

A THERMOGRAVIMETRIC STUDY OF THE SULFATION OF LIMESTONE AND DOLOMITE — PREDICTION OF PRESSURIZED AND ATMOSPHERIC FLUIDIZED-BED DESULFURIZATION *

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ABSTRACT

A pressurized thermogravimetric (TG) analysis system was used to study the isothermal reaction of sulfur dioxide with limestone and dolomite at 1 and 10 atm pressure, and temperatures from 750 to 1050°C. Sorbents of 44–4000 μm particle size were sulfated in gases simulating a 10–300% excess air level in a coal combustion atmosphere. The TG rate data were used to predict the desulfurization performance of limestone and dolomite sorbents in atmospheric and pressurized fluidized-bed combustion systems. The projections are compared to available pilot plant data (i.e., the pressurized Exxon miniplant), and their limitations are discussed.

DEFINITION OF VARIABLES

- a = Stoichiometric reaction coefficient for the solid = 1
- b = Stoichiometric reaction coefficient for the gas = 1
- C = Mole SO_2 cm^{-3}
- D = Diffusion coefficient
- D_p = Pore diffusion coefficient
- F = Volume fraction of particle volume occupied by inerts
- K = Rate constant for sulfur sorption by limestone
- m = Molecular weight
- P = Pressure
- ρ = Particle density, mole Ca cm^{-3}
- R = Gas constant
- \bar{R} = Sulfur retention (%)
- R_a = $(d\alpha/dt)_P / (d\alpha/dt)_{P=1}$
- r = Particle radius
- \bar{r} = Average pore radius
- X = Particle porosity
- z = Gas residence time (expanded bed height/superficial velocity)
- α = Mole fraction of sorbent calcium sulfated
- ϵ = Bed voidage in emulsion fraction

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γ = Volume fraction of bed bubbles

θ_A = Absolute temperature

τ = Tortuosity (2–6)

INTRODUCTION

The sulfation of limestone (CaCO_3) and dolomite ($\text{CaCO}_3 \cdot \text{MgCO}_3$) is a reaction of industrial importance since it is the process by which sulfur emissions are controlled in fluidized-bed combustion systems. Previous work has shown that the reaction ($\text{CaO} + \text{SO}_2 + 1/2 \text{O}_2 \rightarrow \text{CaSO}_4$) is first order in sulfur dioxide [1,2], at least at low partial pressures of sulfur dioxide, the initial reaction rate increases with temperature [3], and the rate and saturation extent of reaction is limited by diffusion of sulfur dioxide into the particle's pores created during calcination ($\text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2$). This limitation arises from the larger molar volume of the sulfate ($46 \text{ cm}^3 \text{ mole}^{-1}$) relative to the oxide ($17 \text{ cm}^3 \text{ mole}^{-1}$) and the carbonate ($37 \text{ cm}^3 \text{ mole}^{-1}$). The pore structure formed during calcination varies from sorbent to sorbent, and is highly dependent on the calcination conditions [4]. The optimum pore structure allows sulfur penetration into the sorbent particle (intergranular diffusion) and into the individual grains or crystallites of CaO (intragranular diffusion).

In a fluidized-bed combustor, coal is injected into an air-fluidized bed of calcined limestone or dolomite. Combustion of the coal in the bed at 700–1000°C liberates heat which is removed by steam tubes immersed in the bed and placed in the freeboard above the bed. The sulfur in the coal is released as sulfur dioxide, which reacts with the calcined limestone or dolomite in the bed to form calcium sulfate. Continuous removal of the bed material and replacement by fresh limestone maintains the desulfurizing action of the bed.

The feed requirements of limestone to maintain sulfur emission standards greatly affect the economics of the fluid-bed combustion system. The limestone must be purchased, received, sized, stored, dried, distributed to the combustor and the spent stone cooled, stored and disposed of; and the heat penalty for endothermic calcination in the bed is great. Much available pilot plant and bench scale data on desulfurization are not collected at steady state. Sulfation kinetics of different limestones vary greatly, and the problem of scaling-up available data for commercial, industrial, and utility uses is present. The development of a model [5,6] based on reaction rate constants determined from thermogravimetric (TG) data has proved to be very useful.

Previous TG results have shown that the effects of operating variables observed in fluid-bed combustors could be predicted from TG experiments. The influence of temperature [5], excess air [5], precalcination [4], bed depth, and fluidization velocity on desulfurization in fluid-bed combustors have been demonstrated with TG data. TG results obtained at 10 atm pressure are outlined here, along with projections made from this data of fluid-bed desulfurization performance in the Exxon miniplant, a 12.5-in. diameter pressurized fluid-bed unit.

EXPERIMENTAL DESCRIPTION

The TG apparatus and data acquisition system have been described elsewhere [4,7] (Fig. 1). A Du Pont 951 thermobalance was modified, according to Ruth [8], to accept corrosive gases by introducing a nitrogen purge through the balance mechanism and feeding the reactant gas mixture through the opposite end of the furnace tube. To study the reaction at pressure, one of the Du Pont 951 thermobalances and furnaces was mounted in a stainless steel pressure shell capable of operation to 3000 kPa.

One of the problems encountered in pressurized data operation was the uncertainty of temperature control. The wall temperature (control thermocouple) has been recorded as over 100°C higher than the sample temperature (thermocouple beside sample basket). To facilitate gas preheating, a section of the furnace tube was packed with an aluminum block. The gas stream was then directed over the sample by constricting the inner tube wall (Fig. 2). Using the configuration, the equilibrium temperature for limestone calcination in 1.4 atm of CO_2 at 10 atm total pressure was $912\text{--}914^{\circ}\text{C}$, in fair

