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UMI
THERMAL DECOMPOSITION OF CALCIUM SULFATE

by

Walter Michael Bollen

A Dissertation Submitted to the
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In Charge of Major Work

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The shortage of Frasch-minable sulfur reserves has led to consideration of other materials as sources of sulfur and sulfuric acid. Naturally occurring calcium sulfate, gypsum and anhydrite, have been considered and in fact used for more than 30 years. However, addition agents have invariably been added to lower the required decomposition temperature and decrease the thermal requirements. The purpose of the work of this thesis was the investigation of processes which would not require the addition of such agents. The maximum possible sulfur dioxide concentration in the dry off-gas from such a process would be 18.0 per cent, based on an overall thermal efficiency of 100 per cent.

The majority of the investigations were with gypsum, but a few studies were also made with anhydrite. Two types of reactors were studied: a shaft furnace and a fluidized bed.

The work with the shaft furnace was limited to nominally oxidizing conditions; i.e. greater than the stoichiometric amount of air required for combustion was supplied. In the
temperature range 2400°F to 2450°F a retention time of 6 1/2 hours was estimated to be required for 95 per cent desulfurization. However, it was not possible to operate with retention times greater than 2 1/2 to 3 hours because of fusion of the surface of the lumps and subsequent sticking of the charge. This fusion would start at about 2375°F. At 2250°F to 2350°F the estimated retention time for 95 per cent desulfurization was 30 hours. At temperatures greater than 2600°F the charge became completely molten but resolidified after a portion of the sulfur trioxide was expelled and completely plugged the shaft. One run in which reducing conditions were present produced an excellent unfused product which was 96 per cent desulfurized. The maximum temperature was 2550°F and the retention time was 4 hours. However, the effect of reducing conditions was not recognized until later work with the fluidized bed, so further investigations under these conditions were not made with the shaft furnace.

The studies with the fluidized bed brought out the importance of the oxidation-reduction characteristics of the bed atmosphere. It was found that with 117 per cent or greater of the stoichiometric air supplied, only very slight desulfurization occurred at temperatures below fusion. However, as the amount of air supplied was decreased and reducing substances, notably carbon monoxide, appeared, desulfurization occurred with no fusion at temperatures above 2100°F.
If the air was decreased to less than 100 per cent of that stoichiometrically required, no appreciable oxygen was present and calcium sulfide formation accompanied the desulfurization and prevented complete desulfurization. Consequently, at a constant gas/air ratio maximum desulfurization (96 per cent desulfurization with a 120 minute retention time) was obtained with 100 per cent stoichiometric air, under which conditions both carbon monoxide and oxygen were present. The sulfide formed under reducing conditions could be rapidly oxidized to calcium oxide and sulfur dioxide by supplying an excess of air.

The reactions involved probably include:

\[
\begin{align*}
\text{CaSO}_4 + \text{CO} & \rightleftharpoons \text{CaO} + \text{SO}_2 + \text{CO}_2 \\
\text{CaSO}_4 + 4\text{CO} & \rightleftharpoons \text{CaS} + 4\text{CO}_2 \\
3\text{CaSO}_4 + \text{CaS} & \rightleftharpoons 4\text{CaO} + 4\text{SO}_2 
\end{align*}
\]

The equilibrium constants for these and other possible reactions were computed over the temperature range of interest. The equilibrium constant for the last reaction above in the range 2000°F to 2400°F is favored by higher temperatures. Because of this, the amount of residual sulfide decreases and hence desulfurization increases with increasing temperature in this temperature range under reducing conditions.

No fusion of particles was observed at temperatures as high as 2450°F when reducing conditions were present, al-
though under oxidizing conditions temperatures of 2400°F caused serious fusion.

Work with anhydrite was limited to the temperature range 2250°F to 2350°F at 80 and 95 per cent of stoichiometric air supplied. Particle size studies were, however, made with this material. With -6+8 mesh particles, the desulfurization was slower than with gypsum under the same conditions, as would be expected since the gypsum is "opened up" by the dehydration process. The particle size studies presented a curious phenomenon. With -8+10 and -10+12 mesh particles the bed was about 600°F to 800°F cooler than with the -6+8 mesh particles at the same fluidizing gas inlet temperature. Consequently, the smaller particle sizes were least desulfurized. This occurred with both constant gas rate conditions and approximately constant bed porosity conditions suggesting an extreme effect of the particle size on the heat transfer characteristics of the fluidized bed.

This work demonstrates that sulfur or sulfur dioxide can be produced from the virtually unlimited supply of natural calcium sulfate without the use of addition agents. The desulfurization of calcium sulfate can be accomplished below its fusion temperature in either a reducing or alternately reducing and oxidizing atmosphere. Economically, it could not compete in the United States with Frasch-mined sulfur, but if these sulfur deposits become depleted such
a process might be competitive with other sulfur producing processes, particularly if there existed a market for the by-product lime produced.
INTRODUCTION

Sulfur is often termed the basic chemical of American industry. It finds application, in one form or another, in the manufacture of a great many items of daily use. Indeed, the statement has been made that all articles have, at some point in their manufacture, directly or indirectly required the use of sulfur.

Most of the sulfur produced is used for the manufacture of sulfuric acid, which is used in such a variety of industries that its consumption is considered an accurate indication of business conditions and may be used as an index of business activity and the nation's economic prosperity.

Sulfur is produced in the United States at present from four sources: (1) underground free sulfur deposits which may be readily mined by the Frasch method; (2) iron pyrites, FeS₂; (3) petroleum gases containing hydrogen sulfide; and (4) smelter gases containing sulfur dioxide and/or sulfur trioxide. In 1953 in the United States 80.4 per cent of the sulfur produced was Frasch-mined sulfur. Roasting of pyrites accounted for 7.7 per cent, hydrogen sulfide from petroleum
gases 5.36 per cent, and smelter gases 4.19 per cent. A total of 6,440,000 long tons was produced, of which 1,250,000 long tons were exported and 4,060,000 long tons went for the manufacture of sulfuric acid. There was no commercial production of sulfur in the United States from gypsum or anhydrite.

At the present time there is apparently an adequate supply of sulfur for both domestic use in, and export from, the United States. However, in 1951 there existed a sulfur shortage such that the National Production Authority, the Office of International Trade, and the International Materials Conference allocated this basic chemical. When the reserves of Frasch-minable sulfur are exhausted, the reserves to which we may turn are pyrites, low grade sulfur ores, smelter gases, sour petroleum gases, coal, and natural sulfate minerals including gypsum and anhydrite.

Deposits of natural sulfates, specifically gypsum and anhydrite, have been described as inexhaustible. In Oklahoma, exposures alone show 30 billion tons of high grade anhydrite and gypsum equivalent to about 560,000,000 tons of sulfur [8].

Calcium sulfate occurs in nature in two forms: gypsum and anhydrite. Gypsum is the term applied to naturally occurring calcium sulfate hydrated with two molecules of water.
per molecule of CaSO₄. Anhydrous calcium sulfate also occurs naturally and is termed anhydrite.

Heating gypsum to a temperature of between 212°F and 399°F drives off three-quarters of the water of hydration, producing plaster of Paris. When heated above 399°F, gypsum loses all of its water of hydration to form anhydrous calcium sulfate, the base of common plasters. The CaSO₄ so obtained is often termed "soluble" CaSO₄ because, although relatively insoluble, continued heating at high temperatures changes the salt to one which is even less soluble. This latter is termed "insoluble" calcium sulfate.

Gypsum has a monoclinic crystal system, a hardness of 1.5 to 2.0 on the Moh scale, a specific gravity of 2.32, and refractive index of 1.523. Its color may be white, gray, yellow, or black. Anhydrite exhibits an orthorhombic crystal structure, a Moh hardness of 3 to 3.5, specific gravity of 2.8 to 3.0, and is white to grayish white in color. It is frequently associated with gypsum deposits. Both have a fusion temperature, in the pure state, of about 2640°F. At 2179°F the rhombic structure of anhydrite transforms to a monoclinic crystal system.

Deposits of gypsum and anhydrite are well scattered throughout the world. In 1950 there were an estimated 13,300,000 metric tons of gypsum produced in 46 countries
exclusive of the United States. Eight other countries for which production data is not available also mined gypsum.

In the United States 8,192,625 short tons of gypsum were mined in 1950 from 57 active mines in 18 states. Seventy-five per cent of this came from the six states of California, Iowa, Michigan, Nevada, New York, and Texas. The remainder was mined in Arizona, Arkansas, Kansas, Louisiana, Colorado, Montana, Washington, Wyoming, Ohio, Oklahoma, Utah, and Virginia [20].

The average value of the crude gypsum mined in the United States in 1950 was $2.78 per ton. Its use was distributed as follows: gypsum board, 43 per cent; lath, 24 per cent; building plasters, 19 per cent; industrial plasters, 2 per cent; tile, 3 per cent; uncalcined uses, 4 per cent.

Anhydrite has not been exploited in the United States as there is little demand for it. Some anhydrite is produced in Canada, largely for export to the southeastern United States where it finds use as a fertilizer for the peanut crop. In Great Britain, where it is used as a raw material for sulfuric acid manufacture, its production is of major importance.

The sulfur in calcium sulfate may be converted to a usable form either by chemical or thermal decomposition. Chemically, the calcium sulfate will undergo a double decom-
position reaction with ammonium carbonate to produce ammonium sulfate and calcium carbonate. This is known as the Merseberg reaction and is being utilized in India.

Thermal decomposition at elevated temperatures results in the formation of sulfurous gases which may be converted to either sulfuric acid or sulfur. Processes based on this thermal decomposition for the manufacture of sulfuric acid have been used in Europe and Great Britain for about 35 years. In these processes slagging materials such as silica, alumina, and various clays are added to decrease the temperature and thermal requirements. The solid by-product material is a usable cement clinker. In the United States these processes have not been able to compete with the Frasch process.

The work described in this dissertation was concerned with the development of a thermal process for the desulfurization of gypsum or anhydrite without the addition of any slagging agents. The solid by-product in such a case would be lime, presumably of an agricultural grade, which would require no further treatment, with the possible exception of slaking. The cumbersome and expensive equipment of a cement plant would thus be eliminated.
Hoffman and Mostowitsch were interested in the effect of heat on calcium sulfate from the standpoint of metallurgical processes in which it was used as a basic flux. They published a paper in 1908 [13] presenting the results of researches in which they found that pure $\text{CaSO}_4\cdot\text{H}_2\text{O}$ subsequent to its dehydration commenced to dissociate at $2190^\circ\text{F}$ and fused at $2480^\circ\text{F}$. When silica was added to the $\text{CaSO}_4$, decomposition began at $1830^\circ\text{F}$ and was complete at $2280^\circ\text{F}$ to $2370^\circ\text{F}$ which was below the melting point of the silicate presumed to have been formed. Ferric oxide was also investigated as an additive and found to lower the temperature at which decomposition commenced to $2010^\circ\text{F}$ for a mixture corresponding to $\text{CaSO}_4\cdot\text{Fe}_2\text{O}_3$.

Subsequent to the above work, they published in 1910 a paper [14] presenting the results of work which indicated that calcium sulfate was reduced by carbon monoxide to calcium sulfide without loss of sulfur, the reduction beginning at about $1300^\circ\text{F}$. Roasting of the resultant sulfide with pure dry air at temperatures of $1470^\circ\text{F}$ or greater gave a
product containing 76 per cent CaSO₄ and 26 per cent CaO.

This was attributed to the reactions

\[
CaS + 2O_2 = CaSO_4
\]  
\[
3CaSO_4 + CaS = 4CaO + 4SO_2
\]

which they claimed could occur only in a neutral or oxidizing atmosphere, the CaSO₄ being too rapidly converted to CaS by the carbon monoxide of a reducing atmosphere.

Marchal [17] presented one of the earliest papers discussing the calculation of free energies and actual measurement of the decomposition equilibrium constants for the reaction

\[
CaSO_4 = CaO + SO_2 + \frac{1}{2} O_2
\]

She measured the equilibrium pressure of the decomposition products of both pure gypsum and mixtures of gypsum with such additives as silica and alumina. She found that dissociation according to the above reaction was first observed at 1760°F. At a temperature of 2246°F, the highest studied, the total decomposition pressure was 97 mm. of Hg.

Subsequent to the work of Marchal, Zawadzki [21] studied the decomposition of gypsum and found that the decomposition pressure decreased appreciably with time at elevated temperatures, approaching that of anhydrite. After 190 minutes of
preheating to 2210°F, the decomposition pressure decreased from 68 mm. of Hg to 14.3 mm. of Hg after 1810 minutes. This was attributed to a change in the crystalline form of the calcium sulfate, specifically from gypsum to anhydrite. The results of both Marchal and Zawadzki are presented later in Figure 3.

Zawadzki also investigated the equilibrium decomposition pressure above a mixture containing CaS and CaSO₄ in a 1:3 mole ratio. The following reactions were assumed to occur:

\[
\text{CaS} + 3\text{CaSO}_4 = 4\text{CaO} + 4\text{SO}_2 \tag{2}
\]
\[
\text{CaS} + 2\text{SO}_2 = \text{CaSO}_4 + \text{S}_2 \tag{4}
\]

At 1652°F the total equilibrium decomposition pressure was 6 mm. of Hg; at 2192°F it was 760 mm. of Hg.

Briner [3] also calculated decomposition pressures for the reaction

\[
\text{CaSO}_4 = \text{CaO} + \text{SO}_2 + \frac{1}{2} \text{O}_2 \tag{3}
\]

at 1880°F and 2061°F. His value for 2061°F agreed very well with the experimental work of Zawadzki.

Briner, Pamm, and Paillard [5] studied the effect of adjuvants as silica and metakaolin on sodium sulfate and potassium sulfate as well as calcium sulfate.
Briner and Knodel [4] found that heating anhydrite in water vapor rather than air resulted in a more rapid decomposition.

Curti [9] studied the decomposition of pure CaSO₄ by X-ray analysis and found that decomposition commenced above 2372°F. He suggested further that a vitreous modification is formed before this decomposition takes place and that during the decomposition a basic sulfate, 3CaO·2CaSO₄, is formed.

Newman [18] in a careful study found the transition of beta calcium sulfate to alpha calcium sulfate to occur at approximately 2217°F, but that this high temperature form was unstable and could not be studied at room temperature. He could not confirm the existence of basic sulfates, but did find what appeared to be an eutectic mixture formed by CaO and alpha CaSO₄ which melted at approximately 2490°F.

Gavanda [11] in a review of German and French patents states that sulfur dioxide is obtained from gypsum by the following thermal methods:

1. Decomposition of gypsum by heating at 2550°F:
   \[
   \text{CaSO}_4 = \text{CaO} + \text{SO}_2 + \frac{1}{2} \text{O}_2 \quad (3)
   \]

2. Reaction with coal:
   \[
   \text{CaSO}_4 + \text{C} = \text{CaO} + \text{SO}_2 + \text{CO} \quad (5)
   \]
   or
   \[
   \text{CaSO}_4 + 2\text{C} = \text{CaS} + 2\text{CO}_2 \quad (6)
   \]
   from which
   \[
   \text{CaS} + \text{CO}_2 + \text{H}_2\text{O} = \text{CaCO}_3 + \text{H}_2\text{S} \quad (7)
   \]
   \[
   \text{H}_2\text{S} + 1\frac{1}{2} \text{O}_2 = \text{H}_2\text{O} + \text{SO}_2 \quad (8)
   \]
3. Reaction with $\text{SiO}_2$ (clinker process):

$$\text{CaSO}_4 + \text{SiO}_2 = \text{CaSiO}_3 + \text{SO}_3 + \frac{1}{2} \text{O}_2 \quad (9)$$

Disintegration begins at 1742°F with 5 per cent $\text{SiO}_2$

1395°F with 35 per cent $\text{SiO}_2$

4. Reaction with $\text{Al}_2\text{O}_3$ at 1715°F:

$$\text{CaSO}_4 + \text{Al}_2\text{O}_3 = \text{Al}_2\text{O}_3\text{CaO} + \text{SO}_3 + \frac{1}{2} \text{O}_3 \quad (10)$$

5. Disintegration of gypsum or anhydrite with the addition of coal, $\text{SiO}_2$, and $\text{Al}_2\text{O}_3$.

Stinson and Mumma [19] have recently studied methods for the regeneration of sulfuric acid from phosphogypsum, the by-product calcium sulfate from wet process phosphoric acid manufacture. Silica and $\text{R}_2\text{O}_3$ were added as adjuvants and the decomposition studied at temperatures both below and above fusion. Calcination at 2372°F resulted in complete desulfurization in 15 to 30 minutes of an agglomerated mixture having a three per cent $\text{R}_2\text{O}_3$ content and a $\text{SiO}_2:5$ mole ratio of one.

Higson [12] lists several European plants producing sulfuric acid from calcium sulfate, including one under construction in England which would produce 165,000 tons of $\text{H}_2\text{SO}_4$ per year. These plants produce cement as a by-product. The process consists of heating in a rotary kiln a mixture of calcium sulfate, carbon, clay, sand, and other ingredients containing alumina, silica, and iron oxides. During this
When anhydrite is used as the raw material, which is the case in England, a SO$_2$ concentration in the off-gas of about nine per cent is obtained. One ton of cement clinker is produced for each ton of sulfuric acid produced. Taking credit for the by-product cement clinker, the net cost is $16.85 per short ton of H$_2$SO$_4$ produced. This compares with $14.06 per short ton for a sulfur burning plant and $17.70 per short ton for a pyrites burning plant (in England).

Cathala [7] has described the results of rather large scale gypsum decomposition by electrothermal means. An arc furnace having inside dimensions of three meters in diameter by three meters in height was used. The feed was a mixture of calcium sulfate and quartz, corresponding to the eutectic with a melting point of 2687°F, plus coke to prevent rapid oxidation of the carbon electrodes by the oxygen liberated by the decomposition. The off-gases contained 50 per cent SO$_2$. Twenty-two hundred kilowatt hours of power and 25 to
30 pounds of carbon electrodes were utilized per ton of 100 per cent $\text{H}_2\text{SO}_4$ produced.

Bell [2] sintered calcium sulfate (plaster of paris) with a low grade "weathered" phosphatic rock at 2102°F to 2282°F and obtained slightly better than 90 per cent desulfurization of the calcium sulfate and 75 per cent conversion of the $\text{P}_2\text{O}_5$ to the citric soluble form.
THEORETICAL CONSIDERATIONS

Equilibrium Considerations

One can speculate on what reactions might be involved during the thermal decomposition of calcium sulfate, and then determine the probability of these reactions by calculating the equilibrium constant from the expression

$$4.576 \log_{10} K = -\left(\frac{\Delta G^o}{T}\right)_T.$$

The equilibrium constant will not in itself establish the rate at which the postulated reactions will occur. This is established by the kinetic relationships, rate of removal of products, and inert materials present. However, the equilibrium constant will indicate which reactions are feasible and which are not.

The thermal decomposition of calcium sulfate, in the absence of other reacting substances, could proceed according to either or both of the following two reactions:
\[
\text{CaSO}_4(s) = \text{CaO}(s) + \text{SO}_2(g) + \frac{1}{2} \text{O}_2(g) \quad (3)
\]
\[
\text{CaSO}_4(s) = \text{CaO}(s) + \text{SO}_3(g). \quad (14)
\]

In the presence of water vapor, it is conceivable that the following might be involved:

\[
\text{CaSO}_4(s) + \text{H}_2\text{O}(\ell) = \text{H}_2\text{SO}_4(\ell) + \text{CaO}(s) \quad (15)
\]
\[
\text{CaSO}_4(s) + \text{H}_2\text{O}(g) = \text{H}_2\text{SO}_4(g) + \text{CaO}(s) \quad (16)
\]
\[
\text{H}_2\text{SO}_4(\ell) = \text{SO}_3(g) + \text{H}_3\text{O}(g). \quad (17)
\]

From thermodynamic considerations equations have been derived relating the equilibrium constants of the foregoing reactions with temperature. The equations so derived are listed in Table II of the Appendix. The method of calculation is also presented in the Appendix. Values of the equilibrium constant, \( K \), have been computed for various temperatures and the results plotted in Figure 1. From this plot the following observations may be made:

1. The temperature required for appreciable decomposition of calcium sulfate by either reaction (3) or (14) will be 2420°F or higher.

2. At the temperatures required for this decomposition, sulfur trioxide is unstable, decomposing into sulfur dioxide and oxygen. Thus reaction (14) would seem to be improbable.
FIGURE 1  EQUILIBRIUM CONSTANTS OF SELECTED REACTIONS
Oxidizing Conditions
3. Reactions (15) and (16) seem improbable inasmuch as sulfuric acid is decomposed into sulfur trioxide and water at temperatures considerably lower than those at which these reactions become appreciable. Thus it may be concluded that the most probable decomposition reaction in oxidizing atmospheres would be that of reaction (3).

When reducing conditions are considered, there are many other reactions which might occur. If the reducing agent is limited to carbon monoxide, the following reactions suggest themselves as of possible interest:

\[
\begin{align*}
\text{CaSO}_4 + \text{CO} & = \text{CaO} + \text{SO}_2 + \text{CO}_2 \\
\text{CaSO}_4 + 3\text{CO} & = \text{CaO} + \frac{1}{2} \text{S}_2 + 3\text{CO}_2 \\
\text{CaSO}_4 + 4\text{CO} & = \text{CaS} + 4\text{CO}_2 \\
\text{CaSO}_4 + 4\text{CO} + \text{H}_2\text{O}(g) & = \text{CaO} + \text{H}_2\text{S} + 4\text{CO}_2 \\
\text{CaS} + \frac{1}{2} \text{O}_2 & = \text{CaO} + \text{SO}_2 \\
\text{CaO} + \text{H}_2\text{S} & = \text{CaS} + \text{H}_2\text{O}(g) \\
\text{H}_2\text{S} + \frac{1}{2} \text{O}_2 & = \text{SO}_2 + \text{H}_2\text{O}(g) \\
\text{CaS} + 3\text{CaSO}_4 & = 4\text{CaO} + 4\text{SO}_2 \\
2\text{H}_2\text{S} + \text{SO}_2 & = 2\text{H}_2\text{O} + \frac{1}{2} \text{S}_2 \\
\text{SO}_2 + 3\text{CO} + \text{H}_2\text{O}(g) & = \text{H}_2\text{S} + 3\text{CO}_2 .
\end{align*}
\]
The equilibrium constants have been evaluated as a function of temperature for the above reactions also. The equations derived are listed in Table 12 of Appendix A and the results of the computations are presented in Figure 2. It is not possible to draw a general conclusion from this set of curves. It appears that decomposition may result in the formation of either or both hydrogen sulfide and sulfur dioxide. If there is any oxygen present, there would be a strong tendency for the sulfides, i.e. hydrogen sulfide and calcium sulfide, to be oxidized to the corresponding oxide and sulfur dioxide.

