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METC Fluid-Bed Hot-Gas Desulfurization PDU

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DISCLAIMER

6.5 METC Fluid-Bed Hot-Gas Desulfurization PDU

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OBJECTIVE

METC is constructing an on-site, hot-gas desulfurization (HGD) process development unit (PDU) to support the U.S. Department of Energy's (DOE's) Integrated Gasification Combined Cycle (IGCC) power systems program. With industrial participation, this PDU will be used for the further development of fluid-bed and transport reactor HGD configurations.

BACKGROUND INFORMATION

Fluid-beds and transport reactors, either alone or in combination, are conceptually attractive for HGD processes because they offer continuous steady-state operation, superior temperature control, and a wide range of achievable regeneration gas sulfur dioxide (SO_2) concentrations. These attributes potentially simplify system control strategies, prolong sorbent activity, and add process flexibility with respect to sulfur recovery options.

During the early conceptualization phase of this project, an economic study failed to show any notable cost and performance differences between IGCC systems with fluid-bed HGD and the same systems with moving-bed HGD (1). Based on testing activities ongoing at that time, relatively low velocity HGD fluid beds were used in this study. A sensitivity analysis showed that costs could be improved by employing higher fluidizing velocities. The study also revealed economic advantages for a system that uses a minimal amount of undiluted air to produce a concentrated SO_2 stream during sorbent regeneration.

These considerations provided the incentive to look at progressively higher velocity regimes and alternative contacting modes during PDU conceptualization (2,3). As a result, the fluid-bed absorber and regenerator in the PDU were designed to operate in a turbulent as well as a bubbling regime. In addition, when encouraging results from a small-scale transport reactor unit became known, the decision was made to incorporate transport reactor provisions on both the sulfidation and regeneration sides of the PDU. Little additional expenditure was required to gain these extra capabilities.

With completion of National Environmental Policy Act (NEPA) documentation requirements, the preliminary process and equipment design, and the April groundbreaking to prepare the project site, the project is now proceeding at a faster, more visible pace. Equipment installation should be completed in about 2 years.

PROJECT DESCRIPTION

As shown by Figure 1, the project is being centrally located in the METC experimental facilities. A nearby natural gas-fired synthesis gas (syngas) generator, which will share the PDU control room, will supply the PDU with up to 4,000 Nm^3/hr (150,000 scfh) of simulated coal gasification fuel gas (4). The PDU equipment will be housed in an open-steel structure with dimensions (excluding stairs) of about 6 by 15 by 24 m in height (20 by 48 by 80 feet).

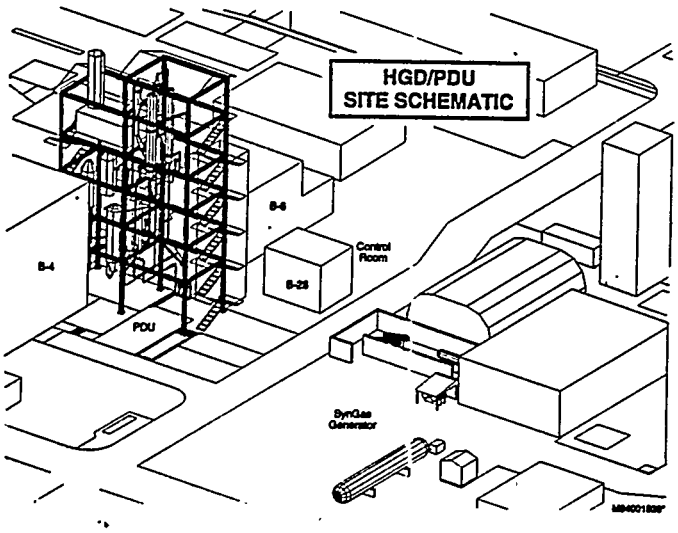

Figure 1. Isometric View of PDU Site

The adjacent fluid-bed vessels will be about 9 m (30 feet) in length, have a top elevation of about 23 m (76 feet) above grade, and have closely coupled external cyclones and diplegs. The vessels will be carbon steel with refractory linings with constant inside diameters throughout the vessel length. Maximum bed depths for the absorber and regenerator will be 3 m (10 feet) and 4 m (12 feet), respectively. A second absorber stage can be added if needed, in which case the vessel will accommodate two 1.5-m (5-foot) beds. The design also has provisions for testing with submerged or freeboard risers and with underflow or overflow standpipes. Standpipe diameters vary from 5 to 15 cm (2 to 6 inch) in diameter. All standpipes and sorbent transfer lines will be unlined, externally insulated alloy pipes.

