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METC's Pilot-Scale Hot-Gas Desulfurization Process Development Unit

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METC's Pilot-Scale Hot-Gas Desulfurization Process Development Unit

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Introduction

The Morgantown Energy Technology Center (METC) has designed and is currently constructing an on-site, hot gas desulfurization (HGD) Process Development Unit (PDU). The PDU is designed to use regenerable solid metal oxide sorbents that absorb hydrogen sulfide from high-temperature, high-pressure simulated coal-gasification fuel gas that is generated by a METC-designed syngas generator. The simulated coal gas is a mixture of partially combusted natural gas, water, carbon dioxide and hydrogen sulfide. PDU process conditions will be representative of anticipated commercial applications in terms of temperatures, pressures, compositions, velocities, and sorbent cycling. The PDU supports the Integrated Gasification Combined Cycle (IGCC) mission at METC by providing a test bed for development of IGCC cleanup systems that offer low capital cost, operating costs, and costs of electricity. METC intends to develop additional industrial involvement opportunities as the project progresses towards operations.

Objectives

The primary objectives of the PDU are to: (1) fill the gap between small-scale testing and large-scale demonstration projects by providing a cost effective test site for transport and fluid-bed desulfurization reactor and sorbent development, (2) demonstrate sorbent suitability over a wide range of parameters and (3) generate significant information on process control for transport and fluidized bed based desulfurization. PDU data is expected to be used to optimize process performance by expanding the experience for larger-scale demonstration projects, such as Sierra Pacific Power Company's Clean Coal Technology project.

Background

During the PDU's early conception (1,2), an IGCC-system economic study showed minimal cost and performance differences when using low velocity HGD fluid beds versus fixed or moving beds. However, costs could be lowered by using higher fluidizing velocities (3). The study also revealed economic advantages for a system that uses a minimal amount of undiluted regeneration air. Given this information and the encouraging results from small-scale transport reactor testing, METC designed the PDU to explore the advantages of higher velocity regimes and alternate contacting modes. Transport reactor provisions were then incorporated into the conceptual design on both the sulfidation and regeneration sides of the

PDU (4). Because the PDU does not require a coal feed or gasifier system, it should cost 25 to 75 percent less per test-hour than would otherwise be required.

Then METC decided to draw upon existing gas-solid processing technology. In particular, the similarity between the continuous, integrated cracking and catalyst regeneration operations used in fluid and transport catalytic cracking (FCC) units and the PDU concept was viewed as a potential link to success. METC took advantage of much of the existing industry expertise by teaming with the M.W. Kellogg Co. (MWK) for preliminary and detailed design activities. MWK designed the PDU reactor system, and METC designed the balance of plant facilities.

METC acted as the general construction contractor, and activities were split between several contractors for underground and above-ground utilities, civil construction and vessel fabrication. METC personnel are doing instrumentation and control, piping field fits and similar activities. In addition, METC will conduct all operations and maintenance.

PDU Description

Design Features

The PDU operates at 400 psia (2,750 kPa) pressure and at temperatures up to 1,200° F (650 ° C) on the sulfidation (fuel gas) side and up to 1,400° F (760° C) on the regeneration (air) side. The unit continuously circulates sorbent material between the sulfidation and regeneration sides of the desulfurization system. The PDU has provisions for fluid bed and transport contacting. When operating in the fluid bed contacting mode, fuel gas is fed into an 18 inch (.457 meters) inside diameter (i.d.) reactor and sorbent is circulated with steam or nitrogen to the 10 inch (.254 meters) i.d. regenerator reactor. When operating in the transport mode, a 5.2 inch (.132 meters) i.d. absorber riser reactor is used along with a 1.7 inch (.043 meters) i.d. regenerator reactor. Density difference is the primary driving potential for circulation. The following are a few of the primary design features of the METC PDU.

- Fuel gas flow: 60,000 to 120,000 scfh typical
- H_2S concentration: 0.5 to 1 volume % typical
- Absorption temperature: 1,000 to 1,200° F design
- Regeneration temperature: 1,100 to 1,400° F design
- Absorber-regenerator differential temp.: 400° F maximum
- Operating pressure: 400 psia maximum
- Fluid-bed absorber: 18-inch i.d., 10-ft bed maximum
- Transport absorber: 5.2-inch i.d., 50-ft length
- Fluid-bed regenerator: 10-inch i.d., 12-ft bed maximum
- Transport regenerator: 1.7-inch i.d., 50-ft length
- Underflow standpipes: 1.7 to 6.8 inch i.d., 20-ft length (approx.)
- Fluid-bed superficial velocities: 1 to 3 ft/s typical
- Riser superficial velocities: 15 to 20 ft/s typical

