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CONTINUING DEVELOPMENT OF REGENERABLE SORBENTS FOR FLUIDIZED BED COMBUSTION

Semiannual Technical Progress Report No. 2, April 1–September 30, 1980

By
C. D. Kalfadelis

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Exxon Research and Engineering Company
Linden, New Jersey

U. S. DEPARTMENT OF ENERGY

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Prepared Under Contract No. DE-AC21-79ET15166

for

Department of Energy

Morgantown Energy Research Center

By

C. D. Kalfadelis

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ABSTRACT

During the period April-September, our efforts were directed primarily to preparation for and/the initial operation of the laboratory-scale hot fluidized bed test system (LSHFB).

The initial test sequence in the LSHFB system was performed with a fixed-bed of 100 grams of barium titanate synthetic sorbent. The sorbent bed was alternately sulfated and regenerated five times. Sulfation was accomplished at 900°C, with a synthetic flue gas mixture comprising 10.1% Cu_2 , 4.95% O_2 , 0.2435% SO_2 and 84.7% N_2 . Regeneration was performed at 1025°C with a gas containing 8.0% CO and 92.0% N_2 .

After an initial drop in sulfation performance after the first sulfation/regeneration cycle, performance held steady, or was shown to be improving, during the succeeding four cycles.

Although the initial operation of this system proceeded relatively smoothly, the reactor was found to have been irreparably damaged by the end of the initial test sequence. A new reactor was subsequently designed, fabricated, and installed in the unit.

Concurrently, sorbent pellet preparation by extrusion was investigated in the Catalyst Preparation Facility at the Baton Rouge Laboratory of Exxon Research and Engineering Company. Preparation of sorbent pellets for use in the LSHFB operation was continued on a laboratory-scale at Linden throughout the reporting period.

Cost and time estimates were prepared for operation of the bench-scale fluidized bed coal combustion and regeneration facilities, including preparation of the requisite volumes of synthetic sorbent pellets needed for that program.

The status of these operations and our projected cost estimate were reviewed with the DOE Project Manager during an onsite visit September 10.

1. INTRODUCTION

Fluidized bed combustion (FBC) may be the way to burn high-sulfur coals in the steam boilers of power plants to achieve environmentally acceptable flue gas emissions at lower costs than competitive technologies. A practical FBC system will require a low-cost sorbent (bed material), resistant to attrition at the conditions of the combustion, which may be repeatedly regenerated to minimize both the rates at which new sorbent must be added, and waste sorbent removed, from the system. Limestone and dolomite have been the principal sorbent materials used to date, but limitations in attrition-resistance and regenerability have been encountered with these substances.

This project is concerned with the continuing development of superior sorbents whose use as sulfur-capture agents in coal-fired FBC boilers will prove cost-effective. Candidate sorbents include calcium aluminate cements (CAC); and formulations of barium and calcium titanates with bentonite clays. The research consists of the following principal tasks:

1. Design and fabrication of a laboratory-scale, fluidized-bed system which may be used to simulate large-scale sorption and desorption performance.
2. Experimental preparation of pellets of the candidate sorbents directed toward optimization of the attrition-resistance and sorption properties determined in the laboratory-scale system.
3. Preparation of optimized sorbent pellet formulations and large-scale testing in an existing pilot-scale, coal-fired fluidized-bed combustor.
4. Economic assessment projected for full-scale systems based on pilot-scale results.

2. WORK PROGRESS

2.1 PRELIMINARY GROUNDWORK FOR LSHFB OPERATIONS

1. Final Pre-operational Safety Review Items

As previously recorded, the final pre-operational safety review of the laboratory-scale hot fluidized bed (LSHFB) pilot plant by an in-house (Exxon) review panel was successfully accomplished. Check items designated by the review panel required only minor additional mechanical revision. Reference should be made to the revised flow plan (Drawing No. 2144-1-C) for the LSHFB system included in the Appendix of our Technical Progress Report for the period January 1, 1980, to March 31, 1980, for details of the operating system.

Most of the safety review check items involved unit-associated "software," including appropriate labelling at the supply gas manifolds, delivery of a marked-up check list, delivery of a marked-up flow plan showing all installed modifications, and the labelling of all valves, lines, and gages. In addition, the initial setting of the velocity-actuated check valves in the incoming gas lines, filling of the effluent gas scrubber, and extension of the unit's thermocouple leads to a panel-mounted temperature recorder were accomplished.

2. Pressure Testing and Calibrations

The unit's inlet gas rotameters were calibrated with nitrogen using a wet-test meter. Figure 1 shows the calibration curve for the inlet sulfating gas flow rotameter.

The entire unit was pressure-tested with nitrogen, and all fittings and components were verified to be gas-tight. The reactor bottom flange was found to be especially difficult to seal.

