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Project Title: **STABILIZATION OF SPENT SORBENTS FROM COAL GASIFICATION** DE-FC22-92PC92521

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ABSTRACT

The objective of this investigation was to determine the rates of reactions involving partially sulfided dolomite and oxygen, which is needed for the design of the reactor system for the stabilization of sulfide-containing solid wastes from gasification of high sulfur coals.

To achieve this objective, samples of partially sulfided dolomite were reacted with oxygen at a variety of operating conditions in a fluidized-bed reactor. The effect of external diffusion was eliminated by using small quantities of the sorbent and maintaining a high flow rate of the reactant gas. The reacted sorbents were analyzed to determine the extent of conversion as a function of operating variables including sorbent particle size, reaction temperature and pressure, and oxygen concentration.

The results of sulfation tests indicate that the rate of reaction increases with increasing temperature, increasing oxygen partial pressure, and decreasing sorbent particle size. The rate of the sulfation reaction can be described by a diffuse interface model where both chemical reaction and intraparticle diffusion control the reaction rate.

The kinetic model of the sulfation reaction was used to determine the requirements for the reactor system, i.e., reactor size and operating conditions, for successful stabilization of sulfide-containing solid wastes from gasification of high sulfur coals (with in-bed desulfurization using calcium based sorbents). The results indicate that the rate of reaction is fast enough to allow essentially complete sulfation in reactors with acceptable dimensions. The optimum sulfation temperature appears to be around 800°C for high pressure as well as atmospheric stabilization of the spent sorbents.

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EXECUTIVE SUMMARY

The sulfur compounds present in coal are converted to hydrogen sulfide when the coal is gasified. To comply with the New Source Performance Standards (NSPS), a high fraction of the sulfur must be removed from the gas stream. Calcium-based sorbents such as limestone and dolomite are among the prime candidates for in-bed capture of sulfur from the fuel gas.

High efficiency advanced electric power generation systems using Integrated Coal Gasification Combined Cycle (IGCC) or advanced/ staged pressurized fluidized-bed combustion, require very low levels of H_2S in the fuel gases. More than 90% of the H_2S in the fuel gas can be removed in the gasifier by using calcium-based sorbents such as limestone or dolomite. An external hot gas cleanup system using regenerable mixed metal oxides such as zinc ferrite or zinc titanate can then be used to further reduce the H_2S content of the fuel gas to acceptable levels for IGCC application.

The removal of sulfur takes place through the reaction of hydrogen sulfide (in-bed or externally) with calcium oxide, calcium carbonate, or calcium hydroxide and produces calcium sulfide. This compound is not stable, and therefore, is not suitable for direct disposal. However, calcium sulfide can be reacted with oxygen (or air) to produce calcium sulfate, a stable and environmentally acceptable compound, for disposal.

The extent of the conversion of calcium sulfide to stable calcium sulfate has been shown to be dependent on the sorbent type, i.e., limestone or dolomite, the extent of sulfidation reaction, i.e., Ca/S ratio in the gasifier, sorbent particle size, and magnesium content of the sorbent. The reaction temperature has been shown to have a significant effect on the overall sorbent utilization. At temperatures below 850°C, calcium sulfide in the partially sulfided dolomite can be nearly completely converted to calcium sulfate. At higher temperatures, stabilization is generally accompanied by significant release of sulfur in the form of SO_2.

The results obtained in previous ICCI-funded projects indicate sulfide-containing solid wastes can be stabilized at around 800°C with minimal release of sulfur as SO_2. However, the kinetics of calcium sulfide oxidation reactions are not known. Such information is needed in designing the gasifier waste stabilization system which can lead to development of an economical process for successful conversion of sulfide-containing solid waste products from gasification or staged combustion of high sulfur Illinois coal to environmentally acceptable products for disposal in landfills.

The objective of this investigation was to measure the rate of reaction between partially sulfided dolomite and oxygen as a function of operating variables such as sorbent particle size, reaction temperature and pressure, and oxygen concentration and use the experimental data to develop a kinetic model for the sulfation reaction which is needed for the design of the reactor system for the stabilization of sulfide-containing solid wastes from gasification or staged combustion of high sulfur coals.

A dolomite used in previous ICCI funded projects (Subgrants 89-04, 90-08, and 91-03) was selected for this study. The selected sorbent was crushed and screened into narrow particle size ranges. Three particle size ranges were selected for testing which includes particles with average diameters of 0.02, 0.035, and 0.07 cm. Samples of all three cuts of the sorbent were sulfided in the fluidized-bed reactor at 900 °C to achieve 50±5% sulfidation level, representing coal gasifier with <u>in-situ</u> desulfurization with a calcium to sulfur ratio of 2 to 1. All three sizes of partially sulfided sorbent were reacted with oxygen in a very shallow fluidized-bed where external diffusion limitation and gas concentration gradient were essentially eliminated. The range of operating variables included temperature: 540° to 730°C; pressure: 1 and 20 atmospheres; oxygen concentration: 0.3 to 5%; and solid residence time: 3 to 240 minutes.

The results of sulfation tests indicate the rate of reaction increases with increasing temperature, increasing oxygen partial pressure, and decreasing sorbent particle size. The rate of the sulfation reaction can be described by a diffuse interface model where both chemical reaction and intraparticle diffusion control the reaction rate.

The kinetic model of sulfation reaction was used to determine the requirements for the reactor system, i.e., reactor size and operating conditions, for successful stabilization of sulfide-containing solid wastes from gasification of high sulfur coals (with in-bed desulfurization using calcium based sorbents). The results indicate the rate of reaction is fast enough to allow essentially complete sulfation in reactors with acceptable dimensions. The optimum sulfation temperature appears to be around 800°C for high pressure as well as atmospheric stabilization of the spent sorbents.

OBJECTIVES

The overall objective of this program was to determine the rate of reaction for the conversion of calcium sulfide in partially sulfided dolomite to calcium sulfate under reaction conditions that promote high conversion levels with negligible SO_2 release.

The program goals were specifically directed toward waste management, Research Priority Section 5.3A: Studies related to disposal and utilization of waste materials generated in gasifiers, or fluidized-bed combustors, or flue gas scrubbers including in-duct injection. The specific objectives of this program were to:

1. Prepare partially sulfided samples of a dolomite that had been used in past ICCI funded projects
2. Obtain experimental data to determine the sulfation reaction rate involving partially sulfided dolomite in atmospheric and high pressure fluidized-bed reactors. The test parameters included solid residence time, sorbent particle size, reactor pressure and temperature, and oxygen concentration.
3. Analyze oxidized sorbents in terms of their physical and chemical properties to determine the extent of sorbent conversion during oxidation.
4. Develop a kinetic model for the oxidation of calcium sulfide in partially sulfided dolomite sorbents

INTRODUCTION AND BACKGROUND

The market-share of Illinois high-sulfur coal can be expanded to industrial users as well as power plants if the coal can be used in an environmentally acceptable manner with minimum gas cleanup costs. For example, an integrated coal gasification combined-cycle (IGCC) power plant (see Figure 1) offers the potential for both lower cost power and lower emissions than coal-fired plants with flue gas desulfurization for power generation.

The sulfur compounds present in coal are converted to hydrogen sulfide when the coal is gasified. To comply with the New Source Performance Standards (NSPS), a high fraction of the sulfur must be removed from the gas stream. Calcium-based sorbents such as limestone and dolomite are among the prime candidates to capture the sulfur compounds from the fuel gas.

The solid wastes produced from the reactions of calcium-based sorbents with hydrogen sulfide in the fuel gas, contain calcium sulfide which is unstable and has the tendency to decompose when it contacts moisture in the air, releasing hydrogen sulfide to the atmosphere. To dispose of the solid waste products in an environmentally acceptable manner, calcium sulfide can be converted to stable calcium sulfate through reaction with oxygen —

$$CaS + 2O_2 = CaSO_4 \qquad (A)$$

However, the calcium sulfate produced by reaction (A), at temperatures of interest to the overall process (800°-1000°C), can also react with the calcium sulfide in an apparent solid-solid reaction to release SO_2 —

$$CaS + 3CaSO_4 = 4CaO + 4SO_2 \qquad (B)$$

Reaction (A) is a highly exothermic reaction (ΔH_{rxn})>225 Kcal/g mole) resulting in a significant increase in the particle temperature. Reaction (B) becomes more favorable as the particle temperature increases, resulting in release of SO_2, and reducing overall sorbent utilization. The highly exothermic nature of reaction (A) and its effect on the reaction temperature significantly affects the final distribution of the product.

The results of investigations on the stabilization of calcium sulfide in previous ICCI funded projects(1-8) indicated that limestone can only be partially sulfated while dolomite can be essentially completely sulfated above 800°C. The extent of sulfation depends not only on the sorbent type but also on the extent of sulfidation in the gasifier. The results of previous ICCI-funded studies, as well as other independent studies reported in the literature(9-15), indicated that the fraction of sulfur in calcium sulfide converted to SO_2 significantly increases with increasing temperature.

These studies suggested that CaS-containing wastes from a gasifier (using dolomite as the sulfur capture agent) can be stabilized at temperatures in the vicinity of 800°C by using either a reactant gas containing low concentrations of O_2, or heat removal devices within the reactor, to control the reactor temperature to minimize SO_2 release. However, further development of an economical and efficient process for stabilization of gasifier solid wastes requires knowledge of the sulfation reaction rate and its dependence on the operating variables.

This study was targeted toward determination of the rate of reaction involving calcium sulfide in partially sulfided dolomite and oxygen, under reaction conditions that promote high conversion levels with minimal SO_2 release. This was accomplished by obtaining experimental data on the effects of sorbent particle size, reactor pressure and temperature, and oxygen concentration on the sulfation reaction rate. The reaction rate data obtained in this study was used to develop a kinetic model for the sulfation reaction to determine the requirements for reactor system, i.e., reactor size and operating condition for the stabilization of the CaS-containing solid wastes produced during gasification of high sulfur Illinois coals.

