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NETL's Gas Process Development Unit for Hot/Warm Gas Cleanup

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Introduction

Hot/warm gas desulfurization is a key component to Integrated Gasification Combined Cycle (IGCC) technologies being advanced by the U.S. Department of Energy (DOE) Gasification Technologies Product Team and is an "enabling technology" in the DOE Vision 21 program. Sorbents that remove sulfurous compounds from synthesis gas (syngas) produced during gasification and that can be regenerated over many absorption-regeneration cycles have been developed under DOE-sponsored work, and independently by research institutes, industry and universities.

As an extension of that work, the DOE's National Energy Technology Laboratory (NETL) has constructed at its Morgantown, WV, site a Gas Process Development Unit (GPDU) pilot plant for testing those desulfurization sorbents at temperatures, pressures, gas compositions and velocities expected in a commercial process. The GPDU facility houses two fluidized-bed reactors and two transport reactors to provide the unique capability of evaluating sorbents in four different continuous operational process modes: (1) transport absorber and transport regenerator, (2) fluidized-bed absorber and fluidized-bed regenerator, (3) transport absorber and fluidized-bed regenerator, and (4) fluidized-bed absorber and transport regenerator.

The GPDU was designed at a scale large enough to produce results scalable to commercial applications, yet small enough to economically collect this information. This pilot-scale project provides a rigorous assessment of desulfurization sorbents under gas-contacting/circulation schemes that would be present in an industrial application. Additionally, because the GPDU offers continuous absorption and regeneration processing, sorbents can be evaluated over many cycles in a short period of time as a means to assess their longevity.

Objective

The long-term objectives for the GPDU project are to: (1) assess transport and fluidized-bed reactor control and performance to determine the most suitable mode for continuous gas desulfurization, and (2) evaluate candidate sorbents for bulk removal of sulfurous compounds from syngas to assess the readiness of sorbents for commercial scale.

The DOE has funded desulfurization and sorbent research for over 20 years and extensive laboratory-scale and bench-scale work has been conducted by government, academia and industry on the development and testing of regenerable sorbents for bulk sulfur removal from syngas (Cicero, et.al, 2000; Mitchell, 1998; Lew, 1989). However, the technologies still need to be proven in controlled conditions at a larger scale. Several Clean Coal Technology projects (i.e, the Toms Creek IGCC Demonstration Project, the Pinõn Pine IGCC Power Project and the Tampa Electric Integrated Gasification Combined-Cycle Project) had proposed demonstrations of hot-gas desulfurization technology, but were not seen to completion (Clean Coal Technology Compendium website, 2002). As a result, there is a lack of data on sorbent and reactor performance under longer-term continuous conditions at a large scale. For commercial acceptance of hot- or warm-gas desulfurization, technology reliability is a question yet to be answered. The GPDU will fill the gap and has the objective to provide the proof-of-concept that is needed to foster commercialization of hot (greater than 538°C (1,000°F)) and/or warm (260 to 427°C (500 to 800°F)) gas desulfurization for IGCC processes.

The GPDU facility, which includes a separate Syngas Generator (SGG) that supplies a simulated coal gas to the GPDU, is in the shakedown phase of operations with an initial reactor configuration of transport absorber-transport regenerator. The status and preliminary results of shakedown activities are presented to provide insight into startup and operations of a continuous transport desulfurization process.

Approach

The current approach to get the project fully operational is independent shakedowns of the Gas Process Development Unit and the Syngas Generator, followed by integrated shakedown that couples the GPDU and the SGG. The general goal of each independent shakedown is to end up with a sufficiently operable and characterized system and adequately trained personnel to proceed with integrated operation. After successful integrated shakedown activities are complete, a continuous proof-of-concept test will be conducted to evaluate the longevity and performance of a candidate hot-gas desulfurization sorbent.

Both units have progressed through various independent shakedown activities and the integrated shakedown has been initiated. The ongoing sequence of planned and completed shakedown activities is given below. Sub-bullets preceded by a check-mark (✓) indicate the activity has been completed.