Initial attempts to calibrate the duPont Model 400 Low-SO₂-Level analyzer were unsuccessful. It was found not possible to flow sufficient gas from our unit to actuate this instrument without exceeding the set points of the pressure relief devices installed for use with our quartz reactor.

As previously indicated, the original design concept for the LSHFB test system incorporated a quartz reactor. Quartz reactor tubes were ordered, and a quartz reactor was fabricated onsite. Moreover, the operating system otherwise was designed around the quartz reactor.

Our subsequent adverse experience with the quartz tubes employed in our sorbent pellet calcination furnace, however, caused

us to have constructed also a metallic reactor as the principal operating component of the LSHFB system. As previously described, the metallic reactor (see Drawing Number 2144-2-D, attached to previous Technical Progress Report, and reproduced in the Appendix to this report) was fabricated of Rolled Alloys, Inc. high-temperature alloy RA-330. RA-330 was designated for this service based on an exhaustive survey of available alloys which might withstand repeated cycling to temperatures of about 1000-1100°C. RA-330 is an austenitic, non-hardenable heat- and corrosion-resistant alloy which possesses good high-temperature strength, oxidation and carbonization resistance to 1200°C (2200°F), and whose properties are enhanced by a 1.25 wt.% silicon content. It is immune to sigma phase formation at all sigma phase forming temperatures. Its nominal composition is 19-35-43-1.5-1.25 (Cr-Ni-Fe-Mn-Si).

The metallic tubular reactor was constructed of a section of RA-330 3/4-inch IPS pipe; and the integral preheat coil was fabricated from a length of RA-330 1/8-inch IPS pipe.

Our intention thereafter was to retain the quartz reactor, and the system's capability to operate with a quartz reactor, should we later deem it advisable to perform experiments of a calibration nature in a non-metallic, or totally inert, system.

Several days were required to track down and rectify wiring errors made while adapting the duPont 400 Analyzer for our unit. During this time, a number of piping changes were made also to reduce the pressure drop in the analyzer inlet gas line. It was eventually possible to achieve satisfactory performance.

Similar difficulties were incurred with the CO analyzer, which was wired into our system to serve as the actuating device for the CO alarm specified by the safety review board. In this case, a replacement chopper belt for the Beckman Model 315A IR CO Analyzer had to be acquired and installed to effect repair of the analyzer; and, again, piping changes were required to get sufficient gas flow to the instrument.

A series of temperature profiles were run with the (empty) reactor installed in position in the electric furnace. It was ascertained that the maximum reactor temperature which could be achieved was about 1125°C (2057°F). The furnace required about 140 minutes to achieve steady-state thermal input to the reactor at the maximum temperature, when fired from room temperature (23°C or 73°F), with nitrogen flowing through the reactor at a superficial velocity of 0.2 meters/second (0.66 feet/second). The design temperature for this system had been specified as 1200°C (2192°F) with nitrogen flowing through the system at a superficial velocity of 1.524 meters/second (5 feet/second).

3. Unit Completion Documented

A series of photographs were taken of the completed unit. These are attached as Appendix Figures 1-3.

2.2 INITIAL LSHFB UNIT SORBENT TEST SEQUENCE

1. Charge Sequence

A 100-gram charge of barium titanate synthetic sorbent prepared in this laboratory was charged to the LSHFB reactor initially on June 3. The sorbent charge was fixed in position in the bottom third of the reactor vessel by virtue of a perforated metallic disk (RA-330 alloy) placed on top of the sorbent charge. The metallic disk had been drilled with thirty-two 3/64-inch holes, and was attached to a Type 316 SS metal positioning rod, which extended internally from the top of the sorbent charge to the underside of the reactor top flange (see LSHFB Assembly and Details, Drawing No. 2144-2-D in the Appendix). The metal positioning rod terminated at a second perforated disk, identical to the first, set in a recess beneath the reactor's top closure flange. The positioning rod was threaded at both ends to allow adjustment for variation in the height of the sorbent charge.

In this case the sorbent charge extended 0.184 meters above the bottom flange. Two thermocouples had been positioned internally, one at a distance of about 0.09 meters above the bottom flange (or at the approximate center of the fixed sorbent charge) and the other at a distance of 0.178 meters (or at about the top of the sorbent charge, and the mid-point in the heated portion of the reactor.)

After reassembly and installation of the reactor, the entire system was again pressure-tested with nitrogen. A very small nitrogen flow was started through the reactor, and the reactor was brought to 200°C. The system was maintained at these conditions overnight (~16 hours).

2. Reactor Temperature Profiles

A sequence of experiments were made on June 4 to determine the thermal limitations on our system with synthetic sorbent in place, and with the sorbent bed fixed in position.

