

One of the more difficult analytical problems was determining carbonyl sulfide in the presence of other sulfur compounds, especially carbon disulfide. A satisfactory method was developed, based on hydrolysis of carbonyl sulfide in dilute potassium hydroxide, with subsequent determination of the sulfide ion by the methylene blue procedure (12). Thiophene, carbon disulfide, and mercaptan sulfur do not interfere with the test.

Sulfur Poisoning of Methanation Catalyst

To make cost estimates on the production of high-B.t.u. gas from coal as realistic as possible, the Southern Natural Gas Co. (and the Tennessee Gas Transmission Corp.) supported in part a study on the effect of sulfur on the poisoning of a nickel catalyst developed and tested in England by the Gas Research Board.

The tests were made using carbonyl sulfide, the organic sulfur compound most likely to be present in unpurified synthesis gas made by reacting coal with oxygen and steam. Five runs were made with gas of about 2:1 hydrogen: carbon monoxide ratio and with sulfur concentrations ranging from 0 to 1.53 grains per 100 std. c.f. (19). At constant space velocity, sulfur concentration times the number of days of operation during which conversion to methane remained above 97 percent was a constant. The heating value of the product gas (on a CO₂-free basis) remained relatively constant at 940 B.t.u. per cu. ft., based on dry gas measured at 60° F. and 30 inches Hg (see fig. 29). When sulfur was present in the gas, catalytic activity decreased as soon as approximately 0.58 gram of sulfur had been adsorbed per 100 grams of nickel. The spent catalyst from one run was only partly regenerated by burning off the sulfur with air at 900° C.

Process Development

Studies of Dust-Removal Processes

Dust Removal in Atmospheric-Pressure Pilot Plant. - The raw gas from the atmospheric-pressure gasifier at Morgantown contained several thousand grains of dust per 100 cu. ft. (22). The dust load was reduced to 2,000 or 3,000 grains per 100 cu. ft. by passing the gas through an unpacked fogging chamber intended merely to cool the gas. A ring-packed scrubber then reduced the dust load to 10 to 30 grains per 100 cu. ft., a removal efficiency of over 99 percent. Half of the remaining dust particles were then less than 20 microns in diameter.

Fine purification was accomplished at times in an electrostatic precipitator. Dust concentrations in the effluent ranged from 0.02 to 0.3 grain per 100 cu. ft. Particle size in the effluent dust was not greatly altered.

Another device used for fine purification was the moving-bed coke filter (8, 9). The gas passed upward through a bed of coke, which periodically moved downward. Fouled coke was removed from the bottom, washed free from dust, and returned to the top of the bed without interference with the filtration operation. The filter could be used at high temperatures or with gases containing much water. Any desired purity could be obtained by controlling the fineness of the filtering material and pressure drop through the apparatus.

