

**5.8**

**MTCI Acoustic Agglomeration Particulate Control**

**CONTRACT INFORMATION**

Contract Number DE-AC21-89MC26288

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Period of Performance June 15, 1989 to June 1, 1995

**Schedule and Milestones**

	1993	1994	1995
Provide Coal Pulse Combustor (Additional Test Facility Modification and shakedown)	_____		
Combined Control Test (Additional Parametric Testing)	_____		
Economic / Engineering Evaluation (Additional Engineering Evaluation)		_____	_____
Commercialization Plan		_____	_____

**OBJECTIVES**

The overall objective of this project is to demonstrate pulse combustion induced acoustic enhancement of coal ash agglomeration and sulfur capture at conditions typical of direct

coal-fired turbines and PFBC hot gas cleanup. The goal of the program is to support the mission of the Department of Energy (DOE) for developing coal-fired combustion gas turbines and advanced PFBC systems.

Specifically, the goals are to:

- Demonstrate the pulse coal combustion, ash agglomeration and sulfur capture,
- Achieve/Meet
  - combustion efficiency > 99%
  - turbine tolerance criteria
    - particulate loading in the 100 - 150 ppmw range
    - particle size < 10 microns with 99% < 3 microns
    - NO<sub>x</sub> @ 15% O<sub>2</sub> < 125 ppm
    - SO<sub>2</sub> @ 15% O<sub>2</sub> < 75 ppm
  - New Source Performance Standards
    - SO<sub>2</sub> < 1.2 lb/MMBtu
    - NO<sub>x</sub> < 0.6 lb/MMBtu
    - particulates < 0.03 lb/MMBtu

## BACKGROUND INFORMATION

Growing concern over global warming, dwindling environmental quality, accelerated waste generation rate, and dependence on foreign oil has spawned an interest in and the need for advanced energy technologies in general and advanced combustion technologies in particular. This, together with the interest in increasing the utilization of coal, entails the development of innovative concepts which promise higher combustion efficiency, higher sulfur capture efficiency, lower NO<sub>x</sub> emissions, lower particulate emissions, and greater fuel flexibility. The advanced combustion technologies currently under demonstration include Fluidized Bed Combustion (FBC), Staged Slagging Combustion (SSC), and Limestone Injection Multistage Burning (LIMB).

While these technologies promise lower SO<sub>2</sub> and NO<sub>x</sub> emissions compared to conventional technologies, each possesses one or more of the following limitations:

- Operates either in the combined cycle format but at a lower peak cycle temperature (e.g., 1550°F rather than at ~ 2300°F) or at atmospheric system pressure and therefore not in the combined-cycle format. This results in lower overall cycle thermal efficiency and consequently higher specific fuel consumption and typically higher emissions levels (CO<sub>2</sub>, CO, SO<sub>2</sub>, NO<sub>x</sub>, and particulate) per pound of coal burned.
- Operates in the slagging mode which poses difficulty with regard to design, reliability, material selection, compliance with emissions standards in the absence of downstream particulate collection equipment, and economics.
- Requires barrier filters to control particulate emissions which pose concerns regarding durability, economics, and limited operating range.
- Requires specially prepared sorbents or some process enhancement to improve calcium utilization and achieve 90% SO<sub>2</sub> retention and this significantly increases the operating cost of the unit.

In response to this challenge, MTCI has developed an advanced compact pulse combustor island for direct coal-firing in combustion gas turbines. This combustor island comprises a coal-fired pulse combustor, a combined ash agglomeration and sulfur capture chamber (CAASCC), and a hot cyclone (**Figure 1**). In the MTCI proprietary approach, the pulse combustion-induced high intensity sound waves improve sulfur capture efficiency and ash agglomeration. The resulting agglomerates allow the use of

commercial cyclones and achieve very high particulate collection efficiency.

Many investigations have confirmed the ability of acoustic fields to agglomerate fly ash to increase particle size. However, the majority of this work focused on the agglomeration of unimodal distributions of fine aerosols which were not fully representative of the conditions within a gas turbine combustor utilizing standard grind pulverized coal or coal-water mixtures, particularly in conjunction with lime sorbent injection processes. Therefore, the conclusions drawn from experimental and theoretical investigations to date using fine unimodal distributions, such as the optimum acoustic sound pressure levels and frequency, may not be valid as applied to the MTCI coal-fired gas turbine technology.

In the MTCI proprietary approach, sorbent particles are injected into a gas stream subjected to an intense acoustic field. The acoustic field serves to improve sulfur capture efficiency by enhancing both gas film and intra-particle mass transfer rates. In addition, the sorbent particles act as dynamic filter foci, providing a high density of stagnant agglomerating centers for trapping the finer entrained (in the oscillating flow field) fly ash fractions. The fly ash fractions have particle sizes which fall primarily in the range from less than 1 to 20 microns. Therefore, by introducing sorbent particles which are primarily concentrated in the size range from 20 to 80 microns, a bimodal distribution is created. The bimodal distribution offers several advantages. First, by increasing the density (in the gas) of large stagnant trap centers, an accelerated agglomeration rate can be achieved. Second, agglomeration can be efficiently performed at a significantly lower acoustic frequency range compared to unimodal distributions containing only finer fly ash fractions.

The effectiveness of particle agglomeration at low frequencies is extremely significant. The

rate of agglomeration is strongly influenced by the acoustic intensity level. Since low frequencies are attenuated less than high frequencies, lower frequency operation is anticipated to be more effective. Furthermore, low frequencies are not expected to affect performance of turbine blades, while frequencies in the kHz range may couple into the system's natural frequencies. Finally, the cut-off particle diameter for 50% entrainment increases with a decrease in frequency and therefore lower frequency operation results in the entrainment of a larger proportion of a given particle feed size distribution and places less constraint on the upper limit for particle growth.

The major advantage of the MTCI combustor island shown in Figure 1 is the ability to use standard grind, unbeneficiated or partially beneficiated coal as fuel. It offers the following additional benefits:

- Pulse combustion provides for a relatively high volumetric heat release rate and high combustion efficiency in a shorter residence time. This gives rise to a compact combustor.
- The pulse combustor is an inherently low  $\text{NO}_x$  burner and therefore  $\text{NO}_x$  emissions are low.
- While a conventional steady flow combustor results in pressure loss, the pulse combustor provides for a combustion-induced pressure boost. The net pressure gain is therefore significant and offers the potential for higher specific power output or lower specific fuel consumption.
- Employs sonic-enhanced coal ash agglomeration and dry ash rejection. This avoids the need for slagging mode of operation which poses difficulty with regard to design, reliability, material selection, compliance with emissions standards, and economics. Ash agglomeration allows the use of conventional cyclones to achieve very high particulate

collection efficiency and eliminates the need for barrier filters which pose concerns regarding durability and economics.

- Efficient in-situ sulfur and alkali capture in sonic-enhanced mode.

## PROJECT DESCRIPTION

The overall objectives of this project are to experimentally develop the basic design framework for scale-up of this technology and to experimentally characterize a laboratory-scale gas turbine combustor island.

The specific objectives of this program are to:

- Perform system shakedown and parametric testing;
- Conduct applied studies for the development of a combined acoustic agglomeration and sulfur capture model and an aerodynamic analysis to establish the aerovalve design data base;
- Conduct engineering and economic evaluations of the system; and
- Develop a design code for combustor island scale-up.

A team has been formed with MTCI as the prime contractor and Penn State University (PSU) and West Virginia University (WVU) as sub-contractors to MTCI. MTCI is focusing on hardware development and system demonstration, PSU is investigating and modeling acoustic agglomeration and sulfur capture, and WVU is studying aerovalve fluid dynamics.

## Apparatus

To demonstrate proof-of-concept, a laboratory-scale bimodal test facility has been designed, fabricated, and integrated for elevated pressure (4 atm.) operation at MTCI (**Figure 2**). It incorporates an advanced tailpipe-agglomeration chamber interface configuration, a coal preheating arrangement, a refractory-lined cyclone to simulate hot gas cleanup, and elaborate instrumentation and controls to enable complete process characterization and safe operation. The test facility comprises the following components/ subsystems:

- Coal and sorbent feed system.
- Air and natural gas supply system.
- Pulse combustor.
- Acoustic agglomeration and sulfur capture chamber.
- Refractory-lined cyclone.
- Fuel preconditioner.
- Heat exchanger.
- Pressure letdown valve.
- Baghouse.
- Steam circuit.
- Cooling water circuit.
- Instrumentation and controls.

Initial tests were performed with one cyclone (primary cyclone) on-line. The design velocity for this cyclone was kept modest (40 to 50 ft/s) to reduce potential agglomerate breakup during transit. This, however, reduced the particulate capture efficiency so that some 10  $\mu\text{m}$

size particles were leaving with the cyclone exit flue gas. Therefore, a secondary cyclone was added (as shown in Figure 2) to enhance overall solids capture efficiency.

### System Tests and Results

At MTCI, system shakedown tests were initially conducted at pressures of 2 and 3 atm. with natural gas and pulverized coal (Seacoal - Pittsburgh No. 8). After verification of satisfactory system operation, 27 screening tests have been performed. The system has been in operation for about 193 test hours.

The parameters varied include pulverized sorbent types, sorbent injection location and Ca/S molar feed ratio. The sorbent types examined include a dolomite (Dolofil by Pfizer), a limestone (Linden Falls), a precalcined lime (Annville by Wimpey Minerals), a pulse combustor calcined and classified (PCC) dolomite (Pfizer Dolofil), and a PCC lime (Annville by Wimpey Minerals).

Tests have been performed with injection of:

- Coal into the pulse combustion chamber and no sorbent injection,
- Premixed coal and sorbent (dolomite or limestone) into the pulse combustion chamber (P.C.),
- Coal into the pulse combustion chamber and sorbent (dolomite, lime, mixture of lime and Baltimore Gas and Electric power plant fly ash, cold air classified lime, PCC dolomite and PCC lime) into the inner section of the agglomeration chamber (A.C.).

The PCC dolomite and PCC lime were generated in the MTCI laboratory-scale pulsed atmospheric fluidized combustion system which

integrates a pulse combustor with a bubbling fluidized bed.

The reader is referred to an earlier paper [1] for test results from the initial test series. The overall test results indicated the following:

- Stable pulse combustor operation was achieved with a variation in firing rate from 1.67 MMBtu/hr to 2.52 MMBtu/hr at 3 atm. system pressure.
- The pressure oscillations were robust and the sound pressure level (SPL) varied from 174 to 186 dB with an increase in firing rate.
- The combustion efficiency exceeded 99%.
- The sulfur capture efficiency ranged from 38 to 98.5%. Calcium utilization was the highest with dolomite followed by lime and then by limestone. Limestone was pretty good in capturing sulfur (77%) at low firing rate but inferior (38% sulfur capture) at medium firing rate probably due to sintering. Sulfur capture exhibited an increase with Ca/S feed ratio for PCC dolomite and PCC lime injection into the A.C. (see **Figure 3**). The calcium utilization was low due probably to the high operating temperature (2000-2200°F) in the A.C.
- NO<sub>x</sub> emissions were in the 82 to 200 ppm range when corrected to 15% O<sub>2</sub> (**Figure 4**). NO<sub>x</sub> emissions tended to increase with dolomite feed rate corroborating the catalytic effect of calcined dolomite on NO<sub>x</sub> formation reactions. With PCC lime injection into A.C., the NO<sub>x</sub> emissions did not increase from the base case (no sorbent injection) level and remained below the 125 ppm @ 15% O<sub>2</sub> target for turbine tolerance.
- The solids loading in the cyclone exit flue gas ranged from 23 ppmw (with two cyclones) to 450 ppmw (with one cyclone). The highest

loading was obtained with dolomite injection into the P.C. and this is attributed to particle fragmentation and fines generation in the high heating rate environment of the pulse combustor. Penn State University (PSU), in an independent study, similarly found increasing decrepitation with an increasing magnesium oxide content. The high purity limestone (Linden Falls) was tested based on the recommendation of PSU and it also was found to decrepitate albeit to a lesser extent than dolomite. The injection of lime into the agglomeration chamber was therefore attempted and the test results indicate the merit of that option. With one cyclone on-line, the cyclone exit flue gas solids loading was below 150 ppmw and within the target goal for gas turbine particulate tolerance. With one cyclone on-line, the baghouse catch indicated about 30% by weight of particles exceeding 3 microns in size. Turbine tolerance criteria require less than 1% by weight of particles exceeding 3 microns in size and therefore a secondary, high efficiency cyclone was added to the system. Ideally, this secondary cyclone should be located downstream of the primary cyclone and upstream of the heat exchanger. However, due to such considerations as space constraints leading to repiping difficulties and cost factors, it was decided to locate the secondary cyclone downstream of the heat exchanger but upstream of the pressure letdown valve. With two cyclones on-line, coal firing and no sorbent injection, the cyclone exit solids loading dropped to 32 to 44 ppmw range (see **Figure 5**). With PCC dolomite injection, the cyclone exit solids loading was higher (72 ppmw) possibly due to sorbent fines generation. With PCC lime injection, the cyclone exit solids loading dropped to the 23 to 27 ppmw range (see **Figure 5**) which is good enough to meet the New Source Performance Standards (NSPS).

- The particle size distributions for the primary and secondary cyclone catch material and the secondary cyclone exit solids are shown in **Figure 6**. The data correspond to the coal-fired test with no sorbent injection. The secondary cyclone exit stream was isokinetically sampled with a pre-calibrated cascade impactor. The two cyclone catch material were sized by the BAHCO method. The d50 cut sizes for the three streams are also shown in **Figure 6**. There seems to be room for improvement of the second cyclone performance and thereby decrease both the larger size (> 3 microns) particle population and the total solids loading in the second cyclone exit stream. For example, the "core separator" concept of LSR Technologies, Inc. [2] could be used in lieu of the two cyclones to achieve higher particulate collection efficiency.
- The size distributions of the particles collected by the cascade impactor in the case of tests without and with PCC lime injection are shown in **Figure 7**. The particle sizes are relatively larger and the quantities/weights are smaller for the case of lime injection in comparison to that for no sorbent injection. This is further evidence for the effectiveness of bimodal agglomeration. Note that the ash generated from coal combustion typically has a bimodal particle size distribution and agglomerates in the presence of an acoustic field even without sorbent injection. For example, based on literature data [3], about 30% by weight of ash generated in conventional combustion corresponds to a size below 6.4 microns. Assuming a linear variation in cyclone collection efficiency up to 6.4 microns and 100% capture efficiency beyond that size, a first order estimate for solids loading in the flue gas corresponding to the combustion conditions of **Figure 6** is 429 ppmw. The measured loading was in the 32 to 44 ppmw range indicating the advantages of acoustic agglomeration. Let the

acoustic agglomeration enhancement factor (AAEF) be defined as:

$$AAEF = 100 (1 - TMA/TMO)$$

where TMO is the mass loading at the exit of the cyclone without acoustic pretreatment and TMA is the mass loading at the cyclone exit with acoustic pretreatment. Then AAEF for the no sorbent and lime injection cases turn out on average to be 91 and 94%, respectively. This is a substantial improvement and verifies the merit of pulse combustion-induced bimodal agglomeration.

- The measured emissions of SO<sub>2</sub>, NO<sub>x</sub> and particulates with PCC lime injection were all below the levels stipulated by NSPS as shown in **Figure 8**.
- CO and total hydrocarbon (THC) emissions were generally below 10 and 5 ppm respectively @ 3% O<sub>2</sub>.

The test results obtained from the MTCI laboratory-scale combustor island are encouraging and meet gas turbine tolerance criteria and New Source Performance Standards.

### PSU STUDY

The objective of the work being conducted at Penn State University is to provide scientific verification of the MTCI pulse combustion technology in the areas of sulfur capture and bimodal agglomeration. The project consists of two parts: 1) investigation of the fundamental behavior of sorbents under pulse conditions, particularly the effect of rapid sorbent particle heat-up and the presence of an acoustic field on calcination and sulfation, and 2) a fundamental investigation of acoustic bimodal agglomeration.

The presence of an acoustic field within the combustion environment influences the mass transfer of SO<sub>2</sub> to particle surfaces and the movement of particles themselves within the gas stream. The result is an enhancement in the rate and extent of sulfation of limestone in the system. Mitigation of SO<sub>2</sub> from the gases produced during the combustion of fossil fuels is necessary given the new SO<sub>2</sub> emission standards. In addition, the agglomeration of very fine particles is necessary for the application of this technology to produce hot combustion gases for gas turbines. Gas turbines have a very low tolerance level for particles within the gas stream. Removal of the coarser size fractions can be accomplished by current technology; however, removal of micron and submicron particles is more difficult. Agglomeration of the micron size ash and sulfated calcine particles forms larger particles that can be removed more efficiently by conventional particle collection technology.

### Calcination and Sulfation Studies and PCGC-2 Modeling

Experimental studies in the area of calcination and sulfation have shown that under high heating rates the fragmentation of sorbents is influenced by the sorbent type, particle size and particle temperature. Sorbent type was the most important factor. Dolomites and limestones containing high levels of magnesium fragment to a greater extent during heating producing significantly finer calcine than high purity limestones.

The extent of calcination of sorbents was relatively insensitive to particle size; however, the extent of sulfation was affected by particle size. Particle size affects heat transfer such that smaller particles calcine at a slightly greater rate than larger particles (**Figure 9**). The extent of sulfation was related to particle size as shown in **Figure 10**. An increase in the S/Ca molar ratio of 26 to 32% was observed for a dolomite and a

high purity limestone, respectively, when the average particle size was decreased from 89 to 45  $\mu\text{m}$ . On the basis of sorbent utilization the performance of lower purity stones was not significantly different than that of high purity stones. This may have implications regarding sorbent selection for the MTCI pulse combustor system due to the stringent requirements for low particle loading of fines.

The experimental data from the calcination and sulfation studies was used to modify an existing combustion model, i.e., PCGC-2. PCGC-2 can model gaseous turbulent diffusion flames and pulverized coal combustion. PCGC-2 has been successfully modified to include mechanisms that define the calcination, sintering and sulfation process. Empirically obtained rate equations were used to model the processes of calcination and sulfation. A shrinking core model was used to model calcination. Processes influencing sulfation include: the rate of calcination, product layer diffusivity, pore diffusion, external heat and mass transfer. Pore diffusion dominates for large particles, i.e., 100  $\mu\text{m}$ , whereas product layer diffusion dominates for submicron size particles. Heat and mass transfer effects are more limiting in larger particles. The model assumes that sulfation is irreversible. Sulfur release during combustion is assumed to be proportional to the coal weight loss and local instantaneous equilibrium chemistry is assumed for the conversion of sulfur to sulfur dioxide.

The model was fitted to the experimental data predicting the calcination and sulfation of particles 45, 63, and 89  $\mu\text{m}$  in size (Figures 9 and 10). The model further predicts that the extent of sulfation increases with increasing sound pressure level due to the increase in mass transfer coefficients (Figure 11). Modeling by PCGC-2 shows that an acoustic field generates large relative velocities between the particles and the gas stream. The increase in slip velocity between the particle and gas stream increases the heat and

mass transfer to and from the particles. The increase in the mass transfer coefficient, i.e., Sherwood number, with increasing sound pressure is shown in Figure 11. An increase in the Sh number results in an increase in the rate at which  $\text{SO}_2$  reaches the surface of the calcine, thereby increasing the rate of sulfation. In addition, highly porous calcines ( $\epsilon = 0.5$ ) show a greater increase in the extent of sulfation than less porous calcines ( $\epsilon = 0.15$ ), i.e., approximately 12% at higher sound pressure levels (Figure 12).

Another benefit of the presence of the acoustic field is due to the agglomeration of small particles to form larger agglomerates. Calcine particles that agglomerate experience a greater rate of diffusion of  $\text{SO}_2$  to the calcine surfaces than smaller calcine particles. The Sh number is proportional to the mass transfer coefficient which determines the rate of  $\text{SO}_2$  diffusion to the particle. Therefore, the rate of  $\text{SO}_2$  diffusion to the surface of smaller particles that make up an agglomerate is greater than the rate of  $\text{SO}_2$  diffusion to individual small particles.

### Acoustic Agglomeration

This work has provided new insight into the interaction mechanisms between small particles under the influence of a strong acoustic field. These mechanisms are associated with what is referred to as acoustic agglomeration caused by the relative motion and collisions between particles in a high intensity sound field. The agglomeration process has potential use in air pollution control to enhance the performance of conventional particle filtering devices. A number of existing acoustic agglomeration models are reviewed and presented graphically in Figure 13. A quantitative analysis of the proposed theories was conducted with parameters representing those of the physical experiments. The evaluation of the different models leads to the conclusion that mutual scattering interaction, an effect proposed as an important agglomeration volume refill

factor, does not contribute significantly to the agglomeration process if gravitational effects are included in the computations. On the other hand, hydrodynamic effects due to asymmetric flow fields around the particles generate significant particle attraction in the direction of the acoustical axis (**Figure 14**). This so-called "acoustic wake effect" is shown to contradict another mechanism referred to as the mutual radiation pressure interaction. A comparative analysis of the two effects suggest that the competing interaction forces might lead to "pseudo" agglomerates, i.e., pairs of particles held together by an acoustically induced captive force field.

To evaluate these findings, experimental analysis were carried out with a small-scale observation chamber using a CCD camera in conjunction with a high resolution video system. A homogenous acoustic velocity field is generated by two rectangular, flat-membrane loudspeakers which comprise two opposing walls in the observation chamber. Glass microspheres (diameters 8,1 and 22.1  $\mu\text{m}$ ) and quartz particles (diameter  $< 50 \mu\text{m}$ ) are used for the observation of interaction and agglomeration trajectories under the influence of an intense acoustic velocity field (1.2-0.53 m/s at 400-900 Hz). The recorded digitized images show a number of similar-sized particles which come together forming larger agglomerates. It is proposed that similarly sized particles first agglomerate to form larger clusters. These larger clusters then find particles of similar size forming larger agglomerates. This process is enhanced at higher sound frequency levels and pressure levels. For dissimilar particle sizes, the particles displayed an axial change of direction resulting missed collisions. In general, this behavior did not lead to particle agglomerations. The experimental evidence suggests the conclusions given in **Table 1** regarding the various acoustic agglomeration models.

## WVU STUDY

The quality of an aerovalve is expressed in terms of diodicity (DIO), defined as the ratio of forward mass flow to reverse mass flow. Thus, diodicity is a strong function of the aerovalve: geometry, size, inlet pressure and temperature and the type of gas used as well as the exit back pressure. The aerovalve operates in a non-steady flow field inside the pulse combustor. The length of the aerovalve ( $L_a$ ) is at least ten times shorter than the length of the combustor tailpipe ( $L_t$ ), the latter controls the combustion pulse frequency. The pulse frequency is approximately equal to  $f_v = 1/2a/L_t$ , where (a) is the speed of sound. Thus the resonance frequency of the short aerovalve by itself is about ten times higher than the combustion pulse frequency. Therefore, non-steady aerodynamic effects are negligible and a quasi-steady state flow analysis can be applied to compute its mass flow rate as a function of pressure differential. This justifies aerovalve diodicity testing using steady flow tests in both the forward and the reverse flow directions. During a pulse combustion cycle, the peak as well as the mean forward and reverse mass flow rates can be calculated by integrating the instantaneous mass flow rates based on pressure as a function of time for any given wave form.

Besides the need for high diodicity and small size, the aerovalve must also have low total pressure loss in forward flow. Next, the pressure differential, where the forward flow starts to choke and the diodicity drops off, should be high. The aerovalve must be easy to manufacture and to keep clean.

The MTCI aerovalves tested incorporate a venturi-type geometry with a rapid contraction to a throat area ( $A_{th}$ ) with a sharp angle transition to a small angle diffuser where the flow expands to area ( $A_2$ ). Reverse flow is unable to negotiate the sharp turn at the throat and therefore separates at

the throat without any diffusion type pressure recovery.

