas cleanup.

A schematic block flow diagram of the 50 MW_e pre-commercial test system and its integration in Tampa Electric Company's (TEC's) Polk Power Station Integrated Gasification Combined Cycle (IGCC) facility is shown in ***Figure 1***. The 50 MW_e pre-commercial system is composed of the following units:

- Warm Gas Desulfurization Process (WDP) – this unit processes a syngas flow of approximately 50 MW_e of power (50 MW_e corresponds to about 1.5 MM scfh of syngas on a dry basis) to produce a desulfurized syngas with a total sulfur (H_2S + COS) concentration that was reduced by ~99.9% (about 10 ppmv for the TEC syngas).
- Water Gas Shift (WGS) – this unit converts sufficient CO into CO_2 to enable 90% capture of the CO_2 in the syngas slipstream. This unit uses conventional commercial sweet high-

temperature shift catalyst in a RTI-designed process that consumes about half as much steam as conventional sweet WGS processes.

- Low Temperature Gas Cooling (LTGC) – this unit cools the syngas to about 110°F needed for the activated methyldiethanolamine (MDEA) carbon capture process and separates any condensed water.
- Activated MDEA Process- this unit employs a non-selective separation for the CO_2 and residual sulfur present in the WDP-treated syngas stream. Because of the selective sulfur removal by the upstream WDP unit, the CO_2 capture target of 90% CO_2 can be achieved with the added benefit that total sulfur concentration in the CO_2 product is <100 ppmv. An additional advantage of the activated MDEA process is the non-selective sulfur removal from WDP-treated syngas reduces the sulfur in the final product syngas to sub-ppmv concentrations, which are required for chemical and fuels production. The specific activated MDEA used in this process unit was BASF's OASE® White absorbent.

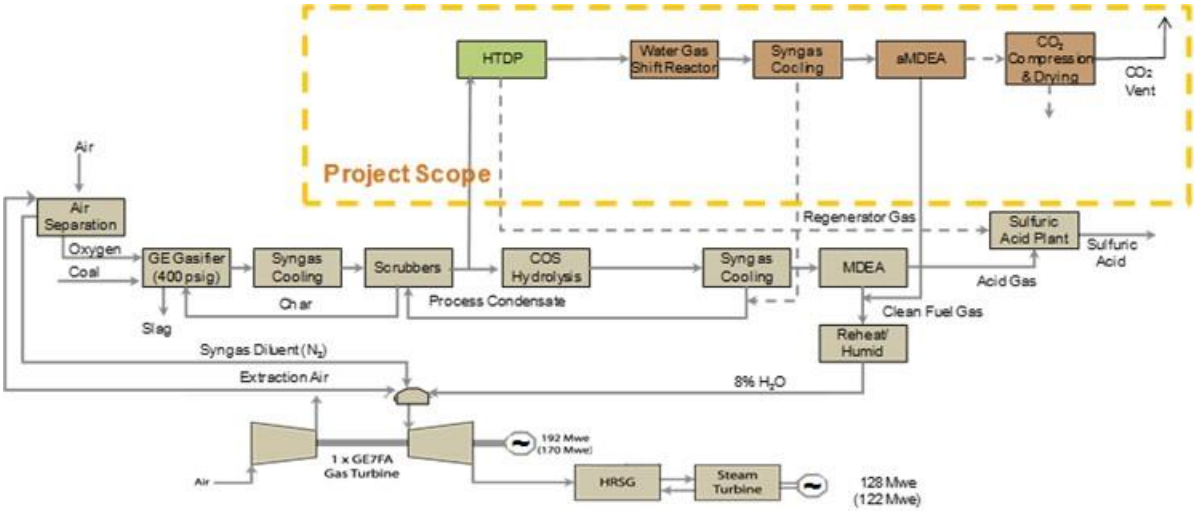

Figure 1. Overall block flow diagram for 50 MW_e pre-commercial system

From the original syngas slipstream for the 50MW_e pre-commercial system, two smaller slip streams were used for additional trace contaminant and syngas conversion testing. One slipstream, which used the desulfurized syngas from the WDP unit, was used to test three sorbent candidates for As, Se and Hg that have shown significant promise in simulated syngas in laboratory testing. The second slipstream, which consisted of fully cleaned syngas from the activated MDEA process, was used to test performance and activity changes associated with using the cleaned syngas from WDP and activated MDEA processes on commercial catalysts used for syngas conversion.

One of the key factors increasing the urgency on this project was TEC's plans to bring their newly installed waste heat recovery generation systems for their natural gas combined cycle plants online in late 2016. Part of this plan included using their annual spring outage to switch the cooling system for their IGCC plant from the existing pond-based cooling system to a new cooling tower system. Unfortunately, when this switch became effective, the 50 MW_e pre-commercial system would be left without access to a cooling system. Although options for providing the 50 MW_e pre-commercial system with cooling water were evaluated, the cost and time delay associated with these options fell outside of the scope of this project. TEC's annual spring outage is scheduled to occur well in advance of their big electric demand period that covers the summer period from early May through late August. Originally, TEC had planned to schedule this annual outage in early March 2016. However, to help support the testing plans for this project, they pushed back this annual outage until the middle of April 2016 (as late as they could) to extend our potential operating widow as much as possible.

Our ability to re-start the 50 MW_e pre-commercial system at the outset of this project was thwarted by delays in repairing the tube bundle for the syngas interchanger just upstream of the WDP unit. Consequently, the available operating window (between completion of this interchanger repair and the start of the TEC spring outage in mid-April 2016) was limited to about four and a half months. During this operating window, the WDP unit was operated at relatively high availability but the TEC gasifier was operated at more typical availability, enabling a total of 2,094 hours of WDP operation to be completed. For the fully integrated system, the key was the integration of the WGS unit, which requires stable operation of WDP to ensure a suitable sulfur concentration to avoid poisoning the WGS catalyst. The plan was to get WDP operating stably for about two weeks and then start WGS. This milestone was achieved by the end of December 2015, but TEC was having issues with their IGCC and planned to bring their system down for repairs in early January 2016. Therefore, we adjusted our plan to bring the WGS unit up after TEC's shutdown. Due to electricity demand and availability of their other generating plants, this planned shutdown was delayed and did not occur until early February 2016. When the pre-commercial system was brought back online after this shutdown, the fully integrated system was also brought online. During the last two months of our operating window, the fully integrated system completed 646 hours of operation. Finally, TEC's IGCC also had several planned and unplanned shutdowns during these operating windows.

In the end, the actual operating time fell short of our planned targets of 1,000 hours for the fully integrated system and 3,000 hours for WDP. However, these targets were just suggested goals used for the objective of minimizing the risks associated with scaling up to a future commercial demonstration. Towards this objective, the project team was successful in maximizing the value of every hour of operation. Over the course of this operating period, continuous incremental improvement in the availability of the WDP, WGS and activated MDEA units were achieved. The WDP unit averaged an availability of 80% for the entire operating period, but had several months where availability was >95%, effectively demonstrating that a commercial availability of greater than 95% is possible. For the fully integrated system, activated MDEA and WGS struggled with equipment failure (primarily an exchanger that used TEC's cooling pond water for cooling and which had biological fouling issues) that could not be effectively replaced without sacrificing operating time. Without fixing this equipment there were maintenance issues that adversely affected availability of these units. Despite this handicap, the availability of these systems downstream of WDP typically ranged between about 50% and 80%, and if time had been available to fully fix these issues, the availability of the fully integrated system would have approached >95% as the problematic equipment was the only cause for the downtime associated with these units.

The performance of the overall system and each unit was thoroughly analyzed. A summary of the desulfurization performance is shown in ***Figure 2***. ***Figure 2*** shows that the WDP technology does effectively remove >99.9% of both the H_2S and COS from the raw syngas. ***Figure 2*** also shows that when WDP is integrated with an activated MDEA unit, the final cleaned product has a sulfur concentration, that with a final polishing guard bed that will be installed for insurance to protect against possible process upsets, approaches that of a commercial Rectisol® system. This validates the assumptions used in the techno-economic analyses completed by Nexant supporting their conclusions relating to the cost, efficiency, and emission benefits associated with WDP compared to other commercial acid gas removal technologies.

Additional support for the applicability of the WDP and activated MDEA technologies for chemicals and fuel production was provided by microreactor testing of commercial iron- and cobalt-based Fischer Tropsch (FT) and methanol catalysts that were fed cleaned syngas from downstream of the activated MDEA unit. These catalysts were tested due to their low tolerance of contaminants typically present in coal-derived syngas which results in a rapid loss in activity. Comparison of catalyst activity through conversion, product selectivity, and productivity for operation on bottled gas, which had no impurities compared to actual product syngas from the 50 MW_e pre-commercial system did not show any evidence of catalyst deactivation. Independent gas analysis by AECOM also showed that the NH_3 and

HCN, Hg, Se, and As concentrations were reduced to < 50 ppbv in the clean syngas from the 50 MW_e pre-commercial system.

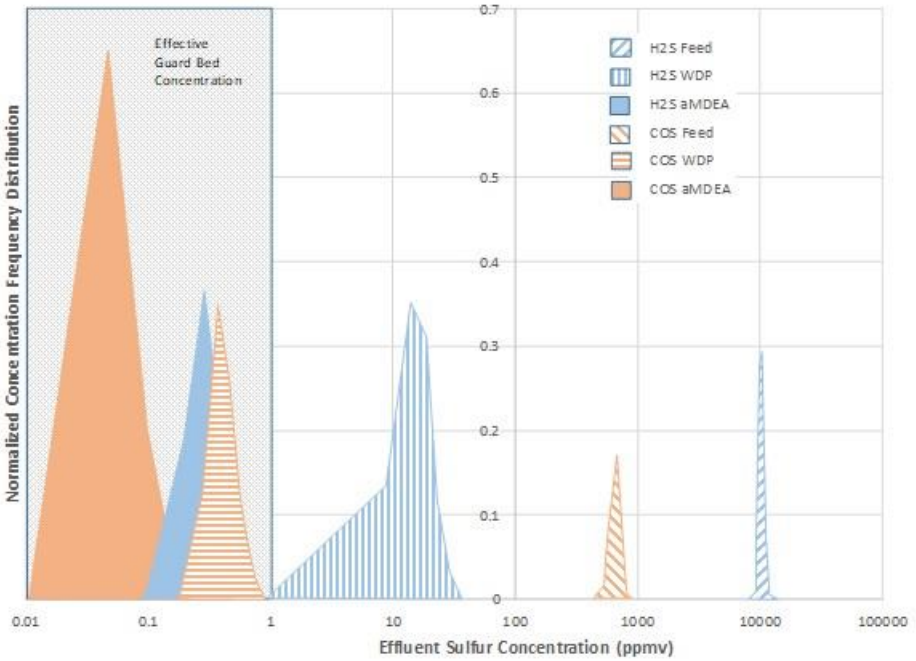

Figure 2. Desulfurization performance of the 50MW_e pre-commercial system

Thorough analysis of the performance of WDP also was also conducted for evidence of deactivation of the sorbent. From analysis of the adsorber and regenerator temperature profiles, the rates of adsorption and regeneration, and testing of the sorbent samples, no evidence of significant deactivation of the sorbent for either the adsorption or regeneration reactions was found. Analysis of the fines collected from the adsorber and regeneration filters was also conducted to establish the rate of sorbent loss due to attrition. Despite the challenges associated with making these measurements, the results show that the attrition rates were significantly less than the typical commercially-accepted rate for fluid catalytic crackers (which are also based on transport reactors). These results continue to show that the assumptions that were used in the techno-economic analyses for WDP have been not only realistic, but conservative.

The fully integrated system was also able to achieve >90% carbon capture. Analysis of the CO conversion over the operation of the WGS unit did not show any conclusive evidence of catalyst deactivation resulting from poisoning by contaminants in the desulfurized syngas. Furthermore, the sulfur effluent of the CO_2 byproduct was consistently below 100 ppmv, which is the U.S. specification for CO_2 transport and sequestration.

Capturing the lessons-learned during this 50 MW_e pre-commercial demonstration was accomplished through several workshops. One of these workshops focused on the technical issues of the system which included design, construction, commissioning, operation and safety. With a focus on a next commercial-scale system, the workshop effectively captured the project team's technical recommendations to eliminate many of the issues they dealt with during the operation of the pre-commercial system. The moderator for this workshop praised the participants, because it was the first workshop he had ever led or heard of that was 100% focused on the project success and did not include any assigning of blame for problems.

The second lessons-learned workshop brought together the leaders and managers from the different participating organizations and project teams (including RTI, TEC, DOE/NETL, and the EPC

firm) to identify key recommendations that would help enable future projects to duplicate the success achieved for this 50 MW_e pre-commercial demonstration. One of the key take-away recommendations was the use of an incentive-based EPC contract for first-of-a-kind (FOAK) projects because it drives the lowest final cost while maximizing the alignment of the engineering firms with the project goals (budget, schedule, quality, and safety) through appropriately designed incentives. By comparison, a lump-sum turnkey approach for FOAK projects often results in higher costs and poor alignment of the engineering firm with project objectives. Other recommendations of this workshop focused on adaptation of the engineering design, construction, and commissioning processes to incorporate tasks/effort that effectively address the FOAK nature of the field demonstration projects. Some examples include the consideration of transient processes such as startup and shut down and the associated equipment requirements, transition of technical knowledge and expertise from design and construction to commissioning and operation, and use of subject matter experts to review not only the design of the FOAK technology, but also the integration of commercial auxiliary equipment into and with the FOAK process.

The ultimate success of this project is visible from the events that took place after the operation was completed on this project. TEC considered and evaluated continued long-term operation of the 50 MW_e pre-commercial system for an expansion that would have resulted in using the full syngas product from the 50MW_e pre-commercial system to produce about 400 tpd of ammonia. Although TEC was convinced that the 50MW_e pre-commercial system was technically able to deliver a clean syngas suitable for ammonia production, the declining price of ammonia associated with low natural gas prices did not adequately justify the additional investment. In November of 2016, RTI completed contract negotiation with Casale SA to officially license and market the WDP technology on a global basis. In November of 2017, RTI completed negotiations with Clariant to be the exclusive manufacturer of the RTI-3 desulfurization sorbent. Both Casale and RTI have been approached to provide budgetary estimates for multiple applications of the WDP technology. At the time of this report writing, several of these potential WDP sub-licensees are scheduled to make a final decision within the next few months, with the anticipation of an actual commercial demonstration project moving forward in 2018.

2. Introduction

Prior testing of the warm syngas desulfurization process (WDP) technology utilizing a slipstream of syngas of about 50 MW_e size from Tampa Electric Company's (TEC's) Polk 1 IGCC facility under the U.S. Department of Energy National Energy Technology Laboratory (DOE/NETL) Cooperative Agreement DE-FE0000489 was very successful at significantly reducing a number of the technical risks associated with scale up of RTI's WDP for commercial application. Key accomplishments associated with this prior testing included:

- On schedule and under budget design and construction of the 50 MW_e pre-commercial test system.
- An outstanding safety record with >500,000 hours of construction and operation with no injuries other than a few minor first aids.
- Performance of the 50 MW_e pre-commercial system that duplicated prior laboratory and pilot plant results and demonstrated that the WDP technology can be confidently scaled up with predictable performance.
- Consistently achieving desulfurization performance of ~99.9 % total sulfur removal with no apparent loss of performance from extended operation, multiple startups and shut downs, and transitory operation conditions for RTI's WDP.
- Demonstration of lower sorbent losses from sorbent attrition for commercial production batches than predicted based on pilot plant operation and pilot plant production batches.
- Significant learnings about appropriate materials of construction, auxiliary equipment reliability, equipment sparing and preventive maintenance plans, and potential WDP design improvements that will lead to more successful design, commissioning, and operation of a full-scale commercial plant
- Demonstration of the effective integration of WDP and existing commercial solvent-based carbon capture technologies that help reduce the sulfur concentration in the final effluent to <0.5 parts per million by volume (ppmv) and produce a carbon dioxide (CO_2) byproduct with ≤ 60 ppmv of sulfur.

In parallel with this testing effort, RTI leveraged the cost information associated with the construction of this pre-commercial system to complete a number of techno-economic analyses for power generation with 90% carbon capture and for chemical and fuels production. This work funded in DOE/NETL Cooperative Agreement DE-FE0012066 revealed that the WDP technology could enable 20 - 50% reductions in capital cost (CAPEX) and up to 50+% in operating costs (OPEX) for the entire cleanup block, which includes WDP, water gas shift (WGS), low temperature gas cooling (LTGC), carbon capture (CC) and the sulfur recovery unit (SRU), when compared with conventional technologies such as Selexol™ and Rectisol®. In addition to these cost improvements, the WDP technology also offered increased process efficiencies and a reduction in sulfur and CO_2 emissions. The ability to simultaneously improve CAPEX, OPEX, process efficiency and lower sulfur and CO_2 emissions illustrates why RTI's WDP is a game-changer technology.

The catch was that total operation of the 50 MW_e pre-commercial unit, and more specifically the WDP unit, was about 1,500 hours at the end of DOE/NETL Cooperative Agreement DE-FE0000489. Although the anticipated goal was higher, problems with operation of certain auxiliary equipment and more importantly an annual outage of TEC's gasifier that lasted 5 months instead of the planned six weeks significantly reduced the total potential operating time. In the eyes of potential end users, this limited operating experience could be viewed as a significant remaining technical risk for commercial deployment of WDP. Based on discussions with potential end users of the technology, their wish list for additional information to successfully support commercial-scale demonstration of this technology included quantifying the following critical technical risks:

- WDP sorbent stability and performance: Operational experience and testing to analyze if the sorbent is able to retain its physical integrity, adequate sulfur-removal capacity, and

regenerability across about 4,000 hours. Long-term effects of syngas contaminants (other than sulfur) on the sorbent stability and performance should also be evaluated.

- Impact of WDP on downstream cleanup and conversion steps: Limited operating experience conducted prior to this project supported the WDP sorbent performance and its expected capability to remove sulfur from syngas by as much as 99.9%. However, long-term integrated testing must be performed to determine to what rate and extent, if any, the cleaned syngas from the WDP process would deactivate the downstream water-gas-shift catalysts and/or cause degradation of the activated amine solvent used for downstream carbon capture. It was anticipated that about 1,000 hours of integrated testing would be needed to adequately determine water-gas-shift catalyst deactivation and approximately 2,000 hours of testing to adequately determine activated amine degradation in the carbon capture system.
- Metallurgy and refractory: Extended testing was needed to determine the long-term impacts of syngas and regenerator off-gas stream corrosion on process piping, and of sorbent flow erosion on the metallurgy and refractory linings of the WDP test unit at the Tampa site.
- Syngas cleanup performance and controllability: Long-term testing was needed to determine the syngas cleanup performance capability and controllability of the WDP operation as syngas composition and process conditions varied across normal ranges of expected operation. The data from this long-term testing would support development of a robust process control strategy and a process simulator for a commercial-scale demonstration plant.
- Carbon capture performance and additional syngas cleanup: The activated amine process (aMDEA®) was previously selected for testing of carbon capture as part of this process development unit. Under the extended testing program in this current effort, the aMDEA® system operation would be optimized to achieve the desired 90% (minimum) carbon capture while also reducing the residual sulfur in the WDP-treated syngas by an additional two orders of magnitude to achieve contaminant control removal performance necessary for production of chemicals/fuels.

An addition consideration was that TEC was in the process of upgrading their existing natural gas facilities at their Polk Power Station to include heat recovery steam generation (HRSG) and a steam turbine. As part of this improvement, TEC had added a cooling tower which had been designed to handle not only the cooling load for the new steam turbine, but also the cooling load for the gasification system. Their anticipated schedule for switching over their existing cooling system for gasification to this new cooling tower was slated to occur in the annual outage in April of 2016. Because the 50 MW_e pre-commercial system draws its cooling water supply from the old cooling reservoir system, it would not be able to operate after the switch to the cooling tower was completed without additional modification to the system and time to complete the modification. To take advantage of this window of opportunity for additional operation of the 50 MW_e pre-commercial system, this project planned to conduct additional operation of this system to achieve a targeted additional ~3,000 hours of WDP operation and ~1,000 hours of continuous operation of the entire integrated syngas cleanup system and to address any remaining issues associated with technical risk associated with scale up for a commercial system.

3. Operation

During the previous operations in DOE/NETL Cooperative Agreement DE-FE00489, we learned that continuous operation of both Furnaces A and B significantly assisted in stable operation of WDP. In addition, when Furnace A is used to superheat steam for preheating the WGS reactors, Furnace A needs to be adequately purged to ensure that all traces of steam and/or condensed water are removed. Failure to remove this steam/water allows it into WDP where it results in sorbent agglomeration that can result in plugging of slide valves (LV-567 and LV-533) or the lock hopper system for removing fines from the Adsorber filter FLT-110. With this operational knowledge, our expectation was that WDP would have to operate between 3 to 5 days without Furnaces A and B.

Our best plan for addressing this and achieving our operational goals was to start up and operate the WDP and the aMDEA® systems until stable operation was achieved, and all operator teams had had at least two weeks operating experience, before attempting to bring the WGS system on line. Once started, the WGS tends to operate stably with minimal operator intervention required and Furnaces A and B could then be returned to supporting continuous operation of WDP.

3.1 WDP Operation

Although this project did get off to a challenging start because of a need to rebuild the syngas interchanger E-110, we began its implementation in early December 2015. In ***Table 1***, we have provided a summary of the overall down time associated with specific types of problems. Using this information as a basis, we created the pie chart in ***Figure 3*** showing the fraction of the overall down time associated with each specific type of problem. The biggest challenge for operating WDP was the required rebuild of the syngas interchanger E-110. This was more of a timing issue for this particular project that an obstacle for commercial deployment. After completing the rebuild of E-110, we did not have any further problems with E-110. The details on the analysis that resulted in the decision to rebuild E-110 are provided in a section entitled Repair of Syngas Interchanger E-110. More details on evaluation of the performance of the new material selected for the rebuild of E-110 are also provided in a later section of this report.

In ***Figure 3***, the second biggest cause that prohibited operating was the TEC's gasification system being down or unavailable. The list of problems that are specifically related to WDP, in order of decreasing overall down time, are slide valve plugging, carryover of sorbent from the regenerator, compressor issues (syngas compressor C-150 and air compressor C-120) and loss of regeneration reaction. Over the course of the operation completed in this project, changes were implemented that significantly reduced or eliminated the issues related with sorbent carry over, compressor issues and loss of regeneration reaction. Issues with plugging of the slide valves were a design-based consequence of the very small opening of the slide valves and their location at the lowest point on the stripper where there is a natural tendency for larger material to accumulate. Once the opening of the slide valve was plugged, the only viable solution was to stop operation and empty the stripper vessel to remove the material blocking the opening of the slide valve. Knowing that this design flaw existed, every effort was made to keep large material from being introduced when sorbent was added and to avoid any situations where conditions would allow in-situ formation of larger chucks of material in the system. This problem can be eliminated or significantly reduced by design changes for any future WDP commercial unit.

The evidence associated with the carryover of sorbent from the regenerator aligned these carryover events with the stopping of the diesel injection near the end of light off of the regenerator (diesel is used to aid in pre-heat of the regenerator prior to introduction of warm syngas to WDP). A majority of this was linked with the specific configuration of the diesel injection system that resulted in a slug of diesel being injected into the regenerator when diesel injection was being stopped. Modifications of the piping network for the diesel injection system and procedures to reduce diesel flow to near zero flow prior to stopping the diesel effectively eliminated this problem after these changes were implemented in January. The addition to track the sulfur balance for WDP, improvements in the

reliability of inlet and outlet sulfur measurements, and better knowledge of the effects of operational changes on regenerator temperatures permitted more stable operation and provided adequate warning to the operators to make changes to maintain the regeneration reaction.

Table 1. Summary of Down Time for the WDP System

Month	Time lost (h)	Explanation/cause
October	744	Rebuild of syngas interchanger E-110.
November	720	Rebuild of syngas interchanger E-110.
December	33	Restart after reinstallation of syngas interchanger E-110.
	18	Failure of temperature sensing device on motor windings of syngas compressor C-150.
	50	Excessive solids carryover from regenerator followed by failure of the slide valve control module on stage 1 of the air compressor C-120.
	95	Excessive solids carryover from regenerator and replacement of damaged filter elements in the regenerator filter FLT-120.
January	4	TEC's sulfuric acid plant tripped and tripped the air compressor C-120 as part of the Emergency Shut Down (ESD) protocol.
	10	Reaction in regenerator extinguished.
	110	TEC had scheduled a 3-day outage to fix their convective syngas cooler (CSC) which they decided not to implement after we had completed our shutdown.
	126	TEC had scheduled a 3-day outage to fix their CSC which they decided not to implement after we had completed our shutdown.
	16	Sorbent carryover from the regenerator, which lead to plugging of the regenerator filter FLT-120.
February	193	TEC completed their planned outage to fix their CSC.
	2	Slide valve LV-567 plugged.
	156	Slide valve LV-533 plugged and regenerator standpipe had to be vacuumed out to remove piece of refractory obstructing slide valve.
March	19	TEC gasifier tripped.
	30	Air compressor C-120.
	90	Regeneration off gas (ROG) leak creating safety hazard.
	176	TEC gasifier tripped due to issues with their nitrogen compressor.
	8	Slide valve LV-567 plugged.
April	17	Slide valve LV-567 plugged.
	41	TEC gasifier tripped due to issues with their nitrogen compressor.

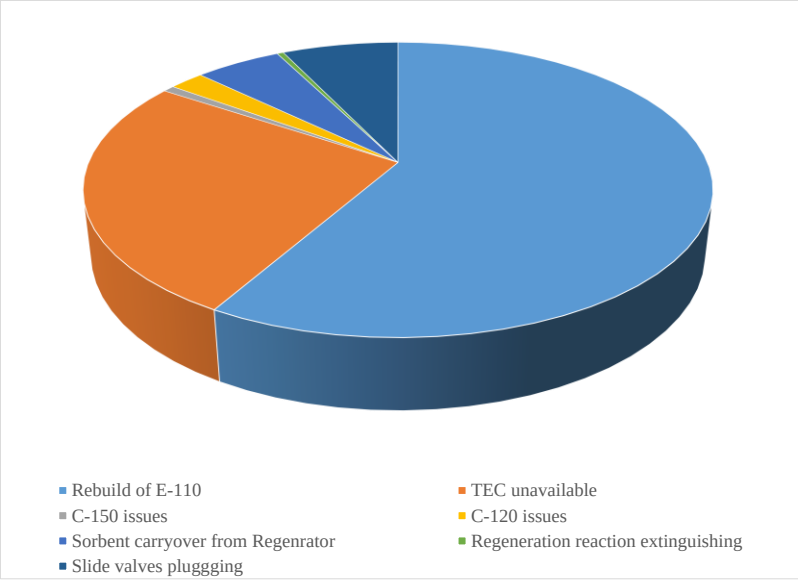

Figure 3. Relative amount of down time for key issues

3.1.1 Repair of Syngas Interchanger (E-110)

Towards the end of the prior project (DE-FE0000489), the tubes in the syngas interchanger, E-110, were failing. Failure of the tubes was identified during operation by an increase in the concentrations of H_2S and COS in the product syngas. Comparison of a syngas sample taken from the adsorber vessel and the syngas sampled downstream of E-110 demonstrated that sulfur concentration in the syngas was increasing as the effluent syngas from the adsorber passed through E-110. This increase in sulfur concentration was caused by some raw syngas with high sulfur concentration on the shell side of the exchanger leaking into the product syngas through holes in the heat exchanger tubes. The head of E-110 was removed to allow inspection of the tubes. A number of tubes were found to be leaking. These leaks were located at the top of the exchanger near the rolled section of the tube sheet which seals the tubes into the tube sheet. MISTRAS conducted eddy current testing of the tubes in E-110 to determine the wall thickness of the tubes. Their findings were that 23 tubes had lost over 60% of their original thickness, 114 tubes had lost between 50 and 59% of their thickness and another 129 had lost between 40 and 49% of their thickness.

At the time, this thinning was assumed to be related to excessive erosion/corrosion of the tubes caused by entrainment of large amounts of sorbent through the tubes that had occurred during some of the initial and early upsets. Because the failures seemed to be located near the connection between the tubes and tube sheet, the assumed cause of failure was associated with the interaction of the thinned tubes and naturally occurring mechanical stresses at or near the tube sheet during startups and shutdowns.

In order to rapidly return the WDP to operation, the failed tubes were plugged. Based on the location of the tube failures, a creative solution was developed in which the existing ferrules, which only extend 3 inches into the 7-inch tube sheet would be removed and replaced with longer ferrules that extended all the way through the tube sheet and 3 inches into the tubes below the tube sheet. By rolling the tubes once inside the tube sheet and once in the ferrule below the tube sheet, the connection between the tubes and tube sheet would be strengthened by the added material from the ferrules reducing the potential for mechanical failure.

A second failure of E-110 allowed this solution to be tested. Unfortunately, when the longer ferrule had been installed, E-110 failed the pressure test. Investigation found a small leak further in the tube than the ferrule extended. Additional investigation showed that many of the leaks were at a location further into the tubes than the new ferrules would cover. At this point, the only solution was to completely replace the tubes in E-110. Upon examining one of the removed tubes, visual inspection indicated that our

assumption that the tube thinning had been caused by particle erosion/ corrosion on the inside of the tubes was incorrect. Inspection of a tube removed from E-110 showed that roughly the top third or about 20 feet of the tube had thinned considerably. The original thickness of the tubes was about 0.097 inches. Near the top tube sheet, the thickness had diminished to about 0.032 inches. The difference in tube thickness can be seen in ***Figure 4***.

Figure 4. Sections of E-110 tube (the thinned tube on the left and normal tube on the right)

The thinning of the tube had occurred due to corrosion on the outside of the tube rather than on the inside. Analysis of some of the tubes removed from E-110 demonstrated that the corrosion had been associated with sulfidation of nickel in the tubes. In addition, a large mass of solid, shown in ***Figure 5***, was eventually found at the top section of E-110 on the shell side. When some of this material was analyzed, the three most predominant elements were nickel (53.7 wt%), sulfur (13.4 wt%), and iron (8.6 wt%). Based on this composition, the main corrosion product was nickel sulfide. As the outside of the tubes were exposed to raw syngas with high concentrations of hydrogen sulfide (H_2S) and carbonyl sulfide (COS) (> 10,000 ppmv), there was plenty of sulfur to promote this corrosion. The high operating temperature created by the hot clean syngas entering through the top tube sheet also accelerated the corrosion kinetics as the highest amount of tube thinning was observed in the top third of the tubes.

Figure 5. Photograph of accumulated material on the top section of the tube bundle from E-110

Although the Inconel 601 material for these tubes was initially selected for its resistance to potential carbon dusting associated with the composition of the product gas, the key corrosion mechanism seemed to be strongly associated with the sulfidation of the nickel in this alloy. As confirmation of this hypothesis, the material of construction for the tubes in Furnace A were evaluated. During TEC's annual 2015 outage, the thickness of these tube was evaluated. This analysis showed no detectable change in tube thickness. The tubes for Furnace A were made of 347 stainless steel (SS), which has a nickel content of about 10 wt %. In addition to this information, several experts in materials of construction for this type of operating environment were consulted. The unanimous recommendation was to use a low-nickel stainless steel. The best procurement time for sufficient tubes to fix E-110 was with 310 SS, which has about 19% nickel, so this alloy was selected.

Although initial attempts were made to remove individual tubes and replace these in the field, this proved to be exceedingly difficult to do because of the length of the tubes, internals within the heat exchanger, and, as was eventually discovered upon taking the exchanger apart, a large mass of corrosion product that had accumulated near the top of E-110. Because of these issues, E-110 was eventually removed and sent out to an external shop for repair. Because of the need to get into the heat exchanger and the difference in thermal expansion between the original and new tubes, a new expansion joint was also needed to complete the repair of E-110. In addition, a 2-inch blinded view port was also added to E-110 near the top tube sheet to permit visual inspection of the tubes during outages. At the end of Project DE-FE-0000489, the plans for repair of E-110 in a local shop had been finalized taking into account the delivery times for the tubes and expansion joint to complete the repair in as short a time as possible.

The plan to accelerate the repair of E-110 worked relatively well. The only problems came with sealing the new tubes at the tube sheet. Multiple iterations were necessary to eliminate all pinhole leaks enabling the heat exchanger to past a 100 psi pressure test. Longer ferrules were also installed. Due to

rewelding that was necessary to get the tubes to seal to the tube sheet, the new ferrules would not fit into all the tubes. The solution was to machine down the ferrules until they fit. On about 10 tubes, longer ferrules could not be installed and shorter ferrules had to be installed. These ferrules were not rolled, as all the rest of the ferrules, to seal them, but bridge welded to adjacent ferrules that had been rolled. When E-110 had successful passed a hydro test at 550 psig, E-110 was returned to TEC and reinstalled on November 24, 2015.

3.2 aMDEA® System

As the aMDEA® system can only be operational if TEC's gasifier and WDP are also operating, we have attempted to segregate the causes of down time for just the aMDEA® system by grouping any down time that directly resulted from the gasifier or WDP into a common category. Although we did, whenever possible, use any down time to repair as much as possible on all systems, the remaining down time can be assumed to be a direct consequence of a problem with primarily the aMDEA® system. A summary of the actions that resulted in shutting down the aMDEA® system and an estimate of the time required to repair the specific problem and return to operation for the entire operational window in this project is provided in ***Table 2***.

Table 2. Summary of the Down Time for the aMDEA® System

Month	Time lost (h)		Explanation/cause
	Gasifier/ WDP	Amine	
October	744		Gasifier/WDP down.
November	720		Gasifier/WDP down.
December	54		Gasifier/WDP down.
	18		Gasifier/WDP down.
		63	Repair of leaks in lean amine exchanger E-506.
	50		Gasifier/WDP down.
	95		Gasifier/WDP down.
		205	Anti-foam pump broke, system upset resulted in loss of amine solvent, and insufficient amine was on hand to refill system.
January		206	Anti-foam pump broke, system upset resulted in loss of amine solvent, and insufficient amine was on hand to refill system.
	120		Gasifier/WDP down.
	142		Gasifier/WDP down.
February	193		Gasifier/WDP down.
	2		Gasifier/WDP down.
		48	Repair of leaks in lean amine exchanger E-506.
	156		Gasifier/WDP down.
March	19		Gasifier/WDP down.
	30		Gasifier/WDP down.
	90		Gasifier/WDP down.
	176		Gasifier/WDP down.
	8		Gasifier/WDP down.
April	17		Gasifier/WDP down.
	41		Gasifier/WDP down.

From ***Table 2***, the two main issues with the aMDEA® system that resulted in down time were failure of the anti-foam agent dosing pump and leaks in the lean amine cooler E-506. When the anti-foam dosing pump broke down and could not be repaired, a creative solution using the amine sump pump was implemented. Unfortunately, this approach was not able to introduce sufficient anti-foaming agent into the system and foaming led to the release of amine solvent through the CO_2 stack. As a consequence of the leaks in E-506 and the release of amine through the CO_2 stack, our inventory of fresh amine solvent was insufficient to refill the amine system and additional fresh amine solvent had to be ordered. Because this occurred so close to the Christmas holidays, the delivery of a new batch of amine did not occur until January 9, 2016. This resulted in a significant loss of operating time for the aMDEA® system (~410 hours).

One of the key challenges with the anti-foaming addition system was that a reliable pump capable of continuously pumping the small amount of anti-foaming agent required for our scale of project was not a standard commercial piece of equipment. Although we did attempt to use periodic dosing as a means to overcome this issue, it required significantly more operator supervision to detect and respond to indications of foaming. We also tried to use dilution of the anti-foaming agent with both fresh amine and process solvent to increase the volumetric flow and enable continuous pumping. However, the anti-foaming agent was only moderately miscible with the amine solvent even at temperatures in excess of 150°F, which meant keeping the feed tank continuously well mixed in addition to pumping at a stable rate from this tank. The solution we found that worked best for us was to have a pump continuously delivering a mixture of anti-foaming agent and a spare backup pump that was plumbed into the system and could deliver a large pulse of anti-foaming agent in a very short time frame. Several indicators were also identified that could be used to tell the level of foaming present in the system and when either an increase in rate of addition or a pulse of anti-foaming agent was needed.

The other piece of problematic equipment on the aMDEA® system was the lean amine cooler. This was a shell and tube heat exchanger using cooling water on the tube side to cool the amine solvent back down to 120°F before being returned to the top of the amine absorber COL-501. In early December, it was noted that the volume of amine in the system and amine concentration were decreasing. When all other potential explanations for these trends had been eliminated, potential sources for leaks were investigated. After confirming that the amine solvent was leaking into the cooling water in E-506, the aMDEA® system was shut down and bypassed to allow work to be conducted on E-506.

When E-506 was opened up for inspection it was found to have a very significant amount of trash accumulated on the surface of the tube sheet and a significant amount of biological growth in the tubes as shown in ***Figure 6***. However, all equipment which had come in contact with TEC pond water used for cooling had shown signs of significant biological growth. After cleaning off this biological growth, we were surprised to find the exposed sections of the tubes were badly corroded as shown in ***Figure 7***. After the tubes on E-506 had been cleaned, only 3 tubes were found to be leaking. These leaking tubes were welded closed and the system reassembled and put back into operation.

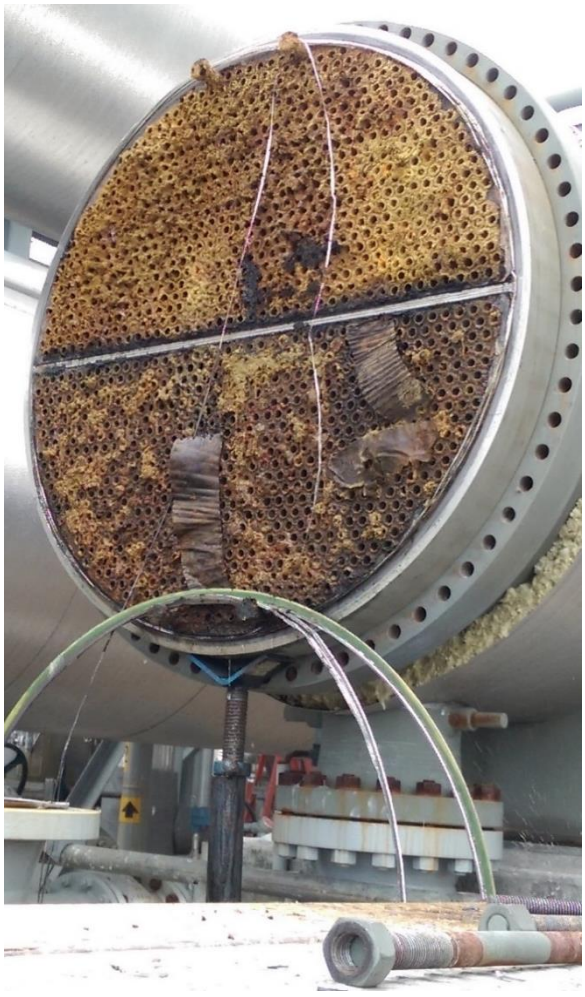

Figure 6. Dirty tube sheet for E-506 in December 2015

The tube bundle for E-506 was made of carbon steel, SA-179. Because the tubes would only come in contact with amine solvent on the shell side and cooling water on the tube side, this material was deemed acceptable. Therefore, the observed level of corrosion was surprising. Part of this corrosion could be the result of a leak of sulfuric acid into the cooling water supply. On August 21, 2015, the 50 MW_e pre-commercial demonstration

system was shut down to make repairs on the syngas interchanger E-110. On August 24, 2015, TEC had an incident in which sulfuric acid leaked into the cooling water system just upstream of the take off point for the 50 MW_e pre-commercial demonstration system. However, this is one of the only places in the entire cooling water system that suffered this level of corrosion. Alternatively, it is possible that this corrosion was the result of microbial induced corrosion (MIC). TEC has observed other cases of MIC in their cooling water system.

In early February, decreases in the level of amine in the system and in the amine concentration prompted E-506 to be retested for leaks. While the 50 MW_e system was down, MISTRAS was also called in to conduct eddy current testing of the tubes. A limitation of this testing technique is that it only can be performed in the straight sections of the tube and not the U-bends at the end of the tubes. The results from the eddy current testing are summarized in ***Table 3***.

Figure 7. Close up of corrosion of exposed tube on tube sheet of E-506 after cleaning

After MISTRAS testing was completed, any tube that was leaking or showed >50% wall loss was plugged. A total of 44 tubes met one or both of these criteria. The total number of plugged tubes rose to 47 with the addition of the 44 tubes plugged during this repair. Based on the information in ***Table 3***, only 22 additional tubes should have been plugged due to their level of wall loss, but almost twice as many tubes were plugged due to leaks. This would suggest that a significant amount of the leaks were potentially occurring at the U-bends that cannot be successfully eddy current tested.

Table 3. MISTRAS Eddy Current Test Results for E-506

# of Tubes	Explanation
13	60%-100% wall loss
8	50%-59% wall loss
46	40%-49% wall loss
87	30%-39% wall loss
92	20%-29% wall loss
59	01%-19% wall loss
1164	No degradation detected
29	Internal obstruction encountered
6	Mechanically plugged

On February 10, 2016, additional tubes were plugged bringing the total number of plugged tubes to 96. This large increase in the number of plugged tubes was assumed to be due to failures in the U-bends of the tubes. Although we could not be sure, we felt that at this point we should have addressed a majority if not all of the most severely corroded tubes.

On February 18, 2016, another 3 tubes in E-506 had to be plugged. The low number of tubes that had developed leaks seemed to confirm our assumption that we had taken care of most of the tubes with the worst corrosion. However, to get to this point, the total number of tubes plugged was now 99. As E-506 has a total of 750 tubes, we had plugged over 10% of the available tubes. At this point, if E-506 was found to be leaking amine solvent, our next course of action would be to drain the shell side of cooling water and seal off the tube side of the exchanger.

This eventually occurred in April 2016. With E-506 effectively cut off from the cooling water flow, the only heat exchange surface was the outer surface of E-506. To promote as much cooling as possible, a soaking hose was used to deliver a continuous stream of cooling water over the surface of E-

506. In spite of this effort to promote cooling of the amine being returned to the top of the amine absorber column COL-501, the temperature of the amine solvent in the effluent from E-506 was 173°F without cooling water flowing in E-506 versus 119°F with cooling water in E-506.

3.3 Water Gas Shift System

During commissioning of the 50 MW_e pre-commercial demonstration unit, the water gas shift (WGS) catalyst was reduced implementing the catalyst activation procedure recommended by the vendor. Following this activation process, the WGS system was maintained with a blanket of nitrogen until system start up. The key objective of the startup procedure was to heat the catalyst to a minimum operating temperature of 650°F. This specific temperature requirement was dictated by the need to be above the dew point of the syngas (or heating gas) and at temperature high enough for sufficient catalyst activity from the WGS catalyst.

Based on these specific requirements, the startup procedure required the initial use of Furnace B with recycled nitrogen to heat the catalyst beds up to the 280°F or the dew point for MP steam. At this point Furnace A would be used to superheat MP steam to continue preheating the WGS reactors to the 650°F starting temperature. The challenge was Furnace A and B were continuously in use to assist in stable operation of the WDP system. Furthermore, previous attempts using this start up procedure had shown that prior to switching back to service for preheating the syngas in Furnace A, the steam had carefully purged from the system to avoid entrainment of the steam and more specifically liquid water into WDP, where this liquid water could result in agglomeration of the sorbent particles which could lead to plugging of the slide valves.

Because the anticipated time that Furnaces A and B would be offline for WDP while preheating the WGS was assumed to be 3 to 4 days, we wanted to get the WDP system operating as smoothly as possible before trying to start the WGS system. Furthermore, when we started the WGS system we wanted the largest possible operating window available. In late December, TEC announced that it foresaw the need for a shutdown to address plugging of their Convective Syngas Coolers (CSCs) in early January. Based on this information, we planned to attempt starting the WGS after TEC's shutdown to clear their CSCs. Unfortunately, TEC's available production facilities also pushed them to keep their gasification system running through January to meet their electricity generation requirements. Thus, it was not until the first week in February, that TEC shut down. When we finally got the WDP and aMDEA® up and running reasonably stable, we started heating the WGS system. Unfortunately, plugging of the slide valves required shutting the WDP system down. Although this did delay us starting the WGS system, we were able to preheat the WGS system and due to the large reactor size, the temperature loss for the bottled-up system was relatively slow.

This provided us with an alternative startup procedure. In this alternative startup procedure, we used Furnace A to superheat the WGS system while the circulation was being started up in WDP. When the WGS system was hot, Furnace A was purged and could be used to preheat and normally start WDP. When WDP was operating stably, steam and syngas could be slowly introduced into the WGS system. When the WGS reaction had started and the temperature stabilized, the flow rate of syngas could be ramped up until all the syngas was being processed in the WGS system. This startup procedure avoided having to run the WDP system without Furnaces A and B.

This alternative procedure was used to startup the WGS system until the system was shut down for TEC's annual outage. As for the aMDEA® system, the WGS system can only be run when both TEC's gasifier and WDP are operational. In order to evaluate the system specific issues that caused down time for the WGS system, we have once again tried to segregate the down time into two categories. The first indicates the down time caused by TEC's system or WDP being down. The second category includes all the additional down time for just the WGS system. ***Table 4*** provides a list of these two categories of down time for the WGS system.

Table 4 shows that there were essentially three reasons that kept the WGS system from being operated. The reason that resulted in the most down time was the challenges with starting the WGS system. In February, after TEC had completed their planned shutdown to clean out the CSC, the WGS was essentially at near ambient temperature (90°F) and the target temperature at which to introduce syngas was 650°F. The large thermal mass of the WGS system, the distance between the heating systems and the WGS system and the limited heat duty of Furnaces A and B resulted in a good portion of February being used to preheat the system. For this reason, during the WDP shut down in the middle of February, Furnace B was used throughout this shutdown to keep the WGS reactors as hot as possible. From the data in ***Table 4***, we can also see that even when the WGS system is at temperature, it takes about 7 to 9 hours to allow the WDP to stabilize and to restart the WGS system.

Table 4. Summary of the Down Time for the WGS System

Month	Time lost (h)		Explanation/cause
	Gasifier/ WDP	WGS	
February		8	Prior to attempted startup.
	193		Gasifier/WDP down.
		10	Prior to attempted startup.
	2		Gasifier/WDP down.
		179	Prior to attempted startup.
	156		Gasifier/WDP down.
		19	Prior to attempted startup.
March	19		Gasifier/WDP down.
		7	Time to stabilize WDP and restart WGS.
		31	Sulfur effluent for WDP exceeding 50 ppmv.
	30		Gasifier/WDP down.
		9	Time to stabilize WDP and restart WGS.
	90		Gasifier/WDP down.
	176		Gasifier/WDP down.
		7	Time to stabilize WDP and restart WGS.
	8		Gasifier/WDP down.
April		1	WDP operated < 3 hours prior to shutdown
	17		Gasifier/WDP down.
		70	WGS not restarted.
	41		Gasifier/WDP down.
		8	Time to stabilize WDP and restart WGS.
		34	Sample valve failure
		39	Sample valve failure

The first reason that the WGS system was shut down specifically because of an issue with the WGS system was during a period when the higher sulfur concentration of the feed had resulted in the effluent sulfur concentration climbing to near 50 ppmv, which is the vendor recommended maximum sulfur concentration for the sweet WGS catalyst. The WGS system was shut down to avoid poisoning the catalyst with sulfur. As mentioned, the sulfur concentration in TEC's syngas was running higher than their design case and the operators were still working on learning to implement the optimized control strategy for WDP.

The second reason the WGS system was shut down because of issues with the WGS system was the failure of sample control valves, which allowed syngas to leak out of the system. Effectively and safely addressing this problem required a shut down and purging of the WGS system with nitrogen. The fact that this shut down protocol also resulted in cooling of the WGS reactors resulted in over 24 hours of downtime before the WGS system could be restarted.

The selection of these valves had assumed that their distance from the full flow in the main process tube would have allowed a significant amount of cooling. However, the high steam concentration and larger sample flow necessary for the stream conditioning system increased the temperature of these valves above their design point, which apparently weakened the valve and caused their premature failure. The orifice approach used to address corrosion issues for the regeneration off-gas stream were then used to replace the valve and improve gas sampling of these syngas streams with very high steam

concentrations. Unfortunately, the timing of TEC's annual outage prohibited evaluating the full effectiveness of this new sampling strategy in the WGS system.

Although the WGS system was challenging to get started, the operators liked operating the WGS system. Their observation about operating the WGS system was that once it was running; its control system did a very good job of maintaining stable operation with essentially no intervention from the operators. The start-up issues can be corrected during design of subsequent commercial systems.

3.4 System Availability

In the previous sections, we have discussed the specific reasons for the down time associated with each of the systems (WDP, aMDEA®, and WGS). In this section, we will look at the time the systems were successfully being operated. ***Figure 8*** shows the total number of hours that each system of the 50 MW_e pre-commercial demonstration unit was operated from December through April. October and November were not included as the entire 50 MW_e pre-commercial unit was down while E-110 was being repaired. As the entire 50 MW_e pre-commercial unit was also shut down on April 15 for TEC's Annual Outage, April only had 360 hours of potential operation for the 50 MW_e pre-commercial unit. ***Figure 8*** also indicates TEC's downtime.

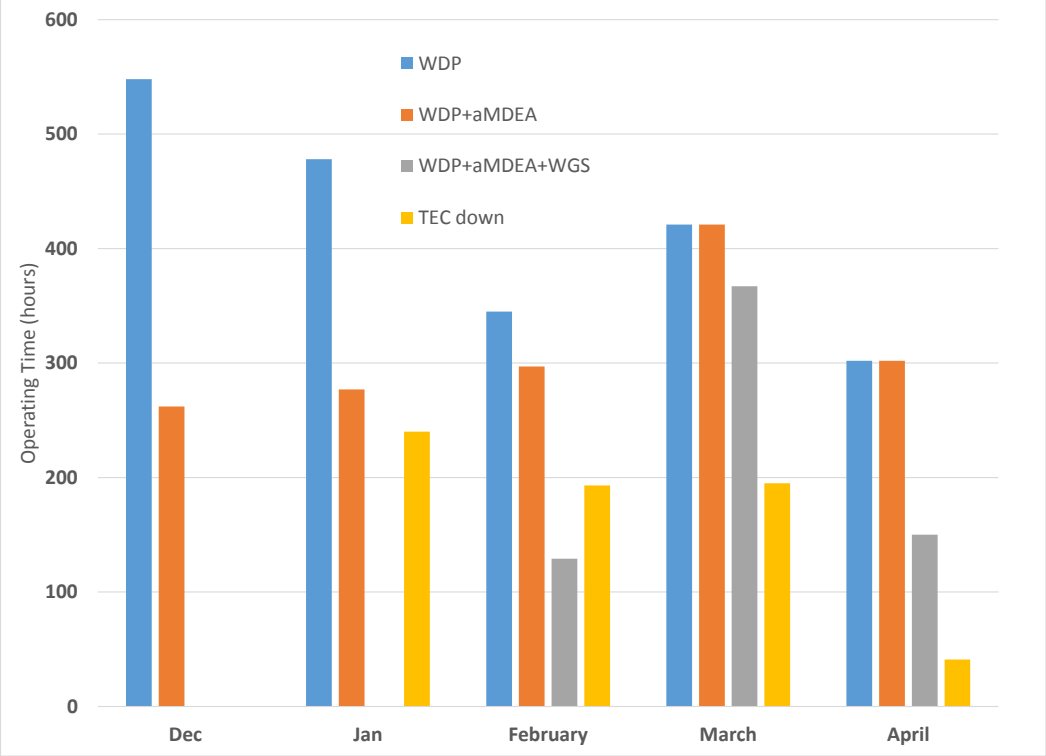

Figure 8. Accumulated operating time for different 50 MW_e unit processes

For ***Figure 8***, the key trend is continuous improvement in operation of the three individual systems as well as the integrated units. After addressing the issues with the anti-foam pump and lean amine cooler E-506, the WDP and aMDEA® system could be run together without any issue as can be seen in March and April. The fully integrated system with WDP, WGS, and aMDEA® also showed significant improvement. For the fully integrated system, all three units completed roughly 400 hours of operation in March. The WGS system is expected to accumulate slightly less operation time than the WDP and aMDEA®, because the WGS system, as designed for the 50 MW_e system, takes 7 to 9 hours to reach stable operation after starting WDP.

As the 50 MW_e pre-commercial unit can only operate when TEC is running, a more convenient means of looking at operating time is to look at the fraction or percentage of the total potential operating time that WDP, WGS, and aMDEA® systems were operated, or their availability. ***Figure 9*** shows the availability for WDP, WGS and aMDEA® from December through April. Over the five-month period, WDP achieved an average availability of about 80%. WDP's lowest availability during this 5-month span was just under 70%. The fact that for two months WDP's availability was about 95% shows that there is the distinct potential for WDP to achieve the high commercial availability (>99%) achieved by Fluid Catalytic Crackers (FCCs) which are very similar in design and operation (except for operation at lower system pressure). The fact that the availability of the aMDEA® and WGS also continuously climbed over the five-month span strongly suggests that the entire syngas cleanup process could easily have an availability identical to that of WDP, with appropriate future design changes to address the downstream issues that should be readily corrected.

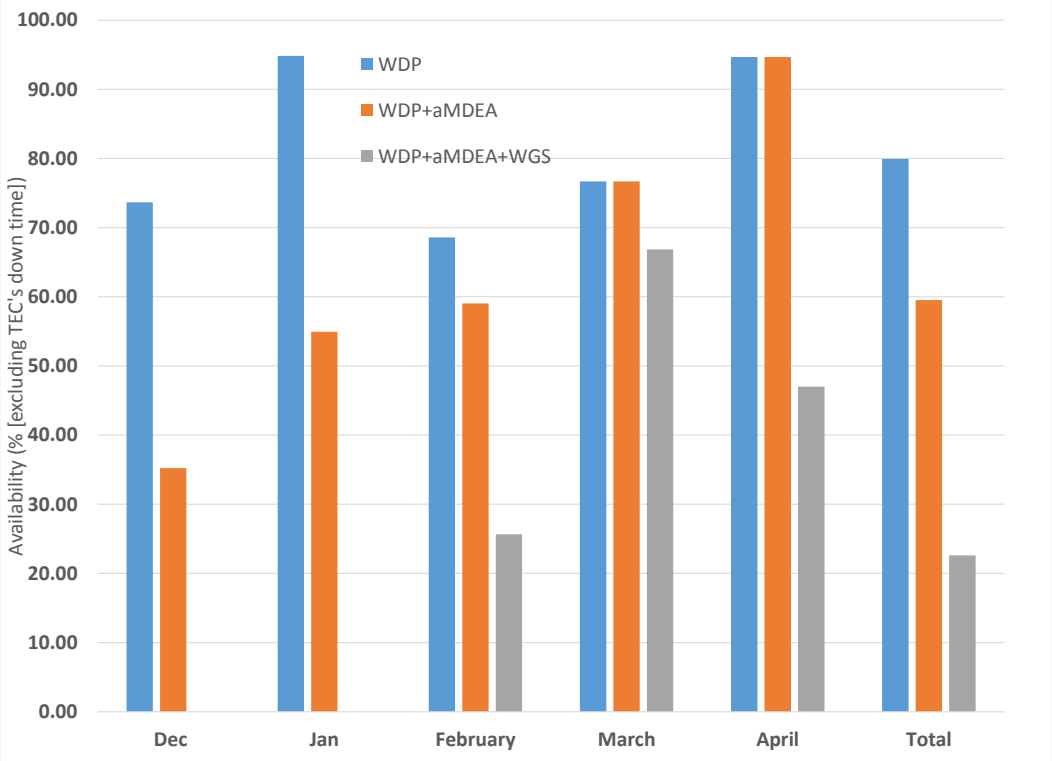

Figure 9. WDP, WGS and aMDEA® system availability

3.5 Post Operation Inspection/Analysis

After the pre-commercial system was shut down on April 15, 2016, the system was purged and sorbent removed to allow entrance into the WDP system to inspect the refractory, the tubes in E-110, the tubes in the heat exchangers on the regenerator, and the tubes in Furnace A.

During internal inspection of the adsorber and regenerator sections of WDP, the refractory was in general found to be in reasonable to fairly good condition. Based on its current condition, the refractory was projected to last for another operational campaign of approximately 2 to 2-1/2 years before major refractory work would be required. At this time, only minor maintenance work was necessary. The areas of most concern centered on the joints in which the refractory was installed in the field, especially where small size hindered accessibility. For these and a few other areas, the recommendation was to monitor these areas using a Forward Looking Infrared (FLIR) camera and Ultra-Sonic Testing (UT) of the

pressure shell on a quarterly basis. The valves on the internal cyclones were also inspected and found to be in good operational order.

For the tubes in E-110, the head of the heat exchanger was removed to expose the tube sheet and inlet to the tubes. Because the ferrules sealing the tubes into the tube sheet impede the eddy current testing method used, the ferrules for approximately 50% of the tubes were removed. The selection of the specific tubes from which the ferrules were removed was made random to ensure that any conclusions drawn were the best possible representation of the entire set of tubes.

The total number of tubes in E-110 is 291. For testing, the ferrules were removed from a total of 148 randomly selected tubes. Of these 148 tubes, eddy current testing was completed on a total of 76 tubes. All 76 tubes which were eddy current tested showed no relevant defects and/or less than 10% loss of the nominal wall thickness.

Based on the fact that these tubes experienced over 2,000 hours of syngas exposure at typical operating conditions without any signs of material loss, 310 stainless steel is deemed to be a suitable material of construction for the syngas interchanger.

The original testing plan was to test the actual pipe inside of the heat exchanger. However, to gain access to these pipes would require cutting open the exchangers to get access for testing. As we have much better access to the pipe leading into or out of these exchangers, the alternative testing approach was to measure the thickness of the entrance or exit pipes to which we had significantly better access. The pipe sections selected for testing were between:

- REV-121 and E-120
- E-120 and E-20A
- E-120A and E-121
- E-121 and E-121A.

For each of these sections of pipe, between 3 and 4 testing sites were selected and ultrasonically tested. To ensure representative measurement of the pipe thickness at each of these points the ultrasonic measurement was performed at 2 specific sites separated by approximately 6 inches and 4 locations around the circumference at each test site. For testing locations around elbows, the thickness at the inner and outer sections of the bend were also measured. The results were that the pipe thickness for each pipe section tested showed little or no change in thickness based on the nominal pipe thickness. Because there is no reduction in pipe thickness in the pipe segments connecting REV-121, E-120, E-120A and E-121, there is no indication of corrosion that would reduce pipe thickness. With this data and the fact that the pipe in the exchangers were exposed to the regenerator off gas with the same composition at temperatures bracketed by those in the different pipe sections, we can conclude that the pipe in heat exchangers E-120, E-120A and E-121 experienced little or no change in thickness caused by corrosion from exposure to regeneration off gas.

A total of five tubes in Furnace A were analyzed using radiographic analysis to ascertain tube status. For each of these tubes, the radiographic analysis was performed on three points around the circumference of the tube. These three locations were on the east and west facing points and bottom of the tube. The results for all tubes at all locations was "no pitting or damage noted". These results indicated that 347 SS would also be a suitable material to use with the high sulfur syngas at high temperatures.

3.6 Summary

During pre-commercial demonstration and development, system availability will increase through improvements in:

- Equipment specification, which includes auxiliary equipment,
- Design criteria, and
- Operational experience.

The key metrics demonstrating this improvement were the steady increase in availability and total number of operating hours for the individual units as well as the overall system. Another change that

occurred during this project was the causes for downtime shifted away from unit equipment and operational issues to inability to operate due to non-operation of an upstream unit.

One of the most problematic issues was with corrosion of heat exchangers. The design specifications used for the syngas interchanger proactively attempted to address one type of corrosion, but actual operation demonstrated that another form of corrosion occurred at our typical operating conditions. Armed with this knowledge, we selected better materials of construction for this syngas interchanger and effectively demonstrated elimination of corrosion for these materials of construction.

Although the semi-lean heat exchanger in the aMDEA® unit was not replaced, a suitable material of construction for this specific environment is known. If sufficient time had been available to design, manufacture and install a new tube bundle made from a more suitable material of construction, both availability and performance of the aMDEA® unit would have improved significantly compared to the system's performance in April.

Other auxiliary equipment that continued to impact operation were the syngas and air compressors and the system for addition of anti-foaming agent for aMDEA®. During the operation achieved in this project, we have been able to identify key specifications for these systems as well as a recommended spare parts list that will enable reducing their downtime.

Finally, there was a significant increase in operational experience. This experience increase came with both the ability to identify the operational data that will result in system failure, if not corrected, and the appropriate corrective actions required to restore/maintain stable system operation. The most promising example of this was the ability of the operators to identify the start of sorbent carryover in the regenerator due to temperature changes and the correct operator intervention required to stop this sorbent carryover.

With these improvements, the design and operation of the next commercial unit will have significantly less technical risk. The operational experience supporting the original design and these improvements has significantly improved end-user's confidence for the technology and is resulting in requests for technical and financial information for a number of potential commercial projects. Accumulating sufficient operating time and experience to attract potential end user interest was one of the primary objectives for this project.

4. Performance

4.1 WDP Effluent Sulfur Concentrations

For WDP, several of the key performance criteria relate to the sulfur concentration in the product streams. For the syngas product, the key performance criteria are the sulfur concentration and amount of sulfur removal achieved. Although the overall sulfur concentration in the product is generally accepted as the required information for establishing specification for any additional desulfurization processes to protect downstream processes, concentrations of both H_2S and COS were measured for both the raw syngas and the WDP product syngas.

The inlet H_2S and COS concentrations of the syngas for the entire operating period are shown in ***Figure 10***.The known sources of variation that cause scatter in the inlet sulfur concentrations are composition and sources of the coal/petcoke mixture fed to the gasifier and transitioning from nitrogen recycle to syngas during startup and shutdown. In addition to these sources of natural variation, there also seems to be an additional source of variation. The additional source of variation is responsible for the higher scatter in the data observed in the data prior to the end of January. No specific change was identified that could have resulted in this change in inlet concentration data scatter. However, as continuous minor changes and improvements were made to the sample conditioning system, it is possible that the cumulative effect of these changes caused this reduction in data scatter. Alternatively, after operating for close to two months, some change, most probably the elimination of a possible pooling of condensed water in the conditioning/sampling loop finally occurred. Based on the data used to generate ***Figure 10***, the average inlet H_2S and COS concentrations during our operation were 10,185 ppmv and 631 ppmv, respectively.

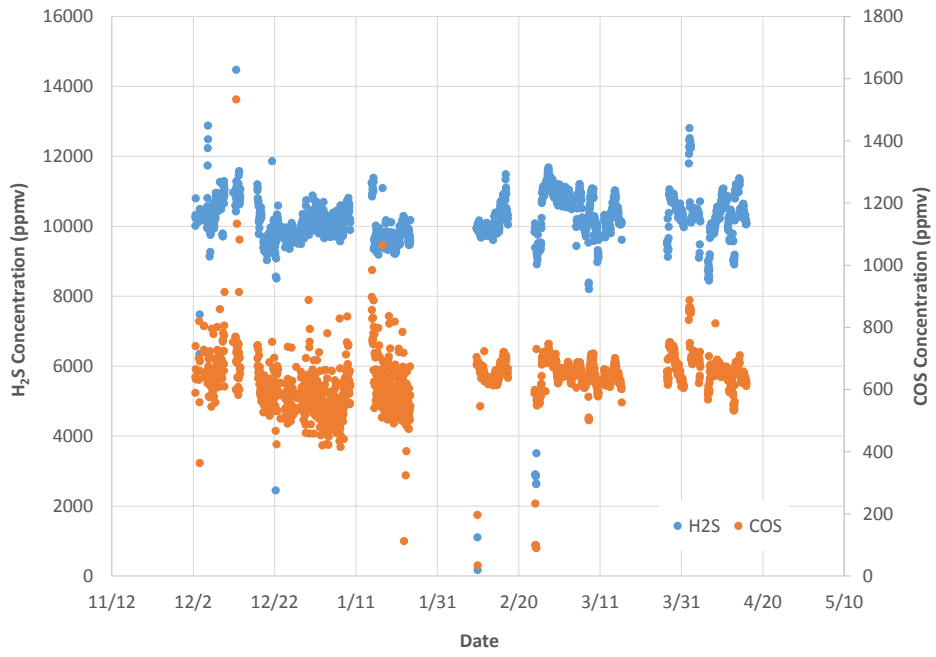

Figure 10. Sulfur concentrations in syngas from TEC

The effluent sulfur concentration data on a daily basis are shown in ***Figure 11***. ***Figure 11*** does show relatively smooth concentration profiles for both H_2S and COS. The average standard deviation for the daily averaging periods for the H_2S concentration was 5 ppmv and 1.2 ppmv for the COS

concentration. With these standard deviations, the effluent concentration for H_2S clearly falls between 10 ppmv and 30 ppmv. Using the standard deviation, the effluent COS concentration is less than 2 ppmv. Because the relative deviation for the effluent COS concentrations was larger than the H_2S concentrations, a closer inspection of the data was conducted. Through this inspection, a systematic shift in the average effluent COS concentration was noticed for the COS concentration data before and after February 20. The specific systematic change that occurred based on the February 20 reference date was the start of operation of the WGS system. Because the effluent sulfur concentrations from WDP are measured upstream of the WGS system, there is no process reason why the operation of the WGS system should affect the effluent COS concentrations from WDP.