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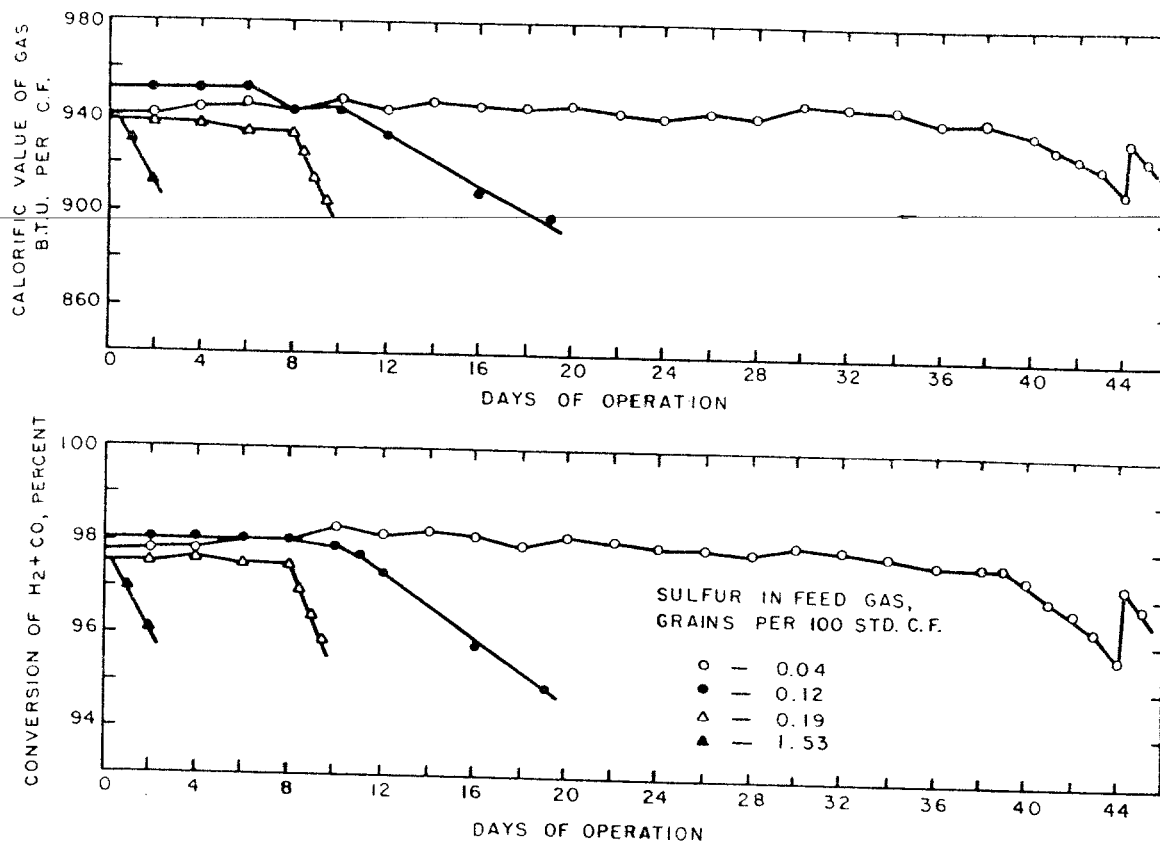


FIGURE 29. - Effect of Carbonyl Sulfide Poisoning on Activity of a Nickel Catalyst Used for Methanation.

On a large scale (3,900,000 std. c. f. per hour) at Oppau, Germany, the moving-bed coke filter was more efficient than an electrostatic precipitator or Theisen disintegrator. The dust load of the gas was reduced from about 5 inches of water. Tests in the atmospheric-pressure gasification system at Morgantown corroborated these results. In one test, dust concentration was reduced from 35 to 0.2 grain per 100 cu. ft. (99.4-percent removal). However, with the filter design used at Morgantown, coke could not be circulated at this pressure drop. Most tests were made at 1.25 to 2.5 inches of water, which usually left outlet dust loads of 0.2 to 3 grains per 100 cu. ft. (85- to 98-percent removal). Used after the electrostatic precipitator, the filter removed usually 86 to 95 percent of the small amount of remaining dust, leaving extremely low concentrations of 0.004 to 0.1 grain per 100 cu. ft.

Process-design information was obtained on the pilot-plant filter and also on a laboratory-scale filter using various sizes of coke. Dry beds of coke removed dust better than wet beds, for the same pressure drop. Probably the water fills cavities in the coke surface and makes the coke act like smooth pebbles, previously found less effective.

Dust Removal in High-Pressure Pilot Plant. - In the high-pressure pilot plant the dust train used was somewhat similar to the low-pressure train just described. An unpacked water-spray chamber in the base of the gasifier first

quenched the gas. Dust determination was impossible at this point, but calculations on the residue indicated that gas leaving the reaction zone contained roughly 3,000 grains per 100 cu. ft. of material fine enough to be called dust, plus much molten slag presumably in larger masses at this point. This initial load was reduced to about 1,500 grains per 100 cu. ft. by the sprays in the gasifier. The next dust-removing device was a cyclonic section in the bottom of the scrubbing tower, which reduced dust concentration to about 77 grains per 100 cu. ft. This was followed by a ring-packed scrubber, which proved very effective at high pressure. The most important variable was pressure (fig. 30); residual dust load decreased greatly as the pressure increased.

