

3. DESCRIPTION OF EXPERIMENTAL UNIT

An experimental unit was constructed in order to make experimental measurements of trace sulfur removal at the actual conditions expected for the SYNTHANE pilot plant process stream. The unit was designed to operate at high pressure, with a completely simulated synthesis gas and to have the capability to handle up to all five of the trace sulfur compounds of interest. The sulfur purification system was to operate at 1000 psig with a synthesis gas composition prior to final sulfur removal of the following approximate composition:

	<u>Mole %</u>
H ₂	45.0
CO	15.0
CO ₂	1.0
CH ₄	35.0
C ₂ H ₆	1.0
N ₂	2.85
H ₂ O	0.15
Sulfur compounds	as indicated below
Total	100.0

The following sulfur compounds and the range of their respective concentrations were to be investigated:

Hydrogen sulfide	15 - 25 ppm (v/v)
Mercaptans	15 - 25 ppm (v/v)
Thiophenes	35 - 45 ppm (v/v)
Carbon disulfide	8 - 12 ppm (v/v)
Carbonyl sulfide	70 - 80 ppm (v/v)

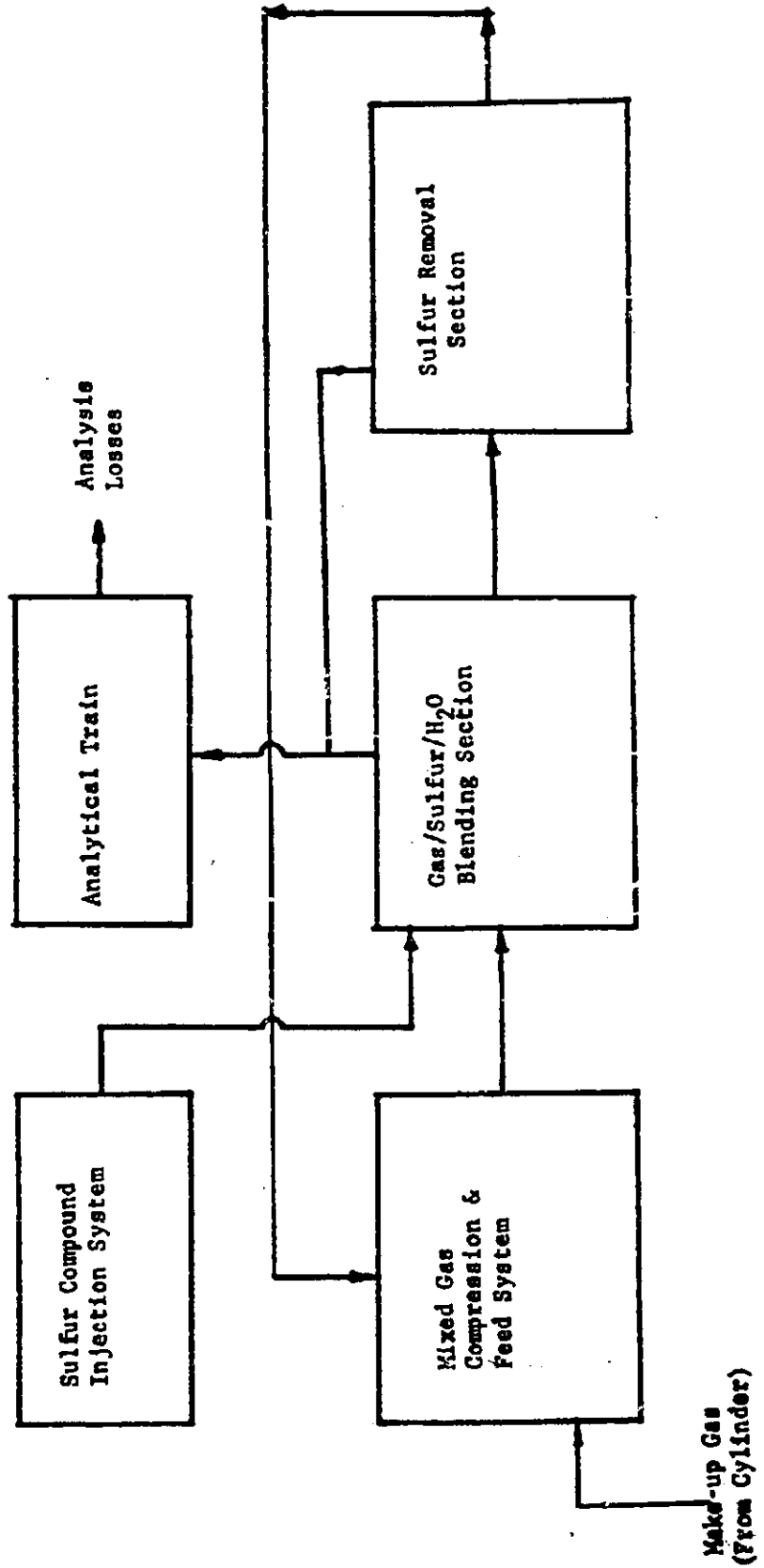
It was desired that the synthesis gas be purified prior to methanation down to a total sulfur content of less than 0.1 ppm (v/v). This objective of removing sulfur down to a final content of less than 0.1 ppm (v/v) was of prime importance.

