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DECOMPOSITION OF CALCIUM SULFATE: A REVIEW OF THE LITERATURE

by

W. M. Swift, A. F. Panek, G. W. Smith,
G. J. Vogel, and A. A. Jonke

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ARGONNE NATIONAL LABORATORY, ARGONNE, ILLINOIS

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Chemical Engineering Division

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ABSTRACT

One of the important issues related to fluidized bed combustion of fossil fuels is the subsequent handling and/or treatment of the partially sulfated lime material removed from the combustor. One alternative would be to regenerate the sulfated additive to recover the sulfur, which would be stored for use, and lime that would be recycled for reuse in the combustor. It is the purpose of this report to review the development of regeneration technology which has progressed rather slowly as compared with the technology relative to the fluidized bed combustion process. The review covers research efforts specifically directed toward the regeneration of sulfated limestones plus those studies which have been made to investigate the decomposition of naturally occurring minerals of calcium sulfate. The report reviews basic thermodynamic and kinetic studies as well as laboratory, bench, and pilot scale process development studies. No attempt has been made in the review to evaluate the engineering, environmental, or economic merits of regeneration or the various regeneration schemes.

INTRODUCTION

The United States Environmental Protection Agency, in keeping with the intent of the Clean Air Act to keep air pollution within acceptable limits, has established in its Standards of Performance for New Stationary Sources the maximum allowable emissions of sulfur oxides and nitrogen oxides and particulate solids from new coal-burning power plants.

Emissions of NO_x can generally be controlled by modifications of the combustion process in existing power plants. Control of particulate solids emissions is a function of the type of solids removal equipment selected. To meet the limit of 0.6 lb of sulfur per million Btu of heat energy, however, existing plants have resorted to the following alternatives: the use of low-sulfur fuel, the use of high-sulfur fuel from which some of the sulfur is removed prior to combustion, or the use of scrubbing devices for removal of SO_2 from the flue gas. These and other techniques for reducing the air pollution problem are being developed for new coal-burning power plants.

A concept that is rapidly gaining recognition as a potentially efficient and economically attractive process for raising steam for electric power generation or process use is the fluidized bed combustion of fossil fuels. In the application of the fluidized bed principle to fossil-fuel combustion, particles of partially sulfated limestone or dolomite are held in suspension by the combustion air, which enters through a grid at the bottom of the combustor. Coal, or any other combustible fuel, is injected and burns in the fluidized bed, which is controlled at a temperature of 800 to 950°C. The sulfur dioxide released during combustion reacts with lime in the fluidized bed and, in the presence of excess oxygen, forms calcium sulfate. Fresh, crushed limestone is injected continuously into the bed and the sulfated lime is removed continuously to maintain a constant bed level in the combustor. The process results in greatly reduced emissions to the atmosphere of both sulfur oxide and nitrogen oxide pollutants.

An important issue related to fluidized bed combustion concerns the subsequent handling and/or treatment of the partially sulfated lime material removed from the combustor. Seemingly, the simplest alternative would be to dispose of the sulfated limestone in landfills or at the site from which the stone was originally mined. This poses potential environmental problems due to possible leaching of trace contaminants from the sulfated limestone, which also contains small quantities of residual ash from the combustible fuel. A second alternative would be to develop useful and environmentally safe applications for the sulfated by-product. This alternative, as does the first, requires that large quantities of fresh limestone be used in the combustion process. A third alternative, and the subject of this review, would be to regenerate the sulfated additive to recover sulfur, which would be stored for use, and lime that would be recycled for reuse in the combustor.

Several regeneration schemes have been considered. They can generally be classified as one-step and two-step regeneration processes.

One-Step Regeneration

The most promising one-step regeneration process involves the reductive decomposition of $CaSO_4$ at 1050 to 1150°C to form CaO and SO_2

$$CaSO_4 + CO \rightleftarrows CaO + SO_2 + CO_2 \qquad (1\text{-a})$$

$$CaSO_4 + H_2 \rightleftarrows CaO + SO_2 + H_2O \qquad (1\text{-b})$$

$$4CaSO_4 + CH_4 \rightleftarrows 4CaO + 4SO_2 + 2H_2O + CO_2 \qquad (1\text{-c})$$

The process could be carried out in a fluidized bed reactor, with partial combustion of a fossil fuel generating the necessary reducing gases.

An alternative one-step regeneration process which has been given some consideration is the straight thermal decomposition of $CaSO_4$ at elevated temperatures (>1200°C) to form CaO and SO_2

$$CaSO_4 \rightarrow CaO + SO_2 + 1/2\ O_2 \qquad (2)$$

This is the reverse of the reaction which occurs in the fluidized bed combustor.

Two-Step Regeneration

The first step in the various two-step regeneration schemes proposed is the reductive decomposition of $CaSO_4$ to CaS at 850 to 950°C

$$CaSO_4 + 4CO \rightleftarrows CaS + 4CO_2 \tag{3-a}$$

$$CaSO_4 + 4H_2 \rightleftarrows CaS + 4H_2O \tag{3-b}$$

$$CaSO_4 + CH_4 \rightleftarrows CaS + CO_2 + 2H_2O \tag{3-c}$$

$$CaSO_4 + 2C \rightleftarrows CaS + 2CO_2 \tag{3-d}$$

The second step which has been most favorably considered is the reaction of the CaS from the first step with CO_2 and H_2O at 550 to 700°C to $CaCO_3$ and H_2S

$$CaS + CO_2 + H_2O \rightarrow CaCO_3 + H_2S \tag{4}$$

Variations in the second step would be: (1) to subject the CaS from the first step to an oxidizing roast at 950 to 1100°C to release SO_2

$$CaS + 3/2\ O_2 \rightarrow CaO + SO_2 \tag{5}$$

or (2) to react the CaS with excess unreduced $CaSO_4$ to form CaO and SO_2

$$3CaSO_4 + CaS \rightleftarrows 4CaO + 4SO_2 \tag{6}$$

The net effect of the second variation of the two-step process would be the same as the one-step reductive decomposition.

While technology relative to fluidized bed combustion has been advancing at an ever-increasing pace toward commercialization, technology related to regeneration has progressed rather slowly. It is the purpose of this report to review the development of regeneration technology. This review covers research efforts specifically directed toward the regeneration of sulfated limestones plus basic and applied studies that may indirectly assist in furthering regeneration technology. Many of the latter studies are those which have been made to investigate the decomposition and/or reduction of gypsum or anhydrite, naturally occurring minerals of calcium sulfate.

The report, insofar as possible, is divided into reviews of the one-step and the two-step regeneration schemes. The discussions of the two types of processes are not sharply defined and there is a degree of overlap in the discussions. It should be emphasized that the report does not attempt to evaluate the engineering, environmental, or economic merits of the various regeneration methods.

ONE-STEP REGENERATION

Thermal Decomposition

The term, one-step regeneration, is generally used in reference to the reductive decomposition of calcium sulfate to calcium oxide and sulfur dioxide. The thermal decomposition of calcium sulfate is, however, a logical introduction to the reductive decomposition processes, both technically and historically speaking. As early as 1903, investigators began to study the thermal decomposition of calcium sulfate alone and with additives to produce sulfur dioxide and a cement clinker. By 1916, an experimental plant was built in Leverkusen, Germany to produce a sufficiently concentrated sulfur dioxide gas and a good cement clinker by the decomposition of calcium sulfate using a carbon reductant.[1] The plant operated successfully from 1918 to 1931, when it was closed for economic reasons. The process, known as the Mueller-Kuhne process, is the basis for several large plants operating in England and Western Europe.

Thermodynamics

The thermal decomposition of calcium sulfate is expressed by the following reaction:

$$CaSO_4 \rightleftarrows CaO + SO_2 + 1/2\ O_2; \quad K_p = P_{SO_2}(P_{O_2})^{1/2} \tag{2}$$

At equilibrium, sulfur trioxide would also be present and can be accounted for by the reaction

$$SO_2 + 1/2\ O_2 \rightleftarrows SO_3; \quad K_p = \frac{P_{SO_3}}{P_{SO_2}(P_{O_2})^{1/2}} \tag{7}$$

The theoretical decomposition pressure for reaction (2) has been calculated as a function of temperature from thermodynamic data by several authors.[2,3,4] A comparison of the calculated decomposition pressures is graphically shown in Fig. 1. The calculated values of Taschappat and Piece[2] and those of Vogel *et al.*[4] agree very well; the values reported by Wheelock[3] are considerably higher.

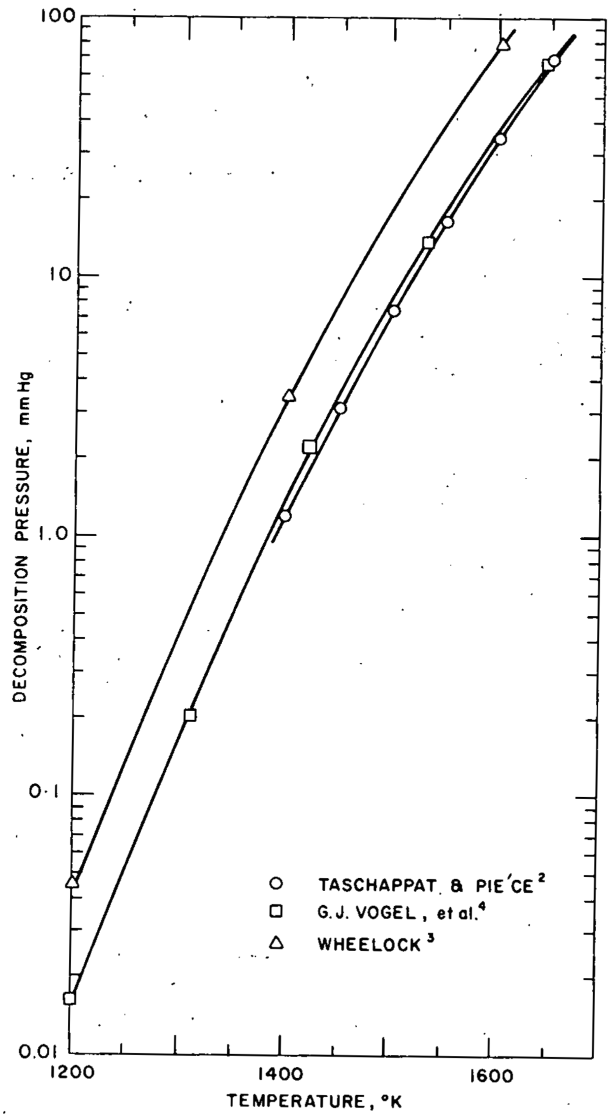

Fig. 1. Decomposition Pressure of Calcium Sulfate as a Function of Temperature as Calculated from Thermodynamic Data by Various Investigators

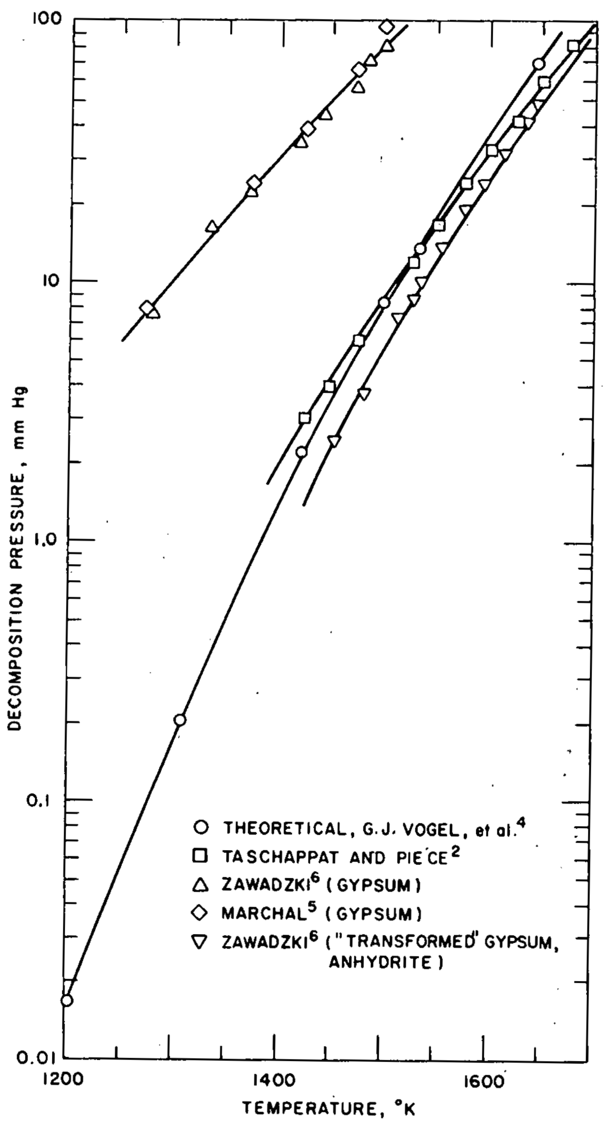

Fig. 2. Experimental Decomposition Pressure of Calcium Sulfate as a Function of Temperature as Measured by Various Investigators

The equilibrium decomposition pressure of calcium sulfate has also been determined experimentally.[2,5,6] These results are shown in Fig. 2 along with the theoretical decomposition curve of Vogel *et al.*[4] Marchal[5] determined the equilibrium decomposition pressure for dehydrated chemically pure gypsum between 1273 and 1503°K. The results, included in Fig. 2, are from one to two orders of magnitude higher than theoretical.

Zawadzki[6] also measured the equilibrium decomposition pressure of calcium sulfate. His values for dehydrated gypsum agreed closely with those of Marchal. Zawadzki observed, however, that when the calcium sulfate was heated for an extended period of time at a temperature near 1200°C, the equilibrium pressure fell to a much lower value which corresponded to that of natural anhydrite and the equilibrium pressure of sulfur trioxide over calcium oxide. Zawadzki thus obtained a second set of value (see Fig. 2) for the "transformed" gypsum which agrees well with the predicted values of Vogel *et al.*[4] Zawadzki's results are in keeping with the fact that all forms of calcium sulfate, when heated for one hour at temperatures in excess of 900°C, will produce the insoluble anhydrite form.

The equilibrium decomposition pressure of calcium sulfate was also measured by Taschappat and Pièce for samples of naturally occurring gypsum, anhydrite, and chemically pure gypsum, with similar results. The values agreed well with the values of Zawadzki for "transformed" gypsum and the theoretical values of Vogel *et al.* (see Fig. 2).

Based on the theoretical decomposition pressure of calcium sulfate, Vogel *et al.*[4] determined the pressures of both sulfur dioxide and sulfur trioxide as a function of temperature, assuming no oxygen was present other than that from the decomposition. Their results are given in Table 1 along with the calculated mole fractions of SO_2 which would result from carrying out the decomposition at different total pressures. Very high temperatures (>1260°C) and very low pressures (<1.0 atm) would be required to produce appreciable levels of SO_2 ($\geq$7%) by thermal decomposition on the basis of these calculations.

TABLE 1. Pressures of SO_3 and SO_2 in Equilibrium with $CaSO_4$ and Resulting Mole Percent of SO_2 at Various Total Pressures

Temperature, °C/°F	Equilibrium Pressure,[a] mm Hg		Mole Percent SO_2 at Indicated Total Pressure in Atm			
	P_{SO_3}	P_{SO_2}	0.5	1.0	5.0	10.0
927/1700	8.82×10^{-6}	1.10×10^{-2}	2.9×10^{-3}	1.4×10^{-3}	2.9×10^{-4}	1.4×10^{-4}
1038/1900	2.24×10^{-4}	1.35×10^{-1}	3.6×10^{-2}	1.8×10^{-2}	3.6×10^{-3}	1.8×10^{-3}
1149/2100	3.28×10^{-3}	1.47	3.9×10^{-1}	1.9×10^{-1}	3.9×10^{-2}	1.9×10^{-2}
1260/2300	2.96×10^{-2}	9.12	2.4	1.2	2.4×10^{-1}	1.2×10^{-1}
1371/2500	2.07×10^{-1}	45.4	11.9	6.0	1.2	6.0×10^{-1}

[a] Assuming no oxygen present other than that from decomposition.

Kinetics

The kinetics of thermal decomposition of calcium sulfate have not been investigated extensively. Early work by Hofman and Mostowitsch[7] indicated that thermal decomposition began around 1200°C, with slagging of the sulfate-oxide mixture at ∿1360°C. After heating for ten minutes at 1200°C, desulfurization was only 0.35% complete. At 1300°C, heating for ten minutes resulted in only 4.4% desulfurization. Budnikoff and Syrkin[8] performed a similar study in which samples of gypsum were heated for three hours at fixed temperatures between 800 and 1375°C. Their results are summarized in Table 2. Even at a temperature of 1300°C, decomposition was only 7% complete after heating for 3 hr. At 1375°C, the sample melted and rapid decomposition of the sample occurred.

