

PERMSELECTIVE MEMBRANES FOR THE  
REMOVAL OF H<sub>2</sub>S FROM COAL GAS

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INTRODUCTION

The integrated combined cycle power plant firing low BTU coal gas is one of the most attractive and efficient systems for production of electricity from coal. H<sub>2</sub>S must be removed from the fuel gas stream when high sulfur coal is used in order to meet emissions requirements.

A permselective membrane which can be used to selectively separate H<sub>2</sub>S from low BTU coal gas is being developed. The membrane is based on the principle of facilitated transport in which permeation is augmented by reversible chemical reaction with a carrier species incorporated in the membrane. In the case of facilitated H<sub>2</sub>S transport, the liquid membrane is a film of immobilized carbonate solution with which H<sub>2</sub>S reacts, yielding permeation rates and selectivities orders of magnitude greater than those of conventional polymeric membranes.

MEMBRANES FOR GAS SEPARATIONS

Membrane gas separations are attractive because they are fundamentally simple and can require less energy than conventional techniques. However, due to their generally low permeation rates and selectivities, the application of membranes to industrial gas separations has been limited. Low permeabilities result in excessively large membrane area requirements reflected in high capital costs. In order to achieve an adequate degree of separation with a membrane of low permselectivity, resort to multiple stage membrane cascades may be required, and both high capital and operating costs accompany this type of operation. To overcome these objections, General Electric is developing a new class of membranes called facilitated transport membranes, which promise both high permeation rates and high selectivity.

Permeation of gases through non-porous polymeric films occurs by a solution/diffusion mechanism. The permeant molecule first dissolves in the membrane phase and then diffuses across the film driven by its concentration gradient. The permeability of such a membrane is given by the product of permeant solubility and diffusivity

$$Pr = D_i \cdot S_i \quad 1)$$

where permeability is generally defined by the equation

$$Pr_i = \frac{N_i \cdot \delta}{A \cdot \Delta P_i} \quad [=] \quad \frac{(\text{cc/sec}) - \text{cm thickness}}{\text{cm}^2 - \text{cm Hg } \Delta P} \quad 2)$$

and

$D_i$  = diffusivity of permeant  $i$  in the membrane,  $\text{cm}^2/\text{sec}$

$S_i$  = permeant solubility,  $\text{cc(STP)/cc membrane-cmHg}$

$N_i$  = permeant flux,  $\text{cc(STP)/sec}$

$A$  = membrane area,  $\text{cm}^2$

$\delta$  = membrane thickness,  $\text{cm}$

$\Delta P_i$  = transmembrane partial pressure difference,  $\text{cm Hg}$

Membrane selectivity is expressed in terms of a separation factor which is simply the ratio of the permeation coefficients of two gases

$$\alpha_{ij} = P_{r_i}/P_{r_j} \quad 3)$$

Unfortunately, both solubilities and diffusivities of gases in polymeric films are generally low and thus gas permeabilities are likewise low. Furthermore, since gas diffusivities and solubilities do not vary greatly for a given polymer, conventional polymeric solution/diffusion membranes also exhibit limited permselectivity as a rule.

Reasonable fluxes and area requirements can be obtained with relatively low performance membrane materials by employing ultrathin membrane technology, and silicone rubber and its copolymers have a number of useful applications when used in this form (1,2,3). Nonetheless, the problem of low selectivity is not resolved by decreasing membrane thickness.

A considerable improvement in performance results from using an immobilized liquid as the membrane phase rather than a polymer. Transport through the "immobilized liquid membrane" (ILM) again occurs by the solution/diffusion mechanism, but permeation rates are now improved because solubilities and diffusivities of permeating gases are generally higher in the liquid phase than in polymers. By immobilizing the membrane liquid by impregnation of a suitable porous support material, it is possible to combine the desirable permeation properties of the liquid with the physical properties and ease of handling of the polymeric support membrane. Such a membrane consisting of a supported polyethylene glycol film has been shown to have high permeability and selectivity for sulfur dioxide (4).

#### FACILITATED TRANSPORT

A more significant feature of immobilized liquid membranes may be that permeabilities and selectivities for gases in liquid membranes can further be augmented, often by orders of magnitude, through facilitated transport. This involves a non-volatile carrier species in the liquid membrane which reacts reversibly with the permeating gas. The reactive carrier shuttles back and forth between opposite sides of the membrane carrying the permeant with it in one direction. This process is very common in biological systems (5).

Consider the simplest case of facilitated transport in which a single permeating species, A, reacts reversibly with a carrier, C, to form a complex, AC; neither the carrier nor the carrier-permeant complex can cross the membrane boundaries. The sequence of events describing facilitated transport is the following:

- (1) Species A dissolves in the membrane liquid;
- (2) A reacts with the carrier near the feed side membrane boundary;
- (3) The AC complex (as well as "free" A) diffuses across the immobilized liquid film;
- (4) Near the other membrane boundary where the partial pressure of A is low, the reaction equilibrium shifts and the AC complex dissociates;
- (5) Free A comes out of solution;
- (6) The carrier diffuses back across the membrane and is again available to participate in the facilitated transport cycle.

The total flux of A is the sum of that by simple diffusion (as free A) and by facilitated diffusion (as AC). Because the concentration levels and gradients in carrier and complex can be made orders of magnitude greater than those of the "free" permeating component, transport of A can be dramatically enhanced by the carrier process. Moreover, membrane selectivity can be extraordinary, as advantage can be taken of the specificity of chemical reaction.

Some of the earliest work by engineers to exploit the separative efficiency of facilitated transport membranes is that of Ward and Robb (6), who identified the use of an aqueous carbonate solution immobilized in a cellulose matrix as a CO<sub>2</sub> transport membrane. They found that not only was CO<sub>2</sub> transport enhanced by orders of magnitude as compared to diffusion through water films, but also that the transport rate could further be enhanced by the addition of a hydrolysis catalyst. A number of mathematical analyses of facilitated transport have been published, including those by Ward (7) and Shultz et al (8).

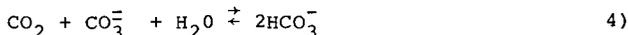
#### FACILITATED TRANSPORT OF H<sub>2</sub>S

Facilitated transport of H<sub>2</sub>S occurs in liquid membranes consisting of aqueous carbonate solutions according to the following process (refer to Figure 1):

- (1) H<sub>2</sub>S dissolves in the membrane liquid at the high-pressure (h.p.) side of the film;
- (2) H<sub>2</sub>S decomposes near the h.p. side of the film by the reaction  
$$\text{H}_2\text{S} + \text{H}^+ + \text{HS}^-;$$
- (3) H<sup>+</sup> produced in step (2) is consumed by CO<sub>3</sub><sup>=</sup> that is diffusing toward the h.p. side by the reaction  $\text{H}^+ + \text{CO}_3^{=} \rightarrow \text{HCO}_3^-$ ;
- (4) HS<sup>-</sup> and HCO<sub>3</sub><sup>-</sup> diffuse from the h.p. to the low pressure (l.p.) side of the film;

- (5)  $\text{HS}^-$  combines with  $\text{H}^+$  near the l.p. side of the film by the reaction  $\text{HS}^- + \text{H}^+ \rightarrow \text{H}_2\text{S}$ ;
- (6)  $\text{H}^+$  for step (5) is supplied by  $\text{HCO}_3^-$  by the reaction  $\text{HCO}_3^- + \text{H}^+ \rightarrow \text{CO}_2$ ;
- (7)  $\text{CO}_2$  produced in step (6) diffuses back to the h.p. side;
- (8)  $\text{H}_2\text{S}$  produced in step (5) leaves the membrane.

Carbon dioxide also reacts with the membrane liquid as described by the overall reaction



and, accordingly, it also experiences facilitated transport. However, because the reaction rate of  $\text{CO}_2$  with the membrane liquid is slow relative to that of  $\text{H}_2\text{S}$ , alkaline absorbents demonstrate an inherent selectivity for absorption of  $\text{H}_2\text{S}$  in preference to  $\text{CO}_2$ . A means of improving this  $\text{H}_2\text{S}/\text{CO}_2$  selectivity still further will be described later.

In its present configuration, the immobilized liquid membrane for facilitated  $\text{H}_2\text{S}$  transport consists of a concentrated (25-30 wt. %) aqueous solution of  $\text{K}_2\text{CO}_3$ , although other membrane liquids including  $\text{K}_2\text{PO}_4$  solutions have been screened. The membrane liquid is immobilized as a film a few thousandths of an inch thick by virtue of surface tension forces in the pores of a hydrophilic polymeric support membrane.

Two approaches have been pursued for maintaining the transmembrane  $\text{H}_2\text{S}$  partial pressure gradient which drives membrane transport. The first and simplest involves "sweeping" one face of the membrane with low pressure steam to dilute the acid gases which permeate across the membrane and keep their partial pressures low. The sweep steam carries the acid gases from the membrane permeator to a condenser, providing a dry mixture of  $\text{H}_2\text{S}$  and  $\text{CO}_2$  at a pressure sufficient for conversion of  $\text{H}_2\text{S}$  to elemental sulfur in a Claus plant or similar process. It is convenient to visualize the liquid membrane functioning as both the  $\text{H}_2\text{S}$  absorption column and steam stripping column which are conventionally used for  $\text{H}_2\text{S}$  removal.  $\text{H}_2\text{S}$  absorption and solution regeneration occur within the membrane liquid film thickness rather than in two separate vessels operated at different pressures with absorbent pumped between them. A drawback to steam sweeping is that a high pressure difference corresponding to the difference between the gasification pressure and the sweep steam pressure must be supported across the liquid film. While the membrane support problem is significant, it is indeed feasible to operate liquid membranes under such conditions, and the steam sweeping approach is being pursued in a parallel program. However, an alternative affords greater  $\text{H}_2\text{S}$  membrane reliability.

The alternative involves sweeping permeated acid gases from the membrane permeator by means of a pressurized liquid which is an  $\text{H}_2\text{S}$  absorbent. This liquid sweep may simply be a concentrated solution of  $\text{K}_2\text{CO}_3$ , identical in composition to the immobilized membrane liquid, which is isolated from the liquid membrane sandwich by a layer of non-wetted microporous polymer membrane which affords no significant resistance to  $\text{H}_2\text{S}$  transport. Relatively little power is required to pressurize the sweep

liquid to coal gas pressure, and by this means no significant pressure difference is applied across the membrane. The price of avoiding the membrane support problem is, of course, introduction of the requirement for absorbent regeneration. Dissolved acid gases are removed from solution by pressure reduction and steam stripping as is conventional practice. In this configuration, the membrane  $H_2S$  scrubbing process resembles a hot potassium carbonate plant in which the conventional packed tower absorber has been replaced by a membrane permeator. The advantages in this are enumerated below.

#### APPARATUS

Figure 2 shows the apparatus used to measure membrane permeability. A membrane is placed in the test cell, and the test cell is inserted into an oven set at the desired operating temperature, usually from  $90^\circ$  to  $130^\circ C$ . Feed and sweep streams pass counter-currently over opposite sides of the membrane. The feed gas--a mixture of  $H_2S$ ,  $CO_2$ ,  $N_2$ , and sometimes small amounts of other gases--is humidified by sparging through a boiler set at the temperature corresponding to the water pressure of the membrane liquid. Helium is likewise humidified and serves to meter the sweep steam. Flow rates of all streams are measured and gas compositions determined by chromatography. In liquid sweeping runs, a sweep liquid stream of appropriate composition pressurized by a metering pump replaces the low pressure sweep gas mixture of helium and steam.

While most tests have employed synthetic coal gas mixtures made from bottled gases, experiments have also been performed with actual coal gas. Coal gas supply pressure has been limited to one atmosphere to date.

#### $H_2S$ MEMBRANE CHARACTERIZATION

The optimum operating temperature of the membrane is in the range of  $90^\circ C$  to  $110^\circ C$ , which coincides with that of the hot potassium carbonate systems. Total feed gas pressure is usually maintained at 300 psig--a typical operating pressure for fixed bed gasifiers. Inlet  $H_2S$  partial pressures are representative of gasification of high sulfur coals--2.5 to 3.5 psi.

Figure 3 shows the dependence of membrane  $H_2S$  permeability on the partial pressure of  $CO_2$  in the feed gas. The inlet  $H_2S$  partial pressure was 2.8 psi, but since substantial amounts of  $H_2S$  were removed from the feed gas stream, the  $H_2S$  feed partial pressure varied several fold from package inlet to outlet and in certain instances significant  $H_2S$  partial pressures were present in the sweep stream. These data demonstrate the strong depressing effect of  $CO_2$  partial pressure on  $H_2S$  permeability which results from competition of the two acid gases for the membrane carrier, the carbonate anion. Such an effect can be predicted qualitatively by the theory of facilitated transport, although a rigorous mathematical description would be extremely complex.

The  $CO_2$  partial pressures of interest in low Btu coal gas range from about 15 to 30 psi, corresponding to an average permeability for  $H_2S$  of  $3000-4000 \times 10^{-9} \text{cc(RTP)-cm/sec-cm}^2\text{-cmHg}\Delta P$ . As a basis for comparison, the room temperature  $H_2S$  permeability of dimethyl silicone

rubber, the most permeable polymeric membrane available, is  $850 \times 10^{-9}$ . Unlike silicone rubber, the immobilized liquid membrane is virtually perfectly selective for acid gases; other coal gas components cross the membrane by the solution-diffusion mechanism, and solubilities in the hot, very concentrated salt solution are quite low.

$H_2S$  permeability is essentially unchanged upon raising the operating temperature from 90 to 110°C, although an increase in  $CO_2$  permeability results in a decreased selectivity for  $H_2S$  over  $CO_2$  at the higher temperature.  $H_2S$  permeability is also relatively insensitive to carbonate solution concentration, apparently due to competing effects between higher carrier loading and decreased diffusivities and activity coefficients at the high concentrations employed.

The permeation coefficient for  $H_2S$  also depends on its own partial pressure in addition to that of  $CO_2$ ; in Figure 4, the feed gas  $CO_2$  partial pressure has been fixed while  $H_2S$  inlet concentration is varied. Since the extent of  $H_2S$  removal from the feed gas was limited to 15-30%, accurate point values of  $H_2S$  permeability were obtained. At high feed partial pressures of hydrogen sulfide, the membrane carrier mechanism is saturated--that is, the extent of the facilitation is limited by the availability of the carbonate carrier for reaction at the feed side of the membrane, and  $H_2S$  permeability falls off sharply at high partial pressures. For  $H_2S$  partial pressures below about 3 psi, the permeation coefficient increases modestly with decreasing reactant partial pressure. This saturation phenomenon is a general feature of facilitated transport systems. The performance of facilitated transport membranes is made more difficult to describe due to the dependence of permeation coefficient on permeant partial pressure. This contrasts with the relatively simple situation for polymeric membranes in which permeability is often a constant characteristic of the identity of the permeating gas but not its pressure.

Membrane permeability to  $H_2S$  depends on sweep side acid gas partial pressures as well as on those in the feed gas. In the liquid sweep runs summarized in Figure 4, the extent of conversion of incoming carbonate sweep solution to the bicarbonate form was varied to simulate different degrees of absorbent regeneration in the steam stripping process. The calculated equilibrium  $CO_2$  partial pressures exerted by the incompletely regenerated sweep liquid are shown in Figure 4. The two dashed lines indicate that  $H_2S$  transport is further hindered by the presence of the competing permeant  $CO_2$  on the sweep side of the membrane.

The presence of  $H_2S$  in the sweep stream influences transmembrane flux in two ways--(1) by decreasing the  $H_2S$  partial pressure difference across the membrane (i.e., the driving force for transport) and (2) by decreasing the facilitation factor due to the decreased concentration gradient in bisulfide and bicarbonate ions resulting from partial membrane liquid conversion by  $H_2S$  in the sweep stream.

As observed earlier, the transport of carbon dioxide is also facilitated by the carbonate membrane system. An important difference between  $H_2S$  and  $CO_2$  facilitated transport is that, while the chemical reactions which augment  $H_2S$  flux are sufficiently rapid that  $H_2S$  transport is essentially diffusion rate limited, the reaction of

CO<sub>2</sub> with the membrane liquid is relatively slow due to the sluggish kinetics of CO<sub>2</sub> hydrolysis. Hence, reaction rates as well as equilibria are important in determining the permeation rate of CO<sub>2</sub>. The significance of the difference in reaction rates is that carbonate absorbents--whether immobilized as liquid membranes or not--exhibit an apparent selectivity for absorption of H<sub>2</sub>S in preference to CO<sub>2</sub>, and membrane CO<sub>2</sub> permeability is much lower than that of H<sub>2</sub>S.

The high degree of control which the membrane designer has over the gas-liquid interface permits him to further improve this inherent selectivity for absorption of H<sub>2</sub>S over CO<sub>2</sub>. Figure 5 shows how H<sub>2</sub>S:CO<sub>2</sub> selectivity can be enhanced by splitting a given total membrane liquid film thickness into two or more liquid layers, each separated by a thin gas-filled space. This so-called "gas gap" is conveniently provided by a layer of a suitable non-wetting microporous polymer membrane. The rate of H<sub>2</sub>S transport, being diffusion-limited, depends only on the total thickness of the membrane liquid films acting as diffusion barriers. Since the mass transfer resistance to H<sub>2</sub>S of the intervening gas gap is entirely negligible, the H<sub>2</sub>S permeability is not effected by this arrangement of the membrane sandwich. In contrast, the transport rate of CO<sub>2</sub> is diminished by dividing the membrane liquid film into multiple layers, since the CO<sub>2</sub> flux is sensitive to the rate of the relatively slow chemical reaction between CO<sub>2</sub> and membrane liquid and since these slow reactions are forced to occur an additional time for each new gas-liquid interface which is created. According to this much oversimplified description, the CO<sub>2</sub> transport rate is approximately halved by a single gas gap, decreased 3-fold with two gas gap interlayers, etc., with a corresponding increase in H<sub>2</sub>S:CO<sub>2</sub> separation factor  $\alpha$  at no cost in reduced H<sub>2</sub>S permeability. It should be observed that the selectivity enhancement requires only that the CO<sub>2</sub> reaction be slow relative to that of H<sub>2</sub>S, since competition between these two reactants for membrane carrier determines selectivity. The CO<sub>2</sub> absorption reaction might be fast compared to the diffusion process.

Figure 6 shows that this simple analysis describes experimental data quite adequately. The ratio of H<sub>2</sub>S and CO<sub>2</sub> fluxes has been determined for three membrane sandwich configurations and plotted as a function of CO<sub>2</sub> partial pressure in the feed stream; inlet H<sub>2</sub>S concentration was fixed. Multilayering is seen to improve H<sub>2</sub>S:CO<sub>2</sub> selectivity as predicted by theory, as the spacing and slopes of the lines drawn through the three data sets indicate. With a double gas gap arrangement (three membrane liquid layers) and a synthetic coal gas feed containing 2.7 psi H<sub>2</sub>S and 20 psi CO<sub>2</sub>, the H<sub>2</sub>S:CO<sub>2</sub> flux ratio is increased from about 0.5 (no gas gap) to 1.5, corresponding to a permeate composition enrichment from 33% to 60% H<sub>2</sub>S in CO<sub>2</sub>. Selectivity for H<sub>2</sub>S absorption is particularly important for integrated combined cycle power generation from low Btu coal gas for reasons discussed below.

Permeation data such as the above are used in predicting the membrane area requirement for any given application. Since the permeability of facilitated transport membranes depends on reaction kinetics and equilibria, it is not possible to characterize membrane performance by a simple permeability "constant" as for polymeric membranes, and in fact the permeation constant varies significantly from permeator inlet to outlet in the following integration:

$$A = \int_0^{N_{H_2S}} \frac{dN_{H_2S}}{Pr_{H_2S} (P_{H_2S} - P_{H_2S,S})} = \frac{\delta \cdot F_t}{P_t} \int_{P_{H_2S,i}}^{P_{H_2S,o}} \frac{dP_{H_2S} \cdot F}{Pr_{H_2S} \cdot \Delta P_{H_2S}}$$

where  $F_t$  and  $P_t$  are the volumetric flowrate and total pressure of the coal gas feed. The  $H_2S$  partial pressure difference across the membrane is calculated by material balance. For typical applications involving desulfurization of low-Btu coal gas produced from high sulfur coal, a range of 1-2 ft<sup>2</sup> of membrane area per kilowatt of generating capacity is predicted.

#### MEMBRANE H<sub>2</sub>S SCRUBBING OF LOW BTU GAS

The conceptual layout of a liquid swept membrane H<sub>2</sub>S scrubbing system is shown in Figure 7; it is very similar to the hot carbonate flowsheet with the exception of the replacement of the conventional absorber with the novel membrane permeator.

