

FLUIDIZED BED COMBUSTION OF OIL SHALE

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ABSTRACT

Two sets of fluid bed combustion experiments have been conducted in which raw shale fines and a simulated low Btu off-gas were burned to produce steam for power generation. The results show that the shale fines and low Btu off-gas can be utilized for energy production, and further, the sulfur removal is effective and efficient. This process eliminates the need for H_2S removal and is not sensitive to small quantities of entrained liquids.

INTRODUCTION

The retorting of oil shale produces a gas which contains significant quantities of sulfur. The largest percentage of this sulfur is in the form of hydrogen sulfide (H_2S); however, measurable quantities of COS and CS_2 exist. The removal of the sulfur is necessary before any processing of the shale can proceed to demonstration or commercial scale. The removal of H_2S from a gas is certainly not new, and many processes exist to accomplish such removal. However, for most shales throughout the world (Morocco, Israel, Western U.S., etc.), the retort off-gas also contains significant amounts of carbon dioxide (CO_2). For the indirect process, this can amount to about 5 times as much CO_2 as H_2S , while for the direct process it amounts to 80 times as much. Since H_2S is an acid gas, as is H_2CO_3 , absorption of H_2S will result in absorption of the CO_2 . This could be a very costly process, making an amine type process unattractive.

The Stretford process has sufficient selectivity to absorb the H_2S in the presence of CO_2 ; however, it is sensitive to the presence of even small quantities of liquids. Recent tests of the Stretford at Occidental Petroleum's Logan Wash site and the Geokinetic test site have shown no better than 70% sulfur removal for an extended period of time (1). While these tests may not be conclusive, they are certainly indicative of a problem with what has been accepted as the "standard" for sulfur removal.

In another arena, significant test work and large-scale demonstration runs have been conducted on sulfur removal from coal-fired power plants using fluidized bed combustion of coal mixed with limestone. The typical limestone-to-coal ratio is 2 to 3.5, and results show 90-95% sulfur removal.

Since oil shale in the Western U.S., Morocco, Israel, and elsewhere in the world contains significant quantities of calcium and magnesium carbonate which decomposes to produce CaO and MgO , it has been assumed that spent shale could be used to absorb SO_2 . Tests have been conducted on such absorption capacity; however, until recently, the idea of using fluid bed combustion to remove the sulfur had not been tested. In addition, retorting processes such as Paraho, Union, Petrosix, Superior, etc., cannot utilize the fines. It was the opinion of some oil shale retorting technologists that discarding the fines was not practical, and that combustion of these fines might allow absorption of all the sulfur if the off-gas was combusted in a fluid bed combustor with the fine shale. The test of this concept is the subject of this paper.

DISCUSSION

A typical gas analysis (2) for indirect and direct processes is given for the Paraho process (Table 1). Note that the H_2S is shown as 0.3 vol % for the direct process and 3.7% for the indirect process. Although not shown, significant quantities of COS and CS_2 exist in this gas. These compounds are poisonous and constitute a health hazard as well as a pollution problem. If virtually all the H_2S were removed (99.5%), the total sulfur removal would be about 97%; thus, some 2-3% of the sulfur is in forms other than H_2S .

A typical Colorado or Utah oil shale analysis (3) is given as Tables 2 and 3, and shows the quantities of CaO and MgO present in such a shale. Also shown is the amount of Na and K in the shales. From Table 2, we note that the dolomite is the largest fraction of the inorganic portion of such a shale.

For a 27 gallon per ton shale, some 83% of the shale is in the form of inorganics.

Two sets of experiments were conducted for Magic Circle Energy Corp in support of their Cottonwood Wash project. The first set of experiments were conducted by Hazen Research using their 4" diameter bench scale unit. The purpose of the combustion testing program was to demonstrate the capability of burning the raw oil shale fines and waste product gas in a fluidized bed. Of special interest was the ability of the base metal oxides in the shale ash to capture the SO₂.