EXPERIMENTAL PROCEDURES

Material

A dolomite used in previous ICCI-funded projects was selected for this study. The sorbent was crushed and screened into narrow particle size ranges. Three particle size ranges were used for stabilization tests. The average particle diameter of the sorbent are 0.02 cm [-60+80 mesh (fines)], 0.035 [-40+50 mesh (medium)] and 0.07 cm [-20+30 mesh (coarse)]. The chemical composition of the sorbent determined in previous ICCI-funded projects is presented in Table 1. The molar ratio of calcium carbonate to magnesium carbonate in this sorbent is 0.98 indicating that the dolomite is reasonably pure.

Table 1. CHEMICAL ANALYSES OF THE SORBENT

Analyses, wt %	Dolomite
Calcium	22.2
Magnesium	13.2
Potassium	0.5
Iron	0.11
Aluminum	0.069
Silicon	0.3
Stontium	0.005
Carbon Dioxide	48.0
Oxygen (by Diff.)	15.616
Total	100

Preparation of Partially Sulfided Sorbents

Sulfidation tests were conducted in quartz fluidized-bed reactors to prepare the partially sulfided sorbents for sulfation tests. Samples of all three cuts of the sorbent were used in these tests. The schematic diagram of the unit is presented in Figure 2. The unit essentially consists of a quartz fluidized-bed rector which is externally heated by two electrical furnaces, equipment for feeding and measuring the flow rates of the gases, measuring and controlling the bed temperature, and monitoring the fluidized-bed pressure. The fluidized-bed distributor is made of a quartz fritted disk.

During a sulfidation test, a known quantity of the sorbent is loaded into the fluidized-bed reactor. The bed is brought to the desired temperature by two electrical furnaces while a stream of nitrogen flows through the reactor. The sorbent is calcined during the heatup period and is kept at 900°C for 30 minutes. Nitrogen and hydrogen sulfide, mixed at a predetermined ratio to achieve the desired mixture composition, are then allowed to enter the reactor at a flow rate of the gas mixture sufficient to fluidized the bed. A slip stream of the reactor off-gases is analyzed to determine the extent of reaction in the fluidized bed. This data is used to determine the solid residence time needed to achieve the desired level of sulfidation (about 50%±5%). After this period, the gas is switched to nitrogen and the sample is cooled. During the run, the temperature is controlled by the temperature controller. The reactor temperature and pressure are monitored by a computer data acquisition system. The reactor off-gases pass through a filter for collection of elutriated fines and then through a liquid scrubber before being vented.

After the run, the partially sulfided sorbent is removed from the reactor and analyzed to determine the extent of sulfidation. The partially sulfided sorbent is then stored for use in the sulfation tests.

EXPERIMENTAL PROCEDURES

Measurement of Sulfation Reaction Rate

Sulfation tests were conducted in the 5-cm-diameter ambient pressure quartz fluidized-bed reactor as well as 7-cm-diameter high pressure/high temperature reactor (HPTR) systems. Schematic diagrams of these units are shown in Figures 2 and 3, respectively. The ranges of operating variables used in this study is given in Table 2.

In a typical sulfation test, about 3 to 5 grams of the partially sulfided dolomite is loaded into the fluidized-bed

Table 2. RANGES OF OPERATING VARIABLES

Variable	Range
Temperature, °C	540-815
Total Pressure, atm	1-20
O_2 Concentration, %	0.3-5
Sorbent Particle Diameter, cm	0.02-0.07

reactor. This shallow bed of solids (1-2 mm thick) is heated by the external furnace, while a stream of nitrogen flows through the reactor until the reactor reaches the desired temperature. The gas flow rate is then increased to fluidized the bed. At this point, the gas is switched to a reactant gas containing the desired concentration of oxygen. The desired composition of the reactant gas is achieved by mixing streams of air and nitrogen at predetermined ratios. The reaction continues until the desired solids residence time is reached. During the test, the temperature is controlled by the temperature controller. The reactor temperature and pressure are monitored by a computerized data acquisition system. The reactor off-gas passes through a filter for collection of elutriated fines and then through a liquid scrubber before being vented. The small quantities of the solids used in these tests combined with high flow rates of the reactant gas eliminate external diffusion limitations and minimize the concentration gradient of the reactant gas across the sorbent bed. The reacted solids are removed from the reactor and are analyzed to determine the extent of conversion of calcium sulfide (CaS) to calcium sulfate ($CaSO_4$).

RESULTS AND DISCUSSION

Sulfidation of Dolomite

Samples of all three cuts (-60+80, -40+50, and -20+30 mesh) of the sorbent were sulfided in the fluidized-bed reactor. The tests were designed to produce partially sulfided sorbent with a sulfidation level in the range of 50±5% for sulfation tests. The partially sulfided sorbents were analyzed and their calcium, sulfide, and sulfate content were determined. The results presented in Table 3 indicate the extent of sulfidation of all three samples is within the desired range.

Determination of Sulfation Reaction Rate

Samples of partially sulfided sorbent with medium particle size ($d_p \approx 0.035$ cm) were sulfated in the 5-cm-diameter quartz atmospheric pressure fluidized-bed reactor.

Table 3. EXTENT OF SULFIDATION IN PARTIALLY SULFIDED DOLOMITE

Sample	Average Particle Diameter, cm	Extent of Sulfidation
Fine	0.02	54.79
Medium	0.035	49.08
Coarse	0.07	48.12

The first sulfation test was conducted at 815°C with the reactant gas containing 5% oxygen. Despite the relatively small quantity of sorbent used, the reactor temperature increased more than 100°C resulting in significant release of SO_2, which directly affects the extent of conversion of CaS to $CaSO_4$. To avoid this problem, a series of four tests was conducted at temperatures of 815°, 730°, 650°, and 540°C using a reactant gas containing 1% oxygen. The operating conditions and the results of these tests are presented in Table 4.

Table 4. EFFECT OF TEMPERATURE ON SULFATION OF CaS

Temperature, °C	Solid Residence Time, min	CaS to $CaSO_4$ Conv., %	CaS to SO_4 Conv., %	O_2 Conv., %
815	6.67	48.88	18.74	66.08
730	6.67	39.03	12.43	50.77
650	6.67	16.32	Nil	17.13
540	60	11.3	Nil	1.32

Although, the equilibrium partial pressure of SO_2 at 815°C (in Reaction B) is about 2×10^{-3} atm (2000 ppm at atmospheric pressure), because of the small quantity of sorbent and the large flow of reactant gas in the tests conducted in this study, a significant fraction of calcium sulfide was converted to SO_2 and CaO. Therefore, to avoid significant loss of sulfur and to minimize concentration gradient of the reactant gas across the solid bed, 650°C was chosen as the baseline temperature. The results of sulfation tests given in Table 4 also indicate that the lower temperature range of the sulfation reaction should be limited to about 540°C. At lower temperature, the reaction rate will be very low requiring a long solid residence time.

Five series of sulfation tests were conducted in this study including the baseline tests and tests for determination of the effects of temperature, oxygen concentration, particle diameter, and reactor pressure. The results of the successful sulfation tests, along with the operating conditions are presented in Table 5. As expected the results indicate that the overall sulfation reaction rate increases with increasing temperature, increasing oxygen partial pressure, and decreasing sorbent particle size.

Development of Kinetic Model for Stabilization Reaction

The sulfation reaction rate data obtained in this program was used in the development of a kinetic model for the reaction. The experimental data for the effect of oxygen concentration suggests that the dependence of the overall reaction rate on oxygen concentration is lower than first order because of "moderate" increase over a "wide" range of oxygen concentrations. The effect of particle size on the overall reaction rate suggests that uniform reaction models cannot be used to describe the data because this model assumes uniform solid conversion throughout the particle, making the reaction rate independent of particle diameter.

Because the sorbent particles do not appear to shrink during the reaction, a shrinking core model (SCM) for particles of unchanging size may be assumed to be suitable. However, significant dependence of the sulfation reaction rate on temperature and pressure strongly suggests that intraparticle diffusion or chemical reaction alone cannot describe the measured reaction rates.

Several classical gas/solid reaction models, including the uniform conversion model, the reaction controlled and the ash diffusion controlled shrinking core models, as well as the grainy pellet model were applied to the experimental data to determine the extent and the direction of modification needed to develop a reliable kinetic model for this reaction. The results of these efforts indicated that a model in which both the chemical reaction and intraparticle diffusion control the overall reaction should better describe the experimental data of the sulfation reaction rate.

The Diffuse Interface Model (DIM) described by Bowen(17,18) includes the effects of both the chemical reaction and the intraparticle diffusion on the overall reaction rate. The Diffuse Interface Model, similar to the shrinking core model, assumes that the reaction proceeds toward the particle center from the surface. However, unlike the "sharp" solid reactants/products interface in the SCM, a diffuse interface zone with a finite thickness is proposed in which concentration gradients of both reactants and products of the reaction are present and in which the reaction proceeds.

Table 5. SULFATION REACTION TEST MATRIX

Temp. °C	Pressure, atm	O_2 Conc. %	Particle Diameter, cm	Solid Residence Time, min	CaS to $CaSO_4$ Conv., %	Remarks
650	1	2	.035	3.33	12.58	Baseline Condition
650	1	2	.035	6.67	17.7	Baseline Condition
650	1	2	.035	13.34	28.76	Baseline Condition
650	1	2	.035	30	40.38	Baseline Condition
650	1	2	.035	60	38.87	Baseline Condition
650	1	2	.035	120	68.26	Baseline Condition
540	1	2	.035	60	14.39	Effect of Reaction Temp.
540	1	2	.035	120	20.89	Effect of Reaction Temp.
540	1	2	.035	240	24.66	Effect of Reaction Temp.
730	1	2	.035	3.33	41.92	Effect of Reaction Temp.
730	1	2	.035	6.67	40.62*	Effect of Reaction Temp.
730	1	2	.035	13.34	57.9	Effect of Reaction Temp.
650	1	0.3	.035	3.33	7.03	Effects of Oxygen Conc.
650	1	0.3	.035	6.67	9.46	Effects of Oxygen Conc.
650	1	0.3	.035	13.34	14.41	Effects of Oxygen Conc.
650	1	0.3	.035	22.2	21.95	Effects of Oxygen Conc.