From the equilibrium constant, it is possible to compute a theoretical decomposition pressure, i.e. equilibrium pressure of sulfur dioxide above calcium sulfate. These have been calculated for reaction (3) and are plotted on Figure 3. The experimental results of Marchal [16] and Zawadzki [20], which have been previously discussed, have also been plotted on this figure.

Thermal Requirements

Use was made of the standard heat of formation data to compute the standard heat of reaction at 18°C for the reactions involving calcium sulfate which appeared to be of interest. The results of these computations are summarized in
FIGURE 2. EQUILIBRIUM CONSTANTS OF SELECTED REACTIONS

Reducing Conditions
Figure 3
Decomposition Pressure of Calcium Sulfate

- DATA OF MARCHAL
- DATA OF ZAWADZKI, GYPSUM
- DATA OF ZAWADZKI, "TRANSFORMED" GYPSUM

Temperature - °F
Calculated Values.
Table 1
Heat of Reaction at 18°C for Selected Reactions

<table>
<thead>
<tr>
<th>Reaction number</th>
<th>$\Delta H_{18^\circ C}$</th>
<th>Heat required</th>
</tr>
</thead>
<tbody>
<tr>
<td>(pp. 14 &amp; 15)</td>
<td>cal./g.mole</td>
<td>Btu/ton sulfur based on $\Delta H_{18^\circ C}$</td>
</tr>
<tr>
<td>3</td>
<td>117,800</td>
<td>13,210,000</td>
</tr>
<tr>
<td>18</td>
<td>50,400</td>
<td>5,650,000</td>
</tr>
<tr>
<td>19</td>
<td>-13,500</td>
<td>-1,515,000</td>
</tr>
<tr>
<td>20</td>
<td>-42,600</td>
<td>-4,785,000</td>
</tr>
<tr>
<td>21</td>
<td>-28,400</td>
<td>-3,190,000</td>
</tr>
<tr>
<td>22</td>
<td>-109,500</td>
<td>-12,300,000</td>
</tr>
<tr>
<td>2</td>
<td>244,100</td>
<td>6,850,000</td>
</tr>
</tbody>
</table>
FIGURE 4. MATERIAL AND ENERGY BALANCE FOR THERMAL DECOMPOSITION OF GYPSUM

Basis: 1 pound gypsum fed
Stoichiometrically required air supplied
Datum: 60°F, H₂O as vapor
Table 1. It is interesting to note that those reactions involving carbon monoxide are exothermic, whereas the thermal decomposition in a neutral or oxidizing atmosphere is quite endothermic. The heat liberated by the oxidation of the carbon monoxide in the former reaction is the cause of this reversal.

A theoretical heat and material balance for one pound of gypsum decomposed according to reaction (3) is presented in Figure 4. This is based on an overall thermal efficiency of 100 per cent, i.e. no heat is lost in the solid or gaseous products which are assumed to transfer their heat to the entering combustion air. The fuel is assumed to be a natural gas containing 96 per cent methane and four per cent inert having a net heating value of 925 Btu per standard cubic foot (0°C, 760 mm. Hg). A datum temperature of 60°F is used. It is also assumed that the amount of air supplied was that required to provide the stoichiometric amount of oxygen required for the combustion less that supplied by the gypsum decomposition.

The calculated analysis of the off-gas indicates a SO₂ content of 11 per cent on the wet basis or 18 per cent on the dry basis.

To illustrate the desirability of recovery of the waste heat in the products, the amount of heat so leaving prior to its recovery by the entering combustion air has been indicated.
MATERIALS USED

Source and Preparation

Gypsum

The gypsum used for these investigations was obtained in three lots from the Fort Dodge, Iowa, works of the United States Gypsum Company. All three lots were designated as Number 2 lump gypsum, which refers to quarry-run rock passed through a 2-inch screen and retained on a 1/8-inch screen.

The first lot was of 100 pounds. A second lot of 900 pounds was obtained about six months after the first, and the third lot of 2100 pounds was obtained about one year after the second.

The as-received gypsum was hand screened to give four size fractions: +1 inch, -1 +3/4 inch, -3/4 +1/2 inch, and -1/2 inch. The feed for the shaft furnace studies was obtained from these latter three fractions. Material from lot number one was used only on the first run with the shaft furnace. Shaft furnace runs 2 through 17 used material from lot number two. Shaft furnace runs subsequent to number 17 were made with gypsum feed from lot number three.
To prepare feed for the fluidization studies, the +1 inch fraction of lots number two and three as well as some of the smaller fractions of lot number three were ground through a pair of Sturtevant crushing rolls 5 inches in width and 8 inches in diameter and thoroughly mixed. The -4+10 mesh fraction was then obtained with a vibrating screen, mixed again, and stored in drums. The feed for fluidization was obtained from this material by sizing with Tyler Standard Screens to give -4+6, -6+8, and -8+10 mesh fractions.

**Anhydrite**

The anhydrite was obtained from an abandoned gypsum mine near Colorado Springs, Colorado. It had been stripped from the gypsum deposit when the mine was worked and piled to one side as waste.

As received, the material was in lumps weighing from 40 to 80 pounds each. These were broken with a sledge, fed into a small Dodge jaw crusher, and finally crushed in the Sturtevant crushing rolls. The final size fractions, obtained with Tyler Standard Screens, were -4+6, -6+8, -8+10, -10+12, and -12 mesh.

The general shape of the crushed anhydrite particles was different from that of the crushed gypsum. The gypsum crushed into particles of more or less equal dimensions
<table>
<thead>
<tr>
<th>Constituent</th>
<th>Source of sample</th>
<th>-4+10 mesh</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Lot No. 1</td>
<td>Lot No. 2</td>
</tr>
<tr>
<td>H$_2$O (combined)</td>
<td>19.7</td>
<td>19.9</td>
</tr>
<tr>
<td>SO$_3$</td>
<td>44.8</td>
<td>44.8</td>
</tr>
<tr>
<td>CaO</td>
<td>31.9</td>
<td>32.1</td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>2.3</td>
<td>2.5</td>
</tr>
<tr>
<td>R$_2$O$_3$</td>
<td>0.6</td>
<td>0.4</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>0.8</td>
<td>0.6</td>
</tr>
<tr>
<td>NaCl</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>MgO</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>Total</td>
<td>100.1</td>
<td>100.3</td>
</tr>
</tbody>
</table>

*Moisture free basis. Expressed as per cent of constituent.*
Table 3

Analysis of Samples of Anhydrite

<table>
<thead>
<tr>
<th>Constituent</th>
<th>Source of sample</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Composite</td>
</tr>
<tr>
<td>$\text{H}_2\text{O}$ (combined)</td>
<td>5.7</td>
</tr>
<tr>
<td>$\text{SO}_3$</td>
<td>54.9</td>
</tr>
<tr>
<td>$\text{CaO}$</td>
<td>37.1</td>
</tr>
<tr>
<td>$\text{SiO}_2$</td>
<td>1.6</td>
</tr>
<tr>
<td>$\text{B}_2\text{O}_3$</td>
<td>0.2</td>
</tr>
<tr>
<td>$\text{CO}_2$</td>
<td>0.4</td>
</tr>
<tr>
<td>$\text{NaCl}$</td>
<td>0.6</td>
</tr>
<tr>
<td>$\text{MgO}$</td>
<td>0.0</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>100.5</strong></td>
</tr>
</tbody>
</table>

$^a$Moisture free basis. Expressed as per cent of constituent.
along the three axes, whereas the anhydrite crushed into long, thin particles.

Analysis

Both the gypsum and anhydrite were analyzed according to the American Society for Testing Materials standard method of testing gypsum, designation C6-42.

The results of analysis of the gypsum are presented in Table 2. This includes the analysis of a composite sample from each of the three lots of gypsum obtained and the analysis of a composite sample of the -4+10 mesh fraction used for the fluidization investigations. No significant difference was found in the composition of the various size fractions used for the fluidization studies.

Table 3 presents the analysis of composite samples of the as-received anhydrite and the -4+10 mesh fraction of the anhydrite.
METHODS OF ANALYSIS OF PRODUCTS

Solid Products

The analyses performed on the solid products were those necessary to compute the per cent desulfurization and, with selected samples, to indicate the quality of the lime obtained. Since the solid product from a successful run contained a high percentage of calcium oxide, it would rapidly absorb moisture and carbon dioxide from the air. Hence if the product had been exposed to the atmosphere, which necessarily occurred in the shaft furnace operation, it was necessary to correlate the sulfur content of the sample with the calcium oxide content by a lime balance to obtain the per cent desulfurization based on the feed composition. For this the following relationship was used:

\[
\text{% desulfurization} = \left( \frac{\% \text{SO}_3 \text{ in feed} - \% \text{SO}_3 \text{ in product}}{\% \text{CaO in feed} - \% \text{CaO in product}} \right) \times 100 . \quad \text{(26)}
\]
The samples removed from the fluidized bed were sealed before moisture or carbon dioxide could be absorbed from the atmosphere so the desulfurization could be computed from the amount of sulfide and sulfate sulfur present. The reliability of this method was checked by the determination of the \( \text{SO}_3/\text{CaO} \) ratio of selected samples, the \( \text{SO}_3 \) including both sulfate and sulfide sulfur.

The analytical determinations thus included residual sulfate, sulfide, total sulfur, calcium oxide, neutralizing value, and caustic value. The total sulfur was determined for some of the samples from the fluidization studies and compared with the sum of sulfate and sulfide sulfur to test for the formation of sulfites.

Residual sulfate was gravimetrically determined by precipitation as barium sulfate in accordance with the American Society for Testing Materials procedure mentioned in the previous section. While dissolving the sample, qualitative tests were made to determine the presence of sulfides in the sample.

An evolution method was used to determine the sulfide content. The sample was placed in a flask and acidulated with hydrochloric acid. The evolved gases, including the hydrogen sulfide from decomposition of the sulfides, were bubbled through an ammoniacal solution of zinc sulfate which converted the hydrogen sulfide to zinc sulfide. This solu-
tion was then acidified with hydrochloric acid to liberate the hydrogen sulfide which was titrated with standard iodine solution.

Total sulfur was determined by oxidizing all forms of sulfur in the sample to sulfate with a mixture of one part of nitric acid with nine parts of hydrochloric acid, removing the nitric acid by evaporation, and gravimetrically determining the sulfate.

Two methods were used for the determination of calcium oxide. In the early part of the investigations, it was gravimetrically determined by precipitation as the oxalate in accordance with the previously mentioned American Society for Testing Materials procedure. However, the time required for this analysis made it desirable to develop a more rapid method. Such a method was developed based on the versenate titration for total hardness in water, which has been described by Diehl, Goetz, and Hach [10]. With this method a weighed sample of solid product is dissolved in hydrochloric acid and filtered. The filtrate is then made up to volume and aliquots removed for titration with ethylenediaminetetraacetic acid (versene) using a hydroxylated azo dye, Erichrome black T, as the indicator. A buffer is added to adjust the pH to about 10. Sodium cyanide must be added to tie up any iron present which would otherwise interfere with the end point, which is very sharp, the solution turn-
ing from red to blue. This method determines both calcium and magnesium oxides; however, no magnesium oxide was present in the gypsum used, so the results were equivalent to calcium oxide. The results obtained by this volumetric method checked with gravimetric results to within ±1.0 percent of the absolute number. As the percent of desulfurization is much more sensitive to the sulfate content than to the lime content, this method of analysis was considered satisfactory.

The neutralizing and caustic values of some of the solid samples were evaluated in accordance with the methods of analysis of the Association of Official Agricultural Chemists for agricultural liming materials. The neutralizing value was obtained by measuring the amount of 0.5 N nitric acid required to neutralize the lime and is expressed as percent calcium oxide. The caustic value was determined by dissolving the sample in a sucrose solution and titrating a filtered aliquot with 0.5 N hydrochloric acid. From the hydrochloric acid required the percent calcium oxide of the sample was computed. The neutralizing value is a measure of the total lime content whereas the caustic value indicates the availability of the lime.
Gas Analysis

The gases from both the shaft furnace and the fluidized bed were composed of the products of combustion of the fuel gas and the gaseous decomposition products of the gypsum or anhydrite. The combustion products included carbon dioxide, carbon monoxide, water vapor, and oxygen and nitrogen from excess air. The gaseous decomposition products included one or more of the following: sulfur trioxide, sulfur dioxide, elemental sulfur, and hydrogen sulfide, depending on the oxidation-reduction characteristics in the furnace.

The products of combustion were determined with the usual Orsat apparatus using potassium hydroxide, alkaline pyrogallol, and ammoniacal cuprous chloride as absorbents for the carbon dioxide, oxygen, and carbon monoxide respectively. However, before this analysis could be made, it was necessary to remove the sulfur dioxide, sulfur trioxide, and hydrogen sulfide from the gases for these would be absorbed by the potassium hydroxide and result in high values for the CO₂ concentration. These were removed by passing the gases through two Milligan gas washing bottles, the first of which was filled with concentrated sulfuric acid to remove sulfur trioxide and the second of which contained a strong iodine solution for the removal of sulfur dioxide.
and hydrogen sulfide. No correction was made to the volume measured in the Orsat burette for the volume of gases absorbed in these solutions. This correction, which would have been no more than eight per cent of the absolute number obtained, would not have affected the relative amounts of carbon dioxide, carbon monoxide, and oxygen and these were of primary interest rather than the absolute values.

The analysis of the off-gases for sulfur dioxide, sulfur trioxide, and hydrogen sulfide, while carried out by slightly different methods depending on the nature of the run and the manner in which the gas sample was obtained, was based on the following reactions:

\[
\begin{align*}
\text{SO}_2 + \text{I}_2 + 2\text{H}_2\text{O} & = 2\text{HI} + \text{H}_2\text{SO}_4 \\
\text{H}_2\text{S} + \text{I}_2 & = 2\text{HI} + \text{S} \\
\text{SO}_3 + 2\text{NaOH} & = \text{Na}_2\text{SO}_4 + \text{H}_2\text{O} \\
\text{SO}_3 + \text{BaCl}_2 + \text{H}_2\text{O} & = \text{BaSO}_4 + 2\text{HCl}
\end{align*}
\]

A measured quantity of off-gas was passed through a measured quantity of iodine solution in a gas washing bottle, either until the blue color produced by some added starch indicator was just removed, or until some given volume had been passed through an excess of iodine, in which case the amount of iodine in excess was determined by back titration with standard sodium thiosulfate solution. From these quantities the combined hydrogen sulfide and sulfur dioxide were
computed. The amount of sulfur dioxide was then obtained by adding methyl orange, titrating the total acid with standard base, and computing the quantity of sulfuric acid formed from the sulfur dioxide.

The total sulfur trioxide and sulfur dioxide was determined in the absence of hydrogen sulfide in a similar fashion by passing the gases through a measured quantity of standard sodium hydroxide solution in a gas washing bottle using phenolphthalein as an indicator. The total sulfur dioxide and sulfur trioxide was computed from this, and the sulfur trioxide obtained by difference, using the value of sulfur dioxide obtained from the iodine absorption. When hydrogen sulfide was present, a gas sample was passed through a scrub bottle containing acidified barium chloride which precipitated any sulfur trioxide present as sulfate which was then determined gravimetrically.

The off-gases from the shaft furnace were continuously aspirated from the stack past the sampling points so that a sample could be withdrawn at any time for analysis. All analyses were made during the run. A similar procedure was used with fluidization studies except for runs F-134 through F-162 from which samples were removed into gas sampling bottles and stored for analysis at any convenient time. The analyses of the samples thus obtained were unsatisfactory.
During the shaft furnace operations every effort was made to operate at oxidizing conditions such that only sulfur dioxide and/or sulfur trioxide would be formed. The gases were passed over moistened lead acetate paper to check for hydrogen sulfide, and the furnace was assumed to be operating incorrectly if hydrogen sulfide was present. Thus these gases were analyzed only for sulfur dioxide and sulfur trioxide. The gases were drawn continuously from the furnace through Fisher-Milligan gas washing bottles by means of an aspirating bottle until the end point was reached, as indicated by disappearance of the blue color in the iodine solution and the pink color in the sodium hydroxide solution. Separate samples were drawn through the two bottles simultaneously. The water displaced from the aspirating bottles was collected and measured and this volume corrected for the temperature and pressure of the gas in the aspirating bottle to obtain the volume at standard conditions of the gas which had passed through the scrub solutions.

A similar procedure was used with the gas samples taken above the fluidized bed, except porous gas diffusion plates in test tubes of the absorbents were used for the washing bottles. A trap containing standard sodium thiosulfate solution followed the iodine wash bottle to remove any iodine which might have been carried over. An excess of iodine was used and subsequently determined with standard sodium
### FIGURE 5. GAS ANALYSIS EQUIPMENT; SHAFT FURNACE

<table>
<thead>
<tr>
<th>Item</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Aspirator bottle</td>
</tr>
<tr>
<td>2</td>
<td>Thermometer</td>
</tr>
<tr>
<td>3</td>
<td>Manometer</td>
</tr>
<tr>
<td>4</td>
<td>Graduated cylinder</td>
</tr>
<tr>
<td>5</td>
<td>Filter—glass wool and asbestos</td>
</tr>
<tr>
<td>6</td>
<td>Standard iodine absorption bottle</td>
</tr>
<tr>
<td>7</td>
<td>Standard sodium hydroxide absorption bottle</td>
</tr>
<tr>
<td>8</td>
<td>Concentrated sulfuric acid absorption bottle</td>
</tr>
<tr>
<td>9</td>
<td>Iodine absorption bottle</td>
</tr>
</tbody>
</table>

### FIGURE 6. GAS ANALYSIS EQUIPMENT; FLUIDIZED BED REACTOR

<table>
<thead>
<tr>
<th>Item</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Aspirator bottle</td>
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<tr>
<td>2</td>
<td>Thermometer</td>
</tr>
<tr>
<td>3</td>
<td>Manometer</td>
</tr>
<tr>
<td>4</td>
<td>Graduated cylinder</td>
</tr>
<tr>
<td>5</td>
<td>Filter—glass wool and asbestos</td>
</tr>
<tr>
<td>6</td>
<td>Tap to remove samples for Orsat analysis</td>
</tr>
<tr>
<td>7</td>
<td>Standard iodine wash bottle</td>
</tr>
<tr>
<td>8</td>
<td>Standard sodium thiosulfate trap</td>
</tr>
<tr>
<td>9</td>
<td>Acidified barium chloride wash bottle</td>
</tr>
</tbody>
</table>
thiosulfate. The sulfur trioxide was precipitated in the acidified barium chloride and gravimetrically determined.

Figures 5 and 6 are schematic sketches of the apparatus arrangements used for continuous sampling and analysis with the shaft furnace and the fluidized bed respectively.
THE THERMAL DECOMPOSITION OF GYPSUM IN A SHAFT FURNACE

Characteristics of a Shaft Furnace

The shaft furnace was selected as one of the reactors for this study because of its efficiency as a countercurrent gas-solids contactor and the high thermal efficiencies which may be obtained with it. The proposed use of a shaft furnace for the thermal decomposition of gypsum is analogous to its use in the lime industry, where it is usually called a shaft kiln, for the thermal decomposition of limestone.

Essentially, the shaft kiln consists of a vertical refractory-lined shaft filled with lumps of solid which pass from their feed point at the top of the kiln to their withdrawal point at the bottom, while gases pass upward from the bottom to the top. These kilns are semi-continuous in operation, being drawn and charged at periodic intervals.

There are three methods of firing a shaft furnace: (1) mixing solid fuel with the aggregate charged at the top; (2) combustion of the fuel in a separate combustion chamber, the hot combustion gases being blown in at a low level of the shaft; and (3) injection of the fuel through nozzles at some
point in the lower portion of the shaft. The latter method was used with the experimental furnaces of this investigation.

A shaft furnace may be divided into three sections: (1) the bottom or solid product cooling section, (2) the middle or reaction (calcining) section, and (3) the top or feed preheating section. The bottom section is usually about one-quarter of the total shaft height. The secondary air passes through it, cooling the solid products and itself becoming preheated. The middle section extends for about one-third of the shaft height. The maximum temperature occurs and decomposition takes place in this section. The top section serves as a heat exchanger in which some of the sensible heat of the gases is transferred to preheat the undecomposed lumps of material moving down the kiln.

In modern shaft kiln design there are many modifications and refinements for the purpose of increasing the thermal efficiency and obtaining more uniform temperature distributions, but the basic design, consisting of the three sections (product cooler and air preheater, reaction chamber or calciner, and gas cooler and feed preheater) remain the same. A shaft furnace thus represents a fairly simple combination of two heat exchangers plus a reactor, and as such provides a means for obtaining excellent thermal efficien-
cies. The thermal efficiencies obtained will depend on the height of the two heat exchange sections and, hence, the overall height.

The optimum height of the kiln may be obtained by a balance between the value of the heat recovered and the additional power and equipment costs. Similar considerations dictate the optimum lump size. Small lumps calcine more rapidly than do large ones, but increase the power required to draw the gases through the charge.

Description of Equipment

Two shaft furnaces of different designs were constructed for the investigations. The first had a square shaft with inside dimensions of 3 by 3 by 40 1/2 inches and a capacity of 19 1/2 pounds of -1 +1/2 inch raw gypsum. The lower nine inches and the top 13 1/2 inches of this kiln were of a silica firebrick (Mexico Refractory Company Mo-Rex). The central portion was constructed of unburned magnesite firebrick (General Refractories Company Ritex A).

Gas was introduced, at the line pressure of 6 1/2 inches of water, at two opposite sides of the shaft through ports 1/2 inch in diameter located 12 1/2 inches above the base of the kiln. Secondary combustion air was introduced through two ports located 7 1/4 inches directly below the gas ports.
There was no primary combustion air supplied. Calibrated orifice meters permitted individual adjustment of each gas line. Orifice meters were also placed in the air line. A bellows type gas meter measured the total gas consumption.