With the reaction system initially at 200°C, and with the ambient room temperature at 23°C, almost exactly one hour was required to achieve isothermal conditions at a reaction temperature of 700°C, while flowing 0.88 standard liters per minute of nitrogen through the reactor.

About 40 additional minutes were required thereafter to achieve isothermal conditions at 900°C.

And about 20 additional minutes were required to achieve steady-state at the maximum available reactor temperature of 1017°C.

These data are plotted in Figure 2. At steady-state, a temperature difference of about 100 Centigrade degrees was observed between a thermocouple placed on the outer skin of the reactor and the thermocouple located in the center of the fixed sorbent bed.

Additional experiments were then run with the electric furnace controller set at maximum (1199°C set point), in which the nitrogen flow through the sorbent bed was increased in stages from 0.88 standard liters per minute to 6.0 standard liters per minute. There was observed essentially no change in the steady-state temperatures indicated either by the reactor skin couple (~1120°C) or by the sorbent bed couple (~1020°C). The highest inlet flow corresponded to a superficial velocity through the reactor of 1.37 meters per second (4.5 feet per second).

The reactor was maintained at 900°C with a nitrogen input flow of about 1.0 standard liter per minute overnight (~16 hours).

3. First Sulfation/Regeneration Cycle

The reaction system furnace required only minor adjustment to achieve steady-state at a reaction bed temperature of 900°C when the inlet nitrogen flow rate was increased from 1.0 standard liter per minute to 8.0 standard liters per minute (corresponding to a superficial velocity of 1.66 meters per second, or 5.4 feet per second.)

The concentration of SO₂ in the reactor off-gas as a function of time is plotted in Figure 3, 4, and 5 for this initial test sequence. Note that concentrations up to 3000 ppm (volume) were measured by a DuPont Model 400 SO₂ Analyzer, and that concentrations higher than this value were indicated by an IR Industries device. The IR device, however, is not accurate below about 0.5 percent (volume), so that reported concentrations in the range 2500-6500 ppm may carry considerable error.

The first sulfation cycle was begun by switching from nitrogen flow, while at steady-state at 900°C, to a gas comprising 10.1 per cent CO₂, 4.95 per cent O₂, and 2435 ppm SO₂ in nitrogen. Inlet flow rate was maintained at 8.0 standard liters per minute. The SO₂ concentration in the gas flowing from the reactor increased from zero to 2175 ppm over a time period of 210 minutes. Reactor total pressure was constant at 22.5 kPa throughout.

At the end of this period, the inlet gas was again switched to nitrogen, and the inlet flow rate was reduced to about 1.0 standard liter per minute. The reactor furnace controller was reset to maximum, and the system then required 30 minutes to achieve steady-state at a reaction bed temperature of 1024°C.

The system was permitted to operate in this condition for an additional 30 minutes, to ensure that the reactor was, in fact, at the highest operating temperature attainable.

As the reactor temperature had been increasing from 900°C to 1024°C, the SO₂ concentration in the nitrogen stream leaving the reactor had also increased, from about 0.22 per cent, to a peak of about 0.56 per cent at 30 minutes, and had then degraded, with the

reactor at a constant temperature of 1024°C, to a level of about 0.30 per cent, 30 minutes later. That is, SO₂ was being removed from the bed by the action of the flowing nitrogen, albeit at a low flow rate, as the sorbent bed was being heated.

The intention then was to switch to the regeneration gas, comprising 5.03 per cent CO in nitrogen. However, the gas mixture which was being used for calibration of the CO alarm was inadvertently switched in instead. The calibration gas mixture comprised 1520 ppm CO and 17.5 per cent CO₂ in nitrogen, and was fed into the reactor at a rate of 8.0 standard liters per minute for a period of about 5 minutes, before the error was determined. During this period, the SO₂ concentration in the effluent gas, after initially exhibiting a very sharp peak rise to about 1.1 per cent, was holding at about 0.6 per cent.

The system was switched back to pure nitrogen flow for 10 minutes, while the proper gas cylinder was being tied in. The nitrogen flow rate was set at 1.0 standard liter per minute during this time, and the SO₂ concentration in the reactor off-gas dropped to about 0.14 per cent.

At a total time of 285 minutes, the proper regeneration gas (5.03 per cent CO in nitrogen) was switched into the unit, at an inlet flow rate of 8.0 standard liters per minute. Again, there was an immediate sharp rise in effluent gas SO₂ content, to a peak of about 1.13 per cent. There was, thereafter, over a period of about fifteen minutes, an almost straight-line drop-off to a level of about 0.21 per cent SO₂, which level then degraded very slowly to about 0.17 per cent at a total time of 330 minutes. At this point the regeneration gas mixture was switched out, nitrogen flow was reinstituted at a low rate, and the reactor furnace was reset downward to bring the sorbent bed back to 900°C.

