

A REACTION WHICH PERMITS THE CYCLIC USE OF CALCINED DOLOMITE
TO DESULFURIZE FUELS UNDERGOING GASIFICATION

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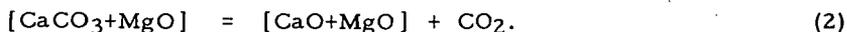
Raw fluid fuels, derived for instance from coal and heavy residual oils by a variety of processes such as gasification, carbonization, or cracking, may be substantially desulfurized by reaction at high temperature with calcined dolomite. This solid can also remove CO₂ from a gas stream; it has the power to convert CO and steam to H₂; and it may participate in the gasification of carbon by steam under a condition of thermal neutrality.

The cyclic use of calcined dolomite for these purposes has previously been hampered by lack of means to recover elemental sulfur from sulfurized calcined dolomite, containing CaS, while at the same time recovering solid in a form suitable for reuse.

The reaction of steam and CO₂ at high pressure with sulfurized calcined dolomite,



can be used to generate a gas stream containing H₂S at a concentration well above the minimum concentration which can be used by a Claus sulfur recovery system. Later, the solid product can be calcined at high temperature to provide a solid containing CaO:



The latter solid can be used to remove H₂S from a fuel gas:



Reactions (1), (2), and (3) can be combined in a cyclic process to desulfurize a fuel undergoing gasification. Heat developed by reaction (1) is at a level suitable for raising or superheating high-pressure steam.

Alternatively, the solid product of reaction (1) can be used directly to remove H₂S from a fuel gas at high temperature by the reverse of reaction (1). The temperature should preferably be just a little below the equilibrium decomposition temperature of CaCO₃ at the prevailing partial pressure of CO₂.

The solid product of reaction (2) can be used to promote CO-shift:



This reaction is the basis of the CO-shift process developed by Gesellschaft für Kohlentechnik during the 1920's (24). The process was conducted in fixed beds, had poor thermal efficiency, and never caught on. An improved version of the process which uses fluidized beds may find modern applications. In this version,

reaction (4) may be combined with reactions (1), (2), and (3) in a cyclic process in which elemental sulfur is recovered.

The solid product of reaction (2) can also participate in the gasification of carbon by steam:



This reaction is the basis of Consolidation Coal Company's Carbon Dioxide Acceptor Gasification Process (16, 18, 19), which eliminates need for oxygen to provide heat to the steam-carbon reaction. The process could be modified for recovery of elemental sulfur by incorporating a step using reaction (1).

Residual oils may be gasified or cracked over calcined dolomite with recovery of elemental sulfur in a cyclic process incorporating reaction (1). A version of this process may find a use in providing sulfur-free fuel to existing power-station boilers in communities which impose restrictions on SO₂ content of flue gases.

These new fuel-desulfurization processes reject very little heat at low temperatures. If a fuel gas is to be used in a combustion, or if the gas is to be subjected to further processing at high temperature -- CO-shift, for example -- the new desulfurization processes have the advantage that the heat exchange required to cool the gases to a low-temperature sulfur-removal step is eliminated. The processes are well suited for use in schemes to produce a clean fuel gas to be burned at high pressure in an advanced power cycle. Indeed, the conception of the new processes was a result of a search for a combination incorporating fuel-gasification at high pressure, fuel-gas cleanup, and an advanced power cycle which could provide electricity at lower cost. Such a combination would be adopted by the power industry as much for reasons of economy as for the advantage that the combination would provide dust-free and sulfur-free effluent. Power cycles which offer the prospect of significant improvement in efficiency are the supercharged-boiler cycle, a cycle incorporating a magnetohydrodynamic device which "tops" the steam cycle, and a top heat power cycle, in which the temperature of steam is raised by direct addition of the products of combustion of a clean fuel with oxygen or air (63, 64).

Dolomite is cheap and widely available, and the solids produced by reactions (1), (2), and (3) are rugged and suitable for use in fluidized beds.

This paper discusses the thermodynamic equilibria which govern the proposed new desulfurization processes; gives results of exploratory bench-scale studies; reviews the relevant dolomite chemistry; and briefly indicates some of the potential applications.

1.0 Discussion of Process Thermodynamics

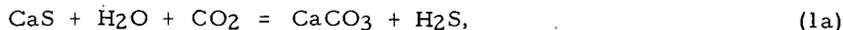
1.01 Review of Thermodynamic Equilibria

Figure 1 gives the equilibrium constant for the reaction



CaO is seen to be an effective desulfurization agent at temperatures as high as 2000° F.

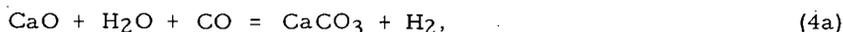
Figure 2, showing the equilibrium constant for the reaction



illustrates the basis for the proposed new desulfurization processes. At temperatures below about 1100° F and at pressures above about 4 atmospheres, say, reaction (1) can be used to derive a gas containing H₂S at a concentration which permits the recovery of elemental sulfur in a Claus system.

The curve of Figure 2 is so steep that the reverse of reaction (1) can be used to desulfurize a gas at temperatures above about 1600° F.

Figure 3 gives the equilibrium constant for the reaction



which must often be considered in finding the composition of gas desulfurized by the new process.

The upper curve of Figure 4 gives an estimate of the equilibrium constant for the reaction



A key to the success of Consolidation's CO₂ Acceptor Process is control of conditions for the calcination of [CaCO₃+MgO] so that sulfur is expelled as SO₂. By using fuel-rich combustion which provides a calciner offgas containing H₂ in an amount greater than called for by the upper curve of Figure 4, one can prevent the oxidation of CaS to CaSO₄ and the "fixing" of sulfur in the latter form. Sulfur is then rejected as SO₂ by reaction between CaS and CaSO₄ (19, 74).

In contrast to Consolidation's procedure, one wishes to preserve CaS unchanged during a calcination step in the new desulfurization process. The lower curve of Figure 4 gives an extremely rough estimate of the equilibrium constant for the reaction



Since CaSO₃ disproportionates to CaS and CaSO₄ at temperatures above about 930° F (46, 70), it would appear that calciner offgas should contain hydrogen in an amount greater than called for by the lower curve of Figure 4 if one wishes to avoid rejecting any sulfur as SO₂. This has been arranged for in studies of the new desulfurization process. If the reaction rejecting SO₂ is slow by comparison with the rate of reduction of CaSO₄ by H₂, less hydrogen may be required to prevent significant loss of sulfur as SO₂.