- Sorbent inventory: 1,000 to 2,000 lb typical
- Sorbent cycles per day: 50 to 100 typical
- Circulation rate: 2,000 to 5,000 lb/hr typical
- Transport absorber recirculation rate: 5,000 to 55,000 lb/hr typical
- Transport regenerator recirculation rate: 0 to 2,000 lb/hr typical
- Riser bulk densities: 2 to 12 lb/ft^3 design
- Sorbent size: 50 to 300 micrometers typical
- Sorbent flux: 100 lb/sec-ft^2 design
- Reactor Vessels Refractory lined, carbon steel
- Major Piping Hot-walled, Inconel 800H alloy

PDU Operation

Overview

Simulated low-Btu coal gasification gas will be supplied to the PDU by a natural gas-fired fuel-gas (syngas) generator. This precludes the ability to test the effects of trace contaminants on sorbent performance. This approach is more cost-effective and presents fewer site environmental issues. A previous description of the fuel gas generator remains generally accurate (5). Notable changes include the decision to use sulfuric acid rather than sulfur dioxide as the source of hydrogen sulfide for the fuel gas, and the use of a direct water quench instead of an indirect heat exchanger for final fuel gas temperature trim. A simple block flow diagram of the PDU is shown in Figure 1. In the absorber, a sorbent, such as zinc oxide, becomes sulfided by absorbing sulfur species from the fuel gas stream. In the regenerator, the captured sulfur in the sulfided sorbent is reacted with air, which restores or “regenerates” the activity of the sorbent. The sorbent is then recirculated back to the absorber, thus providing continuous operation. Inert gases (steam and/or nitrogen) are used to fluidize the sorbent in the standpipes above the valves and to prevent fuel gas and air intermixing.

The project also has two natural gas-fired indirect heaters to preheat inert gases and regenerant gases up to 1,400°F (760 °C), and filter lockhopper arrangements downstream of the cyclones, (as shown in Figure 2) to collect sorbent fines that carry over from the cyclones. Since process gases are cooled to around 600° F (315 °C) prior to entering the filter vessel, the filter elements will be porous metal with a 2-micron pore size. The off-gas from the regenerator, which contains sulfur as SO_2, will be captured in a packed tower absorber using sodium hydroxide and will be disposed of by METC rather than by being recovered as a useful product (such as sulfuric acid) or being recycled to the gasifier as in a commercial system. Similarly, the relatively sulfur free exit gas from the absorber will be burned in the incinerator, to convert any combustible gases prior to venting to the atmosphere. In a commercial unit, the absorber exit gas would be burned in a gas turbine to produce power.

The METC PDU is designed for operation in four distinct modes, which are combinations of fluid bed and transport contacting on both the absorber and regenerator sides. The four distinct modes are shown in Figure 3. Initial METC efforts will focus on transport