Many of the benefits of membrane H<sub>2</sub>S scrubbing in the combined cycle power plant are due to the controllable, high membrane selectivity for H<sub>2</sub>S absorption. Minimizing CO<sub>2</sub> removal increases the fuel gas mass flow to the gas turbine, decreases the turbine compressor air requirement, and thus increases the net shaft work delivered to the gas turbine generator. On the other hand, passage of large amounts of CO<sub>2</sub> through the H<sub>2</sub>S removal and sulfur conversion trains is to be avoided for a number of reasons.

The total amount of acid gas flowing through the sulfur removal and conversion trains is less, of course, for the more selective process; specifically, three times less acid gas must be processed on a molar basis if the product stream from the H<sub>2</sub>S stripper consists of 60% H<sub>2</sub>S in CO<sub>2</sub> rather than 20% H<sub>2</sub>S. A decrease in the total amount of absorbed acid gases to be stripped from solution should reduce the stripping steam requirement. Since insufficient waste heat is available in the plant to raise all the low pressure stripping steam required, a portion must be extracted from the steam turbine at a penalty in reduced power output; this penalty is minimized by high membrane selectivity. In short, less gasification, heat recovery, and gas and steam turbine equipment need be purchased per megawatt of exported power when selective membrane scrubbing is employed, and power plant first costs are thus reduced by more effective use of the energy available in the coal gas. The net plant heat rate is also improved by routing CO<sub>2</sub> to the turbines, reflecting lower operating as well as first costs.

A final consideration as regards the power plant is that a number of H<sub>2</sub>S removal processes, including the membrane scrubber, employ concentrated solutions of alkali metal salts as absorbents. With conventional absorption columns, a possibility exists for alkali metal carryover due to entrainment or foaming. This is unacceptable in view of the extremely low gas turbine tolerance

for alkali metals in the fuel gas due to hot corrosion problems. The carbonate membrane solution, on the other hand, is quite effectively immobilized.

The high absorption selectivity afforded by membrane  $H_2S$  scrubbing also results in equipment and utility savings in the  $H_2S$  scrubbing process itself. Specifically, the effective absorbent carrying capacity for  $H_2S$  increases with selectivity, and a reduced solution recirculation rate is possible at a savings in pumping power. Since gas and liquor flowrates are down, the size of the stripping column is decreased, and a smaller acid gas condenser duty follows from the reduced stripping steam consumption.

The relatively high absorption temperature of 90-110°C is an advantage relative to processes which operate nearer ambient. The higher the absorption temperature, the less heat exchange area and heat rejection capacity that is required in the fuels plant. Energy losses due to incomplete heat recovery are minimized and less polluted condensate is generated. By operating at somewhat higher absorption temperatures and living with increased  $K_2CO_3$  makeup requirements, the alkaline membrane liquid should be capable of absorbing carbonyl sulfide, if required, and hydrolyzing it to  $H_2S$  and  $CO_2$  to facilitate its conversion to elemental sulfur in the Claus plant.

Finally, Claus plant capital cost is sensitive to  $H_2S$  concentration in the acid gas feed. Above 50%  $H_2S$ , the less expensive partial combustion process may be employed; at lower  $H_2S$  concentrations, the split-stream configuration is required in order to achieve stable combustion. Furthermore, since  $H_2S$  conversion to elemental sulfur is limited by equilibrium considerations, sulfur conversion efficiency increases with  $H_2S$  concentration for a given number of catalytic stages. Since the cost of the sulfur conversion plant will be as large as that of the  $H_2S$  removal plant, substantial cost savings can be realized here.

#### MEMBRANE LIFE

Because of the very severe operating environment of coal gas, an extensive life testing effort has been undertaken, focussing on the liquid swept membrane. The membrane has been operated at 90°C and a pressure of 300 psig with synthetic coal gas mixtures. Tests have also been performed on actual coal gas produced by the GEGAS-F atmospheric fixed bed gasifier. Both chemical and physical effects have been sought and solutions developed for membrane life-limiting problems as they have been identified. Promising life test results have been obtained which will soon be reported.

#### CONCLUSIONS

The superior performance of facilitated transport immobilized liquid membranes makes possible the use of membranes to do industrially significant gas separations. The extremely high permeability and  $H_2S:CO_2$  selectivity of carbonate liquid membranes

makes them particularly suitable in low Btu coal gas-combined cycle power plant applications. In addition to high performance, reasonable membrane life is being demonstrated.

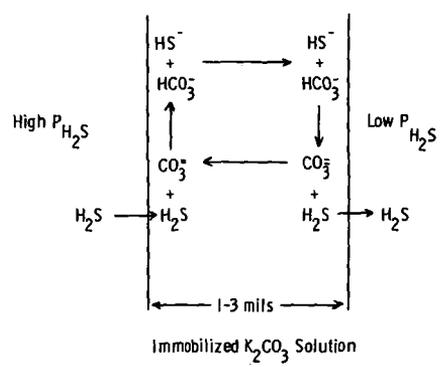
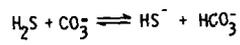
#### ACKNOWLEDGEMENTS

The membrane scrubber development is based in large part on the invention and experimental ingenuity of W.J. Ward and C.S. Herrick of this laboratory.

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FIGURE 1.  
FACILITATED TRANSPORT OF HYDROGEN SULFIDE



SIMILAR REACTION FOR FACILITATED TRANSPORT OF  $\text{CO}_2$

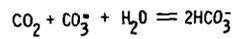


FIGURE 2.

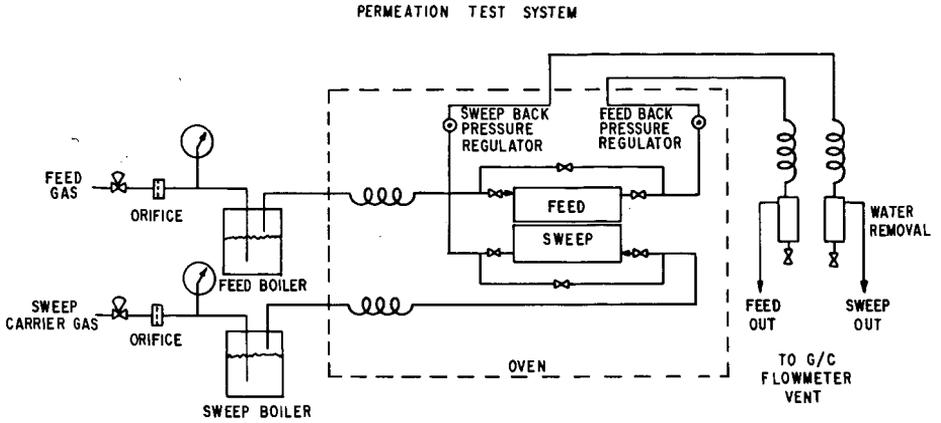


FIGURE 3.

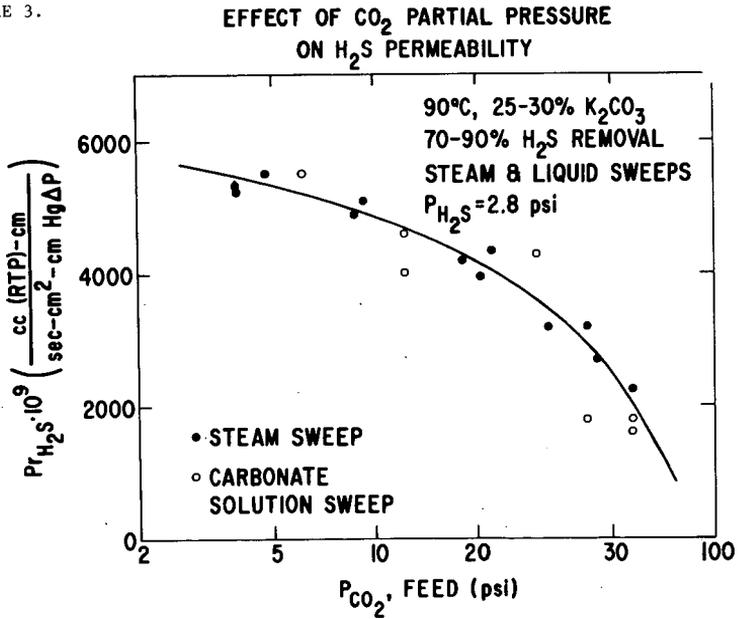


FIGURE 4.

H<sub>2</sub>S PERMEABILITY MAP AT 90°C, 30 PSI CO<sub>2</sub> IN FEED

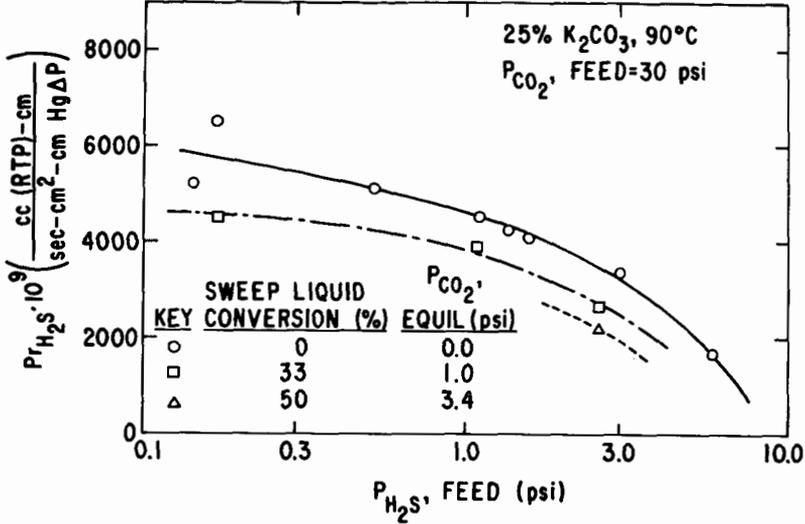


FIGURE 5.

IMPROVEMENT OF H<sub>2</sub>S/CO<sub>2</sub> SELECTIVITY BY GAS GAP

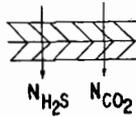
DIFFUSION LIMITED H<sub>2</sub>S TRANSPORT:

$$N_{H_2S} \propto \frac{1}{(\text{TOTAL LIQUID FILM THICKNESS})}$$

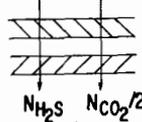
REACTION RATE LIMITED CO<sub>2</sub> TRANSPORT:

$$N_{CO_2} \propto \frac{1}{(\text{NUMBER OF GAS-LIQUID INTERFACES})}$$

I. TWO ILM'S IN CONTACT



II. TWO ILM'S SEPARATED BY GAS GAP



$$\therefore a_{II} \approx 2a_I$$

FIGURE 6.  
 ENHANCEMENT OF MEMBRANE H<sub>2</sub>S/CO<sub>2</sub>  
 SELECTIVITY BY GAS GAP

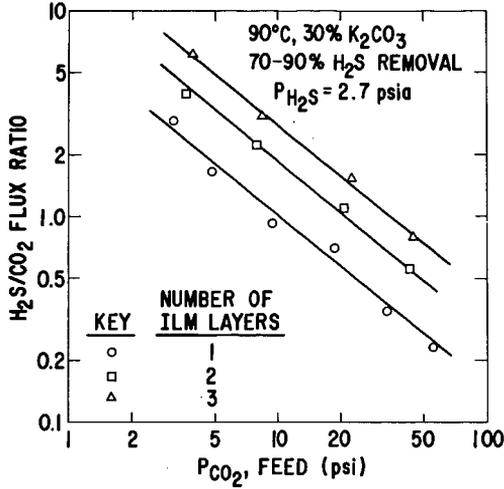
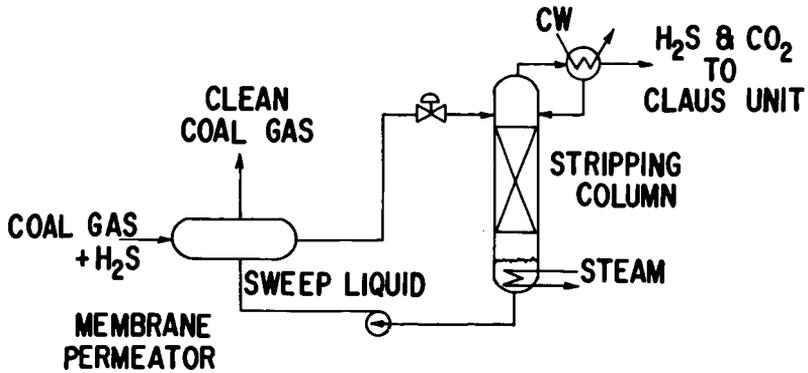


FIGURE 7.  
 MEMBRANE H<sub>2</sub>S SCRUBBING SYSTEM  
 (LIQUID SWEEPING)



Hot Low-Btu Gas Purification with Coal Ash, O. J. Hahn and M. R. Heilig, Institute for Mining and Minerals Research, University of Kentucky, Lexington, KY 40506.

An experimental study was carried out to evaluate the removal of  $H_2S$  and other sulfur compounds from hot low Btu producer gas using gasifier ash. The present work emphasized thermogravimetric studies of the basic absorption and regeneration of ash as a function of temperature, particle gas size composition and residence time. The gas composition studied include ( $H_2S$ ,  $N_2$ ), ( $H_2S$ ,  $H_2$ ,  $N_2$ ), ( $H_2S$ ,  $H_2$ ,  $CO$ ,  $N_2$ ), ( $H_2S$ ,  $CH_4$ ,  $H_2$ ,  $CO$ ,  $N_2$ ), ( $H_2S$ ,  $CH_4$ ,  $H_2$ ,  $CO$ ,  $CO_2$ ,  $N_2$ ) and ( $H_2S$ ,  $COS$ ,  $H_2$ ,  $CO$ ,  $N_2$ ). The temperature range varied from 800 to 1600°F. The absorption of  $H_2S$  in the iron oxide matrix is preceded by the reduction of the iron to the elemental form.

In the case of ( $H_2S$ ,  $N_2$ ) gas the absorption was restricted by the formation rate of  $H_2$ .

HOT GAS CLEANUP PROCESS FOR REMOVING H<sub>2</sub>S  
FROM LOW-BTU GASES USING IRON OXIDE ABSORBENTS

E. C. Oldaker and D. W. Gillmore

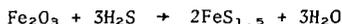
Energy Research and Development Administration  
Morgantown Energy Research Center  
Morgantown, West Virginia

INTRODUCTION

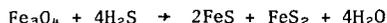
Research is continuing at the Morgantown (West Virginia) Energy Research Center, Energy Research and Development Administration, to develop a hot gas cleanup process using solid regenerable sorbents to remove hydrogen sulfide from hot (1000<sup>o</sup>-1500<sup>o</sup>F) low-Btu fuel gas made from coal. A suitable process is needed whereby sulfur can be removed from low-Btu gases so that high sulfur coals can be utilized to provide clean energy and meet the environmental standards regulating the amount of sulfur released to the atmosphere. Removal of hydrogen sulfide without cooling the gas would conserve the heat lost in conventional gas purification methods, thus increasing the thermal efficiency by 15 percent.

The use of iron oxide to remove H<sub>2</sub>S from industrial gases has been practiced for many years. Indeed, research by the Appleby-Frodingham Steel Company during the late fifties led to the construction and operation of a plant desulfurizing about 2½ million cubic feet of coke oven gas per day followed by construction of a 32 million cubic feet per day plant before operational problems and economic costs shut down the operations. The crude coke oven gas was passed through a fluidized-bed of sintered iron oxide powder (-16 mesh + 100 mesh) where reaction with H<sub>2</sub>S and Fe<sub>2</sub>O<sub>3</sub> took place at temperatures approaching 400<sup>o</sup>C. This process, as reported by Reeves et al (1), removed 95-98 percent of the H<sub>2</sub>S from the coke oven gas. The principal problems encountered, as far as the use of iron oxide was concerned, were massive attrition and replacement of the fines, plugging and erosion of pipes transporting the iron oxide. These difficulties encountered by the Appleby-Frodingham process have been overcome by placing the iron oxide particles on a supporting matrix composed of fly ash, or silica, by thoroughly mixing the two components, extruding the paste-like mixture into 1/4-inch diameter by 3/4-inch long cylinders and sintering at 1800<sup>o</sup>F.

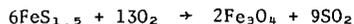
The chemistry involved in absorption and regeneration using iron oxide shows that iron sulfides are produced when H<sub>2</sub>S reacts with Fe<sub>2</sub>O<sub>3</sub> with the empirical composition approaching FeS<sub>1.5</sub>



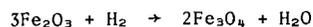
However, according to Imperial Chemical Industries Catalyst Handbook (2), fresh iron oxide is converted to Fe<sub>3</sub>O<sub>4</sub> in the presence of hydrogen and at temperatures above 650<sup>o</sup>F. Therefore, the reaction would be written as



During regeneration, air oxidizes the FeS and FeS<sub>2</sub> to Fe<sub>3</sub>O<sub>4</sub> and SO<sub>2</sub>:



However, in the presence of excess oxygen, the Fe<sub>3</sub>O<sub>4</sub> is converted to Fe<sub>2</sub>O<sub>3</sub>. If this condition exists, then upon the start of another absorption cycle, some hydrogen is consumed from the raw producer gas while conversion to Fe<sub>3</sub>O<sub>4</sub> is taking place



A review of the literature reveals that coke oven gases have been desulfurized in both fixed and fluid beds of iron oxide at temperatures up to 752°F (1). Abel et al (3) and Shultz (4) reported the results of laboratory-scale investigations of solid sorbents to remove hydrogen sulfide from hot (1000°-1500°F), clean, simulated low-Btu fuel gas. Clay and Lynn (5) reported the use of iron oxide supported on alumina to remove NO<sub>x</sub> and SO<sub>x</sub> from powerplant stack gases at temperatures approaching 1000°F, using an injected stream of synthesis gas (CO + H<sub>2</sub>) to reduce the SO<sub>2</sub> to H<sub>2</sub>S and NO to N<sub>2</sub> before passing the flue gases over the catalyst. Oldaker et al (6,7,8,9) reported the results of tests involving fly ash-iron oxide and silica-iron oxide sorbents to remove H<sub>2</sub>S from hot (1000°-1500°F) low-Btu gases.

#### EXPERIMENTAL WORK

The Research conducted thus far has been two-pronged; lab scale investigations for the development of an efficient sorbent for removing H<sub>2</sub>S from hot low-Btu gases made from coal, and process development to identify the major parameters required for scale-up design criteria utilizing data from bench scale operations up to 9000 scfh gas flows.

The absorbent research has been directed toward the development of sorbents with the following criteria:

- a. Efficient removal of H<sub>2</sub>S at temperatures above 1000°F;
- b. Physical strength required to withstand handling;
- c. Economic feasibility; and
- d. Process feasibility--regenerability, form and composition and acceptable life.

Attrition of the iron oxide sorbent resulting in unacceptable carry over and absorbent replacement, plugging or fouling of system components, led to development of a more suitable matrix support for the iron oxide. Fly ash and silica satisfied this requirement and permitted adequate gas contact for removal of H<sub>2</sub>S, while withstanding process temperatures.

The next step toward the development of the sorbent hinged on the necessary preparation techniques required to strengthen these sorbents in the categories of H<sub>2</sub>S absorption capacity and efficiency, physical strength, and economic costs.

Several tests were carried out to determine the effects of additives on the physical strength and absorption capacities. It was found that one percent bentonite added to the fly ash-iron oxide mixture produced a superior sorbent having good physical strength and absorption capacity. This was not true when using silica-iron oxide mixtures as both the physical strength and absorption capacity were reduced. On the other hand, using sodium silicate as the additive produced an excellent sorbent when using either fly ash or silica as the support material. Data are shown in table 1.

Another major difference between the support materials is the amount of iron oxide that can be admixed. It was found that 25 percent iron oxide added to the fly ash was the maximum amount that could be tolerated without reducing both the physical strength and the absorption capacity, whereas 45 percent iron oxide could be added to the silica without any detrimental effects on the physical strength or absorption capacity of the sintered sorbent. This increased amount of iron oxide accounts for the much higher H<sub>2</sub>S absorption capacities shown in table 1 for the silica sorbents.

The temperature limitations imposed on each type of sorbent is significant because of the highly exothermic reaction taking place during the regeneration of the sorbents. Using fly ash as the support material imposes a temperature limitation

of 1500°F for the sorbent to have a good level of absorption capacity and life expectancy. This is because fly ash acts as a glass-fusing at around 1500°F. The fusing characteristic would cause loss of pores thus cutting down on surface area available for good gas contact and eventually rendering the sorbent useless for removing H<sub>2</sub>S from hot producer gas.

Silica, on the other hand, has a much higher fusion temperature permitting higher temperature operation without affecting the ability of the sorbent to perform. The recommended operating temperature indicated by limited data is believed to be in the range of 1700°-1800°F. This range is well above most if not all coal gasification processes being developed at this time. Provided that the present work being carried out on other than low-Btu gases does not contain constituents detrimental to the sorbent material or reactions, the two sorbents could be used on most coal gasification processes efficiently and economically. Particulate matter carried over from the gasification process may cause detrimental effects especially if the fixed bed concept is utilized, although the lab scale investigations indicate the carbonaceous material is burned off during the regeneration cycle. There is much research work going on at the present time on hot particulate removal from coal-derived gases, which is essential to projected combined cycle and turbine applications.