TABLE 1

PARAHO RETORT
TYPICAL GAS PROPERTIES
(Colorado oil shale)

ANALYSIS Dry Gas-vol %	RETORT	
	Direct	Indirect
H ₂	5.5	23.0
N ₂	61.0	0.4
O ₂	-0-	-0-
CO	2.9	2.7
CH ₄	2.4	30.2
CO ₂	24.2	14.8
C ₂ H ₄	0.7	11.3
C ₂ H ₆	0.6	5.6
C ₃	0.6	3.0
C ₄	0.6	0.8
C ₅ ⁺	0.6	4.4
H ₂ S	0.3	2.7
NH ₃	0.6	1.1
TOTAL	100.0	100.0
Water vapor-vol%	17.5	28.8
Heating value-BTU/SCF (DRY)	140	1036

TABLE 2

Average Mineral Composition of Mahogany
Zone Shale, Colorado and Utah

Mineral	Chemical Formula	Composition wt. percent
Dolomite	(Mg,Fe)Ca(CO ₃) ₂	32
Calcite	CaCO ₃	16
Quartz	SiO ₂	15
Illite	KAl ₂ (AlSi ₃)O ₁₀ (OH) ₂	19
Albite	NaAlSi ₃ O ₈	10
K feldspar	KAlSi ₃ O ₈	6
Pyrite	FeS ₂	1
Analcime	NaAlSiO ₄ ·2.5H ₂ O	1
TOTAL		100

TABLE 3

Chemical Analyses of the Inorganic
Mineral Portions of 16 Samples
of 10.5 to 75.0 gal/ton Oil Shale

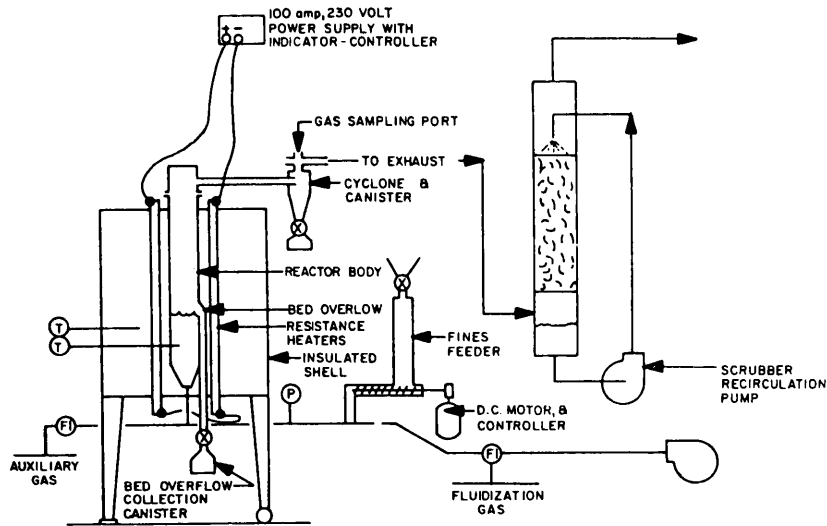
Chemical Component, %	Average
SiO ₂	27.6
Fe ₂ O ₃	2.9
Al ₂ O ₃	7.7
CaO	13.9
MgO	5.9
SO ₃	1.4
Na ₂ O	2.1
K ₂	1.5
Sub-Total	63.0
Mineral CO ₂ in raw shale	17.4
Mineral CO ₂ in spent shale calculated to raw shale	17.0
Mineral CO ₂ in raw shale that was volatilized by the assay	2.3
TOTAL	99.7

The bench scale study and combustion testing of the raw oil shale and waste product gas were conducted in a 4" diameter bench scale fluid-bed reactor. The fluidizing gas was composed of air to effect combustion and a synthetic waste product gas. The synthetic gas stream was made by metering specified volumetric rates of each component to form a total synthetic waste product gas with a composition approximately that expected from an oil shale retort. The fluidizing gas, air plus synthetic product gas, was introduced through the cone at the base of the reactor (Figure 1). A variable speed screw feeder dropped controlled amounts of the oil shale into the fluidizing gas line to be transported to the hot fluidized bed.