Sight holes 3/4 inch in diameter were located in the furnace at heights of 15 inches, 17 inches, 19 1/4 inches, 21 inches, 24 inches, and 28 1/4 inches above the base. These were fitted with short lengths of standard 3/4-inch pipe on the end of which were screwed caps. These caps could be removed to permit determination of the temperature with an optical pyrometer or general observation of the charge. The furnace was also provided with ports, inclined at an angle of approximately 50 degrees, through which the charge could be rodded. These were spaced every four inches beginning from a point eight inches above the gas inlets. There was also a rod port just below the gas inlet.

The solid product was removed from the kiln by a four-inch hand-operated screw conveyor at the bottom of the shaft. The off-gases passed out through the side outlet of a 3 1/2-inch pipe tee, placed at the top of the shaft, into a six-inch stack vented to the atmosphere. An air ejector was placed in this stack to assist in the removal of the gases.

A schematic sketch of this furnace is presented in Figure 7.
OFF GAS STACK

FEED PLUG

3 1/2" STANDARD TEE

GAS SAMPLING TUBE

RODDING HOLES
(CAPS REMOVED)

MO-REX FIREBRICK

SIGHT PORTS
(CAPS REMOVED)

RITEX-A FIREBRICK

AIR

GAS

MO-REX FIREBRICK

SCREW CONVEYOR
PRODUCT OUTLET

FIGURE 7 SHAFT FURNACE - FIRST DESIGN
Difficulty was experienced in the operation of this kiln in that the charge did not fall freely downward after a draw, i.e. removal of product out the bottom. This sticking occurred in two places: the calcining section and the top of the gypsum preheating section. In the former section it was largely the result of fusion and subsequent agglomeration of the particles. In the gypsum preheating section, however, rigid arches of the feed material were being formed, possibly originating with the cool charge and subsequently forming a rigid arch as the lumps expanded on heating. In both sections rodding the charge was not sufficient to permit steady operation and it was frequently necessary to shut-down to clean out the furnace.

These operating difficulties led to the design of the second furnace which was constructed with a circular cross-section tapering from a minimum at the top to a maximum in the firing zone. The overall height of this furnace, from the bottom of the conveyor shaft to the top of the refractory, was 49 inches. The minimum (top) diameter of the shaft was three inches and increased to a maximum of six inches at a distance of 30 inches below the top. This diameter extended for six inches down to the gas burner ports. From the burner ports the shaft tapered to the 4 1/2 by 6 inch oval cross-section of the screw conveyor shaft at the bottom. The upper 18 inches of the shaft had a taper of
1/8 inch per inch; below this a taper of 1/16 inch per inch extended down to the six-inch diameter. The greater taper was used in the upper section since it was in this corresponding section of the first furnace that severe sticking was encountered as a result of arching of the feed material.

The furnace shell was constructed of "Mo-Rex" Arch No. 8 silica firebrick arranged to give an inside diameter of one foot. This was lined with Laclede chrome-plastic fireclay molded to give the desired internal shape to the shaft. The base of the furnace was a four-inch high tier of firebrick into which a four-inch, hand-operated screw conveyor was fitted.

Gas entered through four burner ports spaced 90 degrees apart and located 12 inches above the base of the furnace. Secondary combustion air entered 6 3/4 inches directly below the burner ports. In later experiments the burners were modified to take primary air. Two gas and two air lines, fitted with orifices, supplied the four burners. Secondary combustion air was supplied by the same lines supplying the burners when primary air was used. A valve in the line connecting the secondary air port with the air inlet to the burner served to control the proportion of primary to secondary air. The air lines passed through a small, gas-fired furnace which was used to preheat the air when desired.
Ten rodding holes were located one above the other and approximately equally spaced up the shaft height. Two more were located 65 degrees from these at the 25- and 39-inch levels. These additional ones were installed here since it was in the corresponding position that so much trouble with sticking of the charge had been encountered with the first furnace. The rod holes were fitted with 1/2-inch pipe extending about four inches beyond the furnace. All pipes leading into the furnace were sealed to it with furnace cement.

The sight ports, for visual observation of the charge and measurement of temperatures with an optical pyrometer, were all located 35 degrees from the conveyor. These ports were originally fitted with 3/4-inch pipes extending about four inches beyond the furnace, but were replaced with 1 1/2-inch pipes after run number 17. These ports were kept capped when not in use.

A 3 1/2-inch standard pipe tee with the side outlet horizontal was placed on top of the shaft. A stove pipe was connected to this side outlet through which the off-gases passed to the stack which was fitted with an air ejector. The other opening of the tee was fitted with a plug which could be removed to feed gypsum to the furnace. Leaving diametrically opposite the side outlet and coming up
from the base of this tee was an 1/8-inch pipe for gas sampling. The tee was joined to the furnace top with furnace cement.

The furnace had a volume of 973 cubic inches from the top of the conveyor to the top of the shaft and a capacity of 41 pounds of -1 +3/4 inch lump gypsum.

A sketch of this furnace is given in Figure 8 and a front view photograph is shown in Figure 9.

Variables Considered

Independent variables

The independent variables considered were the maximum temperature in the reaction zone of the kiln, the retention time in the reaction zone, and the particle size of the feed. These independent variables were indirect in that their value was determined by the directly controlled independent variables of gas rate, air rate, air preheat, and feed rate. Each of the controllable independent variables could affect more than one of the independent variables used for correlation, each of which in turn was influenced by more than one of the controllable independent variables.

The maximum temperature attained depended on the gas rate, the air-gas ratio, and the amount of preheat, if any, supplied the combustion air. The retention time depended
Figure 8: Shaft Furnace - Second Design

- Off Gas Stack
- Feed Plug
- 3 1/2" Standard Tee
- Gas Sampling Pipe
- Rodding Holes (Caps Removed)
- Shaft Diameter 3"
- Sight Forts (Caps Removed)
- Shaft Diameter 5 1/4"
- Taper 1/8" Per Inch
- Shaft Diameter 6"
- Taper 1/16" Per Inch
- Burner
- Primary Air
- Secondary Air
- Screw Conveyor
- Product Outlet

Primary and secondary air flows are indicated, along with the shaft furnace design details.
FIGURE 9. SHAFT FURNACE—SECOND DESIGN

Front View
on the feed rate and the volume of the calcining zone. Thus, the gas rate affected not only the temperature but the retention time as well, for if the gas was increased, the calcining zone volume would increase at the expense of the preheating zone. The thermal efficiency of the kiln would also be decreased.

The maximum permissible feed rate was limited theoretically by the fuel rate and the thermal efficiency and practically by the rate of desulfurization, which in turn was influenced by the particle size and temperature. Increasing the feed rate, at a constant gas rate and temperature, would to some point increase the concentration of sulfurous gases in the off-gases as long as the gypsum was completely desulfurized. But, with increasing feed rates a point would be reached at which the retention time was not sufficient for complete desulfurization and the sulfurous gas concentration would start to decrease. The feed rate would also affect the temperature to some extent inasmuch as it affected the rate at which the hot solid product left the calcining zone and entered the secondary combustion air preheating zone.

The maximum particle size was limited by the cross-sectional area of the shaft to a one-inch lump. Particle sizes down to 1/4 inch were studied. The particle size based on the screen analysis is not, however, a good corre-
lating variable since the minimum dimension of the lump has the most bearing on the calcination rate yet is not indicated by the screen analysis.

**Dependent variables**

Dependent variables were the per cent desulfurization of the feed, the quality of the solid product obtained as lime, and the sulfur dioxide and sulfur trioxide concentration in the off-gases.

As discussed in the Analytical Procedures section, the per cent desulfurization was obtained by analysis of the solid product for residual sulfate and calcium oxide. From the \( \text{SO}_3/\text{CaO} \) ratio obtained, the per cent desulfurization was computed. This solid product analysis was performed on the consecutively withdrawn samples and the steady state sample assumed to be one which was bracketed on both sides with samples having analyses of no significant difference.

The concentration of the sulfurous gases in the off-gas is of interest since this is the primary product. The maximum concentration attainable, assuming a thermal efficiency of 100 per cent over the entire kiln, would be 16.9 per cent sulfurous gases (sulfur dioxide, sulfur trioxide, or hydrogen sulfide) on the dry basis and 10.8 per cent with the water from combustion remaining as a vapor. If the feed were added often enough so that the amount of material added to
and removed from the calcining zone at any one time was small in comparison with the total calcining zone volume, the off-gas concentration of sulfur dioxide and sulfur trioxide would be expected to remain fairly constant. However, if charging were infrequent and the entire calcining zone received a fresh batch of undecomposed gypsum which remained until the next charge completely replaced it, the off-gas concentration of sulfurous gases would be expected to fluctuate from a high concentration shortly after charging to a minimum concentration just before its removal.

The lime obtained was evaluated with respect to both caustic and neutralizing value. The former is a measure of chemical activity or availability of the lime. With hard burning the structure of lime becomes more closely packed and its caustic-neutralizing value ratio decreases.

Method of Operation

The same general operating procedure was used with both furnaces. The furnace was filled with partially calcined feed from a previous run to the level of the burner ports and with raw gypsum feed of the desired size for the remainder of the shaft height. The combustion air and ejector were then turned on so as to produce a draft by the burner ports but a slight positive pressure just below the burner
ports. The gas was then turned on, ignited through one of the observation ports just above a burner port and adjusted to the desired rate. The furnace was allowed to warm up for about one hour during which time Orsat analyses were made of the stack gas as a basis for adjusting the air rate to give a stack gas analysis of between eight and twelve per cent carbon dioxide.

When the charge became heated, the gases apparently burned on the surface of the gypsum particle, i.e., surface combustion occurred. This surface combustion produced very high energy liberation rates. It was not unusual to have gas rates which corresponded to an energy release rate of about 1,000,000 Btu per cubic foot per hour, based on the void volume in the shaft reaction zone.

Following this warm-up period, semi-continuous feeding was started, a draw was made and fresh gypsum added every 15 to 30 minutes. The solid product of each draw was identified with a sample number and temporarily stored in a paper sack until it could be sampled, ground, and sealed in an air-tight container. To minimize the occurrence of hollow spots in the charge, it was necessary to rod the charge down thoroughly before adding fresh feed. If such a hollow spot remained, its upper surface would become exceedingly hot and fusion and subsequent sticking of the charge would result.
The stack gas analysis was checked periodically for carbon dioxide as a control on the gas-air ratio. When the steady state was attained, sulfur dioxide and sulfur trioxide were quantitatively determined. Qualitative tests were made for hydrogen sulfide, and the air rate increased when any was present.

At the end of the run the charge remaining in the furnace was removed in samples of from two to five pounds each, labeled as to location, and included with those removed by drawing during operation for subsequent analysis for sulfate, calcium oxide, neutralizing value, and caustic value.

Particle sizes of $-1/2 +1/4$ inch to $-1 +3/4$ inch were investigated. The gas rate used ranged from 49 to 124 standard cubic feet per hour.

The temperature of the charge was determined with an optical pyrometer at various stations in the shaft. The maximum temperature obtained with no primary air preheat was about $2550^\circ F$. With primary air preheat of about $700^\circ F$, temperatures to $3000^\circ F$ were obtained.

The retention times varied from one to about three hours.
Results

The results obtained with the shaft furnace are summarized in Table 4. Those runs which are not listed in this table presented operating difficulties of such a nature that it was necessary to shut down before any pertinent information could be obtained. Runs number one through six were carried out in the first (square cross-section) furnace. Runs subsequent to number six were in the second shaft furnace.

This work with the shaft furnace was directed toward developing a satisfactory operating procedure for desulfurization under oxidizing conditions.

The work may be divided into three sections with respect to the maximum temperature obtained in the calcining or reaction zone:

1. Temperatures in the reaction zone between 2350°F and 2550°F. This was the temperature normally attained with from 10 to 20 per cent excess air.
2. Temperatures in the reaction zone between 2550°F and 3000°F. These were obtained by preheating the combustion air.
3. Temperatures in the reaction zone between 2250°F and 2350°F. Forty to sixty per cent excess air was used to produce these lower temperatures.
Table 4
Shaft Furnace Results

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Maximum temp. °F</th>
<th>Retention time hours</th>
<th>Gas rate cu.ft./hr.</th>
<th>Feed rate lbs./hr.</th>
<th>Particle size inches</th>
<th>CaO %</th>
<th>Sulfate as SO₃ %</th>
<th>Solid size</th>
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<tr>
<td>19</td>
<td>2250</td>
<td>2</td>
<td>52</td>
<td>4</td>
<td>-3/4 +1/2</td>
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<td>61</td>
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<td>-1/2 +1/4</td>
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<td>-3/4 +1/2</td>
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<td>44.6</td>
<td>26</td>
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</table>

aRuns 1 and 4 with shaft furnace number one; all others with shaft furnace number two.
bRetention time above 2300°F, except run 19 at 2250°F.
cReferred to 760 mm. Hg, 0°C.
Table 4

Furnace Results

<table>
<thead>
<tr>
<th>Sulfate as SO₃ %</th>
<th>Desulfur-ization %</th>
<th>Neutralizing value % CaO</th>
<th>Caustic value % CaO</th>
<th>Measured gas analysis maximum concentrations SO₂ + SO₃</th>
<th>Calculated gas analysis average concentration SO₂</th>
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</table>
Temperatures between 2350°F and 2550°F

Thirteen runs were made with this temperature range, six with the first shaft furnace and seven with the second. Of the six with the first shaft furnace, only two were successful to any extent. The others failed because of difficulty encountered with sticking of the charge in the shaft which prevented continuous operation.

The first successful run was at nominally oxidizing conditions and produced an excellent unfused solid product which was 96 per cent desulfurized. Because of this, the conclusion was reached that desulfurization could be obtained with oxidizing conditions without fusing the material. However, later work showed this to be erroneous and indicated that the lack of fusion was the result of reducing conditions existing in the vicinity of the combustion zone. The second successful run produced fusion and agglomeration of the gypsum which eventually forced a shut-down. Sulfur condensed on the feed during the early part of this run, but ceased doing so when the air rate was increased.

Seven runs in this temperature range were made with the second shaft furnace, of which six were moderately successful. In all runs some fusion occurred and ultimately forced a shut-down. Severe rodding from the top best served to keep the shaft free of stoppage, but also mixed the material at the top of the shaft with that in the reaction zone. A max-
imum desulfurization of 78 per cent was obtained. The dif-
ficulty of sticking of the charge prevented retention times
of greater than 2 to 3 hours. It was thus decided to go to
higher temperatures with the thought that this would pro-
duce more rapid desulfurization and an infusible shell might
be formed around the particle.

Temperatures between 2550°F and 3000°F

Three runs using preheated air to obtain higher temper-
atures were performed with the second shaft furnace. In all
cases fusion followed by solidification rapidly occurred in
the high temperature zone of the furnace. This resulted in
solid plugs of material in the shaft, the removal of which
required partial disassembly of the furnace. It was not
possible to remove any product during operation.

Temperatures between 2250°F and 2350°F

Because of the difficulty encountered with fusion, a
series of runs was executed at temperatures below fusion.
To obtain greater retention times, a lower feed rate was
used, but the high temperature zone did not extend as high
as in previous runs causing shorter retention times than ant-
icipated. Four such runs were made, none of which produced
satisfactory desulfurization.

A description of the individual runs is included in
Appendix B.
Discussion

Figure 10 illustrates the correlation obtained by plotting per cent desulfurization versus the maximum temperature attained by the charge. The numbers by the points refer to the run number. Points representing runs number 8 and 21 were given little weight because the retention times were only about one hour and 1 1/2 hours respectively. Run number 4 was at a retention time of about 1 1/2 hours but fits the line well, indicating that retention time is not of as much importance with temperatures above 2500°F. The samples obtained in runs 11 and 12 apparently contained unburned gypsum lumps brought down by the rodding technique. Thus these were also given little weight in fairing the curve. One can also rationalize the misfitting of the point for run number 18 since the maximum temperature of 2450°F was attained for only a short period of the run. A temperature of 2350°F would probably be more representative of this run.

Efforts to correlate the per cent desulfurization with retention time at constant temperature resulted in Figure 11. For this the runs have been divided into the temperature groups >2600°F, 2500-2550°F, 2400-2450°F, 2250-2350°F. This correlation is not as good as that of temperature and, perhaps, is more indicative of the lack of control of the runs.
FIGURE 10

EFFECT OF TEMPERATURE ON DESULFURIZATION OF GYPSUM

SHAFT FURNACE
FIGURE 11  EFFECT OF RETENTION TIME ON DESULFURIZATION OF GYPSUM SHAFT FURNACE
The importance of temperature in reducing retention time is brought out by this plot. Extrapolation of the 2250-2350 curve would indicate an impractically high retention time. However, the retention times for 95 per cent desulfurization obtained by linear extrapolation of the 2400-2450 curve would be about 6 1/2 hours, which, in a large kiln, might be a practical operating condition.

The fact that the temperature has a greater influence than retention time would account for the fairly good correlation obtained between temperature and desulfurization.

No correlation could be made between particle size and desulfurization.

The off-gas analyses were too variable during a run to be useful for correlating purposes. It may be noted, however, that sulfur trioxide was present in greater proportion than sulfur dioxide. This may be attributed to the relatively slow cooling of the off-gases under oxidizing conditions as they pass up the kiln. The experimental values of sulfur dioxide and sulfur trioxide concentration in the off-gases presented in Table 4 were the maximum values observed. These were obtained immediately after a charge had been added, following which the concentration decreased. This higher initial concentration resulted from the rapid desulfurization of the surface of the particles. It will be noted that the values calculated from the gas rate, feed
rate, and per cent desulfurization of the gypsum are much lower, indicating a much lower thermal efficiency after the surface of the solids was desulfurized.

Conclusions

Completely satisfactory operation of the shaft furnace was not attained because of the fusion and resulting sticking of the charge which occurred at the temperatures required for moderate to rapid desulfurization. Most of the work was directed toward establishing a satisfactory operating procedure under oxidizing, desulfurizing conditions.

However, the following conclusions are considered justifiable:

1. The minimum practical temperature range for desulfurization of gypsum in a shaft furnace under oxidizing conditions is 2400°F to 2450°F.

2. Extrapolation of the experimental data obtained indicates that a retention time of 6 to 6 1/2 hours would be required for 95 per cent desulfurization at a temperature of 2400°F to 2450°F. Such retention times could not be investigated in the laboratory shaft furnace because of sticking of the charge in the shaft. It would be easier to prevent sticking in a larger shaft, but it is pos-
sible that at these higher retention times the particles would fuse more severely.

3. In the temperature range of 2400°F to 2450°F the particles fuse together to form larger agglomerated lumps. If the retention time is less than three hours, the particles composing the agglomerate retain at least some of their identity, i.e. fusion is not complete. This could be due to resolidification of the melt as the sulfur trioxide is driven off and the high temperature exterior then serves to contain the interior material when it attains the fusion point. It would seem that either slow heating or rapid heating, which would provide a chance for the exterior of the particle to resolidify before the interior had attained the fusion temperature, might accomplish this, particularly with large particles.

4. At temperatures greater than 2600°F the charge becomes molten and desulfurization is 98 per cent complete in one hour. A different type of furnace than that used for these investigations would be necessary for operation under these conditions.

5. The solid product lime obtained has a low chemical activity, but this would not be detrimental to an agricultural lime.
6. Under reducing conditions, desulfurization occurs without fusion.

7. No conclusions could be reached concerning the effect of particle size in the range \(-1 +1/4\) inch.

8. The off-gases contain a greater proportion of sulfur trioxide than sulfur dioxide as a result of the slow cooling of the off-gases as they pass up the kiln.

From the foregoing it was concluded that desulfurization in a shaft furnace on a laboratory scale was impractical under oxidizing conditions. With a larger shaft, continuous operation might be maintained in the clinkering range. However, to maintain a steady flow down the column of this small furnace it was necessary to keep the temperature down below the point where appreciable desulfurization would occur.

Reducing conditions were avoided in the shaft furnace. However, subsequent work with the fluidized bed, which permitted better control of the variables, indicated the advisability of reducing conditions. A shaft furnace might be designed which would contain both reducing and oxidizing regions such that good desulfurization could be obtained without serious fusion. This is discussed further in a later section.
FLUIDIZATION CHARACTERISTICS OF GYPSUM

It was thought that a furnace in which the decomposition of gypsum could be accomplished with a fluidized bed of particles would offer several advantages not found in the shaft furnace. These would arise in part from the rapid heat transfer characteristics and the uniformity of mixing of the solid particles of a fluidized bed. Furthermore, since the particle size range would be considerably smaller than that used in a shaft furnace, it would be expected that lower retention times and/or temperatures would be required. There was also the possibility that successful operation could be carried out at temperatures greater than the fusion temperature of the feed. The problems in such operation, i.e. at temperatures greater than that of fusion, are discussed further in the Results and Discussion section.

Theoretical Considerations of Fluidization

In these investigations fluidization was used as a tool rather than an object of study in itself. The material presented here is therefore descriptive. A simplified mathemat-
ical treatment and methods of calculation are presented in Appendix C.

As the flow of a fluid through a bed of granular solids increases, the pressure gradient required to overcome the combined effect of fluid friction and the buoyant weight of the bed increases. These frictional and buoyant forces of the fluid tend to raise the particles. Opposing these forces and tending to drag the particles down is the force of gravity, i.e. the weight of the particles. When these opposing forces become equal, the solids become buoyant and begin to move, denoting the start of fluidization.

A further increase in fluid velocity produces only a slight increase in pressure drop which is due to fluid friction alone. If the logarithm of the superficial velocity is plotted versus the logarithm of the pressure drop, a characteristic curve as depicted in Figure 12 is obtained.

![Figure 12. Characteristic Fluidization Curve](image-url)
Subsequent to fluidization there is a transition region during which the pressure falls slightly with increasing velocity before beginning to increase. This is due to the change from a fixed bed to a moving bed.

The incipient fluidization velocity, \( u_f \), is that at which the maximum pressure drop occurs prior to this transition period. Fluidization of particles with a gas results in what is termed aggregative fluidization, the gas bubbles through the bed producing the appearance of a boiling bed. With increasing velocity, the bubbling becomes more violent and the bursting of the bubbles as they reach the top sends streamers of solids into the space above the bed.

Investigation of Fluidization Characteristics of Gypsum at Room Temperature

To become acquainted with the general nature and phenomena of fluidization and to obtain information which could serve as a basis for the design of a high temperature fluidized bed reactor, studies were made on the fluidization characteristics of gypsum particles at room temperature.