TABLE 2. Data of Budnikoff and Syrkin for the Thermal Decomposition of Calcium Sulfate.[8]

Time of Heating (hr)	Temperature (°C)	Weight Loss (%)	Decomposition (%)	Product Composition	
				$CaSO_4$ (wt %)	CaO (wt %)
3	800	0.14	0.33	99.9	0.09
3	900	0.27	0.45	99.81	0.19
3	1000	0.30	0.51	99.79	0.21
3	1100	1.60	2.71	98.86	1.14
3	1200	2.30	3.91	98.35	1.65
3	1300	4.10	6.97	97.00	3.00
3	1375	58.50	99.50	1.33	98.67

The above investigations of thermal decomposition were carried out in an oxidizing (air) atmosphere. The effect of atmosphere on the rate of thermal decomposition was first investigated by Bischoff.[9] Samples of gypsum (99.99% pure) were heated for 4 hr at 1150 and 1200°C in a continuously purged (2 liters/hr) gas flow of either air or water vapor. Decomposition of the calcium sulfate in the water vapor atmosphere was approximately a factor of ten greater than was decomposition in the air environment. Briner and Knodel[10] subsequently compared the decomposition rates in air and in water vapor environments by heating samples of anhydrite (97.6% pure) for 4 hr at 1300°C. Decomposition with the water vapor purge was ∿5 times as great as with the air purge (84% *vs.* 17%, respectively).

Briner and Knodel[10] also investigated the decomposition of anhydrite in a continuously purged water vapor environment as a function of temperature and reaction time. Heating for five hours resulted in 95% decomposition at 1300°C, as compared with only 0.4% at 1050°C. Heating for only 1 hr at 1300°C resulted in decomposition of 42% of the anhydrite.

Wheelock[3] investigated the thermal decomposition of gypsum samples heated to temperatures in the range of 1150 to 1315°C in experiments in which pure nitrogen or pure carbon dioxide or products of the decomposition (sulfur dioxide and oxygen) were passed over the samples. In a nitrogen atmosphere at 1225°C, the gypsum sample was 100% desulfurized in 100 min of reaction time. At higher temperatures, complete desulfurization was obtained in less than 1 hr. When a gas mixture containing only 1.8% sulfur dioxide and 0.9% oxygen in nitrogen was passed over gypsum particles heated to 1150 to 1315°C, the gypsum was only ∿15% desulfurized after ∿90 min. Wheelock's results indicate the adverse kinetic effects of quite low partial pressures of the reaction products, which either prevented thermal decomposition of gypsum or at least reduced the rate of decomposition to an impractically low level.

Additive Effects

The effects of various additives on the thermal decomposition of calcium sulfate have been determined. In the very early work by Hofman and Mostowitsch,[7] the effects of silica, lead oxide, and ferric oxide on the thermal decomposition of chemically pure calcium sulfate were examined. Silica additive was reported to lower the initial decomposition temperature to ∿1000°C from ∿1200°C for the pure sulfate. The rate of decomposition of the sulfate was proportional to the amount of silica added. Ferric oxide reportedly began to decompose calcium sulfate at a slightly higher temperature than silica (∿1100°C), but the decomposition proceeded at a more rapid rate.

Results similar to those of Hofman and Mostowitsch[7] were reported by Cobb.[11] The initial decomposition of calcium sulfate in a flow of dry or moist air (7.2 mole % H_2O in air) with no additive present was observed to occur at ∿1230°C, with the rate increasing gradually up to a temperature of 1380°C (where "rapid" dissociation began). The addition of silica reduced the observed initial decomposition temperature of the calcium sulfate to ∿1010°C, the initial decomposition temperature being independent of the ratio of sulfate to silica. The rate of decomposition was reported to be proportional to the amount of silica added.

A much later study by West and Sutton[12] takes exception to the observations of Hofman and Mostowitsch[7] and Cobb[11] regarding additives lowering the initial temperature at which thermal decomposition takes place. The study was made using the differential thermal analysis technique. Gypsum and mixtures of gypsum with silica, alumina, iron oxide, dialyzed kaolin, or carbon were analyzed in furnace atmospheres of air, nitrogen, carbon dioxide, and carbon monoxide. The results indicated that thermal decomposition of calcium sulfate begins at 1225°C, the temperature at which beta calcium sulfate changes to alpha calcium sulfate. Identical results were obtained for gypsum in air, nitrogen, and carbon dioxide and for the additions of the above additives. X-ray analysis of the sample residues after heating to 1250°C (above the β- to α-anhydrite conversion) identified $2CaO{\cdot}SiO_2$ after the addition of silica, and $CaO{\cdot}Fe_2O_3$ after the addition of iron oxide. No reaction of sulfate with additive was confirmed for alumina or kaolinite.

The effect of additives on the equilibrium decomposition pressure of calcium sulfate was determined in several early investigations. Marchal[5] measured the effects of silica, alumina, kaolin, and iron oxide on the equilibrium decomposition pressure of calcium sulfate. She reported that alumina had a negligible effect and that iron oxide, silica, and kaolin, in that order, were increasingly effective in raising the decomposition pressure of calcium sulfate. Somewhat conflicting results were later reported by Terres,[13] who also measured the decomposition pressures of mixtures of iron oxide, alumina, and silica with calcium sulfate. The decomposition pressure increased with the amount of additive in the mixture; iron oxide, alumina, and silica (in that order) were reported as having an increasing effect in raising the decomposition pressure of the calcium sulfate. The results reported by Terres[13] are shown in Fig. 3.

The effect of silica on the rate of thermal decomposition was investigated by Bischoff[9] in the following gaseous environments: air, oxygen, nitrogen, argon, sulfur dioxide, moist air, and water vapor. After heating samples of anhydrite mixed with silica for 4 hr at 1100°C, decomposition was <5% in the sulfur dioxide, ∿20% in both the air and oxygen, ∿30% in both the argon and nitrogen, and ∿95% in the water vapor environment. In the absence of the silica, decomposition of the calcium sulfate was only 4.3% complete after heating for 4 hr at 1200°C while passing water vapor over the sample.

Briner *et al.*[14] passed a 65% H_2O - 35% N_2 gas mixture over heated samples of calcium sulfate containing additions of silica or kaolin or one of three types of bauxite. Measurable decomposition (∿1%) of the pure calcium sulfate was reported in the water-nitrogen gas mixture after heating for 1 hr at a temperature of only 600°C. The additives increased the rate of decomposition significantly at all temperatures studied between 600 and 900°C. Decomposition was complete after heating a mixture of calcium sulfate and kaolin [$CaSO_4$ + $1/3(2SiO_2, Al_2O_3)$] at 900°C for ∿4 hr.

Hedvall *et al.*[15,16] also investigated the effect of additives on the thermal decomposition of calcium sulfate at low temperatures. They found that the decomposition of calcium sulfate at 1000°C in the presence of quartz, kaolin, feldspar, and coke ash was increased by the addition of 3% sodium chloride, as well as by the use of a stream of moist air to remove the generated gases. Oxides of manganese, chromium, iron, and zinc were also found to be beneficial in the decomposition. Decomposition of 99% was reported as a result of heating mixtures of calcium sulfate and sodium chloride with either quartz or kaolin at 1000°C for 24 hr in moist air.

The thermal decomposition of by-product calcium sulfate from the wet process for the production of phosphoric acid was studied by Stinson and Mumma.[17] In the investigation, the by-product calcium sulfate was pelletized with silica. The rate of decomposition was measured as a function of SiO_2:S mole ratio, temperature, retention time, pellet size, iron-aluminum oxide content, and particle size of silica. When the pellets were heated for 2 hr at 1250°C, the extent of desulfurization increased from 73% to 95% as the SiO_2:S mole ratio was increased from 0.7 to 1.1 The rate of desulfurization increased with an increase in temperature and a decrease in the size of the pellets. At 1250°C and with a SiO_2:S ratio of 1.0, all sizes of pellets (1/4 in. to 1 in.) were ∿90% desulfurized within 60 min. The addition of iron-aluminum oxide strongly increased the rate of decomposition. As the

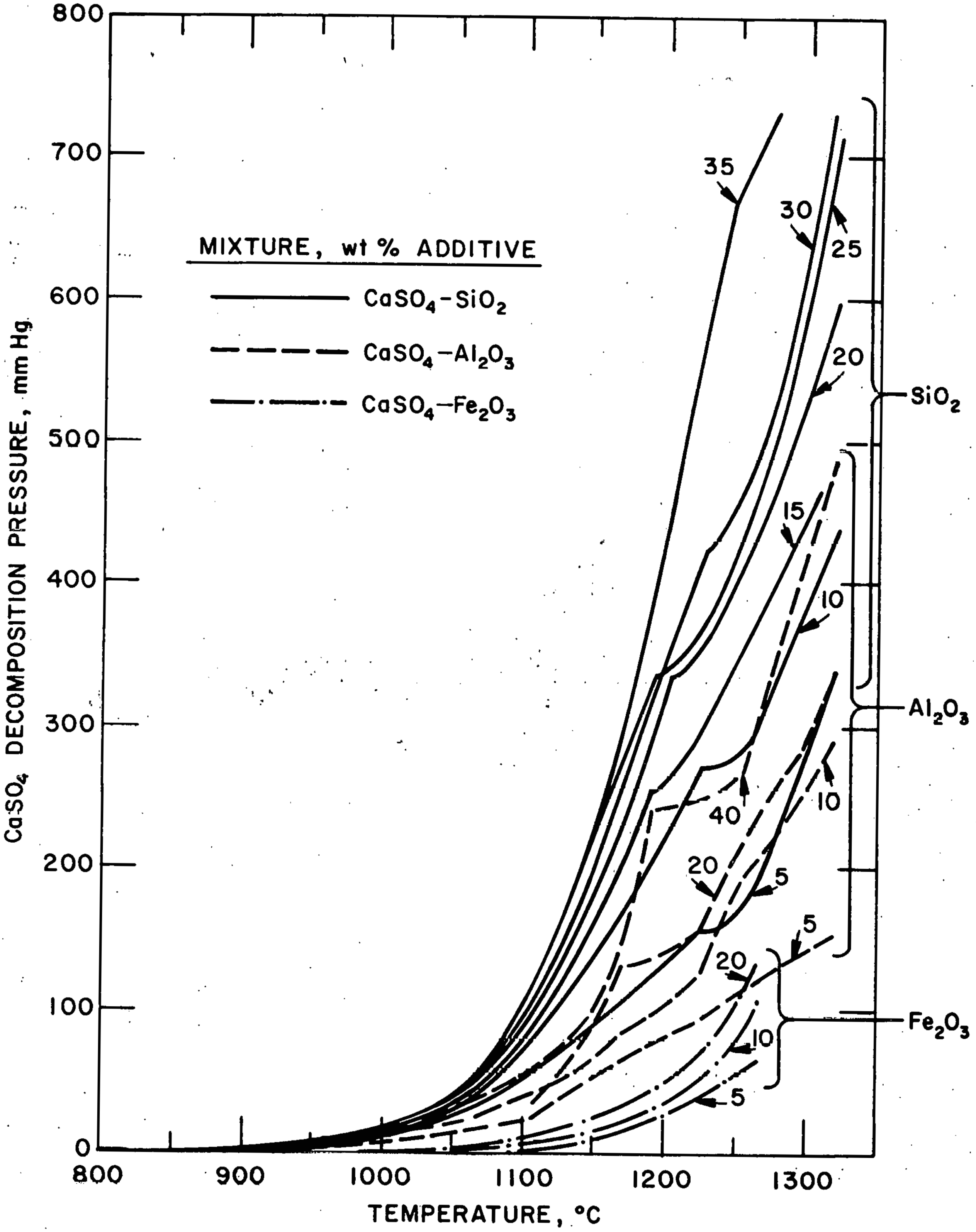

Fig. 3. Decomposition Pressure of Calcium Sulfate as a Function of Temperature and Additive. Additive wt % Indicated on Curves. (Based on Fig. 6 of Ztschr. angew. Chem. 44.(20), 359 (1931). Reproduced by kind permission of Verlag Chemie International Inc., publisher)

iron-aluminum oxide content was increased from 0.7 to 4.1%, the proportion of sulfur volatilized in 15 min from pellets with a SiO_2:S mole ratio of 1.0 at 1250°C increased from 57% to 100%.

Bench-Scale Investigations

In 1951, Bollen attempted to thermally decompose gypsum in a bench-scale shaft furnace in which natural gas was burned with an excess of air in the bed of particles. Under the oxidizing conditions in the furnace, it was found that the thermal decomposition of calcium sulfate was extremely slow, even at temperatures as high as 2450°F. At those temperatures, fusion of particles occurred in the bed, preventing the flow of solids through the furnace. Bollen[18] subsequently attempted to thermally decompose gypsum in a fluidized bed reactor operated at temperatures below fusion. The bed was fluidized with the combustion products of natural gas and air. By changing the natural gas to air ratio, conditions were varied from oxidizing to neutral to reducing. As in the shaft furnace, oxidizing conditions resulted in unacceptably low desulfurization rates.

Reductive Decomposition

The one-step reductive decomposition of calcium sulfate is complicated by the large number of reactions which occur and the variety of end products which can be produced. Depending upon the reductant, the desired decomposition can be considered to proceed according to the reactions

$$CaSO_4 + CO \rightarrow CaO + SO_2 + CO_2 \qquad (1\text{-}a)$$

$$CaSO_4 + H_2 \rightarrow CaO + SO_2 + H_2O \qquad (1\text{-}b)$$

$$4CaSO_4 + CH_4 \rightarrow 4CaO + 4SO_2 + CO_2 + 2H_2O \qquad (1\text{-}c)$$

$$2CaSO_4 + C \rightarrow 2CaO + 2SO_2 + CO_2 \qquad (1\text{-}d)$$

In the same system, however, several other reactions can occur which lead to the formation of undesirable products (for the purposes of the one-step regeneration) such as calcium sulfide, hydrogen sulfide, carbonyl sulfide, and elemental sulfur. For reduction by carbon monoxide and/or hydrogen, these products can be accounted for by the following postulated reactions

$$CaSO_4 + \left\{\begin{matrix} 4CO \\ 4H_2 \end{matrix}\right\} \rightleftarrows CaS + \left\{\begin{matrix} 4CO_2 \\ 4H_2O \end{matrix}\right\} \qquad (3)$$

$$SO_2 + \left\{\begin{matrix} 2CO \\ 2H_2 \end{matrix}\right\} \rightleftarrows 1/2\ S_2 + \left\{\begin{matrix} 2CO_2 \\ 2H_2O \end{matrix}\right\} \qquad (8)$$

$$1/2\ S_2 + \left\{\begin{matrix} CO \\ H_2 \end{matrix}\right\} \rightleftarrows \left\{\begin{matrix} COS \\ H_2S \end{matrix}\right\} \qquad (9)$$

In terms of the one-step regeneration of calcium sulfate, calcium sulfide formation is the most serious because its formation reduces the quantity of calcium available for sulfation upon recycle of the sorbent to the combustor (*i.e.*, the recycle mass flow rate is increased). Its formation also reduces the level of sulfur dioxide obtainable in the off-gas from the regeneration unit. The principal objectives of the one-step regeneration process are, therefore, to minimize calcium sulfide formation in the regenerated solids and to maximize the sulfur dioxide concentration in the off-gas from the regenerator.

Process Thermodynamics

The thermodynamics of the reductive decomposition have been studied by several investigators.[3,4,19,20] Equilibrium constants for the one-step reductive decomposition reactions are plotted in Fig. 4 as a function of temperature. Heats of reaction for the decomposition reactions are given in Table 3. The desired reduction reactions are seen to be endothermic and exhibit increasingly favorable equilibrium constants with increasing temperature.

Several attempts have been made to quantify the effects of temperature and ratio of calcium sulfate to reductant on the equilibrium compositions for both the solid and gas phases. Wheelock[3] observed that the equilibrium expression for the solid-solid reaction of calcium sulfate with calcium sulfide

$$3CaSO_4 + CaS \rightarrow 4CaO + 4SO_2 \qquad (6)$$

is simply:

$$K_p = (\overline{P}_{SO_2})^4 \qquad (10)$$

Thus, the partial pressure of sulfur dioxide in equilibrium with a mixture of calcium sulfate and calcium sulfide is a function of temperature only. From the equilibrium curve in Fig. 4 for this reaction, the equilibrium partial pressure of sulfur dioxide reaches 1 atm at 2120°F (Wheelock[3] reported a temperature of 1990°F). He concluded that a mixture of the reactants heated above this temperature in a closed system at atmospheric pressure would proceed to react (with a corresponding increase in the system volume) until one or the other or both of the reactants was used up.