* Statistically inconsistent experimental data.

Table 5, Cont. SULFATION REACTION TEST MATRIX

Temp. °C	Pressure, atm	O_2 Conc. %	Particle Diameter, cm	Solid Residence Time, min	CaS to $CaSO_4$ Conv., %	Remarks
650	1	1	.035	3.33	11.22	Effects of Oxygen Conc.
650	1	1	.035	6.67	16.32	Effects of Oxygen Conc.
650	1	1	.035	13.34	26.06	Effects of Oxygen Conc.
650	1	5	.035	3.33	18.35	Effects of Oxygen Conc.
650	1	5	.035	6.67	25.55	Effects of Oxygen Conc.
650	1	5	.035	13.34	35.44	Effects of Oxygen Conc.
650	1	5	.035	30	45.75	Effects of Oxygen Conc.
650	1	2	0.02	3.33	16.51	Effect of Particle Diameter
650	1	2	0.02	6.67	24.62	Effect of Particle Diameter
650	1	2	0.02	13.34	29.84	Effect of Particle Diameter
650	1	2	.07	3.33	13.48	Effect of Particle Diameter
650	1	2	.07	13.34	23.69	Effect of Particle Diameter
650	1	2	.07	30	30.20	Effect of Particle Diameter
650	1	2	.07	60	33.53	Effect of Particle Diameter
650	1	2	.07	120	40.81	Effect of Particle Diameter
650	20	1	.02	10	77.07	Effect of Pressure
650	20	1	.02	30	83.99	Effect of Pressure
650	20	1	.035	6.67	48.36	Effect of Pressure
650	20	1	.035	13.34	52.84	Effect of Pressure
650	20	1	.07	30	54.91	Effect of Pressure

Reactant gas must diffuse through the product layer to reach the interface zone. As the reaction proceeds, the product layer becomes thicker, the concentration of gas at the surface of the interface decreases, and the rate of reaction decreases. The global effect of a Diffuse Interface Model is a gas-solid reaction description dependent on both intraparticle diffusion and chemical reaction. The two resistances are combined instead of being additive as in the SCM.

The use of the Diffuse Interface Model leads to a relationship where the time, t, required to achieve a certain solid conversion, x, is given by the form:

$$t = \tau \cdot f(x) \tag{1}$$

in Equation 1, τ is the time required for complete conversion of the solid reactant and can be calculated from —

$$\tau = \frac{\rho_s \cdot D_p \cdot RT}{\epsilon \cdot D_c \cdot P^{0.7} \cdot Y^{0.5} \cdot \exp\left[\frac{-E}{RT}\right]} \tag{2}$$

where ρ_s is the solid molar density, D_p is sorbent particle diameter, P is the total pressure, Y is the mole fraction of oxygen, D_c is the combined overall diffusion coefficient, E is the activation energy, ϵ is the solid porosity, R is the universal gas constant, and T is the reaction temperature. The function f(x) in Equation 1 is described by the expression

$$f(x) = 1 - 3(1 - X)^{2/3} + 2(1 - X) \tag{3}$$

The Diffuse Interface Model was applied to the experimental data obtained in this study and the results are given in Figures 4 through 7. The Diffuse Interface Model fits the experimental data very well. The model assumes uniform solid spheres which leads to greater differences between predicted and measured results as the particle diameter increases and/or its shape deviates from sphere. This is evident in Figure 6.

Modeling of Stabilization Reactor

The kinetic model developed in this program was used to determine the requirements (i.e., reactor size and operating conditions) for the stabilization reactor. Because of the highly exothermic nature of the sulfation reaction, the stabilization step should be carried out in a fluidized-bed reactor. The partially sulfided dolomite particle was assumed to have a uniform size distribution. The calcium sulfide has been shown to be uniformly distributed throughout the particles(1,5) The SO_2 concentration in the product gas was assumed to correspond to the equilibrium partial pressure of SO_2 in Reaction B. Particle attrition and elutriation were not included in this modeling effort. The solids in the fluidized-bed were assumed to be well mixed while the reactant gases were assumed to flow through the reactor as plug flow. This assumption is equivalent to uniform fluidization where the bubbles generated in the bed are small. The interparticle gas-solid diffusion coefficient was assumed to be significantly greater than the combined diffusion coefficient (defined in Equation 2). Successful stabilization was assumed to be at 99% conversion of calcium sulfide to calcium sulfate. Two reactor configuration systems were selected to model the stabilization process at high pressure and low pressure.

In the high pressure stabilization process (See Figure 8), the stabilization reactor is integrated with the coal gasifier (with in-bed sorbent). Hot air is provided from the compressor side of the gas turbine in the Integrated Gasification Combined Cycle (IGCC) at 350°C while the gases leaving the stabilization reactor enter the gasifier. The heat generated in the stabilization reactor is removed by generating steam for the gasifier operation. The hot stabilized solids leaving the stabilization reactor are cooled in a moving bed recuperator where air is heated for injection into the gasifier.

The flow rates for the solids and gases correspond to the operation of a 125-MW gasifier using a high sulfur coal containing 4% sulfur and 10% ash. The range of fluidization velocity in the stabilizer was 0.36 to 1 m/s to ensure good fluidization and to avoid significant solid elutriation and the total flow of gases through the stabilizer was limited to 40% of the total air requirement for the gasifier.

The conversion of calcium sulfide to calcium sulfate as a function of temperature for a fluidized bed reactor operating at 15 atm is shown in Figure 9. The bed diameter and the bed height were 1 m and the fluidization velocity was 50 cm/s. The particle diameter was assumed to be 0.07 cm. The results in Figure 9 indicate that even for such a small reactor, essentially complete sulfation of calcium sulfide (>99%) can be achieved above 800°C. The amount of steam generated at 800°C as a function of fluidization velocity is shown in Figure 10 indicating that this setup can be used over a wide range of excess air for stabilization of partially sulfided dolomite. The amount of steam generated decreases as the heat is used to heat up the excess air. To achieve greater than 99% conversion at 750°C, the bed diameter should be increased to 150 cm (Figure 11). Longer residence times are needed at lower temperatures. At 650°C, the bed height should be about

500 cm for successful stabilization of the spent sorbents as shown in Figure 12.

The conversion of calcium sulfide to SO_2 drastically increases as the stabilization temperature is increased above 800°C. Figure 13 shows that about 10% of sulfur in the spent sorbent is converted to SO_2 at 1000°C. The performance of the stabilization reactor for large particles with a 0.2 cm diameter (10 mesh) as a function of temperature is shown in Figure 14 indicating that more than 20% of the sulfur in the spent sorbent will be converted to SO_2 at 1000°C.

In the low pressure stabilization process (see Figure 15), the stabilizer was assumed to operate at ambient pressure and the feed air enters the reactor at 25°C. The gases leaving the stabilizer are cooled and the sulfur compounds are scrubbed. To minimize the scrubber duty, the excess air was limited to less than 1%. All other operating conditions were similar to those of the high pressure stabilization process. The performance of the stabilizer as a function of temperature is shown in Figure 16 for small and large particles. At low temperatures, i.e., <750°C, the bed height required for successful stabilization of spent sorbents appears to be excessively high while at high temperatures, i.e., 7850°C, a significant fraction of sulfur is released as SO_2.

The results of the reactor modeling efforts indicate that the optimum operating temperature is in the range of 750° to 850°C and that the spent sorbent stabilization process can be successfully carried out at both low pressure and high pressure.

CONCLUSIONS AND RECOMMENDATIONS

The following conclusions can be made from the work performed in this project:

- The rate of conversion of partially sulfided calcium based sorbent to stable calcium sulfate increases with increasing oxygen partial pressure and reaction temperatures, and with decreasing sorbent particle diameter.

- The overall rate of the stabilization reaction is controlled by a combination of chemical reaction and intraparticle diffusion and can be described by the diffuse interface model.

- The rate of reaction between partially sulfided dolomite and air is fast enough to achieve over 99% conversion in a relatively small size reactor at temperatures above 750°C.

- The optimum temperature for stabilization of spent sorbent is in the range of 750° to 850°C.

- A significant fraction of gasifier feed steam and hot air can be achieved by the stabilization process.