Equipment

A sketch of the equipment used is presented in Figure 13.
FIGURE 13  FLUIDIZATION CHARACTERISTICS INVESTIGATION EQUIPMENT
A 3-inch inside diameter "Pyrex" pipe 5 1/2 feet in height was used for the fluidization column. Compressed air from a 1/2-inch supply line passed consecutively through a dirt and moisture trap, a silica gel drying tube, and a needle valve into a vertical expansion section tapering at 7 degrees up to a diameter of 3 inches. At the end of this section was a 20-mesh screen for smoothing the velocity profile, followed by a 6 inch long calming section just before the bed support. A 1/2 inch thick grade 60 "Aloxite" plate was used as a bed support.

A 2-inch standard pipe was flanged to the top of the "Pyrex" pipe in such a manner that the side outlet of the tee was at right angles to this pipe. The air passed through this side outlet down 2 feet of 2-inch standard pipe to a flanged orifice meter and then to a cyclone separator. The top outlet of the tee was fitted with a plug which could be removed for charging of the gypsum particles. The gypsum was removed by disassembling the flanges at the bed support.

The temperature of the air was measured in the 1/2-inch pipe ahead of the expansion section. Provision was made for measuring the static pressure at the following points: (1) in the calming section upstream of the bed support, (2) in the tee located on top of the "Pyrex" pipe, and (3) downstream of the orifice in front of the cyclone. The differ-
ential pressures across the orifice and across the bed support, bed, and "Pyrex" pipe were also measured.

Air flow rates corresponding to velocities in the 3-inch pipe of 0.5 to 10 feet per second were measured with a 0.47-inch orifice plate. To obtain accuracy over this wide flow range, three manometers were used: a mercury manometer, a water manometer, and a methyl alcohol-filled micromanometer. Flow rates less than 0.5 foot per second in the 3-inch pipe were measured with a 0.0781-inch orifice. The orifice meters were not calibrated. Flow rates were computed on the basis of coefficients and equations recommended by the American Society of Mechanical Engineers [1].

Experimental procedure

The gypsum used was crushed with a Dodge jaw crusher set with a discharge opening of 1/2 inch. It was then sized with a set of Tyler Standard Screens using a Ro-tap machine.

A blank run was first made with the grade 60 "Aloxite" porous plate with no charge to determine the pressure drop across the plate alone at various air velocities. A weighed charge of sized gypsum particles was then added through the tee at the top of the fluidization column and a similar series of observations were made, i.e. the combined pressure drop through the plate and the bed at increasing air velocities. The pressure drop at any velocity through the bed
alone was then determined by subtracting the pressure drop through the plate alone at that velocity from the combined pressure drop. The bed height before and during fluidization was also noted to permit computation of the porosity of the bed.

**Experimental results**

The pressure drop through the bed was plotted versus the superficial air velocity in the fluidization column. This produced a characteristic curve from which the fluidization velocity was noted as the velocity at which the pressure drop through the bed ceases to increase and starts to decrease. The curves so obtained are presented in Figures 35 and 36 of Appendix C. A summary of the results is presented in Table 5.

From the observed fluidization velocity the sphericity, or shape factor, of the gypsum particles was computed by the method and data of Brown et al. [6] which is outlined in Appendix C. Consideration was given the air temperature and pressure and the porosity of the bed. These results are also included in Table 5.

From the sphericities thus obtained, the incipient fluidization velocity of the various particle sizes in air at 2600°F and one atmosphere of pressure were computed. As the gypsum calcines, the particle size decreases and the
<table>
<thead>
<tr>
<th>Run No.</th>
<th>Particle size (Mesh)</th>
<th>Air temp. (°F)</th>
<th>Air press. (mm Hg)</th>
<th>Observed fluid veloc. (ft/sec)</th>
<th>Calcd. porosity</th>
<th>Calcd. sphericity</th>
</tr>
</thead>
<tbody>
<tr>
<td>F-5</td>
<td>-4+6</td>
<td>0.127</td>
<td>87</td>
<td>1018</td>
<td>6.0</td>
<td>0.479</td>
</tr>
<tr>
<td>F-7</td>
<td>-6+8</td>
<td>0.1072</td>
<td>110</td>
<td>907</td>
<td>5.0</td>
<td>0.442</td>
</tr>
<tr>
<td>F-3</td>
<td>-12+14</td>
<td>0.0531</td>
<td>78</td>
<td>785</td>
<td>2.65</td>
<td>0.543</td>
</tr>
<tr>
<td>F-8</td>
<td>-20+28</td>
<td>0.0268</td>
<td>95</td>
<td>745</td>
<td>1.27</td>
<td>0.546</td>
</tr>
<tr>
<td>F-2</td>
<td>-28+35</td>
<td>0.019</td>
<td>78</td>
<td>747</td>
<td>0.75</td>
<td>0.582</td>
</tr>
<tr>
<td>F-10</td>
<td>-48+65</td>
<td>0.00946</td>
<td>79</td>
<td>756</td>
<td>0.0498</td>
<td>0.585</td>
</tr>
<tr>
<td>F-11</td>
<td>-65+100</td>
<td>0.0067</td>
<td>79</td>
<td>749</td>
<td>0.025</td>
<td>0.615</td>
</tr>
</tbody>
</table>
FIGURE 14. FLUIDIZATION AND FREE-FALL VELOCITY OF GYPSUM PARTICLES IN AIR AT 2600°F

Based on Experimental Data at Room Temperature
density increases. For these calculations it was assumed that these two effects would cancel each other. The results thus obtained are plotted on Figure 14. Also plotted on this figure is the computed clearing, or free fall, velocity of the particles.

Comparison of these calculated results with the experimentally determined conditions is interesting. For the -6+8 mesh particles, with which most of the high temperature work was done, the minimum gas rate at which good fluidization could be obtained with theoretical combustion air was about 20 cubic feet per hour. This corresponds to a superficial velocity of 6.7 feet per second, whereas the calculated superficial velocity at incipient fluidization was 5.2 feet per second.
Description of Equipment

A photograph of the equipment used is presented in Figure 15. A cross-sectional view of the final form of the reactor which was used for these investigations is shown in Figure 16.

The entire unit was comprised of three separate sections secured together by flanged connections to form an integral unit. Since they were flanged, the sections could be readily dismantled to provide ready access to the various sections of the reactor. The top two sections were fabricated of a 10-inch standard pipe shell lined with Harbison-Walker Chrome-Castable refractory. The bottom section, in its final form, was lined with Plibrico Plicast Hearth Cement to give a circular shaft 3 1/2 inches in diameter in which were placed rings of Babcock-Wilcox K-28 insulating firebrick to give a final inside diameter of 3 inches. The insulating firebrick supported surface combustion and hence permitted higher energy liberation rates.
FIGURE 15. EQUIPMENT USED FOR FLUIDIZED BED STUDIES
FIGURE 16 FLUIDIZED BED REACTOR CROSS SECTION
The bottom section served both as a combustion chamber and a pressure equalizer or windbox below the bed support. A gas burner rated at 60 cubic feet per hour, supplied with primary air alone, was located directly beneath this section and fired up into it. The burner consisted of two concentric pipes, an inner 1/4-inch pipe carrying gas and terminating in a distributing head located 1 1/2 inches below a 1-inch pipe through which the air entered. The end of the burner extended into an insulating firebrick cylinder 3 inches in diameter by 2 inches in height above which was placed a perforated plate fabricated of the same material. This plate was 1/2 inch in thickness and was drilled with thirty 1/8-inch holes approximately equally spaced. This served to distribute the flames uniformly across the area of the combustion chamber.

This bottom section had an overall height of 14 inches, in the top 2 inches of which was encompassed the bed support. A thermocouple was located 1/2 inch directly below the bed support for the measurement of the temperature of the ascending fluidizing gases. This extended in the horizontal plane, to the center of the bed support, parallel to and between two adjoining rows of the gas-passage ports. This was not included, however, until run F-131. Initially, a platinum-platinum, 13 per cent rhodium thermocouple in a "Corundum" protective tube was used. However, when the pro-
tective tube was broken during removal following run F-144
it was replaced with an eight-gauge bare chromel-alumel
thermocouple. Also in this bottom section was a 1/4-inch
port fitted with a plug which could be removed to permit
ignition of the burner.

The bed support, in its final form, was fabricated from
an 1 1/4 by 4 1/2 by 9 inch magnesite firebrick (General Re-
fractories Co. Ritex-A). The center of a 3-inch diameter
circle was located in the center of the brick so as to co-
cide with the combustion chamber and the fluidization
chamber. One-eighth-inch holes spaced on 1/2-inch grids
located with the starting line on the diameter were then
drilled. These were countersunk from the top to a depth
of 1/2 inch with a 1/4-inch drill. A total of 29 holes were
located completely within this circle. The basis for se-
lection of this design for the bed support is discussed
later in this chapter in the Bed Support section.

The middle section of the reactor, in which the fluid-
ized bed was formed, was 2 feet in height. The inside di-
ameter was originally 5 inches, but to reduce the quantity
of feed required this was reduced after the first three runs
to a 3-inch diameter in the lower 8 inches, expanding
abruptly to 5 inches for the upper 16 inches. This enlarge-
ment also provided a freeboard or disengaging space above
the bed to minimize carry-over of solid particles.
Initially, two diametrically opposed burners were located immediately above the bed support. However, the final operating procedure developed did not require them so they were removed.

Internal cooling coils of 3/8-inch copper tubing were provided next to the shell. Water was used as the cooling medium. A pressure tap was provided at the level of the top of the bed support and also at the top of this section to permit measurement of the pressure drop through the bed. Also at the top of this section was a tap through which gases could be removed for analysis. A feed pipe which discharged one inch above the bed support was provided to permit continuous feeding. This was a 1 1/4-inch stainless steel pipe fitted with a screw conveyor fed from a sealed hopper.

To provide for possible continuous operation, three solid product outlets one inch in diameter were provided for the continuous removal of the solid product. These were inclined from 30 to 50 degrees to the horizontal and were of 1 1/4-inch pipe from the shell outward. They entered the reactor interior at 4 1/4-, 8- and 12-inch levels to permit a choice of bed depths for continuous operation. The calcined product flowed by gravity down these pipes into sealed, asbestos-lined collection jars. When not in use, these pipes were capped and plugged with refractory material shaped to the internal contour of the reactor.
The top section of the reactor was a refractory-filled cap 6 inches in height containing an off-gas vent 2 inches in diameter. This vent was staggered to permit location of a chromel-alumel thermocouple for measuring the off-gas temperature with a minimum of radiation error.

An inspection port 2 inches in diameter and fitted with a 2-inch removable sight glass was also located at the top. This permitted visual observation of the bed and measurement of the surface temperature with an optical pyrometer. It could also be removed to permit sampling of the bed during batch operations. A refractory gas sampling tube entered vertically through the top of this section subsequent to run F-134. It could be adjusted to draw samples from any desired depth.

A schematic sketch of the reactor and the auxiliary equipment necessary for its operation is presented in Figure 17. This auxiliary equipment included the gypsum feeder, gas and air metering devices, off-gas sampling and analysis equipment, a cyclone for the removal of fines from the off-gases, and an air preheater.

The off-gases passed out through a standard 2-inch exhaust pipe, which was water jacketed for a distance of 2 feet from the reactor, to a cyclone above which an air ejector was mounted to provide the pressure drop necessary
Figure 17  Fluidized Bed Reactor and Appurtenances
across the bed support and bed by producing a negative pres-
sure above the bed.

The gas passed through a bellows type meter and then
through a calibrated orifice meter before entering the burner.
The air passed through a calibrated orifice meter and option-
ally through an air preheater.

The drive equipment for the gypsum feeder consisted of
a 1/2-horsepower electric motor driving a "Zero-Max" speed
reducer which in turn drove a jack shaft operating the feed
screw. Chain and sprocket drives were used following the
speed reducer to insure positive operation. The speed re-
ducer could be continuously varied and, with the additional
reduction of the jack shaft, provided screw speeds of from
1 to 10 revolutions per minute.

Variables Involved

The variables involved may be divided into two groups.
There is that group of variables which has a direct effect
on the decomposition of the gypsum, such as temperature, re-
tention time, and particle size; and another group which is
that influencing the decomposition indirectly by their ef-
fact on the nature of the fluidized bed. Variables in the
latter group include the Reynolds number and its associated
variables, bed velocity, and particle size and shape factor.
Variables indirectly affecting decomposition

It was not possible to keep these constant for all runs. Particle size and the shape factor associated with it were investigated as a variable directly affecting the decomposition of anhydrite. The effects resulting from its influence on the fluidized bed properties per se cannot readily be separated from its other effects on the reaction. The bed porosity is probably of minor interest since it is a reflection of the Reynolds number or gas velocity.

For any given particle size fraction, the velocity of the fluidizing gases must be between that of incipient fluidization and the clearing velocity. This represents a wide range; for example, considering -6+8 mesh particles, reference to Figure 14 shows the incipient fluidization velocity at 2600°F to be 5.8 feet per second and the clearing velocity to be 60 feet per second. The operating velocity must lie somewhere between these two limits, the choice depending on such factors as entrainment, agitation of the bed, desired fuel rate, and general operating characteristics. It should not be so great that there are excessive losses in the off-gases of the fines produced by attrition, yet it should be great enough to permit a reasonable feed rate of the raw gypsum, as discussed later.
Since the gas velocity obtained will be a function of the fuel rate, gas-air ratio, and gas temperature, it is necessary to fix the latter variables to provide the desired fluidization velocity for any given particle size distribution.

The maximum permissible fuel rate is determined not only by the clearing velocity of the particle, but also by the combustion volume available in the combustion chamber and in the bed itself. This factor was taken into consideration in the design of the reactor, the combustion volume of which was estimated to be sufficient for from 40 to 60 cubic feet of fuel gas per hour.

Efforts were made to keep the indirect variables constant in comparative runs so that their effect could be neglected.

Variables directly affecting decomposition

Bed temperature. This is for two reasons one of the most important variables. The first is its effect on the kinetics of the reaction, and the second is its effect on the physical state of the gypsum particles, i.e. fusion of the particles. From a kinetic standpoint, higher temperatures should increase the rate of the desulfurization reaction. However, even with 1/8-inch particles, the minimum retention time as dictated by the balance of fuel and ve-
locity requirements is 15 minutes. On a commercial scale this would probably be increased, by reason of an increased bed depth, to from 1 to 3 hours. With the relatively fine particle sizes involved this would probably be ample time for the reaction to occur. Bed temperatures greater than necessary to obtain desulfurization in the desired time interval are undesirable from the standpoint of thermal efficiency.

Considering the effect of temperature on fusion and what effect this will have on the fluidized bed, it is necessary to consider what takes place as the gypsum particle is subjected to increasing temperature under oxidizing conditions. At about 2375°F when the decomposition pressure of the gypsum is still low, the calcium sulfate may fuse and become molten. However, as the sulfur trioxide is expelled, which occurs rapidly with slightly increased temperatures, the melting point rises and approaches that of lime which is well over 4000°F. Since there is at complete desulfurization about 10 per cent silica present, the fusion point approaches 3750°F, that of the calcium oxide-silica eutectic. It is apparent that at some stage of desulfurization the particle will again become solid at the temperatures present in the fluidized bed. Since the bed is of uniform composition and the product being discharged is of solid rather than molten nature, it follows that in continuous
operation the majority of the bed would consist of solid particles. The question then arises as to whether or not the introduction of gypsum into such a bed and its subsequent fusion before attaining the solid state will result in fusion and subsequent defluidization of the entire bed. D. Mac-Askill of the Dorr Company [16] in a paper describing their Fluo-Solids reactor has stated:

...fluidized beds consist of essentially finished product. Therefore, if the finished product is not sticky at the temperature ranges selected, there is no reason to fear defluidization. Consequently, providing a material disperses into the bed and it is non-sticky in its finished state, there is nothing to preventing feeding any type of feed, regardless of whether it melts and gets sticky before assuming its calcined form....

Whether or not this is true will depend on what opportunity the material has to agglomerate while in the fused state, and, if an agglomerate is formed, whether or not it breaks up with continued heating. The aspects of this are discussed more fully in the Results section.

Retention time. With batch operation the retention time is a simply determined variable although it is determined with respect to unsteady state conditions of some other variables. With continuous operation the retention time of the solid particles is a function of both feed rate and bed height and is necessarily a statistical average. At a constant bed height it is a function of feed rate. While at a constant feed rate the retention time may be changed
by changing the bed height. If the fuel rate is kept constant, changing the bed height will not alter the fuel/feed rate ratio. Thus investigation of the retention time by changing bed height will indicate the kinetic effects of retention time, whereas its variation by altering the feed rate may show the effect of heat requirements and efficiency as well as kinetic effects. In the interpretation of continuous results care must be exercised to differentiate between kinetic effects and fuel requirements.

The maximum practical feed rate, or minimum retention time, is limited by the rate at which heat is supplied for the endothermic heat reaction, that is, by the fuel rate or, if under reducing conditions, the rate at which the reducing gases are supplied.

It may be noted that in effect the particle size limits the feed rate since the clearing velocity of the former limits the fuel rate and hence the rate of heat or reducing gases supplied for the decomposition reaction. With the smaller sized fractions the minimum retention time is greater than for the larger sized fractions.

Summarizing the foregoing, it may be noted that the particle size determines the limits for the gas velocity, which in turn sets the fuel rate. The fuel rate then limits the maximum allowable feed rate, which at a constant bed height determines the retention time.
Oxidation-reduction characteristics of the fluidizing gases. This was not one of the initially considered variables, but as information was obtained it became obvious that this was a very important consideration.

It was pointed out in the section Theoretical Considerations that whereas temperatures greater than 2400°F were necessary for positive values of the equilibrium constant for the reaction

$$\text{CaSO}_4 = \text{CaO} + \text{SO}_2 + \frac{1}{2} \text{O}_2 \quad (3)$$

the equilibrium constants for several possible decomposition reactions involving carbon monoxide were positive at considerably lower temperatures. Thus the oxidation-reduction (O-R) characteristics of the fluidization gases are of much importance. The modulus of the O-R characteristics was the per cent of the combustion air stoichiometrically required to burn the fuel to carbon dioxide and water.

Method of Operation

Considerations in choice of batch or continuous operation

One of the advantages of a fluidized bed is its adaptability to continuous operation and the steady state conditions which can thereby be attained. However, for investi-
gational work, a batch operation, even though it represents unsteady state conditions, possesses certain advantages over a continuous operation. These include:

1. The effects of retention time may be rapidly and directly studied at any condition of the other variables by the periodic withdrawal of small samples from the bed.

2. The indirectly controlled variables (e.g. fluidizing gas temperature) will remain approximately constant during the time required for a batch operation. However, a series of continuous runs, possibly made over a period of several days, may be at different conditions with respect to these indirectly controlled variables even though directly controlled variables as gas rate and air rate remain constant.

3. A true retention time is obtained rather than a statistical average as in the case of continuous operation.

4. Other advantages are more in the nature of the avoidance of the following disadvantages of continuous operation:
   a. Disturbance of the bed by the entrance of the heavier, cold feed and subsequent channeling.
This is particularly noticeable in a small diameter bed.

b. Attrition of the particles if a screw conveyor is used.

c. Mechanical difficulties in the operation of the feed device.

There are also disadvantages in batch operation which must not be overlooked. These result from unsteady state operation and include:

1. The initial charge preheating period which is required.

2. A decrease in bed depth due to the removal of solid samples.

3. Inability to obtain a gas sample comparable to any steady state conditions.

This last disadvantage is perhaps the most serious. The initial preheating period is small, from 2 to 5 minutes. When small solid samples are removed (10 grams), the effect on bed depth is small during the time of most interest.

The advantages offered by batch operations were considered to be such that the majority of the investigational work was conducted with batch operations. Several continuous runs were attempted but were unsuccessful because of the disadvantages previously mentioned.
Method of batch operation

The reactor was allowed to preheat with no charge for from 2 to 4 hours with a gas rate of from 20 to 25 cubic feet per hour. The stack draft was kept constant at 20 centimeters of water. The air rate was maintained at that necessary to obtain the desired oxidation-reduction characteristics of the bed atmosphere which were characterized by the per cent of the stoichiometrically-required air supplied. Observed values of the Orsat analysis of samples of the fluidizing gases, taken 1 inch above the bed support, are compared in Table 6 with calculated values based on the assumption that carbon dioxide, carbon monoxide, and water are the only products of combustion. It may be noted that with 90 per cent and less stoichiometric air supplied, there was actually less carbon monoxide and more carbon dioxide present than the calculated values would indicate. This discrepancy resulted from soot formation, which was apparent in runs under these conditions. It is also important to note that whereas with 100 per cent stoichiometric air there were small quantities of both carbon monoxide and oxygen present, there was no appreciable carbon monoxide at 105 per cent or greater stoichiometric air and no appreciable oxygen with 95 per cent or less stoichiometric air.

The temperature of the ascending fluidization gases and the temperature of the upper surface of the bed support as
Table 6
Analysis of Fluidizing Gases
Calculated and Observed Values

<table>
<thead>
<tr>
<th>% Stoichiometric air supplied</th>
<th>Calculated values&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Observed values</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>% CO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>% CO</td>
</tr>
<tr>
<td>80</td>
<td>2.6</td>
<td>11.3</td>
</tr>
<tr>
<td>90</td>
<td>7.5</td>
<td>5.1</td>
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<td>95</td>
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<td>100</td>
<td>11.4</td>
<td>0.0</td>
</tr>
<tr>
<td>105</td>
<td>10.8</td>
<td>0.0</td>
</tr>
<tr>
<td>110</td>
<td>10.83</td>
<td>0.0</td>
</tr>
</tbody>
</table>

<sup>a</sup>Dry basis; remainder nitrogen.
measured with the thermocouple located below the bed support and an optical pyrometer, respectively, were measured periodically and the air preheat and/or gas rate adjusted to give the desired fluidization gas temperature. When equilibrium had apparently been established with respect to these two temperatures, a weighed portion of closely sized gypsum was added rapidly through the top sight port. In most of the experiments 700 grams of -6+8 mesh gypsum were charged. This produced an initial bed depth of about 5 1/2 inches. The velocity of the fluidization gases in the range of the gas rates used was not sufficient to fluidize the cold feed. For this reason, in all but the later runs the air was increased until fluidization occurred and then slowly decreased so as to maintain fluidization with a minimum velocity until the desired air rate was reached. The required velocity decreased sharply as dehydration occurred. This procedure was modified subsequent to run F-153, after which the air rate was not increased when the charge was added, that is, dehydration and preheating occurred in a fixed bed which subsequently became fluidized. Stirring of the bed aided in starting fluidization. Approximately the same length of time was required, from 2 to 5 minutes for a 700-gram charge, for this start-up period for both methods.
About 3 minutes after the charge was added, fluidization had been attained and the bed had become very dull red on the surface. At this point the temperature gradient through the bed depth was quite apparent; if the surface was scratched with a rod, particles of much higher temperature were visible beneath the surface.

