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Reductive Decomposition of Gypsum by Carbon Monoxide

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Abstract

Tremendous domestic reserves of gypsum and anhydrite constitute a potential source of raw material for sulfur-based chemicals. As in Europe today, calcium sulfate may become one of our principal raw materials for sulfuric acid. Several European acid plants are based on a process in which sulfur dioxide is freed from anhydrite by heating the latter with coke and shale to a sintering temperature (4). The sulfur dioxide is converted into acid and the clinker is used for portland cement.

Disciplines

Catalysis and Reaction Engineering | Complex Fluids | Other Chemical Engineering

Comments

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Reductive Decomposition of Gypsum by Carbon Monoxide

Sulfur dioxide and lime can be produced from gypsum under newly determined conditions. Process provides a new route for manufacturing sulfuric acid from gypsum

TREMENDOUS domestic reserves of gypsum and anhydrite constitute a potential source of raw material for sulfur-based chemicals. As in Europe today, calcium sulfate may become one of our principal raw materials for sulfuric acid. Several European acid plants are based on a process in which sulfur dioxide is freed from anhydrite by heating the latter with coke and shale to a sintering temperature (4). The sulfur dioxide is converted into acid and the clinker is used for portland cement.

In the work described here a simpler process for freeing sulfur dioxide was investigated. Calcium sulfate reacts with a gaseous reducing agent such as

carbon monoxide at elevated temperatures to produce sulfur dioxide and lime. The solids do not sinter and the lime may be a by-product of value. Because this by-product can be disposed of in more ways than portland cement, the process should be more flexible than the European process.

Thermodynamics

The principal reaction (Reaction 1) is endothermic and therefore favored by higher temperatures. Reaction 2, which is undesirable, is exothermic and is favored by lower temperatures and high carbon monoxide partial pressures. Above 2100° F., under equilibrium con-

ditions at atmospheric pressure, calcium sulfide cannot exist in the presence of calcium sulfate because of Reaction 3. Of course, the kinetics of this reaction may be unfavorable.

To show that a reducing agent is needed for decomposing calcium sulfate, equilibrium constants for Reaction 4 are included.

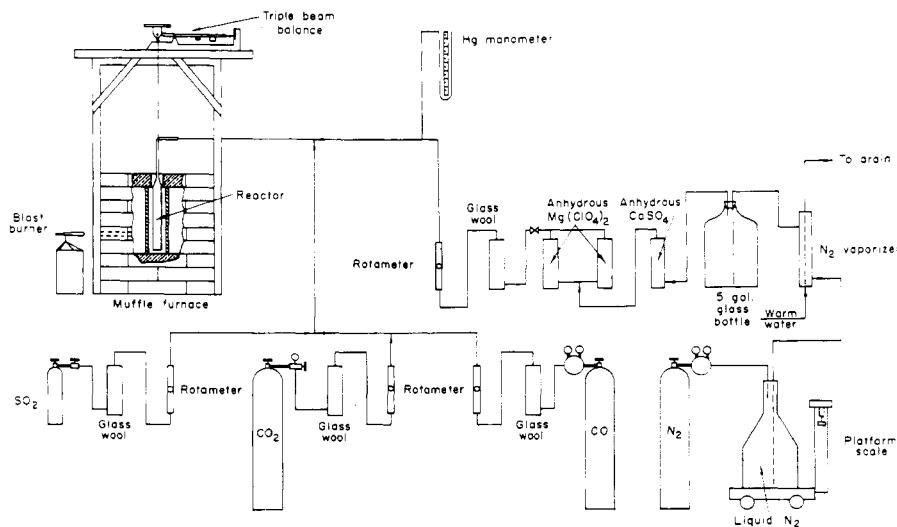
Experimental

For this study natural gypsum having the following composition was used. The gypsum was crushed and then separated by Tyler standard sieves into narrow-size fractions. The -7+8-mesh fraction was used for most runs.