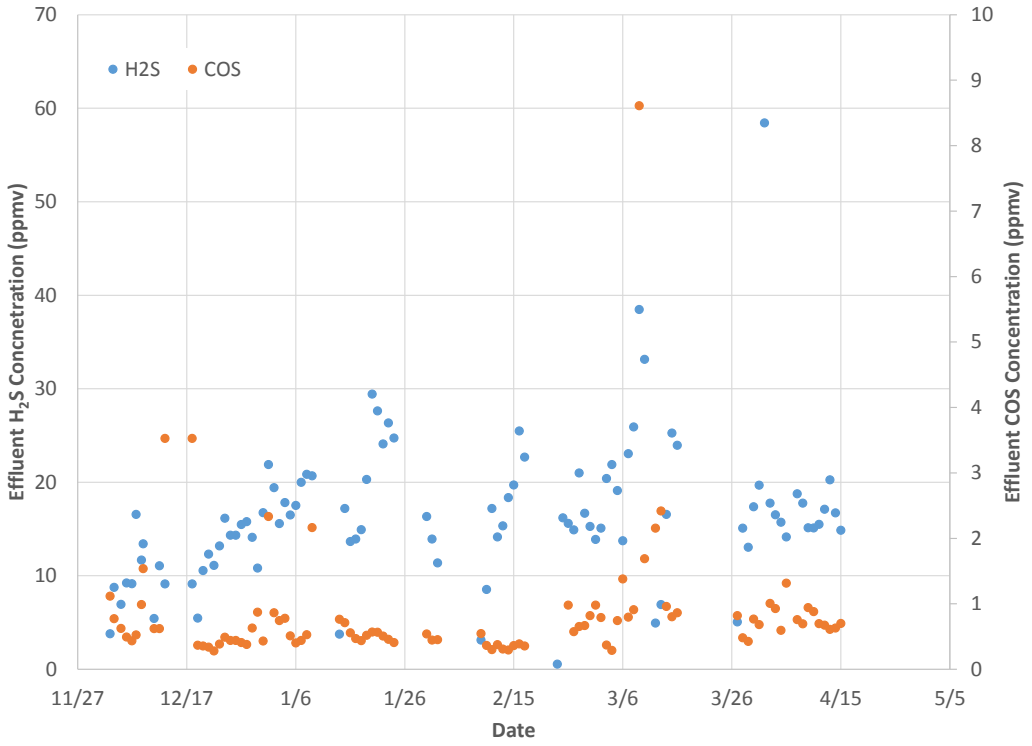

Figure 11. Daily average of effluent sulfur concentrations

Although the data used to generate ***Figure 11*** do show typical averaged effluent sulfur concentrations for WDP, the fact that these data represent a daily average still allows for some significant deviations in effluent sulfur concentration over a 24-hour period. To address this issue, we went back and processed the data in a slightly different manner. In this approach, we broke the expected range of concentrations that were measured into a series of concentration bands. For H_2S, the typical measured effluent concentration range for WDP was between 0 and 50 ppmv. We broke this into roughly 9 concentration bands with a span of roughly 5 ppmv. Because the analytical equipment completes a measurement sequence every 10 minutes, a concentration measurement was collected every 15 minutes to create the concentration data sets. We then counted the number of data points in a data set that were present in each concentration band. The result was the frequency plot shown in ***Figure 12***. The results in ***Figure 12*** show that > 90% of the WDP effluent H_2S concentration data are between 0 and 25 ppmv and > 95% of the data lies between 0 and 30 ppmv. Based on these results, the data clearly demonstrate that the WDP was effectively and consistently reducing an inlet H_2S concentration from about 10,185 ppmv to < 30 ppmv.

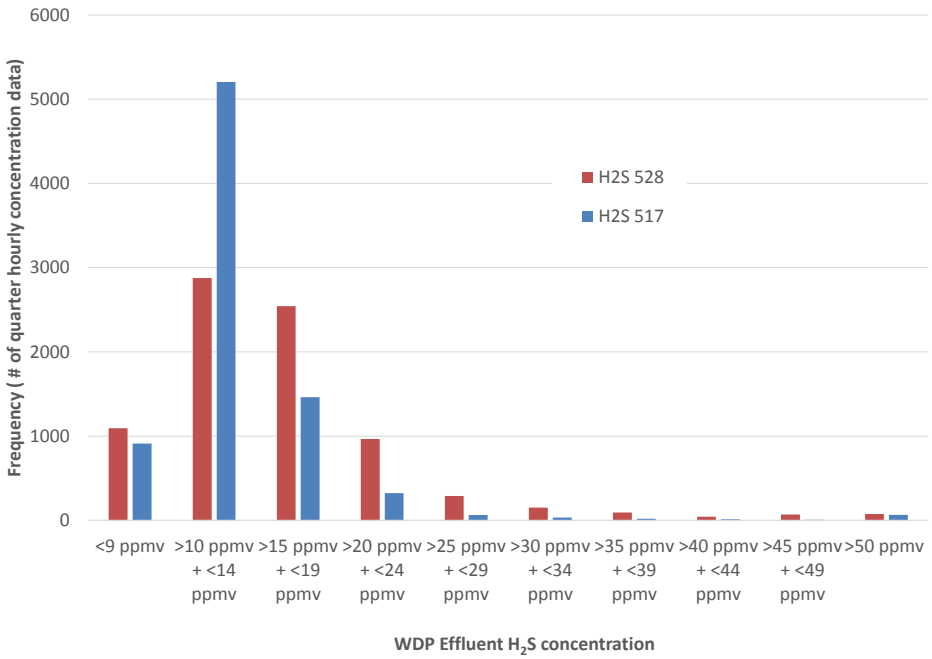

Figure 12. Frequency plot of effluent H_2S concentrations for WDP (528) and LTGC (517)

Figure 12 also has the results for the H_2S effluent concentration for LTGC processed in the same manner. The results in ***Figure 12*** for the LTGC effluent H_2S concentration are essentially identical to those for the WDP effluent for the entire testing period from December through April.

Prior to February 20, the WGS system was being bypassed. Therefore, the only syngas composition changes between the effluent of WDP and LTGC would be the loss of water vapor concentration due to the condensation. As the analytical results are measured on a dry gas basis, there should be no concentration difference between the effluent H_2S from WDP and LTGS prior to February 20, which is confirmed by the data in ***Figure 12***.

For the data after February 20, the two means in which the WGS process would be able to change the sulfur concentrations would be by sulfidation of the metal oxide components in the catalyst or the hydrolysis of COS. At these low concentrations, any sulfidation would be limited to a potential surface layer based on thermodynamics. Development of a sulfided surface layer would lower the effluent H_2S concentration until the surface was saturated. There is also a strong possibility that formation of a sulfide surface layer would effectively poison the catalyst reducing its WGS activity. However, there was no effective loss of WGS catalyst activity observed when this system was started (see Section on WGS Activity). Consequently, there is no solid evidence that the H_2S effluent from the WGS system would be significantly affected by sulfidation of the WGS catalyst

For COS hydrolysis, the effluent COS concentration is already less than 1 ppmv. If any COS hydrolysis does take place in WGS, the net increase in H_2S effluent concentration would have to be a fraction of the COS concentration and numerically < 1 ppmv. For these small changes, we would probably not be able to see a difference in the effluent H_2S concentration. Thus, the observations that the H_2S effluent from WDP and LTGC are essentially identical for the entire operating period confirm that the effluent H_2S concentration from WDP was < 30 ppmv.

We also used this same approach to process the effluent COS concentration data from WDP. The results from this data processing are shown in ***Figure 13***. ***Figure 13*** shows that over 80% of the effluent COS concentration data lies between 200 ppbv and 800 ppbv. However, the frequency distribution in ***Figure 13*** looks like it is a combination of two different distributions with different peak concentrations. Previously, we mentioned that there was a shift in the average effluent COS concentration between data

prior to and after February 20, which marked the beginning of operation of the WGS system. We broke the WDP effluent COS concentration data into these two periods of time and reprocessed the data, which is shown in ***Figure 14***. In addition, we added the effluent COS concentration data from the LTGC for the period prior to February 20, when the syngas effectively bypasses the WGS system and the syngas composition after LTGC should be identical to the syngas composition from WDP.

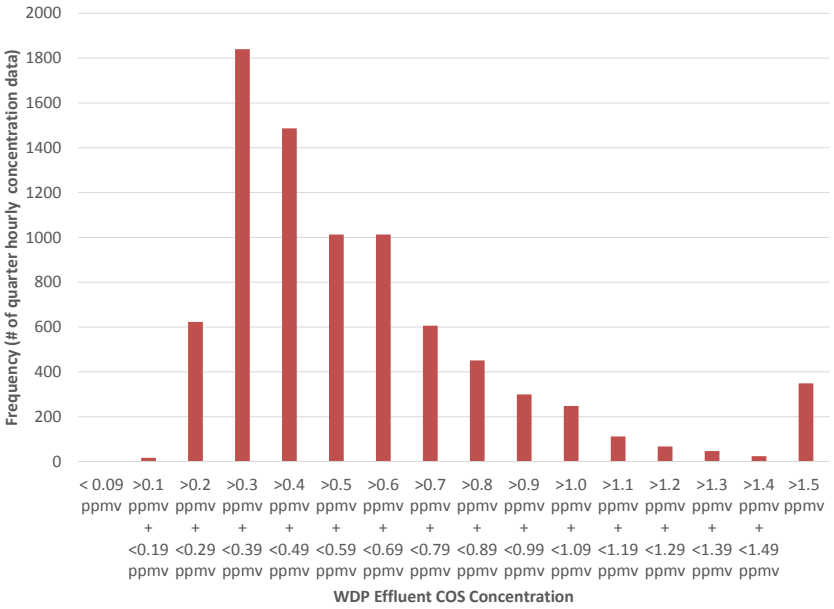

Figure 13. Frequency plot of effluent COS concentrations for WDP (528)

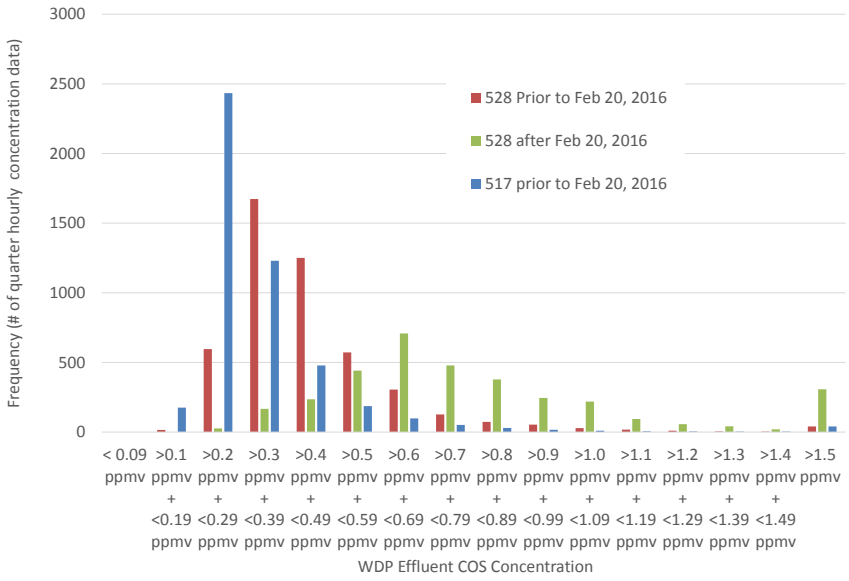

Figure 14. Frequency plot of effluent COS concentrations for WDP (528) and LTGC (517) broken down to periods with and without WGS operation

Figure 14 shows that for the data prior to February 20, both the WDP and LTGC COS effluent concentrations are very similar with over 85% of the COS concentration data between the concentrations of 200 ppbv and 600 ppbv. For the period after February 20, which includes the operation of the WGS system, the most frequent COS concentrations lie between 400 ppbv and 900 ppbv.

These observations about the COS effluent concentration data indicate that there is a distinct difference in the frequency of the effluent COS concentration for the periods before and after February 20. This is unexpected for the difference in the effluent concentration was linked to periods of operation with and without the WGS system, which is downstream of both the WDP and the syngas sampling point. There is no reason a downstream system should have any impact on an upstream system particularly when there is no recycled syngas stream.

Although the syngas source for the TCRP skid was upstream of the syngas sampling point for the effluent from WDP, the TCRP was only taking < 1,000 SCFH of syngas out of a syngas flow of over 1,000,000 SCFH. It is not likely that the TCRP skid operation could have affected the COS concentration and only the COS concentration.

Another possible explanation for the different distributions would be a change in the desulfurization ability of the RTI-3 sorbent. Because the change in desulfurization performance was essentially instantaneous, it should be linked with a sudden poisoning of the RTI-3 sorbent. A constant poisoning would tend to show up as a steady and cumulative decline in desulfurization performance. Because essentially the same batch of RTI-3 was used in the system, there was no significant change in the composition of RTI-3 in the system. Finally, any change in the desulfurization performance should affect both H_2S and COS, but no change in the H_2S effluent concentration before and after February 20 was observed. Therefore, at this time, there is no reasonable technical explanation for the change in the effluent COS concentration that was observed beginning on February 20. Regardless, the data indicated that WDP consistently removed ~99.9% of the inlet COS.

4.2 Regeneration Off Gas Composition

In addition to the sulfur leaving the WDP in the effluent syngas, sulfur also leaves WDP in the regeneration off gas (ROG) as SO_2, which was fed into TEC's Sulfuric Acid Plant (SAP). The SO_2 concentration in the ROG for the December through April operation of WDP can be seen in ***Figure 15***. ***Figure 15*** provides the SO_2 concentration from 2 distinct photometric analyzers. The average ROG SO_2 concentration during this period was 7.5 mol% for the ABB Limas-11 UV photometer (AI 559) and 7.7 mol% for the Ametek UV photometer (AI 559A). The variation in the ROG SO_2 concentration was caused by changes in air flow and nitrogen added to the system for purging differential pressure tap lines, fluidization of the standpipes and sorbent sparging. During stable operation, all the oxygen in the air is consumed by the regeneration reaction. Because the resulting SO_2 concentration is fixed by the concentration of oxygen in air, changes in air flow do not affect the relative concentrations of SO_2 to nitrogen associated with the air flow. However, there is a significant amount of nitrogen added for sparging, fluidization in the stand pipes, and instrument purging. Although this nitrogen addition did vary from run to run, it was generally fairly constant during any particular run. As air flow changes, the constant flow of additional nitrogen would result in changes in the relative SO_2 concentration in the ROG. The correlation between air flow and the ROG SO_2 concentration can also be seen in ***Figure 15***.

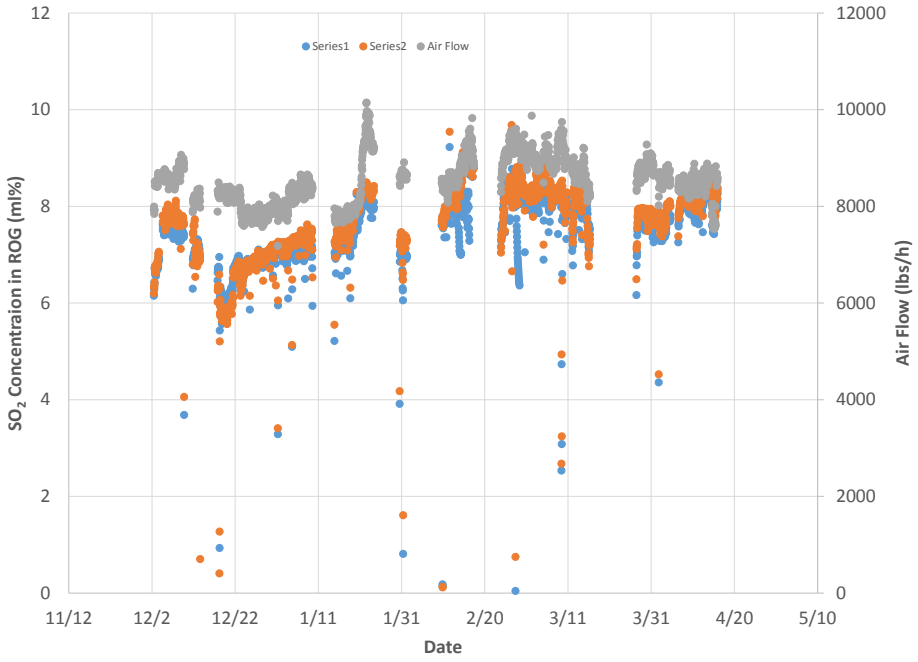

Figure 15. Effluent SO_2 concentrations in ROG

4.3 Adsorber Temperature Profiles

Figures 16 and ***17*** show the temperature profiles for the Adsorber mixing zone and Adsorber riser for all operation between December and April. ***Figure 16*** shows that the temperature span across the mixing zone was approximately 40°F. During operation, the operating window for the temperature in the mixing zone was from 1,070° to about 1,200°F. The data from thermocouple TIT-554 seems to track with the other thermocouples in the mixing zone for the entire operating period. However, after January, the gap between thermocouple TIT-554 and the other thermocouples increased. This is not believed to be an actual process change as thermocouple TIT-555, which is at a higher point in the mixing zone, does not show a similar change. These data would indicate that something happened to skew TIT-554's reading.

From December through the middle of January, the temperature window for the Adsorber mixing zone stayed relatively consistently between 1,110° and 1,180°F. In the middle of January, the syngas flow rate through the Adsorber was significantly increased to see how much syngas the system could process. The higher syngas flow provided additional thermal mass to heat resulting in lower temperatures in the Adsorber. In the runs from February through April, the temperature profile during each run was seen to systematically decrease over the course of the run. In the WDP system, the regeneration reaction provides a lion's share of the heat due to the exothermic regeneration reaction. Consequently, the Adsorber effectively provides a means to cool the system. During operation from February through April, the temperature in the regenerator consistently increased more over the course of a run than had been observed in the December operating period. To help maintain the regenerator outlet temperature below the emergency shutdown limit, more aggressive operator intervention was required to effectively cool the Adsorber. Because of this cooling, the temperatures in the Adsorber decreased over the course of each run.

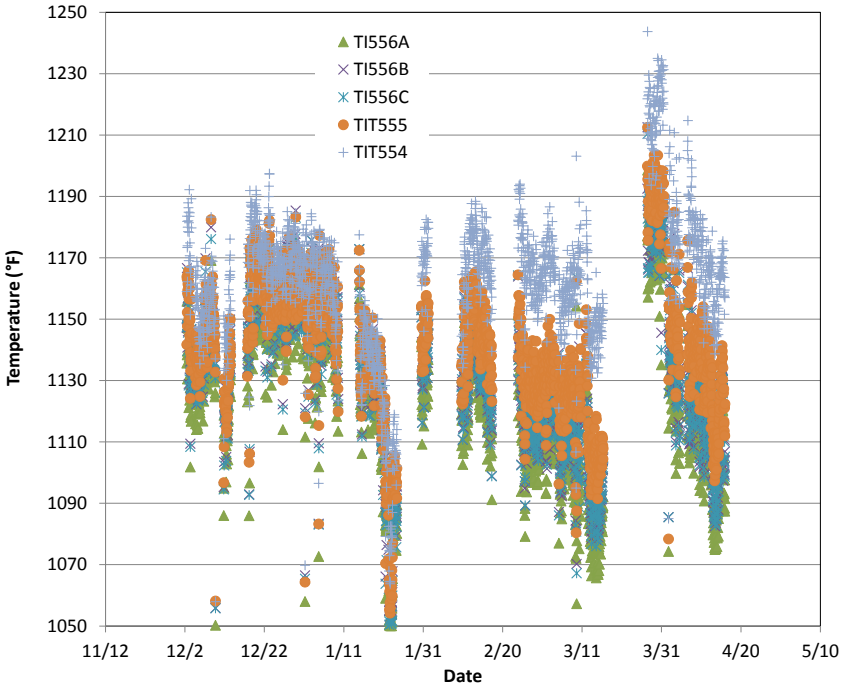

Figure 16. Temperature profiles in adsorber mixing zone

Figure 17 shows the temperature profiles for the Adsorber riser for operation. In general, the same trends that were observed for the Adsorber mixing zone were also observed in the riser temperature profiles. However, the temperature span across the Adsorber riser was about 25°F, which is slightly less than the Adsorber mixing zone, and the temperatures in the riser are about 10°F to 15°F hotter than the Adsorber mixing zone.

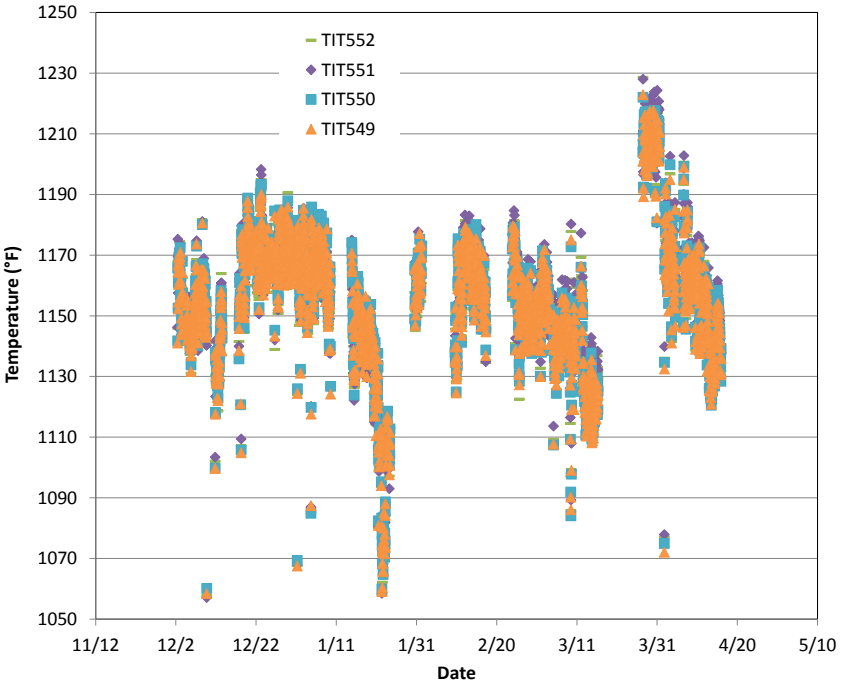

Figure 17. Temperature profiles in adsorber riser

4.4 Regenerator Temperature Profiles

Figures 18 and ***19*** show the temperature profiles for the Regenerator mixing zone and riser during operation from December through April. From December through January, the temperature in the Regeneration mixing zone was between 1,320°F and 1,420°F with the relative temperature difference across the mixing zone of roughly 60°F. From February through the middle of April, the temperature in the Regenerator mixing zone was between 1,300°F and 1,460°F with a temperature span across the Regenerator mixing zone of 80°F. The higher temperatures in the Regenerator and their trend to consistently increase over the course of a run during February through April required additional cooling in the Adsorber, which resulted in the temperatures in the Adsorber consistently decreasing over the course of a run.

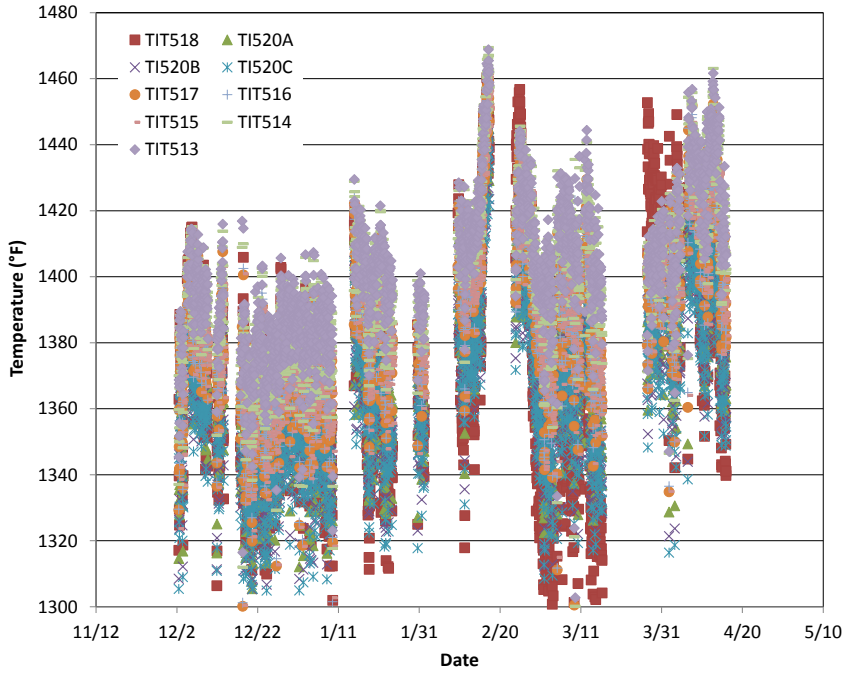

Figure 18. Temperature profiles in regenerator mixing zone

The temperatures in the Regenerator riser run from about 1360°F to about 1420°F during December and January with the temperature span across the Regenerator riser of about 30°F. For February through April, the temperatures in the Regenerator riser run from about 1,380°F to about 1,460°F with a temperature span of about 30°F. As would be expected, the trends in the Regenerator mixing zone and riser are essentially identical.

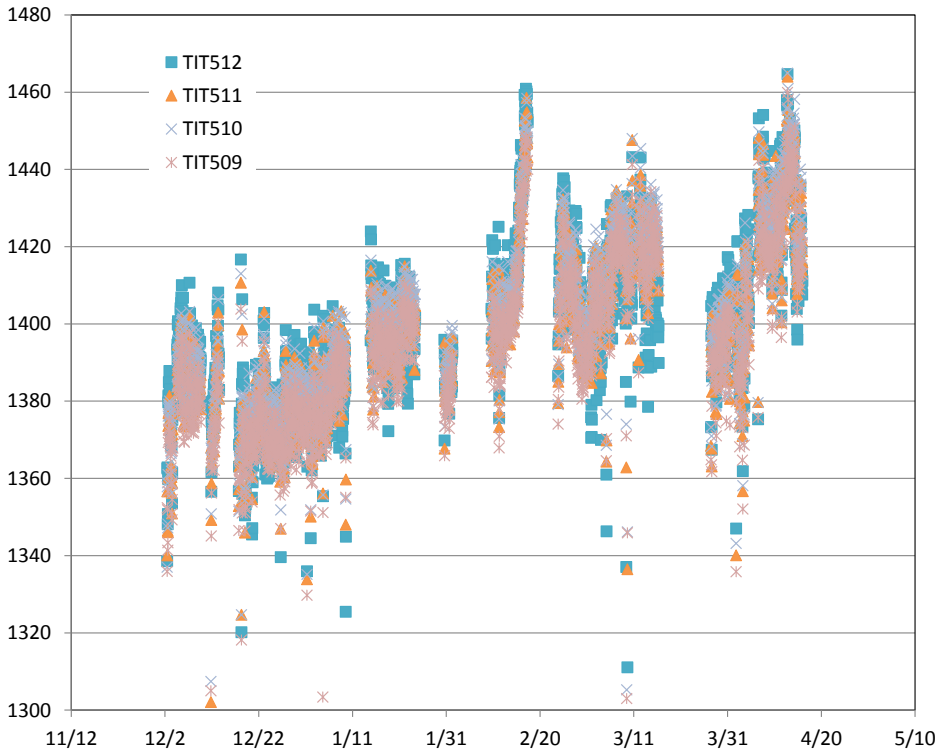

Figure 19. Temperature profiles in regenerator riser

4.5 Sorbent Regenerability

The ability of the RTI-3 sorbent to effectively participate in the paired chemical reactions that allow sulfur to be removed from the syngas in the Adsorber and released in the Regenerator is critical to effective performance of the WDP. In the Adsorber, the reactions are $ZnO + H_2S = ZnS + H_2O$ and $ZnO + COS = ZnS + CO_2$. For the Regenerator, the reaction is $ZnS + 1.5\ O_2 = ZnO + SO_2$. Because the sorbent is effectively recycled in the process, the same sorbent is expected to perform these reactions repetitively for many cycles to achieve long periods of stable operation. It is reasonable to assume that after some period of operation, the sorbent will lose enough of its ability to perform these reactions and that the desulfurization performance of WDP would consequently drop below its target value. When this happens, fresh sorbent must be added and the old sorbent removed to maintain the target desulfurization performance. Sorbent regenerability is the concept we use to try and capture the sorbent's ability to perform these reactions at any point in the sorbent's useful life. Our ultimate goal would be to quantify the addition of fresh sorbent to replace sorbent that is no longer sufficiently active to participate in the paired reactions and achieve the required desulfurization performance.

Ideally, we could operate the system in such a way as to continuously use the same sorbent batch until it failed. In reality, the loss of sorbent due to attrition, which is the other process that requires the addition of fresh sorbent, and process upsets and/or the need to remove sorbent from the vessel for process repair make operating on the same sorbent batch challenging.

During the December through April operation, our remaining inventory of fresh sorbent had been effectively introduced into WDP by early February. After this point, all sorbent added back into the system was obtained from sorbent collected from the system from previous system upsets. In addition, all sorbent additions were introduced into the system during heat up prior to starting a run. Therefore, during any specific run, the sorbent inventory in WDP did not change due to sorbent addition.

Based on the analysis of WDP effluent H_2S and COS concentrations during operation, we did not detect any obvious change in the sulfur removal performance over any specific run or the entire operating

period. The only exception to this was the change in effluent COS concentration that occurred on about February 20, 2016. Although a change in Adsorber reaction rates could be responsible for this change, it appears to only have changed the reaction between the sorbent and COS. No change was detected in the H_2S reaction at the time this change in COS was detected. Furthermore, the similarity between the reactions between the sorbent and H_2S and COS would suggest that any change in COS reaction rate would also change the H_2S reaction rate. The change in the effluent COS concentration from WDP was a lone event that occurred between two runs. These observations strongly suggest that if this change can eventually be linked to sorbent deactivation it was a sudden poisoning probably caused during the shutdown. Thus, there was no indication of deactivation for the reactions in the Adsorber.

The analysis of the effluent SO_2 concentration from the Regenerator had an average value of 7.6 mol% throughout operation of WDP from December through the middle of April. The trends in the effluent SO_2 profile were seen to track with changes made in the air flow to control the process. No systematic decline in the effluent SO_2 was noted over a single run or the entire operating period. During this same operating period, the effluent O_2 concentration consistently remained below 1,000 ppmv. The lack of any systematic decline in effluent SO_2 concentration or increase in unconsumed O_2 indicates that there was no measurable decline in reactivity for the regeneration reaction.

During the last week of operation, sorbent samples were collected from the Adsorber and Regenerator on a daily basis. These samples were analyzed for their zinc and aluminum content. The result of this analysis was used to calculate a zinc to aluminum ratio. The results did not show any significant change in the zinc to aluminum ratio. As one potential deactivation mechanism would be the loss of zinc from the sorbent, the absence of any significant change in the zinc to aluminum ratio indicates that this deactivation mechanism did not occur to any measurable extent during the pre-commercial demonstration.

In combination, these results indicate that any decline in sorbent regenerability is slow enough that over the total operating period of over 3,500 hours during this pre-commercial demonstration, no measurable decline in reactivity for either the Adsorber or Regenerator reactions was noticed. Because 3,500 hours represents about 50% of a full year of operation, we can confidently predict that no addition of fresh sorbent will be necessary for at least 6 months of operation to replace deactivated sorbent. Considering that a significant portion of the sorbent was in the WDP unit for most of two years, it can also be expected that no significant deactivation occurs from simple aging of the sorbent. We do anticipate that sorbent attrition will result in the need to add fresh sorbent during operation. Therefore, the results from this pre-commercial demonstration indicate that sorbent attrition, and not sorbent deactivation, will be the primary factor affecting sorbent replacement rates and costs.

4.6 Sorbent Attrition

Of all the performance metrics, sorbent attrition was potentially the most challenging to measure. The filter systems were designed to effectively capture any entrained fines in the effluents from both the Adsorber and Regenerator. Each filter system also had a lock hopper system to transfer the sorbent fines collected in the filters to storage drums setting on balances that allowed tracking weight changes. In spite of these design efforts to help measure sorbent attrition losses, effective measurement of sorbent losses due to attrition was still challenging.

As part of this pre-commercial demonstration involved learning to operate the system, system upsets would occasionally result in carryover of bed material that was not fines. With increasing operating experience, we were able to significantly reduce the number and frequency of these upsets, but we could not eliminate them 100%. We found that after an upset there was a relatively long period of time during which the amount of carryover decreased. Furthermore, we found that certain ranges of the heating process during startup could result in carry over of sorbent. Because a significant fraction of the sorbent in this carryover material was not fines, attempting to measure sorbent attrition during periods of carryover and for a certain period after a carryover event was not possible.

The lock hopper system on the filters also struggled to effectively transfer the sorbent from the high-pressure filter to an atmospheric drum. Because carryover events resulted in significantly larger amounts of sorbent needing to be removed than the system was designed for, the lock hopper system was used to transfer significantly larger amounts of sorbent, for which the valves were used more frequently than planned. The abrasive nature of the sorbent and the more frequent use of the valves eventually led to significant wear of the valves. Even with periodic rebuilding of these valves, towards the end of our operation, we had cut back the frequency of dumping the lock hopper system to reduce additional wear to a bare minimum.

When the system was effectively operating, the material collected from the filters had the consistency of flour or talcum powder. At this size, the sorbent effectively views gravity as a suggestion and not the law. Thus, transferring sorbent from the high-pressure system to the atmospheric drum was a challenge. The sorbent fines would plug valves, sensors, and even vent lines requiring additional maintenance. As the goal of this maintenance was to get the system to run, loss of sorbent as the system was fixed was not even an issue.

Early during operation, an attempt to use water to effectively rinse the sorbent out of the lock hopper system was attempted. The resulting issues were such that any option involving the introduction of water in the lock hopper system was immediately dismissed by the operating and maintenance teams. However, this did not stop condensation of the steam in the syngas in the system occurring in the Adsorber lock hopper system even with heat traced hoppers. We know this happened as damp material which included actual liquid water was discarded from the lock hopper system on several occasions. There were also periods when no sorbent was removed from the Adsorber for several days. We do not believe that the attrition rate could be this low and assume that enough steam was condensing to trap sorbent in layers on the lock hopper walls.

Finally, to make our inventory of fresh sorbent last as long as possible, we would preferentially load any carryover sorbent prior to fresh sorbent. But any carry over sorbent would have a significantly higher amount of fines than fresh sorbent, which would be slowly entrained out during startup and the early stages of a run.

Despite these challenges, the sorbent losses from the Adsorber and Regenerator were collected and used to calculate a daily mass loss. The total loss for the entire system was assumed to be the sum of Adsorber and Regenerator losses. The results from this analysis are shown in ***Figure 20***. ***Figure 20*** also includes the design value for sorbent losses. When the days with high sorbent losses associated with startup and/or system upsets are ignored, sorbent losses are consistent and significantly below our design value.

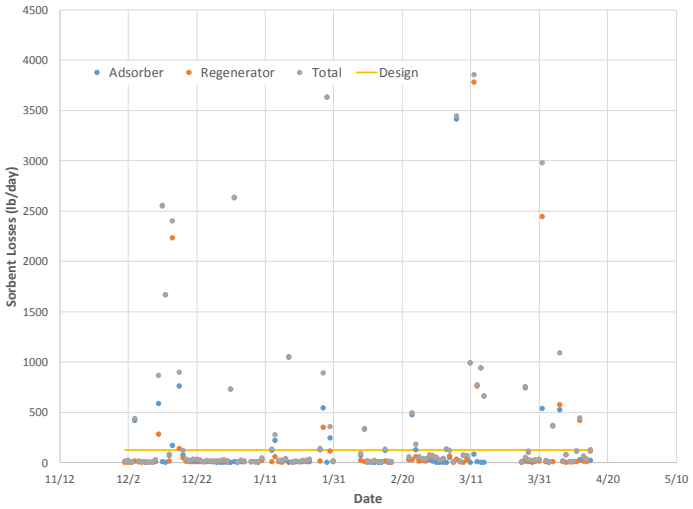

Figure 20. Daily sorbent losses

4.7 Effect of WGS on Effluent Sulfur Concentrations

In the previous section, we have used the effluent syngas sulfur concentration from the LTGC system to confirm the trends observed in the WDP effluent syngas sulfur concentrations. The overall effluent syngas sulfur concentration profiles from LTGC are shown in ***Figure 21***. In general, the H_2S and COS concentration profiles in ***Figure 21*** look very similar to those in ***Figure 2***. It is this similarity that allowed us to use this data as confirmation of trends observed in the WDP effluent syngas sulfur concentration data. To assist with analysis of this concentration data, we have applied the same frequency analysis we used on the WDP concentration data. The results for frequency analysis of the H_2S effluent syngas concentration data have been shown in ***Figure 12***.

Previously, we examined the impact the WGS catalyst would have on the effluent H_2S concentration from the WGS system. Our general conclusion was there would be no significant long-term effect. The primary reasoning for this was if the WGS also catalyzed any COS hydrolysis, the change in the H_2S effluent concentration would be so small it would not necessarily be apparent. This was confirmed by the results shown in ***Figure 12***. However, any COS hydrolysis will have a very significant impact on the effluent COS concentration. Thus, we broke the effluent LTGC COS data into the periods with and without WGS operation. The frequency analysis results for this COS effluent concentration data are shown in ***Figure 22***. To effectively demonstrate any differences, the frequency analysis of all the effluent COS data prior to February 20 was also included in ***Figure 22***.

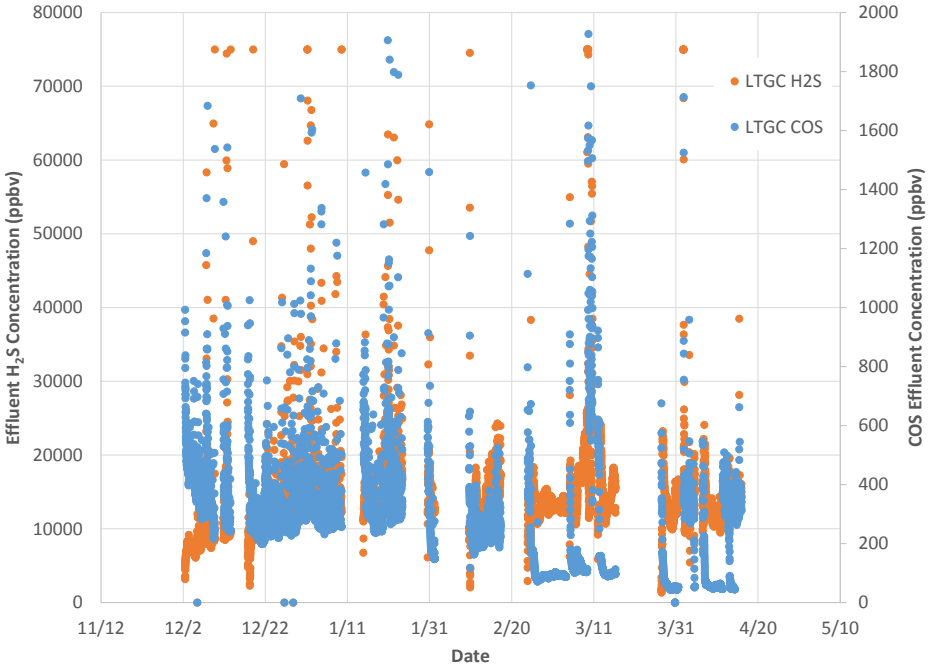

Figure 21. Effluent sulfur concentration profiles for LTGC

The results in ***Figure 22*** show a clear difference. For the data without WGS and data prior to February 20, the frequency analysis of effluent LTGC COS concentration data showed that > 90% of the COS concentration data fall between 200 ppbv and 500 ppbv. The similarity of the data without the WGS and prior to February 20 serves to validate that the effect is due to WGS operation. The effluent COS data during WGS operation shows that about 90% of the effluent COS concentration data has a concentration of < 200 ppbv. Based on our assumption that the WGS catalyst would also catalyze COS hydrolysis, a decrease in the effluent COS concentration is exactly the change we would expect.

A closer look at the data in ***Figure 22*** shows that the frequency profile for the period with WGS operation might be the result of two distributions because of the slight climb of frequency of COS concentration data in the 300 ppbv to 400 ppbv range. The fact that this secondary distribution has a similar COS concentration frequency as the data set without WGS operation suggests that the most probably cause for this was the inclusion of effluent COS data during the period when the syngas flow through the WGS reactors was being increased to full syngas flow. The bypassing syngas would result in a higher effluent COS concentration frequency between 200 ppbv and 500 ppbv (typical effluent concentration without WGS), which is what we observe.

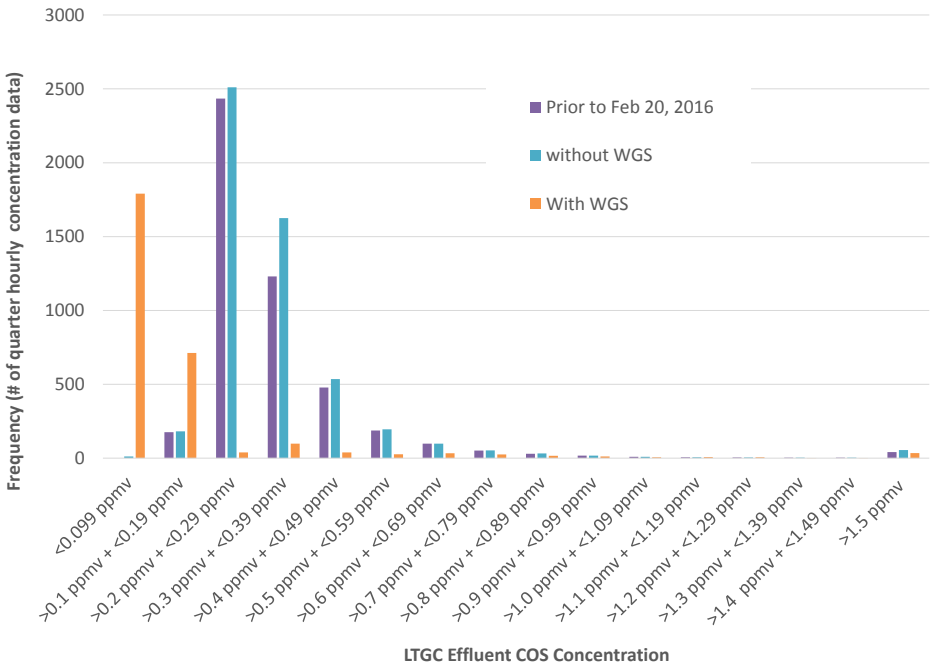

Figure 22. Frequency plot of effluent COS concentrations for LTGC (517) broken down to periods with and without WGS operation

4.8 Effluent Sulfur Concentrations for aMDEA®

The effluent sulfur profiles for the syngas from the aMDEA® system are provided in ***Figure 23*** for the operating period from December through April. ***Figure 23*** clearly shows that there is a reduction in the effluent H_2S and COS concentration when aMDEA® is in operation. Frequency analysis was also performed for these H_2S and COS effluent concentrations from the aMDEA® system. The concentration data was broken into periods during which the aMDEA® was being bypassed and in operation. The results for the H_2S concentration data are shown in ***Figure 24***. ***Figure 24*** clearly shows that when the aMDEA® system is not in operation, the effluent H_2S concentration is > 9 ppmv. Unfortunately, 10 ppmv was the maximum concentration that could be measured by the analytical system used for the aMDEA® syngas effluent. But these results do serve as additional verification of the relative magnitude of the effluent H_2S concentrations from WDP. When the aMDEA® system was operating, about 84% of the effluent H_2S concentrations fall between 100 ppbv and 500 ppbv. This clearly shows that the aMDEA® system effectively removes a large fraction (about 98-99%) of the H_2S remaining in the syngas from WDP.

Because the effluent COS concentration from LTGC was observed to change when the WGS system was in operation, the effluent COS data for periods in which both WGS and aMDEA® were both in operation was also included in the COS frequency analysis for the data for the aMDEA® system. The

results from the frequency analysis are shown in ***Figure 25***. For periods when aMDEA® was not operating, approximately 92% of the concentration data falls between 200 ppbv and 500 ppbv, which are very similar to the results that were seen for the effluent COS concentrations from WDP and LTGC prior to February 20. When the aMDEA® system was in operation, the frequency analysis shows that > 93% of the effluent COS concentration data for aMDEA® was < 150 ppbv. Although the effluent COS concentration data for the LTGC showed a difference between periods with and without WGS, the COS effluent concentration data for aMDEA® does not show a difference between periods of operation with both aMDEA® and WGS and with just aMDEA®.

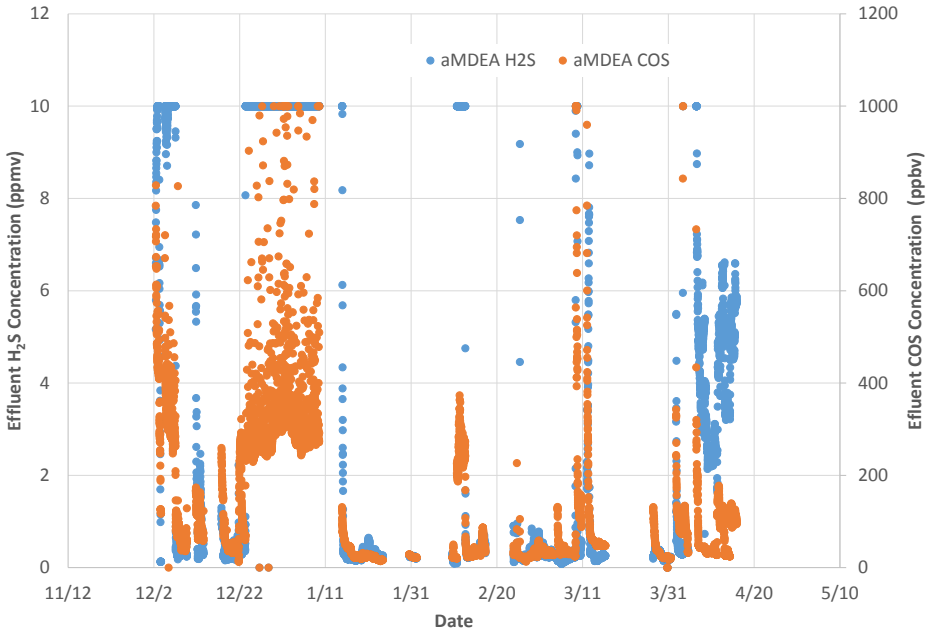

Figure 23. Effluent sulfur concentration profiles for syngas from aMDEA®

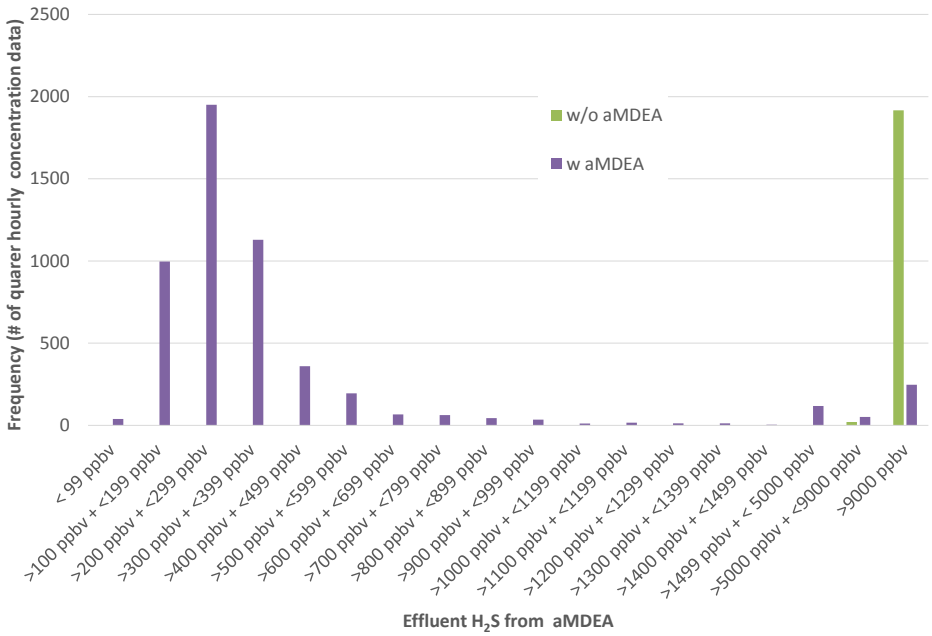

Figure 24. Frequency plot of effluent H_2S concentrations in the product syngas for aMDEA® (586) broken down to periods with and without aMDEA® operation

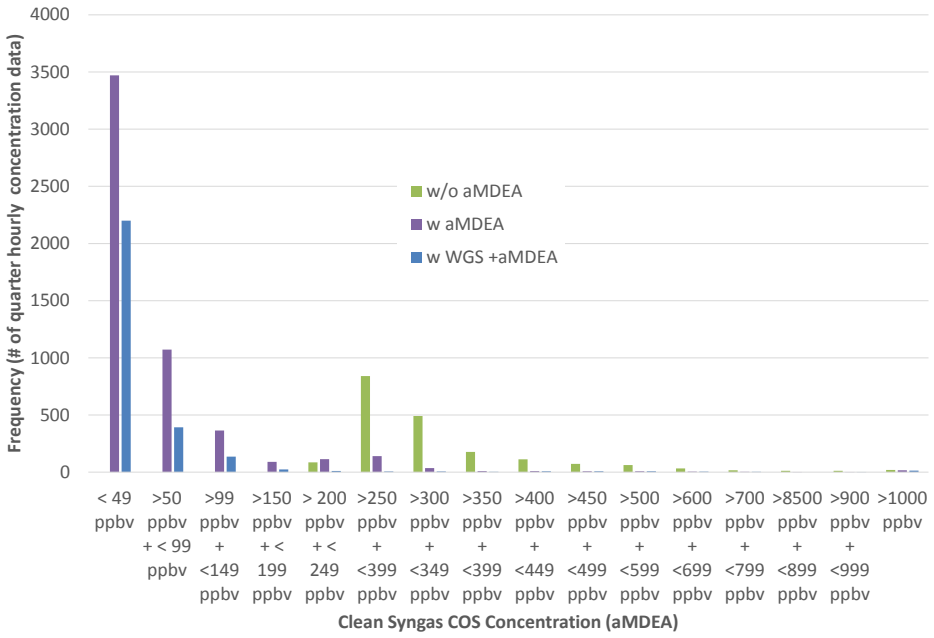

Figure 25. Frequency plot of effluent COS concentrations in the product syngas for aMDEA® (586) broken down to periods with and without aMDEA® operation

Although the primary function of the aMDEA® system was the removal of CO_2, it also results in the removal of other species. H_2S is one of the species which is preferentially removed by the aMDEA® process. The effluent sulfur concentration profiles for the CO_2 byproduct stream for the aMDEA® system are shown in ***Figure 26***. As with most of the sulfur concentration data collected, ***Figure 26*** shows a fair amount of scatter in the concentration data, although most of the scatter in ***Figure 26*** seems to be with startup and shutdown of the aMDEA® process.

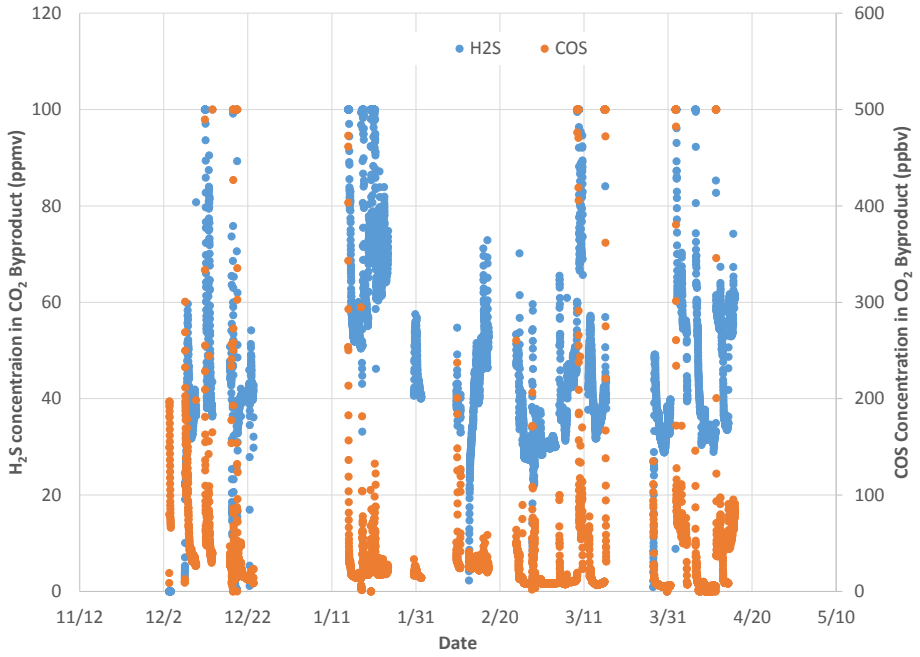

Figure 26. Effluent Sulfur Concentration profiles for CO_2 byproduct from aMDEA®

To investigate any potential patterns in these sulfur concentration profiles, the data was analyzed using the same frequency analysis procedure used previously. The results from this analysis for H_2S are shown in ***Figure 27***. The complexity of the distribution of the H_2S concentration in the CO_2 byproduct indicates that there are multiple individual distribution patterns present. It is also interesting to note that whereas the H_2S effluent concentration in the syngas was relatively constant regardless of the operation of the entire plant, the H_2S effluent concentration of the CO_2 byproduct was affected by system operation. To assist in the identification of the underlying individual frequency distributions, we broke down the operating period into periods with and without WGS operation, syngas capacity testing of the WDP and portions of the operating period. The results for the frequency analysis for the periods without WGS are shown in ***Figure 28***. ***Figure 28*** indicates that there are two distinct frequency distributions. The first covers from December through February when the lean amine exchanger, E-506, was still performing well and the April operating period in which E-506 had been taken offline. With E-506 operating, over 74% of the CO_2 byproduct H_2S concentration data fell between 30 ppmv and 60 ppmv. For the period in April, where E-506 was not operating well, over 80 % of the H_2S concentration data in the CO_2 byproduct were between 50 ppmv and 70 ppmv.

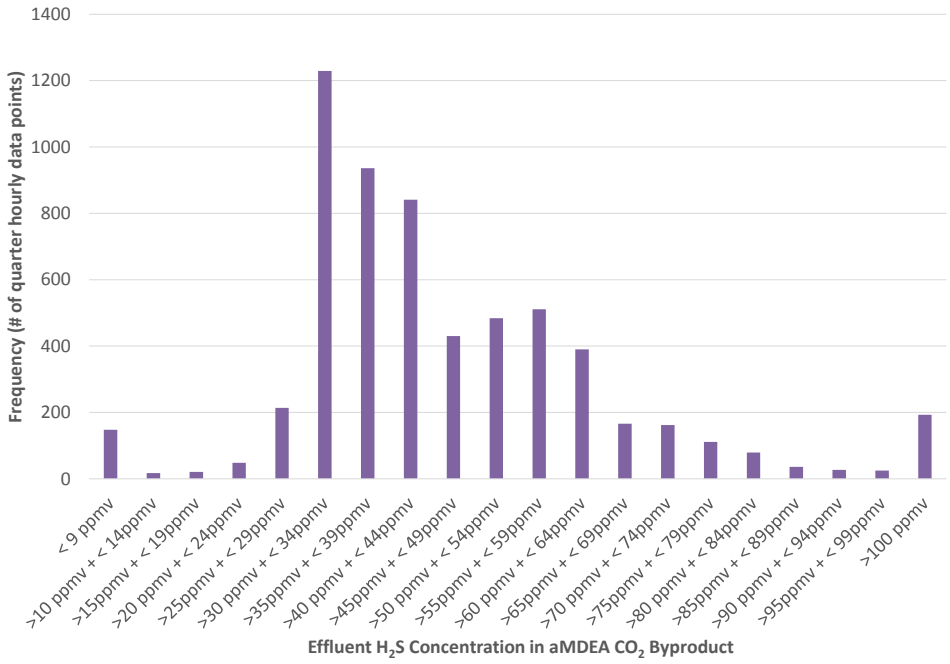

Figure 27. Frequency plot of effluent H_2S concentrations for aMDEA® CO_2 byproduct

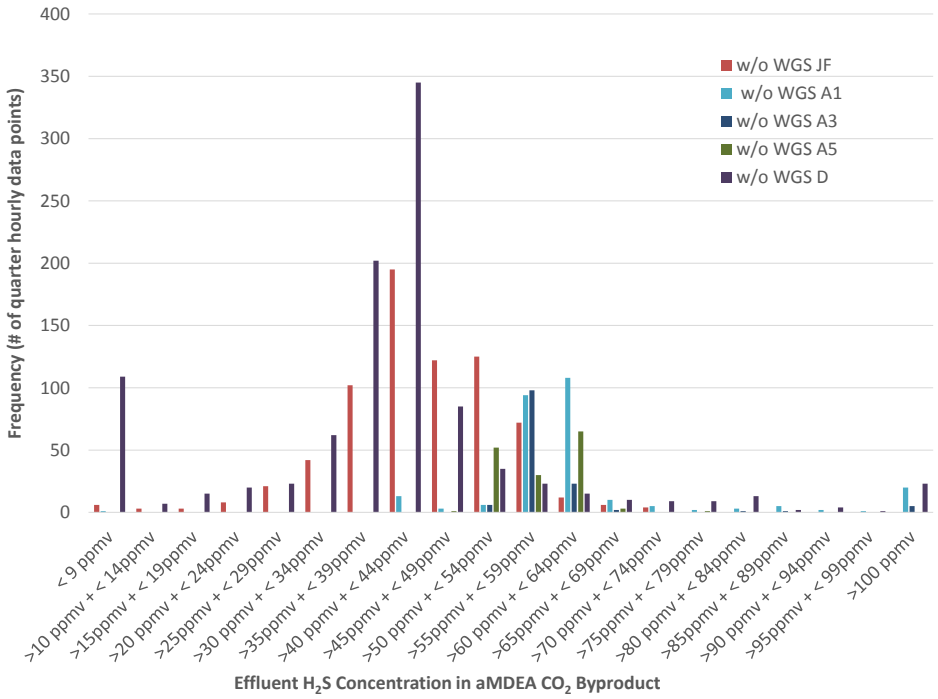

Figure 28. Frequency plot of effluent H_2S concentrations for aMDEA® CO_2 byproduct during operation without WGS

The frequency plot for the operating periods with WGS operation are shown in ***Figure 29***. In ***Figure 29***, there seems to be only a single frequency distribution of the H_2S concentration in the CO_2 byproduct with over 80% of the concentration data falling between 30 ppmv and 55 ppmv.

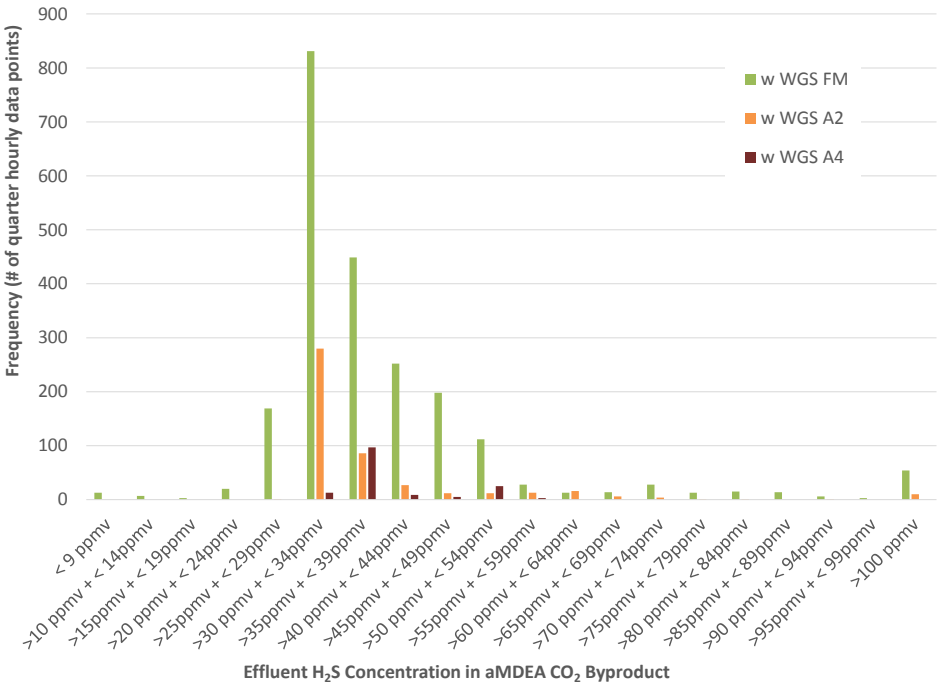

Figure 29. Frequency plot of effluent H_2S concentrations for aMDEA® CO_2 byproduct during operation with WGS

The function of the lean amine cooler, E-506, was to cool the regenerated amine solution back down to about 120°F prior to returning to COL-501 for polishing stripping of the syngas. Because WDP effectively removes over 99% of the sulfur from the raw syngas stream, any additional sulfur removal in COL-501 is polishing. With the reduced sulfur concentration in the syngas entering COL-501 and any removal in the bulk absorption section of COL-501, any additional H_2S removal in the polishing section of COL-501 is probably very small.

Because the CO_2 concentration in the syngas entering COL-501 is much higher than the H_2S concentration, the situation for CO_2 removal in COL-501 is distinctly different than for the H_2S. The polishing section of COL-501 results in a significant amount of additional CO_2 removal. When E-506 is operating well, the additional CO_2 removal in the polishing section of COL-501 results in nearly complete CO_2 removal. When E-506 was not operating well, very limited polishing CO_2 removal is achieved and the total amount of CO_2 byproduct drops. The relative difference in the amount of CO_2 byproduct flow with and without E-506 would cause differences in the H_2S concentration.

Since the difference in the CO_2 byproduct flow when the WGS is not in operation is < 50% of the byproduct flow when WGS is in operation, the largest difference would be noted when WGS was not in operation. From the data, we see about a 20 ppmv shift in H_2S concentration in the CO_2 byproduct with and without E-506 for operation without WGS. When WGS is in operation, there is not sufficient data to convincingly establish that the H_2S concentration changes.

The final frequency distribution for the H_2S concentration data in the CO_2 byproduct was during the period when syngas capacity of WDP was being tested. The results from this frequency analysis are shown in ***Figure 30***. Because a range of different syngas flows from about 90,000 lb/h to 107,000 lb/h were tested, the distribution of H_2S concentrations is more spread out. With the higher syngas flows, over 80% of the H_2S concentration data fell in between 50 ppmv and 85 ppmv.

