9a.3   Fluidization Studies Using Phillips Z-SORB Sorbent

CONTRACT INFORMATION

Contract Number	DE-AC21-88MC25006
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Period of Performance	October 1, 1993 to June 30, 1994

Schedule and Milestones

FY94 Program Schedule

	S	O	N	D	J	F	M	A	M	J	J	A
Z-SORB Sorbent Testing		___	___	___								
Data Analysis				___	___	___	___					
Topical Report								___	___			

OBJECTIVES

The objectives of this project are to determine the long-term chemical reactivity and mechanical durability of a fluidized version of Phillips Petroleum Company's (PPCo's) proprietary Z-SORB sorbent for the desulfurization of coal-derived gases in a high-pressure (20 atm) fluidized-bed reactor under simulated U-Gas conditions and at a moderate operating temperature of 538 °C (1,000 °F).

BACKGROUND INFORMATION

Z-SORB sorbent is a regenerable sorbent for hydrogen sulfide. It is based on zinc oxide supported in a porous matrix and contains a nickel

oxide promoter. Originally, it was developed for tail-gas cleanup (Brinkmeyer and Delzer, 1990), but recently it has been tested for removal of hydrogen sulfide from hot simulated fuel gas that is representative of a coal gasification process. For the latter technology, previous fixed-bed sorbents have shown poor mechanical stability due to spalling when absorbing hydrogen sulfide in reducing gas atmospheres or when being regenerated over many cycles (Mei et al., 1993). Recent tests have shown that Z-SORB sorbent had excellent chemical reactivity and mechanical stability for application in fixed-bed reactors (Campbell et al., 1993).

In an ongoing sorbent research and development program, PPCo has developed a fluidized version of the Z-SORB III sorbent that is the subject of investigation in this paper.
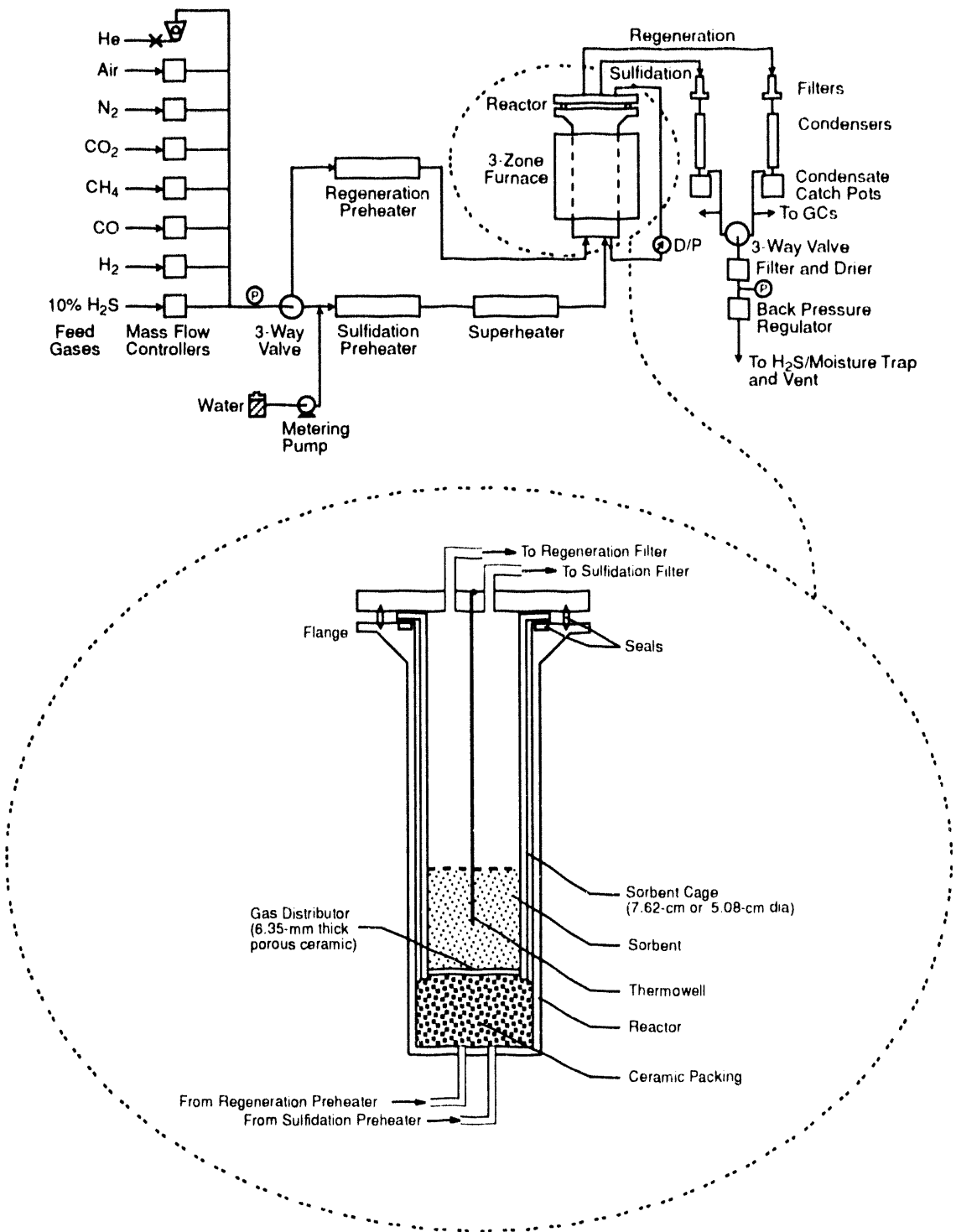
PROJECT DESCRIPTION

Project participants in this study were PPCo and Research Triangle Institute (RTI). This work was part of the project entitled "Enhanced Durability of Desulfurization Sorbents for Fluidized Bed Applications." Sorbents developed for fluidized-bed operation must demonstrate high chemical reactivity, as measured by the rate of sulfur absorption and the sulfur loading capacity, as well as good fluidizing characteristics and mechanical strength characterized by low attrition losses. A fluidized version of PPCo's proprietary Z-SORB III sorbent was prepared by Phillips Research and Development. The sorbent used in this study had an average particle size of 175 μm, a particle size range of 50 to 300 μm and an apparent bulk density of 0.9 to 1.0 g/cc. The sorbent manufacturing process has been demonstrated for 100-lb batch sizes and is believed to be easily scaleable to commercial quantities.

After the initial chemical activity testing at PPCo, the sorbent was provided to RTI for testing

in their bench-scale high-temperature, high-pressure (HTHP) semi-batch fluidized-bed reactor system. The reactor unit, shown in Figure 1, is described in detail elsewhere (Gupta and Gangwal, 1992). From initial thermogravimetric analyzer (TGA) tests, it was evident that this sorbent had high chemical reactivity for sulfur capture at operating temperatures of 482 to 538 °C (900 to 1,000 °F). Consequently, for the 50-cycle (sulfidation and regeneration) long-term testing of this sorbent, an absorption temperature of 538 °C (1,000 °F) was selected. Other test conditions are listed in Table 1, and the composition of simulated air-blown U-gasifier gas is included in Table 2. Testing was done in a 2-in. diameter reactor with 500 g of sorbent. Feed gases entered at the bottom of the reactor vessel and exited at the top. The detailed test procedure is described elsewhere (Gupta and Gangwal, 1993). The sorbent was subjected to alternating periods of sulfidation and regeneration. Sulfidation was accomplished by feeding simulated U-Gas composition produced by mixing of individual metered components upstream of the reactor. For regeneration, air was diluted with nitrogen. Initially, regeneration was initiated at 649 °C (1,200 °F) and 2.5 mol% oxygen in nitrogen.

Online analysis of the exiting gas was performed using a series of gas chromatographs (GCs). Concentrations of sulfurous gases (H_2S, COS, and SO_2) were measured every 5 minutes using a Varian flame photometric detector (FPD), while CO, H_2, N_2, CO_2, O_2, and CH_4 concentrations were measured every 25 minutes using a Carle thermal conductivity detector (TCD). During regeneration, the SO_2 concentration was monitored using a continuous SO_2 analyzer (Model 721AT2 from Western Research).

After 25 cycles of sulfidation (24 cycles of regeneration) the run was stopped, reactor unloaded, and 100 g (20 percent of total inventory) of sorbent was removed from the reactor for analysis and characterization. The

He
Air
N₂
CO₂
CH₄
CO
H₂
10% H₂S

Feed Gases

Mass Flow Controllers

3-Way Valve

Water

Metering Pump

Regeneration Preheater

Sulfidation Preheater

Superheater

Reactor

3-Zone Furnace

Regeneration

Sulfidation

Filters

Condensers

Condensate Catch Pots

To GCs

D/P

3-Way Valve

Filter and Drier

Back Pressure Regulator

To H₂S/Moisture Trap and Vent

To Regeneration Filter
To Sulfidation Filter

Flange

Seals

Gas Distributor
(6.35-mm thick porous ceramic)

Sorbent Cage
(7.62-cm or 5.08-cm dia)

Sorbent

Thermowell

Reactor

Ceramic Packing

From Regeneration Preheater
From Sulfidation Preheater

Figure 1. Bench-Scale Fluidized-Bed Sorbent Test Facility

Table 1. Nominal Test Conditions Used in 50-Cycle Test

Sulfidation

Sorbent	Z SORB III
Temperature	538 °C (1,000 °F)
Pressure	20 atm (294 psia)
Sorbent particle size	100 to 300 µm (d_{50} = 174.3 µm)[a]
Sorbent inventory	500 g (Cycles 1 to 25)[b] 400 g (Cycles 26 to 51)[c]
Total gas flow rate	75 slpm (Cycles 1 to 25) 60 slpm (Cycles 26 to 35) 75 slpm (Cycles 36 to 51)
Sulfidation gas	Simulated U-Gas Gasifier Gas[d]
H_2S content of coal gas	5,000 ppmv (0.5 mol%)
Reactor tube diameter	5.08-cm (2 in.-ID)

Regeneration

Initial temperature	580 to 650 °C (1,076 to 1,200 °F)
Maximum temperature	690 to 780 °C (1,274 to 1,436 °F)
Pressure	20 atm (294 psia)
Gas flow	Same as sulfidation[e]
Regeneration gas	2 to 2.5% O_2 in N_2

[a] d_{50} is the harmonic mean.
[b] Weight of uncalcined sorbent. On heating, sorbent lost 35 g weight due to evolution of 7 percent bound moisture.
[c] Weight of the sorbent in sulfided state containing 12.15 wt% S. The weight of regenerated sorbent would be 375.7 g.
[d] Complete gas composition is specified in Table 2.
[e] The same flow rates were used during regeneration as sulfidation (i.e., 75, 60, 75 slpm).

Table 2. Gas Composition

Component	Vol%
H_2	14.2
H_2S	0.5 (5,000 ppmv)
CO	23.1
CO_2	5.8
N_2	49.8
H_2O	6.6
Total	100.0

had been accumulated on the sorbent. Monitoring of SO_2 in the regenerator off-gas indicated minimum residual sulfate.

RESULTS

The sulfidation runs as indicated in Table 1 were carried out at 20 atm (294 psia) 538 °C (1,000 °F) using 5,000 ppmv (0.5 mol%) H_2S in the feed. The superficial gas velocity of about 9 cm/s was selected based on prior experimental and theoretical information to ensure complete fluidization of the sorbent. This resulted in a superficial gas residence time of 2.38 s based on a slumped bed of density at 72 lb/ft³. Figure 2 shows the hydrogen sulfide breakthrough curves for selected cycles. The sulfur loadings were constant for the first ten cycles with breakthrough (500 ppm H_2S in effluent) occurring in 175 minutes. Estimation of sorbent utilization indicated that nearly 100 percent of the sorbent theoretical loading capacity was utilized over the first 10 cycles. Another interesting feature for this sorbent was its high efficiency for sulfur removal manifested in complete removal of H_2S (to nearly zero ppm) for the first 70 percent of each cycle prior to breakthrough.

During the first 10 cycles, the regenerations were very smooth, completing in about 60 minutes. Typically the regenerations were initiated at

remaining 400 g of sorbent was reloaded to the reactor and regenerated before continuing to Sulfidation Cycles 26 to 50. The test program ended after the 50th sulfidation cycle. The reacted sorbent was subjected to a high-temperature exposure after the normal 50th regeneration cycle in an attempt to determine if excessive sulfates
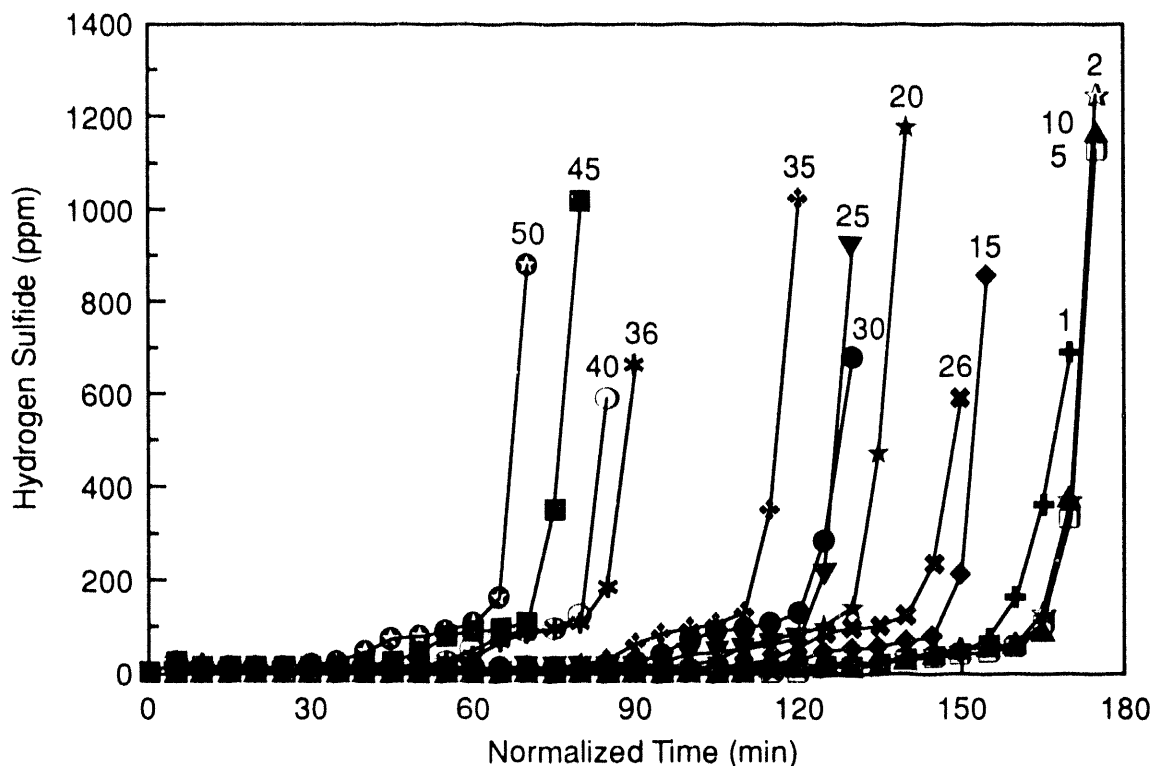
Figure 2. Breakthrough Behavior of Z-SORB III Sorbent U-Gas; 20 atm; 538 °C (1,000 °F)

649 °C (1,200 °F) leading to a peak temperature in the vicinity of 690 °C (1,275 °F). After the first ten cycles of operation, the sorbent suffered, as yet unexplained, exotherms during the start of regenerations resulting in undesired, uncontrolled temperature excursions up to 760 °C (1,400 °F). Breakthrough time declined by 30 percent in the first 25 cycles.