- Conduct independent shakedown of the SGG - *completed March 2002*
  - ✓ First-stage burner light-off outside vessel - *completed July 2001*
  - ✓ First-stage burner light-off inside vessel - *completed August 2001*
  - ✓ Combustion unit refractory dryout - *completed September 2001*
  - ✓ Third-stage firing, transfer line refractory dryout, and transition to syngas mode - *completed November 2001*
  - ✓ Low-sulfur syngas production - *completed December 2001*
  - ✓ High-sulfur syngas production - *completed March 2002*

- Conduct independent shakedown of the GPDU - *completed June 2002*
  - ✓ Sorbent loading - *completed February 2001*
  - ✓ Cold circulation with air - *completed February to April 2001*
  - ✓ Sorbent removal - *completed April 2001*
  - ✓ System heatup with air (no solids) - *completed August 2001*
  - ✓ Medium-pressure heatup with steam (no solids) - *completed April 2002*
  - ✓ Medium-pressure hot circulation of solids - *completed June 2002*

- Conduct integrated shakedown of SGG and GPDU - *ongoing*
  - ✓ Medium-pressure cold integration (no solids) - *completed June 2002*
  - ✓ Medium-pressure cold integration with solids – *completed August 2002*
  - ✓ Medium-pressure hot integration with solids – *completed August 2002*
  - High-pressure SGG test
  - High-pressure batch transport desulfurization shakedown test
  - High-pressure continuous transport desulfurization shakedown test

- Conduct high-pressure (continuous) transport proof-of-concept test

Project Description

The National Energy Technology Laboratory's GPDU facility, shown in Figure 1, houses two fluidized-bed reactors and two transport reactors to provide the unique capability of evaluating desulfurization sorbents in four different operational process modes. Sorbent is continuously circulated between an absorber reactor and a regenerator reactor, and is recirculated when conducting transport reactor tests. Figures 2 and 3 illustrate the dual transport reactor and dual fluidized-bed reactor configurations, respectively.

The GPDU is designed to conduct continuous desulfurization at temperatures up to 649°C (1,200°F) and pressures up 2,655 kPag (385 psig). The four reactors are: (1) a 45.7 cm x 3.0 m (18" x10') fluidized-bed absorber, (2) a 25.4 cm x 3.7 m (10" x12') fluidized-bed regenerator, (3) a 13.2 cm x 15.2 m (5.2" x 50') transport absorber, and (4) a 4.3 cm x 15.2 m (1.7" x 50') transport regenerator. Slide valves regulate sorbent circulation up to 2,270 kg/hr (5,000 lb/hr) between the absorber where fuel gas desulfurization occurs and the regenerator where sorbent is regenerated with air. Slide valves also control sorbent recirculation up to 24,900 kg/hr (55,000 lb/hr) in transport configurations. Depending upon sorbent density and process considerations, generally about 907 to 1,360 kg (2,000 to 3,000 pounds) of sorbent are required for testing.

Sulfur-laden fuel gas for GPDU operation is produced in the NETL-designed Syngas Generator (SGG). Natural gas is combusted with air in the presence of sulfuric acid (which converts to H_2S) in a four-stage combustor to produce fuel gases with an expected composition similar to product gases produced by air-blown coal gasifiers. The SGG provides up to 4,490 kg/hr (9,900 lb/hr) of fuel gas to the GPDU at temperatures up to 746°C (1,375°F) and pressures up to about 4,137 kPag (600 psig). Figure 4 illustrates the SGG design.

Results

Shakedown activities were programmed to address safety and operations issues in a staged fashion: (1) independent shakedown of the GPDU, (2) independent shakedown of the Syngas Generator, and (3) integrated shakedown of both units together. Shakedown was sequenced to develop and optimize procedures for distinct steps in the process, to characterize system performance, and to provide training for 14 operations personnel.