The PDU will have operating pressure capabilities of 2.8 MPa (400 psia) and operating temperature capabilities of 650°C (1,200°F) on the sulfidation side and 760°C (1,400°F) on the regeneration side. Sulfidation temperatures down to about 425°C (800°F) can be accommodated. As shown by Figure 2, fuel gas can be fed to either the 46-cm-i.d. (18-inch) fluid-bed absorber or to the 15-cm diameter (6-inch) absorber transport reactor. During fluid-bed sulfidation testing, the absorber transport reactor will not be used, and sorbent will be circulated with steam or nitrogen from the regenerator to the absorber through the 5-cm diameter (2-inch) absorber riser. Preheated regeneration gas (air, steam, nitrogen) can be fed to either the 25-cm i.d. (10-inch) fluid-bed regenerator or to the 5-cm diameter (2-inch) regenerator transport reactor, which serves as the regenerator riser during fluid-bed regeneration testing.

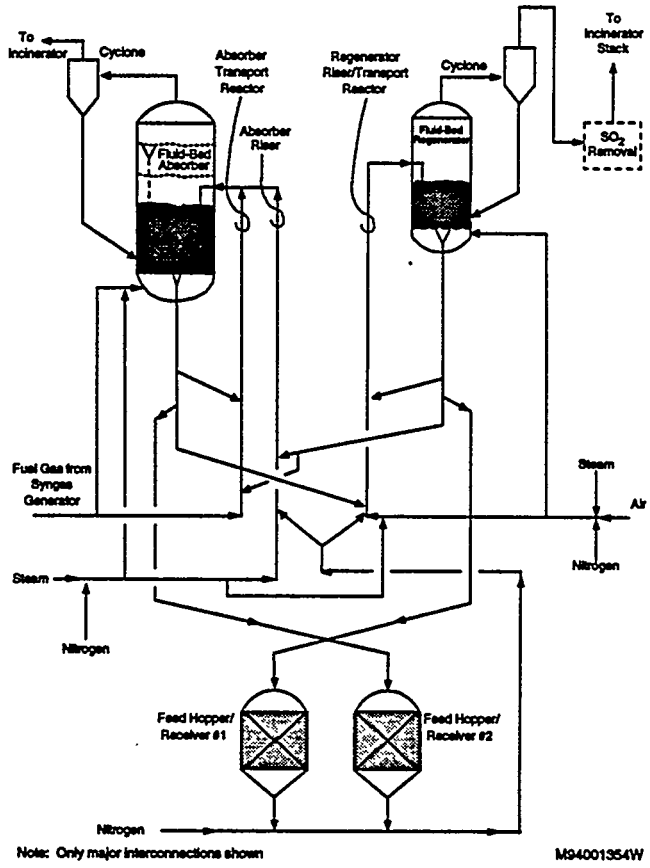

Figure 2. Simplified Flow Diagram of PDU

During transport reactor mode testing and unlike in a commercial configuration, the associated fluid beds will serve as disengagers and remove excess regeneration heat by adjusting the flow rate and temperature of the fluidizing gas. The preheated steam and

nitrogen shown entering on the left side of the diagram provide this service and also serve as aeration/stripping gas and transport gas during fluid-bed mode testing.

Y-bend transfer lines will be used to circulate sorbent between the sulfidation and regeneration sides, and for recirculation to the 15-m long (50-feet) transport reactors. Control valves in the standpipes will be used to control sorbent flow rates. If the circulation control valves in the standpipes prove troublesome at this scale, the Y-bends can be converted to U-bends, which do not require control valves.

Sorbent circulation rates will be in the range of about 900 to 2,300 kg/hr (2,000 to 5,000 lb/hr). Sorbent recirculation rates will range up to about 23,000 kg/hr (50,000 lb/hr) through the absorber transport reactor and about 2,300 kg/hr (5,000 lb/hr) through the regenerator transport reactor. Recirculation is needed on the sulfidation side to improve contacting and to increase sorbent sulfur loading, and on the regeneration side to control temperature. Solids loadings in the absorber and regenerator transport reactors are expected to be respectively about 140 to 190 kg/m^3 (9 to 12 lb/ft^3) and 30 to 190 kg/m^3 (2 to 12 lb/ft^3). The absorber and regenerator transport reactors are respectively sized for superficial velocities of about 8 m/s (25 ft/s) and 5 m/s (15 ft/s). The design is based upon 70 to 250 micrometer-sized zinc titanate and Z-Sorb, the latter being a proprietary material developed by Phillips Petroleum Company.

