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## INTRODUCTION

The importance of sulfur as a natural resource has increased considerably since the year 2,000 B.C. when sulfur was used by the Egyptians to bleach linen textiles. Today, sulfur has many important applications in such areas as cellulose products, chemicals, dyes, fertilizers, iron and steel, pharmaceuticals, rubber, and water treatment. In fact, sulfur has so many varied uses that per capita consumption in a country can be taken as a reliable index of its chemical production and overall industrial activity. In the year 1963 for example, the average annual per capita consumption of sulfur was 81 lbs. in the United States, 56 lbs. in other developed countries, 3 lbs. in less industrialized countries, and 21 lbs. over the entire world (58). Preliminary figures for 1970 indicate that the per capita consumption of sulfur in the United States has increased to 105 lbs. with a total consumption of approximately 9.6 million long tons of sulfur (11).

Considering the importance of sulfur in our nation's industrial activity and its contribution to our nation's high standard of living, it is understandable that the supply and demand situation for sulfur is a matter of vital concern. During the past thirty years there has been a series of violent shifts between periods of oversupply and periods of

shortage. Both situations have produced equally undesirable results and dire warnings that the existing situation would prevail forever. During the years 1963-1967, for example, the sulfur industry was plagued by an acute shortage which saw the inventories of Free World producers of sulfur fall from 43.5 weeks of supply or 84 percent of annual sales to barely 12 weeks of supply or 24 percent of annual sales (28). This decline in inventories was accompanied by higher and higher prices and an ever-increasing concern that the trend would continue (12, 27, 36). Today, however, we find ourselves once more in a situation of over-supply, low prices, and the closing down of several once-profitable sulfur producing mines.

The real question mark lies in the long term outlook for sulfur supply and demand. According to Platou (39), the four main factors which will determine the future supply and demand picture are as follows:

- 1) Growth of "involuntary" sulfur production,
- 2) Amount of "voluntary" sulfur produced,
- 3) Growth rate of existing or traditional sulfur markets,
- 4) Probability and size of new end-use markets for sulfur.

Included in the category of involuntary sulfur are sulfur values recovered from sour natural gas and petroleum, sulfur recovered from flue gases resulting from combustion

of sulfur-containing fossil fuels, and sulfur recovered from metallurgical smelting operations. Voluntary production of sulfur includes mining by Frasch process, mining of other elemental sulfur ores, pyrites mining, and obtaining sulfur values from gypsum and anhydrite. Involuntary sulfur production, free from normal profit motives, is causing a major shift in the source of sulfur supply. In 1968, sulfur recovered from sour natural gas and other sources accounted for 45 percent of the total elemental production with Frasch mined sulfur accounting for the remainder. Smelter gas and other nonelemental sources accounted for 37.6 percent of the nonelemental production with pyrites accounting for the remainder. In 1970, these percentages had risen to 52.7 and 41.7 respectively (57). In fact, the present oversupply situation is largely the result of rapidly increased sulfur production from sour natural gas and oil.

The real threat to the voluntary sulfur industry has yet to be tapped, and that threat is the ominous cloud of sulfur dioxide issuing forth from smelters, power plants, and other sources. It is estimated that in 1970, 18.3 million long tons of sulfur in the form of sulfur dioxide were emitted to the atmosphere in the United States alone, and nearly 75 million long tons worldwide (57). It is further estimated, that if unabated these same emissions in 1980 would amount to approximately 30.5 and 85 million long tons respectively.

With the growing concern over air pollution, however, it won't be long until air pollution control regulations force removal of most of the sulfur dioxide before it reaches the atmosphere. Several factors, however, make it difficult to estimate the full effect of pollution control on the sulfur market. Among these are: (1) the uncertainty of the sulfide content in the next decade's gas, oil, coal, and ores, (2) the uncertainty of fossil/nuclear fuel ratios beyond the next few years, (3) the form of the sulfur recovered from this source could range from the readily marketable elemental sulfur through the possibly marketable sulfuric acid to the unmarketable calcium sulfate.

One thing does seem apparent from all this. In the future, voluntary sulfur production will generally be a function of both the total demand and the involuntary production. With traditional markets expected to continue and grow at a rate parallel to the growth in the gross national product, the key to the future of the voluntary sulfur industry may well lie in new and potentially large markets. According to Platou (39) some potential applications currently being explored include:

- 1) Eliminating the need for mortar between bricks, concrete blocks and building materials; by simply spraying or brushing the exposed surfaces of the stacked bricks with molten sulfur. The resulting

surface bond is stronger than the mortar normally used, is waterproof, and generally exceeds the strength of the masonry materials.

- 2) Using a sulfur foam made with small amounts of additives as a subbase for highways and airport runways in cold climates to prevent freeze and thaw damage. Sulfur foams have a higher compressive strength than most organic foams and it is figured that one inch of foam is equivalent in insulating value to a two foot bed of gravel.
- 3) Using sulfur to impregnate ceramic materials such as tiles and cinder blocks to improve strength and to resist water permeation and frost damage. There are indications that sulfur impregnation could improve the strength of lightweight hollow cinder blocks to that of solid concrete blocks.
- 4) Adding sulfur to asphalt to obtain a crosslinking similar to the vulcanization of rubber. The product appears to have improved resiliency, greater resistance to solvents and increased wear. Since nearly 60 million tons of asphalt are used each year, the addition of any significant percentage of sulfur constitutes a substantial potential market.
- 5) Using sulfur in fertilizers in addition to its

traditional use in fertilizer manufacturing. Sulfur is a macronutrient of plants as is nitrogen, phosphorus, potassium, calcium, and magnesium and must be available in large amounts for good crop growth. Sulfur deficiencies in soils have been observed in 26 states of the United States as well as in many other nations the world over. Already an increasing number of manufacturers are deliberately adding sulfur to their products, guaranteeing and advertising the content of this element.

- 6) Using sulfur in soil and water treatment. Application of sulfur or suitable sulfur compounds directly to the soil or through irrigation water can increase water penetration and adjust soil pH. The potential in the Western United States alone is estimated at one million tons annually.
- 7) Returning to sulfur for use as a fungicide in crop protection. Large quantities of sulfur are still being used for this purpose, but it has been replaced to a large extent by newer and generally more effective organic fungicides. Concern over the environmental effects of these materials may, however, offer a potential opening for a return to sulfur in some cases. Sulfur is virtually non-toxic to man and animals even in large doses.

Together, traditional and new uses for sulfur are expected to result in a growth rate in sulfur consumption of 5.5 to 6 percent during the next decade. While it is true that the recovery of sulfur from flue gases will have a considerable impact on the future supply and demand situation it may not be sufficient. It would not be too surprising on the basis of the changes in the past and the expected changes in the consumption pattern of the future to find that all of tomorrow's sulfur, both voluntary and involuntary, will be needed to meet the demand.

While the future of the sulfur supply and demand situation remains largely a matter for speculation, it is interesting to note that a process for the decomposition of calcium sulfate has applications in both the involuntary and voluntary areas of sulfur production. Regarding the voluntary production of sulfur, the naturally occurring minerals of calcium sulfate, gypsum and anhydrite, are by far the largest single source of reserve sulfur in the world (58). In England and in several other European countries, calcium sulfate has been used extensively as a source of sulfur in the absence of salt dome or surface deposits of sulfur.

Recent developments, however, have suggested that a process for the decomposition of calcium sulfate may also have considerable application in the area of pollution control and

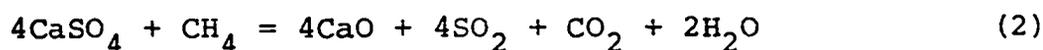
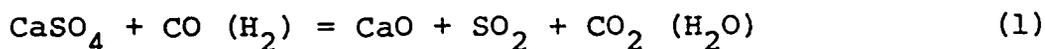
the involuntary production of sulfur.

One particularly promising area of application involves a process currently under investigation for the fluidized bed combustion and desulfurization of coal (14, 24, 44). In the process, limestone is added to the fluidized bed of burning coal to adsorb the sulfur dioxide liberated during the combustion process. Although not considered essential, it does seem desirable that the calcium sulfate formed in the above process undergo a decomposition process to recover the sulfur and regenerate the lime for recycle.

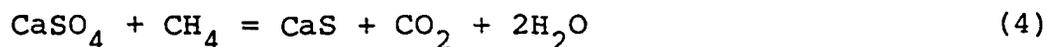
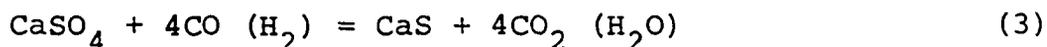
Another promising area of application in the involuntary production of sulfur is in various acid manufacturing and utilizing industries where calcium sulfate is produced as a useless and wasted by-product. In this case, decomposition of the calcium sulfate could be used as a means of regenerating the sulfuric acid for recycle in the plant and the generation of a useful lime by-product.

It would appear, therefore, that a process for the decomposition of gypsum has considerable potential in several different areas of application. An early investigation by Bollen (2) was concerned with the decomposition of gypsum in a fluidized bed reactor employing the hot gases from the combustion of natural gas. The process envisioned was the conversion of calcium sulfate to lime and an off-gas convertible to sulfuric acid. While Bollen's results were not

conclusive, they did show that calcium sulfate decomposed rather rapidly in a reducing atmosphere and that lime could be obtained as a by-product. The following equations were given to explain the decomposition process:



Unfortunately, the results also showed that considerable amounts of calcium sulfide were also formed during the reductive decomposition process. The following equations account for the calcium sulfide formation:



Calcium sulfide formation is undesirable because it reduces the conversion of sulfur and severely contaminates the quality of the by-product lime.

Since Bollen's (2) work, considerable research has been conducted to refine and improve the reductive decomposition process (15, 34, 41, 42, 46, 50, 52). Three United States Patents have also been issued in connection with the process (53, 54, 55).

Preliminary results of a pilot plant investigation conducted at Kent Feeds, Inc., have been encouraging (15).

However, the following problems regarding calcium sulfide formation were encountered which detracted considerably from the process:

1. A significant amount of calcium sulfide is formed in the product except under a very narrow range of operating conditions.
2. The fines elutriated from the reactor are considerably higher in sulfide and unreacted sulfate than the product obtained in the overflow from the reactor.

The fact that calcium sulfide can be readily oxidized, suggested the possibility that the decomposition of calcium sulfate could be accomplished more favorably in a multiple zone reactor, thus alleviating the problems encountered above. It seemed reasonable to assume that if reducing and oxidizing zones could be established in the same fluidized bed, that calcium sulfide formed in the reducing zone would subsequently be eliminated in the oxidizing zone. Such a procedure, it was felt, would considerably broaden the permissible range of operating conditions and reduce the amount of calcium sulfide in the overflow product and elutriated fines.

The following experimental investigations were conducted, therefore, in the development and subsequent testing and evaluation of the multiple zone reactor.

1. The formation of calcium sulfide was investigated in an externally heated fluidized bed reactor having a 1 in. inside diameter. Solid materials containing calcium oxide were reacted with a fluidizing gas mixture of 6.2 percent sulfur dioxide and 6.1 percent carbon monoxide with the remainder nitrogen. Batch experiments were conducted at temperatures between 1900° and 2165°F and sulfur dioxide mass flow rates between  $5.56 \times 10^{-6}$  and  $7.66 \times 10^{-6}$  lb. mole/min. On the basis of the observed reaction to form calcium sulfide, a kinetic model was proposed to account for the reported tendency of smaller particle size calcium sulfate to exhibit a higher calcium sulfide formation than coarser particle size calcium sulfate when reduced under the same experimental conditions. The heterogeneous gas-solid reaction models of Levenspiel (26) were used in the analysis.
2. Relative to the multiple zone reactor, a preliminary investigation was made into the oxidation of calcium sulfide formed during the reduction of calcium sulfate. The investigation was made to determine the general operating conditions favorable to the formation of calcium oxide and sulfur dioxide, the desired end products, as opposed to the formation of calcium sulfate. The study was made in an externally

heated 2 in. fluidized bed reactor which was operated in a continuous manner. The calcium sulfide material was partially reduced calcium sulfate obtained from the Kent Feeds pilot plant reactor (15). The fluidizing gas was an oxidizing mixture of oxygen and nitrogen.

Experiments were conducted at temperatures between 1800° and 2140°F, partial pressures of oxygen in the feed gas between 0.05 to 0.2 atm., oxygen to calcium sulfide feed ratios between 0.75 to 3.0, and solids mean residence times between 7.0 to 47.3 minutes. The results were evaluated on the basis of the degree of calcium sulfide conversion and desulfurization.

Attempts were also made to correlate and model the observed calcium sulfide conversions using the theoretical kinetic models of Levenspiel (26).

3. A qualitative study of gas and solids mixing in fluidized beds was conducted to determine the feasibility of the multiple zone reactor. The experiments were conducted at room temperature in a 4 in. Plexiglas column.

Gas mixing was investigated by fluidizing a bed of coarse, partially reacted calcium sulfate with air at gas velocities of 1 and 2 times the incipient

fluidization velocity. A carbon dioxide tracer gas was continuously injected at a point in the bed above the distributor. Carbon dioxide concentration profiles were then taken across the diagonal of the column at levels 6 and 12 in. above the trace gas inlet.

Solids backmixing was also investigated by the continuous feeding of a tracer of colored solids into a bed fluidized with air at twice its incipient fluidization velocity. The tracer was introduced at a level well above the distributor and below the point at which the solids were continuously removed from the bed. The bed was then observed for uniformity of color above and below the solids addition point. This was done for the case where the bed and tracer materials were the same substance and for the case where the tracer was a very finely divided calcium sulfate and the bed a coarse silica sand.

5. The decomposition of calcium sulfate in a multiple zone reactor was investigated in a fluidized bed reactor having an inside diameter of 4.75 in. A highly reducing mixture of natural gas, air, and oxygen was used as the primary fluidizing gas to provide a reducing zone at the bottom of the fluidized bed. A secondary gas flow of air and

oxygen was introduced at a point above the distributor to provide for an oxidizing zone in the upper portion of the fluidized bed. The combustion of the natural gas supplied the necessary heat to maintain the reactor temperature.

Decomposition experiments were conducted using both gypsum and anhydrite. When operating continuously, the reactor temperature was varied between 1900° to 2250°F, the primary air to gas ratio between 4.2:1 and 5.4:1, the total air to gas ratio between a fairly reducing 8.5:1 to a mildly oxidizing 10.7:1, the solids mean residence time between 10 and 104.2 min., and the mole ratio of natural gas to calcium sulfate between 2.08:1 and 7.85:1. The results were evaluated on the degree of conversion and desulfurization of the solids obtained from the reactor overflow and the fines elutriated in the off-gas from the reactor.

Again the results were correlated using the kinetic models of Levenspiel (26) to determine the over-all rate controlling factor in the multiple zone decomposition process.

6. Preliminary investigations were conducted into the possible decomposition of very finely divided calcium sulfate in a fluidized bed reactor. Since the

material will not fluidize in a conventional reactor because of its caking and channeling tendencies, alternative methods were studied. The possibility of using a vibrated fluidized bed was investigated briefly but was summarily rejected. A more promising approach investigated involved the use of an auxiliary inert coarse material to form the fluidized bed with the calcium sulfate fines being continuously fed into and removed from the bed by pneumatic transport in the feed and off-gas lines respectively. Investigations were made in both the small 2 in. reactor and the multiple zone reactor mentioned above. The primary variables investigated were temperature and gas to solid flow rates with the results being compared on the basis of solids conversion and desulfurization. Attempts were made to decompose phosphogypsum, a finely divided by-product gypsum of the phosphoric acid industry, as well as natural gypsum and anhydrite.

## LITERATURE REVIEW

## Reductive Decomposition of Calcium Sulfate

The decomposition of calcium sulfate has been a subject of scientific investigations for well over 65 years. As early as 1903, Lunge suggested that calcium sulfate could be directly decomposed to sulfur dioxide by heating with clay in a shaft kiln to form a cement clinker as a by-product. Several basic investigations were conducted during the early 1900's to measure the effects of temperature and various additives on the speed of decomposition of calcium sulfate. With pure calcium sulfate, it was generally found that decomposition would begin around 1200°C and that the speed of decomposition would increase with temperature up to around 1400°C where simultaneous melting would occur. It was also found that additives such as iron pyrites, iron oxide, alumina, and silica could be used to both reduce the initial temperature where decomposition would begin as well as increase the rate of decomposition. For a more detailed account of these early investigations, the reader is referred to reviews by other authors (10, 19).

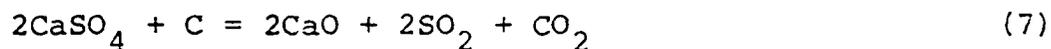
It was in Germany during World War I, however, that the first large scale process for making sulfuric acid and cement from calcium sulfate was developed. Cut off from her iron pyrites supply, then imported primarily from Spain, Germany

was forced to turn to native gypsum and anhydrite deposits as a substitute raw material. Today the process is known as the Mueller-Kuhne process and is the basis for several large plants operating in England and Western Europe and which are being considered for construction in South America (40). Although several other processes for recovering sulfur from calcium sulfate were developed during the war period (17, 18), the Mueller-Kuhne process is the only one to have survived the war's end.

The Mueller-Kuhne process is essentially carried out in the following manner. The raw materials gypsum or anhydrite, coke, fly ash, and sand are blended and fed to the cooler, elevated end of a rotary kiln. As they gravitate to the hot firing zone which is at 2600° to 2700°F, the reaction between the calcium sulfate and coke is thought to take place in two steps as follows:



Reaction 1 begins around 1400°F, whereas higher temperatures of 2000° to 2200°F favor reaction 2. A simplification of the overall process is represented by the reaction

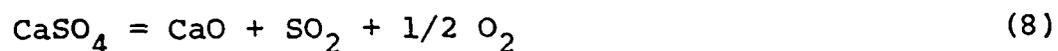


The lime produced during the release of the sulfur dioxide reacts with the fly ash and sand additives to form a cement clinker. The process requires an exact adjustment of the proportions of the reductant coke to the calcium sulfate to avoid the formation of an excess of calcium sulfide or the incomplete reduction of the calcium sulfate. Several excellent and more detailed descriptions and analyses of the Mueller-Kuhne reactions are contained in the literature (9, 10, 19, 33).

During the early 1950's and for most of the 1960's, the United States was faced with temporary sulfur shortages. As a result, considerable attention was given to analyzing available sulfur resources and future requirements. As in Germany, considerable attention was given to exploiting the available pyrites and sulfates more extensively. The Mueller-Kuhne process, although quite successful in Europe, seemed undesirable for use in the United States because of relatively high shipping costs. Such a plant would have to be located near a large supply of gypsum and anhydrite. Consequently, there was a severe limitation on the areas of application for such a process in the United States.

In 1951, Bollen (2) undertook research at Iowa State University to develop a more commercially feasible process for the recovery of sulfur from gypsum in the absence of clinkering agents to produce an off-gas convertible to sulfuric

acid and an agricultural grade lime as the solids by-product. Initially, it was thought that the gypsum could be decomposed thermally under oxidizing conditions in a shaft furnace according to the following reaction:



It was found, however, that the thermal decomposition of calcium sulfate was extremely slow even at temperatures as high as 2450°F. At these temperatures, fusion of particles in the bed prevented the free flow of solids through the furnace.

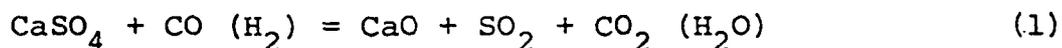
Subsequent attempts by Bollen (2) involved the use of a fluidized bed reactor operated at temperatures below fusion. The bed was fluidized with the combustion products of natural gas and air. By changing the natural gas to air ratio, conditions were varied from oxidizing to neutral to reducing. As with the shaft furnace, oxidizing conditions resulted in very slow desulfurization rates. Under reducing conditions, however, rapid desulfurization occurred at temperatures as low as 2100°F. Unfortunately, a problem of excessive calcium sulfide formation was experienced with highly reducing conditions at low reaction temperatures. Bollen (2) concluded, therefore, that the optimum conditions for moderate desulfurization rates with a minimum of calcium sulfide formation were a neutral atmosphere at a temperature near 2350°F.

Subsequent investigations by Wheelock (50) confirmed the thermodynamic and kinetic feasibility of decomposing gypsum into sulfur dioxide and calcium oxide in a mildly reducing atmosphere. Considerable research has since been conducted at Iowa State University to further develop the process and investigate the factors influencing conversion and desulfurization rates and sulfide formation (34, 41, 42, 46).

In addition to the work at Iowa State University, several other processes for the reductive decomposition of calcium sulfate have been developed in recent years (4, 13, 14, 31, 44, 45). These processes for the most part involve the reduction of the calcium sulfate to calcium sulfide and subsequent treatment of the sulfide to recover the sulfur.

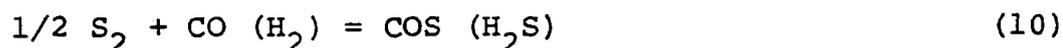
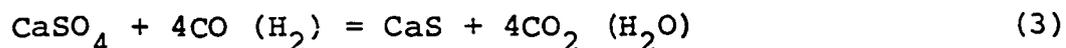
#### Process chemistry

The reductive decomposition of calcium sulfate is complicated by the number of reactions which can occur and the variety of end products which can be obtained. When carbon monoxide or hydrogen is used as the reducing agent, the desired decomposition can be considered to proceed according to the reaction



In the same system, however, several other reactions can occur which lead to the formation of such undesirable products as

calcium sulfide, hydrogen sulfide, carbonyl sulfide and elemental sulfur. These products can be accounted for by the following postulated reactions:



Calcium sulfide formation is the most serious problem in that it represents unrecovered sulfur and at the same time destroys the usefulness and value of the by-product lime. A postulated reaction for the elimination of calcium sulfide from the system is given by the reaction suggested to occur in the Mueller-Kuhne process:



#### Process thermodynamics

Process thermodynamics have been studied by several investigators (24, 44, 50). Wheelock (50), using enthalpy and entropy data, calculated theoretical equilibrium constants and heats of reaction for several of the reaction possibilities. Using updated thermodynamic data, values of these constants for the reactions postulated above were checked, and the adjusted values are presented in Table 1. The desired reactions are seen to be endothermic and exhibit

Table 1. Equilibrium constants and heats of reaction for possible reduction reactions

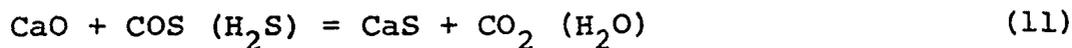
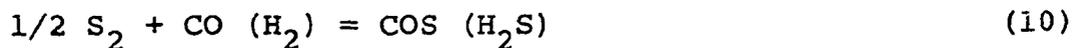
Reaction	$\log_{10} K$			Heat of reaction kcal/g mole		
	1200°K	1400°K	1600°K	1200°K	1400°K	1600°K
(1) $\text{CaSO}_4 + \text{CO} = \text{CaO} + \text{CO}_2 + \text{SO}_2$	0.40	1.66	2.39	42.65	39.85	36.35
(2) $\text{CaSO}_4 + \text{H}_2 = \text{CaO} + \text{H}_2\text{O} + \text{SO}_2$	0.54	1.99	2.87	50.49	47.26	43.35
(3) $\text{CaSO}_4 + 4\text{CO} = \text{CaS} + 4\text{CO}_2$	8.01	6.72	5.61	-50.30	-52.16	-54.56
(4) $\text{CaSO}_4 + 4\text{H}_2 = \text{CaS} + 4\text{H}_2\text{O}$	8.55	7.89	7.50	-18.94	-22.52	-26.58
(5) $\text{SO}_2 + 2\text{CO} = 1/2 \text{S}_2 + 2\text{CO}_2$	3.60	2.39	1.40	-48.23	-47.86	-47.48
(6) $\text{SO}_2 + 2\text{H}_2 = 1/2 \text{S}_2 + 2\text{H}_2\text{O}$	3.86	3.00	2.35	-32.55	-33.04	-33.50
(7) $1/2 \text{S}_2 + \text{CO} = \text{COS}$	-0.13	-0.68	-1.22	-21.38	-21.10	-20.79
(8) $1/2 \text{S}_2 + \text{H}_2 = \text{H}_2\text{S}$	1.36	0.80	0.38	-21.64	-21.66	-21.64
(9) $3\text{CaSO}_4 + \text{CaS} = 4\text{CaO} + 4\text{SO}_2$	-6.40	-0.86	3.94	220.9	211.56	199.96
(10) $\text{CaO} + \text{COS} = \text{CaS} + \text{CO}_2$	4.15	3.41	2.91	-23.34	-23.05	-22.63
(11) $\text{CaO} + \text{H}_2\text{S} = \text{CaS} + \text{H}_2\text{O}$	2.80	2.26	1.92	-15.25	-15.08	-14.79

increasing equilibrium constants with increasing temperatures, while just the opposite holds true for the undesirable reactions. Wheelock (50) also postulated that since the equilibrium partial pressure of reaction 6 equals one atmosphere at 1990°F, any calcium sulfide formed at temperatures greater than 1990°F should be eliminated in the presence of excess calcium sulfate.

A somewhat similar study by Sköpp, et al. (44) attempted to quantify the effects of temperature and various feed gas compositions on the equilibrium compositions for both the solid and gas phases. The equilibrium compositions were calculated subject to material balances by minimizing the total free energy of the system. They concluded that at temperatures below 1880°F only calcium sulfide would be formed, and that no additional advantage in terms of equilibrium conversion would be obtained by increasing the temperature beyond 2060°F. It should be pointed out that similar calculations made by this author tend to confirm the above results in the practical sense, since increases in conversion above 2060°F and the amount of calcium oxide formed below 1880°F tend to be insignificant.

Both investigations tended to discount the presence of significant amounts of elemental sulfur, carbonyl sulfide, and hydrogen sulfide. This appears to be an acceptable assumption since the following reactions can be postulated

to eliminate these compounds from the system:



The theoretical equilibrium constant for reaction 11 is relatively high providing a sink for sulfur, carbonyl sulfide, and hydrogen sulfide. One would expect, therefore, to find only trace amounts of these compounds in the equilibrium gas phase except perhaps under extremely reducing conditions or very low temperatures.

Jonke (24) constructed a phase diagram for a system containing calcium sulfide, calcium oxide, calcium sulfate, and calcium carbonate solid phases and a gas phase containing sulfur dioxide, carbon monoxide and carbon dioxide. The phase diagram he constructed for a total gas phase pressure of 10 atm. is presented in Figure 1. The construction of the diagram is consistent with the basic thermodynamic principle of degrees of freedom and satisfies the theoretical equilibrium constants for the necessary reactions given in the diagram to explain the solid phase relationships.

Although the basic construction of the diagram is correct there is some question concerning the value of the equilibrium constants used in the calculations for the reaction

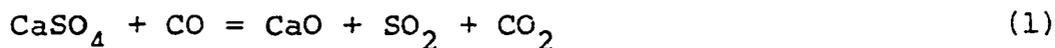
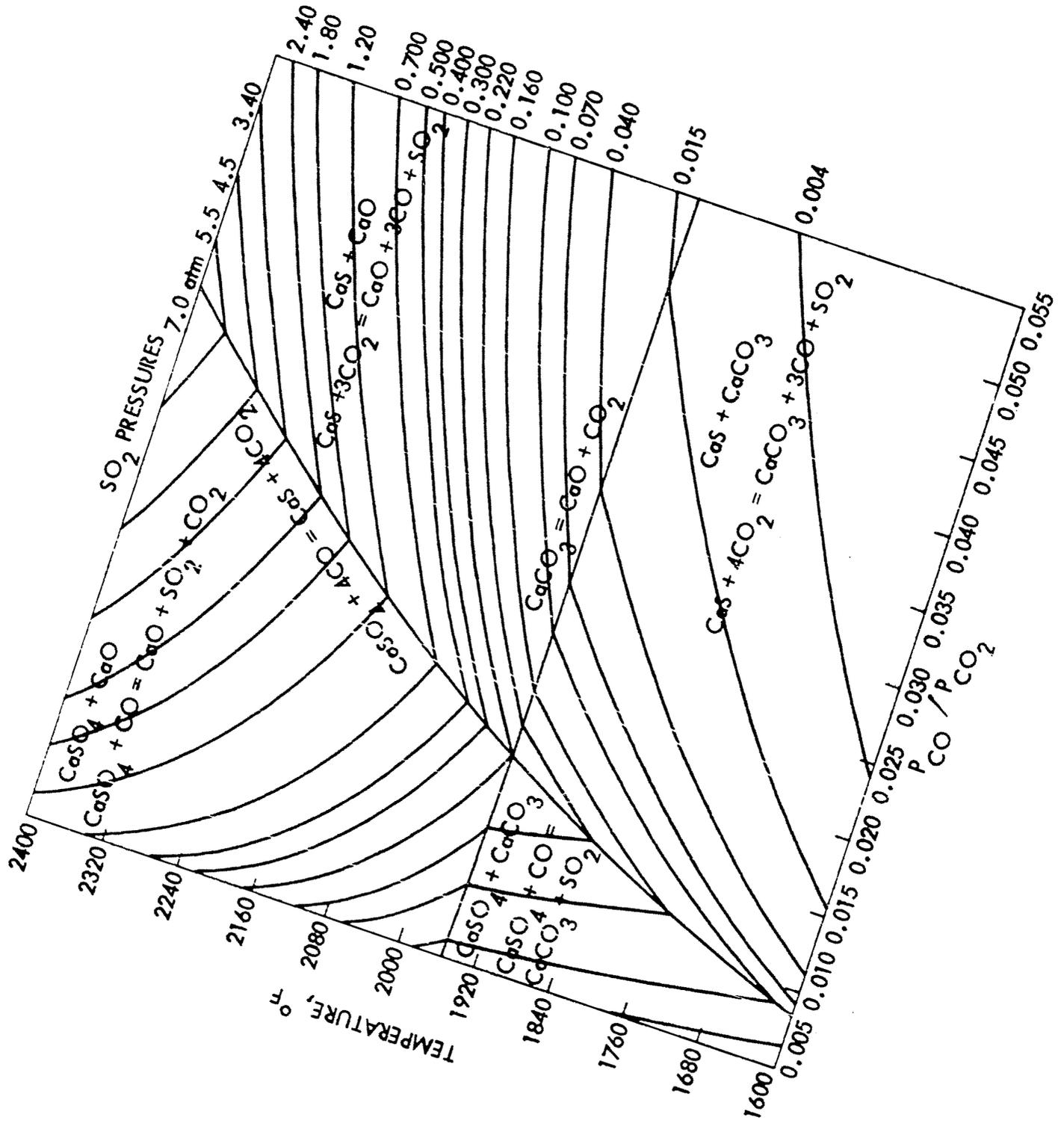


Figure 1. Phase diagram for  $\text{CaSO}_4$  -  $\text{CaS}$  -  $\text{CaO}$  -  $\text{CaCO}_3$  -  $\text{SO}_2$  -  $\text{CO}_2$  -  $\text{CO}$  system  
at 10 atm.



Calculations by this author, for example, determined an equilibrium sulfur dioxide partial pressure of 5.0 atm. at a temperature of 2240°F and a carbon monoxide to carbon dioxide ratio of 0.0149. From the diagram, however, a sulfur dioxide partial pressure of approximately 1.35 atm. is predicted at equilibrium.

Although the accuracy of the diagram is questionable it does indicate the approximate relationship between temperature and ratio of reducing gas to its oxidized species required to prevent the formation of calcium carbonate or calcium sulfide.

#### Process kinetics

Under non-equilibrium conditions, calcium sulfide may be produced regardless of theoretical considerations. Once formed, it represents a loss of sulfur, contamination of the lime by-product, and consumption of an excessive amount of reducing agent. Considerable research has been carried out, therefore, to determine the effects of different operating conditions on conversion rates and sulfide formation. The primary rate consideration is the rate of desulfurization since it is related to the production of the desired products, sulfur dioxide and lime. A very high rate of reaction could represent a very low rate of desulfurization if most of the calcium sulfate were being converted to calcium

sulfide. The percent desulfurization,  $D$ , of a reaction product is calculated according to the following equation:

$$\% \text{ desulfurization} = 100\% \times \left( 1 - \frac{\% \text{ Ca in feed} \times \% \text{ S in product}}{\% \text{ Ca in product} \times \% \text{ S in feed}} \right) \quad (10)$$

A very thorough investigation of operating conditions was carried out by Wheelock (50) and Wheelock and Boylan (51) using a fixed bed reactor. The criteria chosen for evaluating the effects of operating conditions were the rate of desulfurization and the concentration of calcium sulfide in the residual solids. Desulfurization rates were determined by observing the loss in weight of gypsum charged to a reactor as a function of time. Using the total desulfurization calculated from the composition of the final solids and assuming that the instantaneous desulfurization was proportional to the weight lost by the gypsum charge, desulfurization was plotted as a function of time.

Wheelock (50) 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 desulfuriza-

tion occurred during this period. After the initial induction period, the rate rapidly increased to its maximum value during which the greater part of the desulfurization occurred. It was possible to correlate both the initial and maximum desulfurization rates with operating conditions. The results obtained by Wheelock (50) and subsequent investigators (14, 15, 33, 34, 44) are summarized below.

Temperature effects      Wheelock (50) observed that the effect of temperature on the desulfurization rates varied widely according to the feed gas composition. In general, however, the initial desulfurization rate tended to steadily increase with temperature while the maximum desulfurization rate reached a peak value and then dropped off with increasing temperatures. This implies that the mechanism controlling the maximum desulfurization rate shifts as the rate passes through its peak value. It also implies that the mechanism controlling the initial desulfurization rate is independent of the mechanism controlling the maximum desulfurization rate. This same independence is observed for the effects of the other operating variables also.

The percent calcium sulfide in the by-product was found to decrease significantly with increasing temperature. The limiting temperature for the process, however, appears to be around 2300°F. Wheelock (50) observed a drastic

decrease in reaction rates above this temperature and Martin et al. (33) experienced fusion of particles in their fluidized bed reactor. Both investigations suggest an optimum operating temperature of from 2200° to 2250°F to minimize sulfide formation and maintain reasonable rates of desulfurization.

Particle size effects Mehra (34) studied the desulfurization of calcium sulfate by passing reducing gases over solid particles in a horizontal electrically heated furnace. He observed that when reacted under the same conditions for the same length of time, the coarser particles were less reacted and had less of a tendency to form sulfide than finer particles. Similarly, Wheelock (50) observed that at temperatures near 2200°F the maximum desulfurization rate decreased rapidly with increasing particle size. Surprisingly, however, the initial rate of desulfurization seemed to be independent of particle size.

Reducing agent effects Carbon monoxide, hydrogen, methane, coke and coal have all been investigated as possible reducing agents. Skopp et al. (44) reported that carbon monoxide and hydrogen are equally efficient in terms of conversion under the conditions investigated. They also experimented with using methane as a reducing agent, but found it unacceptable because it greatly reduced the desulfurization rate.

Wheelock (50) found that hydrogen had a desulfurization rate two or three times that of carbon monoxide, but that both had an equal tendency to promote calcium sulfide in the residue.

Two investigations have studied the use of the partial combustion of natural gas within the bed of a fluidized bed reactor to supply the necessary heat and reducing components for the reaction. Martin et al. (33), in a very limited investigation, experienced high sulfide formation, but indicated the feasibility of this approach. Hansen et al. (15) employed the same technique in a more extensive study and achieved quite favorable results.

The use of a solid reductant such as coal or coke has also been investigated. Again, air was supplied to affect the partial combustion of the fuel in the reactor bed and promote the reaction. Martin et al. (33), and Brothers (4) explored these reductants and reported comparable results at identical ratios of fixed carbon per mole of calcium sulfate. Average desulfurization of 98 percent was obtained by Martin et al. with cement mixtures at 2200°F and a ratio of 0.6 mole of fixed carbon per mole of calcium sulfate.

It would appear that the choice of reductant is open to that most readily available at a given location. Under the proper conditions, comparable desulfurizations can be obtained for the reductants investigated.