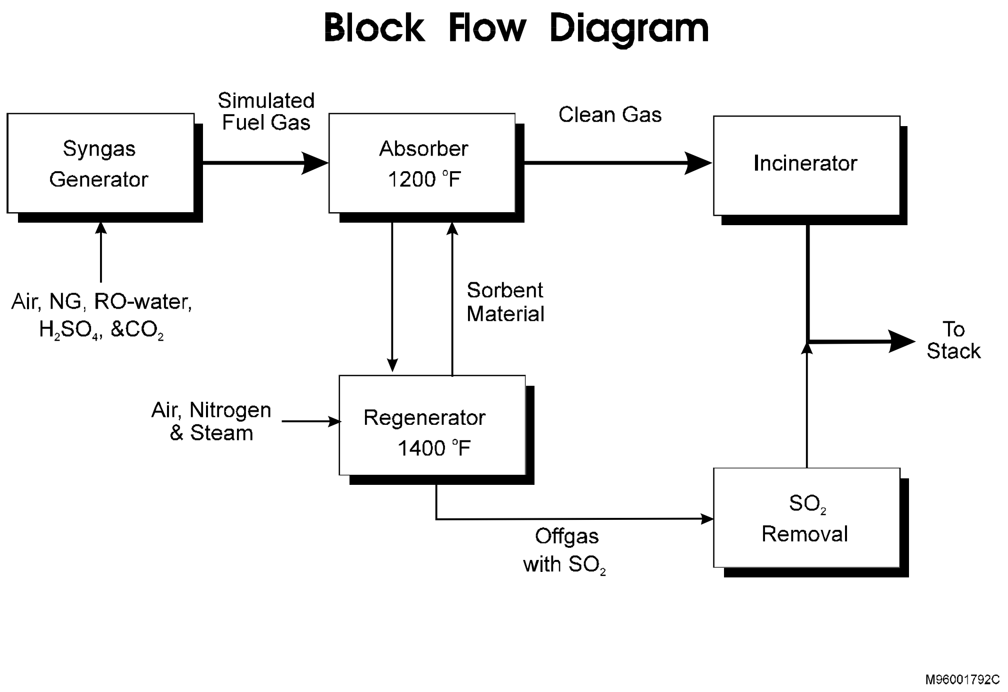

Figure 1

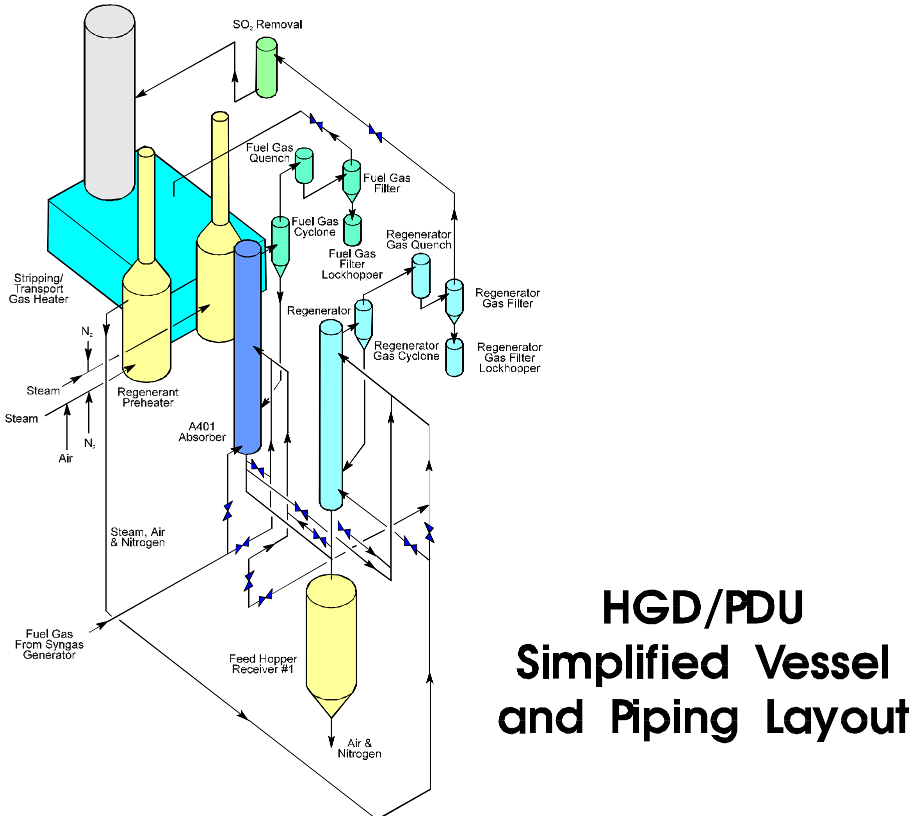

Figure 2

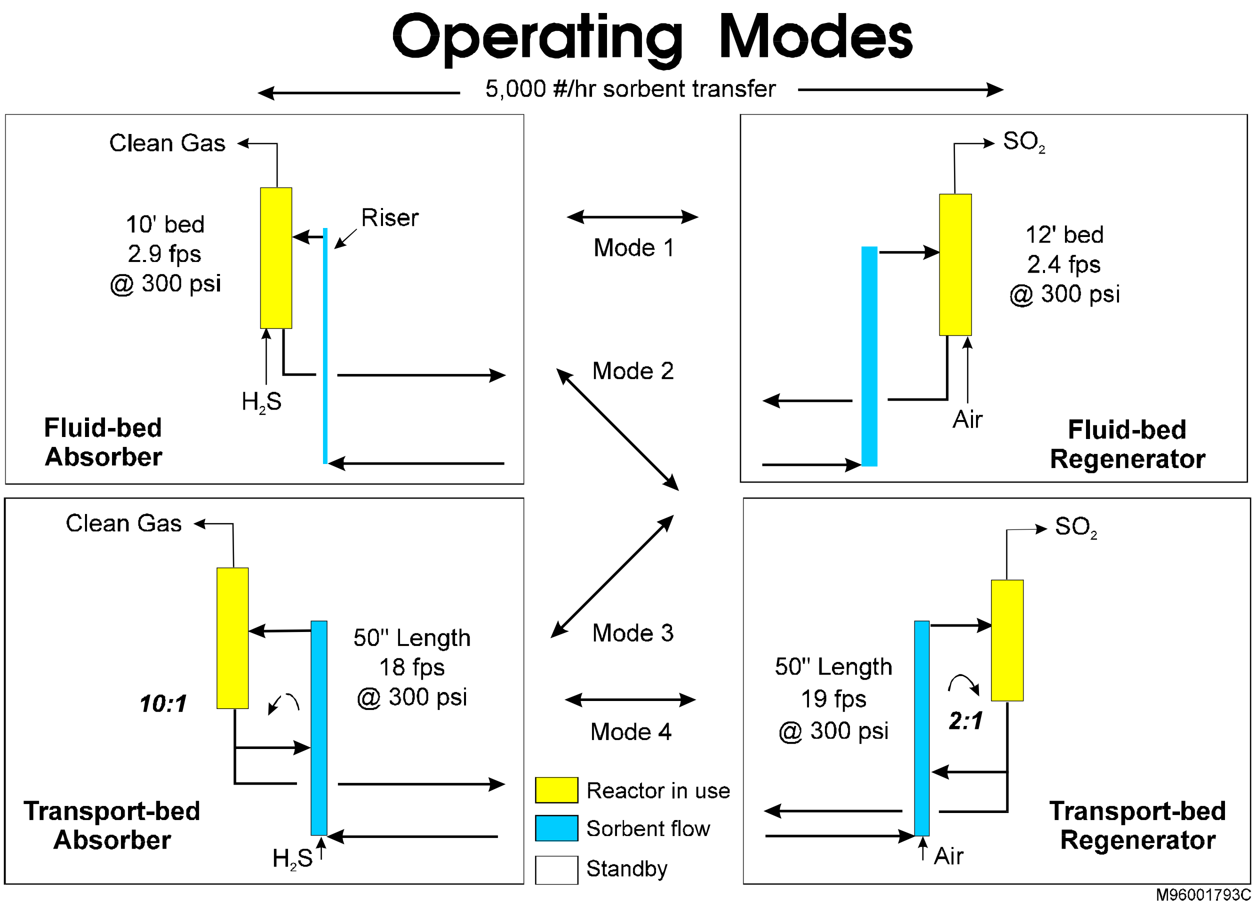

Figure 3

absorption and regeneration (Mode 4) due to the similarities to the Sierra Pacific Power Company's Clean Coal Technology project and because transport-based contacting offers potential economic benefits in both capital investment and operating simplicity.

General Operation

Some of the more important independent process variables to be studied regardless of the configurational mode include: H_2S concentration, sorbent type and particle size, sorbent sulfur loading, regenerant composition, and process temperatures. For fluid-bed modes, additional variables are bed level and fluidization regime (i.e., bubbling or turbulent); and for transport reactor modes, riser velocity and density are important added factors. The dependent variables include: sorbent circulation rate, absorber-regenerator differential pressure, pressure drop across circulation slide valves, amount and type of inert gases, and feed temperatures of the input gas streams.

The general operating strategy for the PDU will be to maintain constant flow rates, temperatures, pressures, and compositions during a specific test run. Values for independent variables will be specified prior to a run, and dependent variables will then be calculated to provide initial control setpoints. In order not to exceed design temperatures, operations will start with both the absorption and regeneration temperatures below the targeted values, and then feed temperatures will be increased. Process changes will be made gradually and the unit will be allowed to stabilize. As a general rule, the sorbent inventory will be cycled a minimum of three times between process state changes.