For the cold flow ideal subsonic isentropic flow venturi-type aerovalve, the diodicity (DIO) equals the venturi area ratio  $\bar{A} = A_2/A_{th}$ . This can be explained as follows. In this case there is no loss in total pressure and the flow adjusts itself such that the exit static pressure equals the back pressure. Thus the exit total to static pressure ratio and exit Mach number are identical for both forward and reverse flow. In cold flow the total temperature for the flow in both directions is the same and thus also the exit velocity and densities are the same. The forward to reverse mass flow ratio equals then the forward flow to reverse flow exit area ratio which is  $\bar{A}$ .

For hot flow, the temperature ratio ( $T_r$ ) between the hot combustion chamber temperature and that of the cold air intake plenum further increases the diodicity. Because the exit Mach number is the same with identical pressure ratio, the exit static temperature ratio will also be equal  $T_r$ , thus the exit density ratio is equal  $1/T_r$  and the exit speed of sound ratio equals  $T_r^{1/2}$  and the exit velocity ratio as well. Consequently, the forward to reverse mass flow ratio equals  $\bar{A}T_r^{1/2}$  (see **Figure 15**). The higher the operating temperature difference between the pulse combustion chamber and the air inlet plenum, the higher the diodicity and the wider the dynamic range. The diodicity, however, becomes lower and poses a problem for gas turbine and vitiated air pulse combustion modes of operation. Further development is therefore needed for superior performance in these cases.

Experiments were conducted in a cold flow test facility at room temperature. **Figure 16** is a plot of the mass flow through an aerovalve of both forward and reverse flow against  $\Delta P$  as measured by the differential manometer. For a  $\Delta P$  of 6 psi, one can see where both the forward and reverse flows choke. This condition restricts

both flow cases to the same throat sonic velocity but the diffuser losses in forward flow actually reduces the density and thus the forward mass flow to less than the reverse mass flow value at the same pressure drop. This makes the diodicity slightly less than one. It is a condition that does not occur in actual operation but it gives a feel of how the diffuser losses can play a significant role in the aerovalve performance.

A quasi-steady flow analysis was also performed using a numerical code. Diodicity of the aerovalve was determined as a function of area ratio, temperature ratio, and pressure ratio. With an increase in pressure ratio, the forward flow was found to choke first and the reverse flow later. This tends to place a limit on the pulse combustor pressure rise/dynamic pressure/SPL that can be achieved. WVU and MTCI have formulated an advanced aerovalve concept to delay the onset of forward flow choking, achieve high diodicity, and permit ease of fabrication.

## FUTURE WORK

MTCI has formulated an alternate advanced concept to meet the DOE mission-oriented criteria for performance, emissions and economics. Additional investigations are planned at MTCI, PSU and WVU to expand the combined control tests and further develop the MTCI advanced coal-fired gas turbine combustion technology.

## REFERENCES

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2. Smolensky, L.A. and B.H. Easom, "Particulate Control for Coal-Fueled Diesel Engine Exhaust," Proc. of the Joint Contractors Meeting: FE/EE Advanced Turbine Systems Conference, FE Fuel Cells and Coal-Fired Heat Engines Conference, DOE/METC-93/6132 (NTIS/DE93011308), August 1993, pp. 327-333.
3. Diehl, R.C., P.J. Loftus, D.B. Stickler, and P.W. Pillsbury, "Emissions Control in a Coal-Fueled Gas Turbine Slagging Combustor for Utility Applications," Proc. Seventh Annual Coal-Fueled Heat Engines and Gas Stream Cleanup Systems Contractors Review Meeting, DOE/METC-90/6110 (NTIS/DE90000480), March 1990, pp. 113-122.

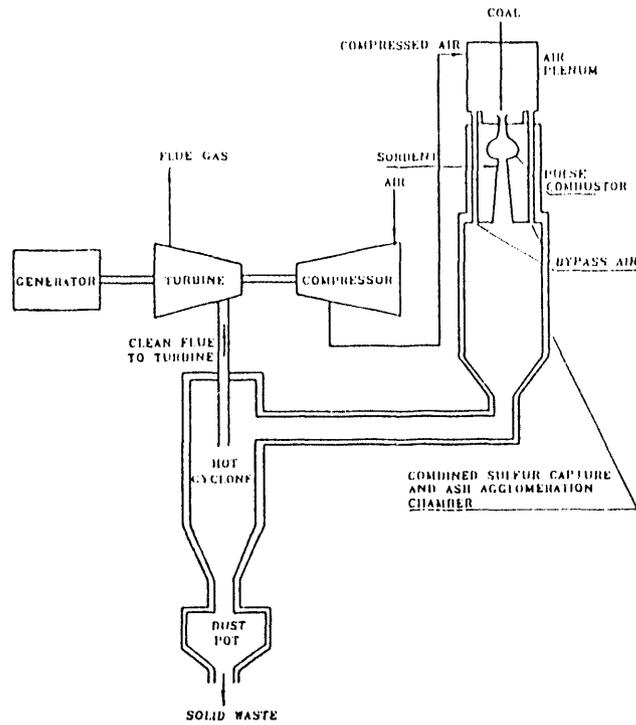


Figure 1. MTCI's Combustor Island for Direct Coal-Fired Gas Turbine Application

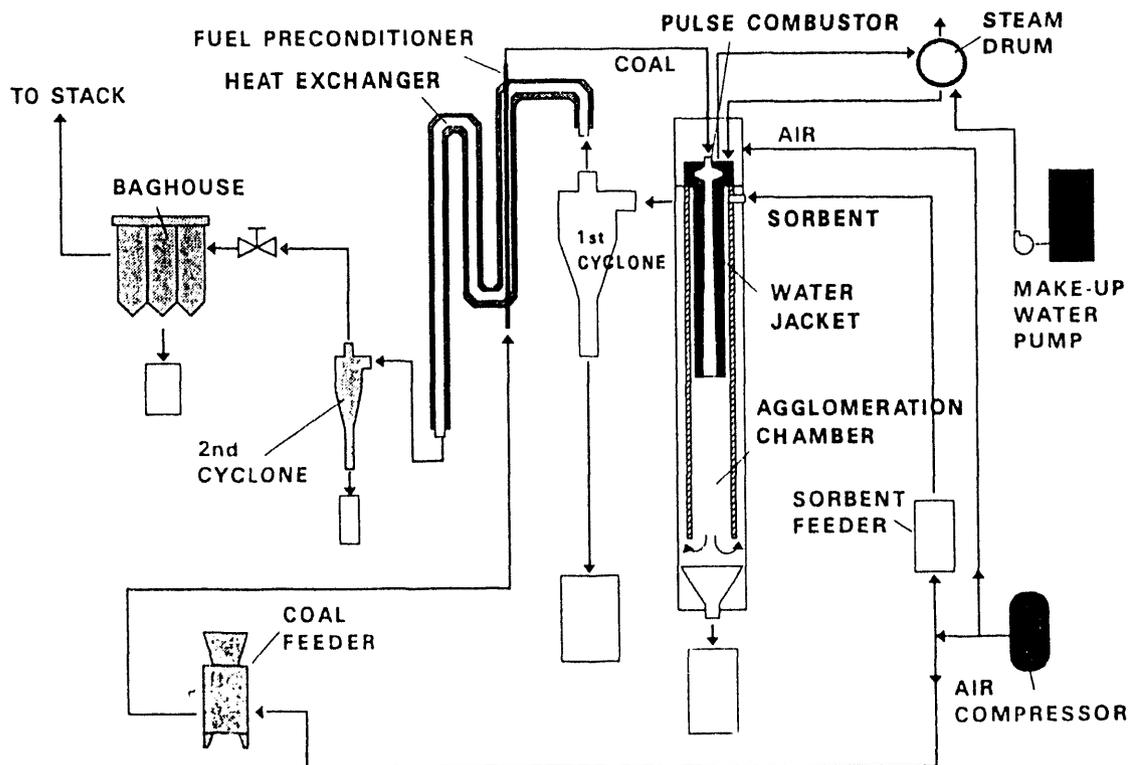


Figure 2. Schematic of the Test System

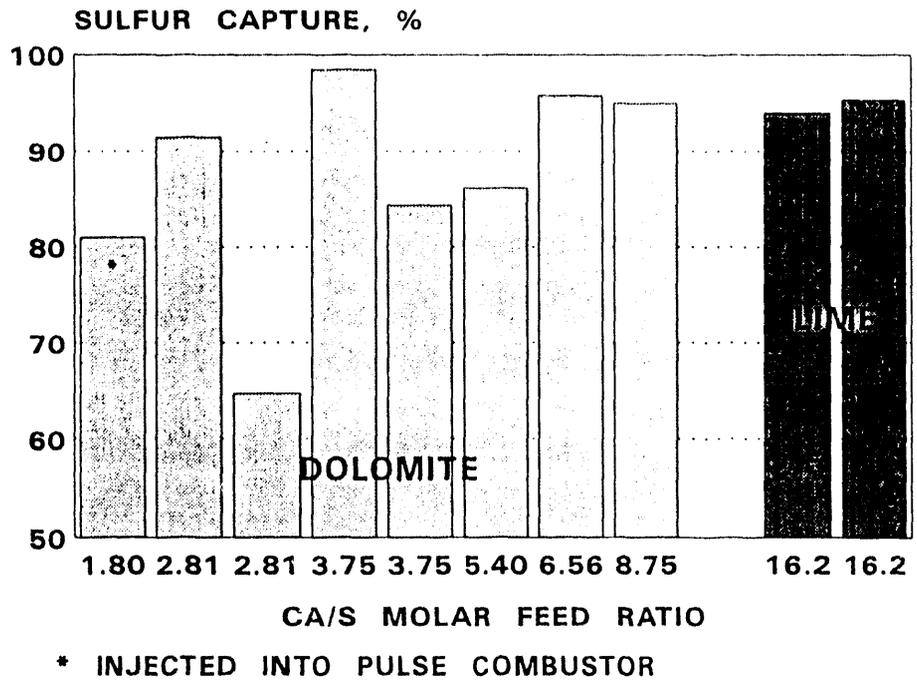


Figure 3. Sulfur Capture Efficiency

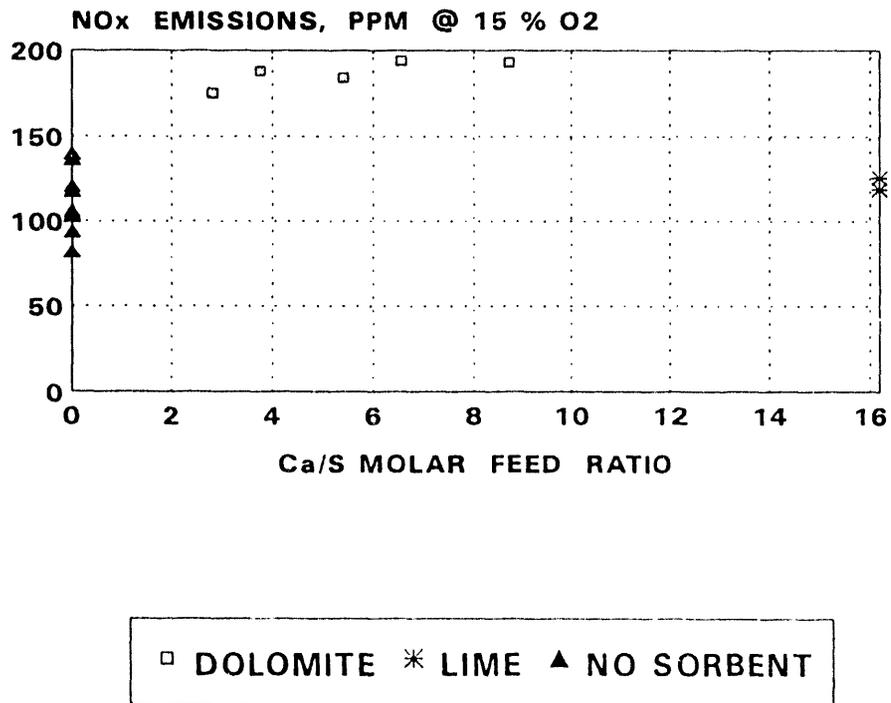


Figure 4. NO<sub>x</sub> Emissions With Coal and Sorbent Feed

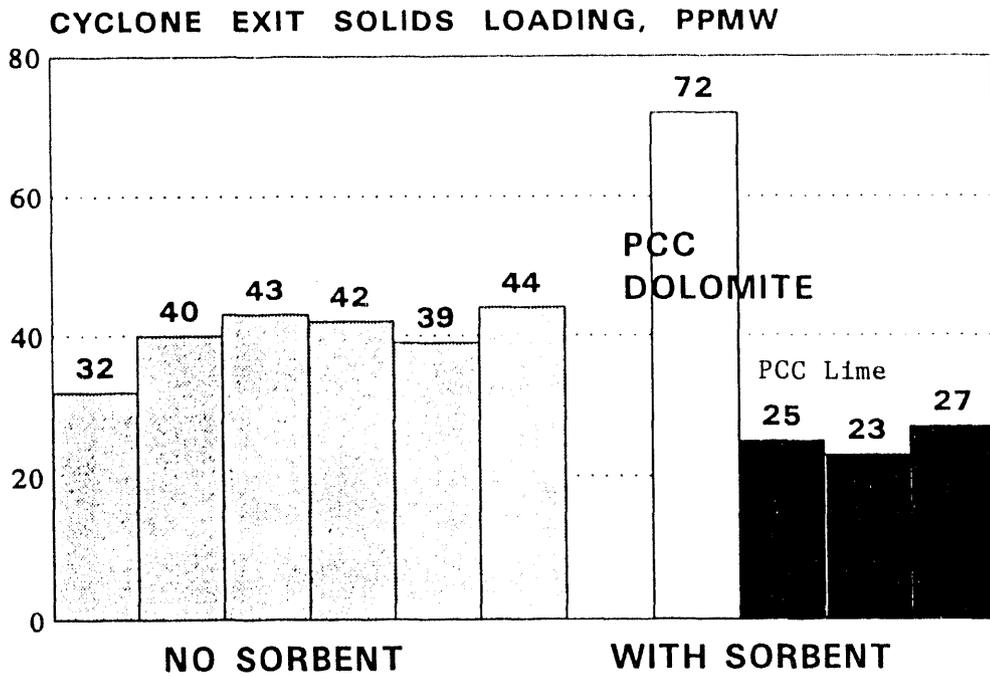
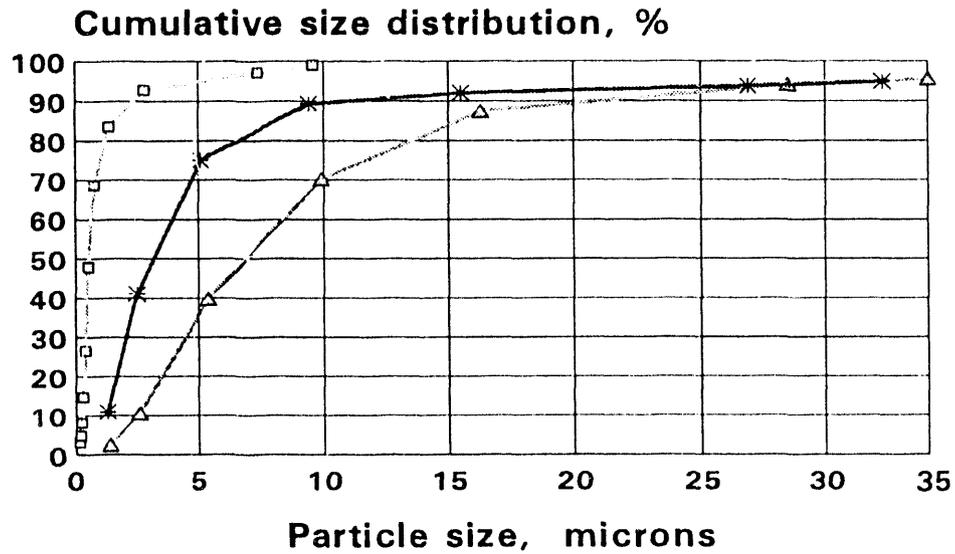


Figure 5. Cyclone Exit Solids Loading With and Without Sorbent Feed



d50, microns		
0.54	3.2	6.9

□ 2nd Cyclone Exit	* 2nd Cyclone Catch	△ 1st Cyclone Catch
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Figure 6. Particle Size Distributions of Different Streams