Figure 2 also shows two vessels that can alternately serve as feed hoppers or receivers. These were included in the design so that the sulfidation and regeneration sides can be operated separately (decoupled). This provision was included to aid process development but may not get constructed for budgetary reasons.

RESULTS

The following figures illustrate certain aspects of transport reactor HGD. These are presented to indicate trends that might be observed when PDU operations commence. All of these figures are based on the use of Z-Sorb to desulfurize fuel gas containing 5,000 ppmv of hydrogen sulfide (H_2S) at 650°C (1,200 °F) and 2.1 MPa (300 psia). Comparable figures could have been prepared for zinc titanate sorbent or for other process conditions.

A transport reactor HGD system has numerous possible operating points depending upon factors such as sorbent characteristics, processing conditions, regeneration scheme, and system performance targets. Sorbent circulation/recirculation rates and utilization levels/swings are interrelated. Figure 3 depicts one possible operating point and is presented here to introduce and illustrate certain concepts. Utilization, expressed here as a fraction, is a measure of the amount of sulfur in a sorbent relative to its completely sulfided state. The sulfur content of the sorbent used for this illustration varies by about 15 weight % as the utilization goes from 0 to 1.0. System utilization swing is the change in utilization as the sorbent circulates between the sulfidation and regeneration sides. Thus, for the example in the figure, the sulfur content of the sorbent circulated to the regenerator is about 2.3 weight % higher (0.15 times 15 weight %) in sulfur content than the sorbent returned to the absorber.

Figure 3 shows that for each time sorbent is circulated from the absorber to the regenerator and back (i.e., one sulfidation-regeneration cycle), it has been recirculated on average about 50 times through the transport absorber, and about 2 times through the transport regenerator. Correspondingly, the sulfur content of the sorbent flowing through the transport absorber

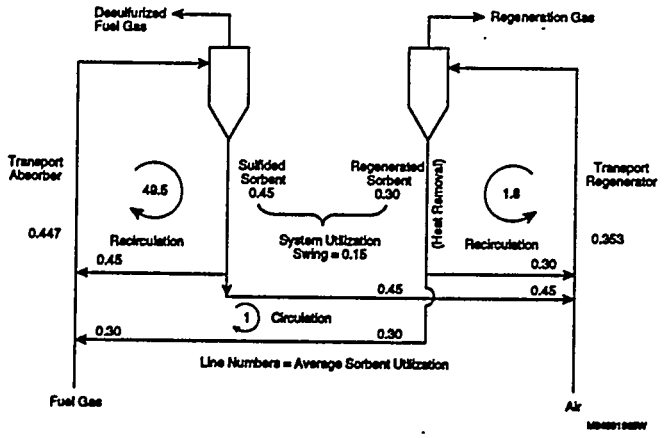

Figure 3. Illustrative Schematic of Transport Desulfurization

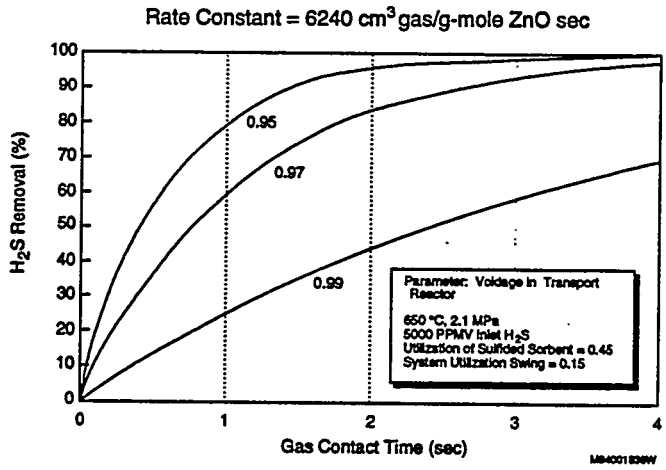

Figure 4. Illustrative Predicted Performance of Transport Absorber

increases by only about 0.04 to 0.05 weight % per pass, and decreases by about 0.8 weight % per pass through the transport regenerator. Since flow splits for circulation and recirculation are purely random, these utilization and sulfur levels are mass-averaged values for a potentially wide distribution. Also, the recirculation levels for this and subsequent figures assume no slip velocity between the sorbent and gas. To the extent that slip occurs, recirculation-circulation ratios will decrease.