Since CaSO₄ is readily reduced by H₂ to CaS at 930° F (51), it would appear desirable that H₂ be present during reaction (1) to avoid oxidation of CaS by steam. Presence of H₂ in excess of the amount called for by the lower curve of Figure 4 has been assumed in studies of the new desulfurization process. Because

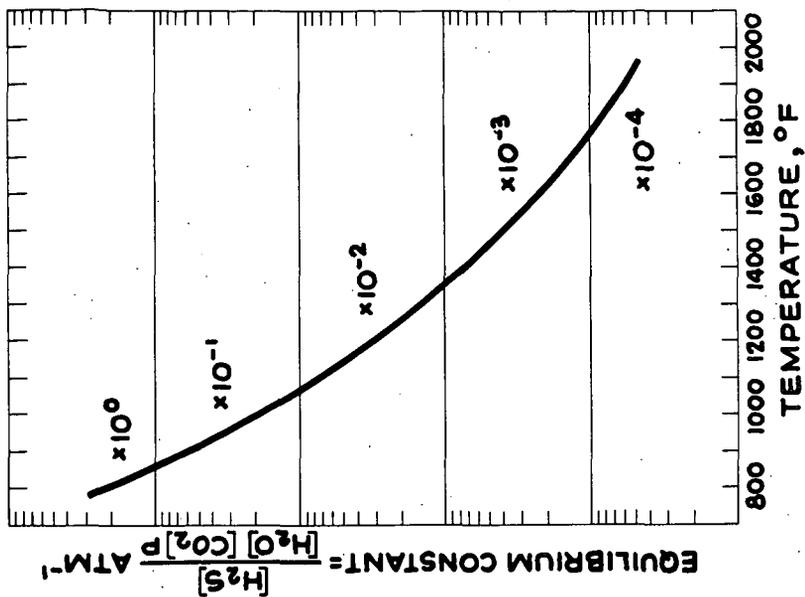


Figure 2. EQUILIBRIUM CONSTANT FOR:
 $CaS + H_2O + CO_2 = CaCO_3 + H_2S$

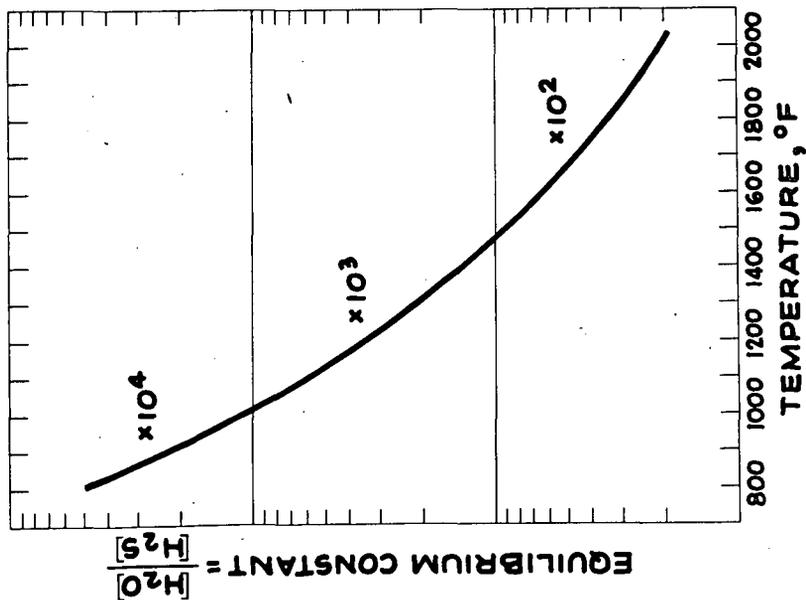


Figure 1. EQUILIBRIUM CONSTANT FOR:
 $CaO + H_2S = CaS + H_2O$

of the tendency of CaSO_3 to disproportionate, less H_2 may in fact be needed to prevent a significant degree of reaction between steam and CaS .

If CaO is present, the steam partial pressure should not exceed the equilibrium decomposition pressure of $\text{Ca}(\text{OH})_2$. As Curran, Rice, and Gorin (19) pointed out, the steam partial pressure should not exceed 13 atmospheres if both CaO and CaCO_3 are present at a temperature around 1650°F ; at higher steam pressures, a melt is formed.

Equilibrium is against the formation of MgS under all conditions encountered in the new desulfurization process.

1.02 Sources of Thermodynamic Data

The curve of Figure 1 is based upon the equation: $\log [\text{H}_2\text{O}] / [\text{H}_2\text{S}] = (3421.5/T) - 0.190$, where p [...] signifies mole fraction and $T = ^\circ\text{K}$. The equation is derived from Rosenqvist (52), who studied the equilibrium over the range 1396° to 2597°F . Uno (69) gave an equation, based upon data between 1652° and 2012°F , which agrees well with Rosenqvist over the range of Uno's data, but which extrapolates to lower values at lower temperatures. Data by Curran et al (19) between 1310° and 1660°F fall above the curve in Figure 1. Additional measurements would be desirable in the low-temperature range, and equilibria for reaction (3a) might well be derived from careful measurements of equilibria for reaction (1a).

Determination of equilibrium decomposition pressures of calcite has proved a durable problem, and dubious values have appeared recently (33, 45). Following Hill and Winter (35), Kubaschewski and Evans (42) adopted the equation: $\log P_{\text{CO}_2} = -(8799.7/T) + 7.521$, where P_{CO_2} = equilibrium decomposition pressure in atmospheres; this equation is used here. Hill and Winter's data were between 840° and 1659°F ; no one else has made such careful measurements at such low temperatures. Their data agree well with Southard and Royster (62) between 1427° and 1652°F , and with Smyth and Adams (61) between 1567° and 1664°F . Smyth and Adams' data extended to 2266°F , and data obtained by Consolidation Coal Company between 1472° and 1895°F agree well with Smyth and Adams' data at higher temperatures (17). Consolidation's measurements were conducted on a dolomite having a Ca/Mg atomic ratio of about 1.03. An ingenious new technique was used: a bed of the solid was fluidized with N_2 and CO_2 , and the temperature of the bed was cycled a few degrees above and a few degrees below the equilibrium decomposition temperature, which was identified by a thermal conductivity cell capable of precisely determining the instant at which the exit gas showed zero change in composition.