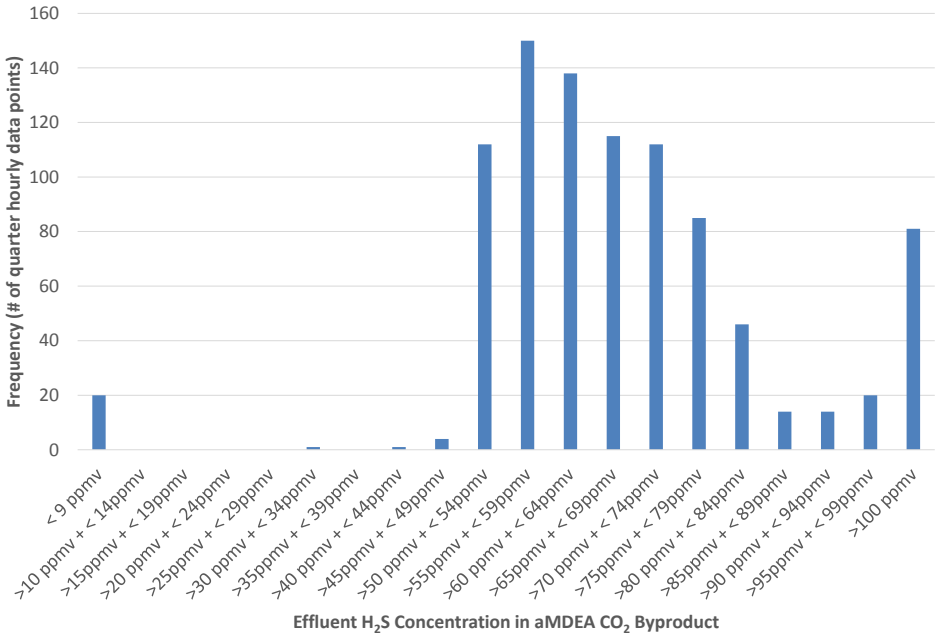

Figure 30. Frequency plot of effluent H_2S concentrations for aMDEA® CO_2 byproduct during syngas capacity testing in WDP

This increase in H_2S concentration in the CO_2 byproduct results from the slightly more H_2S being removed in the aMDEA® system. As the syngas flow to WDP was increased, the effluent H_2S from WDP increased slightly. This increased sulfur in the WDP effluent introduced more H_2S into the aMDEA®

which allowed more H_2S to be removed to the CO_2 byproduct stream. The interesting thing to note is that the effluent H_2S concentration from the aMDEA® only increased from between 200 ppbv and 300 ppbv prior to syngas capacity testing to 300 ppbv to 400 ppbv during the syngas capacity testing. This shows that the aMDEA® provides additional sulfur removal capacity adding an additional layer of protection for downstream catalyst processes. Optimization of the sulfur removal in WDP would lead to lower inlet sulfur concentrations for aMDEA®. With a lower inlet H_2S concentration and achieving similar H_2S removal efficiency, the H_2S effluent concentrations in both the clean syngas and CO_2 byproduct streams will be lower.

The standard frequency analysis was also applied to the COS concentration data for the CO_2 byproduct. The results from frequency analysis of all the COS concentration data for the CO_2 byproduct are shown in ***Figure 31***. ***Figure 31*** shows that >94% of the COS concentration data for the CO_2 byproduct stream is below 100 ppbv. Furthermore, the frequency of the data increases as the concentration decreases. ***Figure 31*** also shows that the overall frequency profile is probably composed on several different distribution profiles.

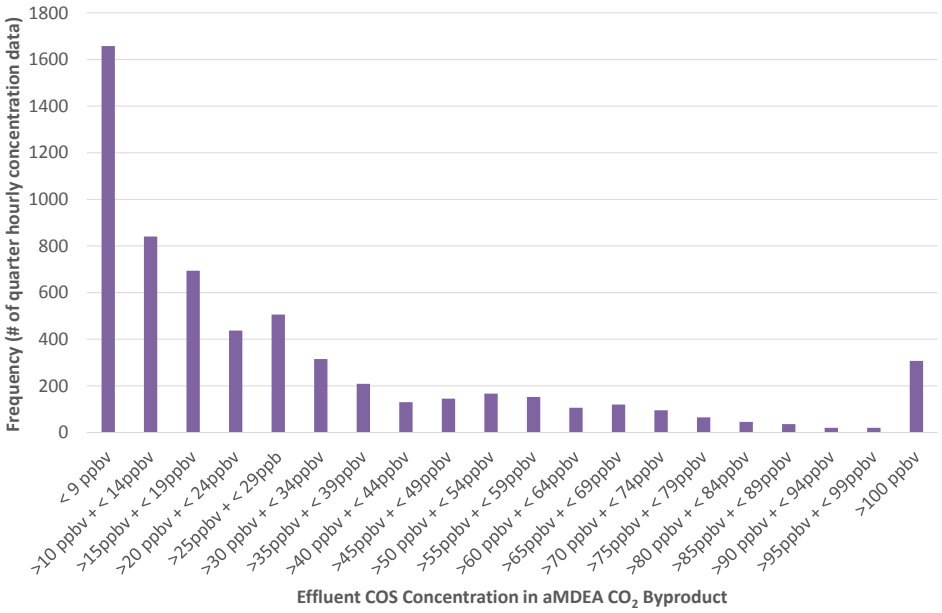

Figure 31. Frequency plot of effluent COS concentrations for aMDEA® CO_2 byproduct

Our initial expectation for this distribution was that they would be similar to those observed for the H_2S concentration data. The first set of data was with operation of aMDEA®, but not the WGS system. The results from the frequency analysis for this data are shown in ***Figure 32***. As with the H_2S data, ***Figure 32*** shows that when E-506 was operating well, over 70% of the COS concentration data was < 50 ppbv. During the April operating period, when E-506 was not operating well, over 80% of the COS concentration data fall between 35 ppbv and 90 ppbv. The same explanation presented for the H_2S concentration data applies to this COS data. One difference that is observed for this COS concentration data is that there still seems to be multiple distributions in these profiles. However, when the data are examined, the cause is the multiple starts for the aMDEA® system coupled with the fact that the COS concentration in the CO_2 byproduct stream seems to always start high and consistently drop. The long term steady state COS concentration in the CO_2 byproduct seems to be between 10 and 30 ppbv, which is achieved after between 48 and 72 hours of operation.

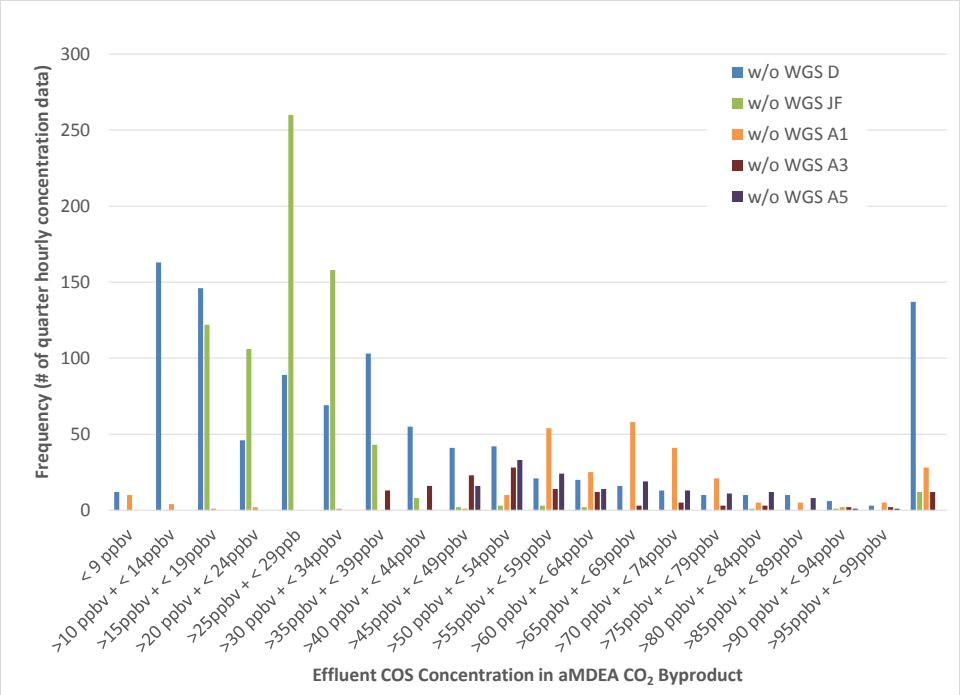

Figure 32. Frequency plot of effluent COS concentrations for aMDEA® CO_2 byproduct during operation of the aMDEA® system

The frequency analysis for the periods during which both aMDEA® and WGS were both in operation is shown in ***Figure 33***. The data show that over 90% of the COS concentration data are < 50 ppbv when both aMDEA® and WGS are in operation.

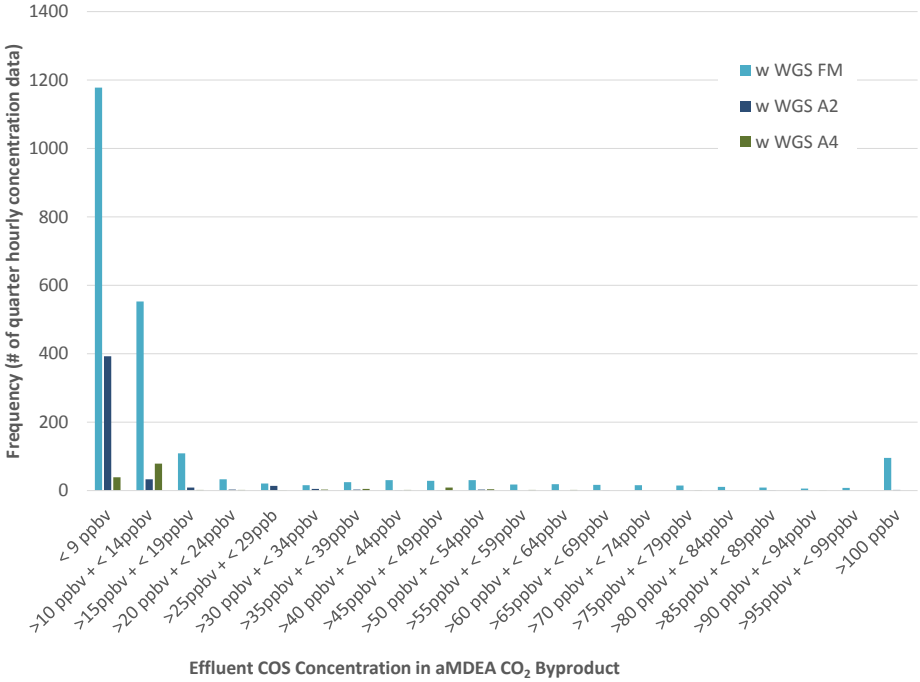

Figure 33. Frequency plot of effluent COS concentrations for aMDEA® CO_2 byproduct during operation of the aMDEA® and WGS systems

The final period of operation shown for the COS concentration data in the CO_2 byproduct was during capacity testing of the WDP. The frequency analysis for the COS concentration data for the syngas capacity testing are shown in ***Figure 34***. Over 83% of the data fall between 15 ppbv and 35 ppbv. The COS concentration during this period initially increased as the syngas flow rate was increased, but eventually settled at a relatively stable COS concentration of around 20 ppbv.

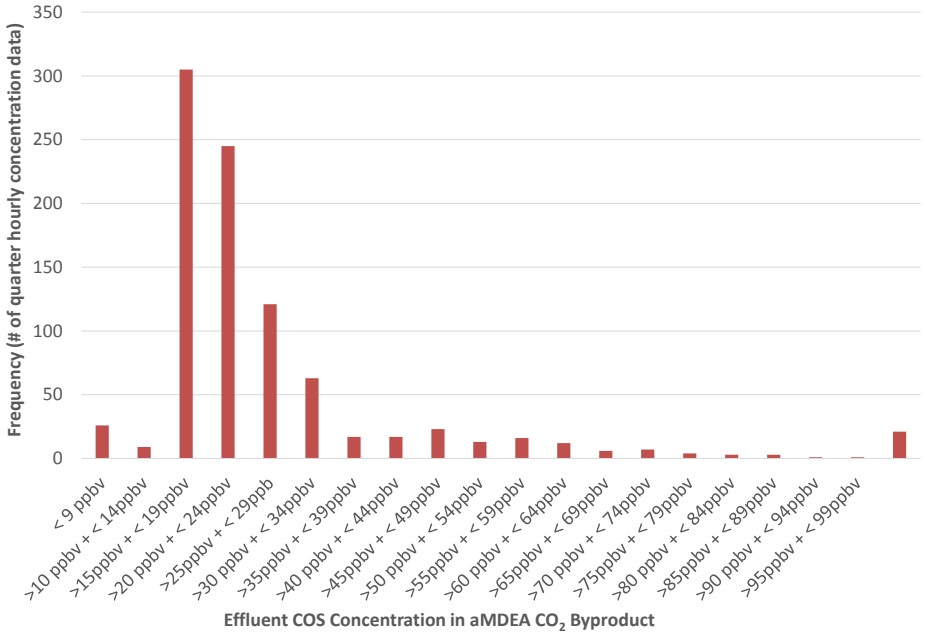

Figure 34. Frequency plot of effluent COS concentrations for aMDEA® CO_2 byproduct during syngas capacity testing in WDP

4.9 WDP Desulfurization Performance

In the previous section, we have discussed the measured concentrations in the various feed and product stream throughout the 50 MW_e pre-commercial unit. However, sulfur removal efficiency for WDP and aMDEA® systems requires solving the mass balance equations for these units. Because of the natural error in the measurement of concentrations and flows and indirect measurements required to get some steam content and purge nitrogen flows, we used data reconciliation to assist in calculation of the mass balances. The data set of concentrations and flows for these mass balance calculations was obtained based on an hourly sampling of the PI data historian. The mass balances were set up to calculate the molar flows of CO, H_2, CO_2, N_2, H_2O, H_2S and COS for syngas and N_2, O_2, and SO_2 for ROG. Based on the calculated molar flows of the effluent gases, the H_2S and COS sulfur removal efficiency for WDP and aMDEA® systems could be calculated.

For WDP, the H_2S and COS removal efficiencies for the operations from December to April are shown in ***Figure 35***. The scatter in the data in ***Figure 35*** are a direct consequence of the variations in the H_2S and COS that have been discussed in the previous sections. To help with the interpretation of this data, we have used a similar approach for conducting the frequency analysis. The key difference is that our balance results were only available for an hourly-based data set. The results from this frequency analysis are shown in ***Figure 36***. Approximately 80% of the data for H_2S removal fall between 99.72% and 99.92% sulfur removal and 90% of the COS data fall between 99.76% and 99.96%.

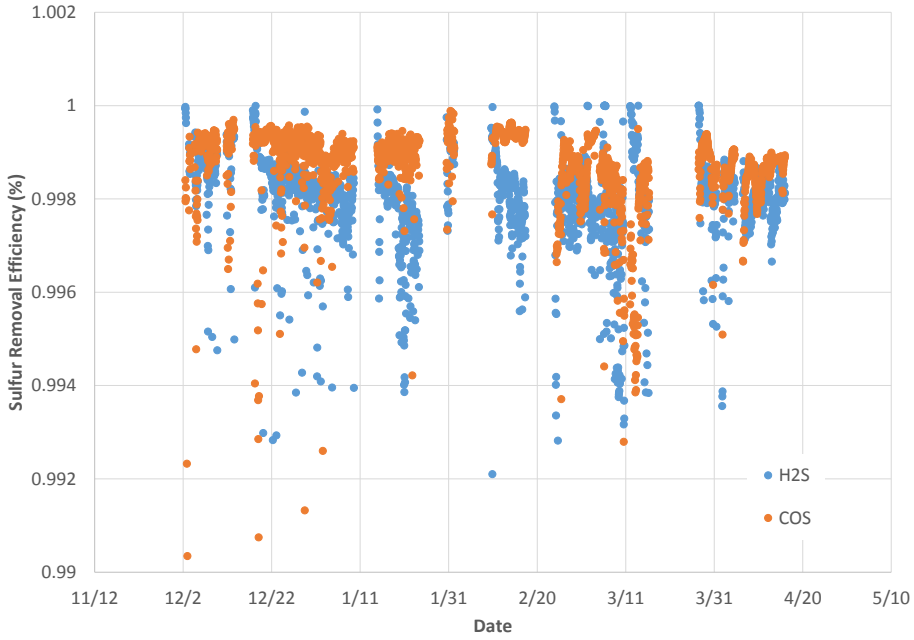

Figure 35. Sulfur removal efficiency from syngas for WDP system

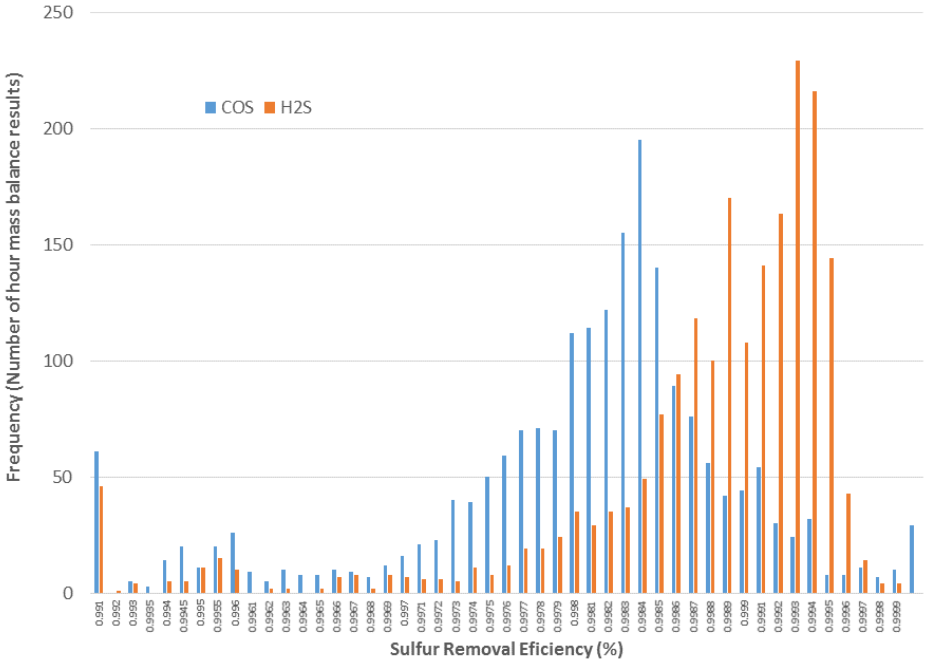

Figure 36. Frequency plot for sulfur removal efficiency for WDP

4.10 WGS Activity

In addition to the sulfur removal, the mass balances could be used to evaluate the extent of any WGS reaction taking place in the WDP. Unfortunately, the effluent syngas sample from WDP is only analyzed for sulfur. For the other syngas components (CO, H_2, CO_2 and N_2), the concentration data from the effluent from LTGC had to be used. ***Figure 37*** shows the CO conversion based on the syngas feed to

WDP and the effluent from LTGC. Prior to the start of the WGS system (i.e., prior to February 20), the concentration measured at the effluent of LTGC was essentially the same as the effluent from WDP and the CO conversion can be attributed to WGS reaction occurring in WDP. From ***Figure 37***, the WGS reaction occurring in WDP results in an average CO conversion of 18.7% with values ranging between 8% and 23%.

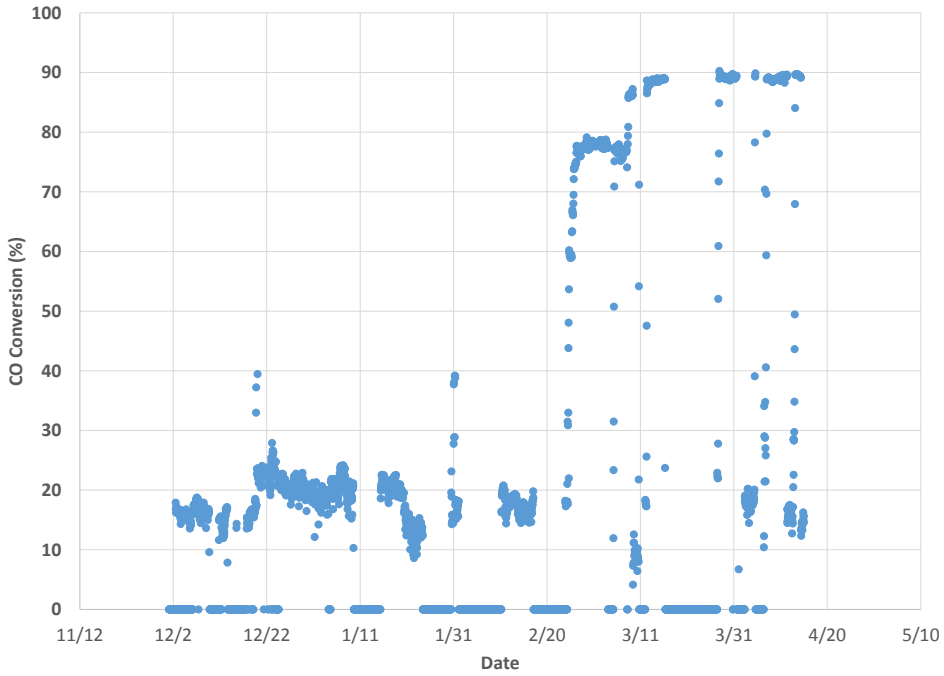

Figure 37. CO conversion using inlet syngas and effluent concentrations from LTGC

After the WGS is started, (i.e., after February 20), the CO conversion reflects the total CO conversion from both WDP and the WGS reactors. During the initial operation, a small portion of the syngas was bypassed around the WGS reactors and only partial CO conversion was achieved. During this period of operation, the average CO conversion was 76.4%. When all the syngas was sent through the WGS reactors, the average CO conversion was 88.9%.

In ***Figure 38***, the CO conversion data for just the period when all the syngas was forced through the WGS reactors have been plotted. This represents about 43% of the operating time completed on this project. In ***Figure 38***, the CO conversion does not remain perfectly constant, but the CO conversion does remain within a very narrow window from 88% to 90%. The gradual changes in the CO conversion in ***Figure 38*** are probably caused by natural variations in process conditions. Despite multiple stops and starts for the system, the system was restarted with the CO conversion always returning to approximately the same level of CO conversion observed prior to the shutdown. This is impressive as one of the stops was a forced shutdown due to a problem with TEC's air separation unit. Although this forced an almost immediate shutdown of the 50 MW_e system, the shutdown was completed with no loss of WGS activity. These data strongly suggest that no measurable amount of deactivation of the WGS catalyst occurred during operation.

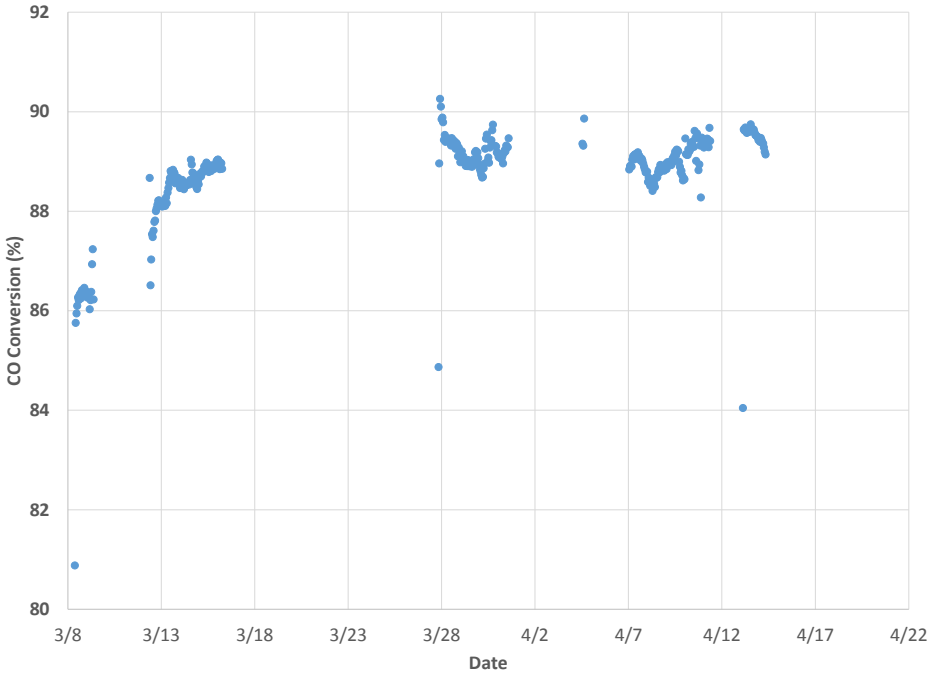

Figure 38. CO conversion for full syngas flow through WGS reactors

4.11 WDP Operational Stability

In addition to completing the mass balance around the Adsorber in WDP, a mass balance was also completed around the regenerator. ***Figure 39*** shows the sulfur removal rate for both the Adsorber and Regenerator. ***Figure 39*** shows that the rate of sulfur removal in the Adsorber consistently tracks the rate of sulfur release in the regenerator, but is typically separated by some bias. This bias seems to remain constant during a run. During January, the bias was essentially zero. From February through April the bias was about 4 lbmoles/h. The primary reason the bias changes between runs is due to differences in the nitrogen added in the Adsorber and Regenerator for fluidization and sparging and differences in solids circulation. ***Figure 39*** also shows that WDP control has improved over the operating period by adding the use of the sulfur balance to adjust operation to respond to changes in sulfur concentration in the raw syngas. Prior to this operating period, better control of the fluidization flows in the standpipes had been implemented. As the use of this improved flow control was implemented in December, control of the fluidization in the standpipes increased allowing better control and more consistent performance between operating periods.

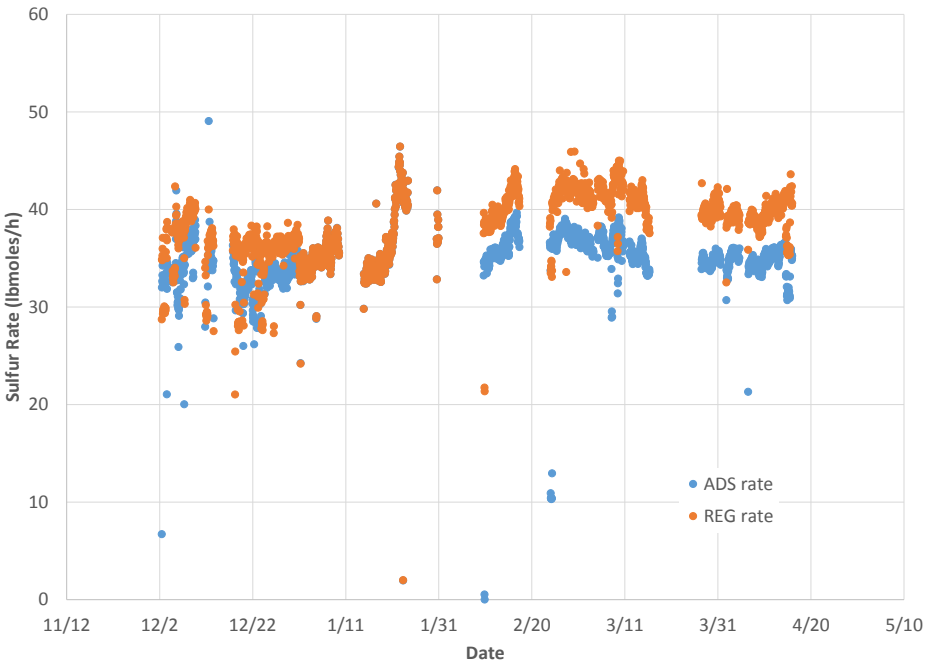

Figure 39. Sulfur rates in adsorber (removal) and regenerator (release from sorbent)

4.12 aMDEA® Desulfurization Performance

Data reconciliation was also used to calculate the mass balance around the aMDEA® system. The results from the mass balances for the different species were used to calculate removal efficiencies for H_2S, COS, and CO_2, which are shown in ***Figure 40***. Similarities in the removal efficiency for H_2S and CO_2 allow the data to be broken into three distinct groups based on time. The first-time period is the month of December. In this month, both WDP and aMDEA® were restarted and operated as an integrated unit. Operators' and engineers' knowledge on the operation of WDP and aMDEA® increased, allowing improvements in consistency of operation and overall performance. This feeds into the second phase of operation that extended from January through April 4, 2016. During this period, the overall system, including the WGS system, were operated consistently with high removal rates for H_2S and CO_2. The final period is from April 4 through April 15, when E-506 had been mechanical bypassed eliminating the potential to cool the amine solvent back down to 120°F and significantly reducing the ability of the aMDEA® system to remove H_2S and CO_2. The average H_2S, COS, and CO_2 removal efficiencies for these three different periods are shown in ***Table 5***.

These results are in line with performance expectations. The aMDEA® system was expected to offer increased removal of H_2S and CO_2. The amine solvent does not have as great an affinity for COS. The fact that the COS removal was relatively constant throughout the entire operating period would suggest that a majority of the COS removal achieved was the result of physical absorption.

Finally, the mass balance data were processed to determine the frequency distributions for H_2S and CO_2 removal with the same procedure used previously. The results from this data processing for H_2S are shown in ***Figure 41***. In ***Figure 41***, the maximum data occurs between an H_2S removal efficiency of 0.98 and 0.99. Approximately 94% of the data from the aMDEA® mass balance data have an H_2S removal efficiency of > 0.96. Approximately 59% of this data result in an H_2S removal of >98%. These results show that the startup data that was included in the calculation of the average values serve to lower the average due to their difference from normal stable operation.

Figure 40. Efficiency removal for H_2S, COS and CO_2 in aMDEA® system

Table 5. Removal Efficiencies for the aMDEA® Unit

Period	H_2S	COS	CO_2
December	0.87	0.43	0.92
January through April 4	0.96	0.44	0.99
April 4 through April 15	0.79	0.40	0.86

The initial results for the frequency distribution for CO_2 removal efficiency from January through April 4 clearly showed 2 distributions. When this data was reprocessed to include periods with and without WGS operation, a single distribution for each of these periods emerged. For the period without WGS operation, which is shown in ***Figure 42***, the peak CO_2 removal efficiency is clearly 0.999. Approximately 89% of the CO_2 removal data for operation without WGS results in >0.998 CO_2 removal efficiency. For the period with WGS operation, which is shown in ***Figure 43***, a clear peak in the CO_2 removal occurs at 0.9997 removal efficiency. Over 74% of the mass balance data have a CO_2 removal efficiency of > 0.999. The higher CO_2 removal with WGS operation is the result of the higher CO_2 partial pressure in the syngas, which enables slightly higher removal efficiency.

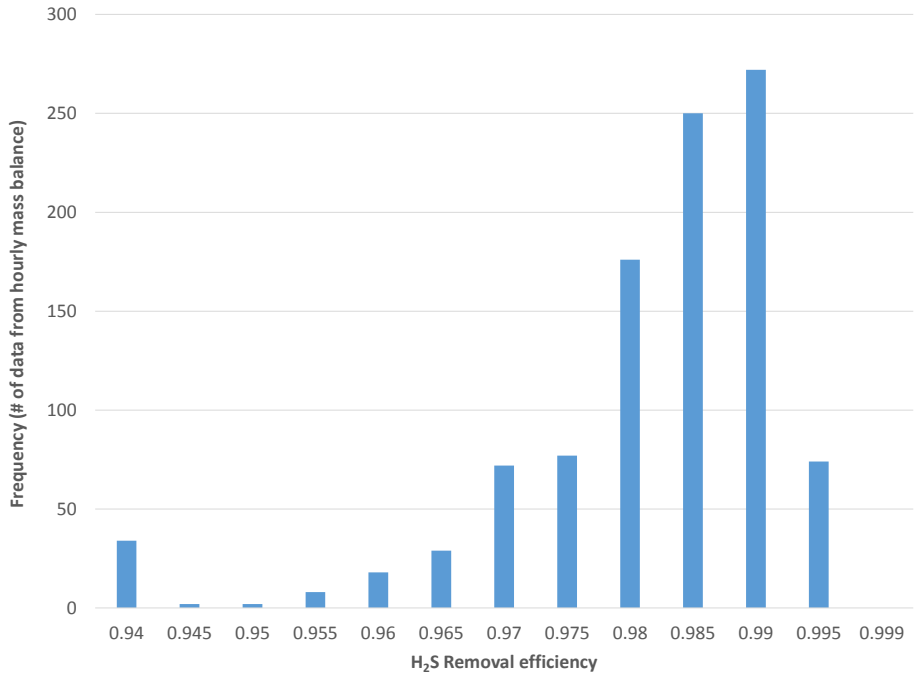

Figure 41. Frequency plot for H_2S removal efficiency from aMDEA® system

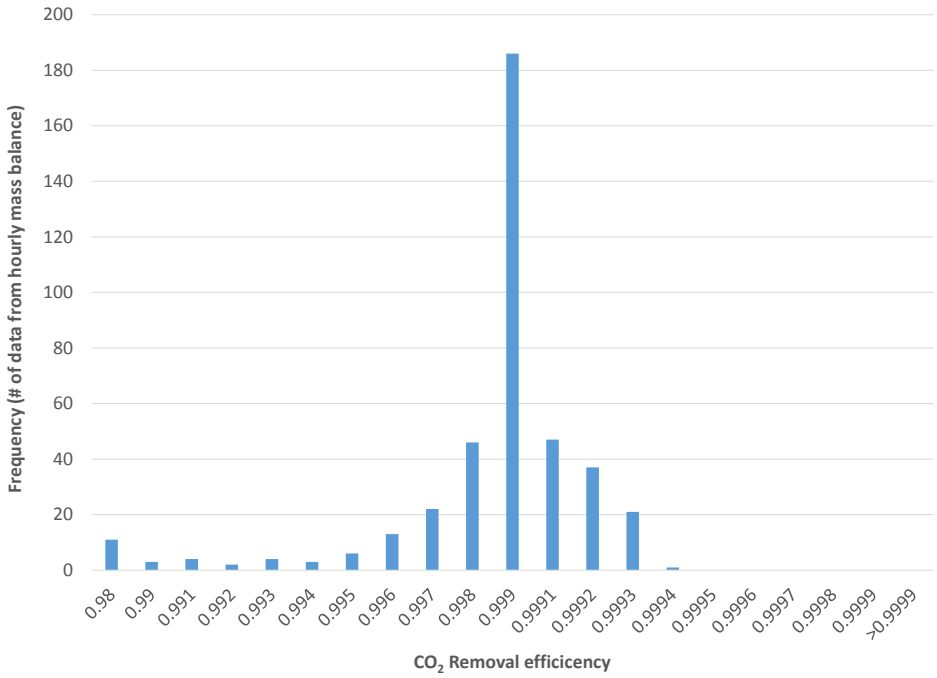

Figure 42. Frequency plot for CO_2 removal efficiency from aMDEA® when WGS was not in operation

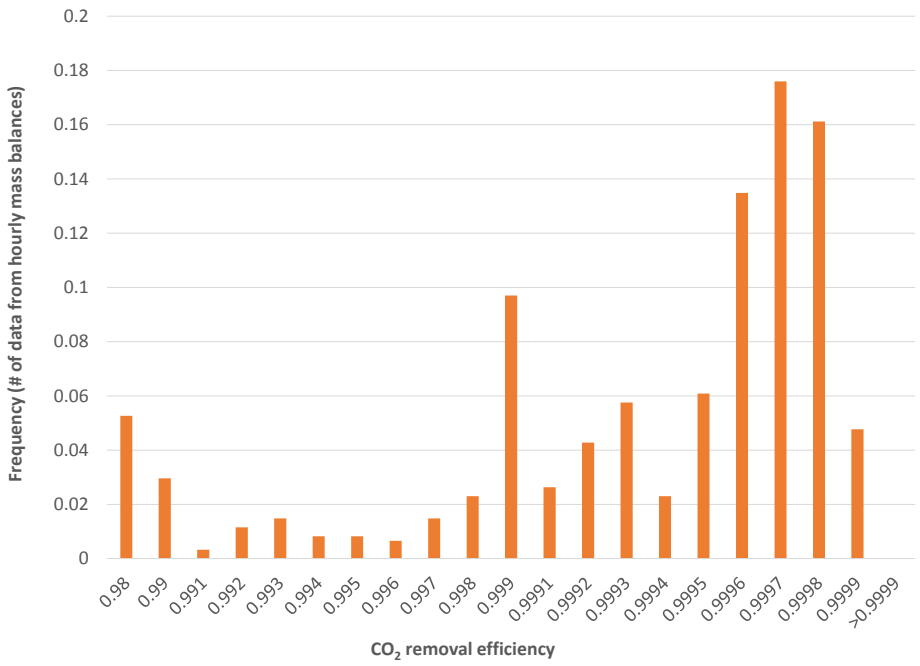

Figure 43. Frequency plot of CO_2 removal efficiency when WGS was in operation

4.13 Overall System Performance

One of the final steps of analyzing the desulfurization performance of the 50 MW_e pre-commercial system was to calculate sulfur removal based on the raw syngas stream and the final clean syngas stream returned to TEC. The results calculating the overall process H_2S and COS removal efficiencies are shown in ***Figure 44***. For H_2S, the removal efficiency seems to consist of two sets of similar data. The transition between these two sets of data occur when E-506 was finally taken offline on April 4, 2016. Prior to this date, the H_2S removal efficiency clearly exceeds the COS removal efficiency. The average H_2S removal efficiency for the period with E-506 operating was 0.9997. When E-506 was taken offline, the temperature of the amine solvent returning to the polishing portion of the absorption column increased significantly reducing the ability to remove H_2S. For the period with E-506 offline, the average H_2S removal efficiency was 0.9994. For COS, the removal efficiency seems to fall into sets, which are with and without WGS operation and operation without E-506. The average COS removal efficiency for these three periods was 0.9996, 0.9997, and 0.9997, respectively.

For an alternative look at this sulfur removal efficiency data, we also performed the same frequency analysis used previously. The results for H_2S removal efficiency are shown in ***Figure 45***. The analysis of the data show that with E-506 operating, approximately 69% of the data resulted in a H_2S removal efficiency of > 0.9997 with about 10% of the data falling below 0.9991 which represent upset conditions associated with startup and shutdown. Without E-506, about 79% of the data fall between an H_2S removal efficiency of 0.9993 and 0.9998.

For COS, the frequency analysis plot is shown in ***Figure 46***. For the data when WGS was not operating, >80% of the data had COS removal efficiencies above 0.9996. For the periods with WGS >98% of the data have COS removal efficiencies > 0.9997. For the period when E-506 was offline, the data splits into two sets based on whether or not WGS is in operation. Although analyzed in detail, the data shows that it would complement the COS removal efficiency observed with and without WGS when E-506 was in operation.

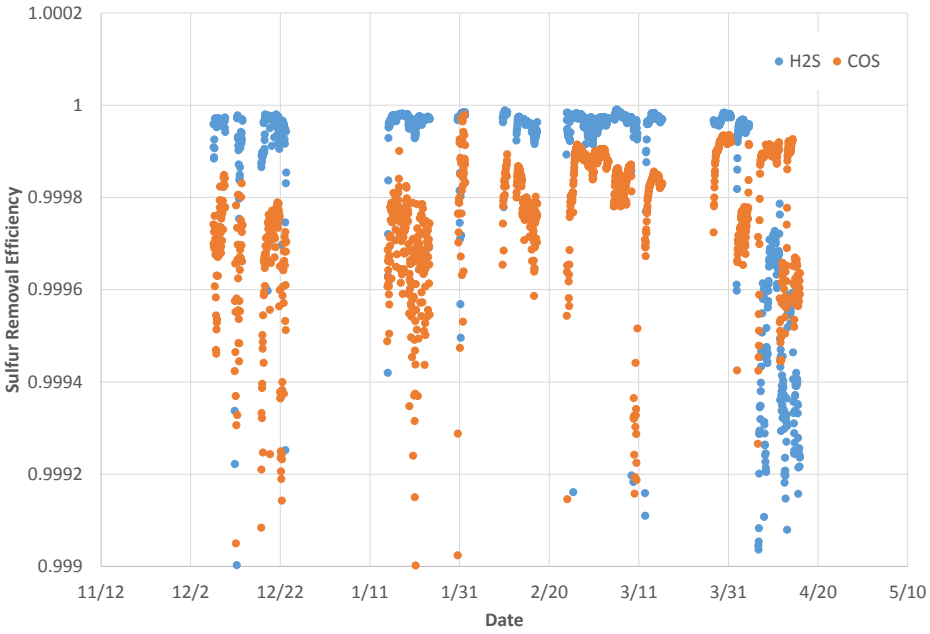

Figure 44. Overall sulfur removal for the entire 50 MW_e system

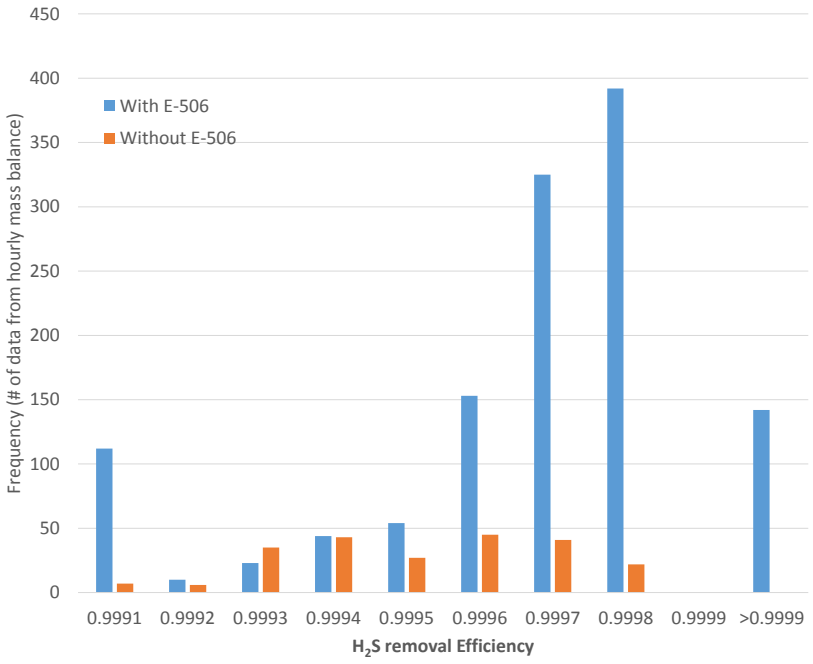

Figure 45. Frequency plot for overall H_2S removal efficiency

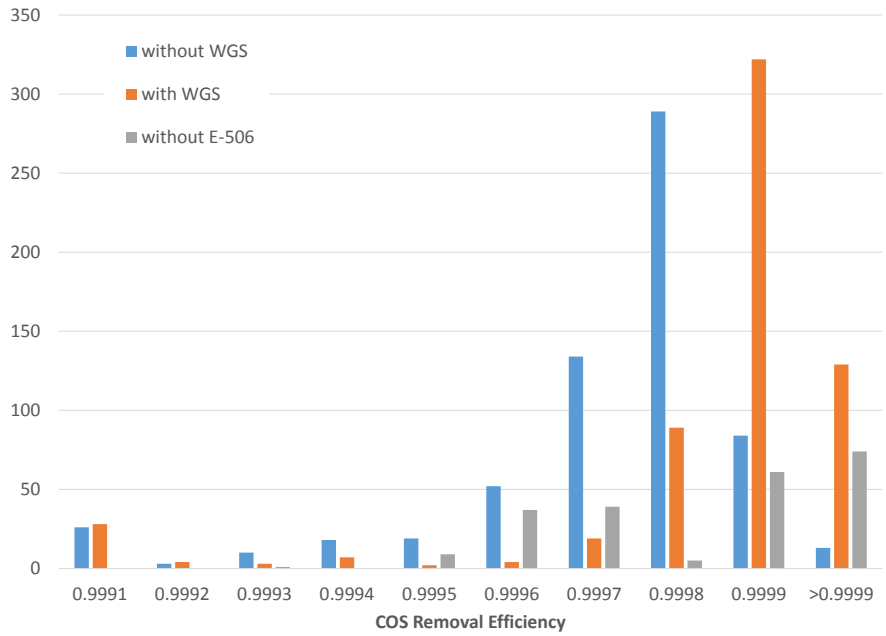

Figure 46. Frequency plot for overall COS removal efficiency

As data reconciliation was performed for the WDP and aMDEA® mass balances, we felt that the final evaluation should look at any molar flow differences between the outlet from the WDP and inlet to aMDEA®. The calculated differences are shown in ***Figure 47***. Although there is some scatter in the data, the general observation is that a majority of the time the difference between the effluent sulfur flow from WDP and inlet to aMDEA® is positive. The fact that a majority of the data is positive rather than roughly uniformly positive and negative suggests that there is sulfur removal occurring after WDP, but prior to aMDEA®. Because LTGC falls in between these two processes and H_2S and COS have some solubility in water, the data confirms that some additional H_2S and COS are removed during LTGC.

The same approach was attempted to evaluate total carbon removal with the 50 MW_e pre-commercial system. The differences in total carbon out of WDP and into aMDEA® were somewhat more random indicating more of a normal distribution. However, negative differences, which result when the flow into aMDEA® is higher than out of WDP resulted in carbon removal efficiencies of >1. The only carbon removal prior to aMDEA® would occur in LTGC and would be limited by the solubility of the gas in water. Because of this fact, the overall carbon removal was calculated based on the carbon into the aMDEA® process and the amount of CO_2 in the CO_2 byproduct. ***Figure 48*** shows this data. Without WGS operation, the average carbon removal was 0.36. With WGS operation, the total average carbon removal efficiency was 0.90. During the full operation of WDP, WGS and aMDEA® which occurred between March 12 and March 31, the 50 MW_e pre-commercial system was able to capture $\geq$90 % of the carbon in the syngas.

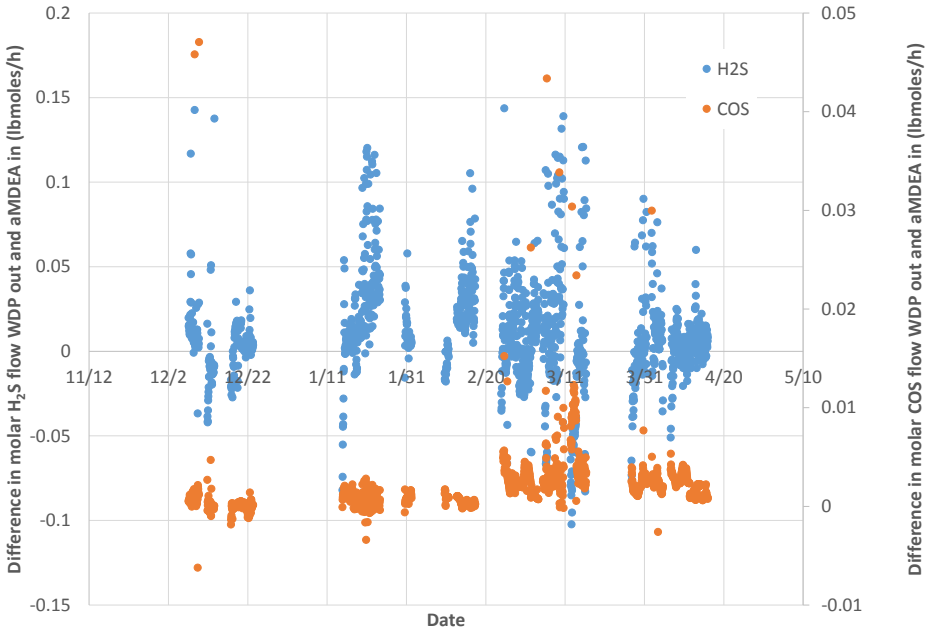

Figure 47. Differences in molar flows of sulfur species out of WDP and into aMDEA® for mass balance calculations

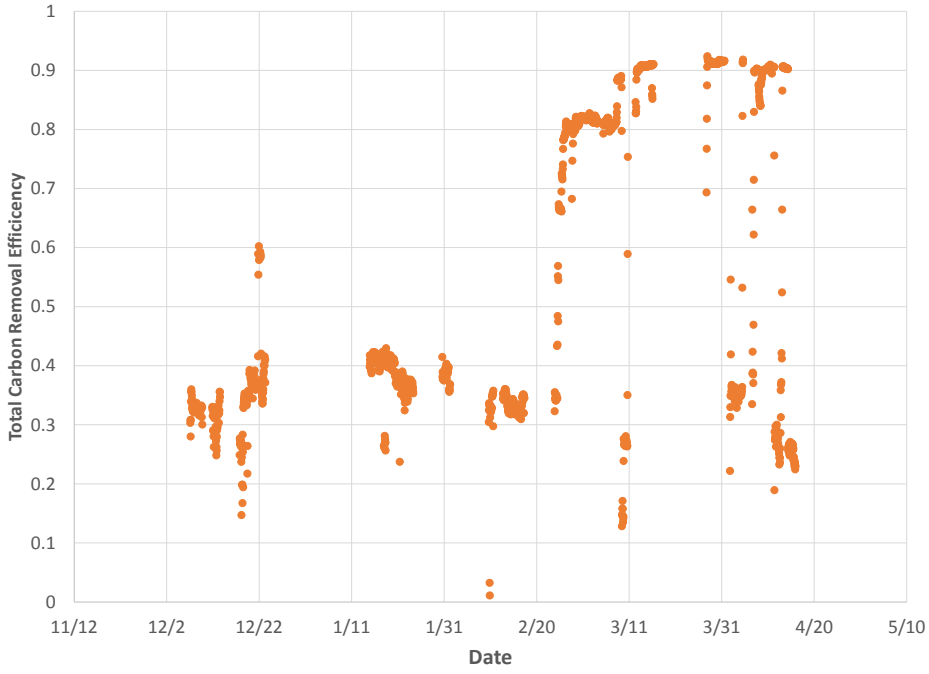

Figure 48. Total carbon removal efficiency for 50 MW_e pre-commercial system.

4.14 Summary

The desulfurization performance can be summarized by ***Figure 49***, which contains the inlet and outlet sulfur concentrations for the WDP and aMDEA® units. ***Figure 49*** shows that WDP effectively reduces the inlet H_2S from about 10,000 ppmv to about 10 ppmv and the COS concentration from about 700 ppmv to 0.5 ppmv. The aMDEA® unit reduced the H_2S concentration from about 10 ppmv to 300 ppbv and the COS concentration from 500 ppbv to about 50 ppbv.

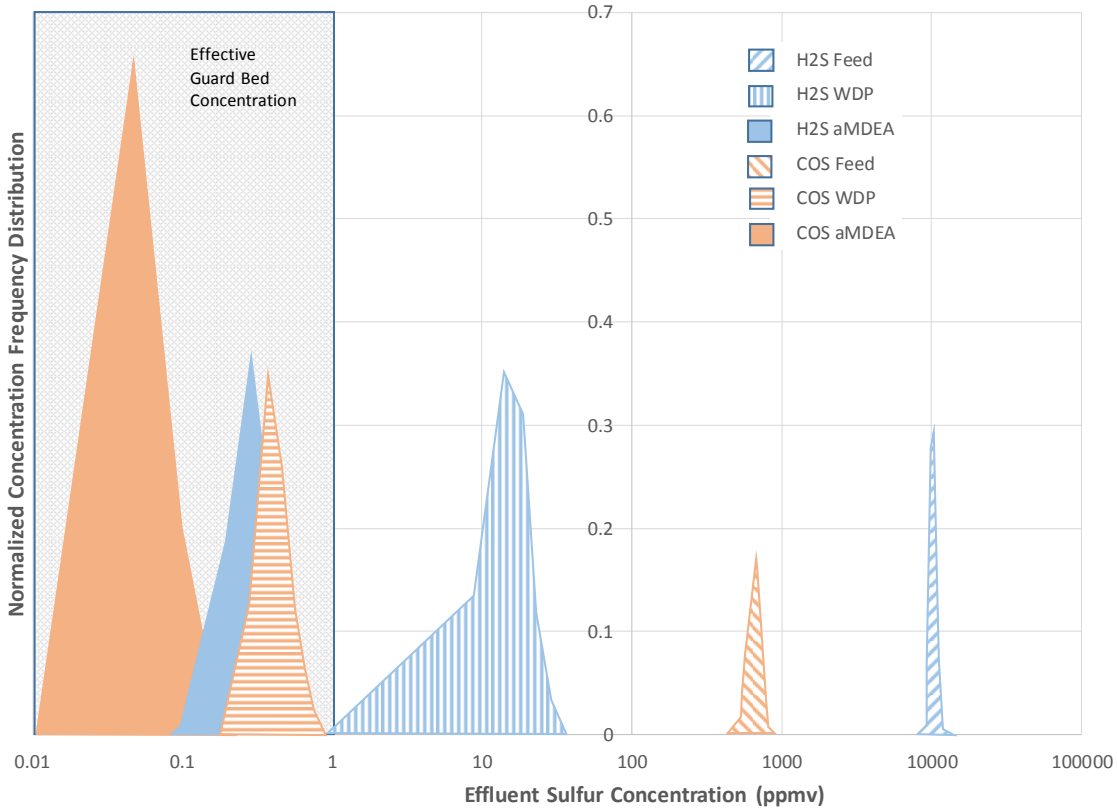

Figure 49. Inlet and outlet sulfur concentration profiles for WDP and aMDEA®

These results confirm several key performance criteria associated with WDP and the integration of WDP and aMDEA® (as well as all available commercial solvent-based acid gas removal technologies). WDP removes H_2S and COS with almost identical removal efficiency. WDP sulfur removal efficiency results in a reduction in total sulfur concentration of about 3 orders of magnitude for inlet sulfur concentrations from about 600 ppmv to 11,000 ppmv. This represents a total sulfur removal efficiency of >99.7% for H_2S and COS (typically 99.8%-99.9% total removal). The integration of WDP and aMDEA® results in a reduction of about 5 orders of magnitude for H_2S and COS. This is equivalent of a sulfur removal efficiency of >99.97% for H_2S and 99.93% for COS (up to as high as 99.999% for total sulfur removal). For practical application, the effluent sulfur concentration from a system with both WDP and aMDEA® is low enough that a conventional sulfur guard bed would economically achieve sulfur effluent concentrations identical to a Rectisol® system.

The aMDEA® unit was also able to achieve over 99.9% removal of the CO_2, which when appropriately coupled with WGS, allowed >90% carbon removal efficiency for the entire 50 MW_e system.

More detailed analysis of performance looking at consistency over the entire operational period coupled with evaluation of chemical composition of sorbent samples has demonstrated that no or minimal

deactivation of RTI-3 sorbent was observed over >3,500 hours of operation. The minimal deactivation observed for RTI-3 indicate that the primary reason for sorbent replacement will be sorbent attrition.

Although the total number of operating hours were significantly lower than for WDP, no deactivation of the WGS catalyst was detected because of changes in CO conversion. This indicates that the combination of WDP and WGS based on Fe-based WGS catalysts can be effectively used together with minimal deactivation of the WGS catalyst due to sulfur in the syngas. Because of this, WDP can be effectively coupled with either sour gas shift or Fe-based high-temperature sweet gas shift processes.

5. Trace Contaminant Removal

Gasification systems convert feedstock such as coal, petroleum coke, natural gas, biofuel, and municipal waste to synthesis gas (syngas) containing highly desirable components such as carbon monoxide, hydrogen, and steam that can effectively be used to produce electricity or value-added chemicals in a very efficient and environmentally friendly process. Challenges faced when utilizing gasification-produced syngas for both power and chemical production include the presence of contaminants in the feedstock that survive the high temperatures and pressures of the gasification step either in their elemental state or are converted to more stable species when the gas is cooled for subsequent use. The presence of these contaminants can be problematic for syngas utilization because they can attack vital metal components in advanced gas turbine systems used to produce power and can also poison expensive catalyst materials used to produce high-value chemicals. In addition, if contaminants survive the utilization step then they may be released to the environment and potentially trigger regulatory issues. For these reasons, control systems designed to reduce syngas contaminants to acceptable levels for both downstream conversion processes and to control emissions is crucial for gasification systems to be a viable alternative to conventional power generation via integrated gasification combined cycle (IGCC) plants and their use as chemical production platforms.

Depending on the feedstock, syngas can be relatively free of contaminants if derived from refined natural gas, but it also can contain a myriad of contaminants that vary widely in their concentrations if derived from coal, petroleum coke, or municipal waste. In the case of coal-derived syngas, results from previous research has led to a fairly good understanding of the contaminant species and expected concentrations for the major contaminants such as sulfur, nitrogen, and chlorine. For the minor contaminants, those present at trace-level concentrations (commonly referred to as trace contaminants) such as mercury, arsenic, and selenium, much less is known about the species type and their concentrations at a specified gas cleaning condition. To overcome this lack of knowledge, researchers have relied on thermodynamic equilibrium calculations to predict chemical species and coal feedstock analyses to predict concentrations for the design of trace contaminant control systems.

Because of the predicted low contaminant concentrations, RTI's approach to trace contaminant removal is based on the interaction of the gaseous contaminant with fixed beds of disposable sorbent materials at temperatures above 400 °F and pressures above 600 psig. This system, known as the trace contaminant removal process (TCRP), was demonstrated along with RTI's warm syngas desulfurization process (WDP) at Tampa Electric Company's IGCC at their Polk Power Station located in Mulberry, Florida and also at Eastman Chemical Company's coal-to-chemicals facility in Kingsport, TN (tested during pilot testing of WDP at Eastman under a previous project). These two processes, when combined, comprise RTI's warm syngas cleanup package capable of producing ultra-clean syngas ideally suited for power and chemical conversion.

The sections that follow describe activities associated with determining the cleanliness of the treated syngas at Polk Station by demonstrating chemical production via micro-reactor testing and gas-phase testing to determine contaminant distribution upstream and downstream of the WDP and TCRP systems.

Within the pre-commercial testing program completed at Tampa Electric's Polk Power Station, evaluation of trace contaminant removal included analysis to measure gas phase trace contaminant concentrations at different stages throughout the syngas cleanup process, collecting operational evidence of suitability of syngas cleanup for commercial catalytic processes with catalysts requiring sub-ppmv concentrations of trace contaminants, and slipstream testing of three sorbents for Hg, As and Se removal. The following sections provide analysis results and discussions from experimental activities performed during pre-commercial testing at the Polk Power Station that extended past the period of performance for the original cooperative funding agreement with DOE (DE-FE0000489).

5.1 Trace Contaminant Testing

Trace contaminant testing was used to determine concentrations of a select group of contaminants present in the syngas during pre-commercial testing of RTI's warm syngas cleanup technology at Polk Power Station that could not be determined using the conventional suite of online analyzers such as gas chromatographs and spectrophotometric instruments that supported the operation of WDP. Trace contaminant testing involved manual sampling methods, which involved collection of contaminants in or on sampling media from a known volume of syngas during real time operation and required analysis of the sampling media afterwards to quantify the amount of a target contaminant captured. The combination of the amount of contaminant collected and known volume of syngas sampled allows calculation of an average contaminant concentration over the sampling period. Although cumbersome to execute compared to real time instrumental measurements that can provide instantaneous analytic results, manual sampling methods are required for accurate detection of extremely low concentrations of contaminants in complex matrices such as syngas. AECOM (Austin, Texas), an industry leader in gas phase sampling and analysis of syngas using manual methods, was selected to provide trace contaminant testing during pre-commercial testing at Polk Power Station. Target contaminants included NH_3, HCN, Hg, As, and Se.

Using these manual sampling methods to simultaneously sample the inlet and outlet of a process allows contaminant removal performance to be determined for any process for the target contaminants. This approach was used to determine contaminant removal performance for the primary processes in the pre-commercial syngas cleanup system and specifically to evaluate three promising sorbent candidates for Hg, As, and Se removal.

As realistic mixtures of syngas contaminants can only be found in syngas mixtures generated from actual gasification of carbonaceous feedstocks, the pre-commercial testing program provided an excellent and unique trace contaminant testing opportunity. Unfortunately, the mixture of trace contaminants in the syngas is dictated in large part by the source of carbonaceous feedstock. Because Tampa Electric Company gasifies a mixture of 85% petroleum coke and 15% coal, the trace contaminant concentrations in the syngas reflect the high Se concentrations in the petroleum coke, but contain significantly less As and Hg than would be generated during gasification of pure coal. As previously mentioned, the pre-commercial testing was a unique opportunity and our best efforts were used to extract the maximum possible value from this contaminant testing.

5.1.1 Trace Contaminant Testing Procedures

A general description of the sampling and analysis methods used by AECOM during onsite testing at Polk Power Station was provided in the final report for DOE Cooperative Agreement DE-FE0000489. Complete details about the sampling and analysis methods are provided in AECOM's final report located in ***Appendix A***.

Gas-phase testing of trace contaminants was conducted at two physical locations. The first location was adjacent to RTI's analyzer shed, which housed all of the analytical instrumentation used to support WDP, WGS, and the amine scrubber unit and provided effective access to conditioned syngas collected for online analysis throughout the entire process. Taps for sample gas withdrawal were installed in the sample conditioning box just upstream from plumbing used to direct sample gas to each instrument in the analyzer shed. Samples collected during this portion of testing were collectively referred to as Warm Gas Cleanup (WGCU) samples and included five sample streams representative of 1) dirty syngas from Polk Power Station's gasifier entering the WDP adsorber, 2) syngas from between the WDP outlet and the inlet of the Low Temperature Gas Cooler (LTGC), 3) syngas from between the LTGC outlet and the amine scrubber inlet, 4) syngas from the outlet of the amine scrubber, and 5) recovered CO_2 from the amine regenerator.

The second sample location was at the TCRP test skid and focused solely on determining the concentration of the trace contaminants entering the test skid and exiting each of the three reactor vessels. These samples were collectively referred to as TCRP samples.

Experimental results from the trace contaminant testing at each to the two sampling points are grouped by contaminant so that the reader can easily track the fate of each contaminant across specific components in either the WGCU or TCRP processes. All concentrations are reported in units of either parts per million dry (ppmvd) or parts per billion dry (ppbvd). In additions, values reported as not detected (ND) were below the method detection limits (MDLs) defined in the AECOM final report. When possible, simultaneous sampling of the different sampling points at each site were conducted. As this is not possible for all contaminants, the key objective was to sample with the shortest time interval separating the testing that would not compromise the use of the data to evaluate contaminant removal performance across the major WGCU and TCRP components. Trace contaminant testing results for WGCU are presented in the next sections and TCRP testing results are presented in the subsequent sections.

5.1.2 Trace Contaminant Testing Results for WGCU

A total of 10 sampling periods, or runs, were completed during WGCU trace contaminant testing. Problems were encountered with balancing flow rates across the five sampling streams for Runs 1 and 2. For this reason, experimental results for these runs are not included in the WGCU results presented here. Runs 3 through 5 were completed between July and August 2015 and Runs 6 through 10 were completed in March 2016.

Table 6 shows the gas phase concentrations of NH_3 determined at each WGCU sampling point.

Table 6. NH_3 Concentrations in WGCU Process Streams (ppmvd)

Process Stream	3	4	5	6	7	8	9	10
WDP Inlet	751	807	465	530	689	485	664	599
LTGC Inlet	547	547	287	556	607	439	466	396
Amine Inlet	0.92	1.00	0.15	1.16	0.15	0.48	0.47	0.44
Amine Outlet	5.40	6.12	1.47	0.43	0.07	0.47	0.31	0.38
Recovered CO_2	1.67	1.50	1.48	0.13	0.28	ND	0.21	0.18

ND = Not Detected. Refer to AECOM report for MDL values.

The first analysis of interest is for the two different periods during which the trace contaminant testing was conducted. The Welch statistical test was used to evaluate the hypothesis that the mean values for the two sampling periods were identical. At a 95% confidence level, the means were identical for the two sampling periods for the WDP inlet, LTGC inlet, Amine inlet, and Amine outlet.

For the Recovered CO_2 samples, the hypothesis that the means for these two different sampling periods were identical had to be rejected. Because AECOM is known to be meticulous about procedures for sampling and analysis and the equivalence of the means for the two sampling periods for the first four points, the result for the Recovered CO_2 samples strongly suggest that the difference is associated with a change in the process and not a consequence of sampling or analytical procedural differences.

A key difference between the two sampling periods was the WGS process was being bypassed during the July/August 2015 sampling period and in full operation during the sampling in March 2016. However, this difference should have caused the Amine inlet samples, which are the first samples collected after the WGS unit, to differ rather than the Recovered CO_2. The statistical analysis for the Amine outlet did not provide sufficient reason to reject the hypothesis that the means for the two sampling periods were identical, but the probability of identical means compared to random variations was significantly lower than for the other sampling points.

These facts suggest that the difference was associated with the amine unit. The main difference in the operation of the amine unit was corrosion of the carbon steel tubes in 1-AML-E-506 (E-506) which resulted in holes in the heat exchanger tubes allowing loss of amine to the cooling water system. Because of our limited supply of amine, this resulted in operating with more dilute amine. In addition, operation of

the amine system improved between these two periods as operational experience increased significantly between December 2015 and March 2016. This improved operation probably resulted in better control of the fresh water wash stage at the top of the absorption column. Although it is not possible to test the impact of these specific differences, they do provide a reasonable explanation for the differences observed for the two sampling periods for the Recovered CO_2 and the lower probability that the Amine Outlet samples are identical.

The principle analysis for which these data were collected was to determine if the process did or did not affect the trace contaminants as they passed through the different processing units. If the process does not affect the trace contaminant, the amount of contaminant into the process should be equal to the amount out of the process. For our syngas cleanup process, the goal would be a reduction in the contaminant amount in the syngas. Because of this objective, our hypothesis is that the amount of contaminant in the inlet syngas is equivalent to the product syngas.