The system was left at these conditions overnight (sixteen hours).

4. Second Sulfation/Regeneration Cycle

The second sulfation cycle on the fixed barium titanate sorbent bed was run June 6, using the same sulfation gas mixture which had been used in the first cycle. Flow rates, system pressures, and system temperatures were essentially identical with those observed in the first cycle. However, it required only ninety minutes for the SO₂ concentration in the effluent gas to rise to a level of 2145 ppm, i.e., sulfation was accomplished in less than half the time required in the first cycle.

It was noted that the SO₂ concentration in the reactor off-gas quickly rose to a high value (about 1.17 per cent) as the sulfation gas (containing 2435 ppm SO₂ and 4.95 per cent oxygen) was started through the system. Within five minutes, the SO₂ level had dropped back to about 1120 ppm, however. There was also observed an accompanying

thermal effect, with the reactor bed temperature appearing to rise very quickly, and then to quickly subside, as the SO₂ emission level dropped. Although not recorded, it appeared the temperature peak may have been as high as 100 Centigrade degrees (above the 900°C starting bed temperature), and the bed temperature may have dipped 10-20 Centigrade degrees below the 900°C datum on the downswing, before the reactor furnace served to reestablish a constant temperature.

At the ninety minute mark, at the termination of sulfation, a low nitrogen flow was again established through the reactor, and the reactor furnace controller was set to maximum to bring the sorbent bed up to regeneration temperature.

The sorbent bed temperature had equilibrated at 1024°C within thirty minutes. During this thirty minute interval, the SO₂ level in the gas passing from the sorbent bed had firstly dropped sharply from 2145 ppm to about 1050 ppm, and had then risen slowly to a peak of about 1480 ppm at the 105 minute mark, by which time the maximum sorbent bed temperature had been achieved. Thereafter, at a constant bed temperature of about 1020°C, the SO₂ level in the effluent gas had dropped off, getting down to 420 ppm at the 120 minute mark.

At the 120 minute mark, a new regeneration gas mixture, comprising 8.0 per cent CO in nitrogen, was started through the unit. In this regeneration cycle, however, the regeneration gas inlet flow rate was set at 0.62 standard liters per minute, in order to attempt to demonstrate a higher SO₂ effluent level than had been observed at the high inlet flow rate used in the first cycle.

As the regeneration gas was switched into the unit, the SO₂ level in the gas passing through the sorbent bed rose to 0.50 per cent. No peak in level was observed at all. Instead the level held essentially constant, rising very slowly to a maximum of about 0.53 per cent forty minutes later, at minute 160, and then slowly dropping again to 0.50 per cent by minute 180.

Regeneration gas flow was continued another hour, to minute 240, by which time the SO₂ level in the sorbent bed off-gas had degraded only to about 0.39 per cent. Sorbent bed temperature had been holding at about 1019°C throughout the regeneration, or was about 5 Centigrade degrees lower than the maximum bed temperature achievable while flowing only nitrogen through the bed.

5. Third Sulfation/Regeneration Cycle

At minute 240, a low nitrogen flow replaced the regeneration gas mixture, as the reactor furnace controller was reset to cool the sorbent bed down to 900°C. A steady-state sorbent bed temperature of 900°C was achieved by minute 255, at which point the sulfation gas mixture was restarted through the system.

During the fifteen minute nitrogen-flow period, SO₂ level in the reactor off-gas was essentially constant at a level of about 0.12 per cent.

The sulfation gas flow rate was set at 8.0 standard liters per minute, identical with the rates used in the two previous sulfations. Again, as sulfation gas was switched in, a sharp temperature rise was observed, in this case reaching at least 45 Centigrade degrees above the 900°C starting datum. The SO₂ level in the reactor off-gas also peaked sharply, to about 0.60 per cent, before falling off to less than 480 ppm, as the reactor temperature re-equilibrated.

In this third cycle, about 96 minutes of sulfation gas flow was required to achieve a level of 2145 ppm SO₂ in the reactor off-gas, effectively duplicating the observations taken in the second sulfation cycle.

At minute 351, sulfation gas flow was terminated, a low nitrogen flow was established, and the reactor furnace controller was reset to maximum. SO₂ effluent level dropped immediately to a low level of about 960 ppm, then rose to a peak of about 1390 ppm some ten minutes later, as the sorbent bed temperature reached its maximum level of 1023°C. By minute 370, five minutes later, the SO₂ level had receded to about 1170 ppm.