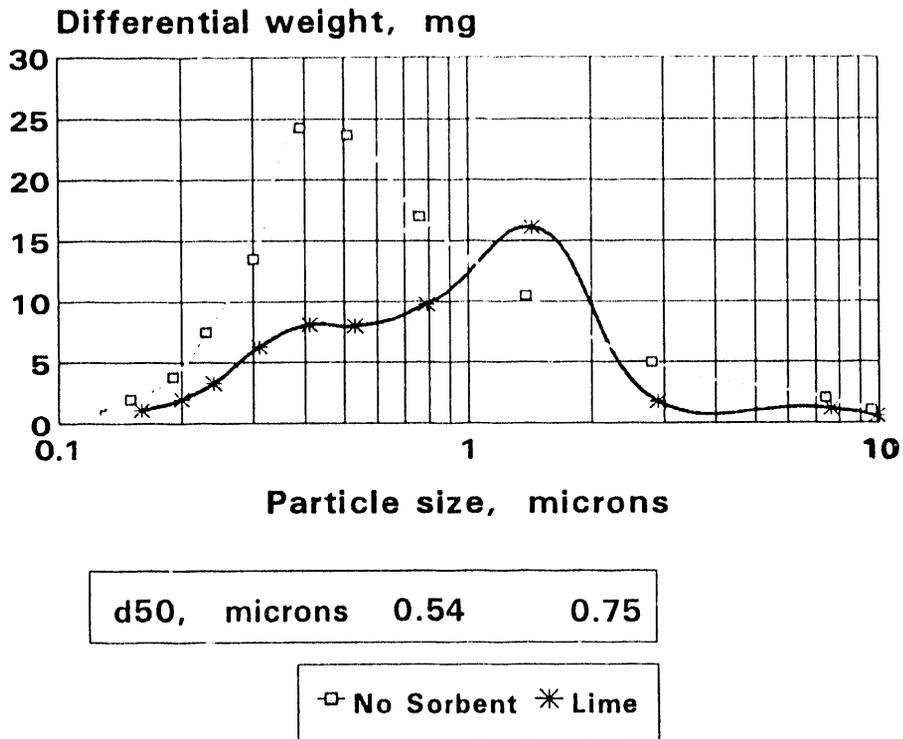


Figure 7. Comparison of Secondary Cyclone Exit Particle Size Distributions

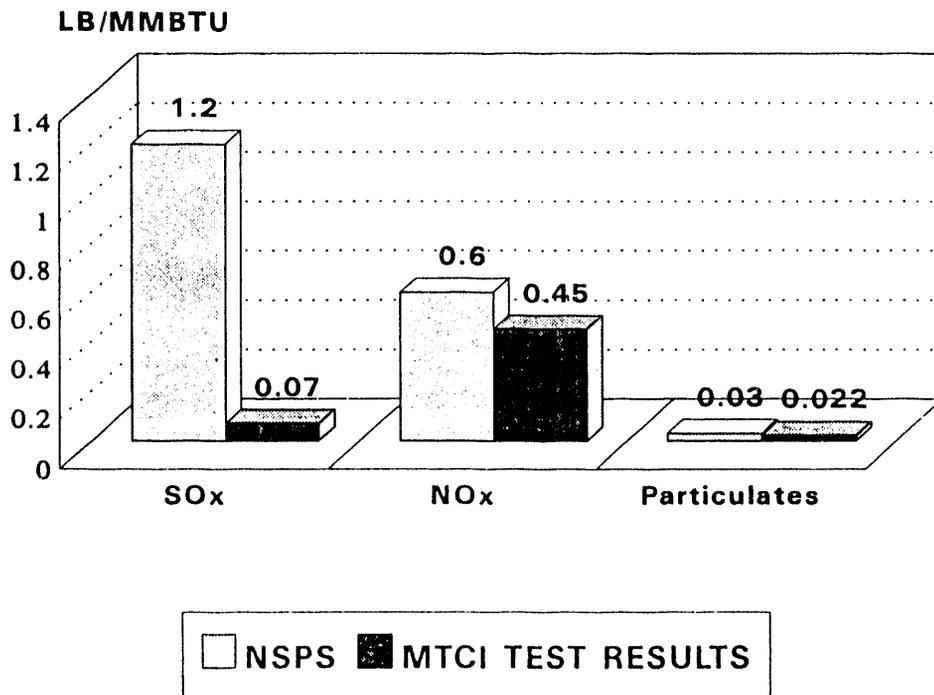


Figure 8. Comparison of Measured Emissions with NSPS

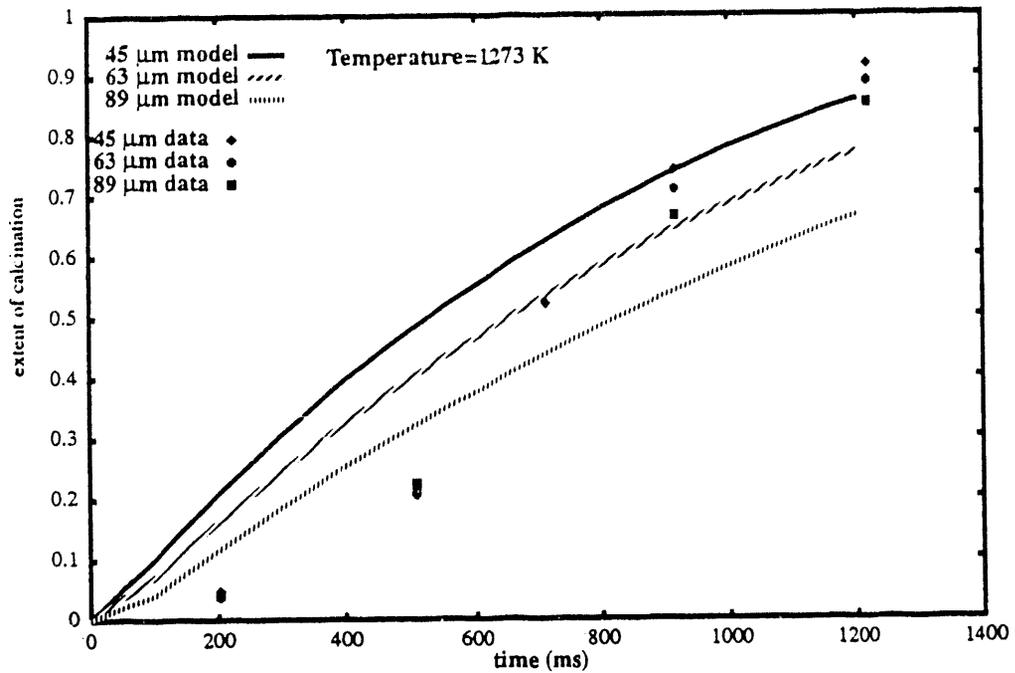


Figure 9. Relationship of Particle Size to the Extent of Calcination with Time

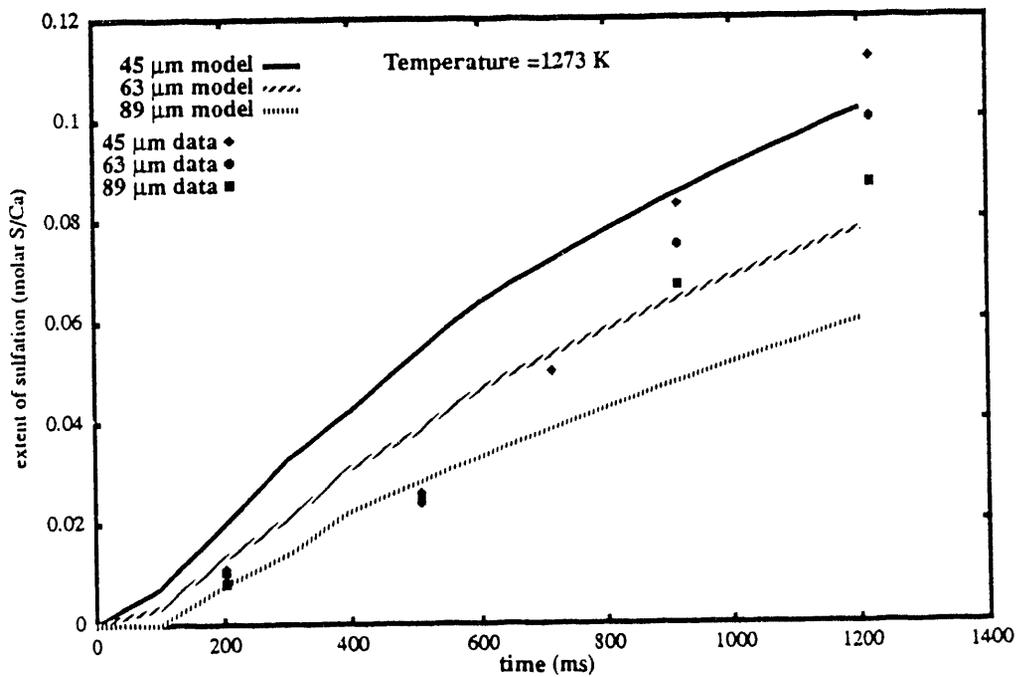


Figure 10. Relationship of Particle Size to the Extent of Sulfation with Time

Diameter = 100  $\mu\text{m}$

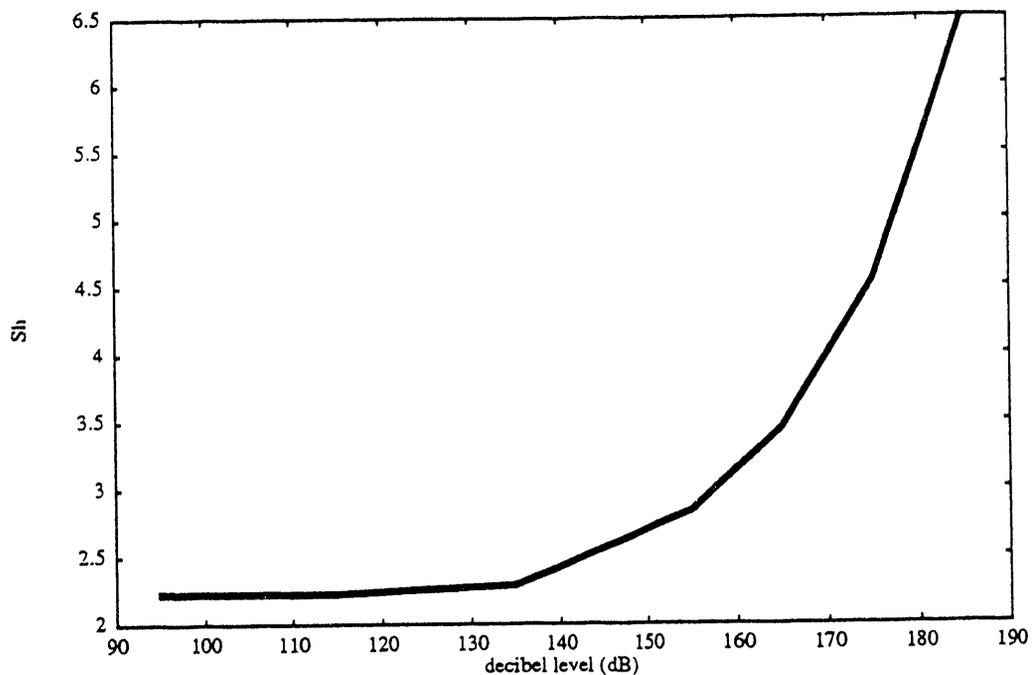
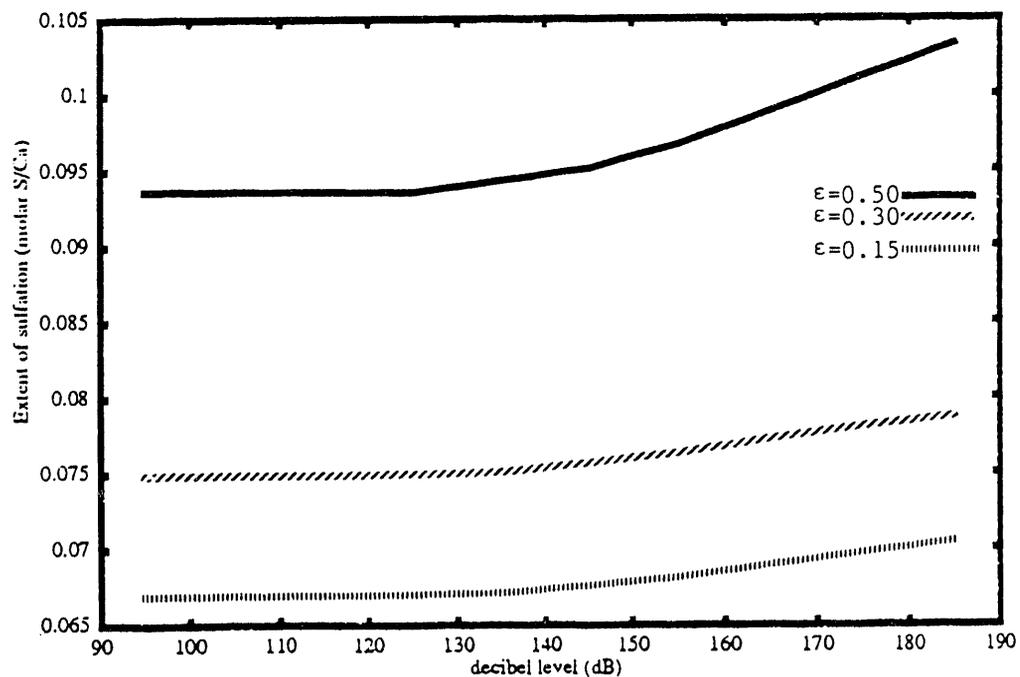


Figure 11. Relationship of Sherwood Number to Sound Pressure (dB)



Diameter of sorbent particle = 100  $\mu\text{m}$

Figure 12. Relationship of the Extent of Sulfation to Sound Pressure (dB) as a Function of Porosity ( $\epsilon$ )

## □ Acoustic Particle Interaction Phenomena

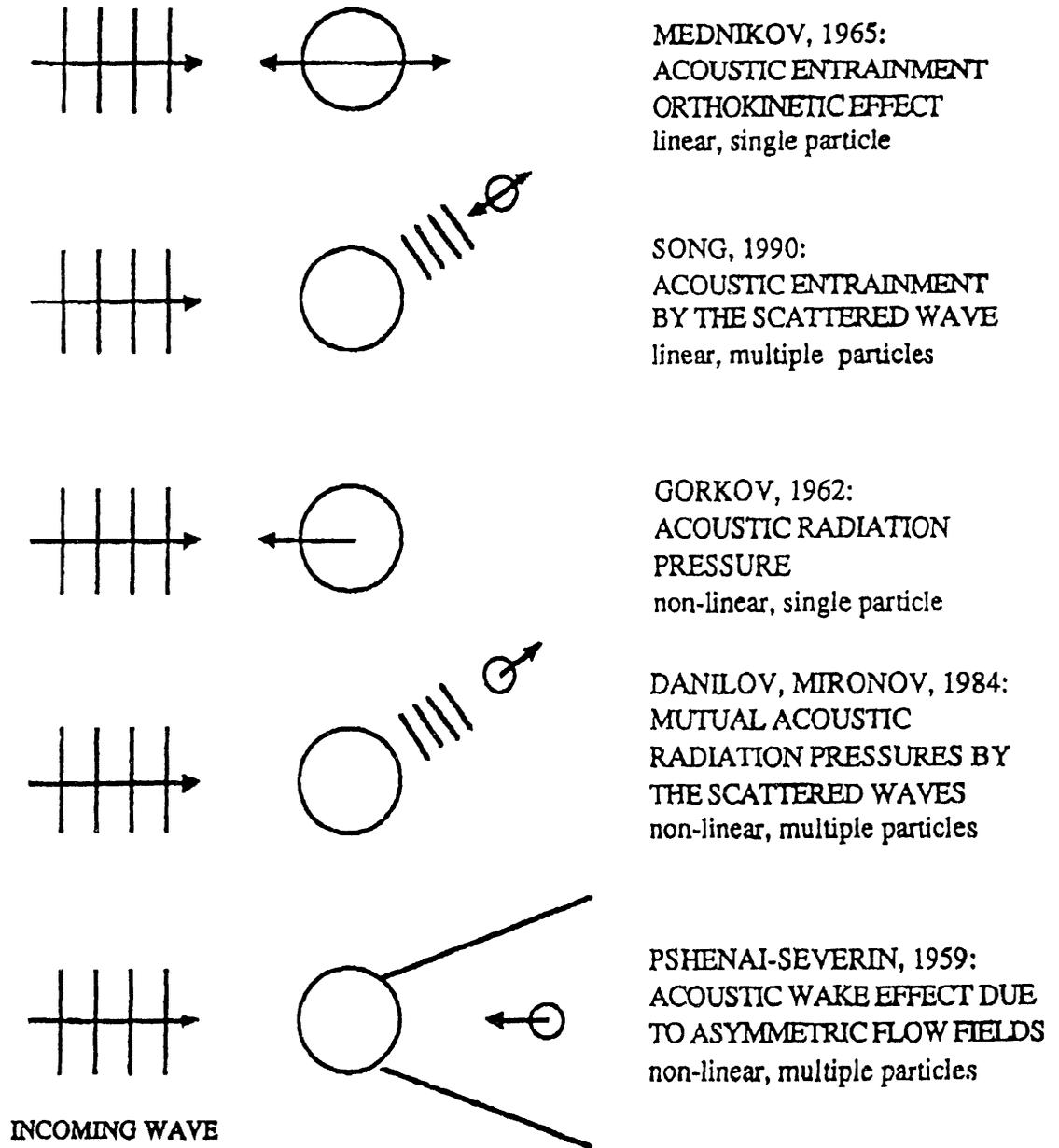


Figure 13. Theoretical Analysis

## □ Acoustic Wake Effect

### ► Caused by Asymmetry of the Flow Field around Moving Particles:

Stokes flow conditions: for dissimilarly sized particles

Oseen flow conditions: for all pairs of particles

### ► The Trailing Particle Moves in the Wake of the Leading Particle:

drag reduction for the following particle leads to convergent velocity

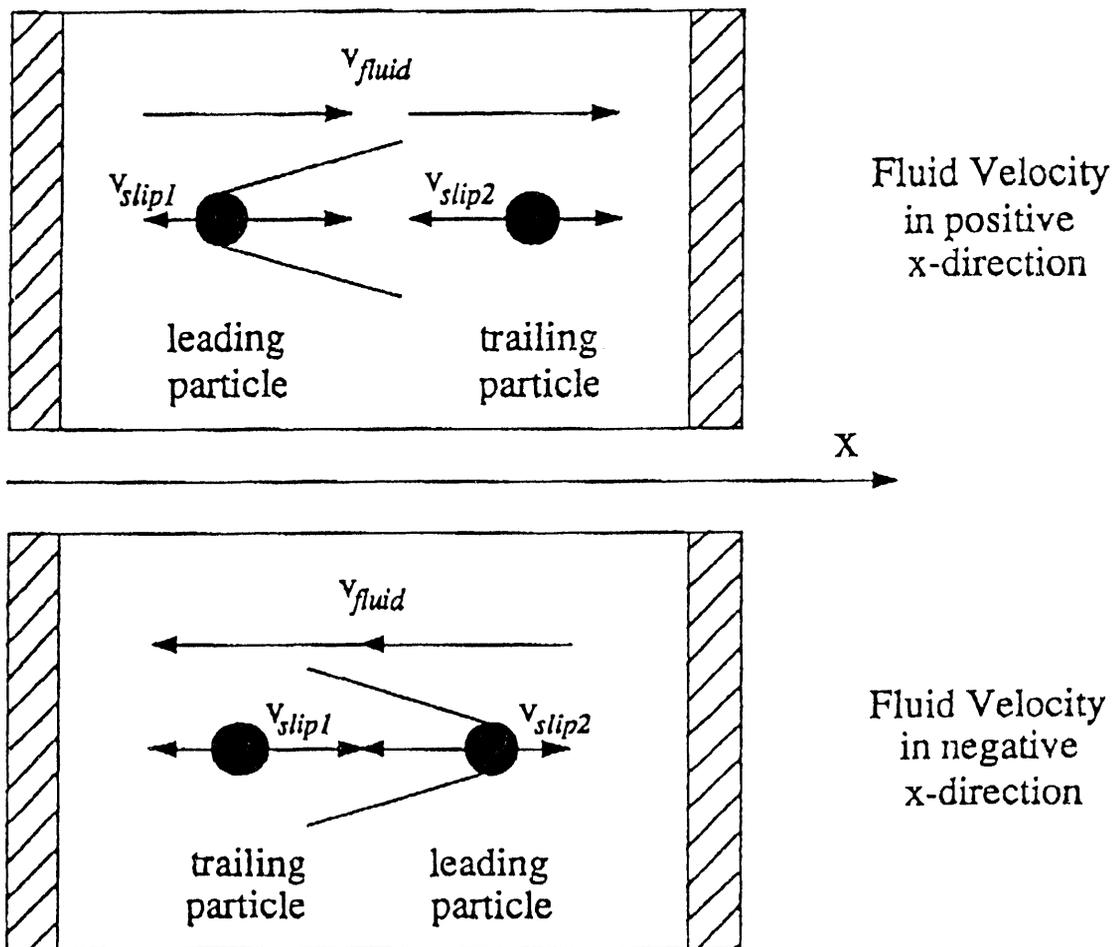


Figure 14.

**Table 1: Summary of Conclusions Regarding Status of  
Proposed Acoustic Agglomeration Mechanisms**

MECHANISM	CONCLUSION
Orthokinetic Agglomeration	Not Supported
Agglomeration Volume and Refill Mechanism	Not Supported
Gravitational Effects	<ul style="list-style-type: none"> <li>- Important for dissimilar sized particles.</li> <li>- Disadvantageous for the agglomeration process.</li> </ul>
Mutual Radiation Pressure Interaction	Captive force field generated by the interaction of mutual radiation pressure and acoustic wake effect explaining the effect of pair building.
Acoustic Wake Effect	Dominant interaction mechanism which accounts for the hydrodynamic agglomerations observed.
Tuning Fork Agglomerations	<ul style="list-style-type: none"> <li>- The determining mechanism for acoustic agglomeration of similarly sized particles.</li> <li>- No agglomeration between dissimilarly sized particles.</li> <li>- Very high sound power leads to excessive kinetic energy of the particles; rebound is possible during collision.</li> </ul>

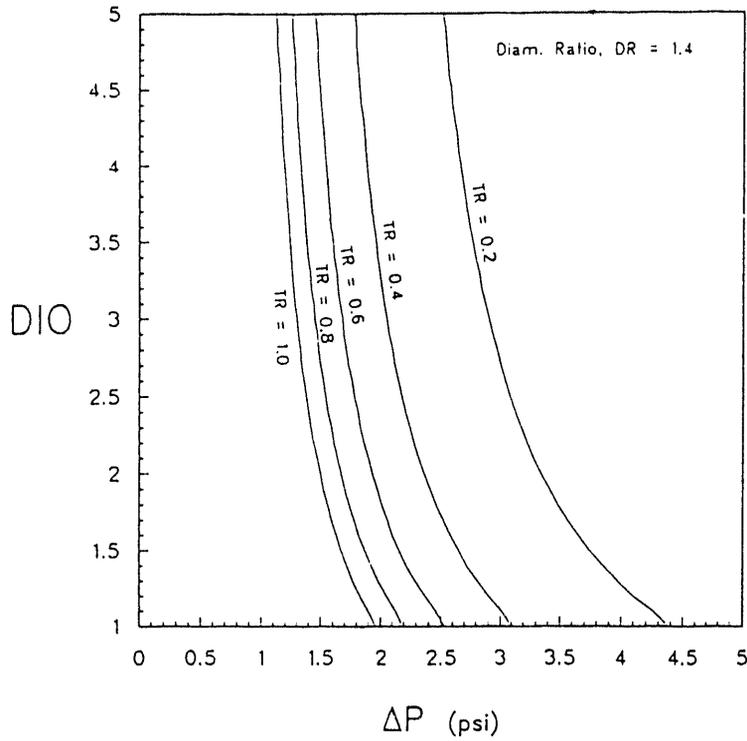


Figure 15. Computed Diodicity vs.  $\Delta P$  for Various  $T_R$

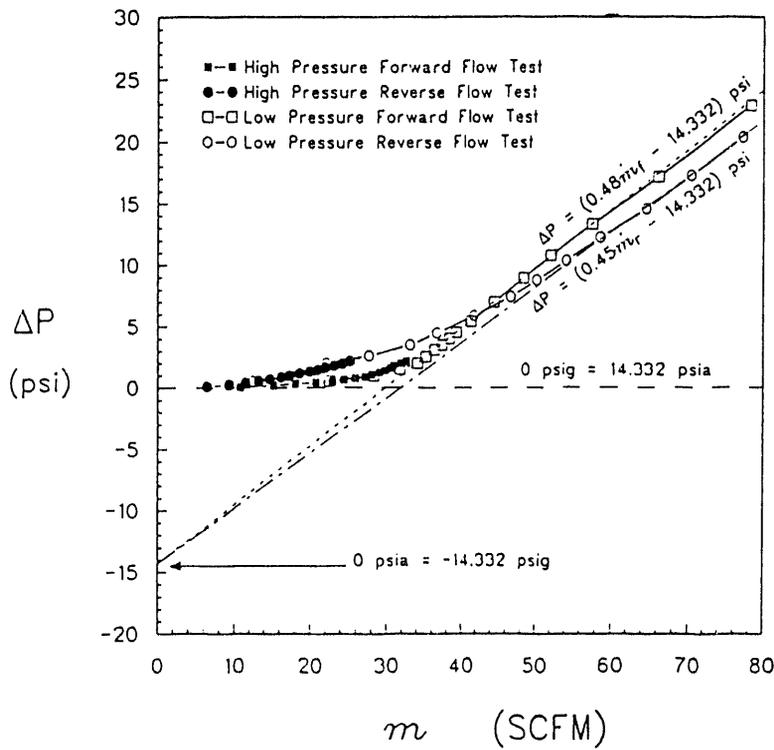


Figure 16. Aerovalve Inlet Pressure Drop vs. Mass Flow

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**Session 6**

*Desulfurization Systems*

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## 6.1

# METC Hot Gas Desulfurization Program Overview

Daniel C. Cicero  
Morgantown Energy Technology Center

This overview provides a frame of reference for the Morgantown Energy Technology Center's (METC's) on-going hot gas desulfurization research. Although there are several methods to separate contaminant gases from fuel gases, that method receiving primary development is absorption through the use of metal oxides. Having completed initial development using iron oxide in the 1970's, METC's research focus in sulfur control was and is set around certain requirements:

- Regenerability -- the primary goal
- Withstand highly reductive gas atmospheres
- Temperatures: 538 to 760°C (1000 to 1500°F)
- Pressures: 2 to 4 MPa (300 to 600 psi)
- Separate small volume percentage of H<sub>2</sub>S from fuel gas (less than 0.5%)
- Regeneration temperatures: 580 to 780°C (1075 to 1450°F)
- Recover reactivity and resist attrition
- Long life at low costs

The temperature requirement for the clean-up subsystem was established to balance the integration between the gasifier and the gas turbine subsystems without the penalties associated with loss of valuable heat. The sorbent must also exhibit and consistently demonstrate less than 100 ppm by volume hydrogen sulfide (H<sub>2</sub>S), with a goal of 10 ppm by volume in the outlet streams. Of course, all of this must be done without loss of absorption effectiveness and with little or no mechanical decrepitation. And most important, such sorbents must demonstrate a very long life and maintain low costs both in their production and disposal.

Research into high-temperature and high-pressure control of sulfur species includes primarily those sorbents made of mixed-metal oxides, which offer the advantages of regenerability. These are predominantly composed of zinc and are made into media that can be utilized in reactors of either fixed-bed, moving-bed, fluidized-bed, or transport configurations. Zinc Ferrite (ZnO-Fe<sub>2</sub>O<sub>3</sub>), Zinc Titanate (ZnO-TiO<sub>2</sub>), Z-SORP<sup>®</sup>, and METC-2/METC-6 are the current mixed-metal sorbents being investigated. Z-SORP<sup>®</sup> is a proprietary sorbent developed by the Phillips Petroleum company originally for use in petro-chemical refining, and METC-2/6 are materials being developed by METC in-house researchers.

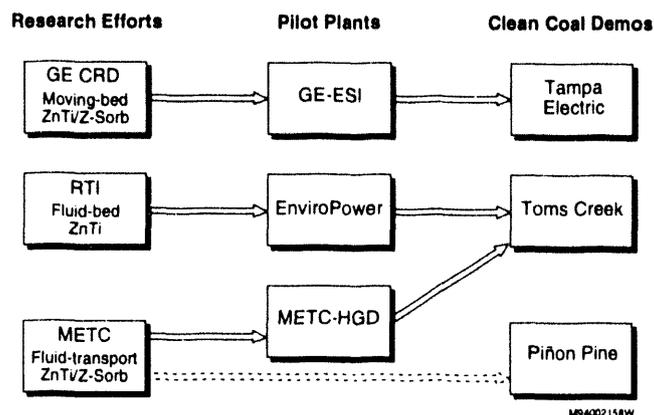
The METC desulfurization program is composed of three major components: bench-scale research, pilot-plant operation, and demonstration that is a portion of the Clean Coal Demonstration projects. Bench-scale research establishes the chemical and physical feasibility of newly conceived sorbents and accommodates quick turn-around testing of varied formulations. The chemical aspects normally investigated include reactivity, sorbent capacity (weight of H<sub>2</sub>S captured per weight of sorbent), loss of active component (ZnO), recovery of absorptivity after regeneration, and attack of contaminant gases, e.g., hydrogen chloride (HCl). Of foremost concern is the mechanical integrity of the sorbent, which is dependent on the reactor configuration in which it is employed. The sorbent must be resistant to attrition, spalling, and the deleterious effects of steam content in the oxidative regeneration gases. The participants in bench-scale research include the GE

Corporate Research and Development Center, Research Triangle Institute (RTI), and METC.

Pilot-plant operation applies candidate sorbents from bench-scale research against real conditions and generates the initial evidence of desulfurization operability in a complete system. This level of investigation uses real gas streams produced by coal-fed gasifiers for removal of H<sub>2</sub>S. It determines the sorbent's tolerance to contaminants at high pressures and extreme temperatures. The sorbent's reactivity and capacity are revealed as they relate to the system's through-put. The particular aspects, such as particle size and shape, and specific issues, such as vessel and valve plugging and sorbent transport velocities, as they relate to the different reactor configurations are uncovered. The players providing pilot-plant facilities are GE Environmental Services, Inc. in Schenectady, New York; EnviroPower, Inc. in Tampere, Finland; and in-house facilities at METC. The GE desulfurizer employs a moving-bed mode, while the EnviroPower unit is a fluidized-bed. The METC hot gas desulfurizer (HGD) is beginning construction and will have dual capability in examining both fluidized and transport reactor modes of operation.

Prior to becoming useful in pilot-plant and commercial operation, sorbents must be produced in larger amounts. Therefore, the technology of manufacture becomes very important in providing not only tonnage production but also constant quality at reasonable cost. The three methods of pelletizing, granulation, and spray drying are all under examination. Companies that are assisting in optimizing manufacturing techniques are United Catalysts of Louisville, Kentucky, Contract Materials Processing of Baltimore, Maryland, and Phillips Petroleum of Bartlesville, Oklahoma. Other catalysts manufacturers have shown interest and possess additional capabilities.