The sulfided sorbent removed from the reactor after 25 cycles was reloaded in the reactor after being stored for about 6 to 7 weeks to complete necessary analyses. The amount of sorbent reloaded was 20 percent less than the initial start-of-the-run loading; therefore, the feed gas flow rate was reduced by 20 percent for cycles 26 to 35, i.e., from 75.0 to 60.0 slpm to maintain the same gas residence time. The initial regeneration (No. 25) was successful and the sorbent reactivity in the 26th cycle was actually higher than what was observed prior to reactor unloading. After the

next several cycles of operation, it became evident that the gas flow rate of 60 slpm was not quite enough to achieve a good quality fluidization of the sorbent; therefore, starting at Cycle 36 the gas flow rate was restored to 75 slpm. This change resulted in more smooth cycling.

The breakthrough curves presented in Figure 2 exhibit the sorbent performance for the entire test. It is quite noteworthy that the sorbent performance remained quite high after 50 cycles of operation. The sulfur capacities of the sorbent during Cycles 1 and 50 were 20.16 and 9.98 g S/100 g of sorbent, respectively, indicating about a 50 percent capacity utilization even after 50 cycles. In Figure 3, the sulfur capacity (g of S pickup per 100 g of sorbent) is plotted as a function of cycle number. Sulfur capacity is calculated using the concentration of H_2S in feed, breakthrough time of 500 ppmv H_2S in the effluent and the amount of sorbent used. Actual sulfur chemical analyses
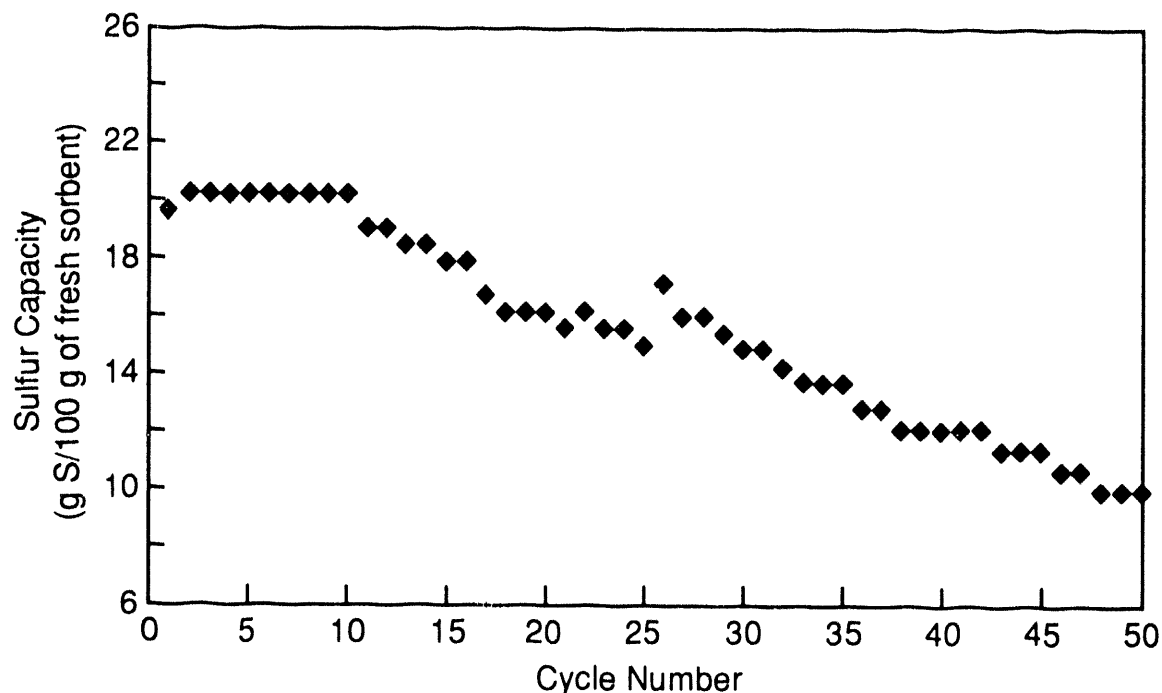
Figure 3. Sulfur Capacity of Z-SORB III Sorbent U-Gas; 538 °C (1,000 °F); 20 atm; 500 ppm Breakthrough.

after 25 and 50 cycles closely corroborated the calculated sulfur capacity.

As mentioned previously, the sorbent for the desulfurization application must have high chemical reactivity. The chemical reactivity is measured by the total sulfur loading capacity as well as the rate of sulfur absorption. In order to measure the latter, standard 1.5-cycle TGA reactivity tests described in Gupta and Gangwal (1992) were carried out for fresh and 25- and 50-cycle reacted sorbents. Figure 4 depicts both the saturation (indicated by the maximum weight gain during the second cycle) and the rate of sulfur pickup (indicated by the slope of the sulfidation curve). While this figure shows that saturation sulfur pickup decreases with increasing number of cycles as expected and observed for conventional desulfurization sorbents, it is important to note that the rate of sulfur pickup for 25- and 50-cycle reacted sorbent remained relatively constant even though the capacity had dropped.

Other notable findings of this test were that in the fluidized-bed reactor there was no evidence of the absorption exotherm that was previously observed in the fixed-bed reactor tests conducted at METC (Campbell et al., 1993) and attributed to methanation reaction promoted by nickel present in Z-SORB sorbent. GC analysis of the absorption effluent gas did indicate an occurrence of water gas shift reaction leading to higher concentration of hydrogen.

Sorbent Loss from the Reactor

The net sorbent loss during the entire 50 cycles was 0.5 percent of the original charge based on the weights of sorbent removed from the reactor and the material deposited on filters and lines. This is indicative of low attrition and high mechanical stability of Z-SORB sorbent. The total sorbent loss from the reactor itself was 2.5 percent.
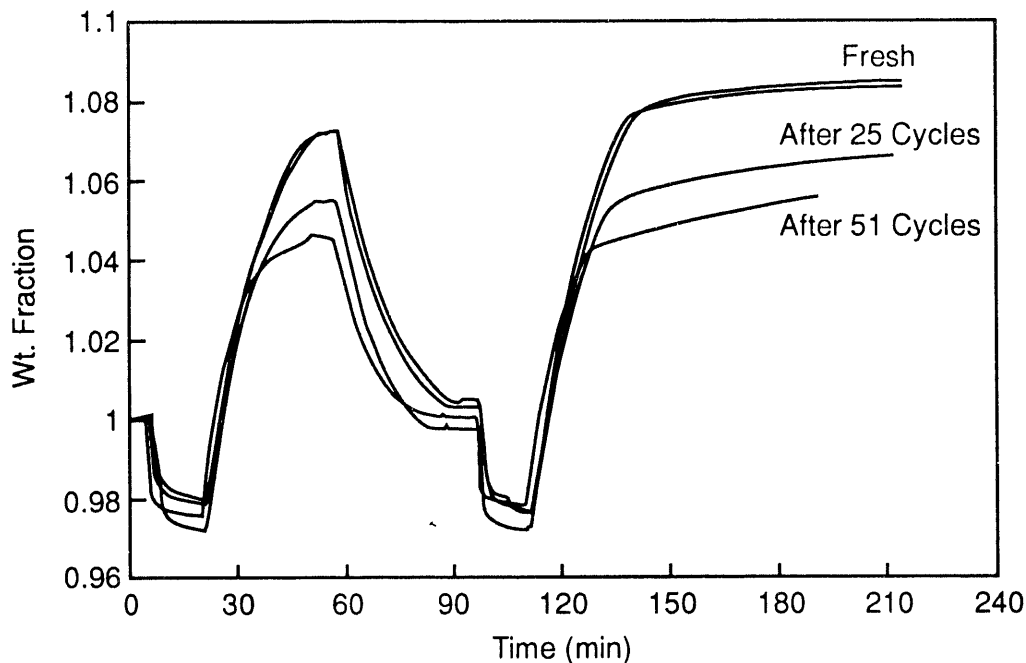
Figure 4. TGA Reactivity of Fresh and Reacted Z-SORB Sorbent

Selected Physical Properties of Fresh and Reacted Sorbents

Selected physical properties of the fresh and reacted sorbents were measured and are presented in Table 3. The average particle size of the sulfided sorbent after 25 and 50 sulfidations remained essentially the same within experimental error. These results corroborate the relatively small sorbent loss observed from the reactor, indicating good mechanical stability of the sorbent. The compacted bulk density of Z-SORB sorbent (66.5 lb/ft^3) increased about 8 percent after 25 cycles of operation, but then it remained essentially the same through the 50 cycles. This indicates that sorbent undergoes some sintering/ shrinking at the beginning, but then the density does not change further and remains relatively constant through the life-cycle test. Attrition tests performed in RTI's 3-hole airjet attrition tester indicated that the attrition resistance of the 25-cycle sulfided sorbent was lower than the fresh material. However, very little change in the attri-

Table 3. Physical Properties of Fresh and Spent Sorbent

	Fresh	After 25th sulfidation	After 51st sulfidation
Average particle size (μm)	174.3	170.8	173.7
Compacted bulk density (lb/ft^3)	66.54	72.12	72.58

tion resistance was found between the 25-cycle sulfided and 51-cycle sulfided materials. It is realized that attrition data from an actual reactor environment is preferable to simulation using a 3-hole attrition test.

CONCLUSIONS

The 50-cycle data show that the fluidizable Z-SORB sorbent has high chemical reactivity and

mechanical durability for hot-gas desulfurization at 538 °C (1,000 °F). Z-SORB sorbent has very high efficiency for H_2S removal to essentially zero levels for a major portion of absorption cycle and a nearly constant rate of sulfur absorption whether fresh or reacted. The sulfur capacity of the sorbent at breakthrough (500 ppm H_2S in the reactor effluent) was 20.16 g S/100 g sorbent in Cycle 1 and 9.98 g S/100 g sorbent in Cycle 50. This sorbent can be easily regenerated at 649 to 704 °C (1,200 to 1,300 °F) with little evidence of sulfate accumulation. During the 50-cycle test only small changes were observed for such important sorbent physical properties as bulk density and particle size. Delineation of the capacity declines observed following Cycle 10 suggests additional research in this area. Definition of the required experiments is currently under assessment.

ACKNOWLEDGMENTS

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9a.4 **Desulfurization Sorbent Development at the Morgantown Energy Technology Center**

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OBJECTIVES

The overall objective of this project is to develop regenerable sorbents for hot gas desulfurization in IGCC systems. The major criteria for the development of novel sorbents included reasonable chemical reactivity and physical durability during repeated sulfidation and regeneration cycles.

BACKGROUND

Various formulations of zinc ferrite and zinc titanate in the form of extrudates and spherical pellets have been studied at the Morgantown Energy Technology Center (METC) for removal of sulfurous gases from coal gasification gas streams (Mei et al. 1993). Problems of decrepitation and spalling have occurred after sulfidation and regeneration of these sorbents. Z-Sorb, a proprietary sorbent developed at Phillips Petroleum Company, showed good physical durability during testing at METC, but there was a continuous decrease in reactivity during multiple cycle tests due to steam regeneration (Delzer et al. 1993). A series of novel sorbents containing zinc oxide have been developed at METC to address these problems. These METC-developed sorbents showed superior performance during a 20-cycle,

high-pressure, fixed-bed test with steam regeneration conducted at METC.

PROJECT DESCRIPTION

Nine sorbents (METC1 through METC9) were prepared, but only some of these sorbents were selected for initial testing. The remaining sorbents will be tested in the future. Two of these sorbents (METC2 and METC6) have been tested both in the low-pressure and the high-pressure reactors. Results of the high-pressure testing of METC2 and METC6 and low-pressure testing of METC7 will be discussed in this paper. METC2 and METC7 were designed for fixed-bed or moving-bed applications, while METC6 was designed for fluid-bed applications. However, these three sorbents were tested in a fixed bed. Twenty (20) cycles of sulfidation reactions were completed for METC2 and 15 sulfidation cycles were completed for METC6 in the high-pressure reactor. Five sulfidations were completed with METC7 in the low-pressure reactor.

Sorbents were prepared at METC by a solid-state mixing method utilizing a mixer pelletizer. The sorbents contained about 50 wt% of zinc oxide. The sorbents were initially tested in a low-pressure (272 kPa/39.7 psia) reactor. This quartz reactor had a diameter of 5.7 cm

(2.2 inches) and a bed height of 15.2 cm (6 inches). Sorbents that showed promising results in the low-pressure unit were then tested in the high-pressure, bench-scale, hot gas desulfurization unit at 1034 kPa/150 psia, which contains a 5.5-cm (2.2-inch) inner diameter reactor system. The reactor is constructed of Incoloy 800HT alloy steel shell. Inside the shell there is a removable 316 stainless steel cage for easy loading and unloading of the sorbent. The sorbent cage is suspended from the top flange of the reactor shell. A gas distributor is fixed at the bottom of the cage to support the sorbent. The inside of the sorbent cage is Alon-processed to prevent corrosion of stainless steel by sulfur gases in the presence of steam. The reactor is housed inside a three-zone furnace equipped with separate temperature controllers for each zone. Quartz wool was installed on top of the sorbent bed to hold the sorbent as well as to capture particulates from the fixed bed for upflow operation. The details of this system are reported by Mei et al. (1993).

A 40.7-cm (16-inch) deep fixed bed of sorbent was subjected to alternating periods of sulfidation and regeneration. Sulfidation was accomplished by feeding a gas, which simulated the expected KRW fuel gas composition, in a downflow mode through the reactor at 538 °C (1000 °F). The sorbent regeneration was performed in the reverse direction (upflow), utilizing air diluted with nitrogen or nitrogen and steam in order to limit the regeneration exotherm and prevent overheating of the sorbent.

RESULTS

High-Pressure Testing

All the sulfidations in the high-pressure reactor were performed at 538 °C (1000 °F) and 1034 kPa (150 psia), utilizing a feed gas containing 800 ppmv hydrogen sulfide (H_2S). The

superficial velocity for all sulfidations in the high-pressure reactor was maintained at 0.3 m/s (1.0 ft/s) and the space velocity was 1363 hr^{-1}. The outlet H_2S concentration was monitored using detector tubes and gas chromatography.