Figure 1 is a flow diagram of the laboratory apparatus used to test and evaluate the various sorbents. Generally, the gases were metered into the system to simulate the actual composition of producer gas. Coal was fed into the system at rates up to 500 grams/hr through the carbonizer to provide the actual tars and particulates found in producer gas. After being preheated, the producer gas flows into the absorber containing approximately 700 grams of prepared sorbents. The H<sub>2</sub>S is monitored at the input and output of the absorber by means of the Tutwiler technique (10) to determine the absorption capacity and efficiency of the particular sorbent being tested. The temperature of the absorbent bed is maintained at operating temperature by means of electric heaters, usually at 1100°F. The gas output is also monitored by analyzers for CO and H<sub>2</sub>.

Life expectancy is another major parameter used to evaluate the worth of a high temperature solid absorbent for H<sub>2</sub>S removal. Therefore, an iron oxide-fly ash absorbent was tested on the lab scale unit using simulated producer gas containing tars and particulates to determine some degree of life expectancy. Thirty complete absorption-regeneration cycles were completed on the same absorbent. It was found that the recycling of the sorbent did not affect the ability of the sorbent to remove H<sub>2</sub>S from the hot producer gas maintaining an average absorption capacity of 10 wt.-% during the tests. Upon completion of these tests, the sorbents were in excellent condition without any signs of physical deterioration or caking between the individual sorbents. Figure 2 indicates the sorption capacities achieved during the thirty runs. These tests were conducted at 1100°F. Regeneration was accomplished by using 12 scfh air flow rate through the absorber for approximately two hours. During regeneration, the bed temperature increased to 1700°F momentarily in the actual wave front or zone of reaction. Although this temperature reached 1700°F momentarily, without apparent harm, it is believed that 1500°F would be the highest temperature fly ash-iron oxide sorbents should be exposed for optimum life expectancy. Further life tests are now being conducted where an optimum sorbent is recycled until the H<sub>2</sub>S absorption capacity decreases significantly so that better defined limits can be predicted. Table 2 shows the typical data from six of the thirty sorption capacity tests using the fly ash-iron oxide sorbent. Note that the H<sub>2</sub>S absorption efficiency is given using 400 grains/100 scf as the break through limit. These percentages would be much higher using 150 grains/100 scf as the stopping point for absorption.

Further testing, using much higher gas flows and increased amounts of sorbent material was believed necessary to generate data that are required for scale-up criteria. A 9000 scfh atmospheric producer and hot gas cleanup facility has been designed, built and installed at MERC for this purpose.

The general overall range of operating conditions include:

Space velocities	500-3500 vol/vol/hr
Coal feed rates	60-200 lb/hr
Pressures	3-15 psig
Temperatures	600 <sup>o</sup> -1500 <sup>o</sup> F
Make gas flows	5000-9000 scfh
Gas analyses	CO-H <sub>2</sub> -CO <sub>2</sub> -H <sub>2</sub> S-N <sub>2</sub> -CH <sub>4</sub> -COS-CS <sub>2</sub> -C <sub>2</sub> H <sub>6</sub> -O <sub>2</sub> -SO <sub>2</sub>

The overall flowsheet is shown in figure 3. The detailed instrumentation has been removed to permit better understanding of the process. Also, it is well to remember that particular designs or instrumentation shown here are only tools needed to procure design criteria and not necessarily the approach that would be used for commercial application.

Air and steam are fed into the 16-inch diameter producer through the revolving, eccentric grate into the combustion zone to gasify the coal. The depth of the coal bed can be varied depending on operating conditions required. Normally, the bed depth averages about 32-36 inches. An agitator-stirrer mechanism providing continuous vertical and circular movement permits stirring in various levels of the coal to minimize agglomeration or break up voids while running on bituminous coal. The coal is choke-fed downward through the coal feed tube, the length of which establishes the bed height. From shakedown operations, it has been necessary to revise the coal feed system. The extremely slow movement of the coal through the coal feed tube permitted the coal particles to become somewhat plastic or sticky and adhere to tube walls eventually blocking coal feed to the producer. This system is now being revised by feeding the coal through a pocket feeder and metering screw. The bed level will be established by the speed of the screw and monitored by nuclear gauges similar to those on the MERC 42-inch diameter pilot scale producer (11).

The make gas exits from the producer into a standard-design refractory cyclone to remove the larger dust particles--above 10 micron--and is then piped into either of the two absorbers, which are loaded with fly ash or silica supported iron oxide absorbents. For testing at 2500 space velocity using 7500 scfh gas flow, around 225 pounds of sorbent would be used. The absorbent bed temperature is held above 900<sup>o</sup>F by maintaining the sensible heat of the exit gas through insulation, refractory, and the circulation of hot gases from a gas-fired POC heater. During regeneration, which is accomplished with air, the heat from the highly exothermic reaction is controlled by dilution gases and/or the natural heat-sink effect of the refractory lined vessel.

The off gases from the absorber are then piped through a back pressure regulator and a metering orifice to the flare stack.

Three sampling ports are located in the flow system for gas analyses. One gas sampling point is located immediately downstream from the cyclone, where the raw producer gas is continuously monitored by a gas chromatograph. Another sampling point is located downstream from the absorbers in the piping system handling the make gas. This point continuously monitors the H<sub>2</sub>S concentration remaining in the make gas after passing through the iron oxide sorbents. The last gas sampling port is located in the exit gas piping carrying the SO<sub>2</sub> enriched stream to the vent stack. This port continuously monitors the SO<sub>2</sub> concentration in the off gas during regeneration cycle.

Figure 4 is a cross sectional view showing the interior arrangement of the producer. The most important parts are the eccentric, cone crusher-type grate, the 16-inch water cooled combustion zone, the agitator-stirrer mechanism, and the coal feed tube.

Figure 5 is a cross sectional view of the refractory lined absorber which is 12-inches inside diameter. The absorber gas flow is down flow during absorption and up flow for regeneration. This flow pattern is presently being reversed in an attempt to prevent build-up of particulates on top of the sorbent bed.

Preheated gas from a gas fired POC heater enters through the bottom of the absorber and passes through the sorbent bed to provide the heat-up necessary before the start of an absorption cycle. As shown, thermocouple ports are located 18 inches apart in order to measure temperatures and thus identify the wave front or zone reaction as it passes through the sorbent bed.

Preliminary data generated thus far on the bench scale unit fairly well parallels data taken on the lab scale apparatus. For instance, the data generated while using the lower temperature extreme of 616°F while using anthracite coal provides almost the same absorption capacity--6.43 wt.-pct., although the space velocity was increased from approximately 500 on the lab unit to 2500 vol/vol/hr on the bench scale facility. Also, a slightly higher bed temperature of 672°F increased the absorption capacity by 18 percent to 7.62 wt.-pct. This shows that increased temperatures give better absorption results. Previous tests on laboratory apparatus showed the highest absorption results were obtained around 1500°F, the limit of the fly ash-iron oxide sorbents. Table 3 shows typical data generated at these lower temperatures on the bench scale facility. The data indicate also that efficiency decreases as temperature during absorption is lowered. More data generated on the bench scale facility will be made available in the immediate future after shakedown operations and equipment design modifications are completed.

#### CONCLUSION

The research results thus far indicate that the hot gas cleanup process is an acceptable alternative for removing H<sub>2</sub>S from low-Btu fuel gases derived from coal. The solid absorbents performed well at temperatures between 1000°-1500°F.

Further engineering development is needed on hot particulate removal and it is being intensely investigated at this time by several firms. Several independent studies are also being made on various regenerative techniques, using recycled SO<sub>2</sub>, for instance, to increase the SO<sub>2</sub> concentration in the effluent gas stream to permit more efficient processing to elemental sulfur. Engineering studies concerning the geometry of the absorber-reactor are being made with particular emphasis on heat transfer mechanisms to handle the high temperatures during regeneration. Fluid bed and moving bed concepts along with the fixed bed are being evaluated and some testing programs are already underway.

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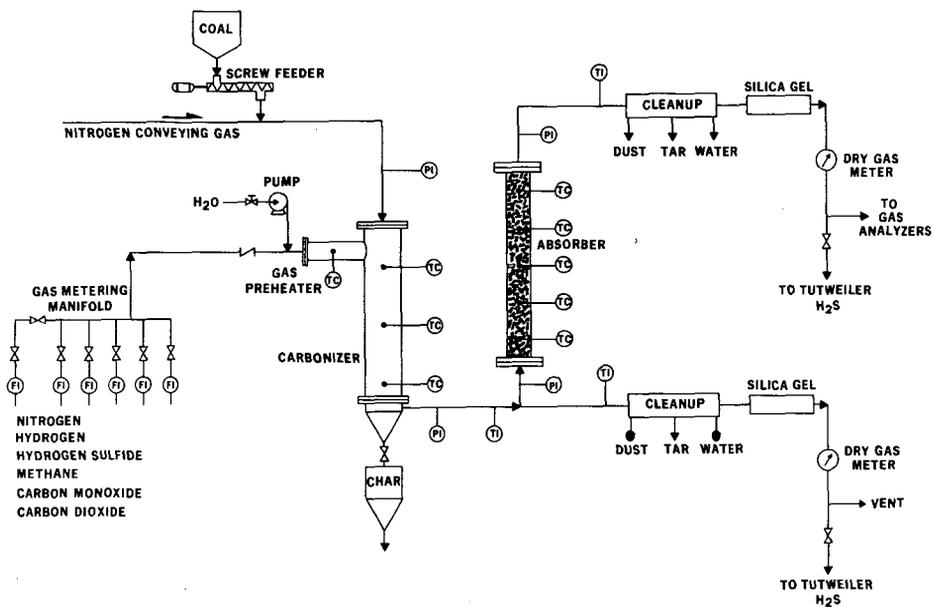


FIGURE 1. — Flow Diagram of Apparatus for Measuring Sorption Capacity

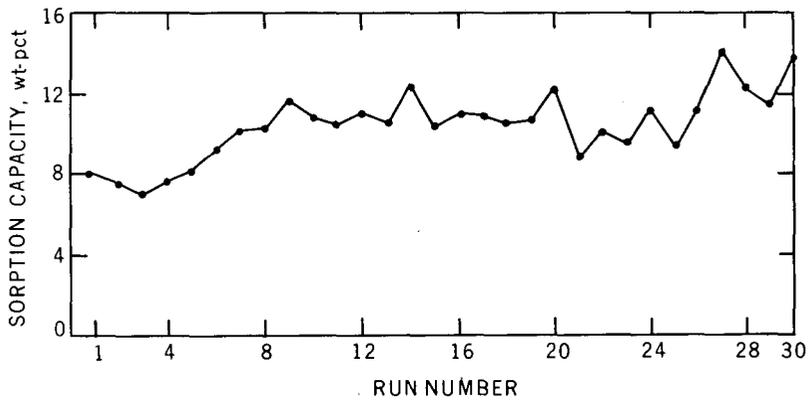


FIGURE 2. — Sorption Capacities Achieved During Thirty Absorption Regeneration Tests

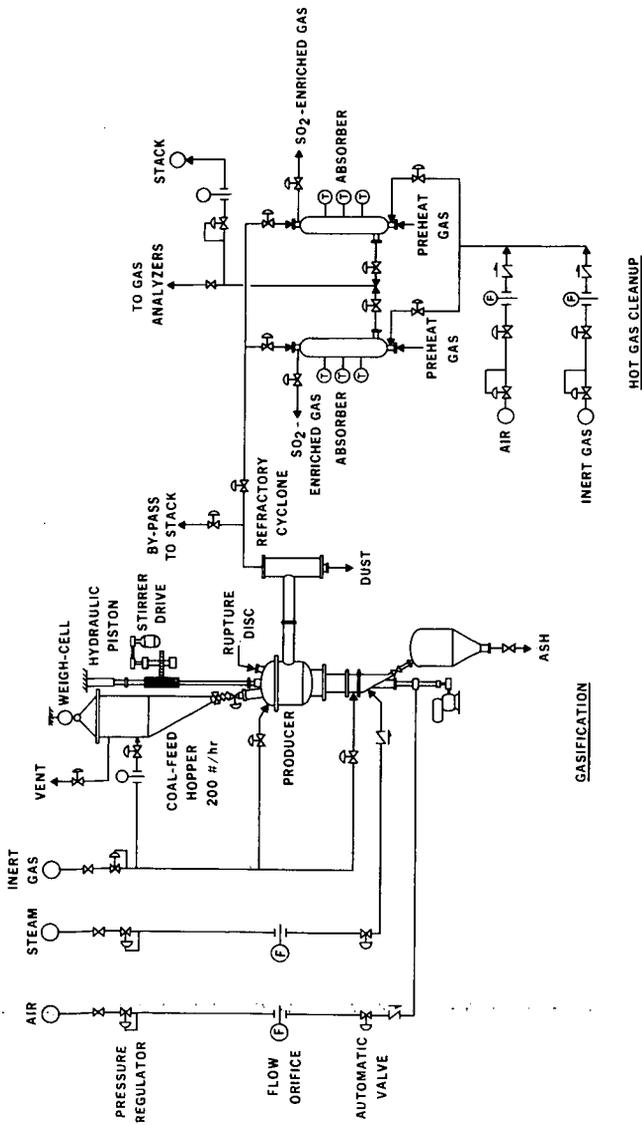


FIGURE 3. — Bench Scale Producer and Hot Gas Cleanup Facility.

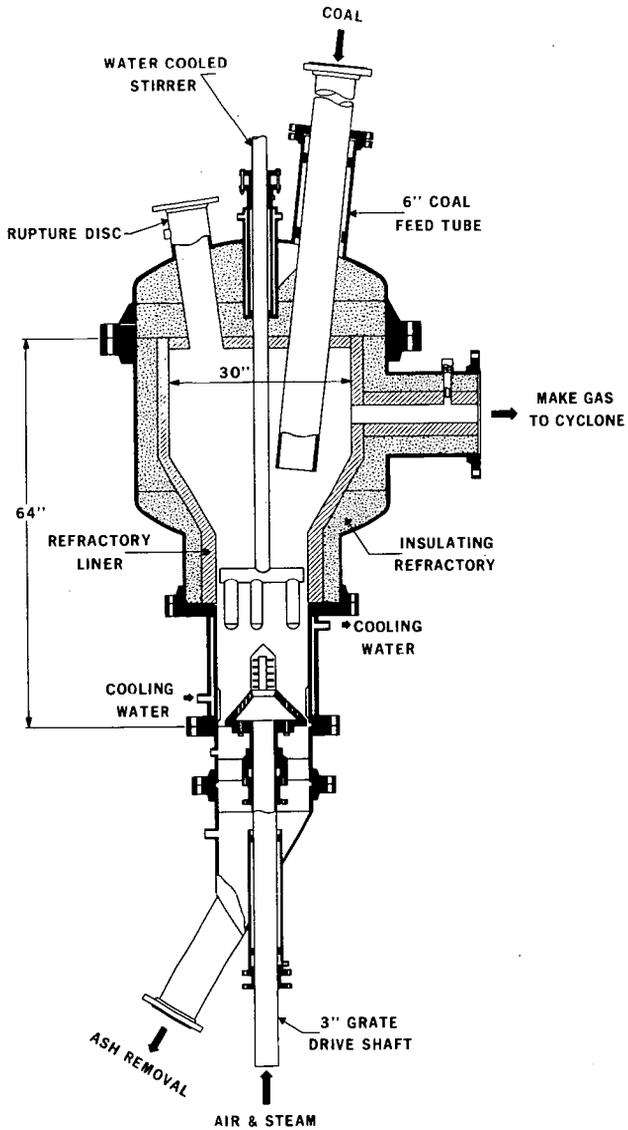


FIGURE 4. — 16-inch Gas Producer for Bench Scale Hot Gas Cleanup Facility. 88

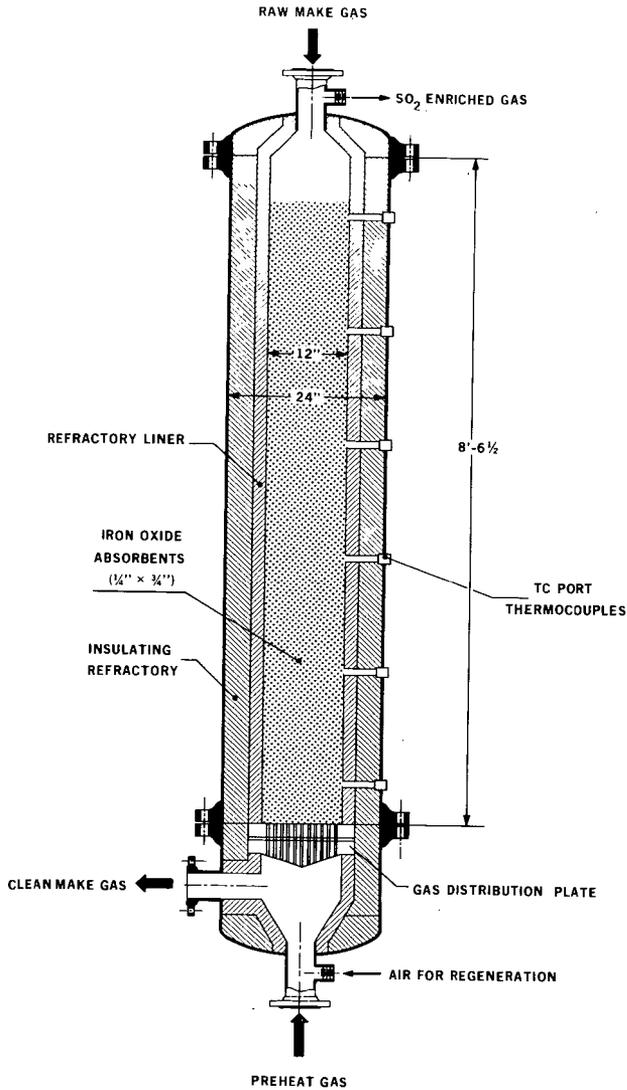


FIGURE 5. — 12-inch Absorber Vessel for Bench Scale Hot Gas Cleanup Facility.

Sorbent Composition	Physical Strength lb/cm	Surface Area m <sup>2</sup> /gm	H <sub>2</sub> S Sorption Capacity wt.-%
55% silica + 45% Fe <sub>2</sub> O <sub>3</sub>	75	2.5	16.1
55% silica + 45% Fe <sub>2</sub> O <sub>3</sub> + 1% bentonite	31	4.3	14.5
55% silica + 45% Fe <sub>2</sub> O <sub>3</sub> + 6 ml sodium silicate/lb	68	2.1	22.8
75% fly ash + 25% Fe <sub>2</sub> O <sub>3</sub>	16	0.9	11.5
75% fly ash + 25% Fe <sub>2</sub> O <sub>3</sub> + 1% bentonite	59	1.5	10.5
75% fly ash + 25% Fe <sub>2</sub> O <sub>3</sub> + 10 ml sodium silicate/lb	69	---	10.4

TABLE 1 — Data Indicating Effect of Additives On Sorption Capacity and Physical Strength

Total gas flow, std. cu. ft.	Gas flow rate, std. cu.ft./hr.	Run duration, hr.	Space velocity, vol/vol/hr.	H <sub>2</sub> S absorption			Total quantities through bed	
				Total grains	wt.-%	Efficiency pct.	Far. gas	Dust, gas
89.62	14.27	6.28	501	1118	10.35	92.5	31.5	.2
91.83	15.97	5.75	563	1193	11.04	95.0	30.8	.6
94.14	16.37	5.75	570	1180	10.92	93.5	28.2	.4
90.07	16.38	5.50	587	1135	10.51	93.1	33.5	.5
91.40	15.23	6.00	529	1159	10.73	94.2	32.3	.5
109.38	15.09	7.25	549	1332	12.33	92.2	33.4	.5

TABLE 2 — Typical Data From Six of Thirty Sorption Capacity Tests

Average Bed Temp.	616°F	672°F
Time to breakthrough, hrs	4.66	5.60
Producer gas flow rate, scfh	7500.00	7322.94
Space velocity, vol/vol/hr	2500	2450
Gas to breakthrough, scf	34,975	40,992
Total H <sub>2</sub> S absorbed, grams	6544.8	7711.2
Weight percent	6.43	7.60
Percent of total (using 100 grains/100 scf as breakthrough)	82.61	82.07

TABLE 3 — Sorption Data Obtained During Regeneration Study on Bench Scale Hot Gas Cleanup Facility

HIGH TEMPERATURE SULFUR REMOVAL SYSTEM DEVELOPMENT  
FOR THE WESTINGHOUSE FLUIDIZED BED COAL GASIFICATION PROCESS

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ABSTRACT

High temperature sulfur removal can be achieved with calcium based sorbents (e.g. dolomite) in fluidized bed coal gasification systems now being developed for power generation. The use of dolomite offers the opportunity to meet environmental emission standards, to minimize energy losses, and to reduce electrical energy costs.