Regeneration gas mixture, comprising 8.0 per cent CO in nitrogen, was started through the unit at minute 370 at a flow rate of 0.62 standard liters per minute. Within four minutes, the SO₂ level in the effluent gas had peaked at 1.54 per cent. The peak was well defined, as the SO₂ level thereafter receded smoothly to about 0.72 per cent eight minutes after the peak. By minute 390, the SO₂ level had dropped to 0.60 per cent. And a half-hour later, at minute 420, the level had receded to 0.34 per cent.

At this point, the regeneration gas flow was terminated, and a very low flow of nitrogen was established through the reactor. The reactor furnace controller was reset downward to 750°C. The system was maintained at these conditions over the weekend (approximately 64 hours).

6. Fourth Sulfation/Regeneration Cycle

The fourth sulfation cycle on the fixed barium titanate sorbent bed was run on June 9, using the same sulfation gas mixture which had been used in the previous cycles. Flow rate was again set at 8.0 standard liters per minute.

Only a slight bed temperature rise accompanied the introduction of the sulfation gas mixture in this case, and the bed temperature was in control at 900°C again within five minutes.

A sulfation time of ninety minutes was required to reach an SO₂ level in the reactor effluent gas of 2175 ppm (inlet gas SO₂ concentration was 2435 ppm). At the ninety minute point, a low flow rate of nitrogen was substituted for the sulfation gas, and the reactor furnace controller was reset to maximum to prepare for regeneration.

SO₂ level in the effluent gas dropped immediately to about 1240 ppm as the nitrogen was introduced, and then rose to a peak of about 1750 ppm fifteen minutes later, as the maximum reactor bed temperature of 1025°C was reached. At minute 120, with the reactor bed

temperature controlling at 1024°C, the regeneration gas mixture was introduced for the fourth regeneration cycle.

The regeneration gas mixture used was again 8.0 per cent CO in nitrogen, but inlet flow rate for this cycle was increased slightly to 0.87 standard liters per minute (from the previously used 0.62 standard liters per minute). The SO₂ level in the effluent gas rose immediately to a smooth peak of 1.85 per cent four minutes after regeneration gas introduction.

By ten minutes after the introduction of regenerating gas, the reactor effluent SO₂ level had fallen smoothly to a level of about 1.12 per cent. It was observed that the sorbent bed temperature had dropped, as the SO₂ level came off the peak, from a high of 1023°C at the peak, to about 1018°C six minutes later.

The SO₂ level then plateaued at about 1.1 per cent for some five minutes, during which time the sorbent bed temperature slowly increased. At minute 131 (21 minutes after start of regeneration) the sorbent bed temperature had increased to 1024°C, and the SO₂ level had risen to 1.27 per cent. At minute 132.5, a second SO₂ peak of 1.32 per cent was observed, as sorbent bed temperature again fell off several degrees.

The SO₂ level, following the second peak, dropped linearly, being 0.54 per cent at minute 150, 0.47 per cent at minute 180, and 0.45 per cent at minute 210, by which time it had again plateaued. Regeneration was terminated at minute 240, with the reactor effluent SO₂ level at 0.44 per cent, and the sorbent bed temperature at 1021°C.

7. Fifth Sulfation/Regeneration Cycle

SO₂ level dropped immediately to about 1250 ppm as nitrogen was again introduced at low rate, while the sorbent bed was cooled to 900°C to prepare for sulfation. The same sulfation gas mixture was reintroduced at 8.0 standard liters per minute at minute 256.

In this case, sulfation appeared to proceed more slowly than in the preceding three cycles. At 104 minutes after the commencement of sulfation, reactor effluent SO₂ level had reached only to 2010 ppm.

Again, nitrogen was switched in at minute 360 as the reactor furnace controller was set to maximum. SO₂ in the reactor effluent dropped immediately to about 1190 ppm. Again, this level then rose to about 1830 ppm fifteen minutes later, as the maximum sorbent bed temperature was reached. At minute 380, as regeneration gas was introduced, the SO₂ level was back to 1670 ppm, and the sorbent bed temperature was holding at 1025°C.

Identical regeneration gas and regeneration conditions were invoked in this cycle, as for the cycle preceding. The SO₂ level described a curve almost identical with that observed in the preceding cycle. A peak level of 1.84 per cent was observed four minutes after the onset of regeneration.

Again, a plateau at 1.25 per cent SO_2 occurred, beginning at minute 390. Reactor bed temperature again showed a decrease after the initial peak, and was increasing during the plateau. At minute 402, SO_2 level was still at 1.25 per cent, and reactor temperature was back to 1026°C . A slight second peak of 1.28 per cent was observed at minute 404, after which a straight-line drop-off again occurred to a plateau level of about 0.68 per cent at minute 420. At minute 450, the run was terminated with the SO_2 level at 0.60 per cent. By this time all thermocouples in our system had failed.