Wheelock[3] further concluded that if calcium sulfate and a reducing gas such as carbon monoxide were reacted at atmospheric pressure in a closed system at a temperature above 1990°F

(1) for a $CO:CaSO_4$ mole ratio of one, the sulfate would be almost entirely converted to calcium oxide with no sulfide formation,
(2) for a $CO:CaSO_4$ mole ratio between 1 and 4, the reaction product would contain both calcium oxide and calcium sulfide, and
(3) for a $CO:CaSO_4$ mole ratio of 4 or greater, the sulfate should be entirely converted to sulfide.

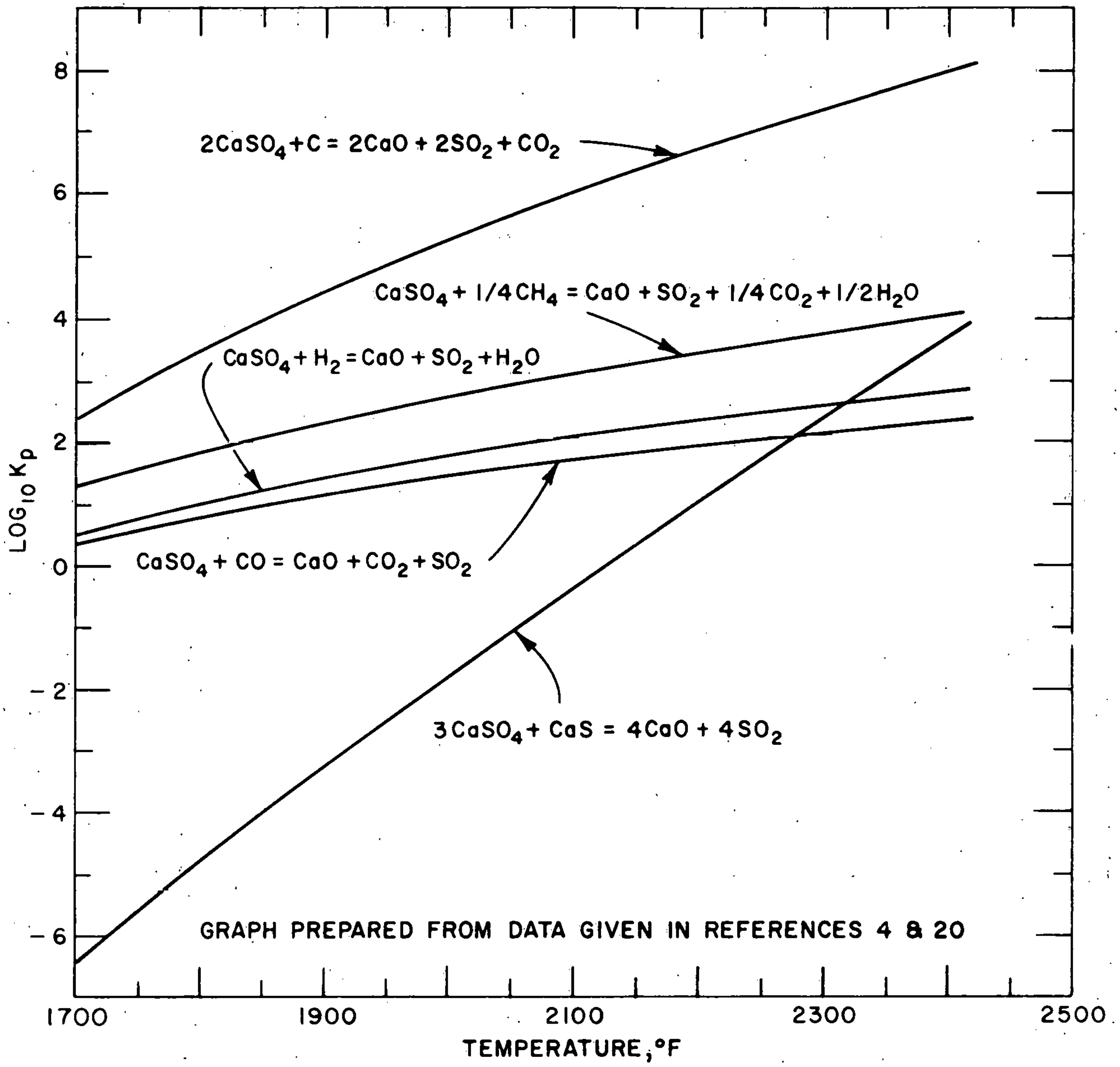

Fig. 4. Equilibrium Constants for One-step Reductive Decomposition Reactions

TABLE 3. Heats of Reaction for the One-Step Reductive Decomposition of Calcium Sulfate[a]

Reaction	Heat of Reaction (kcal/mole $CaSO_4$)		
	1200°K	1400°K	1600°K
$CaSO_4 + CO = CaO + SO_2 + CO_2$	42.6	39.8	36.4
$CaSO_4 + H_2 = CaO + SO_2 + H_2O$	50.5	47.3	43.4
$4CaSO_4 + CH_4 = 4CaO + 4SO_2 + CO_2 + 2H_2O$	62.1	59.0	55.2
$2CaSO_4 + C = 2CaO + 2SO_2 + CO_2$	62.8	59.8	56.0

[a] Table prepared from data given in References 4 and 20.

Wheelock and Boylan[21] then calculated equilibrium conversions at one-atmosphere pressure in a closed system for different ratios of either carbon monoxide or hydrogen to calcium sulfate at two temperature levels (1125 and 1325°C) and at two levels of carbon dioxide or steam to calcium sulfate (1.0 and 4.0). The results of their calculations are shown in Figs. 5a and 5b. The upper halves of the figures represent the conversion to calcium oxide and calcium sulfide, while the lower halves represent the region in which calcium oxide and calcium sulfate are present. The results are interesting in that at atmospheric pressure and within an appropriate range of reducing conditions (as limited by temperature and CO_2:$CaSO_4$ mole ratio), it should be possible to completely convert calcium sulfate to calcium oxide with no calcium sulfide being formed.

Vogel *et al.*[4] performed a somewhat similar analysis for the reduction of calcium sulfate by carbon monoxide at 10-atm pressure. Their calculations

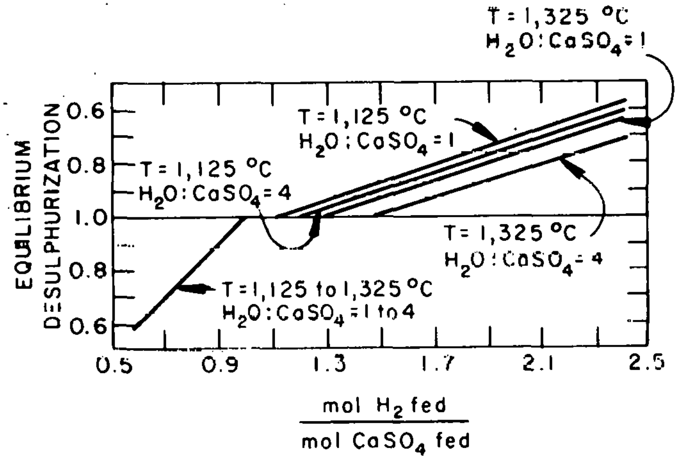

Fig. 5a. Equilibrium Conversion of Calcium Sulfate to Calcium Oxide, Using Hydrogen (Based on Fig. 2, Reference 21. Reprinted by kind permission of Processing.)

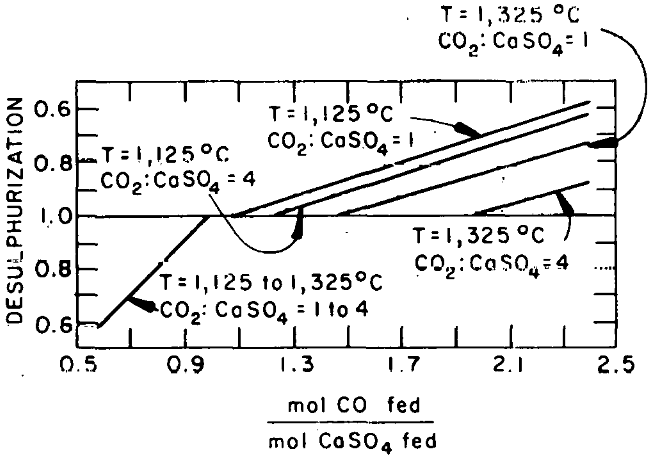

Fig. 5b. Equilibrium Conversion of Calcium Sulfate to Calcium Oxide, Using Carbon Monoxide (Based on Fig. 3, Reference 21. Reprinted by kind permission of Processing.)

resulted in the phase diagram reproduced in Fig. 6 The line extending from the lower left to the upper right of Fig. 6 represents the coexistence line of calcium sulfate and calcium sulfide. To the left of the line, the gas mixture is so rich in carbon dioxide that calcium sulfide would be completely oxidized to calcium sulfate. In the area to the right of this line, the gas is so rich in carbon monoxide that calcium sulfate is completely reduced to calcium sulfide. The diagram assumes, of course, that the equilibrium is not reactant-limited in the solid phase.

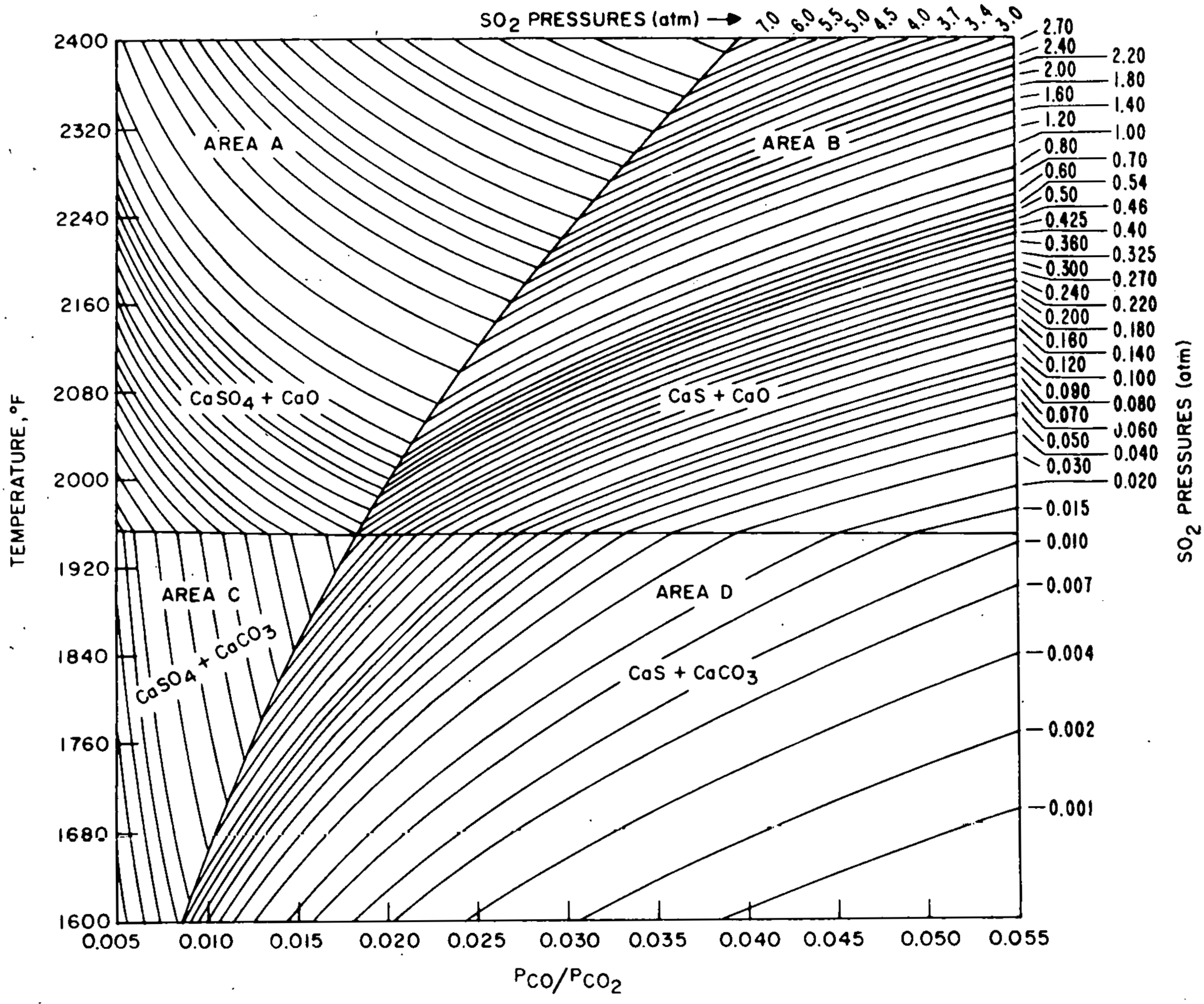

Fig. 6. Solid and Gas Phase Equilibrium Diagram at a Total Pressure of 10 Atm. (Reproduced from Ref. 4).

The following interesting observation was also made concerning the isobars of constant pressure in the phase diagram. In area A, the isobars slant down to the right; in area B, they slant down to the left, meeting those of area A at the calcium sulfate-calcium sulfide coexistence line. At any temperature, therefore, the sulfur dioxide pressure is at a maximum at this junction. Maximizing sulfur dioxide and minimizing calcium sulfide formation at any given temperature would seem to require, therefore, operating just to the left of the coexistence line.

Skopp *et al.*,[19] in order to quantify these effects of temperature and gas composition, determined equilibrium compositions for both the solid and gas phases for a series of hypothetical regeneration systems. The calculations were made by use of a computer program which minimizes the free energy of a system subject to material balance restraints. Table 4 presents the results reported.[19]

TABLE 4. Equilibrium Compositions for the Reduction of Calcium Sulfate[a]

	Inlet Gas Composition (mole %)					Outlet Gas Composition (mole %)				% of Reacted $CaSO_4$ Converted to	
Temp. °F	CO	H_2	CO_2	H_2O	N_2	SO_2	CO_2	H_2O	N_2	CaO	CaS
1880	5	0	10	0	85	0	15	0	85	0	100
1880	0	5	0	10	85	0	0	15	85	0	100
1880	10	0	20	0	70	0	30	0	70	0	100
1880	0	10	0	20	70	0	0	30	70	0	100
1880	15	0	30	0	55	0	45	0	55	0	100
1880	0	15	0	30	55	0	0	45	50	0	100
2060	5	0	10	0	85	4.0	14.4	0	81.6	95	5
2060	0	5	0	10	85	4.0	0	14.4	71.6	95	5
2060	10	0	20	0	70	7.7	27.7	0	64.6	95	5
2060	0	10	0	20	70	7.7	0	27.7	64.6	95	5
2060	15	0	30	0	55	11.1	40	0	48.8	95	5
2240	5	0	10	0	85	3.9	14.4	0	81.7	94	6
2240	0	5	0	10	85	3.9	0	14.4	81.7	94	6
2240	0	10	0	20	70	7.5	0	27.7	64.8	94	6
2240	15	0	30	0	55	10.7	40.2	0	49.1	94	6
2240	10	15	0	30	55	10.8	0	40.2	49.0	94	6
2240	-----100% CH_4 -------					0	33.3	66.7	0	0	100

[a] Data from reference 19.

At 1880°F, conversion of the sulfate was entirely to calcium sulfide. At 2060°F and 2240°F, the equilibrium product compositions were essentially identical in those cases in which the inlet gas composition was the same. There is no indication in the report, however, to explain whether the remaining calcium sulfide at 2060 and 2240°F (particularly for the case of 100% methane in the inlet gas at 2240°F) could have been eliminated by increasing the calcium sulfate to reducing gas ratio as the material balance constraint in the equilibrium calculation. The results did indicate that sulfur dioxide concentrations as high as 11% could be obtained at equilibrium conditions.

The investigations of Vogel *et al.*[4] and Skopp *et al.*[19] both tended to discount the presence of significant amounts of elemental sulfur, carbonyl sulfide, and hydrogen sulfide. Vogel *et al.* did demonstrate that at the temperatures considered for the reduction of calcium sulfate, calcium sulfite could not exist at equilibrium in the presence of carbon monoxide-carbon dioxide mixtures.

Process Kinetics

Under nonequilibrium conditions, calcium sulfide may be produced during the reductive decomposition, regardless of theoretical considerations. Efforts have been made, therefore, to determine the effects of operating conditions on conversion rates and sulfide formation. Of primary interest is the rate of desulfurization since it is related to the production of the desired products, sulfur dioxide and calcium oxide.