The test unit consists of five basic subsystems:

1. Mixed Gas Compression and Feed System
2. Sulfur Compound Injection System
3. Gas/Sulfur/Water Blending Section
4. Sulfur Removal Section
5. Analytical Train

A simplified block diagram illustrating subsystem interaction is shown in Figure 3.1. A brief description of each subsystem follows:

FIGURE 3.1
TEST UNIT BLOCK DIAGRAM



3.1 Mixed Gas Compression and Feed System

Pre-blended synthesis gas (ca 45% H₂, 15% CO, 1% CO₂, 3% N₂, 35% CH₄, and C₂H₆), free of sulfur compounds and water, was purchased from suppliers in conventional compressed gas cylinders. This gas enters the suction side of the gas compressor at ca 2.7 MPa (400 psig). Gas exits the compressor at ca 10.3 MPa (1500 psig) where a certain fraction, dependent on system demand, is sent forward while the remainder is by-passed back into the compressor. Maximum compressor output is 250 SCFH. (As a point of reference, four 0.53 cm I.D. x 30 cm long reactors operating in parallel at a space velocity of 50,000 SCF/hr/SCF bed (equivalent to a space velocity of approximately 700 hr⁻¹ at 1000 psig) requires a total of 48 SCFH.) An accumulator is also provided to dampen compressor pulses while a bicw-by tank is used to monitor mechanical condition of the compressor.

3.2 Sulfur Compound Injection System

The original approach used for injection of sulfur compounds involved volumetric displacement from a syringe-like apparatus containing each of the compounds (H₂S, COS, CS₂, methyl mercaptan, and/or thiophene) as liquids under pressure. The piston is threaded so that it advances 2.54 cm in 16 revolutions. The piston, in turn, is driven by a synchronous motor connected to the piston through a series of precision gears with a gear reduction ratio of 3000/1. The motor has a maximum output of 72 RPM which can be stepped down in 100 equal increments. Operation at full speed results in a piston linear displacement of 0.23 cm/hr. Actual volume displacement would be determined by the surface area of the piston face. (As a point of reference, a piston of 2.54 cm diameter operating at the above maximum setting would result in an 80 ppm level of COS for a gas flow of 250 SCFH.) After leaving the syringe, the sulfur compound is transported through a 0.2 cm I.D. tube where it is combined with the sulfur-free synthesis gas in a blending tee. Contained within the entire tube is a wire which serves to reduce the transport tube volume. In addition, the wire extends beyond the outlet of the tube into the blending tee and serves as the final conduit by which the sulfur compound contacts the flowing gas stream. The net result is that drop formation at the tube outlet is avoided due to the wire's providing sufficient surface area for rapid evaporation of the liquid feed.