A stable pressure balance must be maintained for smooth, uninterrupted sorbent circulation. The absorber-regenerator differential pressure will be set to a constant value to balance the hydrostatic pressure buildups in the fluid beds and standpipes versus the pressure drops across the circulation slide valves and the risers. The normal differential pressure between the absorber and regenerator freeboards is expected to be in the range of +/-2 psi (13.8 kPa), depending upon the operating mode. The pressure drop across the circulation control slide valves should generally be about 5 to 10 psi (35 to 70 kPa). The absorber-regenerator differential pressure will be maintained by modulating the regenerator backpressure valve in response to the differential pressure. To keep the differential pressure as constant as possible, this controller will be tuned for a fast response relative the controller for the absorber backpressure valve.

Sorbent flow rates can not be measured directly. They will be inferred from pressure drops across the standpipe slide valves, which must be calibrated during startup activities. During operation, the circulation rate will be set at a targeted test value by positioning the slide valve in the absorber circulation standpipe (see Figure 4). This will establish a constant flow rate of sorbent from the absorber to the regenerator. The return flow rate of sorbent from the regenerator to the absorber will be automatically controlled by modulating the slide valve in the regenerator circulation standpipe to maintain a preset sorbent bed level in the absorber. The regenerator bed level "floats” in this scheme, but a constant sorbent feed rate is maintained to the regeneration side of the process where temperature concerns are greatest and the need for uniform sorbent flow is therefore more critical. Recirculation rates to the transport reactors will be set by positioning the slide valves in the recirculation standpipes.

Bed levels will be determined from bed differential pressures. Initial bed levels will be established by the amount of sorbent charged to the system. A drop in regenerator bed level during a test will indicate that sorbent inventory is declining because of attrition and carryover from the cyclones into the downstream filters. If necessary, makeup sorbent from the feed hopper can be added to the regeneration side of the process without interrupting the test run.