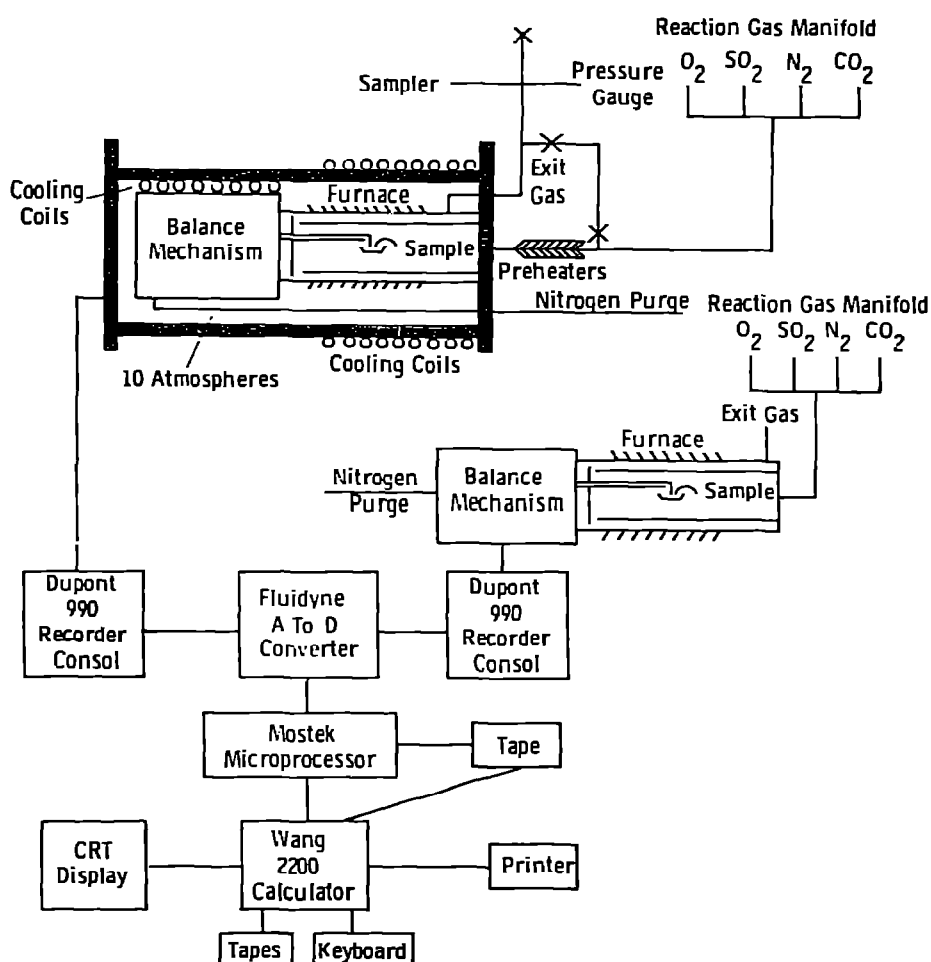


Fig. 1. Schematic of TGA and data acquisition system.

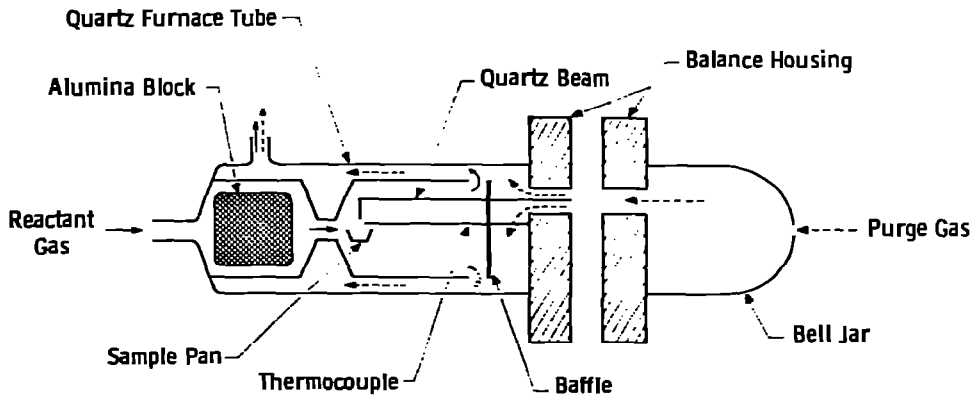


Fig. 2. Schematic of DuPont furnace tube configuration.

agreement with 918°C obtained by extrapolating data on CaCO_3 spheres by Hills [9].

Natural limestones and dolomites characterized in Table 1 were sized to the desired range (74–4000 μm). Samples weighing 10–20 mg were placed in a platinum mesh screen suspended from the balance arm. Samples were calcined before the reaction in premixed gases of CO_2 and N_2 by heating up to the desired temperature at $10^\circ\text{C min}^{-1}$. The sulfating gas atmosphere was then introduced. Flow rates of 600 ml min^{-1} (STP) at atmospheric pressure and 1000 ml min^{-1} (STP) at 10 atm pressure were used.

RESULTS

Sulfation rate data were obtained for a variety of sorbents at 1 and 10 atm pressure under conditions relevant to fluid-bed combustion. The rate data were used to express the rate constant of sulfation as a function of sorbent sulfation extent with a 2nd–4th order polynomial fit of the data.

TABLE 1

Sorbents used in sulfation studies

	Sorbent			
	Grove (1359)	Greer	1337	Tymochtee
Ca as CaCO_3 (wt. %)	96.4	67.8	52.9	51.1
Mg as MgCO_3 (wt. %)	1.5	2.3	45.05	42.2
Al as Al_2O_3 (wt. %)	<0.4	9.8	0.08	2.0
Fe as Fe_2O_3 (wt. %)	1.0	3.7	0.2	0.97
Si as SiO_2 (wt. %)	<0.1	15.4	3.8	3.9
Na as Na_2O (wt. %)	0.008	0.56	0.04	0.075
K as K_2O (wt. %)	0.1	2.3	0.05	0.68
Cl (wt. %)	0.002	0.01	0.05	0.048
Sum (wt. %)	99.5	101.9	102.2	101.0
Ignition wt. loss (%)	42.4	32.4	46.7	44.8

Temperature

Typically, the sulfur removal efficiency of limestone in atmospheric fluidized-bed combustion improves with increasing temperatures up to 820–850°C. Further increasing the temperature reduces the sulfur removal efficiency. This same optimum temperature has been observed in the extent of sulfation of sorbents sulfated in the TG [10]. Several mechanisms have been proposed to explain this effect and the observation that at high pressure (10 atm) no decrease in limestone utilization was observed at temperatures up to 950°C. Two of the mechanisms, the silica deactivating mechanism [3] and the oxidizing/reducing cycle mechanism, are incomplete in that they do not explain results obtained in the TGA. Most other explanations relate to a chemically controlled reaction (i.e., SO₃ formation [11]). It is, however, very likely that pore diffusion limits the reaction rate in the regions of interest. Figure 3 illustrates the effect of temperature on the pressurized sulfation of Greer limestone. Increased sorbent utilization was obtained at higher temperatures to 1010°C. The rates of reaction vary the most with temperature at greater than 30% sulfation, where diffusion of SO₂ into the limestone pores would play an important role in the reaction. This is indicated by the rapid decrease in reaction rate with increased conversion.