Independent shakedowns of the GPDU and the SGG have been completed. The first shakedown tests to integrate the SGG and the GPDU have been undertaken with partial success. Significant accomplishments have included:

- **Independent shakedown of the Syngas Generator was completed** with production of syngas containing reduced sulfur species. The test operations, at a nominal 896 kPag (130 psig), demonstrated that targeted flow rates of reactants to the combustion unit could be achieved and maintained. Most importantly, the process chemistry was confirmed. Several gas grab samples were collected while the SGG was being transitioned to fuel gas operation. Analysis of samples of the resulting process gas verified that the sulfuric acid fed to the combustor was converted to hydrogen sulfide with no detectable oxidized sulfur. Additionally, the gas composition was adequately predicted by a chemical equilibrium code. For instance, one of the grab samples analyzed with a gas chromatograph showed 7,842 ppmv of hydrogen sulfide. Utilizing a chemical equilibrium code, the predicted hydrogen sulfide composition at the conditions that were present in the SGG combustor at that time was 7,607 ppmv.

- **First ever integration of units was demonstrated** with smooth transition of gas (ambient temperature and 2,068 kPa air) flow from the Syngas Generator to the GPDU. The activity demonstrated that the units could be coupled and a nominal 3,628 kg/hr (8,000 lbs/hr) of gas could be transitioned to the GPDU at a pressure of 1,034 kPa (150 psig) in a smooth fashion. There was no sorbent in the GPDU and no reactive gases were used. However, the GPDU and the SGG were pressurized and flow rates were established at setpoints planned for a future sorbent activity. Smooth transitioning is crucial during sorbent work since upsets in pressures or flow rates would adversely affect the operation by interrupting operator control of the sorbent inventory and gas distribution.

- **GPDU operation with steam was demonstrated** to verify adequacy of heating prior to introduction of solids. In a simulation of actual startup, the GPDU was initially heated at 1,034 kPa (150 psig) with hot air from both fired preheaters to get the system above steam saturation temperature (nominal 187°C (369°F)), and then steam at about 538°C (1,000°F) was phased in and run for nearly 2 hours. No major problems were encountered. Although no desulfurization sorbent was in the system, this was an important demonstration because in future test operations, steam would be used for sorbent fluidization and circulation. This operation was significant because had cold spots been observed during this operation, it would signal that steam was condensing which could lead to plugging with sorbent in the system.

- **Independent shakedown of the GPDU was completed** with demonstration of hot sorbent circulation and recirculation at 1,034 kPa (150 psig) and nominal 371°C (700°F). The GPDU was initially heated to about 260°C (500°F) with hot air from both fired preheaters, and then steam was phased in and run for nearly 4 hours during which the unit continued to heat up to nominally 371°C (700°F). Operations went exceptionally well considering this was the first attempt at hot solids operation. Slide valves, standpipes, and riser behaviors were all excellent and superior to cold conditions, and there was little difficulty maintaining stable bed levels on the absorber and regenerator sides of the process during 4.5 hours circulation of EXSO3 sorbent. These conditions were significant since they represent the point at which hot combustion gas from the Syngas Generator would be transitioned to the GPDU to complete systems heatup prior to syngas desulfurization.

- **Integrated shakedown testing of the Syngas Generator and GPDU was initiated.** Sorbent was fluidized and circulated in the GPDU nearly continuously for 3 days straight at 1,034 kPa (150 psig) during which preheated air and steam were utilized to heat the GPDU reactors to nominally 371-427°C (700-800°F). Normally this initial heatup will require less than 24 hours, but was longer for this shakedown test because of some equipment problems. Figure 5 shows a steady sorbent inventory in the fluidized-bed reactors during this extended circulation/recirculation period, suggesting little carryover loss of sorbent from the primary cyclones and thus perhaps a low sorbent attrition rate. The slight decrease in indicated sorbent inventory with the establishment of circulation/recirculation reflects some of the fluidized-bed inventory then being in the risers and lower standpipes. Following this initial heatup and successful startup of the SGG, the GPDU was then integrated with hot, 2,068 kPa (300 psig) SGG process gas. With the SGG in (air-rich) combustion mode, hot gas was smoothly transitioned to the GPDU and sustained for nearly 5 hours, after which the SGG gas was transitioned out of the GPDU in preparation for (fuel-rich) syngas operation (which did not occur due to operational problems). During the integrated period, the GPDU continued to heat up, with the absorber side approaching 510°C (950°F) as shown by Figure 6. The regenerator side showed little temperature change and remained nominally at 371°C (700°F). Sorbent inventory continued to remain steady during integrated operation. This shakedown test successfully demonstrated hot integration and showed that the absorber could be heated to a temperature where desulfurization reactions could be initiated. However, the data also indicated that higher pressure operation (with higher mass flows) and some operational changes would be needed to achieve adequate regenerator temperatures.