The entire output of the syngas generator will be fed to the PDU during normal operations. A slipstream approach is not possible due to air permit restrictions. Delivery pressure is set by a backpressure valve on the feed line to the PDU. The fuel-gas flow rate is established and controlled by input rates to the gas generator. The major composition will be established by firing stoichiometry and the proportional amounts of injected water and carbon dioxide. The hydrogen sulfide content will be controlled by the injection rate of sulfuric acid.

PDU Reactor Schematic

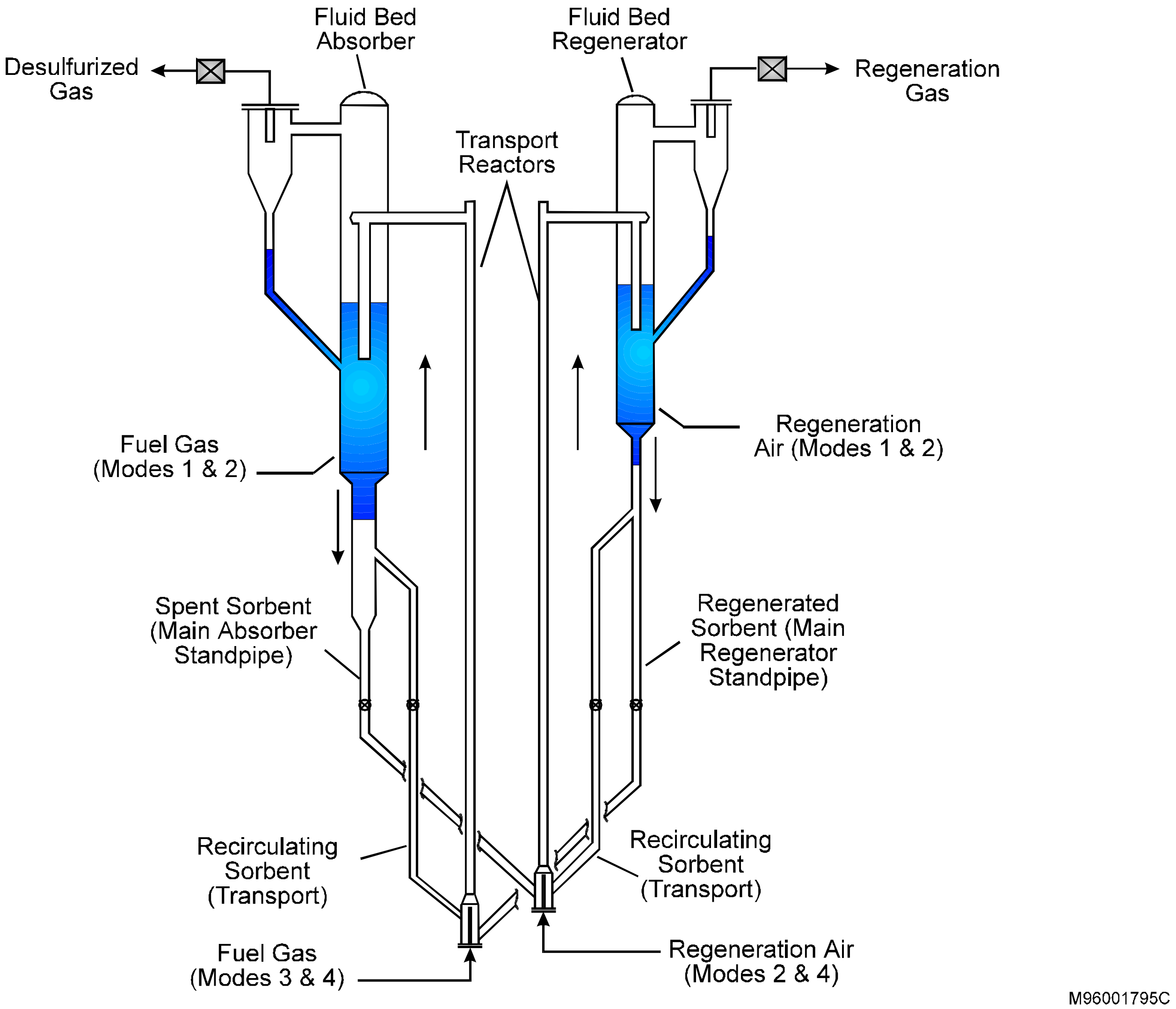

Figure 4

Nearly complete conversion of the sulfuric acid to hydrogen sulfide is expected. This air-blown, partial combustion process is projected to produce a nominal 100 to 130 Btu/scf (3,726 to 4,844 kJ/m^3) gas. Although the unit will be monitored for soot generation, any soot remaining in the gas that is fed to the PDU is not expected to be a significant problem due to the relatively high moisture content of the gas (minimum about 15 mole %), the hot refractory wall temperatures (minimum 1,250° F or 677 ° C), and the long piping length from the syngas unit to the PDU absorber (approximately 200 feet or 61 meters). These three features combined are expected to promote the conversion of soot to gaseous compounds.