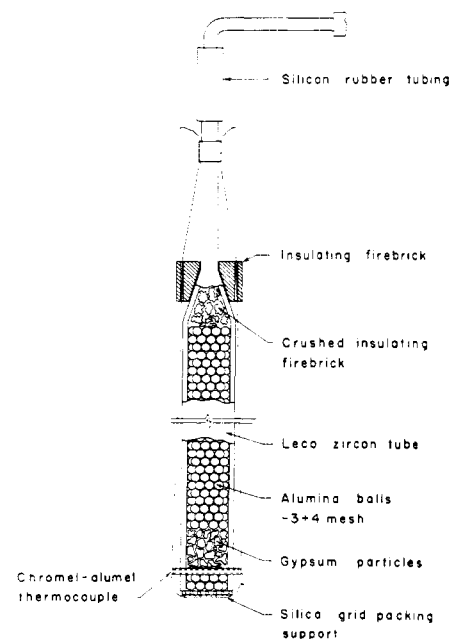
Both commercial and chemically pure grades of carbon monoxide were used. The carbon dioxide was specified as 99.97% pure, and the sulfur dioxide was refrigerant grade. The liquid nitrogen, which after vaporization served as a

Calculated Equilibrium Constants and Heats of Reaction for Reactions Involved in the Process

Reaction	Log ₁₀ K			ΔH _r , Cal./ Mole
	1200° K.	1400° K.	1600° K.	1400° K.
1. CaSO ₄ + CO = CaO + SO ₂ + CO ₂	0.31	1.48	2.28	43,400
2. CaSO ₄ + 4CO = CaS + 4CO ₂	7.92	6.69	5.66	-48,400
3. 3CaSO ₄ + CaS = 4CaO + 4SO ₂	-6.68	-0.77	3.44	222,200
4. CaSO ₄ = CaO + SO ₂ + 1/2 O ₂	-7.42	-4.51	-2.38	110,600



Carbon monoxide and dioxide, sulfur dioxide, and nitrogen, either alone or in combination, were continuously metered, mixed, and passed through the reactor containing gypsum



The reactor (diameters, 0.75 to 1.13 inches) was suspended inside the gas-fired muffle furnace from the triple-beam balance

Average Gypsum^a Composition (1)

Constituent	Weight %
H ₂ O	19.6
CaO	30.9
MgO	0.1
SO ₃	45.1
CO ₂	0.7
R ₂ O ₃	0
SiO ₂	3.3
NaCl	0.3
Total	100.0

^a United States Gypsum Co., Fort Dodge, Iowa.

diluent for the gaseous reactants, contained less than 0.1% oxygen.

The reactor, usually charged with a bed of gypsum 1 inch thick, was suspended inside the preheated furnace, and as its temperature rose, a mixture of sulfur dioxide and air was passed through to prevent the gypsum from decomposing. As operating temperature was approached, nitrogen and carbon dioxide were added. When the reactor temperature had leveled out, the flow of air was stopped and the flow of carbon monoxide was started. This marked the beginning of a run. At regular intervals of 1 to 10 minutes, depending on the rate of decomposition, the reactor weight was noted. Operating conditions were kept constant. After the reactor reached a constant weight, it was slowly withdrawn from the furnace, while nitrogen and a small amount of carbon monoxide were passed through it.

Undecomposed sulfate in the residual solids was determined gravimetrically (7). Sulfide and calcium were determined iodometrically and by Versenate titration (2), respectively.

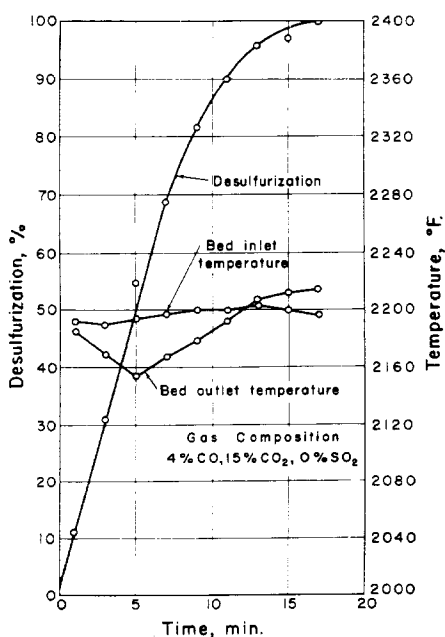


Figure 1. The desulfurization proceeded at a constant rate for much of the run when mixtures of carbon monoxide and nitrogen were fed

Results

Calcium sulfate in the gypsum could be quantitatively decomposed by passing a stream of nitrogen over the gypsum heated to about 2200° F. However, adding as little as 1% of the decomposition products, sulfur dioxide and oxygen, to the nitrogen prevented the decomposition. If several per cent of carbon monoxide were also present, calcium sulfate decomposed in the presence of as much as 7% sulfur dioxide.