Gas composition effects      It would appear that the reduction reaction occurs between gaseous reducing agents such as carbon monoxide and hydrogen and the solid calcium sulfate. Even in cases where solid reductants or natural gas are fed to the reactor, these are first partially converted to carbon monoxide and hydrogen which then act to reduce the gypsum. Therefore, gas composition effects are of considerable interest.

Wheelock (50) observed that both the initial and maximum desulfurization rates varied linearly with carbon monoxide concentration in the feed gas. With a feed containing more than 4 percent carbon monoxide the presence of sulfur dioxide had little effect on the rate of desulfurization. For low carbon monoxide concentrations, however, sulfur dioxide reduced the initial desulfurization rate.

Skopp et al. (44) observed similar results in the off-gas from their fluidized bed reactor. The concentration of sulfur dioxide increased linearly with the concentration of reducing gas in the feed indicating a first order dependence. The reduction appears to be equilibrium limited.

To suppress calcium sulfide formation, Skopp et al. (44) suggests that reducing conditions be kept mild by the use of a 1:2 ratio of reductant to its oxidized species. They observed a decrease in the sulfur dioxide effluent concentration with higher ratios. With as little as 5 percent carbon

monoxide in the feed gas, however, Wheelock reported a 1:6 ratio of reductant to its oxidized species was necessary to eliminate sulfide formation.

Mass velocity effects      Some interesting effects of gas mass velocity on desulfurization rates were observed by Wheelock (50). While an expected increase in the maximum desulfurization rate was noticed when the gas mass velocity was increased, the initial desulfurization rate decreased significantly. Since initial desulfurization rates were only experienced when sulfur dioxide was present in the feed gas, it would appear that the initial rate is controlled by the effective concentration of sulfur dioxide in the bulk gas flow.

#### Reaction mechanism

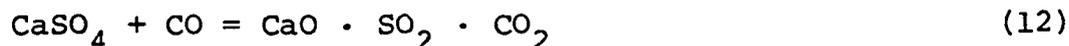
Reactions between gases and solids are very complex in nature and involve several steps which occur successively. Depending on the particular system and set of conditions any one of the steps can control the overall rate of the reaction. A mechanism for the reductive decomposition of calcium sulfate was proposed by Robbins (41). The mechanism is based on gas adsorption studies which he made and Wheelock's desulfurization rate data. The general steps in Robbin's reaction mechanism are as follows:

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

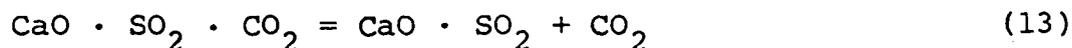
Steps 1 through 4A represent the nucleation of solid product nuclei within the reacting particle. Steps 1 and 2B through 4B represent the growth of solid product nuclei. The implication here is that if the nucleation rate is markedly slower than the growth rate, the decomposition reaction could be characterized by an induction or initial rate period followed by a more rapid or maximum rate period as observed by Wheelock (50). Details of Robbin's proposed mechanism are presented in the following paragraphs.

Calcium oxide formation      Since carbon monoxide does not adsorb appreciably on calcium sulfate, the carbon monoxide proceeds directly to the surface reaction. The product, ac-

According to Robbins (41), is a compound of sulfur dioxide and carbon dioxide adsorbed on calcium sulfide as follows:



Robbins (41) further contended that since the presence of carbon dioxide does not appreciably affect the initial reaction rate as determined by Wheelock (50), it probably desorbs rapidly according to the reaction



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



A similar mechanism has been proposed by Pechkovskii and Ketov (38) who suggest that the formation of calcium oxide occurs in two steps as follows:



The calcium sulfite intermediate in reactions 15 and 16 has also been observed by Marier and Ingraham (32) and Low et al. (30) during an investigation of the reverse reactions.

However, these observations have been made at relatively low temperatures up to 600°C. Jonke (24), in his thermodynamic investigation, proved that calcium sulfite can not exist at elevated temperatures.

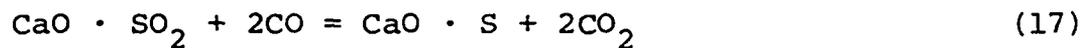
Robbins (41) correlated the initial desulfurization rates determined by Wheelock (50) against the degree of supersaturation of the sulfur dioxide adsorbed on calcium oxide. Supersaturation was determined to be the difference between the equilibrium pressure of sulfur dioxide above calcium oxide and the partial pressure of sulfur dioxide in the bulk gas stream. The data correlated very well, indicating that the nucleation rate is considerably more dependent on supersaturation for 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.

Robbins (41) 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 direct desorption. Evidence that the rate is still desorption controlled is provided by Skopp et al. (44). They observed that if the 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 greater than 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.

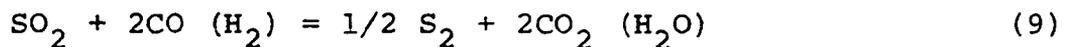
Calcium sulfide formation Robbins (41) proposed that calcium sulfide formation occurs in two steps. First, sulfur dioxide adsorbed on calcium oxide is reduced to elemental sulfur according to the reaction



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



Pechkovskii and Ketov (38) have also proposed a two step mechanism for calcium sulfide according to reactions 9 and 19 as follows:





Robbin's mechanism seems more plausible, however, in that reaction 18 would not require the complicated and improbable molecular interaction expressed in reaction 19.

#### Oxidation of Calcium Sulfide

Since the desulfurization of calcium sulfate is generally complicated by the formation of some calcium sulfide, the possibility of employing an oxidizing roast to remove this contaminate has been given consideration as a solution to the problem.

#### Process chemistry

Early investigations by Neumann (35) and Hofman and Mostowitsch (16) were concerned with the oxidation of calcium sulfide at elevated temperatures. Neumann oxidized pure calcium sulfide with air at temperatures ranging from 600° to 1000°C. and obtained a mixture of calcium oxide and calcium sulfate with calcium sulfate predominating. However, the amount of sulfate tended to decrease with temperature. Hofman and Mostowitsch (16) operated over temperatures ranging from 800° to 950°C and obtained approximately 25 percent calcium oxide and 75 percent calcium sulfate. As a result of their work, Hofman and Mostowitsch concluded that the following reactions were occurring simultaneously with the first

predominating:



Bollen (2), in his early attempts to reduce calcium sulfate in a fluidized bed reactor with a reducing flue gas, subsequently subjected a portion of the solids containing a large percentage of calcium sulfide to an oxidizing roast. Operating at temperatures between 1000 and 1200°C, he was able to increase the desulfurization of the solids from 40 or 50 percent to approximately 90 percent.

#### Reaction thermodynamics

Equilibrium constants and heats of reaction were calculated from thermodynamic data for the two suggested oxidation reactions of calcium sulfide with oxygen and are presented in Table 2. Also included are postulated oxidation reactions employing carbon dioxide as an oxidizing agent. The values given agree with values reported by Loebach (29).

Reactions involving oxygen are highly exothermic and exhibit large positive equilibrium constants. While increasing temperatures reduce the equilibrium constants for both reactions, the difference in the equilibrium values decreases indicating an increased preference for calcium oxide formation over that of calcium sulfate.

Table 2. Equilibrium constants and heats of reaction for possible oxidation reactions

Reaction	$\log_{10} K$			Heat of reaction kcal/g mole		
	1200°K	1400°K	1600°K	1200°K	1400°K	1600°K
$\text{CaS} + \frac{3}{2} \text{O}_2 = \text{CaO} + \text{SO}_2$	15.69	12.97	10.88	-109.1	-109.4	-109.8
$\text{CaS} + 2\text{O}_2 = \text{CaSO}_4$	23.04	17.30	13.22	-219.1	-216.4	-213.1
$\text{CaS} + 3\text{CO}_2 = \text{CaO} + \text{SO}_2 + 3\text{CO}$	-7.62	-4.90	-3.23	92.95	92.01	90.91
$\text{CaS} + 4\text{CO}_2 = \text{CaSO}_4 + 4\text{CO}$	-9.53	-6.72	-5.61	50.30	52.16	54.56
$\text{CaO} + \text{SO}_2 + \frac{1}{2} \text{O}_2 = \text{CaSO}_4$	7.36	4.35	2.32	-110.0	-107.0	-103.3

Reactions involving carbon dioxide, on the other hand, are endothermic and exhibit rather large negative equilibrium constants. This suggests that very little calcium sulfide could be oxidized with carbon dioxide under equilibrium conditions.

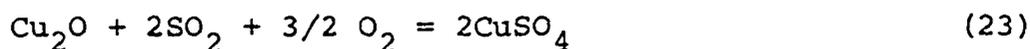
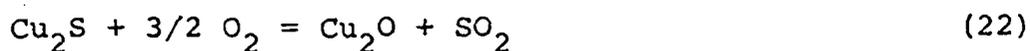
### Reaction kinetics

Loebach (29) carried out some oxidation experiments in a small fluidized bed reactor using a solid material containing high percentages of calcium sulfide and calcium oxide and a small percentage of calcium sulfate. Oxidation was carried out at temperatures ranging from 1700° to 2000°F using mixtures of oxygen with either nitrogen or carbon dioxide. He found that the oxidation reaction was extremely rapid, with lime and sulfur dioxide the favored products. Production of 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 increasing levels of oxidizing agent in the feed gas. Analysis of the gas stream leaving the reactor tended to confirm that the reaction rate was equilibrium controlled.

### Reaction mechanism

While very little is known concerning the actual mechanism by which calcium sulfide is oxidized to calcium oxide and calcium sulfate, an interesting study by Wadsworth et al.

(48) on the sulfating of cuprous sulfide may provide some insight. After subjecting a pellet of cuprous sulfide to an oxidizing roast, an examination of a cross section of the pellet revealed an inner core of sulfide surrounded by a narrow layer of oxide and a subsequent layer of sulfate. It was further found that as the cuprous sulfide reaction front receded towards the center of the pellet, the relative thickness of the oxide layer remained constant. On the basis of their results, they concluded that conversion to oxide was the primary reaction with sulfate being formed secondarily but also simultaneously as follows:



This would tend to suggest that perhaps the formation of calcium oxide and sulfate are formed as follows:



It is interesting to note that this mechanism for oxidation is very similar to the mechanism proposed by Robbins (41) for the reduction of calcium sulfate in that conversion to calcium oxide is the primary reaction in both cases. Formation of calcium sulfate or calcium sulfide

respectively occurs secondarily and simultaneously with the desired reaction.

## ANALYTICAL METHODS

## Solids Analysis

Solids were analyzed for total calcium, sulfate, and sulfide. By making the reasonable assumptions that the sulfate and sulfide were present in the solids as calcium sulfate and calcium sulfide and that any residual calcium was present as calcium oxide, the percentages of these three compounds could be calculated.

Sulfide determinations

Sulfur present as calcium sulfide was determined idiometrically as suggested by Wheelock (50). The sample was placed in a flask to which an excess of a standard solution of the two salts potassium iodate and potassium iodide were added. An excess of hydrochloric acid was then added and the flask tightly stoppered. The acid liberated hydrogen sulfide from the sample and free iodine from the iodide-iodate mixture. The hydrogen sulfide and iodine in turn reacted with each other to form hydrogen iodide and free sulfur. A standard sodium thiosulfate solution was used to titrate the excess iodine to complete the analysis.

Sulfate determinations

Sulfate in the product was determined in one of two ways. Originally, the analyses were carried out gravimetrically by precipitation as barium sulfate in accordance

with the method outlined by the American Society for Testing Materials (1). More recently, the analyses have been made using an ion-exchange technique developed by Robbins (42). With this method, all the cations in the solid are replaced by hydrogen ions with a cation exchange resin. Any sulfide present is liberated from the resulting solution by heating. The sulfate present in the samples was then determined titrimetrically as sulfuric acid using a standard sodium hydroxide solution. Results obtained using both methods are quite consistent.

#### Calcium determinations

Calcium determinations were made for the most part using a method developed by Diehl (7). The calcium is titrated directly against a standard solution of EDTA, disodium dihydrogen ethylenediaminetetraacetate, using calcein as an indicator. Calcein, a derivative of fluorescein bearing two methyleneiminodiacetic acid groups, forms a non-dissociated ion with calcium, the calcium derivative being yellow-green in color and fluorescent. At the end-point in the titration, the calcium is extracted from the calcein-calcium compound by the EDTA and the color changes from yellow-green to brown and the fluorescence disappears. The titration is conducted in a highly alkaline solution to prevent the interference of magnesium.

The end-point in the above procedure is most accurately

determined by the disappearance of the fluorescence. However, a modified calcein composed of calcium, thymolphthalein and potassium chloride mixed together gives a complete color change from green to purple which can be visually determined. Both titration methods have been used successfully.

Some calcium determinations were also made on a Perkin Elmer model 290 atomic absorption spectrophotometer. The samples were dissolved in a standard solution of lanthanum oxide and hydrochloric acid and then diluted to a given volume. The photometer was calibrated using standard solutions of calcium carbonate. Problems with the spectrophotometer have prevented extensive use of this method although it is by far the easiest and most rapid method.

#### Gas Analysis

A special gas chromatograph was used to analyze the resulting off-gas mixtures from the decomposition process. The technique was developed by Robbins et al. (43). The chromatograph consisted of three separating columns and a thermal conductivity cell as a detector. The multiple column arrangement allowed the separation and determination of the following gases: oxygen, nitrogen, hydrogen, carbon monoxide, methane, hydrogen sulfide, carbon dioxide, and sulfur dioxide.

The arrangement of the chromatograph is shown in Figure 1. Column 1 consisted of a 15 ft. long section of 1/4 in. out-

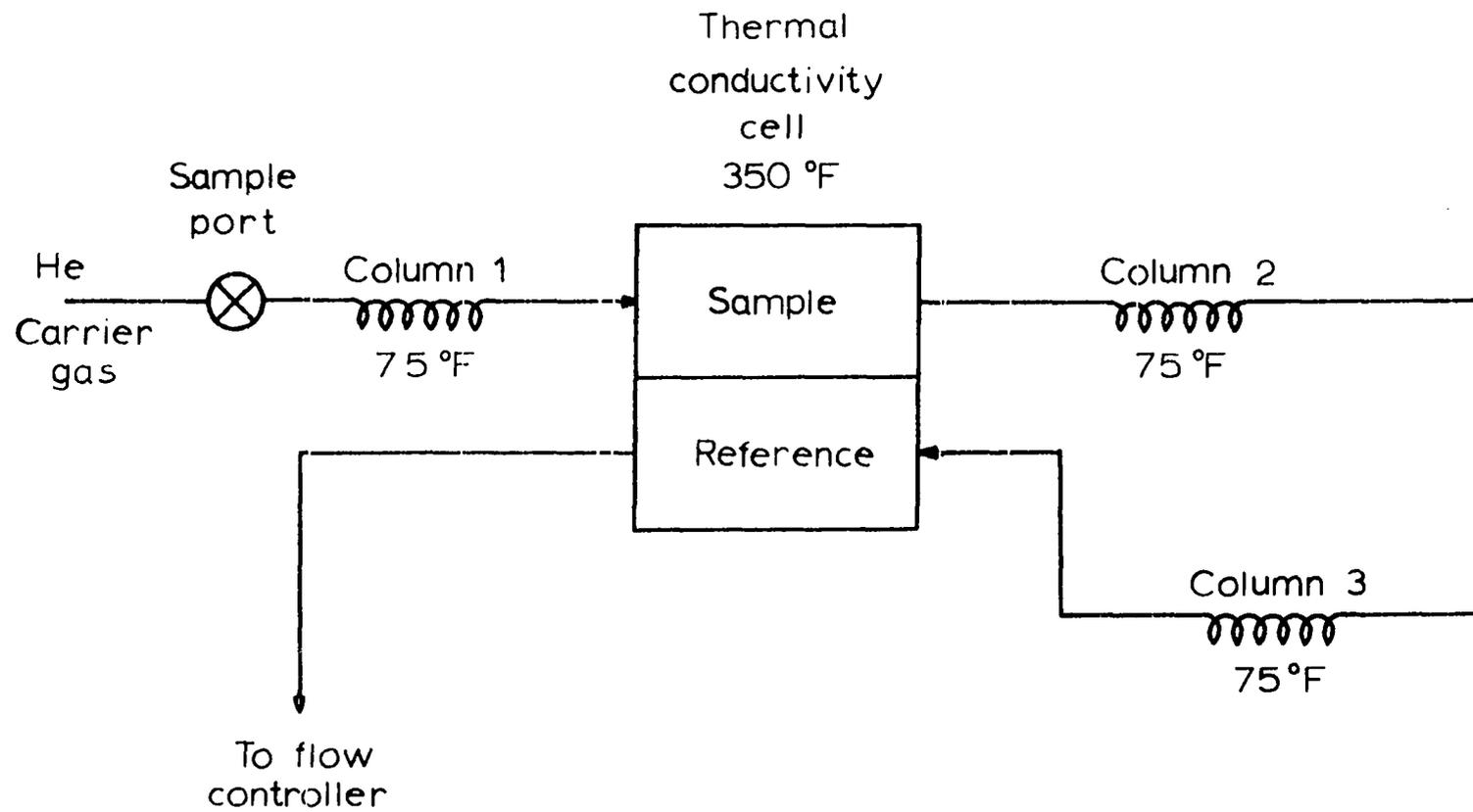


Figure 2. Chromatograph arrangement for gas analysis

side diameter copper tubing filled with 10 percent by weight dibutyl sebacate on a Fluoropak 80 support. Depending of course on what gases were present, the column gave a single peak for a mixture of hydrogen, methane, nitrogen, and carbon monoxide followed by separate peaks for carbon dioxide, hydrogen sulfide, and sulfur dioxide in that order.

Column 2 was a 10 ft. long section of 1/4 in. outside diameter copper tubing filled with a 25 per cent by weight solution of potassium hydroxide on Chromosorb W. The hydrogen sulfide, sulfur dioxide and carbon dioxide were permanently absorbed on the potassium hydroxide while the length of the column provided the proper delay to prevent peak overlaps on the recorder chart output.

Column 3 consisted of a 4 ft. section of 1/4 in. outside diameter copper tubing filled with Linde type 13x molecular sieves. This column selectively absorbed and separated hydrogen, nitrogen, methane, and carbon monoxide in that order.

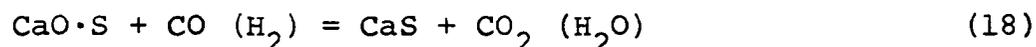
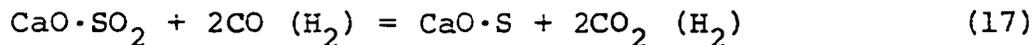
## LABORATORY INVESTIGATIONS

Calcium Sulfide  
Formation

As indicated earlier, a process for the decomposition of calcium sulfate into lime and sulfur dioxide appears to have two promising areas of application. In the area of fluidized bed coal combustion and desulfurization, the process could serve as a means of regenerating the lime for recycle while the sulfur would be recovered as a by-product. In certain acid manufacturing and utilizing industries, the process could serve as a means of regenerating the sulfur for recycle as acid while the lime could be recovered as a by-product. In both instances, the formation of calcium sulfide in appreciable amounts is obviously undesirable.

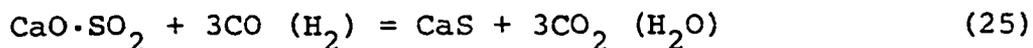
It was decided, therefore, to briefly investigate calcium sulfide formation in a small scale fluidized bed reactor to see what information might be gained concerning the mechanism by which calcium sulfide is formed.

According to Robbins' (41) proposed reaction mechanism, calcium sulfide formation is regarded as a secondary reaction in the reductive decomposition process and is considered to occur in the following manner:



Combining the two equations above suggests that calcium

sulfide formation can be represented as occurring by the overall reaction



The interesting feature of Robbins' (41) mechanism is the role calcium oxide plays as an intermediate in the formation of calcium sulfide. To investigate this mechanism of calcium sulfide formation, solid samples containing calcium oxide were fluidized under varying conditions with a gas mixture containing sulfur dioxide and carbon monoxide.

#### Raw materials

Two different solid samples of calcium oxide containing different amounts of calcium sulfide were used in the investigation. The first material was obtained by calcining very pure limestone in the reactor prior to making a run. This provided a feed material of relatively pure calcium oxide. The second material was an overflow product of the Kent Feeds pilot plant reactor (15) and was designated KF-6. This particular material was selected because of its high calcium sulfide content to see if the presence of calcium sulfide had any influence on the formation of additional sulfide. Screen and chemical analyses of these two materials are presented in Table 3.

The gases used in this investigation were drawn from compressed gas cylinders and had a minimum purity of 99.5

Table 3. Screen and chemical analyses of solids used in the investigation of calcium sulfide formation

Constituent	Chemical Analysis, wt %		Screen Analysis, wt %		
	KF-6	Limestone	Tyler Screen size	KF-6	Limestone
			+20	0.5	0.5
CaO	60.5	54.9	-20+28	2.9	3.2
			-28+35	19.7	14.1
CO <sub>2</sub>	-	43.1	-35+48	32.1	38.0
			-48+65	20.6	21.8
CaSO <sub>4</sub>	0.7	-	-65+100	18.9	14.5
			-100+150	3.4	3.2
CaS	38.6	-	-150+200	1.5	2.6
			-200	0.9	2.2
Total	<u>99.8</u>	<u>98.0</u>	Total	<u>100.5</u>	<u>100.1</u>

percent.

#### Equipment

A flow sheet of the equipment used in this investigation is given in Figure 3. A gas mixture of carbon monoxide, sulfur dioxide and nitrogen was prepared by drawing the individual components from high pressure cylinders and combining them in a large gas mixing tank after they had been dried. The mixing tank was initially purged and evacuated several times with nitrogen to remove any oxygen from the system. Immediately prior to preparing the gas mixture,

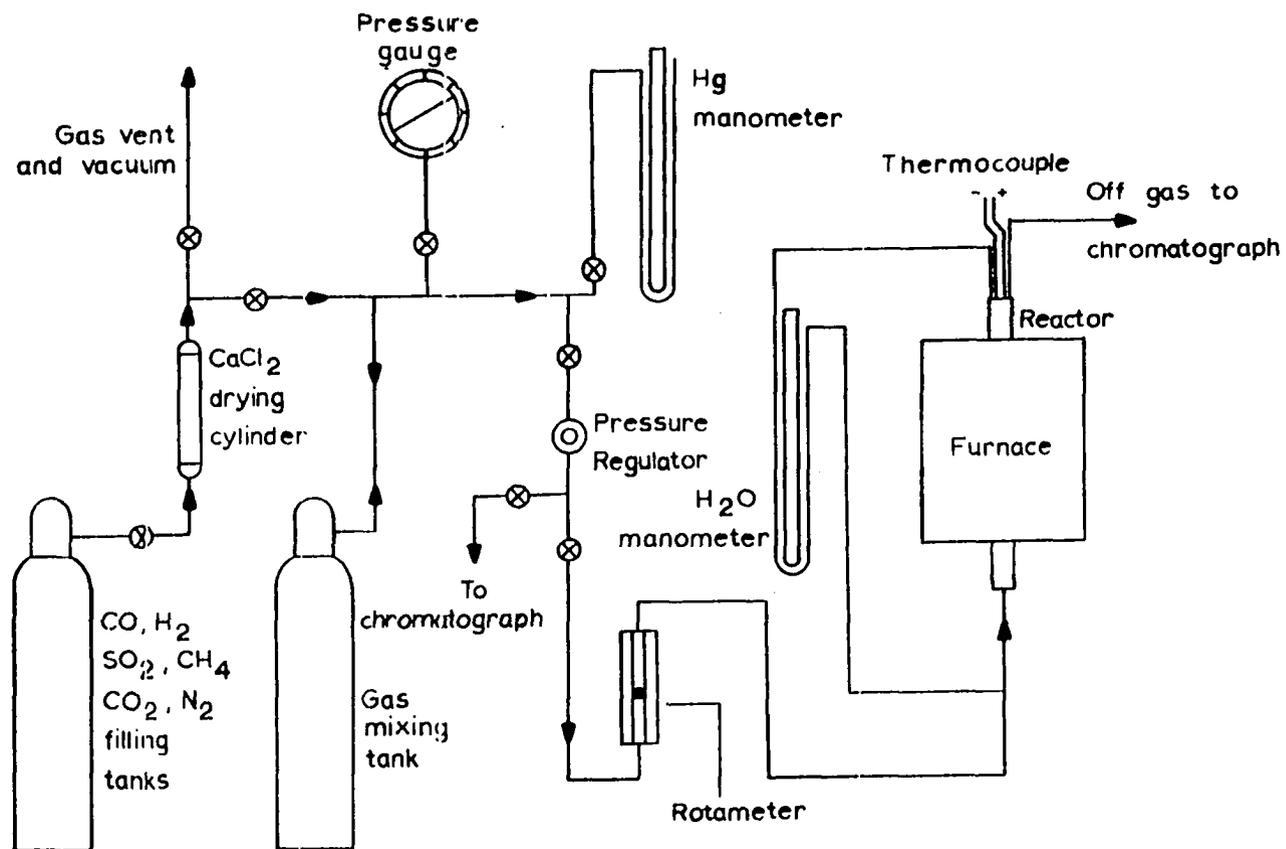


Figure 3. Laboratory apparatus used in the investigation of calcium sulfide formation

the mixing tank was evacuated to an absolute pressure of approximately 2 cm. of mercury. A mercury manometer and a very accurate Heise pressure gauge were used to monitor the partial pressure of each gas as it was fed to the gas mixing tank in order to approximate the desired feed gas composition. Once prepared, the composition of the feed gas was determined by gas chromatography.

When making a run, the gas was delivered to the reactor through a pressure regulator and rotameter to give a controlled flow rate of gas. After leaving the reactor, the gas was filtered, cooled, and dried before being analyzed with the gas chromatograph or vented to the atmosphere.

Reactor      The fluidized bed reactor was made from a Leco ceramic combustion tube having an overall length of 30 in. and inside and outside diameters of 1 and 1.25 in. respectively. A bed support which also served as a gas distributor was fashioned from porous firebrick and inserted into the lower end of the reactor tube. A silicone rubber stopper was cemented to the bottom of the distributor and was used to seal the lower end of the reactor and hold the distributor in place. A ceramic tube having an outside diameter of 3/16 in. and an inside diameter of 1/4 in. was passed up through the center of the rubber stopper and bed support to within 1.5 in. of the top of the bed support. The

gas mixture was introduced to the reactor through this tube.

The top of the reactor was also sealed with a silicone rubber stopper through which an off-gas line and a thermocouple well were passed. These lines were made of quartz glass tubing having inside and outside diameters of 5 and 7 mm. respectively.

Pressure taps to measure the pressure drop across the reactor were located in the inlet and off-gas lines.

Connections to the top of the reactor were made with high temperature silicone rubber tubing. To prevent overheating of the rubber seals and connecting lines it was necessary to place a small water jacket around the upper end of the reactor and pass cooling water through it during a run. A fan also circulated air over the top of the reactor and the connections to the reactor to help dissipate heat.

Furnace The furnace was constructed around a Kanthal tubular heating element type REH 7-60. The heating element had an inside diameter of 2.76 in. and a heated length of 19.7 in. The maximum power rating for the element was 2100 watts. Due to the relatively short length of the heating element, the reactor was situated in the furnace so as to center the bed of material in the heated zone. This was done in an effort to minimize temperature gradients in the fluidized bed.

### Experimental procedure

The sample of calcium oxide material was placed in the reactor and heated to reaction temperature while fluidizing with pure nitrogen. When the desired operating temperature was reached, the fluidizing gas was switched to the premixed mixture of sulfur dioxide, carbon monoxide and nitrogen. The off-gas from the reactor was analyzed periodically using the gas chromatograph. After operating for a suitable length of time during which no changes in the off-gas composition occurred, the gas flow was discontinued and the reactor allowed to cool. The solids were subsequently recovered for chemical analysis for calcium, sulfide, and sulfate.

### Results

Results of a typical run are illustrated in Figure 4 in which the observed off-gas concentrations and fluidized bed temperature are plotted as a function of time.

After making only a very few runs it became apparent that the rate of reaction was being controlled by the mass flow rate of the gas and equilibrium considerations. The conditions and results of the runs which were made are given in Table 4.

Material balances made over the gas phase indicated that the only reaction occurring was the expected reaction

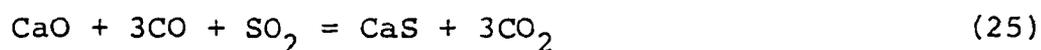


Figure 4. Gas concentration and temperature profiles for typical calcium sulfide formation experiment

Run No. SF-5

Solid charged to reactor: 30 g. of KF-6

Feed gas composition: 6.2% SO<sub>2</sub>

6.1% CO

87.7% N<sub>2</sub>

100.0%

SO<sub>2</sub> flow rate: 7.7 lb. moles/min

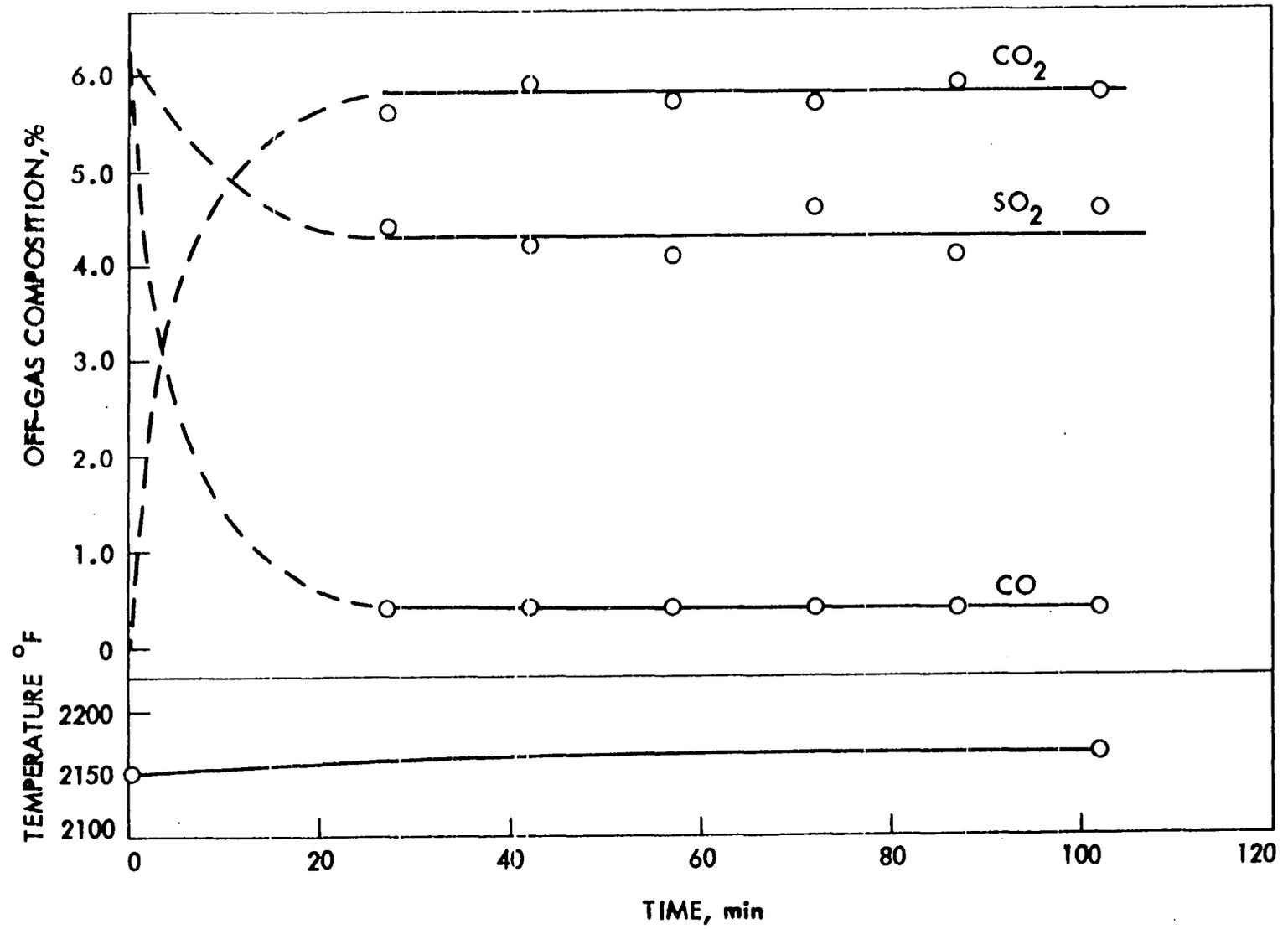


Table 4. Conditions and results of calcium sulfide formation experiments<sup>a</sup>

Run No.	Solid charged to reactor	SO <sub>2</sub> mass flow rate $\frac{\text{lb. mole}}{\text{min.}} \times 10^6$	Temperature °F	Off-gas composition	$\frac{(\bar{P}_{\text{CO}_2})^3}{(\bar{P}_{\text{CO}})^3 (\bar{P}_{\text{SO}_2})}$	Theoretical equilibrium constant for the reaction $\text{CaO} + 3\text{CO} + \text{SO}_2 = \text{CaS} + 3\text{CO}_2$ (24)
SF-2	30g CaO	6.82	1900-1960	4.2% SO <sub>2</sub> 6.2% CO <sub>2</sub> 0.1% CO	$5.68 \times 10^6$	$1.4 \times 10^6 - 5.9 \times 10^5$
SF-3	30g KF-6	5.56	1937-1947	4.3% SO <sub>2</sub> 6.0% CO <sub>2</sub> 0.2% CO	$6.3 \times 10^5$	$7.1 \times 10^5 - 8.1 \times 10^5$
SF-4	30g KF-6	7.66	1950-1975	4.4% SO <sub>2</sub> 5.9% CO <sub>2</sub> 0.3% CO	$1.73 \times 10^5$	$4.8 \times 10^5 - 6.9 \times 10^5$
SF-5	30g KF-6	7.66	2150-2165	4.3% SO <sub>2</sub> 5.8% CO <sub>2</sub> 0.4% CO	$7.1 \times 10^4$	$4.4 \times 10^4 - 3.5 \times 10^4$

<sup>a</sup>All runs were made using a feed gas containing 6.2% SO<sub>2</sub>, 6.1% CO, and 87.7% N<sub>2</sub>.

of reaction 25 may be expressed mathematically as

$$K_{25} = \frac{(\bar{P}_{\text{CO}_2})^3}{(\bar{P}_{\text{CO}})^3 (\bar{P}_{\text{SO}_2})} \quad (26)$$

The last two columns of Table 4 compare the value of the equilibrium constant for reaction 25 calculated from the experimental data with that calculated from thermodynamic data. Considering the probable error involved in both calculations, the agreement between the two values is extremely good.

It would appear, therefore, that the reaction is quite rapid and proceeds to equilibrium. It would also tend to confirm Robbins' (41) theory that calcium sulfide formation in the reductive decomposition of calcium sulfate is a secondary reaction to the formation of calcium oxide.

#### Kinetics of calcium sulfide formation

Mehra (34) has made the interesting observation that calcium sulfide formation tends to increase with decreasing particle size when various sizes of calcium sulfate are reduced under similar conditions. Results obtained by Hansen et al. (15) in the operation of their pilot plant also indicate that fines have an increased tendency toward calcium sulfide formation. This is based on the observation that the fine material elutriated from the bed is consistently less reacted yet higher in sulfide than the coarser material

in the reactor overflow.

Since the above results tend to indicate that calcium sulfide formation is quite rapid and continues until equilibrium in the gas phase is reached, it seems reasonable to suggest that temperature and/or gas concentration gradients throughout a reacting particle could result in a non-uniform distribution of calcium sulfide throughout the particle. It also seems reasonable to expect that gas concentration gradients and temperature gradients are more likely to be a significant factor as the size of a particle increases. With this in mind, the following model is suggested as a possible explanation for the relationship between particle size and sulfide formation.