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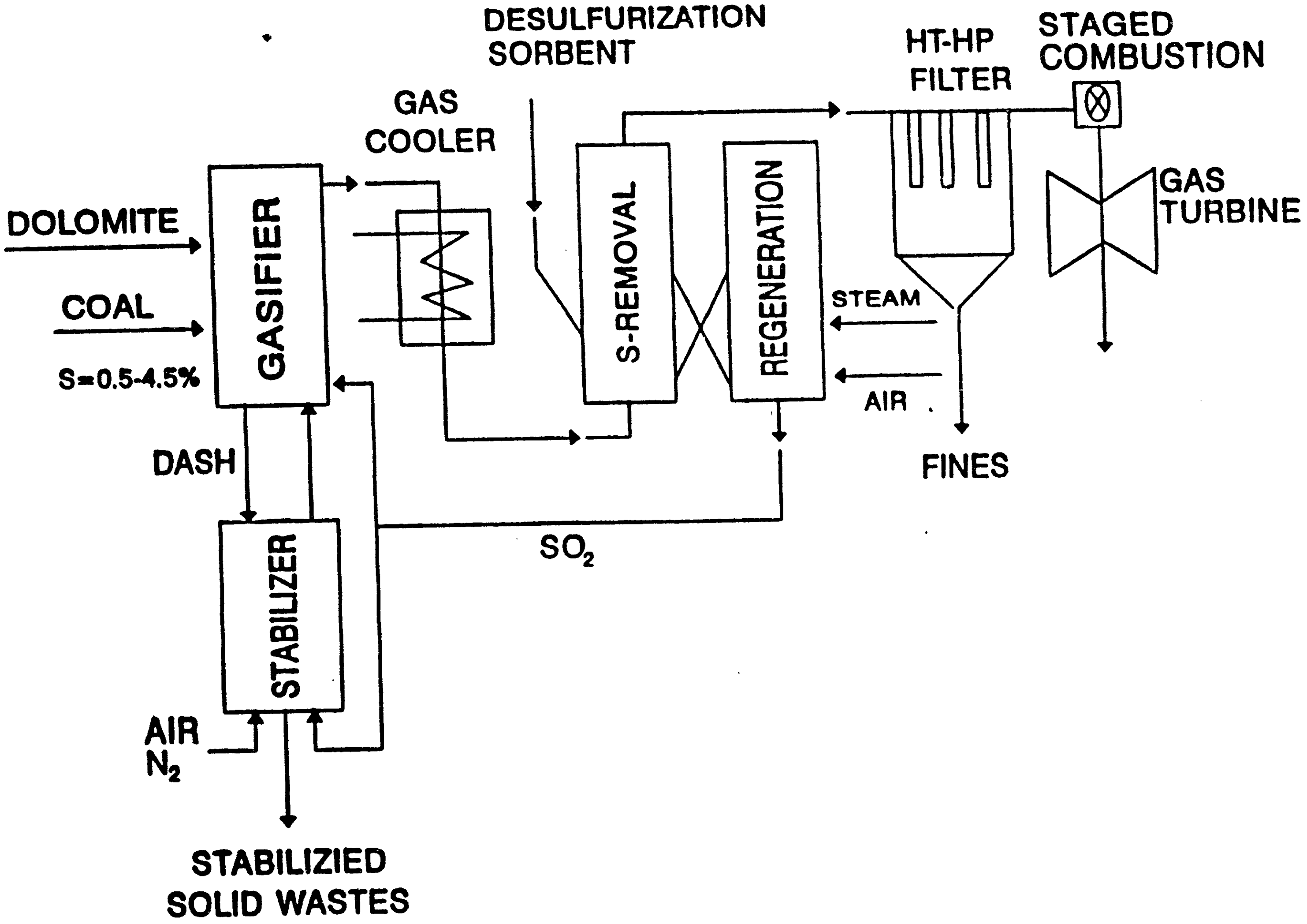