Generally, calcium sulfate was converted to calcium oxide. At times calcium sulfide was produced. Consequently the criteria chosen for comparing the effect of operating conditions were the rate of desulfurization and the concentration of calcium sulfide in the residual solids. The conversion to sulfide was approximately proportional to the percentage of calcium sulfide in the residue.

The total desulfurization or conversion of calcium sulfate to calcium oxide was calculated from the composition of the final solids. By assuming that the instantaneous conversion was proportional to the weight lost by the gypsum charge, desulfurization curves such as those in Figures 1 and 2 were plotted. These curves usually had either one or two constant rate periods for which the rates could be reasonably correlated with reaction conditions. Generally the greater part of the desulfurization took place at a constant rate which corresponded to the maximum rate.

Effect of Temperature. The effect of temperature on the desulfurization rate and on the formation of calcium sulfide was studied between 2100° and 2300° F. using various gas compositions. When the gas mixture fed to the reactor contained 3% carbon monoxide, results were obtained as shown in Figure 2. At 2110° F. the gypsum passed through an initial induction period where little or no decomposition occurred. The reaction rate soon increased, and a relatively constant but rapid desulfurization rate was established. At the end the gypsum was 87% desulfurized, and the solids contained 11% calcium sulfide. Increasing the temperature to 2200° F. increased the initial desulfurization rate, but the maximum rate was unaffected. The total desulfurization was increased to almost 100%, and no calcium sulfide was found in the solids. When the temperature was raised to 2310° F., the initial rate was the same as for 2200° F., but after 8 minutes the rate fell to a much lower but constant value.

When the gas fed contained 4% carbon monoxide, the initial and maximum rates (Figure 3) and the per cent calcium sulfide in the residue (Figure 4) varied with temperature.

When sulfur dioxide was excluded from the gas fed, the maximum desulfurization rate reached a peak value at about 2150° F. with 4% carbon monoxide and 2250° F. with 2%. The variation in the rate with temperature was much greater

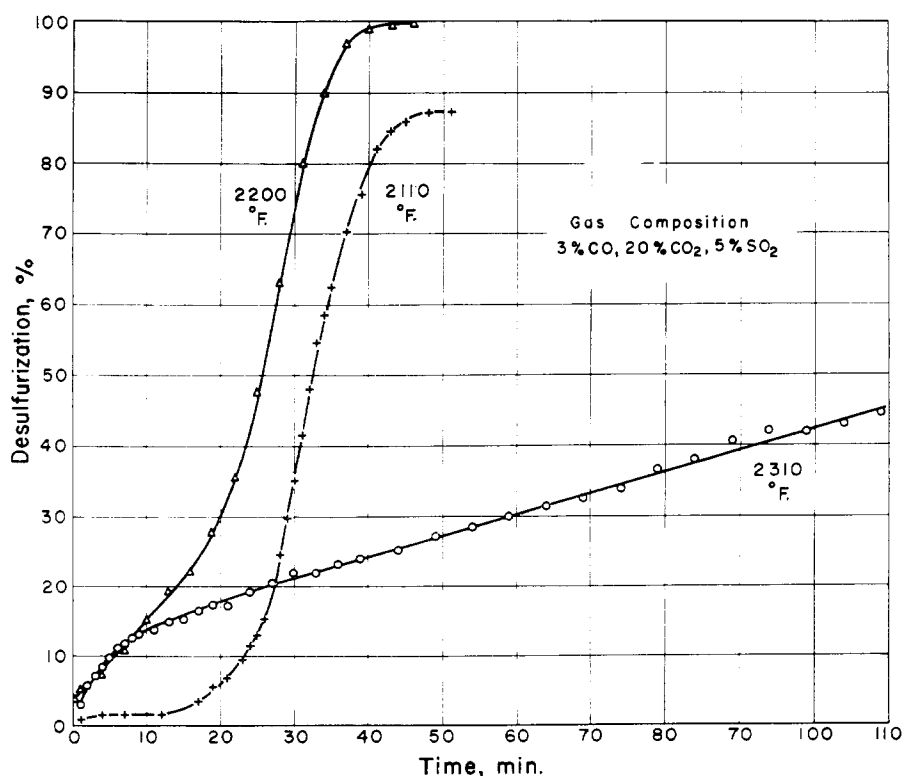


Figure 2. When sulfur dioxide was present in feed gas containing less than 5% carbon monoxide, S-shaped desulfurization curves were obtained