The primary assumptions for the model are as follows:

- 1) Reduction of the calcium sulfate proceeds according to either the unreacted core model or the continuous reaction model as developed by Levenspiel (26).
- 2) Heat transfer is more efficient than mass transfer in the particle.

The second assumption was made on the basis of the overall reaction rates observed by Wheelock (50). These seemed sufficiently slow to eliminate heat transfer as an important consideration.

The models of Levenspiel were chosen because they are very representative of actual phenomena and can be treated

without undue mathematical complexities. The continuous reaction model envisions the reactant gas as entering and reacting throughout the solid particle at all times. The unreacted core model envisions that the reaction first takes place at the outer surface of the particle. The zone of reaction then moves into the solid, leaving behind completely converted material and inert solids referred to as ash. Thus, at any time during reaction, there exists an unreacted core of material which shrinks in size during reaction.

In the case of the shrinking core model, the rate of conversion is usually controlled by either the rate of diffusion of the gaseous reactants and/or products through the ash layer or by the rate of reaction at the surface of the unreacted core.

Kunii and Levenspiel (25) suggest the following general rules regarding the relationship between the particle size and the appropriate reaction model. Small particles follow the continuous-reaction model, whereas large particles follow the shrinking-core model with ash diffusion controlling at high temperatures but reaction controlling at the surface of the unreacted core at low temperatures. The terms large, small, high temperatures, and low temperatures are relative terms, however, which probably vary considerably depending on the particular system being investigated.

On the basis of the above, it is reasonable to assume that the decomposition of a large particle of calcium sulfate

at high temperature would proceed in the following manner. According to Levenspiel's (26) model, the decomposition of the calcium sulfate would begin at the outer surface of the particle. If the partial pressure of carbon monoxide in the reducing gas stream is sufficiently high, the initial reaction products should be a mixture of calcium sulfide and calcium oxide. Reference is made here to the phase diagram for this system constructed by Jonke (24) and illustrated in Figure 1. As the ash layer accumulates, the resistance to diffusion of gases through the ash layer begins to control the rate of reaction. As a result, the ratio of carbon monoxide to carbon dioxide at the surface of the unreacted core should decrease as concentration gradients are developed within the layer of ash. Moving to the left, therefore, along a constant temperature line in Jonke's (24) phase diagram, a point is reached where calcium oxide is the only decomposition product formed at equilibrium. Thus, after a suitable reaction time, the particle is visualized as an unreacted core of calcium sulfate surrounded by a layer of calcium oxide and sulfide. The relative amount of calcium sulfide in the oxide-sulfide layer gradually increases from a minimum at the boundary of the unreacted core to a maximum at the surface of the particle.

As the size of the reacting particle is decreased at the same reaction conditions, the importance of diffusion as the rate controlling mechanism is reduced considerably as indicated

by the shift in Levenspiel's models from a shrinking core to a continuous reaction model. Hence, it is conceivable that in a smaller particle the calcium sulfide formation is uniform throughout the particle and is influenced by the concentration of the carbon monoxide in the reducing gas stream. Thus, the relative amount of calcium sulfide formed in the finer particles occurs uniformly and corresponds to the maximum amount formed near the surface in larger particles.

The possibility that diffusion in large particles at lower temperatures becomes insignificant compared to the rate of reaction at the unreacted core, suggests that at lower temperatures, the amount of calcium sulfide formed in large particles may tend to become more uniform. Thus, the distinction in the amount of calcium sulfide formed between large and small particles may be considerably less distinct at lower temperatures.

As mentioned previously, a mechanism similar to this was observed in the oxidation of cuprous sulfide in that a central core of cuprous sulfide was surrounded by first a layer of cuprous oxide and then by a layer of a mixture of cuprous oxide and sulfate (48).

#### Particle analysis

Some attempts have been made to analyze cross sections of reacted particles of calcium sulfate for calcium and

sulfur using an electron microprobe and a scanning electron microscope in an effort to determine if concentration gradients do indeed exist within the solid phases. Such techniques, however, do not distinguish between sulfur in calcium sulfate or sulfur in calcium sulfide which makes analysis difficult. The extremely limited evidence available to date is both conflicting and inconclusive regarding verification of the model proposed above.

Figure 5, for example, illustrates a sulfur trace obtained using an electron microprobe to analyze the cross section of a partially reduced particle of calcium sulfate. The collection of particles from which the sample was taken had an average chemical analysis of 36.7 percent calcium sulfide, 4.9 percent calcium sulfate, and 51.0 percent calcium oxide. It would appear from the trace made along the particle diameter that the calcium sulfide is a maximum near the surface of the particle and diminishes near the center of the particle. This is in keeping with the model suggested above for large particles reacted at high temperatures.

Similar results were obtained by Jonke<sup>1</sup> when attempting to reduce calcium sulfate to calcium sulfide in a fluidized bed reactor. Microprobe examination of particle cross sections indicated an inner core of unreacted sulfate and

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<sup>1</sup>Jonke, A. A., Argonne National Laboratory, Argonne, Illinois. Results of microprobe analysis. Private communication. 1972.

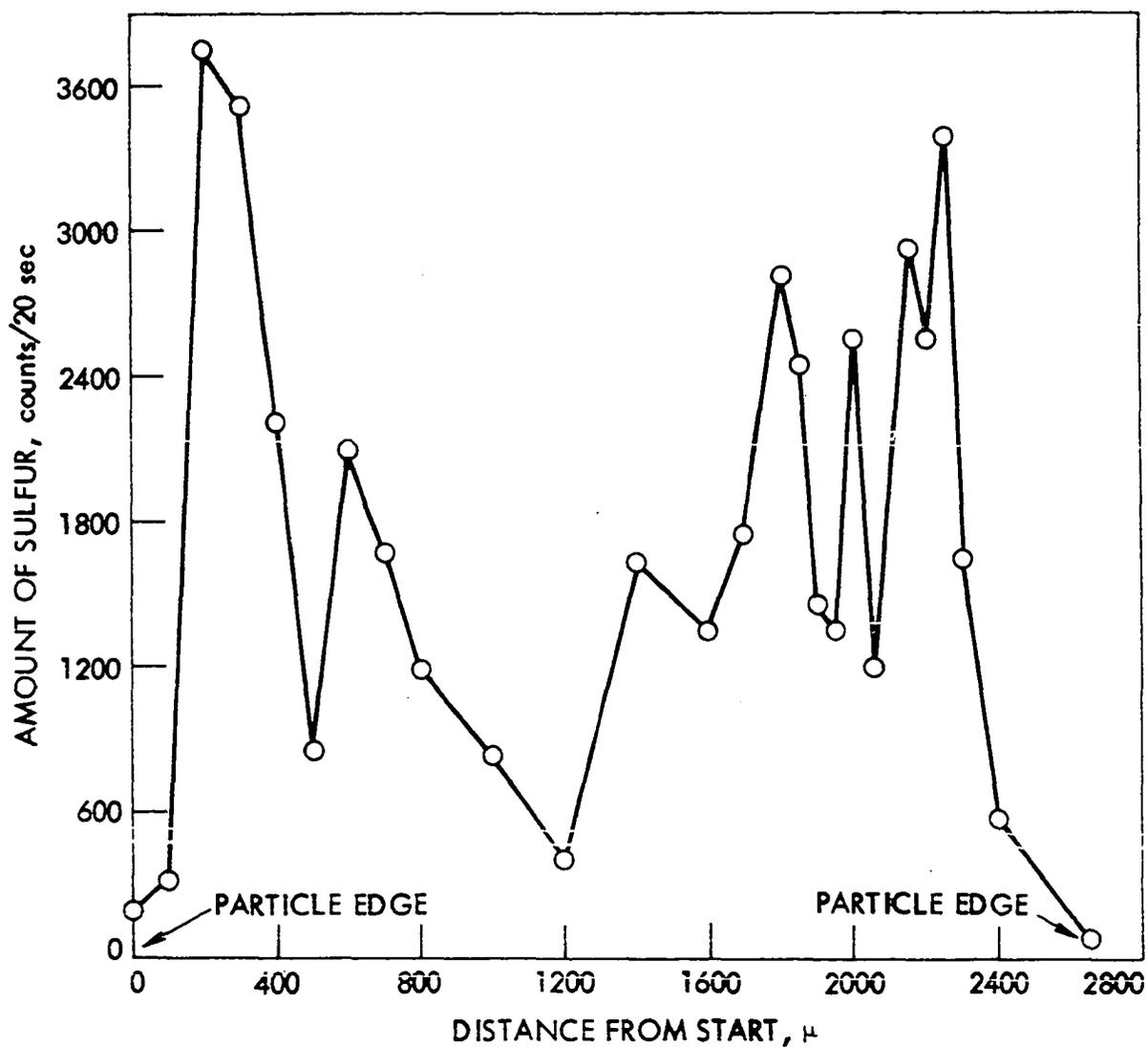


Figure 5. Electron microprobe sulfur trace of partially reduced calcium sulfate particle

Particle approximate composition: CaS=36.7%  
 CaSO<sub>4</sub>=4.9%  
 CaO =51.0%

Approximate particle diameter: 2.5 mm.

Background count: 100 counts/20 sec.

an outer shell of calcium sulfide. The particles were approximately 0.5 mm. in diameter, considerably smaller than the particle examined above.

Recent experiments involving use of the scanning electron microscope, however, have produced results indicating uniform sulfur concentrations in partially reduced sulfate particles containing sulfide in amounts ranging between 9 and 36 percent. The particles examined were also obtained from the Kent Feeds pilot plant reactor and were on the order of 2 mm. in diameter. This is in the same diameter range as the conflicting results obtained above.

Photographs of some of the particles examined on the scanning electron microscope are illustrated in Figure 6. The particles exhibit a slightly porous structure which would be expected in a highly reacted particle. The particles, however, were exposed to the atmosphere for a period of several months before the pictures were taken. It is impossible to tell, therefore, whether the degree of porosity exhibited was caused by the reaction of the particles or by decrepitation of the particles due to exposure to water vapor in the atmosphere.

The difficulty in comparing the above results is further complicated by inadequate information regarding the conditions under which the particles were reacted. It is evident that considerably more work needs to be done in this area

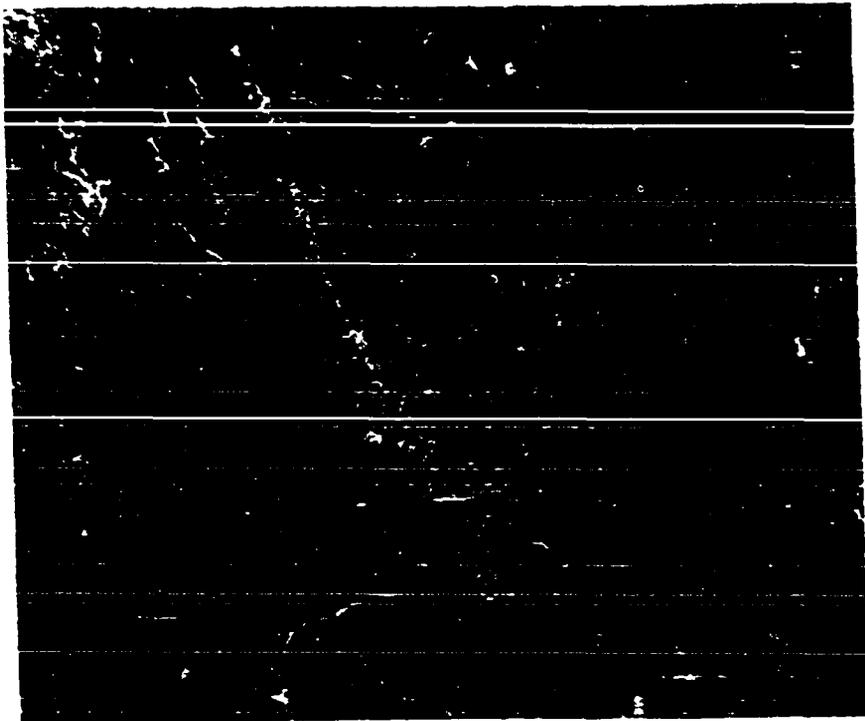
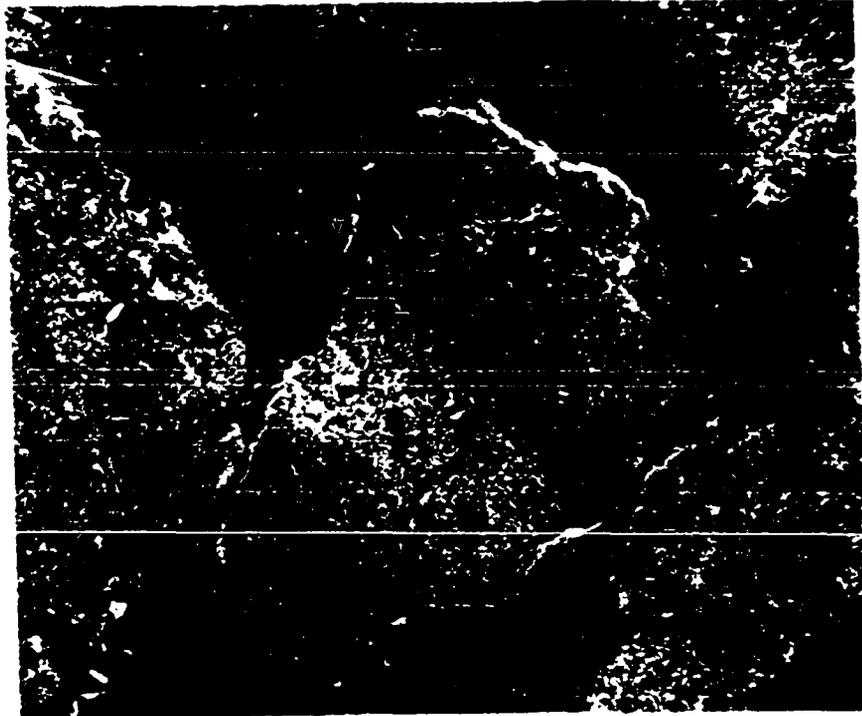
Figure 6. Scanning electron microscope photographs of partially reduced calcium sulfate particle cross sections

Top: Bulk sample analysis: CaS 20%  
CaSO<sub>4</sub> 1%  
CaO 73%

(Magnification: 100X)

Bottom: Bulk sample analysis: CaS 28%  
CaSO<sub>4</sub> 9%  
CaO 63%

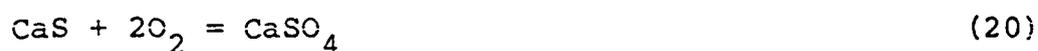
(Magnification: 70X)



to determine the correct kinetic models for the decomposition process and calcium sulfide formation. In particular, particles or particle compacts of widely differing sizes need to be reduced under carefully controlled conditions and examined at differing degrees of conversion to firmly establish the proper kinetic mechanism.

#### Oxidation of Calcium Sulfide

The concept of a two zone reactor having both a reducing zone and an oxidizing zone is based on the assumption that calcium sulfide produced in the reducing zone will be eliminated by reaction in the oxidizing zone. Unfortunately, however, just as in the reduction process, two different reactions can occur. These have been expressed previously as:



Reaction 21 is more desirable of course since it contributes to the process of making lime and sulfur dioxide. However, oxidation studies made in a batch fluidized bed reactor indicated that conversion to calcium sulfate is favored at high oxygen concentrations and at low temperatures (29).

It seemed desirable, therefore, to investigate the oxidation of calcium sulfide in a continuously operated

fluidized bed reactor to determine the effects of different operating variables on conversion and desulfurization and to examine the mechanism by which the reaction takes place.

### Raw materials

This investigation was made using a solid feed material which had been obtained from the overflow of the Kent Feeds pilot reactor (15). The material, designated KF-4, was chosen because of its high sulfide and low sulfate content and because it was a sulfide material which had resulted from the reductive decomposition of anhydrite. Screen and chemical analyses of this material are presented in Table 5.

Gases used in the investigation were again drawn from compressed gas cylinders having a minimum purity of 99.5 percent.

### Equipment

An equipment flowsheet for this investigation is presented in Figure 7. The oxidizing gas mixture was prepared by drawing pure oxygen and nitrogen from compressed gas cylinders and metering the flow of each by means of rotameters. The gas mixture then flowed past a calibrated rotating disc solids feeder which discharged the solids directly into the feed gas line. The solids were entrained in the feed gas and fed to the reactor continuously in this way. Likewise, reacted solids were removed from the reactor

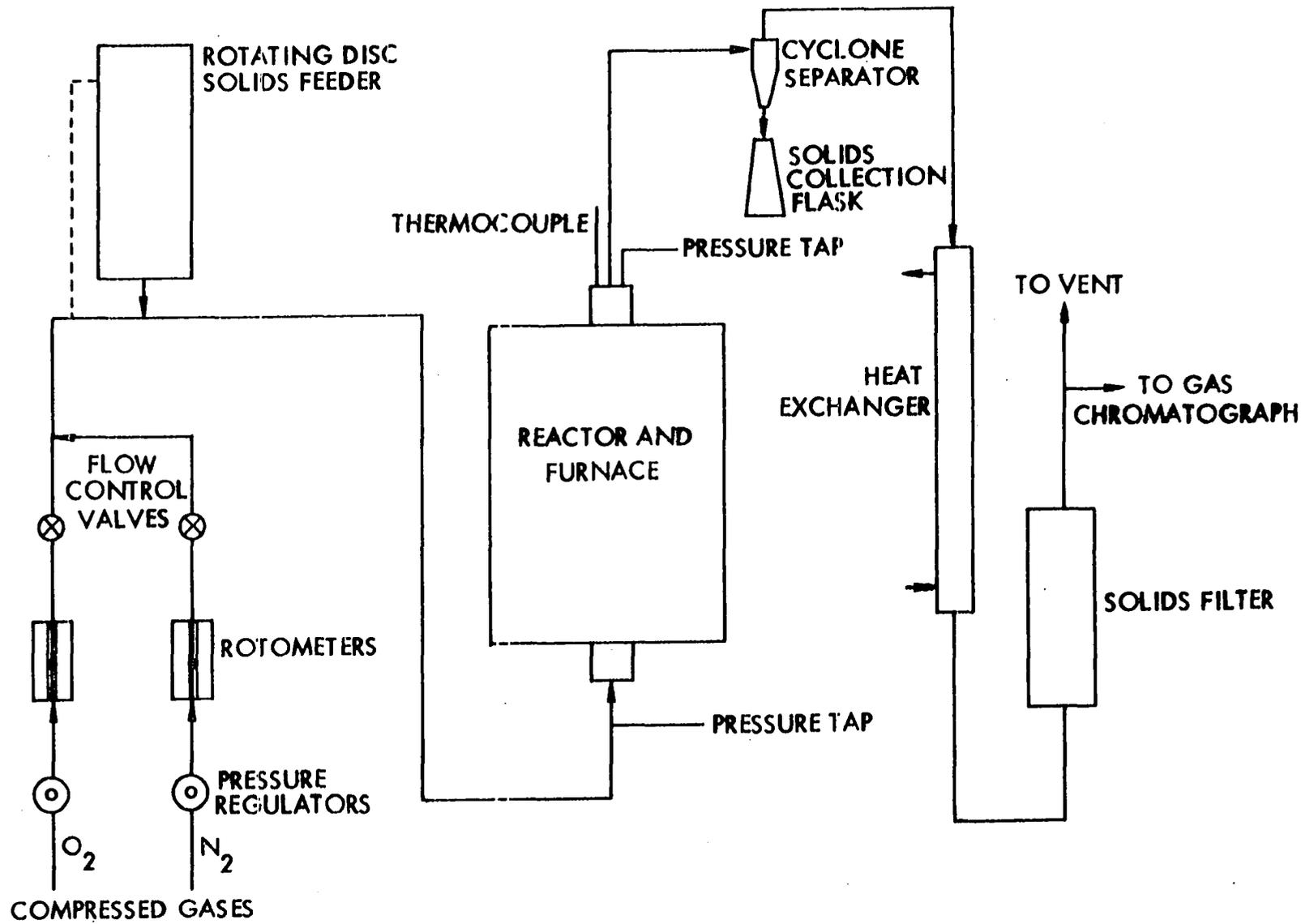


Figure 7. Apparatus used for the oxidation of calcium sulfide

Table 5. Chemical and screen analyses of KF-4

Chemical Analysis		Screen Analysis	
Constituent	Weight %	Size Fraction	Weight %
		+20	0
CaO	43.5	-20+25	2.0
		-28+35	13.6
CaSO <sub>4</sub>	7.3	-35+48	20.8
		-48+65	21.9
CaS	48.9	-65+100	15.9
		-100+150	9.2
Remainder	0.3	-150+200	9.8
		-200	6.8
Total	<u>100.0</u>	Total	<u>100.0</u>

continuously by entrainment in the off-gas line. The solids were then recovered for analysis by means of a cyclone separator and collection flask. The product gas was then cooled and filtered before being vented and/or analyzed with the gas chromatograph.

Reactor The reactor for this investigation was made using a McDanel mullite ceramic tube having an inside diameter of 2 in. and an overall length of 36 in. A conical distributor with a slope of 45° was used so that the solids could be fed to the reactor by entrainment in the gas feed line. For removal of the spent solids from the reactor, the off-gas line was extended down from the top of the reactor to just above the surface of the fluidized bed. Since connections to the reactor were made with silicone rubber

tubing, it was necessary to circulate room temperature air over the top of the reactor to dissipate heat during a run. Details of the reactor are illustrated in Figure 8.

#### Experimental procedure

When making a run the reactor was placed in the Kanthal furnace used in the previous investigation. Care was again taken to ensure that the bed region of the reactor was situated in the center of the heated length. The off-gas line was then adjusted to the desired height above the conical distributor in an attempt to regulate the bed depth.

Once situated in the furnace, the reactor was slowly heated to the desired temperature to prevent thermal damage to the ceramic tube. Oxygen and nitrogen were then fed to the reactor in the proper ratio to produce the desired oxidizing gas conditions. Finally, the flow of solids to the reactor was begun at the desired rate. The reaction was then allowed to continue until it appeared that steady-state conditions had been achieved in the reactor. During the run, the composition of the gas leaving the reactor was sampled at regular intervals. Solid samples were also recovered from the cyclone and saved for analysis. At the conclusion of a run, the flow of solids and oxygen to the reactor was discontinued. The nitrogen flow was continued until the reactor had cooled sufficiently to allow the solid bed residue to be drained from the reactor through the gas inlet

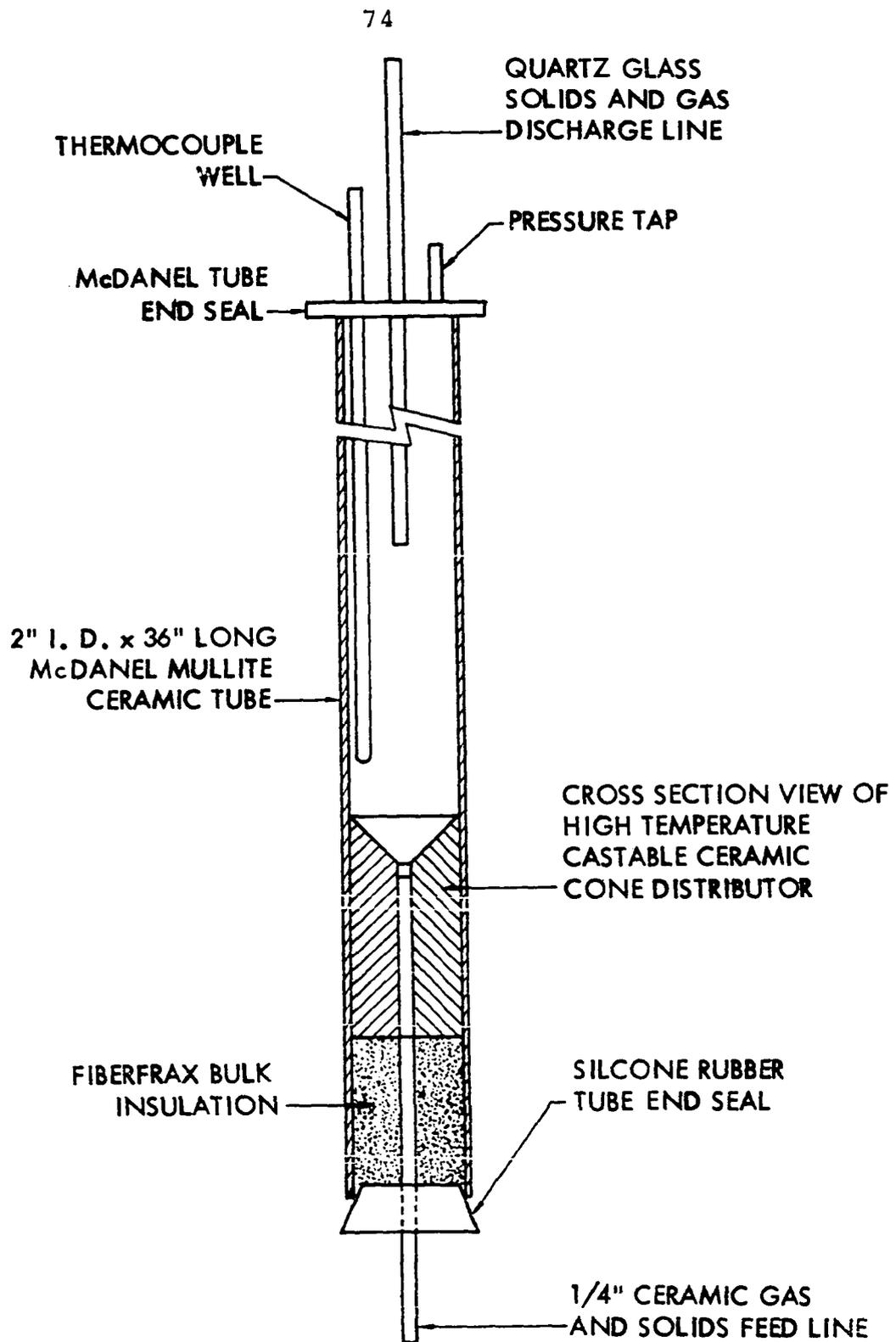


Figure 8. Details of reactor used in oxidation experiments

line.

### Results

The results were evaluated on the basis of the percent calcium sulfide converted in the reactor and on the basis of the percent sulfur in the solids feed converted to sulfur dioxide. The experimental observations for a typical run are presented in Figure 9.

The number of runs made was rather limited due to the short supply of solids feed material available. Therefore, a graphical correlation of the results with experimental conditions was impractical. Instead, the conditions and results of the runs which were made are presented in Table 6 for evaluation.

In Table 6, conversion of calcium sulfide refers to the percentage of calcium sulfide originally present in the feed which is oxidized to either calcium oxide or calcium sulfate. Desulfurization, or percent of sulfur removed, refers to the amount of sulfur originally present in the feed which is removed in the gas phase. Desulfurization may be very low even at high calcium sulfide conversions if most of the calcium sulfide reacts to form calcium sulfate.

Temperature effect      Temperature appears to have a positive effect on conversion which can be seen by comparing runs B and F. A much greater conversion was obtained at the

Figure 9. Results of a typical calcium sulfide oxidation experiment

Run: G  
Feed material: KF-4  
Bed height: 5 in.  
Feed gas: 10% O<sub>2</sub>, 90% N<sub>2</sub>  
Gas flow rate: 0.20 std. cu. ft./min.  
Solids feed rate: 2.5 gm./min.

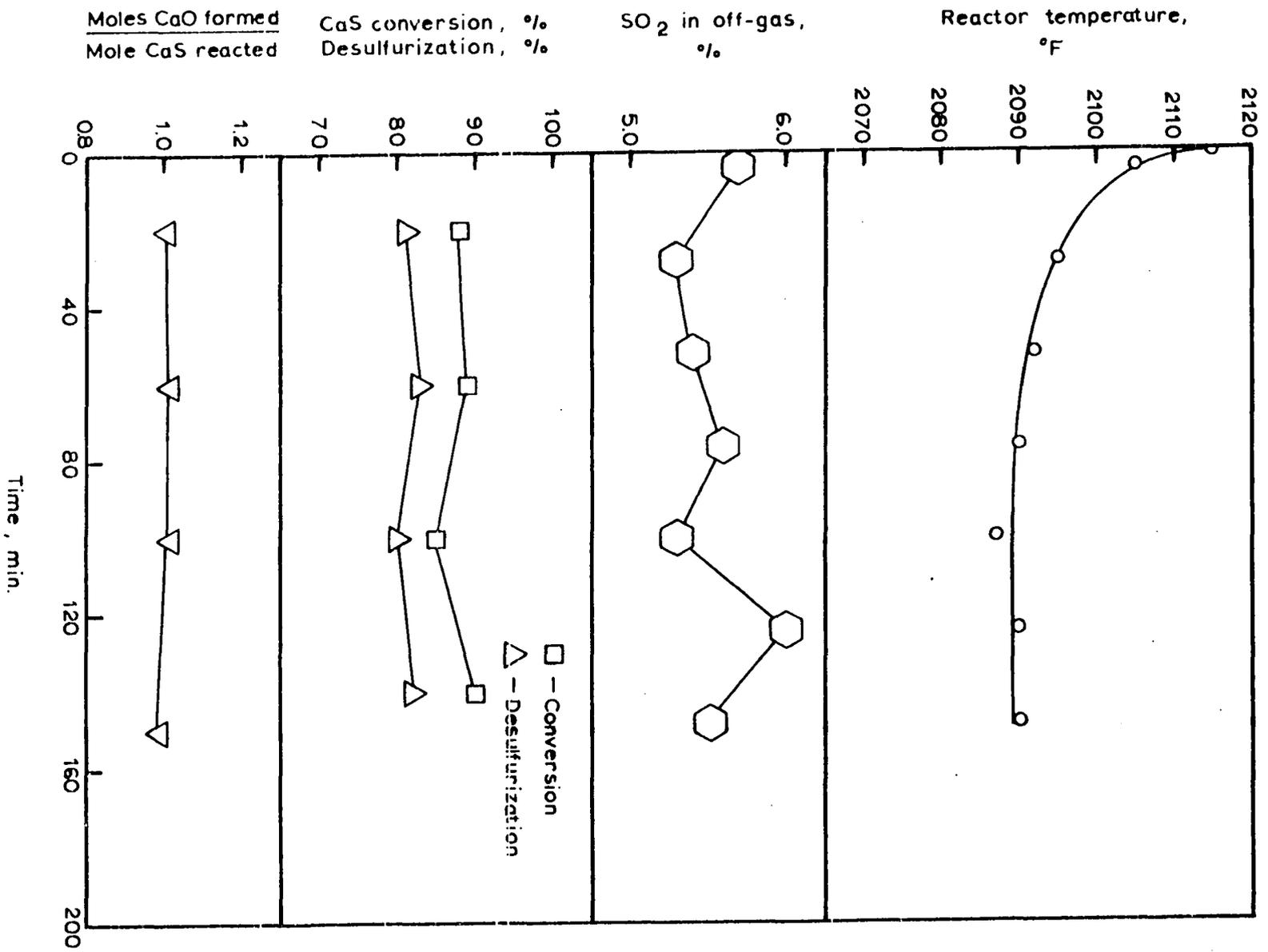


Table 6. Conditions and results of calcium sulfide oxidation experiments<sup>a</sup>

Run No.	Solids Feed gm./min.	Gas Feed		Mole Ratio $\frac{O_2}{CaS}$	Temp. °F	Solids mean res. time min.	CaS conversion %	Sulfur removed %	Off-gas Composition		
		SCFM	$\bar{P}_{O_2}$ atm.						O <sub>2</sub> %	SO <sub>2</sub> %	N <sub>2</sub> %
A	3.72	0.3	0.1	1.5	1934	-	62	40	3.3	2.7	94.0
B	2.76	0.22	0.1	1.5	1987	26.1	52 (99.8)	39 (94.7)	0.8	5.8 (7.1)	93.4
C	1.38	0.22	0.05	1.5	1937	30.1	68 (99.8)	64 (95.4)	1.3	3.0 (3.5)	95.8
D	1.38	0.22	0.1	3.0	2020	29.4	84 (98.2)	15 (53.4)	4.6	0.7 (2.0)	94.7
E	2.76	0.22	0.05	0.75	1935	8.0	31 (61.9)	30 (54.8)	0.4	3.1 (4.0)	96.5
F	2.76	0.22	0.1	1.5	2120	7.0	80 (100.0)	76 (95.7)	2.0	6.1 (7.2)	91.9
G	2.51	0.20	0.1	1.5	2090	31.6	88 (99.9)	81 (95.5)	0.6	5.5 (7.2)	93.9
H	4.14	0.22	0.15	1.5	2050	27.9	92 (99.9)	75 (95.4)	0.5	8.4 (10.9)	91.9
I	5.52	0.22	0.2	1.5	2140	20.7	93 (99.7)	86 (94.4)	0.5	13.5 (14.6)	86.0
J	5.52	0.24	0.2	1.6	1800	27.7	90 (99.9)	30 (65.8)	1.6	2.8 (9.9)	95.6
K	2.76	0.22	0.1	1.5	2014	47.3	99 (99.5)	74 (94.0)	0.4	5.6 (7.1)	94.0

<sup>a</sup>Values in parentheses are theoretical equilibrium values for the experimental conditions.

higher temperature of run F even though the mean residence time of the solids in the reactor was considerably less.

The importance of temperature on desulfurization is also quite obvious in comparing runs B and F. At the higher temperature, the desulfurization was much higher and was significantly closer to the observed value of conversion. Runs I and J also emphasize the importance of temperature on desulfurization. At the high temperature of run I, the conversion and desulfurization were quite close, while at the very low temperature of run J, the desulfurization was very low compared to the conversion. This indicates a significant amount of calcium sulfide was converted to calcium sulfate at the lower temperatures.

Effect of oxygen to calcium sulfide feed ratio      Com-  
paring runs B and D and runs B and E the effect of the oxygen to calcium sulfide feed ratio can be evaluated. Increasing the ratio tends to increase the conversion, but the ratio of desulfurization to conversion drops off rapidly. Apparently as the ratio of oxygen to calcium sulfide in the feed increases, a greater percentage of the calcium sulfide reacted is converted to calcium sulfate.

Effect of solids mean residence time      The solids mean residence time was estimated from the amount of solid material recovered from the reactor at the conclusion of each run.

To account for density changes, the weight of material in the reactor was adjusted to its equivalent weight in unreacted material. This was done on the basis of the conversion and desulfurization which the bed material was analyzed to have undergone. The adjusted weight was then divided by the solids feed rate to obtain the mean residence time.

Although not directly controlled, the solids mean residence time varied considerably from run to run. This was apparently due to differences in gas velocity and particle densities between runs which in turn affected the bulk density of the fluidized bed in each case.

The effect of the solids mean residence time can be seen in runs B and K and runs G and F which are nominally comparable except for residence time. In both cases, the increased residence time resulted in higher conversions and desulfurizations. However, in both cases the ratio of desulfurization to conversion was approximately the same. This was to be expected since residence time should not affect the reaction kinetics or thermodynamics.

#### Effect of oxygen partial pressure in the feed gas

The effect of oxygen partial pressure on conversion and desulfurization is somewhat obscured by the effects of the other variables. Comparing runs B and H, however, does indicate that the increased partial pressure of oxygen was

responsible in some measure for the increased conversion and desulfurization of run H. While not obvious from the data, one would suspect on the basis of thermodynamic considerations that an increase in the partial pressure of the oxygen should shift the equilibrium in favor of more calcium sulfate formation.

Equilibrium considerations      Using the method to calculate chemical equilibrium in complex mixtures discussed in Appendix C, theoretical equilibrium conversions and desulfurizations were calculated for runs B through K assuming that calcium oxide, calcium sulfide, and calcium sulfate were the only solid species in the system and that oxygen, sulfur dioxide and nitrogen the only gaseous species. It is interesting to note that under most of the experimental conditions tested, conversion and desulfurization should have been very high if equilibrium conditions had been reached in the reactor. Only at very low temperatures or ratios of oxygen to calcium sulfide significantly different from 1.5 would low desulfurization values be expected.