The hot combustion gases and entrained ash particles from the fluid-bed passed through a cyclone where the majority of the entrained ash was collected. A venturi scrubber and a packed column scrubber with a circulating water system removed the fine particles carried beyond the cyclone separator.

The fluid-bed temperature was assisted by glow bar heating elements. The temperature was controlled by a thermocouple positioned between the outer wall of the stainless steel reactor and the fire brick forming the insulating wall around the reactor. The fluid-bed temperature was monitored and recorded from a thermocouple encased in a thermowell extending directly into the bed.

FIGURE 1
REACTOR SCHEMATIC



The exhaust gas from the combustion of the oil shale and synthetic waste product gas was sampled at a position between the cyclone overflow and the scrubber system. This gas was analyzed for O_2 , N_2 , CO , CO_2 , CH_4 , and H_2 by gas chromatograph methods, and for SO_2 , H_2S , and NO_x using a Drager sampler with the appropriate sample tubes. The synthetic product gas, prior to mixing with the air, was analyzed in similar fashion. During steady-state operations, samples of the exhaust gas were also analyzed for total hydrocarbon content.

Tables 4 and 5 show the analysis of the feed shale fines. This material was ground to -14 mesh for these tests.

TABLE 4
ANALYSIS OF RAW OIL SHALE

	As-received	Dry
Calorific value (Btu/lb)	2403	2409
Moisture	0.26	-0-
Ash	67.8	67.9
Volatile matter	33.3	33.4
Carbon, organic	10.7	10.7
Carbon, CO_2	4.7	-0-
Hydrogen	1.7	1.7
Nitrogen	0.5	0.5
Sulfur	0.7	0.7
Oxygen	13.8	18.5
Carbon dioxide	15.6	-0-
Modified Fischer Retort		
Oil yield (gal/ton)		28.0
Oil specific gravity		0.8893
Water yield (gal/ton)		4.3
Residue weight (lb/ton)		1708.0
Gas + loss (lb/ton)		49.0

TABLE 5
ANALYSIS OF OIL SHALE ASH

Component	Weight %
Calcium	13.2
Magnesium	4.9
Sodium	2.1
Sulfur	0.9
Carbon	0.1

COMBUSTION TEST PROCEDURE

The combustion testing program was developed to provide ample time to evaluate test parameters and to ensure the ability to operate the system at steady-state conditions over prolonged periods of time. Approximate gas and oil shale rates, which would conform to anticipated commercial plant ratios, included an oil shale feed rate of 1 lb/hr, waste product gas rate of 50.8 ft³/hr, and an air flow of 68.2 ft³/hr. These combinations provided for a calculated excess air of 15%.

The fluid bed was operated at a temperature of 810-820°C for all tests, which was sufficiently high to decompose all of the base metal carbonates in the oil shale to their respective oxides. The superficial space velocity, while operating at these conditions, was 1.3 to 1.4 ft/s.

Each gas component of the synthetic gas stream was metered into a manifold to form a gas mixture having the following approximate composition:

	<u>Percent</u>
CH ₄	3.0
H ₂	7.1
CO	1.6
H ₂ S	0.2
N ₂	56.3
CO ₂	31.8

This gas mixture was combined with the necessary air flow and introduced into the fluid bed.

The fluid bed was operated with a bed temperature of 810°C and a superficial space velocity of 1.5 ft/s, based upon metered gases. The oil shale, synthetic product gas, and combustion air rates were metered to the reactor in amounts proportional to those anticipated in a commercial plant; i.e., 1 lb/hr, 50.8 ft³/hr, and 68.2 ft³/hr.

During the testing, it was demonstrated that while operating at these conditions there were negligible amounts (less than 1 p/m) of H₂S and SO₂ emitted from the stack. The total hydrocarbons in the exhaust gas averaged 0.08 p/m, reported as CH₄. The NO_x concentration in the exhaust gas averaged 325 p/m during the periods of oil shale feeding, whereas there was less than 10 p/m NO_x detected while not feeding the oil shale (see Table 6).