The temperature of the fluidizing gases was periodically checked and, if necessary, the preheater or gas rate adjusted to maintain this temperature. However, in all cases the gas/air ratio was kept constant during a run. The off-gas temperature, bed surface temperature, and ascending hot gas temperature below the bed support were also periodically measured.

Samples of from 5 to 10 grams of the solid material in the reactor were periodically removed with a dipper inserted through the top observation port. At the same time the bed depth was measured and, in some instances, the temperature of the bed surface was noted with an optical pyrometer. Removal of the sight glass from the top observation port resulted in an increase in the pressure in the reactor above the bed. This had little effect on the air since it was supplied at approximately 8 pounds per square inch, but the gas entered at the line pressure which was only about 6 inches of water. Consequently, unless the gas valve was
simultaneously adjusted, the gas rate would drop resulting in more oxidizing conditions in the bed while the cap was removed.

The importance of this was not realized until after run F-143, when consideration of the erratic sulfide formation led to this conclusion. Prior to run F-144 no particular care was exercised to maintain the gas-air ratio at the prescribed value during the 1 or 2 minutes the observation port was open. Subsequent to this, however, care was exercised to maintain this ratio constant by opening the gas valve as the cap was removed from the observation port.

Subsequent to run F-137 gas samples were taken from about 1/2 inch above the bed surface through a refractory tube. Prior to this, the samples had been removed through a port at the top of the reactor. However, air leaks in the upper portion of the reactor diluted these samples. Samples for Orsat analysis were taken with the usual acidulated-water-filled sampling pipette immediately before and 5 to 30 minutes after starting the run.

Samples were removed and stored for subsequent analysis of the sulfurous gases from runs F-146 through F-162. However, the analysis was unsatisfactory. Subsequently, two simultaneous samples were aspirated through a standard iodine solution and an acidified barium chloride solution as outlined in the Methods of Analysis of Products section.
About 15 minutes were required for aspiration of the sample. Three or four such samples were usually collected in the first 90 minutes of operation.

Runs were continued for from 90 to 120 minutes after charging. When reducing conditions existed, the reactions were usually completed within a 90-minute period. Upon completion of a run, the entire bed was removed with a dipper and the furnace either shut down or adjusted to the conditions of the next run.

Experimental Investigation of Bed Supports and Operational Methods

The development of an operational method necessarily accompanied the investigation of the bed support types to determine their utility. Runs F-101 through F-117 were concerned primarily with such investigations. The operational characteristics of most interest were those at temperatures above the fusion point of the feed since this was thought to be possible and considered one of the outstanding advantages of a fluidized bed. Because the conditions were frequently changed during a run and few analyses of the product were made, the information for these runs has not been presented in tabular or graphic form. A description follows.
The first support tried was a perforated plate cast of Harbison-Walker Chrome-Castable refractory. This support was 2 inches in thickness. The gas passageways were 3/16 inch in diameter in the bottom half of the support and tapered from this point to a diameter of 5/8 inch at the top where the holes were close-packed. Starting with an empty bed and feeding continuously, a satisfactory bed could not be established with this support. The particles would pass through the support, although their free fall velocity was calculated to be less than the average velocity through the passageways in the plate. Certain passages seemed to serve as a path for the downward flow of the particles, indicating that perhaps there was channeling through the support. Besides this, the refractory material proved to be completely unsatisfactory, apparently reacting with either the calcium sulfate or calcium oxide formed, or both, resulting in slaggiiing and destruction of the bed support.

The next support was of similar design but was prepared with Laclede Chrome-ore plastic refractory material. It was also 2 inches in thickness, but contained holes 1/8 inch in diameter from the bottom to the midpoint from whence they tapered to a 1/2-inch diameter at the top. The action of this bed support with respect to fluidization was similar to that of the first. At temperatures greater than 2300°F the support was destroyed by reaction with the solid product.
A venturi type of support was tried which tapered from a minimum bottom diameter of 3/4 inch to a top diameter of 3 inches over a height of 6 inches. Laclede Chrome-ore plastic refractory was used for the material of construction and was satisfactory. The walls of this support remained relatively cool and did not attain a sufficiently high temperature to react with the feed material. A bed of high porosity could be obtained in this cone, but particles would fall into the combustion chamber below. This occurred as a result of fluctuations in the gas velocity and turbulent eddy currents which seemed to exist, probably because of the sudden decrease in size of the combustion chamber at the neck of the cone.

This support was then modified by extending the minimum diameter downward for several inches to prevent the particles from falling all the way back to the combustion chamber as a result of the eddy currents. It was moderately successful in this respect, but loss of particles still occurred through this extended neck and prevented formation of a deep bed.

High particle temperatures could be obtained with this bed support as a result of surface combustion, and the violent fluidization minimized the formation of fused agglomerates. However, such agglomerates did form and it is ques-
tionable whether or not sufficiently violent fluidization could be obtained to prevent this formation. Experiments with -6+8 gypsum up to the entrainment velocity indicated that agglomeration could not be prevented. Although with such a bed support it might be possible to adjust the velocity such that the agglomerates would fall out through the bottom from whence they could be removed, this was not possible with the reactor in use because of the previously mentioned eddy currents which carried small particles down as well. Furthermore, agglomerates were formed which were too large to pass through the 3/4-inch neck of the cone. If the gases were burned in a larger chamber and led into the cone via another cone, i.e. a venturi, these eddy currents would probably be minimized and conditions might be adjusted to permit the agglomerates to fall through before attaining too large a size.

Because of the inability to form a deep bed in the cone type of support, perforated plates fabricated from 3 by 4 1/2 by 4 inch magnesite firebrick (General Refractories Company Ritex A) split to give a 1 1/4 by 4 1/2 by 4 inch brick were tried. A 3-inch diameter circle was located in the center and in this were drilled 1/4-inch holes on 1/2-inch centers. The refractory material was satisfactory but the design was poor. Feed particles would fall through into
the combustion chamber at velocities well over the fluidization range.

The next of this type had fewer holes, thirteen, which were spaced on 3/4-inch centers. These holes were of 1/4-inch diameter at the top and bottom, but the middle aperture was only 7/64-inch. With this plate an excellent fluidized bed of raw gypsum could be obtained, firing and burning the gas in the combustion chamber below. However, the support seemed to act as a wire screen in preventing heat from traveling up into the bed. Consequently, the bed, or at least the bed surface, would not attain temperatures over 1800°F unless the gases were burned above the bed support, in which case they would burn by surface combustion in the bed and temperatures to 2500°F were obtained.

Experimentation was carried out with this support to develop a technique for operation at temperatures greater than fusion. First, the reactor was preheated, burning gas above the bed support with an empty bed. Continuous feed was then started into the empty bed at rates as low as 10 per cent of that theoretically possible based on the fuel rate. All such experiments were unsuccessful. The particles would fuse and agglomerate and fluidization could not be maintained. Next, a 4-inch bed of lime was formed by a batch calcination of oyster shell (calcium carbonate). Continuous feed of the gypsum was then started. Again, the
results were unsuccessful and fusion and subsequent defluidization resulted.

Operation with the gases burning below the support but at temperatures greater than 2400°F (obtained with preheated air) also resulted in fusion, even at very low gypsum feed rates (1 pound per hour of gypsum, 30 cubic feet per hour of gas).

The decision was thus made to limit the investigations to temperatures below fusion, using a perforated plate bed support of this last discussed design.

This design was modified following run F-120 to 1/8-inch holes on 1/2-inch centers, counter-sunk 1/2 inch deep from the top to a diameter of 1/4 inch. This reduced the dead area on the surface of the support.

Thermal Decomposition of Gypsum in a Batch Reactor

The independent variables of bed temperature, oxidation-reduction (O-R) characteristics of the bed atmosphere, and retention time are of interest with respect to their effect on the dependent variables of solid product composition (percent desulfurization of the feed and percent of original sulfur converted to sulfide) and nature and quantity of sulfurous gases produced.
The measurement or characterization of the bed temperature was difficult because of the temperature gradient which existed from the bottom to the top of the bed. The surface temperature of the bed as observed with an optical pyrometer was the only related temperature observed through run F-130, although it was apparent that this was not the maximum temperature in the bed. Scratching the surface of the bed with a rod would show the presence of higher temperature particles below the surface. These would also be indicated by the slugs of particles brought to the surface by the fluidization process, which upon attaining the surface would cool rapidly. It was the temperature of these slugs which was measured with the optical pyrometer. This was difficult since they were in constant motion and cooled even before reaching the bed surface. This method was unsatisfactory; no significant difference in the surface temperature could be observed among runs. Direct measurement of the bed temperature with a thermocouple was not possible because no refractory tube could be located which would withstand the fluxing action of the bed. Bare chromel-alumel thermocouples (eight gauge) inserted directly into the bed were destroyed before the potentiometer could be balanced.

Since temperatures within the bed itself could not be measured, it was decided to measure the temperature of the ascending fluidizing gases before they entered the bed. For
this a thermocouple was placed directly beneath the bed support, as discussed in the Description of Equipment section. If all the fuel gases were burned before entering the bed, which appeared to be true, the maximum bed temperature attainable, if the reaction is endothermic, would be the temperature of these gases. The possibility of exothermic reactions exists, but, if a temperature rise occurs in the bed as a result of exothermic reactions, fusion would have been expected in those runs in which the gas temperature was only slightly below the fusion temperature. Such an effect was not observed.

To minimize the effect of the temperature variation in the bed, those runs used in correlation of the data were all carried out with the same weight of charge, 700 grams of -6+8 mesh gypsum.

Results

The O-R characteristics of the bed atmosphere were governed by the gas/air ratio. Ample volume was provided in the combustion chamber below the support to provide complete combustion of the gases entering the bed. The percent of stoichiometrically required combustion air supplied is used to characterize this variable. The retention time for these batch operations was taken as the time elapsed from the addition of the charge.
Table 7 presents the results obtained, grouping the runs with increasing per cent of stoichiometric air supplied and increasing temperature of the fluidization gases below the bed support. The temperature was usually maintained within ±20°F of the nominal temperature of the run. However, fluctuations in the gas or air rate would cause greater deviation for short periods. The maximum deviation from this nominal temperature is also presented. Runs previous to F-131 have no temperatures listed because the thermocouple below the bed support was not in place.

The interrelation among the independent variables must be considered in interpreting the results.

Solid product composition. The results are presented in Figures 18 through 23 which relate the independent variable of retention time to the solid product composition with respect to per cent desulfurization (per cent of original sulfur removed) and per cent of original sulfur present as sulfide sulfur. Note that the difference between 100 per cent and the sum of these two values will equal the per cent of original sulfur remaining as sulfate. Each of these figures represents a constant O-R condition for which lines of constant nominal temperature have been obtained from the experimental data. Because of the lack of control of the O-R conditions in runs previous to F-144, as previously discussed, those runs at reducing conditions prior to this are not in-
NOTE TO USERS

Oversize maps and charts are microfilmed in sections in the following manner:

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Particle size used in all runs was -6+8 mesh except run F-129 for which -4+6 mesh was used.

Sulfate refers to total sulfur present as sulfate expressed as per cent SO₃. Sulfide refers to per cent of sulfur, originally present in the feed, which has been removed.

Sample taken within 1 or 2 minutes of this time. Value presented here interpolated from observations.
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sulfur present as sulfide expressed as per cent $S_2$. Desulfurization was from curve.
NOTE TO USERS

Oversize maps and charts are microfilmed in sections in the following manner:

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cluded in the following discussion. They are discussed in a later section. Those runs prior to P-144 under definitely oxidizing conditions are included as the effect of increasing the oxidative nature of these gases would not be noticeable. A discussion of these is of help in interpreting the summary curves and discussion presented later. They are presented with respect to temperature in order of increasingly reducing conditions.

**Stoichiometric air supplied: 110 to 138 per cent.**

Figure 18 summarizes the results for the oxidizing condition runs. In all runs with 105 per cent or more of the stoichiometrically required air supplied there was negligible sulfide formation. At a nominal temperature of 2375°F with 128 to 139 per cent of the stoichiometric combustion air supplied there was no significant conversion of the sulfate, i.e. under these oxidizing conditions desulfurization did not occur at a temperature which was only slightly below the fusion temperature of the feed.

With the less oxidizing conditions of 110 to 117 per cent stoichiometric air some desulfurization occurred. It is interesting to note that although at all temperatures the desulfurization was small, it was a maximum at the minimum temperature and a minimum at the maximum temperature. This result is discussed in the effect of temperature section.
FIGURE 18 Desulfurization of Gypsum
Oxidizing Conditions

FIGURE 19 Desulfurization of Gypsum
105 Per Cent Stoichiometric Air
Stoichiometric air supplied: 105 per cent. Figure 19 is a similar curve for 105 per cent stoichiometric air. This indicates greater desulfurization at these less oxidizing conditions, and supports the conclusion reached with 110 per cent stoichiometric air that the maximum desulfurization occurs at the lowest temperature, 2150°F, and the minimum desulfurization at the maximum temperature, 2350°F.

Stoichiometric air supplied: 100 per cent. With 100 per cent stoichiometric air, sulfides were formed at all temperatures studied. This is indicated in Figure 20. There is some indication that sulfide formation is favored under these conditions by the lower temperatures. There is no significant difference in the desulfurization between the nominal temperatures 2150°F and 2250°F, but less desulfurization appeared to result from the maximum temperature 2350°F. However, it may be noted that between 30 and 60 minutes there appeared to be an irregularity in this latter curve, after which the slope became approximately equal to that of the lower temperature curves. No explanation can be offered for this lag. If it is assumed that it was the result of some irregular, local action, e.g. effective reduction of the bed area by stoppages in the gas passage ports of the bed support, then the true curve would be off-set toward the ordinate and would lie only slightly below the others. This would support the conclusion that temperature changes between
PER CENT DESULFURIZATION OR PER CENT ORIGINAL SULFUR PRESENT AS SULFIDE

SYMBOL RUN NO.

100 PER CENT STOICHIOMETRIC AIR

DESULFURIZATION OF GYPSUM

RETENTION TIME -- MINUTES
2150°F and 2350°F have little effect on either the desulfurization or the per cent of original sulfur present as sulfide with 100 per cent stoichiometric air.

**Stoichiometric air supplied: 95 per cent.** As previously shown in Table 6, definitely reducing conditions must have existed in the runs with only 95 per cent of the stoichiometrically required air supplied. The relation of solid product composition to retention time at constant temperature is given by Figure 21. Consideration of this figure indicates that under these conditions maximum desulfurization was obtained at the highest temperature and minimum desulfurization at the lowest temperature. The sulfide formation was almost identical for runs F-147 and F-153, which were at approximately 2150°F and 2250°F respectively. At the temperature of 2350°F in run F-156 the sulfide concentration was lower. However, the temperature of 2350°F in run F-163 produced sulfides comparable with those obtained with the lower temperatures of the first mentioned runs, whereas at the lower temperature of 2150°F with run F-166 sulfide formation was initially lower. However, in the latter case this sulfide concentration increased as the sulfate conversion progressed and ultimately attained a value comparable to that of the other low temperature runs.

**Stoichiometric air supplied: 90 per cent.** With 90 per cent of the stoichiometric combustion air there was a
FIGURE 21

DESFULFURIZATION OF GYPSUM

95 PER CENT STOICHIOMETRIC AIR
definite effect of temperature on the sulfide formation. (See Figure 22.) The amount of sulfur present as sulfide increased with decreasing temperature. Because of the decrease in sulfides with increasing temperature, the desulfurization increased with increasing temperature.

*Stoichiometric air supplied: 80 per cent.* Figure 23 presents the data obtained with 80 per cent theoretical air. The curves for the two temperatures 2150°F and 2250°F show little difference in the desulfurization with retention time. The highest temperature (2350°F in run F-168) produced the maximum desulfurization.

The amount of sulfide present was erratic. To 60 minutes there was no difference between the lowest and the highest temperature, while the middle temperature range had considerably more sulfide formation. The curves indicate a maximum sulfide formation at the middle temperature, 2250°F, and a minimum sulfide formation at the highest temperature, 2350°F. This produced the expected effect on desulfurization, i.e. the maximum net desulfurization was obtained at the highest temperature, 2350°F, as with 90 and 95 per cent stoichiometric air. However, the temperature of 2150°F produced slightly greater desulfurization than the middle temperature of 2250°F.
FIGURE 22

DESULFURIZATION OF GYPSUM

90 PER CENT STOICHIOMETRIC AIR
FIGURE 23
DESULFURIZATION OF GYPSUM
80 PER CENT STOICHIOMETRIC AIR
Stoichiometric air supplied: 65 per cent. Only the one nominal temperature of 2250°F, which required an air preheat of 900°F, was investigated under these conditions. Thus no observations may be made regarding the effect of temperature at these reducing conditions. The results obtained are presented and discussed on other summary curves.

Gas analysis. The analysis of the off-gases with respect to the various sulfurous components would be desirable both for determining possible commercial applications and for use in elucidating the possible reactions involved. The nature of the batch operation was such that it was impossible to obtain samples representative of continuous steady state operation. However, samples were taken at various times during a run. This was done as described in the Method of Operation section. The results obtained with runs F-163 through F-168 are presented in Table 8. Also included are selected values of the estimated total sulfur concentration, calculated from the rate of desulfurization and the gas rate over the period of sampling. It may be seen that the measured values do not compare with the estimated. This may be the result either of experimental error or of the combination of sulfur dioxide with hydrogen sulfide to form free sulfur by the reaction

\[2\text{H}_2\text{S} + \text{SO}_2 = \frac{1}{2}\text{S}_2 + \text{H}_2\text{O}\]  

(24)
Table 8

Gas Analysis Results; Batch Investigations in Fluidized Bed\(^a\)

<table>
<thead>
<tr>
<th>Run No.</th>
<th>% stoich.</th>
<th>Fluid. gas temp.</th>
<th>Interval sample taken min.</th>
<th>Observed values</th>
<th>Calc. total S as % SO(_2)</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>% H(_2)S</td>
<td>% SO(_2)</td>
<td>% SO(_3)</td>
<td>H(_2)S</td>
<td>SO(_2)</td>
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<td>2230</td>
<td>35-55</td>
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<td>2245</td>
<td>63-75</td>
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<td></td>
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<td></td>
<td>2350</td>
<td>47-75</td>
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\(^a\)Results corrected for sulfur in fuel gas.
The gases were not analyzed for free sulfur, but none was qualitatively observed, i.e. no sulfur condensed in the gas sampling lines.

The analysis of samples collected from other runs in sample bottles over acidulated water was completely unsatisfactory, probably due to absorption of the gases in the water.

The accuracy of the gas analysis is considered to be too poor to serve as the basis for any but qualitative conclusions. Hydrogen sulfide predominates at conditions of less than 95 per cent stoichiometric air. With greater than 95 per cent stoichiometric air, sulfur dioxide is present. The presence of these gases under the afore mentioned conditions is also indicated by their characteristic odor.

Discussion

The effects of each of the independent variables of temperature and O-R nature of the gases on the desulfurization and per cent of original sulfur converted to sulfide may be determined by preparing cross-plots from the curves presented in the preceding pages. These are discussed below.

Effect of temperature of fluidizing gases. The effect of temperature on the desulfurization is shown on Figure 24. Under nominally oxidizing conditions an increase in temperature appears to decrease the desulfurization. With reducing
FIGURE 24  
EFFECT OF TEMPERATURE ON GYPSUM DESULFURIZATION
conditions the opposite is true, an increase in temperature increases desulfurization, while at nominally neutral conditions there is little effect of temperature.

This indicates that two reactions or sets of reactions may occur, depending on the O-R characteristics. In the presence of oxidizing conditions the reactions involved in desulfurization are apparently hindered by increases in the temperature between 2150°F and 2350°F. Under definite reducing conditions the reactions are favored by higher temperatures within this range.

A definite and consistent effect on the amount of sulfur present as sulfide is produced by temperatures in the range 2150°F to 2350°F. This is indicated by Figure 25 which correlates the per cent of original sulfur present as sulfides after a retention time of 90 minutes at constant O-R conditions with given temperatures. At this retention time, with the exception of some of the lower temperature values, the sulfides had attained an equilibrium value which was the maximum. From this figure it is apparent that the amount of residual sulfide decreases with increasing temperature above 2200°F. This could result from either (1) a decrease in the rate of the sulfide-forming reaction or (2) an increase in the rate, or equilibrium conversion, of the sulfide removal reaction or both. The theoretical equilibrium constant for the reaction
Figure 25: Effect of Temperature on Residual Sulfide
CaS + 3CaSO₄ = 4CaO + 4SO₂  \tag{3}

is zero at approximately 2000°F and rises very rapidly with temperature (see Figure 2). This suggests that (2) above is the cause of this effect. Since conversion of the sulfate will not begin below about 2100°F, the curve of residual sulfide will increase to a maximum and then decrease as the temperature increases from 2100°F. Such a maximum is indicated for 80 per cent stoichiometric air.

The increase in desulfurization with temperature under reducing conditions follows from the consideration relating to sulfide removal, i.e. the reaction between calcium sulfide and calcium sulfate is favored. With oxidizing conditions, calcium sulfide can exist only momentarily if at all, in which case the reaction between the sulfide and sulfate appears improbable. Hence the decomposition reaction involved, which must include a reducing substance as discussed later, is apparently favored by the lower temperatures.

There must also be some temperature below which no appreciable conversion of the sulfate to either a sulfide or a gaseous form occurs. Information from run F-134 with 71 per cent stoichiometric air and run F-141 with 95 per cent stoichiometric air is presented in Figure 26. No sulfides were formed during the portion of these runs presented, so the per cent desulfurization is a direct measure of the ex-
FIGURE 26  EFFECT OF TEMPERATURE ON SULFATE CONVERSION
tent of sulfate conversion. From figures of desulfurization and residual sulfide versus retention time already presented, it may be noted that sulfate conversion begins within a few minutes. In these two runs, however, the temperature of the fluidizing gases decreased on addition of the charge and sulfate conversion did not commence to an appreciable extent until the temperature had increased to about 2100°F.