In obtaining the curves of Figure 4, the free energy of CaS was deduced from Uno's data (69) in order to provide estimates which are probably on the low side. Free energies of CaO , CaSO_4 , H_2 , and H_2O were derived from heats of formation and entropies at 298°K found in Kubaschewski and Evans (42) and from increments in these functions at higher temperatures found in Kelley (38). The heat of formation of CaSO_3 was estimated roughly to be 298,100 calories at 18°C from the heat of formation of $\text{CaSO}_3 \cdot 2\text{H}_2\text{O}$ given in International Critical Tables, vol. V, p. 196. The entropy of CaSO_3 was given by Kelley and Moore (39) to be 24.2 entropy units at 298°K . The heat capacities of CaSO_3 and CaCO_3 are within 0.5% of each other at 298°K , and so Kelley's increments (38) for the heat

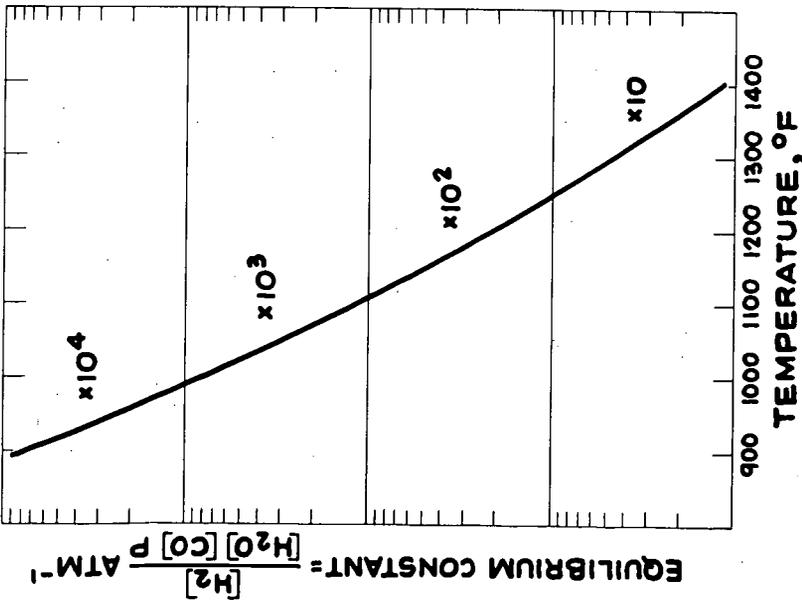


Figure 3. EQUILIBRIUM CONSTANT FOR:
 $\text{CaO} + \text{H}_2\text{O} + \text{CO} = \text{CaCO}_3 + \text{H}_2$

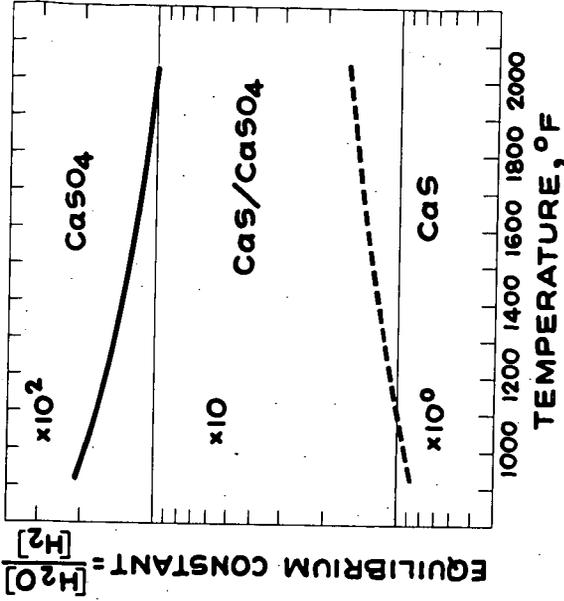
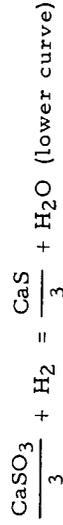
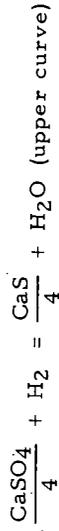


Figure 4. ROUGH ESTIMATES OF EQUILIBRIUM CONSTANTS FOR:



content and entropy of CaCO_3 were used to obtain a rough estimate of the free energy of CaSO_3 at higher temperatures.

The equilibrium decomposition pressure of Ca(OH)_2 may be estimated from an equation based upon data by Tamaru and Siomi (66): $\log P_{\text{H}_2\text{O}} = - (5464.5/T) + 6.949$. These authors measured decomposition pressures over the range 760° to 930° F. Their equation agrees well with data by Halstead and Moore (32) at 950° F, and with data by Dräger between 570° and 830° F (36). Berg and Rassonskaya's data (7) are probably faulty.

2.0 Experimental Studies

Exploratory bench-scale experimental studies were undertaken by Walter C. McCrone Associates of Chicago, Illinois, primarily to demonstrate (a) that reaction (1) is capable of producing a gas containing H_2S at a concentration sufficient for the Claus process, and (b) that the solid does not undergo chemically-induced decrepitation during an operation which includes reactions (1), (2), and (3). This was to be done at the minimum possible cost, and no effort was to be made to determine reaction kinetics or to confirm chemical equilibria.

2.01 Summary of Experimental Results

Dolomite was supplied by Dolese & Shepard Co. of LaGrange, Illinois. This is a typical dolomite of the Chicago area, and has a Ca/Mg atomic ratio of 1.10. Reactions were conducted in a fixed bed of particles of 16 to 30 mesh (NBS sieves).

Reaction (4) was conducted over calcined dolomite at about 1250° F and between about 140 and 315 psia. Two initial gas mixtures were used, containing H_2/CO in ratios 1.0 and 1.6 respectively. The gas mixtures were humidified with steam to afford $\text{H}_2\text{O}/\text{CO}$ ratios between about 1.2 and 1.8. Effluent contained no CO or CO_2 detectable by gas-chromatographic analysis sensitive to less than 0.01% of either constituent. No hydrocarbon synthesis occurred.

Reactions (3) and (4) were conducted simultaneously over calcined dolomite at about 1200° F and between about 140 and 215 psia. The initial gas mixture contained about 1% H_2S , the balance consisting of equal quantities of H_2 and CO. Concentrations of H_2S in effluent ranged from 2 to 140 ppm, and depended upon the quantity of steam in effluent.

Reaction (3) was conducted over calcined dolomite at about 1100° F and atmospheric pressure until the material was substantially all converted to $[\text{CaS}+\text{MgO}]$. The inlet gas mixture contained about 85% N_2 , 10% H_2S , and 5% H_2 . During this operation, effluent contained about 10 ppm of H_2S .

Reaction (1) was conducted over the resulting solid $[\text{CaS}+\text{MgO}]$ at about 1000° to 1100° F and at about 220 psia. The initial gas mixture contained about 82% CO_2 and about 9% each of H_2 and CO. The gas mixture was humidified with steam to afford a $\text{CO}_2/\text{H}_2\text{O}$ ratio of about 1.75. Dry effluent contained 20 to 24% H_2S , levels which are satisfactory for feed gas to a Claus system. It is reasonably certain that a much higher concentration of H_2S could have been obtained by using a lower $\text{CO}_2/\text{H}_2\text{O}$ ratio, since effluent appeared to be substantially at chemical equilibrium for reaction (1).

None of the foregoing chemical manipulations of calcined dolomite produced a decrepitation of the solid, or any evident change in the shape of particles viewed under a microscope; sharp edges and points were still to be seen.