Shakedown of NETL's GPDU facility has proceeded considerably and is nearing full operational status for the purposes of assessing the advantages and disadvantages of different reactor configurations, and for evaluating desulfurization sorbents for bulk sulfur removal from syngas. Work to date has been successful in verifying certain important design aspects.

Application
In the gas cleaning and conditioning area of NETL's Gasification Technologies program, the goal is to achieve near-zero emissions while simultaneously reducing capital and operating costs. The GPDU facility is key to that goal by providing a cost effective test site for transport and fluidized-bed desulfurization reactor and sorbent development. Demonstration of sorbent suitability over a wide range of parameters, and generation of significant information on process control for transport and fluidized-bed based desulfurization will provide the proof of concept desired for commercialization of the hot/warm gas cleaning technology.

The GPDU facility is a highly instrumented pilot plant with 81 flow transmitters, 53 differential pressure transmitters, 25 pressure transmitters, 130 temperature elements, and 5 sampling systems. Data that will be collected will be sufficient to characterize the process and to optimize operations. Valuable knowledge will be gained for scale-up of the process, proof of sorbent readiness at conditions that will be expected in a commercial reactor system, and confidence that the process is reliable.

Future Activities
Although the GPDU has the ability for four different process configurations, the near-term focus will be on process operations and assessment of the transport absorber-transport regenerator mode. The immediate focus will be to complete integrated shakedown of the GPDU with the Syngas Generator. This is envisioned to encompass three additional operational periods: (1) a high-pressure SGG test, (2) a batch transport desulfurization shakedown test, and (3) a continuous transport desulfurization shakedown test.

The GPDU will then be operated in the continuous transport absorber-transport regenerator mode in FY03 with the commercially available EXSO3 zinc titanate hot-gas desulfurization sorbent. Operating conditions will be at the GPDU design conditions of 2,070-2,655 kPag (300-385 psig) and 538-649°C (1,000-1,200°F) sulfidation temperature.

Future work will be programmatically driven and will likely include warm gas conditions, conditions representative of oxygen-blown systems, and/or industrial partnership testing.

References
Cicero, D. C., R. P. Gupta, B. S. Turk, J. W. Portzer, S. K. Gangwal., 2000. Recent Developments in Hot Gas Desulfurization. 4th International Symposium on Gas Cleaning at High Temperatures.

S. Mitchell, 1998. Hot Gas Cleaning for Advanced Coal-Based Power Systems. IEA Coal Research Centre Report.

Lew, S., K. Jothimurugesan, and M. Flytzani-Stephanopoulos. 1989. High Temperature Regenerative H_2S Removal from Fuel Gases by Regenerable Zinc Oxide - Titanium Dioxide Sorbents. *Ind. Eng. Chem. Res.* 28:535-541.

Clean Coal Technology Compendium website, 2002, http://www.lanl.gov/projects/cctc/index.html.

Figure 1. NETL's Gas Process Development Unit is housed in the blue structure.