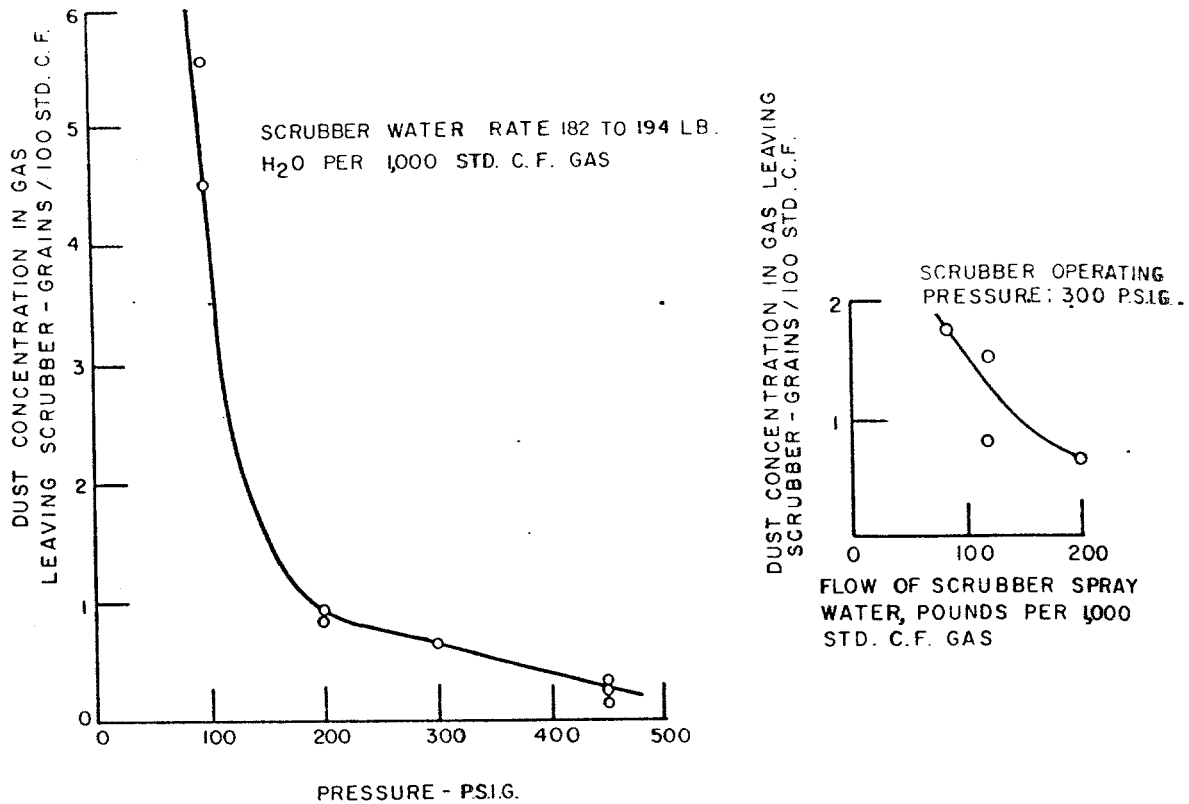


FIGURE 30. - Performance of High-Pressure Dust Scrubber.
(Data from 29 different gasification runs.)

The usual pilot-plant equipment has been described above, but several other dust-removing devices have been tested in the laboratory or in pilot-plant purification trains at different times. In laboratory work, cyclones 2 inches in diameter, with 2 inches of water pressure drop, were found suitable for removing dust particles over 20 microns in diameter. Such cyclones were used satisfactorily for dry removal in the pilot plant for a short time.