The sulfur capture test demonstrated the ability of the oil shale ash to control the emission of SO₂. During the test, a bed of oil shale ash was saturated with sulfur from oxidation of H₂S in the synthetic product gas. While fluidizing with air and a synthetic product gas containing 0.2% of H₂S, the exhaust gas contained approximately 200 p/m SO₂. When the oil shale was introduced at about 3 g/min, the SO₂ concentration decreased to less than 1 p/m over a 25-minute period.

TABLE 6
AVERAGE OPERATING CONDITIONS FOR FLUID BED TESTS

Oil shale feed rate (g/min)	7.7
Fluid-bed temperature, °C	810.0
Fluidizing gas (total), cfm	1.9
Air, cfm	1.1
Synthetic product gas, cfm	0.8
Superficial space velocity, fps	1.4

Component	(Table 6 cont)	
	Synthetic Product Gas, %	Fluid-bed Exhaust Gas, %
O ₂	-	4.1
N ₂	58	74.4
CO	1.9	0.4
CH ₄	3.9	0.08 ppm ^{1/}
CO ₂	32.0	21.3
H ₂	5.0	N.D.
H ₂ S	0.27	1 ppm
SO ₂	-	1 ppm
NO _x	-	325 ppm ^{2/}

^{1/} Analyzed from gas bomb samples taken during the test. Assayed for total hydrocarbons, reported as CH₄.

^{2/} NO + NO₂ reported as NO_x.

The second set of tests was conducted using ERCO's 20" diameter fluid bed pilot plant at Cambridge, Mass. The purpose of the combustion test program was to demonstrate the feasibility of burning raw oil shale fines along with waste product gas (low-Btu gas) in a pilot plant size fluid-bed facility. The conditions under which self-sustained combustion is realized were investigated. This study was a follow-up of a preliminary investigation carried out by Hazen Research, Inc., in February, 1981. In these tests it was demonstrated that almost all the sulfur (in oil shale and from H₂S in product gas) is absorbed by base metal oxides in the shale ash. Stack gas composition was measured, and material balances were made.

In the work performed by ERCO, a 20" diameter fluid-bed reactor was used. Operating conditions were selected for which calculations indicated a stable self-sustained combustion process might be realized. Two different superficial velocities were chosen: 2 ft/sec and 4 ft/sec. The bed temperature was maintained at 1550±50°F. Complete material and energy balances were made. With a few exceptions, most material and energy balances close within 15%. The overall energy balance is very good if heat losses from the reactor are accounted for.

The composition of the low-Btu gas from the retorts is summarized in Table 7. The higher heating value of the gas is 77.8 Btu/scf. In this study, the heating value of the low-Btu gas was simulated with a mixture of natural gas and nitrogen. H₂S was also added to obtain nominally 0.20

volume percent in the synthetic low-Btu gas.

TABLE 7
COMPOSITION AND HEATING VALUE OF LOW-BTU GAS

COMPONENT	VOLUME %
H ₂	7.12
CO	1.64
CO ₂	31.75
H ₂ S	0.21
CH ₄	1.31
C ₂ H ₄	0.27
C ₂ H ₆	0.54
C ₃ H ₆	0.21
C ₃ H ₈	0.27
C ₄ 's	0.20
C ₅ 's	0.19
N ₂ +Ar	56.29
TOTAL	100.0
(HHV)	77.81

The ratio of the synthetic low-Btu gas to the oil shale was set at nominally 50 scf/lb of oil shale. This ratio was specified by Synfuels Engineering & Development, Inc.; it reflects the yield of gas from the retorts relative to the production of oil shale fines. The excess air (based on complete combustion of shale and low-Btu gas) was arbitrarily set at 25-30 percent.

A schematic of the experimental setup used in this study is shown in Figure 2. The combustor unit is a 20" diameter fluid-bed reactor equipped with a solids feed system, appropriate gas feed lines, a gas burner to preheat the bed, a distributor plate, and heat transfer tubes. It is also equipped with a number of thermocouples to measure temperatures at various locations in the bed and the freeboard. Pressure differentials across the distributor plate and across the bed were also measured. The distributor plate was designed specifically for the present combustion test on the basis of a pressure drop of 40 inches of water at a superficial velocity of 4 ft./sec. It has 112-1/8 in. holes on a square pitch of 1.7 inches, and a plate thickness of 1/8 in.