In addition to achieving the removal of sulfur from the low Btu gas, the complete sulfur removal system must be integrated with the total power plant and environment to assure compatibility. Critical requirements to achieve a commercial system include establishing criteria for "acceptable" sorbents, establishing integrated sulfur removal/gasification process design parameters, predicting trace element release, predicting sorbent attrition, developing an economic regeneration and/or once-through process option, developing a spent sorbent processing system, and establishing safe and reliable disposition options for spent sorbent. Design and operating parameters are being developed and potential process limitations identified.

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This work is being performed as part of the Westinghouse Coal Gasification Program. The project is being carried out by a six-member industry/government partnership comprising ERDA, Public Service of Indiana, Bechtel, AMAX Coal Co., Peabody Coal Co. and Westinghouse. This work has been funded with federal funds from the Energy Research and Development Administration under contract E(49-18)-1514. The content of this publication does not necessarily reflect the views or policies of the funding agency.

## INTRODUCTION

The production of a low Btu fuel gas from coal for combined cycle electric power generation provides the potential for improved thermal efficiency and reduced power costs compared with conventional power plants with flue gas desulfurization and can provide acceptable environmental impact. The ability to produce the low Btu gas at elevated pressure (e.g. 1500 kPa) with removal of sulfur and particulates from the high temperature gas (e.g. 800-900°C) will enable the maximum thermal efficiency to be achieved. Calcium-based sorbents, such as limestone and dolomite, have been proposed for the high temperature sulfur removal.

Westinghouse has been working on the development of a multi-stage fluidized bed gasification process for combined cycle power generation since 1970.<sup>(1,2)</sup> The goal of the program is the integration and operation of a gasifier/power-generating plant on a scale which will demonstrate the commercial operation of the process. An integrated program is underway to proceed from bench-scale laboratory research through pilot scale development and system design and evaluation to the operation of a demonstration plant. The pilot development is now being carried out in a 15 ton/day process development unit.

Westinghouse is investigating gas cleaning systems for high temperature operation (800-900°C), intermediate temperature operation (e.g. 650°C), and low temperature operation. Work has been carried out on both sulfur removal and particulate control systems. This document is limited to an overview of the high temperature sulfur removal system development work on calcium-based sorbents. This system was selected for the base concept based on the potential for high system efficiency and the high kinetic efficiency of removing hydrogen sulfide under the proposed operating conditions with an economically available sorbent. Alternate systems, such as the use of iron oxide or low temperature processes, have not been excluded as candidates for the demonstration plant and are also being studied. An intermediate temperature process is attractive in that it reduces the materials problems while maintaining a relatively high plant efficiency.

The approach to the development of the calcium-based sulfur removal system includes laboratory experimental programs utilizing pressurized thermogravimetric analysis, pressurized fluidized bed reactors, and physical and chemical characterization to develop basic data and to develop screening techniques; data analysis to develop design criteria; systems analyses to assess the technical, economic, and environmental impact of alternate sulfur removal system concepts and to assess the impact of these alternatives on the total power plant.

#### SULFUR REMOVAL SYSTEM

The basic gasification process utilizing the high temperature calcium-based sorbent system is illustrated in Figure 1. The gasification process has been described.<sup>(1,2)</sup> The sulfur removal process options are indicated in Figure 1: in-bed desulfurization and external desulfurization. In situ desulfurization of the fuel gas within the recirculating bed devolatilizer combines the sulfur removal and coal devolatilization in a single vessel. This approach requires compatible coal and sorbent behavior and the ability to separate sorbent and char. The external desulfurizer requires a separate vessel and associated components but provides greater flexibility. Both systems are being assessed through process simulations, PDU operation, and engineering analyses.

Two basic sulfur removal systems have been identified and investigated: once-through sorbent operation and regenerative operation. The reference once-through system and regenerative system concepts are illustrated in Figure 1. An alternate once-through system concept is also indicated which has been considered. A number of spent sorbent processing and regeneration processes have been investigated. Similarly, a number of disposal and utilization options are available. These process alternatives will be discussed in the following sections. Other options such as pretreatment of the sorbent to improve its attrition behavior or sulfur capacity and the addition of "getters" to remove alkali metals to prevent gas turbine corrosion are also being considered.

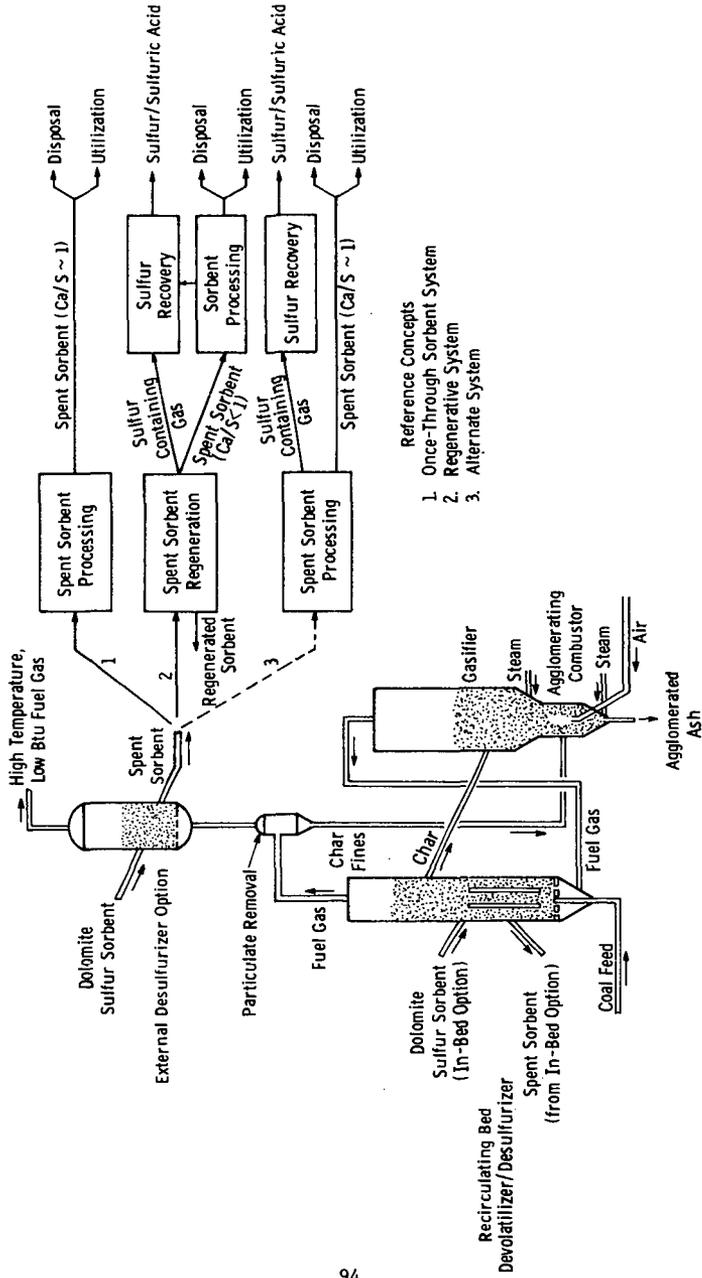


Fig. 1 —Westinghouse multistage fluidized bed gasification/desulfurization process utilizing calcium-based sulfur removal system

## SULFUR REMOVAL

Laboratory and engineering studies are being carried out to evaluate two areas critical to sulfur removal: sulfur removal process options and sorbent selection. These efforts parallel development work planned for the process development unit related to these areas.

### Process Options

The technical and environmental performance and economic aspects of sulfur removal process options are being evaluated in order to provide a basis for selection and to define process development requirements. Two major options have been identified: once-through sorbent operation versus regenerative sorbent operation and in situ (devolatilizer) desulfurization versus external desulfurization.

Both once-through sorbent and regenerative sorbent desulfurization behavior are being developed. The PDU is currently designed for once-through sorbent operation. Trade-offs between once-through and regenerative sulfur removal exist with factors such as sorbent consumption, sorbent attrition, trace element release, and system complexity and operability being important considerations.

### Sorbent Selection

Both limestone ( $\text{CaCO}_3$ ) and dolomite ( $\text{MgCa}(\text{CO}_3)_2$ ) can be used as sulfur sorbents under full gasification conditions at high fuel temperatures, but laboratory studies show that there are several factors which restrict their use under specific design conditions, and which impact on both the desulfurization process, and the overall power generation plant.

Limestone reacts with hydrogen sulfide only when it has calcined, a kinetic rather than a thermodynamic restriction.<sup>(3)</sup> For atmospheric pressure applications, calcined limestone should achieve 90% desulfurization of fuel gases at calcium to sulfur molar feed ratios of  $\sim 1.8/1$ .<sup>(4)</sup> Recent fixed-bed tests by the Bureau of Mines confirm this projection.<sup>(5)</sup> However for desulfurizing low Btu gas at pressure, calcium carbonate is the stable form of the reacting sorbent, and limestone is inactive.<sup>(6)</sup>

For dolomite, at Ca/S feed ratios of  $< 1.2/1.0$ , projections from laboratory data show that almost complete reaction of the calcium content may be attained while fixing 90% of the fuel sulfur in solid form, for particle sizes up to 2000 microns.<sup>(7)</sup> For larger particle sizes reaction is apparently limited by diffusion of reactant into the solid. No significant variation was noted in testing dolomites ranging from the relatively pure massive-grained Canaan dolomite (Connecticut), through the sucrose-type dolomites (Glasshouse, Ohio), to the impure Tymochtee dolomite (Ohio).<sup>(2c)</sup> Fluidized-bed tests by Conoco Coal Development Co.\* have demonstrated the excellent sulfur capture abilities of dolomite with simulated fuel gases.<sup>(8)</sup> The Bureau of Mines tests showed that half-calcined dolomite demonstrated improved sulfur removal at 1500°F over that noted at 1400°F.<sup>(5)</sup> However when they increased the desulfurizing temperature to 1600°F, they noted a drastic loss of desulfurizing action as the dolomite decomposed to the fully-calcined state. While this test has not been simulated in laboratory tests, precalcined dolomites have shown similar sulfidation reaction rates to those noted with half-calcined dolomite. Further tests are evidently required to explore this discrepancy.

The major limitations on using dolomites arise from trace-element emissions, attrition rates, and suitability for processing by direct air oxidation for disposal.

One of the major concerns in operating a gas turbine with the low Btu gas is the extent to which corrosion and erosion will limit the lifetime of the metal alloys used in the blades and stators.<sup>(2c)</sup> The alkali metals, particularly sodium, induce hot corrosion (accelerated oxidation or sulfidation attack of the metal) by depositing oxygen-excluding liquid films of sulfates on the metals. Dolomites contain sodium and potassium as impurities, and they are found both as clay mineral components, and as more volatile compounds - probably chlorides, in the carbonate rock. The range of these impurities in dolomites is enormous, e.g. Na (5-330 ppm), and K(5-6,500 ppm).<sup>(2c)</sup> Recent studies

\* Conoco Coal Development Co. and Consolidation Coal Co. are used in this paper. Consolidation Coal Co. is used when work was performed under that organizational name.

of the release of alkalis from dolomites into fuel gas have demonstrated that significant fractions of the alkali can enter the gas stream, and that this release is essentially complete within a short fraction of the expected sorbent residence times. (2c) The resulting alkali level in the turbine feed gas is substantially in excess of that permitted by current empirical specifications for oil-fired turbines (-10 ppb Na). There are several approaches which may be taken to avoid this problem. First of all, a low-alkali dolomite may be chosen as sulfur sorbent. This is likely to be the result of an unusually fortuitous selection of power plant site. Although the available analysis of dolomites show significant variations in alkali content within a particular geological stratum from quarry to quarry and from stratum to stratum within a quarry, the majority of the analyses are of sufficient vintage to be suspect. However we have noted a consistent increase in alkali content with increasing quarry depth, so that material quarried at a depth of 100 ft may contain one order of magnitude more alkali than that quarried near the surface. (9)

An alternative to selecting a "clean" dolomite, is to pre-heat the material to release the alkalis before using the stone as a sulfur sorbent. The bulk of the alkali release occurs within 20 minutes of heating the stone to ~870°C, and after this initial release the rate of alkali loss is extremely low. The third possibility is to add materials such as aluminosilicates to the sorbent bed, or at a particulate filtration stage to getter the alkalis. It should be emphasized that several critical questions cannot be satisfactorily answered without further research. The extent to which chlorine from the coal may strip alkalis from dolomite and coal char must be investigated. In addition the turbine tolerance to the combined presence of sodium and potassium requires further experimental and theoretical investigation. (2c) The chemical fate of minor elements such as the alkalis in coal gasification is not well known. Recent studies at the Bureau of Mines show considerable

release of chlorine to the gas phase - presumably as HCl. (2c) However the mass balance for alkalis in the input and output solids was not sufficiently precise to estimate the levels of alkali in the gas phase.

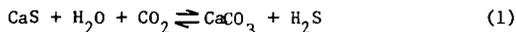
It should also be noted that the turbine tolerance to alkalis is theoretically a function of total chlorine (as HCl) levels in the gas phase. The combination of high chlorine and high alkali levels may avoid corrosive sulfate deposits. This apparent advantage will be limited by direct gaseous attack of the protective oxide scales on the turbine alloys.

#### SORBENT REGENERATION

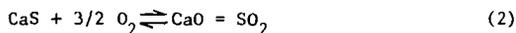
The consumption of sorbent by the power plant sulfur removal system may be minimized by utilizing a processing step to regenerate the utilized sorbent to an active form. Ideally the sorbent would be entirely reconstituted by the regeneration process, but in reality fresh sorbent will be required due to deactivation of the regenerated sorbent and attrition losses. Regeneration of the sulfided sorbent requires that the captured sulfur be converted to some other form, preferably elemental sulfur of commercial quality. The purge stream of spent sorbent must be processed to some environmentally acceptable or useful form. This combination of functions, sorbent regeneration-sulfur recovery-spent sorbent processing, must result in an integrated process which is compatible with the coal gasification process and is economically and environmentally acceptable.

##### Regeneration Process Options

A variety of potential regeneration process concepts have been evaluated for technical feasibility. Two concepts have been selected for further engineering assessment: (1) Sorbent regeneration by reaction of sulfided sorbent with steam and carbon dioxide to generate carbonated sorbent and a hydrogen sulfide gas stream; (2) sorbent regeneration by reaction of sulfided sorbent with oxygen to generate the oxide form of the sorbent and a sulfur dioxide gas stream. The chemical reactions are written, respectively.



and



##### Steam and CO<sub>2</sub> Regeneration Scheme

A schematic flow diagram for the sorbent regeneration system based on the steam and CO<sub>2</sub> regeneration reaction is shown in Figure 2. This process is also being evaluated by Consolidation Coal. (8)

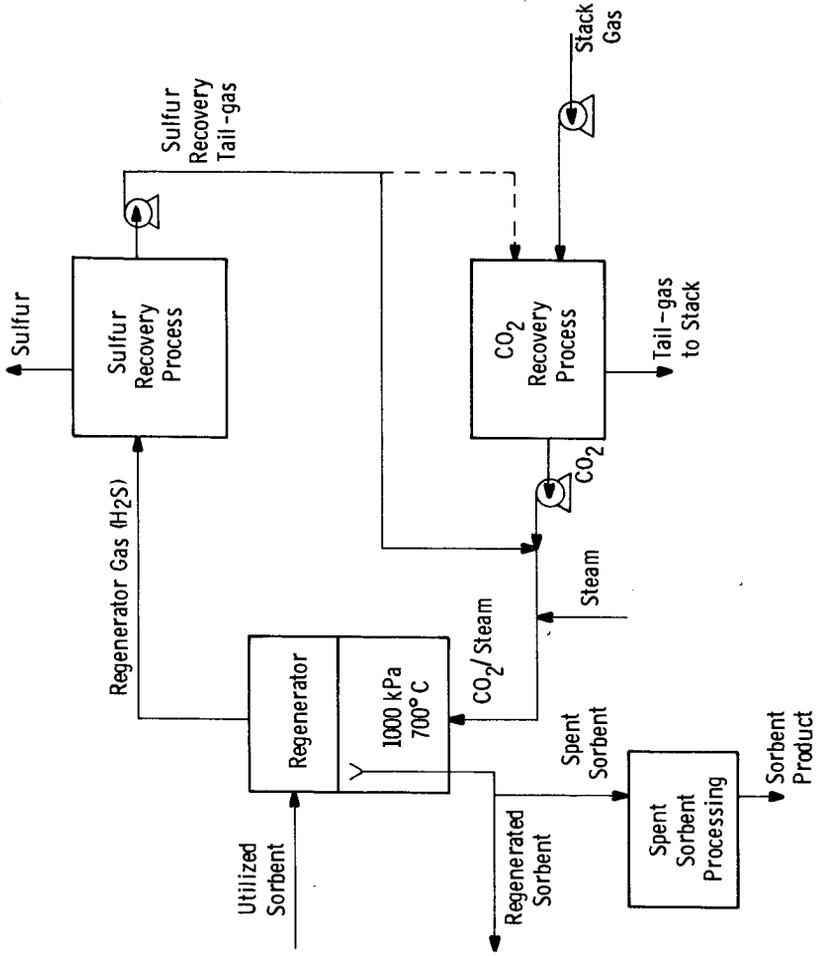


Fig. 2 — Sorbent regeneration by steam and CO<sub>2</sub> reaction

Three major components are involved in the sorbent regeneration system: the regenerator reaction vessel, the sulfur recovery process and the CO<sub>2</sub> recovery process. A number of commercial processes are available for sulfur recovery from H<sub>2</sub>S gas streams. The specific process selection will depend largely on two factors - the level of H<sub>2</sub>S in the regenerator gas and the optimum scheme for steam and CO<sub>2</sub> utilization. An H<sub>2</sub>S volume percent of about 15% will permit the application of conventional Claus process technology. Lower H<sub>2</sub>S concentrations will require either preliminary concentrating of the H<sub>2</sub>S-gas, followed by Claus sulfur recovery, concentrating and recycle of the Claus plant tail-gas, or application of alternate sulfur recovery processes suitable for low H<sub>2</sub>S concentrations such as the Stretford process (Ralph M. Parsons Co. and Union Oil Co. of California).

Make-up CO<sub>2</sub> for the regeneration reaction can be supplied by power plant stack gas purification. A portion of the sulfur recovery tail-gas may also require purification in order to maintain low levels of impurities (N<sub>2</sub>, O<sub>2</sub>, etc.) in the CO<sub>2</sub>/steam reactant stream. Numerous commercial processes are available for CO<sub>2</sub> recovery - Selexol, Benfield, Catacarb, Sulfinol, and many others. The economics and environmental performance of each of these processes will differ for this application and require evaluation.

The single most important factor influencing the economics and performance of this regenerative scheme is the regenerator gas H<sub>2</sub>S concentration. The size of the regenerator reaction vessel, the size and complexity of the sulfur recovery process, and the rate of steam consumption and auxiliary power usage all increase as the H<sub>2</sub>S concentration is reduced. Estimates of the H<sub>2</sub>S concentration based on reaction kinetics and thermodynamics are about 3-5 volume %.

Other factors such as regenerated sorbent activity, the required rate of sorbent circulation, the effect of the regeneration process on the power plant availability, etc., are also important to the process feasibility.

### Oxygen Regeneration Scheme

A schematic flow diagram of the sorbent regeneration system based on the oxygen regeneration reaction is shown in Figure 3. An atmospheric pressure version of this process has been applied by Esso (U.K.) for their CAFB gasification process.<sup>(10)</sup>

This regeneration process is conceptually simpler than the steam/CO<sub>2</sub> regeneration process since only two major process components are involved: the regenerator reaction vessel and the sulfur recovery process. On the other hand, the oxygen regeneration process is necessarily a higher temperature regeneration scheme with the potential for greater sorbent deactivation. The regenerator could be operated at pressures of 200 to 1000 kPa (2 to 10 atmospheres) and temperatures of 1000 to 1100°C with SO<sub>2</sub> volume percents of 2 to 4 expected for the high pressure system and up to 10% for the low pressure system.

Sulfur recovery from dilute SO<sub>2</sub> streams is generally more expensive and complex than from dilute H<sub>2</sub>S streams. The most highly commercialized sulfur recovery process for this application is the Allied Chemical direct reduction process (using methane or clean liquid fuels as reductant) which will work effectively on SO<sub>2</sub> streams down to about 4 volume % SO<sub>2</sub> depending upon the oxygen content of the gas.<sup>(11)</sup> For lower SO<sub>2</sub> concentrations a commercial concentrating step such as the Wellman-Lord process must be used. Other sulfur recovery processes applicable to SO<sub>2</sub> streams which are in early stages of commercialization are the Foster Wheeler RESOX process (which uses coal as the SO<sub>2</sub> reductant), the ASARCO-Phelps Dodge process, the Bureau of Mines Citrate process, the Westvaco activated carbon process, and the Stauffer Aquaclus process.