The system described above was used for the first few single component adsorption test runs. However, because of problems in maintaining the feed concentrations at the desired levels (particularly for low concentrating feeds) a different gasifying system was designed and installed. This alternative approach to feeding of sulfur compounds, consisted of introduction, at ca 6.8 MPa (1000 psi), of sulfur compound(s) in suitable carrier gas into the main synthesis gas stream. This approach, which required purchasing sulfur-containing gas from suppliers, in addition to the current sulfur-free synthesis gas, had associated with it certain penalties. For example, the carrier gas could not be of the same composition as the synthesis gas. In this regard, it was the policy of one of our gas suppliers (Matheson) to not fill any cylinders containing CO and any sulfur compounds above 6.8 MPa (1000 psi) because of their experience with system

instability problems and long-term cylinder corrosion possibilities. (The above pressure also represents our effective cylinder exhaustion pressure.) In addition, they could not guarantee the stability of <1% H₂S gas mixtures unless they were prepared in ultra-pure inert carriers such as H₂ or N₂ or blends, thereof. Furthermore, because of incompatibility problems between COS and H₂S, they could not guarantee stability of mixtures containing both of these gases.

Accordingly, the approach taken regarding purchase of sulfur containing gases was to purchase single sulfur compounds (except H₂S) or 4-component mixtures in CO-free simulated synthesis gas (CO balance made up with N₂), while H₂S was purchased in a 45/55 H₂/N₂ gas. (All were in Teflon-lined cylinders.) These gases, in turn, were metered into the sulfur-free bulk simulated synthesis gas stream in much the same way planned for the liquid microinjection pump.

3.3 Gas/Sulfur/Water Blending Section

After exiting the compressor, synthesis gas enters a temperature-controlled (air bath) insulated box where sulfur compounds are introduced (see above) and water may be added. Addition of water is done by bubbling gas through a saturator whose temperature can be controlled from approximately room temperature up to ca 95°C. Accordingly, for a gas stream at approximately 6.8 MPa (1000 psig), water content could be adjusted from 0.1% to 1%. The option to omit water introduction was also provided. The well-mixed synthesis gas is then sent to a manifolding line where it is split into a maximum of four streams for feeding to reactors at 6.8 MPa (1000 psig). A small slip stream at 100 kPa (15 psig) could also be diverted for analysis.

3.4 Sulfur Removal Section

The sulfur removal section consisted of an air-heated insulated box whose temperature could be controlled from just above ambient to ca 425°C. The reactor arrangement consisted of four parallel reactor tubes of 0.53 cm I.D. and 30 cm length containing test material and equipped with thermocouples to monitor bed temperature. Gas flow may be directed to any number of reactors with flow rate to each capable of independent monitoring and control. Other reactor geometrics and arrangements could be easily accommodated. For example, the compressor output capacity would allow for a single 2.43 cm I.D. x 30 cm long reactor operating at a space velocity of 50,000 SCF/hr/SCF bed. It would also be possible, by minor piping modifications, to increase reactor bed length and monitor gas composition at various points within a bed by arranging the four reactors in series. Thus, a wide range of experimental schemes can be addressed. After exiting each reactor, a small side stream of treated gas could be sent for analysis while the bulk of sulfur-free treated gas is depressurized back to ca 2.7 MPa (400 psig) and dehydrated by cooling and passage through a Linde 3A molecular sieve. In the recycle mode after water removal, each stream is recombined and sent back to the compressor where any sampling losses are continuously made up with cylinder-stored synthesis gas.

3.5 Analytical Train

The analytical train consisted of three gas chromatographs, two of which are F & M Model 720's (thermal conductivity detectors) while the third is a Perkin-Elmer Model 3920 equipped with flame ionization detection for hydrocarbons and flame photometric detection for sulfur compounds. The flame photometric detector is capable of detecting <1 nanogram of sulfur. Thus, in order to detect sulfur levels on the order of 0.1 ppm, gas samples on the order of 10 ml (at standard conditions) were required.

3.6 Unit Shakedown Experience

During the course of our experimental program, several unanticipated equipment difficulties were encountered which considerably delayed the start of experimental work. A synopsis of the major equipment problems encountered is presented in Appendix A. These dealt primarily with the compressor problem, analytical problems and the sulfur delivery system.