8. Discussion of Test Results

The sulfation performance of the 100-gram bed of barium titanate sorbent in this initial test sequence of five alternate sulfation/regeneration cycles is summarized in Table 1. At 900°C , at a constant incoming gas flow rate (8 SLM), with a constant SO_2 concentration (2435 ppm) throughout, the time required for the SO_2 level in the reactor off-gas to reach a value approaching 90% of that in the incoming gas, dropped to half of that demonstrated in the first cycle for each of the succeeding four cycles. Nonetheless, numerical integration of the concentration measurement would indicate that the fraction of the total incoming sulfur retained by the bed remained constant, or was increasing through the test sequence.

Because sulfations were not carried uniformly to a precise SO_2 level for one reason or another during the test sequence, our measured values one hour after the commencement of each sulfation cycle are also included on Table 1. Again, after the dramatic drop in performance from the first to the second cycle, it would appear that the bed's performance was improving steadily.

It was determined (see below) that considerable gas leakage was occurring throughout this test sequence from both the bottom and top flanges of the reactor. Nevertheless, sulfur balance calculations were carried through.

The sulfur balance is summarized in Table 2. The quantity of sulfur dioxide calculated to be on the sorbent bed at the termination of a sulfation cycle is developed as the difference between the total sulfur in the incoming gas and the quantity of sulfur measured to be passing through the reactor. In this case, the quantity of gas incoming would be lower than that deduced from the incoming gas rotameter reading by virtue of the gas leaking from the reactor bottom flange.

The quantity of sulfur passing through the reactor requires numerical integration of the areas under the SO_2 concentration curves measured by our analyzers, as well as the assumption of zero leakage at the top flange. It can be seen that the combined error could be large, depending on the leak at the top flange.

TABLE 1

SULFATION PERFORMANCE
INITIAL TEST SEQUENCE

100-Gram Fixed Barium Titanate Bed @ 900°C
2435 PPM SO₂ in Sulfation Gas

Cycle	Total Sulfation Time (Min.)	PPM SO ₂ In Reactor Off-Gas	Percent Incoming Sulfur Retained on Bed	At Time (Min.)	PPM SO ₂ in Reactor Off-Gas	Percent Incoming Sulfur Retained
1	210	2175	34.4	60	1500	71.3
2	90	2145	36.2	60	1980	46.6
3	96	2145	32.2	60	1835	55.7
4	90	2175	41.6	60	1980	55.0
5	104	2010	41.9	60	1725	58.2

TABLE 2**SULFUR BALANCES
INITIAL TEST SEQUENCE****100-Gm Fixed Barium Titanate Bed**

Cycle	Percent Incoming Sulfur Retained	SO₂ on Bed After Sulfation (Gm-Mol)	SO₂ Removed By Flowing Nitrogen (Gm-Mol)	SO₂ on Bed Before Regeneration (Gm-Mol)	Calculated SO₂ Removed During Regen. (Gm-Mol)	Calculated Percent SO₂ Removed During Regeneration
1	34.42	0.058995	0.048141	0.010854	0.116993	1077.8
2	36.17	0.026649	0.000929	0.025641	0.091467	356.7
3	32.15	0.025189	0.001562	0.023628	0.039672	167.9
4	41.58	0.030541	0.003668	0.026873	0.297834	1108.3
5	41.92	0.035583	0.003610	0.031973	0.182392	570.5

Another complicating factor is the sulfur we measured to be stripped from the bed during periods of nitrogen flow between sulfation and regeneration cycles, as reactor temperature was modified for the succeeding operation. The observed thermal desulfurization of the synthetic titanate sorbent between the temperatures of sulfation (900°C) and regeneration (1025°C) is consistent with our expectation that much higher SO₂ partial pressures may exist over the sulfated titanates relative to those for ordinary sulfates (limestone).

A probable cause for the high SO₂ peaks, and attendant temperature excursions, observed immediately on introduction of sulfation gas in some of our runs is presumed to have been the result of oxidation of sulfide by the oxygen (4.95%) in our synthetic flue gas sulfating mixture. These peaks were too sharp to be measured precisely by our instrumentation, however, and were neglected completely in our sulfur balance calculations.

Our overall sulfur balances were made assuming a perfect system, with no leaks, the tacit assumption that SO₂ was reacting only with the available barium in the sorbent bed, neglecting the high SO₂ emissions associated with the onset of sulfation, and assuming complete accuracy both in our SO₂ measurements and in the subsequent time integrations of our analyzer charts. As shown in Table 2, the cumulative deviation from the ideal system utilized for calculation purposes was large.

Of the available barium in the sorbent bed for this test sequence, 13.7% was calculated to have been utilized after the first sulfation. The utilization dropped to 6.2% for the second sulfation, to 5.9% for the third, and then increased to 7.1% for the fourth, and to 8.3% for the fifth cycle.