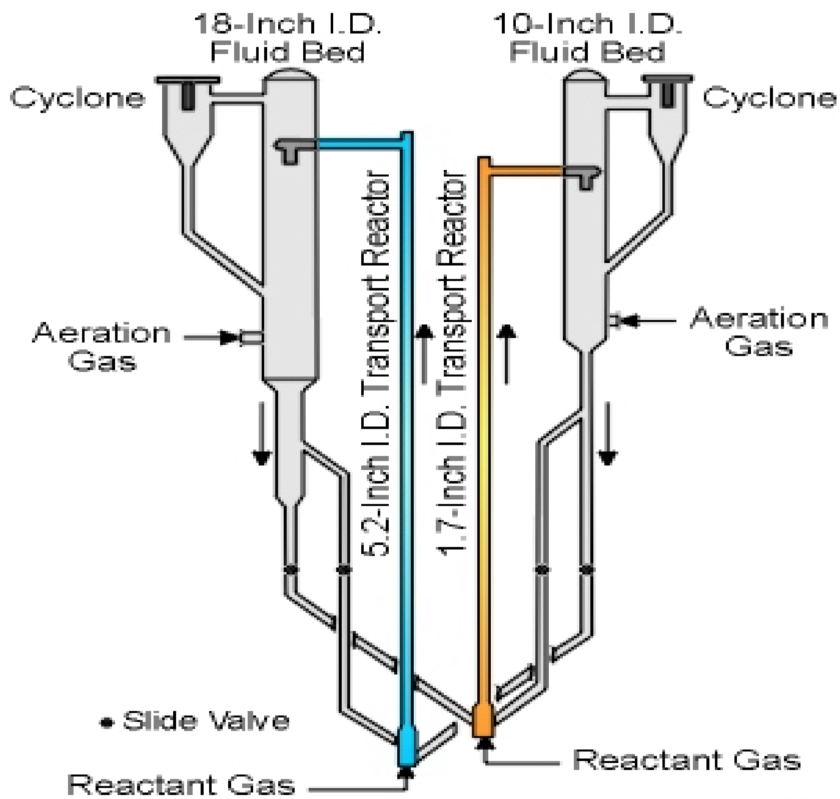

Figure 2. Transport absorber – transport regenerator configuration of GPDU.

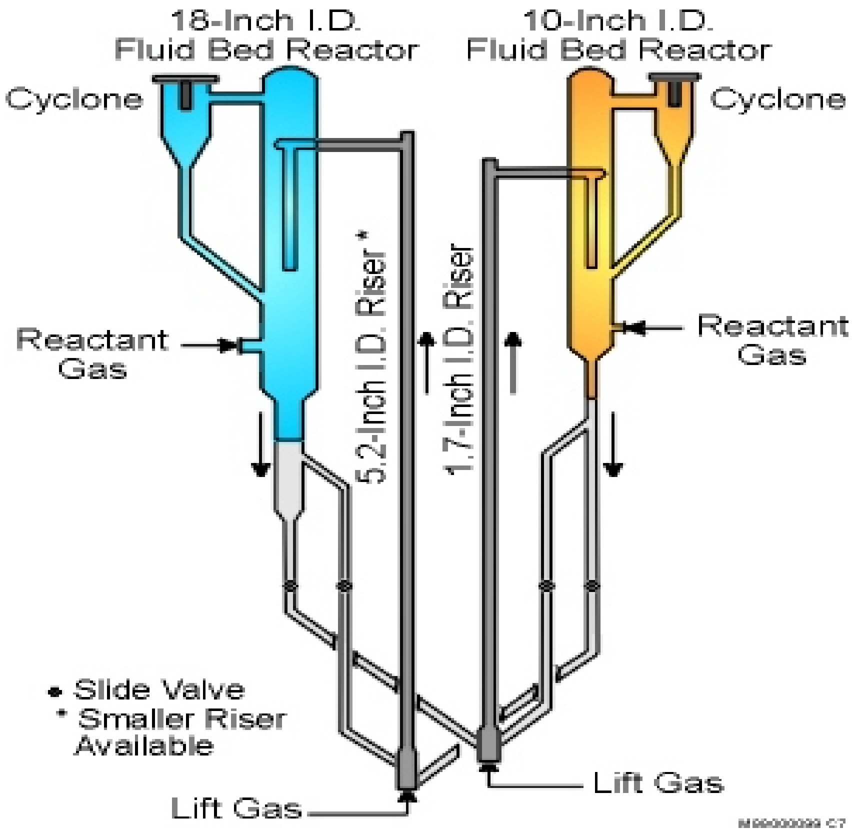

Figure 3. Fluid-bed absorber – fluid-bed configuration of NETL's GPDU.