Regenerant gas will be pure air, or mixtures of air with steam and/or nitrogen. To avoid condensation in the preheater coils, any steam used will be blended in downstream of the regenerant preheater. Required regenerant preheat temperatures can range from about 500° to 1400° F (260 °C to 760 °C) to maintain heat balance. Regenerant flow rates will vary depending upon test objectives. For a regeneration scheme using minimum air, the molar input rate of oxygen (in air) will be set stoichiometrically to be 1.5 times the molar sulfur removal rate of the absorber.

Inert gas will be used for stripping/aeration of standpipes, aeration of cyclone diplegs, and aeration of the mixing chambers at the bases of the transport reactors. Inert gas will also be a transport gas in fluid-bed modes, a fluidizing gas in transport modes, and a regenerant diluent if desired. To minimize operating costs, steam will be used as an inert gas as much as possible; however, pure nitrogen or steam-nitrogen blends can be used in some configurations.

Temperature Control

Temperature control is one of the more important areas of overall process control since temperature has a major impact on process and sorbent performance. Higher temperatures tend to give faster reaction rates and thus potentially better process performance, but can also damage sorbents and equipment. In addition, temperature control strategies must cope with heat of reaction effects. In HGD technology, the reaction effects range from relatively minor on the absorption side (about 926 Btu released per pound of hydrogen sulfide removed) to rather significant on the regeneration side (about 2993 Btu released per pound of sulfur dioxide formed). Therefore, we have outlined the temperature control strategies that will be used initially in the PDU. All of the following strategies take into account the relatively high heat losses that will occur due to the high surface-to-volume ratio of the PDU equipment compared to commercial equipment size.

Fluid-bed Absorber. Absorption temperature primarily depends upon the temperature of the entering fuel gas and, to a much lesser extent, on the temperature of the transport, aeration, and stripping gases. The temperature of regenerated sorbent and the circulation rate also affects absorption temperature but cannot be used as control parameters since these are set by test conditions. Therefore, the fuel-gas feed temperature was selected as the control parameter and the absorber vessel freeboard temperature was selected as the control point. The temperature of the fuel gas exiting the syngas generator will be established by syngas generator operating conditions and will be set higher than that required by the PDU. A temperature controller in the PDU fuel-gas inlet line will provide the final temperature trim by controlling the direct injection of water into the fuel gas transfer pipeline leading to the PDU. The PDU freeboard and fuel-gas inlet temperature controllers will be initially cascaded to provide a faster, smoother response to process upsets. Preliminary runs may indicate that cascading is not required, in which case the final absorption temperature control will come directly from the freeboard controller.

Transport Absorber. For this mode, the temperature control point will be switched from the absorber vessel freeboard to the transport reactor outlet. The control strategy will remain the same as that for the fluid-bed mode, except for additional solids recirculation considerations. The temperature of the recirculated solids will be set by the flow rate and temperature of the inert gas used to fluidize sorbent in the absorber vessel. A fluidizing flow rate will generally be set at a low value to minimize solids entrainment out of the vessel. Once the flow rate is set, it will generally be held constant and the fluidizing gas inlet temperature will then be adjusted so that the sorbent leaving the absorber vessel will be within about 5° F (3.5 °C) of the desired absorption temperature. The heat balance around the transport absorber establishes the necessary temperature of the entering fuel gas with this approach.

Fluid-Bed Regenerator. The temperature of sulfided sorbent, the circulation rate, the regeneration heat release, and the regenerant air rate and composition all affect the regeneration temperature, but these will be set by test conditions and cannot be used as control parameters. Although heat losses from the regenerator vessel/cyclone are significant and are estimated to be about 30 percent of the regeneration heat release for the fluid-bed design case, these losses will remain nearly constant for a given test. Thus, they cannot be incorporated into a control scheme. The regeneration temperature will also be affected by the temperature of the transport, aeration, and stripping gases, but the effect will be too minor for control purposes. Therefore, only the regenerant feed temperature can be used as a control parameter, which is analogous to the fuel-gas feed temperature on the absorption side. Analogously, the regenerator freeboard temperature was selected as the control point. The regenerant feed temperature will be controlled by adjusting the natural gas firing rate of the regenerant gas preheater.