The bed is equipped with five heat transfer tubes (1½", sched. 40) arranged in two separate circuits of cooling water consisting of 3 and 2 tubes, respectively. This particular configuration provides a choice of using 5, 3, 2, or no heat transfer tubes (by cutting off cooling water). Incidentally, hand calculations on bed heat transfer indicated a requirement for two tubes.

The calculated number of heat transfer tubes (1½" schedule 40) for the freeboard (in order to cool the exit gases to 500°F) was 43. However, because of space limitations, only 24 tubes were provided in the free board.

The nitrogen was metered into the plenum. The primary fluidization air (from a positive displacement blower) was metered into the plenum. The natural gas was metered, and injected through a ¼" stainless steel pipe centered in the bed and located 4 inches above the distributor. The pipe diameter was selected based on jet length considerations; with this pipe size, the jet length was calculated to be less than 2". Based on a rule of thumb, only one natural gas feedpoint was used. The oil shale was pneumatically injected through a 1" pipe using transport air. The oil shale was injected 6 inches above the distributor plate. The H₂S flow was measured with a flowmeter; the H₂S was injected into the plenum along with the nitrogen and the primary fluidization air.

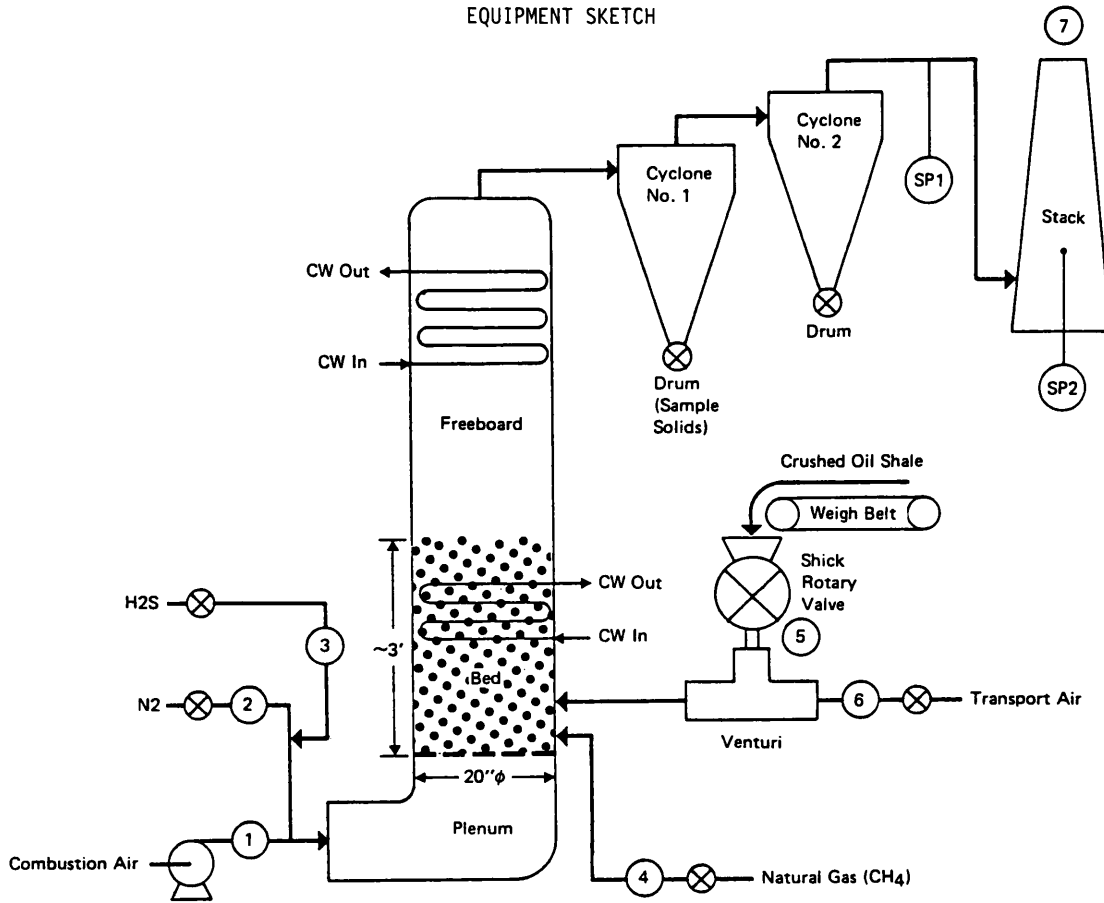
The off-gases from the reactor were sent to two cyclones in series to collect the fly ash. Particulate loading and moisture content of the cyclone off-gases were determined under isokinetic sampling conditions using heated filters and ice-cooled impingers. The stack gases were analyzed for SO_x, NO_x, O₂, CO₂, CO, and N₂.