For removing fine dust particles, the first small gasification system (17) employed two porous metal filter plates, which operated in parallel. One was cleaned while the other was in use. This method yielded gas containing about 0.2 grain of dust per 100 cu. ft. but probably would not be practical on a larger scale.

Final, preferably profitable, disposal of the separated dust poses a difficult problem. Screening and elutriation were tried to separate ash from combustible material, so that the latter could be recycled, but no important separation could be obtained. If much of the solid material were removed as slag, it might be practical to recycle all the recovered dust in the gas. Use of the residue as a rubber compounding agent was investigated. This material showed some reinforcing power and could be used as a filler but is no substitute for carbon black.

Sulfur- and CO₂-Removal Processes

Bench-scale and pilot-plant experimentation, on the removal of organic sulfur compounds from gas, covered catalytic processes operating at elevated temperatures and pressures and adsorption on activated carbon, both at atmospheric and elevated pressures. Of the catalytic processes, the most promising utilized a copper-chromium-vanadium catalyst, which converted the organic sulfur compounds to hydrogen sulfide and acted as an absorbent for the hydrogen sulfide formed (15). This process, although expensive because of the periodic regeneration and reduction of the catalyst, was an excellent means of producing an extremely pure gas at elevated temperatures. Purified gas, containing less than 0.001 grain of total sulfur per 100 std. c. f., was obtained at temperatures of 300° to 400° C. The process was selective and did not remove carbon dioxide from the gas.

Activated Carbon. - A significant improvement in the purification of synthesis gas was the elimination of the alkalized iron process (used in Germany for removing organic sulfur compounds) by substituting activated-carbon drums or adsorbing organic sulfur at elevated pressures. Tests showed that activated carbon alone could reduce the organic sulfur content to less than the specified amount of 0.1 grain per 100 cu. ft. (15, 23). Bench-scale and pilot-plant studies on "GW" carbon^{9/} at 300 p.s.i. showed that:

1. The adsorptive capacity for carbonyl sulfide was a linear function of inlet sulfur concentration, at least between 10 to 30 grains per 100 std. c. f.
2. The presence of carbon dioxide had a marked effect on the capacity of carbon for carbonyl sulfide. Carbon adsorbed twice as much carbonyl sulfide from a gas containing 0.5 percent carbon dioxide as from a gas containing 5 percent carbon dioxide.
3. The effect of pressure on the capacity of an activated carbon for carbonyl sulfide depended on the carbon dioxide content of the gas. With a gas containing less than 0.5 percent carbon dioxide, the carbon adsorbed about seven times as much carbonyl sulfide at 300 p.s.i. as at atmospheric pressure. With a gas containing 20 percent carbon dioxide, this factor was only 1.7.
4. Activated carbon could remove carbonyl sulfide and small quantities of hydrogen sulfide simultaneously. (If traces of oxygen are present in the

An activated carbon made from coal, supplied by the Pittsburgh Coke and Chemical Company.

gas, some of the hydrogen sulfide will be oxidized to elemental sulfur. This would necessitate periodic solvent extraction of the sulfur to regenerate the carbon.)

In 1949, when the Morgantown purification pilot plant was put into operation, special emphasis was placed upon selective removal of hydrogen sulfide and subsequent conversion to elemental sulfur. At the time, substantially complete removal of carbon dioxide was not considered very important, since information based on German practice in the Fischer-Tropsch synthesis indicated that carbon dioxide in the purified gas was not a catalyst poison.