9. Test Sequence Aftermath

It had been found necessary to operate the system at a total pressure of about 30 kPa to obtain sufficient sample gas flow to the duPont low-range SO₂ analyzer, some 70 feet removed from the unit. By the second cycle in the test sequence, it began to be obvious that a substantial amount of gas was leaking from both the top and bottom flanges of the reactor, which were at high temperature within the electrical furnace housing the reactor. By the fifth cycle, operations had become somewhat erratic. Three of four internal thermocouples had failed, and gas was leaking very badly.

Considerable corrosion was found to have occurred when the reactor was opened after this sequence. In fact, there was considerable difficulty disassembling the system to begin with. (See Appendix for photographs of corrosion of some of reactor internals.)

In the next few weeks, considerable effort was expended attempting to modify the flange ends to effect closure at system temperatures. No suitable technique for maintaining a seal at the high temperature was evolved. Accordingly, emphasis was directed to total redesign

of the system. Although a radical shift, as to an all-refractory reactor design, appeared indicated, further slippage in the experimental program due to a long delivery, or to additional detailed design work could not be considered. A modification of the original design, which placed the reactor ends outside the heated zone, was therefore settled on as the most expeditious way to reestablish sorbent pellet testing.

Drawings of the original, and of the modified (second) LSHFB reactors are appended to this report. The second reactor was fabricated and installed in the unit, and was being readied for operation in September.

2.3 SORBENT PELLETT PREPARATION

1. Sorbent Preparation-ERDL

It was realized from our initial laboratory work that substantial scale-up of equipment and operational effort would be required to produce sorbent pellets, according to any of our five basic formulas, in the hundred-pound lots which might be required in the operation of our bench-scale, pressurized, fluidized-bed coal combustor. It was not clear that the original cost and manpower plans had fully considered the impact of this large-scale pellet production.

The quantities of sorbent pellets required for our laboratory-scale (LSHFB) testing program (ten-pound lots), we considered, might be produced in our laboratory by the same equipment and procedures used to produce the very small quantities of pellets used in the TGA work. Such production, however, would prove extremely tedious and time-consuming.

The Catalyst Preparation Facility at ERDL is a special adjunct to that laboratory which undertakes the preparation of developmental quantities of new catalysts. The facility is extremely well-equipped for such manufacture, including a wide variety of mixing and grinding equipment, facilities for extrusion, granulation, and pelletizing, automatically-controlled conditioning and drying ovens, and facilities for calcination and classification of catalyst pellets.

We approached the Commercial Catalyst Development Coordinator at ERDL, Dr. A. H. Neal, relative to our requirements. Dr. Neal, along with the director of the Catalyst Preparation Facility, Mr. F. M. Long, agreed to attempt to produce small quantities of pellets according to our formulation parameters, by way of developing an estimate for the production of the hundred-pound lots we would ultimately require.

In March, 1980, we shipped raw materials required to produce 5-10 pounds of each of our formulations to Baton Rouge. Simultaneously, we were modifying our laboratory equipment and procedures to increase our local rate of pellet production to meet a projected target use in the LSHFB at Linden. A special bottleneck was the electric furnace used for high-temperature (1100°C) calcination, which could accept no more than about 100 grams of pellets per day.

By September, the Catalyst Preparation Facility had produced small quantities of each of our five basic formulations by extrusion. The cement preparations proved especially difficult to extrude, but the titanate formulations extruded readily.

Based on this preliminary effort, Baton Rouge produced an estimate for preparation of larger quantities of sorbent pellets for our program. The estimate letter is appended to this report (F. M. Long to CDK, September 5, 1980).

2.4 COST PLANS AND SCHEDULES

Two major cost and time estimation efforts were completed in late August, relevant to the future program. Because operating time on the bench batch fluidized bed coal combustion system must be shared with other operating groups (also under contract to DOE), it was necessary to prepare a reasonable schedule for such future shared operations. Simultaneously, costs and time required to refurbish and equip the bench regenerator were estimated separately, since this system is not required by other operating groups, and such costs would accrue solely to our account.

The Catalyst Preparation Facility at Baton Rouge estimated costs and time schedules for production of 200-pound lots of test sorbent pellets (see above).

On the basis of the foregoing, and in view of progress on our laboratory and pilot-plant program to date, two separate cost plans were prepared for review with the Project Manager during his visit September 10.

It was our estimate (September, 1980) that we might have completed our original program of testing within the original time frame, or with only minor revision, but at a substantial overall estimated negative variance, at completion. Because preparation of the large batches of test sorbent would impact heavily on operations otherwise scheduled at the Catalyst Preparation Facility, it would have been necessary to commit that facility to such production at an early date to meet our time schedule.