#### Kinetic model

In an attempt to better understand the kinetics of the oxidation process, a search was made for a kinetic model which would explain the results obtained from the oxidation experiments. Although several sophisticated models have been

proposed for the kinetics of gas-solid reactions (3, 6, 21, 22, 47), the shrinking core models and the homogeneous model introduced by Levenspiel (26) and elaborated upon by others (20, 25, 49) are by far the simplest explanations of the kinetics of gas-solid reactions available. With only a limited amount of data available, it seemed reasonable to use Levenspiel's (26) models since the more complicated models require a large number of unknown parameters to be specified.

According to Levenspiel (26), if the resistance to diffusion through the ash layer surrounding the unreacted core controls the rate of reaction, the time,  $\tau$ , required for the complete conversion of a particle of radius  $R$  and density  $\rho_B$  can be expressed as:

$$\tau = \frac{\rho_B R^2}{6bD_e C_{A_g}} \quad (27)$$

where

$b$  = moles of solid which react with one mole of gaseous reactant A.

$D_e$  = effective diffusion coefficient, sq. ft./hr.

$C_{A_g}$  = concentration of gaseous reactant A in the bulk gas stream, moles/cu. ft.

Conversion of the solid reactant,  $X_B$ , can also be expressed as a function of time,  $t$ , by the equation:

$$t/\tau = 1 - 3(1 - X_B)^{2/3} + 2(1 - X_B) \quad (28)$$

In the event that the presence of the ash layer has no influence on the conversion rate, the rate may be controlled by the rate of the chemical reaction at the core interface and the following equations apply:

$$\tau = \frac{\rho_B R}{b k_s C_{A_g}} \quad (29)$$

$$t/\tau = 1 - (1 - X_B)^{1/3} \quad (30)$$

where

$k_s$  = reaction rate constant based on unit surface,  
ft./hr.

A third model developed by Kunii and Levenspiel (25), termed the continuous reaction model, applies when the gaseous reactant is present throughout the entire particle and reacts with the solid reactant everywhere. This model applies to very porous solids or small diameter particles. As a simple first approximation in such a case, the following expression relates the progress of conversion with time:

$$1 - X_B = \exp(-k_r C_{A_g} t) \quad (31)$$

where

$k_r$  is now the rate coefficient based on unit  
volume of solid, cu. ft./mole A·sec.

In applying these equations to the expected performance of a fluidized bed reactor, the following assumptions were made by Levenspiel (26).

1. The bed can be characterized by an average particle size.
2. The solids in the bed are in backmix flow.
3. The concentration of the gaseous reactant can be characterized by an average value and be considered uniform throughout the bed.

With these assumptions, the average conversion of the solids leaving the reactor,  $\bar{X}_B$ , is given by the expression:

$$(1 - \bar{X}_B) = \int_{t=0}^{\infty} (1 - X_B)_{\text{particle}} \frac{e^{-t/\tau}}{\bar{t}} dt \quad (32)$$

where  $\bar{t}$  is solids mean residence time in the reactor.

In addition to the assumptions made by Levenspiel, it was necessary to make the following commonly accepted assumptions concerning the temperature dependence of the rate factors:

$$1. \quad D_e = D_{e_0} e^{-\Delta E/RT} \quad (33)$$

$$2. \quad k_s = k_{s_0} e^{-\Delta E/RT} \quad (34)$$

$$3. \quad k_r = k_{r_0} e^{-\Delta E/RT} \quad (35)$$

where  $D_{e_0}$ ,  $k_{s_0}$  and  $k_{r_0}$  are simply constants,  $\Delta E$  is the activation energy in cal./g.mole,  $R$  the gas law constant, and  $T$  the absolute temperature.

In evaluating the three models, the following values

were used to characterize the solids feed:

$$\rho_B \cong 0.0098 \text{ g.moles CaS/cm.}^3$$

$$R \cong 0.01 \text{ cm.}$$

$$b = 2/3$$

The value of  $b = 2/3$  was used since the primary reaction in the conversion process is considered to be reaction 21.

Analysis of the three models was made by substituting Equations 28, 30 and 31 into Equation 32. On the basis of the experimental conversion, solids mean residence time, and average oxygen concentration observed for each run, it was possible to calculate experimental values of  $D_e$ ,  $k_s$ , and  $k_r$  assuming each of the three models to be correct. Then using Equations 33 through 35, a least squares fit of the rate factors as a function of experimental temperatures was made to determine the best values for the constants in the rate expressions.

On the basis of the least squares fit, all three models were found to fit the experimental data equally well. However, on the basis of the extremely low values of effective diffusion coefficient determined for the diffusion controlling model, this model was rejected.

Using then the theoretical values of the rate constants determined for the shrinking core reaction controlling model and the continuous reaction model, the calculations were

reversed to determine the theoretical conversions predicted by both models at the experimental conditions of each run. The values of the rate expression constants and the conversions predicted by both models are presented in Table 7 for comparison.

Table 7. Comparison of reaction controlling and continuous reaction models

Run No.	Experi- mental CaS Conversion $X_B$	Shrinking core reaction controlling model Parameters determined: $k_{s0} = 5.7 \times 10^3 \text{ cm./sec.}$ $\Delta E = 26,800 \text{ cal./g.mole}$ $\hat{X}_B$	Continuous reaction model Parameters determined: $k_{r0} = 2.16 \times 10^8 \text{ cm.}^3/\text{g.mole.sec}$ $\Delta E = 27,800 \text{ cal./g.mole}$ $\hat{X}_B$
B	52	85	84
C	68	75	75
D	84	91	90
E	31	38	40
F	80	72	72
G	88	91	90
H	92	92	91
I	93	94	93
J	93	85	84
K	99	92	91

Considering the limited amount of data, the agreement is really rather good. Although the standard deviation of the values of the parameters given in Table 7 were quite large due to the scatter in the data, the values determined by both models agree in order of magnitude with similar values reported for the oxidation of zinc sulfide pellets (25).

The results of the modelling study are also consistent with the model suggested previously for calcium sulfide formation. If, indeed, calcium sulfide formation is concentrated near the surface of the particle, the subsequent oxidation of the sulfide could then very easily be expected to be reaction controlled. Also, the fact that the particle is subject to yet another reaction step could conceivably create a highly porous ash and eliminate diffusion as a controlling factor.

Since both reaction models seem to fit the data equally well, more data would be required to determine which one is really better suited to the oxidation reaction.

#### Decomposition of Calcium Sulfate in a Multiple Zone Reactor

It has been shown that during the reductive decomposition of calcium sulfate in a conventional fluidized bed reactor, a significant amount of calcium sulfide may be

produced except under a very narrow range of operating conditions (15, 42). Since it is desirable that calcium sulfide formation be kept at a minimum while easing the restrictions on operating conditions, it seemed that a new method of processing the calcium sulfate might prove more satisfactory. On the basis of the preliminary investigations made regarding the formation and subsequent oxidation of calcium sulfide, the principle of a multiple zone reactor was considered. It was felt that if reducing and oxidizing regions could be established in the same fluidized bed, it would be possible to essentially eliminate the calcium sulfide as it was formed. It was further thought that the oxidizing zone should be in the upper section of the fluidized bed so that all gases leaving the reactor would be in the oxidized state. This should eliminate the presence of such reduced sulfur components as hydrogen sulfide, carbonyl sulfide and elemental sulfur. In principle, the process would be similar to one in which the solids would be treated in a series of alternating reducing and oxidizing fluidized bed reactors as has been suggested (5).

To investigate the possible advantages of a multiple zone reactor it was proposed to carry out some decomposition experiments in which a highly reducing mixture of natural gas and air would be introduced at the bottom of a fluidized bed to form a reducing zone. An excess of air would then be

introduced at a point above the bottom of the bed to form an oxidizing region in the upper portion of the bed. The combustion of the methane would supply both the heat necessary to maintain the reactor temperature and the reducing gases necessary for the decomposition.

#### Raw materials

The majority of the experiments carried out during this investigation were made using a natural anhydrite ore of calcium sulfate obtained from a mine operated by the United States Gypsum Company near Southard, Oklahoma. The approximate composition of the material was determined by Hansen et al. (15) and is given in Table 8. The anhydrite, being a much harder form of calcium sulfate, was preferred in the investigation because of its low attrition rates in fluidized beds. In preparing the material for experimental purposes, it was necessary to crush and screen the material to the desired size range.

A few experiments were made using a natural ore of gypsum. This material was obtained from a mine near Fort Dodge, Iowa, which is also operated by the United States Gypsum Company. It was prepared for use in the same manner as the anhydrite. Its chemical composition is also given in Table 8.

Table 8. Analyses of gypsum and anhydrite

Gypsum <sup>a</sup>		Anhydrite <sup>b</sup>	
Constituent	Percent	Constituent	Percent
H <sub>2</sub> O (combined)	19.7	Anhydrite (CaSO <sub>4</sub> )	73.4
CaO	31.1	Gypsum (CaSO <sub>4</sub> ·2H <sub>2</sub> O)	24.4
MgO	0.1	Ca and Mg carbonates	0.6
SO <sub>3</sub>	45.4	Remainder	1.6
CO <sub>2</sub>	0.7		
SiO <sub>2</sub>	3.3		
NaCl	0.3		
Totals	100.6		100.0

<sup>a</sup>From Wheelock (50).

<sup>b</sup>From Hansen et al. (15).

The gases used in the investigation were air, natural gas, and oxygen. The air and natural gas were taken from service lines to the laboratory while the oxygen was drawn from high pressure cylinders. The natural gas had a nominal composition of 88.2 percent methane, 4.8 percent ethane, and 7.0 percent nitrogen as determined on the gas chromatograph. While composition of the natural gas did vary somewhat from time to time, the changes were minor and disregarded in importance.

Combustion tests were made with the natural gas in air to measure the effect of the air to gas ratio on the combustion products. The tests were carried out in the 2 in. reactor used in the previous investigation. Mixtures of natural gas and air were passed over a bed of inert alumina which was initially heated to a temperature of 1400°F to support the spontaneous combustion of the natural gas. The combustion products were then analyzed on the gas chromatograph after the water had been condensed out. The tests were made at atmospheric pressure and a nominal temperature of 2200°F. Since the gas chromatograph was incapable of separating oxygen and the argon present in the air, both components are recorded as percent oxygen. The results of the study are illustrated in Figure 10. From the graph it appears that an air to natural gas ratio of 10:1 is an essentially neutral mixture while ratios below 10:1 become increasingly more reducing.

#### Equipment

A flowsheet of the equipment used in the investigation is presented in Figure 11. Gas flow rates to the reactor were measured and controlled using pressure regulators and rotameters. The primary gas mixture consisted of oxygen, air, and methane and was fed directly to the reactor below the distributor plate. The secondary gas mixture of oxygen and air went by the solids screw feeder where the solids became

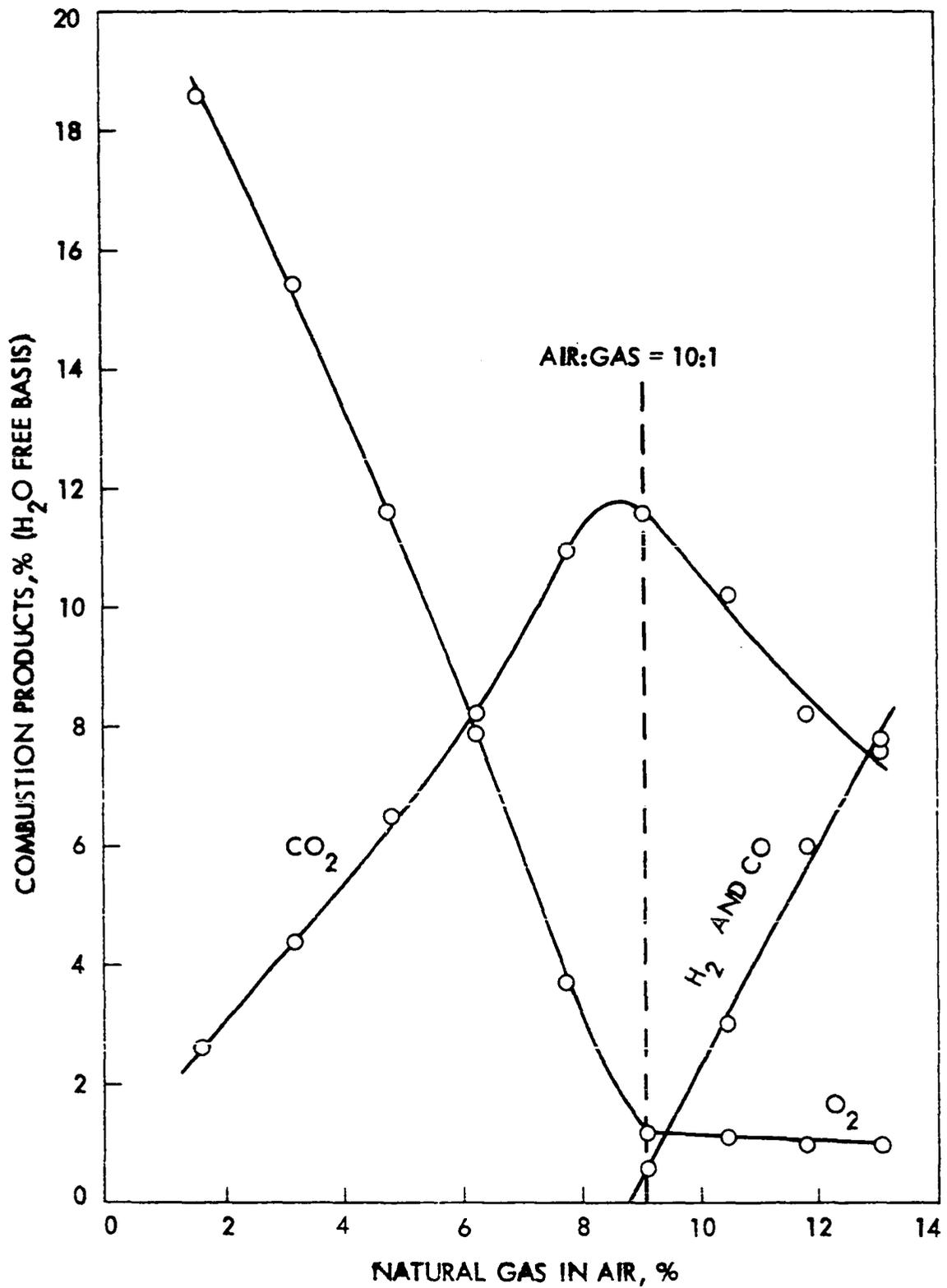


Figure 10. Combustion products of natural gas in air

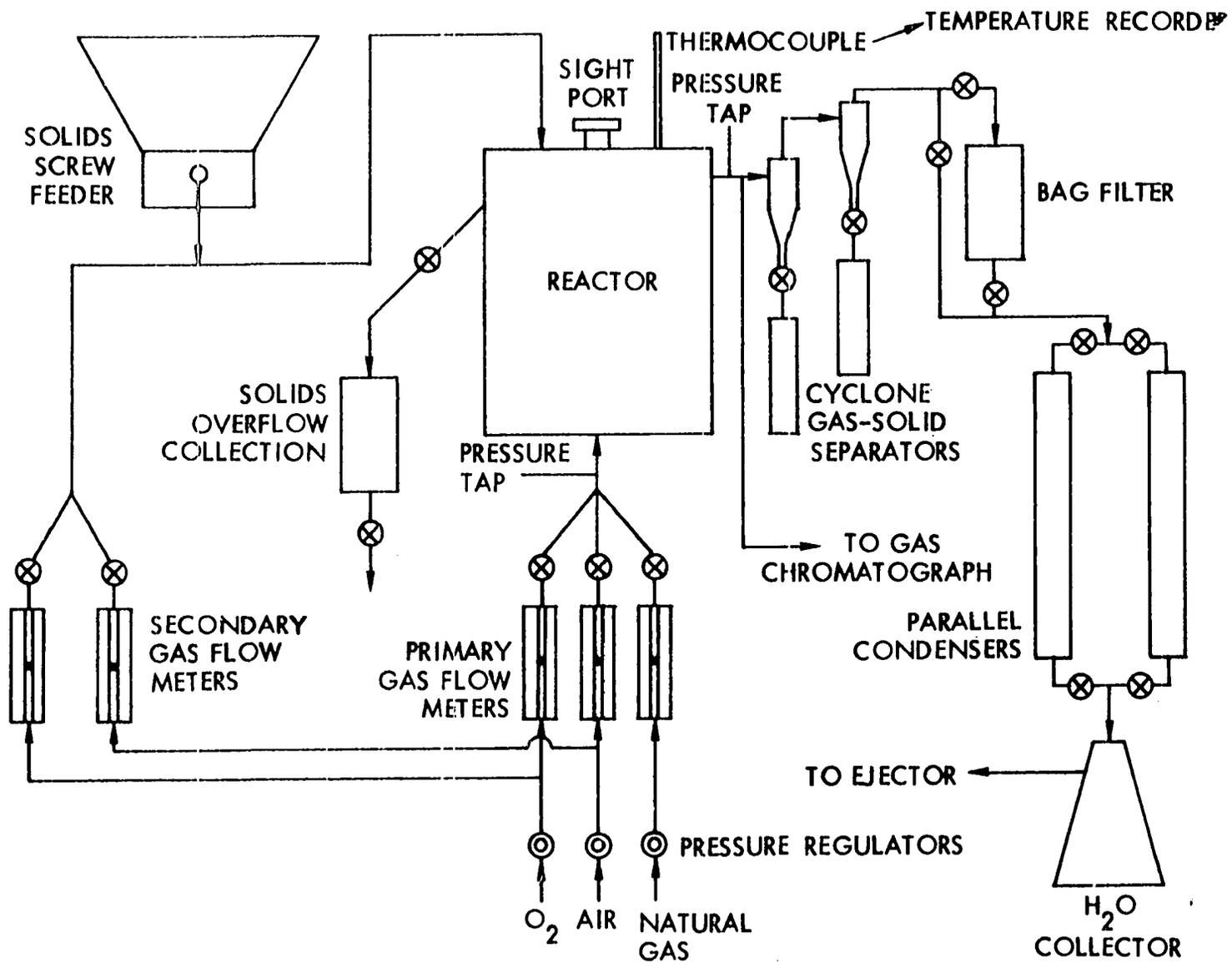


Figure 11. Laboratory apparatus used in the two-zone reactor investigation

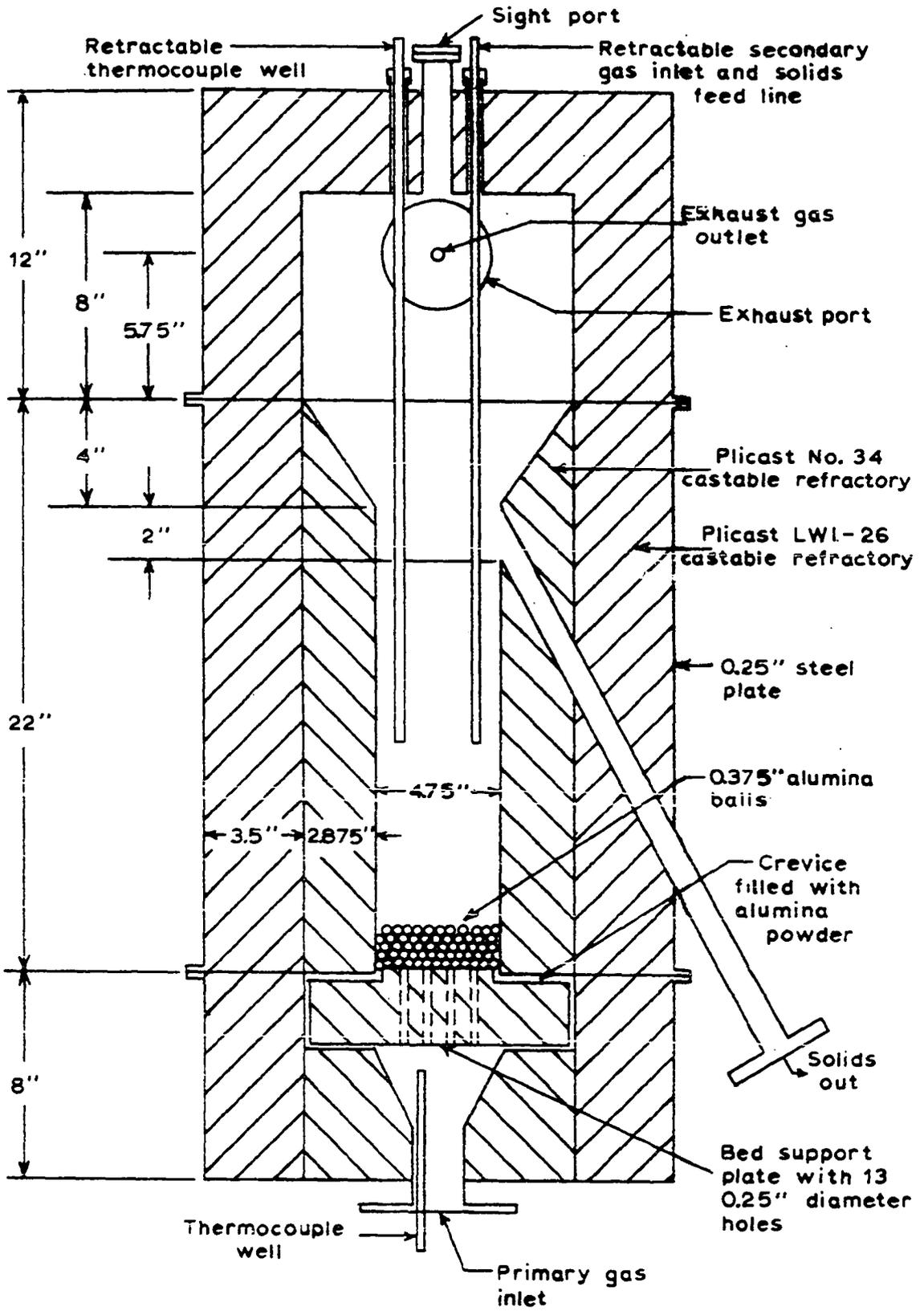
entrained in the gas stream. From there the gas and solids entered the reactor from the top through a dipleg to a point below the surface of the fluidized bed.

Reacted solids were removed from the reactor by means of an overflow as well as by some entrainment of fines in the off-gas. Entrained solids were removed by means of two cyclone gas-solid separators in series. The gas then passed through a bag filter, condensers, and a water removal flask before being vented to the atmosphere through a vacuum ejector.

A thermocouple in a protective well was inserted into the reactor from above to continuously monitor the bed temperature during an experiment. Pressure readings below the distributor and in the reactor were taken to monitor possible problems of plugging in the reactor and in the off-gas lines.

Details of the reactor are illustrated in Figure 12. The inside diameter of the fluidized bed section of the reactor was 4.75 in. The height of the bed was controlled by varying the depth of the alumina balls above the distributor. To prevent the alumina balls from resting in the holes of the distributor plate, thereby blocking the flow of gas, a small amount of bulk Fiberfrax insulating material was used between the balls and the plate. In addition to the insulation shown in Figure 12, an additional 3 in. of Webbers Super 48 Insulating Cement was added to the surface of the

Figure 12. Reactor for investigating  $\text{CaSO}_4$  decomposition in a two-zone fluidized bed



steel shell to further reduce heat losses.

The retractable thermocouple well and secondary gas inlet lines were 3/8 in. outside diameter by 1/4 in. inside diameter mullite ceramic tubes from the McDanel Company. Some attempts were made to insert metal tubes of Kanthal and stainless steel into the reactor, but they were very rapidly corroded away by the hot sulfurous gases generated by the reactions taking place.

#### Experimental procedure

The lack of an external heating source around the reactor created several problems in the starting up and carrying out of experiments. Since the reaction was to be carried out by the combustion of natural gas in the fluidized bed, it was necessary to find a way to bring the reactor to a temperature which would cause ignition to take place. Initially this was accomplished by inserting a long heating element of Kanthal wire wound on a ceramic tube support into the empty reactor through the sight port opening. When the air temperature in the reactor reached 1000°F, the flow of natural gas and primary air to the reactor was initiated and spontaneous combustion occurred. After a short period of time it was then possible to remove the heater from the reactor. The temperature in the reactor was then brought to the desired level by adjusting the flows of the primary and secondary gases.

A second and more reliable method of start-up involved the use of a small pilot light on the end of a long section of 1/4 in. outside diameter stainless steel tubing. By feeding the pilot a mixture of natural gas and oxygen, it was possible to insert the pilot into the reactor through the sight port and rapidly heat the surface of the alumina balls to a temperature capable of supporting combustion. The flow of natural gas and primary air was then started as before.

Once combustion was well established in the fluidized bed zone and the temperature was above 1900°F, the feeding of solids to the reactor was begun. This would generally cause a severe drop in the reactor temperature initially followed by gradual recovery to the desired temperature level. Since there was no external temperature control, it was necessary to adjust the temperature by the flow of natural gas and by varying the relative amounts of oxygen and air in the primary and secondary gas streams. Since the behavior of fluidized beds is not always predictable, the control of the reactor temperature was a very serious problem which was never completely overcome. It also limited the range of variables which could be investigated since the reactor temperature was integrally bound to all of the other variables involving feed rates and feed ratios.

In the early stages of the investigation several batch runs were made while operational techniques were

refined. During these runs, the overflow was sealed off and a specified quantity of material was fed to the reactor. After the feeding of the solids was complete, the flow of gases to the reactor was continued until it seemed the reaction was complete. The gas flows were then discontinued and the contents of the reactor allowed to cool for recovery and analysis. During these investigations problems with the gas chromatograph prevented meaningful gas analyses. However, some solid samples were recovered from the cyclones periodically and subjected to analysis.

The majority of the experiments were made on a continuous basis during which overflow samples from the reactor were collected periodically as well as off-gas samples and cyclone samples. Every attempt was made to let the run continue until it appeared that steady-state conditions had been achieved. In several instances, however, operational difficulties were encountered which prevented this from happening. In these cases, the runs were evaluated on the basis of the degree to which steady state was reached.

As before, when an experiment was terminated, the flow of gases to the reactor was discontinued and the contents allowed to cool for recovery.

## Results

Batch operation As previously stated these runs were made during the preliminary stages of the investigation while

operating procedures and equipment problems were being worked out. During this time, the following conditions for successful operation of the reactor were determined:

1. The optimum particle size range for efficient operation of the reactor was found to be -14 + 35 mesh. Particle sizes larger than this created problems for the pneumatic feeding system. Smaller sizes were a problem since the high gas flow rates required to achieve and maintain the reactor temperature resulted in excessive entrainment.
2. A natural gas flow rate of from 0.5 to 0.6 std. cu. ft./min. was required to furnish the necessary heat for the reaction and maintain the reactor temperature. The exact amount tended to vary quite significantly with the rate solids were introduced into the reactor.
3. Since the amount of natural gas required for heating was so high, it was necessary to use some pure oxygen mixed with air to keep gas velocities at a reasonable level for the particle size range of material being used. In addition, the use of oxygen also reduced the amount of heat required by reducing the amount of inert nitrogen carried along in the air. Therefore, when referring to ratios of air to natural gas it is necessary to think in terms

of equivalent air, or that amount of air equivalent in oxygen to the actual air-oxygen mixture being used.

4. The ratio of equivalent air to natural gas in the primary gas flow was limited to a value below 6:1. Ratios higher than 6:1 were generally not acceptable because of the risk of premature combustion of the natural gas below the distributor. This resulted in severe drops in temperature in the fluidized bed. A primary air to gas ratio of around 5:1 was used during the vast majority of the experimental work.
5. It was found that the overall ratio of air to natural gas in the combined primary and secondary gas flows could be varied quite freely from reducing to oxidizing. From the batch investigations its effects on conversion and desulfurization could not be determined, however.
6. Gas velocities through the bed were nominally maintained between 2.0 and 3.0 ft./sec. or around two to three times the incipient fluidization velocity of the unreacted feed. Since the reacted material was considerably less dense due to its negative change in weight, these velocities were considered adequate for good fluidization. Visual observation of the bed

through the sight port confirmed that the bed was well fluidized.

7. Since it was necessary to maintain the highly reducing conditions in the primary gas stream, a significant portion of the total gas flow entered the reactor in the secondary gas line. This proved to be advantageous for the pneumatic feeding of the solids in the secondary gas line. Operation of the reactor was better, however, when the secondary gas inlet was positioned near the bottom of the bed. For most of the runs, the dipleg was situated at a distance of 1 in. above the bottom of the fluidized bed.

Although the batch runs were made simply in the interest of defining operating conditions for the reactor, some interesting results were observed which bear on the concept of the two-zone reactor. A summary of the conditions and results of four of the runs which were made to try to control the reactor temperature by varying the gas flow rates are presented in Table 9. A complete description of the experimental conditions and results for all the runs made is presented in Table 15 in Appendix A.

One interesting aspect of the results is the difference in composition of the solids taken from the top and bottom of the settled bed. The difference is quite consistent

Table 9. Conditions and results of selected batch experiments

Run No.	Equivalent Ratio		Solids Fed	Temperature Range °F
	Air: Natural Gas Primary	Total		
1-243	6:1	10:1	3100 gm. anhydrite	1895-1930
1-247	4:1-5:1	9.5:1	4000 gm. anhydrite	1725-1968
1-251	5:1	8:1-10:1	3000 gm. anhydrite	2200
1-256	5:1	8.5:1	3000 gm. anhydrite	2150-2250

<sup>a</sup>X = conversion.

<sup>b</sup>D = desulfurization.

Solids Analysis							
Top of Bed				Bottom of Bed			
Composition	X% <sup>a</sup>	D% <sup>b</sup>	X/D	Composition	X%	D%	X/D
CaS = 2.5%				CaS = 4.8%			
CaO = 36.4%	64.7	61.5	1.05	CaO = 51.0%	76.9	71.7	1.07
CaSO <sub>4</sub> = 50.9%				CaSO <sub>4</sub> = 40.0%			
CaS = 0.2%				CaS = 0.2%			
CaO = 19.6%	38.0	37.7	1.01	CaO = 40.4%	64.2	64.1	1.00
CaSO <sub>4</sub> = 78.5%				CaSO <sub>4</sub> = 54.9%			
CaS = 0.6%				CaS = 12.1%			
CaO = 78.5%	93.2	92.6	1.01	CaO = 75.8%	98.1	87.2	1.12
CaSO <sub>4</sub> = 14.1%				CaSO <sub>4</sub> = 4.1%			
CaS = 0.3%				CaS = 0.7%			
CaO = 87.5%	97.1	96.9	1.00	CaO = 88.5%	98.2	97.6	1.01
CaSO <sub>4</sub> = 6.3%				CaSO <sub>4</sub> = 3.9%			

with the premise that oxidizing and reducing conditions of varying degrees are established in the reactor by the addition of the secondary air stream. Samples taken from the bottom of the bed where the reductive decomposition is considered to have occurred consistently exhibited a greater conversion of the calcium sulfate than samples taken from the top of the bed. This is in keeping with the theory that oxidation in the upper part of the bed regenerates a portion of the calcium sulfate during the oxidation of the calcium sulfide. It also indicates the lack of perfect mixing in the fluidized bed.

Another indication that two zones existed in the reactor is the observation that the ratio of calcium sulfate conversion to desulfurization was generally higher near the bottom of the bed indicating that a relatively greater amount of calcium sulfide existed in that region of the fluidized bed. This is reasonable since oxidation in the upper section converted the sulfide to sulfate and oxide.

The results of the batch runs were also very encouraging in that the percentage of calcium sulfide in the upper part of the fluidized bed was less than 0.7 per cent with the exception of one run. It appeared, therefore, that very favorable conversions and desulfurizations could be achieved during continuous operation.

Gas concentration profiles

Numerous attempts were made during the actual continuous steady-state operation of the reactor to obtain vertical gas concentration profiles in the fluidized bed reactor to illustrate more clearly the existence of oxidizing and reducing zones within the bed. The attempts were made by temporarily removing the sight port from the reactor and inserting a probe which could be moved up and down in the bed to take gas samples at various heights in the fluidized bed. When metal tubes were used, they were simply corroded away by the hot sulfurous gases. When ceramic tubes were used, their low mechanical strength at the high temperatures in the reactor caused them to consistently break when attempting to move them up and down in the reactor. Rough concentration profiles were obtained for two runs and the results are illustrated in Figures 13 and 14. The profiles for the two runs are quite similar except for the small oxygen peak which occurs at about the 2 in. level in Figure 13. In both cases the carbon monoxide and hydrogen concentration, which are very high at the very bottom of the bed, drop to essentially zero above the level at which the secondary air is injected into the bed. The puzzling feature of both profiles is the lack of oxygen in the upper reaches of the fluidized bed. Analyses of the off-gases leaving the reactor showed oxygen levels of approximately 6.5 per cent

Figure 13. Vertical gas concentration profile for run 2-28

Bed height: 10 in.