In addition to the clean syngas product, the amine process also creates a CO_2 byproduct. Because the distribution of contaminant between these two streams is valuable knowledge, a slightly different analysis protocol was established for the amine system. For the amine process, the analysis protocol involved three comparison tests. The first test was the comparison of the contaminant amount in the inlet and clean syngas streams as for the other processes. The second test was a comparison of the amount of contaminant in the clean syngas and recovered CO_2 stream. The final test was a comparison of the amount of contaminant in the feed syngas and the total amount of contaminant in the clean syngas and recovered CO_2 products.

The comparison of the contaminant in the clean syngas and recovered CO_2 product provided how the contaminant was preferentially segregated between the clean syngas or CO_2 byproduct. This comparison was based on using the Welch statistical test with the hypothesis that the amount of contaminant in the clean syngas and recovered CO_2 was identical. The comparison of the contaminant in the inlet and outlet gas streams would provide an indication if contaminant was accumulating in the amine solvent. The Welch statistical test was used with the hypothesis that the amount of contaminant in the inlet and total amount in all the effluent gas streams was identical.

Another fundamental difference with this analysis compared to the analysis used for the different sampling periods protocol was that this testing required an amount of contaminant instead of the concentration data available in ***Table 6***. To convert this concentration data into amounts of contaminant, we had to use the total molar flow rates for the various process streams. These molar flow rates were calculated from mass balance analysis completed for the WDP and Amine processes from the PI database for March 2016. This same analysis was not completed for the July through August operations. Consequently, the combination of the concentration data from the Jul/Aug testing and the molar flow rates from March 2016 could lead to improper interpretation of the data. We have limited these specific data combinations to the concentration data where the analysis from the two sampling periods had been shown to be identical. With this limitation, we have assumed that there are no problems associated with using the molar flow rates from March 2016 and concentrations from the Jul/Aug 2015 sampling.

After calculation of the ammonia flows, the Welch test was used to statistically evaluate the different hypotheses. At a 95% confidence interval, the hypothesis of equal molar ammonia flows in the feed and product syngas had to be rejected for the WGS/LTGC process. The hypothesis was accepted at the 95% confidence interval for the WDP and Amine processes. The other analysis for the amine process rejected the hypothesis of equivalent ammonia flow in the clean syngas and recovered CO_2 products and accepted equal ammonia flows in the inlet and outlet gas streams.

For the LTGC process, where cooling in the LTGC results in the formation of liquid water, the high solubility of ammonia in water would explain the large loss of ammonia. The result from the analysis conducted during pilot plant testing at Eastman Chemical Company (Kingsport, TN) indicated the removal of ammonia across WDP. However, during pilot plant testing the syngas stream tested was cooled below its dewpoint enabling water condensation prior to sampling, which would account for the apparent ammonia removal by WDP. In this test, the LTGC inlet gas was sampled at a temperature above its dewpoint. These results confirm that WDP does not remove ammonia and the results obtained during

pilot plant testing were the result of steam condensation prior to sampling. Ammonia removal in the LTGC process was 99.86%.

The results from analysis of the amine process data show that ammonia removal from the syngas and transfer to the recovered CO_2 product is very limited. Because the molar flow of ammonia in the feed gas and product gases is identical at the 95% confidence interval, no ammonia was accumulating in the amine solution. This result suggests that the solubility of ammonia in the amine solution is very limited. This low ammonia solubility does not enable significant ammonia removal from the syngas and prohibits accumulation of ammonia in the amine solution.

Table 7 shows the concentration of HCN around the various WGCU components for Runs 3 through 10. Compared to NH_3, the overall HCN concentrations were much lower. As with the ammonia, the analysis of the data in ***Table 7*** began with comparing the data from the two different sampling periods. The results from the Welch test on the data showed that at a 95% confidence level, the means for the two sampling periods were identical for the WDP inlet and LTGC inlet. The results indicated that the hypothesis of equivalent means had to be rejected for the Amine inlet and Recovered CO_2 sample sets. The fact that the HCN concentration at the Amine outlet was below the detection limit for March samples prohibited numerical analysis. But the observation that the Amine outlet samples from the July/August sampling period had measurable HCN concentrations and no HCN could be detected in the March samples demonstrates the HCN concentration in the Amine outlet for the two samples was different.

Table 7. HCN Concentrations in WGCU Process Streams (ppmvd)

Process Stream	3	4	5	6	7	8	9	10
WDP Inlet	1.52	8.12	6.02	6.49	8.80	6.31	7.60	6.66
LTGC Inlet	1.69	2.01	0.62	0.92	1.12	0.89	0.92	0.98
Amine Inlet	2.32	2.30	1.30	0.036	0.039	0.035	0.027	ND
Amine Outlet	0.010	<0.0042	0.104	ND	ND	ND	ND	ND
Recovered CO_2	1.40	1.57	2.65	0.027	0.028	0.028	0.021	0.0058

ND = Not Detected. Refer to AECOM report for MDL values.

This pattern for the differences between the July/August and March samples for the HCN suggests that the differences began in the WGS/LTGC process. This pattern points to the operation of the WGS unit as the cause of these differences.

For the statistical analyses, which was based on the hypothesis that the processing unit had no effect on the HCN amount in the feed and product syngas, the results showed that this hypothesis was rejected at a 95% confidence interval for WDP and WGS/LTGC processes. The fact that all March HCN concentration data for the clean syngas from the amine unit were below the detection limit prohibited numerical analysis, but demonstrated essentially complete HCN removal for the amine process. The additional analysis for the amine process data required rejection of both the equivalence of HCN amounts in the clean syngas and recovered CO_2 and the equivalence of HCN amounts in the inlet and outlet gas streams. These additional results for the amine process confirm the preferential separation of HCN into the recovered CO_2 over the clean syngas and indicate accumulation and or decomposition of HCN in the amine solution.

In the pilot plant testing, HCN removal for the WDP was close to 99%. But due to the high probability of water condensation prior to sampling, this removal was assumed to be associated with the water as for the ammonia. These results show that WDP does remove a majority of the HCN with the water removing a large fraction of any HCN remaining. The net removal for WDP and WGS/LTGC for the pre-commercial operation was roughly equivalent to the removal observed during pilot plant testing. The total HCN removal in WDP, WGS/LTGC and amine processes was 100% with the HCN removal in the individual processes being 77.65%, 21.62%, and 0.75%, respectively.

Table 8 shows the gas phase concentrations of As determined at all WGCU sampling locations during trace contaminant testing at Polk Power Station. The general observation is that for the July/August sampling period, the As concentration in the syngas feed was typically below the detection limit of the sampling procedure and analytical method used. In the March sampling period, the As concentration in the inlet gas was consistently about 2 ppbvd. Although the increase in the inlet As concentration could be the result of increased As concentration in the fuel fed to the gasifier, the slipstream testing for trace contaminants at Eastman Chemical Company during pilot plant testing showed that new equipment adsorbed a significant amount of the As from the syngas before it became conditioned or saturated with As. If we assume that the accumulated operating time from December 2015 to March 2016 enabled effectively As conditioning of the transfer piping network and WDP, this would explain the increase in As concentration observed in the March samples. This theory is supported by trace contaminant analysis completed by AECOM in February 2014 for the syngas at the source for RTI's 50 MW_e system under DOE Project DE-FE0000489 funding which detected an average of 6 ppbvd in the syngas supplied by Tampa Electric Company. The difference between the As concentration at the original take off point from Tampa and the inlet for the WDP suggest that the transfer pipe was effectively removing As.

Table 8. As Concentrations in WGCU Process Streams (ppbvd)

	Run							
Process Stream	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**
WDP Inlet	ND	ND	1.43	3.00	2.01	1.84	2.33	1.58
LTGC Inlet	ND	ND	ND	1.40	1.05	1.01	1.36	1.01
Amine Inlet	0.573	ND	ND	ND	ND	ND	ND	ND
Amine Outlet	ND	0.695	ND	ND	ND	ND	ND	ND
Recovered CO_2	ND	ND	ND	ND	ND	ND	0.575	ND

ND = Not Detected. Refer to AECOM report for MDL values.

If the Welch test is used to evaluate the hypothesis that the inlet and outlet amounts of As are identical because WDP has no effect on As, the results indicate that this hypothesis must be rejected at the 95% confidence level. The results show that about 31% of the As entering WDP is removed. Unfortunately, as the data from the different sampling periods show that As was accumulating in the 50 MW_e system between the August and March sampling, the As removal for the WDP process does not permit determination if this removal resulted from continued As accumulation in the process or was the result of removal of As by the sorbent materials. The pilot plant testing demonstrated that As did accumulate on the sorbent. It is worth noting that although the pilot plant and pre-commercial demonstration testing both accumulated over 3,000 hours of operation, As accumulation throughout the system was still in progress in the pre-commercial unit at the end of testing while As saturation had been achieved in the pilot plant systems. This difference was a consequence of the As concentration in the raw syngas being between 700 and 900 ppmv (two methods were used for the measurement of As) for the pilot plant and 0.006 ppmv (based on As measurement taken at boundary with Tampa's system) for the pre-commercial testing. This difference is related to the 85% petroleum coke used in the feed to the Tampa Electric Company's gasifier at Polk Power Station.

Table 9 shows the concentrations of Hg at the various WGCU sampling points. The Hg concentrations in the syngas throughout the 50 MW_e system were extremely low but the extremely low MDLs for this sampling and analysis methodology resulted in more measured values at the different sampling points.

Table 9. Hg Concentrations in WGCU Process Streams (ppbvd)

Process Stream	Run							
	3	4	5	6	7	8	9	10
WDP Inlet	0.509	0.435	0.457	0.135	0.929	0.818	0.730	0.579
LTGC Inlet	1.18	0.522	0.644	0.711	0.661	0.627	0.640	0.491
Amine Inlet	ND	ND	ND	0.0763	0.179	0.0938	0.146	0.0513
Amine Outlet	0.0991	0.0612	ND	0.433	0.503	0.394	0.391	0.254
Recovered CO_2	0.104	0.0609	0.0529	0.183	0.0944	0.366	0.0452	ND

ND = Not Detected. Refer to AECOM report for MDL values.

With the available data, the first comparison completed evaluated if the means for the different sampling periods were equivalent with the Welch test. At the 95% confidence level, this hypothesis had to be accepted for the WDP inlet, LTGC inlet, and Recovered CO_2. The hypothesis was rejected for the amine outlet sample sets. Because the Hg concentration in the Amine inlet samples was below the detection limit for the July/August samples, but not the March samples, the hypothesis of equivalent means was rejected based on the detected versus not detected results.

The differences between the two sampling periods are most probably the result of process changes rather than analytical or sampling change. The key process changes included operation versus bypassing of the WGS unit and changes made in the operation of the amine unit to accommodate the issues with E-506 and the improved operational experience. Unfortunately, these changes do not help explain the differences between the sampling periods. The Hg concentration out of the WGS/LTGC process and the Hg concentration in the cleaned syngas for the amine process were lower in the July/August samples than in the March samples. The presence of the WGS catalyst as an additional adsorptive material and/or the additional water added and condensed to achieve the 90% carbon conversion in the WGS unit increased rather than decreased the Hg concentration. Similarly, improved operation of the amine unit resulted in higher Hg concentrations in the clean syngas with no change in the Hg concentration in the Recovered CO_2 product.

As Hg capture on different Hg sorbent materials has been observed to be temperature sensitive with higher removal typically observed at lower temperatures, these observations could be the result of Hg conditioning of the cooler sections of the 50 MW_e system, namely the LTGC and amine system. Based on the data showing the Hg concentration for the original syngas supplied by Tampa being about 1 ppbvd, the Hg concentrations for the amine process streams are much closer to the Hg concentration in the feed syngas from Tampa supporting this theory.

The Welch statistical analysis show that at a 95% confidence interval the equivalence of the amount of Hg in the inlet and outlet syngas streams must be rejected for WDP, WGS/LTGC, and amine processes. For WDP, the data suggest rejection of the hypothesis at a 95% confidence interval, but accepting the hypothesis at a 98% confidence interval. An examination of the results also shows that the amount of Hg out of the process is greater than what is coming into the process. Although this is possible if accumulated Hg in the system is being released, this is not typically observed for steady state processes. Another factor to consider is that the molar flow rates used have been treated as exact values. These values do have some variance, but it is typically very small. However, with the low Hg concentrations, the variance of the molar flow rates may be significant enough to affect analysis. Based on these factors, our assumption is that until additional analysis can prove Hg removal, is that no Hg removal occurs in WDP. This position is supported by laboratory testing, that demonstrated insignificant Hg removal with RTI-3 at standard operating conditions.

For the WGS/LTGC process, the data show about 80% Hg removal. At this level of change in the amount of Hg, the statistical analysis strongly indicates that this difference is not likely caused by random variations in measurements. It is also plausible that a significant amount of Hg does get removed with the condensed water.

For the amine system, the data show that the amount of Hg in the product syngas exceeds the amount of Hg present in the inlet syngas. As mentioned previously, this is not the typical result observed in a stable steady state system. The result from the additional analysis of the amine data indicates rejection of the equivalence of the amount of Hg in the syngas product and recovered CO_2 and rejection of the equivalence of the Hg in the inlet and outlet gas streams. The rejection of the equivalence of the Hg in the inlet and outlet gas reflects the fact already mentioned that the Hg amount in the product syngas exceeded the amount of Hg in the feed gas. The difference in the amount of Hg in the syngas product and recovered CO_2 suggests that minimal amounts of Hg are removed from the syngas by the amine process.

The differences between the analysis results and typical engineering observations for a steady state system and the challenges of effectively measuring these extremely low Hg concentrations cast a reasonable amount of doubt on the results and their interpretations. In light of these differences, the most reasonable course of action is to assume essentially no removal by any of the processes used in the 50 MW_e system until additional data can be accumulated to confirm this assumption.

Table 10 shows the concentration of Se around the various WGCU components for Runs 3 through 10. The high level of Se typically found in petcoke samples, which represents approximately 85% of the gasifier fuel used by Tampa Electric results in the higher concentrations of Se observed in ***Table 10***. The comparison of the July/August and March samples with the Welch test showed that the WDP inlet, WGS and LTGC inlet, Amine inlet and Recovered CO_2 samples had equivalent means at the 95% confidence level. The Amine outlet did not have sufficient data from both periods to apply the Welch test. However, for the subsequent testing of the effect of each processing unit on the Se, all sample data, which resulted in combining the July/August and March samples, was used in the statistical testing.

Table 10. Se Concentrations in WGCU Process Streams (ppbvd)

	Run							
Process Stream	3	4	5	6	7	8	9	10
WDP Inlet	621	519	275	829	401	294	353	267
LTGC Inlet	20.9	11.1	21.9	2.91	4.89	3.44	3.10	3.82
Amine Inlet	0.775	0.783	5.44	ND	0.607	0.962	ND	ND
Amine Outlet	ND	ND	3.09	ND	0.674	0.844	ND	ND
Recovered CO_2	ND	0.746	1.33	ND	0.641	1.18	0.954	ND

ND = Not Detected. Refer to AECOM report for MDL values.

The Welch analysis of the equivalence of amount of Se in the feed and product syngas was accepted at the 95% confidence interval for the amine process, but rejected for WDP and WGS/LTGC. The amount of Se removal in the WDP and WGS/LTGC processes was 97.45% and 2.00%, respectively. During the Eastman pilot plant testing, the WDP unit removed over 90 percent of the Se present in the syngas. Extensive analysis of the adsorber and regenerator sorbent conducted during and after this pilot plant test indicated that the Se accumulated on the sorbent and was not removed during the high temperature regeneration step. Furthermore, this accumulated Se did not have any observed detrimental effect on desulfurization performance of the RTI-3 sorbent. These new results from the operation of the 50 MW_e system confirm these pilot plant results for WDP.

The additional analysis for the amine process resulted in the acceptance of the equivalence of the Se amount in the syngas product and recovered CO_2 and equivalence in the amount of Se in the inlet and out gases. Practically, it is not possible for the amount of Se to be equivalent in the inlet and outlet syngas and in the syngas product and recovered CO_2. After the near complete removal in the WDP and WGS/LTGC processes, the remaining amount of Se is very low and essentially at the detection limit based on the relatively large number of below detection limit results. From Tampa's operation experience, Se tends to accumulate on the filters in their regular amine system. Assuming that the activated amine would have a similar performance, we should anticipate accumulation of Se in the amine solution. However, this 50 MW_e system would need to be operated for a significantly longer period of time to

reach a steady state were this could be tested based on the near complete removal of Se by WDP. However, this does suggest that the removal efficiency of the amine process should be retested at Se concentrations that will result in more reliable Se concentration measurements.

5.1.3 Summary

Manual sampling of the inlet and outlet streams was conducted for the primary processes in the 50 MW_e pre-commercial demonstration system. Because of syngas availability, this manual sampling was conducted in two campaigns. The trace contaminant concentrations collected from these two campaigns were compared using the Welch statistical test with the hypothesis that the sample concentration means for the two sampling periods were identical. The anticipated outcome was identical mean concentrations indicating stable and consistent sampling, sample analysis, and process performance. The analysis indicated differences between the sampling periods occurred. Because procedure and protocols were in place to mitigate differences in the sampling and or sample analysis, potential explanations of these differences have been associated with process changes. ***Table 11*** provides the sample sets for which the sample means were found to be identical (N/C) and samples where the data suggested a process change had occurred (C). ***Table 11*** also includes potential process changes that could explain the specific changes observed and any associated pattern in these changes.

Table 11. Summary of Comparison for Two WGCU Sampling Periods

Contaminant	Location					Explanation
	WDP Inlet	WGS/LTGC Inlet	Amine Inlet	Amine Outlet	Recovered CO_2	
NH_3	N/C	N/C	N/C	N/C	C	Increased operational experience with aMDEA® process and performance issues with work around solutions for corrosion issues with E-506 heat exchanger
HCN	N/C	N/C	C	C	C	Full integration of WGS enables WGS to catalyze decomposition of HCN along with WGS reaction.
As	C	C	N/A	N/A	N/A	As accumulation/passivation of new piping and equipment. This same phenomenon was observed during pilot plant testing
Hg	N/C	N/C	C	C	C	Potential Hg accumulation/passivation of the lower temperature processes.
Se	N/C	N/C	N/C	N/A	N/C	

N/A = Data was not available or insufficient data was available for analysis.

The key objective for this manual sampling for trace contaminants was to determine if and how much trace contaminants removal was occurring in each process in the syngas cleanup system. The Welch statistical test was used to evaluate the hypothesis that the contaminant amounts in the feed and product syngas were equivalent, which would indicate no removal. ***Table 12*** provides the estimated contaminant removal for the cases in which there was a difference in the amount of contaminant in the feed and product syngas. In general, the additional analysis for the amine process supported the removal analysis for the syngas. However, for the Se analysis, the Se concentrations in the amine streams were very low and essentially at the detection limits for this method. Under these conditions, the analysis resulted in an

inconsistent interpretation. For this reason, the Se removal for Se in the amine process has been listed as non-conclusive in ***Table 12***. Similarly, the analysis results for Hg result in several inconsistencies that reduce overall confidence in the analysis and have been listed as non-conclusive in ***Table 12***. Additional data and analysis will be required to define the Hg and Se removal in these cases.

Table 12. Trace Contaminant Removal in Processes in Syngas Cleanup System

Contaminant	Process			
	WDP	WGS/LTGC	Amine	Total
NH_3	None	99.86%	None	99.86%
HCN	77.63%	21.62%	0.75%	100.0%
As	31.74%	N/A	N/A	31.74%
Hg	NC	NC	NC	NC
Se	97.44%	2.00%	NC	99.44%

NC = Non-conclusive analysis results due to low concentration measurements at or near detection limits, variance for molar flows not included in analysis, and/or experimental or engineering reasons for suspecting results.
N/A = No data of insufficient data for analysis

For WDP, these results confirm the pilot plant results observed for Se and possibly As. These results also provide confirmation for interpretations of the NH_3 and HCN removal observed during pilot plant testing. For the ammonia, these results provide confirmation that the removal during pilot plant testing was probably a result of water condensation prior to gas sampling. However, for HCN, these results confirm that WDP does remove a majority of the HCN and that the high HCN removal observed during pilot plant testing was a combination of the WDP removal and subsequent removal in the condensed water prior to sampling.

5.2 Trace Contaminant Sorbent Testing

Even though trace contaminants such as Hg, As, and Se are present in syngas derived from coal and petroleum coke at concentrations much lower compared to S, Cl and N_2, removal of these species to extremely low concentration is critical for successful use of the syngas to produce chemicals. Trace contaminants contained in syngas pose a unique challenge for the development of contaminant control technologies not so much because of concentrations in the actual syngas but because of the extremely low levels required for the treated syngas to meet performance goals set by DOE. These performance goals are expressed as the maximum amount of contaminant that can remain in the syngas after gas cleaning and reflect not only the detrimental effects that these trace level contaminants have on downstream processes during gas utilization in advanced gasification systems but also very low standards set by the U.S. Environmental Protection Agency (EPA) for post utilization emissions. These performance goals are shown in ***Table 13***.

Table 13. DOE Trace Contaminant Performance Goals

Contaminant	Performance Goal	
	Advanced Systems	Emission Limits
Hg	5 ppbw	3 ppbw
As	5 ppbv	5 ppbv
Se	200 ppbv	76 ppbv

Because concentrations of trace contaminants in syngas are relatively low, RTI's approach for removal is based on the use of solid sorbent materials in fixed-bed reactors that interact with, and retain, the contaminant. The candidate sorbent is not regenerated but discarded according to state and local hazardous waste disposal standards after its useful capacity is depleted. Because the sorbent is the key enabling technology for trace contaminant control, much emphasis has been placed on developing materials with high capacities that can meet the challenging DOE performance goals for trace contaminants in syngas at operating conditions higher than 400 °F and greater than 600 psig. RTI and its industrial partners, with funding from DOE, have identified several candidate materials for As and Se removal and one candidate material

for Hg removal from syngas at warm gas cleaning conditions. Together these sorbents comprise RTI's trace contaminant removal process (TCRP).

Pre-commercial testing of WDP at Polk Power Station provided a unique opportunity to test the efficacy of TCRP sorbents to remove the trace contaminants from desulfurized syngas. RTI capitalized on this opportunity by designing a test skid and having it assembled by AMEC personnel onsite during testing at Polk Power Station. Once assembled, the skid was used to expose three materials in separate reactor vessels to desulfurized syngas at nominal 400 °F and 350 psig for over 900 hours. During this time, gas-phase trace contaminant testing was performed by AECOM to determine contaminant concentrations upstream and downstream of the sorbent vessels so that removal efficiencies could be determined. The sections that follow describe construction, skid operation, and test results generated during this TCRP sorbent testing. The one challenge of this testing program was that the As and Hg concentrations in the syngas were substantially below the target effluent concentrations listed in ***Table 13*** making validation of achieving removal targets for these two contaminants impossible based on the current test. However, the test was anticipated to provide valuable data about actual removal under realistic operating conditions.

5.2.1 Design and Construction of the TCRP Test Skid

A P&ID of the TCRP test skid is shown in ***Figure 50***. The skid was configured with three reactor vessels of sufficient volume to expose nominally 1 kg of two mixed-metal oxide candidate sorbents and 0.5 kg of a carbon-based sorbent to syngas at temperatures above 400 °F and pressures up to 600 psig at a nominal flow rate up to 1000 scfh per reactor. Internal plumbing allowed for syngas flow through the reactor vessels either in parallel or in series, but note that all testing at Polk Power Station involved exposing candidate sorbents in the individual reactors to desulfurized syngas in the parallel flow arrangement. Outlet gas from the three reactors was combined in an exit header and returned to the 50 MW_e pre-commercial system at around 50 psig less than it was received. Process control systems to control and monitor the temperature in heated zones and syngas flow rates through the vessels were skid-mounted and their data were conveyed back to the WDP DCS. This enabled the TCRP system to be monitored by operators in the Polk Power Station control room and the data to be recorded in the PI historian.

Syngas is highly flammable and, as such, requires specialized equipment for handling and containment. The TCRP test skid was constructed to meet the electrical classification of Class 1 Division 2 work zones. To meet this classification, specialized heat tracing was used to supply external heat to the skid components and all electrical panels and junction boxes were purged with compressed air to reduce exposure of the flammable gas to potential ignition sources.

Further description of the test skid used to expose trace contaminant sorbents to desulfurized syngas at Polk Power Station can be found in the final report for DOE Cooperative Agreement DE-FE0000489.

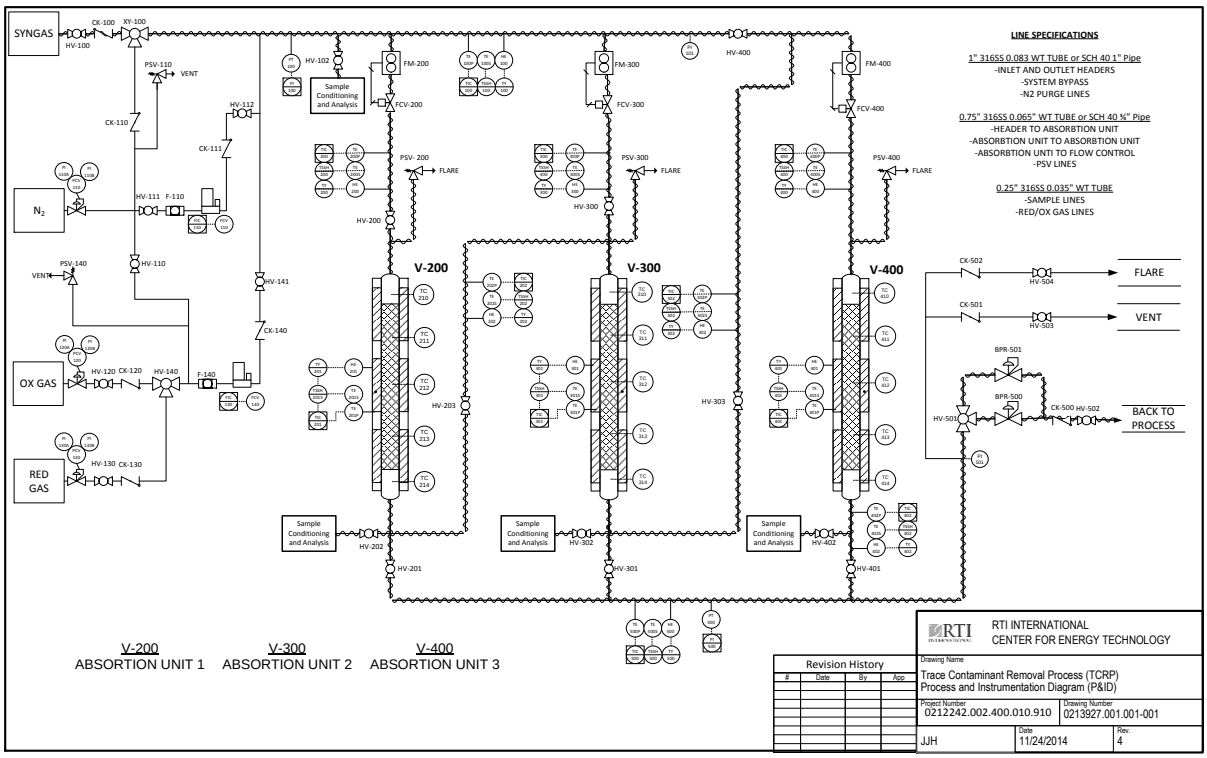

Figure 50. P&ID for TCRP test skid

5.2.2 Operation of the TCRP Test Skid

Details concerning commissioning of the TCRP test skid were provided in the final report for DOE Cooperative Agreement DE-FE0000489. A summary of these details is provided here along with further discussions concerning skid operation with syngas during WDP testing at Polk Power Station. After resolving minor glitches in the on-board control systems and completing initial leak checks, candidate sorbents were loaded in the reactor vessels. ***Table 14*** provides a description of the candidate sorbent loaded into each reactor and the target contaminant.

Table 14. TCRP Sorbent Materials

Reactor Vessel	Candidate Sorbent	Weight (g)	Target Contaminant
V-200	Commercial Sorbent F	976	As, Se
V-300	Commercial Sorbent G	744	As, Se
V-400	Impregnated carbon	489	Hg

The sorbent materials loaded into V-200 and V-300 were mixed-metal oxides and the material loaded into V-400 was an activated carbon material.

The reactors were purged with N_2 supplied from a tube trailer and then heated to their intended operating temperature to perform flow checks. It was at this stage of commissioning when determinations were made that the existing heat tracing would not supply ample heat to the reactors to reach the desired temperature of 400 °F. At this point, further commissioning of the skid was halted until additional insulation was added around the reactor vessels and heat trace lines and a tarp was constructed over the skid to keep the insulated components dry during inclement weather. With these changes, the heat tracing could raise the sorbent bed temperature to the target temperature of 400 °F. A mixture of H_2 and N_2 supplied from compressed gas cylinders was used to chemically reduce the sorbent materials prior to exposure to syngas.

Exposure of the TCRP sorbents to desulfurized syngas commenced on February 11, 2016. Target operating parameters are provided in ***Table 15***.

Table 15. Operating Specifications for TCRP Test Skid

Parameter	Specification
Reactor Temperatures	400 °F
Syngas Pressure	400 psig
Site Classification	Class 1 Division 2
Target Flow Rate	1000 scfh (per reactor)
Gas Hourly Space Velocity	2000 hr^{-1}
Reactor Type	Fixed bed
Nominal Sorbent Bed Dimensions Diameter Length	 7.6 cm 23 cm

Note that the impregnated carbon sorbent packing density was much less compared to the mixed-metal oxides, which resulted in a smaller weight loading for this material. Also note that some of the nominal specifications noted in ***Table 15*** were adjusted for proper operation of individual skid components, most notably the flow rate through the impregnated carbon material in V-400 was reduced during skid operation to nominal 500 scfh to maintain the exposure temperature of the sorbent below 428 °F. Previous laboratory testing indicated that Hg capacity on the impregnated carbon decreases significantly above this temperature.

The trace contaminant sorbents were exposed to desulfurized syngas from the 50 MW_e pre-commercial system when this system was operating stably. This resulted in a total of 911 hours of exposure between February 11, 2016 and April 15, 2016. The operational status of the test skid during this time period is summarized in ***Figure 51***.

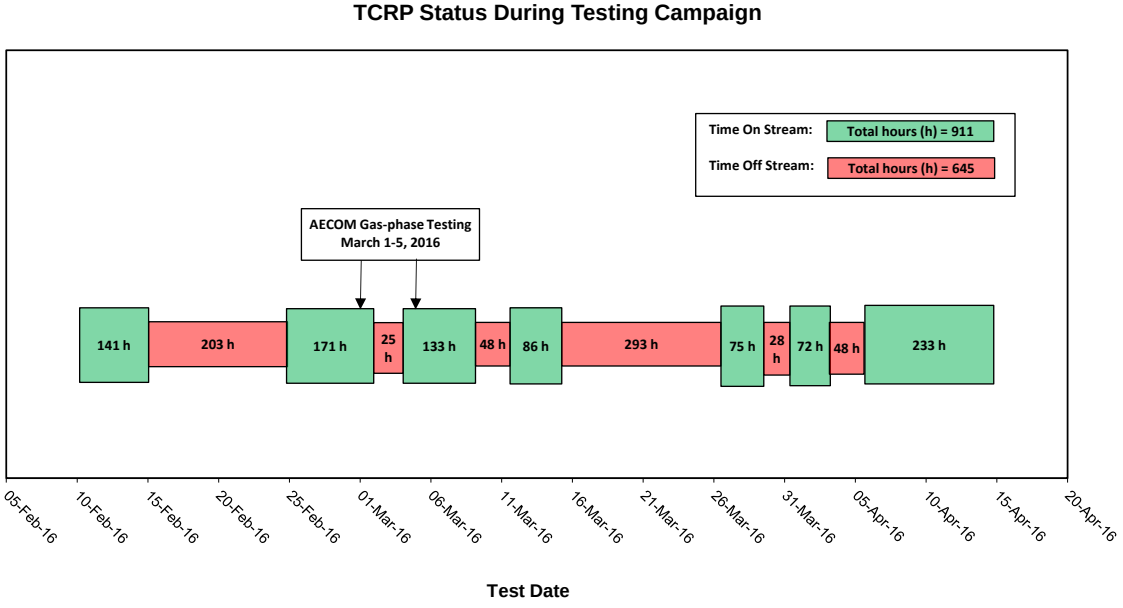

Figure 51. TCRP operational status

The TCRP operational status presented in ***Figure 51*** shows that desulfurized syngas was not always available for exposure to the sorbents during the testing period. This required the test skid to be taken offline and placed in standby mode and then transitioned back to operational mode periodically. To place the system in standby mode, TCRP lines and reactor vessels were purged with N_2 provided by 50 MW_e pre-commercial systems to remove syngas components. Once syngas was purged from the TCRP system, inlet and outlet valves were closed to isolate the TCRP system and external heat tracing was used to maintain the reactor vessels and heat traced lines at nominal 400 °F. To resume testing in the operational mode, the inlet and outlet lines were opened to allow syngas flow through the reactors. The

TCRP system was not cycled back online until WDP was fully operational and desulfurized gas was again available for testing.

After an initial period of 141 hours of continuous operation and an outage that ended on February 25, 2016, the TCRP skid ran uninterrupted for 171 hours. It was during this 171 hours of continuous operation that AECOM started the gas-phase trace contaminant testing described in Section 3.4 of this report. Prior to AECOM completing their full testing schedule for the trace contaminant skid, the skid had to be placed in standby for a short period (about 25 hours) because of a problem encountered with the Polk Power Station gasifier. AECOM resumed their testing schedule for the trace contaminant skid when the system was restarted. AECOM's sampling runs for the TCRP skid were completed on March 5, 2016. No other significant events occurred during TCRP testing other than occasional standby periods when the desulfurized syngas was not available.

The system was purged with N_2 and placed in final standby mode at the conclusion of WDP testing on April 15, 2016. Once testing was completed, the reduced metal in the sorbent beds was passivated using a mixture of O_2 and N_2. Electrical power and all gas connections to the skid were terminated and the skid was shipped by truck to RTI. At RTI, the sorbents were removed from the reactor and submitted for analysis to determine the amount of As, Se, and Hg retained on the materials during testing.

5.2.3 Analysis Procedures for Exposed TCRP Sorbents

The three trace contaminant sorbents exposed to desulfurized syngas during WDP pre-commercial testing at Polk Power Station remained sealed in the reactor vessels until the TCRP test skid was received at RTI. The exposed sorbents were then removed from each individual reactor in five distinct sections that corresponded to the axial position from the top or entrance to the reactor down to the bottom or exit. This resulted in nominal 200 g portions of the mixed-metal oxide sorbents and nominal 100 g portions of the impregnated carbon that corresponded to each position within the reactor vessel. Triplicate analytical aliquots of nominal 0.5 g were removed from the individual well-mixed samples from the five different sample locations for each of the three sorbents. All three individual aliquots for each location and sorbent were submitted for analysis to determine the presence of metals on the sorbents.

Analytical aliquots of the trace contaminant sorbents were subjected to dissolution using hydrofluoric acid (HF) reagent, filtered, and diluted in deionized (DI) water to a final volume before being analyzed by inductively coupled plasma atomic emission spectroscopy (ICP-AES). Analysis results from the triplicate aliquots were averaged and the amount detected was compared back to the individual sample weights to calculate the average concentrations, in units of µg/g, detected for each sample.

5.2.4 Trace Contaminant Sorbent Testing Results

Experimental results for the trace contaminant sorbent testing, which includes results from gas-phase contaminant testing while the candidate sorbents were exposed to desulfurized syngas using the TCRP test skid and results from the analysis of the exposed sorbents at the completion of TCRP testing, are provided in the subsections that follow. For convenience, each subsection is organized by contaminant and the testing results are broken down by vessel so that the reader can track the fate of each contaminant across the TCRP sorbent.

NH_3 Testing Results

Experimental results from the gas-phase trace contaminant testing for NH_3 at the TCRP skid inlet and at the outlet of the three reactor vessels containing TCRP sorbents are presented in ***Table 16***. Problems were encountered maintaining sample gas temperatures above the dew point during Run 1. For this reason, experimental results for this run are not included in the TCRP results presented in this section

The Welch test was used to evaluate the data in ***Table 16*** under the hypothesis that inlet and outlet concentration of ammonia were equivalent. The results from this test showed that at a 95% confidence level, the mean ammonia concentrations in the inlet and outlet gas were identical. There was

no anticipation that these sorbents would remove NH_3. Commercial Sorbent F and G in V-200 and V-300, respectively, have not been tested for NH_3 removal to our knowledge. The impregnated carbon sorbent used during pilot plant testing at Eastman, which is a different impregnated carbon than the material used in this test, did not remove ammonia under similar testing conditions. Because NH_3 was not a target contaminant for retention on the three TCRP sorbents tested, there was no post-exposure analysis for NH_3 or any of its degradation products on the sorbent material.

Table 16. NH_3 Concentrations in TCRP Process Streams (ppmvd)

Process Stream	Run 2	3	4	5	6
TCRP Inlet Header	463	508	541	583	827
Reactor V-200 Outlet	453	529	1035	672	588
Reactor V-300 Outlet	501	474	527	607	756
Reactor V-400 Outlet	513	538	582	415	785

HCN Testing Results

Table 17 shows the concentration of HCN upstream and downstream of the TCRP sorbents.

The Welch test based on the hypothesis of equivalent mean concentrations in the inlet and outlet syngas were used for the data in ***Table 17***. The results all indicated that at the 95% confidence level that the inlet and outlet mean HCN concentrations were identical. The impregnated carbon tested during the pilot plant testing at Eastman did demonstrate about 84% removal of the HCN, but as mentioned previously, a different impregnated carbon was used in this test. As with NH_3, there was no post-exposure analysis for this contaminant or any of its degradation products on the sorbent material.

Table 17. HCN Concentrations in TCRP Process Streams (ppmvd)

Process Stream	Run 2	3	4	5	6
TCRP Inlet Header	0.81	0.74	0.96	0.92	0.95
Reactor V-200 Outlet	0.72	0.74	0.88	0.86	0.92
Reactor V-300 Outlet	0.78	0.61	0.89	0.88	0.88
Reactor V-400 Outlet	0.81	0.67	1.09	1.01	1.08

As Testing Results

Arsenic (As) was one of three contaminants for which two of the sorbents (commercial sorbents F and G) were to be tested under typical operating conditions with actual syngas from a gasifier. Results for both gas-phase testing performed by AECOM and post-exposure analysis were conducted to permit evaluation of the performance of these two candidate sorbents. ***Table 18*** shows the gas-phase concentration of As in the desulfurized syngas upstream and downstream of the TCRP sorbents during AECOM's gas-phase testing conducted after about 300 hours of operation.

Table 18. As Concentrations in TCRP Process Streams (ppbvd)

Process Stream	Run 2	3	4	5	6
TCRP Inlet Header	1.03	0.901	0.816	0.985	1.41
Reactor V-200 Outlet	0.657	1.11	1.17	1.21	1.21
Reactor V-300 Outlet	0.970	0.803	1.04	1.13	1.21
Reactor V-400 Outlet	0.804	0.794	0.980	0.872	1.47

The Welch test of the data in ***Table 18*** based on a hypothesis of equivalent inlet and outlet As concentrations showed at the 95% confidence level that the mean As concentrations for the inlet and outlet of all three reactors were identical. These results indicate that none of the three sorbents was removing As during this gas phase testing.

Figure 52 depicts a graphical representation of the average concentration of As detected in each section of the three sorbents exposed to desulfurized syngas for 911 hours using the TCRP test skid.

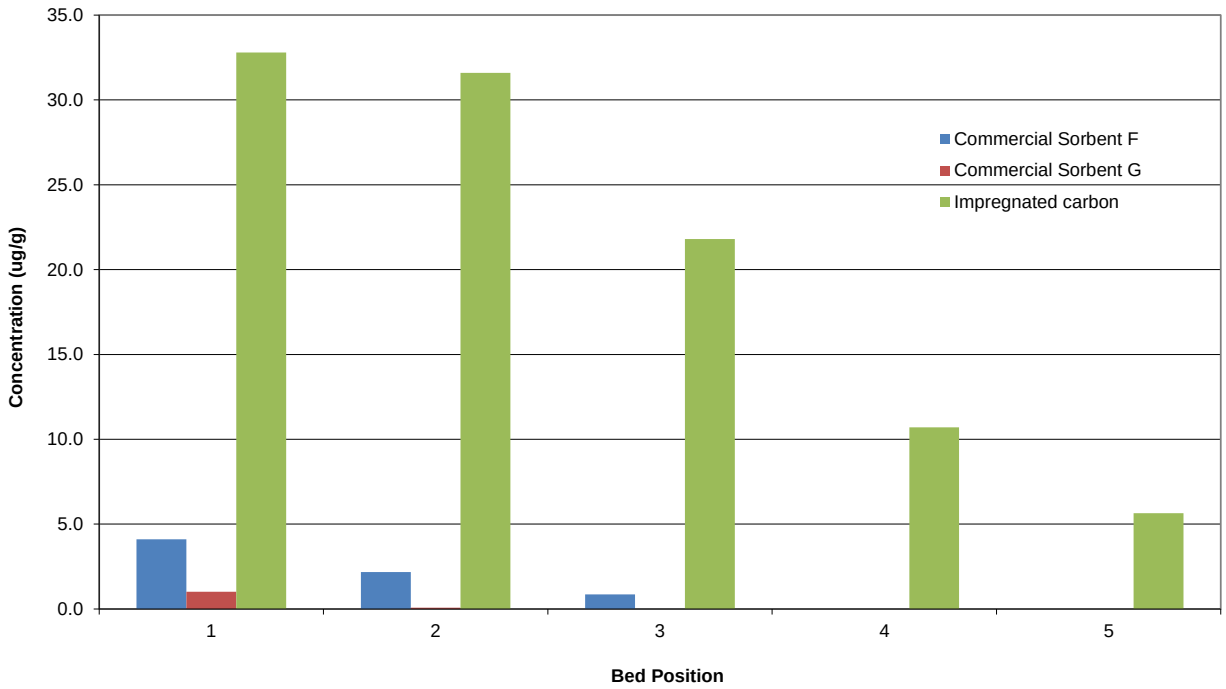

Figure 52. As retention on trace contaminant sorbents

The data in ***Figure 52*** shows that all three sorbents did show accumulation of As. Furthermore, the concentration profiles show a gradual decrease in As accumulation over the length of the sorbent bed, which is the typical concentration profile that would be expected for a sorbent. However, the amount of As accumulated on these sorbents is extremely low and the impregnated carbon showed significantly more As accumulation that did commercial sorbent F or G.

These results are almost exactly the opposite of the results obtained during laboratory testing with simulated syngas. The laboratory tests showed that all three sorbents could reduce the concentration of arsine in simulated syngas from a challenge concentration of 10,000 ppbv to below 5 ppbv and achieve As loadings of > 4 wt%. For all sorbents, there is a limiting concentration at which the driving force for adsorption/removal by the sorbent is too small for any additional removal. In our laboratory testing, this minimum concentration observed during any test was about 5 ppbv. If this is the effective concentration at which the driving force for additional removal becomes essentially zero, we would expect to see essentially no As removal and only minimal As accumulation on the sorbents at the extremely low As concentration (about 2 ppbvd, which would be even lower on a wet basis) in the syngas feed for the TCRP system. Although this result was a distinct possibility based on the As concentration in the syngas available for this slipstream testing, the actual performance of the sorbent under these conditions was not known and the limited number of opportunities to test with actual syngas was too valuable to pass up.

Another possible explanation is the laboratory testing was conducted with arsine (AsH_3) as the source of As in the simulated syngas. AECOM's testing protocol was developed to effectively measure the total As concentration in the syngas and not the concentration of the different compounds that contain arsenic. If multiple As compounds are present in the syngas, as thermodynamic calculations predict, our laboratory screening process might not be effective for all these As compounds. As a result, additional testing with actual syngas is necessary to evaluate the performance of commercial sorbents F and G at more typical As concentrations for coal-derived syngas and/or to identify and quantify the specific As compounds present in actual coal-derived syngas.

Hg Testing Results

An impregnated carbon sorbent was loaded in the V-400 specifically for evaluating Hg removal performance of this sorbent under typical operating conditions with actual syngas from a gasifier. ***Table 19*** shows the gas-phase concentration of Hg in the desulfurized syngas up-stream and downstream of the TCRP sorbents measured by AECOM after about 300 hours of operation.

Table 19. Hg Concentrations in TCRP Process Streams (ppbvd)

Process Stream	Run				
	2	3	4	5	6
TCRP Inlet Header	0.626	0.497	1.25	2.00	0.706
Reactor V-200 Outlet	1.22	0.665	0.704	0.690	0.674
Reactor V-300 Outlet	0.536	1.15	0.734	0.730	1.07
Reactor V-400 Outlet	2.13	2.67	1.44	0.876	0.154

The Welch test of the data in ***Table 19*** based on a hypothesis of equivalent inlet and outlet Hg concentrations showed at the 95% confidence level that the mean Hg concentrations for the inlet and outlet of all three reactors were identical. Consequently, no Hg removal was detected based on gas phase analysis.

Figure 53 shows the average concentration of Hg detected on the three TCRP sorbent materials. The analysis of the impregnated carbon shows that there was Hg accumulation on the sorbent. The Hg profile across the bed is not the typical profile of a higher accumulation at the inlet gradually decreasing to the outlet. Even assuming that the sorbent bed had been saturated, the anticipated profile would show near consistent Hg concentrations across the bed. If during the passivation of the bed at the end of the test in preparation for shipment to RTI, during which heat was generated by the exposure to oxygen, sufficient heat could have been generated to potentially drive off accumulated Hg and lower Hg capacities have been regularly observed at higher temperatures during laboratory testing of all Hg sorbent materials. The phenomenon would also be more visible at the bed inlet, because this is where most of the heat would be generated on exposure to oxygen. This hypothesis would explain the unique Hg profile in the sorbent bed at the end of the test, and if the bed was already saturated when AECOM conducted the gas phase testing (after about 300 hours of testing), the absence of removal during gas phase testing. Based on this assumption, the best estimate of Hg capacity for the sorbent would be based on the Hg accumulated in the last three sections of the bed or about 0.66 wt%.

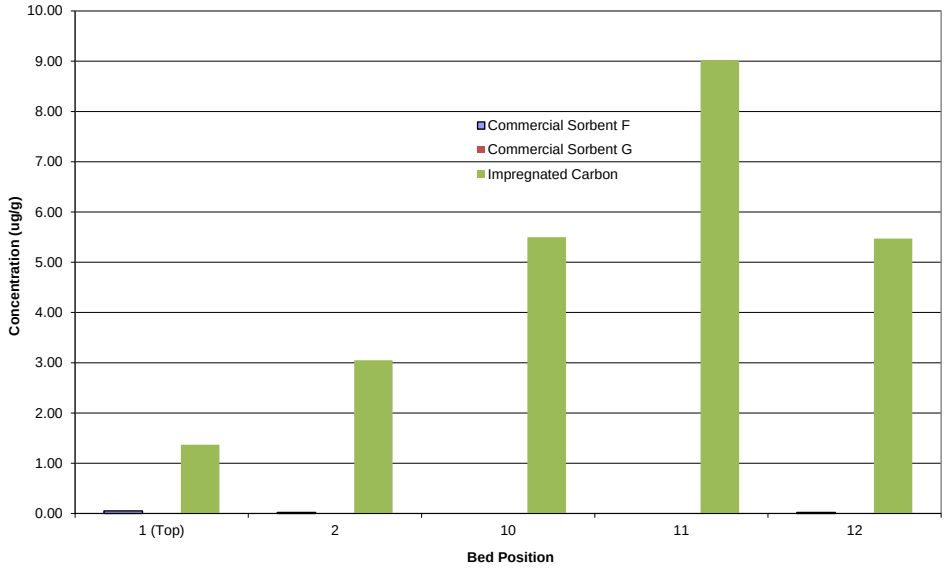

Figure 53. Hg retention on trace contaminant sorbents

For commercial sorbents F and G, the absence of any evidence of Hg removal was the anticipated result as neither of these materials was a candidate for Hg. For the impregnated carbon sorbent, laboratory studies have shown that the impregnated carbon reduced the concentration of elemental Hg in simulated syngas from 240 ppbv to less than 0.31 ppbv (3 ppbw). Thus, the small Hg accumulation observed on the sorbent and the absence of Hg removal based on AECOM's gas phase testing was unexpected, but very promising considering that the Hg concentrations in the syngas feed were approximately equal to the target effluent concentration for removal at which Hg removal would be anticipated to occur much more slowly.

Se Testing Results

Se was the third of three contaminants targeted for retention on the sorbents loaded in the TCRP test skid. ***Table 20*** shows the gas-phase concentration of Se in the desulfurized syngas upstream and downstream of the TCRP sorbents.

Table 20. Se Concentrations in TCRP Process Streams (ppbvd)

Process Stream	Run				
	2	3	4	5	6
TCRP Inlet Header	9.04	3.01	6.16	11.5	1.52
Reactor V-200 Outlet	0.582	1.23	1.17	1.42	1.53
Reactor V-300 Outlet	0.890	ND	1.14	1.26	1.12
Reactor V-400 Outlet	0.805	0.649	0.960	1.10	1.56

ND = Not Detected. Refer to AECOM report for MDL values.

The Welch test was performed on the data in Tab3-8 with the hypothesis that the inlet and outlet concentrations were identical. At the 95% confidence level, this hypothesis was just accepted for Reactor V-200 (Commercial sorbent F). However, the hypothesis was rejected for Reactors V-300 (Commercial sorbent G) and V-400 (impregnated carbon sorbent). The large variability in the inlet and outlet Se concentrations for Reactor V-200 increased the statistical probability that the difference in inlet and outlet Se concentrations could result from just random variations. If the gas-phase testing had included several more test runs, there would have probably been enough data to statistically show a difference in the inlet and outlet Se concentrations for even reactor V-200.

Although these results were expected for commercial sorbents F and G, Se removal by the impregnated carbon was not anticipated. During laboratory testing with a different source of carbon, very little Se retention was observed during testing with simulated syngas, and impregnated carbon had been removed from our list of potential sorbent materials. Apparently, there is something unique about this impregnated carbon that enabled Se removal.

Figure 54 shows the average concentration of Se detected on each section of the three trace contaminant sorbents exposed to desulfurized Polk Power Station syngas using the TCRP test skid.

The general trend in the concentration profile shows gradually decreasing amounts of Se detected between the inlet and outlet. When concentrations of the target contaminant are detected in the last section of the sorbent bed, it demonstrates that the contaminant is reaching this section of the bed and breakthrough is eminent. Although, the Se concentration profiles for all three sorbents show that breakthrough had begun, the gas phase test results indicate that the sorbent was still actively removing a significant amount of Se. Based on AECOM's gas-phase testing, all three sorbents were able to remove > 80% of the Se present in the syngas feed achieving an effluent Se concentration of 2 ppbvd compared to DOE's target of 76 ppbvd. Although the Se loading during laboratory testing with simulated syngas mixtures was typically > 4 wt% for commercial sorbents F and G, the Se loading for the sorbent during this test was <0.001 wt% which could be related to the extremely low Se concentrations in the syngas.

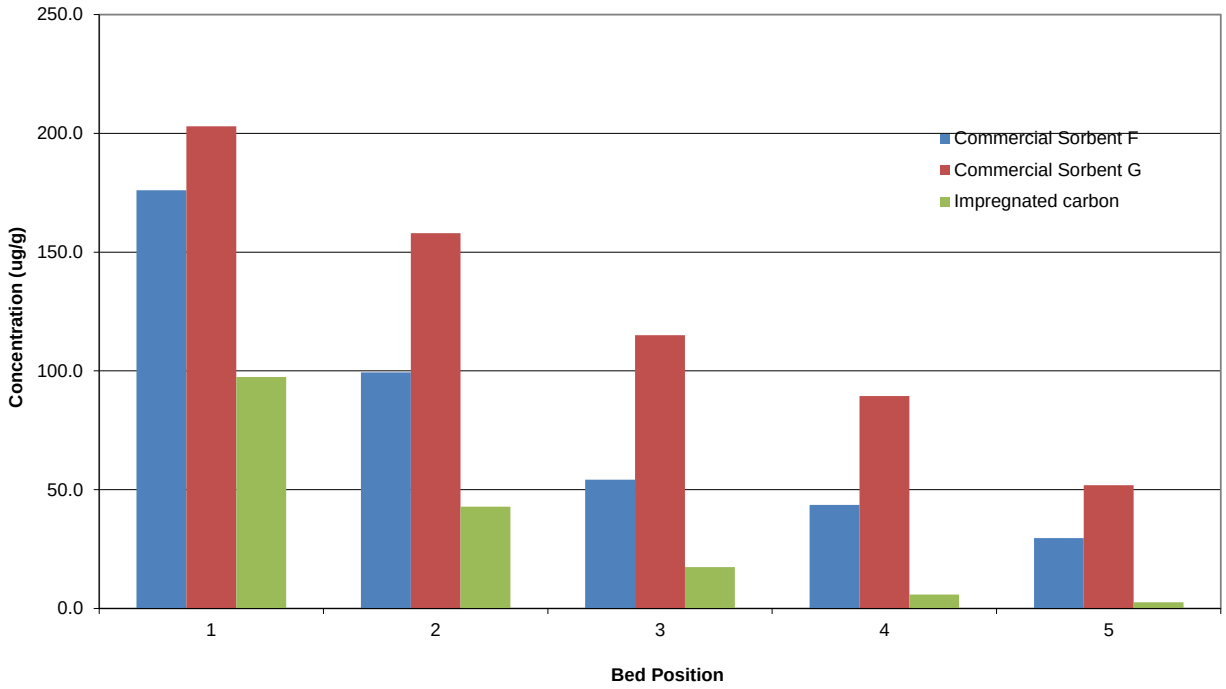

Figure 54. Se retention on trace contaminant sorbents

5.2.5 TCRP Sorbent Testing Summary

One final observation concerning the gas-phase testing for both WGCU and TCRP testing is worth noting. The nominal concentrations of the five target gas-phase trace contaminants detected in the TCRP inlet gas were very similar to the nominal concentrations detected in the LTGC inlet (see Tables 2-1 through 2-5). Both process takeoff points were in fairly close proximity to one another within the syngas flow path but the actual sampling points at the analyzer shed and TCRP test skid were separated by a considerable distance. This is a good indication that sampling lines from both takeoff points were adequately heated and maintained above the dew point of the gas, since several of the target contaminants are soluble in water.

The most promising results from this TCRP testing program was that all three sorbent candidates were able to achieve >80% Se removal and achieve an effluent concentration of 2 ppbvd. The results from this TCRP testing and laboratory testing indicate that Se loading may be a function of the Se concentration in the inlet syngas.

The results for Hg and As did not provide confirmation of the laboratory testing results obtained with simulated syngas. One of the key differences between these two testing programs was the concentration of Hg and As in the syngas feed. During the testing at Polk Power Station, the contaminant concentration was dictated by the coal and petcoke materials gasified and were approximately equal to DOE's target effluent concentration for Hg and below for As. Thus, the driving force for removal of these species was very small. Despite the low inlet concentrations, the impregnated carbon sorbent did show a reasonable accumulation of Hg. Both the gas-phase testing and accumulation of As on Commercial Sorbents F and G were significantly lower than observed during laboratory testing with arsine in simulated syngas. Although this discrepancy may have been caused by the low inlet As concentration, it may also indicate that the arsine used during laboratory testing as a source of As is not the same As species present in actual syngas.

Additional testing will be required to adequately test these sorbent materials for their full potential as trace contaminant sorbents for coal-derived syngas. The preferred means would be with

actual coal-based syngas to ensure testing at actual operating conditions. However, the limited opportunity for this testing warrants a combination of more specific testing with actual syngas to enable improved simulation of laboratory testing conditions and protocols.

5.3 Micro-reactor Testing

Although power production is an important application of gasification, chemicals production via gasification is potentially more important and is the major commercial gasification application. The key challenge for chemical production via gasification is removal of contaminants in the syngas. These contaminants, which survive the gasification step either in their elemental form or as some other more chemically stable species, are known to poison standard catalysts used for conversion of the hydrogen and carbon monoxide in syngas into value-added chemicals. For example, sulfur species such as H_2S should be below 1 ppm and preferably below 0.1 ppm to inhibit deactivation of copper containing catalysts used to produce methanol, and metal species such as arsenic poison Fischer-Tropsch (FT) catalysts based on iron and cobalt.

Measurement of different contaminants provides quantification of the overall effectiveness of removal for these specific measured contaminants. However, the most practical demonstration of the effectiveness of a syngas cleaning process and the one that is most convincing to potential end-users is demonstration in actual operation. Because actual demonstration of all commercial chemical production applications at scale was beyond the scope of this project, a more practical alternative was implemented. In this alternative demonstration, a slipstream of treated syngas from RTI's warm syngas cleanup technology installed at Tampa Electric's Polk Power Station facility was used to produce value-added chemicals in micro-reactors using commercial catalytic processes. The selected catalytic processes, which included methanol and FT synthesis, were chosen based on the stringent syngas cleaning requirements necessary to protect the catalysts from poisoning from sulfur, arsenic, mercury, and other contaminants present in syngas generated via gasification of a mixture of coal and high-sulfur petroleum coke.

In this micro-reactor testing program, the effectiveness of the syngas cleaning process was to be demonstrated by achieving a commercially acceptable level of catalyst deactivation. The catalyst performance was to be monitored with typical reaction performance measures such as carbon monoxide conversion, selectivity to specific products, and productivity of specific reaction products. The baseline performance of these catalysts was to be established during several weeks of 24/7 operation with bottled gas mixtures, which do not have any contaminants. This baseline testing was to be followed with several weeks of 24/7 operation with the actual slipstream of syngas. Any differences in catalyst performance between the bottled gas and actual syngas would be a result of differences in the syngas composition between the two tests. The key difference between the syngas compositions would be the contaminants remaining in the actual syngas after RTI's warm syngas cleanup technology and activated MDEA processes.

For optimal effectiveness of this testing approach, a fundamental assumption was identical testing conditions during the baseline and actual syngas tests. Because of system constraints associated with the actual syngas delivery to the micro-reactors, the composition, gas hourly space velocity, and operating pressure differed between the baseline and actual syngas tests. In addition, starting and stopping the catalytic processes when the pre-commercial demonstration system was down for maintenance and/or TEC's gasification system was down also resulted in significant changes in catalyst performance. Although these factors prohibited using the direct comparison approach originally planned, the data collected from baseline and actual syngas testing were used to identify trends in catalyst performance and reactivity and infer if the changes were due to the different operating conditions or contaminants in the actual syngas.

5.3.1 Catalyst Samples

The three commercial catalysts selected were a copper-based methanol synthesis catalyst, an iron-based FT catalyst, and a cobalt-based FT catalyst. These specific catalysts were chosen because extremely pure syngas is required to reduce deactivation sufficiently to enable cost effective commercial applications of these catalytically processes. Commercially representative catalyst samples were obtained from Clariant. ***Table 21*** provides a description of the selected materials.

Table 21. Catalyst Materials

Catalytic Process	Value-Added Product	Clariant Catalyst
Methanol	Methanol	Megamax 700
FT	FT liquids	D-1140 (Fe-based)
FT	FT liquids	D-1139 (Co-based)

In their as-delivered form, these catalysts were not suitable for optimal testing in the micro-reactor systems. To minimize channeling effects within the catalyst bed, the as-delivered catalysts were crushed and screened to collect catalysts particles with a size between 250 and 355 microns using standard sizing sieves. This ensured that the mean particle diameter was < 0.05 of the reactor's diameter which exceeds the typical recommendation of < 0.1 for testing purposes.

Because these catalytic processes are extremely exothermic, the active catalyst was diluted with an inert material (250 micron alpha-alumina) to reduce the reaction per volume in catalyst bed and achieve more isothermal conditions throughout the catalyst bed. The diluted catalyst samples contained 3 parts by weight of 250 micron alpha-alumina to 1 part by weight of sized catalyst. In addition to being inert, the alpha-alumina particles were carefully selected to minimize stratification of the catalyst and inert particles during loading of the micro-reactors due to hydrodynamic differences between the alpha-alumina and catalyst particles.

5.3.2 Experimental Systems

Three Micromeritics PID/Particulate Systems Effi Micro-reactors were used for the testing. Each PID Effi micro-reactor consisted of an oven containing two furnaces, three 500 mL/minute mass flow controllers for introducing feed gases, a temperature controlled wax trap, a thermoelectrically cooled gas/liquid/liquid separator for condensation and collection of condensable hydrocarbons and water, and a back-pressure control valve for maintaining reactor pressure at up to 100 bar. The oven that housed the reactor furnaces also housed the switching valves and connecting tubing. Housing these devices in a heated oven prevented condensation of hydrocarbon product species before they reached the liquid condensers designed for collection of condensable components in the product gas stream. One furnace in the oven housed a 17 mm ID stainless steel reactor vessel. This reactor was packed with approximately 12 cm^3 of Clariant ActiSorb® S2 (G-72 D) that was heated to 725 °F as a sulfur guard bed. The other furnace housed a 9.1 mm ID stainless steel reactor vessel packed with about 3 cm^3 of catalyst/alpha alumina mixture. This volume of catalyst resulted in a L/D ratio of about 5. These reactors were run in series with the gas flow passing through the sulfur guard bed before entering the catalyst reactor. As mentioned previously, the catalyst mixture that was loaded into the reactor was sized and contained sufficient alpha-alumina to achieve realistic flow patterns and more isothermal conditions throughout the catalyst bed.

In addition to the G-72D sulfur guard bed, a second guard bed consisting of an unheated stainless steel vessel filled with about 50 cm^3 of 20/40 mesh SKC activated carbon was installed on the inlet feed to each reactor system. The G-72D sulfur and activated carbon guard beds are standard guard beds that would be present in any commercial systems to protect the catalyst beds from process upsets. Although these guard bed do provide some additional removal of contaminants, their design was to provide limited

protection against process upsets. During normal operation, they would be rapidly exhausted, if the syngas cleaning system were not removing >99% of the target contaminants.

Analysis of the reactor outlet gas stream was performed with an Inficon 3000 Micro gas chromatograph. Components measured for the FT catalyst systems included hydrogen, carbon monoxide, carbon dioxide, nitrogen, C_1-C_6 alkanes, and C_2-C_6 alkenes. Components measured for the methanol synthesis catalyst system included hydrogen, carbon monoxide, carbon dioxide, nitrogen, and methanol. The nitrogen mass balance around the system along with the nitrogen concentrations in the product gas and in the feed gas and inlet flow rate of syngas were used to determine the outlet gas flowrate.

Liquid hydrocarbons collected from the condensers of the FT catalyst systems were analyzed at RTI by gas chromatography with flame ionization detection to determine the carbon number distribution of the hydrocarbon liquid product.

5.3.3 Procedures

Catalyst Loading

The amount of catalyst/alpha-alumina mixture loaded in each reactor was based on achieving a nominal L/D of 5, which resulted in a bed volume of around 3.2 cm^3. After the mixture was loaded in the reactor, nitrogen was used to initially purge air from the micro-reactor systems. The micro-reactor systems were then pressurized with nitrogen to their expected maximum operating pressure to leak check the system.

Catalyst Activation

In general, the catalyst activation process involves controlled reduction of the active metal oxides using reducing gas mixtures, temperature, and time as control parameters. Although pressure can also affect the reduction, in situ commercial reduction processes typically use standard operating pressure conditions to effectively utilize the existing equipment associated with the reactor system.

Iron-Based FT Catalyst

After the catalyst mixture was loaded into the reactor, the micro-reactor system was pressurized to 3.45 bar using nitrogen. When all the air had been purged out of the micro-reactor system, the activation process began by setting the hydrogen feed rate to 5 sccm (cubic centimeters per minute at standard conditions of 0 °C and 1 atm pressure) and the nitrogen feed rate to 95 sccm. The reactor was heated in this gas mixture to 105°C. Once the reactor had reached temperature, the same gas flow was maintained until GC analysis indicated the effluent hydrogen concentration had stabilized. The feed rate of hydrogen was increased to 10 sccm and nitrogen reduced to 85 sccm. When the GC analysis indicated the effluent hydrogen concentration had stabilized, the hydrogen feed rate was increased to 25 sccm and the nitrogen feed rate decreased to 75 sccm. When the effluent hydrogen concentration had stabilized at these conditions, the hydrogen feed rate was reduced to 5 sccm and nitrogen feed rate increased to 95 sccm and the temperature increased to 120°C. At 120°C, these steps of progressively changing the hydrogen and nitrogen feed rates until the effluent hydrogen concentration had stabilized was continued. When the hydrogen effluent concentration had stabilized at 120°C and 25 sccm of hydrogen and 75 sccm of nitrogen, the hydrogen feed rate was reduced to 5 sccm and the nitrogen increased back to 95 sccm and the temperature was increased to 220°C. Once again, the same procedure of increase the hydrogen and nitrogen flow rates until the hydrogen effluent concentration stabilized was repeated at 220°C. When the effluent hydrogen concentration stabilized at 220°C with 25 sccm of hydrogen and 75 sccm of nitrogen, the catalyst activation procedure was complete and baseline testing could begin.