2.02 Experimental Procedures

The reaction system used components supplied by Autoclave Engineers, Inc. of Erie, Pennsylvania. The reactor was 1" I. D. x 36" inside depth, and was fitted with a 5/16" thermowell containing 5 chromel-P-alumel thermocouples. An active dolomite bed between 8" and 12" in depth was used, the remainder of the reactor being packed with alumina chips. The reactor was situated within two Hoskins furnaces, each affording a heating length of 12". Tanks containing various mixtures of gases at high pressure were obtained from Matheson Company of Joliet. Gases were metered through a rotameter, and were passed through a pool of water in a saturator immersed in a heated oil bath. Gas from the saturator passed upward through the reactor, from the reactor through a filter, thence through a cooling coil, and into a chamber collecting water. Dry gas was let down in pressure across a needle valve, and sent to analysis. Most constituents were analyzed by a gas chromatograph (Perkin-Elmer Model 154) having a column of 1/4" O. D. copper tubing, 5' long, packed with 28-200 mesh silica gel, held at 125°C and swept with helium. Known gas mixtures, analyzed by Matheson, were used to calibrate the chromatograph for CO₂, CO, and H₂. Kitagawa H₂S-Low-Range Detector Tubes were used to analyze for H₂S at low concentrations. The Kitagawa "pump" was not used; a tube was placed in the gas-sampling line, and by trial and error the flow through the tube was adjusted to about 100 ml in 3 minutes. A modification of the Tutwiler method was used to determine H₂S at high concentrations (57). The method was calibrated against a gas mixture analyzed by Matheson and stated by Matheson to contain 10.9% H₂S.

Calcinations were conducted at atmospheric pressure with either N₂ or 90/10 N₂/H₂ flowing through the reactor.

2.03 Selected Results

Figure 5 illustrates the breakthrough of CO and CO₂ at the conclusion of a run using an initial gas mixture containing H₂/CO in the ratio 1.62. Flow of the initial gas at breakthrough was about 250 ml (70°F, 1 atm)/min; pressure was 315 psia; and temperature in the active bed ranged from 1217° to 1290°F. The gas was humidified to a H₂O/CO ratio of 1.83. Neither CO nor CO₂ could be detected in effluent prior to breakthrough. The rise in CO occurred a little earlier than the rise in CO₂. The width of the temperature peak was approximately the same as the time interval during which CO and CO₂ rose to their final steady values. This time interval can be interpreted as the time required for the reaction front to pass any given point in the active bed. The catalytic effect of MgO for the CO-shift reaction is indicated by presence of CO₂ in the gas following breakthrough, for the initial gas mixture contained no CO₂.

Data like those in Figure 5 were presented by Glud et al (24) for operations at atmospheric pressure and about 930°F.

Reaction (3) was conducted at atmospheric pressure with gas containing 85% N₂, 10% H₂S, and 5% H₂, humidified at 79°F. Temperatures in the active bed ranged from 976° to 1138°F, the temperature sharply dropping toward the

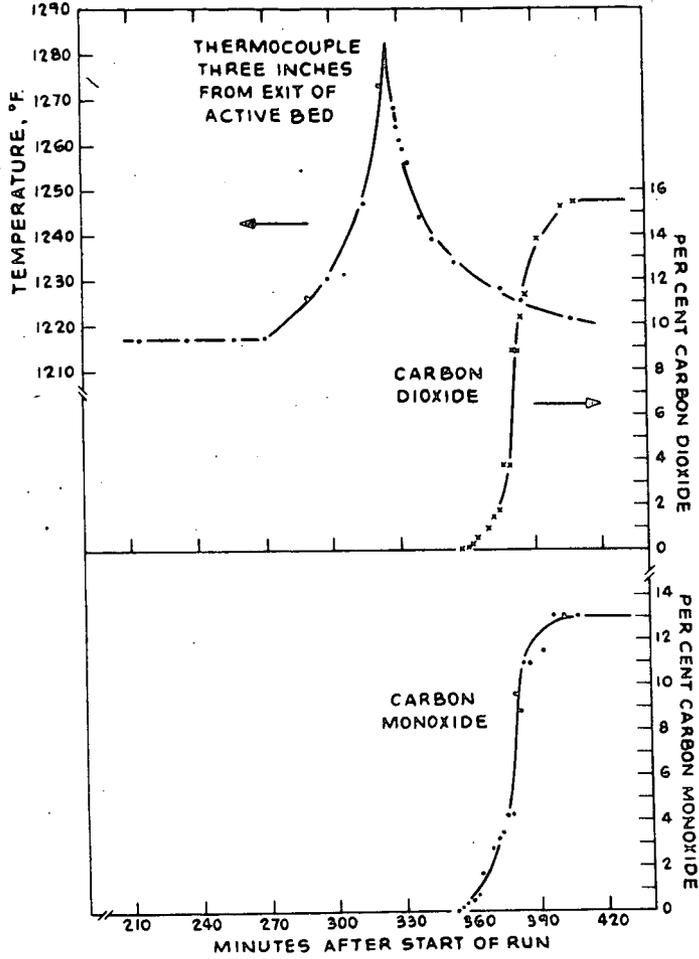


Figure 5. BREAKTHROUGH OF CARBON OXIDES WHEN SOLID IS USED UP BY REACTION (4) IN A FIXED BED AT 315 PSIA

outlet end. The ratio of H_2O/H_2S leaving the bed prior to breakthrough of H_2S was approximately 14,000, a value in close agreement with Figure 1 for the temperature at the outlet of the bed.

After reaction (3), reaction (1) was conducted at atmospheric pressure with gas humidified at 75°F. The initial gas mixture contained 81.7% CO_2 , 9.3% H_2 , and 9.0% CO . Dry gas effluent contained 1.1% H_2S . The active bed temperature ranged from 976° to 1138°F, the temperature sharply dropping toward the outlet end. The value of $[H_2S]/[H_2O][CO_2]P$ in reactor effluent was 0.21, which corresponds to 990°F at equilibrium, according to Figure 2. The purpose of this atmospheric-pressure, low-humidity step was to assure that no CaO remained in the active bed. If this step had been omitted, $Ca(OH)_2$ might have formed at steam partial pressures to which the solid was later subjected.

Later, the pressure was raised to 220 psia, and the saturator temperature was raised to 302°F, providing a CO_2/H_2O ratio of 1.79. The active bed temperature remained as before. Dry gas effluent contained 20.2% H_2S , and corresponded to equilibrium for reaction (1) at about 1040°F. The temperature of the bed was lowered to the range 891° to 1040°F, and the pressure fell to 215 psia, reducing the CO_2/H_2O ratio to 1.73. The H_2S content of dry gas increased to 24.0%, which corresponded to equilibrium at about 1010°F. [Most of the bed was at about 1000°F, and CaS may have been gone from solid near the exit of the bed by this time, for conditions had favored production of H_2S near the exit throughout the experiment.]

