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Integrated Operation of a Pressurized Fixed Bed Gasifier and
Hot Gas Desulfurization System

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Authors:

Cook, C.S.
Gal, E.
Furman, A.H.
Ayala, R.

Contractor:

GE Environmental Services, Inc.
200 N. Seventh Street
Lebanon, PA 17042

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CONTRACT INFORMATION

Contract Number DE-AC21-87MC23170

Contractor GE Environmental Services, Inc.
200 N. Seventh Street
Lebanon, Pennsylvania 17042
(717) 274-7000

Contractor Program Manager Dr. Charles S. Cook

Principal Investigators Dr. Eli Gal
Mr. Anthony H. Furman
Dr. Raul Ayala

METC Project Manager Dr. Justin Beeson

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SCHEDULE/MILESTONES

OBJECTIVES

The primary objective of this contract continues to be the demonstration of high temperature fuel gas desulfurization and particulate removal using a moving bed process with a regenerable metal oxide sorbent. The fuel gas source for test operation is a fixed bed, air blown gasifier located at GE Corporate Research and Development in Schenectady, New York. The demonstration project also includes the design, construction, installation and test operation of a gas turbine simulator which includes a modified GE MS6000 type gas turbine combustor and a film cooled, first stage LM 6000 nozzle assembly. The hot gas cleanup (HGCU) system and the gas turbine simulator have been designed to operate with the full 8000 lb/hr fuel gas flow from the gasification of 1800 lb/hr of coal at 280 psig and 1000 to 1150 F. An advanced formulation of zinc ferrite as well as zinc titanate have been used as the regenerable metal oxide sorbents in testing to date. Demonstration of halogen removal as well as

characterization of alkali and heavy metal concentrations in the fuel gas remain objectives, as well.

BACKGROUND

Fuel gas derived from coal contains sulfur mainly in the form of H_2S and COS . Mixed metal oxide sorbents react with the gaseous sulfur species forming regenerable metal sulfides under reducing conditions in the temperature range from 800 to 1200 F. GE Environmental Services, Inc. (GEESI) has developed a patented moving bed process, which includes the regeneration of the sorbent material along with the production of a marketable sulfur byproduct stream, and has demonstrated the process at 2.5 MWe equivalent scale. The history and continuing test operation of the GEESI moving bed process has been described previously by Smith, et. al. (1987) and Cook, et. al. (1988), (1989), (1990), (1991).

Figure 1: GE Gasifier/Hot Gas Cleanup/Turbine Simulator Process Flow Diagram

PROJECT DESCRIPTION

A demonstration facility has been constructed and operated at GE Corporate Research and Development under the current contract. Completion of construction and preliminary test operation has been described by Cook, et. al. (1990). A simplified process flow diagram for the test facility is shown as Figure 1. A synopsis of system operation, following preliminary test operation, is shown in Figure 2. Test operation has progressed through Long Duration Test 3. Prior long duration testing has resulted in runs 1, 1A, 2, 2A, and 2B. Total long duration test operation to date has totalled 422 hours. Tests 4 and 4A remain a part of the currently scheduled test activity and will be performed in the near future.

RESULTS

Hot Gas Cleanup System Test Operation

Long Duration Test 1 (Runs 1 and 1A) has been discussed previously (Cook, et. al., 1991). The primary reason for Run 1A as an extension of Run 1 was the failure of the system's fuel backpressure control valve which resulted in termination of the test. However, regeneration recycle system performance had also deteriorated sufficiently to require termination of the test. In

addition, it had been concluded that gas and solids mixing and distribution in the regenerator were inadequate and regenerator modifications were indicated. The modifications to the regenerator were accomplished and test operation was resumed as Run 1A. As shown previously (Cook, et. al., 1991), regeneration was significantly improved with more uniform solids temperature distribution, higher SO₂ outlet levels in the tail gas and substantially reduced levels of sulfate in the regenerated zinc ferrite sorbent. Unfortunately, the unanticipated presence of water vapor in the regeneration recycle flow, coupled with the high levels of SO₂, provided large amounts of sulfuric acid and corrosion of the relatively low temperature (150 F) recycle compressor. The water, as well as high levels of CO₂ were present in the recycle gas as a result of the oxidation of tars which were transported to the regenerator on the sorbent, a phenomenon peculiar to the fixed bed gasifier used as the fuel source. Since it would be impossible to eliminate the tars while using the normal Illinois 6 test coal (as opposed to the anthracite startup fuel) it was decided to install a recycle boost blower of a different type with a high tolerance for particulate matter and a suction temperature of 525 F to avoid the acid dew point. Piping and gas cooler modifications were required, as well.