Transport Regenerator. Transport regeneration control is more complicated than fluid-bed mode control due to solids recirculation and other constraints. Consequently, it is likely to change as experience is gained during initial operations. The constraints include the need to maintain a minimum reaction initiation temperature (thought to be around 1,100° F (593 °C) at the bottom of the transport reactor, the need to limit the maximum regeneration temperature (thought to be around 1,400° F (760 °C)), and the need to complete the desired extent of regeneration within the transport reactor length. The location of maximum temperature in the transport reactor is unknown, since this will depend upon sorbent characteristics and process conditions. For example, it is currently believed that increasing sorbent recirculation will spread the riser temperature profile and decreasing recirculation will compress the profile.

The list of variables identified in the fluid-bed mode as being available or unavailable for use as control parameters still applies. However, in the transport mode, the recirculation of sorbent will have a major impact on the regeneration temperature. Therefore, the flow rate and temperature of the recirculated sorbent were selected as the primary control parameters, demoting the regenerant feed temperature to a secondary status. Skin temperature measurements will be made at multiple points along the transport reactor length, and the maximum temperature in this profile will be selected as the control point. To make this selection, sorbent recirculation will be established and set at a sufficiently high flow rate (up to the hydrodynamic limit) to achieve the desired extent of regeneration within the reactor length. Then, with the recirculation rate held constant, the selected control point will be used to adjust the temperature of the recirculated sorbent, thereby controlling the regeneration temperature. Ideally, the selected control point will still correspond to the maximum regeneration temperature along the reactor length. If not, it may be necessary to change the control point at this time and repeat the procedure. The temperature of the recirculated sorbent will be adjusted by controlling the flow rate and the temperature of the inert gas that fluidizes the sorbent in the regenerator vessel. Thus, the temperature rise of the fluidizing gas closes the heat balance around the regenerator/cyclone circuit. Once the desired regeneration temperature profile is obtained, it can be fine-tuned by adjusting the regenerant feed temperature. If sorbent recirculation is not employed, then the regenerant feed temperature becomes the primary control parameter just as in the fluid-bed regeneration mode.

PDU Project Status and Schedule

Structural steel fabrication and steel erection was 100 percent complete in June 1996. The incinerator, barrier filter vessels, fines lock hoppers, sorbent feed vessel, filter blowback accumulator, and air and inert gas preheaters were mounted in the structure. As of June 1, 1996, project construction was 60 percent complete, up from 32% a year ago and progressing according to plan.

The project is on schedule to desulfurize coal-gas by October 1997. The project schedule is given in Figure 5.

Future Activities

In addition to demonstrating fully integrated operations, process and control scale-up data, performance data, and addressing other actual engineering challenges, future tests will concentrate on key operational and sorbent durability issues such as the following. (1) Which is more optimum from a sorbent as well as an overall process economic viewpoint; operating with small changes in sulfur loading on the circulating sorbent and thus at high circulation rate, versus running "deep" cycles with larger changes in sulfur loading but at comparatively lower circulation rates? (2) Which flow regime is best for chemical reaction and/or sorbent life, bubbling, turbulent, or transport?

These data will be generated at METC during six nominal 5-day test periods per year beginning after PDU shakedown in the fall of 1997. Initial testing will involve more numerous but shorter duration test periods. Test planning, operations, data reduction and reporting will be performed by DOE/METC personnel in partnership with industry.