These results demonstrated the ability of reaction (1) to provide a dry gas containing H_2S in a concentration adequate for the Claus process. The results provide an indication that H_2S concentrations approaching thermodynamic equilibrium may be achieved, and it is practically certain that much higher concentrations of H_2S could have been reached by working at lower CO_2/H_2O ratio.

3.0 Review of Relevant Dolomite Chemistry

Primary sources of information are: (a) the series of papers from the Gesellschaft für Kohlentechnik (24), reporting in 1930 on studies of a process to manufacture H_2 by reforming coke-oven gas with steam and thereafter shifting the reformed gas with steam over calcined dolomite; and (b) the series of reports from Consolidation Coal Company on the CO_2 Acceptor Process (16, 18, 19). The latter reports are particularly valuable for the evidence that the solids [$CaO+MgO$], [$CaCO_3+MgO$], and [$CaS+MgO$] are rugged materials which stand up under fluidization, and do not decrepitate under various chemical reactions which convert the solids from one to another.

Dolomite is the mixed carbonate of Ca and Mg , "normal" dolomite being written $CaCO_3 \cdot MgCO_3$. It is a common rock, of wide geographical distribution, and often occurs in a state of high purity. Analyses of typical dolomites were given, for example, in Sikabonyi (59) and Willman (71). Dolomite is a member of a large class of rhombohedral carbonates, which includes calcite and magnesite. These carbonates are built of alternating layers of carbonate ions and cations. In dolomite, ideally, cation planes populated entirely by Mg^{++} alternate with planes populated entirely by Ca^{++} (13). Natural dolomite often diverges from the ideal of one atom of Mg for each Ca , the latter usually being present in excess. True dolomites richer in Mg are seldom encountered (24, 26).

3.01 Formation of [CaO+MgO]

If dolomite is heated in a vacuum, it decomposes in one step, with evolution of CO_2 and formation of a solid comprising an intimate intermingling of tiny crystallites of CaO and MgO. Britton et al (14) studied this process between 640° and 720°C , and believed the decomposition to occur with formation of a transient species $(\text{Ca, Mg})\text{O}$, which quickly breaks up into crystallites of CaO and MgO. The product may be written [CaO+MgO] as a reminder that it is not a true chemical species. Decomposition proceeds from the outside surface inward.

In an atmosphere of CO_2 , dolomite decomposes in two steps (6, 23, 34). Wilsdorf and Haul (72) followed the first step with X-ray diffraction techniques. Decomposition proceeds from the surface inward, and the state of order in the kernel of undecomposed dolomite remains perfect. At around 600°C and 100 mm Hg of CO_2 , predominantly single-crystal patterns for calcite are found, the CaCO_3 crystallites apparently being oriented as in the original lattice. At 800°C and 650 mm Hg of CO_2 , powder calcite patterns are obtained, randomization of the CaCO_3 crystallites having occurred. If dolomite is decomposed at moderate CO_2 pressures, as in a calcination process, the calcite produced is essentially pure CaCO_3 (27), and the product may be written [CaCO₃+MgO]. At extremely high CO_2 pressures, the product is a mixture of crystallites of MgO and of a magnesian calcite, i. e., a calcite containing MgCO_3 in solid solution (29, 33).

Bischoff (10) and MacIntire and Stansel (43) found that both stages in the decomposition of dolomite are catalyzed by steam. Schwob (56) and Graf (28) reported a catalytic effect of alkali. There is evidence that the decomposition of [CaCO₃+MgO] is faster than that of CaCO_3 (34).

From the foregoing, it will be recognized that the intimate mixture of CaO and MgO crystallites which result from the total calcination of dolomite retain no "memory" of the original dolomite structure. Goldsmith (26) believed that this solid would be indistinguishable from one which could be prepared by calcining a mixed precipitate of CaCO_3 and MgCO_3 . Such a precipitate never shows signs of dolomitic order if prepared in the laboratory from solutions at room temperature (27). Artificially-made dolomites are known (29, 30, 33) but these materials and the extensive literature on the problem of the formation of dolomite in nature are not particularly relevant to the new desulfurization process, since [CaO+MgO] can be prepared artificially for use in the process without the material's having passed through the dolomitic state.

Clark et al (15) studied the sintering of MgO at high temperatures. They found a sudden increase in strength to occur at a temperature well below that at which sintering proper with densification sets in, and they interpreted this increase in strength to be a result of destruction of adsorbed moisture films on the surfaces of the particles, i. e., the replacement of hydrogen or hydroxyl bonding between particles by primary ionic bonds.

3.02 Recarbonation of [CaO+MgO] to Form [CaCO₃+MgO]

Glud et al (24) studied the recarbonation, at about 1050°F , of samples of [CaO+MgO] prepared from a wide variety of dolomitic rocks. Uniformly, the initial reaction with CO_2 was extremely rapid. The course of later stages of the reaction was found to depend upon the Ca/Mg atomic ratio of the starting material.

Glud et al recommended that a dolomite be selected having a Ca/Mg ratio as close to unity as could be found. The later stages of recarbonation of $[\text{CaO}+\text{MgO}]$ from a stone having a high Ca/Mg ratio were slow, and the reaction ceased for all practicable purposes far short of complete conversion of CaO to CaCO_3 . Moreover, stones having a high Ca/Mg ratio displayed poor resistance to deactivation when calcined. Working with dolomites having Ca/Mg ratios below about 1.2, Glud et al were able to achieve 90% recarbonation of CaO at good rates, provided the solid had not been exposed to a temperature above about 1920°F . If a dolomite was calcined at 2190°F , its reactivity was drastically reduced. Other workers (9, 14, 49) confirmed that recarbonation is rapid and nearly complete if a Ca/Mg ratio below about 1.1 is used.

Asboth (5) recommended an "artificial dolomite", prepared by precipitating CaCO_3 and MgCO_3 in the molar ratio 40:60 upon freshly made silica gel.

Curran et al (19) subjected a number of dolomites to tests of their suitability for the CO_2 Acceptor Process, which inherently requires use of a high calcination temperature (of the order of 1950°F). Stone from the Greenfield formation of Western Ohio was selected as the best available. This stone has the unusually low Ca/Mg ratio of 0.987. The stone was cycled many times between a calcination at high temperature and a recarbonation at 1650°F . There was no significant loss of reactivity. Calcination temperatures of 1900° , 1950° and 2000°F were used in these tests. Practically no degradation in particle size occurred, although the tests were conducted in fluidized beds. In a similar series of tests, the Greenfield stone was converted to $[\text{CaS}+\text{MgO}]$, from which $[\text{CaO}+\text{MgO}]$ was regenerated at 1950°F by a fuel-rich calcination expelling SO_2 . The latter solid displayed good reactivity after a number of the sulfur cycles.