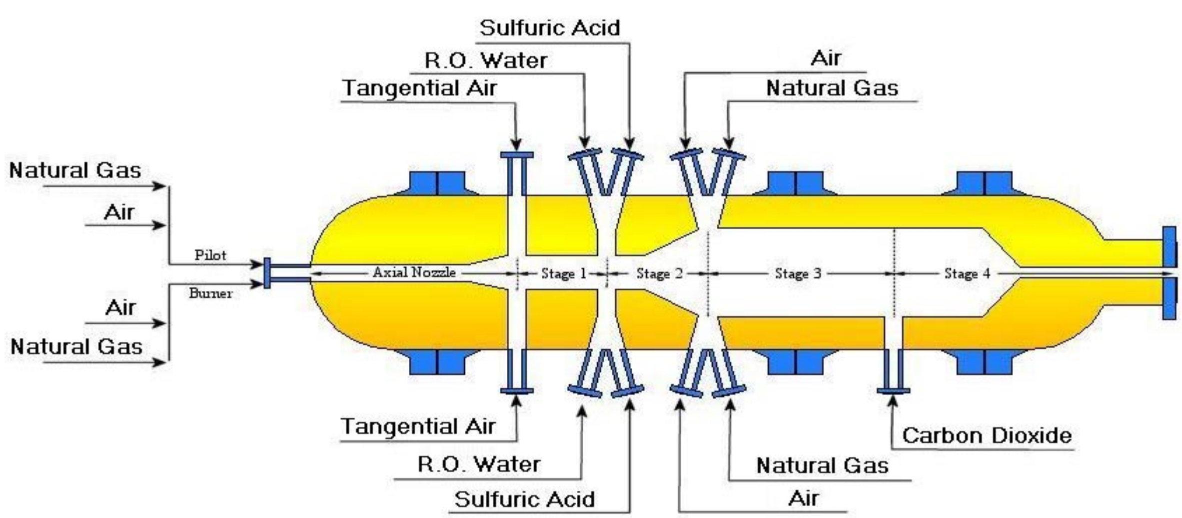

Figure 4. Syngas Generator Combustion Unit.