2.5 PROJECT MANAGER'S VISIT

The DOE Project Manager, Mr. Dana Hewitt of METC, visited the Linden site September 10 to review the status of program studies. Participants in the discussions are listed in Table 1.

1. Operations Review

Dr. Henry Shaw began the discussions with a brief outline of program goals, and of our intended approach in the current program.

Dr. Lawrence Ruth next reviewed the work performed in the predecessor study, which laid the groundwork for the current program. During 1976-1978, an experimental program at EREC, funded by the National Science Foundation, and guided by the U.S. Department of Energy (formerly ERDA), sought to identify sorbent materials superior to naturally-occurring limestone and dolomite for the abstraction of sulfur from gases formed in the fluidized-bed combustion of sulfur-bearing coals.

Dr. Ruth outlined the conclusions of that study, and developed the incentives for larger-scale testing of promising materials which would permit a more accurate assessment of commercial potential.

Mr. Charles Kalfadelis then reviewed operations for the current program, and the cost and time schedule prepared for future work.

Ms. Leslie Goodwin, Engineering Consultant, reviewed the bench-scale fluidized bed combustor and regeneration systems, and of the cost and time schedules developed for that phase of our program.

TABLE 3

PARTICIPANTS IN DISCUSSIONS

PROJECT MANAGER'S VISIT TO EREC

September 10, 1980; Linden, N.J.

1. Dana Hewitt, DOE Project Manager
2. Henry Shaw, EREC Project Director
3. Charles D. Kalfadelis, EREC Principal Investigator
4. Lawrence Ruth, EREC Program Consultant
5. Leslie Goodwin, EREC Engineering Consultant
6. Francis Paciullo, EREC Senior Technician
7. John Fishwick, Technical Service Manager, Lone Star Lafarge, Inc.
8. Paul Ten Hoopen, Manager of Sales, Lone Star Lafarge, Inc.

3. WORK PLANNED FOR SEPTEMBER, 1980-MARCH, 1981

A second test sequence, using calcium aluminate cement sorbent pellets in a fluidized state is planned as the first test sequence in the modified (second) LSHFB reactor.

Cost plans will be revised to reflect a revised scope of work, and a new proposal will be submitted following the guidelines developed by MERC. Laboratory and pilot-plant effort will likewise be redirected to reflect planned revisions.

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Appendix Figure 1

Exxon Laboratory-Scale Hot Fluidized Bed Unit (LSHFB)

May, 1980

Appendix Figure 2

Exxon Laboratory-Scale Hot Fluidized Bed Unit (LSHFB)

May, 1980

Appendix Figure 3

Exxon Laboratory-Scale Hot Fluidized Bed Unit (LSHFB)

May, 1980

Appendix Figure 4

Type 316 SS Internal Reactor Bed Spacer Rod
After Initial Test Sequence, June, 1980

(Approx. 1/3 Size)

Appendix Figure 5

Corrosion Products from Type 316 SS
Internal Reactor Bed Spacer Rod After
Initial Test Sequence, June, 1980

(Approx. Full Scale)

10 LOWER GRID
MAT'L - 316 S.S. REQ'D - 1 PC.

11 BARRIER PLATE
MAT'L - 316 S.S. REQ'D - 1 PC.

13 BOTTOM CAP
MAT'L - 316 S.S. BLIND FLANGE, 150 LB.
REQ'D - 1 PC.

14 REACTOR FLANGE
MAT'L - 316 S.S., 3/4" SLIP-ON FLANGE
REQ'D - 2 PCS.

15 TOP CAP
MAT'L - 316 S.S. BLIND FLANGE, 150 LB.
REQ'D - 1 PC.

17 GASKET
MAT'L - 1/16" THK. COMPRESSED ASBESTOS (IN-5010)
REQ'D - 6 PCS.

16 ELBOW
MAT'L - RA-330 REQ'D - 1 PC.

WELD DETAIL
REACTOR BOTTOM

WELD DETAIL
REACTOR TOP

12 T.C. SLEEVE
MAT'L - 316 S.S. TUBE REQ'D - 2 PCS.

A-8

REFER TO DWG. 2144-2-D FOR OTHER DETAILS.

DATE	REVISION
	LAB SCALE HOT FLUID BED (LSHFB)
	REVISED REACTOR
	ASSY. & DETAILS
EXXON RESEARCH AND ENGINEERING COMPANY RESEARCH TECHNOLOGY SERVICES DIVISION LINDEN, N. J.	
SCALE FULL	PROJECT NO.
ENGR. C. KALPARELIS	DATE 7/1/80
DRAWN BY P. HARRINGTON	DATE 7/1/80
APPROVED/CHECKED BY	DATE
	2144-6-D