Curran et al's experience with the Greenfield stone provides important evidence bearing upon the probable feasibility of the proposed new desulfurization processes. With use of the Greenfield stone, the new processes should be operable in gas-production and gas-purification steps at pressures ranging upward from 100 atmospheres.

Glud et al (24) reported that CO_2 was taken up by $[\text{CaO}+\text{MgO}]$ at 570°F . Dry CaO absorbs only an insignificant amount of CO_2 at this temperature; it reacts markedly at 660° , and rapidly at 790°F (46); but the reaction proceeds readily only to an extent such that about one-half of the CaO is recarbonated (9, 14, 24, 40, 49, 67). The solid $[\text{CaCO}_3+\text{CaO}]$ decomposes at a rate some 4 to 6 times faster than calcite (14). Shushunov and Fedyakova (58) studied the kinetics of $\text{CaO} + \text{CO}_2$.

As Glud et al recognized, calcination of a Mg-poor dolomite probably puts some CaO in a state such that only about one-half of it can absorb CO_2 , in accordance with the behavior of lime. This accounts for the poor performance of dolomites having high Ca/Mg ratios. Glud et al warned against selecting a dolomite having calcite strata.

Although MgO takes up CO_2 readily at atmospheric temperature in presence of water vapor (47), its reaction with CO_2 at high temperature is extremely slow (9, 14, 33). Little recarbonation of MgO will occur even if CO_2 exceeds the equilibrium decomposition pressure of MgCO_3 when reaction (1) is carried out.

3.03 Use of [CaO+MgO] to Promote CO-Shift and the H₂O-C Reaction

DuMotay (21) first proposed use of lime to promote CO-shift in 1880, and this idea received persistent attention without its ever coming into commercial use (1). Greenwood (31) and Taylor (68) reviewed the state of the art in 1920 and 1921 respectively, and Schmidt (55) reviewed the subject in 1935. The most highly developed ideas were advanced by Gesellschaft für Kohlentechnik (24) and Bössner and Marischka (12).

The Gesellschaft für Kohlentechnik recognized that MgO crystallites in [CaO+MgO] are catalytic for CO-shift. Magnesia can be prepared in far more active forms than can any of the other alkaline earth oxides; active magnesias are produced for use as industrial adsorbents having surface areas of the order of 200 m²/gram (48). Gluud et al demonstrated that [CaO+MgO] is catalytic for CO-shift at temperatures above about 750° F, while CaO showed no catalytic activity at any temperature. The catalytic worth of MgO was not altered as the solid was converted to [CaCO₃+MgO]. From this fact, as well as from the ease with which CaO in [CaO+MgO] may be recarbonated, it may be inferred that [CaCO₃+MgO] has an open, porous structure.

The Gesellschaft für Kohlentechnik's CO-shift process was conducted at atmospheric pressure in a fixed bed of [CaO+MgO]. The operation was cyclic, a period of H₂ manufacture being followed by a period in which [CaCO₃+MgO] was calcined, the bed of solid remaining in place in a reactor. Low final CO concentrations, generally below 0.1%, were achieved in operations at 930° F. Break-through of CO occurred at a space velocity of about 130 V/hr-V based upon CO content of gas and upon the [CaO+MgO] remaining in the bed. In operations of a pilot plant on the scale of 200,000 SCF per day, no decrepitation or loss of absorptive capacity was found after many cycles of operation, and it was reported that the life of a dolomite charge should be three months at the very least.

A serious defect in the Gesellschaft für Kohlentechnik's process thinking was exposed when operations were conducted on a large scale. So much heat was generated during the shift step that the temperature became too high for good CO₂ removal unless untreated gases were introduced cold, but this proved infeasible since Ca(OH)₂ formed and the solid quickly decrepitated. The difficulty was got around, after a fashion, by introducing a cooling phase in the cycle, in which the reaction bed was cooled by circulating air at 750° F after the bed had been partly used up. Another defect was that several hundred per cent excess air had to be used in order to keep the calcination temperature below a level at which solid reactivity would suffer. One consequence of the large amount of excess air was that thermal efficiency of the overall process was extremely poor. Another consequence was that both fuel gas and the CO-containing gas to be treated had to be low in sulfur to avoid conversion of large amounts of CaO to CaSO₄, which not only would destroy its usefulness but would probably also lead to losses of H₂ through reduction of CaSO₄ to CaS in the shift step.

DuMotay and Marechal (22) first proposed use of lime to aid the gasification of carbon by steam in 1867, and a large patent literature has ensued (2). Taylor (68) and Schmidt (55) reviewed the art. Dent (20) reported that "trouble occurred due to the caking of the charge" during a test of the idea at 28 atmospheres. The nature of this trouble was identified by Consolidation Coal Company, and was circumvented in the CO₂ Acceptor Process by keeping the

partial pressure of steam below 13 atmospheres.

A patent literature has developed around the idea of using heat from $\text{CaO} + \text{CO}_2$ to supply endothermic heat needed for the reforming of hydrocarbons by steam (3). Marisic (44) visualized using heat from this reaction to sustain catalytic cracking.

3.04 Use of Lime and $[\text{CaO}+\text{MgO}]$ for Desulfurization

An historical method of desulfurizing town gas was treatment with $\text{Ca}(\text{OH})_2$ at atmospheric temperature. The process was used until 1870 in Europe and until 1905 in England. General information may be found in Seil (57).

Mellor (46) reported that dry H_2S does not react with dry CaO in the cold, but when heated, water is evolved, and the mass becomes yellow owing to separation of some elemental sulfur. Wickert (70) showed that the speed of reaction of H_2S with CaO rises sharply between 750° and 1100°F , and stated that CaS is much harder and tougher than CaO . Taylor (68) stated that CaO at around 930° to 1020°F catalytically converts CS_2 in presence of steam to CO_2 and H_2S , both of which are fixed by the lime. A patent literature has grown up about the idea of using lime for fuel desulfurization (4).

Schenck and Hammerschmidt (54) reported that CaS prepared by contacting CaCO_3 with H_2S and CO_2 at 1450° to 1830°F was unsintered and showed no loss of chemical reactivity. It had a pinkish cast, as did the $[\text{CaS}+\text{MgO}]$ prepared by McCrone Associates.

A British patent (8) reported that CS_2 , thiophene, and other organic sulfur compounds are dissociated, with formation of H_2S , if contacted with hot MgO . Carbon is deposited, and may be burned off.

Glud and Klempt (25) stated that organic sulfur compounds are split, with formation of H_2S , when town gas is contacted with calcined dolomite above about 1100°F . Kirillov and Budanov (41) showed that the decomposition of CS_2 over dolomite was a maximum at 1200°F , independent of steam concentration. Kakabadze (37) patented the use of hot calcined dolomite to purify gases of organic sulfur compounds. Zahn (73) reported the calcined ankerite in the Bössner-Marischka process (12) was highly effective in removing organic sulfur, and he claimed that its catalytic worth for CO -shift was not impaired after prolonged use to remove such sulfur.