Solution of the compressor problem required rebuilding of idle compressors after the original unit proved inadequate. Regarding the analytical problems, considerable effort was expended in adapting state-of-the-art techniques where information and experience pertinent to project needs were quite limited, to provide the necessary means to monitor a spectrum of different sulfur compounds in actual synthesis gas over several orders of magnitude in concentration range. The originally conceived sulfur delivery system (sulfur pump) resulted in a large development effort that proved to be beyond state-of-the-art with respect to our requirements. After considerable evaluation of alternative approaches, a new delivery system was installed and its performance proved very favorable. As a result of this effort, a single versatile experimental unit was developed that reproduces the operating conditions expected in the SYNTHANE process and whose data can be used to address many of the questions and possible solution routes that might arise with respect to our objective of recommending a sulfur guard system for the SYNTHANE process.

4. EXPERIMENTAL RESULTS

After careful evaluation of the candidate sulfur guard systems described in Section 2, and giving consideration to the limited time on the program, the experimental effort concentrated on the metal impregnated activated carbon sorbent.

This section discusses the results of single and multicomponent adsorption of trace sulfur compound gases on metal-impregnated (copper and chromium oxides) activated carbon sorbent. This material, designated Katalco 7-2, is the same material planned for eventual use in the 72 TPD SYNTHANE pilot plant unit.

4.1 Selection of Sulfur Compound Feed Concentrations

An important consideration in this study involved the selection of sulfur compound feed concentrations to be addressed in our experimental program. The difficulty in selection of appropriate levels stemmed mainly from the fact that the original sulfur compound levels in the SYNTHANE gasifier effluent are strongly dependent on coal used (variation of one or two orders of magnitude are not uncommon based on the limited data available). In addition, several questions remained regarding the expected performance of the hot potassium carbonate (Benfield) system preceding sulfur guard. After reviewing the situation, it was decided that the original concentration range would define the upper limit of concentrations addressed (i.e. H_2S ~25 ppm, CH_3SH ~25 ppm, CS_2 ~12 ppm, COS ~80 ppm, C_4H_4S ~45 ppm), and thus would provide the most severe test of the adsorbents capacity to breakthrough.

The rationale for selection of the above concentrations as upper limits was based essentially on reviewing recent results for SYNTHANE gasifier effluent concentration (6), selecting these concentrations derived from the worst coal listed (Illinois No. 6), and assuming Benfield performance based on the recent paper of Parrish and Neilson (17). Other factors that entered included the fact that shifting one-half of the gas prior to acid-gas treatment should reduce the organic sulfur by one-half, while some upset in the hot carbonate scrubber might occur. More specifically, for methyl mercaptan, assuming a maximum gasifier effluent of 60 ppm, one-half of the gas shifted, and a minimum 70% Benfield removal efficiency, results in an approximate 10 ppm level as feed to sulfur guard. For carbon disulfide at 10 ppm maximum gasifier effluent, one-half shifting, and 70% minimum removal via Benfield, the result is an approximate 2 ppm level. For carbonyl sulfide at 300 ppm maximum gasifier effluent, half shifting, and 75% minimal removal (as high as 99% apparently has been achieved commercially), the result is ca 40 ppm. For thiophanes at 60 ppm maximum gasifier effluent, half shifting, and no removal by Benfield, a level of 30 ppm is obtained. Other factors, such as removal by some of the unit operations preceding the Benfield (e.g. the oil scrubber) would probably reduce all of the above even further.

Accordingly, the upper concentration limits listed for the above four organic sulfur compounds are quite conservative even if Benfield performance periodically drops below minimum expected levels. The H_2S level of 25 ppm was deemed reasonable based on claims by Benfield that levels of <10 ppm can be routinely achieved with certain versions of their

process. However, this particular impurity must be addressed with more caution since its level in gasifier effluent may be orders of magnitude higher (5,000-15,000 ppm) than the others, and upsets in the Benfield could result in extremely high discharge levels. Special precautionary measures probably would have to be incorporated into a plant design (e.g. routing gas to a furnace, etc.) to handle a major system upset involving large H₂S breakthrough.

In most of the experimental runs, a superficial velocity of 1.36 cm/sec was used. This value was a design value which may not be optimum for the system investigated.

4.2 Single Component Adsorption Studies

Separate adsorption breakthrough studies were conducted with each of the sulfur compound gases of interest in this study. This section describes the tests made with carrier gas (nitrogen or simulated synthesis gas) using only one sulfur compound component at a time. Subsequent studies which were carried out with multiple sulfur compounds are described in Section 4.3.