During the PDU conceptualization phase, a small-scale transport reactor proof-of-concept test was conducted by the M.W. Kellogg Company using Z-Sorb. Excellent desulfurization performance with little sorbent attrition was reported. From the results, a first approximation of the sulfidation rate constant for the transport mode was made assuming pseudo first-order kinetics and plug flow. Figure 4 shows the resulting predicted removal of H_2S as a function of gas residence time and void fraction in a transport reactor. These illustrative trends, which encouragingly indicate that greater than 99 % sulfur removal may be possible in about 3 seconds gas contact time, solidified the decision to have transport reactor provisions in the PDU.

For a given process condition and gas contact time, the extent of desulfurization increases as the initial molar ratio of ZnO-to-H_2S (i.e., reactants) increases. Thus, higher sorbent loadings in a transport reactor (i.e., lower voidages, higher reactor density), and higher zinc oxide contents in a sorbent (i.e., lower utilization levels), increase the probability of achieving a target level of sulfur capture. This analysis assumes that all of the zinc oxide in the sorbent is equally accessible to H_2S. Testing is required to determine to what extent this assumption is valid.

These general trends are illustrated by Figure 5, which shows that as utilization of the sulfided sorbent increases, the transport reactor must be run at a higher density (i.e., lower voidage) to maintain desulfurization performance (in this case, 99 % sulfur removal). Because the sorbent undergoes only fairly small density increases as utilization increases, circulation remains nearly constant for a given system utilization swing. Therefore, higher reactor densities are achieved primarily with higher recirculation

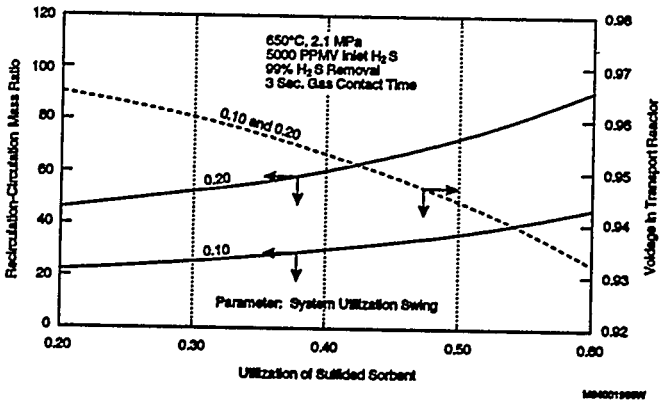

Figure 5. Illustrative Predicted Trends for Transport Absorber

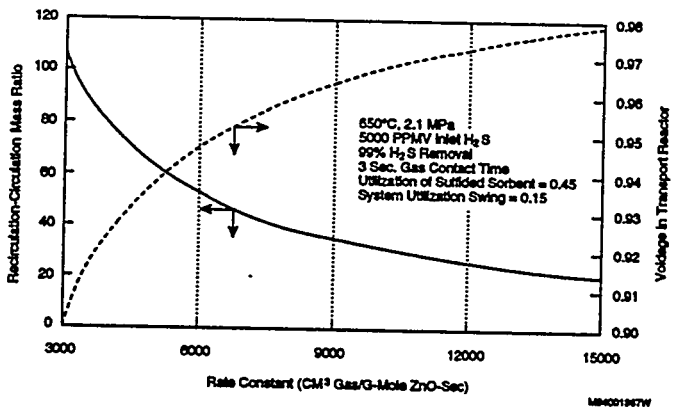

Figure 6. Illustrative Predicted Trends Showing Importance of Sulfidation Rate Constant

rates. The figure also shows that the recirculation ratio increases at higher system utilization swings (due to decreased circulation), and that the needed voidage becomes essentially independent of system utilization swing since, as discussed earlier, the utilization change per pass through the transport absorber is very small.

The ability to achieve a certain level of desulfurization improves as sorbent activity increases. As shown by Figure 6, this lowers the required reactor densities and recirculation rates, which should beneficially translate into lower sorbent attrition tendencies due to reduced sorbent movement. This is also important in the sense that as a sorbent potentially deactivates with use, a higher initial activity provides more operating flexibility to adjust system parameters to maintain performance before limiting factors such as choking are encountered.