Figure 1. SCHEMATIC DIAGRAM OF A TYPICAL IGCC PROCESS

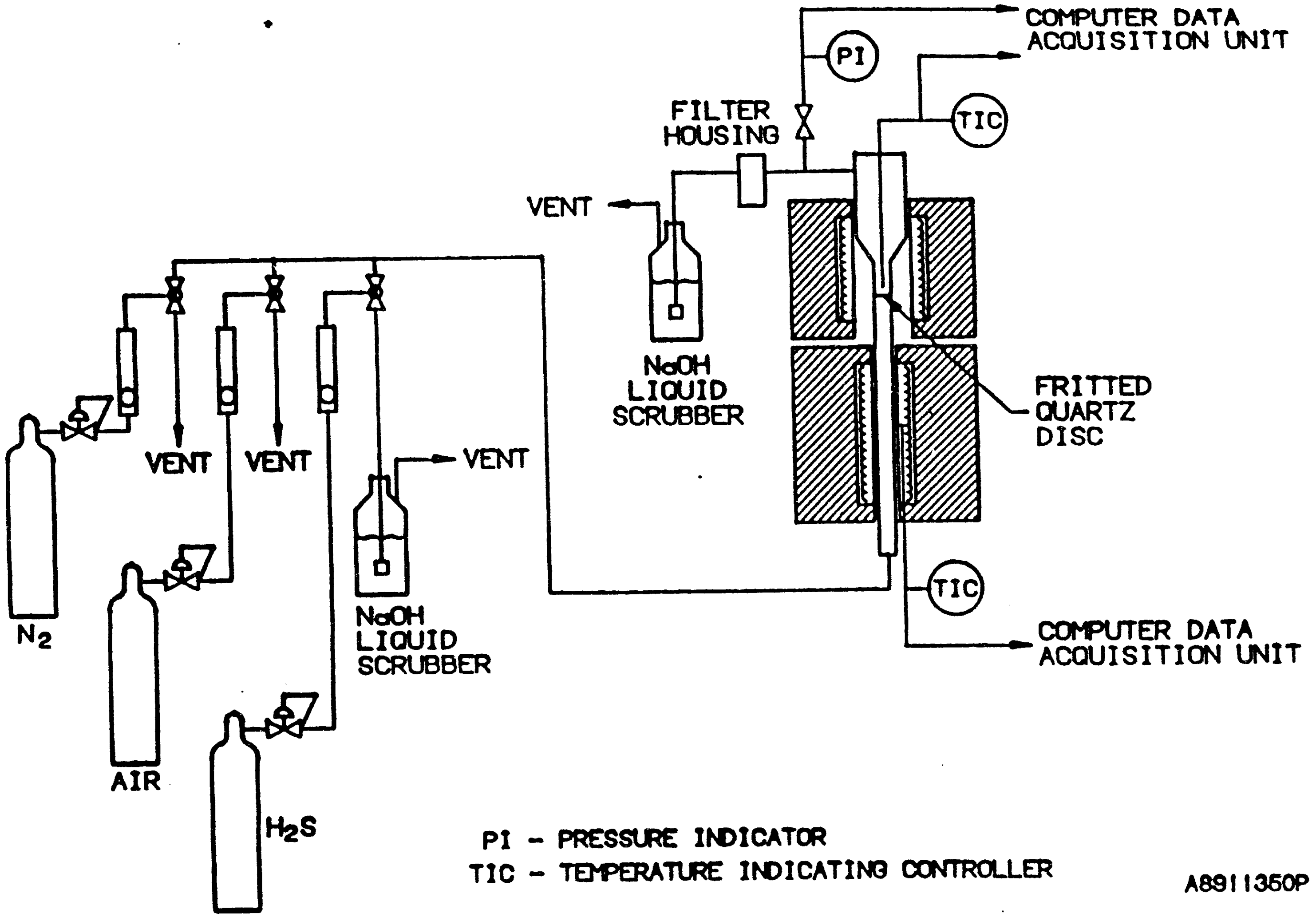


Figure 2. PROCESS FLOW DIAGRAM OF QUARTZ FLUIDIZED-BED UNIT

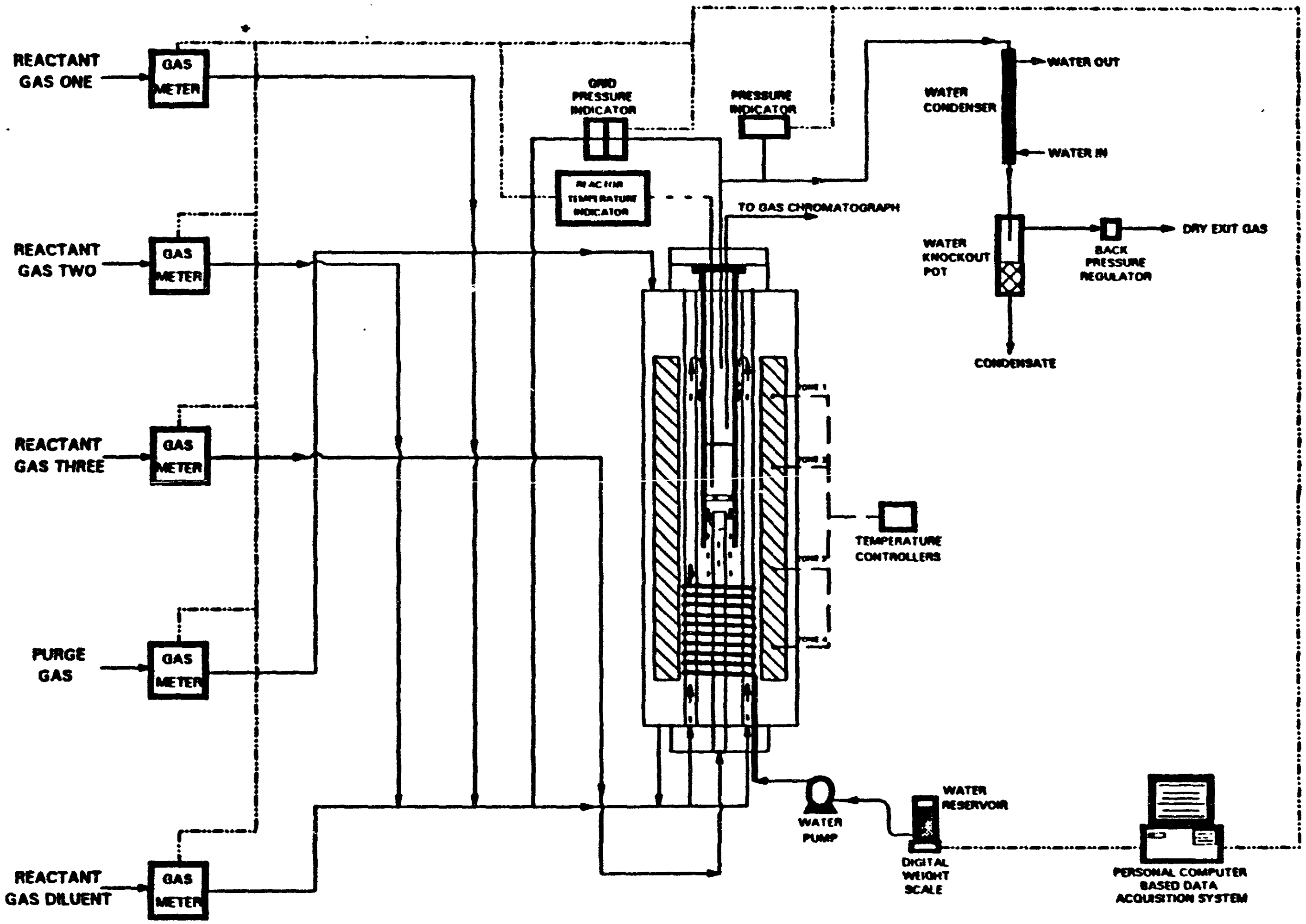


Figure 3. SCHEMATIC DIAGRAM OF THE HIGH-PRESSURE/HIGH-TEMPERATURE REACTOR (HPTR) UNIT

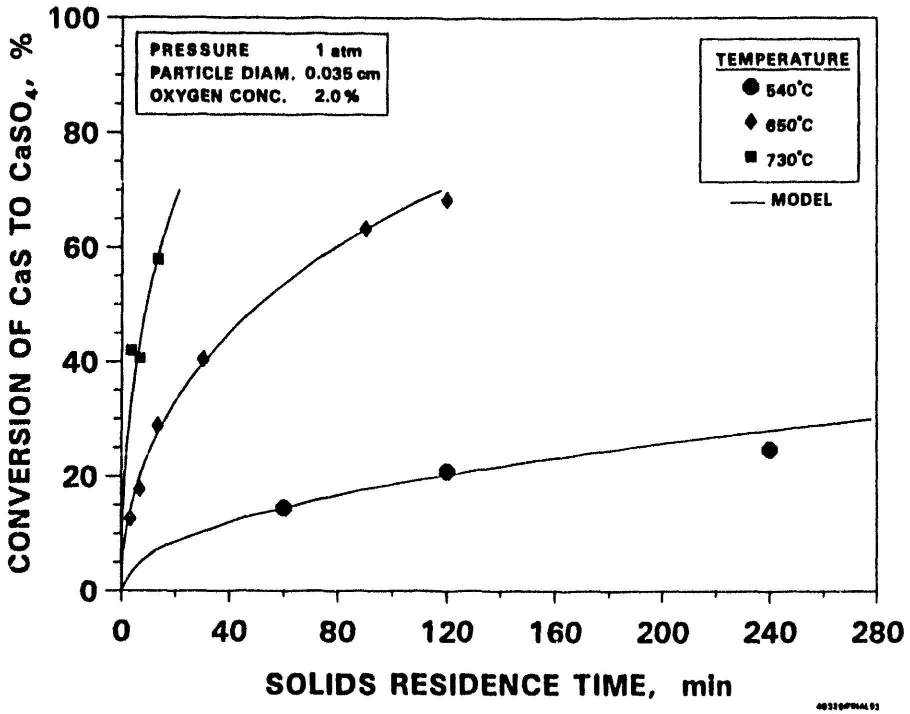


Figure 4. COMPARISON OF EXPERIMENTAL DATA AND MODEL AT DIFFERENT REACTION TEMPERATURES

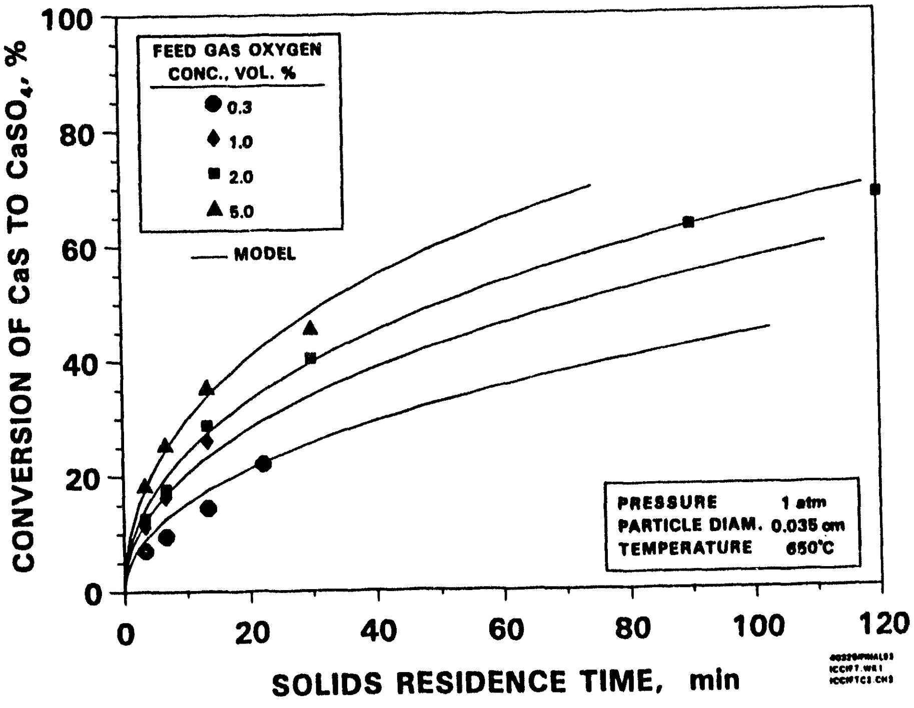


Figure 5. COMPARISON OF EXPERIMENTAL DATA AND MODEL AT DIFFERENT OXYGEN CONCENTRATION

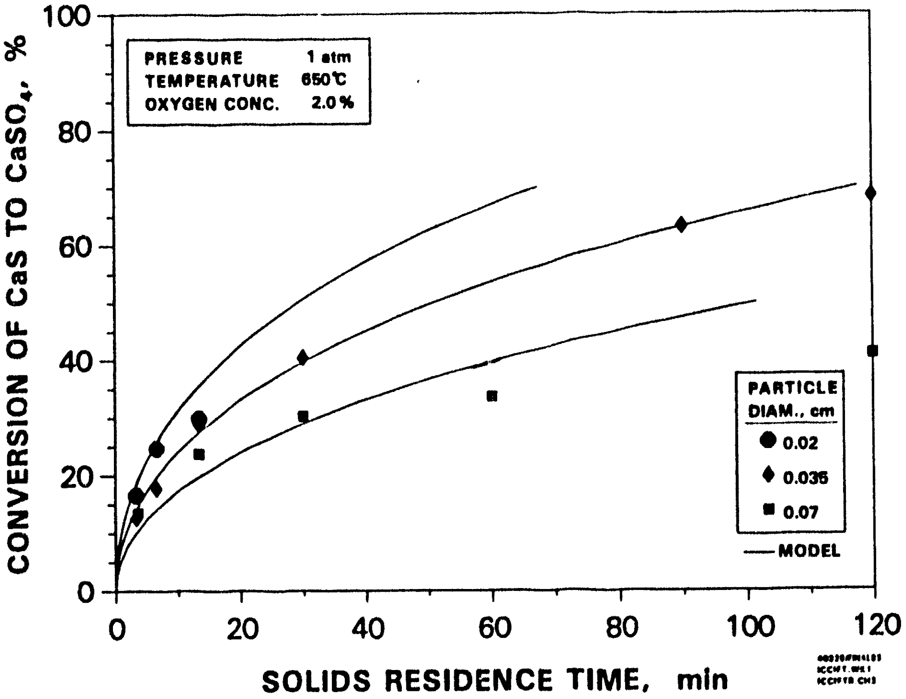


Figure 6. COMPARISON OF EXPERIMENTAL DATA AND MODEL AT DIFFERENT PARTICLE SIZE

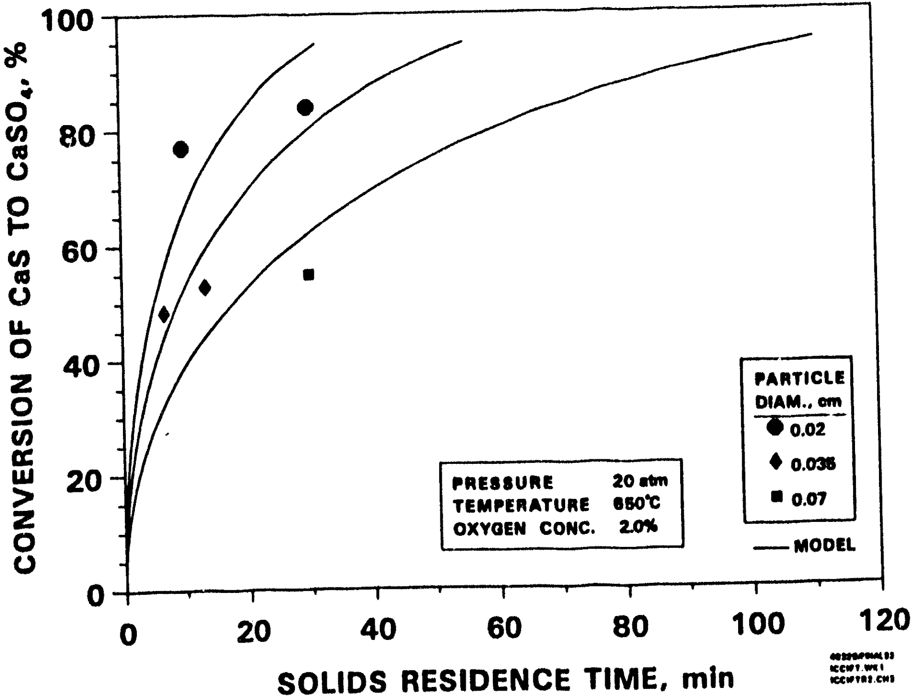


Figure 7. COMPARISON OF EXPERIMENTAL DATA AND MODEL AT ELEVATED PRESSURE

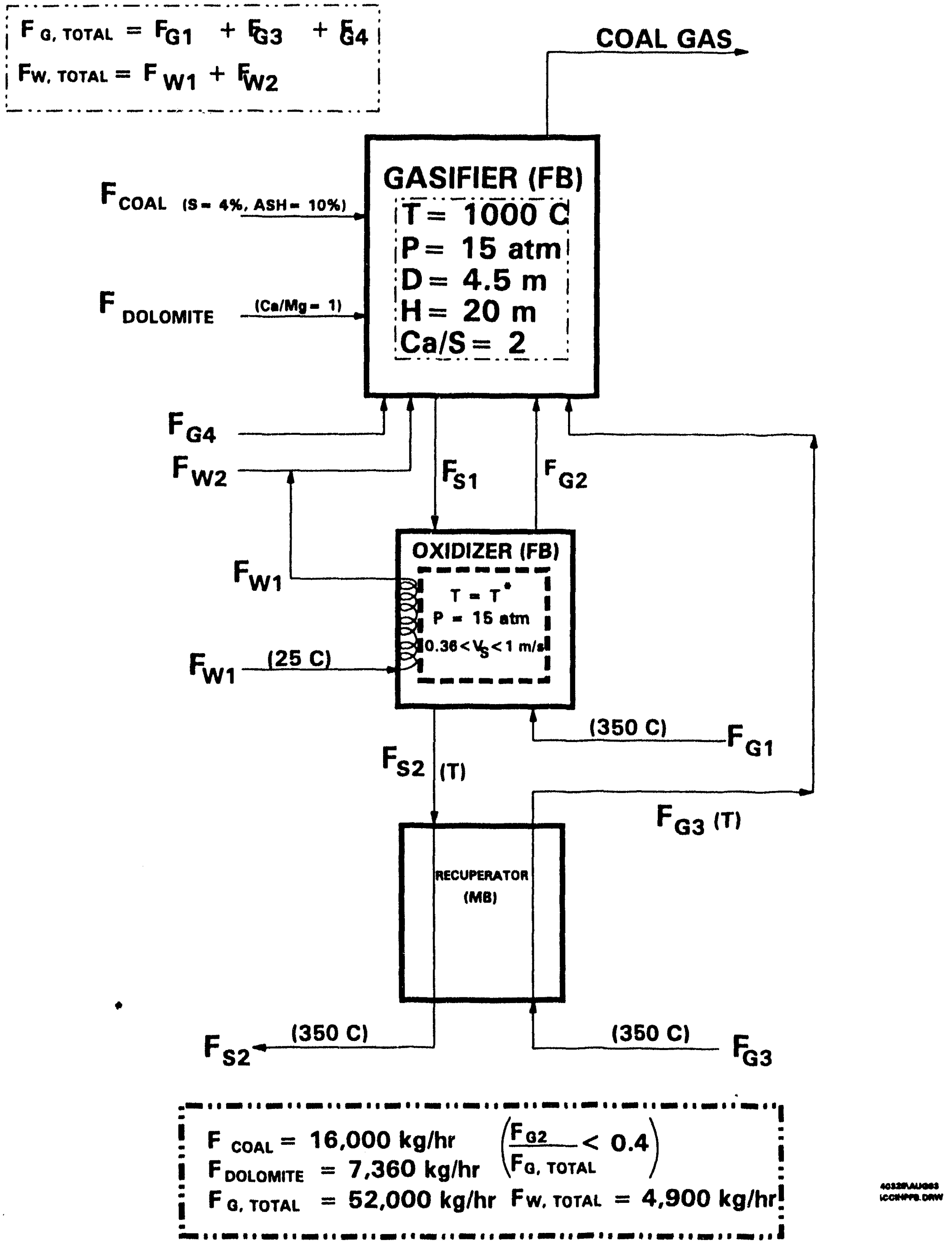


Figure 8. MODEL FOR GASIFICATION WITH HIGH PRESSURE SPENT SORBENT STABILIZATION