In regions of diffusion control, changes in the sorbent pore structure can account for the observed temperature effects. As the temperature increases, the calcination proceeds at a faster rate and, in general, produces a less active sorbent. At pressure, active calcines are formed at higher temperatures because of the higher partial pressures of CO₂ generated. In addition, the

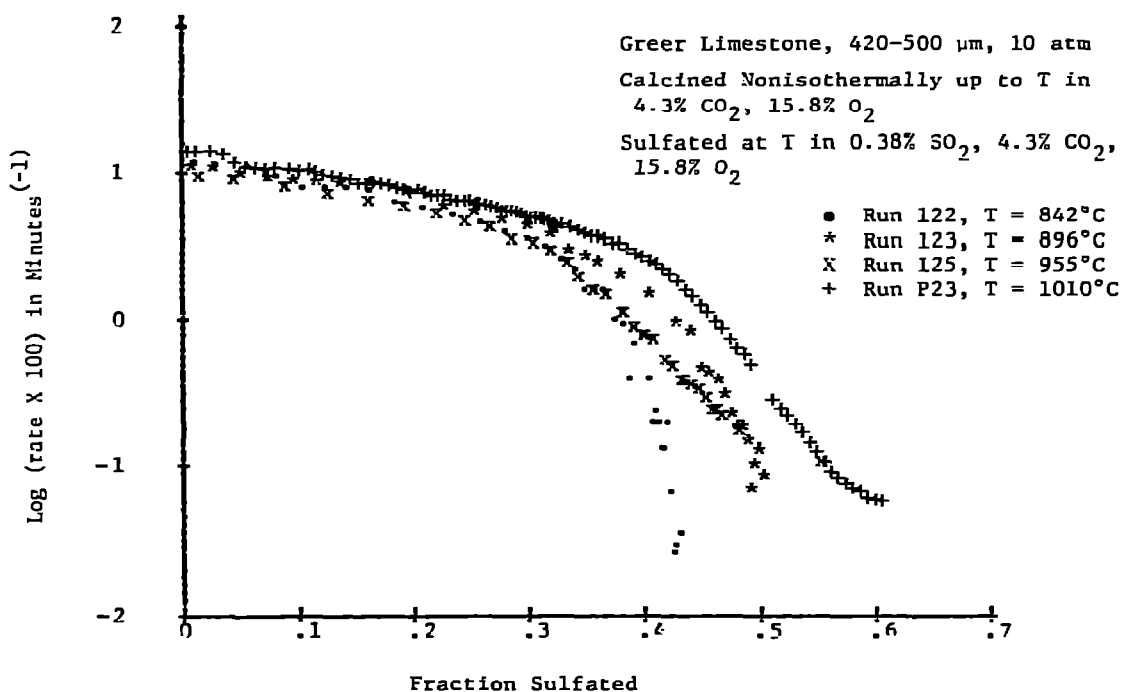


Fig. 3. The effect of temperature on the pressurized sulfation of Greer limestone.

optimum temperature for limestone sulfation has been shown to vary with the pore size distribution of the calcine because of shifts in the relative rates of chemical reaction and pore diffusion with the sorbent's pore structure [4].

Excess air (O_2 and CO_2 concentration) effects

Increasing the excess air in which coal is burned changes the gas composition in which the sorbent sulfates, the partial pressure of oxygen is increased, and the partial pressure of CO_2 is reduced.

Sulfation at atmospheric pressure was found to be zero order in oxygen concentration in the range 2–11% [10]. The influence of oxygen concentration on the pressurized (10 atm) and atmospheric sulfation of Tymochtee dolomite is shown in Figs. 4 and 5. The dolomite was sieved to 16/18 mesh and fully calcined on the TGA at 815°C in 0.15 atm of CO_2 before the sulfations. The results show little influence of the partial pressure of O_2 from 0.075–1.6 atm in pressurized sulfation. The scatter in the atmospheric sulfation data is not related to the oxygen partial pressure. These rate curves indicate fair repeatability of the sulfation kinetics obtained in the atmospheric and pressurized thermobalances.

Previous work has shown that the CO_2 concentration has a great influence on the type of pore structure formed during calcination and thus, indirectly,

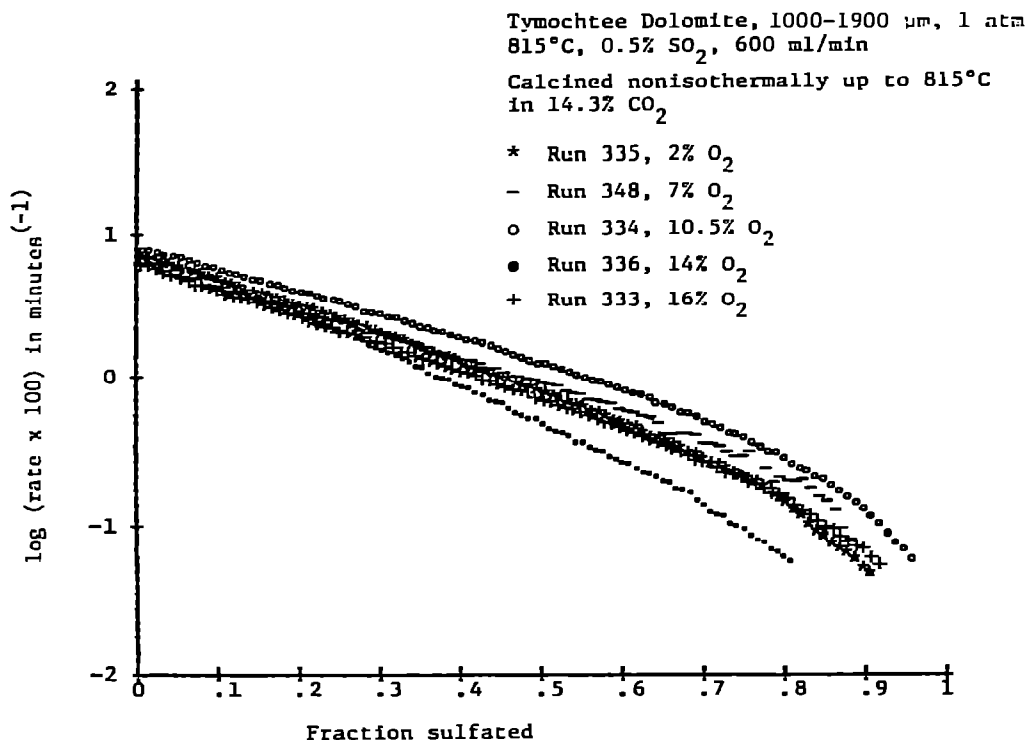


Fig. 4. The influence of oxygen concentration on the atmospheric sulfation rate of Tymochtee dolomite.