All regenerations in the high-pressure reactor were done at 170 kPa (24.7 psia), and the gas velocity was maintained constant at 0.3 m/s (1.0 ft/s). All dry regenerations were performed utilizing a multi-stage technique. With nitrogen as a diluent gas, the oxygen concentration was increased in discrete increments from 0.5 mole % to 21 mole %, while simultaneously increasing the bed temperature from 538 to 760 °C (1000 to 1400 °F). The exit gas was monitored for sulfur dioxide (SO_2) using detector tubes and gas chromatography. All regenerations were performed until the SO_2 concentration dropped to less than 50 ppmv.
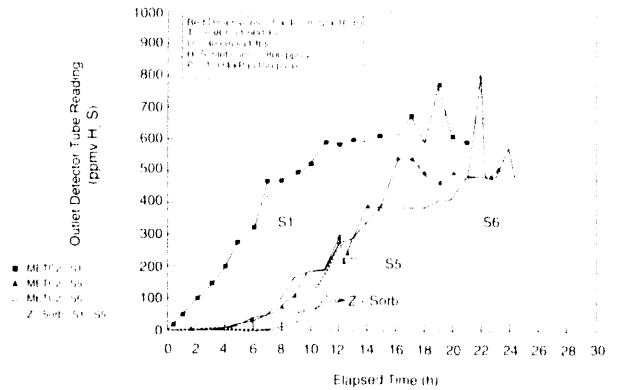
Steam regeneration was conducted in four stages. The temperatures of the four stages were 538, 579, 621, 663 °C (1000, 1075, 1150, and 1225 °F). The steam concentration in all four stages was 50% with a varying concentration of oxygen and nitrogen. The oxygen concentration during the four stages was 0.5, 2.5, 4.0, and 7.0 % respectively.

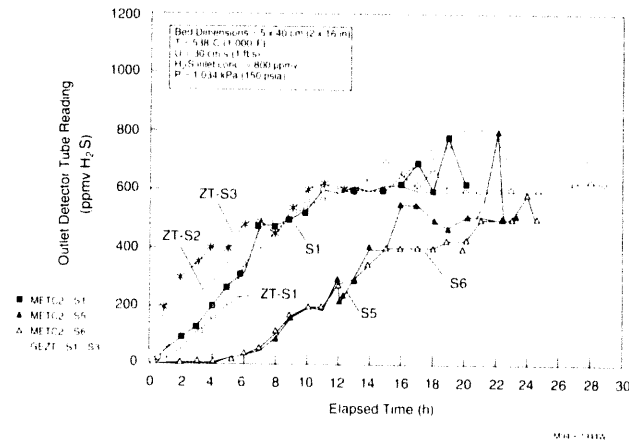### Results of the METC2 Testing in the High-Pressure Unit

The results of the six sulfidation runs for METC2 performed utilizing dry regeneration in the high-pressure reactor are shown in Figure 1. There was a continuous increase in the sorbent sulfur capacity from sulfidation cycle 1 to cycle 5, after which the capacity stabilized. A comparison of the sulfidation breakthrough curves for METC2 and for a molybdenum-containing zinc titanate from General Electric Company tested under identical conditions is shown in Figure 2. For zinc titanate, there was a decrease in the sulfur capacity up to the third
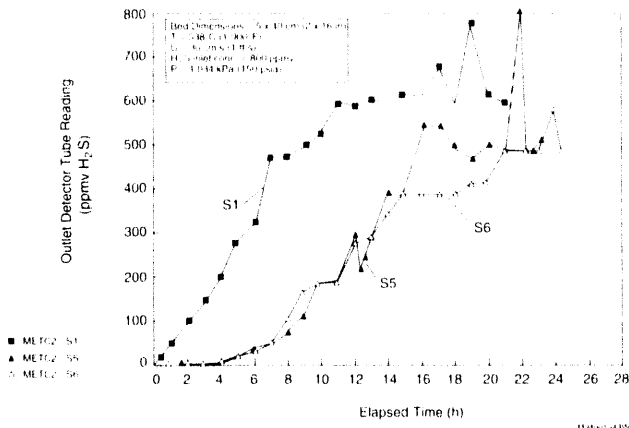
Figure 1. METC2 Sorbent Sulfidations 1 Through 6

Figure 2. Sulfidations of METC2 Sorbent and GE Zinc Titanate

Figure 3. Sulfidations of METC2 Sorbent and Z-Sorb from Phillips Petroleum

cycle, and the sorbent stabilized after the third cycle. The sulfur capacity of METC2 after it stabilized at cycle 5 was significantly better than that of the zinc titanate. A comparison of the sulfidation breakthrough curves for METC2 and Z-Sorb from Phillips Petroleum are shown in Figure 3. The sulfur capacity for METC2 after it stabilized at the fifth cycle is comparable to that of Z-Sorb.

In order to understand how steam regeneration would affect the performance of the METC2 sorbent, regenerations during cycles 6

through 19 were conducted utilizing steam. The sulfidation breakthrough curves from sulfidations 7 through 20 (which all follow steam regenerations) are shown in Figure 4. There was a slight decrease in the sulfur capacity between the sixth (last sulfidation following dry regeneration) and seventh sulfidation (first sulfidation following steam regeneration). However, the breakthrough curves for sulfidations 7 to 11 overlapped,
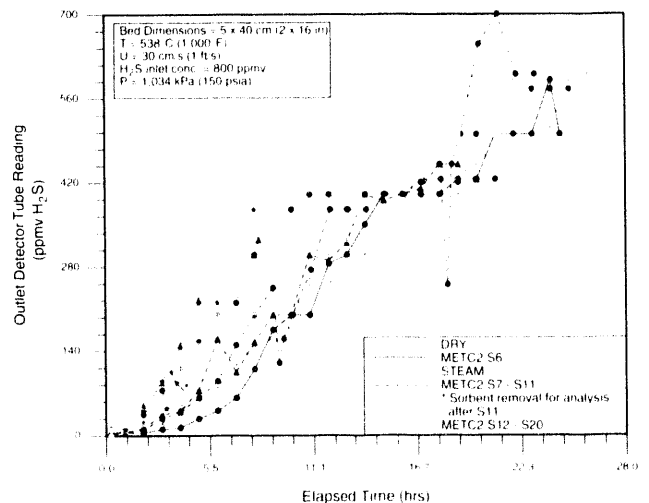
Figure 4. Effect of Steam Regeneration on on METC2 Sorbent During 20-Cycle Testing

indicating that the steam regeneration did not affect the sorbent.

After the eleventh sulfidation some of the sorbent was removed from the reactor for total sulfur analysis. The decrease in breakthrough time between sulfidations 11 and 12 is due to the removal of this material from the sorbent bed. The sulfidation breakthrough curves from cycles 12 to 20, which also follow steam regenerations, overlapped as well, indicating that the sorbent was stable during steam regeneration. The percent total sulfur content from the solid analysis of the sorbent after the 20th cycle was similar to that after the 11th cycle. This further confirmed that the decrease in sulfur capacity during the 11th and 12th cycles was due to the sorbent removal. There was no change observed in the sulfur absorption capacity caused by the steam regenerations in the 7th through 20th sulfidation cycles.

The visual examination of the sorbent after 20 sulfidations indicated that there was no spalling or any other physical deterioration of the sorbent. The crush strength of the sorbent after 20 cycles was higher than that of the fresh sample. Sieve analysis indicated that 92% of the material was unaffected after 20 cycles. This is even after dropping the sorbent in from the top of the reactor during the initial loading and utilizing a vacuum cleaner for sorbent removal from the bed. All of the condensates collected during the 20-cycle test were very clear, indicating that the sorbent did not decrepitate in the bed and that there was no powder lost from the sorbent as observed with zinc ferrite or zinc titanate. The zinc content detected in the condensates was negligible. The METC2 sorbent showed a superior level of performance during the 20-cycle, high-pressure, fixed-bed testing. It is spalling resistant, steam resistant, and had both excellent chemical and physical durability during the 20-cycle test.

Results of METC6 Testing in the High-Pressure Unit

The chemical formulation of METC6 was designed for fluid-bed applications, but the pellets were sized for the testing which was conducted in a fixed bed. Fifteen (15) sulfidation cycles were completed with METC6 in the high-pressure unit utilizing steam regeneration. This test series will be continued for up to a total of 20 sulfidation cycles. The sulfidation breakthrough curves of METC6 are shown in Figure 5. There was an increase in sorbent sulfur capacity between sulfidations 1 and 2, but the capacity decreased again at the third sulfidation cycle. The sulfidation breakthrough curves from the 3rd to 15th cycle overlapped, with a slight decline seen in cycles 14 and 15. This indicates that the sorbent was chemically stable during the 15 cycles of testing and was not affected adversely by the steam regeneration. The condensates collected from the reactor during this test series were very clear. Even though METC6 was formulated for fluid-bed applications, it performed very well with the bigger particle sizes required in fixed-bed testing.
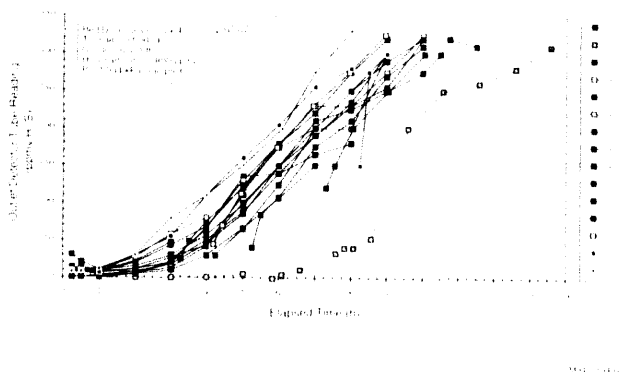
Figure 5. Sulfidations of METC6 Utilizing Steam Regeneration

Results of the METC7 Testing in the Low-Pressure Unit

All of the sulfidations in the low-pressure reactor were performed at 538 °C (1000 °F) and 260 kPa (38 psia), utilizing a feed gas containing 2000 ppmv H_2S. The superficial velocity for all sulfidations in the low-pressure reactor was maintained at 0.09 m/s (0.30 ft/s) and the space velocity was 2000 h^{-1}. The outlet H_2S concentration was monitored using detector tubes and gas chromatography.

All regenerations in the low-pressure reactor were done at 272 kPa (39.7 psia) and the gas velocity was maintained constant during each stage at 0.04 to 0.05 m/s (0.13 to 0.15 ft/s). The steam regenerations were conducted in three stages. The temperatures of the stages were 538, 593, and 649 °C (1000, 1100, and 1200 °F). The steam concentration in all three stages was 50%, with a varying concentration of oxygen and nitrogen. The oxygen concentrations during the three stages were 1.0, 2.5, and 3.5%, respectively.

The sulfidation breakthrough curves of METC7 in the low pressure unit are shown in Figure 6. There was an increase in sulfur capacity from sulfidation 1 to 2, but the sulfur capacity decreased in the third sulfidation. The sulfidation breakthrough curves overlapped after the third sulfidation, indicating sorbent stabilization at that point. As shown in Figure 6, the outlet hydrogen sulfide concentration was zero for about 15 hours, indicating that the efficiency of the sorbent was excellent. A comparison of METC6 and METC7 tested in the low-pressure unit is shown in Figure 7. It is clear that the sulfur capacity of METC7 is better than that of METC6. Since METC7 was the fixed-bed version of METC6, it was expected to have a better capacity in fixed-bed testing. Visual examination of the METC7 sorbent after the fifth cycle

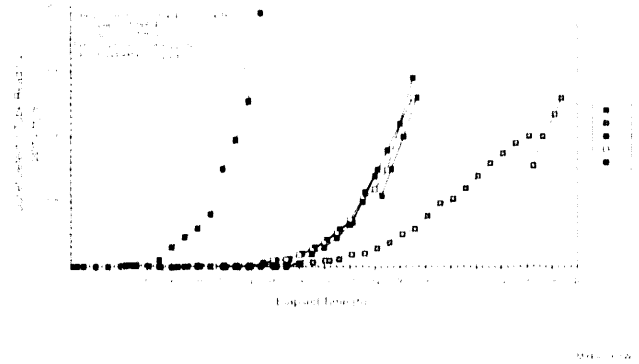
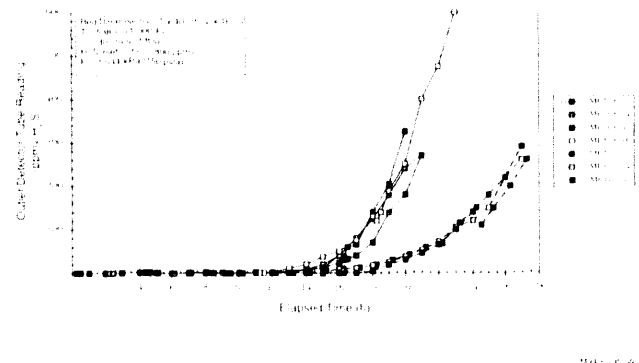**Figure 6. Sulfidations of METC7 Utilizing Steam Regeneration**

Figure 7. Sulfidations of METC6 and METC7

indicated that there was no spalling or any other signs of physical deterioration during the testing.

FUTURE WORK

1. The testing of METC6 in the high-pressure reactor will be continued for a total of 20 cycles.

2. METC2 will be tested using actual coal gas as the feed gas.

3. Other METC formulations will be tested in the thermogravimetric analysis (TGA) and in the low-pressure unit in order to optimize the formulations.

4. The sorbents will be tested in other types of reactors, such as a fluid-bed, moving-bed, or transport reactor.

5. A Cooperative Research and Development Agreement (CRADA) will be initiated.

6. The optimum sorbent may be tested in a Clean Coal Technology demonstration plant.

ACKNOWLEDGMENTS

REFERENCES

Mei, J.S., L.D. Gasper-Galvin, C.E. Everitt, and S. Katta. 1993. Fixed-Bed Testing of a Molybdenum-Promoted Zinc Titanate Sorbent for Hot Gas Desulfurization. In *Proceedings of the Coal-Fired Power Systems 93 -- Advances in IGCC and PPBC Review Meeting*, 315-325. DOE/METC-93/6131. NTIS/DE93000289. Springfield, Va.: National Technical Information Service.

Delzer, G.A., G.P. Khare, and G.J. Greenwood. 1993. *Z-Sorb Absorbent for Hot Gas Desulfurization.* AIChE Annual Meeting, St. Louis, Missouri. Symposium on Gas Purification, Paper No. 130f.

9a.5   Stabilization of Spent Calcium-Based Sorbent

CONTRACT INFORMATION

Contract Number	DE-AC21-91MC27233
Contractor	The M.W. Kellogg Company P.O.Box 4557 Houston, TX 77210-4557 (713) 753-3861
Contractor Project Manager	Philip J. Shires
Principal Investigators	Satyan Katta Gunnar B. Henningsen
METC Project Manager	Thomas P. Dorchak
Period of Performance	June 03, 1991 to October 03, 1994

OBJECTIVES

The overall objective of this project is to obtain experimental data on the reactions of calcium-based sorbents applicable to both air-blown coal gasification systems and second generation fluid bed coal combustion systems (partial gasification). The project is a 40-month effort. A key technical issue for the utilization of calcium sorbents in advanced coal technologies is the subsequent stabilization of the solid wastes (calcium sulfide/ash) produced by such systems.

More specifically, the project objectives are to:

- develop data on the kinetics of in-situ desulfurization reactions (Task 3);

- study the effect of calcium on the kinetics of carbon conversion rate (Task 4);

- study kinetics of oxidation of CaS to $CaSO_4$ and absorption of SO_2 (Task 5);

- develop and identify viable techniques to stabilize CaS;

- carry out further development work on most promising method for stabilization; and

- determine the commercial viability of calcium sulfide stabilization (Task 6).