In this set of runs, the crushed shale was stored in a 5 ft³ bin: the shale was volumetrically metered from the bin with a variable speed, 4" diameter screw. The material was then transferred to a weigh belt which was used as a totalizer. The material was then discharged into a 6" diameter Shick rotary airlock which discharged the material into the venturi tee. The feedrate of the crushed shale was determined from a prior screw calibration and checked by dividing the total feed (by actual weight measurement with a scale) by the run duration.

Temperatures at different locations were measured using Type K thermocouples. Gas compositions were measured using instrumentation specified below:

- CO₂, N₂, O₂, CH₄ - Fisher Gas Partitioner-Model 1200
- CO - Teledyne CO Analyzer
- O₂ - Beckman O₂ Meter/Teledyne O₂ Meter
- SO₂ - Model 40 Thermal Electron Analyzer
- NO_x - Model 10 Thermal Electron Analyzer
- H₂S - Matheson-Kitagawa Toxic Gas Detector Tube

FIGURE 2
EQUIPMENT SKETCH



NOTE: (1) SP1-Sampling point for GC Samples (N_2 , O_2 , CO_2 , CH_4) and H_2S/SO_2 .
(2) SP2-Initial Sampling Point for SO_2/H_2S for Runs on 3/29/82 and 3/30/82.

The GC samples for O_2 , N_2 , and CO_2 were taken at the discharge of the second cyclone.

The solid samples - feed, bed material, cyclone #1 catch, and cyclone #2 catch - from each run were analyzed by Resource Engineering for weight percent C, H, N, CO_2 , S, H_2S , CaO, and MgO; in addition, heating values were determined by Paar Bomb calorimetry.

Ten feedstock samples were collected during the two runs. The average composition for each run and heating value are summarized in Table 8.

There are no fluidization problems at either 2 or 4 fps. It was not necessary to drain bed material during either run because the calcined material elutriated at a sufficient rate to prevent accumulation of bed material. No in-bed tubes were required to remove heat from the bed at either 2 or 4 fps.

Measurements made at bed superficial velocities of 2 and 4 ft/sec., respectively, were analyzed, and

a complete heat and material balance was made in each case.

TABLE 8
OIL SHALE COMPOSITION AND HEATING VALUE^a

Run Date	3/29/82	3/30/82
Run Velocity (fps)	2	4
Composition (wt%)		
Carbon (total)	16.68	16.92
Carbon (organic)	11.94	12.20
Hydrogen	1.71	1.71
Nitrogen	0.54	0.55
CO_2	17.40	17.30
Sulfur	0.69	0.70
Ash	67.53	67.75
CaO ^b	13.30	13.30
MgO ^b	5.70	6.10
N_2S	0.25	0.16
Average HHV [Btu/lb(mf)]	2378.	2379

^aComposition on moisture free bases except H_2O as is.
^bCaO or MgO equivalent.

Run 1 ($V_0 = 2$ ft/sec). The calculated inlet excess air for this case is 30%.