Secondary air inlet: 1 in. from bottom

Air: Natural gas ratio: Primary 5:1

Total 10:1

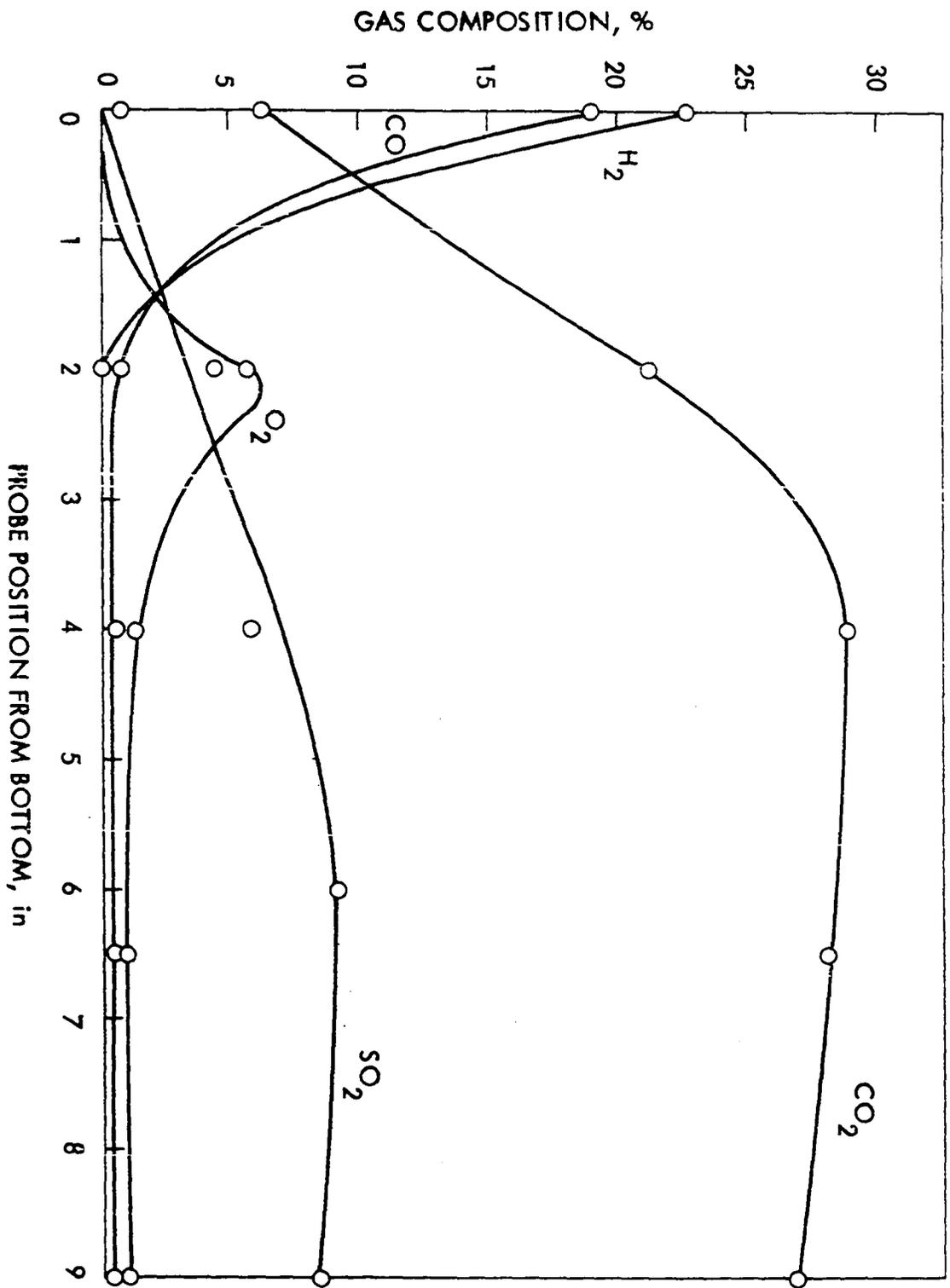


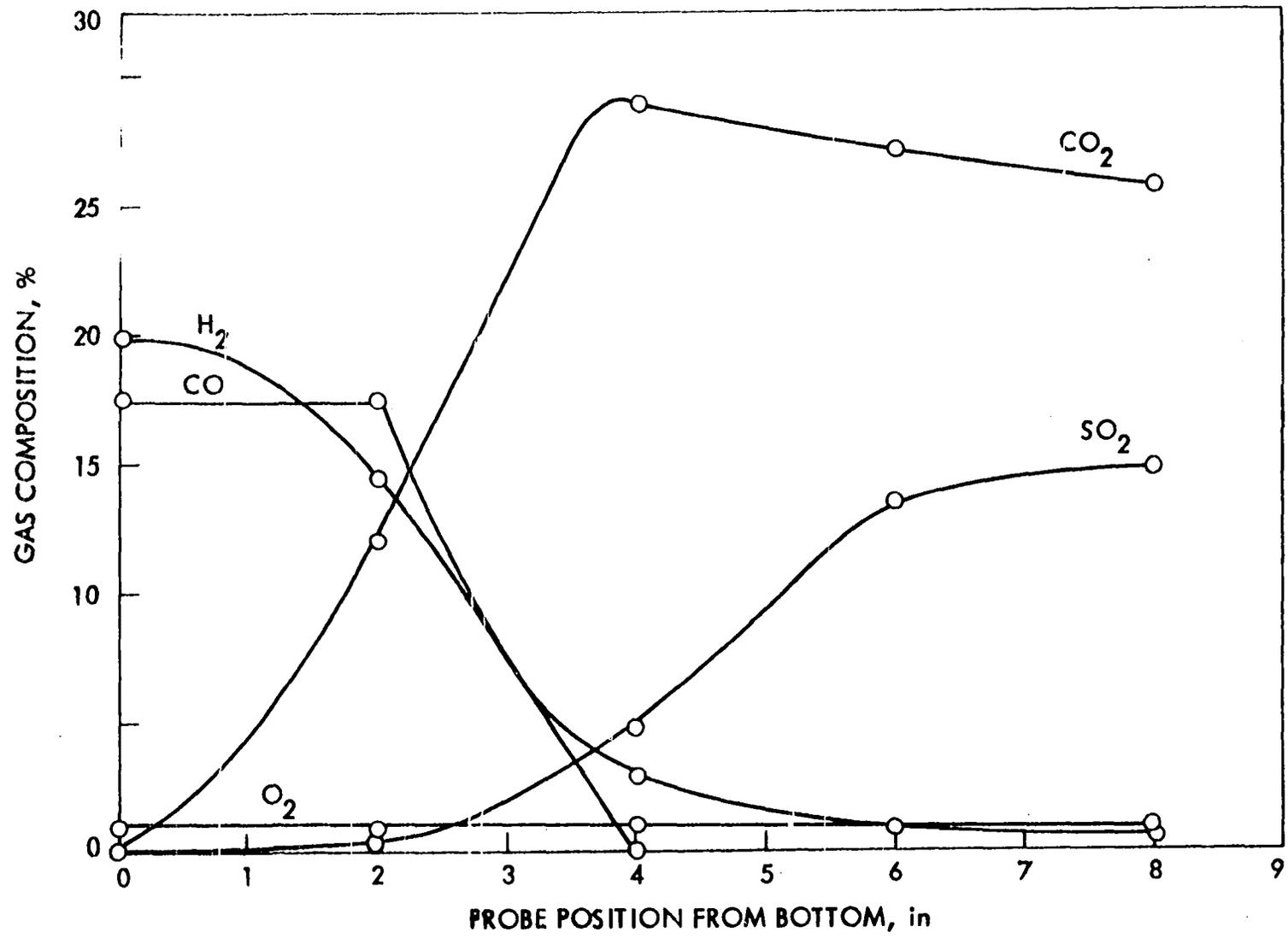
Figure 14. Vertical gas concentration profile for run 2-107

Bed height: 10 in.

Secondary air inlet: 4 in. from bottom

Air: Natural gas ratio: Primary 4.5:1

Total 10.1



and 3.5 per cent for the two runs respectively. Since the probe and the gas inlet were on opposite sides of the reactor and separated by a horizontal distance of approximately 4 in., it is possible that the zone of high oxygen concentration occurred away from the probe. This would tend to suggest that the oxidizing zone occupies a very small percentage of the cross sectional area of the reactor near the secondary gas inlet, but gradually increases in scope as the gas rises through the bed and the oxygen radiates outward. This is entirely in keeping with a small scale investigation which was carried out at room temperature to investigate the radial mixing of a tracer gas injected at a point in a fluidized bed. The results of that investigation are summarized in Appendix B.

These measurements definitely indicate that significant concentration profiles did exist in the fluidized bed reactor and give support to the premise that the reactor has distinct oxidizing and reducing zones.

Continuous operation      The major part of the investigation involved operating the reactor continuously to determine the effects of different operating conditions on the conversion and desulfurization of calcium sulfate, and to see if the two zone reactor would prove valuable in controlling the formation of calcium sulfide. Table 10 lists the

Table 10. List of variables investigated in multiple zone reactor

Directly controlled		Indirectly controlled	
Variable	Range	Variable	Range
Natural gas flow rate	0.51-0.67 SCFM	Temperature	1900-2250°F
		Primary ratio Air: NG	4.2-5.4
Equivalent primary air flow rate	2.56-3.35 SCFM	Total ratio Air: NG	8.5-10.7
		Mole ratio NG: CaSO <sub>4</sub>	2.08-7.85
Equivalent secondary air flow rate	1.85-3.54 SCFM	Gas velocity	2.08-2.81 ft/sec
		Solids residence time	10-142 min
Solids feed rate	17-50 gm/min.		
Secondary gas inlet	1-7 in. from bottom		
Bed depth	9-14 in.		

variables which were either directly or indirectly controlled and the ranges over which the variables were investigated. Since there was no external control on temperature it is included as an indirectly controlled variable. It should be pointed out that the reactor was operated at total equivalent air to natural gas ratios which varied from a mildly reducing 8.5:1 to a mildly oxidizing 10.7:1. In all the experiments, however, the primary air to natural gas ratio was very reducing and ranged from 4.2:1 to 5.4:1.

Figure 15. Results of a typical decomposition experiment

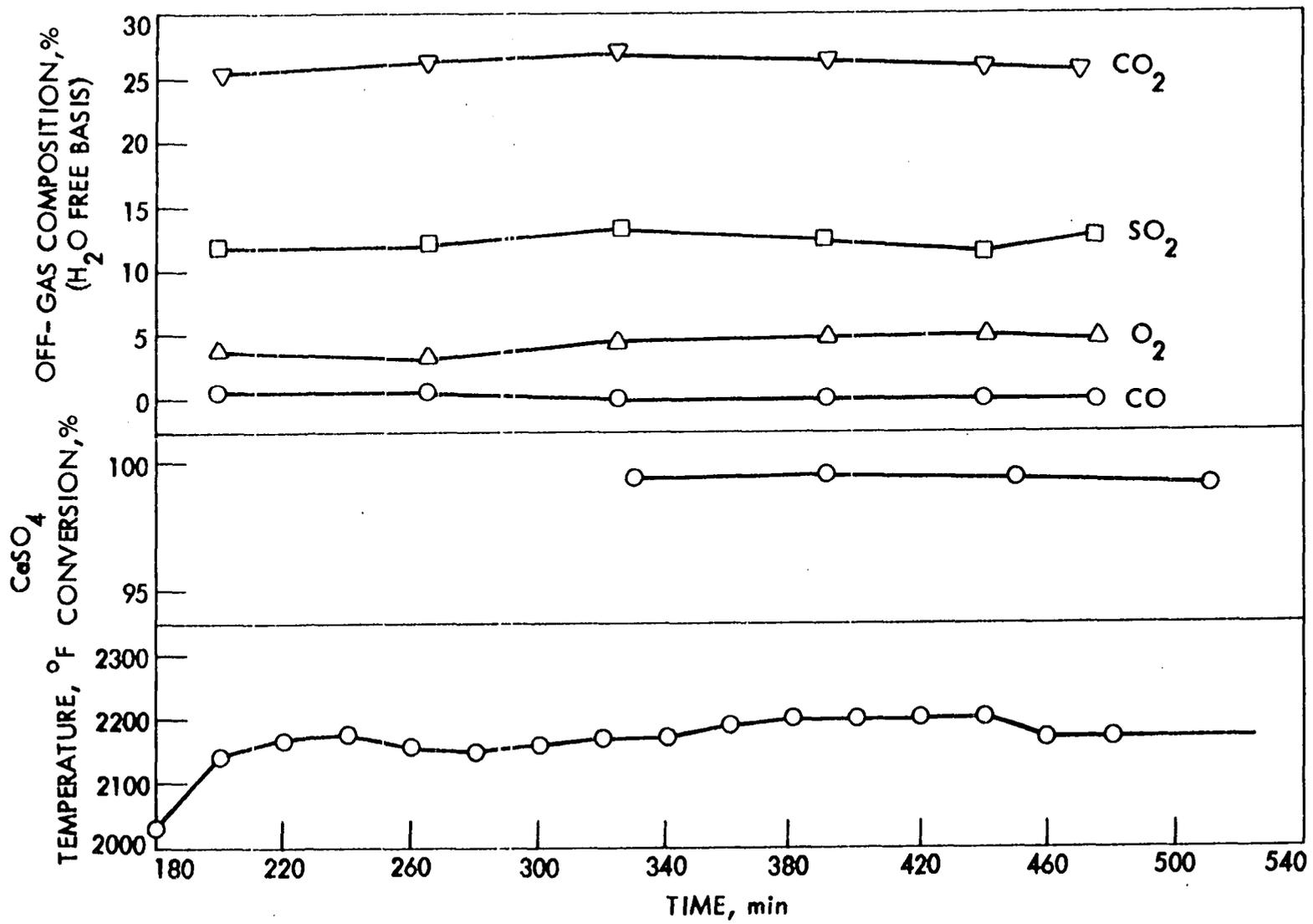
Run: 2-58

Feed: -14+35 mesh anhydrite

Air to natural gas ratio: Primary = 5:1  
Total = 10.7:1

Solid feed rate: 39.3 gm./min.

Bed height: 10 in.



The results obtained using the multiple zone reactor were very encouraging and strongly support the theory of the two zone reactor as a means of controlling calcium sulfide over a wide range of operating conditions. The experimental observations of a typical run are presented in Figure 15. Over the range of operating variables listed in Table 10, conversions in the overflow from the reactor ranged from 45.0 to 99.3 per cent while desulfurizations ranged from 44.7 to 99.2 per cent. With the exception of one run which exhibited 2.5 per cent calcium sulfide in the overflow and another containing 0.9 per cent, the amount of calcium sulfide ranged between 0 and 0.5 per cent.

A brief summary of the conditions and results for several of the decomposition experiments are presented in Table 11 for discussion and evaluation. A complete description of the conditions and results for all the experiments made using anhydrite and gypsum are presented in Tables 16 and 17 respectively in Appendix A.

Examination of the overflow analyses for the selected experiments summarized in Table 11 illustrates the apparent independence of the various operating conditions on the amount of calcium sulfide in the overflow. Examination of the analyses for the elutriated fines does suggest, however, that the total equivalent air to natural gas ratio should be kept fairly oxidizing to prevent excessive amounts of

Table 11. Conditions and results of selected decomposition experiments

Run No.	Temp. °F	Solids fed and rate gm./min.	Bed depth in.	Equivalent ratio air: natural gas		Off-gas analysis	
				Primary	Total	SO <sub>2</sub> , %	O <sub>2</sub> , % <sup>a</sup>
1-268	2150	gypsum 25.0	9	5:1	8.5:1	3.3	1.0
1-274	2020	gypsum 50	9	5:1	8.5:1	5.0	1.0
1-279	1900	anhydrite 50	9	5:1	8.5:1	8.6	2.0
1-298	2250	anhydrite 32.5	10	5:1	8.9:1	6.5	1.0
2-35	2000	anhydrite 44.6	10	5:1	10.4:1	8.5	4.6
2-42	1925	anhydrite 44.6	10	5.1:1	10.6:1	5	9.2
2-49	2190	anhydrite 39.5	11	4.8:1	10.5:1	8	4.0
2-83	2250	anhydrite 31.2	14	4.7:1	10.1:1	7.0	4.5
2-98	2200	gypsum 31.6	10	5:1	10:1	5.2	4.0

<sup>a</sup>Also includes argon present in the air fed to the reactor.

Solids Analysis					
Overflow		Elutriated fines			
CaSO <sub>4</sub>	Conv., %	CaS, %	CaSO <sub>4</sub>	Conv., %	CaS, %
	98.4	0.1	83.4		5.3
	97.2	2.6	72.9		12.0
	93.1	0.0	72.0		4.2
	98.6	0.0	85.0		9.2
	79.9	0.0	40.0		1.0
	45.0	0.2	22.0		0.3
	98.8	0.1	84.0		1.9
	99.2	0.2	80.0		1.8
	99.1	0.4	84.8		2.6

calcium sulfide from occurring in the fines. At the low air to gas ratios between 8.5:1 and 8.9:1 used in runs 1-268, 1-274, 1-279, and 1-298, calcium sulfide in the elutriated fines varied from around 4 to 12 percent. At the higher air to gas ratios of 10.1:1 to 10.6:1 the calcium sulfide levels in the fines drops off considerably to around 1 to 2 percent. This is readily understandable since the higher air to gas ratios resulted in oxygen levels of 4 to 9 percent in the off-gas, ideal for reducing the sulfide content of the fines being elutriated.

Although runs 1-274 and 1-279 appear inconsistent in that the higher temperature run exhibited a higher calcium sulfide formation, the 2.6 percent calcium sulfide in the overflow of run 1-274 suggests that the higher oxidizing air to gas ratios should definitely be used to insure the best results.

Runs 2-35, 2-42, 2-49, and 2-83 demonstrate quite well the ability of the reactor to be operated over a wide temperature range with no apparent adverse affect on the formation of calcium sulfide. Over the temperature range of 1925° to 2250°F, the percent calcium sulfide in the overflow remained between 0 and 0.2 percent.

Comparable results were obtained using either gypsum or anhydrite, although anhydrite did create less of a problem with fines. The fines elutriated during anhydrite

runs represented only about 5 to 10 percent of the solids in the overflow while with gypsum the amount varied from 10 to as high as 41 percent. Since the fines were considerably less converted than the material leaving in the overflow as evidenced in Table 11, it is apparent that recycle or subsequent treatment of the fines would be a necessity, particularly in the case where gypsum is being treated. The relatively poor conversion of the fines is probably due to a much shorter residence time in the reactor.

Reactor model        Since the vast majority of the experiments were made using anhydrite as a feed, an attempt was made to see if some fairly simple model could be used to predict the performance of the reactor in terms of the conversion of calcium sulfate. Since the amount of calcium sulfide formed was minimal, it was felt that it could safely be ignored in the modelling effort.

Initially attempts were made to simply express the conversion of the anhydrite as a linear function of the indirectly controlled variables of operation as listed in Table 10. These variables were selected for the correlation since a similar set of variables had been used with some degree of success to model the Kent Feeds' pilot plant reactor. In the attempt to correlate the data, a linear regression of conversion was made against the different operating variables. From the analysis of variance for

each variable tested, only temperature was found to be significant at the rather poor confidence level of 0.25.

There are several possible explanations for the inability to obtain a good correlation. Perhaps the most obvious of these is the observation that generally very high conversions were obtained in most of the runs made. Therefore, even quite small errors in the analytical results could account for the poor correlations.

Another point which should be raised is the problem of temperature gradients within a fluidized bed which were observed from time to time during the operation of the reactor. This undoubtedly introduced considerable error into the nominal temperature value used in the correlation. While the temperatures recorded as nominal values were those values observed in the bed near the level at which the secondary air was introduced, it may be that under certain conditions this value did not give a true indication of the controlling bed temperature.

To illustrate this problem more clearly, the vertical temperature profile made during a single run of the investigation is presented in Figure 16. In this instance the nominal temperature for correlation was taken as 2250°F. It should be pointed out, however, that most of the reduction may have taken place in the lower 2 in. of the bed where the temperature was well below 2250°F. Unfortunately, temperature profiles were not obtained for all the runs

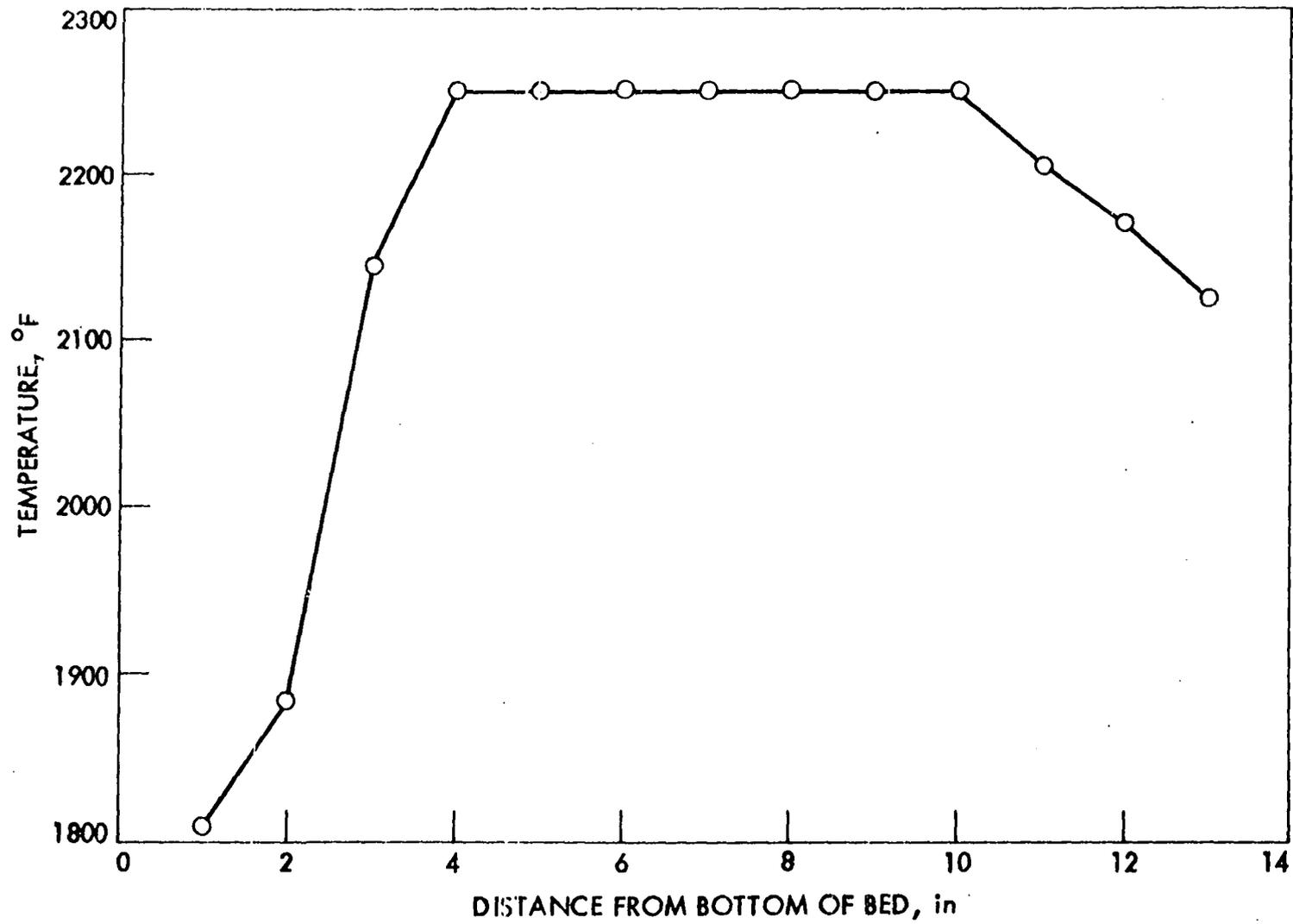


Figure 16. Vertical temperature profile observed during run 2-83

which could have resulted in a serious error in some cases.

Since linear regression offered no insight into the effects of different operating variables on the performance of the reactor, another approach was taken. The results were analyzed by employing the Levenspiel models (25, 26, 49) for gas-solid reactions. The details of the continuous reaction and shrinking core models have been discussed above in connection with the kinetics of calcium sulfide oxidation and will not be repeated here. It is sufficient to point out that the models proposed by Levenspiel suggest that the only factors influencing the conversion of the solids in a fluidized bed are the temperature, the concentration of the reactant gas, and the residence time of the solids in the reactor. In order to implement these models, it was necessary to make the following assumptions:

1. Although several reactions were occurring simultaneously within the reactor, the overall effect from the standpoint of the solids was to convert calcium sulfate to calcium oxide by reaction with methane as expressed by the equation:



The fact that the methane may have been converted to carbon monoxide or hydrogen by partial combustion

before reducing the calcium sulfate is of minor importance since these compounds essentially function as intermediates in the decomposition process.

2. The concentration of the reactant gas can be expressed nominally as the overall concentration of the natural gas in the combined primary and secondary gas lines at the observed temperature in the reactor. Admittedly, this is a very simplified explanation for a rather complex situation, but this value does reflect the overall reducing capabilities of the gas stream.

Referring back to Equations 27 through 32 which mathematically express the various models of Levenspiel, it was possible on the basis of the observed conversions obtained and the experimental methane concentrations and solids residence times, to determine values for  $D_e$ ,  $k_s$ , and  $k_r$  for each run by assuming that ash diffusion controlling, shrinking core reaction controlling and continuous reaction models respectively could be applied to the system. In the case of ash diffusion and shrinking core reaction controlling the following values were used for the average particle diameter, particle density, and constant  $b$  which relates the stoichiometric ratio of solid reactant to gaseous reactant in the overall reaction equation:

$$\bar{d}_p = 0.08 \text{ cm.}$$

$$\rho_B = 0.0218 \text{ g.mole CaSO}_4/\text{cm.}^3$$

$$b = 4.0$$

The values of effective diffusivity calculated assuming the ash diffusion controlling model were on the order of  $10^{-5}$  to  $10^{-8}$   $\text{cm.}^2/\text{sec.}$  Kunii and Levenspiel (25) report an effective diffusivity of  $0.08 \text{ cm.}^2/\text{sec.}$  for the oxidation of zinc sulfide at  $900^\circ\text{C.}$  Since the values of effective diffusivity calculated seemed uncommonly low, the diffusion model was rejected.

Values calculated for the reaction rate constants  $k_r$  and  $k_s$  were on the order of  $10^4$  to  $10^6 \text{ cm.}^3/\text{mole.}^3\text{sec.}$  and  $10^0$  to  $10^{-2} \text{ cm./sec.}$  respectively. Since these values compared quite well with values of  $3.5 \times 10^4 \text{ cm.}^3/\text{mole.}^3\text{sec.}$  and  $2 \text{ cm./sec.}$  reported by Kunii and Levenspiel for the same process mentioned above, it was concluded that the process was essentially governed by the rate of reaction.

To further evaluate the two reaction models, the values of  $k_r$  and  $k_s$  obtained above were plotted against the experimental values of temperature for each run. Assuming that  $k_r$  and  $k_s$  obey the Arrhenius rate equation as expressed in Equations 34 and 35, a least squares linear regression fit of the data was made. Figures 17 and 18 graphically illustrate the results of these calculations.

From the analysis of variance for both regressions,

Figure 17. Least squares fit of  $k_r$  as a function of temperature

$$k_r = k_{r0} e^{-\Delta E/RT}, \text{ cm}^3/\text{g.mole.min.}$$

$$\Delta E = 63,400 \text{ cal/g.mole}$$

$$k_{r0} = 2.0 \times 10^{15} \text{ cm}^3/\text{g.mole.min.}$$

$$R = 1.987 \text{ cal/g.mole.}^\circ\text{K}$$

$$T = \text{temperature, } ^\circ\text{K}$$

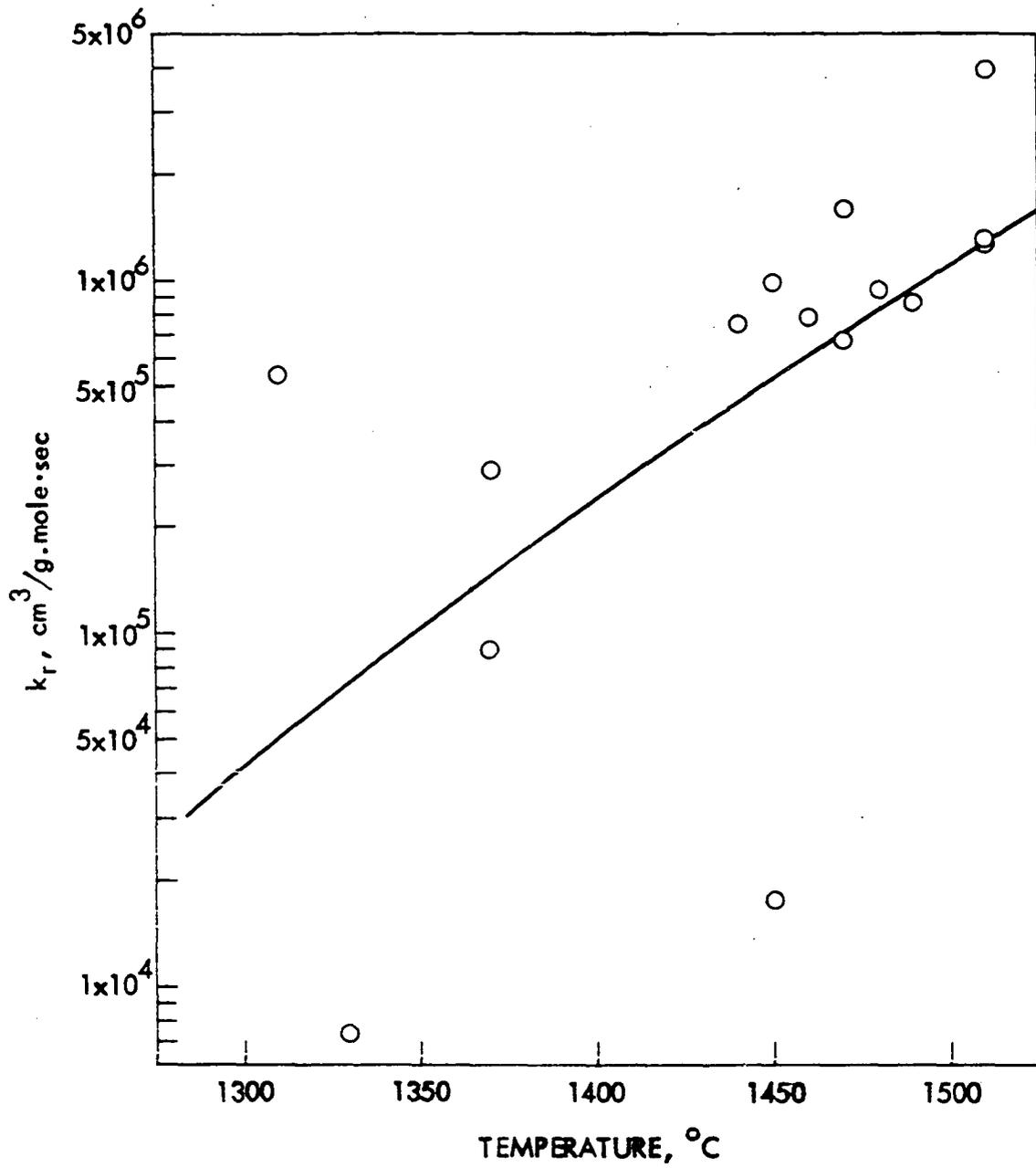


Figure 18. Least squares fit of  $k_s$  as a function of temperature

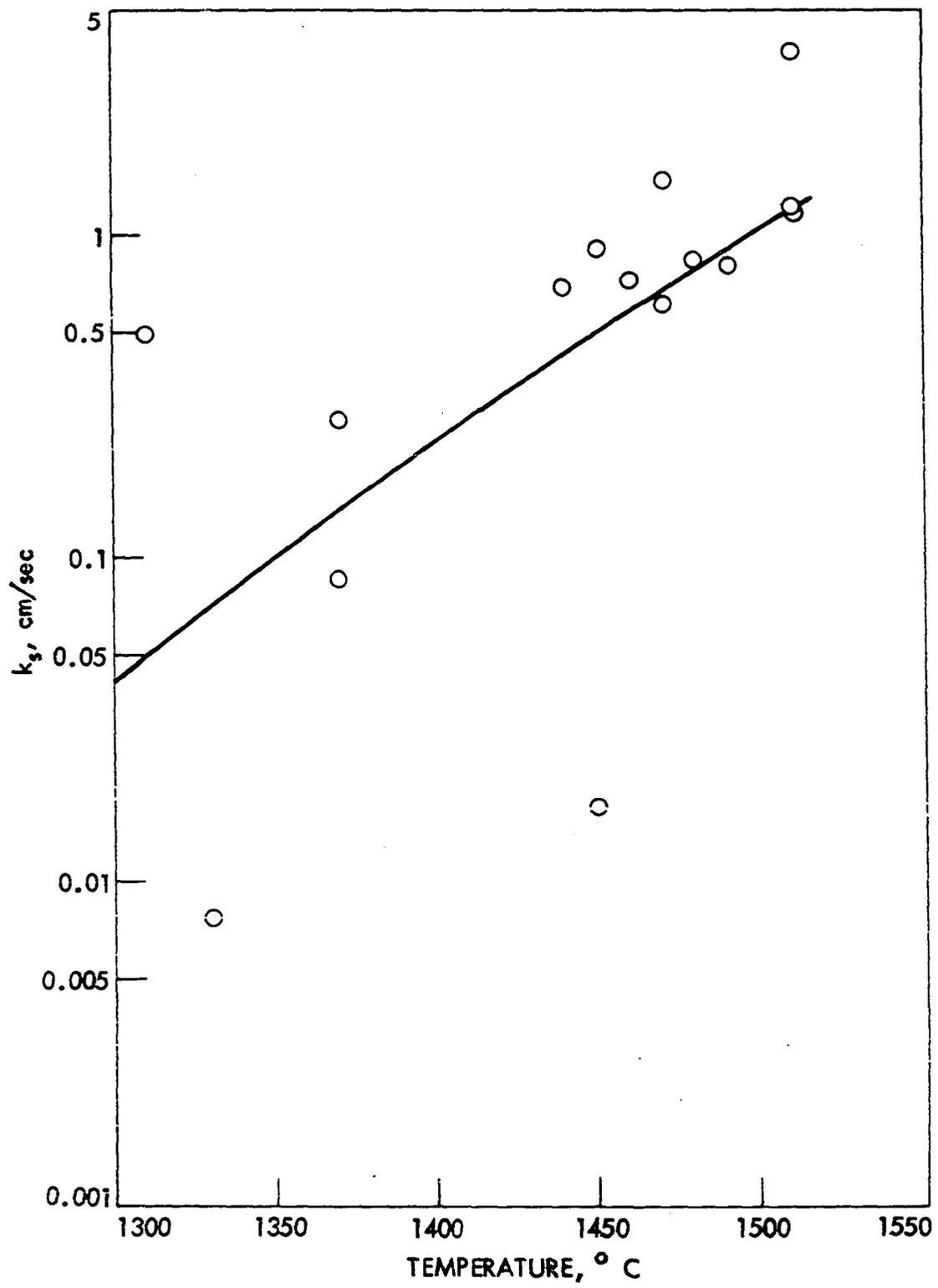
$$k_s = k_{s0} e^{-\Delta E/RT}, \text{ cm/sec.}$$

$$\Delta E = 62,700 \text{ cal/g.mole}$$

$$k_{s0} = 1.32 \times 10^9 \text{ cm/sec.}$$

$$R = 1.987 \text{ cal/g.mole}^\circ\text{K}$$

$$T = \text{temperature, } ^\circ\text{K}$$



the effect of temperature was determined to be significant at the 0.025 level. The correlation coefficients in both cases were a rather poor 0.61 which makes it impossible to favor one model over the other. The considerable scattering of the data in both cases is disappointingly large, but it does tend to further emphasize the probable error involved in the determination of the nominal temperature for each run.

Using the theoretical values of  $k_r$  and  $k_s$  predicted by the linear regression models, theoretical values of conversion were calculated for the different experimental conditions using both models.

A comparison of the predicted results with the experimental results is presented in Table 12. On the basis of the predicted conversions, the results are still inconclusive as to which model might be best used for prediction. The agreement with the experimental conversions is actually quite good considering the scatter in the correlated data. This good agreement is due in part, however, to the fairly high residence times which tend to overpower the value of the rate constants in the theoretical calculations. It is quite conceivable that the models would be considerably less reliable at lower residence times.

It should be mentioned that although the values of  $k_r$ ,  $k_s$ , and  $\Delta E$  were assigned the values of rate constants and

Table 12. Comparison of predicted and experimental conversions

Run No.	Experimental Conversion	Conversion predicted by shrinking core reaction controlling model	Conversion predicted by continuous reaction model
1-279	.931	.550	.561
1-285	.982	.946	.946
1-298	.986	.986	.986
2-21	.983	.963	.963
2-28	.977	.959	.960
2-35	.799	.870	.869
2-42	.450	.894	.891
2-49	.988	.989	.989
2-58	.984	.980	.980
2-63	.988	.987	.987
2-68	.993	.993	.994
2-74	.721	.988	.988
2-78	.973	.950	.949
2-103	.988	.981	.981
2-107	.991	.992	.992

activation energy in the modelling attempts, they are really nothing more than parameters used for correlation. Because of the assumptions made in the analysis it would be foolish to expect these values to apply to a particular reaction.

Instead they serve as pseudo-reaction constants attempting to rationalize a very complicated assemblage of reactions.

Although the modelling attempt was not as successful as might have been hoped, it has been pointed out by Kunii and Levenspiel (25) that even with a good model, the possibility of a change in the controlling mechanism can occur when attempting to extrapolate to new and untried conditions. It is strongly recommended that data always be taken whenever possible at the conditions to be used.

In conclusion, the results of the two zone reactor have been extremely favorable. It would seem that on the basis of the results obtained, such a reactor could be operated over a very wide range of conditions with little or no problem of serious sulfide formation. From the correlations made, it would simply seem that at lower temperatures and hence lower reaction rates a higher residence time will be required to obtain the desired conversion.