A very thorough investigation of the effect of operating conditions on desulfurization rates of calcium sulfate was carried out by Wheelock.[3] The results of this work have also been summarized in two publications by Wheelock and Boylan.[21,22] In the study, a sample of coarse gypsum (-7+8 Tyler mesh) suspended from a triple beam balance was placed inside a small reaction tube, which in turn was inside a gas-fired muffle furnace. The sample was brought to the desired experimental temperature in an atmosphere containing sulfur dioxide and air to prevent the gypsum from thermally decomposing. When the desired temperature was reached, a selected reducing gas mixture was passed over the sample and the loss in weight of the sample was recorded as a function of time. Using the total desulfurization calculated from the composition of the sample residue at the conclusion of a run and assuming that the instantaneous desulfurization was proportional to the weight lost by the gypsum charge, desulfurization was determined as a function of time.

Wheelock[3,21,22] observed essentially two types of desulfurization curves. When the feed gas contained mixtures of carbon monoxide and nitrogen, the curves were characterized by a single constant rate period which prevailed for practically the entire run. When sulfur dioxide was present in the feed gas, the curves were characterized by two relatively constant-rate periods, the initial and the maximum. The initial rate was relatively slow and very little desulfurization occurred during this period. After the initial induction period, the rate rapidly increased to its maximum value, and the greater part of the desulfurization occurred. It was possible to correlate both the initial and the maximum desulfurization rates with operating conditions. The results obtained by Wheelock[3] and subsequent investigators are summarized below.

Temperature Effects. Wheelock observed that the effect of temperature on desulfurization rate varied with the feed gas composition. With a gas composition of 3% CO, 20% CO_2, and 5% SO_2 in nitrogen and a reaction temperature of ∿2100°F, the gypsum passed through an initial induction period when little or no decomposition occurred. The reaction rate then increased to a relatively constant and rapid desulfurization rate of ∿6%/min. After 50 min, the reaction ended with approximately 87% desulfurization and 11% calcium sulfide in the sample residue. At 2200°F, the initial reaction rate was much higher but the maximum reaction rate remained relatively unaffected (∿6%/min). After 45 min, the sample was completely desulfurized.

With a gas composition of 4% CO, 10% CO_2 and 5% SO_2 in nitrogen, both the initial and maximum reaction rates increased with temperature. At 2100°F the maximum desulfurization rate was ∿7%/min, and at 2200°F it was ∿14%.

Particle Size Effects. Wheelock and Boylan[22] reported that with a gas composition of 3% CO, 20% CO_2, and 5% SO_2 in nitrogen and at temperatures of 2160°F to 2220°F, the maximum desulfurization rate decreased from ∿9.5%/min for ∿0.05-in. particles to ∿3.5%/min for ∿0.20-in. particles. The initial desulfurization rate (∿1%/min) was unaffected by particle size, indicating that similarly to the effect of temperature on the initial and maximum desulfurization rates, the mechanism controlling the maximum desulfurization rate is independent of the mechanism controlling the initial desulfurization rate.

Mehra[23] also studied the desulfurization of calcium sulfate by passing reducing gases over solid particles in a combustion boat placed in a horizontal electrically heated furnace. He observed that when reacted under the same conditions for the same length of time, the coarser particles reacted less and had less tendency to form sulfide than did finer particles.

Gas Composition Effects. Wheelock and Boyland[22] observed that both the initial and maximum desulfurization rates varied linearly with carbon monoxide concentration in the feed gas. In the temperature range of 2140 to 2220°F and with 20% CO_2 and 5% SO_2 in the reactant gas, increasing the carbon monoxide concentration from 2% to 5% increased the maximum desulfurization rate from ∿1%/min to ∿14%/min. With more than 5% CO in the reducing gas, the desulfurization rate began to level off with increasing CO concentration due to increasing calcium sulfide formation.

At carbon monoxide levels below 4%, eliminating sulfur dioxide from the reactant gas resulted in increased desulfurization rates. When 4% or more carbon monoxide was present, the desulfurization rate was only very slightly affected by sulfur dioxide concentrations up to 7% in the reactant gas. The desulfurization rate was also influenced to only a very small degree by the presence of carbon dioxide in the reactant gas. Wheelock did report, however, that in decomposition experiments at 2140-2210°F and with 5% SO_2 in the reactant gas, a CO_2/CO mole ratio between 5 and 6 was required to prevent the formation of calcium sulfide.[22]

Wheelock also reported that when hydrogen was used as a reductant the desulfurization rate was two to three times that obtained when carbon monoxide was used, but that the level of calcium sulfide formation was about equal for both reductants.[3]

Skopp *et al.*[19] investigated the decomposition of anhydrite in a small (2-in. ID) batch fluidized bed reactor. The effluent sulfur dioxide concentrations obtained at 10 and 15% reducing gas concentrations and various temperatures were compared with equilibrium predictions. For all reductants tested (hydrogen, carbon monoxide, and methane), the sulfur dioxide was found to have a first order dependence on the concentration of the reductant at the inlet. For carbon monoxide and hydrogen, the reduction was equilibrium-limited.

Mass Velocity Effects. An interesting effect of gas velocity on desulfurization rate was observed by Wheelock.[23] Although an increase in the maximum desulfurization rate was noticed as expected, when the gas mass velocity was increased, the initial desulfurization rate decreased significantly with increased gas mass velocity. Since initial desulfurization rates were observed only when sulfur dioxide was present in the feed gas, it would appear that the initial rate of desulfurization observed by Wheelock[23] is controlled by the effective concentration of sulfur dioxide in the bulk gas phase surrounding the reacting gypsum particles.

Reduction by Carbon. As previously indicated, the decomposition of calcium sulfate using a carbon reductant in the presence of additives is a process used by several large plants operating in England and Western Europe to produce sulfur dioxide and a cement clinker.[1] The results of an excellent recent investigation by Turkdogan and Vinters[24] help outline the basic principles that govern the preferential reduction of calcium sulfate to either sulfur dioxide and calcium oxide or to calcium sulfide.

Experiments were made using a reagent-grade calcium sulfate or powdered natural gypsum. Graphite, charcoal, char, coke and coal were the five types of carbon used in the investigation. Mixtures of sulfate and carbon in various proportions (contained in a platinum crucible) were suspended from an automatic recording balance in a vertical furnace. Oxygen-free dry helium was passed through the reaction tube during the experiments.

Principal conclusions of the work were: (1) complete conversion to sulfur dioxide is achieved by adjusting the molar C/S ratio in the charge to 0.5; for conversion to calcium sulfide with less than 1% loss as sulfur dioxide, the molar C/S ratio should be slightly greater than the stoichiometric value of 2.0, (2) for the minimum C/S stoichiometric ratio of 0.5, approximately one-fourth of the sulfate is converted to sulfide, which subsequently reacts with unconverted sulfate to form the oxide and sulfur dioxide, (3) the rate of conversion of calcium sulfate to calcium sulfide is controlled by the rate of oxidation of carbon by carbon dioxide (from the direct reaction of carbon with calcium sulfate) to carbon monoxide, and (4) coal, char, and charcoal were suitable sources of carbon for the reduction; reduction by graphite was unacceptably slow.

For coal, which was the most reactive of the types of carbon tested, conversion of gypsum to calcium sulfide was $\sim$95% complete after only 8 min at 1000°C and with a C/S ratio somewhat greater than 2.0. At the same temperature and with a C/S ratio of $\sim$0.5, conversion of the gypsum to calcium oxide was $\sim$90% complete after 90 min and was 95% complete after 120 min. At 1100°C and with a C/S ratio of 0.5, reduction of gypsum to calcium oxide was $\sim$90% complete in $\sim$35 min.

Reaction Mechanism

Reactions of gases with solids are very complex and involve several steps which occur successively. Depending on the particular system and the set of conditions, any one of the steps can control the overall rate of the reaction. A mechanism for the reductive decomposition of calcium sulfate was proposed by Robbins.[25] The mechanism is based on gas adsorption studies which he made and on Wheelock's[3] desulfurization rate data. The general steps in Robbin's reaction mechanism are as follows:

1. Diffusion of gaseous reactants to solid reactant surface,
2. Adsorption of gaseous reactants on solid reactant surface,
3. Surface reaction at solid reactant surface,
4. Desorption of gaseous products directly to gas phase,
5. Adsorption of gaseous reactants on solid reactant-product interface,
6. Surface reaction at solid reactant-product interface,
7. Desorption of gaseous products from solid product surface.

Steps 1 through 4 represent a nucleation process with the formation of solid product nuclei within the reacting particle. Steps 1 and 5 through 7 represent the growth of solid product nuclei. The implication here is that if the nucleation rate is markedly lower than the growth rate, the decomposition reaction could be characterized by an induction or initial rate period, followed by a more rapid or maximum rate period, as observed by Wheelock.[3] Details of Robbins'[25] proposed mechanism are presented in the following paragraphs.

Calcium oxide formation. Since carbon monoxide does not adsorb appreciably on calcium sulfate, the carbon monoxide reacts directly at the calcium sulfate surface. The product, according to Robbins[26] theory, is a compound of sulfur dioxide and carbon dioxide adsorbed on calcium oxide as follows:

$$CaSO_4 + CO = CaO \cdot SO_2 \cdot CO_2 \tag{11}$$

Robbins further contended that since the presence of carbon dioxide does not appreciably affect the initial reaction rate as determined by Wheelock,[3] it probably desorbs rapidly according to the reaction

$$CaO \cdot SO_2 \cdot CO_2 = CaO \cdot SO_2 + CO_2 \tag{12}$$

The final step in the formation of calcium oxide nuclei then involves the direct desorption of sulfur dioxide as expressed by the reaction

$$CaO \cdot SO_2 = CaO + SO_2 \tag{13}$$

A similar mechanism has been proposed by Pechkovskii and Ketov,[26] who suggest that the formation of calcium oxide occurs in two steps as follows:

$$CaSO_4 + CO = CaSO_3 + CO_2 \tag{14}$$

$$CaSO_3 = CaO + SO_2 \tag{15}$$

The calcium sulfite intermediate in reactions (14) and (15) has also been observed by Marier and Ingraham[27] and Low *et al.*[28] during investigations of the reverse reactions. However, these observations were made at relatively low temperatures (up to 600°C). Vogel *et al.*,[4] in their thermodynamic investigation, proved that calcium sulfite can not exist at equilibrium at elevated temperatures.

Robbins[25] correlated the initial desulfurization rates determined by Wheelock[3] against the degree of supersaturation of the sulfur dioxide adsorbed on calcium oxide. Supersaturation was determined to be the difference between the equilibrium pressure of sulfur dioxide above calcium oxide and the partial pressure of sulfur dioxide in the bulk gas stream surrounding the reacting calcium sulfate particle. The data correlated very well, indicating that the nucleation rate is considerably more dependent on supersaturation at the lower concentrations of carbon monoxide. In fact, at carbon monoxide levels of 4 percent or greater, the initial desulfurization rate is independent of the degree of supersaturation. This does not negate the possibility that the rate of desorption or diffusion of sulfur dioxide is still the rate-controlling step in the reductive decomposition reaction.

Robbins[25] further contended that once sufficient nuclei are formed, the rate of decomposition increases to its maximum rate, presumably because the surface of the nuclei provides a more rapid route for the desorption of sulfur dioxide than does direct desorption. Evidence that the rate is still desorption-controlled is provided by Skopp *et al.*[19] They observed that if reductant flow to their reactor was stopped, sulfur dioxide was observed in the off-gas at its peak steady-state value for a period of time approximately seven times that of the gas holdup time in the system (from the point of feed gas introduction to the point of off-gas analysis).

The fact that increased mass flow rate decreased the initial desulfurization rate is consistent in that the increased concentration of sulfur dioxide at the particle surface further hindered the desorption of sulfur dioxide during the formation of calcium oxide nuclei.

Calcium sulfide formation. Robbins[25] proposed that calcium sulfide formation occurs in two steps. First, sulfur dioxide adsorbed on calcium oxide is reduced to elemental sulfur by the reaction

$$CaO \cdot SO_2 + 2CO = CaO \cdot S + 2CO_2 \qquad (16)$$

The sulfur can then be further reduced to calcium sulfide as follows:

$$CaO \cdot S + CO = CaS + CO_2 \qquad (17)$$

Pechkovskii and Ketov[26] have also proposed a two-step mechanism for calcium sulfide consisting of reactions (8) and (18) as follows:

$$SO_2 + 2CO\ (H_2) = 1/2\ S_2 + 2CO_2\ (H_2O) \qquad (8)$$

$$2CaO + 3/2\ S_2 = 2CaS + SO_2 \qquad (18)$$

Robbins'[25] mechanism seems more plausible, however, since reaction (17) would not require the complicated and improbable molecular interaction expressed in reaction (18).

Laboratory and Bench-Scale Investigations

Several research and development studies have been made of the one-step reductive decomposition process. Inasmuch as possible, these investigations will be reviewed in the following paragraphs in chronological order and under the investigators' affiliation at the time each study was made.

Early Work at Iowa State University. Mention has already been made of the early bench-scale investigations by Bollen[18] and Wheelock.[3] Bollen[18] first attempted to decompose natural gypsum thermally in a bench-scale shaft furnace in which natural gas was burned with an excess of air directly in the bed of gypsum particles. He subsequently utilized a fluidized bed reactor in which small amounts of gypsum or anhydrite were fluidized by the high-temperature combustion products of natural gas. When combustion was stoichiometric, desulfurization was fairly rapid and complete; when excess air was used for the combustion, the rate of desulfurization was considerable lower; when excess natural gas was used in the combustion, considerable calcium sulfide was found in the decomposition products.

Wheelock[3] in 1958 reported attempts to again decompose calcium sulfate in a shaft furnace. Although he was somewhat more successful than Bollen (89% desulfurization, 2.8% sulfurous gases, and a by-product calcium oxide containing 3.1% calcium sulfide), the results were less than encouraging.

Bureau of Mines. The decomposition of gypsum in a fluidized bed reactor was later investigated by Martin *et al.*[29] Objectives of the investigation were to decompose gypsum in a fluidized bed to produce a gas rich in sulfur dioxide and a lime or portland cement residue.

After preliminary screening tests were performed in a 4-in.-ID fluidized-bed reactor, a 10-in.-ID reactor was constructed and operated. The larger vessel consisted of a silicon carbide tube 6 ft long. Feed was introduced by means of a screw feeder just above the bottom of the bed, and the product was withdrawn at the opposite side of the vessel through a silicon carbide overflow tube. The bed depth could be maintained between 2 and 3 ft. Fluidizing gas was introduced into a cone-shaped bottom section which served as the gas distributor and combustion chamber when natural gas was used as the reductant. External heat was supplied by natural gas burners in the annular space between the reaction vessel and a firebrick-lined shell.

A high-purity gypsum was used in the investigation. Reductants included three types of coke, a lignite char, coal, and natural gas. Additives included quartz, pyrite, and kaolin.

The results obtained were quite favorable. With cement mixtures (gypsum plus additives) containing 0.6 mole of fixed carbon per mole of sulfate, an average of 98% desulfurization was obtained at 1200°C. Sulfur dioxide concentrations in excess of 7% (dry basis) were also reported. The gas velocity was quite low, ∿2 ft/sec, and the solids residence time quite high, ∿1.5 hr, for the tests.

All of the solid carbon reductants gave results comparable to those presented above; a single test using natural gas resulted in only 85% desulfurization.

Exxon. In the late 1960's, several reports related to the one-step reductive decomposition of calcium sulfate began to appear in the literature. Many of these investigations were specifically related to the regeneration of calcium oxide which had been sulfated at high temperatures in either simulated flue gas streams containing sulfur dioxide or in experimental fluidized bed combustors.

Reference has already been made to the work of Skopp *et al.*[19] relative to the thermodynamics of the one-step reductive decomposition process. The report also presented the results of experimental regeneration studies which were made in a small fluidized bed reactor. The reactor consisted of a 2-in.-ID alumina tube, the inlet section of which was packed with alumina cylinders to serve as a gas distributor. The reactor was situated in a small vertical muffle furnace that permitted operation of the reactor at temperatures in excess of 2150°F. Connections to the reactor were made through the gasketed ends of the reactor tube, which extended outside the muffle furnace.

Initial batch experiments with anhydrite were performed at atmospheric pressure, using a reducing gas (carbon monoxide plus hydrogen) concentration of 10 or 15%, a 1:2 ratio of reductant to its oxidized state (carbon dioxide or water) in the reactant gas, a fluidizing gas velocity of 0.8 to 1.6 ft/sec, and a bed temperature of ∿1850°F to ∿2150°F. Conversion appeared to be equilibrium-limited, and sulfur dioxide concentrations in the reactor effluent were 5 to 10%.