BACKGROUND INFORMATION

A number of studies reported a catalytic effect on carbon conversion in the presence of calcium with attendant benefits in lowering capital and operating costs. Additionally, a number of researchers have demonstrated the feasibility of in-situ desulfurization using calcium-based sorbents in fluidized-bed and transport gasifiers

involving combustion or gasification operating at elevated pressures, thereby eliminating the need for conventional external desulfurization to control sulfur emissions. However, much of the previous experimental work on in-situ desulfurization research was performed at atmospheric pressure in contrast to the expected higher operating pressures of the advanced pressurized coal conversion processes.

The benefits to be derived from the utilization of in-situ calcium-based sorbents have led to a requirement for new approaches to solid waste disposal, LASHs and DASHs, (mixtures of coal ash with limestone and dolomite, respectively) due to incomplete conversion of CaS to environmentally acceptable $CaSO_4$. In addition, the solids need to absorb SO_2 in a sulfator/combustor. Prior studies have not produced a viable technique to minimize the reactive CaS in the solids without undesirable concurrent SO_2 evolution. Abbreviations and acronyms are defined at the end of the paper.

PROJECT DESCRIPTION

The project is a 40-month effort to investigate the complex influence of calcium-based sorbents on coal conversion. The work is broken into six tasks. Task 1 and Task 2 deal mostly with project related activities and preparation of test equipment. The experimental part of the project is separated into three separate tasks: Task 3 - studies on sulfidation of calcium-based sorbents, Task 4 - studies to obtain kinetic information and understand the mechanisms of calcium-catalyzed carbon gasification reactions, and Task 5 - studies on oxidation of CaS to $CaSO_4$ in order to identify and investigate different methods to oxidize the sulfide and to further develop a promising method. Task 6 is the economic evaluation of the most promising sulfation technique developed under this program.

EXPERIMENTAL

Description of Bench-Scale Reactor Unit (BRU)

The Bench-scale Reactor Unit (BRU), which is used primarily for sulfation studies, consists of a 2-inch I.D. reactor. Details of the BRU construction and the experimental procedures were described in a previous DOE paper[1]. Experimental conditions used in the BRU are given in Table 1.

Table 1. Experimental-BRU

Particle size	149 to 1000 μm
Distribution	for LASHs and DASHs
	53 to 177 μm for TRTU LASH
	105 to 210 μm for ground solids
Gas comp.	air
Temperature	1500-1700°F
Pressure	atmospheric

An online analyzer is provided for monitoring of SO_2 in the effluent gas of the BRU

Description of Quartz Reactor

The experimental apparatus for gas absorption studies consists of a horizontal quartz reactor containing a fixed bed (1.65-inch I.D. and 15-inch long), with a quartz fritted disc for gas distribution, that is contained in an electrical furnace. The length of the bed generally ranged from 10 to 12 inches. The wall temperature was monitored near the inlet, the middle, and the outlet locations of the bed. There is provision to measure the concentration of H_2S or SO_2 by means of Draeger tubes before the gas enters the bubblers. All the gas absorption experiments were done at atmospheric pressure.

If maldistribution of gas occurs during a test, the test is repeated, and only the results of the final test are considered. Experimental conditions used in the quartz reactor are given in Table 2.

Table 2. Experimental–Quartz Reactor

Particle size   177 to 1000 μm for pure sorbents
149 to 1000 μm for LASHs and DASHs
Gas comp.   1.5% SO_2, 3% O_2, balance N_2
Linear vel. at
temperature   0.43 ft/s
Temperature   1600°F
Pressure   atmospheric

Description of ATGA

An atmospheric thermogravimetric analyzer (ATGA) was used to study the fundamental kinetics of oxidation of LASH at 1700°F in air. It consists of a DuPont 951 thermobalance, a DuPont 9000 console for controlling the heating rate and run time, a data acquisition system, and a personal computer for data storage, retrieval and analysis. Samples are placed in a platinum-mesh screen basket and suspended from the balance arm.

Description of PTGA

A pressurized thermogravimetric analyzer (PTGA), Cahn model TG-151 instrument, was used to study the CaO-SO_2-O_2 reaction producing $CaSO_4$. The PTGA is furnished with a sophisticated computerized data acquisition and control system. The PTGA is capable of operation to temperatures of 2012°F and 1832°F at ambient

pressure and a pressure of 1000 psi, respectively. The experimental conditions used on the PTGA are given in Table 3.

Table 3. Experimental–PTGA

Particle size   707 to 1000 μm
Gas comp.   1.5% SO_2, 3% O_2, balance N_2
Gas flowrate   2.0 liter/min
Operating temp.   1600°F
Pressure   atmospheric

RESULTS

Summary and Conclusions

The results obtained on LASH oxidation in atmospheric pressure air at a temperature of 1700°F for a one hour residence time in the BRU fluidized bed can be summarized as follows:

- Higher sulfide conversions were obtained with KRW LASH compared to FW and TRTU LASHs. This may be attributed to the dolomitic limestone used in producing the KRW LASH.

- For the LASHs studied, the sulfide conversions ranged from about 22% to 80%. With alkali impregnation, the sulfide conversions increased to 90 to 95%.

- Slightly higher conversions were obtained for heavily-sulfided KRW LASHs than lightly sulfided KRW LASHs. Residual sulfide levels depend upon initial sulfide concentration.

- With Tampella and FW DASHs, 100% and 93% sulfide conversions were

achieved showing the advantage of using a dolomite over a limestone.

Fundamental kinetic studies conducted on the ATGA show:

- After about 20 to 50% sulfide conversion is achieved, the sulfide oxidation rate slows down substantially, possibly due to diffusional resistance in the $CaSO_4$ layer.

The results from the SO_2 absorption studies in the quartz reactor and the PTGA can be summarized as follows:

- The absorption of SO_2 in the presence of O_2 by pure sorbents was very good with breakthrough periods (outlet SO_2 concentrations of 100 ppm) of up to 12 hours.

- The absorption of SO_2 by pure limestones in the absence of O_2 was poor, possibly due to the absence of a stable product.

- The absorption of SO_2 by lightly-sulfided as well as heavily-sulfided Sierra Pacific and Greer limestones, and Plum Run dolomite was very good after exposing the sorbents to 10-21% O_2 for a period of time sufficient for the conversion of any CaS to $CaSO_4$ or after they were previously oxidized in a separate step.

- The absorption of SO_2 by KRW LASH, and KRW and Tampella DASHs was very poor. This may be attributed to the relatively high temperatures to which these solids were exposed during the gasification process.

- The absorption of SO_2 by FW DASH was very good, after converting any CaS to $CaSO_4$.

- The absorption of SO_2 by mixtures of LASHs and limestones was better than that expected based on the performance of individual solids. The absorption of SO_2 by a mixture of FW DASH and dolomite was about the same as that expected from individual solids.

- The absorption of H_2S by KRW LASH was as good as that observed for the Sierra Pacific and Greer limestones.

The physical characterization of the various solids by mercury porosimetry shows the following:

- Pores of about 0.05 to 0.5 micron in diameter, which were also found in pure sorbents, were present in FW DASH and TRTU LASH. The good SO_2 absorption capacity of these solids may be attributed to the presence of these larger diameter pores.

- Pores of about 0.05 to 0.5 micron in diameter were not present in the KRW LASH nor KRW and Tampella DASHs possibly contributing to poor SO_2 absorption capacity of these solids.

Recommendations

The following recommendations are made based on the results of this study:

- If complete oxidation of CaS is a requirement, consider using dolomite in the gasifier as it is likely to result in a higher degree of subsequent oxidation of CaS in the sulfator/combustor.

- Examine different options in the design of the gasifier (such as not feeding sorbent directly into the high-temperature jet) to

reduce sorbent exposure to high temperatures. Lower peak temperature exposure is likely to enhance the SO_2 absorption capacity of the sorbent in the sulfator/combustor.

- Consider addition of a portion of the fresh sorbent directly to the sulfator/combustor to reduce the leakage of SO_2.

Oxidation of LASHs

The effects of temperature, grinding the LASHs, and impregnating the ground and unground LASHs with an alkali on the oxidation of CaS were studied using both KRW and FW LASHs. These solids were formed from different sorbents operating at different gasification conditions. KRW LASH was formed in a fluidized bed with a central jet where the temperatures were substantially higher than in the FW carbonizer. The sorbents used to produce KRW and FW LASHs were New Enterprise(dolomitic type) and Longview limestones (high-calcium type), respectively. Thus, studies of these two LASHs are expected to show the effect of both differences on their oxidation characteristics. The TRTU LASH was produced using Longview limestone in Kellogg's Transport Reactor Test Unit under relatively mild conditions and starting with small ($<500\mu m$) particles of sorbent and coal.

The effect of temperature on the oxidation of LSCF KRW LASH was studied at atmospheric pressure over the temperature range of 1500 to 1700°F in air for an hour. An increase in sulfide conversion was obtained with an increase in temperature for both KRW and FW LASHs. Based on these results, 1700°F appeared to be the preferred temperature giving the highest level of oxidation. Hence, subsequent studies were conducted at these conditions. For heavily-sulfided materials, sulfide conversions to 80% were obtained. Table 4 shows a summary of sulfide

conversions achieved for various LASHs and DASHs at 1700°F and atmospheric pressure in air for an hour. Conversions obtained during carbon burnoff in a muffle furnace (carbon-containing solids could not be processed in the BRU) are also shown and are included in the conversions reported for the various solids. The sulfide level (% of Ca as sulfide on a molar basis) in the as-received solids is given below.

HSAR KRW LASH	60
LSAR KRW LASH	33
HSAR FW LASH	42
LSAR FW LASH	21
TRTU LASH	55
FW DASH	55

The effect of impregnating the solids with 2 wt% Na_2CO_3 solution was studied using KRW, FW and TRTU LASHs. The impregnation of LASHs with the alkali increased the sulfide conversions to 90 to 95% for the three LASHs. In order to study the effect of grinding, samples were ground to a size distribution of 70x140 mesh. The combined effect of grinding and alkali-impregnation was also studied. For untreated samples of LASH, sulfide conversions ranged from about 22% to 80%. With alkali impregnation, the sulfide conversions increased to 90 to 95%.

Higher sulfide conversions were obtained for the KRW LASH compared to the FW and TRTU LASHs. This may be attributed to the dolomitic limestone used in producing the KRW LASH. Comparing the lightly-sulfided and heavily-sulfided KRW LASH, slightly higher conversions were obtained for the latter.

Oxidation of DASHs

The oxidation of FW and Tampella DASHs was studied at standard conditions. With the FW and Tampella DASHs, 93 and 100%

Table 4. Summary—Sulfide Conversions of LASHs and DASHs

LASH/DASH	Muffle*	UT	G	D	GD
CFHS KRW LASH	20	72	79	90	85
CFHS FW LASH	0	22	75	86	94
LSCF KRW LASH	20	58	65	94	--
LSCF FW LASH	0	33	-	-	-
HSCF KRW LASH	78	80	80	-	96
HSCF TRTU LASH	12	40	-	79	-
Tampella DASH	100	100	-	-	-
FW DASH	92	93	-	-	-

* sulfide conversion during carbon burnoff in a muffle furnace.

sulfide conversions, that are much higher compared to that of the LASHs, were achieved showing the advantage of using a dolomite over a limestone in the gasifier for subsequent oxidation.

Fundamental Kinetic Studies on the ATGA

The oxidation of CFHS FW and KRW LASHs was studied on the ATGA at atmospheric pressure to obtain rate information. These fundamental studies show that after a certain sulfide conversion is achieved, the rate slows down substantially, possibly as a result of diffusional resistance in the product layer. The results for the FW LASH are plotted to show the sulfide conversion as a function of time in Figure 1. The sulfide conversion profiles for the FW LASH show that much of the conversion occurred in less than 20 minutes. Similar results were obtained for the KRW LASH.
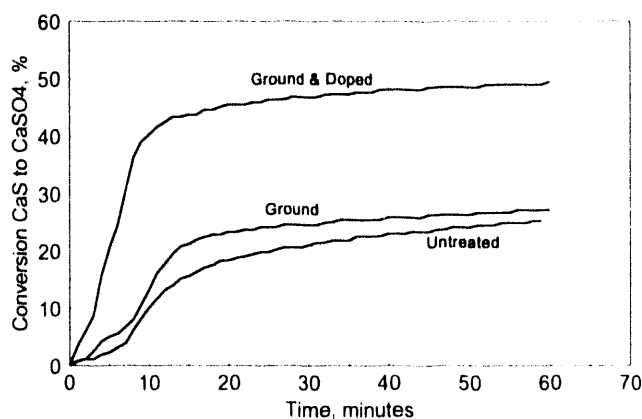
Figure 1. Effect of Grinding and Alkali Impregnation on Oxidation of FW LASH

Weathering Study on Oxidized KRW LASH

A study was conducted with CFHS KRW LASH, that was partially oxidized in the BRU at 1700°F and atmospheric pressure in air, to determine if "weathering" increases the level of oxidation of CaS present in the LASH. The alkali-impregnated and untreated LASH samples

were subjected to weathering by flowing saturated air through a fixed bed of solids for 60 days. The weathering of KRW LASH did not reduce the sulfide level. The LASH sample impregnated with Na_2CO_3 to 2 wt% showed a 32% sulfide conversion. The sulfide level (4.5%) in this sample may not be satisfactory.

Gas Absorption Studies

The objective of the gas absorption studies is to study the ability of various pure sorbents and KRW and FW LASHs to react with SO_2 over the temperature range of 1600 to 1800°F and at atmospheric pressure to enhance fundamental understanding of SO_2 absorption and to simulate the operation of a sulfator/combustor in an IGCC plant. The latter has to absorb the SO_2 evolved from the combustion of carbon as well as SO_2 that is present in the regeneration gas from an external desulfurizer if it is disposed of in the sulfator.

The absorption of SO_2 was studied to investigate the differences between pure sorbents and LASHs and to understand whether gasifier conditions contributed to any changes in the nature of LASHs.

The PTGA was used to study the CaO sulfation reaction with several sorbents and LASHs. The effect of bed weight and gas flowrate on the reaction rate was studied using Plum Run (P.R.) dolomite to establish the sample weight and gas flowrate required to get the true kinetic rate. At these conditions, the absorption of SO_2 on KRW DASH and KRW, FW, and TRTU LASHs was studied. Pure sorbents, LASHs and DASHs were characterized by means of mercury porosimetry to determine their pore characteristics.

SO$_2$ Absorption in the Quartz Reactor

The absorption of SO_2 by KRW LASH and KRW and Tampella DASHs was found to be very poor in the quartz reactor as determined from the breakthrough periods. This may be attributed to the relatively high temperatures at which these solids were processed in the gasifier. The use of a jetting fluidized bed to promote high solid circulation in a gasifier results in substantially higher temperatures in the jet due to the combustion of gases and solids in a confined region. This was substantiated by temperature measurements made in the KRW pilot plant[2]. Hence, the presence of a jet in both KRW and Tampella fluid bed gasifiers caused substantially higher temperatures in the jet than in the bed and exposed the sorbents to these temperature levels.