Run	Date	Run Duration Hours	Coal Type	Temp °F	Press PSIG	Flow Lb/Hr	System Configuration
1	12/3/90	26	16	1000	280	8000	GasIf./HGCU
1A	3/25/91	60	16	1000	280	8000	GasIf./HGCU
2	11/1/91	62	16	1000	280	8000	GasIf./HGCU GT Fuel Valve
2A	12/2/91	102	16	1000	280	8000	GasIf./HGCU GT Fuel Valve
2B	4/20/92	84	16	1000	280	8000	GasIf./HGCU GT Fuel Valve
3	3Q 92	88	16	1000	280	8000	GasIf./HGCU/GT Valve/ MS6000 Simulator
4	4Q 92	100	16	1000	280	8000	GasIf./HGCU/GT Valve/ MS6000 Simulator
4A	4Q 92	50	16	1000	280	8000	GasIf./HGCU/GT Valve/ R-Q-L Combustor

Figure 2: Synopsis of Current and Projected Test Operation

Throughout the testing to date, the outlet levels of H_2S have been in the range of from 10 to 30 ppmv with inlet levels of up to 3500 ppmv, provided that adequately regenerated, or fresh, sorbent has been provided to the absorber. Temperature profiles and the time dependence of pressure drop in the absorber have been within design expectations and easy to control. It appears that the overall absorber design is quite satisfactory and suitable to scaling to commercial size. On the other hand, regeneration has proved to be more difficult with the primary problem being the highly exothermic nature of the process coupled with the difficulty of control of such a reaction in a large volume of solids. Approximately 30 percent of the original sorbent volume in the regenerator was removed through internal flow modifications between Runs 1 and 1A and gas and solids mixing was significantly improved. Even so, periodic, local high temperature excursions were unavoidable while attempting to elevate the entire regenerator solids inventory to 1200 F to avoid sulfate formation.

Long Duration Test 2 eventually resulted in three separate runs; Run 2, 2A and 2B, all runs having been made with the original shipment of zinc ferrite sorbent. Prior to the start of Run 2, a new 13 stage, 525 F suction temperature boost blower, piping modifications and a revised regeneration recycle system gas cooler had been installed in an effort to prevent sulfuric acid condensation. Test 2 was initiated by preheating the regenerator and absorber with electrically heated nitrogen recycle flow allowing verification of the rebuilt recycle system and the new boost blower. Since substantial sulfur was present in the sorbent as a result of prior test operation, the regenerator was operated with admission of air and resulting generation of high temperatures and SO_2 for a period of nearly 40 hours before the absorber and gasifier were brought on line. Although the recycle system temperatures approached design values, regenerator internal temperatures proved difficult to control with excursions as high as 2000 F while portions of the sorbent bed remained substantially below 1200 F. Following a general decline in SO_2 concentration from as high as 10 percent, it was necessary to provide more sulfided sorbent to the regenerator and the absorber was brought on line.

It was decided to use reductive regeneration in the absorber's inlet lockhopper to eliminate much of the sulfated material prior to allowing it into the absorber. This proved unwise since there was substantial sulfated material available and the highly exothermic reduction reaction allowed sorbent temperatures in the absorber inlet piping to rise rapidly. Although no direct temperature measurements were available at this location, absorber bulk temperatures of 1700 F were recorded and sintering of the sorbent in the inlet piping occurred, blocking further solids flow. After solids flow was restored, failure of the overall system's backpressure control valve caused termination of the test at 60 hours. Limited absorber operation was possible and, when in operation, performance appeared normal. The major conclusion from Test 2 was that even with revised regenerator internal geometry and reduced solids content, regeneration temperature control remained difficult.