Regeneration studies were performed by first sulfating batch samples of limestone or dolomite by reaction with simulated flue gas. During investigations of the cyclic capacities of sorbents, a batch of the material was subjected to repeated cycles of sulfation and regeneration in the regenerator unit. The following observations were reported.

1. The rate of sulfur dioxide removal from simulated flue gas was greater for once-regenerated particles than for freshly calcined particles.

2. Addition of as little as 3 to 5% fly ash to a batch of material prior to regeneration was sufficient to cause agglomeration problems at 2000°F.

3. Self-agglomeration of sorbent particles could occur at temperatures between 2000 and 2100°F.

4. Samples of limestone and dolomite were found to retain their reactivity for sorption of sulfur dioxide over eight full cycles. It was theorized that the cyclic capacity of a sorbent is limited by its exposure time to the high regeneration temperatures (∿2000°F) rather than the number of cycles.

5. Regenerability of the sorbents remained essentially constant over the eight cycles. Sulfur dioxide concentrations in the effluent gas were ∿9% and the calcium sulfide level in the regenerated sorbent remained low (1-2%).

6. The amount of attrition was a function of the particular sorbent tested and was not considered representative of what would happen in larger systems.

A later report by Hammons and Skopp[30] presented the results of a series of cyclic experiments in which limestone was alternately sulfated in a 3-in.-dia batch fluidized bed coal combustor and regenerated in the 2-in.-dia batch fluidized bed regenerator described above. These units were operated intermittently, and solids were manually transferred between the reactors. Bed temperatures in the combustor and regenerator were 1600°F and 2000°F, respectively. Superficial gas velocities in the combustor and regenerator were 3 and 2 ft/sec, respectively. The reductant gas for regeneration contained 10 mol % carbon monoxide and 20 mol % carbon dioxide.

The sulfur dioxide concentration in the effluent from the regenerator was relatively constant over a single regeneration cycle, decreasing slightly with time. The maximum sulfur dioxide concentration during each cycle was constant during the seven combustion/regeneration cycles and was essentially the thermodynamic equilibrium value (∿7.5%).

In 1974, Hoke *et al.*[31] reported the results of additional studies at Exxon which were directed toward the development of the one-step regeneration process. A small 1-in.-dia ceramic reactor was used to study the reductive decomposition of calcium sulfate in fixed beds at temperatures up to 2000°F and pressures up to 9.5 atm. A larger, 3.25-in.-ID batch fluidized bed regenerator was also constructed for investigating one-step regeneration at elevated pressures. The fluidized bed unit consisted of a 12-in. carbon steel pipe, refractory lined to accept an inner lining of a 3.25-in.-ID alumina tube. The height of the unit above the fluidizing grid was ∿16 ft. A burner section was located under the grid. Air and fuel required for regeneration entered the regenerator at the bottom of the burner. For some experiments, secondary air and part of the fuel were injected directly into the bed above the fluidizing grid.

A few regeneration runs were made in the ceramic tube fixed-bed regeneration unit at pressures between 1 and 9.5 atm. Temperatures were held at 1900 and 2000°F. Either anhydrous calcium sulfate or sulfated limestone was used as bed material. Carbon monoxide and carbon dioxide concentrations in the feed gas were varied from 10 to 30% and 10 to 20%, respectively. Gas velocity through the bed was varied from 0.16 to 1.45 ft/sec. When the anhydrous calcium sulfate was used at 1 and 3 atm pressure, sulfur dioxide concentrations in the effluent reached ∿7%, corresponding to 35 and 50%, respectively, of the theoretical equilibrium concentrations. At 9.5 atm, the sulfur dioxide concentration dropped to 1.6% cr 34% of the equilibrium concentration. When the sulfated limestone was used, the measured sulfur dioxide concentration at 9.5 atm was only 0.5%, or 10% of equilibrium, and agglomeration problems were experienced at the 2000°F reaction temperature.

In a series of tests in the 3.25-in.-ID fluidized bed regenerator, the following observations were made:

1. Over the pressure range of 3-10 atm, no significant effect of pressure on sulfur dioxide concentration was reported. However, since the equilibrium partial pressure of sulfur dioxide decreases with increasing pressure, the sulfur dioxide concentration increasingly approached equilibrium as the pressure was increased. Sulfur dioxide levels were generally between 1 and 3% (or ∿50 of equilibrium) at 10-atm pressure.

2. Over the temperature range of 1800 to 2080°F, both the sulfur dioxide concentration and the approach to equilibrium increased with increasing temperature.

3. Reducing the space velocity increased the extent of regeneration, *i.e.*, the sulfur dioxide concentration in the effluent gas approached equilibrium more closely.

4. No significant effect of the concentration of reducing gases on the concentration of sulfur dioxide was apparent. The data were insufficient to indicate whether increased ratios of reductants to oxidized species caused increased formation of calcium sulfide.

5. Adding part of the fuel above the fluidizing grid directly into the bed of solids (so that there would be an oxidizing flame at the grid) resulted in more uniform bed temperature profiles, reduced bed agglomeration, and higher permissible bed temperatures at a given fuel consumption.

6. The injection of auxiliary air into the bed at a point 12 in. above the fluidizing grid drastically reduced the calcium sulfide content of regenerated solids--from typical values of 40 to 70 mole % to less than 1 mole %.

Kent Feeds, Inc. The design and operation of an atmospheric pilot plant for demonstrating the reductive decomposition of anhydrite was reported by Hansen *et al.*[32] The reactor was patterned after the Bureau of Mines combustor discussed above. The unit consisted of a 10-in.-ID silicon carbide tube surrounded by a gas-fired heating chamber to provide operating flexibility and reduce heat losses. The solids were fed to the reactor by a rotating valve and screw feeder and were continuously removed through a silicon carbide overflow tube. A flat plate distributor of castable refractory was used, as compared with the Bureau of Mines cone-shaped distributor. Air and natural gas were mixed and entered the bed through the gas distributor where partial combustion of the fuel and reductive decomposition of the anhydrite occurred.

The unit was tested over the following ranges of operating conditions: anhydrite particle size, 1/8 in. or smaller; solids residence time, between 1 and 10 hr; temperature, 2000 to 2300°F; and unspecified ranges of gas and air feed rates. It was claimed that operating conditions were identified which provided up to 90% desulfurization and a product gas containing between 5 and 10% sulfur dioxide. It was claimed that the effluent gas contained over 14% sulfur dioxide intermittently. Calcium sulfide in the reacted solids was reported to vary from "not detectable" to "appreciable" concentrations and was closely related to the reducing characteristics of the system (ratio of reducing agents to calcium sulfate).

Consol. Zielke *et al.*[33] investigated the combustion of coal or low-temperature coal char in a continuous bench-scale unit, using excess air in a fluidized bed of dolomite. Continuous regeneration of the sulfated dolomite using partial combustion of carbon monoxide gas was also demonstrated.

The experimental unit consisted of a continuous, fluidized bed reactor with an inside diameter of 4 in. The bed, 36-in. deep, was supported on a perforated plate above a plenum chamber through which the fluidizing gases were introduced. During combustion studies, dolomite and either coal or char could be pneumatically fed to the reactor. For the cyclic studies (6.5 cycles of alternate sulfur dioxide absorption and regeneration), the reuse of dolomite was explored. During the tests, sulfur dioxide gas was added with the fluidizing air as a major source of sulfur during the absorption cycles; coal was burned to supply heat and a minor amount of sulfur. The regeneration portion of each cycle was conducted at 1950°C with carbon monoxide the reducing gas. Excess carbon monoxide was burned with air to supply the heat. At a gas velocity of 1.5 ft/sec, a solids residence time of ∿1.8 hr, and a carbon monoxide to sulfate ratio of ∿1.0, desulfurization was as high as 93% with less than 0.5 wt % sulfide in the regenerated sorbent. Sulfur dioxide concentrations in the off-gas ranged from ∿3 to 7% as compared with a calculated equilibrium value of 12%. The optimum ratio of carbon dioxide to carbon monoxide in the effluent gas was reported to be 23 to 30, as compared with the equilibrium ratio of ∿46.

Pope, Evans, and Robbins. Researchers at Pope, Evans, and Robbins have long been involved in research and development on fluidized bed boilers. In a report by Gordon *et al*,[34] they also report the results of limited investigations into the regeneration of sulfated sorbent.

The equipment consisted of a combustor, a carbon burnup cell, and a regeneration unit. The combustor consisted of a 18-in. by 72-in. combustion space over an air distributor. Air entered through a plenum chamber below the distributor and up through a grid of bubble caps into the combustion chamber. Coal (or other fuel) and limestone were pneumatically injected into the bed. The fluidized bed was contained in a rectangular enclosure in which each wall was a row of vertical boiler tubes seal-welded to form a gas-tight enclosure.

Appended to the combustor was a fluidized bed carbon burnup cell. It operated in parallel with the combustion chamber, at a higher temperature but with a common bed (*i.e.*, bed material was free to circulate between the two chambers through slots in the dividing water-tube wall). Fuel for the carbon burnup cell was fly ash generated by the combustor, plus its own fly ash and additional coal if required.

A second appendage to the combustor was a regeneration unit which, similarly to the carbon burnup cell, operated in parallel with the combustor but at a higher temperature. The regenerator grid area was 10-in. by 10-in. Coal was the fuel used in the regenerator.

Initial regeneration tests were made using first the fluidized bed combustor and carbon burnup cell in tandem. The theory of operation was to operate the combustor section under conditions favorable to sulfur acceptance by lime (bed temperature <1550°F, excess oxygen >2%) while operating the carbon burnup cell at conditions favorable to sulfur rejection (bed temperature >1800°F, excess oxygen <4%). In a test with the combustor at a 1600°F bed temperature and 5% oxygen in the flue gas and with the carbon burnup cell at 1850°F, the level of sulfur dioxide in the flue gas from the burnup cell varied from 1.6% to 2.4% as the oxygen level decreased from 1.3% to 0.5%. A subsequent test after modifications of the burnup cell resulted in similar regeneration results.

Tests were then made with the three-module system: combustor, burnup cell, and regenerator. During a 156-hr test over an 8-day period, sulfur dioxide levels of 4 to 8% were obtained in the effluent from the regenerator module. The combustor temperature was ∿1500°F; the burnup cell temperature was ∿2000°F; and the regenerator bed temperature was ∿2000°F with <1% oxygen in the flue gas.

A subsequent test was made in which only the combustor and regenerator modules were used. A sulfur dioxide content of 10% in the regenerator flue gas is reported; no details of the test are provided.

Argonne National Laboratory. Argonne National Laboratory, like Exxon and Pope, Evans, and Robbins, has had an extensive research program directed toward the development of fluidized bed combustion. Initial results of investigations into the one-step regeneration process were reported by Vogel *et al.*[35] Experiments were performed in 1-in., 2-in., and 3-in.-dia units.

The 3-in.-dia fluidized bed regenerator, rated for operation at 10 atm and 2000°F, consisted of a refractory-lined 8-in.-dia pipe enclosed by a 12-in.-dia pressure shell. Fluidizing gas entered through a plenum and bubble-cap type distributor. The solids inlet line entered through the top flange of the unit and terminated above the bed. A solids overflow line passed through the gas distributor and the bottom flange of the pressure shell. The fluidizing gas consisted of oxygen and nitrogen, metered separately and then mixed. Carbon monoxide and kerosene entrained in carbon dioxide were injected into the bed as the fuels and reductants for regeneration.

Both batch and continuous experiments were performed at bed temperatures ranging from 1300 to 1900°F, a pressure of ∿2 atm, and gas velocities of 2.3 to ∿6 ft/sec. All tests but one, which was made with sulfated dolomite, were made with pure calcium sulfate. Although high sulfur removal rates were reported (as high as 85% during continuous operation with pure calcium sulfate), sulfur dioxide levels in the flue gas were quite low, ranging between 1 and 4%. Regeneration at the higher temperatures investigated resulted in less residual calcium sulfide in the reacted sulfate.

In addition to the bench-scale experiments, the one-step reductive decomposition was investigated at low temperatures (1200-1650°F) in small

1-in. and 2-in.-dia, batch fluidized bed reactors. A bed of pure calcium sulfate was reacted with a gas mixture of two or more of the following gases: carbon monoxide, carbon dioxide, water, oxygen and nitrogen. Conclusive results were not obtained, but some observations made were:

1. Regeneration appeared to be most effective when conditions of temperature and carbon dioxide concentration favored calcium carbonate formation over calcium oxide formation.
2. A stated observation was that the sulfur dioxide concentration increased with oxygen concentrations. Checking tabulated and graphical presentations of experimental data (Appendix C, Ref. 35) suggests that the observation should have read that the sulfur dioxide concentration increased with increasing carbon dioxide concentration and decreasing oxygen concentration in the regenerator effluent gas.
3. The maximum concentration of sulfur dioxide obtained was approximately equal to the theoretical equilibrium concentration.
4. Small quantities of elemental sulfur were produced.
5. Small concentrations of carbonyl sulfide were detected.

The results of more recent regeneration studies performed at Argonne are available in reports by Vogel *et al.*[36,37] and Montagna *et al.*[38,39] In experiments with the Argonne 3-in.-dia regenerator described above, sulfated dolomite (containing ~10.2 wt % sulfur as calcium sulfate) from the fluidized bed combustion process was regenerated to CaO·MgO by reductive decomposition at 1100°C.[36,38] Methane was combusted in the fluidized bed to generate the heat and the reducing gases required. The effects of temperature, fluidizing-gas velocity, fluidized-bed height, solids residence time, and total reducing-gas concentration in the effluent on the regeneration of calcium oxide and the formation of calcium sulfide were evaluated.

For the study, nitrogen and oxygen were mixed in the desired proportion and introduced through the gas distributor to establish a highly oxidizing zone in the bottom of the fluidized bed. Methane was introduced through multiple injection points rather than one injection point (to reduce hot spots), ranging from 15 to 25 cm above the gas distributor; thus, a reducing zone was established in the top portion of the fluidized bed and an oxidizing zone was established in the bottom portion of the bed. (This concept is similar to the addition of auxiliary air as used by Hoke *et al.*[31] and Swift[20] to create separate oxidizing and reducing zones during regeneration. The work of the former investigator has been discussed above, and a discussion of the latter's work follows.)

The results of the study can be summarized as follows:

1. Increasing the fluidized-bed height at a constant additive feed rate was not beneficial to regeneration. The bed height was increased from 1.5 ft to 2.5 ft with a drop in regeneration from 62% to 54% and a drop in the sulfur dioxide concentration from 5.7% to 4.4%. Poorer fluidizing and mixing in the deeper bed were the suggested causes for the decreased regeneration.

2. Increasing the fluidized-bed height at a constant residence time also resulted in poorer regeneration. Comparable experiments at 1.5 ft and 2.5 ft resulted in regenerations of 57 and 40%, respectively.

3. Increasing the gas velocity from 2.2 to 3.0 ft/sec while the other variables were fixed resulted in a decrease in sulfur regeneration from 65% to 38%. The proportion of gas bypassing in the bubble phase with increasing velocity is a suggested cause for the observed effect.

4. Increasing the temperature from 1010°C to 1100°C increased regeneration from ∿20% to ∿90% in experiments performed under similar conditions. The sulfur dioxide level increased from 0.8% to 7.3% on a dry basis.

5. Very small amounts of sulfide were found in the steady-state regenerated products of all experiments. With ∿3% total reducing gas in the effluent, $\leq$0.1% sulfide was formed. With ∿15% reducing gas in the effluent, the sulfide only increased to 0.3 and 0.7% in two experiments. The use of separate oxidizing and reducing regions was offered as the explanation for the low calcium sulfide formation.

6. Approximately 5 to 15% of the sulfated dolomite feed was decrepitated in the regenerator.

7. Agglomeration of the bed was experienced at temperatures of 1100°C under highly reducing conditions (*i.e.*, 15% reducing gas in the effluent).

In the more recent reports by Vogel *et al.*[37] and Montagna *et al.*,[39] the results of regeneration experiments in which the necessary heat and reducing gases were provided by coal combustion in the bed were reported. For these experiments the inside diameter of the regenerator was increased to 4.25 in.

The effects of solids residence time (7-35 min), regeneration temperature (1000-1100°C), and pressure (1.1-1.5 atm) on the extent of regeneration and the sulfur dioxide concentration in the off-gas were investigated. Significant results were

1. The extent of regeneration improved with increasing bed temperature and increasing solids residence time.

2. The sulfur dioxide concentration in the flue gas increased with increasing temperature, decreasing solids residence time, and decreasing pressure.