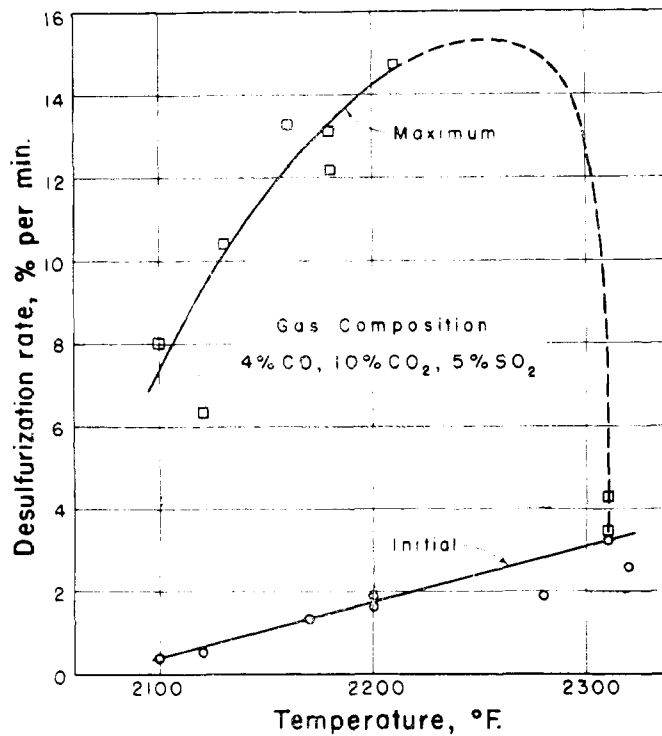


Figure 3. The maximum desulfurization rate reached a peak value at about 2200° F.

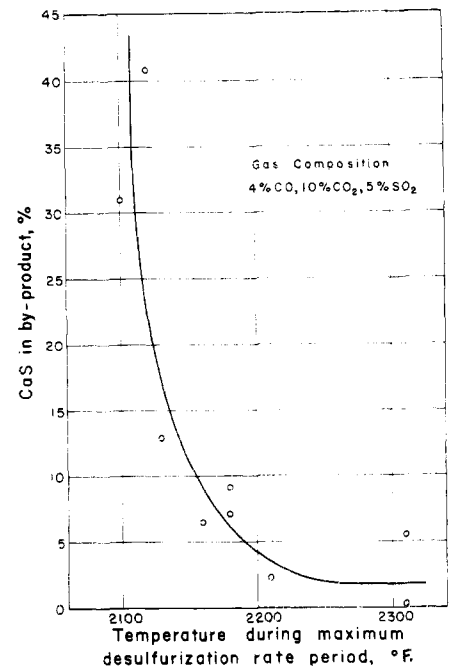


Figure 4. Production of calcium sulfide can be minimized by using high temperatures

for 4% carbon monoxide than for 2%. Again an increase in temperature from 2100 to 2200° F. sharply reduced the calcium sulfide produced.

Although the physical size and shape of the final solids were about the same as for the untreated gypsum, the surface of the treated particles was different in appearance. Gypsum has a relatively smooth surface, while solids recovered from a run made at 2200° F. had a porous surface and solids from a run made at 2300° F. had a glassy surface. The latter must have reached a state of incipient fusion, which may explain the smaller desulfurization rate at this temperature. The glazed surface might offer increased resistance to the flow of the gaseous reactants to the particle interior. On the other hand, the change in rate might have been due to the change in structure which reportedly occurs in this temperature range (3).

In correlating the effect of temperature, the gypsum bed outlet temperature was used because most of the reactors were equipped with only a single thermocouple. In obtaining the data plotted in Figure 1 a reactor equipped to measure both bed inlet and outlet temperatures was used. This provides some measure of the error incurred by not using a mean bed temperature.

Effect of Gas Composition. The effect of gas composition was explored at a temperature level of 2200° F. When a mixture of carbon monoxide, carbon dioxide, sulfur dioxide, and nitrogen was fed, the initial and maxi-

imum desulfurization rates varied linearly with carbon monoxide concentration (Figure 5). For these conditions the rate of decomposition was negligible with less than 1.8% carbon monoxide. With more than 5% carbon monoxide the data points probably fell below the plotted straight line because some calcium sulfide was produced.

When sulfur dioxide was left out of the gas fed to the reactor, the desulfurization rate was again a linear function of carbon monoxide concentration, but the rate of increase in the rate of desulfurization was smaller and the point of origin was different. Thus decomposition took place at an appreciable rate even with no carbon monoxide. With 4% carbon monoxide the rate was about the same as the maximum rate observed for the conditions of Figure 5.