4.2.1 Hydrogen Sulfide in Nitrogen

Very preliminary experimental testing using metal-impregnated (copper and chromium oxides) activated carbon was conducted using H₂S in nitrogen. This material designated Katalco 7-2 was planned for eventual use in the 72 IPD pilot plant. Although supplied by Katalco, it is actually manufactured by Pittsburgh Chemical and designated as their FCA type. In-house analysis indicated this material contained, as metals, 8.00% Cu, 2.73% Cr, and 0.32% Fe. The runs were made to provide a preliminary, ball-park estimate of the maximum activity of the impregnated carbon since published data on this material was not in the open literature.

As previously described, a once-through operation mode using sulfur-containing carrier gas was adopted. The sulfur-containing gas employed in this run consisted of 110 ppm H₂S and 53 ppm H₂S, both in pure nitrogen. Because of supply restrictions, shallow beds (< 15 cm) were used. Low superficial velocities (< 0.64 cm/sec) were also used to contain the mass transfer zone within the bed.

Three tubes were charged with carbon bed depths of 6.4, 7.5, and 15.0 cm, respectively, and 110 ppm H₂S in N₂ at superficial velocities (at run conditions) of 0.64, 0.32, and 0.64 cm/sec, respectively, used as initial feed. (The superficial velocity design value of the pilot unit for the SYNTHANE Process is 1.38 cm/sec, while the 110 ppm H₂S level is greater than the ~25 ppm H₂S maximum levels anticipated.) After nearly 8 hours of run time, the utilizable 110 ppm H₂S cylinder gas was exhausted and switching over to 53 ppm H₂S in N₂ was required to continue the runs. No breakthrough occurred after running for a cumulative time of 31 hours at which time feed gas again was depleted. Accordingly, neither the 7.5 or 15 cm beds produced required capacity data and, thus, detailed discussion will be confined only to the run containing 6.4 cm of carbon. (These runs did serve to support the relatively high capacity levels found in the one good run.) Namely, if one assumes that capacity does not vary with H₂S feed concentration over the range used and uses the capacity levels found in the one good run, together with various assumptions regarding breakthrough curve shape, breakthrough times of ~35 hours are predicted.

Regarding the one run which provided capacity data, breakthrough occurred <10 minutes after 53 ppm H₂S feeding commenced. The transient history of the run is shown in Figure 4.1, with specific details given in Table 4.1. Prior to breakthrough in this run (as well as during the entire length of the two aborted runs) no detectable H₂S (<0.1 ppm) in the effluent was found. Because of the change in feed concentration just prior to breakthrough, the effluent levels plotted in Figure 4.1 are as % of H₂S in feed to the reactor which was continuously dropping toward 53 ppm because of upstream mixing time lags. The feed level to the reactor was, in turn, determined by monitoring the feed concentration to the fourth reactor which contained no carbon.

As indicated in Table 4.1, the H₂S capacity at breakthrough was found to be 5.7 wt % of the carbon charge, or 189,000 standard volumes of gas treated per volume of carbon used. Approximate maximum capacities of 6.7 wt % and 222,000 vols. gas/vol carbon were also calculated using highly idealized models of adsorption which visualize the bed at breakthrough as consisting of a fully saturated zone and a zone of completely unused bed (see, e.g., Lukchis (14)). Such numbers in theory, represent capacities which could be approached in very long beds where the mass transfer zone is assumed to be independent of bed length and, thus, would represent a very small fraction of the total bed length.

Even though the system of H₂S in pure N₂ would be expected to give very high adsorption capacities, the levels found were higher than expected. For example, if it is assumed that all of the Cu is utilized to form the sulfide, given the 8% Cu level found, 4% maximum H₂S loading capacity would be possible from this removal mechanism. It is not possible to account for the balance by assuming physical adsorption on the carbon and using the equilibrium adsorption isotherm data published by Grant et al (8) for H₂S on Pittsburgh BPL carbon (equivalent to unimpregnated Katalco 7-2). For the H₂S partial pressures used in the experiment, the above reference indicates <0.1 wt % H₂S pickup. It is possible that the above cited data is not applicable, or other effects, including total system pressure, were responsible.