DECOMPOSITION OF FINELY DIVIDED  
CALCIUM SULFATE

In some situations, such as with certain by-product gypsums, it may be necessary to carry out the reductive decomposition of very finely divided calcium sulfate. Since powdered gypsum is not very free flowing and is essentially impossible to fluidize even at room temperatures, the possibility of carrying out the reduction in a conventional fluidized bed at high temperatures is almost inconceivable. Consideration was given, therefore, to possible alternative methods of treating calcium sulfate powders. One method proposed was the use of a vibrated fluidized bed to promote fluidization of the powdered gypsum. This method was investigated briefly but was not found satisfactory at high temperatures. The results of the investigation are presented in Appendix B. Another possible solution considered was a dilute fluidized bed where high gas velocities would be used to suspend the particles in a very dilute bed phase with rapid elutriation of the fines in the off-gas. In such an operation it would undoubtedly be necessary to provide for recycle of a significant portion of the fines as they are removed and recovered from the off-gas stream. A third solution considered involved the use of a dense fluidized bed of an

inert coarse material into which very fine gypsum powder would be fed. The fines would continually be elutriated from the coarse bed of material by the relatively high gas fluidization velocities. Recovery of the fines could then be accomplished as before by using a gas-solid separator such as a cyclone.

Of the two methods proposed, the use of an auxiliary bed of coarse material appeared the more promising. A preliminary investigation was conducted, therefore, to test this method for the treatment and desulfurization of finely divided calcium sulfate.

#### Investigation in a 2 in. Reactor

It was proposed to conduct rather small scale experiments initially to form a basis for evaluating the potential of the process. Since the primary interest in desulfurization of fines centers around the possible treatment of certain by-product gypsums, it also seemed advisable to perform some experiments using such a material.

#### Raw materials

The materials selected for investigation were finely divided naturally occurring gypsum and phosphogypsum, a by-product gypsum of the phosphoric acid industry. The phosphogypsum was supplied by the Borden Chemical Company.

As received, the phosphogypsum was quite badly caked and had to be run through a hammer mill to reduce it to a uniform powder. The natural gypsum was also prepared for use in a similar fashion.

The chemical analysis of the phosphogypsum is given in Table 13 along with screen analyses for both the finely divided gypsum and phosphogypsum. The chemical analysis of the gypsum was given previously in Table 8. The analysis of the phosphogypsum suggests that the material is approximately 71 percent calcium sulfate by weight. This compares with the approximately 80 percent calcium sulfate by weight in the natural gypsum.

Table 13. Analyses of phosphogypsum and gypsum

Chemical Analysis of Phosphogypsum <sup>a</sup>		Screen Analyses		
Constituent	Wt %	Size Fraction	Gypsum Wt %	Phosphogypsum Wt %
CaO	31.07	+100	1.4	2.8
SO <sub>3</sub>	41.87			
P <sub>2</sub> O <sub>5</sub>	1.37	-100+150	2.6	5.1
F	0.53			
F <sub>2</sub> O <sub>3</sub>	0.04	-150+200	12.1	28.2
Al <sub>2</sub> O <sub>3</sub>	0.21			
H <sub>2</sub> O	0.66	-200	83.9	63.9
Sinsolubles	6.00			
Total	81.75		100.	100.

<sup>a</sup>Provided by the Borden Chemical Company.

In considering possible materials for use as the coarse bed in the investigation, it was proposed to try using both coarse alumina and gypsum which had been previously reacted and reduced. The gypsum, being the softer of the two, materials would be more subject to undesirable attrition and size reduction than the alumina. The gypsum was also considered less desirable on the basis of the relative chemical inertness of the alumina to possible reactions with the released sulfur. The decision to test gypsum, however, was based on its ready availability and low cost, and the fact that its gradual breakdown in the reactor would not contaminate the fines being treated.

Preliminary investigations revealed that a coarse bed material of -28 +35 mesh was sufficient to allow for good fluidization of the bed and ensure entrainment of the fines in the off-gases from the reactor.

For the sake of simplicity, the reducing gas mixture used contained only carbon monoxide, carbon dioxide and nitrogen. All the gases were drawn from high pressure cylinders with minimum purity levels of 99.5 percent.

### Equipment

The equipment used for this investigation was the same equipment used in the investigation of calcium sulfide oxidation. The process flowsheet and reactor details are illustrated in Figures 7 and 8 respectively. The only

alteration made was to simply raise the off-gas line well above the surface of the fluidized bed to prevent the coarse material from being entrained along with the fines passing through the reactor.

### Procedure

When preparing to make a run, the reactor was placed in the furnace and slowly heated to the desired temperature with the reactor empty. When the reactor was sufficiently hot, the flow of nitrogen to the reactor was initiated and a premeasured amount of coarse gypsum or alumina was pneumatically fed to the reactor. This method of placing the bed in the reactor was necessitated by the cone-shaped distributor which could not support a bed unless gas was flowing through the reactor.

Once the bed was in place, the procedure varied depending on whether gypsum or alumina was being used as the coarse bed material. When gypsum was being used, it was necessary to reduce the gypsum with a gas mixture of 10 percent carbon monoxide, 20 percent carbon dioxide, and 70 percent nitrogen until conversion of the carbon monoxide ceased and no more sulfur dioxide was observed in the off-gas from the reactor. Chemical analysis revealed that this procedure formed a bed material containing approximately 80 percent calcium oxide, 5 percent calcium sulfate and 15 percent calcium sulfide. Although this seemingly presented

a highly undesirable situation, the previous investigation of calcium sulfide formation indicated that even with a bed of pure calcium oxide, sulfide could eventually build up in the bed by reaction with sulfur dioxide released from the fines and carbon monoxide in the feed gas. Experiments were made using this procedure, therefore, to see if the bed composition would seriously affect the results.

Once the bed was in place and the reactor temperature had recovered to the desired value, the gas flow rates were adjusted to the desired reducing gas mixture. A weighed amount of fines was then placed in the feeder and the feeding of fines at a controlled flow rate was begun. As with the coarser material, the fines were pneumatically fed to the reactor with the reducing gas.

Although the rotating disc feeder used was designed for handling fine powders, the flow characteristics of the fine gypsum and phosphogypsum were so poor that it was necessary to add 2 percent by weight of Cab-O-Sil to the powders to make them more free flowing. Even then the feeder could not be relied upon to provide an even flow of fines to the reactor. It was necessary, therefore, to determine the flowrate of solids as an average value based on the amount fed over the time of operation.

As the feeding of fines continued, solid samples were collected periodically from the small glass cyclone in the

off-gas line. Gas samples were also taken periodically to monitor the course of the reaction. Due to the very short retention time of the solids in the reactor, the reactor was essentially operating at steady-state at all times and the runs were made over short intervals. At the completion of a run the flow of reducing gases and fines to the reactor was discontinued. The nitrogen flow was maintained to prevent the hot bed from draining out the bottom of the reactor. Power to the furnace was discontinued, and the solid bed residue drained as soon as possible to conserve nitrogen.

The solid samples were subsequently analyzed and the results were based on the degree of conversion and desulfurization which the fines had undergone.

### Results

In general, the results obtained were not extremely encouraging. It was felt, however, that possible inefficiencies relating to the cone distributor were largely responsible for some of the poor results obtained. As might be expected, the flow of solids in a reactor equipped with a conical distributor is considered to be up in the center of the bed and down at the walls. Poor gas distribution also results in a relatively high gas velocity in the center of the bed as compared to the velocity in the annular

region of the fluidized bed. This combination of flow patterns in the fluidized bed may have resulted in the fines simply passing up through the center of the bed and being elutriated from the bed with little or no back mixing with the coarser material. Perhaps if the fines had been introduced at the wall where the flow of coarse material is generally downward and the gas velocities are lower, better mixing would have occurred and higher conversions resulted.

In addition to the suspected problems of adequate mixing and contacting was the problem of the fines gradually caking up and causing the bed to defluidize at temperatures very much above 2000°F. This was a particular problem when gypsum was used as the bed of coarse material or phosphogypsum was the material being fed to the reactor. Since the conversion of fines is undoubtedly controlled by the rate of chemical reaction, higher temperatures would be necessary to produce high conversions because of the short residence time of the fines in the reactor. Also since the formation of calcium sulfide in fine particles has been suggested previously as being determined by equilibrium considerations, higher temperatures seem a must if sulfide formation is to be controlled.

In terms of the bed material, the alumina proved to be far superior. The gypsum particles underwent considerable attrition during even the short runs which made analysis of

the fines recovered overhead during an experiment virtually impossible. The alumina, however, underwent no perceptible size change and recovery of the bed charge was essentially 100 percent at the end of a run.

The actual operating conditions and results of the runs successfully completed are detailed in Table 18 of Appendix A. Five of the more successful runs are summarized and presented in Table 14 for comparison and evaluation.

Considering the apparent shortcomings of the fluidized bed design, the results given in Table 14 do contain some measure of promise. At the lower level of carbon monoxide concentration, the degree of conversion and the relative amount of calcium sulfide formed increased considerably with the increasing ratio of carbon monoxide to calcium sulfate. The low temperature of run 1-209 also appears to be responsible for the high sulfide formation encountered in that experiment. The results of the runs at the higher level of carbon monoxide are consistent with those of the low level runs except that considerably more calcium sulfide was produced.

Unfortunately, accurate determination of the hold-up time of the fines in the reactor could not be made. Estimates made by dividing the weight of fines elutriated from the bed after the feeding of fines had been discontinued, by the fines feed rate suggested hold-ups of from 1 to 3 min.

Table 14. Summary of selected experiments in the decomposition of fines<sup>a</sup>

Run No.	Fines Fed and Rate, gm./min.	Gas Flow, SCFM	Gas Composition %			Mole Ratio $\frac{\text{CO}}{\text{CaSO}_4}$	Fines Conv. & Desulf. %	Fines Chemical Analysis	SO <sub>2</sub> in off-gas %	Temp. Range °F
			CO	CO <sub>2</sub>	N <sub>2</sub>					
1-191	Gyp. 2.9	0.24	5	20	75	0.91:1	68 63	CaSO <sub>4</sub> 53% CaO 38% CaS 4% Res. 5%	3.9	2125- 2120
1-194	Gyp. 5.3	0.24	10	20	70	0.97:1	72 62	CaSO <sub>4</sub> 45% CaO 40% CaS 8% Res. 7%	6.3	2120- 2095
1-197	Gyp. 5.0	0.24	5	20	75	0.52:1	36 32	CaSO <sub>4</sub> 79% CaO 16% CaS 2% Res. 3%	4.1	2090- 2067
1-199	Gyp. 2.9	0.24	10	20	70	1.75:1	84 69	CaSO <sub>4</sub> 30% CaO 55% CaS 15% Res. -	3.5	2156- 2150
1-209	Phospho. 3.9	0.40	5	20	75	1.24:1	88 67	CaSO <sub>4</sub> 21% CaO 46% CaS 18% Res. 15%	1.8	1960- 1923

<sup>a</sup>Runs 1-191, 1-194, 1-197 and 1-199 used 8 inch alumina beds; 1-205 a 6 inch alumina bed.

In view of this, the 84 and 88 percent conversions obtained in runs 1-199 and 1-205 respectively are quite impressive. The big problem, however, still seems to be the degree to which calcium sulfide is formed. In run 1-101, for example, 4 percent calcium sulfide was present in the residue after only 68 percent conversion of the calcium sulfate. The low 5 percent level of carbon monoxide, high temperature, and low ratio of reducing gas to solid reactant in the run were not sufficient to prevent the calcium sulfide formation.

It seemed, therefore, that to obtain high conversions and low amounts of sulfide, it would first be necessary to increase the residence time of the fines in the reactor or provide for recycle of the fines. Secondly, it seemed apparent that some provision would have to be made for oxidation of the calcium sulfide. Since the concept of the two-zone reactor was so successful in treating coarser gypsum particles, attempts were made to adapt the reactor to the treatment of fines.

#### Investigation in Multiple Zone Reactor

The equipment and reactor used for the investigation were essentially the same as that used in the original investigation of the multiple zone reactor and illustrated in Figures 11 and 12. Several problems were encountered

with the equipment, however, in the feeding and recovery of large amounts of finely divided material which severely limited the investigation. The design of the reactor itself was not suited to the investigation since the large expansion section at the top of the reactor served to prevent elutriation of the fines from the bed. During an investigation, most of the fines fed would settle out and accumulate in the upper section of the reactor making evaluation of the results virtually impossible. Since time did not allow for solutions to be found to all of the problems encountered, no truly quantitative results are available. On the basis of what was accomplished, however, some qualitative judgments can be made concerning the advisability of pursuing the investigation further.

#### Raw materials

Due to the caking problems encountered with phosphogypsum in the investigation above, all the attempted runs were made with anhydrite fines. In general the fines were in the -65 +200 mesh size range. The alumina used to form the inert bed was between 14 and 35 mesh in size. As before, the primary gases to the reactor were natural gas, oxygen and air, while the secondary gases consisted of air and oxygen.

### Procedure

Combustion of natural gas was initiated in the reactor as described previously, and the reactor was then brought to temperature over a period of 2 to 3 hr. After the temperature reached 1800°F, placement of the coarse alumina bed in the reactor was begun. This was accomplished by gradually adding small amounts of alumina through the sight port opening at the top of the reactor. It was necessary to pull a slight vacuum in the reactor during this step of the procedure to allow entry of the solids. A total of approximately 4200 gm. of alumina, or enough for a 10 in. fluidized bed, was placed in the reactor. The reactor overflow was blocked off to prevent the loss of alumina from the bed during operation.

With the alumina in place, the gas flows were adjusted and the reactor raised to the desired temperature of operation. Once the desired temperature was obtained, the feeding of fines to the reactor in the secondary gas flow was initiated. As indicated above, the controlled feeding of the fines was a serious problem which was not completely solved and which prevented quantitative results from being obtained. In all, three different methods of feeding the fines were attempted with equally disappointing results. First, attempts were made to use the screw feeder which had been used quite successfully with the coarser material.

The finer anhydrite, however, would bridge in the hopper above the screw feeder section and the flow of fines would be interrupted. A vibrator attached to the feeder was not sufficient to prevent the bridging from occurring so an alternative method of feeding the fines was investigated.

The second feeder involved the use of an auxiliary fluidized bed of the anhydrite fines in an effort to keep the fines free flowing. A rotating valve in a side exit from the fluidized bed of fines discharged the feed into the secondary gas flow entering the reactor. The discharge of the fines from the valve, however, was very irregular and would frequently fail to discharge entirely again making it impossible to interpret the results quantitatively.

The third feeding method involved the use of a small vibrating commercial Plasmatron feeder designed for the pneumatic feeding of powders. The feeder consisted of a small hopper which discharged the solids in the gas stream flowing through the bottom of the conical base of the hopper. The hopper was mounted on a vibrator which could be varied in intensity. Although this feeder performed significantly better than the first two feeders which were tested, it did not provide a steady, uniform flow of solids either. In fact, the variations in flow as the hopper emptied were quite drastic again making a calibrated flow of solids impossible. The small hopper, holding only 1500

gm. of fines, was rapidly depleted creating additional interruptions in the flow as the feeder had to be recharged.

In addition to the problem of feeding the fines, the recovery of the reacted fines was also a problem. As pointed out previously, the expanded free board section in the upper part of the reactor prevented the elutriation of a significant portion of the reacted material. That portion which was not retained tended to plug the off-gas lines and cyclones causing the pressure in the reactor to become excessive and in many instances forced a termination of the experiments.

In most of the runs, however, it was possible to obtain a few samples of reacted fines from the cyclones before the run had to be terminated. These samples were analyzed to obtain at least a qualitative measure of the effectiveness of the two zone reactor.

When shutting down the reactor, the solid and gas flows were discontinued and the reactor allowed to cool.

### Results

Although very incomplete, the data and results of the runs attempted are presented in Table 19 of Appendix A. It is interesting to note that the highest conversion obtained for any run was only 66 percent as compared to values of 84 and 88 percent obtained in the smaller reactor. The

most significant observation, however, is the relatively small amount of calcium sulfide in the fines compared to the values obtained with the smaller single zone reactor. In general, the sulfide values were around 1.0 percent calcium sulfide or less which indicates that perhaps the two-zone reactor had a favorable effect on suppressing sulfide formation. Compared to the less than 0.5 percent calcium sulfide at 98 and 99 percent conversions observed with the coarser material, the results are somewhat discouraging. For the most part, the conversions were also significantly lower than the conversions observed in the fines elutriated during treatment of coarse gypsum and anhydrite indicating a significantly shorter residence time.

Although the results are too inconclusive to make a sound evaluation of the method for the treatment of finely divided calcium sulfate, the results do seem favorable enough to warrant further investigation as soon as some of the mechanical problems of handling the material can be cleared up. The success of the two-zone reactor in the desulfurization of the coarser calcium sulfate is in itself sufficient reason to investigate its potential even further.

## CONCLUSIONS

Conclusions drawn from the results of the experimental investigation can be summarized as follows:

1. Calcium sulfide formation is a very fast reaction and is controlled by equilibrium considerations.
2. Larger particles of calcium sulfate exhibit less sulfide formation than smaller particles during reductive decomposition because of the increased resistance to mass transport by diffusion in the larger particles. The lower reducing gas concentrations in the interior of the larger particle shift the equilibrium in favor of increased calcium oxide formation.
3. Calcium sulfide formed during the reductive decomposition process can be eliminated by oxidation in a fluidized bed to give a mixture of calcium oxide and calcium sulfate.
4. Calcium oxide formation is favored in the oxidation process by an oxygen to calcium sulfide mole ratio of 1.5:1, which is the theoretical stoichiometric ratio required for complete conversion to calcium oxide. Calcium oxide is also favored at temperatures of 2100°F or above. Although not established experimentally, equilibrium considerations suggest a 5 to 10 percent oxygen concentra-

tion to minimize calcium sulfate formation.

5. The decomposition of coarse calcium sulfate is readily accomplished in a multiple zone reactor consisting of reducing and oxidizing zones. Over the range of conditions tested, the amount of calcium sulfide formed was generally less than 0.5 percent.
6. The successful operation of the two zone reactor is very insensitive to operating conditions.
7. Conversion and desulfurization of the calcium sulfate appeared to be limited only by the residence time of the solids in the reactor. The required residence time for high conversions appeared to be a strong function of temperature indicating a reaction controlling mechanism for the overall process of reduction and oxidation.
8. The multiple zone reactor also contributed to low sulfide levels in the fines elutriated from the reactor. This was attributed to the presence of oxygen in the off-gas from the reactor as a result of the secondary air line.
9. The use of an auxiliary bed of a coarse inert material offers a potential method for the desulfurization of finely divided calcium sulfate, but considerably more work needs to be done in this area.

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APPENDIX A: TABLES OF DATA

Table 15. Conditions and results of multiple zone reactor batch experiments

Run No.	Purpose	Equivalent Ratios		Total Gas	Natural Gas	Solids Fed
		Air: Natural Gas Primary		Flow SCFM	Flow SCFM	gm.
1-243	To test reactor for overall operation	6:1	10:1	2.75- 3.50	0.33- 0.43	~3100 anhydrite
1-247	Increase operating temperature	4:1- 5:1	95:1	2.50- 2.90	0.43	4000
1-251	Increase methane flow-increase temperature	5:1	10:1- 8:1	3.00	0.35- 0.45	3000
1-256	Lower dipleg-use larger particle size to prevent caking	5:1	8.5:1	3.0- 3.6	0.56- 0.37	3000
1-261	Larger screw feeder to handle solids	5:1	8.5:1	3.0	0.49	3100
1-265	Clear-up problems with solids feeding	5:1	8.5:1	2.5	0.52	2700

Time Elapsed During Feeding min.	Total Elapsed Time min.	Temp °F	Dip Leg from bottom in.	Bed Analyses				Comments
				Top		Bottom		
				X%	D%	X%	D%	
190	190		6	64.7	61.5	76.9	71.7	Feed line plug. Low temps. Caking in bed
133	310	1720- 1970	6	38.0	37.7	64.2	64.1	Off-gas lines plug. w/fines Low temps.
100	260	1750- 2200	5	93.2	92.6	98.1	87.2	Some caking around dipleg
150	240	1850- 2250	1	97.1	96.9	98.2	97.6	Feed was too big for disc feeder
50	240	1550- 2200	1	98.0	97.8	99.0	98.1	Solids feed line plugged several times
90	285	1400- 2100	1	98.0	97.4	98.7	98.1	Operation pro- ceeded smoothly

Table 16. Conditions and results of multiple zone reactor investigations using anhydrite

Run	Nominal Temp. °F	Natural Gas Flow SCFM	Air: CH <sub>4</sub>		Total Gas Flow SCFM	Superficial Velocity ft/sec.	Solid Feed Rate gm/min.	CH <sub>4</sub> : CaSO <sub>4</sub> mole ratio
			Primary	Total				
1-279	1900	0.66	5:1	8.5:1	3.92	2.5	50	2.27
1-285	2250	0.67	5:1	8.7:1	3.98	3.0	40	2.88
1-298	2250	0.60	5:1	8.9:1	3.46	2.58	32.5	3.18
2-14	2200	0.60	5:1	10:1	3.74	2.74	32.5	3.18
2-21	2180	0.60	5:1	10:1	3.74	2.72	32.5	3.18
2-28	2150	0.60	5:1	10:1	3.74	2.68	32.5	3.18
2-35	2000	0.54	5:1	10.4:1	3.35	2.27	44.6	2.08
2-42	1925	0.51	5.1:1	10.6:1	3.37	2.21	42.0	2.08
2-49	2190	0.54	4.8:1	10.5:1	3.12	2.29	39.5	2.35
2-58	2175	0.54	5:1	10.7:1	3.35	2.43	39.2	2.36

Table 16 (Continued)

Run	$\bar{t}$ min.	Bed height in.	Dipleg from bottom in.	Amount of fines % overflow	Overflow		Fines		Off-gas Comp.	
					X%	D%	X%	D%	$\frac{SO_2}{\%}$	$\frac{O_2}{\%}$
1-279	16	9	1	~0.1	93.1 CaS=0.0%	93.1	72 CaS=4.2%	67	8.6	2
1-285	10	9	1	~5	98.2 CaS=0.5%	97.7	82 CaS=10.4%	71	7.5	1
1-298	38	10	1	~5	98.6 CaS=0.0%	98.6	85 CaS=9.2%	75	6.5	1
2-14	-	10	1	neg.	98.1 CaS=0.0%	98.1	52 CaS=3.0%	48	8.5	4
2-21	27	10	1	~5	98.3 CaS=0.0%	98.3	80 CaS=2.0%	76	7.5	6
2-28	32	10	1	~6	97.7 CaS=0.1%	97.7	76 CaS=1.2%	75	8.0	6.7
2-35	31	10	1	12	79.9 CaS=0.0%	79.9	40 CaS=1.0%	39	8.5	4.6
2-42	80	11	1	11	45.0 CaS=0.2%	44.7	22 CaS=0.3%	21.7	5	9.2
2-49	85	10	1	3	98.8 CaS=0.1%	98.7	84 CaS=1.9%	82	8	4.0
2-58	58	10	1	4	98.4 CaS=0.2%	98.3	80 CaS=0.9%	79.1	10	5.0

Table 16 (Continued)

Run	Nominal Temp. °F	Natural Gas Flow SCFM	Air: CH <sub>4</sub>		Total Gas Flow SCFM	Superficial Velocity ft/sec.	Solid Feed Rate gm/min.	CH <sub>4</sub> : CaSO <sub>4</sub> mole ratio
			Primary	Total				
2-63	2200	0.56	5.3:1	10.5:1	3.53	2.58	31.3	3.16
2-68	2250	0.56	5.4:1	10.7:1	3.64	2.71	31.3	3.08
2-74	2150	0.54	5:1	10.4:1	3.35	2.41	34.3	2.71
2-78	2000	0.54	5:1	10.4:1	3.35	2.26	35.0	2.66
2-83	2250	0.58	4.7:1	10.1:1	3.39	2.53	31.2	3.17
2-103	2130	0.61	4.4:1	9.5:1	3.42	2.44	36.9	2.84
2-107	2225	0.61	4.4:1	9.5:1	3.42	2.53	36.9	2.84

Table 16 (Continued)

Run	$\bar{t}$ min.	Bed height in.	Dipleg from bottom in.	Amount of fines % overflow	Overflow		Fines		Off-gas Comp.	
					X%	D%	X%	D%	SO <sub>2</sub> %	O <sub>2</sub> %
2-63	71	10	3	10	98.8	98.8	77	74.6	6	4.5
					CaS=0.1%		CaS=2.4%			
2-68	87	10	1	11	99.3	99.2	73	73.7	6.0	6.5
					CaS=0.1%		CaS=1.2%			
2-74	108	14	7	7	72.1	71.9	40.0	39.6	5	7.0
					CaS=0.2%		CaS=0.4%			
2-78	86	14	7	10	97.3	97.0	54.0	48.9	8	9.0
					CaS=0.4%		CaS=3.8%			
2-83	90	14	7	8	99.2	99.0	80.0	78.4	7	4.5
					CaS=0.2%		CaS=1.8%			
2-103	73	10	4	7	98.8	98.8	69.0	67.4	7.5	5.3
					CaS=0.1%		CaS=1.5%			
2-107	86	10	4	9	99.1	98.4	80.1	78.0	7.5	6.0
					CaS=0.9%		CaS=1.9%			

Table 17. Condition and results of multiple zone reactor investigations using gypsum

Run No.	Nominal Temp. °F	Natural Gas Flow SCFM	Air: CH <sub>4</sub>		Total Gas Flow SCFM	Superficial Velocity ft/sec.	Solid Feed Rate gm/min.	CH <sub>4</sub> : CaSO <sub>4</sub> mole ratio
			Primary	Total				
1-268	2150	0.52	5:1	8.5:1	2.90	2.08	25	4.53
1-274	2020	0.67	5:1	50	3.91	2.67	50	2.92
2-89	2250	0.58	4.7:1	10:1	3.39	2.52	34.3	3.73
2-94	2080	0.61	4.2:1	10:1	3.49	2.44	16.9	7.85
2-98	2200	0.64	4.2:1	10:1	3.84	2.81	31.6	4.39

Table 17 (Continued)

Run	Residence Time min.	Bed depth in.	Dipleg from Bottom of Bed in.	Fines % of overflow	Overflow		Fines		SO <sub>2</sub> In Off-gas %	O <sub>2</sub> In Off-gas %
					X%	D%	X%	D%		
1-268	45	9	1	9	98.4 CaS=0.1%	98.4	83.4 CaS=5.3%	78.0	3.3	1.0
1-274	22	9	1	41	97.2 CaS=2.6%	94.9	72.9 CaS=12.0%	59.1	5.0	1.0
2-89	71	10	1	17	96.2 CaS=0.1%	96.2	78.2 CaS=2.1%	76.0	5.5	4.5
2-94	142	10	1	30	98.8 CaS=0.0%	98.8	75.4 CaS=1.6%	73.6	5.0	7.3
2-98	82	10	1	28	99.1 CaS=0.4%	98.7	84.8 CaS=2.6%	81.4	5.2	4.0

Table 18. Conditions and results of decomposing finely divided calcium sulfate

Run No.	Temp. Range °F	Course Material Initially	Course Material Finally	Gas Feed SCFM	Gas Composition %			Gas Velocity ft/sec.	Fines Fed
					CO	CO <sub>2</sub>	N <sub>2</sub>		
1-173	2140-2000	300g. -32 +35 gypsum	50g. 7.5% CaS 4.7% CaSO <sub>4</sub> 79.2% CaO <sup>4</sup>	0.36	5	20	75	1.45-1.37	gypsum
1-176	1995-1980	300g. -32 +35 gypsum	55g. 11.8% CaS 6.0% CaSO <sub>4</sub> 74.4% CaO <sup>4</sup>	0.36	5	20	75	1.37-1.36	gypsum
1-178	1930-1885	500g. -32 +35 gypsum	112g. 10.7% CaS 11.5% CaSO <sub>4</sub> 71.5% CaO <sup>4</sup>	0.36	5	20	75	1.33-1.31	gypsum
1-81	2110-2135	none Comment: Fines caked in reactor	none	0.36	5	20	75	1.43-1.44	gypsum
1-83	1995-2060	none Comment: Fines again caked in reactor	none	0.42	5	20	75	1.60-1.64	gypsum
1-85	1955-1940	400g. -14 +32 gypsum	97g. 14.0% CaS 31.4% CaSO <sub>4</sub> 46.6% CaO <sup>4</sup>	0.36	10	20	70	1.34	gypsum

Table 18 (Continued)

Run No.	Fines Feed Rate gm/min.	Fines Conversion %	Fines Desulfurization %	CaS Amount %	Ratio Conversion to Desulfurization	SO <sub>2</sub> in off-gas %
1-173	4	~57	~52	4.6	1.10	2.3
1-176	4	~40	~36	2.5	1.11	2.2
1-178	4	~46	~42	2.2	1.10	2.2
1-81	4	~ 6	~ 5	0.3	1.20	2.0
1-83	4.4	~ 6	~ 3	1.5	2.0	1.4
1-85	7.2	~24	~20	2.6	1.2	1.5

Table 18 (Continued)

Run No.	Temp. Range °F	Course Material Initially	Course Material Finally	Gas Feed SCFM	Gas Composition %			Gas Velocity ft/sec.	Fines Fed
					CO	CO <sub>2</sub>	N <sub>2</sub>		
1-187	2070-1905	400g. gypsum	75g. 31.2% CaS 20.5% CaSO <sub>4</sub> 41.6% CaO	0.40	10	20	70	1.61-1.51	gypsum
1-189	-	600g. alumina	600g.	0.36	10	20	70	-	gypsum
1-191	2125-2120	800g. alumina	803g.	0.24	5	20	70	0.96	gypsum
1-194	2120-2095	800g. alumina	792g.	0.24	10	20	70	0.96-0.95	gypsum
1-197	2090-1990	800g. alumina	794g.	0.24	5	20	75	0.95-0.91	gypsum
1-199	2150	800g. alumina	793g.	0.24	10	20	70	0.97	gypsum

Table 18 (Continued)

Run No.	Fines Feed Rate gm/min.	Fines Conversion %	Fines Desulfurization %	CaS Amount %	Ratio Conversion to Desulfurization	SO <sub>2</sub> in off-gas %
1-187	8.3	~23	~18	2.3	1.28	-
1-189	8.5	~50	~42	5.2	1.19	3.8
1-191	2.9	~68	~63	1.9	1.08	3.9
1-194	5.3	~72	~62	7.8	1.16	6.3
1-197	5.0	~36	~32	2.1	1.13	4.1
1-199	2.9	~84	~69	15.2	1.22	3.3

Tables 18 (Continued)

Run No.	Temp. Range °F	Course Material Initially	Course Material Finally	Gas Feed SCFM	Gas Composition %			Gas Velocity ft/sec.	Fines Fed
					CO	CO <sub>2</sub>	N <sub>2</sub>		
1-203	1560-1575	600g. alumina	~600g.	0.36	5	20	75	1.13-1.14	Phospho-gypsum
1-205	1825-1845	600g. alumina	~600g.	0.36	5	20	75	1.29	Phospho-gypsum
1-207	~2020	600g. alumina	~600g.	0.36	5	20	75	1.39	Phospho-gypsum
1-209	1923-1960	600g. alumina	~609g.	0.40	5	20	75	1.48-1.50	Phospho-gypsum
1-166	2100-2035	200g. -32 +35 gypsum	~45g. 17.4% CaS 6.1% CaSO <sub>4</sub> 70.1% CaO <sup>4</sup>	0.36	5	20	75	1.43-1.39	gypsum

Table 18 (Continued)

Run No.	Fines Feed Rate gm/min.	Fines Conversion %	Fines Desulfurization %	CaS Amount %	Ratio Conversion to Desulfurization	SO <sub>2</sub> in off-gas %
I-203	6.5	6	6	0	1.00	0.1
1-205	3.1	35	30	2.5	1.17	1.4
1-207	4.4	53	51	3.0	1.04	3.3
1-209	3.9	88	67	18.3	1.31	2.0
1-166	3.9	53	48	3.7	1.10	1.9

Table 19. Conditions and results of decomposing fines in the multiple zone reactor

Run No.	Nominal Temp. °F	Gas Flow		Gas Velocity ft/sec.	Air: Natural Gas	
		N. Gas	Total SCFM		Primary	Total
2-114	-	-	-	-	-	-
2-117	1800-1850	0.61	3.42	2.15	4.4:1	10:1
2-122	2190-2235	0.64	5.10	3.68	5.8:1	10.5:1
2-126	2100-2200	0.54	3.88	2.78	6.1:1	10.2:1
2-131	2000-2250	0.73	4.97	3.54	5.6:1	10.2:1
2-136	2100-2200	0.60	4.78	3.43	6:1	10.5:1
2-149	-	0.60	-	-	6:1	9.6:1
2-150	-	0.60	-	-	6:1	9.6:1
2-151	-	0.60	-	-	6:1	9.6:1

Run No.	Solid Feed Rate gm/min.	Mole Ratio CH <sub>4</sub> : CaSO <sub>4</sub>	Fines		CaS %	O <sub>2</sub> in Off-gas
			Conv. X	Desul. D		
2-114	-	-	58	57	0.5	-
2-117	~8	~13:1	64	63	1.1	-
2-122	-	-	56	55	0.5	4.5%
2-126	-	-	51	48	2.1	2.9%
2-131	~20	~6.3:1	66	64	1.6	3.3%
2-136	-	-	40	40	0.3	5.0%
2-149	~20	~5.2:1	52	51	0.8	-
2-150	~38	~2.7:1	44	43	0.8	-
2-151	~26	~4.0:1	27	26	0.7	-

## APPENDIX B: SUPPORTING INVESTIGATIONS

## Fluidization of Finely Divided Calcium Sulfate in a Vibrated Bed

The fluidization of finely divided calcium sulfate in a vibrated bed was investigated as a possible means for carrying out the reductive decomposition of such material. The fluidization of very fine particle size calcium sulfate was impossible in a conventional fluidized bed because of the tendency for the bed to channel or rathole badly. It seemed logical, however, that energy of vibration could induce sufficient motion of the particles to maintain fluidization and prevent channeling from occurring. It also seemed that the additional energy added by the vibration could substantially reduce the minimum fluidization velocity of the fines thereby permitting lower gas flow rates to be used. If so, the possibility of achieving thermodynamic equilibrium in the reactor would be increased.

Room temperature experiments

Initially, fluidization experiments were carried out at room temperature to examine the effect of vibration on the fluidization of finely divided calcium sulfate.

Equipment      The tests were made in Plexiglas columns having inside diameters of 0.95 and 2.0 in. The columns were transparent so that the effect of vibration on the

behavior of the gypsum particles during fluidization could be readily observed. The columns were equipped with canvas bed supports which served as gas distributors. An electro-mechanical vibrator was used to impart a small amplitude horizontal vibration to the columns at a frequency of 7200 hz. Compressed air was used as the fluidizing gas, and its flow to the columns was regulated by means of a rotameter and a control valve. The pressure drop across the bed of particles and the distributor was measured using a water manometer.

Procedure      A weighed amount of gypsum of a particular size range was placed in the fluidizing column and then aerated with increasing gas velocities in a step-wise manner. At each setting of gas velocity, the bed was allowed to reach a steady state condition and then the pressure drop across the bed and distributor was recorded. To obtain the values of the net pressure drop across the bed alone, it was necessary to subtract the corresponding pressure drop at each velocity determined with the column empty. The same procedure was used whether or not the column was being vibrated.

Results      Three different size fractions of material were included in the investigation: -50+100, -170+200, and -250 mesh. Of the three materials tested, only the coarsest

fraction of -50+100 mesh could be satisfactorily fluidized in either the 0.95 or 2 in. columns. With the finer size fractions, channeling in the beds was sufficient to prevent fluidization with aeration alone. When vibration was used even the finer sizes were readily fluidized. The problems of channeling and slugging encountered with the non-vibrated beds were substantially reduced. Even the coarsest fraction was more evenly fluidized on the basis of visual observation. Particle motion and circulation of the solids was even observed at gas velocities well below the threshold or incipient fluidization velocity as determined from the plots of net pressure drop versus superficial gas velocity through the bed.