Cobalt-Based FT Catalyst

After loading the catalyst mixture, the micro-reactor system was pressurized to 13 bar with nitrogen. After purging air from the system, the same reduction procedure used for the Fe-based FT catalyst was initiated.

Because this was the first catalyst to be activated, a slow heating rate was not selected and the reactor temperature rapidly climbed to 175°C. During this heating, the GC results showed very little

change in the effluent hydrogen concentration indicating that rapid and excessive reduction of the catalyst had not occurred. The reactor was cooled back to 120°C before continuing the activation process using a more appropriate ramp rate for heating the reactor.

When the hydrogen effluent concentration had stabilized at 220°C and 25 sccm of hydrogen and 75 sccm of nitrogen, the hydrogen flow was reduced back to 5 sccm and the nitrogen flow increased to 95 sccm. The reactor temperature was then slowly increased to 300°C. At 300°C, the activation at the progressively higher hydrogen flow rates was completed. When the hydrogen effluent concentration had stabilized at 300°C and 25 sccm of hydrogen and 75 sccm of nitrogen, the activation for the Co-based FT catalyst was complete and baseline testing could begin.

Copper-based Methanol Synthesis Catalyst

The micro-reactor system was purged with 100 sccm N_2 and pressurized to 8 bar. The temperature was increased to 150°C at 1°C /min with a feed gas flow of 5 sccm H_2 and 95 sccm N_2. After confirming that the effluent hydrogen concentration at the reactor outlet was no longer increasing, the temperature was ramped to 180°C at 1°C /min. When the H_2 concentration of the outlet gas stabilized at 5%, the temperature was increased to 230°C at 0.2°C /min. After the reactor temperature had reached 230 °C and H_2 concentration in outlet gas was 5%, the H_2 in the feed was increased to 7%. The outlet concentration of H_2 quickly reached 7%, indicating no further reduction. After switching back to a nitrogen purge, the reactor pressure was increased to 40 bar and the reactor temperature was increased to 250°C in preparation for baseline testing.

Baseline Testing

The selection of the baseline testing conditions was based on standard commercial operating conditions for the catalysts. However, adjustments were made to these conditions to accommodate limitations in the micro-reactor system. Because of the limited size of the wax traps and to minimize the risk of plugging the reactor system with wax and liquid condensate, the syngas composition simulated with bottled gas limited the concentration of reactive gases namely H_2, CO, and CO_2 to < 30 mol% to reduce production of FT wax product. ***Table 22*** provides the baseline exposure conditions.

Table 22. Test Conditions for Baseline Tests

Catalyst	Co-FT	Fe-FT	Methanol
Pressure (bar)	24	24	40
Reactor Temperature (°C)	220	250	250
GHSV * (h^{-1})	1858	1858	3716
Syngas Composition (mol %)			
H_2	16.0	16.0	22.0
CO	7.8	7.8	10.8
CO_2	1.3	1.3	1.7
N_2	Balance	Balance	Balance
Wax Trap (°C)	120	120	
LT Liquid trap (°C)	5	5	5

* GHSV is defined as the gas flow at atmospheric pressure and 0°C based on the catalyst bed volume.

The purpose of baseline testing was to establish performance trends for CO conversion, product selectivity, and catalyst productivity for the three catalysts. The anticipation was that baseline tests could be effectively run 24/7 for several weeks to define natural trends in the key performance criteria for 300 to 500 hours of operation for each catalyst.

The plan was that these baseline performance trends could be compared with the trends collected for testing at identical conditions with actual syngas. Any differences in the performance trends could be attributed to the differences between bottled gas and actual syngas. The primary difference being the contaminants present in actual syngas.

Syngas Testing

Because of the test plans for the 50 MW_e system, the composition of the syngas from the aMDEA® system varied significantly because of the operational status of the Water Gas Shift (WGS) and aMDEA® systems. When the WGS system was not in operation, the syngas from the aMDEA® system

was CO-rich and H_2 addition was necessary to adjust the syngas feed composition for the micro-reactors to achieve about a 2 to 1 H_2 to CO ratio typically used for commercial processes and the baseline test. However, when the WGS was in operation, the syngas from the aMDEA® system was H_2-rich and CO addition was required to lower the H_2 to CO ratio in the syngas feed to the micro-reactors back to about a 2 to 1 H_2 to CO ratio.

The syngas test for the methanol catalyst system was run while the WGS was in operation and the clean syngas was H_2-rich. Commercial methanol synthesis typically includes a small amount of CO_2 (3-6 mol%) to enhance methanol production. With WGS and aMDEA® in operation, the CO_2 concentration in the clean syngas feed to the micro-reactors was < 1 mol%. Simultaneous adjustment of both the H_2 to CO ratio and increasing the CO_2 concentration in the syngas feed to the methanol micro-reactor was accomplished by using a gas mixture containing both CO and CO_2. Because of the concentrations in this gas mixture, the minimum CO_2 concentration in the syngas feed to the micro-reactor was 5.7 mol%. Because of failure of one of the heat exchangers in the aMDEA® process, the aMDEA® performance dropped while the methanol test was in progress and the CO_2 concentration in the clean syngas product increased. This resulted in an increase in the CO_2 concentration in the syngas feed to the methanol micro-reactor system. The maximum CO_2 concentration was about 11 mol%. For the cobalt and iron FT catalyst testing, no additional CO_2 was added to the syngas mixture.

The actual syngas from the aMDEA® system also contained water vapor at about its saturation conditions at the effluent temperature from aMDEA® (~0.5 mol%). As a consequence of these factors, the composition of the actual syngas feed to the micro-reactors was not exactly identical to the simulated syngas used during baseline tests and also had more composition variability than the simulated syngas in the baseline test.

Because of minimum flow constraints for the MFCs for H_2 and CO, the GHSV for the syngas tests was set at 3,716 h^{-1}. For the FT micro-reactor systems, this resulted in an increase in the GHSV of about 2. Similarly, the available pressure from the aMDEA® system limited the operating pressure for the micro-reactor systems to 20 bar. Consequently, the micro-reactor system for methanol production was operated at about half the pressure used during baseline testing. Conditions for testing with syngas feed from after the aMDEA® system in the 50 MW_e pre-commercial system are shown in ***Table 23***.

Table 23. Test Conditions for Clean Syngas Tests

Catalyst	Co-FT	Fe-FT	Methanol
Pressure (bar)	20	20	20
Reactor Temperature (°C)	220	250	250
GHSV * (h^{-1})	3716	3716	3716
Syngas Composition (mol %)			
H_2	16-22	18-22	18-22
CO	9-11	9-11	9-11
CO_2	0-4.7	0-2.2	5.3-11.1
N_2	Balance	Balance	Balance
Wax Trap (°C)	120	120	
LT Liquid trap (°C)	5	5	5

* GHSV is defined as the gas flow at atmospheric pressure and 0°C based on the catalyst bed volume.

Another difference between the actual syngas and baseline tests was syngas from RTI's warm syngas cleaning unit was only available when both TEC's gasifier was in operation and RTI's warm syngas cleaning unit was operating. When either of these systems was brought down, the syngas for micro-reactor testing was also not available and the micro-reactor systems had to be put in hot standby mode in which nitrogen flow was used to keep the reactor at temperature and pressure anticipating the restart of syngas flow from RTI's warm syngas cleaning unit and TEC's gasifier. This resulted in significantly more interruptions in the syngas flow during actual syngas testing than during baseline testing.

The differences in operating conditions between the actual syngas and baseline test prohibited using the micro-reactor test results for a direct comparison where any differences in performance trends would be a consequence of differences in syngas composition, namely contaminant concentration. As a result, the data collected during the baseline and actual syngas tests were used to evaluate the fundamental

reactivity of the catalysts to the reactants and for the products formed to evaluate if contaminants present in the actual syngas were having any impact on catalyst performance.

5.3.4 Micro-reactor Testing Results

For the baseline and actual syngas tests, several key markers of catalyst performance were examined. GC data was used to calculate CO conversion, methane selectivity, CO_2 selectivity, C_2-C_4 olefin selectivity, C_2-C_4 paraffin selectivity, C_5-C_6 olefin selectivity, C_5-C_6 paraffin selectivity, C_2^+ productivity, and C_5^+ productivity for the cobalt and iron FT catalysts. GC data was used to calculate CO conversion, methane selectivity, CO_2 selectivity, methanol selectivity, and methanol productivity for the methanol synthesis catalyst. The data used to calculate these key performance parameters were also examined when necessary to gain insight into the reactivity of the individual reactants and production of specific products.

In addition to these measures of catalyst performance, any wax samples collected from the FT micro-reactor tests were analyzed off-line to obtain carbon numbers. As part of post-test analysis, the catalyst samples were analyzed for trace contaminants.

Iron Catalyst Test Results

Figures 55 and ***56*** show the performance results for the baseline test. The gap in data during the first 100 hours of operation resulted from loss of product composition measurements provided by the gas chromatograph (GC). Despite the loss of GC data, the micro-reactor continued running while the GC was being repaired. In this baseline test, the most change in catalyst performance occurred during the first 100 hours of the test. These changes represent the final activation of the FT catalyst for the FT reaction and are routinely observed when bringing a new Fe-FT catalyst online. After these initial changes in catalyst performance, the only visible trends are a slow increase in CO conversion, C_2^+ productivity, and C_5^+ productivity. If we take a closer look at the product flow rates for the individual alkanes and alkenes shown in ***Figure 57***, the standard preference for alkenes over the corresponding alkanes for Fe-based FT catalyst can be observed. A number of small changes in the different hydrocarbon flow rates occur after the interruption in syngas feed to the micro-reactor after about 350 hours of operation. Upon restarting the micro-reactor after this interruption in the syngas feed, the production of all the alkanes has increased and the production of the alkenes decreased slightly. Another key feature of the hydrocarbon flow rates to observe is that the ethane production flow behaves in an opposite manner to all the other hydrocarbons.

Figures 57 and ***59*** show the standard performance parameters during the actual syngas test. The large gap in the data seen at around 250 hours of operation was not a loss in syngas feed to the micro-reactors system, but a loss of data from the GC measuring the product gas composition. By contrast, the interruptions of syngas feed to the micro-reactor create discontinuities by introducing sudden shifts either up or down in almost all of the performance parameters. If these discontinuities are ignored, the strong trends that are observed are an increase in CO conversion, C_2^+ productivity, and C_5^+ productivity. There is also a steady decline in the C_2-C_4 olefins and paraffins selectivity over the course of the test.

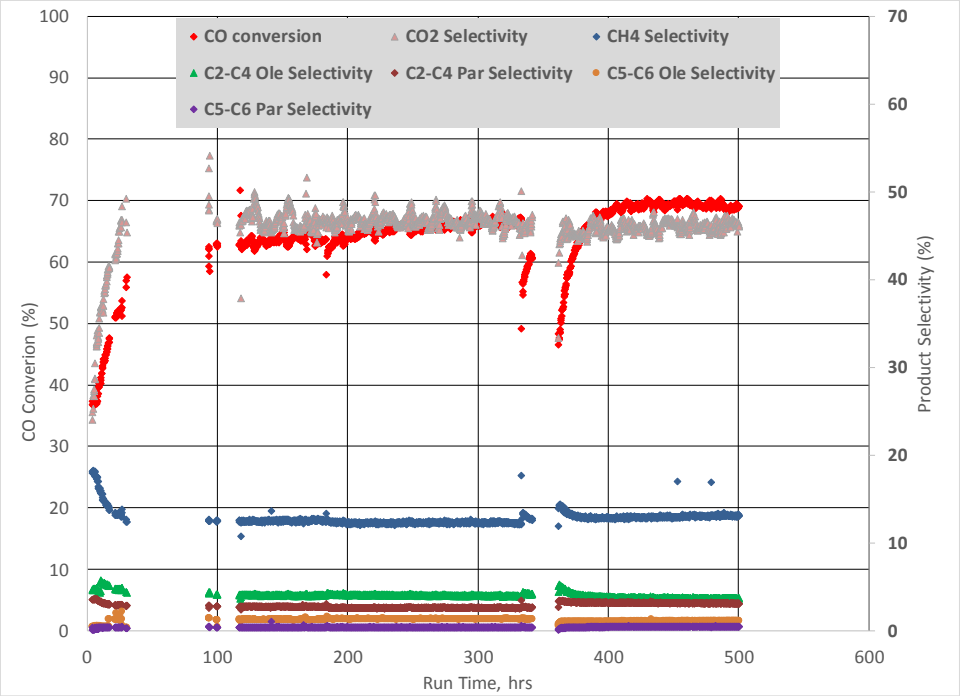

Figure 55. Fe-based FT catalyst CO conversion and product selectivity for baseline test

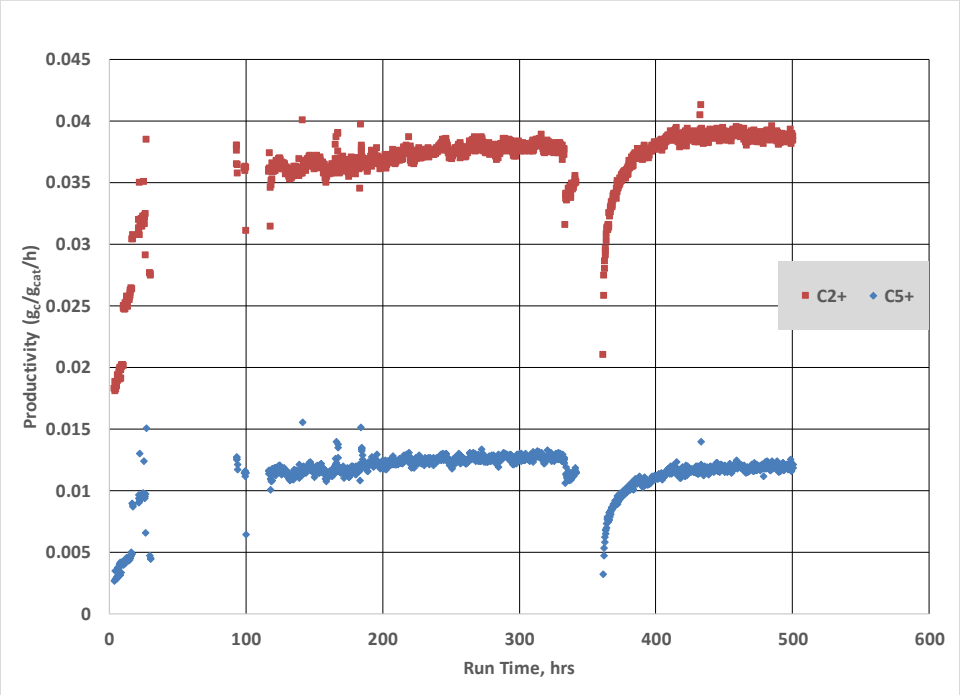

Figure 56. Fe-based FT catalyst productivity for baseline test

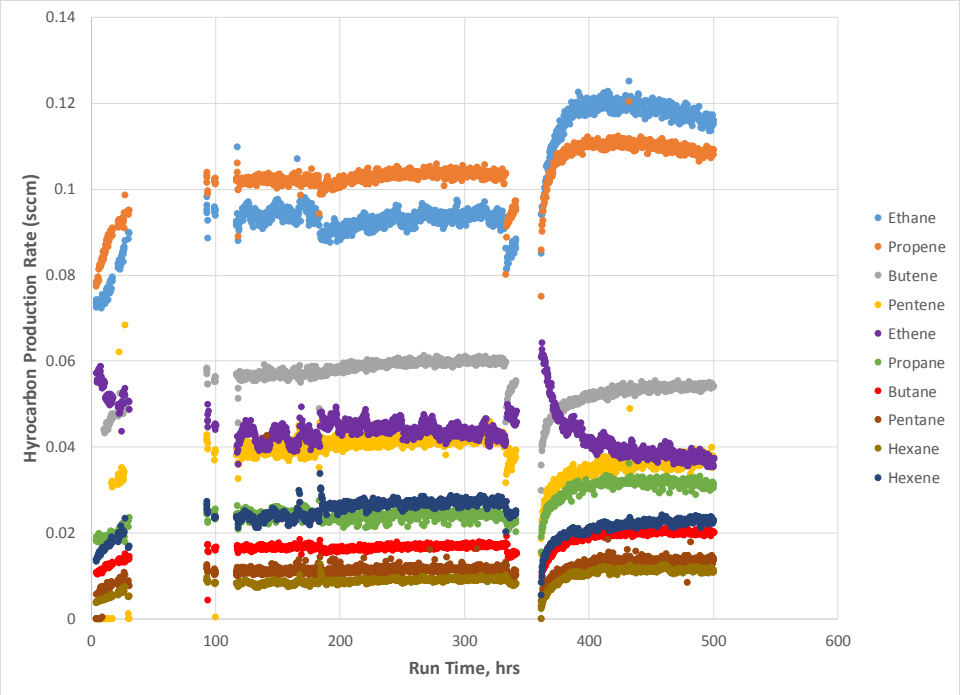

Figure 57. Hydrocarbon production rates for baseline test

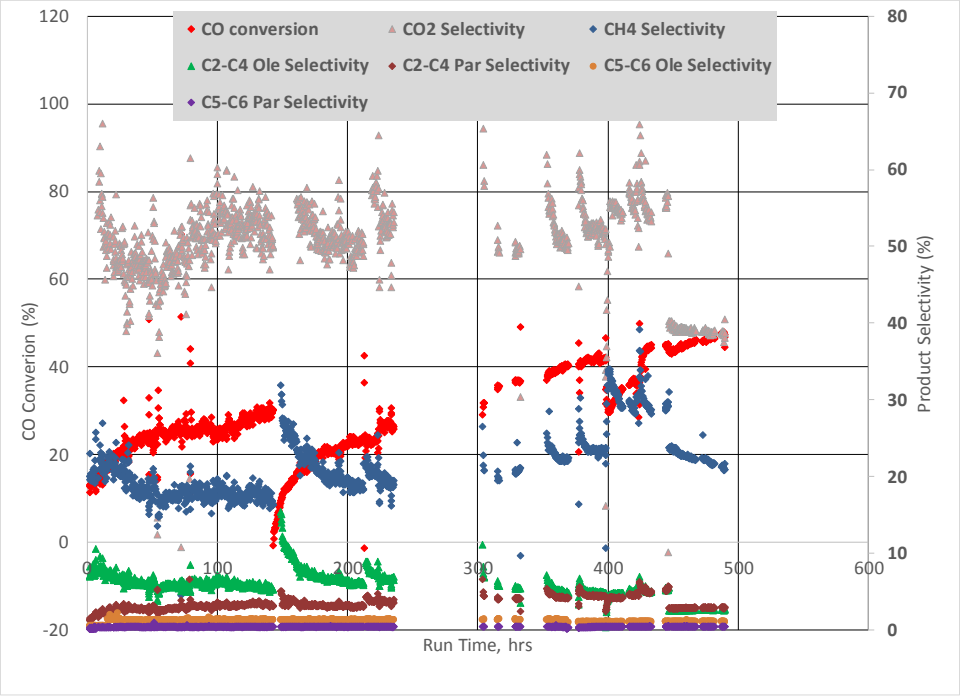

Figure 58. Fe-based FT catalyst CO conversion and product selectivity for actual syngas test

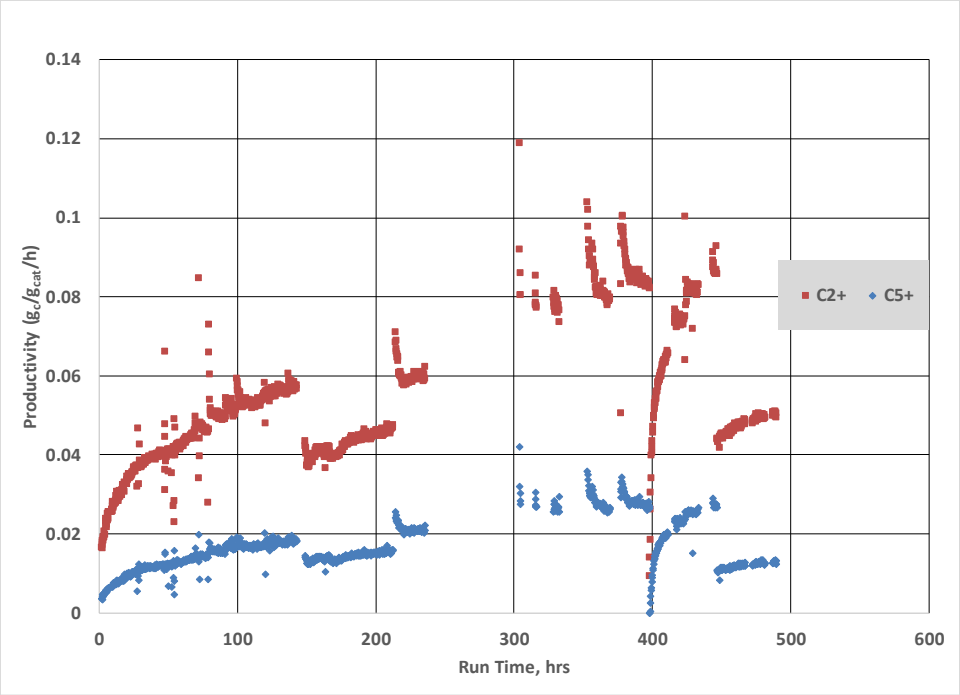

Figure 59. Fe-based FT catalyst productivity for actual syngas test

As one of the key changes between the baseline and actual syngas tests was that the flow rate for the actual syngas test was increased to almost double the GHSV, the trends that were observed are exactly the trends we would expect to see. If we look at the values of these performance parameters, we see that the C_2^+ and C_5^+ productivities are increasing towards a rate that is roughly twice that observed for the baseline test. The increase in methane selectivity and initial higher C_2 to C_4 selectivity align very well with the sudden increase in reactants resulting in a bow wave in shorter hydrocarbon production. The CO conversion for the actual test is lower than the baseline test, but the CO conversion would have been expected to decrease at the higher GHSV used in the actual syngas test.

Figure 60 shows the product hydrocarbon flows for the individual alkanes and alkenes. Interestingly, the same general patterns seen in the baseline test are present in the data from the actual syngas test. Alkene production is favored over alkane production. The ethane production responds in an opposite manner to all the other hydrocarbons in response to syngas interruptions. Finally, after about 350 hours of operation, the same shift in the production rate between the alkanes and alkenes that occurred in the baseline test occurs in the actual syngas test.

Figure 61 shows the liquid hydrocarbon carbon distribution for the baseline and actual syngas tests. For the baseline test, the liquid hydrocarbon product includes hydrocarbons with between 10 and 25 carbons with the more bell-shaped distribution with the peak hydrocarbon having 13 carbons.

No liquid hydrocarbons were collected during the actual syngas test. However, the slight decrease in operating pressure and an increase in syngas flow resulting in doubling the GHSV for the actual syngas test probably resulted in a reduction of the residence time in the liquid condenser to the point there was not sufficient hydrocarbon partial pressure and time to permit capture of a liquid hydrocarbon product for the actual syngas test. This hypothesis seems to be confirmed by the comparison of the carbon distribution for the wax products from the baseline and syngas tests. Although the general shape of the carbon distribution is very similar for these two wax products and consists of a skewed distribution starting at a carbon number of about 10 and tailing off at a carbon number of about 55 with the peak hydrocarbon having about 20 carbons, the wax product for the actual syngas test begins at a slightly higher carbon number than the baseline test and does not begin to match the baseline profile until about a carbon chain length of 25. With less hydrocarbon partial pressure due to lower operating pressure and less

residence time in the cooler due to higher GHSV, the shorter hydrocarbons would be less effectively condensed resulting in lower concentrations in the wax product for the actual syngas test, which is what is observed.

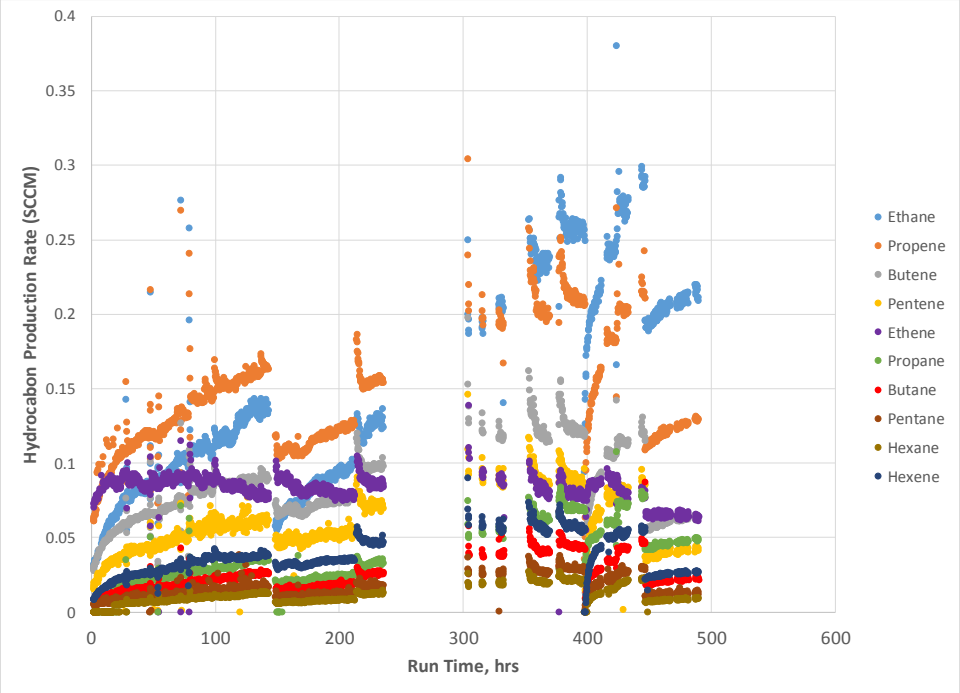

Figure 60. Hydrocarbon production with Fe-base FT catalyst during actual syngas test

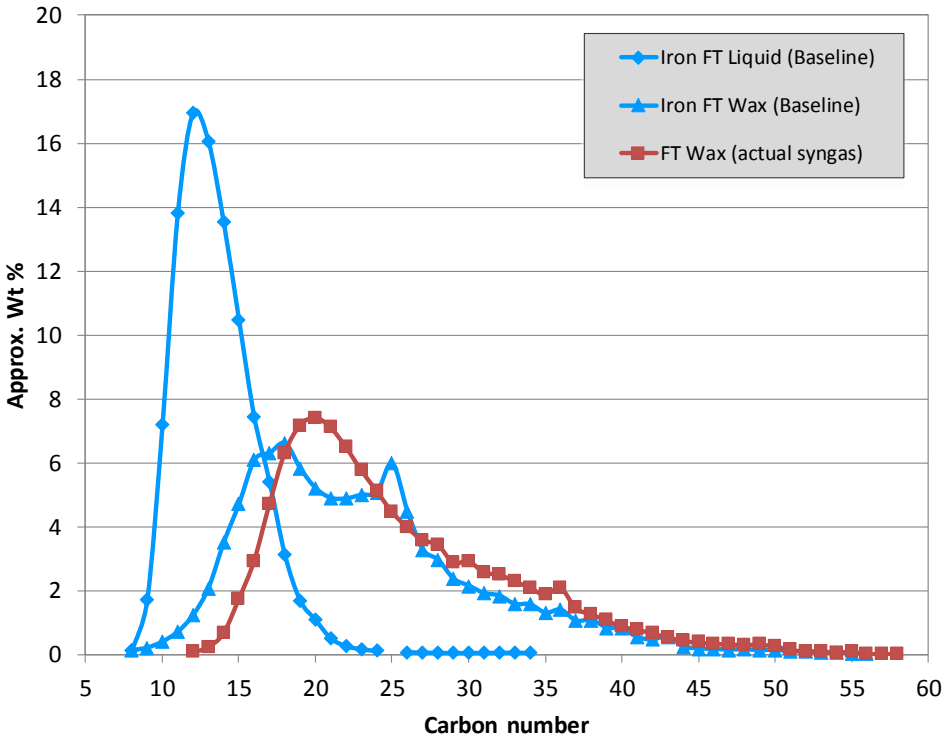

Figure 61. Carbon distribution for liquid and wax products for Fe-based FT catalyst

Finally, post-test analysis of the catalyst for traces of contaminants showed no significant change (< 75 ppmw) in the concentration of any of the trace contaminant concentrations in the catalyst.

The significant change in several of the operating conditions between the baseline and actual syngas test prohibits attributing any differences observed to just the effect of contaminants as there were many other differences. However, the general similarity in the trends observed in the performance parameters and more specifically in the individual hydrocarbon product flows suggests that there were not sufficient contaminants present in the syngas downstream of the aMDEA® process to alter the performance of the Fe-based FT catalyst. Any contaminant poisoning would have preferentially poisoned specific active sites that would have significantly altered at least one of the multiple trends that were observed. Based on the facts, we conclude that no catalyst poisoning for the Fe-based FT catalyst was observed from operation with cleaned syngas from the 50 MW_e pre-commercial system.

Cobalt Catalyst Test Results

Figures 62 and ***63*** show the catalyst performance during the baseline testing for the Co-based FT catalyst. From ***Figures 62*** and ***63***, the factor that seems to have the most impact on catalyst performance is restarting the FT reactions after the syngas was shut off. Continuous operation of the reactor does result in changes in catalyst performance, but these tend to occur at a slow rate. The specific changes that are visible in ***Figure 62*** are the slow and steady decline in the CO conversion and the slow and steady climb in the methane, CO_2, and C_2-C_4 paraffin selectivity. Trends in selectivity for other products are not as readily visible because the overall changes over the baseline test were small. These results show that the Co-based FT catalyst is relatively stable. The slow and consistent decline in CO conversion and increasing methane and CO_2 selectivity, result in a slow decline in C_2^+ productivity despite an increase in C_2-C_4 paraffin selectivity. ***Figure 64***, which shows the hydrocarbon production rates, illustrates typical preference of alkane over alkene production for Co-based FT catalysts. In general, these trends are typical of catalyst performance changes that occur in commercial Co-based FT processes.

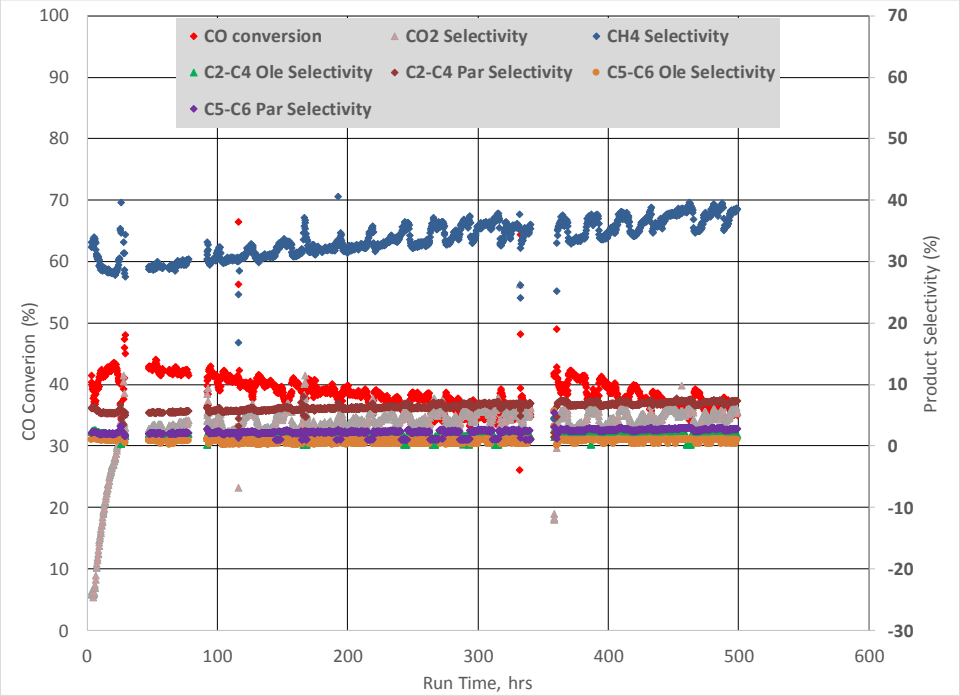

Figure 62. Co-based catalyst conversion and product selectivity for baseline test

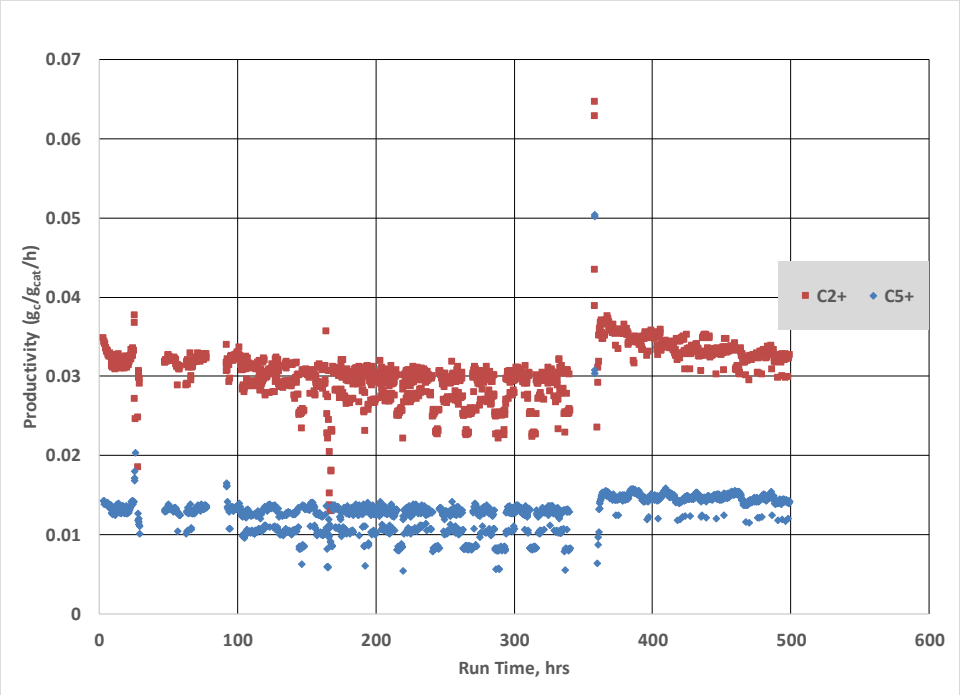

Figure 63. Co-based catalyst productivity for baseline test

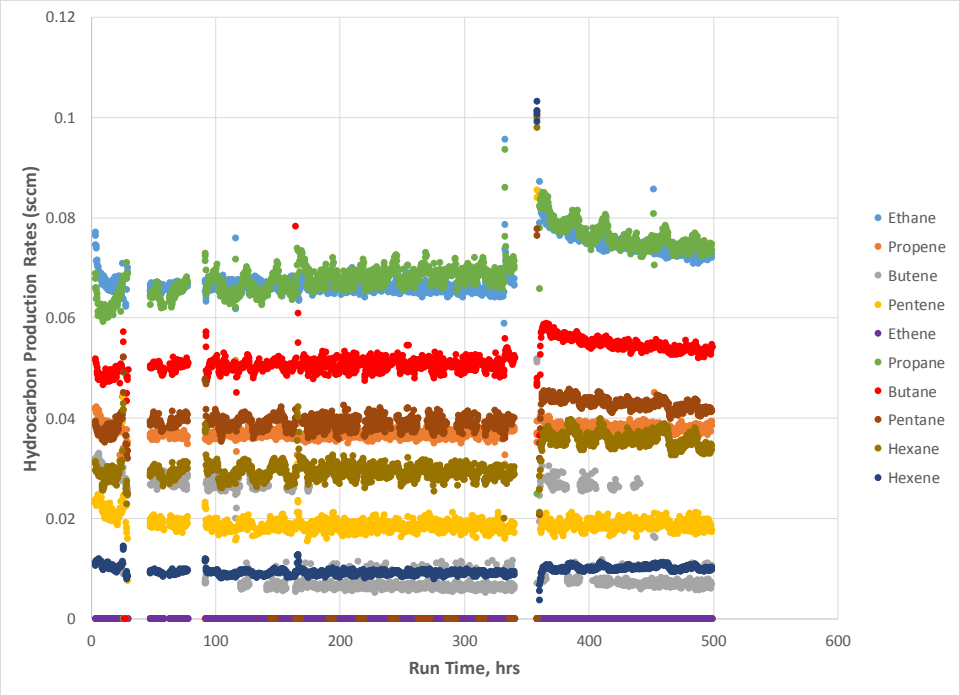

Figure 64. Hydrocarbon production rates for Co-based catalyst during baseline test

As mentioned previously, the operating conditions for the actual syngas test of the Co-based FT catalyst resulted in an increase in the GHSV of about 2. The performance results for the actual syngas test are shown in ***Figures 65*** and 66. These figures show significantly more complex trends in performance changes than for the baseline test.

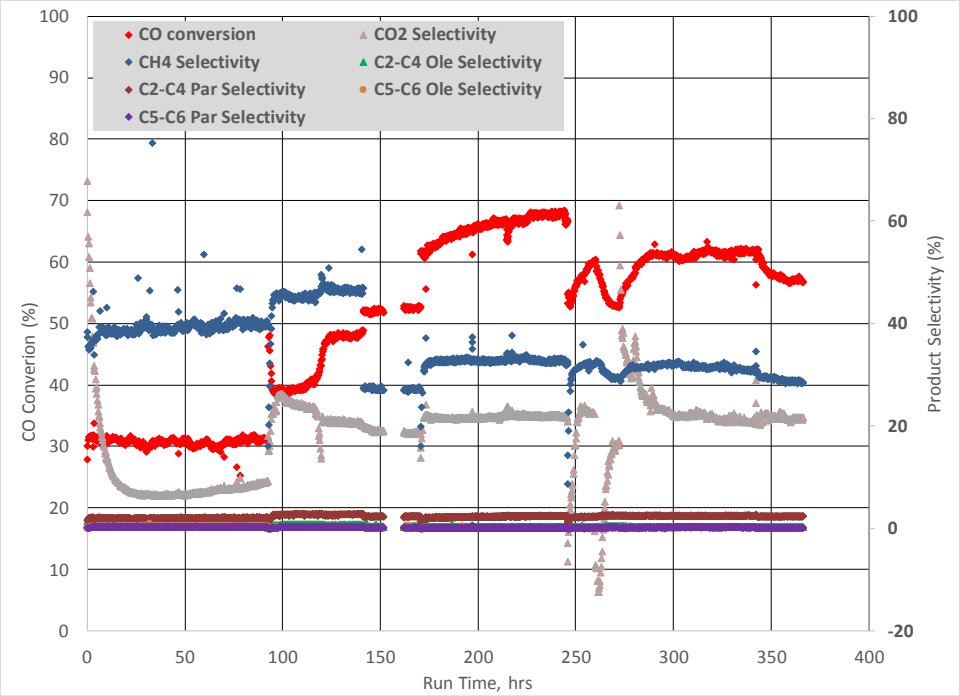

Figure 65. Co-based catalyst conversion and product selectivity for actual syngas test

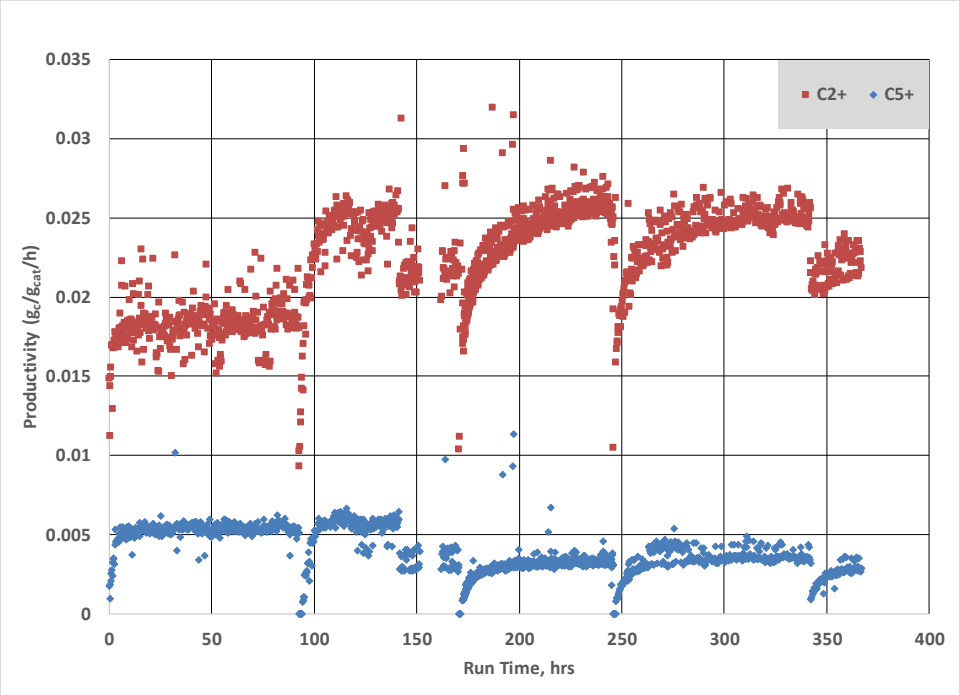

Figure 66. Co-based catalyst productivity for actual syngas test

For roughly the first 100 hours of the actual syngas test, most of the performance criteria show very consistent and stable trends. The only break in this pattern was the rapid decline in the CO_2 selectivity. Although consistent and steady performance is good, there are several factors that are odd. The first is an increase of GHSV results in more reactant flow through the reactor. However, the C_2^+ and C_5^+ productivities for the actual syngas test with almost two times the GSHV were about half that in the

baseline test. Furthermore, when we look at the individual hydrocarbon production rates, shown in ***Figure 67***, the production of the alkenes is as high or higher than the corresponding alkanes. The only exception to this is for butane and butene, where the production of butane still significantly exceeds butene. The high alkene production is very unusual, as Co-based FT catalysts typically favor the formation of alkanes over alkenes as seen in ***Figure 64*** in the baseline test. Finally, ***Figure 67*** shows that H_2 is being produced rather than consumed.

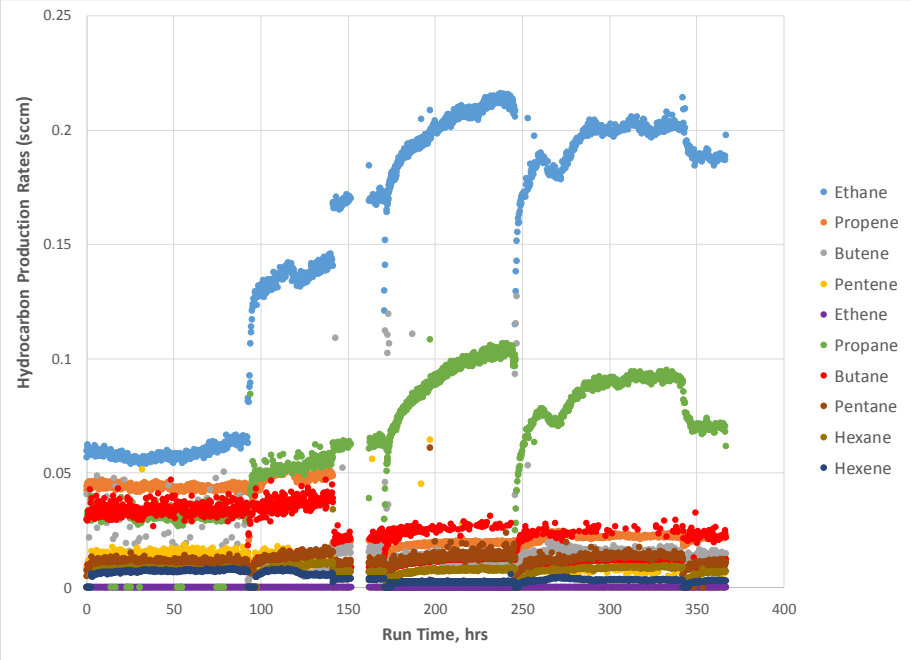

Figure 67. Hydrocarbon production rates for Co-based catalyst during actual syngas test

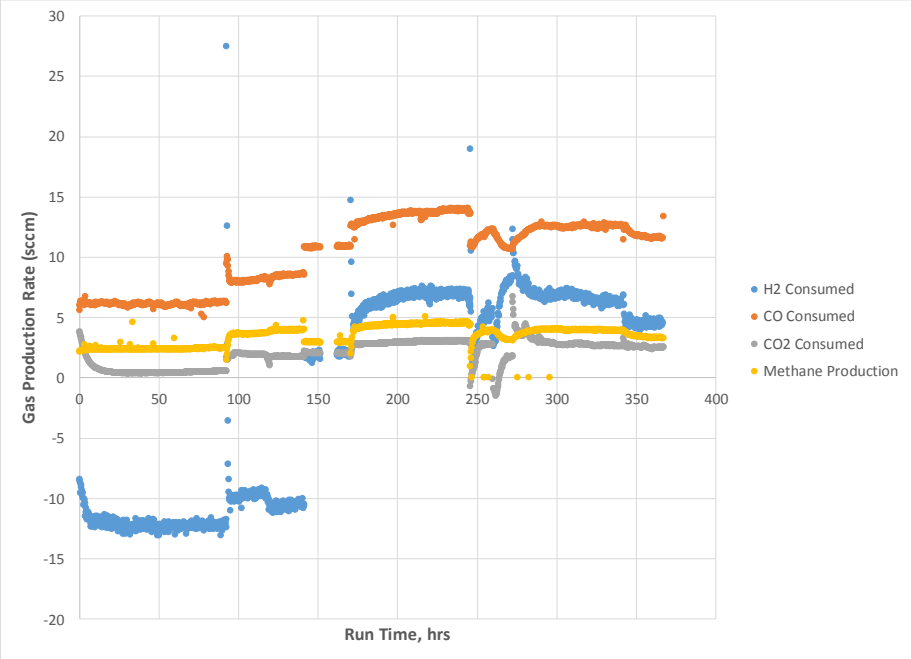

Figure 68. Gas production rates for CO, H_2 CO_2, and CH_4 during actual syngas test

Although a potential production source for the hydrogen could be the WGS reaction, this is unlikely as the CO_2 production is dropping and stabilizes at near zero production levels and CO conversion is low. The higher than typical production of alkene could also potentially be a source of hydrogen, but the hydrogen production rate far exceeds the alkene production rates.

The next couple of restarts of the FT reaction results in some very significant changes in catalyst performance. Hydrogen goes from being produced to being consumed. Alkane production shifts to exceed alkene production. There is also a significant increase in the amount of CO consumption. Production of CO_2, ethane, and propane increase. By contrast, the production of butane drops significantly. The increase in the production of ethane and propane is so large it increases the C_2^+ productivity by between 30% and 40%. The drop in butane production results in a slight reduction of C_5^+ productivity.

After about the first three restarts of the FT reaction, the catalyst performance becomes more consistent. Subsequent restarts of the FT reaction do result in changes in the performance parameters, but the general trends remain relatively consistent for the rest of the actual syngas test.

Figure 69 shows the carbon distribution of the liquid and wax products collected during baseline and actual syngas testing for the Co-based FT catalyst. For the baseline test, the liquid hydrocarbon product includes hydrocarbons with between 10 and 25 carbons with the more bell-shaped distribution with the peak hydrocarbon having 15 carbons. The wax product for baseline testing has a slightly more skewed distribution which favors hydrocarbons with higher carbon numbers and a peak for hydrocarbons with about 20 carbons. No liquid product was collected for the actual syngas test. As for the Fe-based FT catalyst test, the increase in GHSV and slightly lower operating pressure, probably prohibited hydrocarbon condensation at the lower partial pressure and in a much shorter residence time in the condenser. The carbon distribution for the wax product collected during the actual syngas test includes longer hydrocarbon chains with the peak hydrocarbon concentration occurring for hydrocarbons with 30 carbons. The changes in GHSV and operating pressure would make condensation of the shorter chain hydrocarbons more difficult favoring collection of the longer chain hydrocarbons. In addition, the carbon distribution for the wax product for the actual syngas test suggests that the FT reaction was favoring the shorter (C_2-C_4) and longer chain hydrocarbons at the expense of producing medium range hydrocarbons. This carbon distribution does support the trends observed for hydrocarbon production in the C_2 to C_6 range obtained from analysis of the gas phase product.

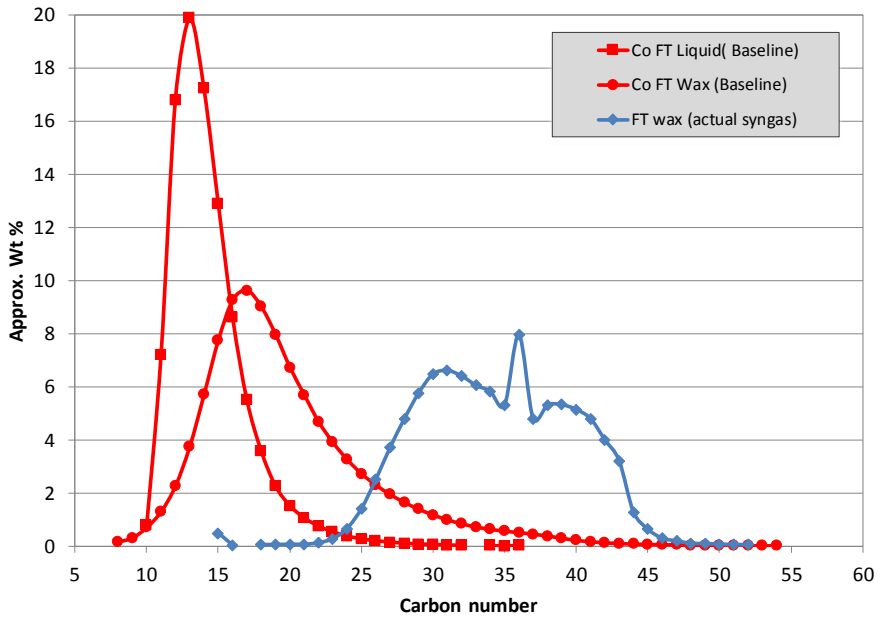

Figure 69. Carbon distribution for liquid and wax products for Co-based FT catalyst

Finally, post-test analysis of the Co-based FT catalyst did not show any significant accumulation (< 75 ppmw) of contaminants.

The baseline test shows that under suitable operating conditions, the performance of the Co-based FT catalyst is extremely stable and consistent. However, the performance results from the actual syngas were very different from the baseline performance and typical performance of Co-based FT catalysts. In general, the most convincing evidence that contaminants present in the syngas were not poisoning the Co-Based FT catalyst is the high levels of catalytic activity and the performance shifts that occur when the FT reaction was restarted. When contaminant poisoning occurs, the poisoned site is rendered inactive. However, all the changes in performance observed did not necessarily show any loss of activity just a different type of activity. This is particularly obvious for the steady and consistent increase in ethane and propane production that was observed during most the actual syngas test. The effects on performance resulting from contaminant poisoning also tend to be gradual and cumulative. All changes in the catalyst performance seem to be relatively sudden and in response to restarting the FT reaction. Although not conclusive, these facts suggest that no contaminant poisoning was observed with cleaned syngas from the 50 MW_e pre-commercial system with the Co-FT catalyst.

Methanol Synthesis Catalyst Test Results

The catalyst performance trends for the baseline test with the methanol catalyst can be seen in ***Figures 70*** and 71. The performance trends in ***Figures 70*** and ***71*** show that the catalyst performance is relatively stable and consistent. However, these performance trends do not tell a consistent story. The CO conversion starts at about 12 % and slowly declines to about 8% over the course of the baseline test. The selectivity for methanol starts at about 11 % and slowly climbs to about 19% during the baseline test. The CO_2 selectivity oscillates between about 5% and 12% throughout the baseline test. The selectivity for methane is essentially zero the entire baseline test. Unfortunately, these selectivities would indicate that about 70% of the CO converted ends up in a product that was not methanol, methane, or CO_2 and was not measured by the GC.

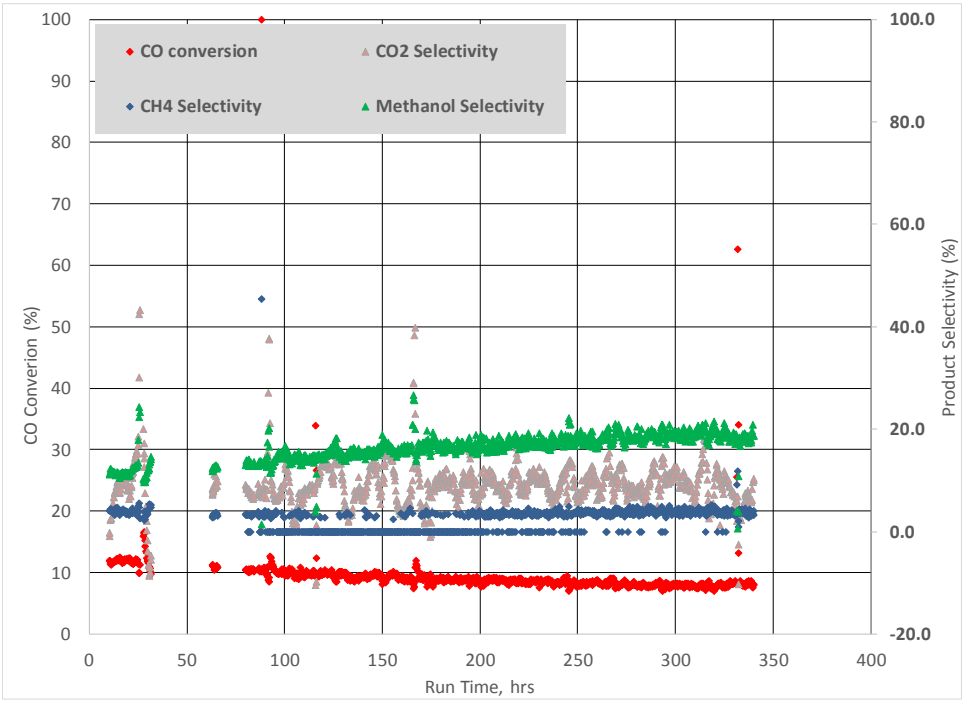

Figure 70. Methanol synthesis catalyst CO conversion and product selectivity for baseline test

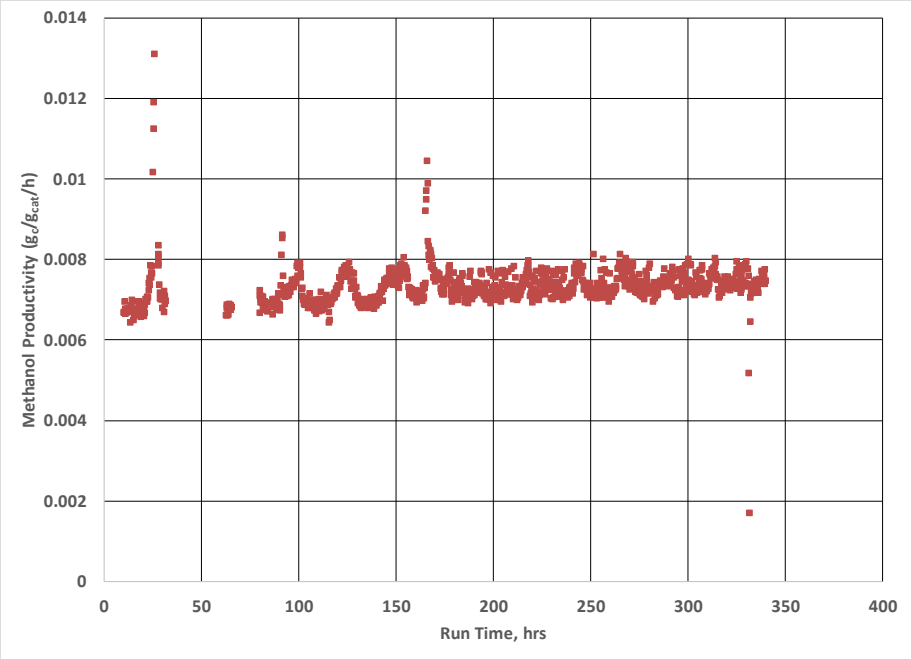

Figure 71. Methanol synthesis catalyst productivity for baseline test

The gas production rates for the different products and reactants detected in the effluent stream are shown in ***Figure 72***. ***Figure 72*** shows that H_2 is consumed at almost twice the rate of CO throughout the entire baseline test. Because this is the exact stoichiometry required for methanol production, methanol must be the major product. If this is correct, the measurement of methanol vapor in the effluent stream must not be accurately measuring the methanol produced in the micro-reactor. Although this might be a GC issue, this is very unlikely due to the calibration procedure implemented and the periodic checks used to ensure GC calibration.

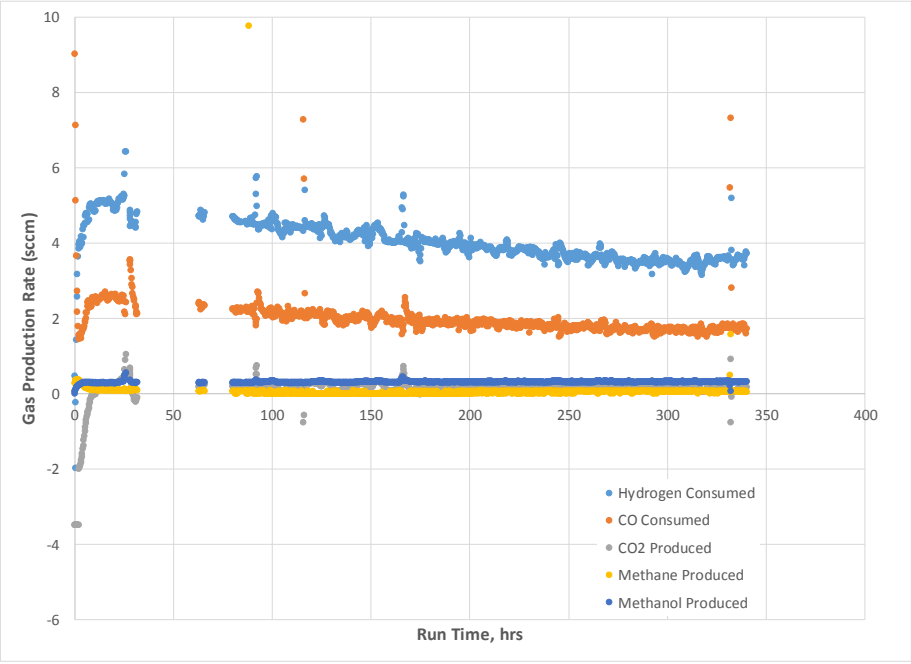

Figure 72. Gas production rates for methanol baseline test

If the GC responses are assumed to be correct, then a significant portion of the methanol is not reaching the GC. The most logical location for this "missing" product to be collected would be the condensation trap for potential liquid products. However, no accumulated liquid product was collected. For the methanol production rate, shown in ***Figure 73***, there is a clear periodic rise and fall in the methanol production rate during the first 150 hours of testing. This trend would suggest that methanol was being captured in the condensed product trap and released. It is possible that although methanol product was being drained, the amount was smaller than the evaporation rate and therefore no liquid methanol product was collected outside of the micro-reactor system. Furthermore, there is a gradual increase in the methanol product detected by the GC over the course of the test. This trend suggests as the methanol trap was filled, more of the methanol remained in the vapor state and was reaching the GC. These interpretations of the data show that the methanol selectivity and production rate calculated based on the methanol concentration in the product effluent from the micro-reactor system were artificially low and that the actual value if based on the total methanol product generated, which included any liquid methanol product condensed and evaporated faster than it accumulated, would be much higher. Furthermore, data reconciliation was performed on the reactant and product flows and confirms that the consumption rates of H_2 and CO should have resulted in near stoichiometric production of methanol. In summary, the baseline test demonstrated that the methanol catalyst was very effective at methanol production and showed great stability and consistency with bottled gases as reactants.

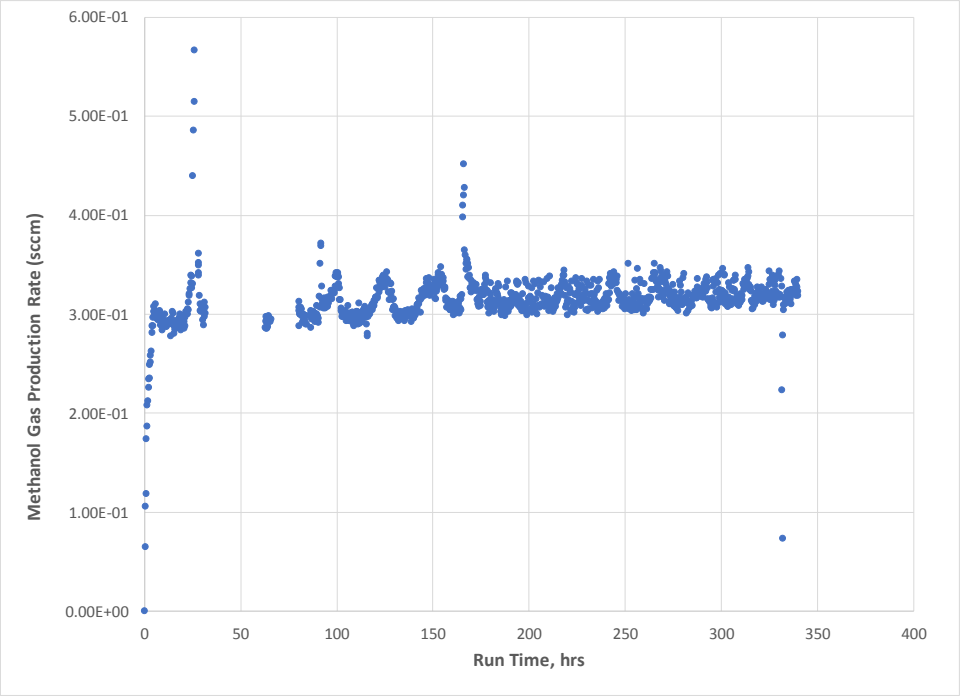

Figure 73. Methanol production during baseline catalyst test

During the testing with actual syngas from the 50 MW_e syngas cleanup system, the operating pressure in the aMDEA®™ system limited the available pressure for operating the micro-reactor system to roughly half of the operating pressure used in the baseline test. As the methanol reactor is operated commercially at high pressures to achieve satisfactory reaction rates, the reduction in operating pressure for the actual syngas testing was not anticipated to favor methanol reactivity. The second parameter that changed was the product syngas from the aMDEA® system had water vapor. Although the concentration of this water vapor was small at ~0.5 mol% (approximately the saturation pressure at 122°F), it was significantly higher than during the baseline test which used dry bottled gas.

The performance parameters for the actual syngas test are shown in ***Figures 74*** and ***75***. As expected at the lower operating pressure, the methanol productivity drops significantly over the test reaching a reasonably stable value towards the end of the test. With the methanol productivity decreasing, it is rather odd that the amount of CO conversion remains relatively constant if not increasing slightly over the test with actual syngas. The implication of a stable level of CO conversion and a decrease in methanol productivity is that some other product(s) were being produced.