While the low pressure oxygen regeneration results in a much greater SO<sub>2</sub> concentration in the regenerator gas, the technological and reliability problems involved in circulating the hot sorbent between vessels with greatly different operating pressures may not be easily overcome. Again, as in the steam/CO<sub>2</sub> regeneration process,

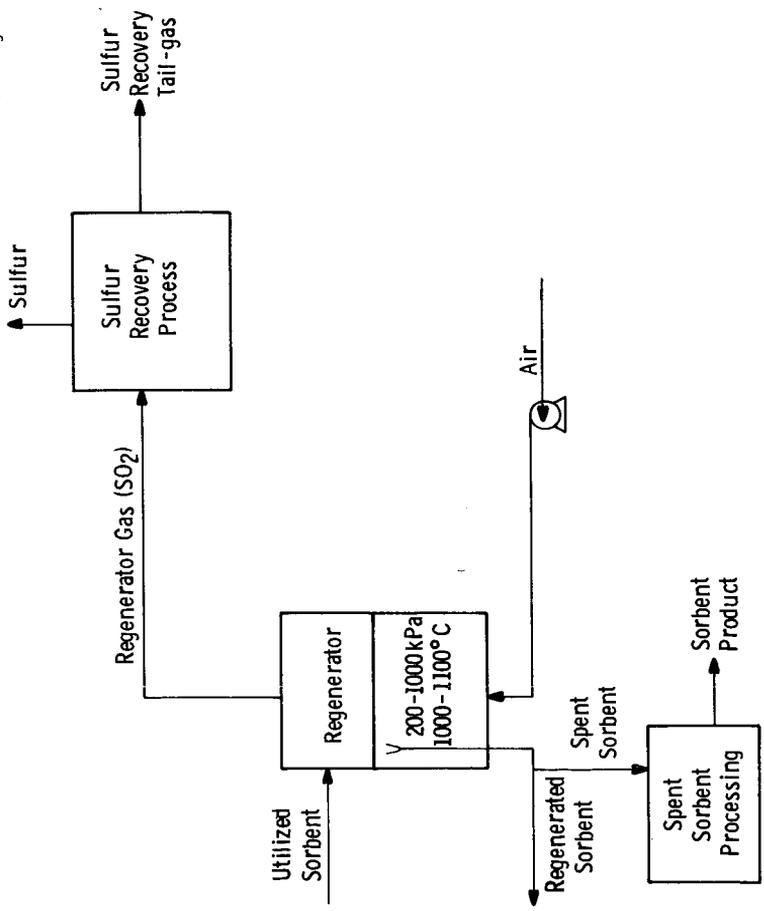


Fig. 3 - Sorbent regeneration by oxygen reaction

the concentration of the sulfur-bearing species in the regenerator gas has a dominant influence on the economics and performance of the regeneration system. Increased operating temperatures will provide greater  $\text{SO}_2$  concentrations (thermodynamically) but may increase sorbent deactivation.

The overall economics, technical performance and environmental impact of these two sorbent regeneration concepts must be evaluated in order to determine the feasibility of sorbent regeneration, in order to select the most promising regeneration scheme and in order to identify the optimum components to be utilized in the regeneration scheme. The critical interfaces between the coal gasification system, the power generation system, the spent sorbent processing system and the sorbent regeneration system are being considered in the evaluation.

#### Regeneration Chemistry

It was noted by Mellor<sup>(12)</sup> that the equilibrium  $\text{CaS} + \text{H}_2\text{O} + \text{CO}_2 \rightleftharpoons \text{CaCO}_3 + \text{H}_2\text{S}$  cannot be used to reform calcium carbonate, because of the low concentration of hydrogen sulfide produced. This problem may be overcome by carrying out the reaction at pressure.<sup>(13)</sup> However the early work by Pell<sup>(14)</sup> showed that calcium sulfide is rapidly deactivated, and TG studies show that only 20% of the calcium sulfide is readily converted to calcium carbonate after 10 cycles of sulfidation/regeneration, at 704°C.<sup>(b)</sup>

An encouraging feature is that the rate of sulfidation decreases very slowly as the stone is recycled and the regenerated sorbent is almost as reactive as fresh stone.<sup>(6)</sup>

The initial rate of regeneration is very fast and is apparently limited by production of the equilibrium level of hydrogen sulfide, since the initial rate increases on dropping the temperature from 700°C to 650°C. However, when the regeneration has proceeded to a certain stage (50% after 2 cycles, or 20% after 10 cycles), the rate

falls off by more than one order of magnitude. At this stage the rate can be increased by increasing the reaction temperature, so that at 870°C, all the sulfide is readily regenerated. However, the equilibrium concentration of H<sub>2</sub>S becomes so unfavorable that this is not a technically feasible solution.

The deactivation of calcium sulfide thus becomes a chemically limiting step in regeneration. An additional clue to the mechanism of deactivation is given by the fact that when calcium sulfide is prepared by reduction of calcium sulfate, at 820 or 850°C, for 2 hours, only 26% of the calcium sulfide is regenerable.<sup>(15)</sup> This increased deactivation may be partly due to the longer residence time at higher temperatures than is customary in sulfidation reactions, since sulfidation takes about 15 minutes. Recent studies by Sun<sup>(16)</sup> have shown that longer exposure at high temperatures (871°C) during sulfidation, reduces the extent of regeneration, as does increasing the temperature of sulfidation to 950°C, while lowering the sulfidation temperature to 750°C increases the extent of regeneration. The deactivation of the calcium sulfide is always accompanied by some growth of calcium sulfide particle size, and by extensive growth of magnesium oxide crystallites in proximity to the calcium sulfide as determined by X-ray diffraction line-widths.

It can be concluded that a continuous regeneration system must operate with a low sulfur differential between the calcium sulfide content of the desulfurizer and regenerator exit streams.

Squires<sup>(17)</sup> has demonstrated that the extent of regeneration improves dramatically with partial pressures of steam of 15 atmospheres, and that 50% of the calcium sulfide is regenerable. While his sulfidation reaction conditions (700°C) may not have been severe enough to cause growth of the magnesium oxide around the calcium containing crystallites, the improved diffusivity of the reactant gases through the solid caused by raising the H<sub>2</sub>O/CO<sub>2</sub> ratio may significantly improve the extent of regeneration before the reaction rate dwindles. Pell's

experiments carried out at a 1/1 ratio at 15 atm indicate little if any improvement over the TG value for extent of regeneration. The average extent of regeneration for 20 cycles is ~13%, so that each mole of calcium will remove 2.7 moles of sulfur via the regenerator, and one mole of sulfur via the spent sorbent stream.

The calcium to sulfur molar make-up feed rate required is therefore 0.25/1 unless attrition losses are greater than 5% of the total calcium per cycle, in which case reducing the attrition loss becomes more important than improving the regenerability of the stone. Consolidation Coal Co. (8) have reported attrition loss rates of less than 1% per cycle; however it is not known if such performance can be projected to large scale units.

#### SPENT SORBENT DISPOSITION

The once-through and regenerative process options will produce a dry, partially utilized dolomite or limestone with particles up to 6 mm in size. In addition, fine particles of sorbent (with some ash and char) will be collected in the gas particulate collection systems. The composition of the sorbent for disposition will depend on the characteristics of the original stone, the coal feed, the selection of the sorbent processing system, and the process operating conditions. The major compounds in the waste stone from the desulfurizer or regenerator utilizing dolomite are calcium carbonate ( $\text{CaCO}_3$ ), magnesium oxide ( $\text{MgO}$ ), and calcium sulfide ( $\text{CaS}$ ). Trace elements from the sorbent and coal will also be present.

Direct disposal or utilization of this material is not considered to be an option which will be generally available. Thus, processing of the spent sorbent has been incorporated in the sulfur removal system. The ultimate selection and development of a spent sorbent processing scheme will depend on many factors related to the development of the desulfurization system and the regeneration system. These factors will determine the nature of the spent sorbent and the processing required for the spent sorbent processing system. Among the factors that will affect the disposition of the sorbent are the quantity of spent sorbent, its chemical characteristics, regulations, geographical location, and the market size in the case of utilization.

#### Processing

A variety of spent sorbent processing schemes have been identified which could potentially convert the spent sorbent produced in a once-through or regenerative operation into a material suitable

for direct disposal or utilization. (4,19) Processing alternatives have been developed to convert calcium-based sorbents containing calcium sulfide to environmentally acceptable forms for disposal or utilization. Work by Westinghouse on the CFB fluidized bed gasification/desulfurization process, under contract to EPA, has identified spent sorbent processing options. (4) Experimental programs are now being carried out as an extension of this work to permit technical and economic assessments of these processes. These tests will provide information directly applicable to the subject coal gasification/desulfurization process. Spent sorbent processing systems being considered include dry oxidation, oxidation plus carbonation, deadburning, slurry carbonation, dry sulfation, high temperature processing with coal ash, and low temperature processing with coal ash.

A dry oxidation process which converts the spent sorbent (calcium sulfide) from a once-through or regenerative operation into a calcium sulfate material has been selected as the base spent sorbent processing scheme. Experimental studies and process studies for the dry oxidation process are being performed as part of the current program.

Thermogravimetric studies of the direct oxidation of calcium sulfide to calcium sulfate have revealed some important features of the reaction which must be considered in process evaluation.

First, in most dolomitic stones, complete oxidation of the sulfided stone occurs rapidly in air at 800°C; while sulfided limestones containing more than 30 molar % CaS and the sulfides of large-grained dolomites are oxidized incompletely.

Secondly, the reaction is extremely exothermic,  $\Delta H_{298} = -912 \text{ kJ mole}^{-1}$ , and if the temperature of the reacting solid is permitted to rise to higher temperatures, sulfur dioxide will be

emitted by one of two mechanisms. In the first mechanism direct oxidation to the oxide may occur:  $\text{CaS} + 3/2 \text{O}_2 \rightarrow \text{CaO} + \text{SO}_2$ . However if low partial pressures of oxygen are developed in the system as a result of the primary reaction, then calcium sulfide and calcium sulfate interact to reject sulfur dioxide according to the reaction



By carrying out the oxidation reaction in a fluidized bed reactor at 800°C in excess air, both of these competing reactions may be avoided. In thermogravimetric tests at 800°C, sulfur dioxide transients in the exit gas stream were accompanied by temperature excesses. Typically 32 moles of cold air per mole of calcium are required for heat balance in a system operating at a 2/1 calcium to sulfur mole ratio in the desulfurizer. Because of the large excess of air entering the system, >3X stoichiometric, the particles should oxidize at much the same rate as they do in the TG apparatus; stone residence times greater than 30 minutes are projected to ensure that oxidation is almost complete (>90%).

The third feature of this reaction is that regenerated stone which has experienced multiple sulfidation/regeneration cycles is not completely oxidizable. A function of the calcium sulfide which is inert in the regeneration reaction is also inert in the oxidation reaction.

Based on the information available, the dry oxidation process is considered attractive for once-through operation with most dolomites. This process does not appear as attractive for once-through operation with limestones or for regenerative operation. The primary concern is the environmental impact from sorbent disposal. Further work is required to permit a comprehensive assessment of dry oxidation. Work is proceeding to investigate other processing options.

### Disposal

The environmental impact of any disposed material is a function of its physical and chemical properties and the quantity involved. Two disposal alternatives will be investigated: land and ocean dumping. Environmental impact tests are planned to study the direct disposal of material from the spent sorbent processing system. These tests will be carried out using material produced in laboratory units to investigate the affect of operating conditions and in the process development unit to determine the environmental impact from material produced in the integrated process.

Westinghouse has carried out environmental impact tests on related materials as part of the CAFB fluidized bed gasification and the fluidized bed combustion programs being carried out under contract to EPA. (4,18;19,20) Leaching and activity tests have been developed at Westinghouse to assess the potential water contamination and heat release from disposing a spent bed limestone directly from a gasification process and from the spent limestone after further processing. These studies indicate the leachability and activity can be significantly reduced by further processing. Spent dolomite from fluidized bed combustion processes has also been tested<sup>(18)</sup> which indicates that if the calcium sulfide in the dolomite can be converted to calcium sulfate through the dry oxidation process, the material will be environmentally acceptable.

### Utilization

The direct disposal of sorbent may not be possible or permitted in all cases. Utilization of spent sorbent is an alternative which has the potential to provide technically and economically attractive by-product. Potential applications of processed or unprocessed spent sorbent include soil stabilization, land fill, concrete, refractory brick, gypsum, municipal waste treatment. Preliminary work has been carried out in this area. (4,20,21)

## ASSESSMENT

High temperature sulfur removal with a fluidized bed coal gasification system appears attractive based on available information. A number of processing options are being developed which consider integration of the sulfur removal system with a low Btu gasification - combined cycle power plant and consider the total sulfur removal system from sorbent selection to sorbent disposition. Assessment of the sulfur removal system includes:

Sulfur Removal: Dolomites are the preferred sorbent for the Westinghouse coal gasification process. Sulfur removal efficiencies of 90% are projected with mean particle sizes between 1000 and 2000  $\mu$  and a calcium to sulfur molar ratio of 1.2/1.0 for a once-through system. Combined devolatilization/desulfurization is considered attractive but compatibility must be demonstrated. The external desulfurizer option offers an alternative with greater flexibility. There appear to be ample supplies of dolomite available.

Sorbent Regeneration: Two regeneration concepts have been selected for further study. Regeneration by carbon dioxide and steam is technically feasible and is the preferred option. Calcium to sulfur molar feed make-up is projected to be 0.25/1 based on attrition losses < 5% of the sorbent per cycle. Commercial technology is available for sulfur recovery from dilute  $H_2S$  or  $SO_2$  gas streams and for  $CO_2$  recovery. Advanced systems, which may reduce costs, are not being incorporated into the current development effort.

Spent Sorbent Disposition: In general, spent sorbent processing will be required for once-through or regenerative operation due to the calcium sulfide present in the sorbent. Alternate processing schemes are under investigation to permit disposal or utilization of the material.

A dry oxidation process is attractive for once-through operation with most dolomites. Preliminary oxidation tests and environmental impact tests indicate this processing option will be economic and environmentally acceptable. Preliminary tests on related materials indicates utilization of the spent sorbent may be practical.

Sorbent Selection: General factors to be considered in the selection of a sorbent are the desulfurization performance, the sorbent regenerability, the spent sorbent properties, sorbent attrition behavior and trace metals release behavior. Sodium, potassium, and chlorine release is of particular importance to control gas turbine corrosion. Trace metals release to the fuel gas may be controlled by selecting a "pure" sorbent, pretreating the sorbent or utilizing a getter in the fuel gas cleaning system. Available data indicate the trace elements can be controlled to meet turbine protection requirements. Further work is required to specify the preferred method of operation.

A once-through sulfur removal system utilizing dolomite with a dry oxidation spent sorbent processing system has been selected for the reference design. Further development evaluation of the technical performance, economics, and environmental impact of the alternative sulfur removal systems under consideration must be carried out to select the most promising system. The integration of the alternative processing schemes into an optimum high temperature sulfur removal system which is compatible with the coal gasification power plant is the object of the development effort.

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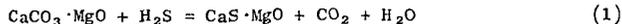
## REACTION OF H<sub>2</sub>S WITH HALF-CALCINED DOLOMITE IN A REGENERABLE PROCESS

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### Introduction

The Conoco hot desulfurization process makes use of the reaction of half-calcined dolomite with H<sub>2</sub>S,



to remove H<sub>2</sub>S from a fuel gas and also to regenerate sorbent dolomite. The Conoco gasification process yields a gas fairly high in H<sub>2</sub>O, about 13%. This necessitates a high desulfurization temperature if a goal of 95% desulfurization is to be met. The conditions called for in the current design are as follows:

Desulfurization: 914°C; 13% H<sub>2</sub>O, 8% CO<sub>2</sub> inlet; 0.02% H<sub>2</sub>S exit  
Regeneration: 704°C; 35% H<sub>2</sub>O, 64% CO<sub>2</sub> inlet; 3.6% H<sub>2</sub>S exit

The entire process runs at 15 atmospheres. Desulfurization operates at the equilibrium H<sub>2</sub>S concentration, and regeneration is assumed to operate at about 90% approach to equilibrium. The above conditions provided the base case point about which experimental work was conducted. However, equipment limitations required the desulfurization temperature to be reduced to 871°C for most of our work.

### Continuous Cycling Runs

Experiments were carried out in a three-inch diameter gas desulfurizer and a two-inch diameter regenerator. Both vessels contained fluidized beds and were continuously fed with both gas and solids. Details of the experimental technique have been given elsewhere.<sup>(1,2)</sup> Dolomite was cycled through the vessels for numerous cycles so that the nature of the decline in activity could be studied. Detailed data on the conditions of these cyclic runs are presented in Tables 1 and 2.

It was found that the desulfurization reaction proceeded rapidly, and that a low concentration of H<sub>2</sub>S was maintained until the supply of CaCO<sub>3</sub> was essentially exhausted. However, the regeneration reaction was incomplete, typically yielding but a fraction of the original CaCO<sub>3</sub> in an hour's residence time.

The regeneration activity, defined as mols CaCO<sub>3</sub> produced/100 mols CaS fed, declined as the stone was cycled. The activity decline is pictured in Figure 1. It can be seen that the decline is logarithmic in character. Thus, although a severe decline occurs in cycles 1 to 10, the stone contains modest residual activity even out to 100 cycles. This means that a regenerable process is feasible. The data presented in Figure 1 are for Canaan dolomite, our base case stone. Similar data were obtained for other dolomites.

Figure 2 presents deactivation data for three regeneration temperatures. The data lines are roughly parallel, but this is believed to be fortuitous and unlikely to hold for all conditions. The data indicate that at 593°C, the fractional regeneration is quite low, amounting to less than 10% within only 7 cycles. Only at low regeneration temperatures is the equilibrium H<sub>2</sub>S concentration high enough for processing by a conventional Claus process. The Conoco process, however, uses a liquid-phase Claus reaction which is uniquely suited to handling low H<sub>2</sub>S concentrations. Our interest therefore centered around the 704°C temperature where stone utilization is higher.

TABLE I

Conditions and Results for Gas Regalizer with Canaan Dolomite Feed

System Pressure: 15 atm (206 psig)  
System Temperature: 871°C (1600°F)

Run Number	A7	A13	A15	A20A	A21	A22A	A36A
Canaan Dolomite Batch Number	1	35	48	2	2	20 x 28	2120
Acceptor Size Consist, Tyler Mesh	28 x 35	3040	1500	1810	1840	1892	42
Feed Rate, gm/hr (half-calculated basis)	33	32	65	52	51	50	42
Nominal Solids Residence Time, min							
Inlet, SCFH <sup>(1)</sup>	175	178	178	148	148	148	310
Recycle to Bed							
H <sub>2</sub> O	33	33	33	21	21	21	90
H <sub>2</sub>	40	40	40	25	25	25	90
CO	33	33	33	23	23	23	55
CO <sub>2</sub>	21	21	21	8.3	8.3	8.3	52
N <sub>2</sub>	96	96	96	66	66	66	152
H <sub>2</sub> S	3.5	3.5	1.8	1.6	1.6	1.6	1.8
Purges (CO <sub>2</sub> ) to Bed				5			
Purges (N <sub>2</sub> ) above Bed				15			
Recycle Acceptor Lift Gas, above Bed				71			110
Output in Cycle No.	2	6	1	23	18	8	4
Exit Gas Rate, SCFH (dry basis)	215	213	215	143	144	144	338
Composition, Mol %							
H <sub>2</sub>	17	17.5	18.2	16.5	16.6	16.6	17.5
CO	18	17.9	18.0	17.0	16.8	16.1	17.0
CO <sub>2</sub>	12	9.9	9.7	9.8	9.9	10.3	9.4
N <sub>2</sub>	53	54.4	54.0	56.6	56.3	57.0	56.0
H <sub>2</sub> S	0.05	0.207 <sup>(2)</sup>	0.048	0.03	0.03	0.03	0.04
Outlet Gas, Top of Bed							
Composition, Mol %							
H <sub>2</sub> O	9.7	10.0	9.5	8.1	8.0	8.5	8.3
H <sub>2</sub>	15.4	16.4	17.1	16.0	16.1	16.0	16.5
CO	15.9	16.8	16.9	16.3	16.3	15.5	16.0
CO <sub>2</sub>	11.2	9.3	9.2	9.5	9.6	10.0	8.9
N <sub>2</sub>	47.7	47.3	47.3	49.9	49.6	50.0	50.3
H <sub>2</sub> S	0.046	0.194	0.045	0.029	0.029	0.029	0.038
Flow Rate, SCFH, Top of Bed	416	418	418	300	301	303	690
Fluidizing Velocity, ft/sec	0.33	0.33	0.33	0.43	0.43	0.43	0.89 <sup>(3)</sup>
Attrition % of Feed Rate	0.7	0.77	0.89	0.68	0.68	0.68	1.45
Duration of Circulation with H <sub>2</sub> S Feed, hr	25.2	35.1	42.7	11.7	14.5	8.9	71
Removal of Feed Plus Recycle Sulfur, %	95.3	79	90	94.6	94.5	94.5	86.7
% H <sub>2</sub> S in Outlet/Equilibrium % H <sub>2</sub> S	1.4	6.8	1.7	1.3	1.3	1.1	1.7
Conversion of Acceptor/Pass, Mol % of Total Cs	19	16	18	13.8	13.6	13.2	12.6

(1) Inlet is given after shift reaction and hydrolysis of CS<sub>2</sub> have taken place.  
(2) Gas sample taken after breakthrough had occurred.  
(3) Includes 20-30% +100 mesh particles.