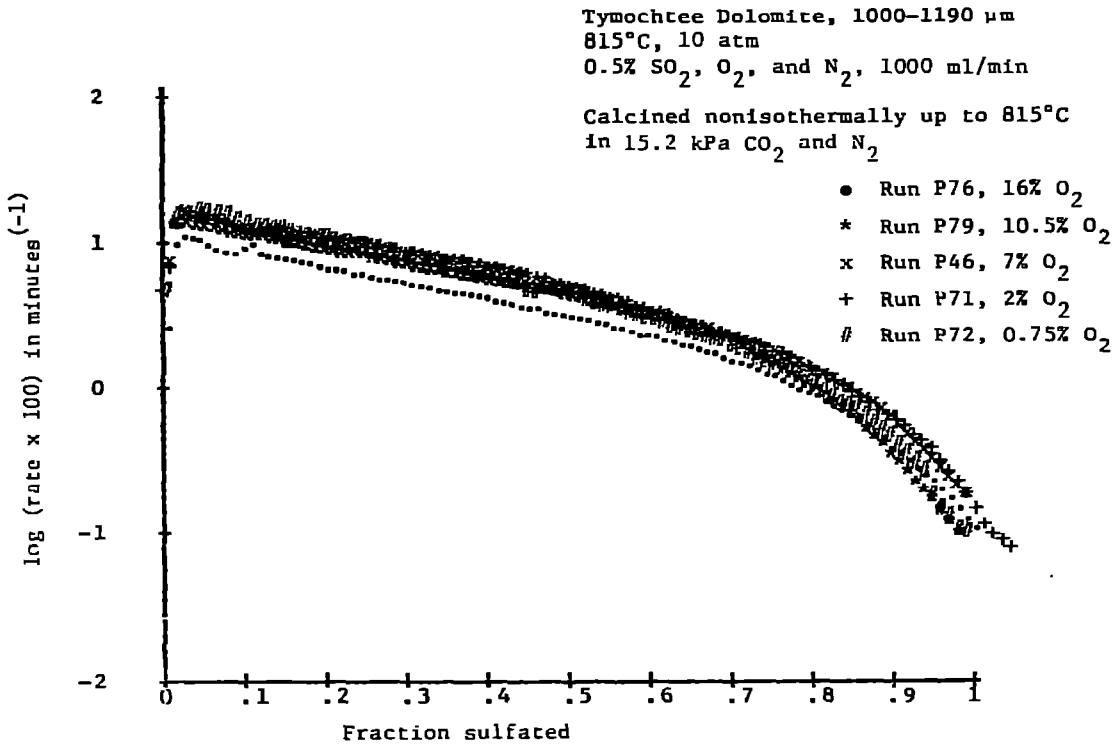


Fig. 5. The influence of oxygen concentration on the pressurized sulfation rate of Tymochtee dolomite.

on the sulfation kinetics [4,10]. Little direct effect of CO_2 concentration was found on the sulfation of calcined sorbents. During pressurized operation of combustion units, the partial pressures of CO_2 generated are often in excess of the equilibrium pressure for calcination of the calcium carbonate. For this reason, the sulfation of some limestones at 10 atm in the carbonated state was studied. (Past studies have concentrated on the use of half-calcined dolomites [5].) A pure limestone, Grove, with small, tightly interlocking grains had little ability to absorb sulfur (<5% sulfated) in the carbonated state. Greer limestone, however, a stone with many impurities and a loosely-packed structure of calcite crystallites, was active in the carbonated state if the partial pressure of CO_2 was close to the equilibrium value. At 815°C, the equilibrium pressure for calcination is 0.25–0.30 atm. In 1.5 atm of CO_2 , less than 5% of the limestone could be sulfated. Some improvement in the sulfation extent was achieved by lowering the CO_2 partial pressure to 0.87 atm. At 0.58 atm of CO_2 , the carbonated stone was approaching the reactivity of the calcined sorbent (Fig. 6). Diffusion of CO_2 away from the stone in a high partial pressure of CO_2 evidently limits the sulfation of carbonated sorbents. Some limestones, such as Greer, may be useful sorbents in the carbonated form, provided the CO_2 partial pressure is not much greater than the equilibrium for calcination.