3. A maximum sulfur dioxide concentration of ∿8% was obtained at ∿70% regeneration.

4. The presence of reducing and oxidizing zones in the fluidized bed resulted in negligible ($\leq$0.1 wt %) calcium sulfide in the regenerated sorbent.

5. A mass and energy balance constrained model was developed using the experimental results for preliminary process evaluation.

6. Favorable preliminary results were also presented of a cyclic study (first three utilization cycles) to evaluate the reactivity of the sorbent over several cycles.

Later Work at Iowa State University. Reports by Swift[20] in 1973 and Swift and Wheelock[40] in 1975 present the results of experiments investigating the two-zone reactor for the decomposition of calcium sulfate. A small 4.75-in.-ID reactor made by installing a refractory lining in an 18-in. pipe was used in the investigation. A fixed solids overflow line was 16 in. above the ceramic bed-support plate. Bed height was varied by placing layers of alumina balls on the surface of the distributor. Solids were introduced pneumatically through a dip-leg penetrating the top of the reactor and extending below the surface of the bed.

Two reaction zones were achieved by limiting the ratio of air to natural gas which entered through the gas distributor. Secondary air was introduced as the transport gas conveying the solids feed into the combustor. A reducing zone was established in the lower portion of the fluidized bed and an oxidizing zone in the upper portion of the bed, as verified by measured concentration profiles.

Both gypsum and anhydrite were tested in the reactor. In a number of tests made at temperatures from ∿1900 to ∿2200°F, the effect of the two-zone reactor was demonstrated. In most instances, the overflow solids were well desulfurized (95-99%) with very little calcium sulfide formed (<0.5%).

TWO-STEP REGENERATION

Two-step regeneration of sulfated additives (dolomite or limestone) depends upon first reducing the calcium sulfate to calcium sulfide and subsequently recovering the sulfur from the sulfide by an acid-base reaction, by roasting, or by a solid-solid reaction between the calcium sulfide and excess calcium sulfate from the first step.

For the reduction step, several reducing agents may be involved as indicated by the reactions

$$CaSO_4 + 4CO \rightleftarrows CaS + 4CO_2 \qquad (3\text{-a})$$

$$CaSO_4 + 4H_2 \rightleftarrows CaS + 4H_2O \qquad (3\text{-b})$$

$$CaSO_4 + CH_4 \rightleftarrows CaS + CO_2 + 2H_2O \qquad (3\text{-c})$$

$$CaSO_4 + 2C \rightleftarrows CaS + 2CO_2 \qquad (3\text{-d})$$

Once calcium sulfide has been formed, calcium carbonate can later be regenerated by the acid-base reaction:

$$CaS + H_2O + CO_2 \rightleftarrows CaCO_3 + H_2S \tag{4}$$

Alternative regeneration reactions include roasting of the sulfide to yield calcium oxide and sulfur dioxide,

$$CaS + 3/2\ O_2 \rightleftarrows CaO + SO_2 \tag{5}$$

or the solid-solid reaction of calcium sulfide with calcium sulfate,

$$3CaSO_4 + CaS \rightleftarrows 4CaO + 4SO_2 \tag{6}$$

Reduction of Calcium Sulfate to Calcium Sulfide

Thermodynamics

The free energy changes and heats of reaction for the reduction reactions of calcium sulfate to calcium sulfide as calculated by Zadick *et al.*[41] are presented in Table 5. It can be seen that the free energy change favors all the reduction reactions at temperatures of $\sim$200°C and higher, with reduction by hydrogen and CO favored at temperatures below 25°C. Reduction by carbon monoxide and hydrogen is highly exothermic and reduction by carbon and methane is highly endothermic.

Equilibrium constants for the reduction reactions have been compiled from a number of sources (references 3, 20, 35, 41, 42, and 43), and representative values are plotted in Fig. 7. The relatively large values of the equilibrium constants indicate that high equilibrium conversions of sulfate to sulfide should be achievable with all the reductants at stoichiometric conditions.

It should be emphasized, however, that mixtures of calcium sulfide and calcium sulfate have an equilibrium partial pressure of sulfur dioxide as indicated by the regeneration reaction:

$$3CaSO_4 + CaS = 4CaO + 4SO_2 \tag{6}$$

As indicated in the discussion of the one-step reductive decomposition kinetics, reductive decomposition of calcium sulfate results in either a mixture of calcium sulfate and calcium oxide or a mixture of calcium oxide and calcium sulfide, depending on the temperature and reducing gas concentrations (see Fig. 5a, 5b, and 6).[4,21] Calcium sulfide formation is favored over calcium oxide at low temperatures (1600-1800°F) and high reducing gas concentrations.[4,21]

TABLE 5. Calculated Free Energy Changes and Heats of Reaction for the Reduction of Calcium Sulfate to Calcium Sulfide by Various Reducing Agents[a]

Reaction	Free Energy Change, kcal/mole $CaSO_4$				Heat of Reaction, kcal/mole $CaSO_4$	
	298°K	500°K	1000°K	1500°K	500°K	1000°K
$CaSO_4 + 4CO \rightarrow CaS + 4CO_2$	-44.3	-44.9	-46.4	-47.9	-44.1	-46.2
$CaSO_4 + 4H_2 \rightarrow CaS + 4H_2O$	-17.1	-25.9	-47.7	-69.5	- 6.0	-12.6
$CaSO_4 + CH_4 \rightarrow CaS + CO_2 + 2H_2O$	+ 6.6	-12.7	-61.2	-109.4	+35.7	+33.9
$CaSO_4 + 2C \rightarrow CaS + 2CO_2$	-12.9	- 4.7	-48.4	-92.1	+38.8	+35.4

[a] Data of Zadick *et al.*[41]

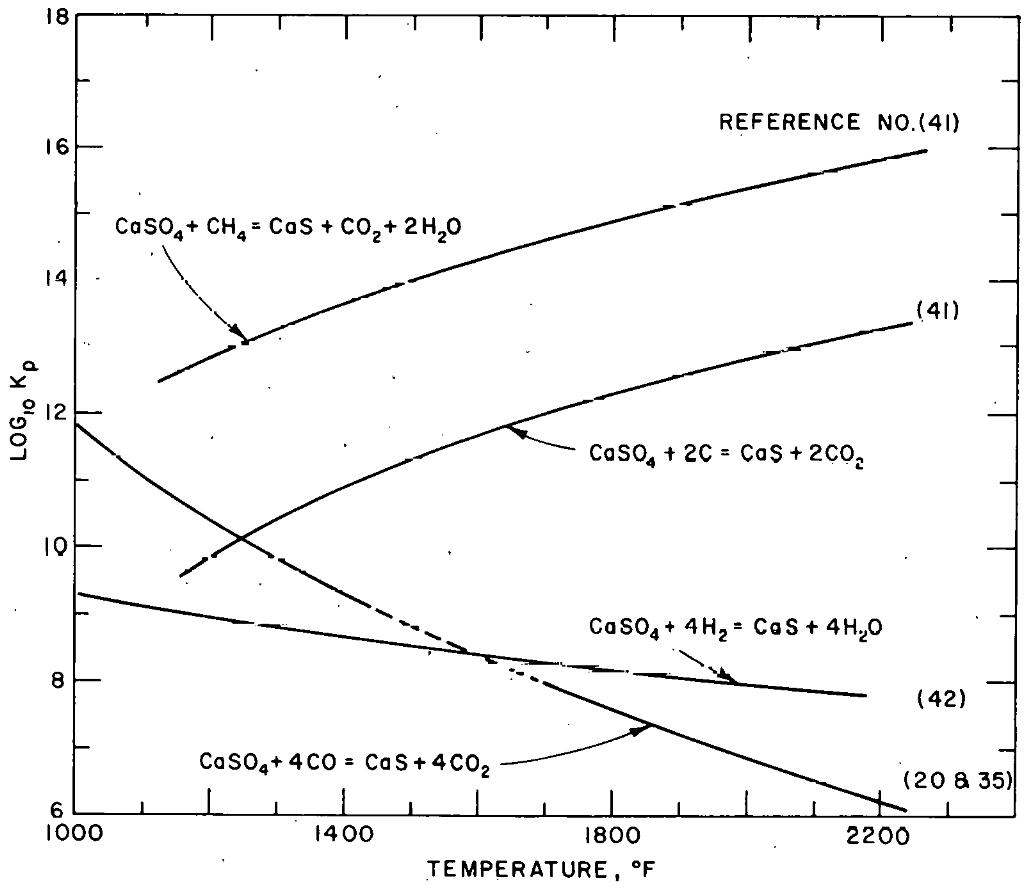

Fig. 7. Equilibrium Constants for the Reduction of Calcium Sulfate to Calcium Sulfide

Kinetics

A very early work by Hofman and Mostowitsch[44] investigated the reductive decomposition of pure calcium sulfate by carbon and carbon monoxide. Reduction by carbon was carried out in a nitrogen-purged environment, and reduction by carbon monoxide in a pure carbon monoxide purged environment. The results of the work are summarized in Table 6. The results indicate an expected higher rate of reaction with carbon monoxide. Even at 900°C, however, approximately 1 hr was required to reduce the sulfate to sulfide in a pure carbon monoxide reactant stream.

TABLE 6. Reduction of Calcium Sulfate by Carbon Monoxide and Carbon[a]

Temperature (°C)	Time of Reduction (hr)	Reduction of Calcium Sulfate (%)	
		Carbon Monoxide	Carbon
700	1	1.0	0.4
750	1	3.3	1.7
800	1	3.6	9.3
850	1	92.0	67.0
900	1	100.0	90.0
1000	1	-	96.0

[a] Data of Hofman and Mostowitsch.[44]

O'Neil *et al.*[45,46] performed thermogravimetric analysis experiments in which sulfated dolomites were reduced to calcium sulfide. The experiments were performed in the temperature range of 750 to 850°C with 80 to 90% conversion. At 10 atm and 820°C, 85% conversion of the sulfate to sulfide was achieved in ~65 min using a reactant gas containing 20% carbon monoxide, 40% carbon dioxide, and 40% nitrogen. The sulfidation reaction was indicated to be first order in sulfate concentration.[45]

A thermogravimetric analysis of the sulfidation reaction with hydrogen was performed by Vogel *et al.*[47] Results reported were that temperatures of 900°C were required for complete reaction and that the presence of water vapor had no effect on the rate of reaction. No details of the tests are given.

The catalytic reduction of calcium sulfate to calcium sulfide was investigated in a small fluidized bed reactor by Zadick *et al.*[41] Of the catalysts tested, ferric oxide, stannous sulfate and vanadium pentoxide were found to have the greatest effect. When the bed was fluidized at 4 ft/min with pure carbon monoxide at 700°C and with no catalyst present, conversion of calcium sulfate to sulfide was ~5% after ~50 min. With the addition of 12.5% ferric oxide, conversion was ~97% after only 45 min. In addition, calcium sulfide was found to autocatalytically favor its own rate of formation.

Regeneration by Acid-Base Reaction

Thermodynamics

For regeneration by the acid-base reaction,

$$CaS + CO_2 + H_2O \rightleftarrows CaCO_3 + H_2S \tag{4}$$

thermodynamic data has been used to calculate values for equilibrium constants.[4,42,43] The equilibrium constants reported by different investigators agree well with each other, as evidenced in Table 7. The equilibrium constants indicate that increases in temperature have an adverse effect on equilibrium conversion. This effect can be seen in Table 8, in which calculated theoretical concentrations of hydrogen sulfide are presented as a function of temperature.[4] Calculations by Squires[42] indicate that at temperatures below ∿1100°F and pressures above ∿4 atm, the acid-base regeneration reaction should yield a product gas containing hydrogen sulfide at concentrations which permit recovery of elemental sulfur in a Claus system.

TABLE 7. Equilibrium Constants for the Acid-Base Regeneration Reaction

Temperature (°F)	Equilibrium Constant K_p (atm^{-1})		
	Vogel *et al.*[4]	Squires[42]	Curran *et al.*[43]
1000	0.153	0.200	-
1100	0.058	0.070	0.082
1200	0.023	0.030	0.030
1300	0.010	0.015	0.013
1400	0.0055	0.007	0.006
1500	-	0.004	0.004

TABLE 8. Hydrogen Sulfide Concentrations at Equilibrium in Dried and Undried Product Gas Stream as a Function of Temperature for the Acid-Base Regeneration Reaction[a]

Temperature (°F)	Hydrogen Sulfide Concentration[b] at Equilibrium (%)	
	Undried	Dried
1000	23.0	37.0
1100	11.0	20.0
1200	4.7	9.9
1300	2.7	5.1
1400	1.4	2.8

[a] Data of Vogel *et al.*[4]

[b] Assumes 10-atm total pressure, 50% H_2O and 50% CO_2 inlet gas.

Kinetics

Experimental work reported by Squires[42] verified the high equilibrium yield of hydrogen sulfide predicted by thermodynamics. Fully calcined dolomite was first converted to calcium sulfide at atmospheric pressure and ∿1100°F, using a gas mixture of 85% N_2, 10% H_2S, and 5% H_2. The sulfided dolomite was then regenerated at ∿220 psia and 1000-1100°F to obtain a dry effluent gas containing 20-24% hydrogen sulfide. This is very close to the predicted equilibrium concentration for hydrogen sulfide (20 to 37%) given in Table 8 for temperatures between 1000 and 1100°F.

Experimental work by other investigators, however, seems to indicate that such high yields of hydrogen sulfide may not be obtainable in actual operation. The results of cyclic sulfidation-regeneration experiments performed in a small, 2-in.-dia fluidized bed reactor have been reported by Vogel *et al.*[4,35] A sample of dolomite was sulfated, reduced to calcium sulfide at 10 atm and 1600°F (using pure hydrogen or carbon monoxide), and then regenerated at 10 atm and 1000°F with a CO_2/H_2O mixture. The peak concentration of hydrogen sulfide in the effluent gas during the regeneration step decreased from 13% for cycle 1 to 0.5% for cycles 5 and 6. The percent sulfide regenerated decreased from 9.7% to a very low indeterminant value.

Experiments were also performed in which calcium carbonate was reacted directly with hydrogen sulfide and then reacted with CO_2/H_2O at 1000-1200°F. Again the sulfur removal was poor, generally 50% or less. In cyclic studies, the peak hydrogen sulfide concentration in the effluent gas stream steadily decreased with each regeneration.

The decrease in the ability to regenerate calcium sulfide during cyclic operation has also been reported by Curran *et al.*[48] In the cycling of dolomite between a hydrogen sulfide absorption unit and a regenerator, the level of calcium sulfide in the sorbent gradually increased due to poor conversion in the regenerator.

An additional interesting observation was made in a report by O'Neill *et al.*[45] Regeneration of calcium carbonate from calcium sulfide produced by the reduction of sulfated dolomite was quite rapid initially. After ∿25% conversion (in 10 min), however, the rate became extremely low. In contrast, yields greater than 70% (∿18 min) were achieved when the calcium sulfide was formed by the direct sulfidation of the dolomite with hydrogen sulfide.

Laboratory and Bench-Scale Studies

Very little development work has been done that is directly related to the two-step regeneration of calcium oxide from calcium sulfate materials produced in fluidized bed combustors. The process studies cited above[43,48] for the regeneration of calcium sulfide formed directly from the reaction between calcium oxide and hydrogen sulfide during coal gasification indicate that poor kinetics limits the hydrogen sulfide concentration in the off-gas, as well as the extent of regeneration. The results of O'Neill *et al.*[45] (TGA experiments) cited above indicate that calcium sulfide produced by the reduction of calcium sulfate is even less reactive.

Vogel *et al.*[35] have reported the results of a preliminary investigation of the two-step regeneration process in which the acid-base regeneration method was used. The experiments were performed in the 3-in.-dia, bench-scale regenerator described previously in this report. In the experiments, a batch of pure calcium sulfate was reduced at ∿1700°F with carbon monoxide, which served as both the fuel and the reductant. Following reduction, the bed was cooled to ∿1000°F and then a mixture of carbon dioxide and steam was passed through the bed. The pressure of the system was varied between ∿2 and 10 atm. The final samples contained large amounts (54 to 77%) of calcium sulfate, indicating poor reduction during the first step. The final samples, with the exception of the experiment at 10 atm, also contained residual sulfide (17 and 26%), indicating that regeneration was incomplete in the second step. No hydrogen sulfide was detected in the reactor effluent.

The results of the limited kinetic and bench-scale efforts investigating two-step regeneration by the acid-base regeneration step have not been encouraging. It has been suggested that more favorable kinetics at higher temperatures may make the process acceptable if special techniques are used to recover the low hydrogen sulfide content that would be present in the reactor effluent.