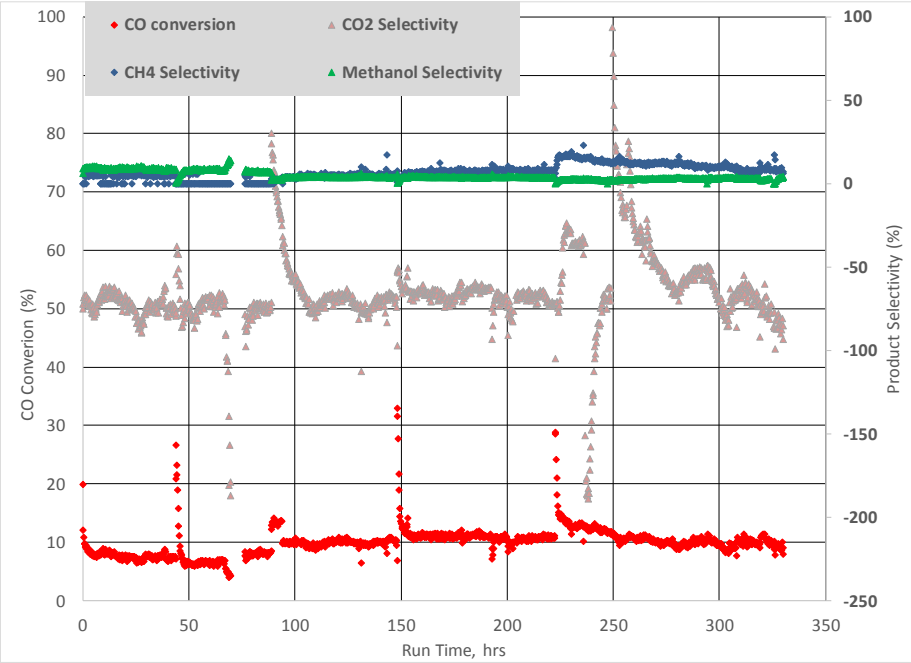

Figure 74. Methanol synthesis catalyst CO conversion and product selectivity for actual syngas test

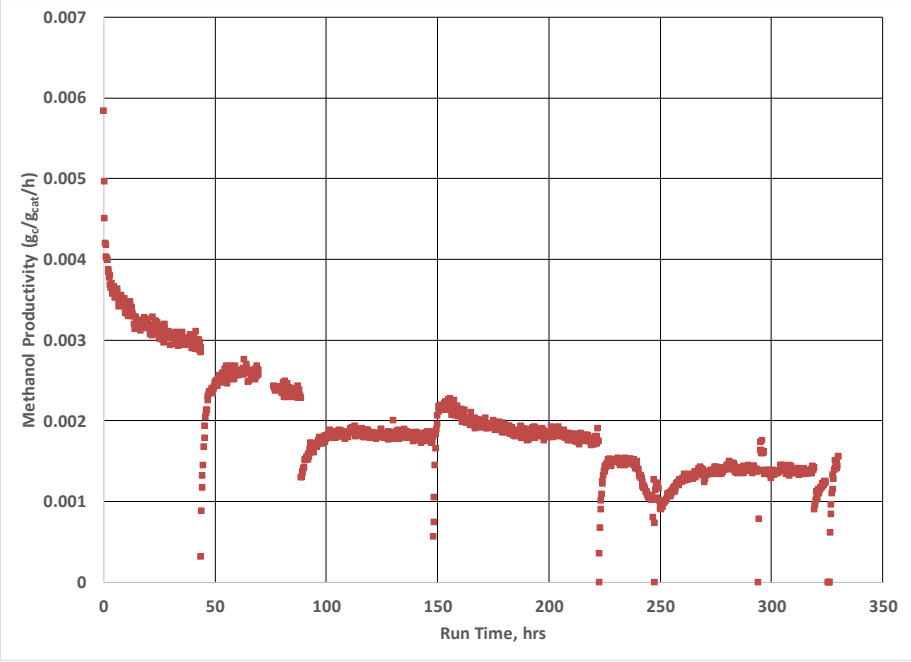

Figure 75. Methanol synthesis catalyst productivity for actual syngas test

Figure 76 shows the change in flow rate across the reactor for H_2, CO, CO_2, methane and methanol. The results in ***Figure 76*** show that CO and CO_2 are continuously consumed during the test with actual syngas, whereas H_2, methane, and methanol are the primary products. The magnitude of the rate of CO and CO_2 consumption and H_2 production are roughly similar. The production rate for methane and methanol is about an order of magnitude smaller than the rate of change for CO, CO_2 and H_2. These differences in rates create the fundamental problem that reactant carbon species (CO and CO_2) are disappearing faster than product carbon species (CH_4 and methanol) are appearing. Although the water gas shift, which involves CO, CO_2, H_2 and steam could account for the similarity in rate change for CO, CO_2 and H_2, reacting, water gas shift activity would result in consumption of CO, but production of H_2 and CO_2. Although other carbon species were not reported as part of the analysis method, there was no additional peaks in the GC chromatograph to indicate the production of other carbon-based products.

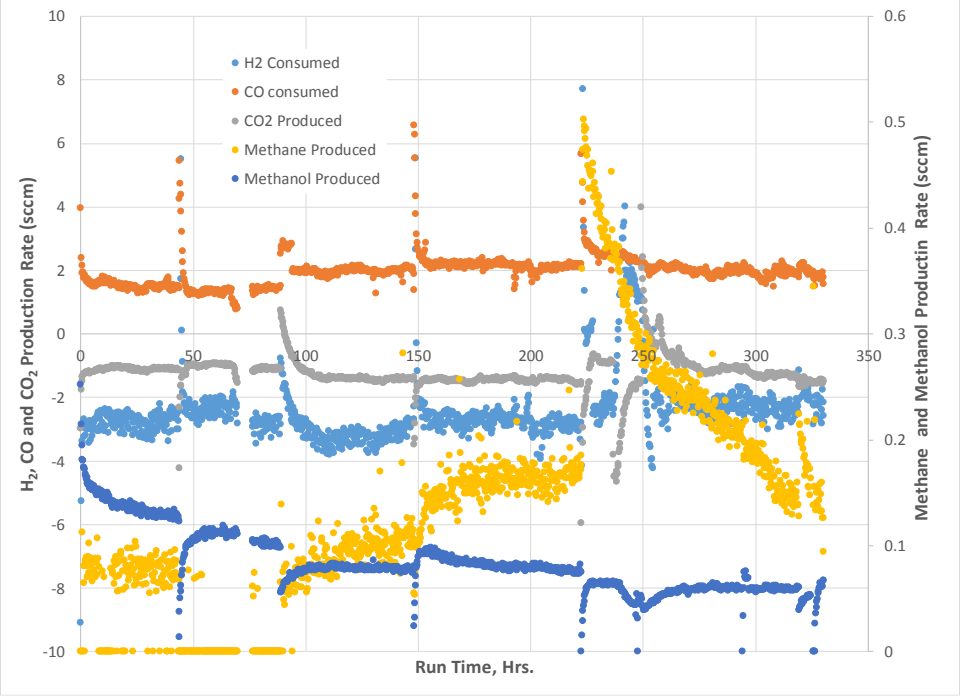

Figure 76. Consumption and production flow rates for H_2, CO, CO_2, methane, and methanol for raw data

The potential that methanol product was being made, but not collected, as in the baseline test was considered. However, unlike the baseline test, the consumption of CO and production of H_2 did not support this possibility. Furthermore, the observed methanol production rate was much lower and more stable without the periodic cycling that would result from methanol draining from the liquid condensation pot.

With no obvious explanation, we were forced to look a little closer at the data. Because of the need to add CO to generate a feed gas with a H_2 to CO ratio of 2 and to add a small amount of CO_2, roughly 3 to 6 mol%, to promote the methanol reaction, all three of the feed gases (syngas, CO and CO_2 in N_2 balance, and N_2) contained nitrogen. Unfortunately, N_2 was also used as an internal standard for calculating the product gas flow rate. Because of this, small errors in the measurement of both N_2 concentration and flow rate of the three feed streams could have introduced error in the calculation of the product flow. Because of the relatively large flow of nitrogen compared to the other reactant gases, even a small error in the calculation of the N_2 flow would cause a significant error in the CO, CO_2 or H_2 flows. Furthermore, the very small production rate of methanol and methane suggests very limited conversion for any the reactants.

Data reconciliation was used to estimate actual species flow rates rather than using N_2 as an internal standard. The data was reconciled in three distinct manners. In the first approach, the methanol reaction and methane reaction were considered as variables to be solved for. In the second reconciliation, the methanol and methane reactions were considered, but their rates were fixed based on the observed output flow rates. In the final reconciliation, the methanol and methane reactions were ignored. The predicted flow rates for H_2, CO, and CO_2 into and out of the micro-reactor for all three of these reconciliations was identical. The result from the third reconciliation are shown in ***Figure 77***. In ***Figure 77***, the methanol and methane production rates are the measured production rates.

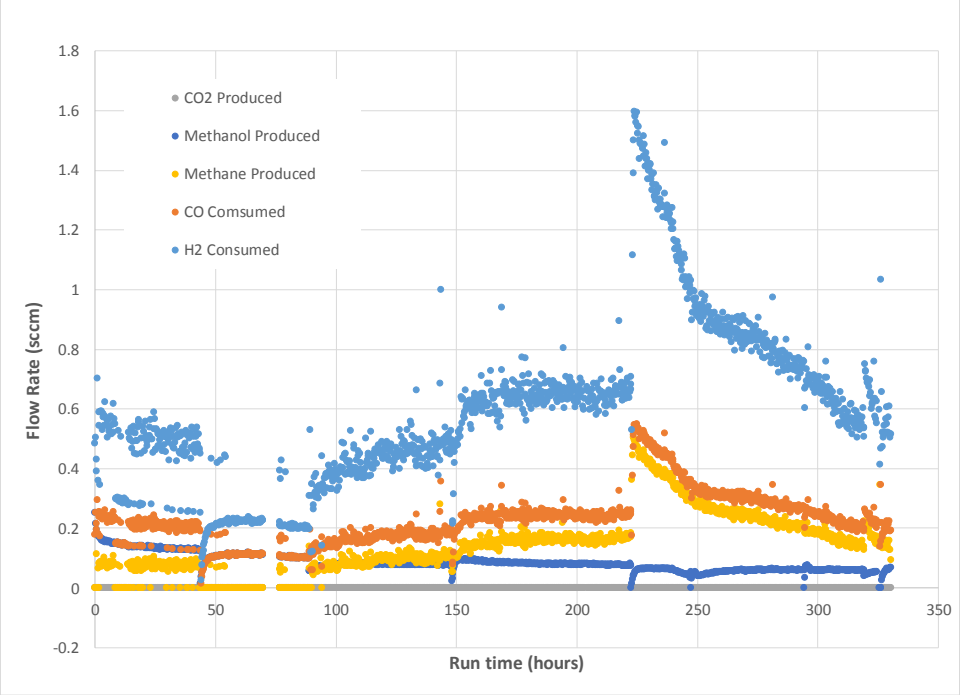

Figure 77. Consumption and production flow rates for H_2, CO, CO_2, methane, and methanol after data reconciliation

The flow rates of H_2, CO, and methane all seem to follow the same pattern indicating that methanation is the primary reaction. The slight difference between the CO consumption and methane production rates account for the small amount of methanol production.

In terms of catalytic activity, the changes in methanation activity are the most significant. For the first 220 minutes of operation, all the changes in methanation activity are essentially step changes that occur because of starting or stopping syngas flow. At about 220 minutes of operation, there is a very sudden increase in methanation activity. Unlike previous changes in methanation activity, where the activity remains relatively constant after the change, the methanation activity begins a rather rapid decline. At about 250 minutes of operation, there is another change and the rate of decline in the methanation activity drops and declines at a lower rate for the rest of the run.

These periods of steadily declining methanation activity are the only results obtained during this micro-reactor testing that are typical of contaminant poisoning of catalytic activity. However, there are several factors that suggest that this decay in methanation activity is not the result of contaminant poisoning. The first is the fact that at the start of the baseline test, there is about a 10- to 20-minute period where the methanation activity rapidly declines to a final stable activity level. This change cannot be related to contaminates, because the gases are bottled gas mixtures. This change is more than likely due to changes in the redox state of the active component associated with the methanol reaction. As conditions in the baseline case favored the methanol reaction, this change was very rapid reflecting the high

methanol production rate. In the syngas test, the condition for the methanol reaction are much less favorable as demonstrated by the lower methanol production rate. Consequently, the decay of methanation activity is also much slower than in the baseline test.

The second fact is that the failure of a key heat exchanger in the aMDEA® system resulted in a large reduction in the efficiency of CO_2 capture with a corresponding increase in CO_2 concentration in the clean syngas product after about 250 hours of operation. This change in syngas composition was large enough that it caused the H_2 concentration in the feed to the micro-reactor system to drop below the targeted 2:1 H_2 to CO ratio. This lack of sufficient H_2 caused the slight decline in methanol production, which eventually recovered as the aMDEA® was fixed and concentrations returned to normal. These significant changes in the available H_2 concentration would also alter the reducing potential of the feed gas and the decay in methanation activity that was being caused by this reducing potential.

Most of the changes in methanation activity were observed in response to stopping and starting the syngas, which is when changes in the reducing potential of the feed gas would cause changes in the redox state of the active catalytic component. As the rate of change in the decay of methanation activity occurred during a period when the H_2 concentration and reducing potential of the feed gas were changing supports the assumption that this is the more probable cause of the decay in methanation activity than contaminant poisoning. The final facts are that contaminant poisoning should have been occurring through the entire syngas test rather than suddenly start after 220 hours of operation and contaminant poisoning is typically permanent and there were multiple times the methanation activity increased after stopping and starting the syngas.

Finally, post-test analysis of the methanol catalyst did not show any significant accumulation (< 75 ppmw) of contaminants.

5.3.5 Summary of Micro-Reactor Catalyst Testing

Even though changes in the operating conditions for the syngas test prohibited using a direct comparison of the results from the baseline and syngas tests to identify effects of contaminant poisoning, the baseline and syngas testing provided supporting data that contaminants in the syngas were not causing catalyst deactivation. This supporting data consisted of the lack of trends or changes in performance and activity that could be attributed to contaminants in the syngas for a total of almost 1,000 total hours of operation with three different commercial catalysts. Because the primary reason for selection of these specific catalysts was their known deactivation associated with even low concentration of contaminants, these results provide operational confirmation that the clean syngas from the combination of WDP, WGS and aMDEA® processes are sufficiently contaminant-free to fully enable commercial chemical production for the production processes possessing the most stringent specifications for allowable contaminants and their concentrations.

6. Lessons-Learned Workshops

To facilitate the collection and documentation of the knowledge gained over the course of this project from the entire project team, lessons-learned workshops were conducted. As the plans for the lessons-learned workshop were refined, the wealth of knowledge which covered the full diversity of the roles and responsibilities of the full project team was just too broad to capture in a single workshop. The first workshop brought back together most of the technical team members with the objective of identifying, collecting, and documenting the technical knowledge accumulated during construction, commissioning, and operation of the 50 MW_e pre-commercial system. The second workshop focused more on project management and execution and brought together the leaders for the different team members. The objective of this second workshop was to identify and document strategies and approaches that will promote successful future projects based on the performance of the strategies and approaches implemented in this project. A summary of these workshops is provided in the following sections.

6.1 Technical Lessons-Learned Workshop

Although the primary goal of this workshop was to identify, capture, and document overall process technical knowledge gained, the stretch goal for this workshop was to also identify and capture the specific knowledge gained and/or recommendations from this pre-commercial demonstration that would enable success for the first commercial WDP plant.

The participants included the technical staff involved in the design, construction, commissioning and operation of the 50 MW_e pre-commercial system for the entire project team. This technical staff included the process engineers responsible for design, construction team members, commissioning team members, operation team members including lead engineers, field operators and board operators as well as technical consultants that managed our DSC system. In preparation, all members of the technical staff were provided with a questionnaire to be filled out and submitted prior to the workshop. A copy of this questionnaire is provided in ***Appendix B***. The workshop was led and moderated by an AMEC senior process engineer and the technical discussions during the workshop were recorded by another AMEC engineer. Neither the senior engineer that moderated the workshop nor the engineer that recorded the workshop discussions actively worked on this project, enabling them to provide an objective perspective, which served as a basis, enabling the team to effectively explain topics to non-team members rather that to a team colleague that would have an extensive prior understanding of the project and its technical issues.

Although most of the technical staff proactively completed the questionnaire, Mr. Lou Stengl, the operations manager, monitored questionnaire submission and politely reminded even the busiest staff that their responses to the survey were important and would make the final product more valuable. Because a strong contingent of the process engineers that started on this project transitioned through commissioning and operations, Mr. Stengl worked hardest to ensure that these individuals completed the survey and attended the workshop. These engineers provided a strong element of continuity to the project and valuable insight into the technical reasons for the original design and how commissioning and operation provided additional information that was used to modify and improve parts of the design over the course of the project.

The following section contains the questions and their responses. Rather than use the structure and/or order used in the questionnaire, the workshop addressed the questions in an order that was selected to foster audience participation with respect to getting input from the largest cross section of the technical team and capturing as much technical data as possible.

1. **What are the hallmarks of the pre-commercial demonstration project?**
   The hallmarks of this project ranked according to their perceived importance were:
   - Great project team performance
   - Phenomenal safety record

  - 500,000 manhours without a lost time incident (LTI) during construction
  - 150,000 manhours without LTI during operation
- Commitment of the project team to achieve the project objectives
- Cost, schedule, and construction performance
  - Approximately $5MM was returned to DOE at the end of the project which was a first for any DOE demonstration project
- Operational achievements reaching >3,500 hours for WDP, >2,300 hours of integrated operation of WDP and aMDEA®, and >681 hours of fully integrated operation of WDP, WGS and aMDEA®.
- Effectively demonstrating proof of concept and reducing scale up risk for the commercial deployment
- Sorbent performance

This impressive list of hallmarks demonstrates the success of this project. Several of the technical achievements of this project were the successful scale up from the pilot plant (0.3MW_e) to 50 MW_e, which is a scale up of about 150. Subsequent scale up for commercial applications will be between 2 and 6 times. The integration of WDP and aMDEA® was anticipated to result in several key benefits. One of these benefits was that the effluent sulfur in the syngas was expected to be < 500 ppbv. The results from this project confirmed that effluent sulfur concentrations in the syngas < 500 ppbv could be achieved. Previously, the only technology available that could achieve this level of syngas cleaning was Rectisol®. The other benefit of the integration of WDP and aMDEA® is the cost reduction, which has been extensively evaluated in techno-economic analyses in DOE cooperative agreement DE-120006. This creates a unique situation in which "market pull" will help drive this cleaner technology into the market because of its cost and efficiency benefits.

2. What unit operations or areas need improvement?

The ranked list of areas needing improvements was:

- Warm desulfurization process (WDP)
- Water gas shift process (WGS)
- Area 500 which consisted of
  - Low temperature gas cooling (LTGC) and
  - Activated MDEA (aMDEA®)
- Utilities
- Water treatment package

Specific areas or opportunities for improving these unit operations as part of future scale-up were discussed. Note: These opportunities for improvement have been described in previous sections in this report.

3. Does the Gen #2 (future commercial-scale demonstration) project need input from third party organizations?

Because of the benefits associated with extensively engaging subject matter experts (SMEs) during this project for the design and operation of WDP, the team recognized that continued engagement of these SMEs would be beneficial for commercial deployment to ensure efficiently leveraging as much of the available commercial expertise as is available from Fluid Catalytic Cracking (FCC) and transport reactor technology as possible. There was also the anticipation that the SMEs could also recommend additional improvements based on the data collected from this pre-commercial demonstration.

Other areas were SMEs would be recommended was metallurgy, filter design and operation, and foam detection and control in the aMDEA® unit. The required metallurgy for this system was challenging because of the complex and diverse composition, temperature, and pressure conditions across the entire system.

SMEs were also recommended for improving the DCS system. In this project, SMEs would have been helpful as the DCS system had to emulate Tampa Electric Company's 20-year-old system with a

recently upgraded version of the software used. Because there was essentially no existing SME's for the new software, the project team faced the steep learning curve to master this software without any SMEs. The team realized that during commercial deployment that SMEs would be extremely beneficial in setting up an optimal DCS system. The team also recognized that using the available project data to create a simulation model would provide the opportunity to effectively train operators for commercial plants.

4. Are you comfortable with process transformations such as yield, residence time, and performance?

Although the sorbent performance was excellent and met or exceeded expectations, the operating team felt that there were several modifications that could result in improved performance and/or operability of the WDP. These included design modifications to increase riser heights, to expand the range of operating temperatures, and to improve sorbent fines separation from the product gases. The specific details of their recommendations were documented for inclusion in future designs.

5. Would you change any of the key equipment selections?

For this question, the responses focused on recommendations for future equipment selection processes. These recommendations attempted to incorporate criteria for selecting equipment that would improve reliability, maintenance and/or repair, and improve information available to board operators.

Because one of the key properties of the sorbent was high attrition resistance, the sorbent was extremely hard and abrasive. Consequently, all valves that contacted gas containing sorbent or sorbent fines experienced significant seat wear. The recommendations to overcome this issue were:

- Investigate if valve vendors offer valves with seat materials that can be renewed or replaced.
- Evaluate valves that incorporate a means of wiping/cleaning or gas purging of the gate to drive sorbent from the valves during operation
- Evaluate alternative valve technologies.

Many of the auxiliary subsystems were specified with their own PLC and a station for local operation. The key problem with this approach was the wealth of process information available to the field operator at the field operating station was/could not be transferred to the DCS system enabling the board operators to monitor this equipment. In future projects, these PLC systems should be linked to the DCS with at least a minimum of information to enable the board operator to monitor the activity of PLC controlled subsystems.

Accurate flow measurement was an extremely important function for the flow meters used in this project. The flow meters at the plant interfaces required high levels of accuracy, because of their use for revenue/billing purposes. To enable sufficient accuracy from the flow meters, key selection criteria should be the ability to compensate the flow response for temperature and pressure. If a flow meter is to be used during normal/stable and transient operation, the compensation response also needs to account for any differences in gas composition as well as temperature and pressure during startup, normal/stable operation, and shut down.

Because the startup heaters were only anticipated to run during startup, shut down, and hot standby operation, the startup heater design was adjusted to facilitate permitting (a single versus independent exhaust stacks) and multiple uses (i.e. the regenerator startup furnace was also used to preheat the WGS system). For a first-of-a-kind (FOAK), we strongly recommend planning for dedicated startup heaters for each process despite the added cost.

To meet our specification for a single stack, the vendor used a single stack to vent the effluent from two fired heaters. Although the individual heaters probably would have been effective and reliable, if operated independently, the common stack interfered with the operation of both heaters. This made operation of these startup heaters difficult especially when starting up and the board operators need to focus on other systems than the startup heaters.

The obvious tradeoff is ease and success of the permitting process versus success and simplicity of operational start up. If an existing commercial package with multiple heaters tied to a common stack is available, this system would be acceptable to simplify the permitting process. However, if only independent heaters are available, our recommendation is that they be operated as independent units and the necessary efforts be made to permit their independent stack emissions.

When examining the equipment failures in this project, more heat exchangers failed than any other type of equipment. Corrosion, erosion, and adverse interaction with the process gas were the enabling cause of many of the failures. However, as a group, the heat exchangers that failed were also almost exclusively of a fixed tube-sheet design. Furthermore, for one of the heat exchangers that failed due to corrosion/erosion, the original tube thickness was only 0.083 inches. Although increasing thickness would not have necessarily avoided the ultimate failure, it was probably not the wisest design decision to use such thin tubes. The project team's recommendation is in future projects to add a process into the overall design process that critically reviews the design selection for all equipment, especially for FOAK projects, to ensure design features are selected rather than accepting the default design.

6. **Do you think the proper design standards were applied?**

The response from the survey was proper design standards were applied.

7. **Could a high-fidelity 3D model provide needed insight into improved equipment access and result in a decrease in personnel safety exposure?**

The project team did not feel a high-fidelity 3-D model would decrease personnel safety exposure by increasing insight or improving equipment access.

8. **Can you identify any site constraints or restrictions that had a negative impact to the construction installation?**

The survey response indicated that there were no negative impacts on construction due to site constraints or restrictions. The detailed discussion during the workshop pointed out that the decision to install a DCS system that was the same as currently used by Tampa Electric Company for compatibility did have an impact on commissioning and operation. This impact and potential recommendations have been discussed under the discussion on Question 5.

9. **Did Gen#1 project have clear definitions of roles and responsibilities?**

The survey response was that the roles and responsibilities did have clear definition. During the workshop, an amendment to this response was that during the transition between construction and commissioning, turn over "by system" rather than "by area" would increase efficiency of the turn over process.

10. **Did the project have the proper execution strategy for contracts, allocation of risk, shared incentives, and pain for poor performance?**

The survey response was the project did have the proper execution strategy. During the workshop, the importance of implementing the strategy was emphasized with the extension for the WDP reactor delivery from 50 weeks to 72 weeks. Although only having a single available vendor for this equipment limited options, poor monitoring of milestones, which was part of the strategy, did not catch this issue until it required an aggressive recovery rather than a simple mitigation strategy.

11. **Can you identify any environmental restrictions or constraints that could be reduced in Gen #2?**

The survey response provided no list for reducing environmental restrictions or constraints. The discussion at the workshop mentioned that the limit for H_2S in the CO_2 byproduct in China is lower than in the United States. However, if needed Haldor Topsøe offers a commercial technology that can cost-effectively remove residual sulfur from the CO_2 byproduct. There was also the general impression that environmental restrictions or constraints for a greenfield site might be less than for a brownfield site.

12. **Does the Gen#1 program represent a minimum effective design and a low-cost solution?**

The project team's response for this survey question was the pre-commercial demonstration plant was an effective design and low-cost solution. The comments during the workshop added that the pre-commercial demonstration plant was also properly instrumented. Major revamps were associated with heat exchangers, for which the most significant loss was in operating time. A strategy for spare equipment needs to be incorporated into plans for the next plant.

13. **What improvements and/or operational best practices can you suggest for a safe emergency shut down?**

Development of the Emergency Shutdown system (ESD) for this project effectively incorporated information and prioritization from the host site, personnel safety, equipment failure and equipment

safety. The challenge came with incorporating changes in host site restrictions. Because of a major construction project on Tampa Electric Company's Polk Power station facility, the original calculation completed relating stack height to ground level concentrations for SO_2 emission were no longer valid, as they did not account for this new construction. As this occurred after all the hardware had been installed, the stack height was not sufficient to reduce the SO_2 concentration to an acceptable level by the time it reached the construction site, particularly at locations above ground level. The only real solution was through coordination of system startup and construction activities to prohibit unsafe operations on the construction site when the pre-commercial system was starting up the regenerator. However, if the sulfuric acid plant had tripped, which would have tripped our regenerator to release the SO_2-rich regeneration off gas to the stack, evacuation of the construction site would have been required for personnel safety and forced the shutdown of the pre-commercial system.

Although not a personnel safety issue, system upsets that increase the sulfur concentration to > 50 ppmv in the syngas feed to the downstream water gas shift unit could result in poisoning of the water gas shift catalyst. To avoid this situation, the project team recommended that a single shutoff button that would prohibit the sulfur-rich syngas from entering the water gas shift reactors be installed and improvement in the frequency and accuracy of the sulfur concentration in this syngas stream be made to permit using this signal as a trigger for shutdown of the water gas shift unit.

Another challenge with the EDS was falsely triggered shut downs. During initial setup of the ESD logic, the triggering events were carefully considered by the process engineering team and implemented. Unfortunately, this made starting the syngas compressor (C-150) difficult, because too many events would effectively trigger shut down of C-150. When this happened and attempts were being made to restart the compressor, there was no convenient means of rapidly and effectively identifying which permissives were and were not engaged. This difficulty with identifying the status of ESD permissives also occurred with several other systems with complex ESD logic. To ensure that the necessary information is always readily available to the operator, the project team recommended providing the necessary permissives list in the DCS control graphics.

As part of their response to this question, the project team also considered implications of an emergency shut down that would adversely affect subsequent restarting of the system. For the WDP, this means actively considering how to most effectively purge the syngas out of the system as well as a stagnant sorbent. During an emergency shut down, syngas, which contains a significant amount of moisture, becomes trapped as the sorbent settles. As the system cools, this steam condenses creating liquid water potentially causing the sorbent bed to aggregate. To avoid this, the sorbent bed must be adequately purged to get enough of the syngas out of the system to lower the dew point of the remaining gas to below room temperature. During an emergency shut down, sufficient nitrogen may not be readily available and the hardware for normal fluidization and stripping may not be adequate for effectively purging syngas from the stagnant bed. The project team recommended evaluating effective purging strategies for an emergency shut down as part of the design planning for the next WDP plant.

Typically, the flare header operates at a lower pressure (< 5 psig) providing a convenient and safe location to vent small quantities of process gas to prohibit their environmental or local release. During this project, the flare header would occasionally have enough pressure to push process gas back into the pre-commercial system when it was down. The solution was to shut down and lock out the flare header when the pre-commercial system was shut down. As locking out the flare system is probably not the best solution, the project team recommended evaluating alternative means of dealing with back flow of process gas in the flare header system to protect personnel working on shut down equipment, while maintaining access to the flare header.

14. What improvements can you suggest for the startup sequencing, procedures for cold and hot starts, and warm standby conditions?

In their response to this question, the project team focused their responses on WDP and WGS units. The single response for the WGS unit was it should have a dedicated startup heater, which has been discussed previously. The responses for the WDP unit included recommendations for the syngas compressor (C-150) to facilitate its startup (but note that most commercial WDP units would not need or

have a syngas compressor upstream) and several recommendations that would provide more structure/definition to the sequence of startup procedures. There was also a request to include more automation for more routine control functions to enable the operators to concentrate on the overall process.

A more general recommendation was to develop a process simulator that includes start up and shutdown as well as normal operation. Tampa Electric Company developed a process simulator for their system and found that it was very useful in evaluating and optimizing start up procedures, developing a standard set of operating procedures and training operators.

The project team also recommended for future WDP plants that the use of the warm standby mode be based on a detailed set of criteria with a fixed or maximum operating window.

15. Can you identify any site constraints or restrictions that had a negative impact to the startup and/or operations?

The survey responses to this question identified the following constraints or restrictions

- Availability of process gases (nitrogen, syngas and steam) when required,
- Availability of cooling water in sufficient amounts and of a suitable cleanliness,
- Selection of the same DCS system as used by the host site,
- Permitting the startup heater with only one stack emission point,
- Minimal transfer of information from PLC-controlled skid-mounted subsystems.

All except two of these constraints have been mentioned and discussed in response to previous survey questions. The new constraints are the availability of process gas and cooling water. The primary gas was nitrogen for startup and shutdown. Because this was recognized as an important issue, a bullet tank was installed that could store 1,300 SCF of nitrogen at 1,000 psig. The intention was to use this stored gas for nitrogen purging during emergency shutdown when nitrogen was not available from Tampa Electric Company. The second problem was the manually-adjusted metering valves for the instrument taps and the original magnetic flow meters for fluidization allowed extremely large nitrogen flows. These nitrogen flows were large enough to consume almost all of Tampa Electric Company's surplus nitrogen flow. When the flow orifices were installed to control fluidization flows, control and reliability of these flows increased significantly. For the next plant, it would help to install metering valves that provided better control of gas flow to the instrument purges.

The limitation on the availability of cooling water was discovered during detailed engineering. The solution was to reuse the cooling water a second time. This required additional hardware to pull used cooling water back from the return pipe on Tampa Electric Company's pond cooling water system. Considering the cleanliness of the pond water, this resulted in significant fouling of all heat exchangers using cooling water. The cleanliness of the pond was cited as one of the potential causes of failure of a carbon steel heat exchanger (E-506) in the aMDEA® process. When Tampa Electric Company started up their new water cooling system for their new combined cycle plants, all cooling water availability for the pre-commercial demonstration system ended.

The limited availability of these two key utilities supports careful evaluation of available utilities as part of the FEED package and the value of dedicated utility systems for key utilities for the overall success of the project.

16. Can you identify any design or operational gaps that required significant field modification from the original design and installation?

The survey results for this question effectively captured both the modifications made during this pre-commercial testing program and recommendations for future plants. The list of changes implemented included:

- Modifications and improvements to the air compressor,
- Improvements to the sorbent fines lock hoper systems,
- Modification of heat exchangers,
- Improvement of the sorbent sampling system,
- Improvement to the diesel feed system, and

- Modification of the damper system on the startup furnaces.

The list of recommendations for future plants included:

- Increasing slide valves to full port openings,
- Increasing design temperatures for WDP,
- Increasing differential pressure window on recycle compressors to compensate for full system pressure loss, and
- Relocation of the low-pressure steam generator on the syngas effluent to the recirculation loop for the syngas compressor.

17. Can any of the key equipment or systems be converted from custom design and fabrication to off-the-self supply?

The survey results for this question recommended standardization on size to reduce parts inventory (pumps, compressors and valves) and modular design and shop fabrication where cost efficiency could be realized. The project team also recommended the use of off-the-self systems for:

- The filter systems, the adsorber and regenerator,
- The antifoam injection system in the aMDEA® unit, and
- Sorbent sampling systems.

18. Can you identify any process safety improvements for design engineering? For startup?

The survey response generated the following list of process safety improvements:

- For startup, shutdown and normal operations:
  - Improve flexibility in temperature and pressure ranges,
  - Improve identification of operational mode on control screen, and
  - Improve control ability for different operating modes, and
  - Increase the number of control screens dedicated to subsystems;
- Eliminate the use of flanges in the WDP unit,
- Improve operator access to root valves on WDP system;
- Implement additional operator training;
- Consider insulation of adsorber and regenerator vessels;
- Select more reliable fire and gas detection system and include a maintenance and testing schedule;
- Ensure safety is adequately addressed during design:
  - Design pressure for vessels should exceed normal maximum operating pressures,
  - Incorporate realistic/code required safety limits and shutdowns,
  - Ensure that emergency shutdown venting includes home for all streams, and
  - Improve DCIP for utility of process safety relief valve design.

19. Would you recommend a change in metallurgies?

The recommendations relating to metallurgies/materials of construction consisted of:

- Selection of different materials of construction to allow higher operating temperature of the adsorber filter,
- Review of the service performance of the different metallurgies for the diesel fuel nozzles,
- Implementing a cost review analysis comparing hot- versus cold-wall reactor design, and
- Re-examination of optimal metallurgy in the presence of high hydrogen concentrations.

20. Suggested cost reductions?

The list of suggested operational changes that could reduce cost include:

- Reducing nitrogen consumption in WDP,
- Increasing water recycle and reuse,
- Adjust aMDEA® operating conditions to achieve CO_2 capture targets with minimum solvent flow to reduce anti-foam and filter costs,
- Include a subsystem to separate fines from sorbent materials captured during process upsets.

21. Would you rate the field instruments and local controls as adequate or deficient? What improvements should be incorporated for Gen #2?

This set of questions generated the most responses compared to all the other survey questions. Furthermore, the responses predominantly provided recommendations for improvements for future plants. The recommendations for measurement improvements included:

- Flows:
  - Improve mass measurement for addition of fresh sorbent additions to the system
  - Improve the measurement and control of flow for
    - Fluidization gas
    - Instrument purges
    - Flow meters at the boundary limits used for billing/revenue calculation
    - Diesel during regenerator light off
- Temperature:
  - Ensure thermocouples are correctly positioned for proper temperature measurements
- Differential pressure (DP)
  - For the aMDEA® unit pipe low side legs to top of vessel to enable operation as either "wet" or "dry" leg
  - Review design of differential pressure measurement systems
    - Avoid the use of common lines between pressure transducers

Several general recommendations for instrument and hardware selection included:

- Standardize on field calibration of instrumentation rather than factory calibration because actual installation typically requires calibration making factory calibration an unnecessary cost
- DCS/ESD I/O cards should include capability for BOTH "4-wire field powered" analog signals and "2-wire" to simplify field wiring installation
- DCS/ESD terminal blocks should use "pin" connectors on the end of conductors to enable rapid and effective connection to communicators and test meters

Some recommendation that merit mentioning again include:

- Tie local PLC systems on subsystems into DCS to enable operators to monitor these subsystems remotely
- Evaluate alternative valve designs and/or other options for protecting the valves from wear in gas containing sorbent or sorbent fines
- Increase port opening on slide valves

22. What are the critical design/project documents to update to help sell Gen#2?

Although a list of design documents to update that are critical for the success of any future plant could be developed, preparation of as complete a set of design /project documents was identified as important for the following reasons:

- If Murphy's law applies, some key piece of information for the future plant will be in a document not deemed critical.
- It is impossible to have too much information when evaluating potential technical options
- Multiple descriptions of complex problems can provide different viewpoints that enable better problem identification/definition and selection of an optimal solution
- The success achieved in the project was unique and should be thoroughly documented to enable identification and emulation of the successful strategies

Because of the experience and wisdom of several of the project team's leaders, updating documentation was part of a continuous effort. Although the time to work on these updates was restricted during periods of normal operation, during Tampa Electric Company's annual outages, one of the key milestones for an outage became to complete updating of project documentation. Thus, the remaining

effort was to collect and complete updating the project documentation made during the March 2015 and April 2016 outages.

6.2 Summary

The success of this project is a testament to the hard work and perseverance of the project team. As with any FOAK project, there were issues and imperfections in the design that were identified. The fact that the project team consisted of individuals from multiple organizations and yet managed to achieve almost singular alignment of purpose to complete construction ahead of schedule and on budget and complete over 3,500 hours of operation despite overwhelming challenges with a phenomenal safety record was nothing short of miraculous. Perhaps the best evidence of the exceptional dedication of the project team is that this is the first Lessons-Learned workshop that the moderator is aware of where negative comments and recriminations were utterly absent.

Although a milestone for this project was the proof of concept for WDP at the demonstration scale, the project team continually worked past this original milestone focusing on overcoming all technical challenges to ensure the success of a commercial plant. The goal for this workshop has been to capture recommendations and improvements that can be made to make the next plant even more successful. Through the active participation of the project team, many issues that hindered or made operation more difficult were identified and valuable recommendations for corrective action collected. The specific recommendations for commercial WDP plants have been summarized in ***Table 24***.

Table 24. Recommendations for Commercial WDP Plants

Topic	Recommendations
Design	• Leverage available subject matter expertise associated with design, operation and maintenance of commercial fluid catalytic crackers, metallurgy recommendations, and adsorber and regenerator filter designs. • Specify ESD/DCS components with objective of facilitating installation, operation, troubleshooting and maintenance. • Establish field set up and calibration as standard to avoid cost of factory set up and calibration that must typically be redone after field installation. • Consider standardization for filter and sorbent sampling systems.
Host site utilities	• Carefully evaluate availability of fluidization, aeration, and stripping gas for startup, normal operation, and shutdown scenarios. • Carefully consider the amount and cleanliness of cooling water available at the host site.
Safety	• Optimize the information and resources available in the DCS to facilitate the board operator's job. • Eliminate flanges in the WDP. • Improve safe access by the field operators to root valves for fluidization, aeration, and, stripping in WDP. • Increase operator training. • Incorporate more safety criteria into the design criteria.
Shutdown	• Ensure ESD action adequately addresses need to purge steam present in the syngas to avoid water condensation during shutdown. • Include ESD logic and adequate instrumentation to protect downstream systems from high sulfur that could result from WDP process upsets.

(continued)

Table 24. Recommendations for Commercial WDP Plants (continued)

Topic	Recommendations
Process and control equipment	• Identify valve design and/or purging systems that will reduce wear for valve used in gas service that contain entrained sorbent or sorbent fines. • Ensure specification for flow meters achieves desired levels of accuracy not only at normal operating conditions, but also during transient conditions and due to ambient temperature and pressure variability. • Modify specification on flow meters for fluidization, aeration and stripping to enable more accurate and controlled delivery of the gases. • Improve measurement of fresh sorbent additions during sorbent replacement. • Avoid use of common lines for differential pressure transducers as this complicates maintenance. • Use full port openings on the slide valves. • Maximize information and data transfer from any subsystem PLC-controlled process. • Ensure adequate and properly specified equipment is available to support startup, normal operation, and shutdown.
Operator training	• Consider development of a process simulator.

The action item for this workshop was to collect, update as necessary, and deliver a repository of documentation relating to the design, operation, and modifications developed and implemented on this project to RTI.

6.3 Project Lessons-Learned Workshop

This lessons-learned workshop differed from the other lesson learned workshop conducted as part of the project, which focused on technical, engineering, and construction aspects associated with the 50 MW_e pre-commercial demonstration system. This lessons-learned workshop took a broader view of the project to evaluate and discuss the pros and cons of the non-technical aspects of this project like team integration and management, project execution, legal/contractual issues, and risk and goal management. The objective of this lessons learned workshop was to identify answers to the following questions:

- What worked well,
- What could have been improved, and
- How can and should these learnings be used to benefit future projects?

With the specific goal of identifying practices that DOE could use and/or avoid in future projects to enhance successfully completing project goals on time, under budget, and with maximum benefit to DOE's programmatic goals.

For this workshop, the participants included key leaders of the engineering, construction, and operation teams; legal/business teams; and project/program managers from DOE/NETL, DOE/headquarters, Tampa Electric Company (TEC), AMEC Foster Wheeler (AMEC), and RTI. The approaches/tactics implemented by this group of individuals effectively shaped and managed this project. Using a presentation format enabled the different participants to provide a description, the details and outcome of their approaches/tactics, and identify the key components that contributed to the project's success. The presentation broke the project down into thirteen topics, which are provided in ***Table 25***. In addition to providing structure, this format was anticipated to elicit discussion and group participation to identify the important factors for success and failure.

In this section, we have attempted to refine and organize the information collected during the workshop by project task and/or structure to maximize the value for future projects. These tasks and/or structure components included project selection and definition, team building, Pre-FEED, FEED, EPC, commissioning and operation, and legal. In each of these sections, we collected recommended actions for success and where appropriate provided supporting information.

6.3.1 Project Selection and Definition

Table 25. Workshop Presentation Topics—Project Breakdown Topics

• Project Background and Goals	• Permitting	• Commissioning
• Project Structure	• Risk Management Program	• Startup and Operation
• Pre-FEED	• EPC Contract	• ARRA Issues
• FEED	• Construction	• Summary
• Site-Access Agreement		

The two key criteria for a technology that is being considered for pre-commercial or demonstration testing are:

1. A successful pilot plant testing campaign and
2. Techno-economic analysis supported by the pilot plant data that shows a significant economic advantage of the technology.

For pre-commercial demonstration projects, one of the primary objectives is to reduce the risk for subsequent scale up for a commercial plant. Our recommendation is that the pre-commercial system be at minimum one tenth of a full-scale commercial system. In this project, the size of our 50 MW_e pre-commercial demonstration system was between one half for older retrofit opportunities to one sixth of newer commercial gasifier systems. All prospective clients that have demonstrated an interest in evaluating a potential commercial system have found the scale up risk between the pre-commercial system and a commercial system for their application acceptable.

During project definition, the natural tendency is to evaluate technical, structural, organizational and scheduling components for the project. Our recommendation is to double check and verify that the project sequence matches with project structure, management, and milestones. In this project, some of the key information required for approval for Budget Period 2 (BP2) was to be developed during BP2. Although this issue was solved by a partial release of BP2 funds to acquire the necessary information and permit approval for BP2 funding, it delayed the schedule and required legal intervention.

When structuring a project, there is always the realization that there will be future events beyond the project. As this future is contingent on the results of the project, there is the general rationalization that the details can be worked out at some future date. In this project, we struggled with two disconnects between our plans and legal/contractual requirements that extended past the period of performance for this project.

For this project, EPA insisted that a Class 6 well permit was required for CO_2 sequestration. One of the requirements for a Class 6 permit was well monitoring that extends up to 50 years after CO_2 injection has been completed. Our team successfully negotiated with the EPA to reduce this monitoring period to 10 years for our project, but the funds to support this monitoring, which amounted to about $10 million, were not available past the period of performance because of the fixed termination date for the ARRA funding. Because the project team could not come up with these funds, the project was only able to capture the CO_2 and not sequester it, despite this being one of the key reasons several team members chose to initially support this project.

To effectively showcase this pre-commercial unit to potential clients to demonstrate the technology readiness, there was a desire to maintain the pre-commercial system for a period of about 2 years beyond the period of performance of the project. This required postponing the decommissioning of the unit past the period of performance of the project. In addition, another disposition option was for TEC to acquire the plant for continued operation supporting their IGCC plant. Because of DOE's ownership of the unit, these options for the pre-commercial unit required complicated legal arrangements for the transfer of title and/or decommissioning of the unit at some future date past the period of performance. Although our team developed solutions for these challenges, these challenges might have been handled better during project definition.

To fully address every possible future event is impossible, however we do feel that it is worth a careful examination of the project and future events to be aware and structure the project to ensure the smoothest possible transition.

6.3.2 Team Building

One of the most crucial aspects of successful team building for a project is communication. Clearly identifying, consolidating, and documenting the reasons for participation and expectations of all team members is a fundamental first step to ensure that all team members benefit in the shared project outcomes. Next, it is essential to effectively communicate the execution plan and document the specific agreed upon roles and responsibilities of each team members. With these two documents, the expectations and the effort necessary to achieve these anticipated outcomes are defined for each team member. Preparation of these documents should begin as soon as possible because they will facilitate preparation of agreements that will be needed to initially assemble the team and subsequently negotiation of the legal and contractual agreements to support project activities.

The three key roles that were considered most important for the success of this project were the project manager, the EPC contractor, and project champions.

Our project manager, Mr. Ben Gardner, used his previous experience (particularly with plant construction) to implement key strategies that he had found to be extremely beneficial for first-of-a-kind (FOAK) plants. These strategies included development of a comprehensive risk registry at the beginning of the project, evaluation of process start up and shutdown as part of detailed engineering, and evaluating win-win approaches for engaging the EPC contractor in the success of the project. Mr. Gardner enabled his goal of proactively dealing with risks, delays, and unforeseen circumstances by weekly review meetings on schedule, risk, costs incurred, and mitigations strategies to address any pending issue. Mr. Gardner also successfully implemented a shadow estimate approach to provide a means to gauge appropriate FOAK project costs and schedule by multiple EPC contractors and from historical data.

Mr. Gardner also recognized that plant construction was an accomplishment on the path to the operational goal and not the goal itself. From this viewpoint, he envisioned a more effective transition between construction and commissioning in which construction and commissioning activities overlapped in the last few months prior to mechanical completion. This approach allowed the commissioning team to inspect the subsystems prior to insulation, which greatly improves visibility of the subsystems. In addition, the construction team maintained a significant presence on site, which enabled rapid and effective repair or modification of any issues or discrepancies that the commissioning team discovered. Finally, it jumpstarted commissioning activities leading to a more rapid transition into operation.

The result of Mr. Gardner's efforts was that the pre-commercial system for this project was completed on schedule and under budget and with a phenomenal safety record.

In most EPC projects, the objective is to build a n^{th} version of a commercial plant, for which EPC contractors have developed standardized methodologies, protocols and practices to effectively complete these tasks in the most cost effective means possible. Because larger projects are also more profitable, many EPC contractor focus on larger projects. Unfortunately, FOAK projects tend to be smaller and have significantly more unknowns and risks than the n^{th} version of a commercial plant. FOAK projects benefit from a more flexible approach that maximizes the use of the available information for detailed engineering and adapts to accepting the best available information when information is not available. Because this can be at odds with the conventional engineering approach, FOAK projects benefit from EPC vendors that have a proven record with FOAK plants. AMEC Foster Wheeler had this experience and continued to demonstrate their capabilities in this area with this project.

With any project, there will be challenges. The difference in this project was there were numerous project champions that dedicated themselves to overcoming the challenges with their creativity, resourcefulness or at times good old-fashion hard work. The first tier of project champions was the team leaders from the different organizations. This group recognized the shared benefits and served as the cohesive force that kept the team together. Beyond this, there were the project champions in the different functional teams that could lead and motivate their teams to get done whatever was necessary to keep the project moving.

This project was extremely fortunate to have had an abundance of project champions in the right place at the right time enabling the success of this project. Not all projects will have this good fortune.

However, when building the team identifying people who could be project champions is extremely valuable Furthermore, it is also essential to ensure that prospective project champions are suitably motivated by the anticipated benefits that the project will bring them, their team, and their organization. This re-enforces the importance of communication of shared project outcomes. However, it also points out that communication of the benefits needs to occur regularly and remain current as things change.

The best example of the positive effect of effective team building can be seen in project permitting activities. For the air permits, TEC worked proactively with their permitting contractors and the Florida Environmental Permitting Agency (FLEP) so that all sides saw the benefits of a successful air permitting process. Similarly, Mr. Mark Lusk from DOE, was instrumental in coordinating collection of the necessary and required information from TEC, AMEC, and RTI to efficiency complete the Environmental Assessment of the project.

By contrast, the EPA and in particular the Washington, D.C. EPA office, failed to see the value the rest of the team saw for CO_2 sequestration on this project and in this unique geological formation. Because they lacked a project champion and a perceived benefit from the project, the Class 6 well permitting process was not successful and all the CO_2 captured on the project was released and not sequestered.

6.3.3 Pre-FEED

Pre-commercial demonstration projects are by nature FOAK projects. As the primary reason for conducting pre-commercial demonstrations is to eliminate as much risk for subsequent commercial deployment, there are a lot of unknowns relating to the technology, its integration with auxiliary commercial equipment and ultimately integration with the existing host site facility. In the face of all these unknowns, a Pre-FEED package is a critical element of the pre-commercial demonstration project. A Pre-FEED task allows the process engineers to do what they do best, which is assemble possible operational process configurations based on set of known constraints. From this set of possible process configurations, a Pre-FEED task effectively enables optimization of the process configuration and effective integration with the host site facility with its available utilities to be fixed for the subsequent FEED effort while incorporating the maximum probability of success.

A Pre-FEED task also provides the perfect opportunity for construction of a comprehensive risk registry. The function of the risk registry is to help manage risk. In the beginning, any project will have many risks with consequences which range from minor to devastating. Management of these risks entails proactively implementing mitigation strategies that reduce or eliminate the risks. A successful risk management plan progressively reduces the number and potential consequences of risks over the course of the project. Thus, it is extremely important to have the risk registry available to enable reduction of technical risks through effectively incorporating mitigation strategies into the design. This risk registry also helps with team building activities in that team members become aware of the importance of their roles and responsibilities.

Another key activity to include in the Pre-FEED task would be establishing a resource loaded schedule with as much detail as possible. The risk registry helps the team members see the importance of their roles and responsibilities, the schedule shows when their services and talent will be required. With a resource loaded schedule, integration/transition between tasks can be planned with maximum efficiency. This was what Mr. Gardner was trying to accomplish through his planned transition from construction to commissioning. As the date for mechanical completion approaches, the construction team should be shrinking. When the commissioning team finds issues with the system that need repair of modification, their progress will be hindered until this repair is completed. With a skeleton construction crew, the challenge becomes having the individual or more realistically enough individuals with the right talent to fix the problem.

In this project, the Pre-FEED task enabled a rapid transition to expand the pre-commercial system to include water gas shift and carbon capture and sequestration adding additional benefits for the team

members and taking advantage of the availability of ARRA funding. Thus, we recommend including a Pre-FEED task in a pre-commercial demonstration project that involves:

- Down selection of process configurations to achieve optimal integration with the host facility and maximum success of technology demonstration,
- Construction of a comprehensive risk registry, and
- Establishing a resource loaded schedule with the maximum detail possible.

6.3.4 FEED

One of the key activities in the FEED task is to fix the scope as soon as possible. Hopefully, the Pre-FEED task has provided an optimized process configuration which includes integration with the host site facility, which can rapidly be converted into a fixed scope of work. However, even if this Pre-FEED process configuration is not available, the scope must be fixed as early as possible to effectively prohibit scope, schedule and cost creep that will inevitably occur if the scope is left open ended. One of the advantages of using a Pre-FEED task to define the process configuration is that the risk and consequences can be evaluated and known. The key disadvantage of rapidly fixing the scope early in the FEED task is that it will inevitably lead to some sub-optimal choices. However, sub-optimal choices can be more effectively dealt with than continued and uncontrolled scope creep.

With FOAK plants, mitigation of technical risk is extremely important. One of the key means of managing this risk is to effectively and proactively incorporate mitigation strategies into the design of the pre-commercial plant. Two specific activities that were performed as part of this project were evaluation of transient conditions and design evaluation by an expert review panel.

In the typical n^{th} commercial plant, there is no need for the engineering team to consider transient operation as part of the FEED task, because clear and effective startup, shutdown, and responses to key process changes have already been identified and built into the design package. However, for a FOAK, this knowledge does not exist. Therefore, it is critical for the engineering team to effectively evaluate these transient scenarios and ensure that the process design can do what is required to get to full operation or complete a safe shutdown. As part of this exercise, the engineers need to proactively think about instrumentation to ensure that key process deviations can be detected and sufficient instrumentation is available to troubleshoot problems. A full or completely instrumented system would be ideal, but this would be too cost prohibitive, this exercise also enables a realistic check to identify if an acceptable level of instrumentation is present to effectively start, operate, and shut down the system safely and effectively with the available operators.

In this project, we brought together a team of fluidization experts with extensive commercial experience with Fluid Catalytic Cracking systems (FCCs) to evaluate and critique the process design for our WDP. Based on recommendations made by this team, the design for our WDP was extremely successful in operation and evaluation of the unit at the end of operation showed that with minor repairs/modifications that the system could be easily operated for several more years prior to the next required maintenance event.

From the perspective of our design team, the biggest perceived risk was with the technology we had developed. However, for both this pre-commercial demonstration and also the pilot plant testing conducted at Eastman Chemical Company, it was the integration of the commercial auxiliary equipment that ended up causing most of the operation issues that had to be overcome. Thus, our recommendation would be to also include expert technical review of the auxiliary equipment and its integration and intended operation as part of the FEED task.

Finally, the most important activity that must be performed as part of the FEED task is regularly tracking progress. The three key factors to tracking progress are schedule, incurred cost, and risk management. In this project Mr. Gardner, the project manager, owned the schedule and was responsible for ensuring that all teams incorporated their updates to the main schedule on a weekly basis. Mr. Gardner also used Primavera software to track project costs. The key benefit of the Primavera software was its versatility at being able to provide high level budget snapshots, tracking of key project cost metrics, and

being able to effectively focus in on fine details by any of a number of factors. Including a review of the risk registry as part of the weekly review process enabled a proactive approach to risks rather than a reactionary response approach. Although a proactive approach cannot exclude the occasional need for a reactionary response, incorporating the risk review as part of the weekly review ensured that even the reactionary responses were caught and mitigation strategies implemented at the earliest possible stage. Two of the risk management software packages that are available are @Risk and Crystalball.

6.3.5 EPC

As mentioned in the Team Building section, one criteria to consider is a corporate culture that adapts its work breakdown and patterns to efficiently and effectively execute FOAK or smaller projects. Just as financing a FOAK is different than a conventional n^{th} commercial plant, the EPC tasks for a FOAK will need to be different. The consequence is that strict and rigorous implementation of the typical EPC approach for a large n^{th} commercial plant cannot achieve its typical efficiency and cost-effectiveness and will result in significantly higher cost and perform key activities that are not important for the success of smaller FOAK projects.

For the n^{th} commercial plant, historical data provides an extremely reliable estimate for estimating the cost for designing, constructing, and commissioning a plant. For a FOAK project, the use of historic data would be of value, but EPC firms typically do not track these project as an independent subset because of their limited number. Because of DOE's programmatic goals to get technologies implemented, they fund and monitor a large number of projects that include pilot plant testing, pre-commercial demonstration, and even subsidize commercial demonstrations. By effectively mining cost information from these projects, DOE could create a historical data base that could improve cost estimation for commercialization plants from pilot plant testing through commercial demonstration. We strongly recommend that DOE consider compiling this data base for their own use and potentially to help emerging technologies do a better job of cost estimation for their commercialization efforts.

Although historical data does improve cost estimation for FOAK projects, each FOAK project has its own unique requirements, circumstances, and challenges. This uniqueness tends to create more differences that are considered important than similarities even to other FOAK projects. By obtaining shadow estimates from several EPC firms for the same basic FOAK design package, multiple estimates for the same FOAK package are generated reducing differences in these proposals relating to the design package and highlighting the different EPC's approach, cost and schedule. If shadow estimates were to be coupled with historical data, especially for FOAK projects, evaluation of cost estimates for FOAK projects could be significantly improved.

For the n^{th} commercial plant, a lump-sum turnkey contract structure is extremely effective, because the risks are known and can be controlled. For a FOAK project, all risk is significantly higher. But it is the large technical risk, which EPC firms do not understand, particularly when they have not been involved in the technology's development, which causes the problem with a turnkey contract approach for FOAK projects. For an EPC to be successful, it must be profitable. When requested to provide a cost estimate for a FOAK project, the cost estimate will need to include enough contingency to cover all unknowns to ensure the project is profitable. Because the EPC firm probably has very little understanding of the technology, it can only assume the worst-case scenario and include a high contingency to cover potential costs for as many unknown problems as it can identify. For this reason, turnkey contracts will be the most expensive approach for a FOAK project.

Another problem with turnkey contracts for FOAK projects is that the EPC firm has little or no motivation to help make the project a success. Their role is to deliver a plant that works. There is no incentive for the EPC firm:

- To help optimize the process allowing the FOAK technology to showcase its potential performance,
- To help identify the most cost-effective plant design and configuration, and
- To assist in achieving the commercialization goals of the FOAK project.

The solution to the challenges with a turnkey contractual approach for FOAK projects is to use an incentive based contract, where the EPC is financially rewarded for aligning their efforts with key project goals. When properly structured, these incentive-based contracts effectively result in the lowest cost when EPC firm achieves the most value addition. Incentive-based contracts are probably the best approach for FOAK project. However, be sure to include safety and quality as well as budget and schedule in the incentive requirements. Although this is an advantage for the project, it also helps improve the host site's perception and lower their reservations about the risk associated with the installation of the FOAK at their site.

Another important aspect of the EPC contract will be the definition of substantial completion for the FOAK system. Unlike the conventional n^{th} commercial plant, the FOAK plant is essentially being built to help define its performance. Thus, the FOAK plant's performance will not be the best definition for substantial completion. It is the performance of certain key pieces of equipment, like heat exchangers and compressors that enable the FOAK process, that are critical to being able to operate the FOAK plant. A definition of the performance of this enabling equipment provides a definition for substantial completion that can be effectively measured demonstrating that the EPC firm has completed their work, but also enabling effective operation of the FOAK process.

As we recommended for the Pre-FEED task, we also strongly recommend that

- Regular weekly review of the schedule, incurred cost and risk management plan be completed
- A detailed transition plan between construction, commissioning and even operation be established and implemented, and
- Documented plans for key transitory processes, like start up and shutdown, be developed to ensure the appropriate equipment and instrumentation are present to complete these processes in a safe and effective manner.

6.3.6 Commissioning and Operations

In the Pre-FEED, FEED, and EPC tasks, we have recommended a transition plan between construction, commissioning, and operation. Our reason for this recommendation is continuity of knowledge and ensuring the effective transfer of knowledge between teams. The commissioning team's technical and practical physical knowledge of the system is invaluable to them for the commissioning task. By using the commissioning team to walk down/check out systems as part of mechanical completion, the commissioning team effectively learns the system. Scheduling these walk down/check activities while the system is not insulated allows a more rigorous and through evaluation of the piping and equipment by the commissioning team, and achieves a greater appreciation of the equipment and piping networks.

In this project, continuity was achieved through the transfer of key process engineers from the process engineering team onto the commissioning team and ultimately the operating team. Similarly, the operators provided by TEC were actively involved in the setup, installation, and commissioning of the system and specifically the control and emergency shutdown systems. Although this approach may not work for all projects, it was an extremely valuable and effective use of staff for this project.

With any system, some issues can be expected during commissioning and start up, but FOAK typically face more problems during this phase. Because of this, it is essential for project engineers and operators to be well trained and knowledgeable about the system and its operation for identification of abnormal operation, behavior, or performance and to assist in the troubleshooting activities.

In addition to transferring some of the process engineers to the commissioning and then operating teams on this project, the operation team also include a support team from the construction crew. Although the size of this construction support team was somewhat larger that might be associated with a normal commercial plant, this team was extremely effective for understanding the issue and assisting in implementing creative solutions. We strongly recommend maintaining a strong construction team to support the operation team through commissioning and operational start up. The strength of this

supporting construction team can be reduced to more normal levels when operational approaches near commercial level of onstream availability.

One final recommendation for operation is to make documentation a key priority. Although a data acquisition system will effectively store all the process data from the process instrumentation, written documentation by the operators and engineers is required to establish control strategies and actions being implements, to link consequences to a specific event or sequence of events, and keep track of when, why, and how improvements or issues with process instrumentation occur. A good general rule of thumb is that there can never be too much documentation.

6.3.7 Legal

DOE's involvement in this project and the use of ARRA funding created a unique set of legal requirements that required effective blending of federal assistance regulations and more typical commercial/industrial contractual arrangements. The legal objectives of these two systems are relatively distinct and it required an expert understanding of each system and considerable creative thinking to craft the legal documents that effectively align and protect all parties while satisfying the legal requirements/constraints. For future DOE projects, the project prime would be wise to consider building a legal team which is well versed in both areas.

As with team building, communication amongst the team members is extremely important to identify the legal roles and responsibilities of each team member. For this project, this specific communication was the key means by which the liability was distributed amongst the team members in the most cost-effective and fair manner.

The combination of team members with diverse objectives and roles and responsibilities and the complex legal arrangements fulfilling both federal and commercial legal requirements require perseverance, patience, creativity, and time. The fixed expiration data on the ARRA funds for this project made time an extremely important factor to consider. For this reason, the key legal risk items were completion of the different contractual arrangements. The weekly review of the risk registry assisted with keeping the legal discussions on track. However, the negotiation and completion of the legal arrangements consumed a significant amount of effort and time. We recommend that future projects recognize this and dedicate appropriate resources and time to get this work done. We found that tracking these activities through the weekly review of the risk registry enabled efficient management of these efforts. Finally, this was also an area where having project champions was extremely important to the point that each team had a legal project champion.

6.4 Summary

The workshop discussions broke the project into the following topics: project selection and definition, team building, Pre-FEED, FEED, EPC, commissioning and operation, and legal. The two factors that were critical components of all discussions about this project were effective communication and continuing dedication of project champions to the success of this project. The most important recommendations from each of these topics have been collected in ***Table 26***.

Table 26. Workshop Recommendations

Topic	Recommendations
Project selection and definition	• Minimal selection criteria – A successful pilot plant testing campaign – Techno-economic analysis supported by pilot plant data that shows a significant economic advantage for technology. • Minimal size for pre-commercial demonstration should be one tenth of anticipated commercial plant. • Review technical, structural, organization and scheduling components of project, but ensure optimal alignment of the components to achieve success. • Successful projects appear to anticipate future events when part of a detailed and comprehensive overall commercialization strategy.
Team building	• Begins with documentation of – Reasons and expectations for all team members – Roles and responsibilities for all team members • Key roles – Project manager – EPC contractor – Project champions who dedicate themselves to overcoming challenges with the creativity, resourcefulness and good old-fashion hard work.
Pre-FEED	• For a pre-commercial demonstration including a Pre-FEED enables: – Down selection of process configurations to achieve optimal integration with the host facility and maximum success of technology demonstration, – Construction of a comprehensive risk registry, and – Establishing a resource loaded schedule with the maximum detail possible. • For FOAK projects, there is also the need to carefully evaluate transient operation, like start up and shut down to ensure appropriate design criteria are included to support these transient operations.
FEED	• The first milestones should be a fixed process configuration to achieve optimal integration with the host facility and maximum success of technology demonstration, a completed risk registry, and resource loaded schedule, which effectively fixes the scope and minimizes scope creep. • Regular tracking of scheduling, incurred cost, risk by all team leaders as a group. • Technical review for: – FOAK process – Integration of auxiliary commercial technologies/equipment with FOAK technology.
EPC	• Use shadow estimates from multiple EPC firms to acquire cost, schedule, and project approaches to bracket actual project costs and identify alignment with project goals. • DOE should consider using their project data records to create a historical basis for the costing of pilot plants through commercial demonstration plants. • An incentive-based contract results in significantly higher alignment of the EPC firm with project goals and results in the lowest cost especially when the EPC earns the maximum incentives. Be sure to include safety and quality as part of the incentive requirements. • Other recommendations for EPC included: – Regular weekly review of the schedule, incurred cost and risk management plan be completed – A detailed transition plan between construction, commissioning and even operation be established and implemented, and – Documented plans for key transitory processes, like start up and shutdown, be developed to ensure the appropriate equipment and instrumentation are present to complete these processes in a safe and effective manner.

(continued)

Table 26. Workshop Recommendations (continued)

Topic	Recommendations
Commissioning and operation	• Implement transition plans that maximize the transfer of knowledge and optimize resource usage. • Consider transitioning of process engineers to commissioning and operational teams. • Retain a strong contingent from the construction team to assist with dealing with the increased level of modification, repair and maintenance associated with pre-commercial demonstration plants at least until operational availability approaches commercial targets. • Make documentation a key priority by supplementing the data collected from instrumentation via the data acquisition system with operator and engineer documentation of modifications, changes in instrumentation, calibration, and maintenance of equipment, and modification of operational strategy and process control logic.
Legal	• The legal team for a pre-commercial demonstration project needs to include specialists that understand both federal assistance regulations and more typical commercial/industrial contractual arrangements. • Because legal negotiations are an extremely important part of the project, but are segregated from the technical efforts, the regular reviews of schedule, risk registry, and cost need to include the legal team's efforts to ensure that negotiations are completed in a timely manner to maintain strong team and project momentum.