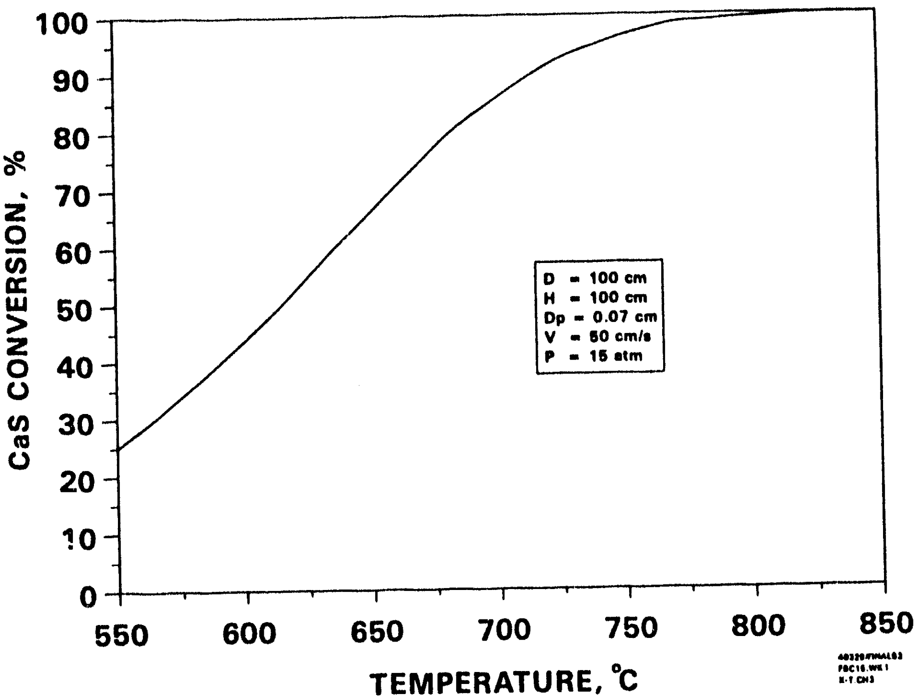


Figure 9. EFFECT OF TEMPERATURE ON CaS CONVERSION IN THE OXIDIZER

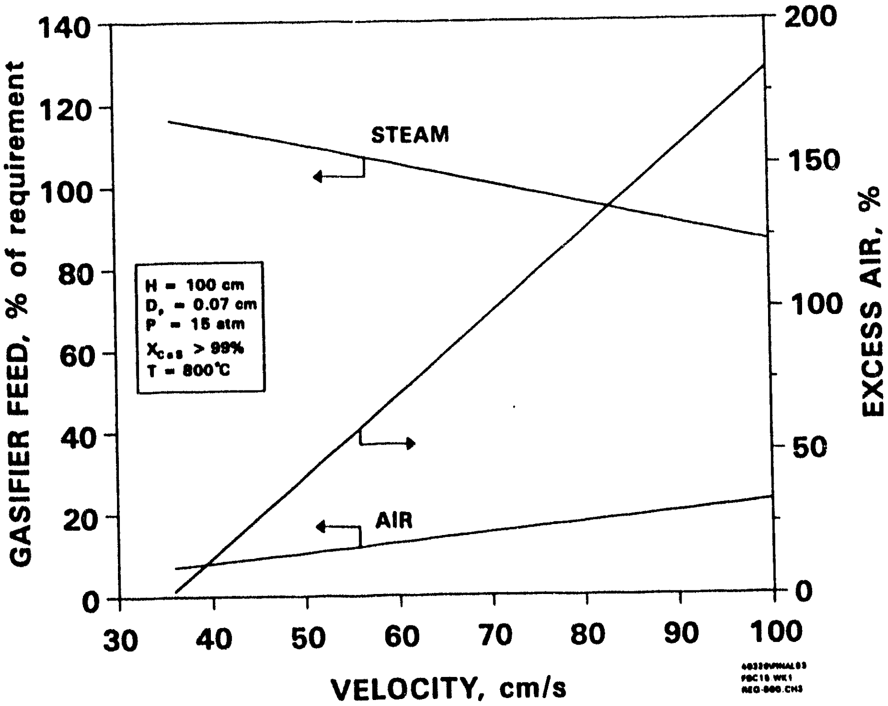


Figure 10. OXIDIZER PERFORMANCE AT 800°C

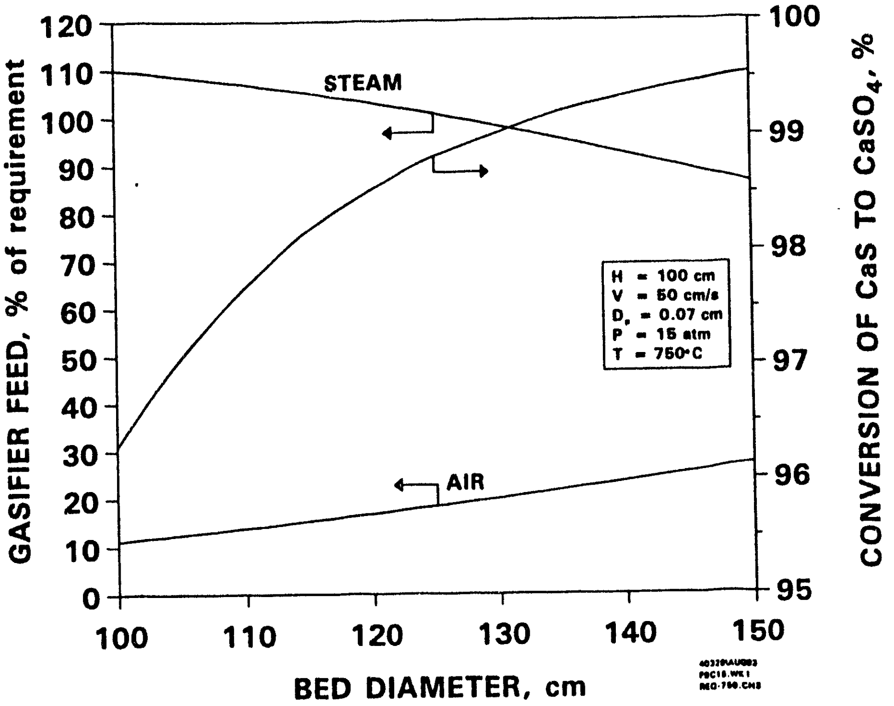


Figure 11. OXIDIZER PERFORMANCE AT 750°C

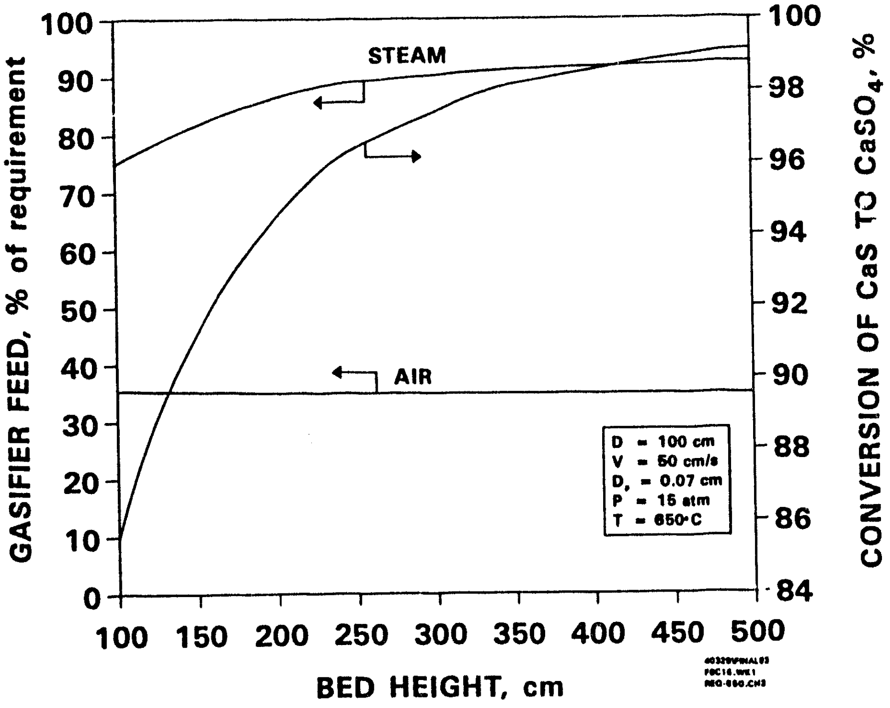


Figure 12. OXIDIZER PERFORMANCE AT 650°C

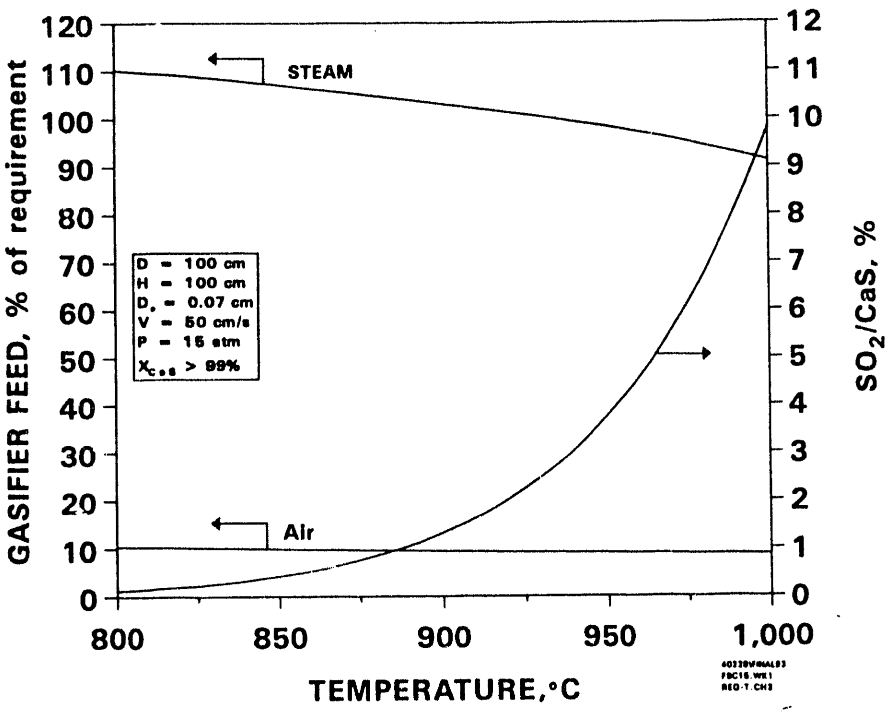


Figure 13. OXIDIZER PERFORMANCE FOR SMALL PARTICLES

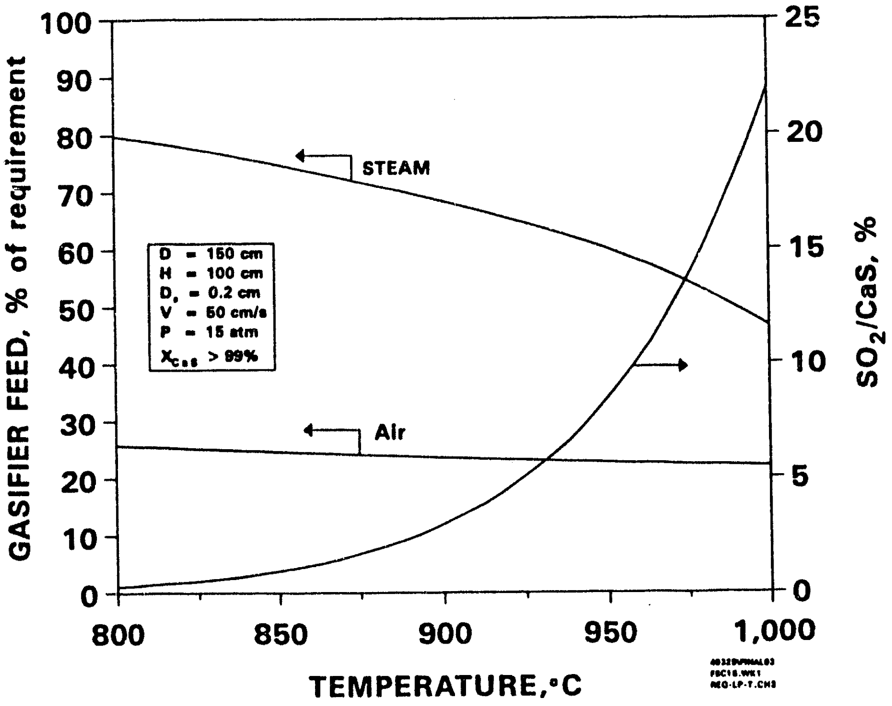


Figure 14. OXIDIZER PERFORMANCE FOR LARGE PARTICLES

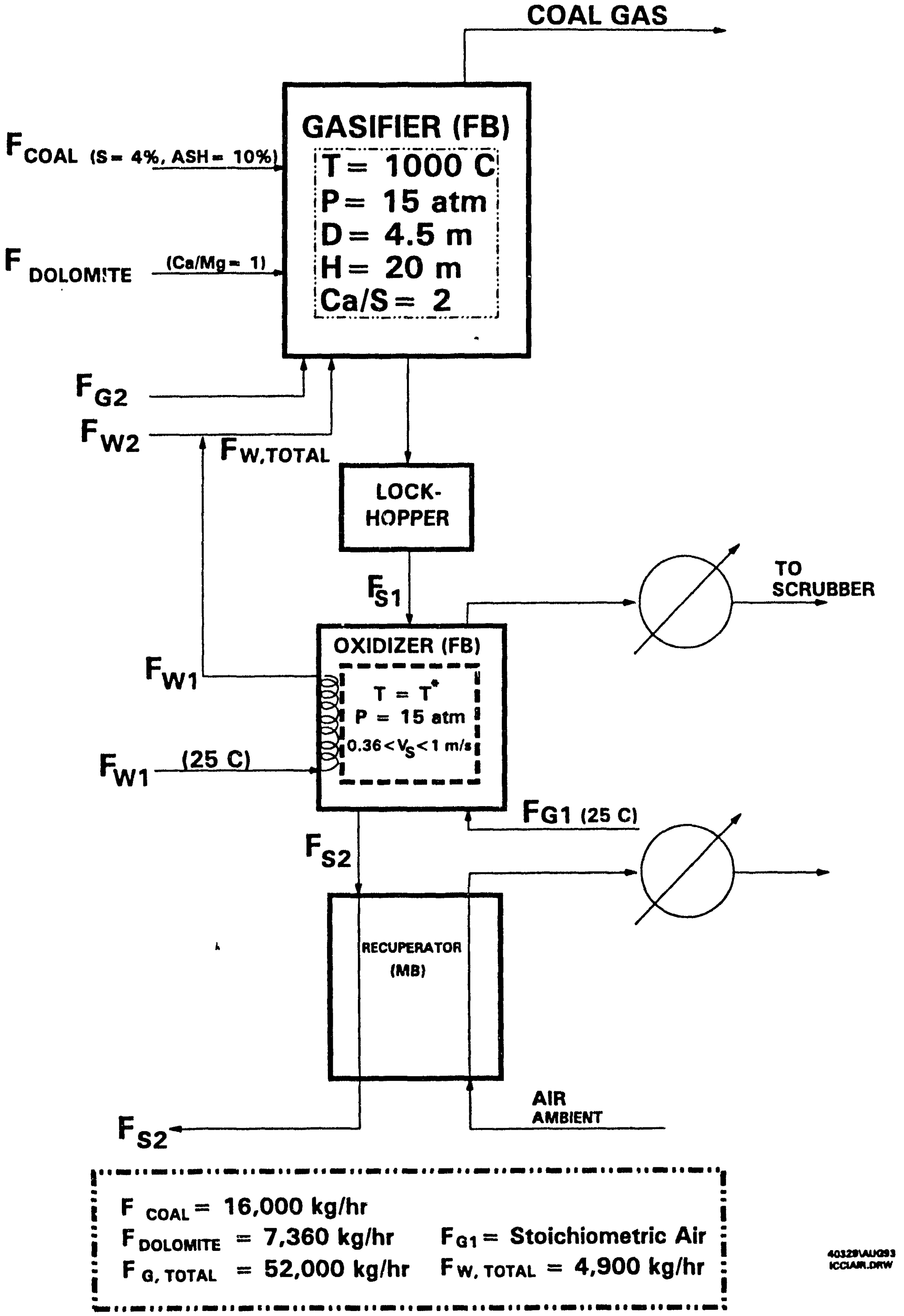


Figure 15. MODEL FOR GASIFICATION WITH AMBIENT PRESSURE SPENT SORBENT STABILIZATION

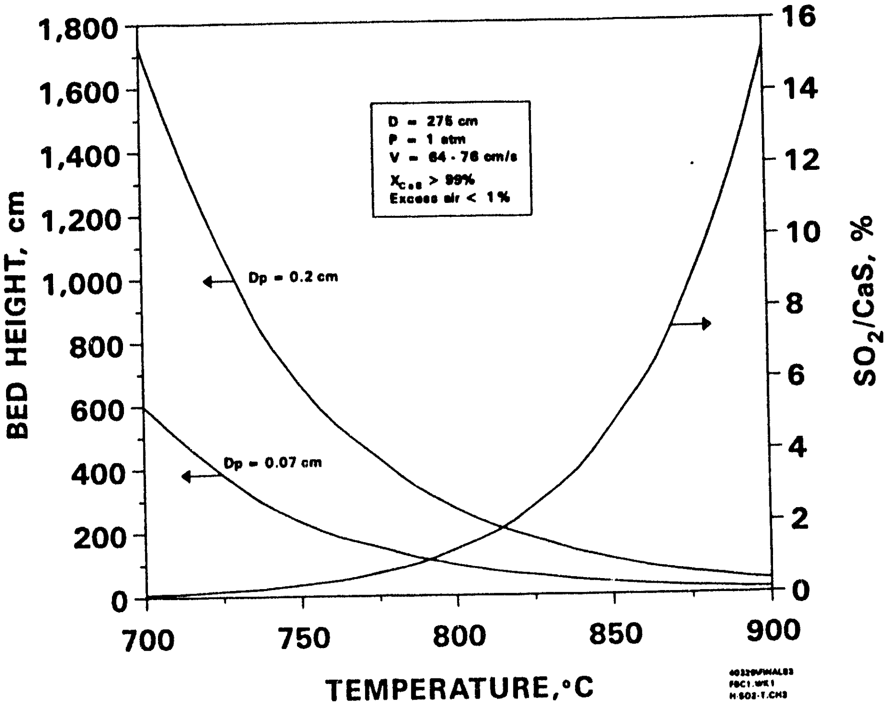


Figure 16. LOW PRESSURE OXIDIER PERFORMANCE

PROJECT MANAGEMENT REPORT
June 1, 1993 through August 31, 1993

Project Title:	**STABILIZATION OF SPENT SORBENTS FROM COAL GASIFICATION**