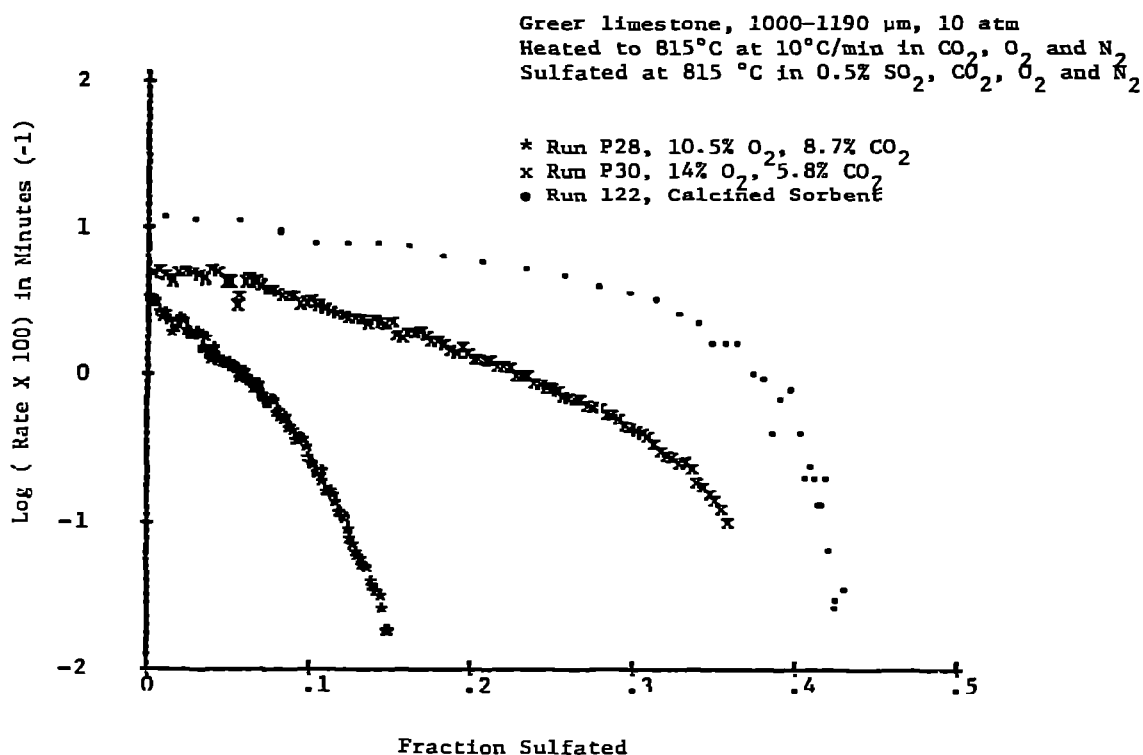


Fig. 6. The influence of carbon dioxide partial pressure on the pressurized sulfation of carbonated Greer limestone.

Sorbent residence time

Sorbents used in fluidized-bed combustion will typically have residence times of 12 h at temperatures of 800–1000°C. TG tests on sorbents were run with 0.5% SO_2 so that the complete reaction could be studied in about 2 h. The rate constants derived from the TG data were based on assuming a first-order reaction in SO_2 . The longer residence times and lower SO_2 concentrations in the fluid bed could cause sintering of the sorbent, changing its pore structure and reactivity toward SO_2 . The effect of residence time at various temperatures on the sulfation kinetics of limestones at 1 and 10 atm was studied by varying the SO_2 concentration in the gas.

The rate of sulfation at 10 atm in 0.1% SO_2 was predicted for Greer limestone using TG data from runs with 0.05–0.5% SO_2 in the gas and assuming first-order kinetics (Fig. 7). The predicted curve is fairly consistent, indicating that a first-order reaction is followed and the sorbent is unaffected by the time held at temperature (the time required for 37% utilization varied from 15 to 89 min). The same analysis using Grove limestone, however, indicates sintering of the stone decreases its reaction rate with temperature exposure (Fig. 8). (The time of exposure when sulfated 8% varied from 4 to 66 min.) Similar results were obtained for Grove and Greer limestone at atmospheric pressure.

We conclude that the residence time of a sorbent at temperature may

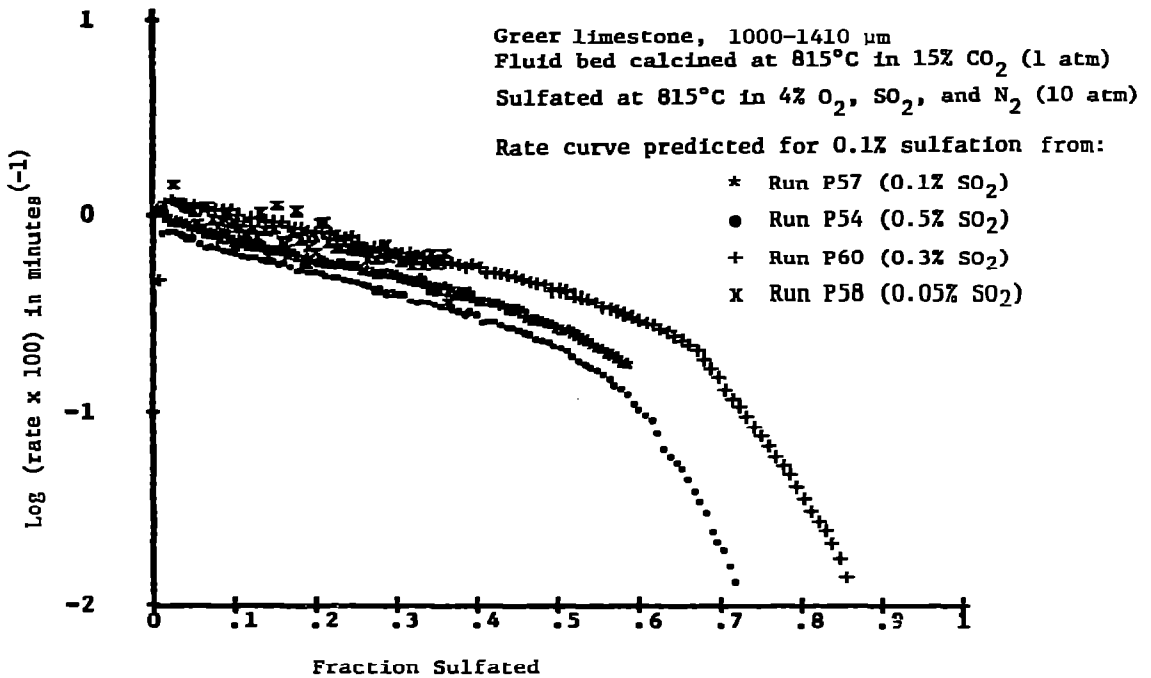


Fig. 7. The influence of sorbent residence time on the pressurized sulfation of Greer limestone.