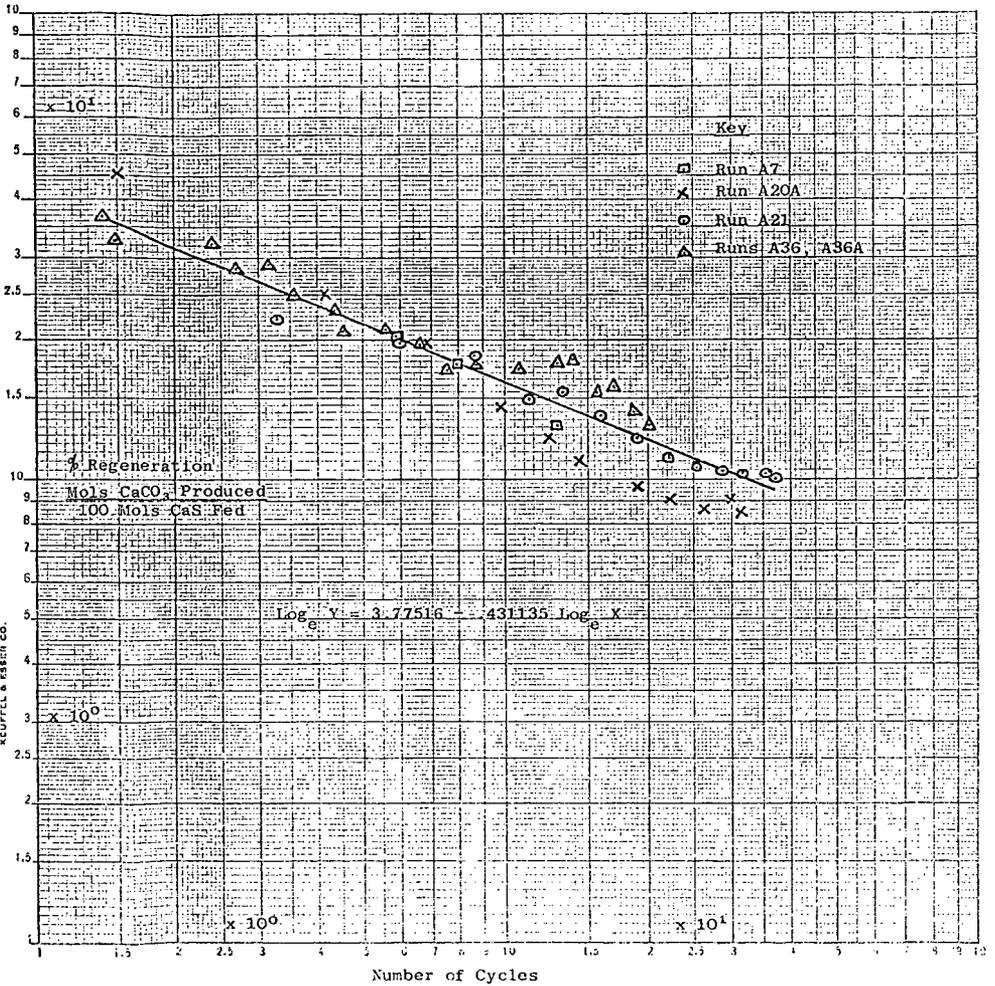
TABLE 2

Conditions and Results for Regenerator with Canmat Dolomite Feed  
System Pressure: 45 atm (200 psig)

Run Number	A7	A15	A16	A20A	A21	A22A	A35A
Temperature, °C (°F)	704 (1300)	593 (1100)	593 (1100)	704 (1300)	704 (1300)	760 (1400)	704 (1300)
Nominal Solids Residence Time, min.	37	36	74	60	59	57	52
Innit. SCFH	0.0						
Recycle to Bed	0.0						
H <sub>2</sub> O	110	100	109	53	102	0.0	0.0
H <sub>2</sub>	0.0	12	12	8.0	47	48	108
CO <sub>2</sub>	110	118	118	91	3.0	8.0	11
Purges (H <sub>2</sub> ) to Bed	8	8	8	7	50	86	205
Purges (N <sub>2</sub> ) above Bed	10	10	10	10	10	10	10
Purges (CO <sub>2</sub> ) above Bed	5	5	5	4	0.0	10	0.0
					15	4.5	15
Output in Cycle No.	1	6	1	23	18	8	4
Exit Gas Rate, SCFH (dry basis)	133	194	152	120	33	116	236
Concentration, Mol %							
H <sub>2</sub>	ND	8.0	8.3	5.0	3.9	3.9	2.1
CO	ND	0.76	1.01	3.95	5.2	3.7	2.6
CO <sub>2</sub>	85.7	78.4	77.4	71.8	83.1	71.4	94.1
N <sub>2</sub>	13.5	11.4	12.8	18.3	5.2	19.4	0.6
H <sub>2</sub> S	0.7	1.41	0.46	0.82	2.54	0.94	0.62
COS	ND	0.02	Trace	0.04	0.11	0.04	0.03
Outlet Gas, Top of Bed							
Composition, Mol %							
H <sub>2</sub> O	46.3	41.6	44.1	32.9	29.0	32.9	33.5
H <sub>2</sub>	--	5.15	5.14	3.8	3.1	3.0	1.5
CO	--	0.49	0.63	3.0	4.1	2.8	1.8
CO <sub>2</sub>	47.8	48.5	46.0	52.0	57.5	51.8	62.4
N <sub>2</sub>	3.5	3.2	3.9	7.6	4.1	8.3	0.4
H <sub>2</sub> S	0.4	0.91	0.28	0.82	2.03	0.72	0.44
COS	--	0.01	Trace	0.03	0.09	0.031	0.02
Flow Rate, SCFH Top of Bed	298	238	245	159	159	151	333
Fluidizing Velocity, ft/sec	0.63	0.60	0.61	0.44	0.47	0.44	0.92
% H <sub>2</sub> S in Outlet/Equilibrium % H <sub>2</sub> S	0.99	0.94	0.91	0.18	0.61	0.43	0.11
Regeneration of Acceptor/Pass, Mol % of Total Ca	5.1	11.5	7.5	8.8	7.4	9.3	11.0

ND - Not determined.

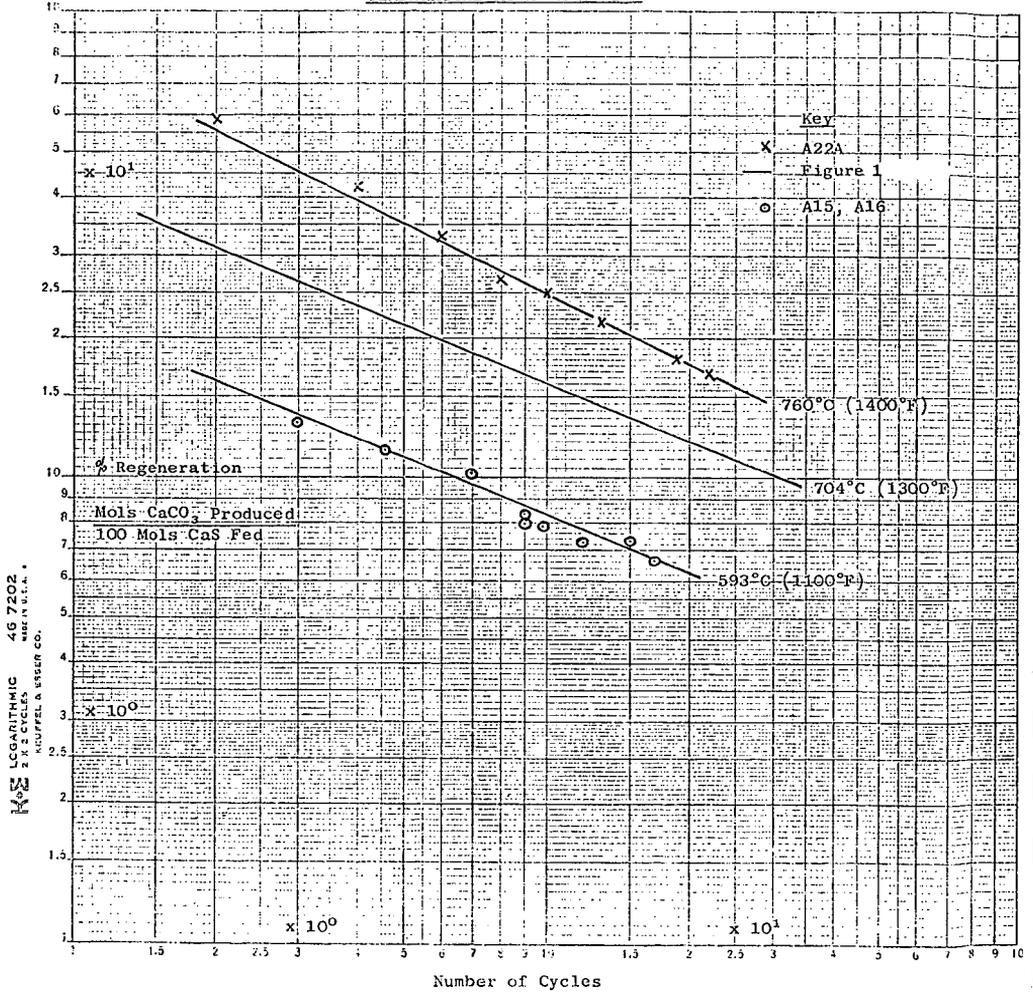
**FIGURE 1**  
**DEACTIVATION OF CaS IN CANAAN DOLOMITE**  
**AT 704°C (1300°F)**



46-7203  
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 2 X 2 CYCLES  
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FIGURE 2

DEACTIVATION OF CaS WITH  
TEMPERATURE AS A PARAMETER



### Batch Regeneration

As a limiting step appeared to be regeneration, a batch regeneration program was set up to further explore the variables affecting the system. Results of these runs are given in Table 3. A statistical analysis of the data showed percent regeneration to increase with increasing temperature and decreasing age of stone. The effect of increasing temperature causing an increase in conversion was more pronounced for cycled stone than for fresh stone.

The effect of bed depth was unusual. It was expected that since the deeper bed ran at an  $H_2S$  outlet concentration closer to equilibrium, there would be less driving force for reaction and the regeneration conversion would be lower. In all six test pairs exactly the opposite was found. The runs with the deeper beds, i.e., higher  $H_2S$  outlet concentration, gave higher conversions. This is consistent with earlier conclusions that increasing the  $H_2S$  concentration does not adversely affect conversion in the regenerator.

In the course of running cyclic operations, the  $H_2S$  concentration in the outlet gas of the regenerator ranged from about 10% to 100% of the equilibrium value, and there was no detectable change in the rate of regeneration as the  $H_2S$  content approached equilibrium. It had been concluded that there would be no difficulty in running the regenerator close to the equilibrium  $H_2S$  concentration in the outlet gas.

### Regeneration Kinetics

Regeneration kinetics were examined by recording the  $H_2S$  concentration in the exit gas as a function of time as the batch runs progressed. The total mols of  $H_2S$  produced were normalized to match the total mols of CaS reacted, and conversion as a function of time was then plotted. These results are presented in Figures 3 to 5 in the form of  $(1 - X)$  versus time, where X is the fractional conversion of the CaS feed.

In all cases, the rate continuously decreased. It appeared that the reaction would eventually cease while there was still considerable CaS left. This is consistent with the notion that much of the CaS is simply unreactive. The initial reaction rate was faster for fresh stone than for cycled stone at all temperature levels. Additionally, the rate seemed to slow sooner for the cycled stone. The curves also show that the effect of bed depth is present even at the early stages of all reactions; the deeper beds had a higher reaction rate at all times.

While the reaction kinetics are complicated, they may be approximated by a simple first order rate constant for the short times (about an hour) of interest to the process. The reaction model would then be:

$$Kt = -\ln(1 - X)$$

where  $K$  = rate constant,  $hr^{-1}$ , whose function of gas concentration is yet to be determined.  
 $t$  = time, hours  
and  $X$  = fractional conversion of the CaS fed.

The value of  $K$  was taken from the slope of the data from 5 to 50 minutes in Figures 3 to 5, and is tabulated in Table 4. The data of Table 4 are plotted in Figure 6. The activation energies for cycled and fresh stone are shown to be the same, about 19 kilocalories.

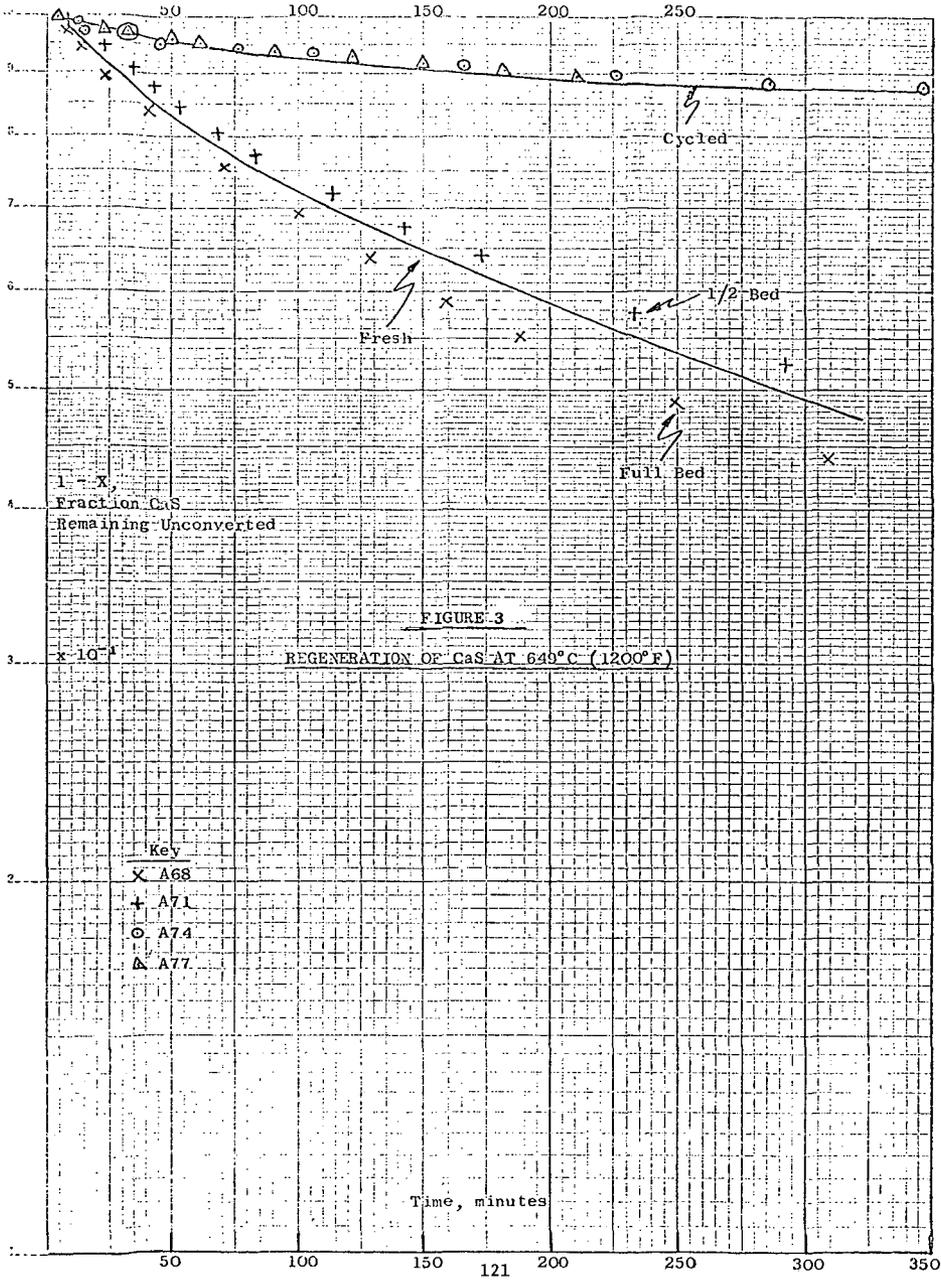
The kinetic mechanism proposed here allows one to calculate the effect of changing conditions of temperature or residence time upon fractional conversion of CaS (percent regeneration).

TABLE 3

Results of Regenerator Runs  
All Runs 15 atm, 60% CO<sub>2</sub>, 35% H<sub>2</sub>O Inlet

Run No.	Dolomite	Bed Height, inches	Regeneration %	Equilibrium, %	Maximum Approach to Equilibrium, %	Run Time, hours	Maximum Dry Basis, % H <sub>2</sub> O	Temperature, F (C)	Gas Residence Time, sec	10 <sup>3</sup> x Moles CaS Available Moles (CO <sub>2</sub> + H <sub>2</sub> O)/hr
A68	Sulfided	35.3	61.6	13.0	1.77	7.2	1200 (649)	4.9	20.6	
A69	Fresh	36.1	41	47.4	2.78	8.0	1300 (704)	4.7	24.8	
A70		36.3	80.8	93.7-102.6(1)	5.7	2.68-2.94(1)	1400 (760)	4.6	28.5	
A71		16.1	57.5	3.0	.41	8.4	1200 (649)	2.2	8.6	
A72		16.2	71.2	13.5	.79	8.0	1300 (704)	2.2	11.0	
A73		16.2	78.3	50.0	1.43	4.7	1400 (760)	2.0	11.4	
A74	Sulfided	37.9	14.5	2.8	.38	9.1	1200 (649)	5.3	5.39	
A75	Cycled	36.5	31.5	14.2	.83	8.1	1300 (704)	4.8	10.8	
A76		38.9	55.4	31.5	.90	10.0	1400 (760)	4.8	19.9	
A77		15.9	10.9	0.7	.09	3.7	1200 (649)	2.0	1.71	
A78		15.3	23.0	3.4	.20	7.8	1300 (704)	2.0	3.38	
A79		17.1	42.6	13.6	.39	8.0	1400 (760)	2.1	6.8	

(1) The high value is extrapolated where a portion of the chart was unreadable.