4.2.2 Hydrogen Sulfide in Dry Synthesis Gas

Experimentation using Katalco 7-2 (equivalent to Pittsburgh 80A) metal-impregnated (Cu and Cr oxides) continued using H₂S in dry synthesis gas. Other analytical results showed this carbon to have S = 0.69%, C = 72.7%, H = 0.78%, N = 1.51%, ash (@788°C) = 18.3%, and surface area (BST) = 727 m²/g. This material was the same as planned for use in the 72 TPD pilot plant.

One of the four reactor tubes was left empty, while the remaining three were charged with 1.6, 1.6, and 3.2 gms of carbon, respectively, which represented bed depths of approximately 6.4, 6.4, and 12.7 cm, respectively. Superficial velocities of 0.66, 1.33, and 1.33 cm/sec (the latter being comparable to the 1.33 cm/sec 75 TPD PDU design value), respectively, were used. Dry synthesis gas was used as the carrier gas, with H₂S being injected via the sulfur pump.

TABLE 4.1

REMOVAL OF H₂S IN PURE N₂ USING METAL-IMPREGNATED ACTIVATED CARBON

Carbon:

Katalco 7-2 (12-30 mesh)
Impregnants (as metals) = 8.0% Cu; 2.7% Cr
Packing Density = 0.53 g/ml (33 lb/ft³)
Bed Depth = 6.37 cm
Bed Diameter = 0.775 cm
Charge = 3.0 ml = 1.59 g

Feed Gas:

110 ppmv H₂S in pure N₂ (t ≤ 8 hrs)
53 ppmv H₂S in pure N₂ (t > 8 hrs)

Run Conditions:

Pressure = 6.9 MPa (1000 psi)
Temperature = 27°C
Vol. Feed Rate = 19.7 std. ml/sec (2.5 SCFH)
Superficial Velocity (actual) = 0.64 cm/sec
Space Velocity (STP) = 23,600 hr⁻¹

Results:

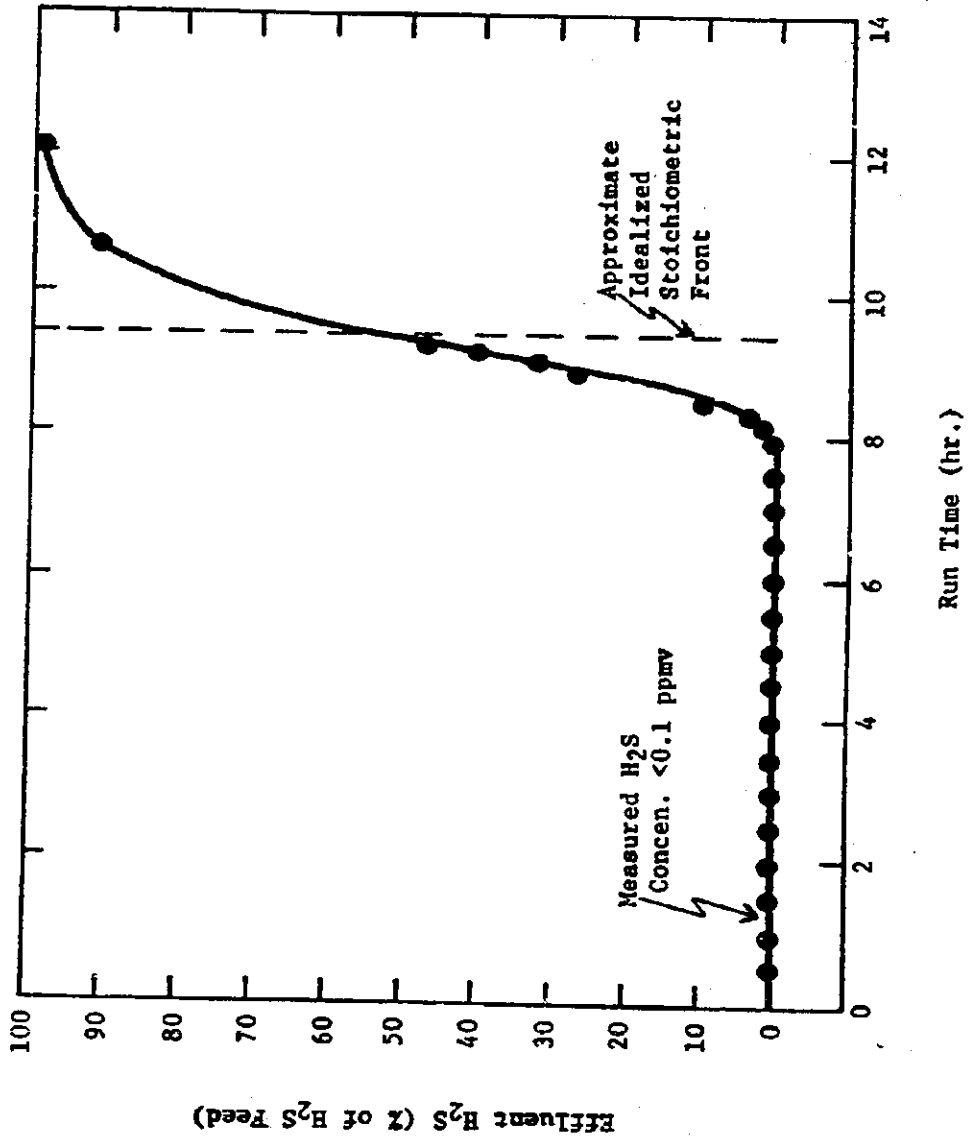
Time to Breakthrough = 8.0 hrs
Effluent H₂S Before Breakthrough = < 0.1 ppmv
H₂S Capacity @ Breakthrough = 5.7 wgt % of Carbon
Approx. Max. H₂S Capacity* = 6.7 wgt % of Carbon
Vol Gas (STP)/Vol Carbon @ Breakthrough = 189,000
Approx. Max. Vol Gas (STP)/Vol Carbon* = 222,000