Effect of oxidizing-reducing characteristics of the fluidizing gases. The effect of the O-R characteristic of the fluidizing gases on the desulfurization of calcium sulfate is illustrated in Figure 27, which correlates the percent desulfurization at a constant retention time of 90 minutes with the percent of stoichiometrically required combustion air supplied for each of the three temperature ranges studied. At the 90 minute retention time the desulfurization had in most cases reached a maximum and "equilibrium" value. The notable exception to this was at 100 percent theoretical air in which case desulfurization was rapidly increasing.

The effect of an increase in the reducing conditions is greatest between 105 and 95 percent stoichiometric air. It would be in this range that reducing substances, specifically carbon monoxide, would start to appear. No desulfurization is observed with about 130 percent excess air at temperatures below 2400°F. With this amount of excess air,
FIGURE 27. EFFECT OF OXIDATION-REDUCTION CHARACTERISTICS OF ATMOSPHERE ON DESULFURIZATION OF GYPSUM
Per Cent Desulfurization or Per Cent Sulfur Present as Sulfide

Retention Time - 90 Minutes
Solid Lines - Desulfurization
Broken Lines - Sulfide

Per Cent Stoichiometric Air Supplied

120 110 100 90 80 70 60

2350 °F
2250 °F
2150 °F
complete oxidizing conditions may be assumed to exist, but
with 110 and 105 per cent excess air occasional slight re-
ducing conditions may exist, while with 100 per cent stoi-
chiometric air both moderate reducing and moderate oxidizing
conditions would be expected simultaneously. Thus the de-
sulfurization of gypsum at temperatures below 2400°F must
require the presence of a reducing substance which in these
investigations was undoubtedly carbon monoxide.

The importance of the proper O-R relation is evident
from Figure 27. Optimum desulfurization at all temperatures
is effected near 100 per cent of the stoichiometric air.
With this condition, the atmosphere is probably alternately
reducing and oxidizing. Thus the reducing conditions nec-
essary for conversion of the sulfate are present, yet the
sulfides formed are removed by oxidation by the small amount
of oxygen present.

With increasingly reducing conditions, higher residual
sulfide concentrations are obtained which decrease the de-
sulfurization. At more oxidizing conditions, the lack of
the apparently necessary reducing material in the gas phase
prevents desulfurization.

Figure 27 also indicates the effect of the O-R condi-
tions on sulfide formation. It is apparent that decreasing
the stoichiometric air increases the sulfide formation. One
exception is the point of 65 per cent stoichiometric air for
which no explanation can be offered. A similar effect is observed with other retention times.

It may be noted that with both oxidizing and reducing conditions the amount of desulfurization approached an equilibrium value of less than 100 per cent with time. With reducing conditions this is the result of the residual sulfide present when the sulfate concentration approaches zero. However, with oxidizing conditions no noticeable sulfide is formed, yet the desulfurization ceases before completion. This is explainable as follows. Although the conditions are nominally oxidizing, there is some reducing material present, probably occurring sporadically as the result of varying conditions. The reducing agent reacts readily with the exterior of the particle, but it must diffuse through part of the particle to reach the interior. If its presence is sporadic, there is a maximum depth to which it will penetrate before conditions are such that it will diffuse back into the gases. This then limits the maximum per cent desulfurization which may be obtained.

**Effect of retention time.** The effect of retention time may be observed from Figures 28 and 29. These correlate retention time with per cent desulfurization and residual sulfide for the nominal temperature of 2250°F.
Figure 28
EFFECT OF RETENTION TIME ON DESULFURIZATION OF GYPSUM

NOTE: TEMPERATURE - 2250 °F
PER CENT STOICHIOMETRIC AIR SUPPLIED

RETENTION TIME - MINUTES
FIGURE 29  EFFECT OF RETENTION TIME ON SULFIDE FORMATION

NOMINAL TEMPERATURE — 2250°F
From Figure 28 it may be seen that equilibrium with respect to desulfurization was generally attained at from 45 to 60 minutes retention time with reducing conditions. However, with 95 to 105 per cent stoichiometric air equilibrium was not attained in this time interval, indicating perhaps a limitation due to the low reducing substance content.

The retention time required may be a function of variables not studied, as bed depth and gas rate. A constant charge weight of 700 grams and gas rates between 20 and 25 cubic feet per hour were used. The thermal efficiency was low so the gas rate probably did not limit the heat supply. The rate at which the reducing material became available for the reaction could, however, be a limiting factor for the rate of sulfate conversion, particularly at only slightly reducing conditions. With 95 per cent stoichiometric air the carbon monoxide necessary to react with 700 grams of charge on a mole per mole basis could be supplied in a minimum of about 20 minutes at a gas rate of 20 cubic feet per hour. The contact efficiency in a bed of 700 grams (about 4 inches deep) would not be good, however, and much of the carbon monoxide would pass through unreacted. Thus the availability of carbon monoxide was undoubtedly a limiting factor with 100 per cent stoichiometric air and probably also at 95 per cent stoichiometric air. With less than 90 per cent
stoichiometric air, however, this effect ceased to be as noticeable. Thus, increasing the gas rate might increase the rate of sulfate conversion at 95 and 100 per cent stoichiometric air, but would have little effect at O-R conditions corresponding to 90 per cent or less stoichiometric air. A change in the bed depth might produce changes in the required retention time because of the temperature gradients which are involved. Furthermore, at some point there will be thermal limitations unless the gas rate is increased correspondingly with bed depth. Thus for a given retention time, the bed depth is limited by the maximum permissible fluidizing gas velocity which in turn governs the gas rate.

The sulfide concentration also reached an equilibrium value at about 60 minutes, with the exception of 65 per cent stoichiometric air which continued to increase slightly (see Figure 29). At the lower temperature range, not plotted, approximately 90 minutes were required for the equilibrium sulfide concentration to be reached with 95 and 80 per cent stoichiometric air, and 45 minutes with 100 and 90 per cent stoichiometric air. This decrease is explainable with 100 per cent stoichiometric air (a maximum sulfide depth may be obtained before it is oxidized) but that with 90 per cent cannot be explained. At the highest temperature range, equilibrium was reached at 60 minutes.
Comparison of the desulfurization and residual sulfide curves shows that with respect to residual sulfate nominally reducing conditions reduced the sulfate content to 5 per cent or less in from 50 to 70 minutes, the longer period being required for the less reducing conditions. Thus the retention time required depends, in this range, more on factors other than the concentration of reducing substances. With 100 per cent stoichiometric air, considerably more time is required, 110 minutes, to reach 5 per cent residual sulfate. Here the reducing substance concentration is probably a limiting value.

Interpretation of the foregoing observations combined with a study of the equilibrium constants presented in Figure 2 may be used to determine the probable reactions involved.

It is apparent that a reducing substance is necessary for the desulfurization at temperatures below 2400°F. This is undoubtedly carbon monoxide. The solid products obtained under reducing conditions are calcium oxide and calcium sulfide. The gases include hydrogen sulfide, which must arise from some source other than the reaction of calcium sulfide with water vapor, since desulfurization ceases when only sulfide remains.
Some reactions involving calcium sulfate would be:

\[ \text{CaSO}_4 + \text{CO} = \text{CaO} + \text{SO}_2 + \text{CO}_2 \]  
(18)

\[ \text{CaSO}_4 + 4\text{CO} = \text{CaS} + 4\text{CO}_2 \]  
(20)

\[ \text{CaSO}_4 + 4\text{CO} + \text{H}_2\text{O} = \text{CaO} + \text{H}_2\text{S} + 4\text{CO}_2 \]  
(21)

\[ \text{CaS} + 3\text{CaSO}_4 = 4\text{CaO} + 4\text{SO}_2 \]  
(2)

It will be noted that equation (21) is the sum of reaction (18) plus the reaction

\[ \text{SO}_2 + \text{H}_2\text{O} + 3\text{CO} = \text{H}_2\text{S} + 3\text{CO}_2 \]  
(25)

and that (20) is the sum of reaction (21) plus the reaction

\[ \text{H}_2\text{S} + \text{CaO} = \text{CaS} + \text{H}_2\text{O} \]  
(23)

Thus desulfurization may proceed first by reaction (18), the sulfur dioxide from which is subsequently converted to hydrogen sulfide. Some hydrogen sulfide may then recombine with calcium oxide to form calcium sulfide. The calcium sulfide formed can react with calcium sulfate by reaction (2) above.

The theoretical equilibrium constant for this reaction is zero at 2000°F and 100 at 2150°F. Thus at higher temperatures this reaction may become quite effective for sulfide removal when sulfate is present and explains the lower final sulfide concentrations with higher temperatures. This also accounts for the effect of temperature on desulfurization.
at the more reducing conditions, i.e. reaction (2) becomes
effective with increasing temperature in addition to reac-
tion (21) and/or (18) which are apparently not greatly in-
fluenced by the temperature in the range 2150°F to 2400°F.

The sulfur dioxide may also react with hydrogen sulfide
to form free sulfur. Thus the probable reactions involved
may be summarized as:

\[
\begin{align*}
\text{CaSO}_4 + \text{CO} &= \text{CaO} + \text{SO}_2 + \text{CO}_2 \quad (18) \\
\text{SO}_2 + \text{H}_2\text{O} + 3\text{CO} &= \text{H}_2\text{S} + 3\text{CO}_2 \quad (25) \\
\text{H}_2\text{S} + \text{CaO} &= \text{CaS} + \text{H}_2\text{O} \quad (23) \\
\text{CaS} + 3\text{CaSO}_4 &= 4\text{CaO} + 4\text{SO}_2 \quad (2) \\
2\text{H}_2\text{S} + \text{SO}_2 &= 1\ 1/2 \ \text{S}_2 + 2\text{H}_2\text{O} \quad (24)
\end{align*}
\]

and under oxidizing conditions, calcium sulfide if formed is
removed by

\[
\text{CaS} + 1\ 1/2 \ \text{O}_2 = \text{CaO} + \text{SO}_2 . \quad (22)
\]

Effect of oxidizing roasts following reducing conditions.
If calcium sulfide is present in a high temperature bed sub-
jected to oxidizing conditions, it will rapidly oxidize to
calcium oxide and, initially, sulfur dioxide. As has been
previously mentioned, such oxidizing roasts occurred inadver-
tently in the runs previous to F-144. The solid products
from these runs varied with respect to the sulfide content,
which would generally appear as a maximum of about 10 per
cent (as SO₃) at a residual sulfate concentration of 10 percent and then drop rapidly, effecting complete desulfurization.

To study this phenomenon the beds of solid product remaining at the completion of some of the runs were subjected to oxidizing roasts. The conditions and results are presented in Table 9.

The roast was effected at the end of runs F-163 through F-165 by increasing the air rate to give 140 percent of stoichiometric air. The bed temperature immediately began to increase and attained a maximum at from 3 to 6 minutes after starting the roast. The maximum bed surface temperature observed ranged from 1850°F to 2000°F. Much higher temperature particles could be observed, however. A higher bed temperature, 2200°F, was attained in the roast following run F-166 by using air alone with no gas. This did not produce significantly better desulfurization.

At the end of run F-167 the gas was shut completely off and the air increased somewhat. This produced a bed surface temperature greater than 2400°F, but probably less than 2500°F. Measurement was difficult as the maximum was rapidly attained and then cooling immediately started. The bed had cooled at the end of 5 minutes to a dull red. The gas was turned on and combustion occurred completely above the bed support on the surface of the particles. This was con-
Table 9

Effect of Oxidizing Roasts

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Solid product analysis before roast</th>
<th>Sulfate % SO₃</th>
<th>Sulfide % SO₃</th>
<th>Desulfurization %</th>
<th>Stoich. air in roast %</th>
<th>Duration of roast min.</th>
<th>Max. bed temp. observedᵃ °F</th>
<th>Sulfate % SO₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>F-163</td>
<td></td>
<td>0.61</td>
<td>15.7</td>
<td>87</td>
<td>140</td>
<td>10</td>
<td>1850</td>
<td>8.5</td>
</tr>
<tr>
<td>F-164</td>
<td></td>
<td>1.91</td>
<td>62.3</td>
<td>41</td>
<td>140</td>
<td>13</td>
<td>1905</td>
<td>12.0</td>
</tr>
<tr>
<td>F-165</td>
<td></td>
<td>0.56</td>
<td>57.6</td>
<td>49</td>
<td>140</td>
<td>15</td>
<td>1985</td>
<td>8.6</td>
</tr>
<tr>
<td>F-166</td>
<td></td>
<td>15.6</td>
<td>34.9</td>
<td>49</td>
<td>140</td>
<td>7</td>
<td>2200</td>
<td>8.0</td>
</tr>
<tr>
<td>F-167</td>
<td></td>
<td>3.26</td>
<td>54.4</td>
<td>48</td>
<td>140</td>
<td>8</td>
<td>2450</td>
<td>13.7</td>
</tr>
<tr>
<td></td>
<td>Gas turned on</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>F-168</td>
<td></td>
<td>1.23</td>
<td>41.0</td>
<td>63</td>
<td>140</td>
<td>5</td>
<td>2350</td>
<td>4.1</td>
</tr>
<tr>
<td></td>
<td>Gas turned on</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

ᵃTemperature observed with an optical pyrometer.
Table 9

Effect of Oxidizing Roasts

<table>
<thead>
<tr>
<th>Stoich. air in roast %</th>
<th>Duration of roast min.</th>
<th>Max. bed temp. observed°F</th>
<th>Solid product analysis after roast</th>
<th>Gas analysis SO₂</th>
<th>SO₃</th>
<th>Total SO₂ + SO₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>140</td>
<td>10</td>
<td>1850</td>
<td>8.59 0.57 92.5 1.8 0.6 2.4</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>140</td>
<td>13</td>
<td>1905</td>
<td>12.05 0.58 89 3.4 6.1 9.5</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>140</td>
<td>15</td>
<td>1985</td>
<td>8.81 0.72 92 5.8 3.2 9.0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>140</td>
<td>7</td>
<td>2200</td>
<td>8.07 0.96 93</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>8</td>
<td></td>
<td>2450</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>140</td>
<td>13(total)</td>
<td>2150</td>
<td>13.76 2.94 85</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>140</td>
<td>23(total)</td>
<td>2150</td>
<td>7.36 1.55 93</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>140</td>
<td>5</td>
<td>2350</td>
<td>4.13 0.85 97</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>140</td>
<td>11(total)</td>
<td>2200</td>
<td>0.60 0.22 99</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

ical pyrometer.
tinued for ten minutes during the last five of which the de-
sulfurization increased from 85 to 93 per cent.

The next roast, on the product of run F-168, was carried out in a similar manner. The product following the pure air roast was 97 per cent desulfurized and was more than 99 per cent desulfurized following six minutes of combustion in the bed.

The gas analyses obtained were high in both sulfur di-
oxide and sulfur trioxide. No hydrogen sulfide was detected. The sulfide first forms sulfur dioxide, some of which oxidi-
dizes further at lower temperatures to form sulfur trioxide. This could be prevented by rapid cooling of the gases. This was impossible with the gas sampling tube used, which cooled gradually from the bed temperature to room temperature over a distance of about 30 inches.

From the solid product analysis it is apparent that some of the sulfur dioxide recombines with calcium oxide and oxygen to produce calcium sulfate. This is to be expected as the equilibrium constant for this reaction is positive below 2600°F. If the roast could be carried out above this temperature, little recombination would occur. The calcium sulfate formed may be decomposed by burning gas directly in the bed following the roast. Sufficiently high temperatures are thus obtained to eliminate the residual sulfate.
Operating condition limits. Operation of the bed must be at temperatures below the fusion temperature of the lowest melting material present. With gypsum, this maximum temperature is about 2375°F.

Calcium sulfide, however, appears to be infusible at temperatures below 2600°F. Its melting point was not found in the literature. Calcium oxide also has a melting point (4650°F) well above any probable operating temperature. If operation is to be at high temperature levels, it is necessary that the surface of the particles be either sulfide or oxide to prevent fusion and defluidization. This surface depth must be sufficient to adequately isolate the calcium sulfate in the center.

With reducing conditions this protective surface is rapidly formed and there is little chance for fusion after about ten minutes of operation. However, when subjected to an oxidizing roast, some calcium sulfate may be formed on the particle surface which will fuse and agglomerate with other calcium sulfate particles.

Under oxidizing conditions it is necessary to keep the temperature below 2350°F for a longer period of time before a protective coating of oxide is formed. Furthermore, since at and below this temperature desulfurization is exceedingly slow with time, it may be a practical impossibility to oper-
ate above this temperature at oxidizing conditions, unless the sulfide or oxide is first produced with reducing conditions.

Conclusions

The following conclusions may be reached with respect to the batch thermal decomposition of gypsum in a fluidized bed:

1. Desulfurization of gypsum in a fluidized bed in the absence of reducing substances requires temperatures above its fusion temperature (ca. 2375°F).
2. Temperatures greater than 2100°F produce desulfurization of gypsum under reducing conditions.
3. Carbon monoxide was probably the reducing agent involved, effecting the desulfurization by either or both of the reactions

\[ \text{CaSO}_4 + \text{CO} = \text{CaO} + \text{SO}_2 + \text{CO}_2 \] (18)

\[ \text{CaSO}_4 + 4\text{CO} + \text{H}_2\text{O} = \text{CaO} + \text{H}_2\text{S} + 4\text{CO}_2 \] (21)

4. Calcium sulfide is formed under reducing conditions, probably as a result of the combination of hydrogen sulfide and calcium oxide. It attains a maximum equilibrium value when there is no residual sulfate.
5. Calcium sulfide may be removed either by oxidation if oxygen is present or in either oxidizing or re-
ducing conditions by reaction with calcium sulfate:

\[ \text{CaS} + 3\text{CaSO}_4 = 4\text{CaO} + 4\text{SO}_2 \]  \( (2) \)

This last reaction is very sensitive to temperature
in the range 2000°F to 2400°F. Slightly increased
temperatures greatly favor the equilibrium constant.
Because of this, the amount of residual sulfide de­
creases, and hence desulfurization increases, with
increasing temperature.

6. The amount of residual sulfide increases with de­
creasing stoichiometric air.

7. When slightly oxidizing conditions exist alternate­
ly with slightly reducing conditions, e.g. 100 to
105 per cent stoichiometric air, residual sulfides
are negligible and lower temperatures favor the de­
sulfurization.

8. Desulfurization occurs under nominally oxidizing
conditions of 105 and 110 per cent stoichiometric
air but attains a low equilibrium value because the
sporadic presence of the carbon monoxide limits its
diffusion into the particles.

9. A decrease in theoretical air below 100 per cent
increases the overall rate of sulfate conversion
but decreases the amount of desulfurization as a
result of increased sulfide formation.
10. The optimum condition for complete desulfurization when operating at a constant O-R condition is 100 per cent stoichiometric air at 2350°F.

11. Most rapid and complete desulfurization is obtained by alternating reducing conditions with oxidizing conditions.

Thermal Decomposition of Anhydrite in a Batch Reactor

The equipment and operating procedure used for the investigation of anhydrite were the same as those used for gypsum. However, the investigations were not as comprehensive as were those with gypsum. The studies were limited to two oxidizing-reducing conditions, produced by 95 and 80 per cent stoichiometric air, and no temperature variation studies were made since the results obtained with gypsum indicated that temperature variations of the fluidizing gases above 2150°F did not greatly affect the results.

Inasmuch as no water of hydration is present in anhydrite, the particles will remain more dense during calcination than the gypsum particles which are opened up by the dehydration process. If diffusion is involved, the particle size would then be expected to influence the rate at which the reaction is completed because of its effect on surface
and the particle's minimum dimension. For this reason it was thought that particle size studies would be of more interest with this material than with gypsum. Accordingly, three particle size fractions were studied: -6+8, -8+10, and -10+12 mesh.

The results obtained are presented in Table 10 and plotted in Figures 30, 31, and 32.

Comparison of anhydrite with gypsum

Figure 31 compares the results obtained with anhydrite with those of gypsum under similar conditions for the particle size -6+8 mesh. The following may be observed from this figure:

1. The rate of desulfurization of gypsum is more rapid than that of anhydrite, particularly under the more reducing conditions. This would be expected if diffusion of a gas into the solid particle is necessary, since the anhydrite would be more dense.

2. The rate of sulfide formation is not significantly different for the first 60 minutes. This suggests that a sulfide forming reaction occurs independently of some other sulfate conversion reaction; in the case of the anhydrite it continues after 60 minutes as there is still residual sulfate.

Thus, in the case of the sulfide forming reaction, the additional surface and/or decreased diffusion path which are
Table 10
Fluidized Bed Results
Anhydrite

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Per cent stoichiometric air</th>
<th>Inlet temp. (°F) fluidizing gases</th>
<th>Gas rate (^a) cu.ft./hr.</th>
<th>Charge weight gm.</th>
<th>Particle size mesh</th>
<th>Analyzed for (^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>F-174</td>
<td>80</td>
<td>2300 -15±25</td>
<td>32</td>
<td>700</td>
<td>-6±8</td>
<td>Sulfate Sulfide Desulf.</td>
</tr>
<tr>
<td>F-175</td>
<td>80</td>
<td>2220 -15±10</td>
<td>26</td>
<td>700</td>
<td>-8±10</td>
<td>Sulfate Sulfide Desulf.</td>
</tr>
<tr>
<td>F-176</td>
<td>80</td>
<td>2220 -30±5</td>
<td>23</td>
<td>700</td>
<td>-10±12</td>
<td>Sulfate Sulfide Desulf.</td>
</tr>
<tr>
<td>F-169</td>
<td>95</td>
<td>2350 -30</td>
<td>25</td>
<td>700</td>
<td>-6±8</td>
<td>Sulfate Sulfide Desulf.</td>
</tr>
<tr>
<td>F-170</td>
<td>95</td>
<td>2350 -10±20</td>
<td>25</td>
<td>700</td>
<td>-8±10</td>
<td>Sulfate Sulfide Desulf.</td>
</tr>
<tr>
<td>F-171</td>
<td>95</td>
<td>2350 -20±25</td>
<td>25</td>
<td>700</td>
<td>-10±12</td>
<td>Sulfate Sulfide Desulf.</td>
</tr>
</tbody>
</table>

\(^a\)Referred to 760 mm. Hg, 0°C.