The absorption of SO_2 by FW DASH, after converting the CaS to $CaSO_4$, is very good reflecting the advantage of using a dolomite over a limestone in the FW carbonizer and the moderate temperatures that prevailed in the latter compared to the KRW and Tampella gasifiers.

The absorption of SO_2 by pure limestones in the presence of O_2 is very good with a maximum observed at 1700°F for Greer limestone[1]. The absorption of SO_2 by lightly-sulfided as well as heavily-sulfided Sierra Pacific and Greer limestones, and Plum Run dolomite is very good after exposing the sorbents to 10-21% O_2 for a period of time to supply enough O_2 for both oxidation of CaS and SO_2 absorption or after the sample is oxidized in a separate step. The absorption of SO_2 by pure limestones in the absence of O_2 is poor, possibly due to the absence of a stable product.

Kinetic Studies on the PTGA

The sample weight and gas flowrate required to obtain a true kinetic rate that is free from the gas film diffusional effect were established by studying the rate of CaO sulfation reaction at 1600°F and atmospheric pressure on a PTGA using P.R. dolomite (18x25 mesh) and these conditions were employed for all the subsequent tests. The reaction rate at any time is defined as the weight of CaO reacting per minute per unit weight of CaO present at this time. In the case of LASHs, DASHs and pure sorbents, the composition of the solids, as determined from gravimetric analysis, was used in calculating the reaction rate.

Figure 3. Sulfation of KRW, FW and TRTU LASHs—Conversion vs. Time

Sulfation Rate of KRW, FW and TRTU LASHs

The sulfation rate ($CaO-SO_2-O_2$ reaction) of the KRW, FW and TRTU LASHs was studied at standard conditions and the results are presented in Figures 2 and 3 showing the reaction rate as a function of CaO conversion and the latter as a function of time, respectively. For the various solids studied on the PTGA for reaction with SO_2, the PTGA results are in qualitative agreement with the results obtained in the quartz reactor.
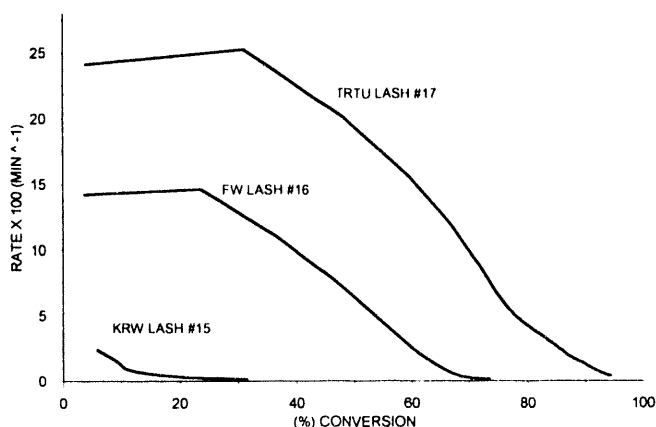

Figure 2. Sulfation of KRW, FW and TRTU LASHs—Rate vs. Conversion

The reaction rate of TRTU LASH is much higher than that of the KRW and FW LASHs. This higher rate may be attributed to the mild conditions at which the TRTU LASH was prepared in the TRTU since the same sorbent was used in the preparation of FW LASH as well. Due to high solid circulation rate and the absence of a high-temperature jet in the TRTU, the LASH is not exposed to localized temperatures as high as in fluidized beds.

Sulfation Rate of FW, Tampella, and KRW DASHs

The sulfation rate of FW, Tampella, and KRW DASHs was studied at standard conditions. The results are presented in Figures 4 and 5 showing the reaction rate as a function of CaO conversion and the latter as a function of time. The poor reaction rates of KRW and Tampella DASHs corroborate the SO_2 absorption results obtained in the quartz reactor. The reaction rate of the KRW DASH is just as poor as that of the Tampella DASH and the KRW LASH.

Based on the qualitative agreement between the results obtained in the quartz reactor and in

the PTGA, it appears that, if a suitable model is developed, the SO_2 absorption capacity of a sorbent in either the quartz reactor or in a fluidized bed reactor can be predicted from the results of fundamental tests on the PTGA.
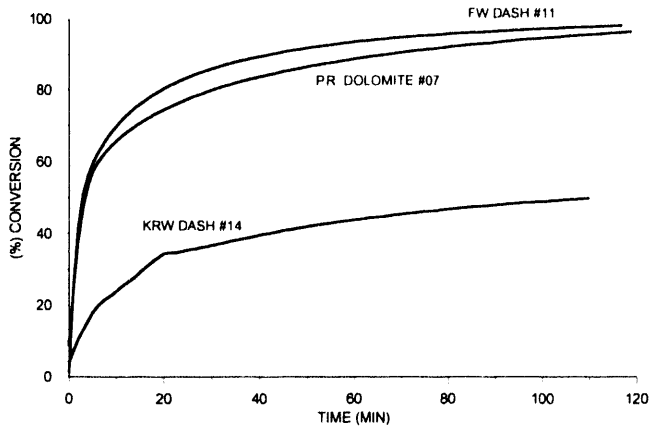
Figure 4. Sulfation of DASHs and P.R. Dolomite—Converson vs. Time

Figure 5. Sulfation of DASHs and P.R. Dolomite—Rate vs. Conversion

Effect of Heat Treatment Temperature on SO_2 Absorption

Pure sorbents were exposed to different temperatures in the range of 1600 to 2100°F and then their reactivities were studied on the PTGA at standard conditions. For exposure temperatures of about 2100°F, subsequent SO_2 absorption capacity was significantly reduced for both Longview limestone and Plum Run dolomite. The data on CaO conversion as a function of time for both of these solids are shown in Figures 6 and 7, respectively.
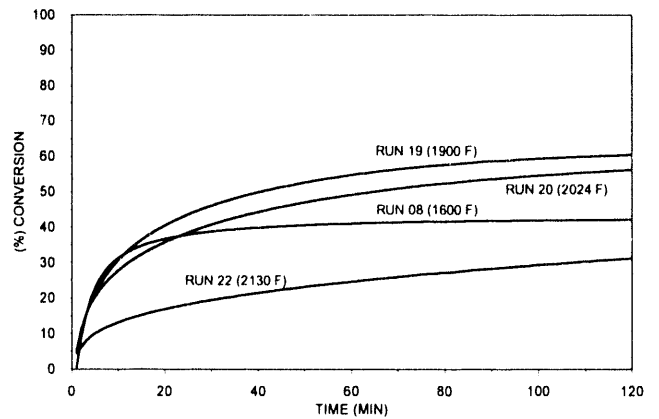
Figure 6. Effect of HTT on Sulfation of Longview Limestone
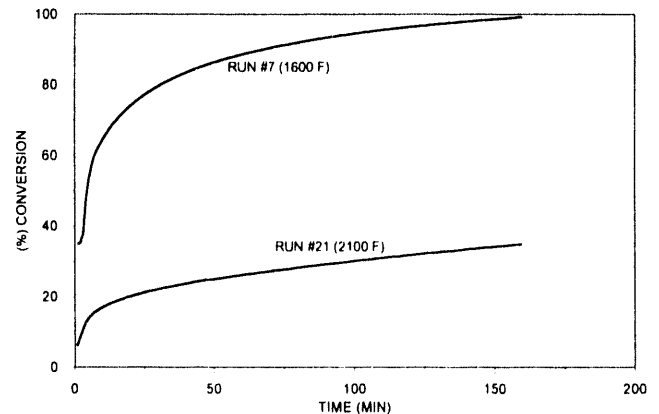
Figure 7. Effect of HTT on Sulfation of P.R. Dolomite—Conversion vs. Time

Characterization of Sorbents and LASHs and DASHs by Mercury Porosimetry

Calcined sorbents and carbon-free LASHs and DASHs were characterized by mercury porosimetry to measure the variation of pore surface area and pore volume as a function of pore size on a Micromeritics Autopore II 9220. The pressure was increased from 1.6 to 60,000 psia that covers pores from about $117\mu m$ to $0.003\mu m$ in diameter. Based on the SO_2 absorption capacity of the various solids and pore characteristics, no correlation appears to exist between either the total pore surface area or the total pore volume and SO_2 absorption capacity.

The differential pore volume divided by differential pore size for each incremental change in pressure, called differential intrusion, is plotted as a function of pore diameter in Figures 8 and 9. This type of plot appears to be the best in discerning the differences in SO_2 absorption capacity of the LASHs, DASHs and pure sorbents. A comparison of FW LASH and Longview limestone used in its production, given in Figure 8, shows a partial loss of pores of 0.05 to $0.5\mu m$ in diameter, while a comparison of KRW DASH and the P.R. dolomite, given in Figure 9, shows complete loss of these pores. Comparison of the pore characteristics of pure sorbents with KRW LASH, KRW and Tampella DASHs (not presented here), shows that in the case of the LASH and the two DASHs, larger pores present in the pure sorbents are not present in these solids and only pores smaller than about $0.01\mu m$ in diameter are present. This leads to the premise that larger pores beneficial for SO_2 absorption disappeared from the sorbents when they were processed in the KRW and Tampella gasifiers. The pore characteristics of FW DASH and TRTU LASH compare favorably with that of the pure sorbents, presumably due to lower processing temperatures in these gasifiers.
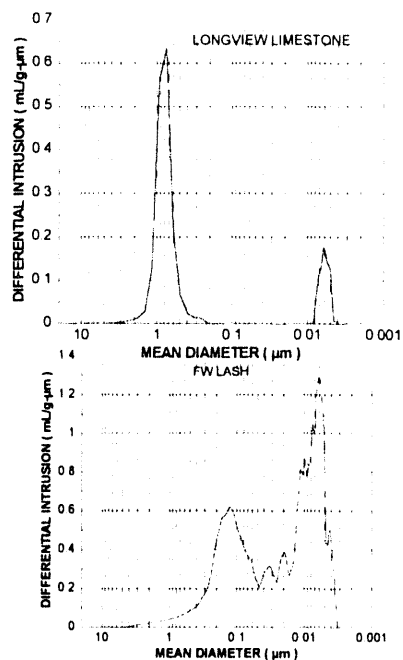

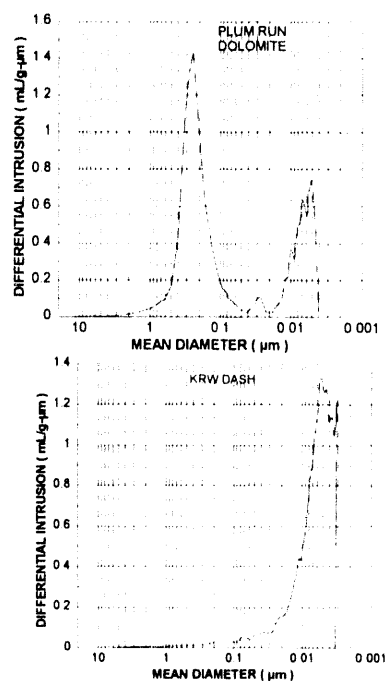**Figure 8. Characterization of Longview Limestone and FW LASH**

Figure 9. Characterization of P.R. Dolomite and KRW DASH

REFERENCES

1. Katta, S., G.B. Henningsen, and P.J. Shires, "LASH Oxidation, Waste Management," Proceedings of the Coal-Fired Power Systems 93 - Advances in IGCC and PFBC Review Meeting (June, 1993).

2. Katta, S., Principal Investigator, "Process Analysis Topical Report on Pressurized Ash-Agglomerating Fluidized-Bed Gasification System," FY-1984 & 1985, submitted by KRW Energy Systems to U.S. DOE, FE-21063-26 (1986).

FUTURE WORK

The effect of pressure at 150 psi, and a different O_2 partial pressure on the oxidation of KRW LASH at 1700°F, identified as the preferred temperature in this study, will be investigated. After completing Task 5, studies will be performed in support of Tasks 3 and 4.

ACKNOWLEDGEMENT

ABBREVIATIONS

AR	As Received solids
ATGA	Atmospheric Thermo-gravimetric Analyzer
BRU	Bench-scale Reactor Unit
CF	carbon-free solids
CFHS	processed in the muffle furnace first to burn off carbon and then sulfided in the quartz reactor
DASH	mixture of dolomite and ash
DT method	Draeger Tube method to determine CaS content in solids
FW LASH	LASH produced in the Foster Wheeler carbonizer using Longview limestone
FW DASH	DASH produced in the Foster Wheeler carbonizer using Plum Run dolomite
HSAR	Heavily sulfided and as received (carbon-containing)
HSCF	Heavily sulfided and carbon free
HTT	Heat Treatment Temperature (maximum temperature to which the solids are exposed in processing)
IGCC	Integrated Gasifier Combined Cycle System
KRW LASH	LASH produced in the KRW pilot plant using New Enterprise limestone (a dolomitic limestone)
KRW DASH	DASH produced in the KRW pilot plant using Plum Run dolomite
LASH	mixture of limestone and ash
LSCF	lightly sulfided and carbon-free
LSAR	lightly sulfided and as received (carbon-containing)
P.R.	Plum Run
PTGA	Pressurized Thermogravimetric Analyzer
S.P.	Sierra Pacific-supplied
Tampella DASH	DASH produced in the Tampella pilot plant gasifier using a dolomite
TRTU	Transport Reactor Test Unit
TRTU LASH	LASH produced in the TRTU using Longview limestone

9a.6   Market Assessment and Technical Feasibility Study of PFBC Ash Use

CONTRACT INFORMATION

Cooperative Agreement Number	DE-FC21-93MC30127
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METC Project Manager	Mary Beth Ashbaugh
Period of Performance	10/93 to 1/96

Schedule and Milestones

FY 94-95 Program Schedule

	FY '94												FY '95								
	J	F	M	A	M	J	J	A	S	O	N	D	J	F	M	A	M	J	J	A	S	O
Market Assessment																						
Ash Selection/Acquisition																						
Ash Laboratory Testing																						
Demonstration Strategy (FY95)																						
Field Demonstrations (Projected FY96/97)																						

OBJECTIVES

The overall objectives of this study are to determine the market potential and the technical feasibility of using PFBC ash in high volume ash use applications. The information will be of direct use to the utility industry in assessing the economics of PFBC power generation in light of ash disposal avoidance through ash marketing. In addition, the research is expected to result in the generation of generic data on the use of PFBC ash that could lead to novel processing options and procedures. The specific objectives of the proposed research and demonstration effort are:

- define present and future market potential of PFBC ash for a range of applications (Phase I);

- assess the technical feasibility of PFBC ash use in construction, civil engineering and agricultural applications (Phase II); and
- demonstrate the most promising of the market and ash use options in full-scale field demonstrations (Phase III).

BACKGROUND INFORMATION

Market assessment studies for advanced SO_2 control wastes have concluded that the market potential for PFBC materials is promising (Baker, 1990). Potential markets and the projected market volumes include: road construction (high); structural fill (high); concrete (high); asphalt (medium); brick (medium); cement production (medium); and synthetic aggregate (medium). Table 1 shows the market assessment for these applications and others.

These markets have the potential to consume large volumes of PFBC ash. Unfortunately, the value of the market products and the availability of competing materials has restricted transportation distances. A number of competing materials are established in these markets, thereby offering substantial performance records. However, the disposal avoidance costs associated with a power plant may encourage the penetration of PFBC ash into these markets, if documented technical performance of uses can be made available.