The effect of vibration on the pressure drop across the bed of particles is illustrated in figure 19. Values of the net pressure drop across the vibrated and non-vibrated beds of the -50+100 mesh material are plotted against the corresponding values of superficial gas velocity through the column. In the case of the non-vibrated bed there was a distinct incipient fluidizing velocity around 1 ft./sec. Below this velocity the bed was fixed and above this velocity the bed was fluidized. The vibrated bed, however, did not exhibit a distinct incipient fluidization point. As indicated by the smooth curve of gradually decreasing slope in

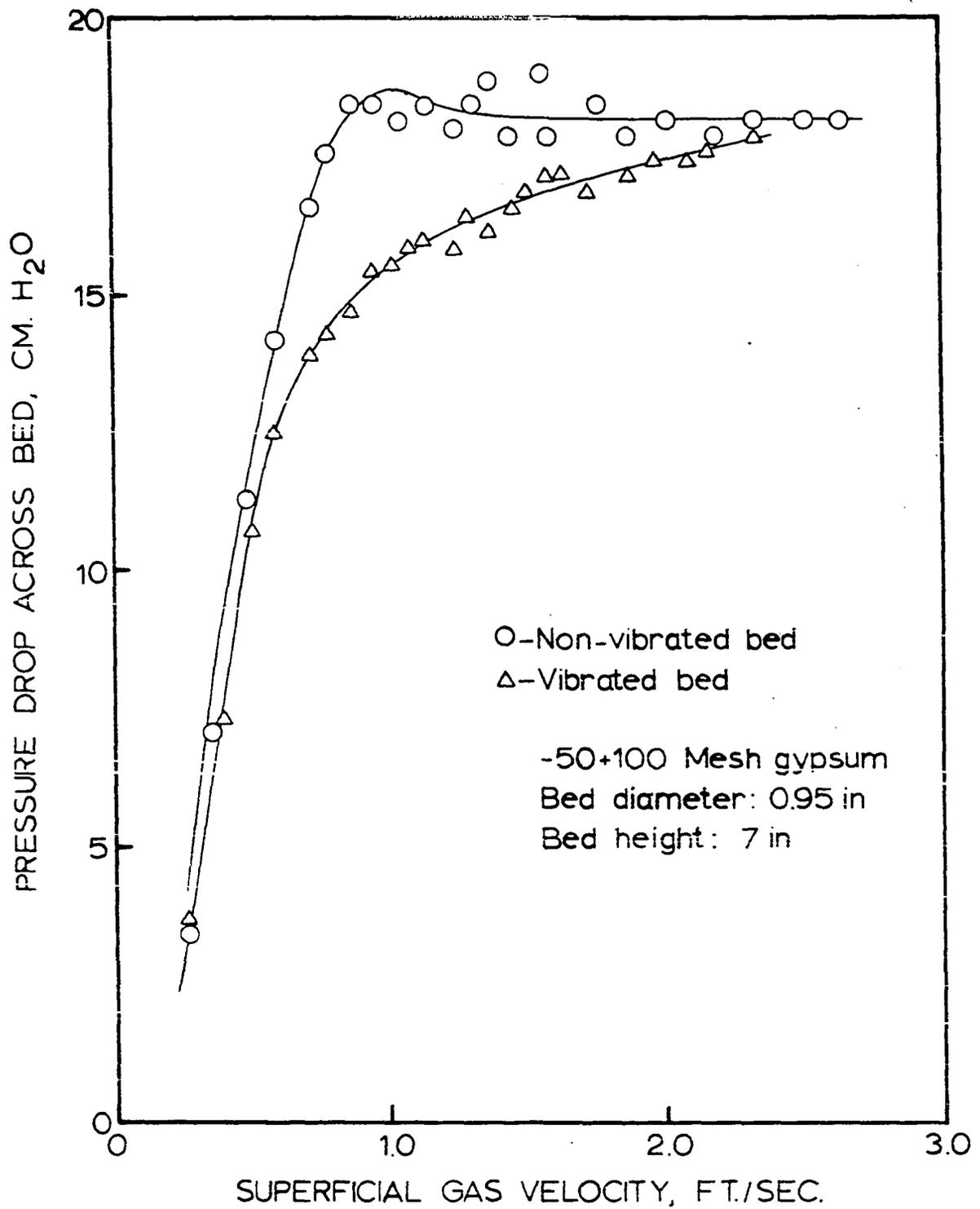


Figure 19. Fluidization of -50+100 mesh gypsum with and without vibration

Figure 19, the bed underwent a gradual and barely perceptible transition between fixed and fluidized states. The difference in pressure drop between the two cases appears to be a maximum near the incipient fluidizing velocity of the non-vibrated bed and a minimum at either end of the velocity extremes.

Pressure drop curves for the other two size fractions were also obtained for the situation where vibration was applied. As can be seen in Figure 20, for the case of the -170+200 mesh material, the results were identical to those obtained for the coarser material. The finer material did exhibit a much lower velocity required for fluidization, and the pressure drop increased much more rapidly to the maximum value over a much narrower range of gas velocity.

#### High temperature experiments

Encouraged by the results obtained at room temperature, attempts were made to fluidize and reductively decompose finely divided gypsum in a high temperature reactor.

Equipment and procedure      The reactor and equipment used for the study were the same as that used in the investigation of calcium sulfide formation as described in the main text and illustrated in Figure 3. The only significant difference was the addition of a small electric vibrator with a vibrational frequency of 7200 hz. The vibrator

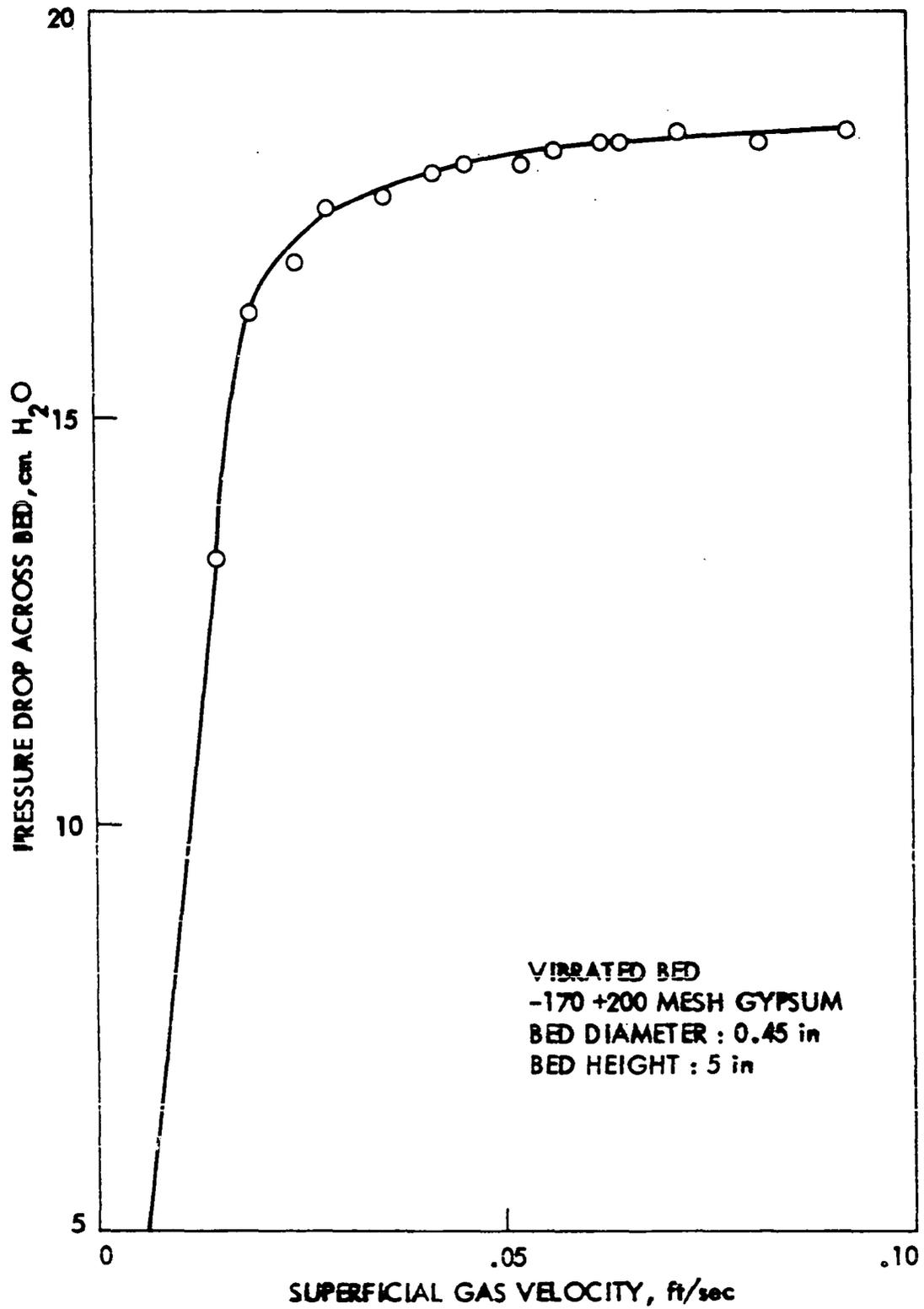


Figure 20. Fluidization of -170+200 mesh gypsum in air with vibration

transmitted the vibrations to the reactor at its lower end where it extended beneath the furnace.

When attempting a run, a weighed amount of calcium sulfate was charged to the reactor and fluidized with air while the reactor was gradually heated to temperature. The system was constantly plagued with the problem of maintaining fluidization during the heating up procedure. Even with the vibrator operating, gas velocities several times the minimum fluidization velocity determined at room temperature were required to keep the bed from channeling and defluidizing with materials coarser than 100 mesh. With material finer than 100 mesh, fluidization could not be maintained even with the vibrator operating. The material would adhere to the walls of the reactor and gradually build up until defluidization and channeling occurred. As a result, use of the vibrator was discontinued and the investigation abandoned.

#### Gas and Solid Mixing in a Fluidized Bed

In connection with the concept of the two-zone reactor, gas and solids mixing are primary considerations. With fresh particles being added to the reactor at a point above the distributor in the secondary gas stream, it is desirable that the solids be well backmixed to ensure that each particle is alternately exposed to reducing and oxidizing conditions

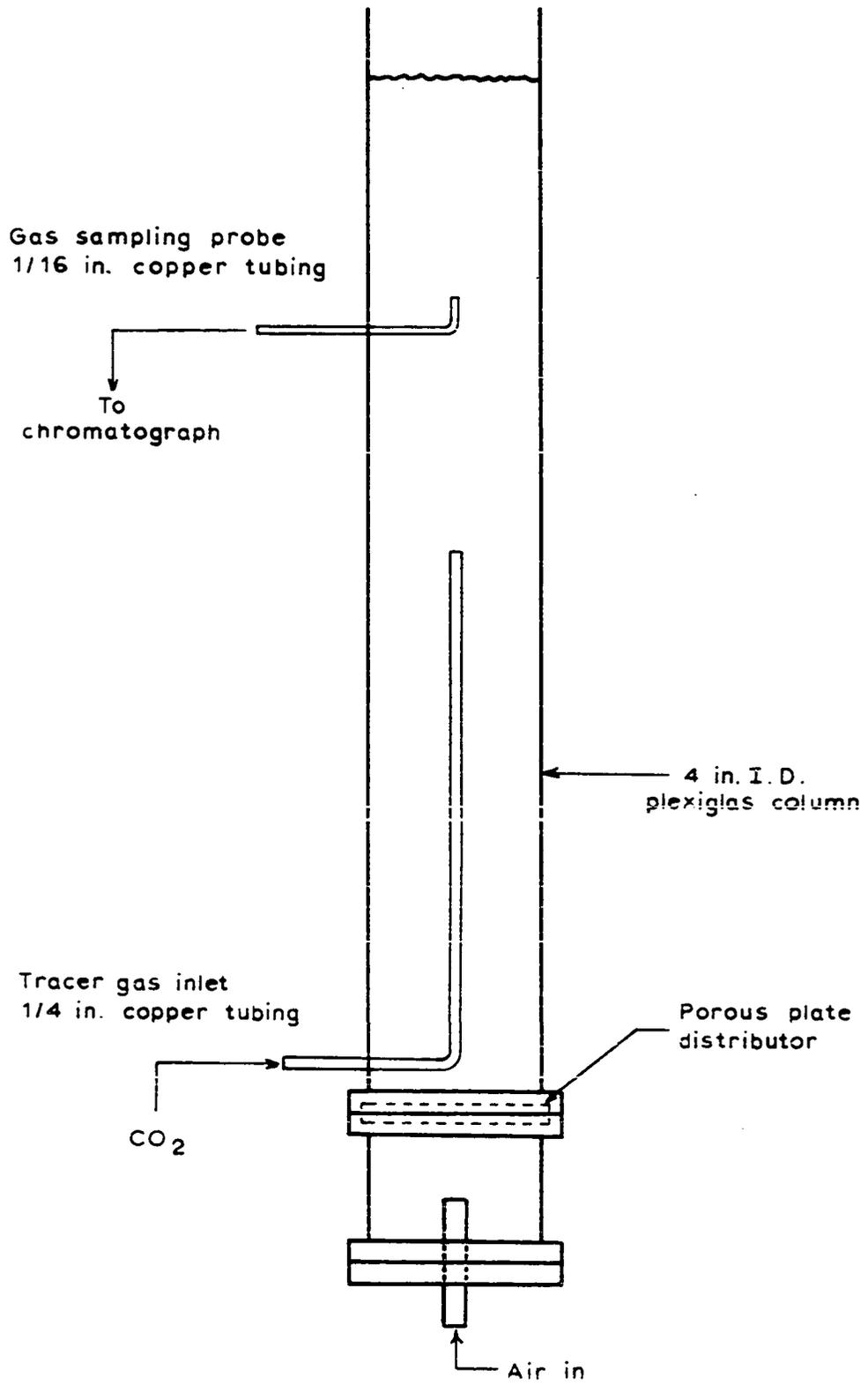
many times in passing through the reactor. On the other hand, it is desirable that gas mixing be limited to ensure the establishment of reducing and oxidizing conditions in different regions within the reactor.

To justify the concept of the two zone reactor, some very simple experiments were carried out to obtain some insight into gas and solids mixing in a gas fluidized bed.

Gas mixing      The gas mixing study was carried out in the Plexiglas column arrangement illustrated in figure 21. The bed of solids was composed of partially reduced calcium sulfate obtained from the Kent Feeds pilot plant reactor (15). This was the same material used in the study of calcium sulfide oxidation and is described in Table 5. The primary air flow rate was varied from 1.125 to 2 times the incipient fluidization velocity of 0.8 std. cu. ft./min. for a 4 in. column at room temperature. The carbon dioxide tracer gas flow varied from 0.1 to 0.5 times the incipient velocity.

Gas samples were taken at different radial positions in the column using the probe which was inserted at a height of 6 to 12 inches above the tracer gas inlet. Typical carbon dioxide concentration profiles are illustrated in Figure 22. The lack of symmetry in the profiles is probably due to the tracer inlet being somewhat off center and

Figure 21. Apparatus for gas and solid mixing investigations



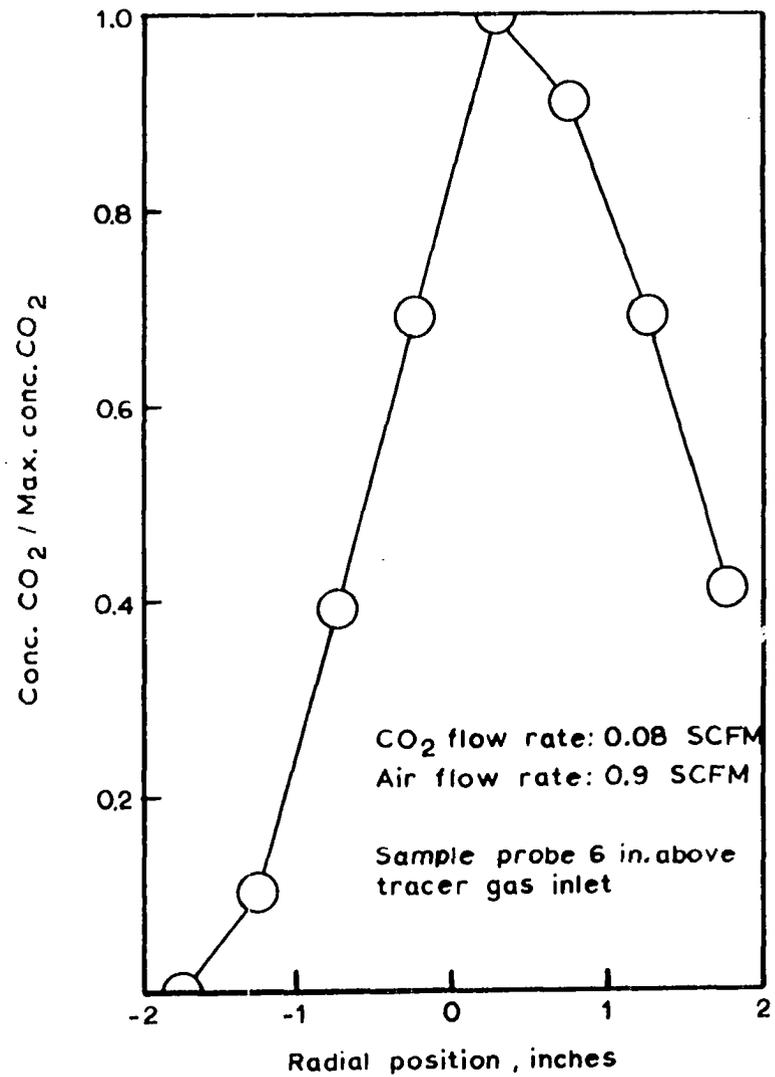
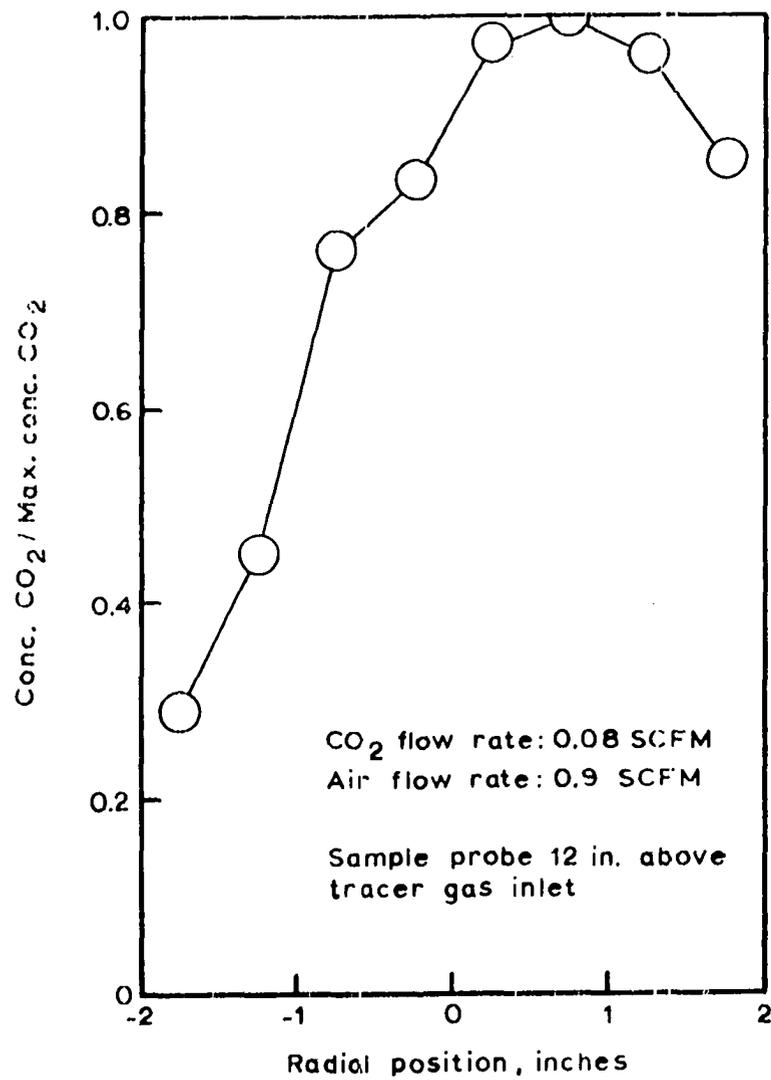


Figure 22. Concentration profiles across bed in gas mixing investigation

inaccuracies in measuring the position of the sample probe. The results do demonstrate, however, the gas concentration gradients which can exist in a fluidized bed. At higher velocities, the profiles at 12 in. above the tracer inlet flattened out considerably, but at the 6 in. level the gradients were still quite steep.

The results tend to confirm the possibility of establishing reducing and oxidizing regions in a fluidized bed by feeding a highly reducing mixture of natural gas and air at the bottom of a fluidized bed and an excess of air at a point above the distributor.

Solids mixing      The mixing of solids was investigated to see how solids introduced into the upper half of a fluidized bed would tend to backmix and be uniformly distributed throughout the entire bed. The equipment used was essentially the same as used for the gas mixing investigation.

A bed of white sand having a size distribution primarily in the -28+65 mesh range was placed in the column and fluidized with air at twice its incipient fluidization velocity. Colored sand was then pneumatically fed to the column through the tracer gas inlet at a point midway in the fluidized bed. The height of the fluidized bed was maintained at 26 in. by continuously removing sand from the top of the bed. After only 15 min. of operation the distribution of the colored sand appeared to be uniform throughout the

entire bed indicating that solids backmixing is very effective and rapid when the same materials are being considered.

These results indicate that solids fed to a reactor at a point above the distributor, as in the secondary gas line of a two-zone reactor, should become well mixed throughout the reactor.

To roughly determine the effects of particle size and density variations on backmixing, the following experiment was made. Once again a bed of colored sand was fluidized as before except the level of the bed was maintained at 24 in. This time, however, finely divided gypsum of the size shown in Table 13 was pneumatically fed to the reactor through the tracer gas inlet at approximately the mid-point of the bed. This time the color variations throughout the bed were quite noticeable, with a significantly higher proportion of the much smaller and less dense gypsum being observed in the upper half of the bed than in the lower half. It seemed that backmixing of the fines was very poor.

The limited backmixing of the fines suggests a problem in attempting to decompose finely divided calcium sulfate in a multiple zone reactor which uses a bed of coarse, dense material to maintain fluidization. The very limited results obtained in the operation of the two-zone reactor in treating fines as discussed in the text tends to confirm this observation.

APPENDIX C: CHEMICAL EQUILIBRIUM IN COMPLEX  
MIXTURES

Although used very sparingly during the preceding investigation, a very useful computer program for the calculation of equilibrium compositions in complex gas-solid mixtures was developed and is listed in Appendix D. The program is based on the theory of minimizing the total free energy of the system subject to material balances as developed by White et al. (56). Opsahl (37) and Dunshee (8) developed computer programs for determining the equilibrium of complex gas phase reactions, and the program presented here is an extension of their work.

The mathematical development of the procedure for gas phase reactions is presented in great detail by White et al. (56) and Opsahl (37). Since the extension to gas-solid reaction systems is straightforward, the mathematical development will not be duplicated here. In addition to the original assumption that the gases can be treated as ideal gases, however, it was necessary to assume that the activities of the solid species can be taken as unity.

Program Guide

Although the program as presented in Appendix D is well annotated to facilitate its use, the following guide is presented to assist the user in entering the proper data and

interpreting the results obtained. To illustrate the steps in the procedure, an example involving the reductive decomposition of anhydrite will be given.

Step 1: Decide the basis for the problem to be solved. For the example, 2 moles of calcium sulfate are to be reacted with 1 mole of carbon monoxide at temperatures from 1000° to 1600°K at 100°K intervals and at a pressure of 10 atmospheres. The problem could also be solved for the case of constant volume in the gas phase if desired.

Step 2: From the basis established, determine the different atom types present. In the example, calcium sulfate and carbon monoxide are composed of Ca, S, O, and C.

Step 3: Decide what and how many species will be included in the equilibrium mixture. The program can accommodate as many as 10 solid species and 20 gaseous species for a total of 30 components. For the example, the species selected were  $\text{SO}_2$ ,  $\text{CO}_2$ ,  $\text{CO}$ ,  $\text{CaSO}_4$ ,  $\text{CaO}$ , and  $\text{CaS}$ . You can include as many different combinations of atom types as you wish within the limits set above. However, you must list the gaseous species first.

Step 4: Obtain the free energy functions of the different species in the desired temperature range. The JANAF Thermochemical Tables (23) are an excellent source for this

data. The free energy function is expressed as  $(F^\circ - H_{298}^\circ)/T$  in the JANAF tables and is entered into the program in this form. To obtain the free energy, therefore, it is also necessary to enter  $\Delta H_{f298}^\circ$ , the standard heat of formation of the species at 298°K. This then makes the elements at 298°K as the reference state for the free energies used in the calculations. Express both values in cal/mole.

Step 5: Using the basis selected, calculate the number of moles of each atom type present initially. For the example being used, 2 moles of calcium sulfate and 1 mole of carbon dioxide represent 2 moles of Ca, 2 moles of S, 9 moles of O, and 1 mole of C.

Step 6: Set up the A(I,J) matrix, where A(I,J) is the number of atoms of type I in species J. The order of the species is the same as determined in Step 3. The order of the atom types is the same as determined in Step 2. For the example the A(I,J) matrix would be:

	Ca	S	O	C
SO <sub>2</sub>	0.0	1.0	2.0	0.0
CO <sub>2</sub>	0.0	0.0	2.0	1.0
CO	0.0	0.0	1.0	1.0
CaSO <sub>4</sub>	1.0	1.0	4.0	0.0
CaO	1.0	0.0	1.0	0.0
CaS	1.0	1.0	0.0	0.0

The  $A(I,J)$  matrix is read into the program by rows.

Step 7: Determine an initial estimate for the equilibrium mole numbers. The actual numbers selected are unimportant, but the total moles of each atom type in the initial guess should balance with the total moles of each atom type in the initial statement of the problem. It is best if all the mole numbers in the initial estimate are greater than zero. For the example the following initial estimates were made:

<u>Specie</u>	<u>Initial Estimate</u>	<u>Moles of each atom type</u>			
		<u>Ca</u>	<u>S</u>	<u>O</u>	<u>C</u>
SO <sub>2</sub>	0.8	0.0	0.8	1.6	0.0
CO <sub>2</sub>	0.9	0.0	0.0	1.8	0.9
CO	0.1	0.0	0.0	0.1	0.1
CaSO <sub>4</sub>	1.175	1.175	1.175	4.7	0.0
CaO	0.8	0.8	0.0	0.8	0.0
CaS	0.025	<u>0.025</u>	<u>0.025</u>	<u>0.0</u>	<u>0.0</u>
Totals		2.0	2.0	9.0	1.0

Step 8: The data is now ready to put on computer cards to be used in the calculations. The order of the data cards and the FORTRAN format used with each set of information is outlined below:

- Data 1 This card is the label for the equilibrium calculations being made and anything may be typed on this card. In the example the label was "REDUCTIVE DECOMPOSITION OF ANHYDRITE." The label is read in under a 10A8 format.
- Data 2 M, N, NS, NP, and MP are entered in a 5I4 format. M is the number of atom types, N is the total number of species, NS is the number of solid species, NP is the number of values in the free energy table for each specie, and MP is the number of temperatures at which equilibrium is to be calculated. Referring to the example, these numbers are 4, 6, 3, 7 and 7 respectively.
- Data 3 This data set is a list of B(I), the number of moles of each atom type initially present and is entered under a 10F7.2 format. The program will accommodate up to 10 distinct atom types. In the example, the values for B(I) are 2.00, 2.00, 9.00, and 1.00 for Ca, S, O, and C respectively.
- Data 4 This card contains BCD(K), the names of the species. They are entered under a 20A4/10A4 format. In the example, these were listed as SO<sub>2</sub>, CO<sub>2</sub>, CO, ANHY, LIME, and CAS. Note

that the gaseous species must be entered first.

Data 5 This card contains the A(I,J) matrix as previously determined. It is essential to remember that the atom types and species must be in the same order as determined by Data 3 and 4. The format for the reading of this data is 20F4.1. Referring to Step 3, the example data would be read in as follows:

0.0, 1.0, 2.0, 0.0, 0.0, 0.0, 2.0, 1.0,  
0.0, 0.0, 1.0, 1.0, 1.0, 1.0, 4.0, 0.0, 1.0,  
0.0, 1.0, 0.0, 1.0, 1.0, 0.0, and  
0.0.

Data 6 Since the program is an iterative procedure which may require interpolation of the free energy tables for the species, it is necessary to specify NNI, the maximum number of iterations allowed for calculation at each temperature, and DFR, the accuracy required for interpolation. This data is entered in a I4, F10.7 format. Values of 100 and 0.0005 were used in the sample calculations.

Data 7 This card contains the word true or false. If true is used, each iteration in the calculation is printed out. This is only necessary when attempting to pinpoint problems in the program.

- Data 8 This card contains the values for T, PT, V, TC, DZ, DT, and ZS and is in a 7F11.4 format. T is the Rankin temperature of the first calculation. PT is the pressure at which all calculations are to be made, V is the volume on which the calculations will be based if PT is zero, TC is the Kelvin temperature of the first calculation. DZ is the difference in temperature between successive calculations, and ZS is the temperature of the first value in the free energy table. Note that the first calculation is to be made at the highest temperature. Therefore, for the example the following values were used: 2880.0, 10.0, 7.0, 1600.0, 100.0, -100, 1000.0.
- Data 9 These cards contain  $FI(I,J)$ , the free energy values for  $J=NP$  temperatures and  $I=N$  species. The set of free energy values for each specie concludes with  $H(I)$ , the heat of formation at 298°K Kelvin. These must be arranged in the order of species as determined in Data 4. The data is read in using a 8F10.3 format.
- Data 10 These cards contain  $X(I)$ , the initial guesses for the mole numbers of the species. From Step 7 we see that for the example the following

numbers would be entered: 0.8, 0.9, 0.1, 1.175, 0.8, 0.025 for  $\text{SO}_2$ ,  $\text{CO}_2$ ,  $\text{CO}$ ,  $\text{CaSO}_4$ ,  $\text{CaO}$ , and  $\text{CaS}$  respectively.

### Program Results

The output for each calculation made includes the following information:

1. The label for the data
2. The temperature in degrees Kelvin
3. The total pressure of the gas phase, or volume in a constant volume calculation
4. A list of the major components including the number of moles of each specie at equilibrium and its mole fraction in its respective phase.
5. A list of the trace components including the number of moles of each and the ppm of each in its respective phase. Any solids which appear in this list should be regarded as completely consumed at equilibrium.
6. A list of negligible components of less than 1 ppm listed with mole fraction and number of moles.
7. The total moles in the gas phase
8. The total free energy
9. Assorted miscellaneous information regarding the number of iterations made and the step size of certain factors used in the calculations

A summary of the results obtained in the example used are presented in Table 20. The program is very easy to use and would be extremely helpful in the performance of theoretical equilibrium calculations.

Table 20. Results of equilibrium calculations for example problem<sup>a</sup>

Temp. °K	Solid Phase			Gas Phase		
	Component	Moles	Mole %	Component	Moles	Mole %
1600	CaSO <sub>4</sub>	1.006	50.33	SO <sub>2</sub>	0.993	49.84
	CaO	0.993	49.67	CO <sub>2</sub>	0.993	49.84
	CaS	-	-	CO <sub>2</sub>	0.006	0.32
1500	CaSO <sub>4</sub>	1.015	50.73	SO <sub>2</sub>	0.985	49.63
	CaO	.985	49.27	CO <sub>2</sub>	0.985	49.63
	CaS	-	-	CO <sub>2</sub>	0.015	0.74
1400	CaSO <sub>4</sub>	1.584	79.18	SO <sub>2</sub>	0.226	18.47
	CaO	.226	11.32	CO <sub>2</sub>	0.986	80.37
	CaS	.190	9.49	CO <sub>2</sub>	0.014	1.17
1300	CaSO <sub>4</sub>	1.719	85.97	SO <sub>2</sub>	0.004	4.24
	CaO	.044	2.21	CO <sub>2</sub>	0.990	94.78
	CaS	.236	11.82	CO <sub>2</sub>	0.010	0.96
1200	CaSO <sub>4</sub>	1.746	87.32	SO <sub>2</sub>	0.007	0.71
	CaO	0.007	0.35	CO <sub>2</sub>	0.993	98.65
	CaS	0.247	12.33	CO <sub>2</sub>	0.007	0.66
1100	CaSO <sub>4</sub>	1.750	87.48	SO <sub>2</sub>	0.001	0.09
	CaO	.002	0.12	CO <sub>2</sub>	0.994	99.17
	CaS	.248	12.40	CO <sub>2</sub>	0.004	0.42
1000	CaSO <sub>4</sub>	1.751	87.53	SO <sub>2</sub>	-	-
	CaO	-	-	CO <sub>2</sub>	0.998	99.76
	CaS	0.249	12.47	CO <sub>2</sub>	0.002	0.24

<sup>a</sup>Calculations made at 10 atmospheres pressure.

APPENDIX D: COMPUTER PROGRAM

```

      READ(5,51) NNI,DFR
51  FORMAT(I4,F10.7)
C   DATA 7 CHECK TRUE OR FALSE WHETHER EACH ITERATION IS TO BE
C   PRINTED OUT
      READ(5,500) CHECK
500 FORMAT(L6)
C   DATA 8 T THE RANKINE TEMPERATURE OF THE FIRST CALCULATION. THE
C   HIGHEST TEMPERATURE TO BE COMPUTED IS THE FIRST.
C   PT THE PRESSURE AT WHICH ALL CALCULATIONS WILL BE MADE
C   V THE VOLUME ON WHICH CALCULATIONS WILL BE BASED IF PT=0
C   TC THE KELVIN TEMPERATURE OF THE FIRST CALCULATION
C   DZ THE DIFFERENCE BETWEEN SUCCESSIVE VALUES OF TEMPERATURE
C   IN THE FREE ENERGY TABLES IN DEGREES KELVIN
C   DT THE DIFFERENCE IN TEMPERATURE BETWEEN SUCCESSIVE
C   CALCULATIONS IN DEGREES KELVIN
C   ZS THE TEMPERATURE OF FIRST VALUE IN THE FREE ENERGY TABLE
C   IN DEGREES KELVIN
      READ(5,120) T,PT,V,TC,DZ,DT,ZS
120 FORMAT(7F11.4)
C   DATA 9 FI(I,J) THE VALUES OF (F-H)/T FROM THE FREE ENERGY TABLES
C   FOR J TEMPERATURES AND I SPECIES
C   H(I) THE HEAT OF FORMATION AT 298 DEG. KELVIN FOR
C   EACH SPECIES
      DO 7 I=1,N
7  READ(5,20) (FI(I,J),J=1,NP),H(I)
20 FORMAT(8F10.3)
C   DATA 10 X(I) THE INITIAL GUESSES FOR THE MOLE NUMBERS OF THE
C   SPECIES. THESE SHOULD BE BALANCED BY STOICHIOMETRY TO
C   FIT THE NUMBER OF MOLES OF EACH ATOM TYPE FOR BEST
C   RESULTS
      READ(5,1120) (X(I),I=1,N)
1120 FORMAT(8F10.6)
      DO 1122 I=1,N
1122 NO(I)=I
C   WRITE DATA IN SAME FORMAT AS READ
      WRITE(6,1)
1  FORMAT(1H1,'DATA READ IN BY OPERATOR')

```

C THIS IS A PROGRAM FOR COMPUTING EQUILIBRIUM COMPOSITIONS OF A  
C GAS-SOLID MIXTURE. THE MIXTURE MAY CONSIST OF N SPECIES (UP TO A  
C MAXIMUM OF 30) OF WHICH NS (UP TO A MAXIMUM OF 10) MAY BE SOLIDS.  
C THE PROGRAM ALLOWS FOR M (UP TO A MAXIMUM OF 10) UNIQUE ATOMIC  
C TYPES TO BE PRESENT IN THE MIXTURE.