7. Conclusions

A complete conclusion for the 50 MW_e pre-commercial testing project must include the work completed on this project as well as under DOE Cooperative Agreement DE-FE0000489. Details on background, design, construction, and commissioning of the 50 MW_e pre-commercial demonstration system are documented in the final report for DOE Cooperative Agreement DE-FE0000489. This report documents the operational phase of the 50 MW_e pre-commercial testing project and trace contaminant testing. This report also pulls together specific technical knowledge for the system and recommendations for more general project definition, implementation, and management strategies that were collected from lessons-learned workshops that covered the full pre-commercial testing effort.

By far, the biggest outcomes of this pre-commercial testing effort have been the dramatic increase in the interest in the technology by end users and the investment of resources by end users to evaluate commercial applications for their specific projects. These outcomes are the confirmation that the overall project objective of reducing the technical risk for scale-up to a commercial demonstration plant with a commercially acceptable level of technical risk was accomplished. This accomplishment was built upon the system performance achieved during this pre-commercial testing effort as well as the meticulous planning and design criteria selected to showcase this system's performance.

By the end of the operational phase of this pre-commercial testing project, more than 680 hours of operation of the entire integrated system consisting of the WDP, WGS, LTGC, and aMDEA® processes had been completed. But more importantly, over 3,500 operational hours for WDP were completed. During this final operational phase, there was a clear shift in the causes of downtime from being system issues associated with the pre-commercial units (but primarily with auxiliary equipment associated with these units) to being because of non-availability of upstream equipment. During the five months of operation completed during this project, the average availability of WDP was 80% with the lowest availability of just under 70% and with multiple months of greater than 95% availability. Although the WGS and aMDEA® processes did not achieve this same high level of availability due to system issues that would have required a prolonged shutdown to fix, their availability had systematically improved and would have allowed >95% availability of the fully integrated systems after the necessary repairs were completed.

During integrated operation of the full system, the full system achieved >90% carbon capture and sulfur removal efficiencies of > 99.95% for both H_2S and COS. At these levels of sulfur removal, the effluent H_2S and COS concentrations in the clean syngas from the full system were <500 ppbv and <50 ppbv, respectively. The typical sulfur concentrations in the CO_2 byproduct generated by the aMDEA® process were 30 ppmv to 60 ppmv for H_2S and < 40 ppbv for COS. This CO_2 byproduct also had several thousand ppmv of H_2 and CO. Independent analysis by AECOM to measure NH_3, HCN, Hg, Se, and As in the clean syngas demonstrated that effluent concentrations of these contaminants had all been reduced to sub-ppmv concentrations in the clean syngas product. AECOM's analysis of the CO_2 byproduct also showed sub-ppmv effluent concentrations of these contaminants. This demonstrates that the integration of WDP and aMDEA® processes can produce an ultra-pure syngas.

Although AECOM's measurements showed extremely low concentrations of contaminants, additional microreactor testing was conducted with three different commercial syngas conversion catalysts to evaluate changes in activity and/or reactivity when using the clean syngas from the integrated system. The three conversion catalysts were cobalt- and iron-based Fischer-Tropsch (FT) catalysts and a methanol catalyst. These catalysts were selected because they require the lowest contaminant concentrations for syngas conversion. Although our approach was to compare performance with bottled gas mixtures (which are contaminant-free) with the cleaned syngas, differences in the operating conditions and syngas compositions complicated the overall analysis. However, detailed analysis of performance trends and changes in catalyst activity failed to find any changes in catalyst performance for any of these three catalysts that indicated deactivation caused by contaminants in the syngas.

These results provide technical confirmation that integration of WDP with aMDEA® can clean syngas (with suitable guard beds for added protection against process upsets) that is suitable for the most stringent of syngas conversion processes. Previously, this level of syngas cleanup could only be provided commercially with a Rectisol® process. Techno-economic analyses completed outside of this project (DOE/NETL project DE-FE0216606) have demonstrated that WDP coupled with aMDEA® also offers significant reductions in CAPEX (20-50%) and in OPEX (up to 50+%) when compared with other conventional acid gas removal technologies such as Selexol™ and Rectisol®. This ability to simultaneously improve CAPEX, OPEX, and process efficiency, without trading one improvement area off versus another, illustrates why RTI WDP is a game-changer technology.

For WDP, the analysis showed that the average raw inlet syngas concentrations provided by TEC for H_2S and COS were 10,185 ppmv and 631 ppmv, respectively. The sulfur effluent concentrations from WDP were predominantly < 25 ppmv for H_2S and < 500 ppbv for COS. This resulted in >99.7% removal (normally 99.8-99.9% removal) for both H_2S and COS. This confirms the previous results at lab-, bench-, and pilot-scale that demonstrated near identical removal of both H_2S and COS. The results from AECOM's trace contaminant analysis of the inlet and outlet syngas to WDP also showed the WDP process removed about 78% of the HCN, 32% of the As and 97% of the Se.

One of the key operating costs to be confirmed during this pre-commercial operation was sorbent replacement costs. Analysis of the WDP temperature profiles, adsorption and regeneration rates, and the absence of changes in sorbent composition during operation did not provide any evidence of deactivation for either the desulfurization or regeneration reactions over >3,500 hours of operation. The other factor that affects sorbent replacement rates is attrition losses. Analysis of the sorbent losses from the system demonstrated that the sorbent losses due to attrition were <0.25% per day, which was used as a design basis for the pre-commercial demonstration system and is less than the standard commercially acceptable limit for Fluid Catalytic Crackers (FCCs). Based on these results, sorbent replacement will be dictated by sorbent attrition and not sorbent deactivation. Furthermore, the estimated attrition loss assumption of 0.25% per day (design basis for pre-commercial demonstration system) used in all the techno-economic analysis for WDP represents a highly conservative estimate for sorbent replacement rates.

Another slipstream test conducted during this 50 MW_e pre-commercial demonstration testing was for Hg, As, and Se sorbents that have showed promise in laboratory testing at RTI at temperatures >200°C. The sorbents consisted of two commercially available mixed-metal oxide materials (Commercial Sorbent F and Commercial Sorbent G) for As and Se and a commercial impregnated carbon for Hg. Although this slipstream testing unit could only operate when WDP was operating, a total of over 900 cumulative hours of syngas exposure was completed. As part of this testing, AECOM tested the inlet and outlet gas for these trace contaminants after about 300 hours of syngas exposure. After the syngas exposure was completed, the sorbents were removed from the reactors and analyzed for Hg, As and Se content at RTI. The results from both AECOM's gas phase testing and RTI's post-exposure testing of the sorbents demonstrated an 80% removal of Se, reducing the effluent Se concentration to about 2 ppbvd. The test results for Hg and As were not able to conclusively confirm the removal levels observed in laboratory testing, but these results were complicated by the fact that the levels of these contaminants seen in TEC's raw syngas (produced from an 85% petcoke and 15% coal feed mixture) were extremely low.

One of the key challenges for this exposure test was that the Hg and As concentrations in the raw syngas provided by TEC were approximately equal to DOE's target effluent concentrations for Hg and below for As. The Se concentration in the raw syngas was higher due to the high concentration of petcoke (which has a high concentration of Se) in the fuel for the gasifier, but the WDP removed approximately 97% of this Se prior to reaching the sorbent slipstream reactors. Despite these low challenge concentrations, the impregnated sorbent did show Hg accumulation and all three sorbents also showed some As accumulation. Although the extremely low contaminant concentrations could be an explanation for this difference between the laboratory and slipstream testing, it is also possible that the contaminant species used in the laboratory testing is not the same species present in the actual syngas. This is especially true for As, where arsine (AsH_3) is used in the laboratory testing, but thermodynamics predicts

that several arsenic species such as As_4 could be present. It is through slipstream tests like this that we are learning more about both the concentration and chemistry of the trace contaminants present in coal-derived syngas and the requirements for an effective contaminant removal solution.

During the lessons-learned workshops, one of the key attributes of the project team that could be clearly identified was their alignment and dedication to the success of the project. In the workshop focused on technical issues, the team focused primarily on solving the problems and not on assigning blame, which was the first time the moderator had witnessed this type of behavior. Another key attribute of the successful project team that was identified by the workshops was the value of communication. Throughout the project, the importance of communication had been emphasized. Because of this emphasis, active communication became part of the project team's culture and everyone who attended the workshop felt comfortable, able, and willing to share their knowledge and information.

For commercial WDP plants, the recommendations from the technical lessons-learned workshop were related to design, EPC contracting, host site utilities, safety, shutdown, process and control equipment, and operator training. One of the key themes in these recommendations was effective integration with the host site. Based on experience in this project, it was very important to fully understand not only what utilities the host site could provide, but also the quality of these utilities and the availability of these utilities under different operating scenarios. This was especially important for the purge gas, which was nitrogen for this system, during emergency shutdown. Because of TEC's limited availability of nitrogen during an emergency shutdown, this required additional equipment and control strategies to effectively ensure that steam in the syngas was purged from the system prior to WDP shutdown. Cost reduction recommendations included standardization of the filters and sorbent sampling systems and reducing nitrogen consumption by improving the flow control of aeration, fluidization and stripping gases. By far the strongest recommendation for process and control equipment was for a valve design or modifications that would reduce valve seat and seal wear for gases containing sorbent and/or sorbent fines. Other key recommendations for process and control equipment included improving the flow meter selection process to achieve more accuracy and include temperature, pressure, and density compensation, improving the ability to measure the amount of fresh sorbent being added to the system, using full port slide valves, and fully tying the information available in the PLC of subsystems back into the DCS to enable board operators to effectively monitor these subsystems. A final suggestion that would help with training and WDP operation would be development of a process simulator. As an action item from this technical workshop, a repository of documentation relating to the design, operation, and modifications developed and implemented on this project was submitted to RTI.

Because the focus of the first lessons-learned workshop was technical relating to design, engineering, equipment, operation and maintenance, a second lesson-learned workshop was conducted that focused on lessons-learned during project execution. The specific goal of this workshop was to identify recommendations for achieving greater success with pre-commercial demonstration projects. Some of the recommendations highlighted the conventional wisdom of effective team building, effective intra-organizational communication, regular meetings to track progress and identify and implement risk mitigation strategies. Additions to the conventional wisdom included the approach of incorporating risk mitigation strategies into process design, the importance of identifying and actively cultivating project champions into key leadership roles of all teams and organizational members, and incorporating transition plans between EPC and commissioning and commissioning and operation that most effectively transfer process knowledge. Some of the recommendations deviated from conventional practices to embrace the unique and different circumstances that arise from a pre-commercial demonstration that involves FOAK processes. The recommendations included:

- Expanding the design efforts to consider the process and equipment required for transient operations like startup and shutdown,
- Bringing in subject matter experts to assist with both the FOAK process and the integration with auxiliary commercial equipment,
- Using a Pre-FEED to allow process engineering design to evaluate and optimize for host site integration, integration of commercial auxiliary equipment, incorporate risk mitigation

strategies into the design, and enabling rapid fixing of scope during FEED to avoid scope creep,
- Using shadow estimates from multiple EPC firms to better estimate the project cost for the specific FOAK project in question,
- Using an incentive-based contract structure to increase alignment of the EPC firm with the project goals and minimize project costs, and
- Advocating that DOE use its available information and data on pilot-scale, pre-commercial, and demonstration projects for FOAK processes to develop a cost data base that is similar to what industry uses to better evaluate the cost bids for n^{th} commercial plants.

One of the final recommendations was the recognition that with DOE funding, projects that include pre-commercial and/or commercial demonstration testing require legal expertise for both standard commercial contracting as well as federal assistance regulation. To meet these needs, the project legal team needs to possess both these areas of legal expertise for efficiency and optimal success.

From the perspective of accumulating additional operation hours and experience of the 50 MW_e pre-commercial system for supporting reducing barriers for a commercial demonstration, this project has been very successful. The operational data accumulated has conclusively demonstrated that the pre-commercial system achieved the same levels of sulfur removal and lower attrition losses than demonstrated in bench-and pilot scale testing. These data support many of the assumptions that were made in techno-economic analyses of the WDP process that show improvements in CAPEX, OPEX, and process efficiencies over conventional acid gas removal technologies. The operational data from this project has also demonstrated that coupling of WDP with aMDEA®, and more generally with any other conventional solvent-based CO_2 capture technologies, enables achieving syngas cleanup levels approaching that of commercial Rectisol®. The techno-economic analysis shows that the integration of WDP with conventional solvent-based CO_2 capture processes also results in significant reductions of CAPEX and OPEX and improved efficiency over conventional acid gas processes. These benefits enable use of WDP in IGCC as well as for chemical production, creating a situation where market forces will drive implementation of the technology to realize cost benefits and efficiency improvements over conventional technologies. The decoupling of the sulfur and CO_2 capture also enables staged implementation of CO_2 capture in IGCC applications that align capital investments with promulgation of CO_2 regulations, which cannot be done with conventional acid gas removal technologies.

Appendix A:
RTI WGCU Test

Test Results for Trace Metals, Ammonia, and Hydrogen Cyanide in Syngas through a Warm Gas Cleanup and Trace Contaminant Removal Process

Final Report

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Statement of Limitations

This report is intended for the sole use of RTI International. The scope of services performed for this work may not be appropriate to satisfy the needs of other users, and any use or re-use of this document or of the findings, conclusions, or recommendations presented herein is at the sole risk of said user. This report is for RTI's use only and is not to be distributed to third parties beyond the intended scope of services or outside RTI's organization.

1.0 Introduction

This report presents test results from the analysis of syngas and the carbon dioxide product gas produced from a 50 MWe production scale warm gas cleanup (WGCU) system. A slipstream of the clean syngas from the WGCU was also introduced into a small pilot scale Trace Contaminant Removal Process (TCRP), using various solid sorbents for trace contaminant removal. The WGCU and TCRP systems were located and tested at Tampa Electric Company's (TECO) Polk Power Station near Mulberry, Florida.

Testing was conducted during two test periods, July-August 2015 and March 2016, by AECOM under contract with RTI International (RTI). The purpose of the test was to characterize numerous syngas streams and the CO_2 product gas for ammonia (NH_3), hydrogen cyanide (HCN), and four selected trace elements: arsenic (As), cadmium (Cd), selenium (Se), and mercury (Hg) across key components of the WGCU and TCRP.

2.0 Test Narrative

The process gas streams that were sampled from the WGCU system and TCRP are described in Tables 2-1 and 2-2, respectively. Tables 2-3 and 2-4 summarize the dates and sampling times for each test parameter measured on the WGCU and TCRP gas streams. A total of ten (10) sampling runs for NH_3, HCN, and trace elements were conducted for each WGCU gas stream, and a total of six (6) runs were conducted for each TCRP gas stream. The initial sampling runs on the WGCU highlighted some sampling system limitations with respect to balancing sample flow rates and gas moisture condensation. These are described in more detail in Section 2.1.

2.1 WGCU Sampling

A portable sampling manifold system was used to collect samples from the WGCU process. The sampling manifold was designed to take pressurized gas from the process, and by controlling the sample flow to a low-pressure (flare) vent header, maintain a sufficient sample flow that ensures representativeness, retains latent heat and prevents condensation of gas moisture, and provides sufficient sample pressure for gas delivery to the sampling trains. The manifold system controls four process gas streams and it directs all four gas streams to a single header for venting to a single flare header connection. This common vent header and the connection to the flare header required some modifications that were implemented after the two initial sampling runs on the WGCU.

Immediately after the beginning of Run 1, it became apparent that the sample flow and temperature of the Sour Syngas was insufficient to prevent condensation within the sample line upstream of the sample flow control valves. Run 1 was interrupted until heating elements and insulation could be installed on supply line tubing for the Sour Syngas (manifold line 1), Clean Syngas to LTGC (manifold line 2), and Clean Syngas to the Amine System Inlet (manifold line 3).

Sample flow control was sporadic through Runs 1 and 2 even after heating the manifold sample lines. It was determined that a large delivery pressure difference between the line pressures for the first three process gases (Sour Syngas, Clean Syngas to LTGC, and Syngas to the Amine System Inlet) at a nominal 35-45 psi, and the supply pressure for the Syngas from the Amine System Outlet (manifold line 4) at nearly 250 psi was creating flow control problems in the manifold. The large delivery pressure differential, and a ⅜” to ¼” reducing union at the flare header return produced a condition where an excess flow of the high pressure sample caused sufficient backpressure in the vent header line to restrict the flow of the lower pressure samples.

This situation was corrected before Run 3 by installing a pressure regulator (set at 45-50 psi) at the Amine System Outlet syngas sample root valve. The regulator reduced the delivery pressure at the manifold so sample flow and temperature control could be balanced for the four manifold streams. The problem of moisture condensation in the sample manifold was not apparent during further test runs on the WGCU. Test Runs 6 through 10 were conducted without incident between March 6 and March 8, 2016.

The samples from Runs 1 and 2 on the Sour Syngas stream are not considered to be representative of the incoming process gas to the WGCU due to the disproportionate amount of moisture collected and the uncharacteristic results for those test parameters that exhibit some solubility in water, particularly NH_3, As, Se, and to a lesser extent, HCN. The samples from the two clean syngas streams upstream of the amine scrubber may also have been affected, but possibly to a lesser extent based on the lower moisture content. Samples of the clean, dry syngas from the amine scrubber and the CO_2 stream are not expected to be affected by the circumstances described above. There is little to no measurable moisture in the clean syngas from the amine scrubber, and the CO_2 stream was collected independent of the four-gas sampling manifold. All test results for the WGCU are presented in Section 3.0, and qualified results are flagged and footnoted.

2.2 TCRP Sampling

The same portable sampling manifold system was used to control the sample pressure of the four gas streams from the TCRP. The TCRP gas sample delivery pressure was not reduced like those gas streams at the WGCU analyzer manifold. While this did not pose any problems with gas sample flow, a higher sample line temperature was required to maintain the gas sample above the dewpoint. During the first test run at the TCRP, the sample lines were heated to 250°F and some evidence of gas condensate formation within the sample lines was observed. The relative percent difference between the measured moisture results from the ammonia/hydrogen cyanide and charcoal (metals) train was noticeably higher indicating a lower degree of precision and higher degree of sample variability (see Table 3-8). The Run 1 results from the TCRP are flagged accordingly. Results for the more water-soluble species (NH_3, As, Se, HCN) should be viewed as potentially non-representative.

Following the observations from Run 1, heating of the sample lines was increased to 350°F - 375°F and no other sampling issues were observed for Runs 2 through 6. However, syngas flow to the TCRP skid was interrupted for about 24 hours between around 0600 hrs on March 4 and 0700 hrs on March 5. Run 6 was started on March 5 at 1025.

Table 2-1. WGCU Process Gas Streams [1]

Sample ID	Process Stream	Description
SG	Sour Syngas to the WGCU Absorber	Syngas from the COS hydrolyzer outlet to the WGCU absorber inlet.
CG	Clean Syngas to LTGC	Syngas (after sulfur removal) from the WGCU absorber to the low-temperature gas cooler (LTGC).
ASI	Clean Syngas from LTGC to the Amine Scrubber	Syngas from the low-temperature gas cooler to the amine scrubber inlet (low moisture content).
ASO	Clean Syngas from the amine scrubber	Syngas from the amine scrubber outlet (acid gas and CO_2 removal)
CO2	Recovered carbon dioxide	Recovered gases from the rich amine stripper.

[1] All WGCU process gas streams were collected from the gas analyzer sample supply manifolds located at the gas analyzer housing.

Table 2-2. TCRP Gas Streams [1]

Sample ID	Process Stream	Description
SG	Inlet Syngas to the TCRP Reactors (Clean Syngas to LTGC)	Syngas (after sulfur removal) from the WGCU absorber to the low-temperature gas cooler.
R1	Syngas from TCRP Reactor Vessel 1	Syngas from the outlet of TCRP reactor vessel 1.
R2	Syngas from TCRP Reactor Vessel 2	Syngas from the outlet of TCRP reactor vessel 2.
R3	Syngas from TCRP Reactor Vessel 3	Syngas from the outlet of TCRP reactor vessel 3.

[1] All TCRP gas samples were collected locally at the TCRP skid.

Table 2-3. WGCU Sampling Schedule

Run No.	Date	Test Parameters	Sour Syngas from COS Hydrolysis	Clean Syngas to LTGC	Clean Syngas from LTGC to Amine System Inlet	Clean Syngas from Amine System Outlet	Recovered CO_2
July 29, 2015: WGCU start-up at approximately 1700 hrs.							
1	July 30, 2015	As,Cd,Hg,Se	10:05-15:30	09:55-15:30	09:55-15:30	09:55-15:30	09:55-15:30
		NH_3 / HCN	10:58-13:00	12:35-13:00	14:05-14:25	14:05-14:25	15:00-15:30
2	July 30, 2015	As,Cd,Hg,Se	18:00-21:00	18:00-21:00	18:00-21:00	18:00-21:00	18:00-21:00
		NH_3 / HCN	18:05-18:25	18:05-18:25	18:45-19:05	18:45-19:05	19:15-19:46
3	July 31, 2015	As,Cd,Hg,Se	10:00-13:00	10:00-13:00	10:00-13:00	10:00-13:00	10:00-13:00
		NH_3 / HCN	08:02-08:22	10:05-10:26	10:50-11:15	10:50-11:15	11:35-12:05
4	July 31, 2015	As,Cd,Hg,Se	15:30-18:30	15:30-18:30	15:30-18:30	15:30-18:30	15:30-18:30
		NH_3 / HCN	15:35-15:55	15:35-15:55	16:15-16:40	16:15-16:40	16:55-17:25
Aug 1-10, 2015: Main gasifier experiencing plugging problems. WGCU shut down on short notice the morning of August 1. Syngas to the WGCU was resumed around 20:00 hrs on August 10.							
5	August 11, 2015	As,Cd,Hg,Se	10:10-13:10	10:10-13:10	10:10-13:10	10:10-13:10	10:10-13:10
		NH_3 / HCN	10:15-10:35	12:16-12:36	10:52-11:17	10:52-11:17	11:30-12:00
August 11, 2015: Problem with the WGCU Syngas compressor interrupts operation at 13:40, shortly after finishing Run 5. WGCU down for several days. Balance of testing rescheduled.							
February 23, 2016: WGCU Start-up at approximately 2100 hrs. WGCU off of syngas (TECO gasifier trip) at approximately 0600 hrs on March 4. WGCU resumed operation on syngas at approximately 0300 hrs on March 5.							
6	March 6, 2016	As,Cd,Hg,Se	10:20-13:21	10:22-13:22	10:24-13:24	10:26-13:26	10:48-13:48
		NH_3 / HCN	10:59-11:19	11:00-11:20	12:42-13:02	12:42-13:02	13:19-13:53
7	March 7, 2016	As,Cd,Hg,Se	08:00-11:00	08:02-11:02	08:04-11:04	08:06-11:06	08:08-11:08
		NH_3 / HCN	08:15-08:35	08:16-08:36	09:05-09:31	09:06-09:31	10:00-10:30
8	March 7, 2016	As,Cd,Hg,Se	12:30-15:30	12:32-15:32	12:34-15:34	12:36-15:36	12:38-15:38
		NH_3 / HCN	13:07-13:27	12:47-13:07	13:30-13:55	13:31-13:56	14:20-14:50
9	March 8, 2016	As,Cd,Hg,Se	07:50-10:50	07:52-10:52	07:54-10:54	07:56-10:56	07:58-10:58
		NH_3 / HCN	08:02-08:22	08:05-08:25	08:50-09:15	08:51-09:16	09:30-10:00
10	March 8, 2016	As,Cd,Hg,Se	12:45-15:45	12:47-15:47	12:49-15:49	12:51-15:51	12:53-15:53
		NH_3 / HCN	13:07-13:27	13:08-13:28	13:55-14:20	13:56-14:21	14:33-15:05

Table 2-4. TCRP Sampling Schedule

Run No.	Date	Test Parameters	Clean Syngas to LTGC/TCRP	Clean Syngas from Reactor Vessel 1	Clean Syngas from Reactor Vessel 2	Clean Syngas from Reactor Vessel 3
February 25, 2016:TCRP Start-up at approximately 1900 hrs						
1	March 1, 2016	As,Cd,Hg,Se	11:35-14:45	11:40-14:40	11:46-14:46	11:48-14:48
		NH_3 / HCN	13:07-13:27	13:07-13:27	15:05-15:25	15:05-15:25
2	March 2, 2016	As,Cd,Hg,Se	08:27-11:31	08:30-11:31	10:45-13:45	08:33-11:33
		NH_3 / HCN	09:15-09:35	09:15-09:35	10:50-11:10	10:50-11:10
3	March 2, 2016	As,Cd,Hg,Se	13:27-16:27	13:29-16:29	14:13-17:13	13:31-16:31
		NH_3 / HCN	14:00-14:20	14:00-14:20	15:05-15:25	15:05-15:25
4	March 3, 2016	As,Cd,Hg,Se	08:00-11:00	08:02-11:02	08:04-11:04	08:06-11:06
		NH_3 / HCN	08:45-09:05	08:45-09:05	09:30-09:50	09:30-09:50
5	March 3, 2016	As,Cd,Hg,Se	12:24-15:24	12:26-15:26	12:28-15:27	12:30-15:30
		NH_3 / HCN	13:21-13:41	13:21-13:41	14:09-14:29	14:09-14:29
The TCRP test unit was taken off of syngas at approximately 0600 on March 4 (TECO gasifier trip) and placed in hot-standby mode under nitrogen until syngas feed was resumed the morning of March 6, at approximately 0700 hrs.						
6	March 5, 2016	As,Cd,Hg,Se	10:25-13:25	10:05-13:05	10:07-13:07	10:09-13:09
		NH_3 / HCN	10:30-10:50	10:30-10:50	11:10-11:30	11:10-11:30

3.0 Test Results

The test results are presented in this section by process unit and by individual analyte so that the fate of each can be easily compared in the data tables. The test results for the process gas streams associated with the WGCU are presented in Section 3.2 and the streams associated with the TCRP are presented in Section 3.3. All concentration results for ammonia, hydrogen cyanide, and trace elements are reported on a dry gas basis. Section 3.1 discusses the reporting convention used to determine and report the test results.

3.1 Reporting Convention

In most cases, a single analytical fraction was prepared to quantitatively represent the entire gas sample. In other cases, multiple sample fractions were analyzed separately to determine collection efficiency or breakthrough. With the separate analysis of multiple sample fractions, a convention for managing the summation of results that could include concentrations both above the method detection limit (MDL), and undetected concentrations (below MDL) was necessary to calculate a meaningful net result.

The following convention was used for determining the reported results for the NH_3 and HCN sampling trains:

- The full MDL value was used for all non-detect results where the analytical sample fraction represents the entire gas sample (NH_3 and HCN impinger train samples).
- Where three HCN impinger fractions were analyzed individually, all detectable measured values were summed to provide a total result for the sample. Non-detect results were treated as follows: ½ the MDL was used for the second impinger in series, and an ND result for the last impinger in series was assigned a value of zero. There were no occurrences where the first of three impinger fractions reported a non-detect result.

For the trace element sampling trains, the sum of the numerous analytical fractions using full MDLs raises the reported detection limits and makes comparisons of results difficult. After evaluating all of the analytical results it was apparent that each individual target element is preferentially collected in specific recovered sample fractions.

Arsenic and selenium appear to be preferentially collected in the condensate knock-out impinger upstream of the charcoal sorbent tubes. Only in the samples of the sour syngas was selenium detected in the charcoal sorbent sample fraction, likely due to the higher concentrations present in that gas stream, and for the sour syngas samples, there were no non-detect results.

For the remaining samples, only the MDLs for the condensate fraction were used to represent the non-detect results for arsenic and selenium.

Mercury was measured almost exclusively in the charcoal sorbent sample fraction. In only 4 out of 67 samples was mercury detected in the condensate fraction. For samples with all non-detect results, the MDL for the charcoal sample fraction (or the first charcoal tube section when available) were used to represent non-detected mercury results.

Cadmium was also found preferentially in the charcoal fraction with only 3 out of 18 samples reporting detected concentrations being associated with the condensate fraction. For the non-detected cadmium results however, the sum of the MDLs for both the charcoal and condensate fraction was used to represent the total non-detected cadmium result.

All samples that reported a measurable concentration of the target trace element were reported on the measured concentration basis alone, and any other analytical fraction reporting a non-detect value was treated as zero. The highest MDL determined from the sample with the lowest gas sample volume was reported consistently for all samples. Detailed results for the individual analyses of the condensate and charcoal sorbent fractions and the determination of the total mass/concentration reported are provided in Section 5 on Quality Control Sample Results.

3.2 WGCU Process Gas Streams

The five WGCU process gas streams sampled during the course of this test program were each measured for moisture content, ammonia, hydrogen cyanide, arsenic, cadmium, mercury, and selenium concentrations. Ten samples were collected for each parameter on each of the five gas streams. The gas streams sampled included:

1. Sour Syngas to the WGCU absorber;
2. Clean Syngas from the Absorber to the Low-Temperature Gas Cooler;
3. Clean Syngas to the Amine Scrubber;
4. Clean Syngas from the Amine Scrubber; and
5. Carbon Dioxide product gas from the Amine Stripper Column

Runs 1 and 2 were collected while syngas sample flow through the sampling manifold was being adjusted in an attempt to stabilize and balance sample gas temperatures and flow rates. The effect of these adjustments on the manifold sample streams other than sour syngas is difficult to assess, but appears to be minimal, especially for the low-moisture gas streams (i.e., Amine System Inlet and Amine System Outlet).

Runs 3 and 4 were collected after the sampling system adjustments were made to reduce the Amine System Outlet syngas sample pressure. This balanced the delivery pressure for all syngas streams on the sampling manifold and resulted in more stable and consistent sample flows. The samples for Runs 3 and 4 collected on July 31 were collected without incident.

Run 5 was collected after an outage period of 9 days. The test run started about 14 hours after syngas feed was restored to the WGCU. Shortly after Run 5 sampling was completed, a problem with the WGCU syngas compressor forced a shutdown of the WGCU. The shutdown period required a rescheduling of the remaining samples for a later date.

The WGCU was started up on February 23, 2016, and operated continuously for 10 days until March 4 when a gasifier trip brought down the WGCU for approximately 21 hours before resuming operation on March 5 at 0300 hrs. Sampling of the WGCU was resumed on March 6, approximately 31 hours after the restart of the WGCU. WGCU Runs 6 through 10 were collected without incident.

The following Sections (3.2.1 through 3.2.7) present the test results for moisture, ammonia, hydrogen cyanide, and the trace elements arsenic, cadmium, mercury, and selenium on the five WGCU process gas streams.

3.2.1 Moisture

Table 3-1 presents all WGCU test results for gas moisture content. Moisture was determined by measuring the total net weight gain of the impingers due to water vapor condensation and absorption within the ammonia/cyanide (NH_3/HCN) sampling trains. The percent moisture results are used as an indicator of sample representativeness, particularly with respect to the sour syngas and clean syngas to the LTGC. The LTGC removes most of the moisture from the gas by cooling and condensation, so downstream syngas samples are relatively dry. This is evident from the test results which also indicate the gas flow and condensation problems associated with the sour syngas during Runs 1 and 2.

During test Runs 6 through 10, the metals sampling trains were also weighed for the determination of moisture as an additional check against the moisture determined from the NH_3/HCN trains. The NH_3/HCN sampling train processes a significantly larger volume of gas and is considered more reliable for the determination of moisture. However the sampling train is operated for a very short time during the overall sampling period and only reflects the moisture content for that relatively short sampling period.

The metals sampling train collects a much smaller volume relative to the NH_3/HCN train, but is collected for the entire duration of the sampling run. However, the small gas sample

volume and difficulty in recovering and accounting for all of the gas condensate from the sample line introduces the potential for more significant errors. For the gas streams with easily measurable moisture content (i.e., sour syngas and clean syngas to the LTGC) the two separate moisture results are in relatively good agreement with relative percent differences between the measurements less than 5% with two exceptions at 7.4 and 10.7 RPD (sour syngas Runs 6 and 7, respectively).

3.2.2 Ammonia

Ammonia measurement results for the WGCU process gas streams are presented in Table 3-2 as nitrogen in parts per million by volume on a dry gas basis (ppmvd NH_3 as N). Ammonia is generally water soluble and is typically removed from the syngas by water scrubbing and removal of gas condensate. This is evident from the test results as the removal of gas moisture by condensation in the LTGC is reflected in both the reduction in the moisture concentration and the ammonia concentration downstream of the LTGC.

Ammonia measurements are easily affected by any moisture condensation within the sample manifold lines upstream of the sample transfer line to the impinger train. Problems with sample flow control, heat retention, and moisture condensation in the sour syngas sample manifold as described in Section 2.1 are reflected by uncharacteristic sour syngas results for Runs 1 and 2. While not as evident from the ammonia concentrations measured for the other gas streams during runs 1 and 2, the difficulty maintaining consistent sample gas flow through the manifold during the first two runs may have affected the representativeness of the other syngas streams. The recovered CO_2 gas stream was collected through a separate low-pressure sample connection so it would not be affected.

3.2.3 Hydrogen Cyanide

The hydrogen cyanide concentrations measured in the WGCU process gas streams are presented in Table 3-3 in parts per million by volume HCN on a dry gas basis (ppmvd HCN). Like ammonia, HCN also exhibits water solubility, especially at higher pH conditions. It appears from the test results that in addition to some removal of HCN with the gas condensate in the LTGC, the high pH condition in the amine scrubber may also be effective at removing HCN as an acid gas.

3.2.4 Arsenic

Table 3-4 presents the arsenic results for WGCU process gas streams. Nearly all of the gas samples collected and analyzed during test Runs 1 through 5 returned non-detect results. Of the fifteen samples collected, only three reported detectable arsenic concentrations; sour syngas, clean syngas from the LTGC, and clean syngas from the amine scrubber.

For Runs 6 through 10, arsenic was detected in all of the sour syngas and clean syngas samples from the absorber. Arsenic was not detected in any of the clean syngas samples after the low temperature gas cooler, and was detected in only one sample of the recovered carbon dioxide stream (Run 9). The five measured arsenic concentrations in the clean syngas from the absorber appear very consistent ranging from 1.0 to 1.4 ppbv. Sour syngas results ranged between 1.6 to 3.0 ppbv.

All detectable arsenic concentrations were measured in the gas condensate sample fraction. Arsenic was not measured in any of the charcoal sorbent fractions. More details on the recovery of arsenic in the sampling train fractions are presented in Section 5.0.

3.2.5 Cadmium

Cadmium was measured at least once in each of the five WGCU gas streams sampled during the first five test runs. Only two of the WGCU gas streams reported measurable cadmium concentrations during Runs 6 through 10; sour syngas (Runs 7, 8, and 9), and clean syngas from the absorber (Runs 7 and 9). During Runs 6 through 10, cadmium was not detected in any of the clean syngas samples after the low temperature gas cooler, or in the recovered carbon dioxide stream. The cadmium results are presented in Table 3-5. Sporadic and infrequent results above the MDL indicate that cadmium is not easily measured at this level under the sampling conditions of this test.

3.2.6 Mercury

Mercury was measured in nearly all of the WGCU gas streams, including the recovered carbon dioxide. All samples of sour syngas and clean syngas from the absorber had detectable concentrations of mercury. Mercury was not detected in the clean syngas samples from the LTGC outlet to the amine scrubber during Runs 1 through 5, but it was detected during Runs 6 through 10. The mercury results are presented in Table 3-6.

3.2.7 Selenium

Selenium results for the WGCU process gas streams are presented in Table 3-7. All samples of the sour syngas and clean syngas from the absorber reported measurable concentrations of selenium.

Similar to arsenic, all of the samples containing measurable selenium reported selenium in the condensate fraction of the sampling train. Selenium was also measured in the first section of the carbon sorbent tube of the sour syngas samples. The collection of selenium in the condensate and first carbon bed is consistent with the collection of selenium in the sour syngas collected during the February 2014 Baseline Tests.

3.3 TCRP Process Gas Streams

The four TCRP gas streams were sampled March 1 through March 5, 2016. Each process stream was measured for moisture content, ammonia, hydrogen cyanide, arsenic, cadmium, mercury, and selenium concentrations. Six samples were collected for each parameter on each of the four gas streams. Gas flow from the four process sample points was initiated at a reduced flow rate to condition the sampling system approximately 12 hours prior to collecting the first sample.

Run 1 on the TCRP was conducted with the set points on the sample line heaters at 250°F. This may have been too close to the dew point of the sample gas as some minor condensation was observed in the sample lines. The moisture results suggest the samples may have been compromised to some degree. The Run 1 test results however, do not appear to be unusual or show any particular indication of being unrepresentative in comparison with subsequent test runs. Nevertheless, the Run 1 results are flagged to indicate the potential for uncertainty, particularly with the target species more closely associated with the gas condensate. Runs 2 through 5 on the TCRP were conducted without incident after increasing the sample line heaters to 350°F to 375°F.

Following Run 5, the TCRP experienced a loss of syngas feed and was placed in hot standby on plant nitrogen on March 4. Syngas flow was restored the following day and Run 6 was conducted approximately 27 hrs after the TCRP was back on syngas.

The following Sections (3.3.1 through 3.3.7) present the test results for moisture, ammonia, hydrogen cyanide, and the trace elements arsenic, cadmium, mercury, and selenium on the four TCRP process gas streams.

3.3.1 Moisture

Table 3-8 presents the syngas moisture results for the TCRP gas samples. In the same manner as described in Section 3.2.1 for Runs 6 through 10 at the WGCU, both the NH_3/HCN sampling trains and the charcoal-metals sampling trains were weighed before and after sampling to determine moisture content. For the clean syngas streams of the TCRP, the two separate moisture results are in relatively good agreement (i.e. a relative percent difference <10%) for all four streams during Runs 2 through 6. As suspected, the lower sample line temperature during Run 1 appears to be a factor in obtaining representative and consistent samples. The moisture results appear inconsistent and exhibit greater variability between the two moisture measurements (RPD between 12.4% and 48.9%).

3.3.2 Ammonia

Ammonia measurement results for the TCRP process gas streams are presented in Table 3-9 as nitrogen in parts per million by volume on a dry gas basis (ppmvd NH_3 as N). The TCRP is heated to maintain the gas temperatures above the dew point and prevent gas cooling and condensation of moisture. Changes in ammonia concentration between the inlet and the outlet of each reactor vessel should therefore not be affected by anything other than the media within the test reactors, or condensation within the sampling system manifold (results for Run 1 are flagged for this reason). All NH_3 results for Run 1 represent the lowest concentration measured during all six test runs. Whether this is coincidental or a function of the sample header temperature and moisture condensation within the sample line is unknown.

3.3.3 Hydrogen Cyanide

The hydrogen cyanide concentrations measured in the TCRP gas streams are presented in Table 3-10 in parts per million by volume on or dry gas basis (ppmvd HCN). Similar to the ammonia results in Table 3-9, all HCN results for Run 1 represent the lowest concentration measured during all six test runs. The results for Run 1 have been flagged.

3.3.4 Arsenic

The arsenic results presented in Table 3-11 appear consistent for Runs 2 through 6 with no apparent or significant change through any of the three reactor vessels. Results for the TCRP clean syngas also appear consistent with the subsequent test results for the same gas stream collected from the WGCU analyzer header that ranged between 1.0 and 1.4 ppbv arsenic.

3.3.5 Cadmium

Cadmium results for the TCRP are shown in Table 3-12. Similar to the WGCU test results for the Clean Syngas to LTGC, the results for the clean syngas through the TCRP are sporadic and near the MDL indicating that cadmium is not consistently detected at these concentration levels.

3.3.6 Mercury

Mercury was detected in all of the TCRP gas sample streams as shown in Table 3-13. The concentrations are well above the MDL of 0.036 ppbv, but are widely scattered across the data set. The results for the clean syngas to the TCRP are comparable to the mercury concentrations measured for the same clean syngas stream on the WGCU. Since mercury was typically not measured in the gas condensate of the metals sampling trains, the variable moisture results associated with Run 1 samples may not have produced a significant impact on the mercury results.

3.3.7 Selenium

The selenium results for the TCRP are presented in Table 3-14. With the higher inlet concentration of selenium, these results indicate a reduction of selenium through all three reactor vessels. All detected reactor outlet concentrations were measured at levels less than 3 times the MDL (<3 times the MDL).

The selenium results for Run 1 should be considered non-representative as the sampling system may not have been heated sufficiently to prevent condensation within the sample lines. As evident from the results of the fractional analysis of the charcoal sampling train, selenium's association with the condensate fraction and the potential for disproportionate collection of condensate in the sample lines would potentially bias these results.

The Run 6 selenium result for the Clean Syngas to the TCRP (collected after the TCRP was in a nitrogen purge mode for 24 hours) was noticeably lower than the previous four test runs. Run 6 started at 10:25 am, approximately 3 hours after syngas to the TCRP was restored. No sampling anomalies were noted or observed to explain the drop in selenium concentration from previous runs and there does not appear to be a similar reduction in the results for the other trace elements associated with that sample.

Table 3-1. WGCU Process Gas Moisture Results (Mol %)

Process Gas Stream	Sampling Train	Run 1	Run 2	Run 3	Run 4	Run 5	Run 6	Run 7	Run 8	Run 9	Run 10
Sour Syngas to WGCU Absorber	NH_3/HCN	3.08 [1]	1.75 [1]	25.57	29.15	25.51	28.22	30.72	24.92	26.99	23.10
	Charcoal	NA	NA	NA	NA	NA	26.20	27.60	24.74	28.29	23.63
Clean Syngas from Absorber to LTGC	NH_3/HCN	9.38 [1]	8.41 [1]	6.86	8.65	7.33	13.67	14.63	14.68	15.29	14.23
	Charcoal	NA	NA	NA	NA	NA	14.02	15.04	15.27	15.40	14.49
Syngas from LTGC System Outlet	NH_3/HCN	3.22 [1]	0.96 [1]	ND	ND	0.19	0.49	0.33	0.35	0.76	ND
	Charcoal	NA	NA	NA	NA	NA	0.69	ND	0.74	ND	0.62
Syngas from Amine System Outlet	NH_3/HCN	0.45	0.04	ND	ND	0.64	ND	0.37	0.17	0.29	ND
	Charcoal	NA	NA	NA	NA	NA	0.15	0.55	0.64	0.70	0.15
Recovered CO_2	NH_3/HCN	8.14	4.22	5.37	4.15	4.79	5.55	3.76	2.92	2.40	3.48
	Charcoal	NA	NA	NA	NA	NA	2.94	1.62	4.84	1.77	3.96

NA = Not analyzed. The mini-impingers were not weighed for moisture determination during the first five test runs for metals by charcoal.

ND = Not detected. A negative net weight gain was measured for the impinger train.

[1] Test results from Runs 1 and 2 on the sour syngas (and possibly the two clean syngas streams upstream of the amine scrubber) are not considered representative of the source due to the apparent condensation of moisture within the sample delivery system.

Table 3-2. WGCU Process Gas Ammonia Results (ppmvd NH_3 as N)

Process Gas Stream	Run 1	Run 2	Run 3	Run 4	Run 5	Run 6	Run 7	Run 8	Run 9	Run 10
Sour Syngas to WGCU Absorber	111 [1]	20.2 [1]	751	807	465	530	689	485	664	599
Clean Syngas from Absorber to LTGC	825 [1]	694 [1]	547	547	287	556	607	439	466	396
Syngas from LTGC System Outlet	1.36 [1]	1.62 [1]	0.92	1.00	0.15	1.16	0.15	0.48	0.47	0.44
Syngas from Amine System Outlet	7.29	6.27	5.40	6.12	1.47	0.43	0.07	0.47	0.31	0.38
Recovered CO_2	2.55	2.56	1.67	1.50	1.48	0.13	0.28	ND	0.21	0.18

ND = Not detected. Highest estimated MDL = 0.18 ppmvd NH_3 as N. Results reported below this MDL reflect positive analytical results and a larger sample volume resulting in a lower sample-specific MDL.

[1] Test results from Runs 1 and 2 on the sour syngas (and possibly the two clean syngas streams upstream of the amine scrubber) are not considered representative of the source due to the apparent condensation of moisture within the sample delivery system, and the high degree of solubility of ammonia in the condensate.

Table 3-3. WGCU Process Gas Hydrogen Cyanide Results (ppmvd HCN)

Process Gas Stream	Run 1	Run 2	Run 3	Run 4	Run 5	Run 6	Run 7	Run 8	Run 9	Run 10
Sour Syngas to WGCU Absorber	1.52 [1]	1.62 [1]	1.52	8.12	6.02	6.49	8.80	6.31	7.60	6.66
Clean Syngas from Absorber to LTGC	1.72 [1]	1.56 [1]	1.69	2.01	0.62	0.92	1.12	0.89	0.92	0.98
Syngas from LTGC System Outlet	1.58 [1]	1.47 [1]	2.32	2.30	1.30	0.036	0.039	0.035	0.027	ND
Syngas from Amine System Outlet	ND	0.030	0.010	<0.0042 [2]	0.104	ND	ND	ND	ND	ND
Recovered CO_2	0.92	1.10	1.40	1.57	2.65	0.027	0.028	0.028	0.021	0.0058

ND = Not detected. Highest estimated MDL = 0.0077 ppmvd HCN. Results reported below this MDL reflect positive analytical results and a larger sample volume resulting in a lower sample-specific MDL.

[1] Test results from Runs 1 and 2 on the sour syngas (and possibly the two clean syngas streams upstream of the amine scrubber) are not considered representative of the source due to the apparent condensation of moisture within the sample delivery system, and the potential for HCN to be biased by its solubility in the condensate.

[2] One or more sample fractions summed to obtain the total mass of HCN recovered was a non-detect result.

Table 3-4. WGCU Process Gas Arsenic Results (ppbvd As)

Process Gas Stream	Run 1	Run 2	Run 3	Run 4	Run 5	Run 6	Run 7	Run 8	Run 9	Run 10
Sour Syngas to WGCU Absorber	ND [1]	ND [1]	ND	ND	1.43	3.00	2.01	1.84	2.33	1.58
Clean Syngas from Absorber to LTGC	ND [1]	ND [1]	ND	ND	ND	1.40	1.05	1.01	1.36	1.01
Syngas from LTGC System Outlet	ND [1]	ND [1]	0.573	ND	ND	ND	ND	ND	ND	ND
Syngas from Amine System Outlet	ND	ND	ND	0.695	ND	ND	ND	ND	ND	ND
Recovered CO_2	ND	ND	ND	ND	ND	ND	ND	ND	0.575	ND

ND = Not detected. Highest estimated MDL = 0.66 ppmvd As. Results reported below this MDL reflect positive analytical results and a larger sample volume resulting in a lower sample-specific MDL.

[1] Test results from Runs 1 and 2 on the sour syngas (and possibly the two clean syngas streams upstream of the amine scrubber) are not considered representative of the source due to the apparent condensation of moisture within the sample delivery system, and the apparent association of arsenic with the condensate fraction.

Table 3-5. WGCU Process Gas Cadmium Results (ppbvd Cd)

Process Gas Stream	Run 1	Run 2	Run 3	Run 4	Run 5	Run 6	Run 7	Run 8	Run 9	Run 10
Sour Syngas to WGCU Absorber	ND [1]	ND [1]	0.445	ND	ND	ND	1.15	0.715	1.02	ND
Clean Syngas from Absorber to LTGC	ND [1]	ND [1]	2.07	ND	ND	ND	0.0730	ND	0.456	ND
Syngas from LTGC System Outlet	ND [1]	ND [1]	0.376	ND	ND	ND	ND	ND	ND	ND
Syngas from Amine System Outlet	0.377	ND	ND	0.223	ND	ND	ND	ND	ND	ND
Recovered CO_2	0.0762	0.102	ND	ND	ND	ND	ND	ND	ND	ND

ND = Not detected. Highest estimated MDL = 0.58 ppmvd Cd. Results reported below this MDL reflect positive analytical results and a larger sample volume resulting in a lower sample-specific MDL.

[1] Test results from Runs 1 and 2 on the sour syngas (and possibly the two clean syngas streams upstream of the amine scrubber) are not considered representative of the source due to the apparent condensation of moisture within the sample delivery system, however cadmium was measured in only a few of the total condensate sample fractions recovered and may not be affected by the disproportionate amount of condensate in these samples.

Table 3-6. WGCU Process Gas Mercury Results (ppbvd Hg)

Process Gas Stream	Run 1	Run 2	Run 3	Run 4	Run 5	Run 6	Run 7	Run 8	Run 9	Run 10
Sour Syngas to WGCU Absorber	0.365 [1]	0.516 [1]	0.509	0.435	0.457	0.135	0.929	0.818	0.730	0.579
Clean Syngas from Absorber to LTGC	0.747 [1]	0.764 [1]	1.18	0.522	0.644	0.711	0.661	0.627	0.640	0.491
Syngas from LTGC System Outlet	ND [1]	ND [1]	ND	ND	ND	0.0763	0.179	0.0938	0.146	0.0513
Syngas from Amine System Outlet	0.0717	0.0783	0.0991	0.0612	ND	0.433	0.503	0.394	0.391	0.254
Recovered CO_2	0.0860	0.0879	0.104	0.0609	0.0529	0.183	0.0944	0.366	0.0452	ND

ND = Not detected. Highest estimated MDL = 0.036 ppmvd Hg

[1] Test results from Runs 1 and 2 on the sour syngas (and possibly the two clean syngas streams upstream of the amine scrubber) are potentially not representative of the source due to the apparent condensation of moisture within the sample delivery system. However, mercury was found associated with the gas condensate in only a few of the recovered samples, and therefore may not be as affected by the disproportionate condensate volume recovered.

Table 3-7. WGCU Process Gas Selenium Results (ppbvd Se)

Process Gas Stream	Run 1	Run 2	Run 3	Run 4	Run 5	Run 6	Run 7	Run 8	Run 9	Run 10
Sour Syngas to WGCU Absorber	25.6 [1]	336 [1]	621	519	275	829	401	294	353	267
Clean Syngas from Absorber to LTGC	15.7 [1]	20.4 [1]	20.9	11.1	21.9	2.91	4.89	3.44	3.10	3.82
Syngas from LTGC System Outlet	ND [1]	2.07 [1]	0.775	0.783	5.44	ND	0.607	0.962	ND	ND
Syngas from Amine System Outlet	ND	0.968	ND	ND	3.09	ND	0.674	0.844	ND	ND
Recovered CO_2	1.18	1.40	ND	0.746	1.33	ND	0.641	1.18	0.954	ND

ND = Not detected. Highest estimated MDL = 0.82 ppmvd Se. Results reported below this MDL reflect positive analytical results and a larger sample volume resulting in a lower sample-specific MDL.

[1] Test results from Runs 1 and 2 on the sour syngas (and possibly the two clean syngas streams upstream of the amine scrubber) are not considered representative of the source due to the apparent condensation of moisture within the sample delivery system, and the apparent association of selenium with the condensate fraction.

Table 3-8. TCRP Gas Moisture Results (Mol %)

Process Gas Stream	Sampling Train	Run 1 [1]	Run 2	Run 3	Run 4	Run 5	Run 6
Clean Syngas to the TCRP	NH_3/HCN	16.3	14.7	13.9	14.0	13.1	14.6
	Charcoal	12.4	14.3	15.2	13.8	13.7	14.1
	RPD (%)	27.2	2.8	8.9	1.4	4.5	3.5
Syngas from TCRP Reactor Vessel 1	NH_3/HCN	16.3	14.4	14.6	14.1	13.5	14.3
	Charcoal	14.4	13.8	14.1	14.9	13.4	14.5
	RPD (%)	12.4	4.3	3.5	5.5	0.7	1.4
Syngas from TCRP Reactor Vessel 2	NH_3/HCN	14.5	14.4	14.8	13.5	13.6	14.1
	Charcoal	8.8	14.9	14.6	14.3	14.5	14.9
	RPD (%)	48.9	3.4	1.4	5.8	6.4	5.5
Syngas from TCRP Reactor Vessel 3	NH_3/HCN	16.1	14.0	14.0	14.1	13.3	13.9
	Charcoal	13.9	15.3	14.3	14.1	14.5	15.0
	RPD (%)	14.7	8.9	2.1	0	8.6	7.6

[1] Test results from Run 1 may have been affected by insufficient heating of the sample lines to maintain the gas above the dewpoint and prevent condensation within the sample lines. The relative percent difference between the moisture measured by the NH_3/HCN and the charcoal (metals) sampling trains demonstrates an elevated level of imprecision.

Table 3-9. TCRP Gas Ammonia Results (ppmvd NH_3 as N)

Process Gas Stream	Run 1 [1]	Run 2	Run 3	Run 4	Run 5	Run 6
Clean Syngas to the TCRP	394	463	508	541	583	827
Syngas from TCRP Reactor Vessel 1	340	453	529	1035	672	588
Syngas from TCRP Reactor Vessel 2	370	501	474	527	607	756
Syngas from TCRP Reactor Vessel 3	293	513	538	582	415	785

[1] Test results from Run 1 may have been affected by insufficient heating of the sample lines to maintain the gas above the dewpoint and prevent condensation within the sample lines.

Table 3-10. TCRP Gas Hydrogen Cyanide Results (ppmvd HCN)

Process Gas Stream	Run 1 [1]	Run 2	Run 3	Run 4	Run 5	Run 6
Clean Syngas to the TCRP	0.51	0.81	0.74	0.96	0.92	0.95
Syngas from TCRP Reactor Vessel 1	0.43	0.72	0.74	0.88	0.86	0.92
Syngas from TCRP Reactor Vessel 2	0.47	0.78	0.61	0.89	0.88	0.88
Syngas from TCRP Reactor Vessel 3	0.52	0.81	0.67	1.09	1.01	1.08

[1] Test results from Run 1 may have been affected by insufficient heating of the sample lines to maintain the gas above the dewpoint and prevent condensation within the sample lines.

Table 3-11. TCRP Gas Arsenic Results (ppbvd As)

Process Gas Stream	Run 1 [1]	Run 2	Run 3	Run 4	Run 5	Run 6
Clean Syngas to the TCRP	ND	1.03	0.901	0.816	0.985	1.41
Syngas from TCRP Reactor Vessel 1	ND	0.657	1.11	1.17	1.21	1.21
Syngas from TCRP Reactor Vessel 2	ND	0.970	0.803	1.04	1.13	1.21
Syngas from TCRP Reactor Vessel 3	ND	0.804	0.794	0.980	0.872	1.47

ND = Not detected. Highest estimated MDL = 0.66 ppmvd As. Results reported below this MDL reflect positive analytical results and a larger sample volume resulting in a lower sample-specific MDL.

[1] Test results from Run 1 may have been affected by insufficient heating of the sample lines to maintain the gas above the dewpoint and prevent condensation within the sample lines. Arsenic results may have been affected due to the apparent association of arsenic with the condensate fraction.

Table 3-12. TCRP Gas Cadmium Results (ppbvd Cd)

Process Gas Stream	Run 1 [1]	Run 2	Run 3	Run 4	Run 5	Run 6
Clean Syngas to the TCRP	0.800	1.30	ND	ND	ND	ND
Syngas from TCRP Reactor Vessel 1	0.400	0.461	ND	ND	ND	ND
Syngas from TCRP Reactor Vessel 2	ND	ND	ND	ND	0.479	ND
Syngas from TCRP Reactor Vessel 3	ND	0.491	ND	ND	ND	ND

ND = Not detected. Highest estimated MDL = 0.58 ppmvd Cd. Results reported below this MDL reflect positive analytical results and a larger sample volume resulting in a lower sample-specific MDL.

[1] Test results from Run 1 may have been affected by insufficient heating of the sample lines to maintain the gas above the dewpoint and prevent condensation within the sample lines.

Table 3-13. TCRP Gas Mercury Results (ppbvd Hg)

Process Gas Stream	Run 1 [1]	Run 2	Run 3	Run 4	Run 5	Run 6
Clean Syngas to the TCRP	0.573	0.626	0.497	1.25	2.00	0.706
Syngas from TCRP Reactor Vessel 1	1.51	1.22	0.665	0.704	0.690	0.674
Syngas from TCRP Reactor Vessel 2	0.783	0.536	1.15	0.743	0.730	1.07
Syngas from TCRP Reactor Vessel 3	0.927	2.13	2.67	1.44	0.876	0.154

[1] Test results from Run 1 may have been affected by insufficient heating of the sample lines to maintain the gas above the dewpoint and prevent condensation within the sample lines. However, mercury was found associated with the gas condensate in only a few of the recovered samples, and therefore may not be as affected by any disproportionate condensate volume recovered.

Table 3-14. TCRP Gas Selenium Results (ppbvd Se)

Process Gas Stream	Run 1 [1]	Run 2	Run 3	Run 4	Run 5	Run 6
Clean Syngas to the TCRP	9.71	9.04	3.01	6.16	11.5	1.52
Syngas from TCRP Reactor Vessel 1	ND	0.582	1.23	1.17	1.42	1.53
Syngas from TCRP Reactor Vessel 2	ND	0.890	ND	1.14	1.26	1.12
Syngas from TCRP Reactor Vessel 3	ND	0.805	0.649	0.960	1.10	1.56

ND = Not detected. Highest estimated MDL = 0.82 ppmvd Se. Results reported below this MDL reflect positive analytical results and a larger sample volume resulting in a lower sample-specific MDL.

[1] Test results from Run 1 may have been affected by insufficient heating of the sample lines to maintain the gas above the dewpoint and prevent condensation within the sample lines. Selenium results may have been affected due to the apparent association of selenium with the condensate fraction.

4.0 Sampling and Analytical Approach

WGCU process gas samples were collected from the sample headers delivering process gas samples to the on-line analyzer system. The WGCU gas streams sampled were:

- Sour Syngas to the WGCU absorber;
- Clean Syngas to the Low-Temperature Gas Cooler;
- Clean Syngas to the Amine Scrubber;
- Clean Syngas from the Amine Scrubber; and
- Carbon Dioxide product gas from the Amine Stripper Column

The sample delivery pressures were reduced by pressure regulators installed at the process sample origination point. The pressure regulators and sample points were maintained in heated enclosures and the sample lines were heat traced to maintain the sample temperature above the dew point. Sample delivery pressures on the WGCU analyzer manifold were nominally between 35 and 50 psi. With the exception of the recovered CO_2 sample line, the four sample lines connecting the sampling manifold to the process sample lines at the analyzer housing were heat traced and maintained at a minimum of 250°F.

The TCRP unit syngas samples were collected directly from sample taps on the TCRP test skid through ¼" OD stainless steel tubing. Those syngas sample points were:

- Inlet Syngas to the TCRP Reactors (Clean Syngas to LTGC);
- Syngas from TCRP Reactor Vessel 1;
- Syngas from TCRP Reactor Vessel 2; and
- Syngas from TCRP Reactor Vessel 3.

The sample lines connecting the sampling manifold to the process sample points were heat traced and maintained at 350°F to 375°F (except as noted in Section 2.2 for Run 1). Sample delivery pressures were at the nominal process gas pressure of 350 psi.

The sampling system manifold was operated to allow continuous sample gas flow to a low pressure flare header, with a back-pressure control valve adjusted to maintain sample delivery pressures of 25 psi at the individual sample flow control valves to the sampling trains. Teflon tubing was used to convey the sample gas to the sampling trains described in this Section.

4.1 Ammonia and Hydrogen Cyanide

A gas impinger sampling train was used to collect NH_3 and HCN from the process gas streams. The sampling train consisted of two impingers containing 100 ml each of 0.5 Normal sulfuric acid for NH_3 collection, followed by four impingers containing 2% zinc acetate solution for hydrogen sulfide (H_2S) precipitation and HCN collection, an empty impinger to catch any carryover, and an impinger containing silica gel for removing moisture.

Gas sample volumes (nominally 5 dscf at 0.35 to 0.50 scfm) were measured by calibrated dry gas meters and the measured gas volume was adjusted to account for the removal of H_2S by the zinc acetate. The moisture content of the syngas was determined by measuring the weight gain of the impingers due to collected condensate.

The recovered samples for NH_3 were analyzed by the automated phenate colorimetric method (APHA Standard Method SM 4500 G NH_3). HCN samples were distilled and measured spectrophotometrically by EPA SW-846 Methods 9010 and 9014. Multiple impinger samples were collected during one run for each of the gas streams sampled. Of the four impingers containing zinc acetate solution, the first two impingers were recovered as the first fraction, the third zinc acetate impinger was recovered as the second fraction, and the last zinc acetate impinger was recovered as the third analytical fraction. These were recovered and analyzed separately for cyanide to determine the HCN collection efficiency. The results of the individual impinger analyses are presented and discussed in Section 5.0.

4.2 Trace Elements

Trace elements (As, Cd, Se, and Hg) were collected on coconut shell charcoal (CSC) sorbent following gas condensate removal by a small impinger in an ice bath. Gas samples (nominally 65 – 90 liters at 0.35 to 0.5 lpm) were collected through sorbent tubes containing three 1-gram sections in series, each separated by quartz wool. All individual sorbent tube sections were digested with the preceding quartz wool separator. The three digestate samples were then combined to form a single sample for analysis. Individual charcoal sections for one run from each sample gas stream were analyzed separately to determine collection efficiency and the trace element distribution in the sampling train.

Each charcoal sorbent and quartz wool section was digested in 20 ml of aqua regia (5 ml HCl + 15 ml HNO_3) for two hours at 85°C to 90°C. Each digestate was rinsed from the charcoal with deionized water and brought to a final volume of 100 ml. A 50 ml aliquot of the digestate was removed and preserved with 1 ml of 5% $KMnO_4$ for mercury analysis by cold vapor atomic absorption spectroscopy (CVAAS). The remaining 50 ml was analyzed for As, Cd, and Se using trace-level, inductively coupled plasma emission spectroscopy (ICPES). Combined digestate

samples representing the whole gas sample were prepared by combining the individual aliquots from each digestate fraction for mercury and ICPES elements.

The gas condensate collected from the first impinger in the trace elements sampling train was recovered using 0.1 Normal nitric acid and then analyzed directly by ICPES for As, Cd, and Se and by CVAAS for Hg. The clean syngas samples downstream of the LTGC typically did not produce a measurable volume of condensate in the first impinger, but the impinger was rinsed with 0.1 N HNO_3 and the rinse samples were analyzed by ICPES and CVAAS.

5.0 Quality Control Sample Results

Numerous samples were specifically collected and analyzed to assess the collection efficiency of the sampling trains and the accuracy and precision of the sampling and analytical measurements. HCN and metals sampling train fractions were recovered and analyzed separately for at least one run on each sample gas stream, and a matrix spike was prepared at the laboratory for each analytical batch. There was a direct effort to specify matrix spikes on gas samples representing a cross section of the various gas matrices sampled.

The collection efficiency for ammonia was not directly assessed since sufficient 0.5 N sulfuric acid solution was present to maintain the pH < 2 in both of the ammonia collecting impingers. Due to the extremely high affinity for ammonia in acidic aqueous solutions and that the use of sulfuric acid solutions is a well-established and accepted method for the collection of ammonia, analysis of individual impinger solutions was not considered necessary and was not performed.

This section presents and discusses the results of the fractional sample analyses and the other quality control samples that qualify the reported data.

5.1 HCN Collection Efficiency Measurements

The zinc acetate solutions used for collecting HCN (and precipitating H_2S) have been used successfully in syngas applications. However, in the absence of any promulgated test methods, performance measures were introduced in this test program to demonstrate the collection efficiency and effectiveness of the HCN sampling method for the variety of actual gas streams specifically measured in this test program.

To measure the HCN collection efficiency and the effect that H_2S and high CO_2 concentrations have on the zinc complexing solution, selected impingers were recovered separately and submitted for analysis. For the sample streams collected during the first five test runs on the WGCU, the contents of the first, the second and third, and the fourth zinc acetate impingers were the three fractions recovered and analyzed. For the TCRP gas samples, the contents of the first and second, the third, and the fourth impinger made up the three sample fractions.

Table 5-1 presents the sample gas streams, the test run, and the fractional train analysis results for HCN. The key performance objective is to find less than 10% of the total mass recovered in the final (fourth) zinc acetate impinger. Less than 2.5% of the total cyanide measured in the impinger train fractions was found in the final impinger sample, with the exception of the carbon dioxide stream which reported 8.6% breakthrough to the final impinger.