Potential Ash Uses

Conventional power plant ashes and the new desulfurization residues have been used successfully in a number of industries, including building construction, road and highway construction, coal mining and reclamation, agriculture and recently environmental restoration industries. These industries consume enormous quantities of raw materials and fly ash has found acceptance in each of these industries.

Table 1.
Overall Marketability Projection for Advanced Coal Combustion By-Products

Utilization Market	Potential Market Volume	Marketability Projection*		Comments
		Short Term	Long Term	
Agricultural/Soil Amendment	Low	Good	Good	Seasonal
Asphalt	Medium	Fair	Fair	Abundance of inexpensive competing materials
Brick	Medium	Poor	Possible	Mine-mouth industry; unique contribution needed
Cement Production	Medium	Good	Good	
Concrete	High	Poor	Good	Current specifications may limit use
Grout	Low		Excellent	
Road Construction	High		Excellent	
Structural Fill	High		Excellent	
Synthetic Aggregate	Medium		Good	
Waste Stabilization	**		Possible	Liability issues must be resolved.

* Marketability projection for technically suitable coal ash assuming technical suitability is demonstrated.
** Presently indeterminate.
Source: Modified from Baker (1990) DOE/MC/25042-2872

An example of the market magnitude and potential of ash use can be seen in road and highway construction (Table 2). The road construction industry consumes a tremendous amount of raw materials including earth borrow, aggregates, portland cement, asphalt cement, and mineral fillers. Lesser amounts of lime are also used. Earthen borrow is used as a fill, backfill, or embankment material. Aggregates are used as subbase or base material, as well as in concrete and asphalt paving. Mineral fillers, such as rock fines and ash are used in asphalt paving mixtures. Lime is also used as a stripping agent in asphalt, as well as a stabilizing agent for soils and road subbases and bases. Ash has found its way into this industry/market at a level of 4 to 5 million tons per year.

The building industry has used fly ash as a raw material in cement production, cement replacement in concrete and concrete products, such as masonry units. Production of lightweight aggregate for concrete and concrete products has also been commercially practiced. Recently, FBC ash and FGD sludge have also use in the building materials industry, such as wall board production.

Conventional power plant ash and FBC residue use as an engineering and construction material have been investigated for over a decade. A summary of FBC ash use in construction applications was provided by Bland (1994). Construction applications include road and highway construction, airport runways, and dams and other earthen and concrete structures. Road construction has traditionally involved a number of techniques and materials, such as roller compacted concrete (RCC), soil stabilization, stabilized road subbases and bases, embankments and fills, engineered material for structural fills, synthetic construction aggregate production for concrete, asphalt paving, and road base construction.

Table 2.
Raw Materials Use in Road and Highway Construction Industry*

Materials Consumed	Potential PFBC Ash Uses	Road Bases/Subbases (million tons)	Asphalt Paving (million tons)	Concrete Paving, Bridges,etc (million tons)
Aggregate	Synthetic Aggregate			
Crushed Stone	from PFBC Ash	200	215	200-240 Crushed Stone
Sand and Gravel		150	100 to 125	& Sand and Gravel
Total		350	315 to 340	200-240
Cement	Replacement in Cement/Concrete & Soil Stabilization	1 (est.)		15 to 20
Lime	No Substitution	0.8	0.1	
Asphalt	No Substitution		25	
Mineral Filler	PFBC Ash as Filler		25	
Fly Ash	PFBC Fly Ash	0.5	0.1	3 to 4
Bottom Ash	PFBC Bed Ash	0.4 to 0.5		
Total Conventional Ash Production (1987) 68.9 million tons Total Conventional Ash Use (1987) 18.3 million tons				
*Does not include earthen materials used for fills and embankments, for which 2 million tons of fly ash used. (1987)				

Source: Compiled from data presented by Baker (1990) DOE/MC/25042-2872

The mining industry has used ash for a number of years as a reclamation and soil/spoil amendment, for subsidence control in underground mines, for haul road stabilization, and for numerous embankments and fills.

The agricultural industry is becoming a market for conventional ashes and FBC ashes. The ash is used as a lime and sulfate source, micro- and macro-nutrient source, soil texture modifier, and moisture barrier for root growth. FBC ash, in particular, is finding acceptance in a number of states in agricultural applications.

The use of conventional ashes and more recently FBC ash in these applications provides a basis for believing that PFBC ash can also penetrate these markets. The following provides a brief description of potential applications.

Cement Production. Approximately 82.5 million tons of cement were produced in the United States in 1992. Of that amount approximately 800,000 tons or approximately 1% of the conventional fly ash produced by power plants was used for clinker production. The fly ash is used as a raw material in the clinker production, as a source of silica and alumina; or as a material blended with ground clinker in the formulation of a blended Type P pozzolanic cement.

PFBC ash appears to show promise for this application. PFBC ash can also be used as a set retarder (normally gypsum or anhydrite is used) that is interground with the cement clinker. Competing materials for this application remain limestone and shales as well as conventional fly ashes. The use of dolomite as a sorbent in FBC can result in excess MgO, a detrimental (<4%) component in cement.

Replacement of Cement in Ready Mix Concrete and Concrete Products. In 1987, over 6 million tons of conventional fly ash were used as a cement replacement or portland cement in ready mix concrete and concrete products. This represented approximately 82% of all of the fly ash used in the United States. Approximately 42% of all ready mix concrete used fly ash at an average of 20% replacement of the cement.

The use of PFBC ash in concrete and concrete products relies on the pozzolanic property of the ash. Fly ash, including FBC ash is known to be a pozzolan, and therefore is used as a cement replacement (supplement) in portland cement concretes. However, ASTM requires that the SO3 content of the ash can not exceed 5% if the ash is to be used as a pozzolan. This will restrict the use of certain PFBC ashes. Ashes from low-sulfur coal fired units (i.e., low sulfur subbituminous coals) will meet the specifications and represent excellent pozzolans (unpublished Western Research Institute data). Those from the combustion of high sulfur coal will not meet the SO3 limits

No-Cement Concrete and Concrete Products. The use of FBC ash in the production of no-cement concrete and concrete products has also been the subject of extensive development in the United States and Canada during the 1980s (Minnick 1982; Bland et al. 1987, 1989, 1991a,b; Burwell et al. 1993). This material, originally developed as a material for subsidence control in underground mines, has been modified to have engineering properties comparable to portland cement concrete.

Bland et al. (1991a) concluded that AFBC concretes show promise as a construction material. The engineering properties of the concrete varies considerably due to the nature of the coal burned and the sulfur content which dictates the sorbent usage. Low-sulfur coal ash seems to exhibit the best durability characteristics, but may be short on unreacted sorbent, thereby limiting the strength

development. The AFBC no-cement concrete has been tested in field demonstrations as a road base material, including roller compacted concrete (RCC), as a ready mix concrete, and as masonry block mix.

PFBC ash may have potential in this application, when used in conjunction with lime. PFBC ash, unlike AFBC ash, is not expected to contain sufficient free lime for the required pozzolanic reactions to occur.

Soil and Road Sub-Base/Base Stabilization. The use of FBC residue for stabilization of soils has been proposed by a number of researchers. This application is similar to the cement stabilization of soils commonly applied in the construction industry. Soil stabilization is based on the lime treatment of clay soils and the self-cementing characteristics of the FBC ash. Unfortunately, the high-sulfate content of some FBC residue may create swelling due to the sulfate induced heaving of the soils. This is due to the formation of hydration products, such as ettringite and thaumasite in the soil/FBC residue mixture. Both of these mineral phases are known to cause expansion and swelling in cement or lime stabilization of high-sulfate soils. The use of relatively low-sulfate PFBC residue or the use of PFBC residue in low concentrations with the soil appear to show promise, although caution is warranted.

Bigham et al. (1993) has successfully demonstrated the application of FBC residue for the stabilization of cattle lots. In this application, the FBC residue is mixed into the soft cattle lot soils and allowed to cure. The FBC residue removes water from the cattle lot soil and hardens. The resultant cattle lots show improved stability and the cattle penetration into the soils is eliminated.

The largest stabilization area is related to the stabilization of subbases and bases for road and highway construction. There are essentially two forms of stabilized road bases: (1) stabilization of a base material as a soil cement application; or (2) production of a stabilized road base material in a form such as roller compacted concrete (RCC). Both of these road base materials have potential (Bland et al. 1989, 1991b). The first road base material form employs the principals of soil cement application and as such may be susceptible to dimensional instability for certain FBC residue compositions. On the other hand, roller compacted concrete, is a lean zero slump concrete mixture that resembles the texture of a damp aggregate. The RCC mixture is emplaced using typical asphalt paving equipment. The mixture is spread and compacted using roll compactors in lifts. The cured RCC mixture then has a wear surface placed on it in the case of road bases. RCC is used for other applications, such as dams and parking lots (Pitman, 1986).

RCC made from FBC ash has been demonstrated as part of the Tennessee Valley Authority (TVA)/Electric Power Research Institute (EPRI) sponsored research program (Bland et al 1989, 1991b; Hunsacker et al. 1987). FBC residue from the TVA 20 MW FBC facility in Paducah, Kentucky was used in a demonstration of RCC in McCracken County (Bland et al 1989, Hunsacker et al. 1987). PFBC ash is expected to be usable in this application, particularly in combination with controlled amounts of lime or cement.

Structural Fill and Embankments. The application of FBC residue as an engineered material for structural fills and embankments represents a large-scale use option. Structural fills and embankments are numerous in the road construction, mining and industrial construction industries. Structural fills and highway embankments using conventional ash materials

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have been well documented through EPRI sponsored research and demonstration activities.

The application of FBC residue for these construction applications relies on the development of the stable properties of the ash. Ash Management Engineering and Jacques Whitford and Associates investigated the potential for the structural fill of a quarry using ash from the AES Barbers Point CFBC facility, Oahu, Hawaii (Georgiou et al. 1993). The study concluded that the construction of a structural fill using FBC ash was technically feasible and that the ash produced a fill with a high degree of strength and stability. However, the ash was a low-sulfate residue and the environmental conditions were warm temperatures and relatively low precipitation. Other high-sulfur residues may not produce a stable fill under these or more humid conditions.

A construction material has been produced by AES Barbers Point called 'Ash Rock', which can be used for structural fill applications. 'Ash Rock' material has not been able to meet the abrasion resistance requirements specified by ASTM or AASHTO for consideration as an aggregate material. Instead, this material is presently being produced as a structural fill material and has received designation as 'borrow' material on the island of Oahu.

PFBC ash is expected to be marketable in these applications. In fact, Bigham et al. (1993) have successfully used ash from the AEP Tidd PFBC facility in an embankment/fill application for a U.S. DOE-sponsored road field demonstration.

Synthetic Aggregate. The aggregate market in the United States is enormous. In 1992, approximately 1.2 billion tons of crushed stone and approximately 0.8 billion tons of sand and gravel were produced for a market valued in excess of $8 billion. The aggregate market encompasses conventional aggregate products,

such as masonry units and ready mix concrete. Also with crushing, aggregates can be produced for use in asphalt paving, road base construction and even RCC. There is evidence that lightweight aggregate can also be produced from certain CFBC ashes.

Two CFBC ash pelletizing plants have been built in the United States at AES Thames and U.S. Generating Cedar Bay Cogeneration plants (Bland et al. 1993; Bland 1994). These plants have the capacity of pelletizing 500 to 800 tons/day, respectively. The pelletization of FBC ash was selected for ease of handling and for the possible subsequent use as a synthetic aggregate. Preliminary testing of the pelletized ash as an aggregate indicates that the material meets the strength, abrasion resistance, and other engineering requirements for its use as an aggregate (Bland et al. 1993).

Although the availability of free lime is not characteristic of PFBC ashes, this option still poses a major market for PFBC ashes, as well as a method for storage in the construction off-season.

Ash Use in Agricultural/Soil Amendment Applications. There are a number of benefits that result from the application of FBC residue to agricultural soils or mine spoils. The benefits include the modification of soil pH, supply of essential plant nutrients for crop production, increasing water infiltration, soil aggregation, and modification of texture of clay soils promoting root growth. This data base has resulted from years of research by universities and especially the U.S. Department of Agriculture (USDA).

Previous work has verified that the chemical composition of FBC residues includes compounds of interest in agriculture, such as lime and gypsum (Korcak 1980; Stout et al. 1988). This material has potential as both a soil amendment and a nutrient source. Greenhouse studies have

determined that the FBC residue was as effective as that of Ca(OH)$_2$ in increasing soil pH when the materials are applied in equivalent free lime amounts. The residue, when applied as a lime source, also increased the sulfur and manganese contents of tall fescue. The research to date indicates that application rates of FBC residue at 1 to 5 tons per acre to agricultural lands with acidic soils, soils high in heavy metals, or soils deficient in trace metals are beneficial.

The potential application of FBC residue as a soil amendment and nutrient source for revegetation of disturbed lands resulting from mining has received considerable attention (Bennett et al 1985; Stout et al. 1982; Sidle et al. 1978). The application of FBC residue to acidic soils and strip mine spoil can reduce the mobility of heavy metals through pH adjustment. Also beneficial micro- and macro-nutrients have been observed to move into the subsoil of infertile acidic soils and mine spoils after application of FBC residue, thereby promoting root penetration.

The application of FBC residue to agricultural lands has been commercially pursued in Hawaii for sugar cane applications (Sundstrom, personal communication); in New York at the Fort Drum facility (Tom Nickeson, personal communication) and in California at the Stockton facility (Lewnard 1991). Additional testing is ongoing at the USDA using FBC residue for orchard applications (Korcak, 1994, personal communication).

PFBC ash is expected to also meet the requirements for agriculture/soil amendment applications. Recent studies sponsored by the U.S. Department of Energy (DOE) using the ash from the AEP Tidd PFBC facility have examined the use of FBC residue in a variety of greenhouse studies. The technical feasibility of FBC ash use in agricultural applications was noted, but the potential of magnesium imbalance was also noted as a potential side-effect (Stehouwer and Sutton

1992; Bigham et al. 1993). This is specific to those units using dolomite as a sorbent.

PROJECT DESCRIPTION

The chemical characteristics of PFBC ash compared to AFBC ash has generated interest in the use of the PFBC ash for various construction and agricultural applications. However, before commercial entities are ready to commit to the concept of using PFBC ash, the performance of the ash in these high volume ash use applications must be documented. The first step must be a preliminary evaluation at the laboratory scale. If successful at that level, then full-scale demonstration projects will be required before acceptance is received by the contractors and regulatory agencies.

A research and development program composed of three phases is being conducted. Phase I focuses on an evaluation of the markets for PFBC ash. Phase II addresses the technical feasibility of PFBC ash use including chemical/physical characteristics, construction and civil engineering properties, and agricultural amendment properties. Phase III addresses the development of a strategy for demonstrating the most promising of the ash use applications defined in Phases I and II.