Both the carbon efficiency and combustion efficiency for the oil shale are high (approximately 99%). This is not surprising, since at this low superficial velocity, most of the oil shale feed burns either in the bed or in the freeboard; very little feed material is able to escape the reactor without combusting. On the basis of negligible hydrocarbon levels in the stack gases, it is assumed that the combustion efficiency for natural gas is 100%.

The overall sulfur retention (based on SO_2 concentration in exit gas) was 95.5%; the exit SO_2 concentration was 60 ppm (dry basis), and the exit H_2S concentration was zero. This SO_2 concentration corresponds to 0.55 lb SO_2 /MMBtu (shale only). The Ca/S ratio was 5.2 for this run. If MgO is considered, the Ca+Mg/S ratio was 8.3. The exit CO concentration was 400 ppm.

The elemental balances agree within 12%, except the sulfur balance (only 60.9%). The overall material balance agrees within 2%. The sulfur balance is low because of sulfur accumulation in the bed.

The overall heat balance is off by 14%; this discrepancy is attributed primarily to reactor heat losses.

Run 2 ($V_0 = 4$ ft/sec). The calculated inlet excess air for this case is 26%.

The carbon efficiency and combustion efficiency are about 97%, which is somewhat lower than the corresponding values for the 2 ft/sec case. This decrease in combustion efficiency at the higher superficial velocity is expected, since a larger fraction of feed is likely to be entrained at the higher velocity.

Overall sulfur retention by the bed material is 85.5%; the exit stack gas contained 50 ppm H_2S and 170 ppm SO_2 . It is noted that the inlet H_2S concentration in the plenum was 1100 ppm (determined with a Drager tube); this is in reasonable agreement with the calculated value of 883 ppm. The discrepancy is attributed to imperfect mixing in the plenum chamber and the inaccuracy of the Drager tube.

The exit NO_2 concentration was 200 ppm, and the exit CO concentration was 500 ppm.

The most elemental balances agree within 10%, and the overall material balance agrees within 2%.

The overall sulfur balance is 78%; the discrepancy is again attributed to sulfur accumulation on the bed.

The overall heat balance agrees within 5%; this is better than the previous run because of the higher through-put.

Assuming natural gas combustion is complete within the bed, an energy balance around the bed alone (without water cooling) at 4 fps indicates that 30-40% of the oil shale burns in the bed and the remainder burns in the freeboard. Bed heat losses and calcination heat requirements make this calculation somewhat tenuous.

From these tests, we conclude that combustion of the oil shale/synthetic low-Btu gas feedstock in a fluidized bed reactor results in excellent combustion efficiency (>95%) at fluidization velocities of 2 and 4 fps and a bed temperature of $1550 \pm 25^\circ\text{F}$. Fluidization characteristics were excellent. No in-bed tubes were required to maintain the bed at this temperature. Sulfur removal efficiency was 95.5 and 85.5% at 2 and 4 fps, respectively, without the addition of a separate limestone stream. At the operating conditions evaluated, the Ca/S mole ratio was nominally 5/1 or 8/1 if Ca+Mg is utilized. Material and energy balances for the two runs were satisfactory.