The first pilot-plant runs were therefore made to study the selective properties of aqueous solutions of triethanolamine (TEA), tripotassium phosphate (K_3PO_4), and potassium N-dimethyl glycine (Alkazid DIK) (20-22). The purification pilot plant (fig. 31) and the solution and gas cycle have been

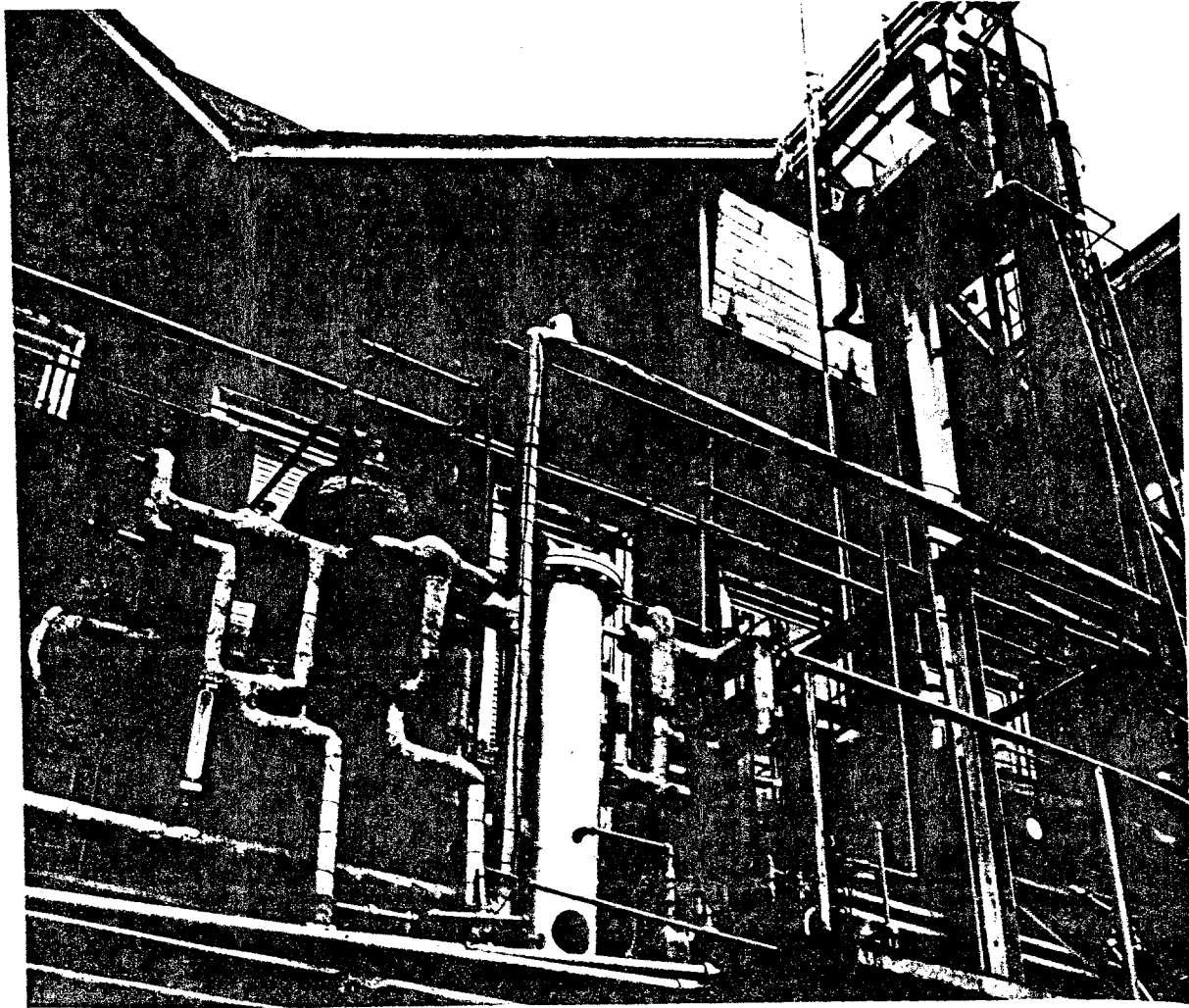


FIGURE 31. - View of Gas-Purification Pilot Plant.