C THE PROGRAM IS KINETICS FREE AND IS BASED ON THE METHOD OF  
C WHITE, ET.AL., (J. OF CHEM. PHYS. 28:5, P.751-755, 1958.) WHICH  
C MINIMIZES THE TOTAL FREE ENERGY OF THE MIXTURE. THE FREE ENERGY  
C FOR EACH SPECIE AT THE DESIRED TEMPERATURE IS OBTAINED FROM TABLES  
C OF FREE ENERGY VALUES READ IN FROM DATA CARDS. AN INTERPOLATION  
C SCHEME IS USED TO OBTAIN VALUES BETWEEN TABLED VALUES.

C AFTER THE FREE ENERGY REACHES A CHANGE OF LESS THAN 0.00002  
C PERCENT BETWEEN ITERATIONS, THE SPECIES WITH A MOLE FRACTION OF  
C LESS THAN ONE PPM ARE SEPARATED OUT AND THE MINIMIZATION IS  
C CARRIED OUT USING ONLY THE MAJOR COMPONENTS.

C THE GAS PHASE COMPONENTS HAVING A MOLE FRACTION OF LESS  
C THAN 0.01 ARE CALCULATED USING A SPECIAL METHOD.  
C

```
DIMENSION NI(3),NO(30),NOL(30),NOS(30)
DOUBLE PRECISION XPK(30)
DIMENSION BCD(30),FI(30,25),H(30),IER(30)
DOUBLE PRECISION G(30),DEL(30),XMF(30),F(30)
DOUBLE PRECISION C(30),RP(11,11),APP(11,30),P(10)
DOUBLE PRECISION CP(10),CK(10),FX(25),FR(30),TI(30)
DOUBLE PRECISION X(30),B(10),XN(30),A(10,30),FRT(30)
DOUBLE PRECISION PPPA(30),PPA(10),XX(30),XXMF(30)
LOGICAL CHECK
DOUBLE PRECISION XB,FT,XBN,DELB,DFDL,DL,DLOG,DZ,ZS
DOUBLE PRECISION DABS,TC,FTN,XBL,DEXP,XBS,XBB
DOUBLE PRECISION XMFS(30),XS(30),BCDS(30),FS(30)
DOUBLE PRECISION XMFL(30),XL(30),BCDL(30),FL(30)
DOUBLE PRECISION FRTL(30),FRTS(30),AL(10,30),AS(10,30)
DOUBLE PRECISION HL(30),HS(30),FIL(30,25),FIS(30,25)
DOUBLE PRECISION CL(30),CS(30),NAME(10),ATF(11)
```

C  
C READ IN DATA  
C DATA 1 NAME(I) IS THE LABEL FOR THE TABLE OF VALUES PRINTED OUT.

```

      READ(5,2)(NAME(I),I=1,10)
2  FORMAT(10A8)
C   DATA 2  M IS THE NUMBER OF ATOM TYPES
C             N IS THE TOTAL NUMBER OF SPECIES
C             NS IS THE NUMBER OF SOLID SPECIES
C             NP IS THE NUMBER OF VALUES IN FREE ENERGY TABLES
C             MP IS THE NUMBER OF TEMPERATURES AT WHICH EQUILIBRIUM IS
C             TO BE CALCULATED
5  READ(5,10) M,N,NS,NP,MP
10 FORMAT(5I4)
C   DATA 3  B(I) IS THE NUMBER OF MOLES OF EACH ATOM TYPE PRESENT
      READ(5,8) (B(I),I=1,M)
8  FORMAT(10F7.2)
      MP1=M+1
      NOR=N
      RT=1.987
      R=0.7302
      NG=N-NS
      NGOR=NG
      NSOR=NS
      NGP1=NG+1
      NGPL=NGOR+1
C   DATA 4  BCD(K) IS THE NAME OF EACH SPECIE.  THE ORDER OF BCD MUST
C             BE PRESERVED FOR OTHER VARIABLES.  LIST GASEOUS PHASE
C             SPECIES AHEAD OF SOLID PHASE SPECIES
      READ(5,11) (BCD(K),K=1,N)
11 FORMAT(20A4/10A4)
C   DATA 5  A(I,J) IS THE NUMBER OF ATOMS OF ATOMIC TYPE I IN
C             SPECIES J.  A(I,J) IS READ IN BY ROWS.  J MUST FOLLOW
C             THE ORDER ESTABLISHED BY BCD(K) ABOVE.
      READ(5,12) ((A(I,J),I=1,M),J=1,N)
12 FORMAT(20F4.1)
C   DATA 6  NNI IS THE MAXIMUM NUMBER OF ITERATIONS TO BE CARRIED OUT
C             FOR EACH TEMPERATURE FOR WHICH FREE ENERGY IS BEING
C             MINIMIZED.
C             DFR IS THE ACCURACY REQUIRED FOR INTERPOLATION IN THE FREE
C             ENERGY TABLE.

```

```

WRITE(6,222) (NAME(I),I=1,10)
222 FORMAT(1H0,10A8)
WRITE(6,10)M,N,NS,NP,MP
WRITE(6,8)(B(I),I=1,M)
WRITE(6,11)(BCD(K),K=1,N)
WRITE(6,12)((A(I,J),I=1,M),J=1,N)
WRITE(6,51)NNI,DFR
WRITE(6,500)CHECK
WRITE(6,120)T,PT,V,TC,DZ,DT,ZS
DO 77 I=1,N
77 WRITE(6,23)(FI(I,J),J=1,NP),H(I)
23 FORMAT(8F11.3)
WRITE(6,1120)(X(I),I=1,N)
15 DO 906 L=1,MP
MXP=1
C INTERPOLATE FREE ENERGY AT DESIRED TEMPERATURE FROM FREE ENERGY
C TABLES FOR EACH SPECIES
DO 41 I=1,N
DO 905 K=1,NP
905 FX(K)=FI(I,K)
CALL DATSE(TC,ZS,DZ,FX,NP,1,TI,FR,NP)
CALL DALI(TC,TI,FR,FRT(I),NP,DFR,IEL)
IER(I)=IEL
IF(NP.EQ.1) FRT(I)=FI(I,1)
FRT(I)=FRT(I)+H(I)/TC
41 FRT(I)=FRT(I)/RT
C IF CHECK IS TRUE, WRITE OUT IER AND TEMPERATURE AND VOLUME AND/OR
C PRESSURE.
IF(CHECK)GO TO 410
GO TO 6951
C IF PRESSURE IS NEGATIVE, PROGRAM TERMINATES
410 IF(PT)691,18,19
18 WRITE(6,22)TC,V
22 FORMAT(5X,"TEMPERATURE = ',F7.1,'DEGREES KELVIN ',
1' VOLUME = ',F10.3,' CUBIC FEET')
GO TO 413
19 WRITE(6,21)TC,PT

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21 FORMAT(5X,'TEMPERATURE = ',F7.1,' DEGREES KELVIN ',
1' PRESSURE = ',F9.4,' ATMOSPHERES')
413 WRITE (6,411) (IER(I),I=1,N)
411 FORMAT(1H0,5X,5HIER =,5X,20I4)
6951 CONTINUE
C COMPUTE INITIAL FREE ENERGY FUNCTION
MPNS =M+NS
FT=0.0
NI(MXP)=0
IF(N-NS)5003,5005,7001
7001 XB=0.0
DO 7110 I=1,NG
IF(X(I).EQ.0.0) X(I)=1.E-60
7110 XB=XB+X(I)
DO 7004 I=1,NG
7004 XMF(I)=X(I)/XB
IF(PT)691,7005,7006
7005 DO 7007 I=1,NG
C(I)=FRT(I)+ALOG((R*T)/V)
F(I)=X(I)*(C(I)+DLOG(X(I)))
7007 FT=FT+F(I)
GO TO 7010
7006 DO 7011 I=1,NG
C(I)=FRT(I)+ALOG(PT)
F(I)=X(I)*(C(I)+DLOG(X(I)/XB))
7011 FT=FT+F(I)
7010 IF(NS)7000,7118,5005
5005 XBS=0.0
DO 7094 I=NGP1,N
IF(X(I).EQ.0.0) X(I)=1.E-60
7094 XBS=XBS+X(I)
DO 7095 I=NGP1,N
7095 XMF(I)=X(I)/XBS
DO 5006 I=NGP1,N
C(I)=FRT(I)
F(I)=X(I)*C(I)
5006 FT=FT+F(I)

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7118 CONTINUE
    IF(CHECK) GO TO 305
695 CONTINUE
    NI(MXP)=NI(MXP)+1
    IF(NI(MXP).GT.NNI) GO TO 245
C    COMPUTE R MATRIX
    DO 40 I=1,M
    CP(I)=0.0
    DO 17 J=1,N
    17 CP(I)=CP(I)+X(J)*A(I,J)
    IF(NI(MXP).LE.1.0)GO TO 502
    IF(CK(I).LE.1.E-60)GO TO 501
502 CK(I)=CP(I)-B(I)
    GO TO 40
501 CK(I)=0.0
    40 CONTINUE
    IF(NS)7000,7014,7016
C    SOLVE FOR CASE NS=0
7014 DO 70 K=1,M
    DO 70 J=1,M
    RP(J,K)=0.0
    DO 70 I=1,N
    70 RP(J,K)=RP(J,K)+A(J,I)*A(K,I)*X(I)
    IF(PT)691,71,74
    71 DO 72 J=1,M
    RP(J,M+1)=0.0
    72 RP(M+1,J)=0.0
    RP(M+1,M+1)=1.0
    GO TO 76
    74 DO 75 J=1,M
    RP(M+1,J)=CP(J)
    75 RP(J,M+1)=CP(J)
    RP(M+1,M+1)=0.0
    76 DO 80 I=1,M
    DO 80 J=1,N
    80 APP(I,J)=A(I,J)
    IF(PT)691,700,833

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700 DO 850 I=1,M
    ATF(I)=0.0
    DO 840 J=1,N
840 ATF(I)=ATF(I)+APP(I,J)*F(J)
850 ATF(I)=ATF(I)+CP(I)-CK(I)
    ATF(M+1)=0.0
    DO 845 J=1,N
845 ATF(M+1)=ATF(M+1)+F(J)
    GO TO 820
833 DO 835 I=1,MP1
    ATF(I)=0.0
    DO 835 J=1,N
800 APP(M+1,J)=1.0
835 ATF(I)=ATF(I)+APP(I,J)*F(J)
    DO 836 I=1,M
836 ATF(I)=ATF(I)-CK(I)
820 IF(CHECK) GO TO 810
    93 CALL SIMEQ(RP,ATF,MP1)
    90 DO 95 J=1,M
    95 P(J)=ATF(J)
    U=ATF(M+1)
    IF(CHECK) GO TO 85
    99 DO 98 I=1,N
    G(I)=0.0
    DO 98 J=1,M
    98 G(I)=G(I)+A(J,I)*P(J)
    IF(PT)691,91,96
    91 XBN=-U
    DELB=XBN-XB
    DO 102 I=1,N
101 XN(I)=X(I)*G(I)-F(I)
    DEL(I)=XN(I)-X(I)
102 CONTINUE
    GO TO 100
    96 XBN=(1.+U)*XB
    DELB=XBN-XB
    DO 140 I=1,N

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139 XN(I)=-F(I)+X(I)*XBN/XB+G(I)*X(I)
    DEL(I)=XN(I)-X(I)
140 CONTINUE
    GO TO 100
C    IS NS LT. OR EQ TO N
7016 IF(N-NS)5003,7017,7018
7017 DO 7120 K=1,M
    DO 7120 J=1,M
7120 RP(J,K)=0.0
    DO 7121 J=1,M
    DO 7121 K=MP1,MPNS
    JJ=NG+K-M
    RP(J,K)=A(J,JJ)
7121 RP(K,J)=A(J,JJ)
    DO 7122 J=MP1,MPNS
    DO 7122 K=MP1,MPNS
7122 RP(J,K)=0.0
    DO 7123 I=1,M
7123 ATF(I)=CP(I)-CK(I)
    DO 7124 I=MP1,MPNS
    MM=NG+I-M
7124 ATF(I)=FRT(MM)
    IF(CHECK) GO TO 1501
7125 CALL SIMEQ(RP,ATF,MPNS)
7126 DO 7127 J=1,M
7127 P(J)=ATF(J)
    DO 7128 J=MP1,MPNS
    JJ=J-M
7128 XN(JJ)=ATF(J)
    DO 1600 I=1,N
1600 DEL(I)=XN(I)-X(I)
    IF(CHECK) GO TO 1502
    GO TO 100
7018 DO 7100 K=1,M
    DO 7100 J=1,M
    RP(J,K)=0.0
    DO 7100 I=1,NG

```

```

7100 RP(J,K)=RP(J,K)+A(J,I)*A(K,I)*X(I)
      IF(PT)691,7200,7300
7200 DO 7220 J=1,M
      DO 7220 K=MP1,MPNS
      JJ=NG+K-M
      RP(J,K)=A(J,JJ)
7220 RP(K,J)=A(J,JJ)
      DO 7230 J=MP1,MPNS
      DO 7230 K=MP1,MPNS
7230 RP(J,K)=0.0
      DO 7240 I=1,M
      ATF(I)=0.0
      DO 7250 J=1,NG
7250 ATF(I)=ATF(I)+A(I,J)*F(J)
7240 ATF(I)=ATF(I)+CP(I)-CK(I)
      DO 7260 I=MP1,MPNS
      JJ=NG+I-M
7260 ATF(I)=FRT(JJ)
      IF(CHECK) GO TO 1504
      94 CALL SIMEQ(RP,ATF,MPNS)
7265 DO 7270 J=1,M
7270 P(J)=ATF(J)
      IF(CHECK) GO TO 1505
1506 CONTINUE
      DO 7275 I=1,NG
      G(I)=0.0
      DO 7275 J=1,M
7275 G(I)=G(I)+A(J,I)*P(J)
      DO 7280 I=1,NG
      XN(I)=X(I)*G(I)-F(I)
7280 DEL(I)=XN(I)-X(I)
      DO 7285 I=NGP1,N
      JJ=NGP1-NG+M
      XN(I)=ATF(JJ)
7285 DEL(I)=XN(I)-X(I)
      XBN=0.0
      DO 7286 I=1,NG

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7286 XBN=XBN+XN(I)
      DELB=XBN-XB
      GO TO 100
7300 DO 7305 J=1,M
      RP(J,M+1)=0.0
      RP(M+1,J)=0.0
      DO 7310 I=1,NG
      RP(J,M+1)=A(J,I)*X(I)+RP(J,M+1)
7310 RP(M+1,J)=RP(M+1,J)+A(J,I)*X(I)
7305 CONTINUE
      DO 7315 J=1,M
      DO 7315 K=MP1,MPNS
      LL=NG+K-M
      RP(J,K+1)=A(J,LL)
7315 RP(K+1,J)=A(J,LL)
      DO 7320 J=M ,MPNS
      DO 7320 K=M ,MPNS
7320 RP(J+1,K+1)=0.0
      DO 7325 I=1,M
      ATF(I)=0.0
      DO 7330 J=1,NG
7330 ATF(I)=ATF(I)+A(I,J)*F(J)
7325 ATF(I)=ATF(I)+B(I)
      ATF(M+1)=0.0
      DO 7331 I=1,NG
7331 ATF(M+1)=ATF(M+1)+F(I)
      DO 7335 I=MP1,MPNS
      LL=NG+I-M
7335 ATF(I+1)=C(LL)
      NN=MP1+NS
      IF(CHECK) GO TO 1516
7340 CALL SIMEQ(RP,ATF,NN)
7341 DO 7342 J=1,M
7342 P(J)=ATF(J)
      U=ATF(M+1)
      XBN=U*XB
      DELB=XBN-XB

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        IF(CHECK) GO TO 1507
7343 CONTINUE
        DO 7344 I=1,NG
            G(I)=0.0
            DO 7344 J=1,M
7344 G(I)=G(I)+A(J,I)*P(J)
            DO 7345 I=1,NG
                XN(I)=-F(I)+X(I)*XBN/XB+G(I)*X(I)
7345 DEL(I)=XN(I)-X(I)
            DO 7346 I=NGP1,N
                LL=MP1+I-NG
                XN(I)=ATF(LL)
7346 DEL(I)=XN(I)-X(I)
C COMPUTE MAXIMUM ALLOWABLE CHANGE
100 CONTINUE
        FTN=0.0
        DL=0.0
145 DL=DL+0.1
        IF(DL.GT.1.0) GO TO 155
        DFDL=0.0
        DO 147 I=1,N
            XN(I)=X(I)+DL*DEL(I)
            IF(XN(I).LT.0.0) GO TO 155
147 CONTINUE
        IF(N-NS) 5003,1300,1400
1400 XBN=XB+DL*DELB
        IF(PT) 691,146,148
146 DO 149 I=1,NG
149 DFDL=DFDL+DEL(I)*(C(I)+DLOG(XN(I)))
        GO TO 1300
148 DO 150 I=1,NG
150 DFDL=DFDL+DEL(I)*(C(I)+DLOG(XN(I)/XBN))
1300 IF(NS) 7000,151,1402
1402 DO 1302 I=NGP1,N
1302 DFDL=DFDL+DEL(I)*FRT(I)
151 IF(DFDL.LE.0.0) GO TO 145
155 DL=DL-0.1

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        IF(DL.GT.0.0) GO TO 200
        DL=0.05
169   DFDL=0.0
        DO 160 I=1,N
        XN(I)=X(I)+DL*DEL(I)
        IF(XN(I).LT.0.0) GO TO 158
160   CONTINUE
        IF(N-NS) 5003,1321,1325
1325  XBN=XB+DL*DELB
        IF(PT) 691,156,159
156   DO 1331 I=1,NG
1331  DFDL=DFDL+DEL(I)*(C(I)+DLOG(XN(I)))
        GO TO 1321
159   DO 153 I=1,NG
153   DFDL=DFDL+DEL(I)*(C(I)+DLOG(XN(I)/XBN))
1321  IF(NS) 7000,161,7600
7600  DO 1424 I=NGP1,N
1424  DFDL=DFDL+DEL(I)*FRT(I)
161   IF(DFDL.LE.0.0) GO TO 200
158   DL=DL/2.0
        IF(DL.LT..005) GO TO 1250
        GO TO 169
200   DO 1412 I=1,N
1412  X(I)=X(I)+DL*DEL(I)
        IF(N-NS) 5003,1440,1441
1441  XB=XB+DL*DELB
        XBL=0.0
        IF(PT) 691,201,208
201   DO 207 I=1,NG
        XMF(I)=X(I)/XB
        F(I)=X(I)*(C(I)+DLOG(X(I)))
        XBL=XBL+X(I)
207   FTN=FTN+F(I)
        GO TO 1440
208   DO 210 I=1,NG
        XMF(I)=X(I)/XB
        F(I)=X(I)*(C(I)+DLOG(X(I)/XB))

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      XBL=XBL+X(I)
210  FTN=FTN+F(I)
1440 IF(NS) 7000,211,1450
1450 DO 1451 I=NGP1,N
      F(I)=X(I)*FRT(I)
1451 FTN=FTN+F(I)
      XBS=0.0
      DO 1452 I=NGP1,N
1452 XBS=XBS+X(I)
      DO 1453 I=NGP1,N
1453 XMF(I)=X(I)/XBS
211  IF(CHECK) GO TO 300
240  DFT=FT-FTN
      FT=FTN
      DDFT=DABS(FTN/(10.0**7))
      IF(DFT.LT.DDFT) GO TO 1250
      GO TO 695
C    SEGREGATION OF LARGE AND SMALL COMPONENTS
1250 MXP=MXP+1
      IF(MXP.EQ.3) GO TO 2500
      DLA=DL
      II=0
      III=0
      IV=0
      NGS=0
      IF(N-NS) 5003,3070,3000
3000 DO 3001 I=1,NG
      IF(XMF(I).LT..000001) GO TO 3003
3006 II=II+1
      XMFL(II)=XMF(I)
      XL(II)=X(I)
      BCDL(II)=BCD(I)
      FL(II)=F(I)
      CL(II)=C(I)
      FRTL(II)=FRT(I)
      NOL(II)=NO(I)
      HL(II)=H(I)

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DO 3102 J=1,NP
3102 FIL(II,J)=FI(I,J)
DO 3002 J=1,M
3002 AL(J,II)=A(J,I)
GO TO 3001
3003 III=III+1
XMF(III)=XMF(I)
XS(III)=X(I)
BCDS(III)=BCD(I)
FS(III)=F(I)
CS(III)=C(I)
FRTS(III)=FRT(I)
HS(III)=H(I)
NOS(III)=NO(I)
DO 3104 J=1,NP
3104 FIS(III,J)=FI(I,J)
DO 3004 J=1,M
3004 AS(J,III)=A(J,I)
3001 CONTINUE
NG=II
NGP1=NG+1
NGS=III
3070 IF(NS) 7000,3109,3030
3030 DO 3078 I=NGP1,N
IF(XMF(I).LT..000010)GO TO 3079
II=II+1
XMFL(II)=XMF(I)
XL(II)=X(I)
BCDL(II)=BCD(I)
FL(II)=F(I)
CL(II)=C(I)
FRTL(II)=FRT(I)
NOL(II)=NO(I)
HL(II)=H(I)
DO 3080 J=1,NP
3080 FIL(II,J)=FI(I,J)
DO 3081 J=1,M

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```

3081 AL(J,II)=A(J,I)
      GO TO 3078
3079 III=III+1
      XMFS(III)=XMF(I)
      XS(III)=X(I)
      BCDS(III)=BCD(I)
      FS(III)=F(I)
      CS(III)=C(I)
      FRTS(III)=FRT(I)
      HS(III)=H(I)
      NOS(III)=NO(I)
      DO 3082 J=1,NP
3082 FIS(III,J)=FI(I,J)
      DO 3083 J=1,M
3083 AS(J,III)=A(J,I)
3078 CONTINUE
3109 IF(II.EQ.0) GO TO 3084
      DO 3085 I=1,II
      XMF(I)=XMFL(I)
      X(I)=XL(I)
      BCD(I)=BCDL(I)
      F(I)=FL(I)
      NO(I)=NOL(I)
      C(I)=CL(I)
      FRT(I)=FRTL(I)
      H(I)=HL(I)
      DO 3086 J=1,NP
3086 FI(I,J)=FIL(I,J)
      DO 3087 J=1,M
3087 A(J,I)=AL(J,I)
3085 CONTINUE
      IF(III.EQ.0)GO TO 3092
3084 IIA=II+1
      DO 3093 I=IIA,N
      IV=IV+1
      XMF(I)=XMFS(IV)
      X(I)=XS(IV)

```

```

NO(I)=NDS(IV)
BCD(I)=BCDS(IV)
F(I)=FS(IV)
C(I)=CS(IV)
FRT(I)=FRTS(IV)
H(I)=HS(IV)
DO 3094 J=1,NP
3094 FI(I,J)=FIS(IV,J)
DO 3095 J=1,M
3095 A(J,I)=AS(J,IV)
3093 CONTINUE
3092 NS=II-NG
NSS=III-NGS
N=II
IF(N.LT.M) GO TO 2500
GO TO 6951
245 WRITE(6,246)
246 FORMAT('1****ITERATION LIMIT EXCEEDED****')
IF(PT)691,9970,9980
9970 WRITE(6,22)TC,V
GO TO 909
9980 WRITE(6,21)TC,PT
GO TO 909
2500 K=0.0
NA=N+1
NAA=N+NGS
NAAA=NAA+1
NGA=NG+1
IF(NG.EQ.0) GO TO 2520
DO 2620 I=1,NG
K=K+1
XL(K)=X(I)
XMFL(K)=XMF(I)
BCDL(K)=BCD(I)
FL(K)=F(I)
NOL(K)=NO(I)
CL(K)=C(I)

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```

      FRTL(K)=FRT(I)
      HL(K)=H(I)
      DO 2621 J=1,M
2621  AL(J,K)=A(J,I)
      DO 2622 J=1,NP
2622  FIL(K,J)=FI(I,J)
2620  CONTINUE
2520  IF(NGS.EQ.0)GO TO 2623
      DO 2624 I=NA,NAA
      K=K+1
      XL(K)=X(I)
      XMFL(K)=XMF(I)
      BCDL(K)=BCD(I)
      FL(K)=F(I)
      NOL(K)=NO(I)
      CL(K)=C(I)
      FRTL(K)=FRT(I)
      HL(K)=H(I)
      DO 2625 J=1,M
2625  AL(J,K)=A(J,I)
      DO 2626 J=1,NP
2626  FIL(K,J)=FI(I,J)
2624  CONTINUE
2623  IF(NS.EQ.0)GO TO 2627
      DO 2628 I=NGA,N
      K=K+1
      XL(K)=X(I)
      XMFL(K)=XMF(I)
      BCDL(K)=BCD(I)
      FL(K)=F(I)
      NOL(K)=NO(I)
      CL(K)=C(I)
      FRTL(K)=FRT(I)
      HL(K)=H(I)
      DO 2629 J=1,M
2629  AL(J,K)=A(J,I)
      DO 2630 J=1,NP

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```

2630 FIL(K,J)=FI(I,J)
2628 CONTINUE
2627 IF(NSS.EQ.0)GO TO 2631
      DO 2632 I=NAAA,NOR
        K=K+1
        XL(K)=X(I)
        XMFL(K)=XMF(I)
        BCDL(K)=BCD(I)
        FL(K)=F(I)
        NOL(K)=NO(I)
        CL(K)=C(I)
        FRTL(K)=FRT(I)
        HL(K)=H(I)
        DO 2633 J=1,M
2633 AL(J,K)=A(J,I)
        DO 2634 J=1,NP
2634 FIL(K,J)=FI(I,J)
2632 CONTINUE
2631 K=0.0
      IF(NOR-NSOR) 5003,2503,2525
2525 DO 2529 I=1,NGOR
      IF(XMFL(I).GT..01)GO TO 2529
      PPPA(I)=0.0
      DO 2530 J=1,M
      PPA(J)=AL(J,I)*P(J)
2530 PPPA(I)=PPPA(I)+PPA(J)
      XL(I)=XB*DEXP(-C(I)+PPPA(I))
      XMFL(I)=XL(I)/XB
2529 CONTINUE
      DO 2531 I=1,NGOR
      IF(XL(I).GT.1.E-25) GO TO 2532
      XL(I)=0.0
      GO TO 2531
2532 K=K+1
      X(K)=XL(I)
      XMF(K)=XMFL(I)
      BCD(K)=BCDL(I)

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      NO(K)=NOL(I)
      F(K)=FL(I)
      C(K)=CL(I)
      FRT(K)=FRTL(I)
      H(K)=HL(I)
      DO 2536 J=1,M
2536  A(J,K)=AL(J,I)
      DO 2537 J=1,NP
2537  FI(K,J)=FIL(I,J)
2531  CONTINUE
      NG=K
2503  IF(NSOR) 7000,2501,2533
2533  NGORA=NGOR+1
      DO 2538 I=NGORA,NOR
      IF(XL(I).GT.1.E-25) GO TO 2542
      XL(I)=0.0
      GO TO 2538
2542  K=K+1
      X(K)=XL(I)
      XMF(K)=XMFL(I)
      BCD(K)=BCDL(I)
      F(K)=FL(I)
      NO(K)=NOL(I)
      C(K)=CL(I)
      FRT(K)=FRTL(I)
      H(K)=HL(I)
      DO 2543 J=1,M
2543  A(J,K)=AL(J,I)
      DO 2544 J=1,NP
2544  FI(K,J)=FIL(I,J)
2538  CONTINUE
2501  N=K
      NS=N-NG
      NSOR=NS
      NGOR=NG
      NOR=N
      WRITE(6,13)

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13 FORMAT(1H1)
3664 WRITE(6,14)(NAME(I),I=1,10)
14 FORMAT(5X,'EQUILIBRIUM COMPOSITIONS FOR ',10A8)
   IF(PT) 691,710,712
710 WRITE(6,22)TC,V
   GO TO 714
712 WRITE(6,21) TC,PT
714 WRITE(6,4001)
4001 FORMAT(5X,'MAJOR COMPONENTS')
   WRITE(6,4002)
4002 FORMAT(10X,'COMPONENT      MOLE FRACTION      NO OF MOLES')
   DO 4003 I=1,NOR
   IF(XMF(I).LT..0001)GO TO 4003
   WRITE(6,4004)BCD(I),XMF(I),X(I)
4004 FORMAT(13X,1A4,8X,F9.6,8X,D15.5)
4003 CONTINUE
   WRITE(6,4005)
4005 FORMAT(5X,'TRACE COMPONENTS')
   WRITE(6,4006)
4006 FORMAT(10X,'COMPONENT      PARTS PER MILLION      NO OF MOLES')
   DO 4007 I=1,NOR
   IF(XMF(I).GE..0001.OR.XMF(I).LT..000001)GO TO 4007
   XPPM=XMF(I)*10.0**6
   WRITE(6,4008)BCD(I),XPPM,X(I)
4008 FORMAT(13X,1A4,8X,F6.2,11X,D15.5)
4007 CONTINUE
   WRITE(6,4009)
4009 FORMAT(5X,'NEGLIGIBLE COMPONENTS')
   WRITE(6,4002)
   DO 4010 I=1,NOR
   IF(XMF(I).GE..000001)GO TO 4010
   WRITE(6,4011)BCD(I),XMF(I),X(I)
4011 FORMAT(13X,1A4,8X,D10.3,7X,D15.5)
4010 CONTINUE
   WRITE(6,4012)XB,FT,NI(1),NI(2)
4012 FORMAT(5X,'TOTAL MOLES = ',F10.5, /
15X,'TOTAL FREE ENERGY = ',F15.5, /

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    25X,'TOTAL ITERATIONS BEFORE SEPARATION = ',I3,/
    35X,'TOTAL ITERATIONS AFTER SEPARATION = ',I3,/
    IF(DLA.LT..005)GO TO 4014
4013 WRITE(6,4015)DLA
    GO TO 4017
4015 FORMAT(5X,'STEP SIZE BEFORE SEPARATION = ',F8.5)
4014 WRITE(6,4016)
4016 FORMAT(5X,'STEP SIZE BEFORE SEPARATION NOT FOUND')
4017 IF(DL.LT..005)GO TO 4019
4018 WRITE(6,4020)DL
4020 FORMAT(5X,'STEP SIZE AFTER SEPARATION = ',F8.5)
    GO TO 909
4019 WRITE(6,4021)
4021 FORMAT(5X,'STEP SIZE AFTER SEPARATION NOT FOUND')
    909 TC=TC+DT
        T=T+DT*1.8
        N=NOR
        IF(CHECK) GO TO 5001
        GO TO 906
C    CHECK PROCEDURES
    305 IF(N-NS)5003,7116,7112
    7112 WRITE(6,313) (BCD(I),X(I),XMF(I),F(I), I=1,NG)
    313 FORMAT(10X8HCOMPOUND,12X,5HMOLES,12X,13HMOLE FRACTION,6X,
    111HFREE ENERGY/(11X,1A4,8XD19.12,8XD19.12,8XD19.12,/))
        IF(NS)7000,7117,7116
    7116 WRITE(6,313) (BCD(I),X(I),XMF(I),F(I), I=NGP1,N)
    7117 WRITE(6,215)FT,NI(MXP)
    215 FORMAT(10X19HTOTAL FREE ENERGY =,F15.5,
    12X,'ITERATIONS = ',I3)
        GO TO 695
    810 IF(NI(MXP).GT.3) GO TO 93
        WRITE(6,403)
    403 FORMAT(10X3HRP )
    83 WRITE(6,82) ((RP(I,J),I=1,MP1),J=1,MP1)
    82 FORMAT(/20F6.1,/ )
        WRITE(6,404)
    404 FORMAT(10X3HATF)

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      WRITE(6,84) (ATF(I),I=1,MP1)
84  FORMAT(/10F12.3,/)
      GO TO 93
85  WRITE(6,405)
405  FORMAT(10X27H U AND LAGRANGE MULTIPLIERS)
      WRITE(6,97) U, (P(I),I=1,M)
87  FORMAT(10X,11F10.5)
      GO TO 99
1501 IF(NI(MXP).GT.3) GO TO 7125
      WRITE(6,403)
      WRITE(6,82) ((RP(I,J),I=1,MPNS),J=1,MPNS)
      WRITE(6,404)
      WRITE(6,84) (ATF(I),I=1,MPNS)
      GO TO 7125
1502 WRITE(6,1503)
1503 FORMAT(10X23H LAGRANGE MULTIPLIERS )
      WRITE(6,97) (P(I),I=1,M)
      GO TO 100
1504 IF(NI(MXP).GT.3) GO TO 94
      WRITE(6,403)
      WRITE(6,82) ((RP(I,J),I=1,MPNS),J=1,MPNS)
      WRITE(6,404)
      WRITE(6,84) (ATF(I),I=1,MPNS)
      GO TO 94
1505 WRITE(6,1503)
      WRITE(6,97) (P(I),I=1,M)
      GO TO 1506
1516 IF(NI(MXP).GT.3) GO TO 7340
      WRITE(6,403)
      WRITE(6,82) ((RP(I,J),I=1,NN),J=1,NN)
      WRITE(6,404)
      WRITE(6,84) (ATF(I),I=1,NN)
      GO TO 7340
1507 WRITE(6,1503)
      WRITE(6,97)(P(I),I=1,M)
      GO TO 7343
300 WRITE(6,215) FTN, NI(MXP)

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```

WRITE(6,1510)DL
1510 FORMAT(10X11HSTEP SIZE =,D14.6)
IF(N-NS) 5003,1508,1511
1511 WRITE(6,214) XB,XBL
214 FORMAT(10X,13HTOTAL MOLES =,F10.5,5H AND ,F10.5)
WRITE(6,313) (BCD(I),X(I),XMF(I),F(I),I=1,NG)
1508 IF(NS) 7000,907,908
908 WRITE(6,313)(BCD(I),X(I),XMF(I),F(I),I=NGP1,N)
907 WRITE(6,400)
400 FORMAT(10X8HRESIDUES)
WRITE(6,216) (CK(I),I=1,M)
216 FORMAT(/12F10.5,/)
GO TO 240
5001 WRITE(6,5002)
5002 FORMAT('1')
906 CONTINUE
GO TO 6
C ERROR MESSAGES
691 WRITE(6,692)
692 FORMAT(10X20HPRESSURE IS NEGATIVE)
GO TO 6
7000 WRITE(6,694)
694 FORMAT(10X14HNS IS NEGATIVE)
GO TO 6
5003 WRITE(6,5004)
5004 FORMAT(10X20HNS IS GREATER THAN N)
6 STOP
END
SUBROUTINE SIMEQ (A,B,N)
C SOLVES A SET OF SIMULTANEOUS EQUATIONS
DOUBLE PRECISION A(11,11), B(11)
DO 11 I=1,N
IF (A(I,I)) 1,25,1
25 I1 = I + 1
DO 29 L=I1,N
IF (A(L,I)) 30,29,30
29 CONTINUE

```

```

WRITE (6,1000)
STOP
30 DO 35 K=I,N
   F = A(L,K)
   A(L,K) = A(I,K)
35 A(I,K) = F
   F = B(L)
   B(L) = B(I)
   B(I) = F
1 DO 6 K=1,N
   IF (K-I) 5,6,5
5 A(I,K) = A(I,K)/A(I,I)
6 CONTINUE
   B(I) = B(I)/A(I,I)
   A(I,I) = 1.0
   DO 10 J=1,N
   IF (J-I) 7,10,7
7 DO 9 K=1,N
   IF (K-I) 8,9,8
8 A(J,K) = A(J,K) - A(J,I)*A(I,K)
9 CONTINUE
   B(J) = B(J) - A(J,I)*B(I)
   A(J,I) = 0.0
10 CONTINUE
11 CONTINUE
1000 FORMAT (28HDETERMINANT = 0, NO SOLUTION)
RETURN
END

```