When 4% or more carbon monoxide was present, the desulfurization rate was not affected much by sulfur dioxide in concentrations up to 7%. For smaller concentrations of carbon monoxide, sulfur dioxide reduced the initial desulfurization rate. Its effect on the maximum rate was not fully determined.

The desulfurization rate was influenced only to a small degree by carbon dioxide in concentrations up to 30%.

The per cent calcium sulfide in the residual solids increased with carbon monoxide concentration but decreased with carbon dioxide concentration (Figure 6). In the presence of 5% sulfur dioxide the concentration of carbon dioxide must be five to six times greater

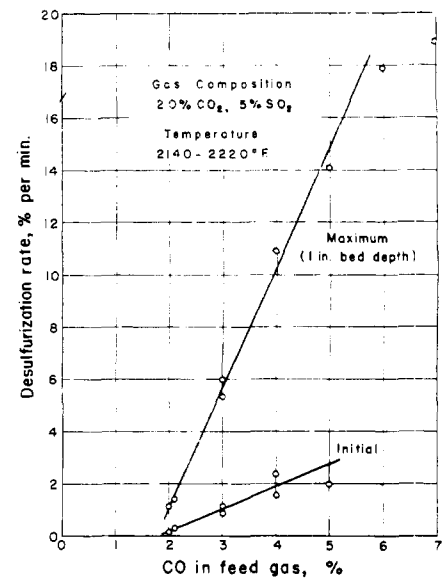
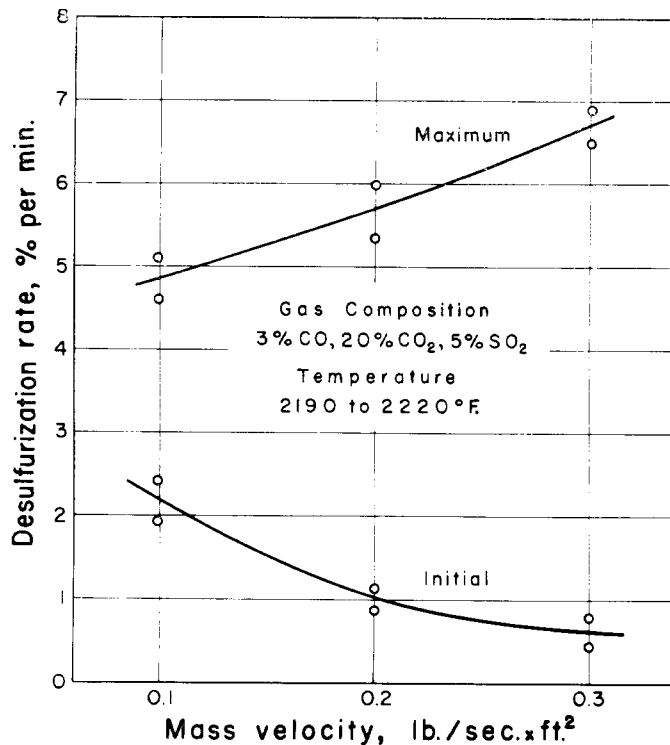
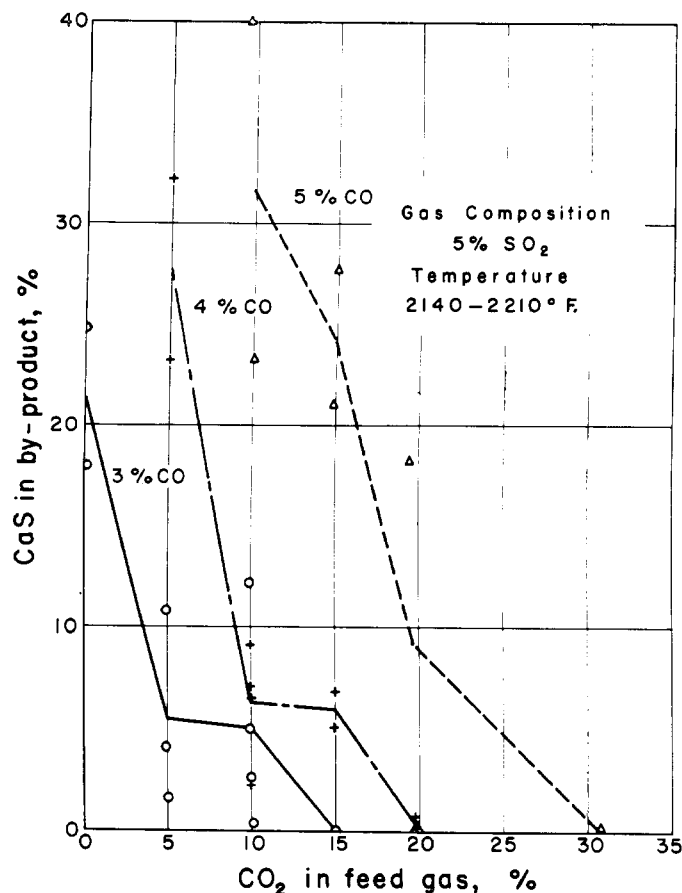