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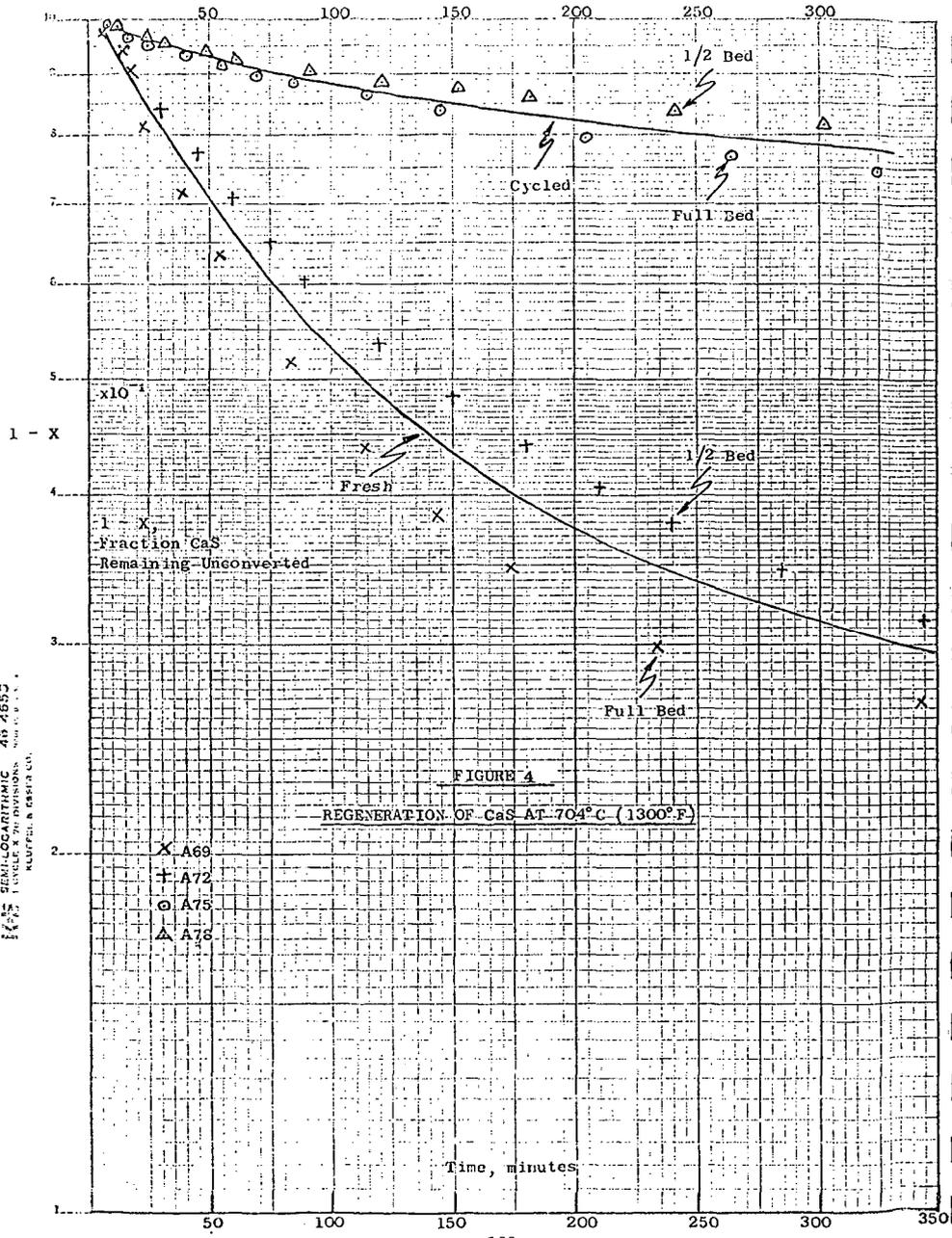


FIGURE 4  
 REGENERATION OF CaS AT 704°C (1300°F)

- X A69
- + A72
- o A75
- Δ A78

1455 SEMI-LOGARITHMIC AS 4850  
 1 1/2" x 1 1/2" x 1 1/2" 1/4" DIA. BORE  
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1 - X

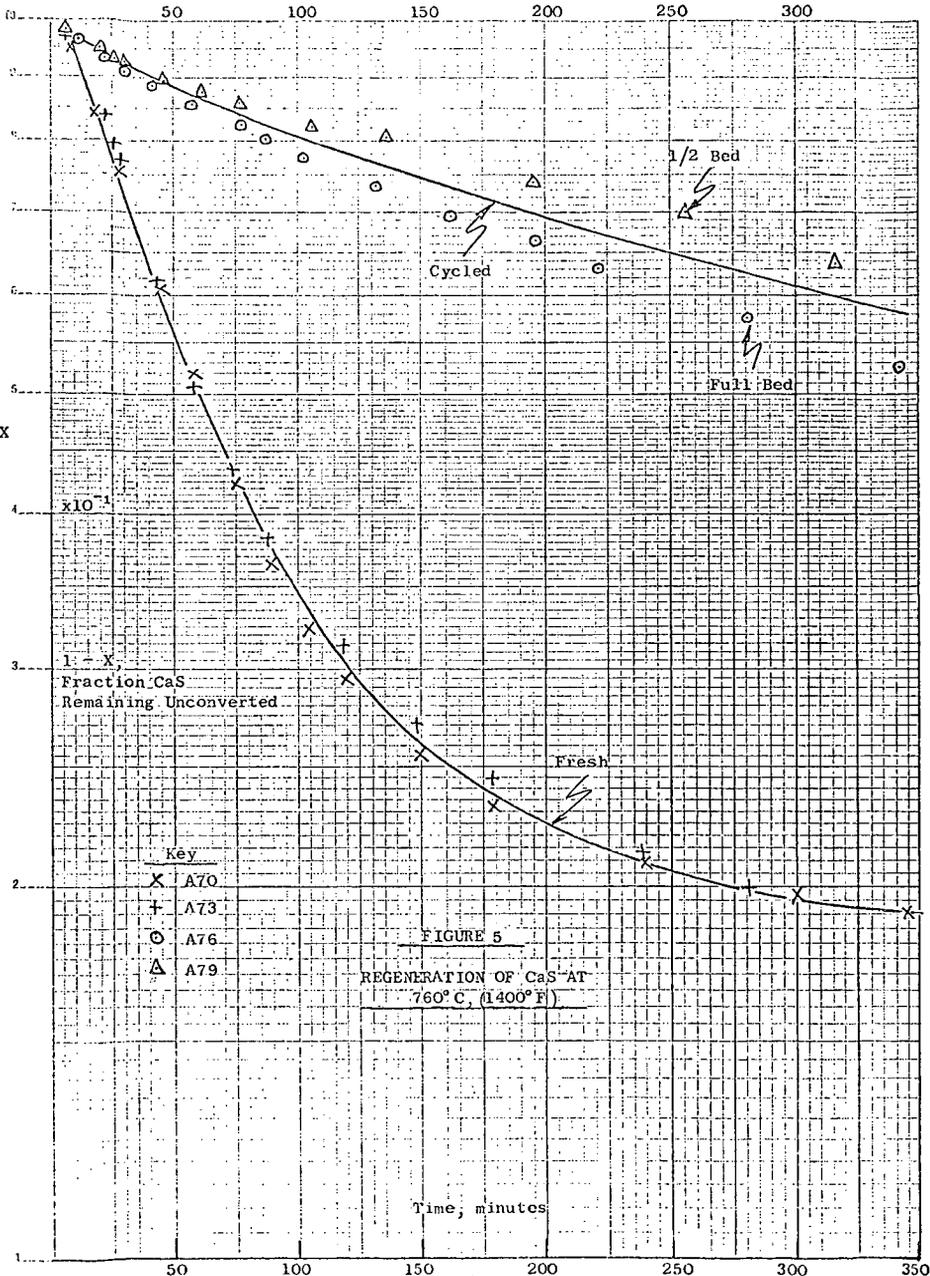


TABLE 4

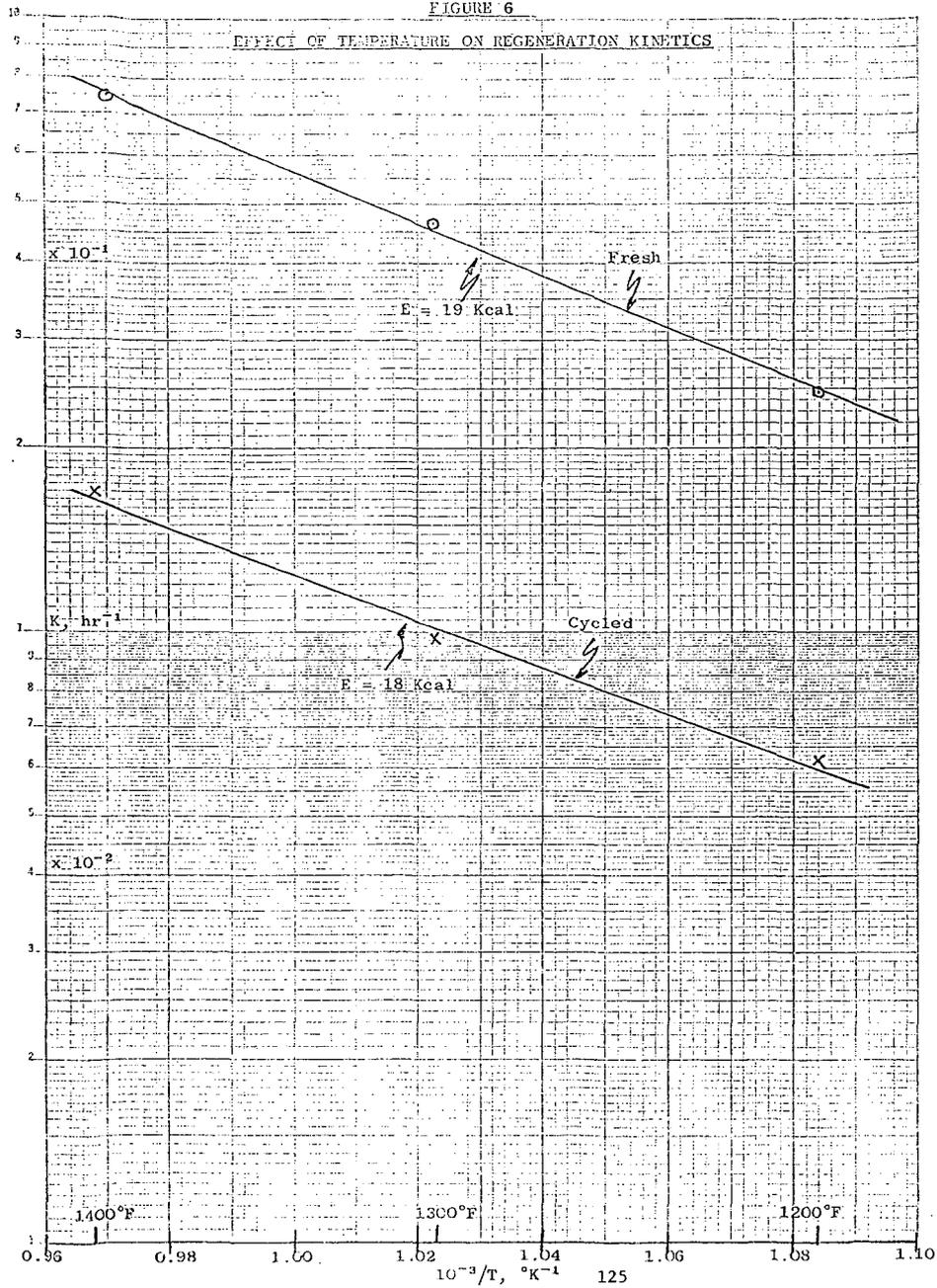
Initial Rate Constants for Regeneration Kinetics

System Pressure: 15 atm  
Feed: 35% H<sub>2</sub>O, 60% CO<sub>2</sub>, 5% H<sub>2</sub>

Temperature, °C (°F)	k, hr <sup>-1</sup>	
	Cycled	Fresh
649 (1200)	.063	.247
704 (1300)	.098	.468
760 (1400)	.170	.747

FIGURE 6

EFFECT OF TEMPERATURE ON REGENERATION KINETICS



SCHLÖSSELMAN 46 4973  
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### Cycling with Varying Residence Times

Four batch cycling runs were made employing the possible combinations of 20 or 60 minutes residence time for sulfur absorption and regeneration. Results are presented in Figure 7. Tymochee 11 dolomite was the feedstock, and each run lasted for 11 cycles.

The effect of reducing residence time in the gas desulfurizer was striking. At 10 cycles, going from 60 to 20 minutes in the gas desulfurizer increased regeneration activity from 15 to 40% at 60 minutes regenerator time and from 15 to 23% at 20 minutes regenerator time. Conversely, going from 60 to 20 minutes regenerator time had no effect at the 60 minute desulfurizer level. Another effect observed was that attrition rates were highest at the short gas desulfurizer residence time, 2.3% average for 20 minutes versus 0.8% for 60 minutes.

It is believed that deactivation of stone takes place primarily in the gas desulfurizer due to crystal growth and particle sintering. This would explain the dramatic effect of time on activity. The results of the above runs are highly significant since they indicate the potential for greatly increasing the stone's capacity for sulfur absorption.

### Scanning Electron Microscope Data

Selected samples of cycled stone were examined under an electron microscope equipped for energy dispersive X-ray analysis. It was found that cycled stone contained very large grains of CaS. The CaCO<sub>3</sub> which was present tended to be concentrated in smaller sizes. Both of the calcium species were larger than the MgO crystals or grains. It is believed that the larger CaS grains are unreactive in the regeneration step of the process.

### Model for the Deactivation Process

The regeneration reaction suffers from deactivation of the CaS even from cycle 1. The model postulated below fits the behavior of the system so far. The part dealing with regenerator variables was developed jointly with A. M. Squires of The City College Clean Fuels Institute.

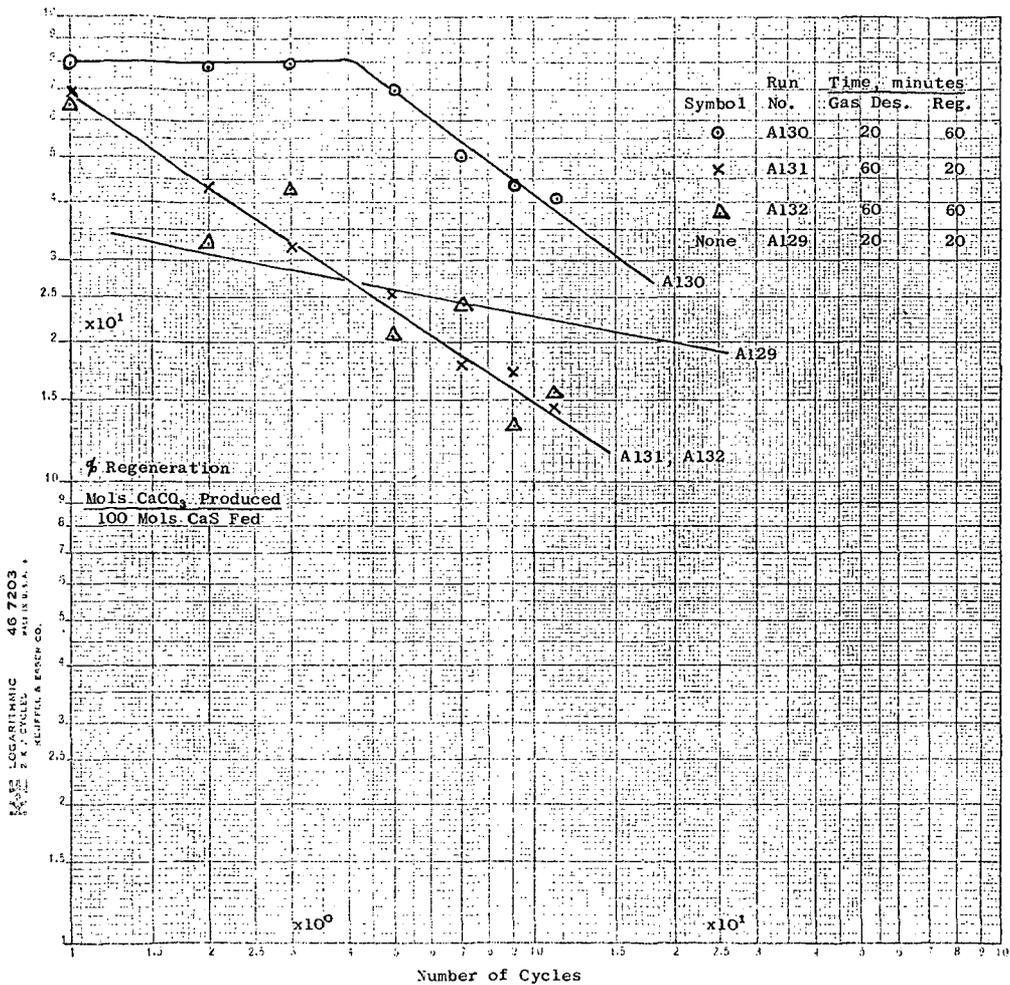
Deactivation of the dolomite occurs mainly in the gas desulfurizer due to the elevated temperature. Two mechanisms are operating. Crystal growth of CaCO<sub>3</sub> and CaS segregates the calcium crystals from the MgO and produces a material tending toward a limestone rather than a dolomite. Simple sintering and densification take place as well, and this both hardens the stone and tends to reduce porosity.

In the regenerator, densification does not occur. However, the reaction starts rapidly and then tails off to an insignificant rate. Using the same feed, it can be shown that the conversion at which reaction essentially ceases is a strong function of temperature, the lower temperature producing the lower conversion. It has further been observed that introducing product H<sub>2</sub>S does not retard the rate of reaction, but conversely increases the ultimate level of conversion attainable.

The phenomenon of the products of reaction increasing the conversion of calcium in the sulfur-calcium system is not new. Peil<sup>(3)</sup> found that H<sub>2</sub>O increased the conversion of CaO to CaS in the reaction of H<sub>2</sub>S with calcined dolomite, and Ruth<sup>(4)</sup> showed that either CO<sub>2</sub> or H<sub>2</sub>O could increase the conversion of CaCO<sub>3</sub> to CaS in the reaction of H<sub>2</sub>S with half-calcined dolomite. Furthermore, both studies demonstrated the effect of the reaction flagging at lower and lower conversion levels as the reaction temperature decreased. Ruth<sup>(5)</sup> proposed the following mechanism after examination of electron microscope results on various samples. "High levels of CO<sub>2</sub> . . . may promote the formation of large numbers of fine

FIGURE 7

Runs A129 to A132 - Deactivation of  
CaS at 704°C (1300°F)



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SCALE  
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crystallites of CaS that do not protect the underlying CaCO<sub>3</sub>. . . . On the other hand, at low levels of CO<sub>2</sub> a smaller number of large CaS crystals formed and grow together to close off the surface, thereby protecting the remaining CaCO<sub>3</sub> from further reaction."

Ruth's careful analysis of his data showed that in the presence of reaction products, the reaction was indeed slower initially. However, within a short time the conversion associated with the product-rich environment soon surpassed that in the product-poor environment.

It is postulated that a similar model fits the regeneration reaction. At low levels of H<sub>2</sub>S, the CaCO<sub>3</sub> formed grows in large crystals shutting off the interior of the grain from further reaction. At high levels of H<sub>2</sub>S, the reaction nucleates at many sites to produce many small crystals which leave the interior of the grain open to further reaction. Via such a mechanism, the presence of H<sub>2</sub>S would enhance conversion in the regenerator. This is in full concordance with our experimental results.

#### Acknowledgment

Appreciation is expressed to the Environmental Protection Agency for financial support of the work presented in this paper and for permission to publish the results given.

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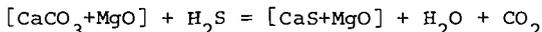
High Pressure TGA Studies on the Cyclic Use of Half-Calcined Dolomite to Remove Hydrogen Sulfide

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New York, N.Y. 10031

Candidate solids for absorption of hydrogen sulfide from a fuel gas at elevated pressure are the composite of iron oxide and fly ash developed by the U.S. Bureau of Mines (1), fully-calcined dolomite (2-4), and half-calcined dolomite (2,5).

Half-calcined dolomite absorbs hydrogen sulfide by the reaction:



For a given fuel gas at a given pressure, desulfurization by this reaction is best accomplished at a temperature just a bit below the temperature at which calcium carbonate would decompose at the partial pressure of carbon dioxide prevailing in the fuel gas.

Regeneration of the solid absorbent is by the reverse reaction, preferably conducted at the lowest possible temperature in order to obtain the highest possible concentration of hydrogen sulfide in the offgas, facilitating conversion of this species to elemental sulfur in a subsequent operation.

Absorption and regeneration cycles at atmospheric pressure and 750°C give the results seen in Figure 1. Although the absorption reaction is rapid, the regeneration reaction is slow, requiring more than 1 hour. There is a decline in capacity of the solid to about 23% of the total calcium after 6 cycles.

Cycling trials at elevated pressure have been carried out with a duPont thermogravimetric analyzer modified for operation at total pressures up to 30 atmospheres, with high partial pressures of steam, and with corrosive gases such as hydrogen sulfide. This equipment is described in reference 6.

In contrast to the results at one atmosphere, cycling at elevated pressure gives little change in capacity or reactivity beyond the first several cycles. Figure 2 gives results from 15 cycles carried out at 300 psig and 731°C. Absorption for 15 minutes was alternated with regeneration for 10 minutes. The capacity settles out at 40%. Figure 3 shows the course of the reactions in the first, 7th, and 15th cycles, and illustrates our finding that the reaction rates do not change much with cycling; only capacity changes. The regeneration reaction at 300 psig is extremely fast, running most of its course in the order of one minute.

Figure 4 shows 30 cycles with absorption for 19 minutes and regeneration for 5 minutes at 550°C. The 19 minutes absorption time

includes 13 minutes at 700°C and 6 minutes cooling time.

Figure 5 shows sulfur capacity versus cycle number for three runs, and illustrates the decline in capacity with decline in regeneration temperature.

Figure 6 illustrates the course of reactions in the last cycle of each of the three cycles plotted in Figure 5. It is fascinating that the observed reaction rates do not seem much to depend upon temperature. This suggests that the true rates are extremely fast, and that the observed rates are controlled by diffusion.

In the series of runs depicted in Figure 7, we varied the ratio of steam to carbon dioxide in the regeneration step to see if this is an important factor in the final capacity of the solid. It appears from Figure 7 that the capacity suffers at a low ratio of steam to carbon dioxide, such as 25/75. Above about 50/50, the ratio does not seem to have much effect. It may be noted that we have succeeded in a run of 15 cycles with a steam partial pressure in the vicinity of 19 atmospheres.