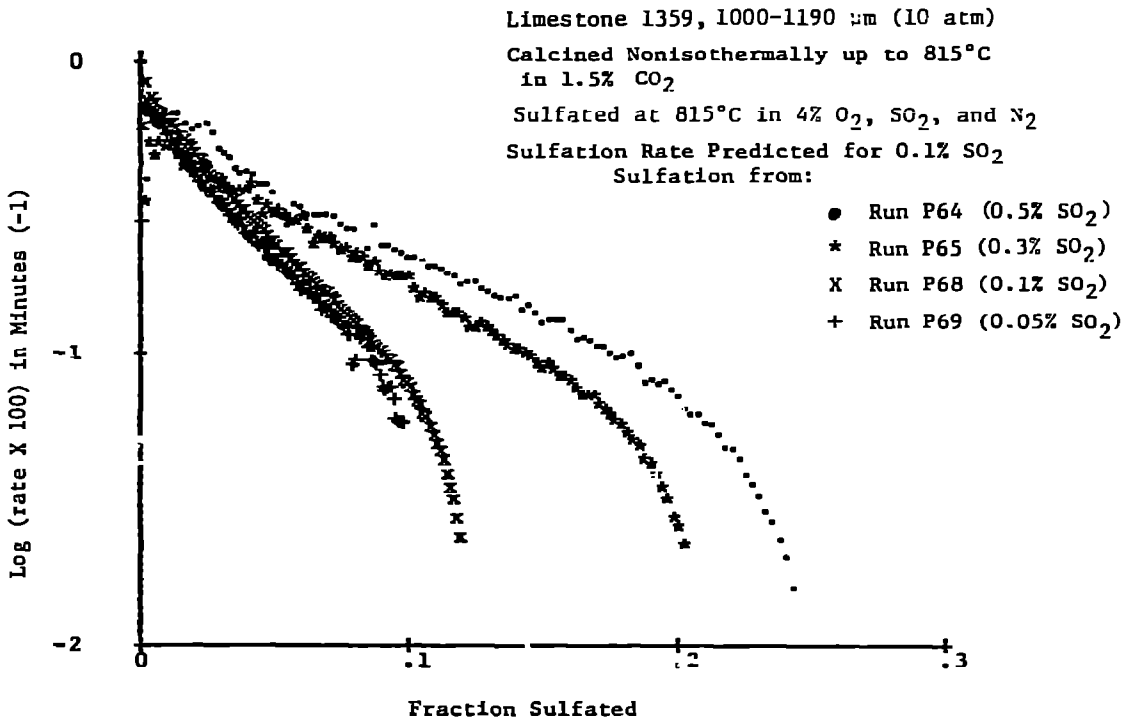


Fig. 8. The influence of sorbent residence time on the pressurized sulfation of Grove limestone.

change the sulfation kinetics, by varying the sorbents pore structure, from the first-order relationship observed at initial reaction periods. Depending on the type of sorbent, this effect could lead to errors in rate constants projected from TG data. Unfortunately, the types of sorbent that will show varied kinetics with residence time have not yet been identified.

Pressure

The ratio of the rate of sulfation at 10 atm to the rate at 1 atm is shown in Fig. 9 for Tymochtee dolomite sulfation. The dolomite was sieved to 16/18 mesh and calcined at 815°C in 0.15 atm of CO₂ before sulfation. Increasing the pressure from 1 to 10 atm has increased the reaction rate by a factor of 2–3 [10] over most of the sulfation. This relationship can be rationalized by considering the rate of pore diffusion in a shrinking core model

$$\frac{d\alpha}{dt} = \frac{1}{2\theta[(1-\alpha)^{-1/3} - 1]}$$

where

$$\theta = \frac{apr^2}{6bD_p C}$$

The gas concentration, C , is proportional to P and the pore diffusion coefficient, D_p , is the sum of two terms, one representing Knudsen diffusion in small pores where collisions between gas molecules and the pore walls are more frequent than collisions between gas molecules.

$$D_p = \frac{X}{\tau} \left[\frac{3}{4\bar{r}} \left(\frac{\pi m}{2R\theta_A} \right)^{1/2} + \frac{1}{D} \right]^{-1}$$

Now the ratio of the rate at pressures to that at atmospheric, R_a , is

$$\begin{aligned} R_a &= \frac{(d\alpha/dt)_P}{(d\alpha/dt)_{P=1}} = \frac{\theta(P=1)}{\theta(P)} = \frac{D_p \cdot C_{SO_2}(\text{at } P)}{D_p \cdot C_{SO_2}(\text{at } P=1)} \\ &= \frac{P[(3/4\bar{r})(\pi m/2R\theta_A)^{1/2} + 1/D(P=1)]}{[(3/4\bar{r})(\pi m/2R\theta_A)^{1/2} + 1/D(P)]} \end{aligned}$$

If no small pores are present, Knudsen diffusion is unimportant and

$$R_a = \frac{P \cdot D(P)}{D(P=1)} = 1$$

Since $D \propto (1/P)$, the rate is not affected by pressurization. If only Knudsen diffusion were important, the rate would be proportional to the pressure. In reality, limestone particles have a broad distribution of pore sizes so D_p is a function of the fractional conversion and this function could vary with pressure. Therefore the ratio of the diffusion controlled rates could exceed 10. As the stones reach 100% conversion the rates as well as the ratio should approach zero.

The reaction, however, does not proceed by a simple shrinking core

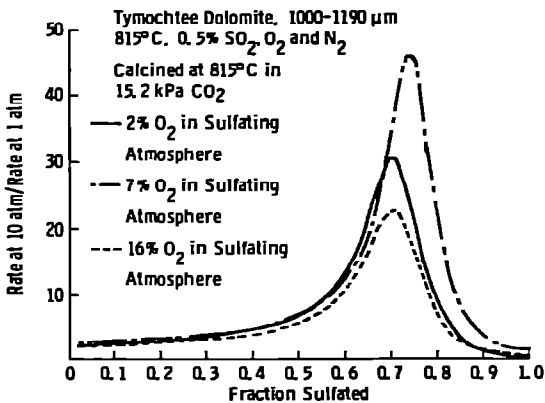


Fig. 9. The effect of pressure on the sulfation rate of Tymochee dolomite.

mechanism, and the combined effects of pore diffusion with chemical reaction control and, possibly, mass transfer resistance must be considered to project accurately the effect of pressure on the sulfation reaction.

APPLICATION

Modeling with thermogravimetric data

A simple process model [5,6] for sulfur sorption by sorbents in a fluidized-bed combustor expresses the sulfur retention, \bar{R} , by a sorbent in terms of an average rate constant for sulfur sorption in the bed, K , as

$$\bar{R} = 1 - \frac{1}{K'z} (1 - e^{-K'z})$$

where

$$K' = K \frac{(1 - \gamma)\epsilon(1 - F)}{\gamma + (1 - \gamma)\epsilon}$$

z = gas residence time = expanded bed height/superficial gas velocity

γ = volume fraction of bed bubbles

ϵ = bed voidage in emulsion fraction

F = volume fraction of particle volume occupied by inerts

The assumptions in the above model were:

- sulfur is uniformly generated as SO_2 throughout the bed;
- sulfur released passes upward through the bed in plug flow;
- absorption of SO_2 by the sorbent is a first-order reaction in SO_2 ;
- there is steady-state operation in the bed;
- diffusion resistance in the sorbent's pores controls the reaction rate;
- there is perfect solids mixing in the bed.