\(^b\)Sulfate refers to total sulfur present as sulfate expressed as per cent SO\(_3\). Sulfide refers to total sulfur present as sulfide expressed as per cent S. Desulfurization refers to per cent of sulfur, originally present in the feed, which has been removed.
### Table 10

**Fluidized Bed Results**

**Anhydrite**

<table>
<thead>
<tr>
<th>Particle size mesh</th>
<th>Analyzed for[^b]</th>
<th>Analysis of solid product at specific time from addition of charge (time: minutes)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Sulfate</td>
<td>10</td>
</tr>
<tr>
<td>-6+8</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Sulfate</td>
<td>50.1</td>
</tr>
<tr>
<td></td>
<td>Sulfide</td>
<td>2.9</td>
</tr>
<tr>
<td></td>
<td>Desulf.</td>
<td>16</td>
</tr>
<tr>
<td>-8+10</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Sulfate</td>
<td>49.1</td>
</tr>
<tr>
<td></td>
<td>Sulfide</td>
<td>2.2</td>
</tr>
<tr>
<td></td>
<td>Desulf.</td>
<td>21</td>
</tr>
<tr>
<td>-10+12</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Sulfate</td>
<td>51.4</td>
</tr>
<tr>
<td></td>
<td>Sulfide</td>
<td>2.3</td>
</tr>
<tr>
<td></td>
<td>Desulf.</td>
<td>10</td>
</tr>
<tr>
<td>-6+8</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Sulfate</td>
<td>50.1</td>
</tr>
<tr>
<td></td>
<td>Sulfide</td>
<td>0.0</td>
</tr>
<tr>
<td></td>
<td>Desulf.</td>
<td>24.5</td>
</tr>
<tr>
<td>-8+10</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Sulfate</td>
<td>55.2</td>
</tr>
<tr>
<td></td>
<td>Sulfide</td>
<td>0.5</td>
</tr>
<tr>
<td></td>
<td>Desulf.</td>
<td>7</td>
</tr>
<tr>
<td>-10+12</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Sulfate</td>
<td>57.3</td>
</tr>
<tr>
<td></td>
<td>Sulfide</td>
<td>0.0</td>
</tr>
<tr>
<td></td>
<td>Desulf.</td>
<td>0.0</td>
</tr>
</tbody>
</table>

[^b]: per cent SO\(_3\). Sulfide refers to total sulfur present as sulfide expressed as per cent SO\(_3\).

The feed, which has been removed.
FIGURE 30

COMPARISON OF DESULFURIZATION OF GYPSUM AND ANHYDRITE
FIGURE 31

THERMAL DECOMPOSITION OF ANHYDRITE
95 PER CENT STOICHIOMETRIC AIR
**NOMINAL TEMPERATURE**

<table>
<thead>
<tr>
<th>SYMBOL</th>
<th>RUN NO</th>
<th>TEMPERATURE</th>
</tr>
</thead>
<tbody>
<tr>
<td>O</td>
<td>F-174</td>
<td>2300 °F</td>
</tr>
<tr>
<td>□</td>
<td>F-175</td>
<td>2220 °F</td>
</tr>
<tr>
<td>△</td>
<td>F-176</td>
<td>2220 °F</td>
</tr>
</tbody>
</table>

**OPEN - DESULFURIZATION**

**SOLID - SULFIDE**

**FIGURE 32**

**THERMAL DECOMPOSITION OF ANHYDRITE**

60 PER CENT STOICHIOMETRIC AIR
undoubtedly present with the calcined gypsum do not seem to increase the rate of sulfide formation. This indicates that some factor other than diffusion must be controlling. This is most probably the concentration of carbon monoxide, four moles of which are required for each mole of calcium sulfide formed.

Since the more rapid desulfurization indicates that the overall sulfate conversion is slower for the anhydrite, it must, to some extent, be independent of sulfide formation. Furthermore, this reaction appears dependent on the surface or porosity of the particle whereas the carbon monoxide concentration is of less importance, which might be expected inasmuch as only one mole of carbon monoxide is required per mole of sulfur removed when no sulfide is formed.

**Particle size studies**

To investigate the effect of particle size on the reactions, three particle size fractions were studied. These were -6+8, -8+10, and -10+12 mesh. The first series of runs was made at a constant gas rate with 95 per cent stoichiometric air and an essentially constant fluidization gas temperature of 2350°F. The results of these runs, presented in Figure 31, were contrary to what was expected. The desulfurization decreased with increasing particle size. A partial explanation of this was apparent from observation of the bed
during the runs. With the -6+8 particles, there was a definite temperature gradient from the bottom to the top of the bed. The bed surface was dull red, about 1450°F, but white-hot particles were present below the surface. With the -8+10 and -10+12 particles, however, the bed temperature was more uniform at the relatively cold surface temperature of about 1450°F. Only a few white-hot particles could be observed. Although the literature indicates increasing particle to retaining wall heat transfer coefficients with decreasing particle size [15], such a pronounced effect was not expected.

It was thought that perhaps the more violent agitation and mixing of the bed at the lower particle sizes, resulting from the relatively greater fluidization velocity, contributed to producing the uniformly low temperature bed. Consequently, another series was executed in which efforts were made to maintain constant bed porosity by decreasing the gas and air rate with decreasing particle size. To minimize the effect of the carbon monoxide concentration, 80 per cent stoichiometric air was supplied. The fluidizing gas temperature varied from a minimum of 2200°F with the smallest particle size to 2375°F with the largest. This temperature variation was not found to be of great importance with the gypsum, and hence was not considered to be a variable affecting the results. With these runs a bed temperature ef-
fect similar to that obtained with a constant gas rate was noted with decreasing particle size. A decrease in particle size produced a bed at a more uniform but lower temperature, between 1400°F and 1500°F at the surface and apparently not much hotter below the surface.

The results of these runs are presented in Figure 32. With decreasing particle size, the rate of desulfurization decreases. As would be expected under the more reducing conditions, more sulfides were present than in the previous series with 95 per cent stoichiometric air. The lower desulfurization in both series is unquestionably the result of the lower temperature in the bed, or perhaps more correctly, fewer particles in the bed at the required temperature. From this it appears that the particle size, at least with the reactor used for these investigations, influences the bed temperature to such an extent as to mask its effect per se on the reactions involved. That is, the effect of particle size on the characteristics of the fluidized bed itself cannot be neglected. In a larger diameter bed of greater depth perhaps this would not be true and an effect of particle size on the sulfate conversion might be observed and attributed solely to particle size. However, from the foregoing, no conclusion may be drawn with respect to particle size other than that it has a pronounced effect on the bed temperature in the equipment used for these investigations.
EVALUATION OF PROCESSES INVESTIGATED

Economic Considerations

Although the investigations presented in this thesis are not sufficient to prepare a complete economic study, it is of interest to compute the net raw material and fuel cost. For this, a basis of one ton of sulfur produced will be used.

The thermal requirements for the dissociation of one ton of sulfur from gypsum, assuming an overall thermal efficiency of 80 per cent, would be 16,600,000 Btu. Assuming complete desulfurization, 5.39 tons of gypsum would be required and 1.75 tons of by-product lime produced. The average value of the crude gypsum mined in the United States during 1950 was $2.78 per ton [20]. The cost of fuel would probably range from $0.10 to $0.30 per million Btu, depending on the location. For this analysis, a value of $0.20 per million Btu is used. The current (1954) value of agricultural lime is $14.50 per ton and of chemical quick lime $10.25 to $12.50 per ton. A value of $11.00 per ton is used as the credit for the by-product lime. The costs for raw materials and fuel per ton of sulfur obtained are then:
It is apparent from the above figures that the cost of the gypsum is of major importance. The fuel cost, on the other hand, may vary 100 per cent without greatly distorting the above result. It is also apparent that, because of the large gypsum cost, a market for the by-product lime produced would probably be necessary to justify the production of sulfur by this method.

The current value of sulfur is $26.50 per ton on a contract basis. Thus the net value of the products obtained would be $27.44 for every 5.39 tons of gypsum processed. This would need to be sufficient to provide a profit after the operating costs, fixed costs, amortization costs, etc. were deducted. As mentioned previously, it is not possible to estimate these at this time, but the margin involved is sufficient to warrant further consideration of this method.
Analysis of Results
with Respect to Possible Future Work

To assist in the planning of future work, it is felt that a general discussion of the results presented in this thesis and some of the ideas and methods they suggest is warranted at this point. The factors to be considered in such a discussion are: (1) desired composition of the off-gases, (2) range of operating variables, and (3) type and arrangement of the furnaces used to carry out the reaction.

Desired composition of the off-gases

The final treatment and usefulness of the off-gases will depend upon their composition. Originally, it was hoped to produce a gas containing at least 7 per cent sulfur dioxide, with no hydrogen sulfide, which would be suitable for feed to a sulfuric acid plant following removal of the dust. However, to obtain such a gas with one step it would be necessary to operate under oxidizing conditions and the results obtained indicated the charge would fuse during the process and resolidify before complete desulfurization.

With reducing conditions, a mixture of hydrogen sulfide and sulfur dioxide is obtained when operated under a constant but reducing atmosphere. If the ratio of these two components could be adjusted to the stoichiometric proportions for
the Claus reaction

\[ \text{SO}_2 + 2\text{H}_2\text{S} = \frac{1}{2} \text{S}_3 + 2\text{H}_2\text{O} \] (24)

sulfur would be formed in the gases and could be subsequently removed by condensation. This method would be advantageous in that the sulfur could be recovered from low concentration off-gases. Furthermore, there would be advantages in producing the sulfur rather than sulfuric acid if the market for the latter was some distance from the gypsum or anhydrite source. The question then arises as to whether or not these proportions of the two gases could be obtained. Unfortunately the gas analyses were too unsatisfactory to answer this question for a one stage process. However qualitative indications were that hydrogen sulfide was the major constituent particularly when less than 90 per cent of the stoichiometric air was supplied. Let us, however, consider three possible cases which might arise with reducing conditions: (1) sulfur dioxide is the major constituent produced in the gas phase, (2) both hydrogen sulfide and sulfur dioxide are present in similar quantities, and (3) hydrogen sulfide is the major constituent produced in the gas phase. In all cases it will be assumed that some calcium sulfide is formed as a solid product and may be decomposed to CaO and SO$_3$ by an oxidizing roast.
Case 1: Sulfur dioxide the major constituent. If this is the case, the hydrogen sulfide present would react with the necessary sulfur dioxide to produce free sulfur, which could be condensed and recovered. The sulfur dioxide might then be suitable for preparation as a feed to a contact sulfuric acid plant. A final step might be required to remove the last traces of hydrogen sulfide. The roasting of the solid calcium sulfide would produce additional sulfur dioxide.

Case 2: Both hydrogen sulfide and sulfur dioxide present in similar quantities. If the sulfur dioxide were present in excess of that stoichiometrically required for the Claus reaction, the final gas could be assumed to contain sulfur, from the combination of sulfur dioxide and hydrogen sulfide, and sulfur dioxide, presumably in too weak a concentration for use as feed gas to a sulfuric acid plant. This could be passed over a bed of hot coke which would reduce the sulfur dioxide either to sulfur or hydrogen sulfide for reaction with the excess sulfur dioxide. The sulfur dioxide produced by roasting of the calcium sulfide could be treated in a like manner. Thus the final product would be sulfur. If the hydrogen sulfide were present in excess, the gases could be treated as in Case 3 below.
Case 3: Hydrogen sulfide the major constituent produced in the gas. In this case it would be necessary to add to, or produce sulfur dioxide in, the gas so that the proportion required for the Claus reaction would be present. Since the concentration of the sulfur is not critical, air could be introduced and the hydrogen sulfide burned to sulfur dioxide if the former were present in high enough concentrations (lower explosive limit is 4.1 per cent hydrogen sulfide by volume in air). However, it would be more reasonable to obtain the necessary sulfur dioxide from an oxidizing roast of the calcium sulfide present in the solid product. This sulfur dioxide could be added to the hydrogen sulfide in the correct proportion. As discussed below under equipment, two beds, one operating under reducing conditions and one under oxidizing conditions, could be used with the gases from the two being continuously combined. Consideration of the data presented in this thesis indicates that the desired $\text{H}_2\text{S}/\text{SO}_3$ ratio could be obtained and controlled by varying the O-R conditions of the bed atmosphere. Reference to Figure 27 indicates that from 5 to 60 per cent of the sulfur originally present may be converted to sulfide, depending on the per cent of stoichiometric air supplied and, to a lesser extent, the temperature. During the roast this would be converted to sulfur dioxide. The conditions could thus be set such that the sulfur dioxide liberated in this roast was one-half the
quantity of hydrogen sulfide produced under the reducing conditions. For example, if operation at a temperature of 2250°F is considered, and the assumption made that all the sulfur removed under reducing conditions is as hydrogen sulfide, conditions must be such that the per cent of sulfur remaining as sulfide is one-third of the total sulfur originally present. This condition may be obtained with approximately 90 per cent stoichiometric air and a 90 minute retention time.

Operating variables

It has been shown that carbon monoxide, or some other suitable reducing substance, must be present for desulfurization to occur at temperatures below the normal fusion point of gypsum. Furthermore, when the reaction has partially progressed, the temperature may be increased to higher temperatures with no danger of fusion. This work was not extended to these higher temperatures, except in the oxidizing roasts in some of which the temperature reached 2600°F with no serious fusion. From the standpoint of rapidity of reaction, it is best to use strongly reducing atmospheres followed by an oxidizing roast. This might produce a gas sufficiently concentrated in SO₂ to yield a feed gas for an acid plant after the sulfur formed by combination of the hydrogen sulfide and sulfur dioxide was removed.
Type and arrangement of reaction furnaces

It may be seen that for the optimum desulfurization of the gypsum either two furnaces or a two-stage furnace would be required. In the first furnace or stage the material would come into contact with reducing gases at high temperatures. Following this the material would be subjected to an oxidizing roast to complete the desulfurization. Otherwise, complete desulfurization may be approached only with the stoichiometric amount of air supplied which requires high retention times.

The shaft furnace presents, in many ways, an ideal reactor for this. Figure 33 presents one possible arrangement of such a furnace, not unlike the first shaft furnace used in this work. In the region where the gas enters, the solids would be subjected to a reducing atmosphere. In the upper portion of this region where the temperature would be below fusion this would produce a surface of calcium oxide or calcium sulfide necessary to prevent fusion when the particle reached the higher temperature region farther down. The O-R characteristics of this zone would be closely controlled by adjusting the amount of primary air introduced with the gas. Secondary air passing up from the bottom would result in an oxidizing zone directly below the gas burners. The roasting of sulfides is exothermic, and hence no heat would need to supplied; however, unless the temperature were maintained
FIGURE 33  SCHEMATIC SKETCH OF SHAFT FURNACE PROPOSED FOR DESULFURIZATION OF CALCIUM SULFATE
above 2500°F the sulfur dioxide liberated would recombine with the calcium oxide to produce calcium sulfate. Consequently, some burners might be placed in this section or gas could be introduced with the secondary air to maintain the temperature of the roasting area above 2500°F. This uprising air and gas would, of course, be preheated as it cooled the descending roasted material. The sulfur dioxide evolved would probably combine, in the reducing zone, with the hydrogen sulfide evolved to produce sulfur which could be condensed from the stack gases as previously mentioned. If too much sulfur dioxide was formed, it would be necessary to increase the oxidizing conditions in the reducing zone to decrease the amount of calcium sulfide and hence sulfur dioxide formed. It might also be possible to introduce air above the reducing zone and burn the hydrogen sulfide to sulfur dioxide. Any sulfur present would also be burned to sulfur dioxide. The off-gases would then be suitable as a raw feed for a sulfuric acid plant.

It would also be possible to use two separate shaft furnaces. One would operate under oxidizing conditions and the other under reducing conditions. If steady conditions were maintained in each furnace, it would be necessary to transfer the solid product from the reducing furnace to the oxidizing furnace. However, the furnaces could be operated
alternately, such that one was reducing while the other was oxidizing. The solid product from each would then be lime, but the off-gases would vary depending on the cycle, although the off-gas composition of the mixed off-gases would remain unaffected. One disadvantage to such an alternating procedure is the relative rates of the two reactions. The oxidation of the sulfide occurs more rapidly than its formation. Consequently, if two furnaces were used, each at a constant condition, they could be sized accordingly.

Were two furnaces used, it would also be possible to pass the gases from the oxidizing furnace up through the reducing furnace. This would produce the same effect as obtained in the single furnace which was first discussed.

Since at least some of the reactions involved are gas-solid reactions, there is the possibility that the desulfurization would be exceedingly slow after the surface of the particles had reacted. If this should be the case, it would be necessary to revert to a high temperature treatment following formation of the protective surface in the reducing atmosphere such that the reaction

\[
\text{CaSO}_4 = \text{CaO} + \text{SO}_2 + \frac{1}{2} \text{O}_2 \quad (3)
\]

would occur within the particle. This could be done by modification of the single furnace arrangement of Figure 33 so that the majority of the gas would be burned under oxidizing
conditions. Two separate furnaces could also be used. In either case the primary gaseous product would be sulfur di-oxide and hence burners or air inlets would be required above the reducing zone to oxidize any hydrogen sulfide present.

Similarly, there are several arrangements which could be obtained with a fluidized bed reactor. The simplest would be a single bed, semi-continuous operation in which alternately oxidizing and reducing conditions were produced by adjusting the gas-air ratio. The solid product would be withdrawn after the oxidizing roast. This would produce an off-gas of varying composition. Consequently, it would have to be operated either in conjunction with another unit which operated on alternate cycles, or the gas would have to be stored in some type of surge tank to permit mixing. Alternatively, the two furnaces could be in series, the solid product from the reducing furnace passing to the oxidizing furnace and thence out as lime. The off-gases could be combined, as sketched in Figure 34, or the off-gas from the oxidizing furnace could be used as fluidization gases for the reducing furnace. In the latter case, one bed could be placed above the other as in the Dorr Company Fluo-Solids roaster.
OFF-GAS, RICH IN SULFUR

OFF-GAS
RICH IN H₂S

OFF-GAS
RICH IN SO₂

REDUCING BED

CaSO₄

CaO + CaS

AIR - FUEL MIXTURE

OxIDIZING BED

CaO

AIR

FIGURE 34  SCHEMATIC SKETCH OF FLUIDIZED BED ARRANGEMENT PROPOSED FOR DESULFURIZATION OF CALCIUM SULFATE
Separate fluidized beds to provide preheat of the feed and cooling of the product to increase the economy could also be provided.

In comparing the fluidized bed with the shaft furnace, it should be pointed out that the shaft furnace is basically a much simpler piece of equipment, although the fluid-solid contact may not be as efficient. However, its operation is more difficult to control and the larger particles involved require greater retention time. Should further investigations be made, it is recommended that operation of a shaft furnace with reducing conditions be considered.
LITERATURE CITED


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APPENDICES
APPENDIX A

Method of Calculation of Equilibrium Constants

The equilibrium constant, $K$, of a reaction at any temperature, $T$, may be found from the standard free energy change, $\Delta G^\circ$, of the reaction at that temperature. The relationship is:

$$\left(\frac{\Delta G^\circ}{T}\right)_T = -RT \ln K .$$  \hspace{1cm} (31)

The standard free energy change may be obtained from the expression

$$\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ$$  \hspace{1cm} (32)

where $\Delta G^\circ$, $\Delta H^\circ$, and $\Delta S^\circ$ are the changes in free energy, enthalpy, and entropy, respectively, which accompany the reaction with all reactants and products in their standard state; and $T$ is the absolute temperature. If $\Delta H^\circ$ and $\Delta S^\circ$ are expressed as a function of temperature, then $\Delta G^\circ$ and hence $K$ may also be expressed as a function of temperature.

If heat capacities of each of the individual reactants and products of a general reaction
\[ n_bB + n_C + \ldots = n_R + n_S + \ldots \]  

are expressed by the general type of equation

\[ C_p = a + bT + cT^2 \]  

then \( \Delta C_p \), the heat capacity change of the entire system at constant pressure, is

\[ \Delta C_p = n_R C_R + n_S C_S + \ldots - n_B C_B - n_C C_C - \ldots \]
\[ = n_R a_R + n_R b_R T + n_R c_R T^2 + n_S a_S + n_S b_S T + n_S c_S T^2 \]
\[ + \ldots - n_B a_B - n_B b_B T + n_B c_B T^2 \]
\[ + n_C a_C + n_C b_C T + n_C c_C T^2 - \ldots \]

Collecting terms and defining the quantities \( \Delta a \), \( \Delta b \), and \( \Delta c \) gives:

\[ \Delta a = n_R a_R + n_S a_S \ldots - n_B a_B - n_C a_C \ldots \]  

\[ \Delta b = n_R b_R + n_S b_S \ldots - n_B b_B - n_C b_C \ldots \]  

\[ \Delta c = n_R c_R + n_S c_S \ldots - n_B c_B - n_C c_C \ldots \]  

so that

\[ \Delta C_p = \Delta a + \Delta bT + \Delta cT^2 \]  

The heat of reaction at any temperature, \( T \), is then given by the equation

\[ \Delta H_T = \Delta H + \Delta aT + \frac{1}{2} \Delta bT^2 + \frac{1}{3} \Delta cT^2 \]
If the heat of reaction is available for one temperature, e.g. the standard heat of reaction at 18°C, the constant $I_H$ may be evaluated.

The entropy change at constant pressure is given by

$$ds = \frac{CpdT}{T}.$$  \hspace{2cm} (41)

Thus, for a general reaction

$$\Delta S^o = ds = \frac{\Delta CpdT}{T} = \frac{\Delta a + \Delta bT + \Delta cT^2}{T}$$

$$= I_s + \Delta alnT + \Delta bT + 1/2 \Delta cT^2.$$  \hspace{2cm} (42)

If the standard molal entropy change of a reaction is available at one temperature, $I_s$ may be evaluated.