The effect of temperature in absorption and regeneration is shown in Figures 8 and 9. In both figures the duration of the absorption and regeneration steps are 21 and 4 minutes respectively, the time required for heating and cooling being included in the absorption time. Increasing absorption temperatures reduces capacity. The data in Figure 8 show a "deactivation energy" of 22 kcal/gmole. Capacity increases with regeneration temperature, but the temperature effect is not as strong as in absorption. From the data of Figure 9, the "activation" energy is 9 kcal/gmole.

Figure 10 shows the last cycle reaction rates for the four runs plotted in Figure 8. Figure 11 shows the capacity versus cycle number for the same runs.

The effect of steam and CO<sub>2</sub> level on regeneration rate was explored in the presence of partial pressures of H<sub>2</sub>S. Figures 12 and 13 show five regeneration steps for the same stone in which only the regeneration atmosphere was changed from one cycle to the next. The sample reactivity was first stabilized by conducting 6 cycles in the same regeneration atmosphere (50% H<sub>2</sub>O, 40% CO<sub>2</sub>, 10% H<sub>2</sub>). In all cases the absorption conditions were unchanged. Lower initial rates result from the presence of H<sub>2</sub>S as well as decreased H<sub>2</sub>O and CO<sub>2</sub> partial pressures. With high CO<sub>2</sub> pressures (Figure 12), increasing the steam partial pressure increases the initial rate and the capacity. The effect is much more dramatic at low CO<sub>2</sub> pressures (Figure 13).

The complexities of the kinetic situation illustrated in Figures 12 and 13 are reminiscent of the "kinetic curiosities" reported earlier for the absorption reaction (5), and like them, the new complexities appear to reflect differences in the way in which crystallites of  $\text{CaCO}_3$  or  $\text{CaS}$  grow within the solid microstructure. Examinations of microstructural properties of solids arising in this research will be reported elsewhere (7).

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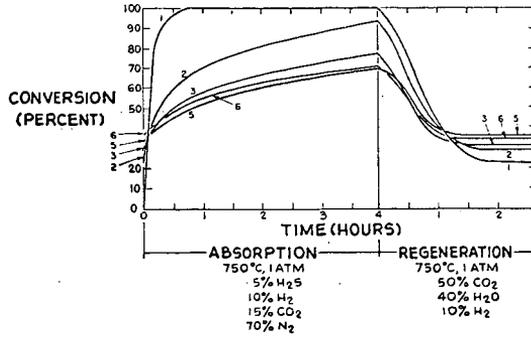


Figure 1. Sulfur absorption and regeneration cycles for half-calcined dolomite at 1 atm and 750°C.

300 Psig (21.4 ATM)

<p>ABSORPTION: 0.5% H<sub>2</sub>S, 4.8% H<sub>2</sub>, 5% CO<sub>2</sub>, Bal. N<sub>2</sub>          15 min. @ 731°C</p>	<p>REGENERATION: 50% H<sub>2</sub>O          10 min. @ 731°C    40% CO<sub>2</sub>          10% H<sub>2</sub></p>
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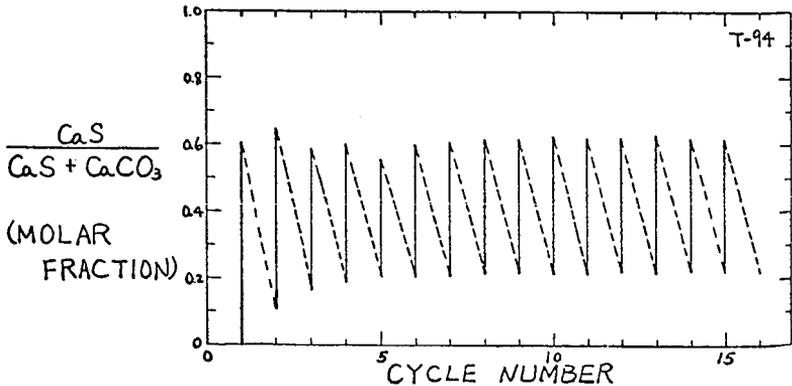


Figure 2. Molar fraction of calcium sulfide in half-calcined dolomite used in 15 cycles for absorption of hydrogen sulfide from simulated fuel gas.

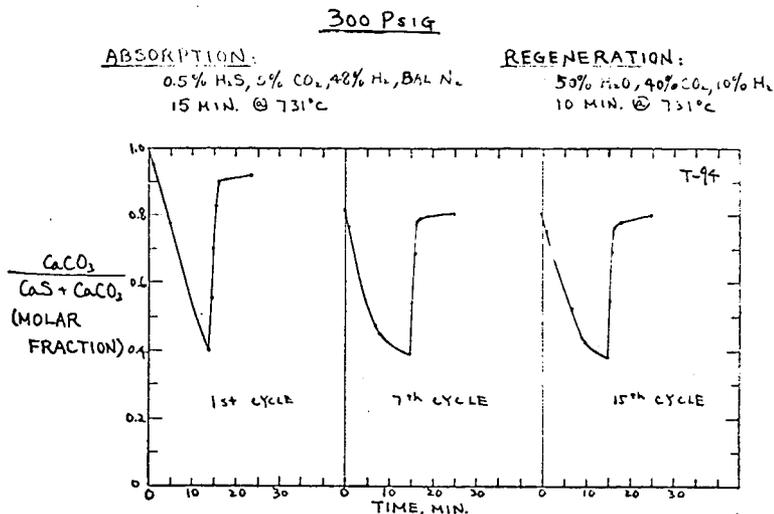


Figure 3. Course of reactions in first, 7th, and 15th cycles of Figure 2.

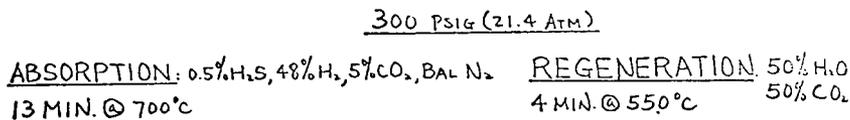


Figure 4. Molar fraction of calcium sulfide in half-calcined dolomite used in 30 cycles for absorption of hydrogen sulfide from simulated gas. Heating took about two minutes without H<sub>2</sub>S present, cooling took about 6 minutes with H<sub>2</sub>S mixture present.

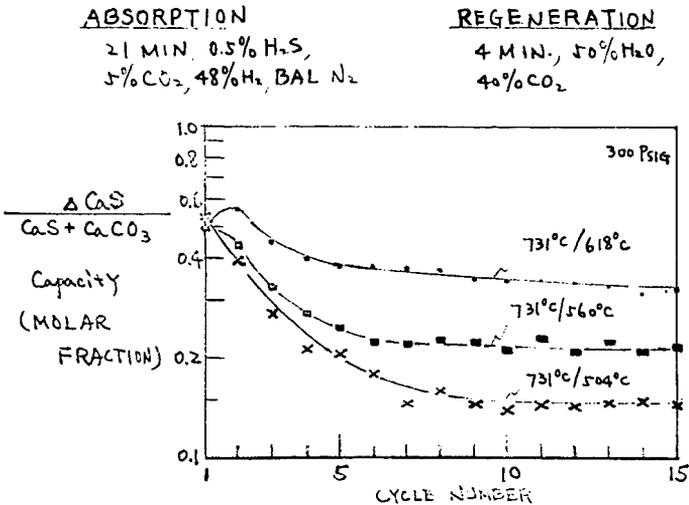


Figure 5. Capacity versus cycle number for three runs with absorptions at 731°C (the first temperature designated alongside each curve) and regenerations at 618°C, 560°C, and 504°C (the second temperature).

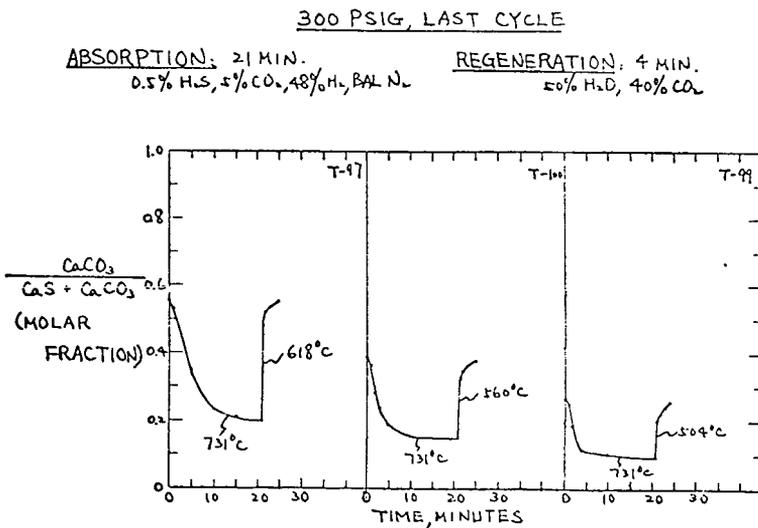


Figure 6. Cycle of absorption and regeneration for each of the three runs of Figure 5.

300 P.S.I.G

ABSORPTION: 731°C  
 0.5% H<sub>2</sub>S, 5% CO<sub>2</sub>, 48% H<sub>2</sub>, BAL N<sub>2</sub>

REGENERATION: 760°C

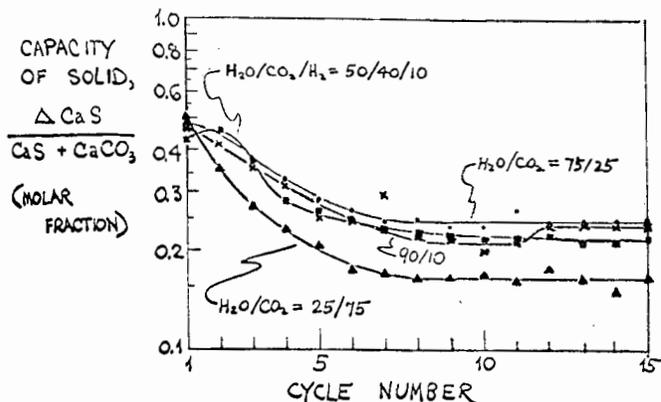


Figure 7. Capacity versus cycle number for four runs with steam/carbon dioxide/hydrogen ratios in regeneration gas as shown alongside the curves.

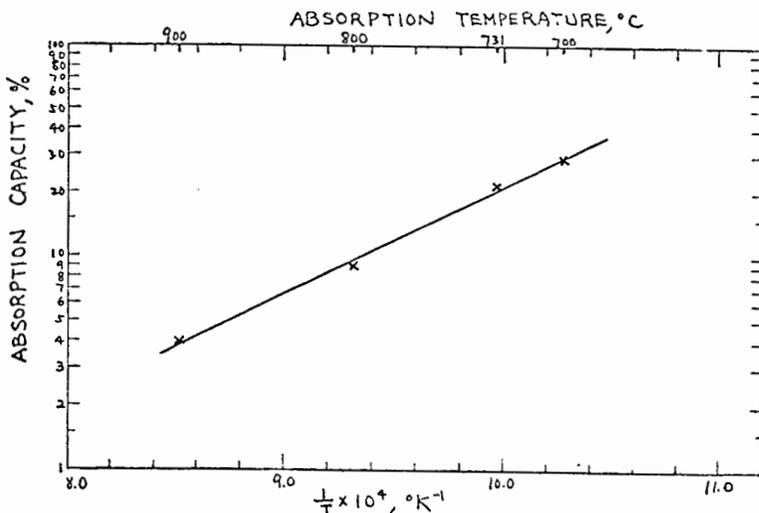


Figure 8. Variation in solid capacity with absorption temperature, for regeneration at 560°C. Absorption = 21 minutes (including heating and cooling); regeneration = 4 minutes.

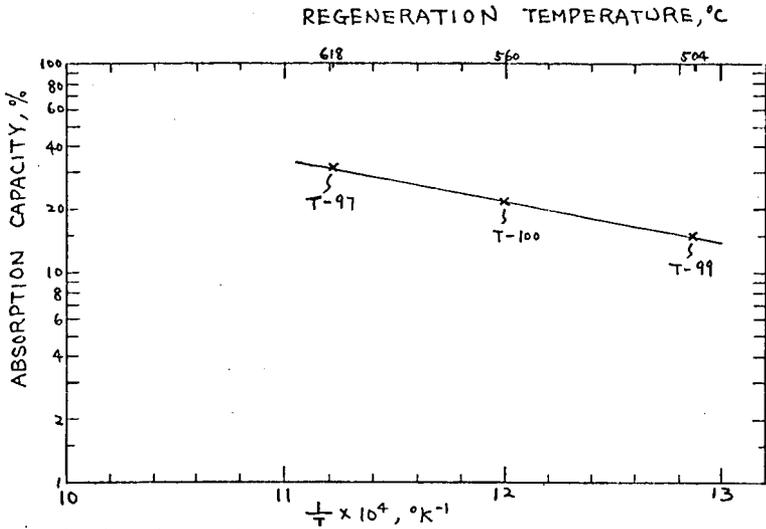


Figure 9. Variation in solid capacity with regeneration temperature, for absorption at 731°C. Times are same as in Figure 8.

### 300 PSIG, LAST CYCLE

<u>RUN</u>	<u>ABSORPTION</u>	<u>REGENERATION</u>
T-110	*26 MIN., 0.5% H <sub>2</sub> S, 30% CO <sub>2</sub> , 48% H <sub>2</sub> , Bal. N <sub>2</sub>	4 MIN., 50% H <sub>2</sub> O, 50% CO <sub>2</sub>
T-111	*21 MIN., 0.5% H <sub>2</sub> S, 10% CO <sub>2</sub> , 48% H <sub>2</sub> , Bal. N <sub>2</sub>	4 MIN., 50% H <sub>2</sub> O, 50% CO <sub>2</sub>
T-112	*19 MIN., 0.5% H <sub>2</sub> S, 5% CO <sub>2</sub> , 48% H <sub>2</sub> , Bal. N <sub>2</sub>	4 MIN., 50% H <sub>2</sub> O, 50% CO <sub>2</sub>
T-114	*19 MIN., 0.5% H <sub>2</sub> S, 5% CO <sub>2</sub> , 48% H <sub>2</sub> , Bal. N <sub>2</sub>	4 MIN., 50% H <sub>2</sub> O, 40% CO <sub>2</sub> , 10% H <sub>2</sub>

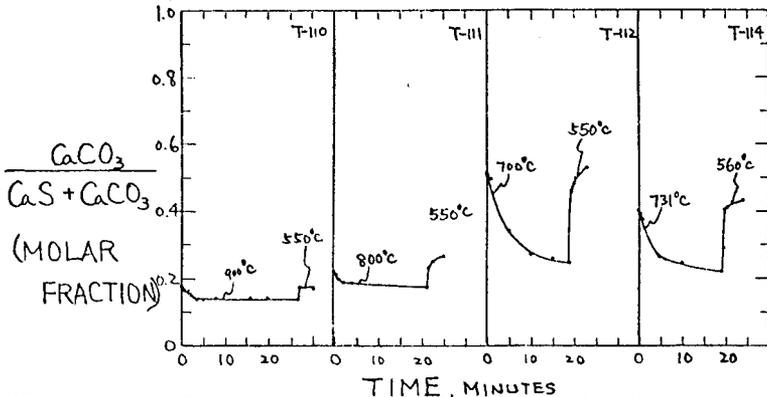


Figure 10. Last cycle of absorption and regeneration for each of the four runs of Figure 8.

RUN	ABSORPTION	REGENERATION
T-110	900°C, "2.6 MIN.", 0.5% H <sub>2</sub> S, 30% CO <sub>2</sub> , 42% H <sub>2</sub> , BAL. N <sub>2</sub>	550°C, 4 MIN., 50% H <sub>2</sub> O, 50% CO <sub>2</sub>
T-111	800°C, "2.1 MIN.", 0.5% H <sub>2</sub> S, 10% CO <sub>2</sub> , 42% H <sub>2</sub> , BAL. N <sub>2</sub>	550°C, 4 MIN., 50% H <sub>2</sub> O, 50% CO <sub>2</sub>
T-112	700°C, "19 MIN.", 0.5% H <sub>2</sub> S, 5% CO <sub>2</sub> , 42% H <sub>2</sub> , BAL. N <sub>2</sub>	550°C, 4 MIN., 50% H <sub>2</sub> O, 50% CO <sub>2</sub>
T-114	731°C, "19 MIN.", 0.5% H <sub>2</sub> S, 5% CO <sub>2</sub> , 42% H <sub>2</sub> , BAL. N <sub>2</sub>	560°C, 4 MIN., 50% H <sub>2</sub> O, 40% CO <sub>2</sub> , 10% H <sub>2</sub>

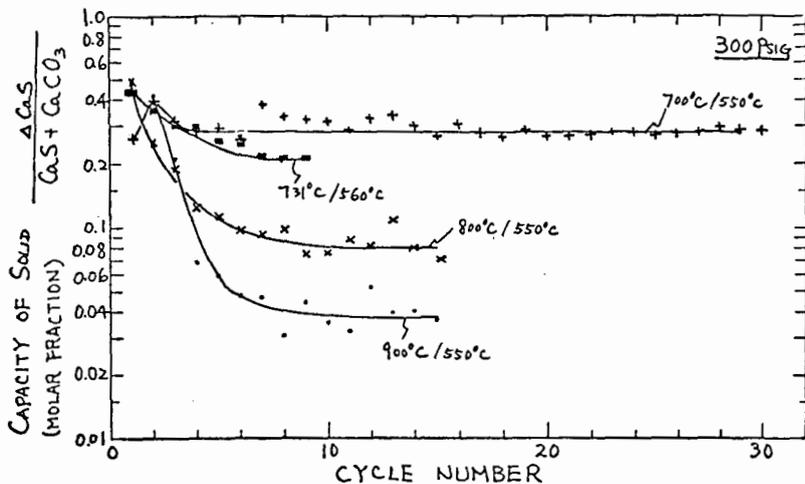


Figure 11. Capacity versus cycle number for the four runs of Figure 8.

300 PSIG, 550°C

REGENERATION:

GASES: H<sub>2</sub>O/CO<sub>2</sub>/H<sub>2</sub>S/H<sub>2</sub>, BAL. N<sub>2</sub>

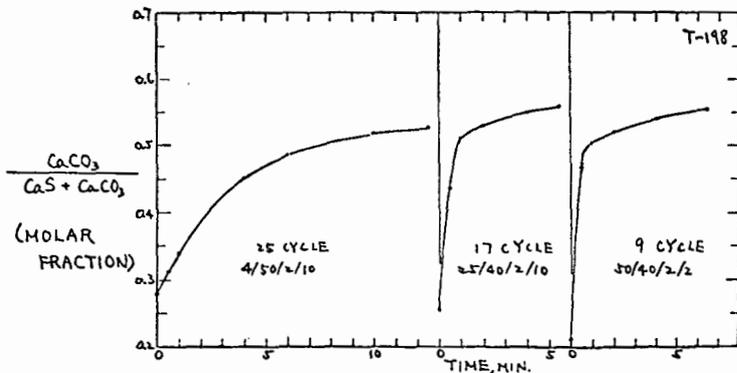


Figure 12. Effect of steam on regeneration rate at high CO<sub>2</sub> partial pressure in presence of H<sub>2</sub>S. Three cycles of the same sample. Absorption at 700°C, 0.5% H<sub>2</sub>S, 5% CO<sub>2</sub>, 48% H<sub>2</sub>, balance N<sub>2</sub>.

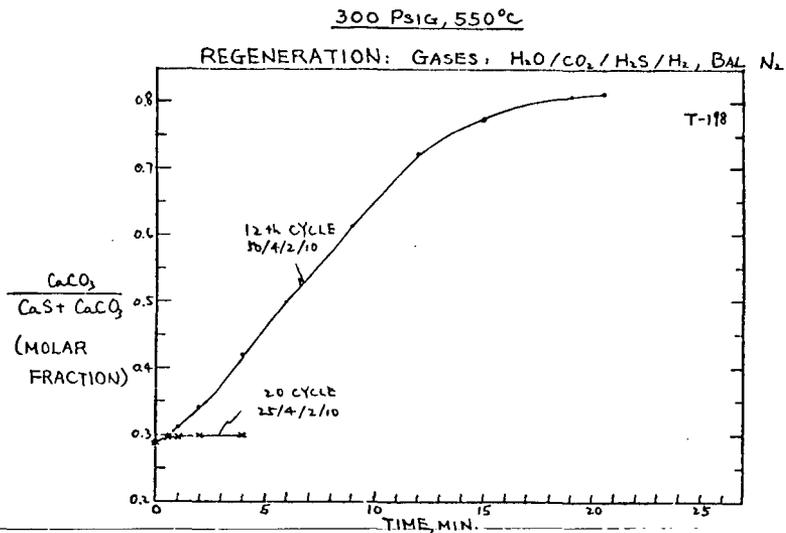


Figure 13. Effect of steam on regeneration rate at low CO<sub>2</sub> partial pressure in presence of H<sub>2</sub>S. Same sample and absorption conditions as in Figure 12.