Figure 5. The reaction was first-order with respect to carbon monoxide concentration

than the carbon monoxide concentration to prevent production of calcium sulfide.

When sulfur dioxide was excluded from the gas fed, a much lower concentration of carbon dioxide was effective in suppressing calcium sulfide.

In correlating the results, the composition of the gas fed to the reactor was used, as it approximated the composition in the reaction zone and the latter could not be accurately determined.



▲ Figure 7. The decrease in the initial desulfurization rate when the mass velocity was increased was unexpected

◀ Figure 6. Production of calcium sulfide can be minimized by using small concentrations of carbon monoxide and large concentrations of carbon dioxide

Effect of Mass Velocity. Most of the runs were carried out using a gas mass velocity of 0.2 lb./sec. \times sq. ft. When a four-component gas mixture was fed, the initial and maximum desulfurization rates varied with mass velocity (Figure 7). The increase in the maximum rate with mass velocity was probably due to an increase in the average carbon monoxide concentration within the reaction zone rather than to an increase in the rate of mass transfer.

The decomposition rate increased to a greater extent for the same increase in mass velocity when the feed gas contained 2% carbon monoxide and 98% nitrogen. For this case the increase in rate seemed due to an increase in the mass transfer rate rather than to an increase in the average carbon monoxide concentration.

Effect of Particle Size. The effect of particle size on the desulfurization rate was determined by using three size fractions of gypsum: $-3\frac{1}{2}+4$, $-7+8$, and $-12+14$ -mesh. The initial and maximum rates are plotted against the average screen opening in Figure 8. Because the maximum rate increased with decreasing particle size, and mass transport in the gas phase did not seem to be limiting, the rate of internal diffusion might have been the rate-controlling mechanism during the maximum desulfurization rate period for the conditions common to both Figures 7 and 8.

Because the initial and maximum rates were not affected in the same way by

temperature, gas composition, mass velocity, or particle size, it is apparent that more than one mechanism is rate-controlling during the desulfurization of a single batch of gypsum.

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Reductive decomposition of gypsum using carbon monoxide in low concentration is both thermodynamically and kinetically feasible. The reaction appears to be first-order with respect to carbon monoxide concentration, and the optimum temperature is 2200° to 2250° F.

Desulfurization rate is a function of temperature, gas composition, gas mass velocity, and particle size. Side reactions yielding calcium sulfide can be limited by employing a high temperature, a low concentration of carbon monoxide, and a concentration of carbon dioxide five to six times greater than the carbon monoxide concentration in the reaction zone.

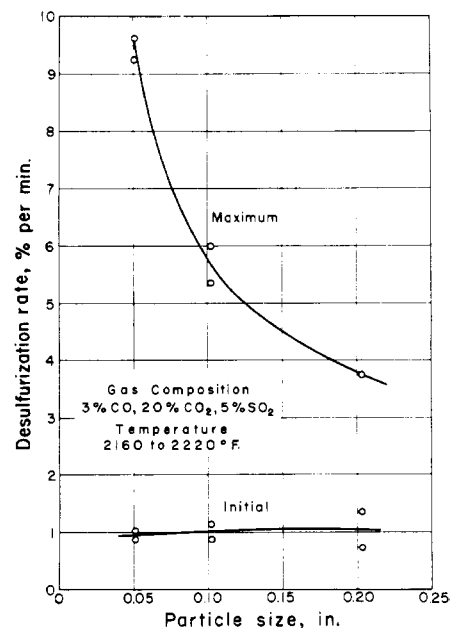


Figure 8. The maximum desulfurization rate can be increased by reducing the particle size

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