Substituting their value as a function of temperature for $\Delta H^o$ and $\Delta S^o$ in equation 32 (i.e., equations 40 and 42) gives:

$$\frac{\Delta G^o}{T} = \frac{I_H}{T} + \Delta a - I_s - \Delta alnT - \frac{\Delta bT}{2} - \frac{\Delta c}{6} T^2.$$  \hspace{2cm} (43)

This is the general form of the equation which was used to calculate the standard free energy change at any temperature. The constant $I_H$ was evaluated from the standard heat of reaction computed from heat of formation data. The constant $I_s$ was evaluated from the standard entropy change computed from standard molal entropy values.
If \( \left( \frac{\Delta G^o}{T} \right)_T \) is expressed in cal./g.mol °K, equation 31 becomes

\[
4.576 \log_{10} K = - \left( \frac{\Delta G^o}{T} \right)_T .
\]  
(13)
Table 11
Equations Expressing the Equilibrium Constant as Function of Temperature for Selected Reactions
Neutral or Oxidizing Conditions

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Expression</th>
<th>Equilibrium Constant</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1) CaSO₄(s) = CaO(s) + SO₂(g) + 1/2 O₂(g)</td>
<td>[ \log K = \frac{-25.600 + 10.58 + 1.681 \log T - 1.005 \times 10^{-3} T - 0.0893 \times 10^{-6} T^2}{T} ]</td>
<td></td>
</tr>
<tr>
<td>(2) CaSO₄(s) = CaO(s) + SO₃(g)</td>
<td>[ \log K = \frac{-20.750 + 10.45 + 0.181 \log T - 0.80 \times 10^{-3} T + 0.1165 \times 10^{-6} T^2}{T} ]</td>
<td></td>
</tr>
<tr>
<td>(3) CaSO₄(s) + H₂O(ℓ) = H₂SO₄(ℓ) + CaO(s)</td>
<td>[ \log K = \frac{-13.450 - 10.29 + 4.02 \log T - 1.79 \times 10^{-3} T}{T} ]</td>
<td></td>
</tr>
<tr>
<td>(4) CaSO₄(s) + H₂O(g) = H₂SO₄(g) + CaO(s)</td>
<td>[ \log K = \frac{-16.900 + 15.9 - 1.715 \log T - 1.18 \times 10^{-3} T}{T} ]</td>
<td></td>
</tr>
<tr>
<td>(5) H₂SO₄(ℓ) = SO₃(g) + H₂O(g)</td>
<td>[ \log K = \frac{-10.290 + 42.3 - 9.1 \log T + 0.96 \times 10^{-3} T - 0.131 \times 10^{-6} T^2}{T} ]</td>
<td></td>
</tr>
</tbody>
</table>
Table 12
Equations Expressing the Equilibrium Constant as Function of Temperature for Selected Reactions
Reducing Conditions (CO present)

\[ T = \text{temperature, } ^\circ \text{K} \] \[ \log = \log_{10} \] \[ K = \text{equilibrium constant} \]

(1) \( \text{CaSO}_4(s) + \text{CO}(g) = \text{CaO}(s) + \text{SO}_2(g) + \text{CO}_2(g) \)
\[ \log K = \frac{-11,000 + 9.36 + 0.442 \log T - 0.47 \times 10^{-3} T - 0.0731 \times 10^{-6} T^2}{T} \]

(2) \( \text{CaSO}_4(s) + 3\text{CO}(g) = \text{CaO}(s) + \frac{1}{2} \text{S}_2(g) + 3\text{CO}_2(g) \)
\[ \log K = \frac{2.835 + 7.65 - 0.969 \log T + 0.236 \times 10^{-3} T - 0.221 \times 10^{-6} T^2}{T} \]

(3) \( \text{CaSO}_4(s) + 4\text{CO}(g) = \text{CaS}(s) + 4\text{CO}_2(g) \)
\[ \log K = \frac{9.040 + 7.64 - 2.292 \log T + 0.716 \times 10^{-3} T + 0.29 \times 10^{-6} T^2}{T} \]

(4) \( \text{CaSO}_4(s) + 4\text{CO}(g) + \text{H}_2\text{O}(g) = \text{CaO}(s) + \text{H}_2\text{S}(g) + 4\text{CO}_2(g) \)
\[ \log K = \frac{6.190 - 3.90 + 1.002 \log T + 2.96 \times 10^{-3} T - 0.325 \times 10^{-6} T^2}{T} \]

(5) \( \text{CaS}(s) + \frac{1}{2} \text{O}_2(g) = \text{CaO}(s) + \text{SO}_2(g) \)
\[ \log K = \frac{23.800 - 1.29 - 1.009 \log T + 0.38 \times 10^{-3} T - 0.0328 \times 10^{-6} T^2}{T} \]
Table 12 (continued)

(6) \[ \text{CaO}(s) + \text{H}_2\text{S}(g) = \text{CaS}(s) + \text{H}_2\text{O}(g) \]
\[ \log K = \frac{3.135 - 0.52 + 0.242 \log T + 0.070 \times 10^{-3} T - 0.0306 \times 10^{-6} T^2}{T} \]

(7) \[ \text{H}_2\text{S}(g) + \frac{1}{2} \text{O}_2(g) = \text{SO}_2(g) + \text{H}_2\text{O}(g) \]
\[ \log K = \frac{27,000 - 3.05 - 0.332 \log T + 0.00765 \times 10^{-3} T - 0.00109 \times 10^{-6} T^2}{T} \]

(8) \[ \text{CaS}(s) + 3\text{CaSO}_4(s) = 4\text{CaO}(s) + 4\text{SO}_2(g) \]
\[ \log K = \frac{-53,100 + 30.25 + 4.06 \log T - 2.58 \times 10^{-3} T - 0.31 \times 10^{-6} T^2}{T} \]

(9) \[ \text{SO}_2(g) + 2\text{H}_2\text{S}(g) = \frac{1}{2} \text{S}_2(g) + 2\text{H}_2\text{O}(g) \]
\[ \log K = \frac{7,660 - 9.57 + 2.56 \log T - 1.15 \times 10^{-3} T + 0.138 \times 10^{-6} T^2}{T} \]

(10) \[ \text{SO}_2(g) + 3\text{CO}(g) + \text{H}_2\text{O}(g) = \text{H}_2\text{S}(g) + 3\text{CO}_2(g) \]
\[ \log K = \frac{16,890 - 0.693 - 3.38 \log T + 1.61 \times 10^{-3} T - 0.175 \times 10^{-6} T^2}{T} \]
APPENDIX B

Description of Shaft Furnace Runs

Temperatures between 2350°F and 2550°F

Run number 1. This was of a preliminary nature designed to determine the general operating characteristics of the first shaft furnace. The initial charge of 19 1/2 pounds of -1 +1/2 inch gypsum filled the shaft. The gas was introduced at the rate of 58 cubic feet per hour and 20 per cent excess air was supplied. The run extended over a period of 6 1/2 hours. Two draws were made, each removing a volume equivalent to 2 pounds of feed. The first draw was made after 3 hours of operation and the second 1 1/2 hours after the first. Gypsum equivalent to that removed was added immediately after each draw. Continuous operation would not have been possible because of sticking and "hanging up" of the charge in the upper portions of the shaft. The maximum temperature observed was 2550°F. This was subsequent to the second draw at a height of 11 1/2 inches above the gas inlet ports. After the run the contents of the kiln were removed and labeled as to location, each 4 1/2-inch depth of material
being taken as a sample. The results of the analysis of these samples are presented in Table 13.

Some fusion and resulting clinkers occurred in the upper portion of the kiln, but the material which had been in the vicinity of the gas ports at the start of the run was well desulfurized but not fused. These particles were yellowish white in color and quite friable.

From this run the conclusion was reached that desulfurization could occur, under oxidizing conditions, without fusing the material. However, this was subsequently shown to be erroneous, and later work with the fluidized bed suggested the following explanation. In the vicinity of the gas ports poor air-gas mixing resulted in temperatures below fusion, but reducing conditions brought about decomposition by the reaction

$$\text{CaSO}_4 + \text{CO} = \text{CaO} + \text{SO}_2 + \text{CO}_2 \quad (18)$$

In the zone above the gas burners gas-air mixing and combustion had been completed producing higher temperatures and an oxidizing atmosphere. This resulted in some thermal decomposition but also brought about fusion and agglomeration.

**Run number 2.** This run lasted less than 90 minutes because of failure of the gas line pressure.

**Run number 3.** A feed rate of 5 pounds per hour at a gas rate of 30 cubic feet per hour was proposed for this run.
Table 13

Results of Run No. 1

<table>
<thead>
<tr>
<th>Sample location in kiln distance from top towards base</th>
<th>Approximate time-temperature conditions on sample</th>
<th>% SO$_3$ in sample</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gypsum feed</td>
<td></td>
<td>43.5</td>
</tr>
<tr>
<td>0&quot; - 4 1/2&quot;</td>
<td></td>
<td>43.5</td>
</tr>
<tr>
<td>4 1/2&quot; - 9&quot;</td>
<td>Estimated max. temp. of 1800°F for 2 hr.</td>
<td>36.4</td>
</tr>
<tr>
<td>9&quot; - 13 1/2&quot;</td>
<td>2200°F for 2 hr.</td>
<td>27.6</td>
</tr>
<tr>
<td>13 1/2&quot; - 18&quot;</td>
<td>1800°F to 2550°F for 1 hr., 2550°F to 2400°F for 1 hr.</td>
<td>13.9</td>
</tr>
<tr>
<td>18&quot; - 22 1/2&quot;</td>
<td>2100°F for 1 1/2 hr., 2450°F for 2 hr.</td>
<td>8.7</td>
</tr>
<tr>
<td>22 1/2&quot; - 27&quot;</td>
<td>2200°F to 2500°F for 1 hr., 2500°F to 2400°F for 1 hr., 2200°F for 2 hr.</td>
<td>7.2</td>
</tr>
<tr>
<td>27&quot; - 31 1/2&quot;</td>
<td>2200°F for 2 hr., 2400°F for 2 hr., 2200°F for 1 1/2 hr.</td>
<td>3.8</td>
</tr>
</tbody>
</table>
However, sticking of the charge in the upper portion of the kiln prevented continuous operation.

**Run number 4.** This was the first run during which gas samples were taken. A gas rate of 49 cubic feet per hour with 10 per cent excess air was used. The particle size was -3/4 +1/2 inch and the feed rate 8 pounds per hour fed at approximately 2 pounds per 15 minutes. In spite of the excess air, sulfur was noticed condensing on the feed during the early part of the run. The semi-continuous operation lasted 2 1/2 hours, after which plugging of the upper portion of the furnace forced a shut-down. The steady state solid product of this run was 82 per cent desulfurized. The particles obtained in the product were definitely fused on the exterior and quite hard. Some shrinkage had taken place so that the particles were about one-half of their original size. Their color was predominantly a yellow-brown, but ranged from white to black. Few were obtained as discrete particles, most being in an agglomerated form but retaining at least some of their identity. This appearance was characteristic of the products obtained in this temperature range, with the exception of those from run number 1.

**Run number 5.** A gas rate of 30 cubic feet per hour with 20 per cent excess air was used. It was thought that the lower gas rate would decrease the extent of fusion. Gypsum was fed at the rate of 5 pounds per hour. A -3/4
+1/2 inch particle size was used. After 3 hours of operation the furnace became so severely plugged that it was necessary to dismantle the top 13 inches of the furnace to remove the plug. Hollow spots existed above and below the plug. No analysis was made of the products.

Run number 6. Conditions were identical with those of run number 5 except that a lower gas rate of 21 cubic feet per hour was used, again in an attempt to reduce fusion. However, in charging some hollow spots were apparently left unfilled, the upper surface of which became molten and re-solidified forming a very tight plug within one-half hour after firing.

Run number 7. This was the first run with the second shaft furnace. Some operating troubles were experienced in developing a satisfactory operating procedure, specifically in adjusting the gas-air ratio to the desired quantity. The gas rate of 124 cubic feet per hour was quite high. Fusion occurred after about 8 hours of running and it was necessary to shut down to unplug the furnace. A feed rate of 8 pounds per hour of -3/4 +1/2 inch gypsum was used.

Run number 8. In an effort to decrease the difficulty encountered with fusion, a lower gas rate and a higher feed rate were used in run number 8. With a gas rate of 82 cubic feet per hour and a feed rate of 14 pounds per hour fed at about 4 1/2 pounds per 20 minutes, it was possible to keep
material passing downward. However, when the shaft was cleaned after the run a solid clinker was found located across one-half the cross-section of the shaft from a height of 8 inches to a height of 14 inches above the burner port. The Orsat apparatus did not function because of a plugged sample line, but conditions were apparently reducing, as evidenced by sulfur condensing on the feed and hydrogen sulfide in the off-gases.

**Run number 9.** In continuance of the efforts to minimize fusion, a lower gas rate of 57 cubic feet per hour and a larger particle size of -1 +3/4 inch were used for this run. Notwithstanding this, it was necessary to shut down because the shaft plugged after about 9 hours of operation.

**Run number 10.** Since run number 9 was moderately successful in maintaining continuous operation, run number 10 was designed to duplicate the conditions of this run except for a slightly higher feed rate of 8 pounds per hour and more frequent rodding. However, operation was less successful and the furnace plugged after about 3 hours of operation. Difficulty was also encountered with the gas analysis equipment and no gas samples were taken.

A comparison of the results of runs number 9 and 10 would indicate that the combustion conditions varied between runs as the result of some unmeasured variable and resulted in localized effects. This unmeasured variable was probably
the distribution of the lumps in the shaft and its effect on gas and solid channeling as well as possible partial stoppage of some of the burner ports.

Run number 11. This run was a repetition of run number 10 with the rodding technique altered. Rodding was accomplished by driving a bar down the center of the shaft and vigorously moving it up and down. This was repeated at about 10- to 15-minute intervals. Although the shaft was kept free and continuous operation was permitted by this technique, it apparently caused vertical mixing of the charge and brought fresh feed down into the reaction zone prematurely, resulting in a lower temperature in this zone and a final solid product diluted with relatively unburned feed. As a result, the desulfurization of the final product was low.

Run number 12. The conditions for this run were the same as with run number 11 except that -1/2 +1/4 inch particles were used with the thought that these smaller particles would be more thoroughly decomposed. The same rodding technique was used as in run number 11. There was no significant increase in the desulfurization over the previous run, and relatively unburned lumps of solid gypsum were noted in the solid product obtained as a result of the rodding technique. No sticking of the charge occurred, but one large piece of agglomerated particles did form; this was dislodged and removed during the run.
Run number 13. The product removal conveyor jammed before this run reached steady state conditions. No samples were taken. Six pounds per hour of -1/2 +1/4 inch particles were charged at 1.5 pounds per 15 minutes. The gas rate was 57 cubic feet per hour. This was the first run in which air preheat was used. The secondary air was preheated to about 200°F.

Subsequent to run number 13 the gas burners were modified to accommodate primary combustion air.

Run number 14. A particle size of -3/4 +1/2 inch and a feed rate of 6 pounds per hour with a gas rate of 57 cubic feet per hour were used for this run. Some fusion occurred but no large clinkers formed. Desulfurization was incomplete.

The foregoing runs, with the exception of the first, produced incomplete desulfurization. At the same time, difficulty was generally encountered with fusion and agglomeration of the charge which prevented retention times of greater than 2 or 3 hours with a continuous operation. It was thus decided to go to higher temperatures with the thought that this would produce more rapid desulfurization and an infusible shell might be formed around the particle. Higher temperatures were attained by preheating the primary combustion air.

Temperatures greater than 2550°F

Run number 15. A gas rate of 106 cubic feet per hour
was used with 20 per cent excess air preheated to 575°F. Primary air only was used. In the vicinity above the burner ports the charge heated rapidly, became molten, and trickled down into the particles below the gas burner. This fused material subsequently resolidified as a hard, green material filling the space around these particles and forming a well-cemented mass. Material further up in the shaft then became molten and formed a puddle on top of this in the region just above the burner ports. As the sulfur trioxide was expelled, this puddle became solid and very hard-burned, forming a tight plug in the shaft. (The analysis at 1-hour retention time presented in Table 4 is for a sample of this clinker.) After about 50 minutes a draw was made, but the plug apparently did not move. However, the charge had dropped enough due to decomposition and the trickling downward of the charge that about 14 pounds of fresh charge could be added. The maximum temperature observed during the run was 2750°F, observed 12 inches above the burner port. The temperature observed during the run was probably low because of the draft through the observation port, which would cool the charge very rapidly.

Analyses were made of both the fused material above the burner ports, which was hard-burned, and that below the burner ports, which by virtue of the fact that it had escaped from the hottest zone was, relatively speaking, "soft"
burned. The hard-burned material was almost completely desulfurized but had a low caustic value. The less hard-burned material was only partially desulfurized but also had a low caustic value (7.25 per cent) as compared with its neutralizing value (16.2 per cent).

Run number 16. The severe rodding during and after run number 15, to remove the clinker which formed, dislodged some of the furnace brick and severely cracked the lining. This was not noted until run number 16 was in progress and gases escaped from this lower section to such an extent that it was necessary to shut down. Conditions for this run were to be identical with run number 15 but more frequent rodding was planned. However, the noxious fumes which escaped prevented rodding and the run was stopped within an hour of starting.

The bottom, back tier of bricks were removed and the chrome-plastic lining below the burners chipped away to facilitate the downward passage of any clinkers which might form above them. The bricks were then cemented back into place.

Run number 17. A gas rate of 102 cubic feet per hour with 20 per cent excess air preheated to 500°F was used. Gypsum of -3/4 +1/2 inch particle size was fed at the rate of 10 pounds per hour. However, the charge became molten and plugged the burner ports about 3 hours after semi-continuous operation began. Again it was necessary to re-
move some of the bottom bricks to dislodge the fused product. There was a solid fused plug from about 2 inches above the screw conveyor to about 7 inches above the burner ports. No analyses were made on the solid product.

These two high temperature runs indicated that this furnace design was unsatisfactory for operation in a temperature range where the material became molten. If such operations were planned, the furnace design would need to provide for removal of the molten material and subsequent solidification at a high temperature to produce discrete lumps followed by heating of these lumps at a temperature below the fusion point to expel the remaining sulfur trioxide.

Subsequent to run number 17 the entire furnace was dismantled and rebuilt, using the same design as before except that the observation ports were enlarged to accommodate 1 1/4-inch pipe.

Temperatures between 2250°F and 2350°F

Run number 18. Six pounds of -1/2 +1/4 inch gypsum were fed per hour. Gas was supplied at the rate of 58 cubic feet per hour with about 40 per cent excess air. Some fusion and clinkering were encountered, but did not seriously interfere with the operation. A maximum temperature of 2450°F was attained for about one hour, but throughout most of the run the maximum temperature was about 2350°F. Little desulfurization was obtained.
Run number 19. Four pounds of $-\frac{1}{2} + \frac{1}{4}$ inch gypsum were fed per hour. A gas rate of 52 cubic feet per hour with about 60 per cent excess air was used. The maximum temperature noted was $2250^\circ F$. The desulfurization obtained was very low.

Run number 20. Three pounds of $-\frac{1}{2} + \frac{1}{4}$ inch gypsum per hour were fed with a gas rate of 61 cubic feet per hour and about 60 per cent excess air. A maximum temperature of $2350^\circ F$ was observed. The desulfurization was very small.

Run number 21. The conditions were the same as for run number 20 except that $-\frac{3}{4} + \frac{1}{2}$ inch particles were used. A higher maximum temperature of $2400^\circ F$ was obtained. Desulfurization was greater than with run number 20 but was still low.

It had been hoped that the lower feed rate of these latter three runs would result in higher retention times. However, because of the lower temperatures, the reaction zone did not extend for more than about 6 inches above the burner ports as compared to about 12 inches when higher temperatures were used. Consequently, the retention times were low and the desulfurization obtained was unsatisfactory.
APPENDIX C

Theoretical Considerations of Fluidization

As the flow of a fluid through a bed of granular solids increases, the pressure gradient required to overcome the combined effect of fluid friction and the buoyant weight of the bed increases. These frictional and buoyant forces of the fluid tend to raise the particles. Opposing these forces and tending to drag the particles down is the force of gravity, i.e. the weight of the particles. When these opposing forces become equal, the solids become buoyant and begin to move, denoting the start of fluidization. Thus, at incipient fluidization we may write:

\[
\frac{g}{g_s} (1-\varepsilon)(LA) \rho + (-\Delta P_f)A = \frac{g}{g_s} (1-\varepsilon)(LA) \rho_s
\]  

(44)

where

\( A \) = cross-sectional area of the bed

\( L \) = bed depth

\( -\Delta P_f \) = pressure drop required for fluidization

\( \varepsilon \) = porosity of the bed = \( \frac{\text{void volume}}{\text{bulk volume}} \)
\[ \rho = \text{density of fluidization gas} \]
\[ \rho_s = \text{density of solid particles} \]
\[ g = \text{acceleration of gravity} \]
\[ g_c = \text{gravitational constant} . \]

Solving for \( \frac{-\Delta P_f}{L} \) gives

\[ \frac{-\Delta P_f}{L} = (\rho_s - \rho)(1 - \epsilon) \frac{S}{g_c} . \tag{45} \]

The superficial velocity, \( u \), at which the above value of \( \frac{-\Delta P_f}{L} \) is obtained will be the incipient fluidization velocity. This velocity may be computed by a solution of the equations relating the flow of fluids through porous media.

The nature of the flow of a fluid through a porous bed will depend on the nature of the free space and passageways in the bed, which in turn will depend on the variables of bed porosity, and the particle size, shape, and orientation.

If we define a Reynolds number \( Re' \) based on the particle diameter and including a factor \( F_{Re} \) which is a function of the variables mentioned above, and a friction factor \( f' \) which includes a factor \( F_f \) also a function of these variables, then, by analogy to flow through circular pipes we may write
\[ \text{Re}' = \frac{D_p F \text{Re} u \rho}{\mu} \quad (46) \]

and

\[ f' = \frac{2g c D_p (-\Delta P)_f}{F_f L u^2 \rho} \quad (47) \]

where

\( D_p \) = mean particle diameter = \((1.155)\) (diameter retaining screen) when screened through a screen of diameter \( (\sqrt{2}) \) (diameter retaining screen)

\( u \) = superficial fluid velocity

\( \rho \) = fluid density

\( \mu \) = fluid viscosity

\( L \) = bed depth.

Values of \( F \text{Re} \) and \( F_f \) are obtained from plots obtained from experimental data which relate these factors to the bed porosity and the particle sphericity or shape factor.

The friction factor \( f' \) is obtained from an experimental plot relating it to the modified Reynolds number, \( \text{Re}' \), and the particle orientation.

The superficial velocity at the point of incipient fluidization for particles of a given sphericity and packing is computed from \( \Delta P_f \) and a trial and error solution of equations (46) and (47). A value of \( u \) is assumed and \( \text{Re}' \) com-
puted. From this $f'$ is obtained from a plot of experimental data and the value of $-\Delta P_f$ computed from equation (47). This is repeated until the value so obtained agrees with that given by equation (45).

The calculation may also be reversed and the sphericity or shape factor computed by a trial and error solution of equations (47) and (46) if $-\Delta P$ and $u$ are known. Values of $F_f$ and $F_{Re}$ are obtained at assumed values of the sphericity until the proper relation between $f'$ and $Re'$ is obtained.
FIGURE 35. FLUIDIZATION DATA

Gypsum
**Figure 36**  Fluidization Data

**GYPSUM**