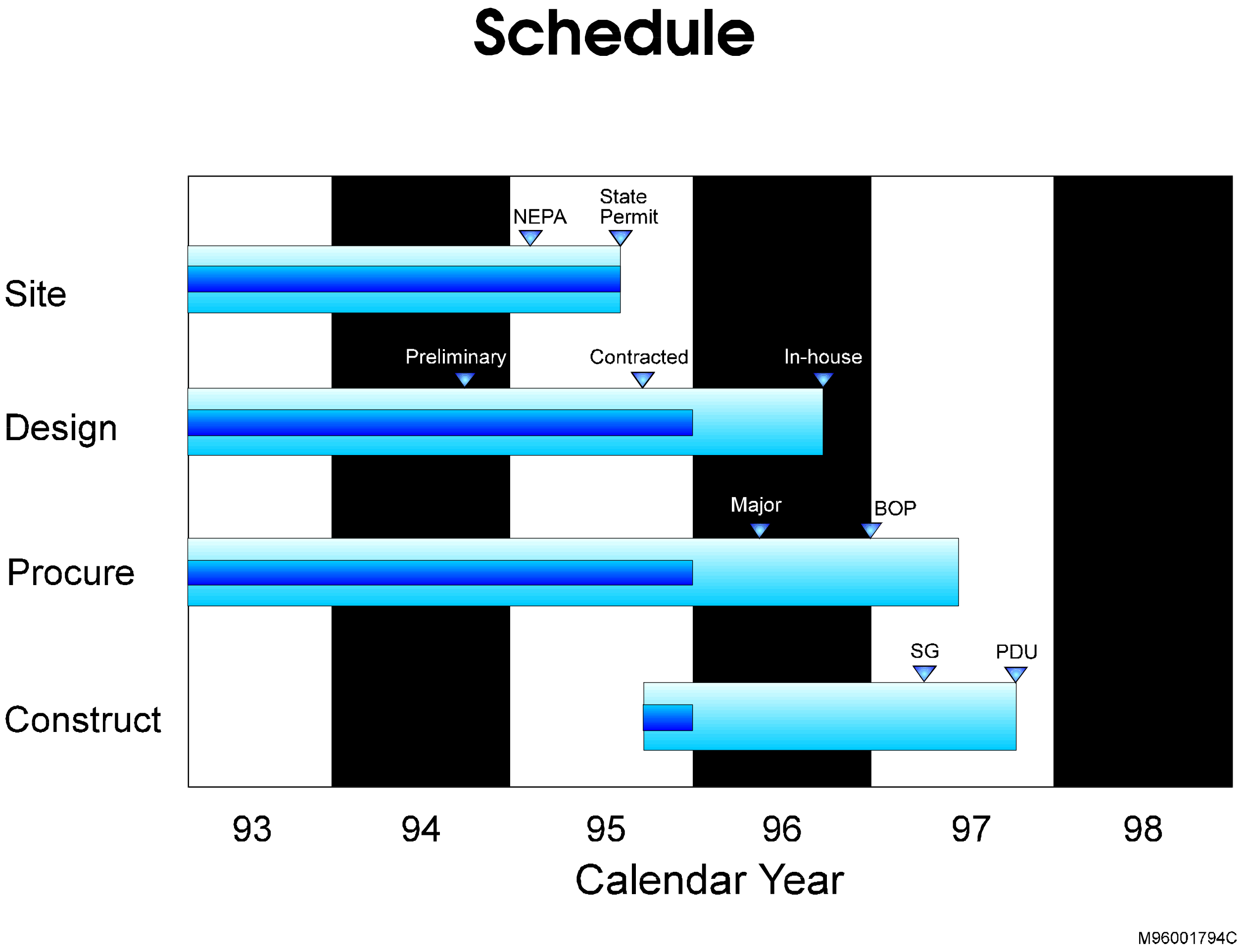

Figure 5

Summary

The PDU offers coupled system operation of various reactor configurations to optimize gas/solids contacting and to prove system safety and control aspects. The operating flexibility, and high degree of instrumentation mean that the PDU will provide design data on this complex HGD process over a broad operating window for about a dozen major operating variables.

At this point the PDU is not linked to a single developer. Therefore, intellectual property provided by the PDU will be available for application to other IGCC systems, including those using oxygen-blown gasifiers. The expected cost savings can thereby be realized by a much broader market than if the technology were limited in use to only one gasifier supplier. METC is interested in pursuing industrial cost sharing of PDU activities through arrangements such as cooperative research and development agreements, whereby intellectual property rights can be obtained by the industrial partner.

References

1. Bissett, L.A., J.M.Rockey, and S.C.Walczak. 1991. Preliminary Conceptualization of METC's Fluid-Bed, Hot-Gas Desulfurization PDU. In *Proceedings of the Eleventh Annual Gasification and Gas Stream Cleanup Systems Contractors Review Meeting*, 556-565, DOE/METC-91/6123, Vol. 2. NTIS/DE92001102. Springfield, VA.: National Technical Information Service.

2. Bissett, L.A. 1993. Fluid-Bed HGD PDU. In *Proceedings of the Coal-Fired Power Systems 93 -- Advances in IGCC and PFBC Review Meeting*, 302-306. DOE/METC-93/6131, NTIS/DE93000289. Springfield, VA.: National Technical Information Service.

3. Rutkowski, M.D., H.T. Chen, and M.G. Klett. 1993. Sensitivity of Hot-Gas Desulfurization on IGCC Cost of Electricity. *Proceedings of the 12th Annual Gasification and Gas Stream Cleanup Systems Contractors Review Meeting*, 263 -279. DOE/METC-92/6128, Vol. 1, NTIS/DE93000228. Springfield, VA: National Technical Information Service.

4. Bissett, L.A., 1994. METC Fluid-Bed Hot-Gas Desulfurization PD. *Proceedings of the Coal-Fired Power Systems 94 -- Advances in IGCC and PFBC Review Meeting Vol. I,* 256 -262. DOE/METC-94/1008, Vol.1, NTIS/DE94012252. Springfield, VA. National Technical Information Service.

5. Monahan, M.J., 1992. METC’s Synthetic Gas Generator Project. *Proceedings of the Eleventh Annual Gasification and Gas Stream Cleanup Systems Contractors Review Meeting*. 533-540. DOE/METC-91/6123, NTIS/DE92001102. Springfield, VA. National Technical Information Service.