Figure 1 shows the relationship between the research work, the pilot plant tests, and the Clean Coal demonstration plants. The desulfurization modules of the Tampa Electric and Toms Creek projects have been and are being supported by the laboratory studies done by GE, RTI, and METC. GE's fixed-bed gasifier pilot plant has been in operation for many years, but has only recently tested zinc titanates and Z-SORP® in a moving-bed desulfurizer. The EnviroPower integrated fluidized-bed gasifier and fluidized-bed desulfurizer plant have likewise begun testing different formulations of zinc titanate, albeit for fluidized applications. METC has supported the Piñon Pine fixed-bed zinc-based cleanup system for many years, although the METC-HGD will now be exploring the fluidized and transport configurations.



**Figure 1. Desulfurization Research with Reference to Clean Coal Demonstration Projects**

Future METC-sponsored research in desulfurization will involve projects in Advanced Sulfur Control Concepts and Advanced Sorbent Development. The goal of the sulfur control project is to develop simpler and economically superior processing concepts of regenerable sorbents and to produce by-product elemental

sulfur. A recent award has been made to Louisiana State University and is to be guided by Professor Douglas Harrison. A second award was made to RTI, where Dr. Santosh Gangwal is serving as principal investigator. Recent system studies have shown that pushing the upper temperature envelope above 760°C (1400°F) will not improve overall system efficiency. Since this is the case, the inherent increase in capital and operating costs associated with higher and higher temperatures may be avoided. Thus, METC has decided to explore a milder range of temperature operation, i.e., from 343°C to 538°C (650 to 1000°F) for what may promise to be more practical design and operating considerations and to yield more economical systems. Initial indications are that the existing slate of zinc-based sorbents can effectively absorb H<sub>2</sub>S at these lower temperatures, although possibly somewhat less than optimally. Other metal oxides, such as iron oxide, could also achieve equilibrium concentrations down to below 100 ppm by volume. This advanced sorbent development project should see its beginning in late 1994.

## 6.2 Integrated Operation of a Pressurized Gasifier, Hot Gas Desulfurization System and Turbine Simulator

### CONTRACT INFORMATION

**Contract Number** DE-AC21-87MC23170

**Contractor** GE Environmental Services, Inc.  
200 N. Seventh St.  
Lebanon, PA 17042  
(717-274-2400)

**Contractor Project Manager** Steve Bevan - GEESI, David Najewicz - GE-CRD

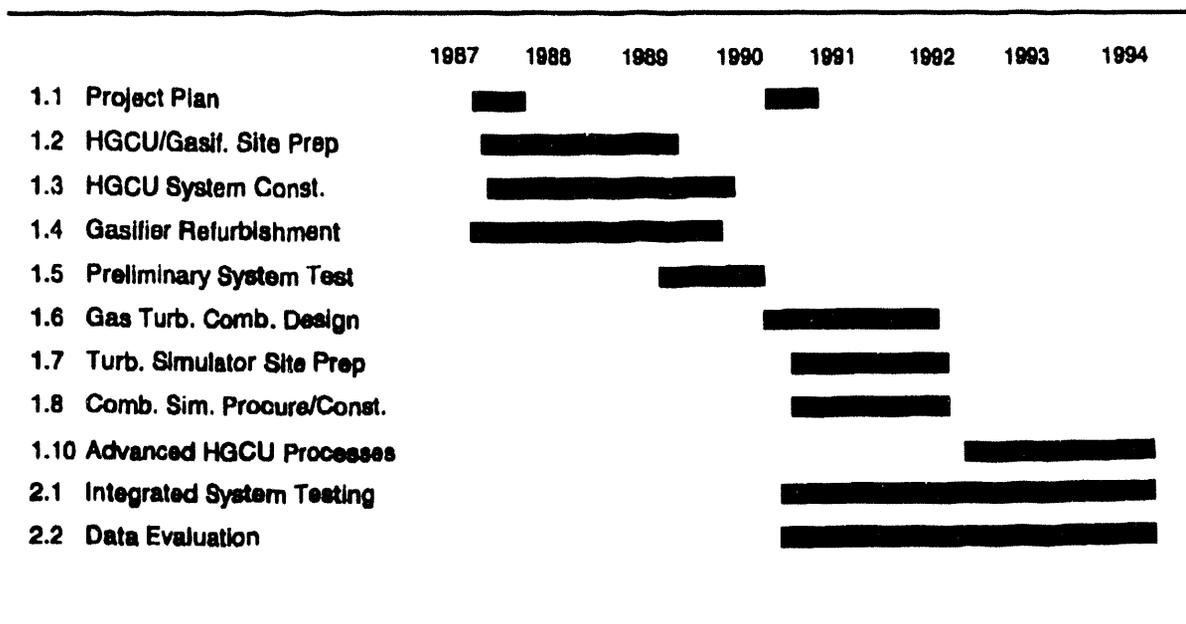
**Principal Investigators** Eli Gal  
David Najewicz  
Anthony H. Furman  
Raul Ayala  
Alan Feitelberg

**METC Project Manager** Justin Beeson

**Period of Performance** September 30, 1987 to September 30, 1994

**Schedule and Milestones**

### Project Schedule



## OBJECTIVES

The overall objective of the General Electric Hot Gas Cleanup (HGCU) Program is to develop a commercially viable technology to remove sulfur, particulates, and halogens from a high-temperature fuel gas stream using a moving bed, regenerable mixed metal oxide sorbent based process. This technology will ultimately be incorporated into advanced Integrated Gasification Combined Cycle (IGCC) power generation systems. In IGCC applications, HGCU will improve overall power generation cycle efficiencies by 1 to 2% compared with conventional low-temperature cleanup technologies, and will also offer the potential for reducing plant capital and operating costs.

The HGCU Program is based on the design and demonstration of the HGCU system in a test facility made up of a pilot-scale fixed bed gasifier, a HGCU system, and a turbine simulator in Schenectady, NY, at the General Electric Research and Development Center (GE-CRD). A modified GE MS6000 gas turbine combustor and a film-cooled, first-stage LM6000 nozzle assembly are incorporated into the turbine simulator.

The objectives of the turbine simulator testing are (1) to demonstrate the suitability of fuel gas processed by the HGCU system for use in state-of-the-art gas turbines firing at "F" conditions (2350°F rotor inlet temperature) and (2) to quantify the combustion characteristics and emissions of such a combustor. The turbine simulator program also includes the development of experimental combustors based on the rich-quench-lean concept to minimize the conversion of ammonia and other fuel-bound nitrogen species to NO<sub>x</sub> during combustion.

The HGCU system and turbine simulator have been designed to process approximately 8000 lb/hr of low heating value fuel gas produced by the GE fixed bed gasifier. The raw fuel gas is provided to the HGCU and turbine simulator systems at 280 psig and 1000°F. The HGCU system has utilized several mixed metal oxide sorbents—including zinc ferrite, zinc titanate, and Z-Sorb (a proprietary zinc-based sorbent developed by Phillips Petroleum Company)—with the objective of demonstrating good sulfur removal and mechanical attrition resistance as well as economic cost characteristics. Demonstration of halogen removal and the characterization of alkali and trace metal concentrations in the fuel gas are subordinate objectives of the overall program.

## BACKGROUND

As a result of the availability of advanced gas turbine combined cycles that fire at temperatures of over 2350°F and the advent of integrated gasification/oxygen separation technology, IGCC plants now offer overall plant efficiencies of 42–44% with extremely low emissions of SO<sub>x</sub>, NO<sub>x</sub>, and particulate.

Although the capital cost of IGCC technology is higher than conventional coal-fired steam turbine plants, it is rapidly dropping and is approaching competitive levels. As IGCC power generation technology reaches the early stage of demonstration and commercialization, the first plants built will use conventional low-temperature gas-cleaning technology. However, the goal of HGCU is that when fully developed, it will represent a "second generation" clean-up technology offering further improvements in IGCC power generation efficiency and operation flexibility, as well as reduced capital and operating costs.

Fuel gas derived from coal by gasification processes contains sulfur in the form of H<sub>2</sub>S and COS at concentrations of up to several thousand parts per million (ppm). In order to comply with increasingly stringent environmental regulations and to meet the conditions required for the long life of gas turbine components, it is necessary to reduce both the sulfur and particulate in coal-derived fuel gas to low levels. In the temperature range of approximately 800–1200°F, mixed metal oxides, such as zinc oxide, react with these gaseous sulfur species, forming metal sulfides under reducing conditions. These metal sulfides can then be regenerated to their original oxide state, producing a sulfur-dioxide-rich off-gas suitable for conversion either to sulfuric acid or to elemental sulfur. GE Environmental Systems, Inc. (GEESI) has patented a moving bed process to utilize mixed metal oxide sorbents to remove sulfur from a high-temperature fuel gas stream and regenerate the sorbent for reuse while producing a byproduct stream suitable for the recovery of sulfur. The history

of this project and the concurrent development of high-temperature particulate removal systems based on cyclones has been documented by Smith et al. (1987) and Cook et al. (1988, 1989, 1990, 1991, and 1992). In addition, the previous development of the mixed metal oxide sorbents and turbine simulator have been documented by Ayala et al. (1992, 1993) and Feitelberg et al. (1993).

## PROJECT DESCRIPTION

The HGCU Program is based on the design and demonstration of gas cleaning technologies at GE-CRD's Process Evaluation Facility (PEF). This work is being carried out under a current DOE contract, with the most recent schedule shown in the Schedule and Milestones section at the beginning of this paper. Construction of the basic facility was completed in late 1990, with continuing modifications and test operation taking place since that time. A summary of the test runs performed to date is shown in Table 1. These tests include 9 long dura-

**Table 1. Gasifier/HGCU/Turbine Simulator Test Operation – 20 atm, 1000°F**

<u>Run</u>	<u>Date</u>	<u>Run Hours</u>	<u>Coal Type</u>	<u>System Configuration</u>
1-2B	12/90-4/92	230	I 6	Gasifier/HGCU/GT Valve
3	8/30/92	88	I 6	Gasifier/HGCU/GT Valve/MS6000 Simulator
3A	2/7/93	120	Anthracite	Gasifier/HGCU/GT Valve/MS6000 Simulator
4	6/13/93	100	I 6, Crown II	Gasifier/HGCU/GT Valve/Simulator/Halogen
5	11/1/93	103	I 6, Crown II	Gasifier/HGCU/GT Valve/Halogen/"F" Simulator 2300°F
6	5/1/94	85	I 6	Gasifier/Guard Bed/HGCU/GT Valve/Halogen/"F" Simulator 2500°F
4A	4Q94	24	I 6	Gasifier/HGCU/GT Valve/R-Q-L Sub-Scale
7A	3Q94	100	I 6, Crown II	Gasifier/HGCU/GT Valve/Halogen/"F" Simulator 2500°F
7B	3Q93	100	I 6, Crown II	Gasifier/HGCU/GT Valve/CFB Halogen/R-Q-L Full Scale
8	4Q94	100-200	I 6, Crown II	Gasifier/HGCU/GT Valve/CFB Halogen/R-Q-L Full Scale

tion runs (approximately 100 hours each), incorporating a variety of new hardware features and sorbents. Tests 4A, 7A, 7B, and 8 are scheduled for later in 1994.

A schematic of the PEF facility, as configured at the conclusion of Test 6, is shown in Figure 1. The GE-CRD fixed bed, pressurized air-/steam-blown gasifier is shown on the left. The gasifier includes a water-cooled bed stirrer, alternating pressurized coal feed lock-hoppers, and a rotating grate for ash removal. The PEF also includes a primary cyclone immediately downstream of the gasifier, the HGCU system consisting of the absorber and associated upper and lower lock-hoppers, regenerator with recycle gas system, fines screen, and elevator. A secondary cyclone is located downstream of the HGCU system, and the cleaned fuel can be directed either to the MS6000 turbine simulator or to the system flare. Using analytical instrumentation in "real time" to allow process

control, both the process fuel gas and the recycle gas are sampled extensively during the run. Solid flow is sampled hourly for later chemical analysis and to support the preparation of overall heat and mass balances.

## RESULTS

Testing of the GE HGCU system has been underway since December 1990. During this period, a variety of sorbents and system configurations have been tested, including zinc ferrite and zinc titanate sorbents, single/double stage open cylindrical regenerators, and alternate recycle blower configurations. The two most recent tests, Test 5 (completed in November 1993) and Test 6 (completed in May 1994), represent the latest advancements in regenerator configuration, type of sorbent, and chloride control systems. Test 5 was based on the use of zinc titanate sorbent and included a revised regenerator configuration and a

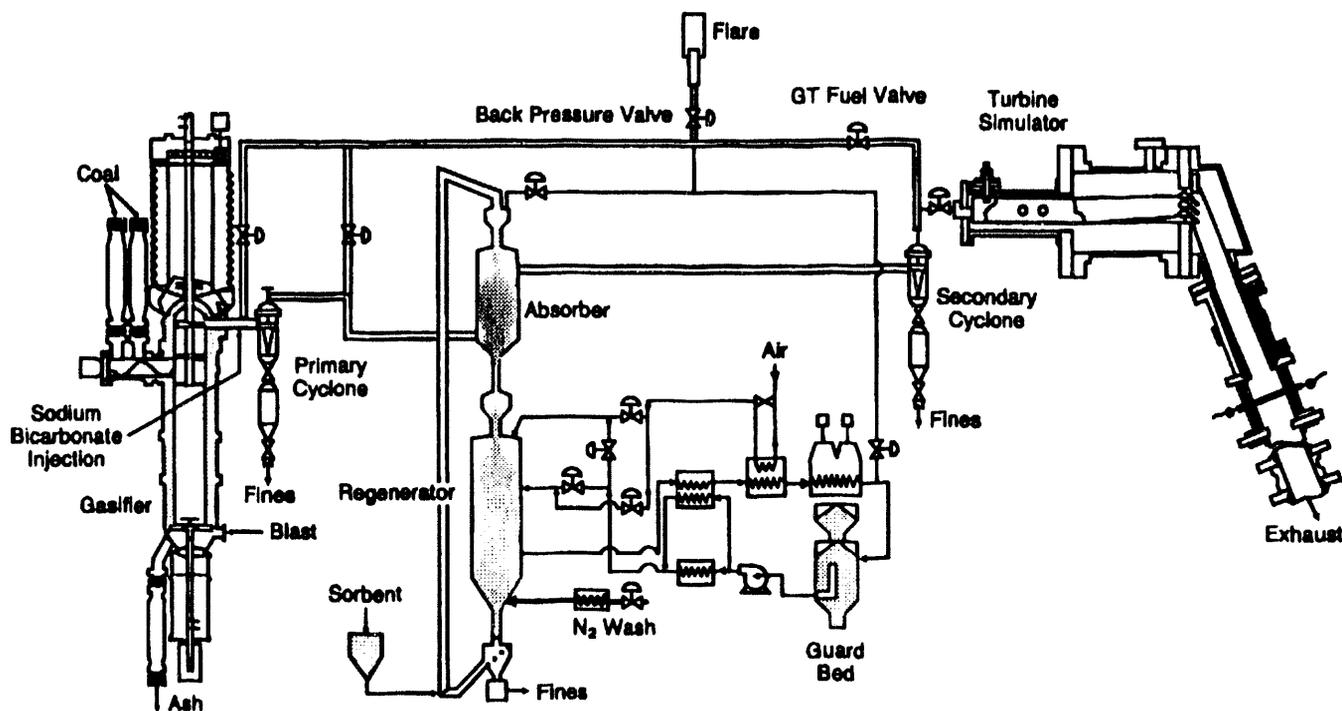


Figure 1. GE Gasifier/Hot Gas Cleanup Process Flow Diagram

sodium bicarbonate injection system for chloride control. Test 6 incorporated the use of Z-Sorb, a chloride guard in the regenerator recycle loop, and further modifications to the regenerator internal configuration. The following sections describe the test conditions in detail and discuss the test results.

### Test 5 Conditions and System Modifications

Long Duration Test 5 was performed in early November 1993 at GE-CRD's PEF using zinc titanate (L2535M) sorbent. This sorbent had been used in previous tests and had been subjected to periodic high-temperature regeneration conditions during those tests. A blend of Illinois #6 (1.9% sulfur) and Crown II (3.7% sulfur) coals were used, resulting in effective sulfur levels in the range of 2.5–3.0%.

The regenerator, previously modified in Test 4 to include a single-stage annular configura-

tion, was further modified for Test 5 to include a two-stage annular configuration. These modifications are shown in Figure 2.

The regenerator modifications were made to improve control of sorbent temperature in the regenerator, which was found to be a problem in Test 4. Freshly sulfided sorbent, which also includes tar (associated with the GE fixed bed gasifier) entering the top of the regenerator is very reactive. For that reason, the oxygen content of the recycle gas must be reduced in order to control the sorbent temperature rise caused by the exothermic regeneration and tar oxidation reactions at the top of the regenerator bed. To complete the regeneration of sorbent in the middle and bottom of the regenerator, however, additional oxygen is required. In a single-stage configuration it was difficult to satisfy both criteria.

To solve this problem, a two-stage regeneration approach was reinstated in the regenerator. In the

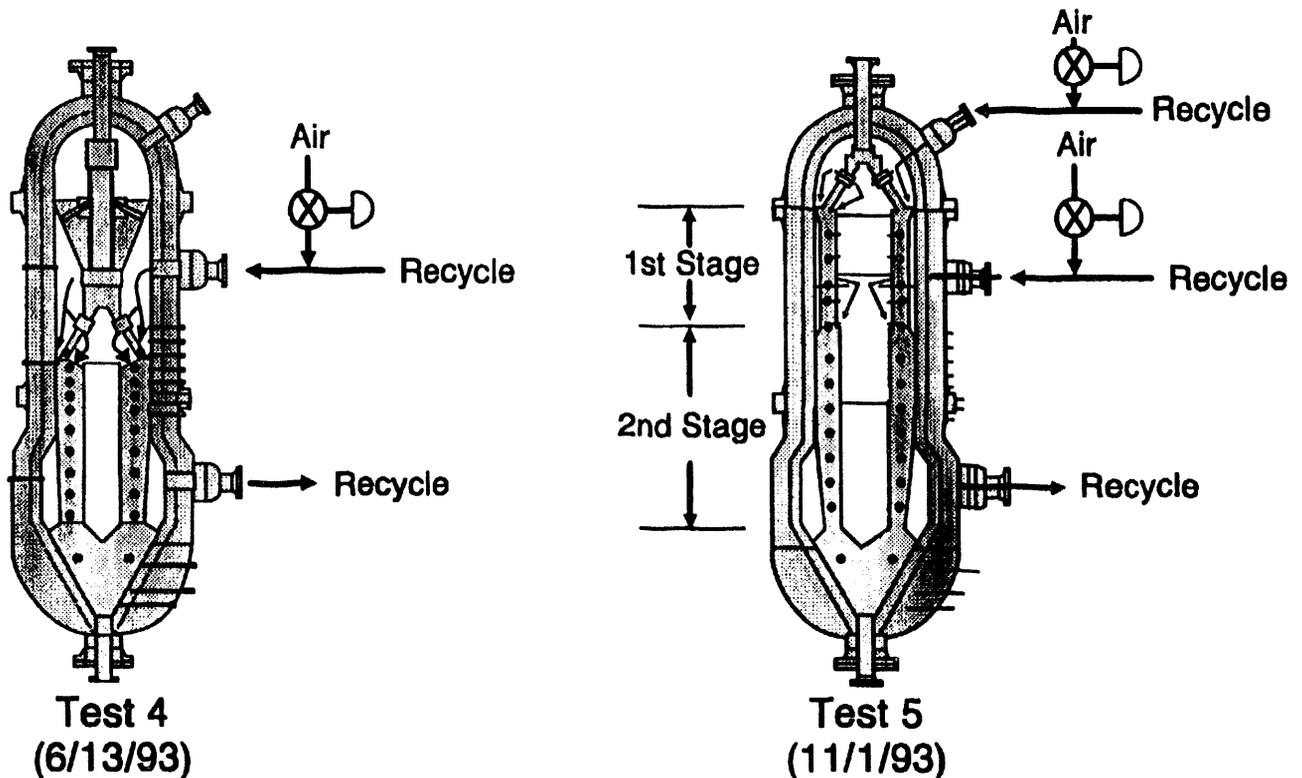


Figure 2. Hot Gas Cleanup Regenerator Modifications – Test 5

modified regenerator configuration, the sorbent passes through two regeneration stages, each with an independent air (oxygen) control, allowing control of the oxygen content and temperature of the sorbent in each stage. In addition, larger valving and piping were installed in the air feed and off-gas bleed lines to increase the flow capacity of these systems.

As previously reported, chlorides in the coal gas cause problems to the HGCU system by adsorbing onto the sorbent in the absorber and being transported to the regenerator, where they are released in the recycle gas. In the recycle gas, the chlorides react with both the sorbent and the  $\text{SO}_2$  in the recycle gas to form zinc sulfate and zinc chloride deposits in the recycle loop heat exchangers. This condition causes blockage of the heat exchangers after several days of operation. To prevent this problem, a fuel gas chloride removal system was designed and installed for demonstration in Test 5. The chloride removal system consists of a pressurized sodium bicarbonate powder injection system located upstream of the primary cyclone. The sodium bicarbonate powder flow is metered through a feeder and transported to the coal gas piping using a dilute phase nitrogen transport system. Sodium bicarbonate powder injected into the hot fuel gas stream at  $1000^\circ\text{F}$  rapidly calcines to sodium carbonate, forming highly porous particles. The sodium carbonate reacts with the hydrogen chloride in the coal gas to form solid sodium chloride within the particles. The particles, consisting of unreacted sodium carbonate and sodium chloride, are captured by the primary cyclone. The location of the sodium bicarbonate injection system is shown on the system schematic (Figure 1).

The MS6000 turbine simulator configuration was not modified significantly from the

previous test. Improvements were made to the nozzle cascade cooling circuits to improve cooling flows to the leading and trailing edges of the vanes. In addition, an automatic temperature control system was incorporated to maintain a constant firing temperature despite variations in the fuel gas heating value caused by the movement of the gasifier stirrer.

### Test 5 Results

The results of Test 5 are summarized in Figure 3. The figure plots the inlet and outlet temperature of the absorber and the outlet  $\text{H}_2\text{S}$  levels of the gas leaving the absorber. The data is shown for the entire week's operation; periods when the absorber was off line are indicated by decreases in the absorber temperatures. The turbine simulator was operational for 41 hours. Most of the turbine simulator operation was at  $2100^\circ\text{F}$  combustor exit temperature, with two hours of operation at  $2300^\circ\text{F}$ .

The gasifier was operated for 103 hours in Test 5, with 65 hours of integrated operation of the HGCU system. The input sulfur loading ranged from 4000 ppm  $\text{H}_2\text{S}$  on Monday to nearly 6000 ppm  $\text{H}_2\text{S}$  on Tuesday and was lowered to approximately 4000 ppm Wednesday through Friday. As shown in Figure 3, the  $\text{H}_2\text{S}$  levels in the fuel gas downstream of the absorber ranged from 50–500 ppm during the test. This corresponds to a sulfur removal range of 90–97% overall.

The test was interrupted several times when the absorber was taken off line. The first two interruptions, on Tuesday evening and Wednesday morning, were caused by poor performance of the regenerator, as evidenced by outlet  $\text{H}_2\text{S}$  levels in the 300–400 ppm range. This degraded performance was caused by incomplete regeneration of the sorbent in the regenerator. As a result, the absorber was removed from the coal gas stream, allowing the regeneration process to continue without the addition of freshly sulfided material to the regenerator.

Post-test material analysis indicated that the sulfur levels in the sorbent leaving the regenerator during these periods were in the range of 2–3%, indicating that regeneration of the sorbent was incomplete. Although both periods of off-line regeneration were successful in improving the performance for several hours, the outlet H<sub>2</sub>S levels again increased to the 300–400 ppm range.

The period the absorber was off line on Thursday morning was associated with plugging of the recycle loop heat exchanger. This condition required disassembly of the heat exchangers for cleaning to restore full recycle gas flow. Subsequent problems on Thursday evening associated with the sorbent elevator electrical system took approximately 12 hours to correct. The final operation on Friday demonstrated improved operational and regeneration conditions and the ability to reduce outlet H<sub>2</sub>S levels to below 100 ppm under proper control conditions.