Regeneration by Air Oxidation

Regeneration of calcium oxide from calcium sulfide by oxidation is expressed by the reaction.

$$CaS + 3/2\ O_2 \rightleftarrows CaO + SO_2 \qquad (5)$$

A competing and undesirable reaction is the oxidation of the sulfide to sulfate, as expressed by the reaction.

$$CaS + 2O_2 \rightleftarrows CaSO_4 \qquad (19)$$

Hofman and Mostowitsch,[44] cited earlier for their investigation of the reduction of calcium sulfate with carbon monoxide and carbon, also investigated the air oxidation of calcium sulfide. Air was passed over samples of calcium sulfide heated to temperatures between 350 and 950°C. Decomposition became noticeable at ∿500°C and active at ∿800°C. The calcium sulfide was completely oxidized to a mixture of calcium oxide and calcium sulfate, with the indication that evolution of sulfur dioxide increased with increasing temperature.

Thermodynamics

Equilibrium constants and heats of reaction for the calcium sulfide oxidation reactions reported by Swift[20] are presented in Table 9. The values agree well with those also reported by Loebach.[49] The reactions are highly exothermic and exhibit highly favorable equilibrium constants, which decrease slightly with increasing temperature.

TABLE 9. Equilibrium Constants and Heats of Reaction for Oxidation Reactions of Calcium Sulfide with Oxygen[a]

Reaction	$\text{Log}_{10}K_p$			Heat of Reaction (kcal/g mole $CaSO_4$)		
	1200°K	1400°K	1600°K	1200°K	1400°K	1600°K
$CaS + 3/2\ O_2 \rightleftarrows CaO + SO_2$	15.7	13.0	10.9	-109.1	-109.4	-109.8
$CaS + 2O_2 \rightleftarrows CaSO_4$	23.0	17.3	13.2	-219.1	-216.4	-213.1

[a] Data of Swift[20]

An interesting analysis of the roasting of calcium sulfide was made in a report by Vogel *et al.*[4] The equilibrium constant for reaction (5) which is expressed as

$$K_p = \frac{\overline{P}_{SO_2}}{(\overline{P}_{O_2})^{3/2}} \tag{20}$$

indicates that at any given temperature, the partial pressure of sulfur dioxide increases with the partial pressure of oxygen. It also follows from the equilibrium constant for reaction (19)

$$K_p = \frac{1}{(\overline{P}_{O_2})^2} \tag{21}$$

that above some definite oxygen partial pressure given by equation (21) for any given temperature, calcium sulfide is no longer stable and is converted to calcium sulfate. Thus, the maximum sulfur dioxide partial pressure obtainable is along the coexistence line of calcium sulfide and calcium sulfate.

Kinetics

Very little kinetic information has been found relative to the reaction of calcium sulfide and oxygen. Loebach[49] carried out some experiments in a small 2-in.-dia fluidized bed reactor in which a solid product (from the reductive decomposition of anhydrite) containing high percentages of calcium sulfide and calcium oxide and a small percentage of calcium sulfate was oxidized. Oxidation was carried out at temperatures ranging from 1700 to 2000°F, using mixtures of oxygen with either nitrogen or carbon dioxide. He reported that the oxidation reaction was extremely rapid, with calcium oxide and sulfur dioxide the favored products. Oxidation to calcium sulfate was found to increase, however, with decreasing temperatures and with increasing oxygen levels in the oxidizing gas stream. The rate of reaction increased with the level of oxidizing agent in the reactant gas. Conversion in the reactor was reported to be equilibrium-controlled.

Swift[20] performed similar experiments except that the reactor was operated at steady state by the continuous feeding and removal of solids. These experiments were also performed in a 2-in.-dia reactor. Conversion of calcium sulfide was quite high, ranging from 52 to 99%, but desulfurization (rejection of sulfur as sulfur dioxide) ranged from 15 to 86%. Conversion of the sulfide to sulfate was enhanced at low temperatures and high O_2/CaS molar feed ratios. At a 1.5 O_2/CaS mole ratio, increasing the temperature from $\sim$2000°F to $\sim$2100°F increased the conversion from 52 to 80% and the desulfurization from 39 to 76%. Increasing the O_2/CaS mole ratio to 3 at $\sim$2000°F increased the conversion to 84% but the desulfurization decreased to only 15%. The mean solids residence time for the solids in the reactor ranged from 7 to 32 min.

Keairns *et al.*[50] have reported the results of thermogravimetric experiments in which sulfided limestones and dolomites were oxidized at low temperatures with the intention of forming calcium sulfate. Results reported were:

1. Oxidation became perceptible at $\sim$750°F when air was used.
2. Isothermal runs made with sulfided limestone at $\sim$930°F, $\sim$1290°F, and $\sim$1650°F, yielded conversions to the sulfate of 3.5% in 750 min, 8% in 35 min, and <1%, respectively. In the experiment at $\sim$1290°F, $\sim$50% of the sulfide was oxidized in only 150 sec and $\sim$65% was oxidized after 50 min.
3. Oxidation of sulfided dolomite at $\sim$1290°F was 70% complete in <50 sec, after which oxidation ceased.
4. Oxidation of partially sulfided dolomite was performed at temperatures between 1020°F and 1470°F. The degree of oxidation attained before the reaction rate essentially ceased was 16% at 1020°F, 60% at 1200°F, and 92% at 1470°F.
5. Residual sulfide, after oxidation, was concentrated in a thin band at the outer edges of the stone.
6. The oxidizability of sulfided limestones and dolomites increased with decreasing calcium content of the original stone.

The report fails to indicate the relative degree of conversion to the oxide or sulfate for each of the oxidation experiments performed.

Bench and Pilot-Scale Investigations

The Esso Petroleum Co., England, has developed a process known as the CAFB (chemically active fluidized bed) for the gasification and desulfurization of oil and coal. The process uses a fluidized bed of calcium oxide, which reacts with the hydrogen sulfide released during gasification to form calcium sulfide. The spent bed material, rich in calcium sulfide, is then transferred to a fluidized bed regenerator where the calcium sulfide is air-oxidized to lime (for recycle to the gasifier) and sulfur dioxide. Results of batch bench-scale and continuous pilot-plant experiments of the air-oxidation regeneration process have been reported.[51]

The batch, bench-scale experiments were on both a single-cycle and multiple-cycle basis. Batches of limestones were first sulfided by the substoichiometric combustion of fuel oil directly in the bed. Upon completion of the sulfidation cycle, the fuel supply to the fluidized bed was discontinued, allowing air alone to contact the bed. When the supply of fuel was discontinued, the temperature of the bed was generally between 900 and 1000°C. During oxidation of the calcium sulfide, the bed temperature would rise to between 1000 and 1100°C and then decrease rapidly as oxidation decreased. The concentration of sulfur dioxide during the tests was as high as 15%.

Batch cyclic tests were also performed in which beds were alternately sulfided and then regenerated by air oxidation for up to 80 cycles. The maximum temperature during regeneration was ∿1050°C for most of the tests, with sulfur dioxide levels (maximum) ranging around 7 to 9%.

Results in the pilot plant were just as encouraging. When sorbent was continuously recycled between the gasifier and regenerator during a ten-day test, sulfur dioxide concentrations in the regenerator off-gas were consistently between 6 and 8%.

Keairns *et al.*[52] have issued a design report for a demonstration gasification facility based on the CAFB process. The design calls for a 4.5-ft-dia regenerator operated at 2000°F (1090°C), a maximum bed depth of 4 ft, and a gas velocity of 6 ft/sec. Expected sulfur dioxide concentration in the regenerator effluent is 8%.

Thus, regeneration by air oxidation may be a viable process for the two-step regeneration. It should be tested, however, since (as in the case of regeneration by the acid-base reaction) the oxidation of calcium sulfide from reduced sulfate may be considerably different from the oxidation of calcium sulfide from the sulfidation of limestone.

Regeneration by Sulfide-Sulfate Reaction

Thermodynamics

Regeneration by the solid-solid reaction of calcium sulfide with calcium sulfate is expressed by the reaction

$$3CaSO_4 + CaS \rightleftarrows 4CaO + 4SO_4 \qquad (6)$$

The thermodynamics of the reaction have been considered by several investigators.[4,41,43] Table 10 lists values for the free energy change, heat of reaction, and equilibrium constant for the reaction as a function of temperature, as presented (or derived from data presented) by different investigators. The published values are generally in good agreement.

The equilibrium constant values derived from data presented by Vogel *et al.*[4] are plotted in Fig. 8 along with both the theoretical equilibrium concentration of sulfur dioxide at 1 and 10 atm total system pressure. The curves indicate that a gas containing ∿10% sulfur dioxide should be obtainable at temperatures of ∿1000°C and ∿1150°C at system pressures of 1 and 10 atm, respectively.

Equilibrium constants for the solid-solid reaction have also been determined experimentally. In a very early work by Zawadzki,[6] the partial pressures of sulfur dioxide and sulfur in nitrogen over calcium sulfide were determined, using static and dynamic methods. Curran *et al.*[53] also experimentally measured the decomposition pressure of sulfur dioxide over a mixture of calcium sulfide and calcium sulfate. The latter experimenters used a thin-walled stainless steel reactor (1-in.-ID by 6-in. long) contained along with its heating furnace in a high-pressure autoclave. The reactor internal pressure was balanced by adding sulfur dioxide from an external source to the autoclave. A sulfur dioxide-nitrogen mixture of known composition and pressure was used to fluidize a mixture of calcium sulfide and calcium sulfate. The effluent gas was throttled to atmospheric pressure and passed through a thermal conductivity cell where the feed gas served as a reference gas. The thermal conductivity cell was able to detect a change in sulfur dioxide concentration of ±0.01%. The solid phases were heated to the temperature anticipated to correspond to the sulfur dioxide partial pressure imposed on the system. The temperature was then cycled at a maximum rate of 5°F/min below and above the anticipated equilibrium temperature. The effluent gas then showed a deficiency or excess of sulfur dioxide, as compared with the inlet gas. The temperature corresponding to the equilibrium sulfur dioxide pressure was recorded at the point where the effluent gas showed zero change in composition. The theoretical equilibrium values determined by Curran *et al.*[53] and Zawadzki[6] are also shown in Fig. 8. The experimental results, which exhibit good agreement with each other, indicate somewhat lower equilibrium constants than those predicted from theory.

TABLE 10. Thermodynamic Values for the Solid-Solid Reaction of Calcium Sulfide with Calcium Sulfate as a Function of Temperature[a]

	Zadick et al.[41]			ln K_p		
Temp. (°K)	ΔF_r (kcal/mole)	ΔH_r (kcal/mole)	ln K_p	Vogel *et al.*[4]	Swift[20]	Curran *et al.*[43]
298	65.3	*	-110.2	*	*	*
500	52.8	83.6	- 53.2	*	*	*
1000	21.8	80.0	- 11.0	-11.5	*	*
1200	*	*	*	- 4.9	-4.91	-5.78
1400	*	*	*	- 0.3	-0.66	-1.12
1500	- 9.1	*	+ 3.5	+ 1.4	*	*
1600	*	*	*	+ 2.90	+3.02	*

[a] Reaction expressed as $CaSO_4 + 1/3\ CaS = 4/3\ CaO + 4/3\ SO_2$.

Vogel *et al.*[4] made the observation that the solid-solid reaction can be expressed as the sum of the reactions:

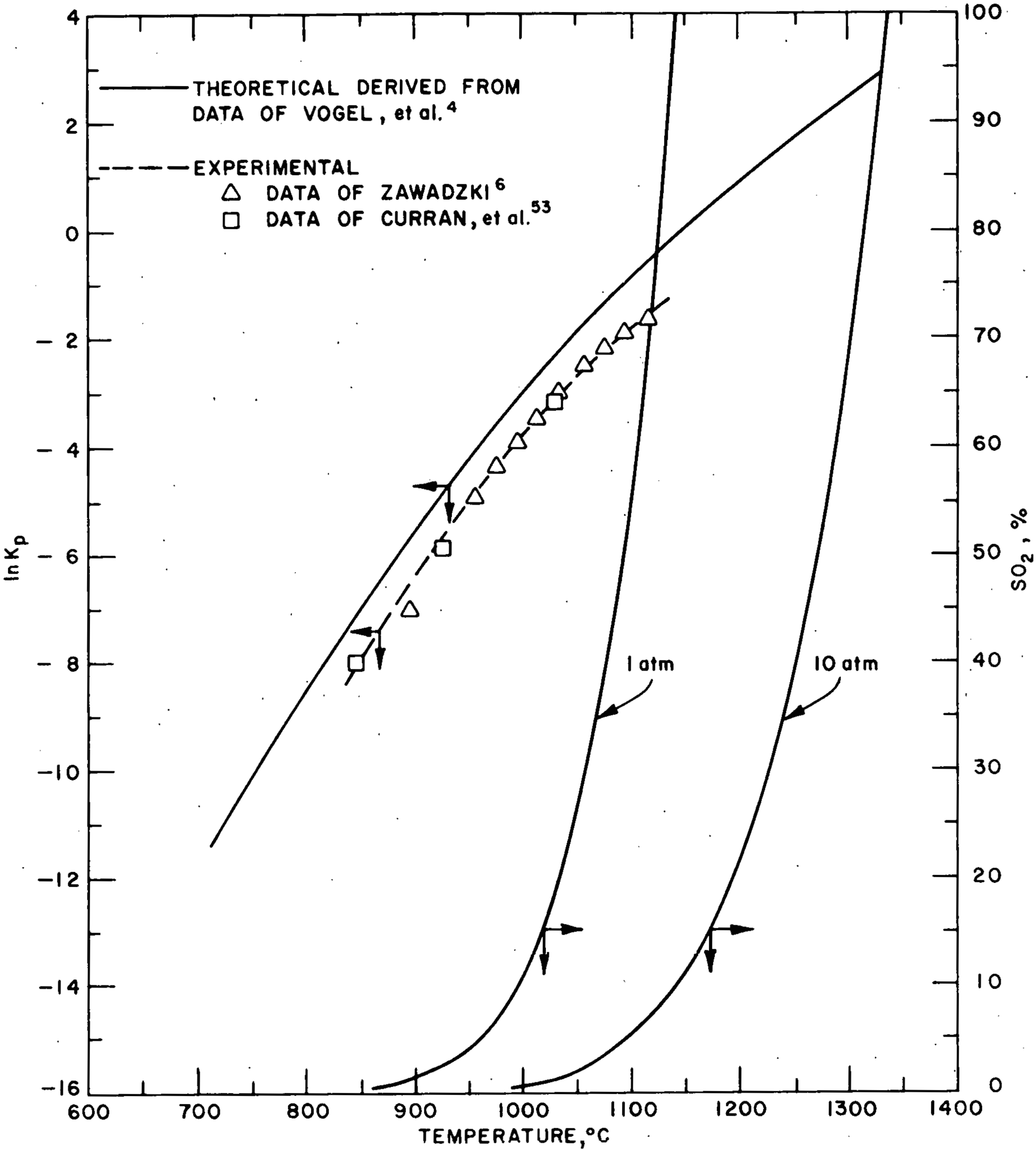

Fig. 8. Theoretical and Experimental Equilibrium Constants for $CaSO_4 + 1/3\ CaS = 4/3\ CaO + 4/3\ SO_2$ and Theoretical Sulfur Dioxide Concentrations at 1 and 10 atm

$$CaSO_4 + CO \rightleftarrows CaO + SO_2 + CO_2 \qquad (1\text{-a})$$

and

$$1/3\ CaS + CO_2 \rightleftarrows 1/3\ CaO + CO + 1/3\ SO_2 \qquad (22)$$

Thus, the sulfur dioxide partial pressure for the solid-solid reaction (Eq. No. 6) must be that calculated from either reaction (1-a) or reaction (22) at the coexistence line for calcium sulfide and calcium sulfate (see Fig. 6 and refer to the discussion of one-step reductive-decomposition thermodynamics). The presence, therefore, of both calcium sulfide and calcium sulfate determines an oxidizing potential for the atmosphere with which it is in equilibrium, and this oxidizing potential determines the carbon monoxide/carbon dioxide ratio of the atmosphere. The resulting conclusion is that although the presence of the reducing agent does not increase the equilibrium concentration of sulfur dioxide over calcium sulfide-calcium sulfate mixtures, the gas phase components may serve as a facile route for the production of sulfur dioxide so that rapid reaction rates for mixtures of the two solids are possible.