Dolomite is used in a moving bed to remove sulfur from hot "carburettor gas" of the Wiberg process used in Sweden for production of sponge iron (65). The quantity of dolomite charged is the temperature control on reducing gases to the Wiberg furnace, and dolomite is discharged typically containing only about 5% to 10% sulfur. No decrepitation of the dolomite lumps is experienced. (11)

3.05 Converting $[\text{CaS}+\text{MgO}]$ to $[\text{CaCO}_3+\text{MgO}]$ and H_2S

Riesenfeld (50) studied the reaction of steam and CO_2 with CaS at atmospheric pressure, conducting four exploratory experiments between 896° and 1526°F . He did not intend to measure equilibria for the reaction, and he did not estimate equilibria from his data. The measurement at 1526°F was more

carefully made than the other three, and one can derive a reasonably good estimate of the equilibrium from Riesenfeld's results at this temperature: the estimate falls only about 10% above the curve of Figure 2. Crude estimates of equilibria from Riesenfeld's other three points lie 20% below, 50% below, and 120% above the curve of Figure 2. Riesenfeld did not report H_2S concentrations in product gas, but one can deduce (very roughly) that about 2% H_2S was present in a run at 941°F, and lesser amounts at other temperatures. Riesenfeld concluded that the conversion of CaS to $CaCO_3$ by its reaction with steam and CO_2 is not a practicable proposition, although his results may now be regarded as confirmatory evidence in support of the conclusions which have been drawn from the tests conducted by McCrone Associates at higher pressure.

The reaction of liquid water and CO_2 with CaS has been recognized since 1817, when the towns gas industry adopted dry purification with slaked lime. Used-up lime was decomposed by action of water and CO_2 when left in the open air, a process which contributed to the poisoning of air around old-time gas works (46, 60). The reaction was put to commercial use in the Claus-Chance process (53), which recovered H_2S from CaS waste from the Leblanc soda process.

Wickert (70) incorporated the reaction in a proposed process to eliminate sulfur from flue gases derived from heavy residual fuel oil. Wickert would employ partial oxidation of the oil with air; would desulfurize the resulting lean fuel gas with $CaCO_3$ at around 1460° to 1830°F; and would cool the resulting CaS to atmospheric temperature, slurry this solid with water, and react the slurry with CO_2 -bearing flue gases. By comparison with the new desulfurization processes proposed here, Wickert's scheme has disadvantages including: (1) much heat would be discharged at low temperature and could not be put to use; and (2) $CaCO_3$ would probably be recovered in such finely divided form that its separation from desulfurized fuel gases might be difficult.

4.0 Process Applications

A cataloging and evaluation of potential applications of the new desulfurization processes would fall outside the scope of this paper, which can only indicate briefly some of the possibilities.

Figure 6 illustrates a scheme for making a rich fuel gas from heavy residual oil, suitable for use in a top heat power cycle (63, 64) in which the temperature of steam is raised by direct addition of the products of combustion of the rich fuel gas with oxygen. A solid comprising mainly [$CaCO_3+MgO$] is fed to a fluidized bed in which oil is gasified by oxygen and steam. The temperature should preferably be a little below the equilibrium decomposition temperature of $CaCO_3$, so that CaO is not produced in the fluidized bed. Gaseous products are desulfurized by the reverse of reaction (1). Wickert (70) reported that CaS is catalytic for the steam-carbon reaction, and one may be able to operate the gasification step in Figure 6 with only a small excess of steam beyond the amount called for by steam-carbon equilibrium. Solid is conveyed from the gasifier to an elevated cyclone, which delivers solid via a standpipe to the sulfur desorber. Here reaction (1) is conducted in a fluidized bed with use of CO_2 supplied from the heat exchange in which steam is condensed from top heat cycle fluid. Heat from reaction (1) is used to raise or superheat high-pressure steam. In a top heat cycle using Kuwait heavy residue (4.73% sulfur), this heat amounts typically to about 1.5% of the total water-heating, steam-raising, and steam-superheating

duty. Offgas from the sulfur desorber is cooled to condense excess steam, and gas rich in H_2S is sent to a sulfur plant. Rich fuel gas for use in a top heat cycle must be absolutely free of dust. Various arrangements for removing dust from the gas may be considered (63), but schemes which work at high temperature are preferred. An interesting possibility is to use oil to be fed to the gasifier in a scrubber working at about $600^\circ F$, say, which removes at least a major part of the dust.

Figure 7 shows equipment for sulfur recovery when desulfurization is accomplished by means of reaction (3), so that the solid charged to the sulfur desorber contains CaO . The sulfur desorber in Figure 7 houses two fluidized beds: a lower bed for conducting reaction (1), and an upper bed in which reactive values of CaO in the solid are converted to $CaCO_3$ in the absence of steam. Provision of the upper bed allows one to use a higher steam partial pressure in reaction (1) than would otherwise be possible, for one does not have to worry about the formation of $Ca(OH)_2$.

In the context of the top heat power cycle, there is advantage in operating the Claus system under pressure, since equipment exists both to provide high-pressure air and to recover power from Claus-system offgases.

Figure 8 illustrates an application in which CO-shift is conducted by means of reaction (4). Shift is carried out in reactor A, which houses two fluidized beds, the upper bed being held at a lower temperature. Spent solid is calcined in reactor B. Flow of gas and solid in reactor A is countercurrent. By conducting the greater portion of the shift reaction in the lower bed, at higher temperature, the calcining duty in reactor B is reduced. Also, the upper bed of reactor A can be operated at a much lower temperature than that needed in a single-bed reactor in order to avoid $Ca(OH)_2$.

The scheme of Figure 8 is obviously more attractive if one has need for high-level heat, available to the heat-transfer surfaces shown in reactor A, as well as need for H_2 . The scheme of Figure 8 would permit the production of extremely cheap byproduct hydrogen in future power stations which employ some combination incorporating pressurized fuel gasification, fuel-gas cleanup, and an advanced power cycle.

Figure 9 illustrates representative schemes in which oil-cracking is practiced together with desulfurization. In general, reactor A of Figure 9 would operate at a lower temperature than the gasifier of Figure 6. If less steam is used than the amount called for by steam-carbon equilibrium, coke generated by cracking reactions in reactor A could serve as at least part of the fuel used to calcine the solid in reactor B. The splitting of the oil into two fuel fractions, one rich in hydrogen and the other lean, is advantageous in the context of the top heat cycle. H_2 in rich fuel gas is ultimately discharged from the cycle as liquid water. There is an advantage in putting as much of the fuel's H_2 content as possible into the rich-fuel-gas path, in order to keep the water-vapor content of flue gas generated by combustion of the lean fuel gas from reactor B as small as possible.