The rate constant for sulfur sorption is dependent on the sorbent type, its extent of sulfation, its treatment (i.e., calcination conditions) and particle

size, and the bed temperature, pressure, and gas composition. Because the reaction is very complex, involving inter- and intragranular diffusion of SO_2 through the sorbent, reaction models have not been successful in predicting the reaction rate as a function of utilization for varied sorbent types and operating conditions. The rate data as a function of utilization can, however, be easily obtained for any sorbent type and operating condition using a properly designed TG experiment. (A mass balance on the TG gives the reaction rate constant as a function of the fractional rate of reaction, $d\alpha/dt$, as

$$\frac{d\alpha}{dt} = \frac{KC\epsilon}{p(1-\epsilon)}$$

where C is the moles of SO_2 cm^{-3} in the TG gas and p is the solids density, mole Ca cm^{-3} .) Thus, the reaction rate constant necessary to maintain any required level of sulfur removal can be calculated from the model. The fractional utilization, U , of any given sorbent at any specified condition that corresponds to the required reaction rate constant is determined from TG data. Given the sulfur retention and the fractional utilization of the sorbent, the amount of limestone necessary to feed along with the coal and maintain emission standards is easily calculated on a moles of calcium to moles of sulfur (Ca/S) basis as

$$\text{Ca/S} = \frac{\bar{R}}{U}$$

TG projections describe the dependence of limestone feed requirements, expressed as a Ca/S molar feed ratio, to maintain 90% sulfur removal for dolomite 1337 at typical fluid-bed operating conditions as a function of sorbent particle size and the gas residence time in the bed (expanded bed height/superficial gas velocity) as shown in Fig. 10. Increasing the gas resi-

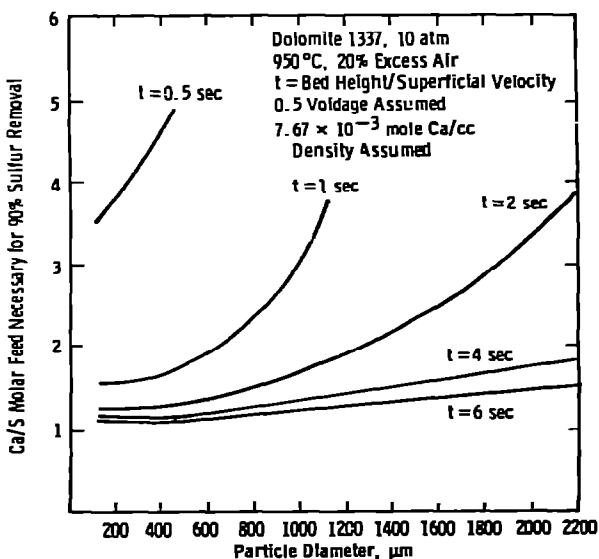


Fig. 10. Ca/S molar feed requirements projected for 90% sulfur removal in pressurized fluid-bed combustion using TG data.

dence time lowers the Ca/S molar feed requirements, but at a decreasing rate. This type of relationship is illustrated by the TG rate data in Fig. 11. Increasing the gas residence time decreases the rate constant necessary to maintain a given level of desulfurization (by the model). As the particle of limestone is more highly sulfated, however, the reaction rate drops off as the pores become plugged with sulfate. In this region of reaction, changes in the rate requirement have little effect on the sorbent utilization obtainable. Changes in sorbent particle size have less effect on limestone requirements at longer gas residence times because particle size had less effect on the reaction rate at lower reaction rates (for this particular sorbent and operating condition).

Comparison to pilot plant data

The projection of atmospheric fluid-bed combustion data from TG data and its comparison with results obtained in bench and pilot scale fluid-bed combustion units are outlined in a contract report [6]. An example of the TG projection of atmospheric results obtained in Argonne National Laboratories [12] bench scale unit is shown in Fig. 12. Projections of pressurized results obtained in the Exxon miniplant were made using TG rate data collected at 10 atm pressure. Projections of the desulfurization obtainable at varied Ca/S molar feed rates using dolomite 1337 are compared to results obtained in Run 27 [13] of the miniplant and are shown in Fig. 13. More

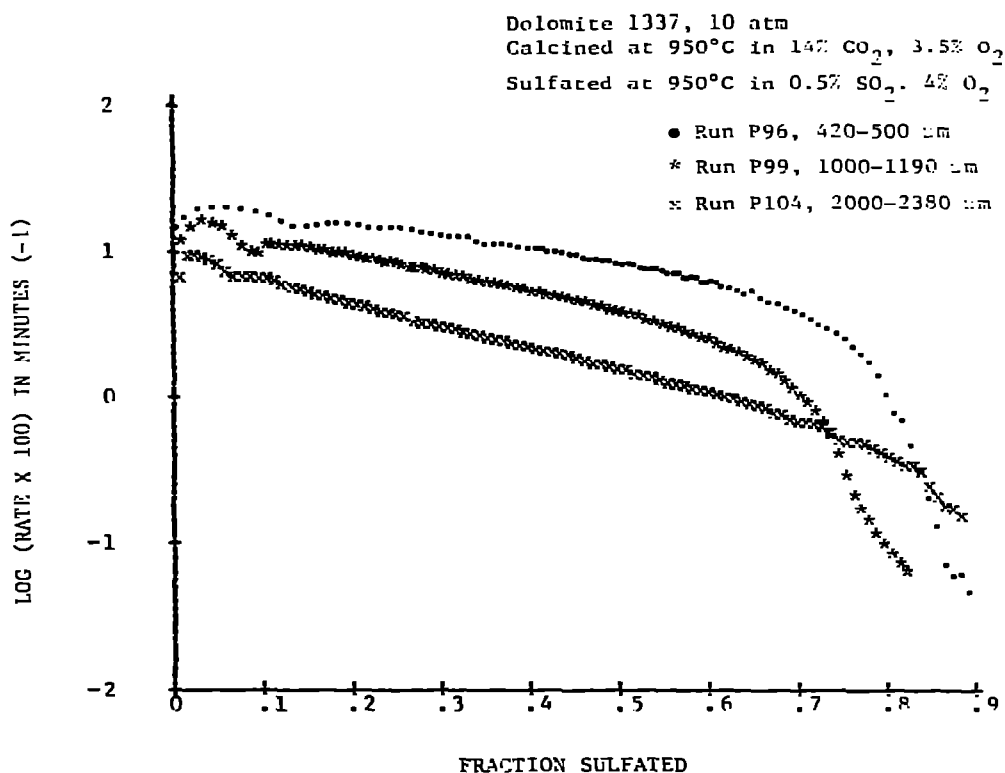


Fig. 11. TG rate data used for pressurized fluid-bed projections.