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H₂S IN ACID GAS, PERCENT

FIGURE

described in detail in previous publications. The following data were obtained for a gas containing 10 percent carbon dioxide and 0.5 percent hydrogen sulfide and treated at 300 p.s.i. so that hydrogen sulfide in the scrubbed gas was reduced to 25 grains per 100 std. c. f.:

Absorbent	H ₂ S absorbed, pound per gallon	H ₂ S in gas leaving reactivator, percent
35 percent K ₃ PO ₄	0.025	19.0
Alkazid DIK (sp. gr., 1.1380).....	.033	11.5
30 percent TEA.....	.030	12.5

The effect of carbon dioxide:hydrogen sulfide ratios in the raw feed gas on the hydrogen sulfide content of the gas coming from the reactivator was determined for tripotassium phosphate (fig. 32) and for Alkazid DIK (fig. 33).

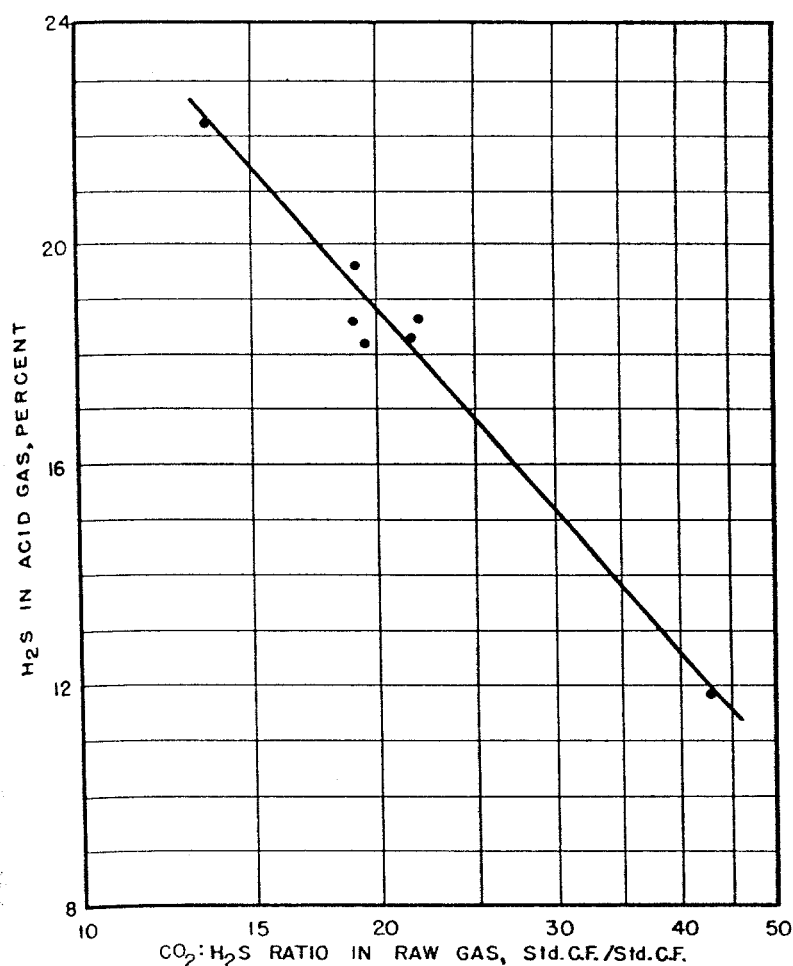


FIGURE 32. - Correlation of Carbon Dioxide:Hydrogen Sulfide Ratios in Raw Gas With Composition of Acid Gas From Reactivation of Foul Phosphate Scrubbing Solution.

In later research by the Bureau it was learned that carbon dioxide in rather large amounts has a deleterious effect on the Fischer-Tropsch synthesis. Therefore, pilot-plant research was directed toward simultaneous removal of hydrogen sulfide and carbon dioxide (20, 22). As already discussed, removal of most of the carbon dioxide would assist in adsorbing carbonyl sulfide on activated carbon. Also, simultaneous removal would not preclude the recovery of elemental sulfur from the acid gases stripped from the spent absorbent.