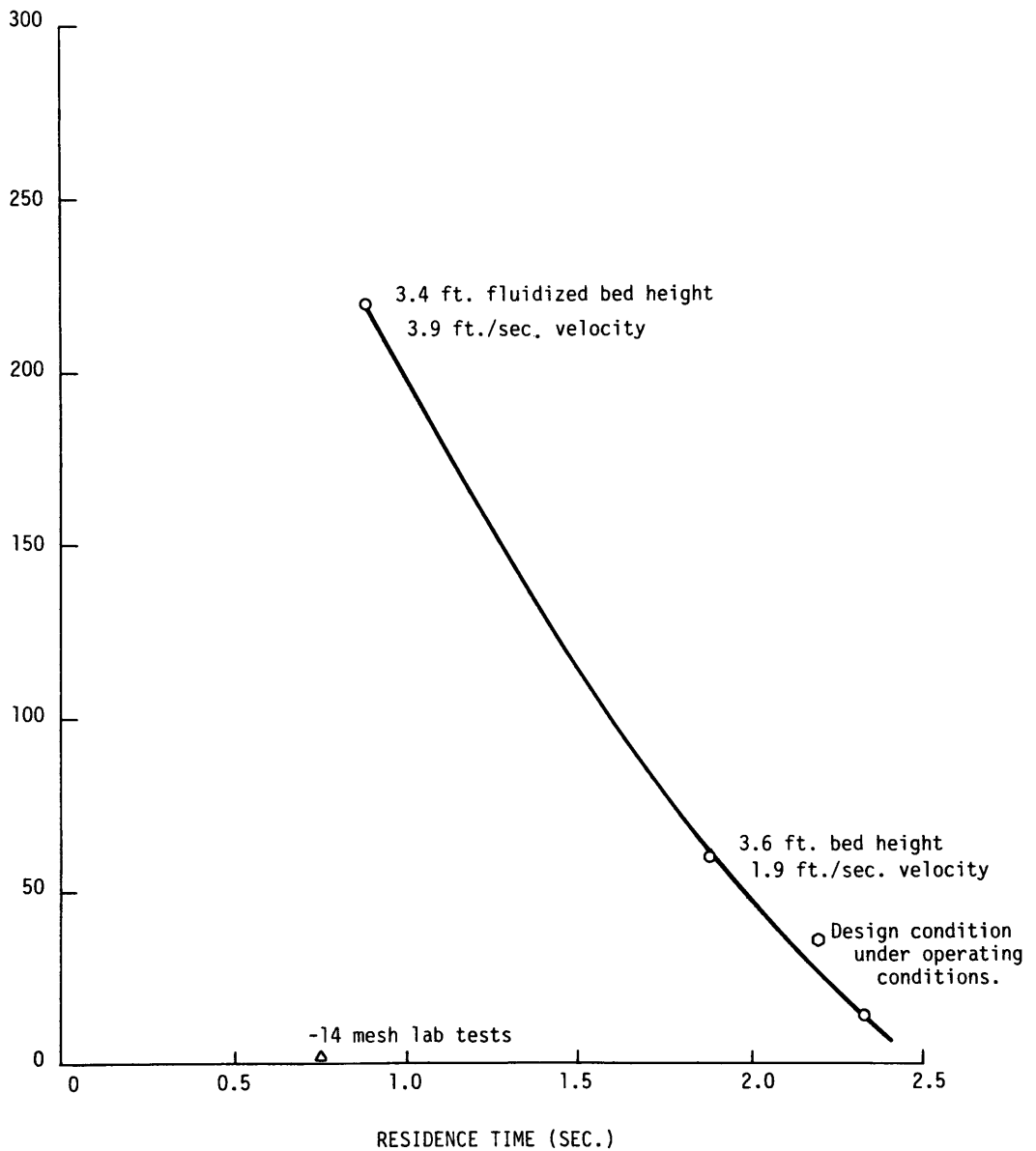
An interesting observation is that the initial SO_2 data, which suggested essentially 100% SO_2 removal, was in error because of SO_2 absorption by reactive particulate coating the tube wall. This SO_2 removal occurred at low temperatures (150 - 225°F). One can speculate that a baghouse, which is an essential component of a fluid-bed combustion facility, will also be an effective SO_2 scrubber. In this instance, it is possible that the SO_2 can be removed in two stages: The first, high temperature stage being the bed, and the second, low temperature stage being the baghouse. Possibly one would want to design the plant with inefficient cyclones to increase the solids (i.e., Ca/S ratio) to the bag house.

CONCLUSION

The above sets of tests are summarized in Figure 3. This figure shows that, using a residence time of about 2.2 sec, we would expect to absorb more than 97% of the SO_2 from the shale. This matches the proposed, but unproven, removal efficiency of the Stretford units, and can be considered best available control technology. In ad-

FIGURE 3

FLUID BED COMBUSTION TESTS
USING NOMINAL CONDITIONS



dition, this process allows burning of the low-Btu gas in a safe, tested manner.

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