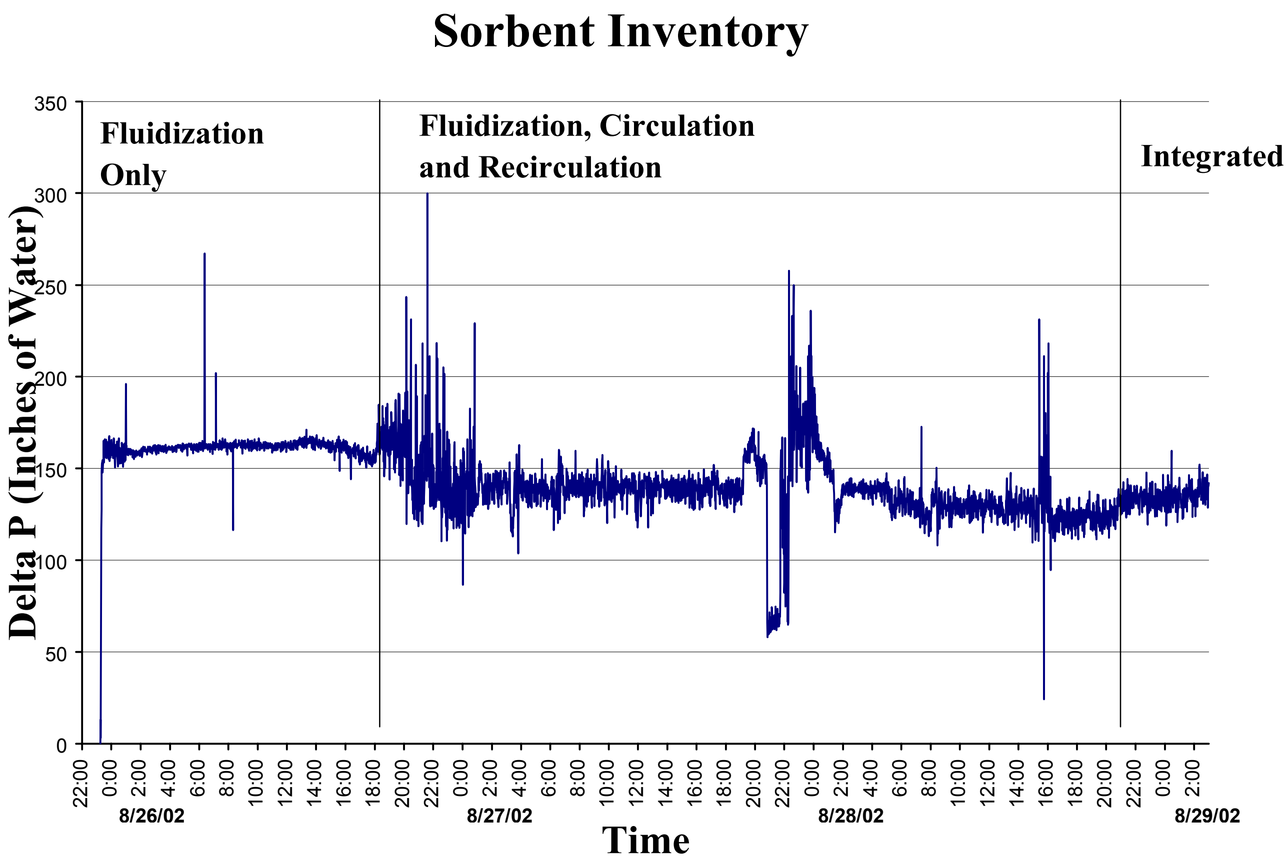

Figure 5. Sorbent inventory was maintained for over three days.

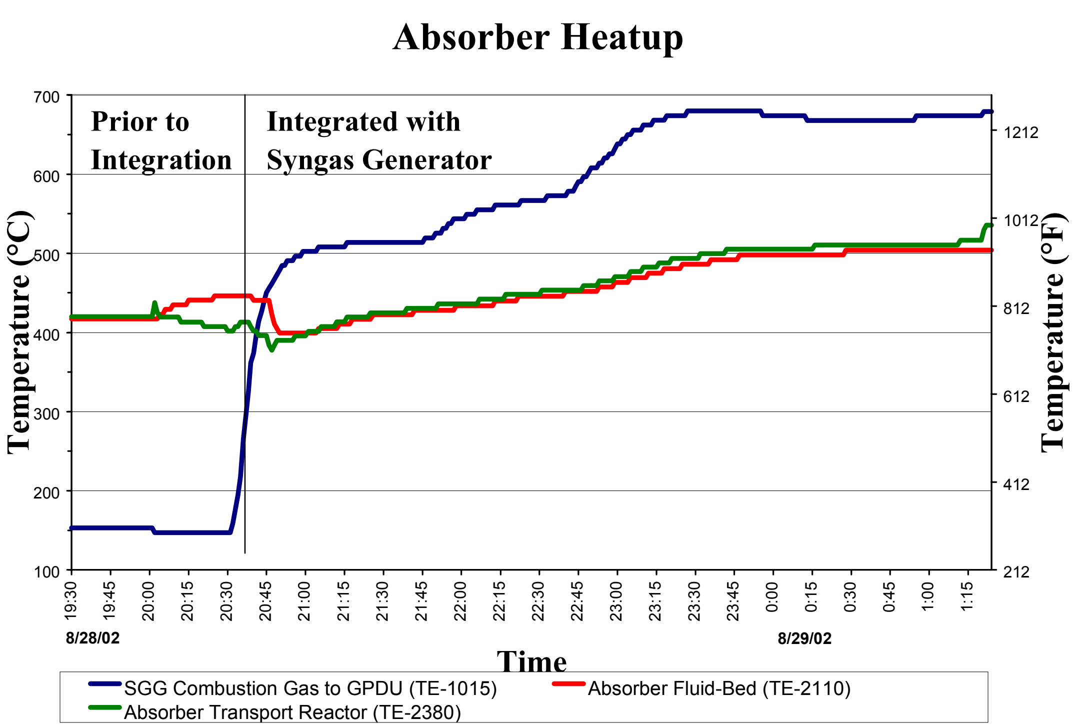

Figure 6. Hot combustion gas from the SGG completes the heatup of the GPDU.