Overall, sulfur removal performance during Test 5 degraded in comparison with previous tests. We concluded that the performance was due to incomplete regeneration and higher sulfur input levels. Despite the incomplete regeneration, the regenerator recycle gas attained SO<sub>2</sub> levels of 10% for over 36 hours of operation. During shut-downs and restart periods, the regenerator loop was able to recover to high SO<sub>2</sub> levels quickly. These SO<sub>2</sub> levels are much higher than the 7–8% required by the input stream of the sulfuric acid conversion process.

Other results from Test 5 included the demonstration of greatly improved temperature control of the sorbent. The first stage of the regenerator was operated in an automatic control mode, which controlled the input oxygen level based on the peak temperature measured in the first stage. This control approach allowed the maximum temperature in the first stage to be maintained at less than 1500°F throughout the test. The second

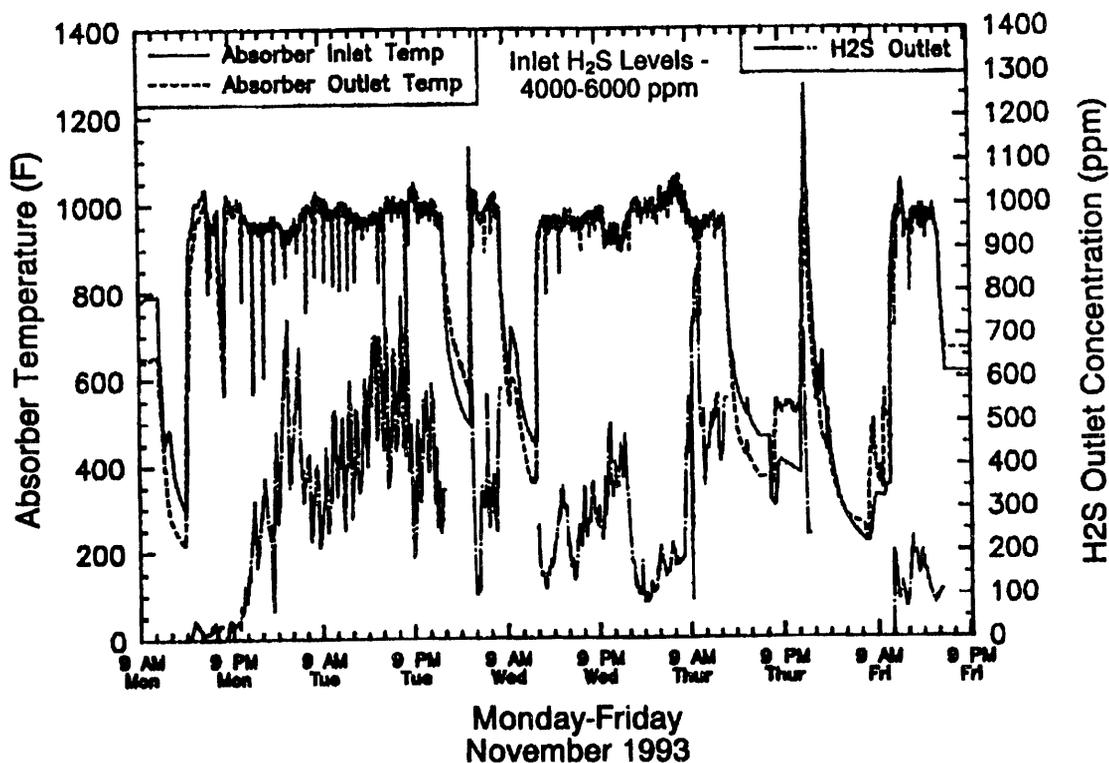


Figure 3. Absorber Performance – Test 5

stage was manually controlled to maintain desired sorbent temperatures.

The pressurized sodium bicarbonate injection system functionally performed as designed. Approximately 20–23 lb/hr of sodium bicarbonate were injected into the coal gas stream using a nitrogen carrier gas upstream of the first-stage cyclone. The sodium bicarbonate had a residence time of approximately 1.5 seconds prior to being removed by the cyclone. The mean particle size was relatively coarse, 85% greater than approximately 75 microns and 98% less than 150 microns, and the stoichiometry was approximately 2.5:1. However, based on measurements in the fuel gas stream and a post-test solids analysis, the chloride mass balance around the system indicated that only 35% of the chloride was removed from the gas.

The mass balances for chloride and sodium are shown in Figure 4. Measurements of the chloride in the recycle loop gas were also

performed periodically throughout the test. Chloride levels in the recycle gas were found to range from 1000 to 2000 ppm, as measured in previous tests. Since the plugging of the recycle loop heat exchangers sharply limited test operation of the PEF and represented a significant problem, it was decided to add a chloride “guard bed” to remove chlorides directly from the recycle loop.

To improve our understanding of the kinetics of sodium bicarbonate reactions with HCl in hot fuel gas streams, testing was performed at the University of North Dakota Energy and Environmental Research Center’s pressurized drop tube furnace (PDTF). The tests used various powder sizes, residence times, and stoichiometry of sodium bicarbonate in simulated coal gas containing HCl. The results demonstrated that removal rates of over 90% were possible using longer gas/solids residence times, finer powder, or increased stoichiometry. The conclusion of the PDTF testing was that the PEF residence time was too short and that an improved configuration to increase both the residence time

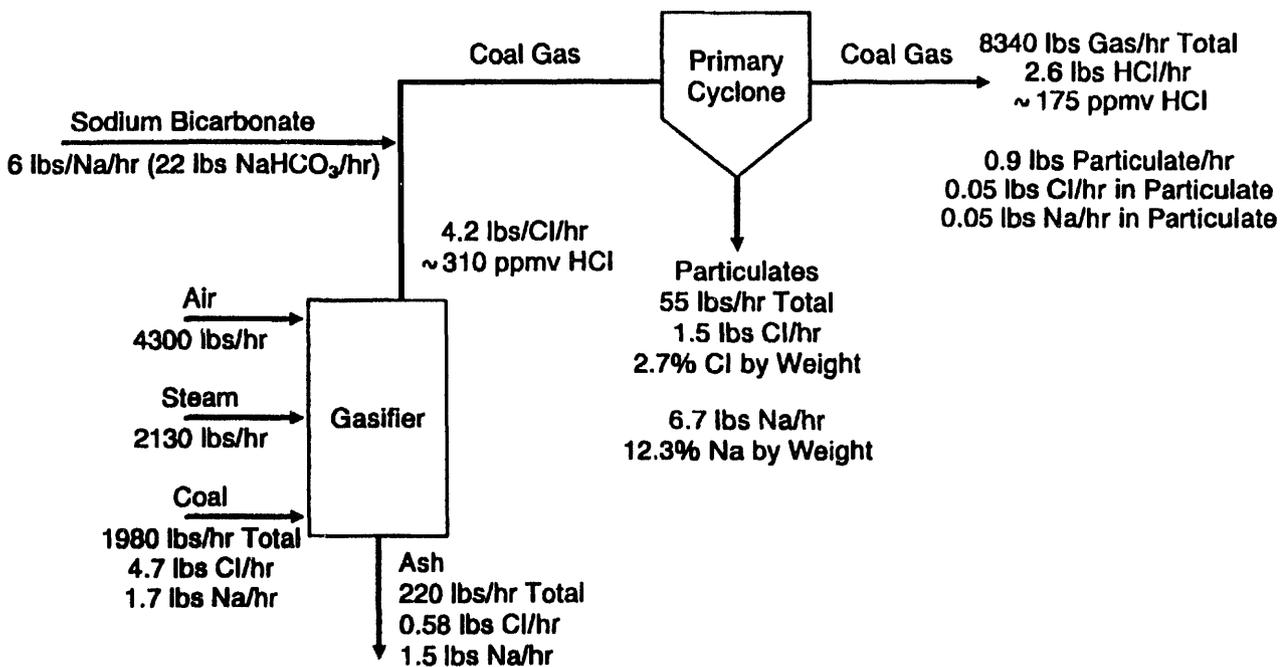


Figure 4. Gasifier Sodium and Chloride Balance for Run 5

and stoichiometry by use of a recycle cyclone should be incorporated into the facility. However, because of the time required to revise the plant high-temperature fuel piping, this modification has been postponed until after Test 6.

During Test 5, it was observed that the sorbent pellets leaving the regenerator were not uniform in color, indicating that some pellets were not fully regenerated. This observation led to the hypothesis that the pellets were not moving through the regenerator in a uniform plug flow condition. It appears that some sorbent pellets were moving through the regenerator more quickly and did not have enough residence time to be fully regenerated, while other pellets were moving very slowly and were fully regenerated at the exit. This hypothesis was tested by constructing scale models of the regenerator geometry and flowing sand through the model to observe the behavior of a colored

tracer layer of sand. From tests on a modified regenerator model, it was determined that a diverter located in the discharge of the regenerator would greatly improve the uniformity of the solids flow in the annular section of the regenerator. The data from this testing is shown in Figure 5, indicating the ideal flow characteristics and the modified and non-modified flow characteristics. On the basis of these results, modifications to the regenerator exit were designed and incorporated into the PEF regenerator.

Disassembly of the turbine simulator after Test 5 indicated that although the simulator operated without apparent problems, the cap/cowl louvers in the head end of the combustor had been damaged. Several of the cooling louvers were damaged. The appearance of the combustor suggested that the flame structure was located very close to the head end of the combustor and was the cause of the overheating of the cap/cowl assembly. This condition was reviewed with GE Power Generation

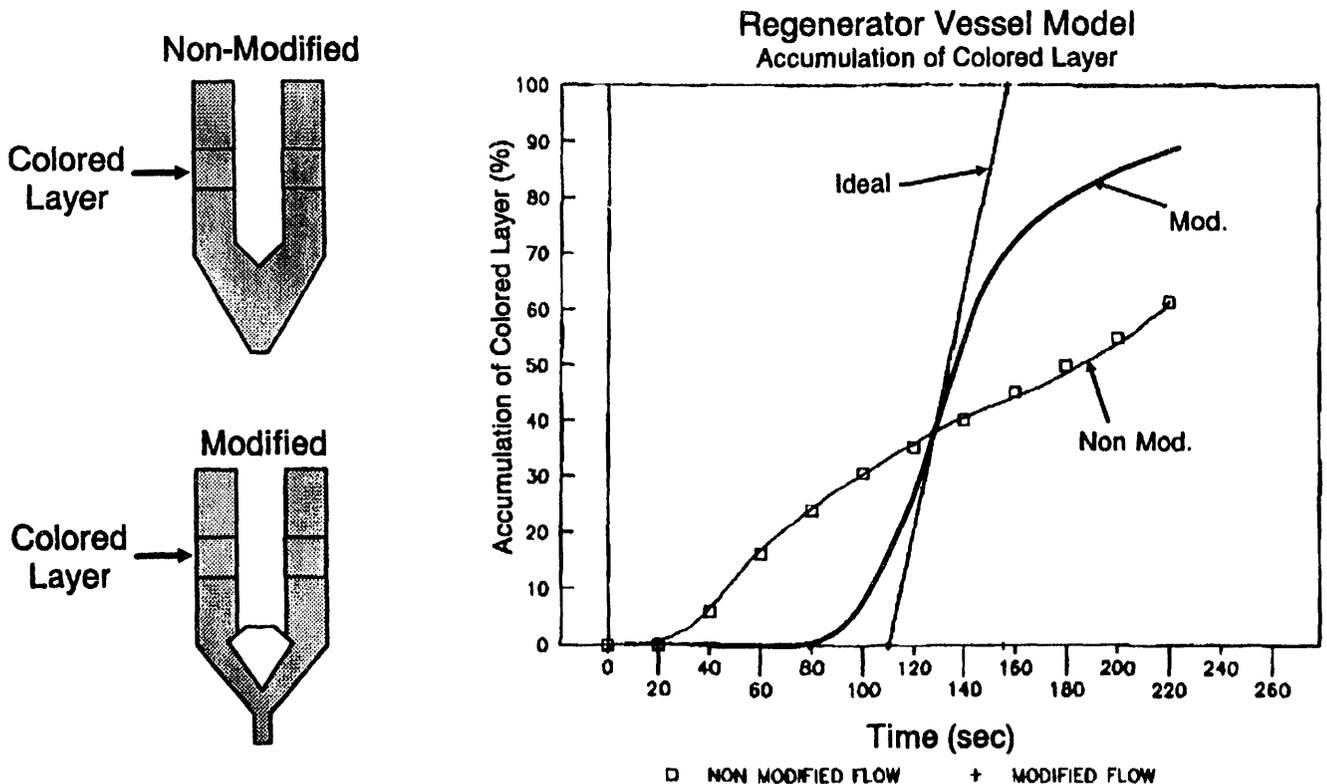


Figure 5. Solids Flow Test - Regenerator Discharge

Engineering, and minor modifications to the axial location of the air and fuel swirler were made. In addition, the swirl angles of the air and fuel swirlers were reduced, thus modifying the location of the flame within the combustor.

### Test 6 Conditions and System Modifications

Long Duration Test 6 was performed during the period of May 1 to May 5, 1994. Several significant modifications and changes were made to the HGCU and turbine simulator systems in preparation for Test 6. The most significant change from previous tests was the use of Z-Sorb sorbent. Characteristics of Z-Sorb are detailed in a paper presented in the sorbent development session of this conference (Ayala et al., 1994).

Modifications to the lower section of the regenerator internal configuration, as shown in Figure 6, were fabricated and installed with the

objective of improving the uniformity of sorbent solids flow. The annular, two-stage regenerator configuration was retained from Test 5.

A "guard bed" was added to the recycle loop to continuously remove chlorides from the recycle gas. The guard bed is a small fixed bed contains an active volume of approximately 300 pounds of sodium bicarbonate pellets (3-4 mm). Since sodium bicarbonate will react with  $\text{SO}_2$  as well as chlorides, the guard bed was located in the lowest temperature position in the loop, upstream of the recycle compressor. Bench-scale testing of sodium bicarbonate pellets in simulated recycle gas demonstrated that at temperatures of 500 to 550°F, reactions with  $\text{SO}_2$  are minimized and chloride reactions will proceed rapidly.

In addition to the modifications made for Test 5, minor modifications were made to the primary cyclone to improve performance of particulate

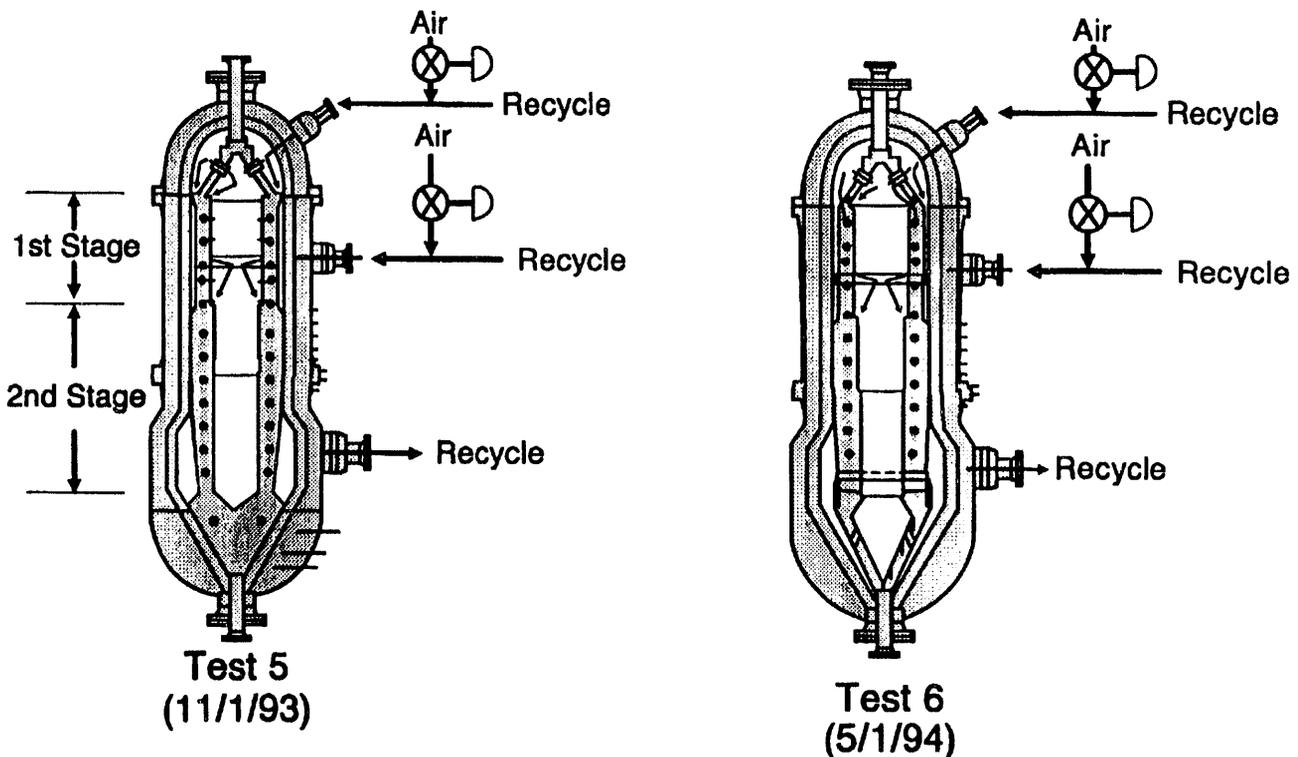


Figure 6. Hot Gas Cleanup Regenerator Modifications – Test 6

collections during lock-hopper operation. Sorbent transfer valves manufactured by two vendors were installed in the HGCU system to evaluate alternate valve designs in high-temperature, high-solids loading applications.

Test 6 utilized Illinois #6 (1.9% sulfur) as the gasifier input fuel, producing approximately 3500–4000 ppm H<sub>2</sub>S in the coal gas. Sodium bicarbonate injection into the coal gas was also retained during Test 6. The system was tested with finer grades of sodium bicarbonate. Because the finer grades caused bridging of the feeder, the original grade of sodium bicarbonate was used for Test 6 and no improvement in this system's performance was expected.

Modifications to the turbine simulator, as previously noted, included relocation of the air swirler/fuel nozzle, changes to the swirl angle, and blocking of dilution holes in the liner. An

improved cooling scheme for the nozzle cascade mounting flange area was also incorporated to prevent problems caused by thermal growth of the cascade relative to the mounting flange.

### Test 6 Results

Test 6 resulted in approximately 80 hours of integrated gasifier/HGCU system operation and represents the longest integrated test operation to date in the program. The only hardware problem encountered during Test 6 was the failure of the sorbent elevator cable on Wednesday evening. This failure resulted in severe damage to the elevator bucket; however, repairs to the bucket and elevator were made in a very short time, and the system was returned to operation on Thursday morning.

The overall results of Test 6 are shown in Figure 7. The performance of Z-Sorb was very encouraging. Removal of H<sub>2</sub>S from the gas stream was very good, with long periods of testing with

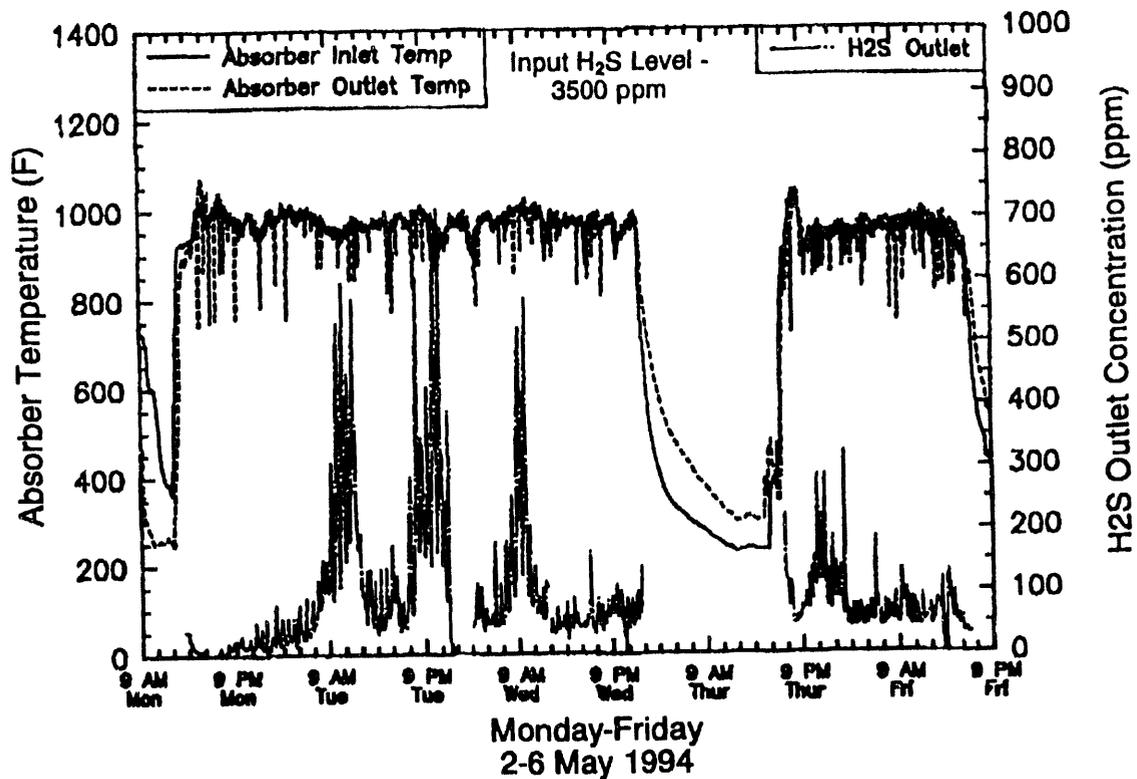


Figure 7. Absorber Performance – Test 6

less than 50 ppm H<sub>2</sub>S in the absorber outlet stream. No problems were encountered with the use of Z-Sorb in a moving bed system. The sorbent flowed well and no significant water gas shift in the absorber was observed. Although an exothermic methanation reaction was predicted during the first sulfidation cycle of the material, that reaction was not observed. Post-test inspection did not reveal any agglomeration of sorbent or other signs of physical degradation.

As shown in Figure 7, the performance of the HGCU system fell off slightly during three periods on Tuesday and Wednesday. This decrease in absorber performance was associated with adjusting the regeneration control conditions to determine the best regeneration strategy for Z-Sorb. Once the proper regeneration conditions were met, the performance of the Z-Sorb returned to predicted H<sub>2</sub>S performance levels.

One difference between Z-Sorb and the zinc titanate previously tested was the limitation on the upper temperature of the sorbent. Phillips Petroleum Company recommended that the peak regeneration temperature of Z-Sorb be limited to approximately 1350°F, significantly lower than the 1500°F peak temperature used for zinc titanate. This operational limitation required that close control be maintained over the regeneration process.

Due to the different regeneration characteristics of Z-Sorb compared to zinc titanate, several operational changes (e.g., lowering the temperature of the inlet recycle gas) were necessary to maintain the proper temperatures. For most of the test, a nitrogen purge through the regenerator exit area was maintained to decompose any sulfate that might have formed during regeneration. Post-test analysis indicates that sulfate levels in the

sorbent leaving the regenerator were very low, generally less than 0.5%. Total residual sulfur in the sorbent leaving the regenerator was approximately 1% for those periods of good regeneration. These levels are significantly lower than the regenerator sorbent sulfur levels observed in Test 5. Although the use of Z-Sorb improved performance of the HGCU system, the test results continued to indicate that improved control of sorbent temperature (i.e., sufficient heat rejections), while maintaining sufficient oxygen content in the recycle gas to complete regeneration is the key to HGCU performance.

Fines were collected under the vibrating sorbent screen at the bottom of the regenerator in order to measure the attrition loss of Z-Sorb. The attrition resulting from movement of fresh sorbent through the HGCU system at ambient temperature was approximately 0.2% of the total material circulated through the system. The overall attrition loss over 8 cycles of absorption/regeneration in Test 6 was approximately 0.4% of the total sorbent moved. This attrition rate is considered to be very low at the scale of the PEF and is significantly better than the attrition rate of zinc titanite in Test 5.