It was possible to obtain a replacement backpressure control valve body quickly and to install it in the preferred direction for reduced erosion in the particulate laden flow encountered during startup operation. This allowed resumption of Long Duration Test 2 as Run 2A within two weeks. Test 2A resulted in 102 hours of total test operation although not all as full integrated operation. Several interruptions were due to non-process related events such as rupture disc and coal elevator failures. Sintering of sorbent in the absorber's solids inlet pipe and inability to transport solids out of the regenerator caused interruptions, as well. During periods of successful absorber operation, characteristically low (10 - 30 ppmv) levels of H_2S were observed. Regeneration system operation during periods of adequate recycle flow produced the expected high (10 - 12 percent by volume) levels of SO_2 , accompanied by short term peak levels of CO_2 of more than 20 percent. Test operation was eventually terminated as a result of an inability to transfer sorbent from the regenerator. Post test examination revealed the presence of a number of sintered clumps of zinc ferrite,

presumably the result of high regenerator temperatures, as well as a significant amount of fines. The high fines content can be attributed, in part, to extensive sulfation of the sorbent in prior testing due to low regeneration temperature.

The next scheduled test operation, Long Duration Test 3, was to include zinc titanate sorbent, as well as initial gas turbine simulator operation. Just as final procurement arrangements for the zinc titanate were being completed, a new formulation of the sorbent with superior mechanical properties was identified in a parallel GE-CRD/DOE program (Ayala, 1992). It was decided to procure the modified material, even though a program delay was unavoidable, and to proceed with a further test under Long Duration Test 2 as Run 2B. The objectives for Run 2B were to utilize the remaining large size fraction of the existing zinc ferrite with a further modified regenerator and increased recycle temperature to demonstrate the viability of complete regeneration.

Prior to starting Run 2B, the electric heater in the regeneration recycle loop was upgraded to provide 1200 F gas temperature to allow a higher preheat temperature for the sorbent prior to oxidative regeneration. In addition, the

regenerator was modified from a three to a two stage system to minimize the mass of sorbent and reduce heat loss.

Figure 3 shows regenerator outlet temperature, gasifier flow rate and absorber internal temperature vs. test time for Run 2B. During the first 24 hours of the test the regeneration system was heated electrically with the internal sorbent temperature exceeding 900 F and the outlet gas temperature achieving 800 F prior to starting oxidative regeneration. Solids were moved through the system six times prior to the start of integrated operation as shown by the stepped increases in absorber bed temperature. Following inert gas electric preheat, oxidative regeneration was started at test hour 26 and resulted in continuing increase in regenerator outlet gas and solids temperature for approximately 12 hours until the supply of sulfided material began to decline. At this point the gasifier was brought on line rapidly while sorbent transport frequency was increased to preheat the absorber in preparation to bringing the absorber on line at 48 hours into the test. Integrated operation proceeded from this point until voluntary shutdown at 84 test hours. As shown in

Figure 3: Test Operating History for Long Duration Test 2B Showing High Temperature Regenerator System Preheat (0-26 hrs), Off-line Oxidative Regeneration (26-48 hrs), and Integrated Operation (48-84 hrs)

Gasifier

Pressure	20 Atm
S/A Ratio	0.5
Coal Rate	1800 lb/hr
Gas Flow	8000 lb/hr
Gas Temp	1050°F

Gas Composition

	Absorber Inlet Vol %, Wet	Absorber Outlet Vol %, Wet
N ₂	33.9	35.5
CO ₂	11.8	14.1
CO	10.4	8.8
H ₂	15.8	18.5
CH ₄	3.1	3.1
H ₂ S	0.23	0.003
COS	0.03	0.000
H ₂ O	25.0	20.0

Figure 4: Typical Gasifier and HGCU Fuel Gas Conditions During Operation with Illinois 6 Coal

Figure 5: HGCU System Absorber Performance, Run 2B, Illustrating Effect on H₂S Outlet of Complete Regeneration of Sorbent

Figure 3, the regenerator outlet temperature reached 1350 F near the end of the period and was above 1200 F during the period from hour 60 through hour 80.