Principal Investigator:	Javad Abbasian, Institute of Gas Technology
Other Investigators:	Andy H. Hill, Institute of Gas Technology David M. Rue, Institute of Gas Technology James R. Wangerow, Institute of Gas Technology
Project Manager:	Daniel D. Banerjee, Illinois Clean Coal Institute

COMMENTS

The project was completed on schedule and all objectives of the project were achieved.

STABILIZATION OF SPENT SORBENTS FROM COAL GASIFICATION

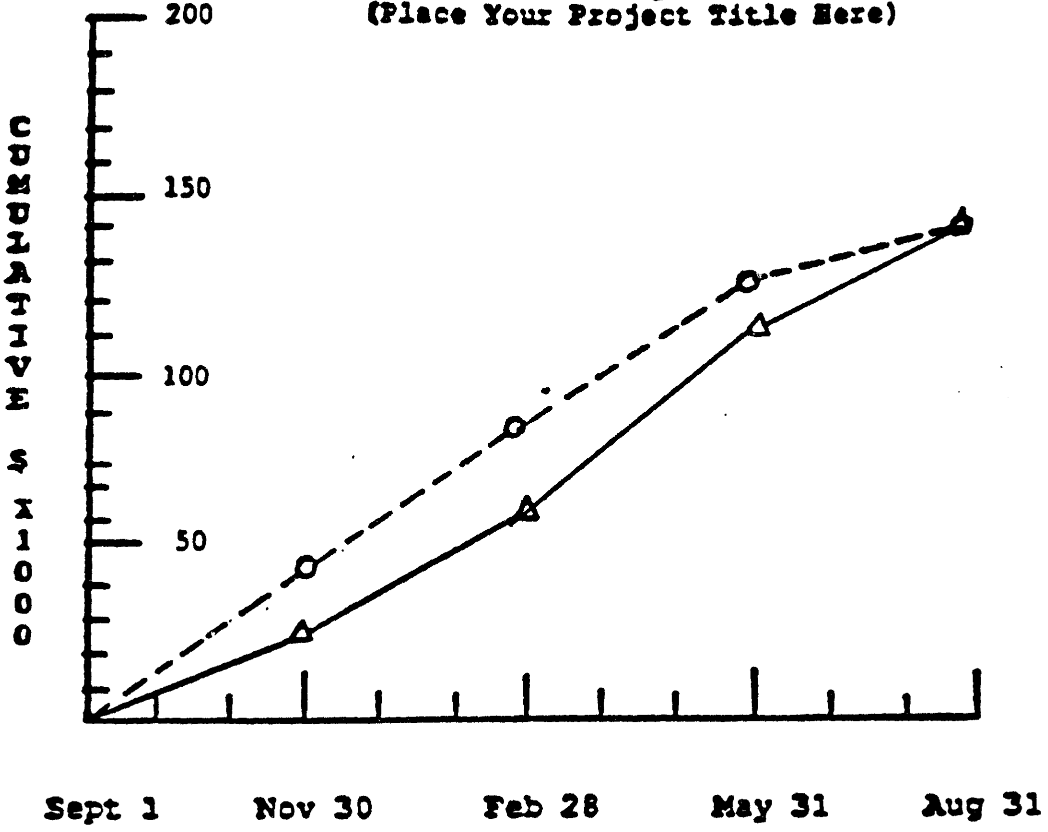
Projected and Estimated Expenditures by Quarter

Quarter*	Types of Cost	Direct Labor	Fringe Benefits	Materials & Supplies	Travel	Major Equipment	Other Direct Costs	Indirect Cost	Total
Sept. 1, 1992 to Nov. 30, 1992	Projected	14572		3000				26,964	44,536
	Estimated	8182		1200				14,641	24,023
Sept. 1, 1992 to Feb. 28, 1993	Projected	29145		4500				53,615	87,260
	Estimated	22174		2700				39,558	64,432