A major achievement of Test 6 was the demonstration of effective chloride removal by the regenerator recycle guard bed. Chloride levels downstream of the guard bed averaged 308 ppm compared to 1000–2000 ppm in previous tests. This reduction enabled us to maintain full recycle gas flow throughout the test. The heat exchanger pressure drop was constant throughout the test.

Test 6 was the first test that did not require cleaning of the recycle loop heat exchangers during a long duration test. The sodium bicarbonate material in the guard bed did react with chlorides as expected; however, SO<sub>2</sub> in the recycle loop also reacted with the sodium bicarbonate and reduced the SO<sub>2</sub> levels to 6–7% during the test. The use of

sodium bicarbonate in the recycle loop guard bed was effective in removing chlorides; although an improved guard bed material, demonstrating lower reactivity to SO<sub>2</sub> while maintaining reactivity towards chlorides, is under investigation.

The performance of the sodium bicarbonate injection system for removal of chlorides in the fuel gas was found to be of the same level as demonstrated in Test 5. The system removed 25–35% of the chlorides from the fuel gas, and an improved sodium bicarbonate/recycle design is in progress.

Turbine simulator testing totaled 67 hours of fired operation. The simulator operated for over 24 hours at 2300°F combustor exit temperature and at 2500°F for three hours. The modifications to the turbine simulator were successful, resulting in low metal temperatures both in the cap/cowl area and in the combustor liner. No deposits were observed on the turbine simulator nozzle or liner after the conclusion of the test. The NO<sub>x</sub> emissions from the turbine simulator were approximately 200 ppm (@ 15% oxygen) due to the conversion of fuel-bound nitrogen species, such as ammonia, to NO<sub>x</sub>. Ammonia in the fuel gas was measured at 4100 ppm. Carbon monoxide (CO) and unburned hydrocarbon emissions were also found to be very low.

Vapor phase alkali measurements in the hot fuel gas (850°F) were performed by the research staff of Ames Laboratory during Test 6. This testing was performed using an on-line atomic absorption spectrometer to measure alkali directly in the vapor phase of the fuel gas. Preliminary results of this testing indicated that the alkalis in the fuel gas were present at levels well below 10 ppb. This level is well below the turbine alkali tolerance specification required by GE. Details of the turbine simulator testing and

alkali testing are discussed in a concurrent paper presented by Feitelberg et al. (1994) in these proceedings.

Overall, Test 6 was the most successful test of the HGCU program to date. Sulfur removal efficiency of 98 to 99% was demonstrated, and sorbent attrition was very low. The guard bed prevented plugging of the recycle heat exchanger during the test period and all HGCU mechanical systems (with the exception of the elevator) performed well. The turbine simulator reached “F” class turbine firing conditions with no damage to the hardware.

## **FUTURE WORK**

Several additional tests are planned for the gasifier/HGCU/turbine simulator in calendar year 1994. Two 100-hour tests are planned for August and October to demonstrate an improved internal sorbent flow configuration for the absorber and the addition of the recirculating sodium bicarbonate chloride removal system to the fuel gas stream. The test year will culminate with a longer term test (100 to 200 hours) in December 1994. A 24-hour test of an experimental rich-quench-lean combustor will also be performed during the fourth quarter of 1994. All remaining testing in 1994 is based on the use of Z-Sorb and will be focused on demonstrating long-term durability of the HGCU system and the sorbent.

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### 6.3

## Enviropower Hot Gas Desulfurization Pilot

### CONTRACT INFORMATION

**Cooperative Research and Development Agreement Number:** 93-016

**Contractor:** Enviropower Inc.  
P.O. Box 35  
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Gabor Feher

**Principal Investigators:** Jukka Konttinen  
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Wahab Mojtahedi

**METC Project Manager:** Thomas P. Dorchak

**Period of Performance:** September 8, 1993 to December 31, 1995

**Schedule and Milestones:**

#### 1993-95 Program Schedule

	<u>1993</u>	<u>1994</u>	<u>1995</u>												
	S	N	J	M	M	J	S	N	J	M	M	J	S	N	D
CRADA Agreement															
Pilot Installations															
Pilot Commissioning															
Pilot Tests with Sorbent															
DSRP Pilot Design															
DSRP Commissioning															

## OBJECTIVES

In September 1993 Enviropower Inc. entered into a Cooperative Research and Development Agreement (CRADA) with the Department of Energy in order to develop and demonstrate the major components of an IGCC process such as hot gas cleanup systems.

The objectives of the project are to develop and demonstrate 1) hydrogen sulfide removal using regenerable zinc titanate sorbent in pressurized fluidized bed reactors, 2) recovery of the elemental sulfur from the tail-gas of the sorbent regenerator and 3) hot gas particulate removal system using ceramic candle filters.

## BACKGROUND INFORMATION

Enviropower Inc. is a subsidiary of Tampella Power Inc. which is the parent company of the Tampella Power Corporation in the U.S.A. Enviropower Inc. is actively involved in the development of IGCC process. Enviropower's IGCC concept incorporates pressurized fluidized bed gasification of different solid fuels, applying air-blown gasification and hot gas clean-up. The IGCC process diagram can be seen in Figure 1.

As part of the Clean Coal IV-program in 1992, Tampella's IGCC technology was chosen by the United States Department of Energy (DOE) to be demonstrated in the U.S.A. Currently, an IGCC demonstration plant to be built in Finland is being designed by Enviropower Inc. to utilize biomass and coal. The IGCC process and the demonstration projects have been described in detail elsewhere /1, 2/.

Enviropower's U-GAS-based gasification pilot plant is located in Tampere, Finland. The thermal input of the gasifier is 15 MW (or 35 tons of coal per day) and maximum

operating pressure of 30 bar. The pilot plant has the capability of gasifying coal, biomass and different waste materials. It also includes the components for hot gas cleanup including hot gas desulfurization and fine particulate removal using ceramic candle filters. The components of the pilot-process are described in Figure 2.

In the Enviropower's present concept of IGCC, the bulk of fuel bound sulfur is removed in the gasifier by means of a calcium based sorbent such as limestone or dolomite and the rest is removed externally in a fluidized bed system using a regenerable sorbent such as zinc titanate. The sulfur removal options in Enviropower's IGCC process can be seen in Figure 3. Novel zinc titanate sorbents suitable for fluidized bed application has been tested and the plan is to use the regenerable sulfur removal system as the sole method of sulfur removal in the future. This will reduce the bulk of solid waste from the gasifier and improve the system performance and economy.

Cyclic sulfidation and regeneration tests with zinc titanate have been carried out in a 3-inch I.D. batch fluidized bed reactor which is located at the Institute of Gas Technology in Chicago. The reactor is capable of operating at temperatures up to 1000°C and pressures up to 30 bar with synthetic gas mixtures containing all the gaseous components for sulfidation and regeneration reactions. The 3-inch pressurized fluidized bed reactor assembly has been described in detail elsewhere /5/ and a schematic diagram can be seen in Figure 4. A typical H<sub>2</sub>S breakthrough curve in cyclic tests for one of the sorbents is shown in Figure 5. Figure 6 shows the corresponding regeneration curve. The laboratory- and bench-scale test results have been reported in more detail elsewhere /3, 4, 5/.

## PROJECT DESCRIPTION

The CRADA-project consists of the following subtasks:

- Laboratory-scale tests will be conducted on selected sorbents for removal of hydrogen sulfide. These tests will be performed in a 3 inch pressurized fluidized bed under conditions simulating the real situation with respect to temperature, pressure, gas composition and contaminants. Sorbents will be fully analyzed for their physical, chemical and mechanical durability characterization.
- Full-scale pilot-plant testing of the sorbents will be carried out in Finland, using a pressurized fluidized-bed absorber and regenerator. The sulfur removal efficiency and long term durability of the sorbent will be evaluated in these tests. Sorbent samples from the pilot-plant tests will be analyzed the same way as fresh sorbents by Enviropower, IGT and METC.
- The tail gas from the regeneration contains sulfur dioxide which can be converted to usable elemental sulfur. A technology called the Direct Sulfur Recovery Process (DSRP) has been developed at Research Triangle Institute (RTI) /6/ to achieve this objective. A skid-mounted DSRP unit will be designed and built in METC and will be shipped to the pilot plant in Finland for installation and testing with a slipstream of the U-gas process coal gas. Suitability of the DSRP process and sulfur conversion efficiency will be examined during testing. Design data will also be obtained for scale-up for commercial-sized systems.
- The collection efficiency and operability of ceramic candle filters for removing solid particles from the hot gas will be examined in full scale pilot plant tests in Finland. The filter ash, fuel and U-gas gasifier fly ash will be analyzed for their physical properties.

## RESULTS AND FUTURE WORK

### Pilot design and testing

The installation of the sulfur removal pilot was under way in September 1993 when CRADA was signed. The major part of the installation took place in 1993 and it was completed in January 1994. The pilot consists of HTHP fluidized-bed type sulfider and regenerator reactors and systems for fresh sorbent feeding, sorbent circulation between reactors and gas preheating/cooling for regenerator. In February 1994, the operational check-out of the pilot at actual process conditions was carried out with the objective of testing the mechanical integrity of the system as part of the pilot plant. Inert sand was used as bed material in sulfider and regenerator reactors. The tests showed that the sorbent feeding and circulation systems could be operated as designed, and the automation and control systems were working well. Bed material samples from both reactors could be taken without difficulty.

In March 1994, two tons of zinc titanate sorbent produced by the United Catalysts, Inc. was received from U.S.A. The average particle size of the sorbent batch is about 200  $\mu\text{m}$  and particle density about 2  $\text{g}/\text{cm}^3$ , which is in the region of well fluidizable particles according to Geldart classification /7/. Another batch of zinc titanate sorbent (ZT-4) with about the same fluidization properties has been ordered by DOE to be shipped to Finland by September 1994.

In May 1994, the commissioning of the pilot was accomplished with zinc titanate sorbent at actual process conditions with coal gas. Bituminous (Polish) coal was used as gasifier feedstock. The test run was successful and several operation test points was run. The data are presently being analyzed and some of the results are shown in Figures 7, 8 and 9.

The following preliminary conclusions from the pilot commissioning with zinc titanate sorbent can be drawn:

- several steady-state operation test points of the sulfider and regenerator fluidized bed reactors linked together near and at design pressures and temperatures was obtained
- the regeneration of the sorbent with steam+air mixture seemed to work without problems
- it was possible to keep the regenerator bed temperature in the range of 650-750°C and SO<sub>2</sub> outlet content between 0-4 vol-% (mainly 2 vol-%) by controlling the air flow into the reactor
- As can be seen in Figures 7, 8 and 9, the continuous transport of the sorbent between the fluidized bed-type reactors seemed not to interrupt regeneration or sulfidation much.
- Very high sulfur removal efficiencies in sulfider were obtained by adjusting the bed height and gas superficial velocity (Figure 7)
- more tests are needed to obtain larger steady-state runs to optimize the system. These will be undertaken in 1994.

The tests with the pilot will continue in fall 1994 by using the current and ZT-4 sorbent.

### **Laboratory-scale work**

Bed samples taken from the pilot tests and fresh zinc titanate samples will be tested by the DOE and IGT according to the project plan.

### **Other subtasks**

The performance of ceramic filters with coal gas was and will be tested during the same test runs with sulfur removal pilot unit.

The data from the test run in May 1994 are currently being analyzed. The preliminary results show however that the filtration efficiency is high enough to satisfy gas turbine requirements.

The design of the DSRP-pilot equipment is proceeding with the preliminary objective to test the unit in connection with the pilot-plant in Finland by mid-1995.

### **Modelling efforts**

A steady-state kinetic model for hot gas desulfurization system has been developed based on laboratory- and bench-scale tests on zinc titanate sorbents. The model has been used in the preliminary dimensioning of the commercial-scale sulfur removal system. The results from the pilot test run in May show that the model predictions were in good agreement with the test results.

A dynamic model for the pilot and commercial-scale post-bed sulfur removal system is under development. The objective is to use it for predicting the effects of the changes in regenerator inlet gases, sorbent transport velocity, fluidization velocities etc. on the overall performance. This information can be used to adjust the control system of the process. After the verification of the dynamic model with pilot test results it will be added as a module into the Enviropower's existing IGCC-plant dynamic simulator for design and training purposes.

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2. SALO K., *Using Biomass-Gasification Combined Cycle Technology in Power Generation*. In: Energy in Finland 1993, pp. 32 - 35

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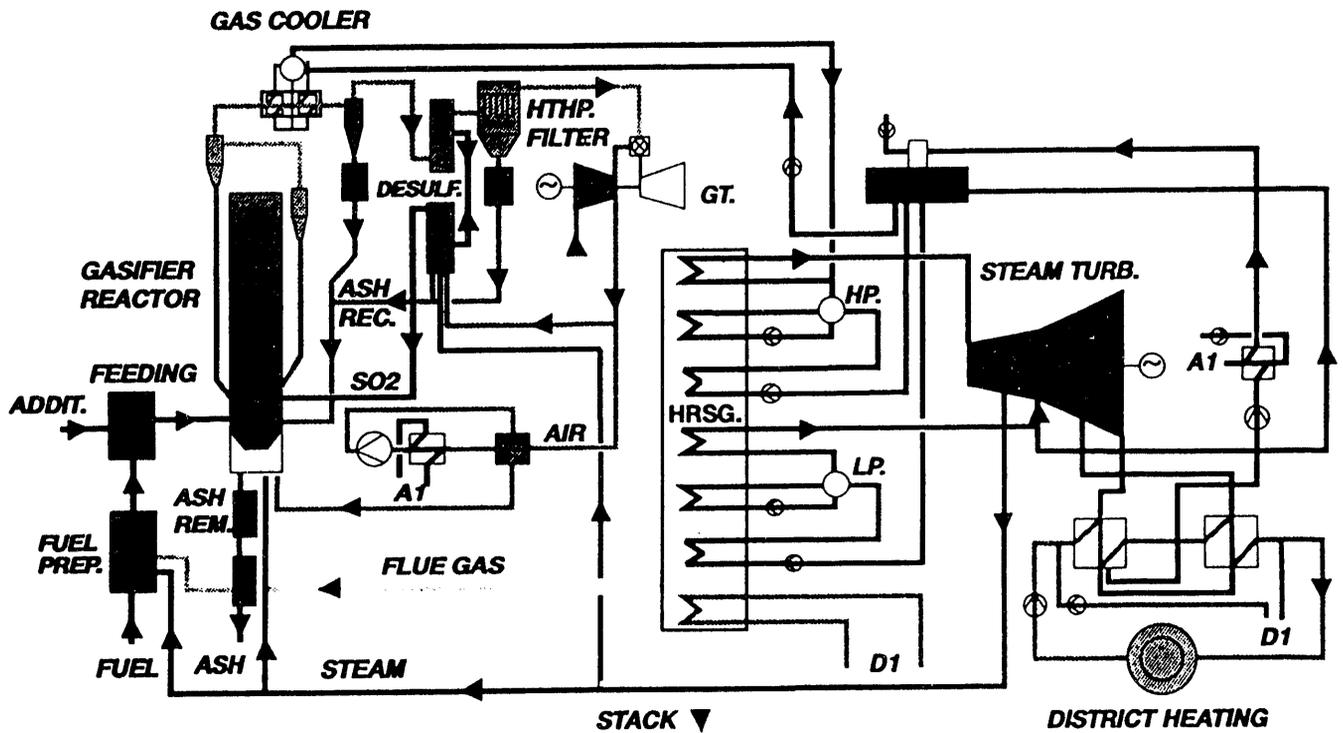


Figure 1. Tampella's IGCC process scheme.

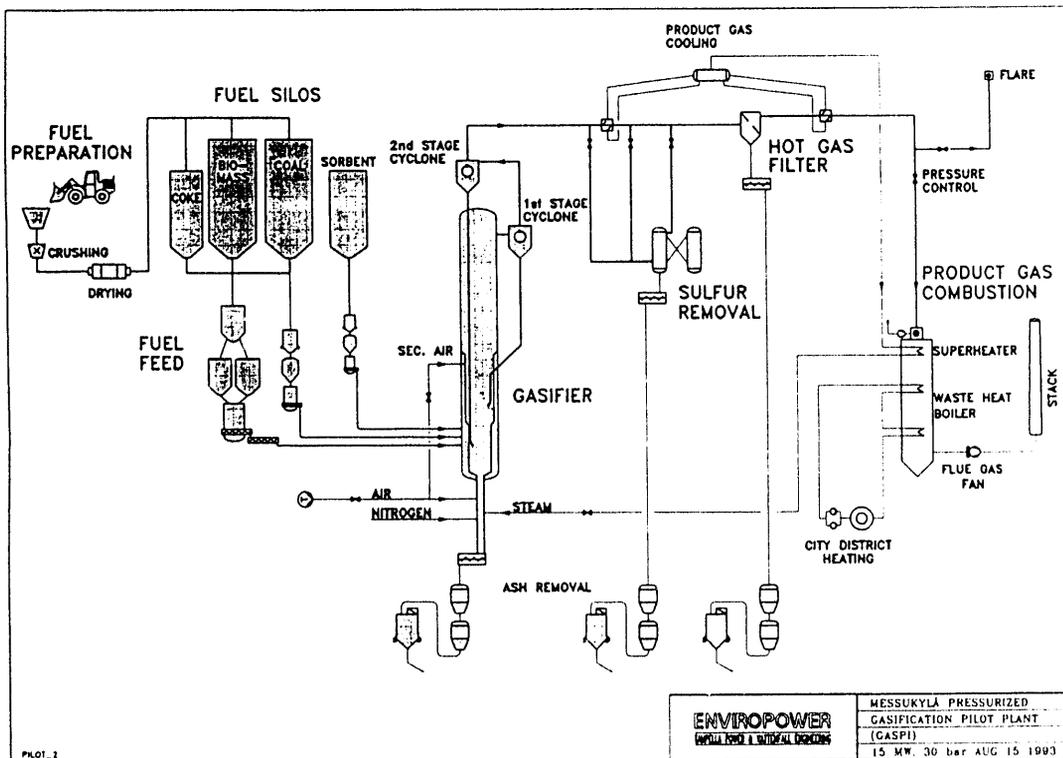
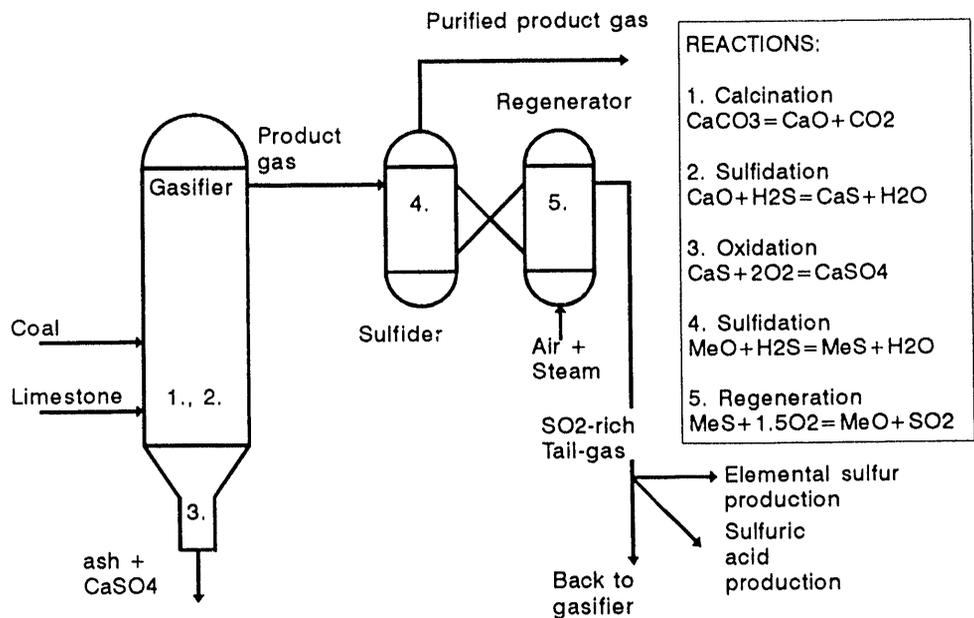


Figure 2. Scheme of the Enviropower's pressurized gasification pilot plant.



## ENVIROPOWER

Figure 3. Different stages in Tampella's IGCC sulfur removal.

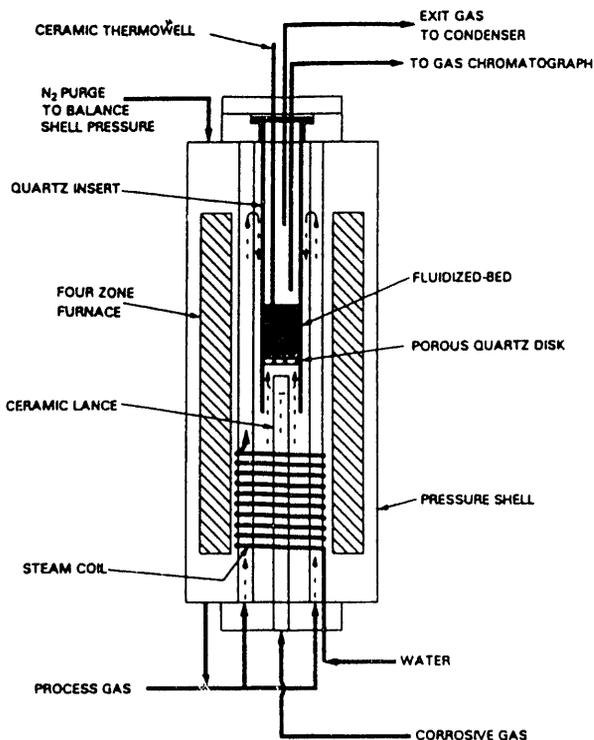


Figure 4. High-temperature/high pressure 3-inch batch fluidized bed reactor assembly.

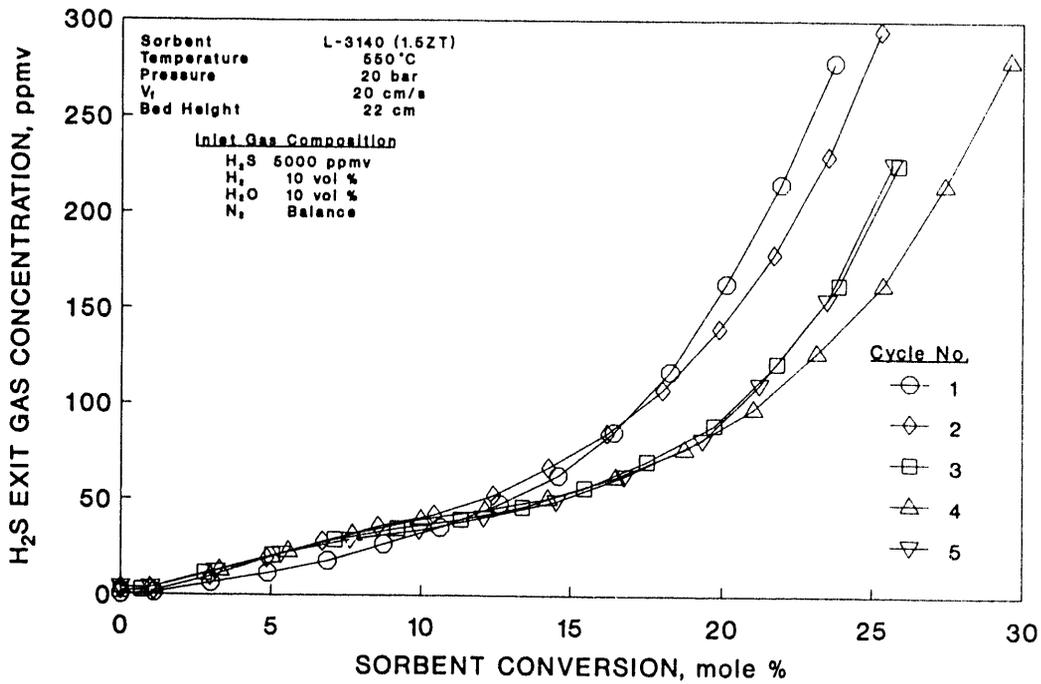


Figure 5.  $H_2S$  breakthrough curve for L-3140 zinc titanate sorbent in the 3-inch batch reactor.