Phase I. Market Assessment of PFBC Ash

Potential market penetration of the existing markets will be assessed according to a protocol agreed to by DOE and EPRI. The market assessment will be an evaluation of the market potential in a number of areas including: **structural fill** as used in construction of highways, embankments and bridge abutments; **soil stabilization/road base material** used in building roads, parking lots, factory floors, etc.;

supplementary cementing material for concrete and concrete products; **bricks and blocks**; **synthetic aggregate** in concrete and asphalt paving of roads, etc.; and **agriculture/soil amendments** for agricultural and reclamation lands as a soil conditioner, liming and gypsum agents.

Each of these markets for PFBC ash are to be addressed and assessments of the magnitude of the market, competing materials and likely growth potential determined. The properties of the materials presently used in the markets will be determined and compared with known properties of PFBC ash to determine delimiting properties and/or required properties of the PFBC ash.

The market assessment will also provide an evaluation of the market trends and related opportunities, speculation about the market in the year 2000, and the nature of technical developments and marketing needed for market penetration by PFBC ash. A ranking of the potential applications for PFBC ash will be made, based on the results of the market assessment.

Phase II. Technical Feasibility of PFBC Ash Use

The scope of the proposed testing focuses on ash characterization and conditioning studies, geotechnical characteristics of the ash as related to stabilized fill applications, use of the PFBC ash as a supplementary cementing material, the production of a synthetic aggregate via pelletization of the ash, and the use of the ash in agricultural/soil amendment applications.

It is anticipated that two PFBC ashes will be evaluated as part of this study. Previous experience has indicated that the sulfur content of the coal is the primary controlling parameter affecting ash composition and resultant ash

properties. Based on the use of ash from these coal sulfur content extremes, the determination of the range of technical performance of PFBC ash can be made.

The characterization of the ash includes both the chemical and the physical properties. The chemical characterization of the ash consists of the chemical analysis for the elemental composition of the ash, the identification of the phases present in the ash, and the leachate characteristics of the ash as a result of the standard Toxicity Characteristic Leaching Procedure (TCLP). Both the elemental concentration and the mineral phases are to be determined.

The geotechnical properties are the basis for evaluating the general feasibility of the ash for use in construction-related applications. In general, the geotechnical evaluation will determine those properties of the ash related to its use in **structural fill** applications.

The testing of the PFBC residue as a **supplementary cementing material** will consider both partial cement replacement and addition to standard portland cement mortar mixes. Applicable ASTM and AASHTO specifications and limits for (1) grouts and flowable fills, (2) ready mix or roller compacted concretes, and (3) soil-cement applications will be evaluated.

The production of **synthetic aggregate** from PFBC fly ash will be addressed through a series of laboratory tests and pelletizing trials and subsequent testing of the cured and hardened ash pellets. The pelletization trials will include the ash conditioning requirements, the water demand requirements for pelletizing, the curing requirements, and the definition of the engineering properties as related to materials handling.

The pellets produced from the pelletizing tests will be subjected to a series of standard ASTM

and AASHTO tests for aggregates to be used in concrete and masonry blocks, highway base construction, and asphaltic paving. The testing will determine the abrasion resistance, strength, and durability characteristics.

The use of PFBC ash as a **soil amendment** in reclamation and/or agricultural applications has potential due to the presence of macro and micro-nutrients and lime, calcium sulfate, and calcium carbonate in the ash, all of which could be beneficial to plant growth. Specifically, the available lime and sulfates are considered to be of value relative to replacement of fertilizers.

An evaluation of the potential of PFBC ash as a soil amendment will be made both in laboratory equilibration testing and in a greenhouse plant productivity study. The laboratory equilibration study will compare PFBC ash to agricultural lime in the treatment of two soil types with low pH. The greenhouse plant productivity testing will evaluate both the PFBC ash and the agricultural lime on several plant species of varying acid tolerances. The vegetation will be evaluated for elemental composition, production rates and root conditions.

Phase III. Ash Use Demonstration Strategies

Phase III will evaluate the results of the Phase I and II research in order to develop a strategy for the demonstration of the most promising of the PFBC ash uses in full-scale field demonstrations. The purpose of the Phase III activities is to develop a game plan for the implementation of Phase I and II results into field demonstrations with prospective commercial developers and or marketers.

The activities will identify potential developers and marketers as well as potential sites for field demonstrations. The details of Phase III activities are difficult to quantify until the results of the Phase I and II are complete. The detailed scope of work for this phase will be developed jointly with EPRI, DOE, and the others sponsors as the project progresses.

The results of the Phase III activities will lead to the implementation of one or more field demonstrations, under future funding opportunities. These field demonstrations will allow the developers, ash generators, ash management companies, and ash users to all participate and thereby develop confidence and the engineering data necessary to take these ash use options to a commercial business status.

RESULTS

The project is underway and ash sources for the technical feasibility study are being finalized. Ashes from the Ahlstrom Pyropower's Hans Ahlstrom Laboratory pilot PCFBC unit in Karhula, Finland are being made available for this study. The ashes represent the material from the combustion of low-sulfur Powder River Basin subbituminous coal with and without limestone sorbent. Sulfur capture of approximately 90 to 95% was achieved in the limestone sorbent tests. These tests are being conducted in support of the Des Moines Energy Center (DMEC) Clean Coal projects. The Powder River Basin coal (western U.S. subbituminous) and the Iowa Industrial Lime No. 1 are the proposed fuel and sorbent for the DMEC-1 PCFB demonstration project.

The Ahlstrom PCFBC pilot plant is of square cross-section. It is housed in an 11.8-ft (3.6-m) diameter pressure vessel. A high-pressure high-temperature, gas cleaning unit downstream of the PCFB exhaust is installed in a separate 8.5-ft. (2.6-m) diameter pressure vessel. The maximum plant operating pressure is 16 bar (232 psia). The fuel is fed as a slurry and the sorbent is also fed along

with the fuel. A separate dry sorbent feed system is also installed for trimming the sulfur oxides emissions during load swings. The plant has provisions for startup with gas and/or oil. A detailed description of the facility is provided in earlier papers (Isaksson et al. 1990; Sellakumar et al. 1993) and the design conditions is given in Table 3.

Table 3.
Summary of the Operating Conditions of the Ahlstrom Pyroflow PCFB Pilot Plant in Karhula, Finland

Heat Input	34 MM Btu/hr (10 MWth)
Max. Fuel Feed Rate	15870 lb/hr (2 kg/s)
Max. Air Flow Rate	43650 lb/hr (5.5 kg/s)
Operating Temperature	1616 °F (1153 °K)
Max. Operating Pressure	232 psia (16 bar)

FUTURE WORK

The project is just being initiated. The scope of the project as defined earlier will be conducted over the next three years.

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Co-Firing Waste Materials in an Advanced Pressurized Fluidized-Bed Combustor

CONTRACT INFORMATION

Contract Number	DE-AC21-89MC25177
Contractor	Gilbert/Commonwealth, Inc. P.O. Box 1498 Reading, PA 19603 (610) 775-2600
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Principal Investigators	Michael R. DeLallo Roman Zaharchuk
METC Project Manager	Donald L. Bonk Heather M. McDaniel
Period of Performance	August 26, 1992 to September 30, 1994

OBJECTIVES

A study has been undertaken to investigate the technical and economic feasibility of co-firing a pressurized fluidized-bed combustor (PFBC) with coal and municipal or industrial wastes. Focus was placed on the production of electricity and the efficient disposal of wastes for application in a central power station and distributed locations. Wastes considered for co-firing include municipal solid waste (MSW), municipal sewage sludge, and industrial de-inking sludge. Issues concerning waste material preparation and feed, PFBC operation, plant emissions, and regulations are addressed. This paper describes the results of the performance evaluation completed as part of this study, and provides recommendations for further evaluation.

BACKGROUND INFORMATION

The Environmental Protection Agency's (EPA) 1990 estimates place the amount of MSW generated in the United States at over 195 million tons per year, up approximately 44 million tons since 1980[1]. EPA estimates that 4.3 pounds of MSW are generated per person per day. Together with industrial process waste and municipal sewage sludge, the resultant burden on our capacity to dispose of these wastes, in a cost-effective and environmentally acceptable manner is an enormous management problem.

One method of waste management is through combustion or incineration with energy recovery. This alternative has been plagued with a legacy of inefficient, dirty, and poorly operated incinerators, resulting in environmental problems leaving communities searching for solutions. However, advanced power systems that can meet new stringent environmental regulations have been developed and operated successfully. Additionally, electric utilities and non-utility generators have shown significant interest in waste management through waste-to-energy facilities.

Co-firing waste with coal in a utility scale boiler has emerged as an effective approach to produce energy from waste. Fluidized-bed combustors are becoming a primary method of burning wastes. The fluidized-bed, with its stability of combustion and temperature, provides enhanced energy recovery and environmental control while achieving cost-effective waste management.

Waste Material Characteristics

The characteristics and analyses of the three waste fuels under consideration were obtained from facilities that presently co-fire these materials. The wastes are municipal solid waste, municipal sewage sludge, and industrial de-inking sludge

Municipal Solid Waste. Waste classified as MSW is extremely variable in composition both on a seasonal and location basis. To produce a fuel that can be fed to a PFBC, it must be processed to remove metal, glass, and other non-combustibles to produce what is called refuse derived fuel (RDF). Methods currently used process about 50 percent of MSW to RDF. A typical 3-inch shredded material is prepared by shredding, magnetic separation, and air classification. It can be burned as is, pelletized, or slurried. A representative RDF proximate and ultimate analysis is shown in Table 1.

Municipal Sewage Sludge. The incineration of sewage sludge has a long history in the United States. Initially, multiple hearth units were used; now the majority of new installations are FBCs.

Treatment plant sludges generally are less than 7 percent total solids (t.s.). Combinations of processes such as chemical addition, flocculation, thermal conditioning, gravity thickening, and centrifugation are used to thicken sludge prior to burning. Feed sludges range from 20 percent to 40 percent t.s., but 25 percent t.s. is a reasonable average.

Sludge analyses vary from plant to plant and from season to season in the same plant. The fibrous nature of sewage sludge greatly affects the fluidity. A 7 percent t.s. sludge has the consistency of wet cement. At 25 percent t.s., sludge can be conveyed "dry" on a conveyor belt. Table 2 is an ultimate analysis of a sludge that has 13.85 percent t.s. On a dry basis the Higher Heating Value (HHV) of sludge can be as high as 6,500 Btu/lb.

De-Inking Sludge. The amount of de-inking sludge produced is increasing as the use of recycled paper is gaining popularity. In the manufacture of newsprint, the repulping generates a large quantity of high ash sludge, which previously was disposed of in lagoons. Now incineration in fluidized-bed combustors is preferred since overall energy costs can be reduced and environmental requirements can be satisfied. The pulping process in a typical size facility produces 250 dry tons of de-inking sludge per day from a feed of 1,600 dry tons per day of old newsprint.

The sludge is concentrated from a 2 percent t.s. stream to 7 percent and is further de-watered to 45 percent t.s. using screw presses. The character of 45 percent sludge is such that storage bins are not used. The sludge is processed and conveyed directly to the boiler on conveyor belts. Table 3 shows a representative sludge analysis.

Design and Operation Issues

Although there is considerable data on the operation of PFBCs when feeding coal both dry and as a slurry, wastes have not been co-fired with coal. There is, however, considerable information on co-firing wastes in atmospheric fluidized-bed combustors (AFBC) that is relevant. Except for pressure, AFBCs have similar operational requirements. Feeding the wastes into the combustors has been the most common problem. This prompted an investigation as to what equipment is available to feed RDF and sludges into a PFBC.

Table 1. Representative RDF Analysis

Proximate Analysis As Received		Ultimate Analysis As Received	
Moisture	30.73 %	Moisture	30.73 %
Ash	11.59	Ash	11.59
Volatile	48.93	Sulfur	0.32
Fixed C	8.75	Nitrogen	0.61
	100.00 %	Carbon	28.30
		Hydrogen	4.20
Btu/lb, HHV	4,801	Oxygen	24.25
		Total	100.00 %

Table 2. Municipal Sewage Sludge Ultimate Analysis

Carbon	3.08 %
Hydrogen	0.46
Nitrogen	0.37
Sulfur	0.07
Ash	6.80
Oxygen	3.07
Moisture	86.15
Total	100.00 %
Btu/lb, HHV	464

Table 3. De-Inking Sludge Analysis

Proximate		Ultimate	
Moisture	55.00 %	Moisture	55.00 %
Ash	9.76	Ash	9.76
Volatile	28.74	Sulfur	0.11
Fixed C	6.50	Nitrogen	0.35
	100.00 %	Carbon	19.58
		Hydrogen	2.40
Btu/lb, HHV	3,562	Oxygen	12.80
		Total	100.00 %

The flow and handling characteristics of the waste materials considered in this study are affected by quality, moisture content, particle size, and extraneous contaminants. Feeding these materials into pressure vessels differs greatly from feeding into atmospheric processes due to pressure influences on the tension and compression strength of the feed material. Recently, there has been activity in developing pressurized feeders for biomass waste materials and both dry and slurry feeders have been tested. Dry feed systems include double lockhoppers, rotary valve feeders, piston feeders, screw feeders, and pneumatic systems. Slurry feeders include progressive cavity pumps, piston pumps, and rotary feeders. However, these options have not had substantial operating experience at PFBC conditions, but it is assumed that eventually a reliable system will be available. The slurry feeders have had the advantage based on experience feeding coal slurries, but there is a penalty effect on performance especially when feeding high moisture slurries. Table 4 presents some of the dry feeders evaluated.

PROJECT DESCRIPTION

Design and performance analyses were developed for PFBC advanced generation plant configurations with nominal ratings of 110 MWe and 250 MWe. Performance considerations were given to fuel handling, emission control, and residual solids handling. Thermal performance for all cases was calculated by using an Aspen/SP™ modular computer program. The program modeled the PFBC, gas turbine, heat recovery and steam generator, and the steam turbine cycle in a single, integrated calculation process. Plant material and energy balances were developed along with the net plant power, thermal efficiency, and net heat rate. Comparisons were made to firing with and without waste materials to define the effects on plant performance from waste co-firing.

RESULTS

The design and performance analyses for the PFBC power plant co-fired with RDF and/or sludge waste followed two application scenarios. The first assumed a utility base load application with electrical production in the 100 to 120 MWe range, and the second assumed a capacity of 240 to 250 MWe. Application specifics were then based on these scenarios including the definition of site and ambient conditions -- fuel, waste, and sorbent feedstock -- and method of fuel/waste handling. The PFBC 1.5-Generation plant configuration as presented in Figure 1 was the basis for this study and is used to establish the baseline performance. The study utilized defined plant boundary conditions including ISO ambient conditions, Pittsburgh 8 coal, Plum Run dolomite, and waste feedstock for each PFBC application analysis.

The ratio of coal-to-waste fuel was established on the following criteria: (1) an 80:20 coal-to-waste ratio on an as-received weight basis was used to define the maximum amount of co-fired waste products, and (2) co-fired amounts for municipal sewage sludge were based on the volume produced from a typical population center of 250,000, employing a typical sludge treatment process.

Design Review

Major subsystems specifically influenced by the waste material feedstock are fuel handling, emission control, and residual solids handling. Of particular concern to this study is the impact on system performance from variations in the fuel/waste handling process.