In the absence of relevant kinetic information, comparable illustrations of transport regeneration can not be prepared. Given the likely high rate of reaction, obtaining sufficient regeneration in a transport reactor of reasonable length should not be a problem. However, the possibility of particle overheating may be encountered if the reaction rate is too rapid and outpaces heat transfer. This could prove to be especially troublesome for a process that uses a minimal amount of undiluted air (i.e., 21 percent oxygen) for regeneration. Depending upon temperature regimes and kinetics, sulfate formation may also be encountered since oxygen and SO_2 will both be present in considerable concentrations. In addition to being potentially detrimental to a sorbent, this would increase the regeneration air requirement and generally lower efficiency.

A simple heat balance can illustrate some transport regeneration trends and may ultimately prove to be more relevant than kinetic considerations for establishing sorbent flow rates. During regeneration, sorbent serves as a heat sink and limits overall temperature rise. As shown by Figure 7, the amount of sorbent circulated per unit of sulfur regenerated decreases as system utilization swing increases. Consequently, more heat is released per unit of circulated sorbent, which translates into the need for more sorbent recirculation to limit the higher potential temperature rise. With temperatures used for this figure, the total amount of circulated and

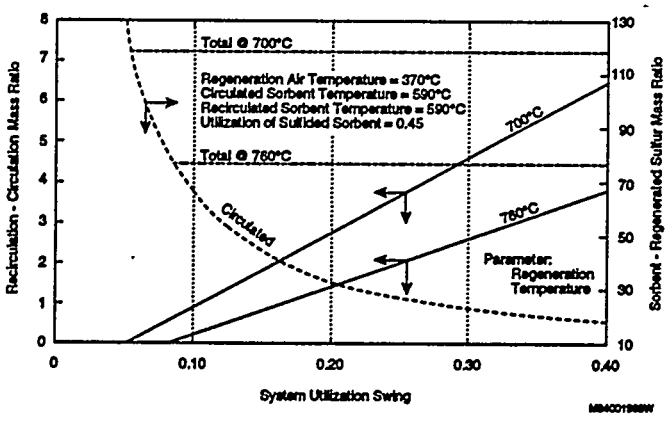

Figure 7. Illustrative Trends for Transport Regenerator

recirculated sorbent necessary for any given regeneration temperature is constant (horizontal lines) throughout the range of system utilization swings. Higher total amounts are needed for lower regeneration temperatures. The difference between total and circulated is the amount of sorbent that must be recirculated. The resulting recirculation ratio is graphically shown as constant-temperature operating lines for two regeneration temperatures.

Where the operating lines meet the horizontal axis, or where the total and circulated sorbent trends intersect, the recirculation requirement becomes zero. For the conditions used, this occurs for the two regeneration temperatures plotted when about 0.8 and 1.3 weight % sulfur is regenerated from the sorbent. These regeneration amounts would change for different assumed regenerant and sorbent temperatures. From a systems viewpoint, this becomes a tradeoff between having a large circulation rate and a once-through regenerator without heat removal versus a smaller circulation rate and a regenerator with recirculation and heat removal. The once-through system is simple, and has the additional potential benefit of maximizing the transfer of regeneration heat to the absorber. On the other hand, the more complex system with recirculation appears to offer better process flexibility. The PDU, which is configured to test both systems, should begin to sort out the operational problems and capabilities associated with each.

WRAP-UP

DOE is making a sizeable investment in this facility and believes it can accelerate HGD development and commercialization. With its ability to demonstrate fully coupled sulfidation-regeneration operations at a meaningful scale, the PDU represents an essential step beyond the small-scale batch reactors used to date. Since a number of technologies can likely emerge as winners in the HGD market due to site-specific factors, the PDU can provide the opportunity to explore candidates and serve as an initial proving ground.

Industrial participation is considered essential for maximizing the effectiveness and outcome of the project. Both sorbent and process developers are encouraged to participate, preferably through the Cooperative Research And Development Agreement (CRADA) program.

REFERENCES

1. Rutkowski, M.D., H.T. Chen, and M.G. Klett. 1992. Sensitivity of Hot Gas Desulfurization on IGCC Cost of Electricity. In *Proceedings of the Twelfth 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.

2. 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.

3. 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.

4. Monahan, M.J. 1991. METC's Synthetic Gas Generator Project. In *Proceedings of the Eleventh Annual Gasification and Gas Stream Cleanup Systems Contractors Review Meeting*, 533-540. DOE/METC-91/6123, Vol. 2. NTIS/DE92001102. Springfield, Va.: National Technical Information Service.

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