Sept. 1, 1992 to May 31, 1993	Projected	42720		6200				80,218	130,130
	Estimated	39518		4500				70431	114850
Sept. 1, 1992 to Aug. 31, 1993	Projected	47261		6200	1380			87009	141,850
	Estimated	48437		5535	1268			86610	141,850

*Cumulative by Quarter

STABILIZATION OF SPENT SORBENTS FROM COAL GASIFICATION

COSTS BY QUARTER
(Place Your Project Title Here)



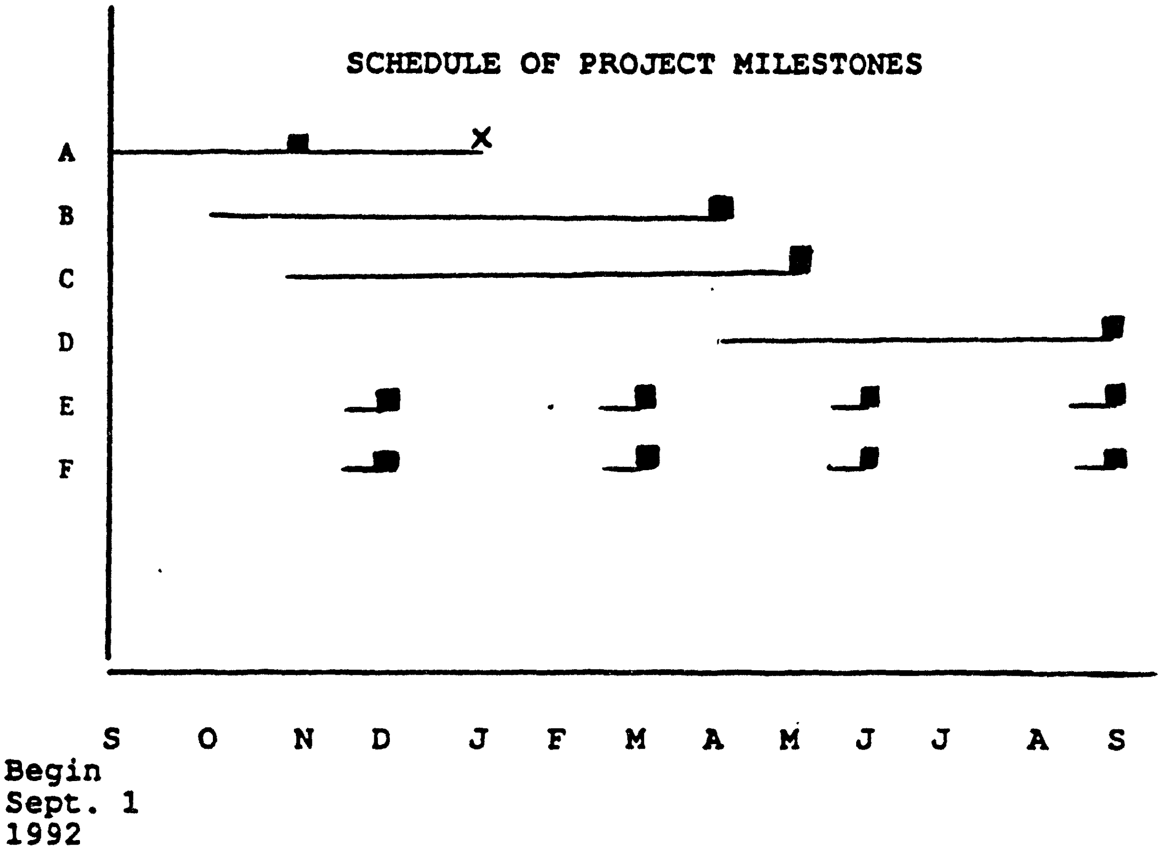
Months and Quarters

0 = Projected Expenditures 141,850

▲ = Estimated Actual Expenditures 141,850

Total Illinois Clean Coal Institute Award $ 141,850

STABILIZATION OF SPENT SORBENTS FROM COAL GASIFICATION



A. Preparation of Partially Sulfided Sorbents

B. Measurement of Sulfation Reaction Rate

C. Physical and Chemical Analyses of the Reacted Sorbents

D. Development of Kinetic Model for Stabilization Reaction

E. Preparation of Technical Reports

F. Preparation of Project Management Reports