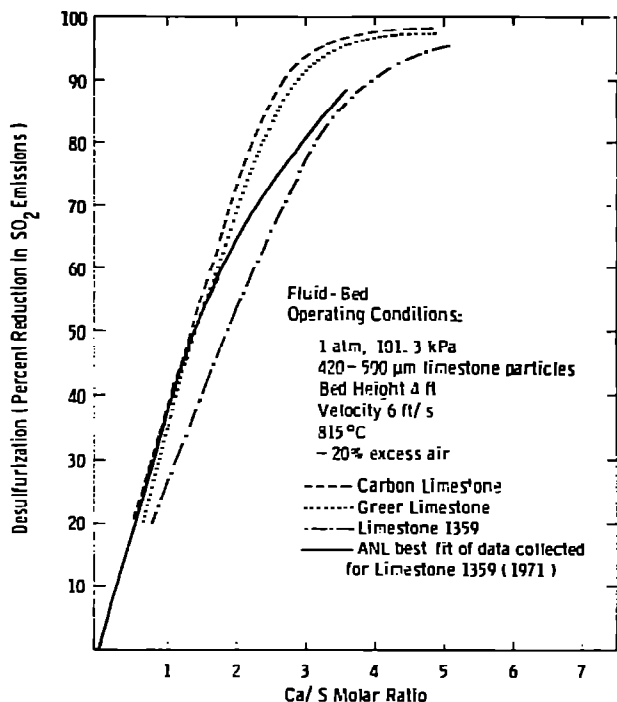


Fig. 12. Comparison of atmospheric TG projections with data from ANL.

recent results from runs [14] designed to investigate higher levels of sulfur removal could also be projected with accuracy (Fig. 14).

The TG projections are limited by the availability of complete pilot plant data (particle size distribution in the bed, fraction of inert particles in the bed, bed expansion data), the accuracy of pilot plant data (including fluctua-

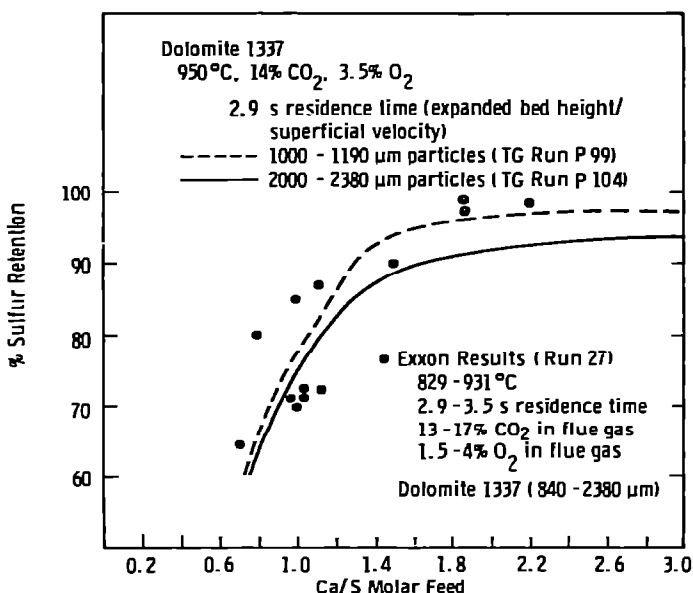


Fig. 13. Comparison of pressurized TG projections with data from the Exxon miniplant.

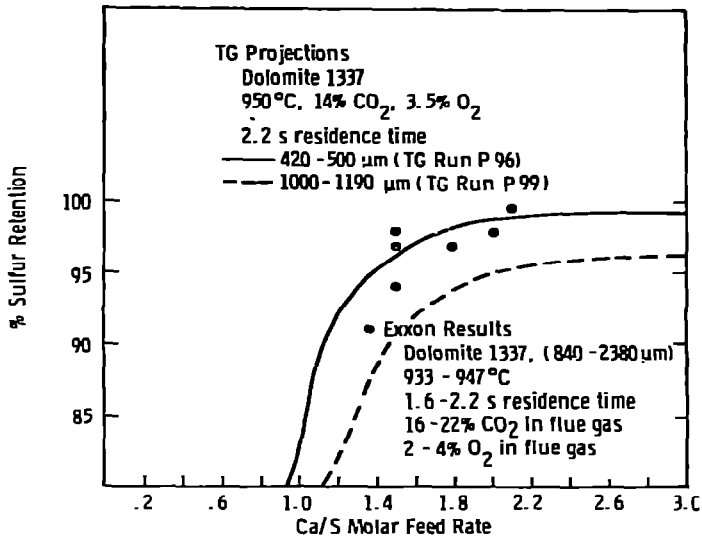


Fig. 14. Comparison of TG projections for >90% sulfur removal with Exxon data for dolomite 1337.

tions in coal and sorbent properties and nonsteady-state operation) as well as the basic assumptions applied in the projections.

CONCLUSION

Thermogravimetric rate data can be successfully used to determine the rate constant of sulfation as a function of sorbent utilization for calcium-based sorbents. By judiciously selecting operating conditions that represent conditions in fluid-bed combustion, the rate constant can be used to predict sulfur retention in fluid-bed units. The agreement between fluid-bed data and TG projections has been demonstrated using data collected at 10 atm pressure, as well as atmospheric data.

TABLE 2

Limitations of TG projections

Model assumption	Limitation	Comment
Diffusion control	Mass transfer may influence initial reaction rate	
First-order reaction	No account for sorbent sintering	
Uniform sulfur generation	No variation in sulfur generation pattern is accounted for	Can be included in the model
Generation and sorption of sulfur all occur in main bed by limestone	Ash can absorb sulfur Sulfur can be generated and absorbed outside of bed	Can be included in the model

Limitations to the accuracy of the model arise from the modeling assumptions (Table 2) and the representability of the 20 mg sample to the limestone bulk used.

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