The air or oxygen requirements for reactor A can be considerably reduced by drawing upon heat of recarbonation of CaO , as well as heat from reaction (4). A fuel gas of high calorific content can be produced even with the use of air. Such a gas is well suited for use in a top heat cycle using air instead of oxygen.

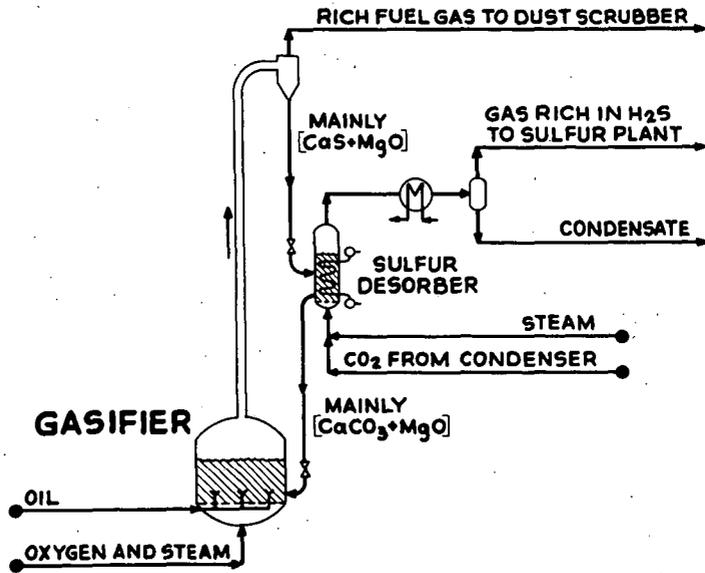


Figure 6. SCHEME FOR MAKING RICH FUEL GAS FOR TOP HEAT POWER CYCLE

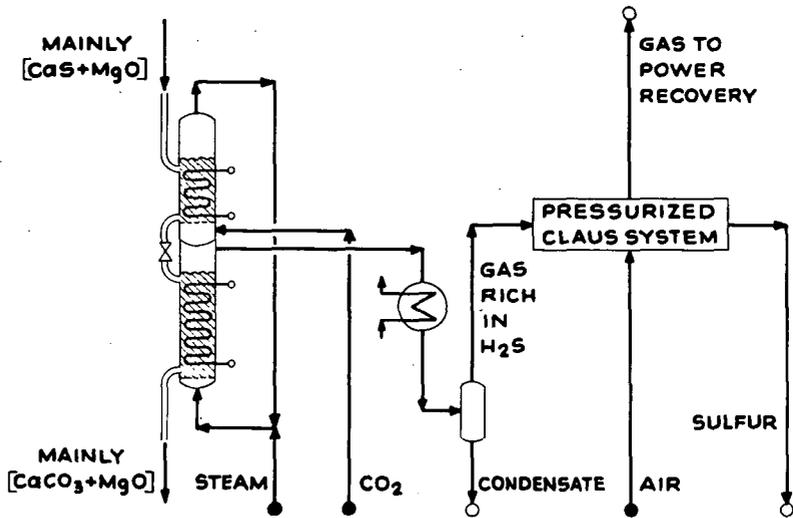


Figure 7. SULFUR DESORBER AND SULFUR RECOVERY

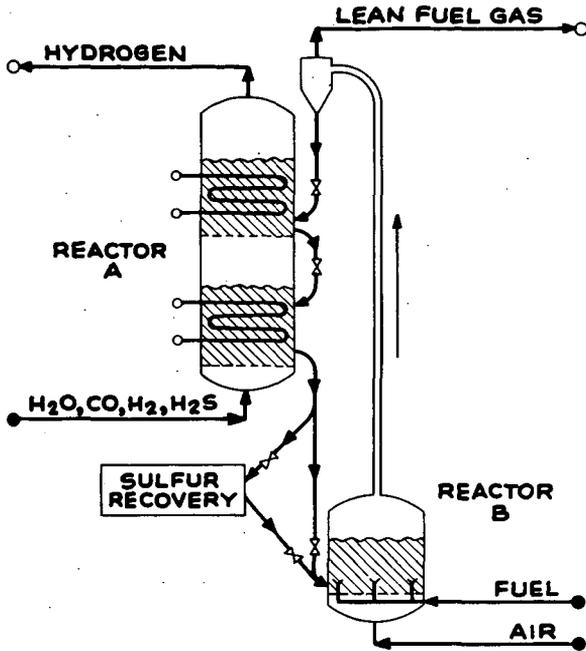


Figure 8. CONDUCTING CO-SHIFT IN A POWER-STATION CONTEXT

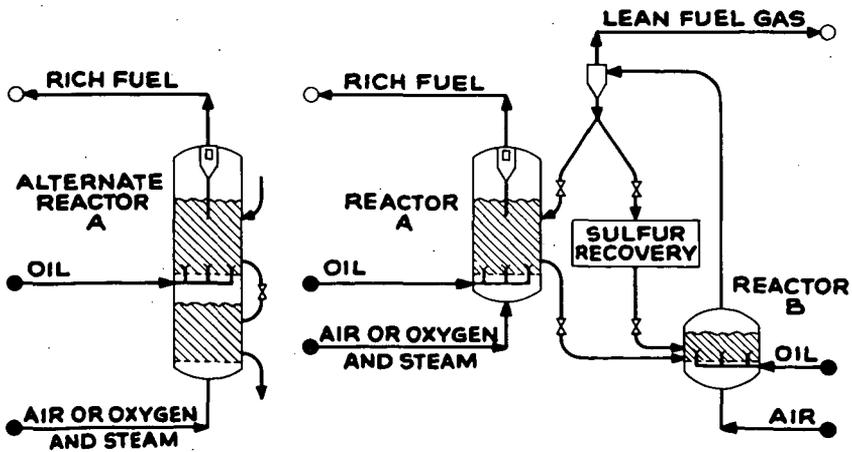


Figure 9. REPRESENTATIVE SCHEMES INVOLVING OIL CRACKING

An interesting possibility is to use air in reactor A to produce clean fuel of high calorific value for existing power-station boilers in communities which place restrictions upon SO_2 in flue gas. A gas-turbine plant would be required to supply air to reactor B and to recover power from the lean fuel gas. Power generated in this gas-turbine plant would represent a small fraction of the capacity of the existing power station to which clean fuel is supplied.

Alternate reactor A in Figure 9 provides for gasification of oil in two steps: oil is cracked in an upper bed in an atmosphere containing H_2 , the H_2 being generated from coke in a lower bed.

The foregoing examples by no means exhaust the possibilities. Modifying Consolidation's CO_2 Acceptor Process to incorporate the recovery of elemental sulfur has been mentioned. Hydrocracking or hydrogasifying oil, by using H_2 as the fluidizing gas to reactor A of Figure 9, is an interesting possibility.

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