Gasifier operating conditions, typical for the fixed bed gasifier being used during the entire test series, are shown in Figure 4. The effect of the water gas shift reaction on composition can be seen in the modified hydrogen and carbon dioxide content of the fuel gas. This shift is accompanied by the 50 to 80 F temperature rise seen across the absorber in Figure 5. The negative temperature spikes seen in the absorber outlet gas temperature are the result of transport of cooler sorbent into the absorber from the inlet lockhopper and bucket elevator and provide a reference for sorbent movements. The data shown in Figure 5 are for the test period where optimum regeneration temperatures were obtained and illustrate the steady decline in outlet H₂S peaks that were obtained as sorbent regeneration was driven to completeness. When regeneration has been carried out at lower than 1200 F, zinc sulfate is formed and recycled to the absorber with a resulting hydrolysis to H₂S under reducing conditions. The lack of an H₂S peak following transport of sorbent at the 78 test hour point is direct evidence of the completeness of

regeneration.

Further evidence for proper regeneration is shown in Figure 6 where, in addition to regenerator internal temperatures, total residual sulfur as well as percent residual sulfur reporting as sulfate, is shown vs. test time. The total sulfur curve shows that approximately 1 percent total sulfur remains in the sorbent following regeneration when the sorbent loading during absorption is approximately 4 to 10 percent by weight. Further, it can be seen that there is a steady decrease in the sulfate content with improving regeneration temperature to the point of nearly zero sulfate content at the 78 hour point. It should be pointed out that the lower temperature trace, associated with thermocouple location 239, is at the exit of the regenerator and in a nearly pure air environment where sulfation is not expected to occur. The results of regenerator operation during the 60 to 84 hour test period are shown in Figure 7 where tailgas concentrations of SO₂ and CO₂ are plotted vs. test time. The sharp CO₂ peaks are believed to be peculiar to the fixed bed gasifier's tar production as a significant amount of condensed tars are brought into the regenerator on the sorbent.

Figure 6: HGCU System Regenerator Performance, Run 2B, Illustrating Decreasing Sulfate Content in Regenerated Sorbent Resulting from Higher (> 1200 F) Regeneration Temperatures

Figure 7: Regenerator Tailgas Composition vs. Time, Run 2B

Figure 8: HGCU System Performance vs. Time, Run 3, Illustrating H_2S Performance with Fresh and Regenerated Zinc Titanate as well as Increased Regenerator Preheat and Integrated Operation

This tar, as well as any char deposited, is oxidized first and starves the oxygen supply for sulfur regeneration. Even so, SO₂ levels were generally in the 8 to 10 percent range expected from complete regeneration of the sorbent.

Figure 8 shows the effect of periodic sorbent movement on pressure drop in the absorber and, conversely, illustrates the need for moving the bed, independent of sulfur saturation. The absorber acts as a granular bed filter and operates predictably and within the design values of from 40 to 100 inches of water during steady operation.

Following delivery of the new zinc titanate sorbent, preparations were made for Long Duration Test 3 since no further testing with the remaining zinc ferrite was intended. The system was emptied of zinc ferrite and filled with 11,614 lbs of fresh zinc titanate with the regenerator still reduced to two stage operation (second and third stages operational relative to the original configuration) and nearly continuous solids flow capability in the regenerator. The latter feature was implemented by arranging for control of pulsed operation of the regenerator's outlet rotary feeder while using the regenerator's inlet lockhopper as a storage vessel and the elevator bucket as a receiving bin. The absorber remained

unmodified while the primary cyclone was replaced with a potentially higher efficiency insert which had been supplied with the original cyclone system but not utilized.

The gas turbine simulator and its associated piping and controls were assembled, pressure checked and operated with natural gas firing just prior to the start of Run 3, making it possible to include them in the test program with Lbtu fuel.

A portion of Long Duration Test 3 is shown in Figure 8. The portion shown for test hours 16 through 22 illustrates the sulfur removal performance of fresh zinc titanate during a period when the regenerator was at steady state, inert gas preheat status with sulfided sorbent being transported from the absorber. The absorber was on line during this period providing the sulfided material so that oxidative regeneration could be started. The regenerator thermocouple traces (222d and 222a) represent temperatures at the positions shown in Figure 6 and demonstrate that reasonably well controlled regeneration temperature was possible with nearly continuous sorbent movement but that near the end of the test, with deteriorating recycle flow, uniformly high temperature levels could

Figure 9: Gas Turbine Simulator Configuration as Operated on Lbtu Fuel Gas During Run 3

not be maintained. SO₂ levels in the tail gas were the expected 10 percent when adequate recycle flow was available. Absorber outlet H₂S concentrations were at the expected 20 to 30 ppmv when properly regenerated sorbent was returned to the absorber. Full analysis and data reduction remain to be performed and will be reported in the future.