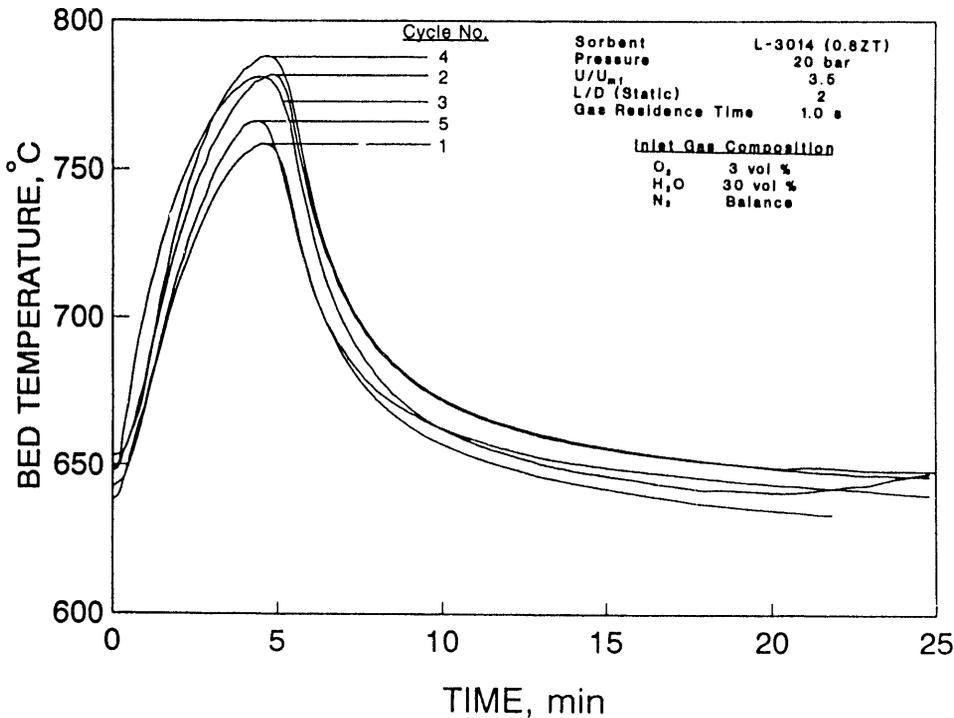


Figure 6. Bed temperature rise in 3-inch batch fluidized bed reactor due to exothermic regeneration reaction.

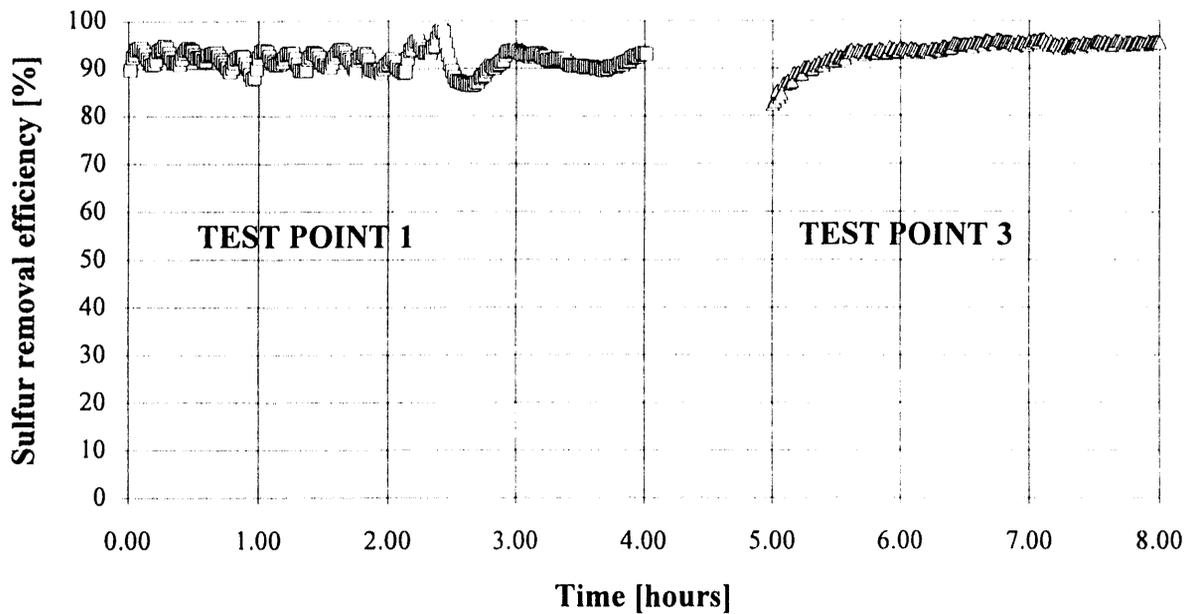


Figure 7. Hot gas desulfurization pilot test run in May 1994. Calculated sulfur removal efficiencies in sulfider during two test points.

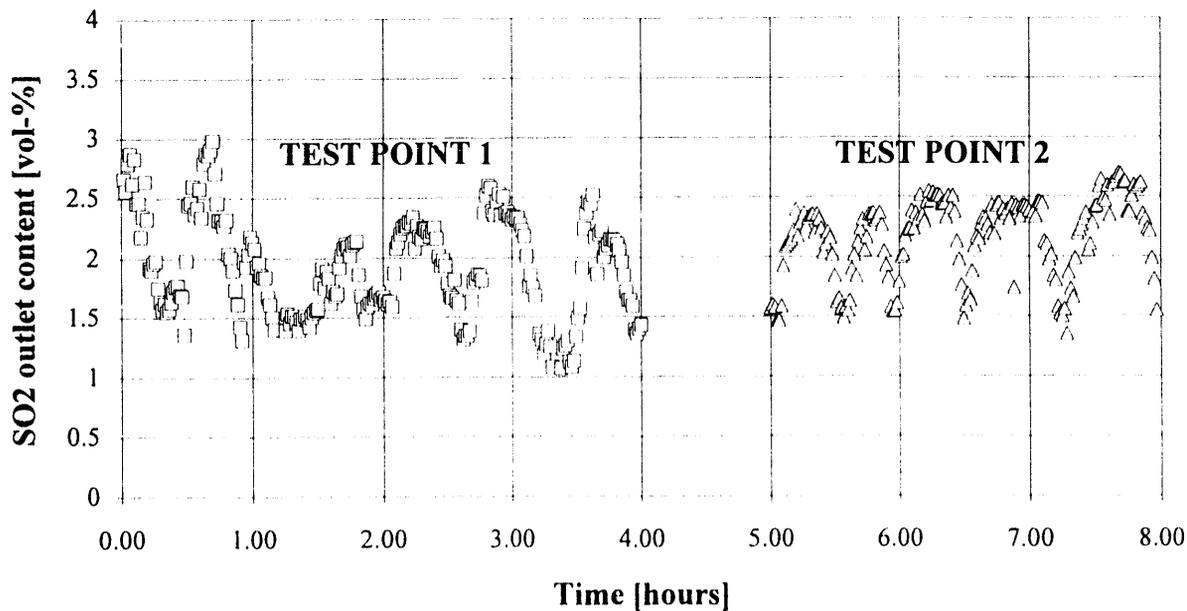


Figure 8. Hot gas desulfurization pilot test run. SO<sub>2</sub> outlet content [vol-%] in the regenerator off-gas during two test points (manual regenerator air inlet control).

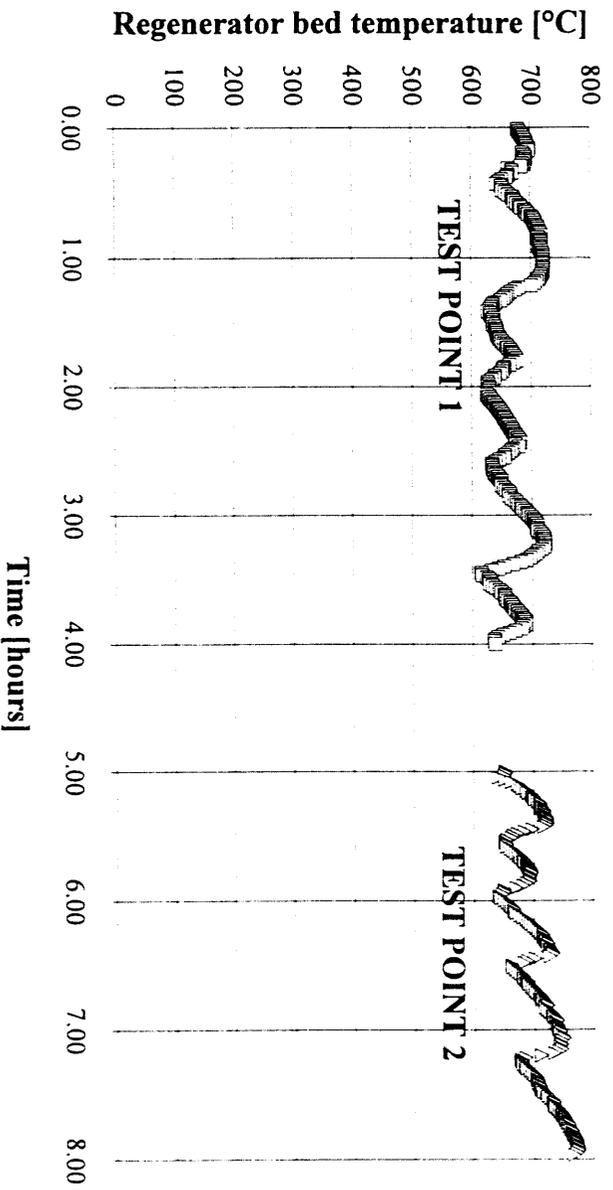


Figure 9. Hot gas desulfurization pilot test run. Regenerator bed temperature during two test points.

## 6.4 Slipstream Testing of the Direct Sulfur Recovery Process

### CONTRACT INFORMATION

**Contract Number** DE-AC21-93MC30010

**Contractor** Research Triangle Institute  
P. O. Box 12194  
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**Principal Investigators** Jeffrey W. Portzer  
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Daniel H. Chen (Lamar University)  
Michael H. McMillian (DOE/METC)

**METC Project Manager** Thomas P. Dorchak

**Period of Performance** July 1, 1993 to December 12, 1994

### Schedule and Milestones

#### FY94-95 Program Schedule

	J	A	S	O	N	D	J	F	M	A	M	J	J	A	S	O	N	D
MET Field Test	<hr/>																	
Large-Scale System	<hr/>																	

### OBJECTIVES

The objective of this work is to continue further development of the zinc titanate fluidized-bed desulfurization (ZTFBD) and the Direct Sulfur Recovery Process (DSRP) technologies for hot gas cleanup in integrated gasification combined cycle (IGCC) power generating systems. There are three main goals of this project:

- Development of an integrated, skid-mounted, bench-scale ZTFBD/DSRP reactor system;
- Testing the integrated system over an extended period with a slipstream of coal gas from an operating gasifier to quantify the degradation in performance, if any, caused by the trace contaminants present in coal gas (including heavy metals, chlorides, fluorides, and ammonia); and

- Design, fabrication, and commissioning of a larger, pilot-plant scale DSRP reactor system capable of operating on a six-fold volume of gas greater than the reactors used in the bench-scale field tests.

## BACKGROUND INFORMATION

Hot gas desulfurization processes for IGCC and other advanced power applications utilize regenerable mixed metal-oxide sorbents to remove hydrogen sulfide ( $H_2S$ ) from raw coal gas. Regeneration of these sorbents produces an off-gas typically containing 1 to 3 percent sulfur dioxide ( $SO_2$ ). Reduction to elemental sulfur is a highly desirable option for the ultimate disposal of the  $SO_2$  content of this off-gas. Elemental sulfur, an essential industrial commodity, is easily stored and transported. The DSRP is a simple and attractive process for production of elemental sulfur from the regeneration off-gases.

As shown in Figure 1, the DSRP consists of two catalytic reactors, each followed by a sulfur condenser. Hot regeneration off-gas is mixed with a hot coal gas slipstream (to act as the reducing gas) and is fed to the first DSRP reactor. Approximately 95 percent of the combined sulfur in the inlet stream of the first reactor is converted to elemental sulfur. The outlet gas of the first DSRP reactor is cooled, condensing out sulfur. The flow of reducing gas to Stage I is controlled so that there is a 2-to-1  $H_2S$ -to- $SO_2$  ratio at this point. This cooled gas stream is then sent to the second DSRP reactor where 80 to 90 percent of the remaining sulfur compounds are converted to elemental sulfur via the modified Claus reaction at high pressure. The total efficiency of the two reactors for the conversion of sulfur compounds to elemental sulfur has been demonstrated to be 99 percent.

The development of the DSRP has proceeded from lab-scale experiments utilizing 25- to 50-cc

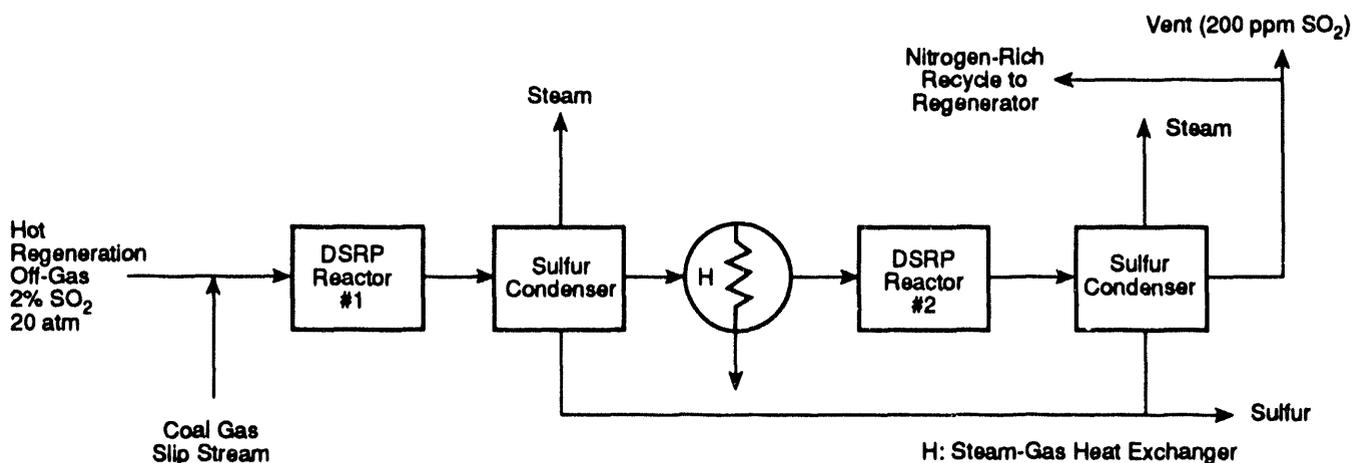


Figure 1. DSRP Process

fixed-bed reactors (McMichael and Gangwal, 1990) through bench-scale (Gangwal and McMichael, 1991; Gupta et al., 1992; Gangwal et al., 1992), and fluidized-bed testing (Gangwal et al., 1993). The composition of the regeneration off-gas has been varied to as high as 12.4 vol% SO<sub>2</sub>; pressures have ranged from 1.7 to 24.8 atm. The results indicate the effectiveness in obtaining up to 96 percent conversion to sulfur in one stage of reaction and up to 99 percent in two stages with efficient interstage sulfur removal. Independent studies by Gilbert Commonwealth, Texaco, and the Research Triangle Institute (RTI) have shown the economic attractiveness of the DSRP (Robin et al., 1993; Buchanan et al., 1994; McMichael and Gangwal, 1990).

Through bench-scale development, both fluidized-bed zinc titanate and DSRP technologies have been shown to be technically and economically attractive. The demonstrations to date, however, have only been conducted using simulated (rather than actual) coal gas and simulated regeneration off-gas. Thus, the effect of trace contaminants in actual gases on the sorbent and DSRP catalyst is currently unknown. Also, ZTFBD and DSRP have not been demonstrated in an integrated manner. Finally, data from a larger reactor size are needed for realistic scaleup to commercial scale. Thus, this project continues further development of the zinc titanate desulfurization and DSRP technologies by testing with a slipstream of actual coal gas in bench-scale and larger equipment.

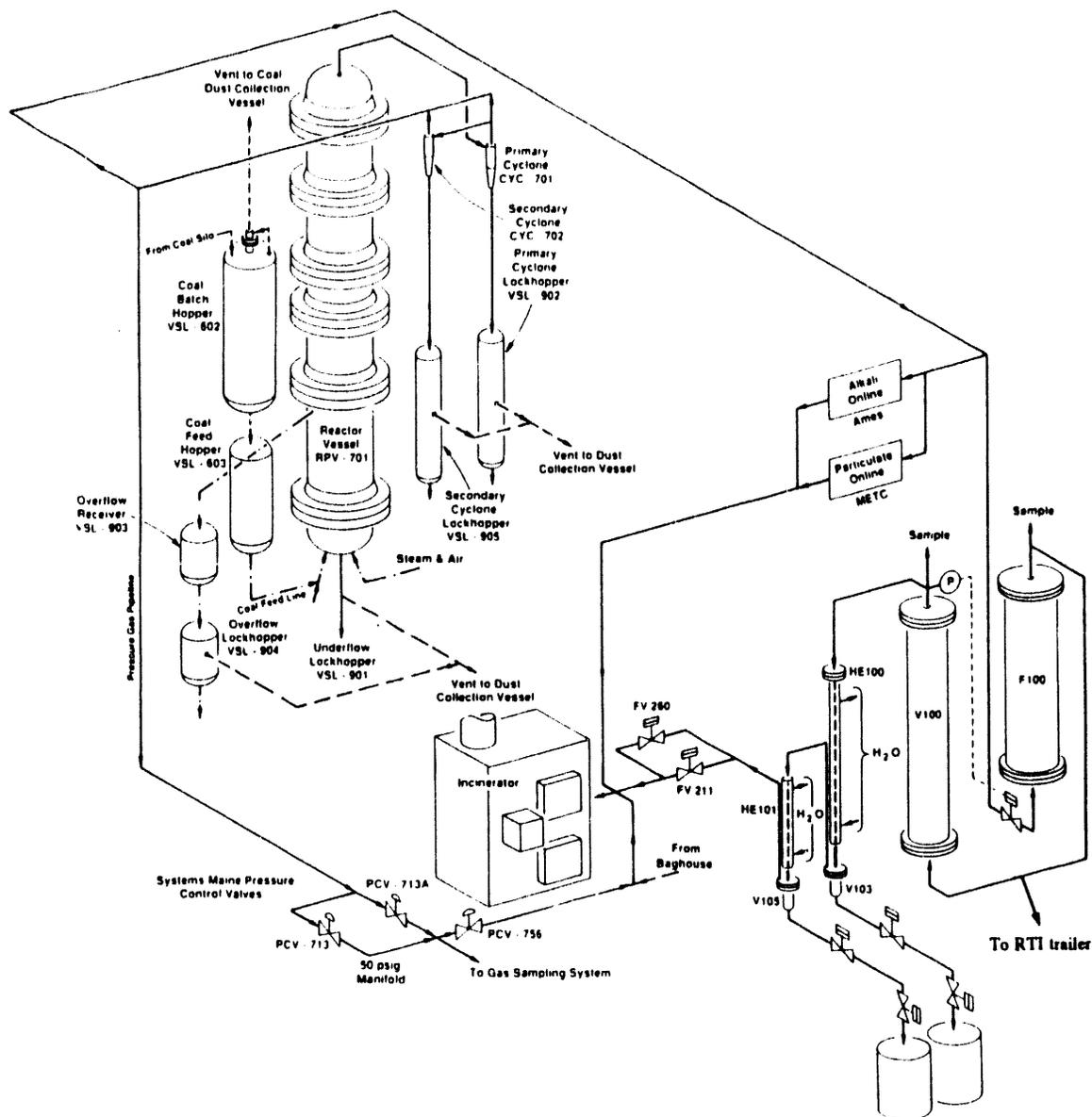
## PROJECT DESCRIPTION

The slipstream testing activities that are the subject of the present project will be conducted in two distinct phases. The first will be at the Morgantown Energy Technology Center (METC), using a slipstream from the 10-in. experimental gasifier directed to the ZTFBD/DSRP system housed in a mobile unit. The second phase will

be design and commissioning of a larger scale DSRP unit that is to be eventually tested at the Enviropower pilot plant employing a 10 MWE (thermal) U-gas gasifier coupled to a ZTFBD system. Enviropower, a subsidiary of Tampella Power Corporation, is commercializing IGCC systems in the United States.

METC operates an air-blown, fluidized-bed, 10-in. dia gasifier capable of providing approximately 300 lb/h—approximately 4,750 standard cubic feet per hour (scfm)—of low-Btu coal gas from a nominal charge rate of 80 lb/h of coal. A simplified vessel and piping layout showing the gasifier, modular gas cleanup rig (MGCR), and the location of the slipstream are provided in Figure 2. Table 1 shows the typical coal gas composition following gasification of a medium-sulfur coal. The raw coal gas is supplied at 538 °C (1,000 °F) and 425 pounds per square inch gage (psig) pressure to downstream cleanup devices. The system includes several particle removal stages that provide the capability to tailor the particle loading to the cleanup section. The cleanup test section consists of a closely coupled MGCR. To supply the ZTFBD and DSRP test apparatus, a coal gas slipstream of approximately 185 scfh (4.3 percent of the gasifier flow) at 538 °C (1,000 °F) and 350 to 400 psig is taken from the MGCR section between the filter vessel and the MGCR sorbent reactor, vessels F100 and V100, respectively. The particulate-free coal gas slipstream is transported through an insulated, heat-traced process line to the RTI ZTFBD/DSRP system.

All of the process equipment, control equipment, and sampling and analysis equipment for field testing at METC is housed in a specially modified office trailer (mobile laboratory). The experimental apparatus is being fabricated, assembled, installed, and commissioned in the lab trailer while it is conveniently located at an RTI site. Provision has been made for a full pressure, full-power checkout of all equipment before relocating the trailer at METC. The system will be pres-



**Figure 2. B-12 Fluidized-Bed Gasifier and Cleanup Rig Simplified Vessel and Piping Layout**

sured up with inert gases, and the electrically heated furnaces, mass flow controllers (MFCs), computer data loggers, flow control valves, and automatic shutdown system can be operated and checked out. All equipment will be leak-tested prior to installing the insulation. In addition, the

toxic gas sensors will be calibrated and the emergency shutdown procedures will be operated.

The fully configured relocatable laboratory will then be transported to the METC site. Only minimal construction on site will be required to

**Table 1. Typical Coal Gas Composition (vol%)**

N <sub>2</sub>	46
H <sub>2</sub>	16
CH <sub>4</sub>	3.8
CO	10.4
CO <sub>2</sub>	12
H <sub>2</sub> O	11.5
H <sub>2</sub> S	0.30

connect electric power, potable water, sewer, cooling water, and the process gases—a slipstream of coal gas, high-pressure nitrogen, high-pressure air, and instrument air. The systems will be checked out, and automatic safety shutdowns and other safety features verified. The continuous runs will be made in coordination with operating campaigns of the METC 10-in. gasifier. Following completion of the test runs, the process and utility lines will be disconnected. The mobile laboratory will then be returned to the RTI site. It can be reinstalled at RTI for additional test programs, or it could be relocated to another site for future additional slipstream testing.