Table 4. Summary of Dry Feed Systems for High Pressure

Feeder Type	PSI Pressure (Max)	m3/h Capacity (Nominal)	Suitable For	Remarks
Lockhopper Gravity Feed	500	40	All Wastes	Unless double LH are used, compression gas use could be excessive.
Lockhopper Screw Feed	360	14	All Wastes	A larger capacity unit has not been designed.
Rotary Valve	175 to 350	200 to 280	All Wastes	Size should be <5 cm. Other Vendors offer <200 psi max. feeders.
Piston Feeders	333 to 2175	50 to 115	All Dry Wastes	Feeders are more suitable for dry fuels. Sludges would have to be tested.
Screw Feeders	250 to 1450	20 to 45	All Wastes	Expensive. Fibrous and abrasive materials are a problem.
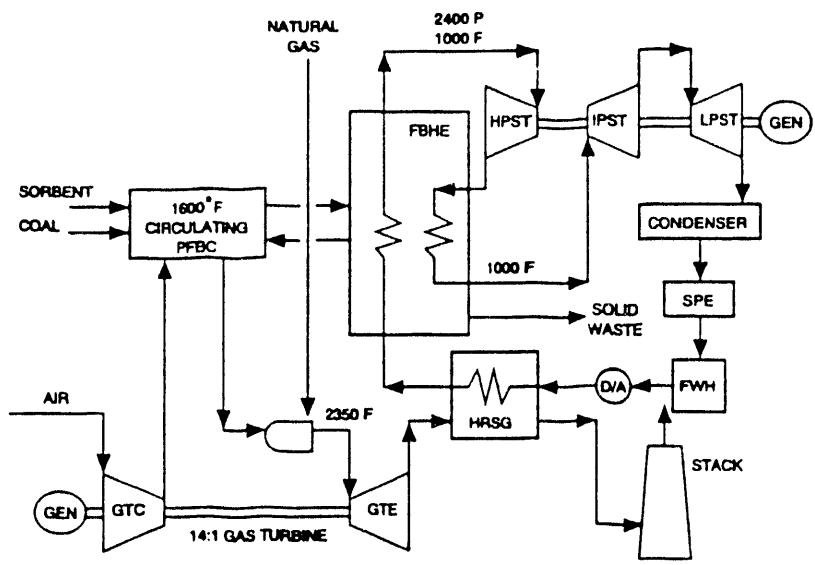
Figure 1. 1.5-Generation PFBC Cycle

Fuel Handling Options. The analyses investigated slurry processing of the coal and sorbent in either: (1) separate combustor feed of the coal/sorbent and waste streams, or (2) combined coal/sorbent and waste fired in a slurry media. As an alternative approach to slurry feeding, a sensitivity study of dry feeding of coal, sorbent, and the co-fired RDF was completed at the 250 MWe level. The analysis compared overall plant efficiency and cost-of-electricity to determine if an advantage exists in dry versus slurry feed. In the slurry feed approach, the coal and sorbent are transported via a water media at 75 percent total solids.

Waste Material Handling. For the 250 MWe system, RDF is fed to the PFBC as a slurry or pneumatically to determine which method proved higher system efficiency and lower economics of operation. For the slurry feed analysis, RDF is combined with coal and sorbent and slurried with water to 75 percent t.s. The slurry is then pumped into the PFBC. The inherent moisture of RDF was not considered to be used as part of the slurry water content.

In the case of dry feed, the RDF is fed to the PFBC via a screw conveyor. In this case, coal and sorbent are pneumatically conveyed to PFBC. Separate feed systems allow different fuel injection points in the combustor. In this manner the relatively light RDF material can be fed to the PFBC at a point to assure complete combustion.

For municipal sludge, it was assumed to be dewatered to 24 percent t.s. and fed in a separate flow stream to the combustor. A value of 24 percent t.s. corresponds to the industry achievable de-watering capability with conventional belt filter or screw press.

Based on a population value of 250,000 supplying the municipal sludge, a feed rate of 35,000 lb/day was assumed in both the 250 MWe and 110 MWe performance analysis. At this input rate, the coal-to-waste feed ratio, on an as received weight basis, is 95:5 and 91:9, respectively.

An additional case analysis examined the potential use of as-received municipal sludge at 6 percent t.s. as the slurry media for the PFBC fuel and sorbent. The limiting factor for this analysis was the requirement to maintain a 75 percent t.s. in the fuel and sorbent feed.

For the analysis of de-inking sludge, it was assumed that a 40 percent t.s. is fed to the PFBC via piston feeder. At this percent solids, de-inking sludge can not be pumped in a conventional fluid pump. A sludge total solids value of 40 percent was chosen to represent the industry standard in recycled newsprint facility operation. Separate feed systems for the coal/sorbent slurry and de-inking sludge allow for different fuel injection points. In this manner, the relatively light sludge material can be fed to the PFBC at a point that will inhibit rapid ascension of the sludge material assuring complete combustion. The coal-to-waste firing ratio of 80:20 was assumed, on a weight basis, and is based on as-received coal and "bone-dry" de-inking sludge.

Performance Analysis Assumptions

The design and performance analyses for a PFBC power plant co-firing RDF and/or sludge waste followed similar application scenarios. Operational conditions were established assuming a utility base load application located in the United States mid-Atlantic region.

The 250 MWe application includes the use of a Westinghouse 501D5 gas turbine with an 1800/1000/1000 steam turbine bottoming cycle. The performance for the 110 MWe is based on using a Westinghouse W251B12 gas turbine with a 1450/1000/1000 steam turbine bottoming cycle.

The PFBC combustor design parameters were assumed to follow the design assumptions defined in Gilbert/Commonwealth Report No. 2985[2]. The PFBC is a circulating bed with an operating temperature in the 1600°F range. A 99.3 percent carbon conversion efficiency

was assumed for performance modeling along with a 93.3 sulfur removal.

The performance analysis for the various PFBC power plants co-fired with waste feedstocks were developed according to the application and waste material used.

The case profiles used to define the performance assumptions are as follows:

250 MWe Application

250 MWe with Pittsburgh 8 coal and municipal solid waste as RDF in a combined slurry feed at the 80:20 coal-to-waste ratio.

250 MWe Pittsburgh 8 coal and municipal solid waste as RDF as-received in separate dry feeds at the 80:20 coal-to-waste ratio.

250 MWe Pittsburgh 8 coal and municipal sewage sludge de-watered to 24 percent t.s. with separate feed at a waste feed volume based on a 250,000 population.

250 MWe Pittsburgh 8 coal and de-inking sludge de-watered to 40 percent t.s. with separate feed at the 80:20 coal-to-waste ratio.

110 MWe Application

110 MWe with Pittsburgh 8 coal and municipal solid waste as RDF in a combined slurry feed at the 80:20 coal-to-waste ratio.

110 MWe with Pittsburgh 8 coal and municipal sewage sludge de-watered to 24 percent t.s. with separate feed at a waste feed volume based on a 250,000 population.

110 MWe Pittsburgh 8 coal at 6 percent t.s. municipal sewage sludge to provide a combined slurry feed (coal, sorbent, and waste) at 75 percent t.s. with the slurry media supplied by the waste stream.

110 MWe Pittsburgh 8 coal and de-inking sludge de-watered to 40 percent total solids with separate feed at the 80:20 coal-to-waste ratio.

Performance Analysis Results

To further enhance the results of this study, performance comparisons were developed for the 1.5-Generation PFBC with and without co-firing of waste. The PFBC plant, as presented in Reference 2, is the basis for this study and was used to establish nominal performance without co-firing waste.

250 MWe Results. The performance for the 250 MWe PFBC plant without co-firing is shown in Table 6. Also shown are performance values for the same facility co-firing RDF as a slurry and in a dry form, co-firing municipal sewage sludge, and co-firing industrial de-inking sludge.

As indicated, an overall conversion efficiency of 41.38 percent was defined for the facility without co-firing of waste materials. With waste co-firing, conversion efficiencies decreased in the range of 1.0 percent to 2.7 percent depending on the waste co-fired and method of fuel handling. The lowest efficiency is attributable to the highest waste co-firing (industrial de-inking sludge), on a weight basis; thus a lower coal feed rate of approximately 13.6 percent.

In the comparison of alternative fuel and waste handling techniques, the pneumatic feed of coal, sorbent, and RD had a slightly higher overall conversion efficiency of 40.98 percent compared t, 40.39 percent for the slurried case. However, it was determined in follow-up work that the cost-of-electricity was also higher as a result of the required equipment capital cost for pneumatic feed.

110 MWe Results. The performance for the 110 MWe PFBC plant without co-firing is shown in Table 7. Performance values for the same facility co-firing RDF as a slurry, co-firing municipal sewage sludge, and co-firing industrial de-inking sludge are also presented for comparison.

Table 6. 250 MW PFBC Plant Performance Comparison

	W/O Waste Co-firing	RDF	(DRY) RDF	Municipal Sludge	De-Inking Sludge
ENERGY INPUT					
Coal Feed, lb/hr	128,861	118,313	117, 691	128,885	111,329
Coal HHV, Btu/lb	12,450	12,450	12,450	12,450	12,450
Natural Gas, lb/hr	19,257	19,635	19,251	19,553	19,710
Natural Gas HHV, Btu/lb	21,799	21,799	21,799	21,799	21,799
Waste Feed, lb/hr		29,578	28,367	6,076	69,581
Waste HHV, Btu/lb		4,103	4,103	804	3,166
Plant Energy Input, MW	595.181	592.713	588.256	596.628	596.710
ENERGY OUTPUT					
Gas Turbine, MW	87.501	98.882	89.139	96.908	103.182
Steam Turbine, MW	169.369	151.897	163.932	156.514	152.661
Auxiliaries, MW	10.590	11.407	12.030	10.166	10.583
Net Plant Power, MW	246.272	239.373	241.041	243.256	240.271
Thermal Efficiency, %	41.38	40.39	40.98	40.77	40.27
Net Heat Rate, (Btu/kWh)	8,246	8,449	8,327	8,369	8,474

As indicated, the overall conversion efficiency of 40.22 percent was defined for the facility without co-firing waste materials. With the additional waste co-firing, conversion efficiencies decreased in the range of 1.3 percent to 2 6 percent depending on the waste co-fired and method of fuel handling. As in the previous analysis, the lowest efficiency is attributable to the co-firing of industrial de-inking sludge.

The RDF co-fired analysis is based on a combined slurry feed system. As indicated, the overall conversion efficiency for the case of co-firing RDF was determined to be 39.29 percent, which represents a 2.3 percent decrease in thermal efficiency from the base case without co-firing.

Alternatives in co-firing municipal sewage sludge were investigated at the 110 MWe level. In the first analysis the coal was co-fired with municipal sewage sludge de-watered to 24 percent t.s. using a separate feed approach. A second analysis assumed a 6 percent t.s. municipal sewage sludge for use in providing a slurry media to transport the combined sludge, coal, and sorbent mixture at 75 percent t.s. This analysis was performed at the 110 MW nominal plant size to investigate the benefits of using the existing as-received municipal sludge as the transport media for the complete fuel, sorbent, and waste feedstock.

Table 7. 110 MW PFBC Plant Performance Comparison

	W/O Waste Co-firing	RDF	Municipal Sludge (24%)	Municipal Sludge (6%)	De-Inking Sludge
ENERGY INPUT					
Coal Feed, lb/hr	61,581	56,814	61,634	61,634	53,457
Coal HHV, Btu/lb	12,450	12,450	12,450	12,450	12,450
Natural Gas, lb/hr	7,781	7,853	7,902	7,890	7,880
Natural Gas HHV, Btu/lb	21,799	21,799	21,799	21,789	21,799
Waste Feed, lb/hr		14,200	6,076	24,306	33,410
Waste HHV, Btu/lb		4,103	804	201	3,166
Plant Energy Input, MW	275.345	274.550	276.844	276.767	276.434
ENERGY OUTPUT					
Gas Turbine, MW	38.107	43.760	43.491	44.025	44.735
Steam Turbine, MW	77.408	69.320	71.028	73.048	68.354
Auxiliaries, MW	4.774	5.204	4.608	7.039	4.806
Net Plant Power, MW	110.741	107.875	109.911	110.035	108.284
Thermal Efficiency, %	40.22	39.29	39.70	39.76	39.17
Net Heat Rate, (Btu/kWh)	8,484	8,684	8,594	8,582	8,711

As indicated in Table 7, there is no significant performance difference in the combined slurry approach over separate feed. However, a follow-up economic analysis indicated a savings in capital cost and lower cost-of-electricity with this approach. However, by combining the fuel, sorbent, and waste fuel streams, process control and combustor stability may be affected. Further data and analysis of the PFBC combustion parameters is required before accepting the benefits of the combined fuel feed approach.

FUTURE WORK

This study's objective was to investigate co-firing a pressurized fluidized-bed combustor with coal and refuse-derived fuel and/or sludges for the production of electricity and the efficient disposal of waste. Performance evaluation of the PFBC power plant co-fired with RDF and/or sludges showed only slightly lower overall thermal efficiency than similar sized plants without waste co-firing. Major contributors to the slightly lower performance include the waste material preparation and feed systems, and the additional water to support slurry feed of both the coal/sorbent and waste feedstock.

The results also indicate that there are no technology barriers to the co-firing of waste materials with coal in a PFBC power plant. The potential to produce cost-competitive electrical power and support environmentally acceptable waste disposal exists with this approach. However, as part of technology development, there remain several design and operational areas requiring data and verification before this concept can realize commercial acceptance.

Throughout the analysis, key issues concerning waste material preparation and feed, PFBC operation, plant emissions, and regulations were identified and addressed to the limits of available data. It is important to note that presently there are no known PFBC facilities co-firing coal and waste materials. Available information and performance data is limited to utility and municipal-owned facilities co-firing waste in AFBCs and private and government-funded research and development programs in PFBCs. Correlation of this data is difficult due primarily to the differences in operational parameters, combustion kinetics, and particulate removal temperature profiles. However, data on air/fuel distribution, primary emissions, and in-bed gas residence lend confidence to the use of existing AFBC operational information.

Specific R&D needs are listed below as major challenges.

Feeding waste materials against pressure using either dry feeders or slurry pumps,

waste material feed point spacing and location,

solids handling that includes circulating material and fly ash,

removal of tramp metal and other non-combustible material from the bed when feeding RDF,

corrosion effect of chlorine in waste materials,

levels of trace elements (organics and metals) in the gas and ash streams, and

storage of municipal sewage sludge and RDF at the power plant site.

In summary, the key issues for co-firing are feeding waste materials against system pressures (solids handling), materials concerns due to the addition of potentially corrosive constituents, and envi-

ronmental impact of solid wastes and gaseous emissions. In order to address these issues, pilot-scale testing co-firing waste materials should be performed and the results used to predict commercial-scale performance. The testing should be performed in a facility of adequate size so that commercially representative fuel feed sizes and gas residence times can be evaluated.

REFERENCES

1. Franklin, W.E. and Franklin, M.A. "Putting the Crusade into Perspective" EPA Journal, Volume 18, No. 3 July/August 1992.

2. Gilbert/Commonwealth Report No. 2985, Conceptual Design and Optimization of a 1-1/2 Generation PFBC Plant, Draft Report, September 1993.