Kinetics

Several investigators[24,43,53] have proposed that the actual mechanism of the reaction between calcium sulfate and calcium sulfide involves first the thermal decomposition of calcium sulfate

$$CaSO_4 \rightleftarrows CaO + SO_2 + 1/2\ O_2 \qquad (2)$$

followed by the oxidation of calcium sulfide

$$1/3\ CaS + 1/2\ O_2 \rightleftarrows 1/3\ CaO + 1/3\ SO_2 \qquad (23)$$

Turkdogan and Vinters[24] observed during the reductive decomposition of calcium sulfate that the carbon reacted rapidly to convert some of the sulfate to sulfide and that subsequently the sulfide reacted with excess sulfate to release sulfur dioxide. They also performed experiments in which a mixture of reagent grade calcium sulfate and calcium sulfide were mixed in a 3:1 molar ratio and heated in a stream of helium at temperatures of 1050 and 1100°C and helium pressures of 0.03 and 1 atm. The results of these experiments, expressed as the percent sulfur dioxide evolved as a function of time, are reproduced in Fig. 9. At 1100°C and 1 atm, between 85 and 90% of the sulfur was evolved as SO_2 in 20 min.

If the reaction follows the mechanism suggested by reactions (2) and (23), the kinetics might logically be expected to be limited by the kinetics of the thermal decomposition step. However, the kinetics of the solid-solid

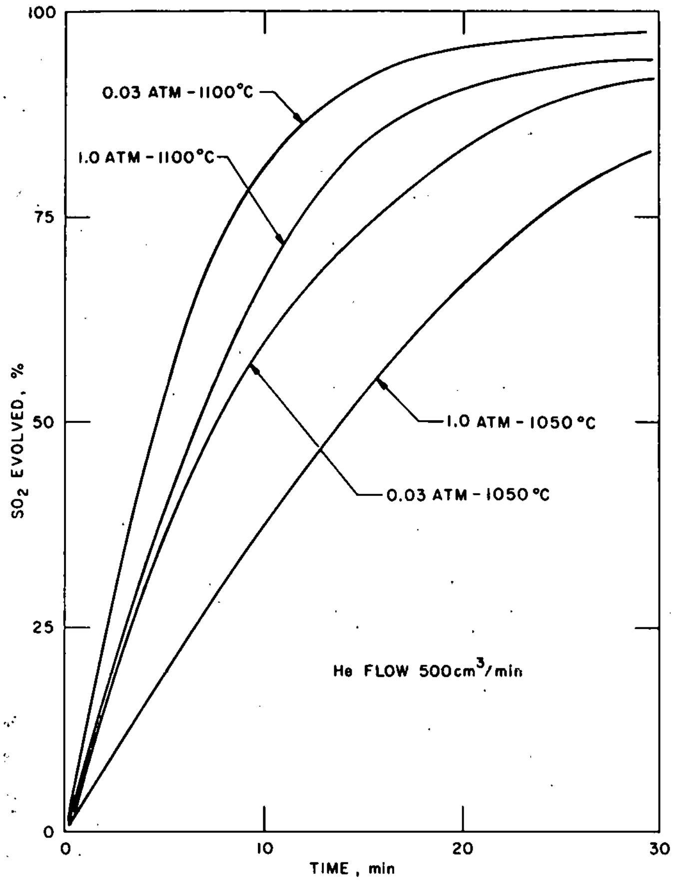

Fig. 9. Evolution of Sulfur Dioxide from 3:1 Stoichiometric Mixture of Calcium Sulfate to Calcium Sulfide. (Based on Fig. 7 from Ref. 24, Reproduced by permission of the Institution of Mining and Metallurgy.)

reaction appears to proceed considerably faster than the thermal decomposition of calcium sulfate would permit. As previously stated, Wheelock[3] attempted to thermally decompose calcium sulfate in nitrogen atmospheres in the temperature range of 1050 to 1315°C. Even at a temperature of 1225°C and a pressure of 1 atm, ∿100 min was required to completely decompose the sample of calcium sulfate. Wheelock[3] did observe, however, that even the slightest impurity of oxygen (0.5%) in the nitrogen atmosphere resulted in a significant reduction in the rate of thermal decomposition. The rapid removal of the oxygen from the thermal decomposition step by oxidation of the calcium sulfide present probably accounts, therefore, for the kinetics of the solid-solid reaction being better than the kinetics for the straight thermal decomposition.

A very early work by Neumann[54] investigated the kinetics of the reaction of calcium sulfate with calcium sulfide. Samples of a mixture containing 82.8% calcium sulfate, 15.6% calcium sulfide, and 1.6% calcium oxide were heated in either air or nitrogen for 0.5 hr at temperatures between 800 and 1100°C. The molar ratio of sulfate to sulfide was ∿2.8, indicating a slight excess of calcium sulfide according to the stoichiometry of the solid-solid reaction. The results of the experiments are noted in Table 11. Heating of the solid mixture in air apparently resulted in oxidation of the calcium sulfide with little or no decomposition of the calcium sulfate. Increasing the temperature increased the sulfur release since the calcium sulfide was increasingly oxidized to calcium oxide, instead of being oxidized to calcium sulfate. When samples were heated in nitrogen, however, the solid-solid reaction went to completion when heated at 1000°C for 0.5 hr (the product contained a small percentage of the excess calcium sulfide present in the original mixture).

In comparison with the results of Turkdogan and Vinters[24] (see Fig. 9), the results of Neumann[54] indicate a somewhat higher rate of decomposition. The rate of decomposition, however, is undoubtedly a function of the reactant particle sizes and the degree of mixing of the sulfide-sulfate mixture, which could easily account for the apparent variation in decomposition rates in the two investigations.

Table 11. Decomposition of a Calcium Sulfate-Calcium Sulfide Mixture Heated for 0.5 hr as a Function of Temperature and Gaseous Environment (Data of Neumann[54])

	Heated in Air Flow				Heated in Nitrogen Flow			
	Sulfur	Product Composition			Sulfur	Product Composition		
Temp (C°)	Expelled (%)	CaS (%)	$CaSO_4$ (%)	CaO (%)	Expelled (%)	CaS (%)	$CaSO_4$ (%)	CaO (%)
800	0.9	14.0	85.1	0.9	2.1	15.3	81.0	3.7
900	2.1	5.8	92.5	1.7	17.0	14.2	75.4	10.3
1000	9.7	0	93.7	2.3	100.0	2.2	0	97.8
1100	18.0	0	94.5	5.5	--	--	--	--

Vogel *et al.* have also reported results of experiments investigating the feasibility of the solid-solid reaction for regenerating sorbent material in the fluidized-bed combustion process.[36,55,56,57] Results are also presented in separate reports by Hubble *et al.* [58,59] In two particularly interesting experiments, dolomite which had been sulfated in the Argonne National Laboratory, 6-in.-dia combustor was reacted with an excess of calcium sulfide in a small fixed-bed, tubular quartz reactor.[55] In one experiment, the sulfated dolomite was in the half-calcined condition ($CaSO_4$, $CaCO_3$, MgO), and in the other experiment, the sulfated dolomite was preheated to the fully calcined state ($CaSO_4$, CaO, MgO). The mixture was heated to 1025°C in a purge stream of nitrogen gas. The off-gas was monitored continuously for sulfur dioxide content.

Very little reaction was observed between the half-calcined sulfated dolomite and calcium sulfide. The explanation offered was that the calcium sulfide was oxidized by the carbon dioxide released from the partially calcined dolomite. The reaction of calcium sulfide with the fully calcined sulfated dolomite produced much more favorable results. Figure 10 illustrates the concentration of sulfur dioxide produced (and hence the rate of sulfur

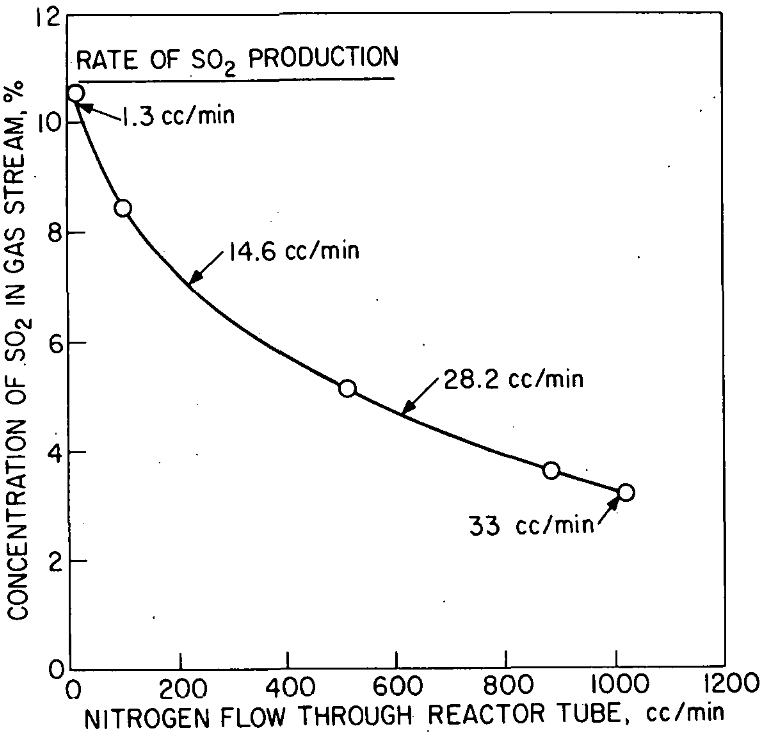

Fig. 10. Concentration of Sulfur Dioxide in Nitrogen Purge Gas as a Function of Nitrogen Purge Flow Rate in the Solid-Solid Reaction of Calcium Sulfate with Calcium Sulfide at 1025°C. (Data of Vogel *et al.*[55])

dioxide production) at 1025°C as a function of the nitrogen purge rate. The concentration of sulfur dioxide in the reactor off-gas varied from a high of 10.5% at 12 cm^3/min nitrogen purge to a low of 3.3% at 1000 cm^3/min nitrogen flow. At zero nitrogen flow, the equilibrium curves of Fig. 8 indicate a maximum sulfur dioxide concentration of ∿18% at 1-atm total pressure. Thus, the reaction appeared to be approaching equilibrium as the nitrogen purge rate approached zero. The reaction rate, however, was highest at the highest nitrogen purge rate due to the reduction of sulfur dioxide concentration in the bulk gas flow. This strongly indicates that the rate of the reaction is mass-transfer limited.

The kinetic results of Vogel *et al.*[55] can be compared with the results of Turkdogan and Vinters.[24] At a nitrogen purge rate of 500 cm^3/min, the concentration of sulfur dioxide in the off-gas reported by Vogel *et al.*[55] was ∿5.2% (see Fig. 10). This corresponds to a fractional rate of conversion of the calcium sulfate of ∿4.0 x 10^{-3}/min. At the same purge rate of 500 cm^3/min of inert gas, the data of Turkdogan and Vinters (by extrapolation to 1025°C of their data taken at 1100 and 1050°C) indicate a fractional rate of calcium sulfate conversion of ∿2.2 x 10^{-2}/min (corresponding to a sulfur dioxide concentration of ∿1% in the purge gas). The slow kinetics reported by Vogel *et al.*[55] were obviously due to the considerably larger initial charge of solid reactants. This further emphasizes the mass transfer limitations on the rate of conversion.

Vogel *et al.* have also reported the results of TGA experiments primarily designed to investigate the effects of varying the composition of the starting material for the solid-solid reaction.[55,56,57] The general procedure for the TGA experiments has been to half-calcine a high-purity dolomite, to sulfate the stone using a simulated off-gas mixture containing 4% SO_2 and 5% O_2, to reduce a fraction of the sulfate to sulfide at 880°C using a reducing gas mixture of 3% H_2 in helium, and then to allow the solid-solid reaction to proceed in an atmosphere of helium at 950°C. It was reported on the basis of these experiments that a starting material containing greater than 25 mol % sulfide (the stoichiometric percentage for the solid-solid reaction) was necessary to permit consumption of most of the sulfide and sulfate before the reaction ceased. When the starting material contained 25 mol %, the calcium sulfide was completely consumed while a substantial amount of calcium sulfate remained unreacted.

An explanation of the requirement for excess calcium sufide in the solid-solid reaction is found in reports by Fleck[60] and by Hull *et al.*[61] They both report that in addition to the desired solid-solid reaction to yield sulfur dioxide, an undesirable side reaction can occur in which sulfur vapor is formed. Hull *et al.*[61] suggest the following overall stoichiometry to account for the formation of elemental sulfur:

$$3CaS + CaSO_4 \rightarrow 4CaO + 2S_2 \qquad (24)$$

Fleck suggests that a more likely mechanism for the formation of elemental sulfur is the reaction:

$$2SO_2 + CaS = CaSO_4 + S_2 \qquad (25)$$

where the sulfur dioxide could be generated by both the thermal decomposition of calcium sulfate (Eq. 2) and the oxidation of calcium sulfide by oxygen from the thermal decomposition (Eq. 23). Another mechanistic possibility for the formation of elemental sulfur is the gas-phase reaction:

$$2SO_2 \rightleftarrows S_2 + 2O_2 \qquad (26)$$

Both Zawadzki,[6] whose work was cited above for the experimental determination of the sulfur dioxide partial pressure over calcium sulfide-calcium sulfate mixtures, and Schenck and Hammerschmidt[62] measured the partial pressure of sulfur over calcium sulfide-calcium sulfate mixtures. Fleck[60] extrapolated the data of Schenck and Hammerschmidt and calculated the equilibrium ratio of elemental sulfur to total sulfur as a function of temperature and total pressure. His results are presented in Fig. 11. The curves of Fig. 11 represent the equilibrium relationship for reaction (25) and do not consider the presence of oxygen or calcium oxide at equilibrium. Although the presence of the additional phase and compounds at equilibrium would certainly alter

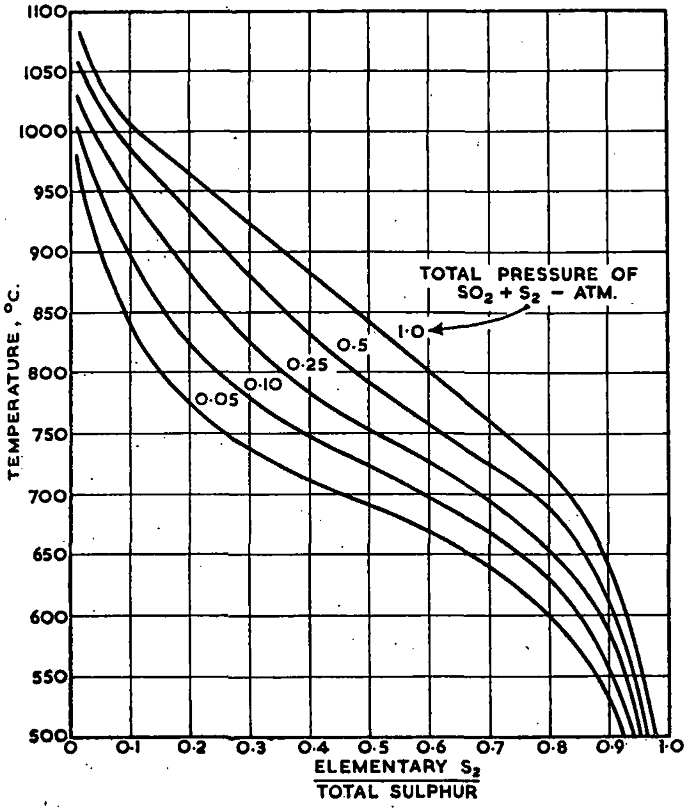

Fig. 11. Effect of Temperature and Pressure on the Ratio of Sulfur Vapor to Total Sulfur in the Gas Phase over Calcium Sulfide-Calcium Sulfate Mixtures (from Fleck[60])

the sulfur to sulfur dioxide ratio and reduce the thermodynamic degrees of freedom, Fig. 11 does serve to indicate that as the system temperature is reduced, the fraction of elemental sulfur to total sulfur in the gas phase can become quite significant.

Zawadzki[6] also reported that at a temperature of 900°C, the partial pressures of elemental sulfur and sulfur dioxide were one-third and two-thirds, respectively, of the total system equilibrium pressure. Thus, at equilibrium, elemental sulfur could account for a significant proportion of the sulfur released from a mixture of calcium sulfate and calcium sulfide. The fact that the formation of elemental sulfur requires an excess of calcium sulfide over the stoichiometric amount required to produce only sulfur dioxide is consistent with the observations of Vogel *et al.* that a starting material containing greater than 25 mol % calcium sulfide is necessary to permit consumption of both the sulfide and the sulfate.[37,55,56,57]

Hull *et al.*[61] also reported that the rates of reactions which produce sulfur dioxide and elemental sulfur have about the same order of magnitude between 900°C and 1000°C. At higher temperatures, the kinetics are favorable to the formation of sulfur dioxide.

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