In addition, 78% of the total cyanide measured in the sour syngas sample was measured in the first impinger fraction where a significant portion of the zinc was precipitated as zinc sulfide. The zinc acetate method performance data indicate excellent capture of the HCN from the samples and support the application of the zinc acetate method for these process gas matrices.

5.2 Trace Element Collection Efficiency Measurements

The collection efficiency of the charcoal sorbent for the selected trace elements was assessed by analyzing the condensate fraction removed from the sample gas upstream of the charcoal sorbent tubes, and by analyzing each of the three sorbent tube sections separately. The distribution of the target analytes in the sampling train indicates the retention and collection efficiency.

Based on the results presented in this section, it would appear that analyte detection may be improved in future tests by analyzing only the condensate fraction and first charcoal bed, with the second charcoal bed (and possibly the third) analyzed only if the target analyte was detected in the first charcoal bed.

5.2.1 Arsenic

Table 5-2 presents the distribution of arsenic recovered in the trace elements sampling trains when the fractional samples were analyzed separately. Arsenic, when detected, was only detected in the condensate/impinger rinse fraction. For all other test runs where the three individual charcoal section digestates were combined to form a single digestate per train, arsenic was only detected in the condensate/impinger rinse fraction. Tables 5-3 and 5-4 present the arsenic results for the condensate and combined charcoal fractions. These fractional train analysis results provide the basis for determining the arsenic detection limit on the MDL for the condensate fraction only.

5.2.2 Cadmium

Cadmium was detected sporadically in about one quarter of the samples collected; 12 of 50 WGCU samples, and 6 of 24 TCRP samples. The distribution of cadmium measured in the fractional train samples was also sporadic and inconsistent. Table 5-5 presents the cadmium distribution in the trace elements sampling trains. Of the nine trains with individual fraction analysis, all of the measured cadmium was found in the charcoal sections with none detected in the condensate/rinse fraction.

However, cadmium distribution in the charcoal did not always follow the expected pattern with charcoal sections 1, 2 and 3 having decreasing mass, respectively. Cadmium was detected in the second and third tube sections at higher levels than the first section in three of the

four samples reporting measurable cadmium, albeit at relatively low concentrations. All of the cadmium measured in these fractional samples was less than three times the charcoal MDL. At these low concentrations and absent any clear pattern of detection, the degree of uncertainty in these results is high and the data may only suggest that cadmium is potentially present, but only at the limits of detection for this method.

Tables 5-6 and 5-7 present the cadmium for all other test runs where the three individual charcoal section digestates were combined to form a single digestate per train. Cadmium was detected in 18 samples, three of which were the condensate/rinse fraction only. Given the inconsistent findings of cadmium in both the charcoal and condensate/rinse fractions, the basis for determining the cadmium detection limit was to include the sum of the MDLs for the condensate/rinse and charcoal fractions combined.

5.2.3 Mercury

Mercury was measured in the charcoal fraction alone in 94% of the samples reporting measured mercury concentrations. Only four of sixty-seven samples reported any measurable mercury in the condensate/rinse fraction, and those measured concentrations accounted for between 4% and 26% of the total. Table 5-8 presents the mercury results for the condensate/rinse and individual charcoal sections. Tables 5-9 and 5-10 present the mercury results for the remaining test runs on the WGCU and TCRP gas streams. Mercury capture is overwhelmingly favored in the charcoal sample fraction. These results support the use of the charcoal sample MDL as the basis for the sample MDL.

5.2.4 Selenium

The distribution of selenium measured in the trace element sampling train for each of the sample sets is shown in Tables 5-11, 5-12, and 5-13. Selenium was measured only in the condensate/nitric acid impinger rinse fraction for all samples except those associated with the sour syngas. At the higher concentrations present in the sour syngas, selenium was also detected in the charcoal sorbent fraction in all samples.

The only sour syngas sample analyzed in separate train fractions was WGCU Run 1, which reported the lowest selenium concentration due to loss of gas condensate in the sampling manifold. Of the 6,190 ng of selenium measured in the Run 1 sample, 60.7% (3,760 ng) was found in the first charcoal section, 7.3% (450 ng) was found in the second charcoal section, and there was no selenium detected (<430 ng) in the third charcoal section.

Whether this distribution can be reasonable expected for the other samples is not clear from the available data. However, for the remaining sour syngas samples, the mass found in the condensate/rinse fraction accounts for at least 59% of the total selenium measured (WGCU Run 6), up to 97% (WGCU Run 3). More typically, the amount in the condensate/rinse fraction accounts for 70% to 95% of the total selenium.

The most selenium measured in the combined charcoal fraction was 101,400 ng during WGCU Run 6. Whether this sample, or any other combined charcoal fraction experienced any breakthrough of selenium is unknown. The results of the breakthrough tests conducted on the sour syngas during the February 2014 baseline tests (RTI Subcontract C000600823) indicate that samples containing up to 80,000 ng of selenium, greater than 98% of the total is collected in the condensate and first charcoal fractions, and an average of 80% is retained in the condensate fraction, similar to the findings during the WGCU test runs.

Clean syngas to the LTGC in Run 2 was found to have 5,360 ng of selenium in the condensate-rinse sample, and no detectable selenium in the first charcoal sorbent section. Selenium was measured at 2,176 ng/sample in the condensate fraction in the clean syngas to the LTGC during Run 1 of the TCRP test and again, no selenium was detected in the first charcoal section. Breakthrough of selenium to the charcoal fraction was not observed in any other gas samples downstream of the WGCU absorber, with the Run 5 sample of Clean Syngas to the TCRP being the only exception. For the clean syngas samples downstream of the WGCU absorber and the recovered CO_2 stream, the basis for the selenium MDL is the condensate fraction only.

5.3 Matrix Spike Results

In addition to the quality control samples analyzed to demonstrate the effectiveness of the sampling systems, analytical quality control samples were prepared for a measure of analytical precision and accuracy. Matrix spike and matrix spike duplicate (MS/MSD) samples were included for each preparation and analytical batch for ammonia, cyanide, and trace element analysis. The project data quality objectives for spike recovery are 80% - 120% of the known spike amount, and <20% for the relative percent difference (RPD) between duplicates.

The MS/MSD results for accuracy (% recovery) and precision (RPD) are presented in Tables 5-14 and 5-15 for NH_3/HCN and trace elements, respectively. The percent recovery results for the ammonia matrix spikes fell in the range of 86% to 109% recovery when sufficient spike levels were applied. There was one sample (Run 4 - Clean syngas to the LTGC) that failed to meet the 80%-120% spike recovery objective and it was directly related to an insufficient spiking level that was overwhelmed by the native concentration.

The ammonia spiking levels were increased from 5 mg/L to 3000 mg/L for the high ammonia samples from the March 2016 test period. This is an overcorrection by the lab to the low spike problem as the native concentration in the impinger samples was in the 100-350 mg/L range.

One sample that was arbitrarily selected by the laboratory for spiking was the 0.5 Normal sulfuric acid reagent blank. The MS was recovered at 96%, but the MSD was recovered at only 29%. This is a likely indication that the full strength acid reagent, undiluted by gas condensate or deionized water recovery rinses, was not completely neutralized by the analytical system and ammonia was not fully dissociated for color development. This sample does not reflect the more diluted sample matrix recovered from the sampling trains.

Matrix spikes in the zinc acetate impinger samples for cyanide analysis were recovered at acceptable levels between 102% and 114% when spiked at appropriate levels relative to their native concentration. Two of the four samples collected during the July – August 2015 test period were spiked at relatively low levels (<10%) and demonstrated spike recovery percentages outside of the 80%-120% objective. The two samples were from the clean syngas to the amine system and the recovered carbon dioxide stream. During the March 2016 test period, the recovered carbon dioxide stream was also selected for matrix spiking and the MS/MSD recovery was 106% and 102%. All other cyanide-spiked samples from the March 2016 test period were spiked appropriately for the native concentrations and were recovered within the data quality objectives.

The charcoal sorbent tubes used to collect the gas samples represent the only sample fraction available to determine the gas concentration, and consequently cannot be spiked directly before digestion. In lieu of spiking actual charcoal sorbent samples, blank charcoal sorbent tubes from the same carbon batch were spiked prior to digestion with liquid standards containing the trace elements of concern. The spiking solution was added to the digestion vial with the carbon and digested along with the samples in each digestion batch. The parent concentration for determining the spike recovery was the results for the charcoal media blank sample prepared in the same batch. All charcoal media blanks reported “non-detect” results for all analytes with only one exception for selenium. Non-detect results for blank charcoal concentrations were assigned the value of zero for the determination of the matrix spike recovery.

Table 5-15 presents the MS/MSD results for the charcoal digestion and analysis. The spiking solution was prepared by AECOM from single element standard solutions in a nitric acid/hydrochloric acid (3% HNO_3/1% HCl) matrix. The composition of the spiking standard was:

- Arsenic (2.0 ppm)
- Cadmium (1.0 ppm)
- Mercury (0.1 ppm)
- Selenium (3.0 ppm)

Three milliliters of this spiking solution was added to the charcoal digestion vials for matrix spikes. All of the spike recovery and RPD results were within the data quality objectives of 80%-120% recovery and <20% RPD for all elements except selenium in the July-August 2015 sample sets.

A solution preparation error was discovered when the results of the July-August 2015 samples were received. A dilution error in the preparation of an intermediate selenium standard resulted in selenium spikes being delivered at 10% of the desired spiking level. The resulting spiking level of 9 ppb was only two times the laboratory's MDL, and the selenium accuracy and precision data for the July-August 2015 preparation batches reflect the lower accuracy and precision associated with low level measurements. A new spiking standard was prepared and used for the March 2016 digestion batches and the selenium results for spike recovery were all within 91.3% to 97.1%.

The gas condensate samples were spiked at the analytical laboratory and the spike recovery results are shown in Tables 5-16 and 5-17. Low spike recoveries observed for the sour syngas condensate samples appear related to the low amounts of selenium spiked relative to the parent concentrations.

In summary, the valid matrix spike recovery data that are not disqualified for inappropriate spiking levels indicate that the accuracy and precision of the analytical measurements are within the stated data quality objectives and do not indicate any matrix effects that would measurably bias the analytical results.

5.4 Laboratory Check Standard Results

Laboratory check standards were prepared by the analytical laboratory and by AECOM during the digestion of the charcoal sorbent samples. Laboratory check standards and laboratory check standard duplicates (LCS/LCSD) are known standard samples processed through the entire sample preparation and analytical procedure and the results are used to demonstrate the accuracy and precision of that process. Since the LCS/LCSD standards are "clean" solutions that do not

involve the sample matrix, the performance expectations are greater. The data quality objectives reflect this higher expectation and the desire for demonstrating sample preparation and analytical systems are in control. The project data quality objectives for LCS/LCSD spike recovery are 90% - 110% of the known spike amount, and <20% for the relative percent difference (RPD) between duplicates.

Tables 5-18 and 5-19 present the LCS/LCSD recoveries for the NH_3/HCN and trace element analyses, respectively. The analytical laboratory's standard procedure is to prepare and analyze a LCS, but not an LCSD for ammonia or cyanide analyses. For the charcoal digestions, AECOM prepared the LCS/LCSD pair for each digestion batch.

All of the LCS recoveries for ammonia, cyanide, and mercury analyses in the gas condensate (Table 5-20) were within the 90%-110% data quality objective. For the trace element digestions, the LCS/LCSD recovery results are generally within the 90%-110% data quality objective. Where the LCS recovery objective was not met, many of the results are just outside (within 5%) of the objective range. The digestion batch identified as RTI-LCS-MTL-150803 is the only batch where the LCS and the LCSD recovery results for all four trace elements in both samples were outside of the recovery objective range. There is no clear explanation for this occurrence, and the accompanying MS/MSD samples prepared during the same digestion batch demonstrated spike recoveries for all four trace elements between 95% and 104%, well within the LCS/LCSD recovery objective. The spike recovery of the LCS/LCSD does not appear to be associated with the digestion process during that batch.

5.5 Blank Sample Results

Blank samples were analyzed representing sample digestions (Laboratory blanks and Laboratory Digestion blanks) and the reagents used during sample collection and recovery (Reagent Blanks). Table 5-20 presents the laboratory method blanks for the gas condensate samples prepared for mercury. All results were reported as non-detected. Table 5-21 provides the method blank results and the blank charcoal media results for each of the trace metal digestion batches. Table 5-22 presents the results of the reagent blank analyses. Only four blank samples reported hits above the MDL, one for cadmium and three for selenium. All of the results were at very low levels, less than two times the MDL.

5.6 Method Detection Limits

The method detection limit (MDL) values shown in Tables 5-23 and 5-24 and other tables throughout this report for "non-detect" (ND) results are based on the analytical laboratory's MDLs for a selected sample fraction and the lowest gas sample volume collected during this study. The primary sample fraction selected for determining each MDL is shown in Tables 5-23 and 5-24 and is based on the results of the fractional train analyses indicating the predominant sample fraction retaining the species of interest. The associated sample fraction volume and the minimum gas sample volume collected during the sampling events provide a reasonable and conservative estimate of the achievable measurement levels.

Samples collected with greater gas volumes will produce lower sample-specific MDLs. In some cases, results are reported below the MDLs shown in Tables 5-23 and 5-24. This reflects a circumstance where the laboratory reported a positive result above the MDL, and the actual gas sample volume led to a sample specific MDL that is lower than the conservative MDL. Rather than report a positive result as a "less than" value below the highest estimated MDL value, the actual result is reported.

Table 5-1. HCN Collection Efficiency

Process Gas Stream	Run No.	Train Fraction	Zinc Acetate Volume (ml)	Test Results	
				µg/sample	% of Total
Sour Syngas	WGCU-1	ZnOAC Impinger 1	700	347.1	78.1
		ZnOAC Impingers 2&3	400	93.9	21.1
		ZnOAC Impinger 4	200	3.4	0.8
Clean Syngas to LTGC	WGCU-2	ZnOAC Impinger 1	100	260.3	58.9
		ZnOAC Impingers 2&3	200	171.5	38.8
		ZnOAC Impinger 4	100	10.3	2.3
Clean Syngas to the Amine Scrubber Inlet	WGCU-3	ZnOAC Impinger 1	100	99.6	11.5
		ZnOAC Impingers 2&3	200	753.2	86.6
		ZnOAC Impinger 4	100	16.8	1.9
Clean Syngas from Amine Scrubber Outlet	WGCU-4	ZnOAC Impinger 1	100	1.2	67.1
		ZnOAC Impingers 2&3	200	ND (1.1)	<32.9
		ZnOAC Impinger 4	100	ND (0.7)	0.0
Recovered CO_2	WGCU-5	ZnOAC Impinger 1	100	463.6	42.2
		ZnOAC Impingers 2&3	200	540.5	49.2
		ZnOAC Impinger 4	100	93.9	8.6
Clean Syngas to the TCRP	TCRP-1	ZnOAC Impingers 1&2	200	120.5	91.7
		ZnOAC Impinger 3	100	9.0	6.8
		ZnOAC Impinger 4	100	1.9	1.5
Syngas from TCRP Reactor Vessel 1	TCRP-2	ZnOAC Impingers 1&2	200	191.3	88.1
		ZnOAC Impinger 3	100	20.6	9.5
		ZnOAC Impinger 4	100	5.2	2.4
Syngas from TCRP Reactor Vessel 2	TCRP-3	ZnOAC Impingers 1&2	200	158.1	90.6
		ZnOAC Impinger 3	100	12.7	7.3
		ZnOAC Impinger 4	100	3.7	2.1
Syngas from TCRP Reactor Vessel 3	TCRP-4	ZnOAC Impingers 1&2	200	283.5	88.2
		ZnOAC Impinger 3	100	31.2	9.7
		ZnOAC Impinger 4	100	6.8	2.1

Table 5-2. Arsenic Collection Efficiency

Process Gas Stream	Run No.	Train Fraction	As Test Results	
			ng/sample	% of Total
Sour Syngas	WGCU-1	Condensate/Imp. Rinse	ND (132)	NA
		Charcoal Section 1	ND (330)	NA
		Charcoal Section 2	ND (330)	NA
		Charcoal Section 3	ND (330)	NA
Clean Syngas to LTGC	WGCU-2	Condensate/Imp. Rinse	ND (132)	NA
		Charcoal Section 1	ND (330)	NA
		Charcoal Section 2	ND (330)	NA
		Charcoal Section 3	ND (330)	NA
Clean Syngas to the Amine Scrubber Inlet	WGCU-3	Condensate/Imp. Rinse	**132**	**100%**
		Charcoal Section 1	ND (330)	NA
		Charcoal Section 2	ND (330)	NA
		Charcoal Section 3	ND (330)	NA
Clean Syngas from Amine Scrubber Outlet	WGCU-4	Condensate/Imp. Rinse	**160**	**100%**
		Charcoal Section 1	ND (330)	NA
		Charcoal Section 2	ND (330)	NA
		Charcoal Section 3	ND (330)	NA
Recovered CO_2	WGCU-5	Condensate/Imp. Rinse	ND (132)	NA
		Charcoal Section 1	ND (330)	NA
		Charcoal Section 2	ND (330)	NA
		Charcoal Section 3	ND (330)	NA
Clean Syngas to the TCRP	TCRP-1	Condensate/Imp. Rinse	ND (132)	NA
		Charcoal Section 1	ND (330)	NA
		Charcoal Section 2	ND (330)	NA
		Charcoal Section 3	ND (330)	NA
Syngas from TCRP Reactor Vessel 1	TCRP-2	Condensate/Imp. Rinse	**184**	**100%**
		Charcoal Section 1	ND (330)	NA
		Charcoal Section 2	ND (330)	NA
		Charcoal Section 3	ND (330)	NA
Syngas from TCRP Reactor Vessel 2	TCRP-3	Condensate/Imp. Rinse	**208**	**100%**
		Charcoal Section 1	ND (330)	NA
		Charcoal Section 2	ND (330)	NA
		Charcoal Section 3	ND (330)	NA
Syngas from TCRP Reactor Vessel 3	TCRP-4	Condensate/Imp. Rinse	**244**	**100%**
		Charcoal Section 1	ND (330)	NA
		Charcoal Section 2	ND (330)	NA
		Charcoal Section 3	ND (330)	NA

Table 5-3. WGCU Process Gas Samples – Arsenic Results by Sampling Train Fraction (ng/sample)

Process Gas Stream	Train Fraction	Run 1	Run 2	Run 3	Run 4	Run 5	Run 6	Run 7	Run 8	Run 9	Run 10
Sour Syngas to WGCU Absorber	Condensate/Imp. Rinse	ND (132)	ND (132)	ND (132)	ND (132)	**428**	**860**	**420**	**412**	**548**	**404**
	Charcoal-Combined Digestate	NA	ND (990)	ND (990)	ND (990)	ND (990)	ND (990)	ND (990)	ND (990)	ND (990)	ND (990)
Clean Syngas from Absorber to LTGC	Condensate/Imp. Rinse	ND (132)	ND (132)	ND (132)	ND (132)	ND (132)	**404**	**272**	**276**	**340**	**260**
	Charcoal-Combined Digestate	ND (990)	NA	ND (990)	ND (990)	ND (990)	ND (990)	ND (990)	ND (990)	ND (990)	ND (990)
Syngas from LTGC System Outlet	Condensate/Imp. Rinse	ND (132)	ND (132)	**132**	ND (132)	ND (132)	ND (132)	ND (132)	ND (132)	ND (132)	ND (132)
	Charcoal-Combined Digestate	ND (990)	ND (990)	NA	ND (990)	ND (990)	ND (990)	ND (990)	ND (990)	ND (990)	ND (990)
Syngas from Amine System Outlet	Condensate/Imp. Rinse	ND (132)	ND (132)	ND (132)	**160**	ND (132)	ND (132)	ND (132)	ND (132)	ND (132)	ND (132)
	Charcoal-Combined Digestate	ND (990)	ND (990)	ND (990)	NA	ND (990)	ND (990)	ND (990)	ND (990)	ND (990)	ND (990)
Recovered CO_2	Condensate/Imp. Rinse	ND (132)	ND (132)	ND (132)	ND (132)	ND (132)	ND (132)	ND (132)	ND (132)	**160**	ND (132)
	Charcoal-Combined Digestate	ND (990)	ND (990)	ND (990)	ND (990)	NA	ND (990)	ND (990)	ND (990)	ND (990)	ND (990)

Table 5-4. TCRP Gas Samples – Arsenic Results by Sampling Train Fraction (ng/sample)

Process Gas Stream	Train Fraction	Run 1	Run 2	Run 3	Run 4	Run 5	Run 6
Clean Syngas to the TCRP	Condensate/Imp. Rinse	ND (132)	**300**	**228**	**224**	**248**	**412**
	Charcoal-Combined Digestate	NA	ND (990)	ND (990)	ND (990)	ND (990)	ND (990)
Syngas from TCRP Reactor Vessel 1	Condensate/Imp. Rinse	ND (132)	**184**	**304**	**304**	**340**	**348**
	Charcoal-Combined Digestate	ND (990)	NA	ND (990)	ND (990)	ND (990)	ND (990)
Syngas from TCRP Reactor Vessel 2	Condensate/Imp. Rinse	ND (132)	**248**	**208**	**256**	**284**	**312**
	Charcoal-Combined Digestate	ND (990)	ND (990)	NA	ND (990)	ND (990)	ND (990)
Syngas from TCRP Reactor Vessel 3	Condensate/Imp. Rinse	ND (132)	**216**	**204**	**244**	**216**	**392**
	Charcoal-Combined Digestate	ND (990)	ND (990)	ND (990)	NA	ND (990)	ND (990)

Table 5-5. Cadmium Collection Efficiency

Process Gas Stream	Run No.	Train Fraction	Cd Test Results	
			ng/sample	% of Total
Sour Syngas	WGCU-1	Condensate/Imp. Rinse	ND (20.4)	NA
		Charcoal Section 1	ND (51.0)	NA
		Charcoal Section 2	ND (51.0)	NA
		Charcoal Section 3	ND (51.0)	NA
Clean Syngas to LTGC	WGCU-2	Condensate/Imp. Rinse	ND (20.4)	NA
		Charcoal Section 1	ND (51.0)	NA
		Charcoal Section 2	ND (51.0)	NA
		Charcoal Section 3	ND (51.0)	NA
Clean Syngas to the Amine Scrubber Inlet	WGCU-3	Condensate/Imp. Rinse	ND (20.4)	NA
		Charcoal Section 1	**130**	**100%**
		Charcoal Section 2	ND (51.0)	NA
		Charcoal Section 3	ND (51.0)	NA
Clean Syngas from Amine Scrubber Outlet	WGCU-4	Condensate/Imp. Rinse	ND (20.4)	NA
		Charcoal Section 1	ND (51.0)	NA
		Charcoal Section 2	**77.0**	**100%**
		Charcoal Section 3	ND (51.0)	NA
Recovered CO_2	WGCU-5	Condensate/Imp. Rinse	ND (20.4)	NA
		Charcoal Section 1	ND (51.0)	NA
		Charcoal Section 2	ND (51.0)	NA
		Charcoal Section 3	ND (51.0)	NA
Clean Syngas to the TCRP	TCRP-1	Condensate/Imp. Rinse	ND (20.4)	NA
		Charcoal Section 1	**73.0**	**28.6**
		Charcoal Section 2	**82.0**	**32.2**
		Charcoal Section 3	**100**	**39.2**
Syngas from TCRP Reactor Vessel 1	TCRP-2	Condensate/Imp. Rinse	ND (20.4)	NA
		Charcoal Section 1	ND (51.0)	NA
		Charcoal Section 2	**64**	**33.0**
		Charcoal Section 3	**130**	**67.0**
Syngas from TCRP Reactor Vessel 2	TCRP-3	Condensate/Imp. Rinse	ND (20.4)	NA
		Charcoal Section 1	ND (51.0)	NA
		Charcoal Section 2	ND (51.0)	NA
		Charcoal Section 3	ND (51.0)	NA
Syngas from TCRP Reactor Vessel 3	TCRP-4	Condensate/Imp. Rinse	ND (20.4)	NA
		Charcoal Section 1	ND (51.0)	NA
		Charcoal Section 2	ND (51.0)	NA
		Charcoal Section 3	ND (51.0)	NA

Table 5-6. WGCU Process Gas Samples – Cadmium Results by Sampling Train Fraction (ng/sample)

Process Gas Stream	Train Fraction	Run 1	Run 2	Run 3	Run 4	Run 5	Run 6	Run 7	Run 8	Run 9	Run 10
Sour Syngas to WGCU Absorber	Condensate/Imp. Rinse	ND (20.4)	ND (20.4)	ND (20.4)	ND (20.4)	ND (20.4)	ND (20.4)	ND (20.4)	ND (20.4)	ND (20.4)	ND (20.4)
	Charcoal-Combined Digestate	NA	ND (153)	**165**	ND (153)	ND (153)	ND (153)	**360**	**240**	**360**	ND (153)
Clean Syngas from Absorber to LTGC	Condensate/Imp. Rinse	ND (20.4)	ND (20.4)	ND (20.4)	ND (20.4)	ND (20.4)	**28.4**	ND (20.4)	ND (20.4)	ND (20.4)	ND (20.4)
	Charcoal-Combined Digestate	ND (153)	NA	**840**	ND (153)	ND (153)	ND (153)	ND (153)	ND (153)	**171**	ND (153)
Syngas from LTGC System Outlet	Condensate/Imp. Rinse	ND (20.4)	ND (20.4)	ND (20.4)	ND (20.4)	ND (20.4)	ND (20.4)	ND (20.4)	ND (20.4)	ND (20.4)	ND (20.4)
	Charcoal-Combined Digestate	ND (153)	ND (153)	**130**	ND (153)	ND (153)	ND (153)	ND (153)	ND (153)	ND (153)	ND (153)
Syngas from Amine System Outlet	Condensate/Imp. Rinse	ND (20.4)	ND (20.4)	ND (20.4)	ND (20.4)	ND (20.4)	ND (20.4)	ND (20.4)	ND (20.4)	ND (20.4)	ND (20.4)
	Charcoal-Combined Digestate	**153**	ND (153)	ND (153)	**77.0**	ND (153)	ND (153)	ND (153)	ND (153)	ND (153)	ND (153)
Recovered CO_2	Condensate/Imp. Rinse	**22.8**	**38.0**	ND (20.4)	ND (20.4)	ND (20.4)	ND (20.4)	ND (20.4)	ND (20.4)	ND (20.4)	ND (20.4)
	Charcoal-Combined Digestate	ND (153)	ND (153)	ND (153)	ND (153)	NA	ND (153)	ND (153)	ND (153)	ND (153)	ND (153)

Table 5-7. TCRP Gas Samples – Cadmium Results by Sampling Train Fraction (ng/sample)

Process Gas Stream	Train Fraction	Run 1	Run 2	Run 3	Run 4	Run 5	Run 6
Clean Syngas to the TCRP	Condensate/Imp. Rinse	ND (20.4)	ND (20.4)	ND (20.4)	ND (20.4)	ND (20.4)	ND (20.4)
	Charcoal-Combined Digestate	**255**	**570**	ND (153)	ND (153)	ND (153)	ND (153)
Syngas from TCRP Reactor Vessel 1	Condensate/Imp. Rinse	ND (20.4)	ND (20.4)	ND (20.4)	ND (20.4)	ND (20.4)	ND (20.4)
	Charcoal-Combined Digestate	**159**	**194**	ND (153)	ND (153)	ND (153)	ND (153)
Syngas from TCRP Reactor Vessel 2	Condensate/Imp. Rinse	ND (20.4)	ND (20.4)	ND (20.4)	ND (20.4)	ND (20.4)	ND (20.4)
	Charcoal-Combined Digestate	ND (153)	ND (153)	NA	ND (153)	**180**	ND (153)
Syngas from TCRP Reactor Vessel 3	Condensate/Imp. Rinse	ND (20.4)	ND (20.4)	ND (20.4)	ND (20.4)	ND (20.4)	ND (20.4)
	Charcoal-Combined Digestate	ND (153)	**198**	ND (153)	NA	ND (153)	ND (153)

Table 5-8. Mercury Collection Efficiency

Process Gas Stream	Run No.	Train Fraction	Hg Test Results	
			ng/sample	% of Total
Sour Syngas	WGCU-1	Condensate/Imp. Rinse	ND (24.8)	NA
		Charcoal Section 1	**224**	**100%**
		Charcoal Section 2	ND (6.3)	NA
		Charcoal Section 3	ND (6.3)	NA
Clean Syngas to LTGC	WGCU-2	Condensate/Imp. Rinse	ND (24.8)	NA
		Charcoal Section 1	**510**	**100%**
		Charcoal Section 2	ND (6.3)	NA
		Charcoal Section 3	ND (6.3)	NA
Clean Syngas to the Amine Scrubber Inlet	WGCU-3	Condensate/Imp. Rinse	ND (24.8)	NA
		Charcoal Section 1	ND (6.3)	NA
		Charcoal Section 2	ND (6.3)	NA
		Charcoal Section 3	ND (6.3)	NA
Clean Syngas from Amine Scrubber Outlet	WGCU-4	Condensate/Imp. Rinse	ND (24.8)	NA
		Charcoal Section 1	**37.7**	**100%**
		Charcoal Section 2	ND (6.3)	NA
		Charcoal Section 3	ND (6.3)	NA
Recovered CO_2	WGCU-5	Condensate/Imp. Rinse	ND (24.8)	NA
		Charcoal Section 1	**32.6**	**100%**
		Charcoal Section 2	ND (6.3)	NA
		Charcoal Section 3	ND (6.3)	NA
Clean Syngas to the TCRP	TCRP-1	Condensate/Imp. Rinse	ND (24.8)	NA
		Charcoal Section 1	**326**	**100%**
		Charcoal Section 2	ND (6.3)	NA
		Charcoal Section 3	ND (6.3)	NA
Syngas from TCRP Reactor Vessel 1	TCRP-2	Condensate/Imp. Rinse	ND (24.8)	NA
		Charcoal Section 1	**918**	**100%**
		Charcoal Section 2	ND (6.3)	NA
		Charcoal Section 3	ND (6.3)	NA
Syngas from TCRP Reactor Vessel 2	TCRP-3	Condensate/Imp. Rinse	ND (24.8)	NA
		Charcoal Section 1	**796**	**100%**
		Charcoal Section 2	ND (6.3)	NA
		Charcoal Section 3	ND (6.3)	NA
Syngas from TCRP Reactor Vessel 3	TCRP-4	Condensate/Imp. Rinse	**40.0**	**4.2%**
		Charcoal Section 1	**918**	**95.8%**
		Charcoal Section 2	ND (6.3)	NA
		Charcoal Section 3	ND (6.3)	NA

Table 5-9. WGCU Process Gas Samples – Mercury Results by Sampling Train Fraction (ng/sample)

Process Gas Stream	Train Fraction	Run 1	Run 2	Run 3	Run 4	Run 5	Run 6	Run 7	Run 8	Run 9	Run 10
Sour Syngas to WGCU Absorber	Condensate/Imp. Rinse	ND (24.8)	ND (24.8)	ND (24.8)	ND (24.8)	ND (24.8)	ND (24.8)	ND (24.8)	ND (24.8)	ND (24.8)	ND (24.8)
	Charcoal-Combined Digestate	**224**	**275**	**337**	**294**	**367**	**102**	**510**	**480**	**450**	**390**
Clean Syngas from Absorber to LTGC	Condensate/Imp. Rinse	ND (24.8)	ND (24.8)	ND (24.8)	ND (24.8)	ND (24.8)	ND (24.8)	ND (24.8)	ND (24.8)	ND (24.8)	ND (24.8)
	Charcoal-Combined Digestate	**490**	**510**	**857**	**367**	**398**	**540**	**450**	**450**	**420**	**330**
Syngas from LTGC System Outlet	Condensate/Imp. Rinse	ND (24.8)	ND (24.8)	ND (24.8)	ND (24.8)	ND (24.8)	ND (24.8)	ND (24.8)	ND (24.8)	ND (24.8)	ND (24.8)
	Charcoal-Combined Digestate	ND (19.0)	ND (19.0)	NA	ND (19.0)	ND (19.0)	**60.0**	**135**	**69.0**	**102**	**36.0**
Syngas from Amine System Outlet	Condensate/Imp. Rinse	ND (24.8)	ND (24.8)	ND (24.8)	ND (24.8)	ND (24.8)	**44.0**	**104**	ND (24.8)	**40.0**	ND (24.8)
	Charcoal-Combined Digestate	**52.0**	**55.1**	**61.2**	**37.7**	ND (19.0)	**270**	**300**	**270**	**264**	**189**
Recovered CO_2	Condensate/Imp. Rinse	ND (24.8)	ND (24.8)	ND (24.8)	ND (24.8)	ND (24.8)	ND (24.8)	ND (24.8)	ND (24.8)	ND (24.8)	ND (24.8)
	Charcoal-Combined Digestate	**45.9**	**58.1**	**70.4**	**49.0**	**32.6**	**126**	**69.0**	**276**	**33.0**	ND (19.0)

Table 5-10. TCRP Gas Samples – Mercury Results by Sampling Train Fraction (ng/sample)

Process Gas Stream	Train Fraction	Run 1	Run 2	Run 3	Run 4	Run 5	Run 6
Clean Syngas to the TCRP	Condensate/Imp. Rinse	ND (24.8)	ND (24.8)	ND (24.8)	ND (24.8)	ND (24.8)	ND (24.8)
	Charcoal-Combined Digestate	**326**	**490**	**337**	**918**	**1,346**	**551**
Syngas from TCRP Reactor Vessel 1	Condensate/Imp. Rinse	ND (24.8)	ND (24.8)	ND (24.8)	ND (24.8)	ND (24.8)	ND (24.8)
	Charcoal-Combined Digestate	**1,071**	**918**	**490**	**490**	**520**	**520**
Syngas from TCRP Reactor Vessel 2	Condensate/Imp. Rinse	ND (24.8)	ND (24.8)	ND (24.8)	ND (24.8)	ND (24.8)	ND (24.8)
	Charcoal-Combined Digestate	**428**	**367**	**796**	**490**	**490**	**734**
Syngas from TCRP Reactor Vessel 3	Condensate/Imp. Rinse	ND (24.8)	ND (24.8)	ND (24.8)	**40.0**	ND (24.8)	ND (24.8)
	Charcoal-Combined Digestate	**551**	**1,530**	**1,836**	**918**	**581**	**110**

Table 5-11. Selenium Collection Efficiency

Process Gas Stream	Run No.	Train Fraction	Se Test Results	
			ng/sample	% of Total
Sour Syngas	WGCU-1	Condensate/Imp. Rinse	**1,980**	**32.0%**
		Charcoal Section 1	**3,760**	**60.7%**
		Charcoal Section 2	**450**	**7.3%**
		Charcoal Section 3	ND (430)	NA
Clean Syngas to LTGC	WGCU-2	Condensate/Imp. Rinse	**5,360**	**100%**
		Charcoal Section 1	ND (430)	NA
		Charcoal Section 2	ND (430)	NA
		Charcoal Section 3	ND (430)	NA
Clean Syngas to the Amine Scrubber Inlet	WGCU-3	Condensate/Imp. Rinse	**188**	**100%**
		Charcoal Section 1	ND (430)	NA
		Charcoal Section 2	ND (430)	NA
		Charcoal Section 3	ND (430)	NA
Clean Syngas from Amine Scrubber Outlet	WGCU-4	Condensate/Imp. Rinse	ND (172)	NA
		Charcoal Section 1	ND (430)	NA
		Charcoal Section 2	ND (430)	NA
		Charcoal Section 3	ND (430)	NA
Recovered CO_2	WGCU-5	Condensate/Imp. Rinse	**324**	**100%**
		Charcoal Section 1	ND (430)	NA
		Charcoal Section 2	ND (430)	NA
		Charcoal Section 3	ND (430)	NA
Clean Syngas to the TCRP	TCRP-1	Condensate/Imp. Rinse	**2,176**	**100%**
		Charcoal Section 1	ND (430)	NA
		Charcoal Section 2	ND (430)	NA
		Charcoal Section 3	ND (430)	NA
Syngas from TCRP Reactor Vessel 1	TCRP-2	Condensate/Imp. Rinse	**172**	**100%**
		Charcoal Section 1	ND (430)	NA
		Charcoal Section 2	ND (430)	NA
		Charcoal Section 3	ND (430)	NA
Syngas from TCRP Reactor Vessel 2	TCRP-3	Condensate/Imp. Rinse	ND (172)	NA
		Charcoal Section 1	ND (430)	NA
		Charcoal Section 2	ND (430)	NA
		Charcoal Section 3	ND (430)	NA
Syngas from TCRP Reactor Vessel 3	TCRP-4	Condensate/Imp. Rinse	**252**	**100%**
		Charcoal Section 1	ND (430)	NA
		Charcoal Section 2	ND (430)	NA
		Charcoal Section 3	ND (430)	NA

Table 5-12. WGCU Process Gas Samples – Selenium Results by Sampling Train Fraction (ng/sample)

Process Gas Stream	Train Fraction	Run 1	Run 2	Run 3	Run 4	Run 5	Run 6	Run 7	Run 8	Run 9	Run 10
Sour Syngas to WGCU Absorber	Condensate/Imp. Rinse	**1,980**	**65,200**	**157,200**	**131,200**	**80,800**	**149,200**	**74,400**	**51,600**	**63,600**	**48,400**
	Charcoal-Combined Digestate	**4,210**	**5,280**	**4,530**	**6,720**	**6,120**	**101,400**	**14,100**	**17,790**	**23,820**	**23,880**
Clean Syngas from Absorber to LTGC	Condensate/Imp. Rinse	**4,040**	**5,360**	**5,960**	**3,072**	**5,320**	**888**	**1,336**	**992**	**816**	**1,032**
	Charcoal-Combined Digestate	ND (1,290)	NA	ND (1,290)	ND (1,290)	ND (1,290)	ND (1,290)	ND (1,290)	ND (1,290)	ND (1,290)	ND (1,290)
Syngas from LTGC System Outlet	Condensate/Imp. Rinse	ND (172)	**484**	**188**	**180**	**1,280**	ND (172)	**184**	**284**	ND (172)	ND (172)
	Charcoal-Combined Digestate	ND (1,290)	ND (1,290)	NA	ND (1,290)	ND (1,290)	ND (1,290)	ND (1,290)	ND (1,290)	ND (1,290)	ND (1,290)
Syngas from Amine System Outlet	Condensate/Imp. Rinse	ND (172)	ND (172)	ND (172)	ND (172)	**728**	ND (172)	**216**	**232**	ND (172)	ND (172)
	Charcoal-Combined Digestate	ND (1,290)	ND (1,290)	ND (1,290)	NA	ND (1,290)	ND (1,290)	ND (1,290)	ND (1,290)	ND (1,290)	ND (1,290)
Recovered CO_2	Condensate/Imp. Rinse	**248**	**364**	ND (172)	**236**	**324**	ND (172)	**188**	**356**	**280**	ND (172)
	Charcoal-Combined Digestate	ND (1,290)	ND (1,290)	ND (1,290)	ND (1,290)	NA	ND (1,290)	ND (1,290)	ND (1,290)	ND (1,290)	ND (1,290)

Table 5-13. TCRP Gas Samples – Selenium Results by Sampling Train Fraction (ng/sample)

Process Gas Stream	Train Fraction	Run 1	Run 2	Run 3	Run 4	Run 5	Run 6
Clean Syngas to the TCRP	Condensate/Imp. Rinse	**2,176**	**2,784**	**804**	**1,784**	**1,696**	**468**
	Charcoal-Combined Digestate	NA	ND (1,290)	ND (1,290)	ND (1,290)	**1,350**	ND (1,290)
Syngas from TCRP Reactor Vessel 1	Condensate/Imp. Rinse	ND (172)	**172**	**356**	**320**	**420**	**464**
	Charcoal-Combined Digestate	ND (1,290)	NA	ND (1,290)	ND (1,290)	ND (1,290)	ND (1,290)
Syngas from TCRP Reactor Vessel 2	Condensate/Imp. Rinse	ND (172)	**240**	ND (172)	**296**	**332**	**304**
	Charcoal-Combined Digestate	ND (1,290)	ND (1,290)	NA	ND (1,290)	ND (1,290)	ND (1,290)
Syngas from TCRP Reactor Vessel 3	Condensate/Imp. Rinse	ND (172)	**228**	**176**	**252**	**288**	**440**
	Charcoal-Combined Digestate	ND (1,290)	ND (1,290)	ND (1,290)	NA	ND (1,290)	ND (1,290)

Table 5-14. Matrix Spiked Sample Results – NH_3 / HCN [1]

Parameter	Sample ID	Parent Conc.	Units	Amount Spiked	MS		MSD		RPD
					Result	% Recvry	Result	% Recvry	%
Ammonia	WGCU-ASO-NH3-H2SO4-1	3.73	mg/L	5.00	9.13	108	9.16	109	0
	WGCU-CG-NH3-H2SO4-4	279	mg/L	5.00	**NC [2]**	**NC**	**NC**	**NC**	**NC**
	TCRP-R1-NH3-H2SO4-2	187	mg/L	3000	2880	90	2900	90	0
	TCRP-SG-NH3-H2SO4-4	200	mg/L	3000	2790	86	2930	91	5
	TCRP-R3-NH3-H2SO4-6	337	mg/L	3000	3120	93	3010	89	4
	WGCU-CG-NH3-H2SO4-6	239	mg/L	3000	2910	89	2860	87	2
	WGCU-ASI-NH3-H2SO4-7	0.0937	mg/L	5.00	4.76	93	4.75	93	0
	WGCU-ASI-NH3-H2SO4-9	0.268	mg/L	5.00	5.1	97	5.43	103	6
	WGCU-ASO-NH3-H2SO4-10	337	mg/L	3000	3120	93	3010	89	4
	RTI-NH3-H2SO4-RB2	0.0761	mg/L	5.00	4.88	96	1.52	**29 Q**	**105 Q**
Cyanide	WGCU-SG-HCN-ZNOAC-2	210	µg/L	100	318	108	326	117	3
	WGCU-ASI-HCN-ZNOAC-3b	3100	µg/L	200 [3]	3040	**-21 Q**	2940	**-69 Q**	3
	WGCU-CO2-HCN-ZNOAC-4	990	µg/L	100 [3]	1150	**160 Q**	1130	**139 Q**	2
	WGCU-ASO-HCN-ZNOAC-5	62	µg/L	100	166	104	164	102	1
	TCRP-SG-HCN-ZNOAC-2	320	µg/L	500	862	107	860	107	0
	TCRP-R2-HCN-ZNOAC-4	360	µg/L	500	852	98	884	104	4
	WGCU-SG-HCN-ZNOAC-6	950	µg/L	500	1520	114	1520	114	0
	WGCU-CG-HCN-ZNOAC-7	540	µg/L	500	1080	109	1050	102	3
	WGCU-CO2-HCN-ZNOAC-8	19	µg/L	500	547	106	529	102	3

[1] The data quality objective for matrix spikes is 80% – 120% recovery of the known spiked amount. The objective for precision between duplicates is <20% relative percent difference.

[2] NC = not calculated. The spiking level was insufficient relative to the native parent sample concentration.

[3] The spiking level was insufficient relative to the native parent sample concentration.

Table 5-15. Matrix Spiked Sample Results – Trace Elements [1]

Parameter	Preparation Batch ID	Parent Conc.	Units	Amount Spiked	MS		MSD		RPD
					Result	% Recvry	Result	% Recvry	%
Arsenic	RTI-MS-MTL-150730	ND	µg/L	60	53.1	88.5	51.6	86.0	2.9
	RTI-MS-MTL-150731	ND	µg/L	60	50.5	84.2	49.9	83.2	1.2
	RTI-MS-MTL-150801	ND	µg/L	60	51.1	85.2	51.4	85.7	0.6
	RTI-MS-MTL-150802	ND	µg/L	60	57.3	95.5	57.8	96.3	0.9
	RTI-MS-MTL-150803	ND	µg/L	60	58.8	98.0	57.6	96.0	2.1
	RTI-MS-MTL-150804	ND	µg/L	60	59.5	99.2	58.0	96.7	2.6
	RTI-MS-MTL-150805	ND	µg/L	60	59.7	100	57.5	95.8	3.8
Cadmium	RTI-MS-MTL-150730	ND	µg/L	30	30	100	29.9	99.7	0.3
	RTI-MS-MTL-150731	ND	µg/L	30	28.7	95.7	28.8	96.0	0.3
	RTI-MS-MTL-150801	ND	µg/L	30	29.7	99.0	30.6	102	3.0
	RTI-MS-MTL-150802	ND	µg/L	30	30.9	103	31.0	103	0.3
	RTI-MS-MTL-150803	ND	µg/L	30	31.3	104	30.8	103	1.6
	RTI-MS-MTL-150804	ND	µg/L	30	30.6	102	30.1	100	1.6
	RTI-MS-MTL-150805	ND	µg/L	30	31.3	104	30.5	102	2.6
Mercury	RTI-MS-MTL-150730	ND	µg/L	3	2.55	85.0	2.65	88.4	3.9
	RTI-MS-MTL-150731	ND	µg/L	3	2.65	88.4	2.55	85.0	3.9
	RTI-MS-MTL-150801	ND	µg/L	3	2.75	91.8	2.75	91.8	0
	RTI-MS-MTL-150802	ND	µg/L	3	2.96	98.6	2.96	98.6	0
	RTI-MS-MTL-150803	ND	µg/L	3	3.06	102	2.96	98.6	3.4
	RTI-MS-MTL-150804	ND	µg/L	3	2.86	95.2	2.96	98.6	3.5
	RTI-MS-MTL-150805	ND	µg/L	3	2.96	98.6	2.86	95.2	3.5
Selenium	RTI-MS-MTL-150730	**5.3**	µg/L	9	12.1	**75.6 Q**	14.0	96.7	**24.5 Q**
	RTI-MS-MTL-150731	ND	µg/L	9	9.3	103	7.6	84.4	**20.1 Q**
	RTI-MS-MTL-150801	ND	µg/L	9	11.0	**122 Q**	11.0	**122 Q**	0
	RTI-MS-MTL-150802	ND	µg/L	90	84.9	94.3	85.0	94.4	0.1
	RTI-MS-MTL-150803	ND	µg/L	90	87.4	97.1	85.7	95.2	2.0
	RTI-MS-MTL-150804	ND	µg/L	90	82.2	91.3	82.7	91.9	0.6
	RTI-MS-MTL-150805	ND	µg/L	90	87.3	97.0	85.4	94.9	2.2

[1] The data quality objective for matrix spikes is 80% – 120% recovery of the known spiked amount. The objective for precision between duplicates is <20% relative percent difference.

Table 5-16. Post-Digestion Spike Results – Trace Elements (Condensate)

Parameter	Sample ID	Parent Conc.	Units	Amount Spiked	PDS		PDSD		RPD
					Result	% Recvry	Result	% Recvry	%
Arsenic	WGCU-SG-MTL-COND-3	ND	µg/L	100	82.5	82.5	86.4	86.4	4.6
	WGCU-SG-MTL-COND-4	ND	µg/L	100	96.6	96.6	96.8	96.8	0.2
	TCRP-SG-MTL-COND-3	5.74	µg/L	100	109	104	109	103	1.0
	TCRP-SG-MTL-COND-4	5.64	µg/L	100	108	102	111	105	2.9
	WGCU-CG-MTL-COND-10	6.49	µg/L	100	115	108	114	108	0
	WGCU-SG-MTL-COND-7	10.5	µg/L	100	112	101	110	99.6	1.4
Cadmium	WGCU-SG-MTL-COND-3	ND	µg/L	50	53.7	107	53.5	107	0.4
	WGCU-SG-MTL-COND-4	ND	µg/L	50	54.7	109	55.0	110	0.9
	TCRP-SG-MTL-COND-3	0.11	µg/L	50	52.1	104	51.8	103	1.0
	TCRP-SG-MTL-COND-4	ND	µg/L	50	50.6	101	51.5	103	2.0
	WGCU-CG-MTL-COND-10	ND	µg/L	50	52.3	105	52.7	105	0
	WGCU-SG-MTL-COND-7	ND	µg/L	50	48.0	95.9	47.3	94.7	1.3
Selenium	WGCU-SG-MTL-COND-3	3926	µg/L	150	4036	**72.9 Q**	3991	**43.0 Q**	**51.6 Q**
	WGCU-SG-MTL-COND-4	3283	µg/L	150	3350	**44.8 Q**	3341	**38.2 Q**	**15.9 Q**
	TCRP-SG-MTL-COND-3	20.1	µg/L	150	195	116	197	118	1.7
	TCRP-SG-MTL-COND-4	44.6	µg/L	150	219	116	222	118	1.7
	WGCU-CG-MTL-COND-10	25.8	µg/L	150	204	119	204	119	0
	WGCU-SG-MTL-COND-7	1864	µg/L	150	2008	96.0	2003	92.9	3.3

Table 5-17. Matrix Spiked Sample Results – Mercury (Condensate)

Parameter	Sample ID	Parent Conc.	Units	Amount Spiked	MS		MSD		RPD
					Result	% Recvry	Result	% Recvry	%
Mercury	WGCU-ASO-MTL-COND-2	ND	µg/L	1.00	1.00	100	1.06	106	5.8
	WGCU-SG-MTL-COND-5	ND	µg/L	1.00	0.982	98.2	0.984	98.4	0.2
	TCRP-R2-MTL-COND-1	ND	µg/L	10	9.76	97.6	9.65	96.5	1.1
	TCRP-R1-MTL-COND-6	ND	µg/L	10	9.34	93.4	9.28	92.8	0.6
	WGCU-ASO-MTL-COND-10	ND	µg/L	10	9.88	98.8	10.2	102	3.2
	WGCU-ASI-MTL-COND-6	ND	µg/L	10	10.4	104	10.4	104	0

Table 5-18. Laboratory Control Sample Results – NH_3 / HCN

Parameter	Sample ID	Units	Amount Spiked	LCS		LCSD		RPD
				Result	% Recvry	Result	% Recvry	%
Ammonia	LCS 490-276862/5	µg/L	5.0	5.34	107	NA	NA	NA
	LCS 490-276887/4 LCSD 490-276887/5	µg/L	5.0	5.40	108	5.37	107	1
	LCS 490-327736/4	µg/L	5.0	5.48	110	NA	NA	NA
	LCS 490-328035/4	µg/L	5.0	5.49	110	NA	NA	NA
	LCS 490-328036/4	µg/L	5.0	5.49	110	NA	NA	NA
	LCS 490-329137/4	µg/L	5.0	4.95	99.0	NA	NA	NA
	LCS 490-329149/4	µg/L	5.0	5.34	107	NA	NA	NA
Cyanide	HLCS 180-151434/2-A	µg/L	250	248	99.2	NA	NA	NA
	LCS 151434/3-A	µg/L	200	199	99.5	NA	NA	NA
	LLCS 151434/1-A	µg/L	50	50.5	101	NA	NA	NA
	HLCS 180-151833/2-A	µg/L	250	257	103	NA	NA	NA
	LCS 151833/3-A	µg/L	200	206	103	NA	NA	NA
	LLCS 151833/1-A	µg/L	50	51.2	102	NA	NA	NA
	HLCS 180-172251/2-A	µg/L	250	240	96.0	NA	NA	NA
	LCS 172251/3-A	µg/L	200	195	97.5	NA	NA	NA
	LLCS 172251/1-A	µg/L	50	49.6	99.2	NA	NA	NA
	HLCS 180-172345/2-A	µg/L	250	241	96.4	NA	NA	NA
	LCS 172345/3-A	µg/L	200	200	100	NA	NA	NA
	LLCS 172345/1-A	µg/L	50	49.9	99.8	NA	NA	NA
	HLCS 180-171992/2-A	µg/L	250	258	103	NA	NA	NA
	LCS 171992/3-A	µg/L	200	210	105	NA	NA	NA
	LLCS 171992/1-A	µg/L	50	52.1	104	NA	NA	NA

Table 5-19. Laboratory Control Sample Results – Trace Elements

Parameter	Sample ID	Units	Amount Spiked	LCS		LCSD		RPD
				Result	% Recvry	Result	% Recvry	%
Arsenic	RTI-LCS-MTL-150730	µg/L	100	90.5	90.5	91.9	91.9	1.5
	RTI-LCS-MTL-150731	µg/L	100	90.2	90.2	89.8	**89.8 Q**	0.4
	RTI-LCS-MTL-150801	µg/L	100	89.0	**89.0 Q**	87.7	**87.7 Q**	1.5
	RTI-LCS-MTL-150802	µg/L	100	83.9	**83.9 Q**	101	101	18.5
	RTI-LCS-MTL-150803	µg/L	100	56.3	**56.3 Q**	39.0	**39.0 Q**	**36.3 Q**
	RTI-LCS-MTL-150804	µg/L	100	98.4	98.4	87.6	**87.6 Q**	11.6
	RTI-LCS-MTL-150805	µg/L	100	102	102	101	101	1.0
Cadmium	RTI-LCS-MTL-150730	µg/L	50	50.7	101	51.7	103	2.0
	RTI-LCS-MTL-150731	µg/L	50	51.0	102	50.6	101	0.8
	RTI-LCS-MTL-150801	µg/L	50	51.3	103	50.7	101	1.2
	RTI-LCS-MTL-150802	µg/L	50	44.1	**88.2 Q**	53.0	106	18.3
	RTI-LCS-MTL-150803	µg/L	50	29.6	**59.2 Q**	19.9	**39.8 Q**	**39.2 Q**
	RTI-LCS-MTL-150804	µg/L	50	51.2	102	45.7	91.4	11.4
	RTI-LCS-MTL-150805	µg/L	50	53.4	107	53.3	107	0.2
Mercury	RTI-LCS-MTL-150730	µg/L	5	4.90	97.9	4.59	91.8	6.5
	RTI-LCS-MTL-150731	µg/L	5	4.90	97.9	4.79	95.9	2.1
	RTI-LCS-MTL-150801	µg/L	5	5.20	104	4.90	97.9	6.1
	RTI-LCS-MTL-150802	µg/L	5	6.53	**131 Q**	5.61	**112 Q**	15.1
	RTI-LCS-MTL-150803	µg/L	5	7.45	**149 Q**	8.47	**169 Q**	12.8
	RTI-LCS-MTL-150804	µg/L	5	5.20	104	5.92	**118 Q**	12.8
	RTI-LCS-MTL-150805	µg/L	5	5.30	106	5.20	104	1.9
Selenium	RTI-LCS-MTL-150730	µg/L	15	17.2	**115 Q**	17.6	**117 Q**	2.3
	RTI-LCS-MTL-150731	µg/L	15	14.5	96.7	13.4	**89.3 Q**	7.9
	RTI-LCS-MTL-150801	µg/L	15	13.8	92.0	14.7	98.0	6.3
	RTI-LCS-MTL-150802	µg/L	150	124	**82.7 Q**	147	98.0	17.0
	RTI-LCS-MTL-150803	µg/L	150	84.1	**56.1 Q**	59.2	**39.5 Q**	**34.8 Q**
	RTI-LCS-MTL-150804	µg/L	150	143	95.3	128	**85.3 Q**	11.1
	RTI-LCS-MTL-150805	µg/L	150	151	101	147	98.0	2.7

Table 5-20. Laboratory Blank and LCS Sample Results – Trace Elements (Condensate)

Parameter	Preparation Batch ID	Units	Method Blank	Amount Spiked	LCS	
					Result	% Recvry
Mercury	5231022	µg/L	ND (0.20)	5.00	5.09	102
	5231028	µg/L	ND (0.20)	5.00	5.25	105
	6081012	µg/L	ND (0.20)	5.00	5.07	101
	6081014	µg/L	ND (0.20)	5.00	5.07	101
	6083022	µg/L	ND (0.20)	5.00	5.36	107

Table 5-21. Laboratory Digestion Blank Sample Results – Trace Elements

Parameter	Sample ID	Method Blank	Charcoal Blank
		Result (µg/L)	Result (µg/L)
Arsenic	RTI-MB / RB-MTL-150730	ND (3.3)	ND (3.3)
	RTI-MB / RB-MTL-150731	ND (3.3)	ND (3.3)
	RTI-MB / RB-MTL-150801	ND (3.3)	ND (3.3)
	RTI-MB / RB-MTL-150802	ND (3.3)	ND (3.3)
	RTI-MB / RB-MTL-150803	ND (3.3)	ND (3.3)
	RTI-MB / RB-MTL-150804	ND (3.3)	ND (3.3)
	RTI-MB / RB-MTL-150805	ND (3.3)	ND (3.3)
Cadmium	RTI-MB / RB-MTL-150730	ND (0.51)	ND (0.51)
	RTI-MB / RB-MTL-150731	ND (0.51)	ND (0.51)
	RTI-MB / RB-MTL-150801	**0.78**	ND (0.51)
	RTI-MB / RB-MTL-150802	ND (0.51)	ND (0.51)
	RTI-MB / RB-MTL-150803	ND (0.51)	ND (0.51)
	RTI-MB / RB-MTL-150804	ND (0.51)	ND (0.51)
	RTI-MB / RB-MTL-150805	ND (0.51)	ND (0.51)
Mercury	RTI-MB / RB-MTL-150730	ND (0.062)	ND (0.062)
	RTI-MB / RB-MTL-150731	ND (0.062)	ND (0.062)
	RTI-MB / RB-MTL-150801	ND (0.062)	ND (0.062)
	RTI-MB / RB-MTL-150802	ND (0.062)	ND (0.062)
	RTI-MB / RB-MTL-150803	ND (0.062)	ND (0.062)
	RTI-MB / RB-MTL-150804	ND (0.062)	ND (0.062)
	RTI-MB / RB-MTL-150805	ND (0.062)	ND (0.062)
Selenium	RTI-MB / RB-MTL-150730	**4.7**	**5.3**
	RTI-MB / RB-MTL-150731	ND (4.3)	ND (4.3)
	RTI-MB / RB-MTL-150801	ND (4.3)	ND (4.3)
	RTI-MB / RB-MTL-150802	ND (4.3)	ND (4.3)
	RTI-MB / RB-MTL-150803	ND (4.3)	ND (4.3)
	RTI-MB / RB-MTL-150804	ND (4.3)	ND (4.3)
	RTI-MB / RB-MTL-150805	ND (4.3)	ND (4.3)

Table 5-22. Reagent Blank Results

Parameter	Sample ID	Result	Units
Ammonia	RTI-NH3-H2SO4-RB	ND (0.05)	mg/L
	RTI-NH3-H2O-RB	ND (0.05)	mg/L
Cyanide	RTI-HCN-ZnOAc-RB	ND (3.8)	µg/L
	RTI-HCN-H2O-RB	ND (3.8)	µg/L
Arsenic	RTI-MTL-COND-RB	ND (3.3)	µg/L
	WGCU-RB-MTL-HNO3	ND (3.3)	µg/L
Cadmium	RTI-MTL-COND-RB	ND (0.51)	µg/L
	WGCU-RB-MTL-HNO3	ND (0.51)	µg/L
Mercury	RTI-MTL-COND-RB	ND (0.62)	µg/L
	WGCU-RB-MTL-HNO3	ND (0.62)	µg/L
Selenium	RTI-MTL-COND-RB	5.4	µg/L
	WGCU-RB-MTL-HNO3	ND (4.3)	µg/L

Table 5-23. Method Detection Limits for Trace Elements [1]

Parameter	Primary Sample Fraction [2]	Analytical MDL (µg/L)	Sample Volume (ml)	MDL (ppbv-dry)
Arsenic	Condensate	3.3	40	0.66
Cadmium	Condensate + Charcoal	0.51	40 + 300	0.58
Mercury	Charcoal	0.062	306	0.036
Selenium	Condensate	4.3	40	0.82

[1] The MDLs are based on a 63.8 dry standard liter sample volume, the minimum gas sample volume collected during these tests. Greater gas sample volumes will result in lower sample-specific MDLs.

[2] The MDLs are also based on the analytical detection limits for the primary sampling train fractions found to contain the element of interest at moderate to low concentrations.

Table 5-24. Method Detection Limits for NH_3 and HCN [1]

Parameter	Sample Fraction	Analytical MDL (µg/L)	Impinger Sample Volume (ml)	Gas Sample Volume (dscf)	MDL (ppmv-dry)
Ammonia	H_2SO_4 Impingers	50	400	6.8	0.18
Hydrogen Cyanide	Zinc Acetate Impingers	3.8	650	6.8	0.0077

[1] The MDLs are based on a sample gas volume of 6.8 dry standard cubic feet (the minimum NH_3/HCN gas sample volume collected during these tests) and a nominal recovered impinger sample volume. Greater gas sample volumes will result in lower sample-specific MDLs.

Appendix B:
Questionnaire

RTI Warm Syngas Project
Improvements to Gen #2 Deployment
Questionnaire

GENERAL:

Name:
Title: President
Email Address:

Company:
Phone No:

Please give a brief description of your current title/position and what specific role you provided for the Gen #1 deployment at the TECO facility in Mulberry, Florida.

QUESTIONNAIRE OBJECTIVE:

To prepare our team and stakeholders for alignment to the lessons learned from Gen #1
To collect information about the process, operational and facility requirements for Gen #1
To gain a general understanding of specific improvements required for Gen #2

CONTENTS:

This questionnaire has four sections:

1. **Introduction**
2. **Design Improvements**
3. **Gaps and Constraints**
4. **Risk Factors**

Questionnaires will be distributed to all interview participants prior to the Gen#2 workshop. This will allow all team members/stakeholders an opportunity to have input in the identification of required improvements to Gen #2 deployment.

Any response is appreciated and we will receive comments in any form. You can email or write (fax) your response. A timely response is needed in order to compile the information before the workshop.

RTI Warm Syngas Project
Improvements to Gen #2 Deployment
Questionnaire

Section 2 – Design Improvements

- Are the core design documents in a usable form or do they need improvements?

  1. Process Descriptions, Capacities, Product Specifications
  2. Mass and Energy Balance
  3. Process Modeling
  4. Block Flow Diagrams
  5. Utilities and Required Site Services

- What unit operations or WBS areas need improvements? Rank in importance if possible.

  1. 100 – Desulfurization
  2. 400 – Water Gas Shift
  3. 500 – Amine
  4. 900 - Utilities

- Can you identify any process safety improvements for design engineering? For startup?

- Would you recommend a change in the selected metallurgies? If yes, describe.

RTI Warm Syngas Project
Improvements to Gen #2 Deployment
Questionnaire

- Do you think that the proper design standards were applied? If not, what should change?

- Would you rate the field instruments and local controls as adequate or deficient? What improvements should be incorporated for Gen #2?

- Are you comfortable with the process transformations such as yield, residence time, and performance? If no, describe improvements required?

- Does the next project need additional design input from any third party organizations?

- Would you change any of the key equipment selections? If yes, describe.

RTI Warm Syngas Project
Improvements to Gen #2 Deployment
Questionnaire

Section 3 – Gaps and Constraints

- Can you identify any design or operational gaps that required significant field modifications from the original design and installation?

- Could a high fidelity 3D model provide needed insight into improved equipment access and result in a decrease in personnel safety exposure?

- Can you identify any site constraints or restrictions that had a negative impact to the **construction** installation?

- Can you identify any site constraints or restrictions that had a negative impact to the **startup and/or operations**?

- Can you identify any environmental restrictions or constraints that could be reduced in Gen #2?

RTI Warm Syngas Project
Improvements to Gen #2 Deployment
Questionnaire

Section 3 – Risk Factors

- Did the Gen #1 project have clear definitions of roles and responsibilities? If not, what is needed for Gen #2 deployment?

- Did the project have the proper execution strategy for contracts, allocation of risks, shared incentives, and pain for poor performance? If not, what needs to improve?

- What improvements can you suggest for the startup sequencing, procedures for cold and hot starts, and warm standby conditions?

- What improvements and/or operational best practices can you suggest for a safe emergency shut down?

- Can any of the key equipment or systems be converted from custom design and fabrications to off-the-shelf supply?

Section 3 – Risk Factors

RTI Warm Syngas Project
Improvements to Gen #2 Deployment
Questionnaire

- Gen #1 is considered to be a 50 MW unit. Should Gen #2 be a larger scale or the same? If larger, what scale and what would be the challenges?

- What is the hallmark of the Gen #1 deployment?

  1. Great team performance?
  2. Achieved 2500 hours of integrated run time?
  3. Proved economical carbon sequestration technology?
  4. DOE objectives were achieved?

- Does the Gen #1 program represent a minimum effective design and a low cost solution? If not, what cost reductions could be incorporated into the Gen #2 program?

- Describe any other improvements that should carry forward to the Gen #2 program.