Turbine Simulator Test Operation

Long Duration Test 3 was the first opportunity for operation of the MS6000 gas turbine combustor and turbine simulator, shown in Figure 9, with Lbtu gas from the integrated gasifier/HGCU system. The combustor, Lbtu fuel nozzle, impingement cooled transition piece and nozzle cascade are intended to verify ignition, flame stability, combustion efficiency, emission characterization and short term erosion and deposition performance related to coupling the HGCU system to a GE gas turbine.

Following several short duration operation periods early in the test, a leak was observed in the fuel control valve upstream of the turbine simulator. This required shutting down the simulator and removal and inspection of the valve. Valve repairs were initiated and completed in time to allow further test operation near the end of Run 3. During this latter period, nearly continuous operation was obtained for 8 hours. Nozzle inlet temperature was restricted from the planned 2020 F to 1550 F due to a cooling air leak at the exit of the nozzle cascade assembly. This prevented an adequate supply of cooling air to the leading edge blade cooling holes and caused the local metal temperatures to approach the gas temperature. Post test examination has confirmed the leakage path and a design modification is in progress.

In general, the combustor proved easy to ignite and ran stably with the 900F to 1000F Lbtu fuel gas. The only non-intentional period of loss of combustion appears to be associated with an upset in gasifier operation which altered the heating value of the fuel. Post test examination of

the internal metal surfaces revealed essentially no detectable deposition or erosion during the short duration of testing. A more complete analysis of gas samples and overall turbine simulator performance will be reported in the proceedings of the upcoming 10th Annual Heat Engines Conference.

FUTURE WORK

Long Duration Test 4 and Test 4A remain to be completed and will involve further test operation with the existing turbine simulator configuration, as well as Nahcolite injection for halogen removal, and diagnosis of alkali and heavy metal species. Test 4A will utilize a rich-quench-lean (RQL) slipstream combustor being developed in parallel for limited duration testing of the RQL process for reduction of NO_x related to fuel bound nitrogen species. Gasifier and absorber performance continue to be well understood and overall process operation interruptions have been less frequent. Future testing will utilize zinc titanate sorbent and will involve continuing emphasis on optimizing the regeneration process and sorbent.

REFERENCES

- Smith, D.P., E. Gal, C.S. Cook, A.H. Furman, June 1987. "Design Studies for Hot Gas Cleanup System in a Load Following Mode," Seventh Annual Gasification and Gas Stream Cleanup Systems Contractor's Review Meeting, Report DOE/METC/87/6079
- Cook, C.S., Gal, E., Furman, A.H., Ayala, R., Tucker, R.M., May, 1988. "Integrated Operation of a Pressurized Fixed Bed Gasifier and Hot Gas Desulfurization System," Eighth Annual Gasification and Gas Stream Cleanup Systems Contractors' Review Meeting, Report DOE/METC/88/6092.

Cook, C.S., Gal, E., Furman, A.H., Tucker, R.M., Parekh, B., June, 1989. "Integrated Operation of a Pressurized Fixed Bed Gasifier and Hot Gas Desulfurization System," Ninth Annual Gasification and Gas Stream Cleanup Systems Contractors' Review Meeting, Report DOE/METC/89/6107, Vol. I.

Cook, C.S., Gal, E., Furman, A.H., Tucker, R.M., Parekh, B., August, 1990. "Integrated Operation of a Pressurized Fixed Bed Gasifier and Hot Gas Desulfurization System," Tenth Annual Gasification and Gas Stream Cleanup Systems Contractors' Review Meeting, Report DOE/METC/90/6115, Vol. I.

Cook, C.S., Gal, E., Furman, A.J., Ayala, R., August, 1991. "Integrated Operation of a Pressurized Fixed Bed Gasifier and Hot Gas Desulfurization System," Eleventh Annual Gasification and Gas Stream Cleanup Systems Contractors' Review Meeting, Report DOE/METC/91/6123, Vol. I.

Ayala, R., September, 1992. "Enhanced Durability of High Temperature Desulfurization Sorbents for Moving-Bed Applications", Twelfth Annual Gasification and Gas Stream Cleanup Contractors' Review Meeting, Report DE/AC21-88MC25003.

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