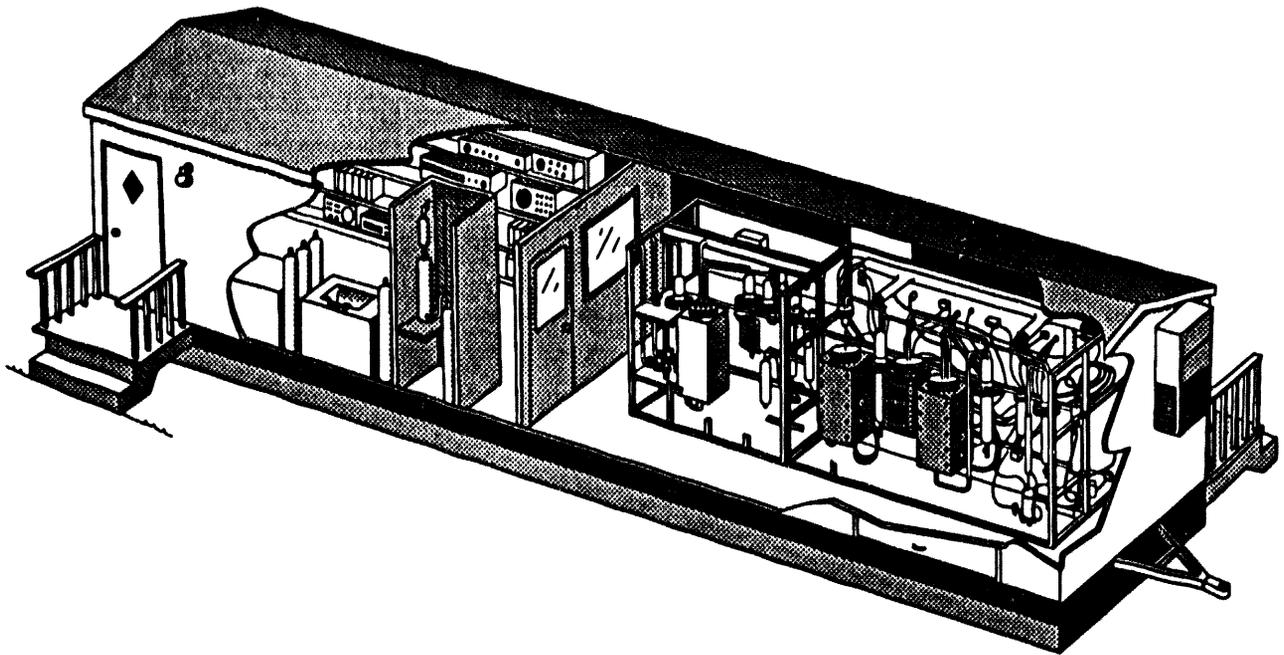
The ZTFBD/DSRP system consists of a newly constructed bench-scale skid-mounted ZTFBD reactor system and a renovated and modified existing skid-mounted bench-scale DSRP reactor system. The bench-scale DSRP unit has been described previously (McMichael and Gangwal, 1990). It is configured for this project with two stages of reaction using a fixed bed of catalyst in each stage, with interstage sulfur condensation and removal. The reactor designs for both the ZTFBD and DSRP reactors are similar. A pipe cylinder, flanged at one end, is capped with a porous alumina plate to act as a gas distributor. This "cage" holds the fluidizable sorbent or fixed-bed catalyst, as appropriate. The cages are inserted vertically into reactor shells made from 4-in.

(nominal) Schedule 160 stainless-steel pipe; the sorbent and catalyst cages are made from 3-in. (nominal) stainless-steel pipe. With the ZTFBD reactor utilizing a 3-in. diameter sorbent cage, the size is more than a two-fold scaleup from that used for much of the previous bench-scale sorbent testing.

The ZTFBD reactor system is integrated with the existing renovated DSRP reactor system, i.e., the regeneration off-gas from the ZTFBD becomes the feed to the DSRP reactor system. Additionally, the DSRP unit can be operated independently of the ZTFBD by using simulated regeneration off-gas—a mixture of nitrogen and (vaporized) liquid SO<sub>2</sub>. In both DSRP modes of operation, the reducing gas required for the process is a slipstream of actual coal gas.

Figure 3 shows the layout of the mobile laboratory built into a 12 ft wide × 50 ft long × 8 ft high (open height inside) modified office trailer. The trailer is partitioned into two rooms, with one room housing the reactor systems and the other acting as the control and instrumentation room. A single door provides access between the rooms. A window in the door and another window in the partition provide visual access to the equipment from the control room. Each room has a separate personnel exit door. In addition, the reactor systems room is equipped with a roll-up door that provided access for installing the shop-fabricated, skid-mounted reactor system units. This door has subsequently been blocked off with a semipermanent closure.

Shelving along one wall of the control room holds the analytical instruments, computer data acquisition system, and toxic gas alarm monitors. On the opposite wall of the control room, a counter with base cabinets provides a sink, a hot water heater, and an eyewash fountain so that simple laboratory procedures can be undertaken. A control panel with automatic controls for the reactor systems is located on the partition wall.



**Figure 3. ZTFBD/DSRP Mobile Laboratory**

Also in the control room section of the trailer is a 3-ft  $\times$  3-ft vented closet to house a liquid  $\text{SO}_2$  supply system.

Special provisions have been made to protect the operating personnel from hazards associated with elevated pressure and temperature, and the use of toxic gases in enclosed spaces. A sophisticated toxic gas monitoring and alarm system has been installed. The design philosophy is that the high-temperature, high-pressure (HTHP) reactor systems will be operated semi-remotely. The equipment is isolated in the equipment room, and operating personnel will normally stay in the control room when the system is operating at elevated temperature and pressure. The gas flow rates can be adjusted from the control room, the modes of operation can be switched, using the remotely actuated valves, and data can be logged from the control room. Only occasional hands-on action is required to turn a valve or to draw liquid

samples of condensate and molten sulfur. Special procedures will be followed on these occasions.

To operate the ZTFBD/DSRP reactor systems remotely, the process units have been equipped with 14 pneumatically operated control valves and shutoff valves. The coal gas feed line from METC is additionally controlled by two pneumatically operated shutoff valves on the exterior of the trailer and interlocked with the RTI control system. The pneumatic valves in the process can be operated with operator intervention from the control panel, or they can be placed in automatic mode where their operation is controlled by a programmable logic controller (PLC). The PLC will shut down part or all of the reactor system process units in response to inputs from the process pressure sensors, oxygen analyzers, flow meters, or emergency. For instance, a drop in system pressure, indicating a significant leak, or a rise in differential pressure across the coal gas

filter, indicating pluggage, will trigger a shutdown and purging of process gases from the system.

The ZTFBD/DSRP system can be operated in four modes of operation shown in Table 2. Actual coal gas is flowing to the trailer at all times during testing. Modes A and B could be considered to be "startup" modes in which only one reactor system is operating, each independent of the other. The fully integrated operation is shown as Mode C and could be considered to be "normal operation," in which the regeneration off-gas from the ZTFBD is used as the feed to the DSRP. Mode D would normally alternate with Mode C so that the DSRP can be operated continuously while the ZTFBD is being sulfided.

**Table 2. Operating Plan**

Mode	ZTFBD		DSRP	
	Sulfidation	Regeneration	Actual Regeneration Off-gas	Simulated Regeneration Off-gas
A	X			
B				X
C		X	X	
D	X			X

The basic plan for the field test is that the DSRP will be operated continuously, 24 hours per day, through a 7-day campaign of the METC gasifier, with additional startup and shutdown periods. Table 3 summarizes the operating conditions that will be used in the continuous field test. The DSRP will be operated with both simulated and actual regeneration off-gas each day. The cycle times for the various modes will be on the order of 1.5 to 3 hours. With this frequent changing of modes, a fair amount of operator attention will be required. It is envisioned that two teams of two operators each will split coverage of each 24-h period.

**Table 3. Field Testing — Range of Operating Conditions**

Desulfurization Reactor	
Pressure:	250 to 350 psig
Sulfidation temperature:	600 °C (1,112 °F)
Regeneration:	Inlet gas temperature = 650 to 725 °C (1,202 to 1,337 °F) Inlet gas O <sub>2</sub> = 1% to 3%
ZT-4 sorbent loading:	1,000 g (50 to 150 µm)
Gas flow rate:	40 to 80
DSRP Reactors	
Pressure:	250 to 350 psig
Stage I:	Temperature = 550 to 650 °C (1,022 to 1,202 °F) Fixed-bed operation Inlet gaseous sulfur = 1 to 3 vol% 600 g catalyst
Stage II:	Temperature = 280 to 320 °C (536 to 608 °F) Fixed-bed operation 600 g catalyst
Flow rate:	40 to 80 slpm

The process control strategy (independent of the remote operator control and automatic shutdown systems) incorporates significant use of automatic controls. In both reactor systems, the pressure is maintained by a pair of self-regulating back-pressure regulators. The hot coal gas flow to the ZTFBD unit during the sulfidation half cycle is regulated by a lab-scale pneumatically operated flow control valve operating at HTHP conditions. In the regeneration mode, the ZTFBD requires a hot nitrogen stream containing 2 percent oxygen as a feed gas. This is accomplished by blending air from compressed gas cylinders with high pressure nitrogen supplied by METC. MFCs are used to meter the flows and the gas is preheated prior to delivery to the reactor.

When the ZTFBD and DSRP are operating in the integrated mode, the DSRP is receiving actual regeneration gas (100 percent of the ZTFBD gas flow) as the feed gas. The flow through the system is controlled by the MFCs supplying the regeneration nitrogen/air mixture. When the DSRP is operating independently of the ZTFBD, using simulated regeneration off-gas, the flow through the DSRP is controlled by the MFC supplying nitrogen to the simulated regeneration off-gas system. In this system, the nitrogen that makes up the bulk of the regeneration off-gas (the "SO<sub>2</sub> carrier" nitrogen) is preheated and a small quantity of liquid SO<sub>2</sub> is mixed with it prior to the first-stage reactor. The liquid SO<sub>2</sub> is pressure-transferred from a reservoir equipped with a dip tube by using a metered quantity of nitrogen flowing into the head space (the "motive" nitrogen).

An innovative scheme has been designed for controlling the flow of coal gas to the DSRP. As with the ZTFBD, the flow is adjusted by a lab-scale control valve operating at HTHP conditions. The valve position is set by a flow ratio controller receiving feedback signals from a continuous analysis of the composition of the exit gas. The goal is to maintain the ratio of H<sub>2</sub>S to SO<sub>2</sub> at 2:1 throughout the DSRP reactor system. Increasing the flow of reducing gas will tend to increase the conversion of SO<sub>2</sub> to elemental sulfur and H<sub>2</sub>S, thus raising the H<sub>2</sub>S:SO<sub>2</sub> ratio. Similarly, decreasing the flow of reducing gas will decrease the conversion, lowering the H<sub>2</sub>S:SO<sub>2</sub> ratio. The ratio controller will adjust the flow of coal gas, in response to changing operation, so that composition ratio is maintained at the set point.

In order to operate this control scheme, continuous analysis of the DSRP exit gas is required. Separate analyzers have been installed in the control room to measure the H<sub>2</sub>S and SO<sub>2</sub> concentrations in the DSRP exit gas. A small sample stream is continuously bled off the process and feeds these instruments. Their electrical output signals go to the flow controller. To

monitor the progress of the zinc titanate sorbent regeneration, and for safety reasons, a trace oxygen analyzer has been installed. Finally, to provide a more detailed understanding of the process operation, additional gas analyses, will be by gas chromatograph (GC). One objective will be a complete sulfur balance around the system so that the conversion efficiency can be tracked during optimum operation.

As the test runs in this project will use actual coal gas, trace contaminants are expected to be present. A scheme has been incorporated in the design of the process equipment and the layout of the mobile laboratory to permit sampling of the process streams for heavy metals, fluoride, chlorides, and ammonia. There are several sampling points located throughout the process to identify the input levels and potentially to identify any sequestering or removal of the trace compounds by the sorbent, the catalyst, or the filters. The heavy metal compounds, As, Be, Cd, Co, Hg, Se, Sb, V, Zn, will be analyzed using a modification of the U.S. Environmental Protection Agency (EPA) Reference Method 29. The chloride and fluoride species will be analyzed from 0.1 N NaOH solution through which the sample has been passed. The ammonia (NH<sub>3</sub>) will be captured in a 1.0 N H<sub>2</sub>SO<sub>4</sub> solution.

## RESULTS/STATUS OF FABRICATION AND CONSTRUCTION

The results so far on the first phase of this project are limited to design and construction of the test apparatus. The period July through December 1993 was occupied with experiment design, process design, equipment design, and procurement issues. The construction permit application for a project at METC was drafted, and the site safety review was held.

Starting in January 1994, the fabrication of the apparatus proceeded in earnest. A new aluminum frame was built for the ZTFBD unit, and the exist-

ing frame for the DSRP was modified so that it could mate with the ZTFBD and be mounted in the trailer. The pressure vessels and the electric furnaces required to heat them were mounted on the frame. The pneumatic valves were located, and process tubing between them was installed. The sample points and connections for analyzer sample tubing were installed.

The trailer was received at RTI's facility in early April. RTI Facilities and Maintenance personnel completed outfitting the unit with shelves, electric service, steps, emergency lighting, and framework to support additional small apparatus. In late April the two equipment skids were moved into the trailer through the large roll-up door provided in the side.

In May, with the two skids installed together, the system process piping was integrated. In addition, all the control and analysis systems were installed in the control room, and tubing and cables routed between the two halves of the trailer. The toxic gas alarm system was installed, as well as the smoke detectors, fire extinguishers, and eyewash fountain. The two vent headers intended to be connected to the METC incinerator and stack were installed, and the exhaust fan was mounted temporarily on the roof of the trailer. May was a period of intense activity with several technicians and construction tradesmen working in the mobile laboratory simultaneously.

In June, the systems are being checked out for mechanical integrity (pressure- and leak-testing) and for operability. The analyzers and GCs are being calibrated and the sample system operation verified. The control panel is being checked out for remote operation of the valves, automatic shutdown features, proper operation of the flow controllers, and correct display of digital data. The heat-trace lines are being tested to verify that proper temperatures can be maintained, and the furnaces are being exercised to verify that the reactors can be held at the desired operating

temperatures. The computer-based data logger is being set up to record key flows, pressures, and temperatures.

## **FUTURE PLANS**

### **Mobile Laboratory Testing at METC**

In the remainder of June 1994, it is anticipated that checkout of the process and control systems at RTI will be completed, and the mobile laboratory can be prepared for transport to METC. An operating permit application will be prepared and submitted to METC for review. Shutdown and pack-up will entail a fair amount of disassembly of sensitive equipment and special packing procedures.

In early July 1994, the packed-up mobile laboratory will be transported to METC. At approximately 20,000 lb gross weight, it is relatively heavy compared to a typical mobile home or office trailer of this size, 12 ft x 50 ft. It will be installed at METC at a spot behind building B-12. METC support personnel will temporarily block it in position, and reconnect the utility lines—electricity, instrument air, potable water, and sewer. In addition, the process lines—hot coal gas, high pressure nitrogen, and process water—will be connected. This is all scheduled to be completed by the end of July, so that the laboratory and experimental apparatus will be available for use in time for the scheduled August 1 gasifier run.

During the August 1994 gasifier campaign, the process apparatus will be checked out with coal gas. Although no specific problems are foreseen, it is not unrealistic to expect that some equipment may need to be modified, or operating strategy modified, in order to achieve a successful extended period continuous run. The time period

of late August to early September is available for repairs and modification.

The extended run of slipstream testing is scheduled to coincide with the mid-September gasifier campaign. When the run is complete, the reactors will be opened and the sorbent and catalyst removed for final analysis. The equipment in the trailer will then be secured for transit. The process and utility lines at METC will be disconnected, and the trailer will be transported back to RTI's facility. In the October to December 1994 time frame, the data analysis will be completed and a topical report will be written.

### Larger Scale DSRP Unit

Work has already begun on the preliminary process design and equipment sizing for the larger scale DSRP unit. The specifics of utility availability, control system interface, and equipment layout are being coordinated with Enviropower. The DSRP slipstream testing by Enviropower is tentatively scheduled for August through December 1995.

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## 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<sub>2</sub>) 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

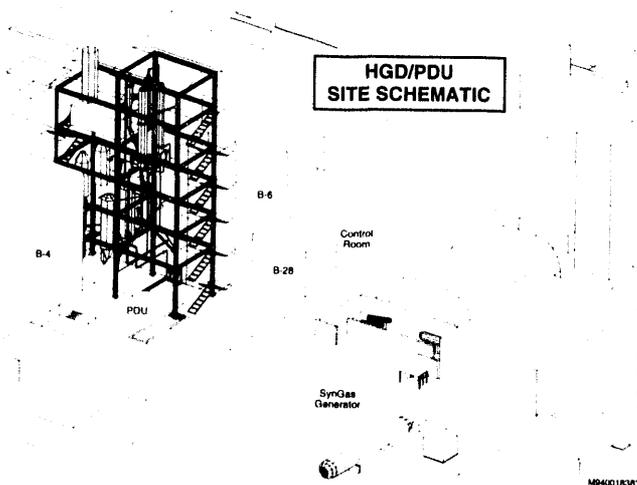
produce a concentrated SO<sub>2</sub> stream during sorbent regeneration.

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<sup>3</sup>/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).

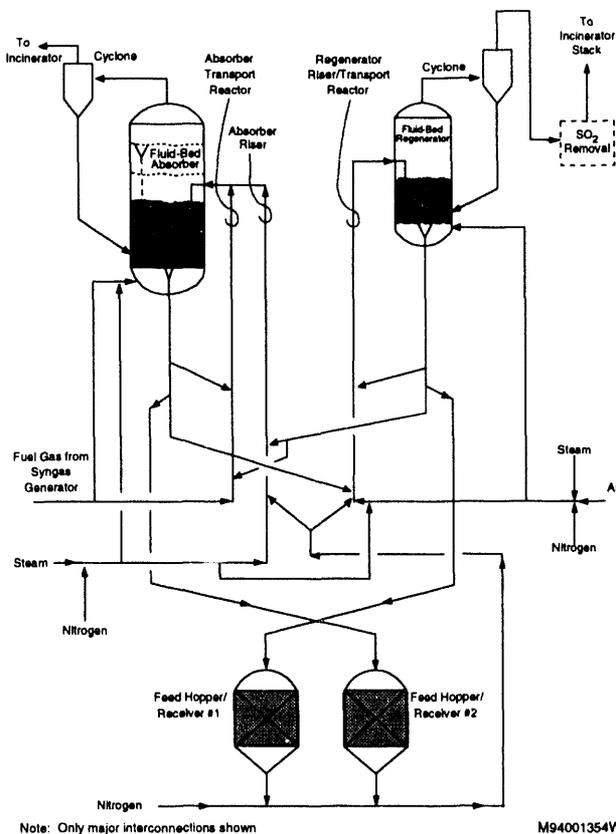


**Figure 1. Isometric View of PDU Site**

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-foot) 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<sup>3</sup> (9 to 12 lb/ft<sup>3</sup>) and 30 to 190 kg/m<sup>3</sup> (2 to 12 lb/ft<sup>3</sup>). 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.

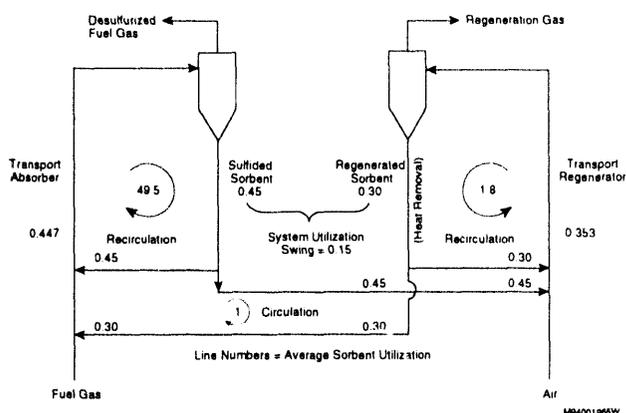
Figure 2 also shows two vessels that can alternately serve as feed hoppers or receivers. These were included in the design so that the sulfidation and regeneration sides can be operated separately (decoupled). This provision was included to aid process development but may not get constructed for budgetary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

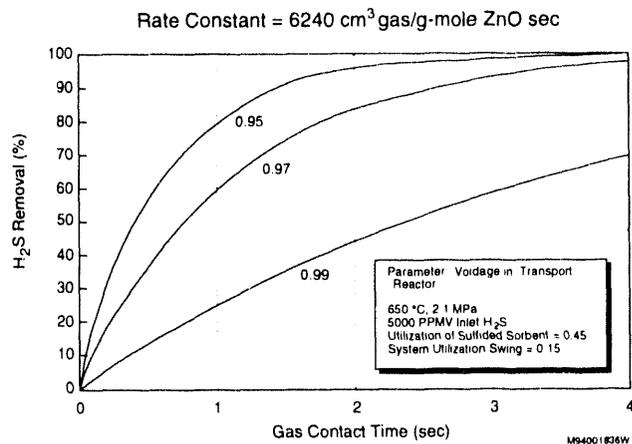
Figure 3 shows that for each time sorbent is circulated from the absorber to the regenerator and back (i.e., one sulfidation-regeneration cycle), it has been recirculated on average about 50 times through the transport absorber, and about 2 times through the transport regenerator. Correspondingly, the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



**Figure 3. Illustrative Schematic of Transport Desulfurization**

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

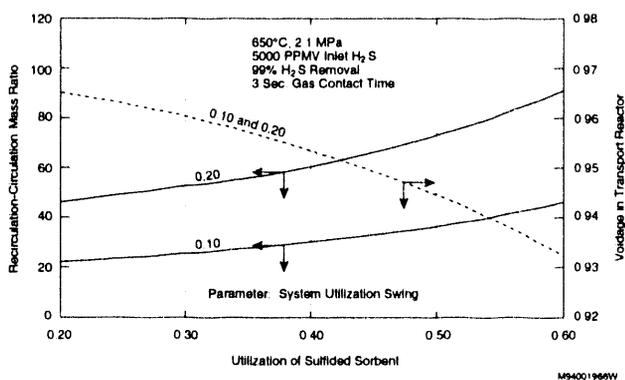


**Figure 4. Illustrative Predicted Performance of Transport Absorber**

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

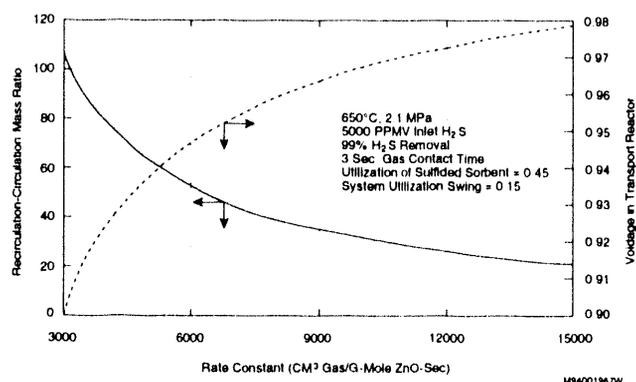


**Figure 5. Illustrative Predicted Trends for Transport Absorber**

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.

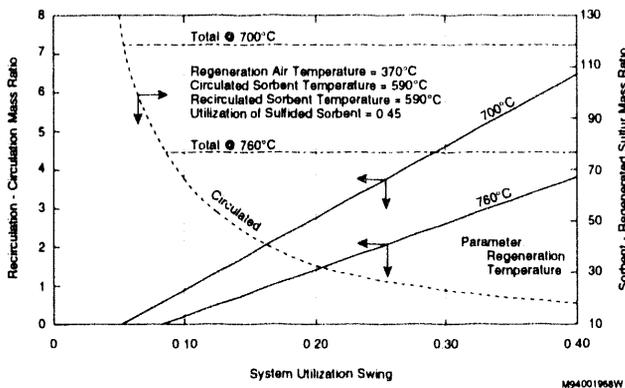
In the absence of relevant kinetic information, comparable illustrations of transport regeneration can not be prepared. Given the likely high rate of reaction, obtaining sufficient regeneration in a transport reactor of reasonable length should not be a problem. However, the possibility of particle overheating may be



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

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  $\text{SO}_2$  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.

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