About 60 percent of the cost of removing hydrogen sulfide and carbon dioxide by liquid scrubbing is the expense for steam to regenerate the spent solution. Under cooperative agreement with the Turbo-Mixer Division, General American Transportation Corp., small pilot-scale experiments were initiated to find whether costs could be reduced by replacing the conventional packed absorber

with an agitator absorber (see fig. 34). Preliminary results indicated about 30 to 50 percent greater pickup of carbon dioxide, per volume of solution, with this absorber than with either a packed or bubble-cap column (23).

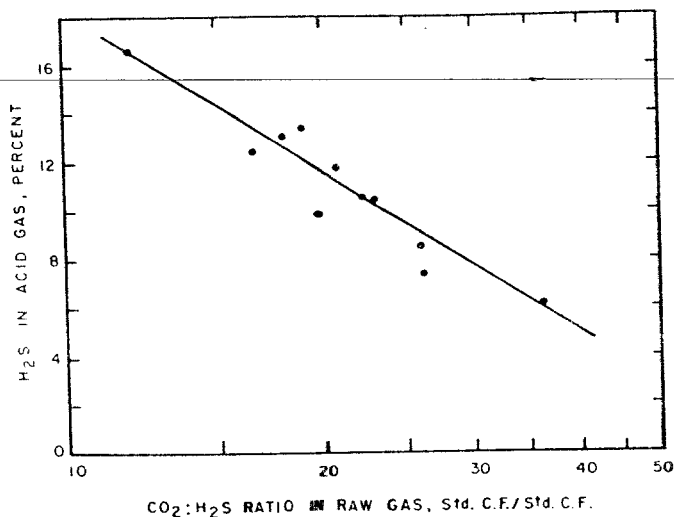


FIGURE 33. - Effect of Carbon Dioxide:Hydrogen Sulfide Ratios in Raw Gas on Composition of Acid Gas Obtained in Reactivation of Potassium N-Dimethyl Glycine Absorbent.

process was developed for removing hydrogen sulfide and carbon dioxide from synthesis gas, using a hot, concentrated solution of potassium carbonate. A description of this process follows.

Hot Carbonate Scrubbing

During the production of synthetic liquid fuels from coal via gasification and the Fischer-Tropsch process, some 200 cu. ft. of carbon dioxide per gallon of gasoline must be removed. Hydrogen sulfide (from sulfur in the coal) must also be removed, as it poisons the catalyst.

To reduce the cost of purification, a process employing absorption by a concentrated solution of potassium carbonate, at elevated pressure and temperature, has been developed at the Bruceton laboratory. The most practical range of concentrations of carbonate solution was between 30 and 45 percent; above this range precipitation occurred at relatively low concentrations of bicarbonate. The spent carbonate solution, after leaving the absorber, was regenerated by depressurizing and steam stripping. Because absorption and regeneration occur at about the same temperature (about 230° to 250° F.), no heating and cooling were required between steps so steam requirements were lowered and the cost of heat exchangers was eliminated (1, 2, 4, 6, 7).

Two pilot plants employing continuous countercurrent absorption were operated from 1951 to 1955 (5) (fig. 35). The principal components were an insulated absorber and regenerator and a flash drum where the spent solution

During the research on gas purification at Morgantown two major contributions were made elsewhere. In Germany a one-step, low-temperature process known as "Rectisol" was developed for removing hydrogen sulfide, carbon dioxide, organic sulfur compounds, gum formers, and water. Essentially, raw gas is cooled by the purified gas and fed to the bottom of an absorber, where it is scrubbed with methanol at elevated pressures and -30° F. At the Bureau of Mines, Bruceton, Pa., an economically attractive

FIGURE 35
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