* Calculated by assuming idealized stoichiometric front (vertical breakthrough curve) occurs at 50% of feed concentration, or from Fig. 4.1 at ca. t = 9.4 hrs. Accordingly, the 6.37 cm bed at breakthrough is idealized as consisting of 5.42 cm (6.37 x 8.0/9.4) of fully saturated carbon and 0.95 cm of completely unused bed. Maximum capacities and volumes calculated thus represent (using such an idealized model) levels which could be approached in very long beds.

FIGURE 4.1

REMOVAL OF H₂S IN PURE N₂ USING
METAL-IMPREGNATED ACTIVATED CARBON

Reactor 1, Run 1, 4231-6
(See Table 4.1 for Run Details)



Because of performance problems with the sulfur pump, the run was characterized at various times by widely differing H_2S concentrations in carrier gas. However, there did exist one period of approximately 3 hours duration where the effluent concentration from the empty reactor remained between 250-300 ppm H_2S . (This level represents approximately one order of magnitude higher than desired in feed.) After calculating the amounts of H_2S fed to the reactors during the entire run, it turned out that approximately 80% of the total H_2S fed up to the breakthrough point of each reactor occurred during this period. Furthermore, breakthrough for each charged reactor occurred during this somewhat stable interval. Accordingly, this interval served as a basis upon which the entire run was quantified. The average effluent concentration from the empty reactor (275 ppm) during this period was used as the equivalent feed concentration. Coupling this with the value of total H_2S fed to each reactor up to their breakthrough points, an equivalent time to breakthrough for each reactor was calculated in order to put the entire run on a better comparative basis. Breakthrough curves, themselves, were determined by direct comparison of the effluent levels from each charged reactor to the actual effluent value from the empty reactor existing during breakthrough. For the case of reactors 2 and 4, the empty reactor effluent H_2S level remained essentially in the 255-270 ppm range during their respective breakthroughs, while this level began to fall (eventually to the ~150 ppm range) shortly after the last (reactor 1) breakthrough curve began to develop.

Although the aforementioned ~3 hour interval was generally classified as one of relative stability, there did exist an inexplicable peculiarity; namely, the H_2S feed concentration measured considerably upstream of the reactors averaged about 20% less than the effluent level from the empty reactor during the majority of the 3-hour interval. One can only speculate that wall desorption phenomena may have been occurring. In any event, the effluent from the empty reactor was considered to be a less biased estimate of the actual feed to the charged reactors.

A summary of run conditions and results are given in Table 4.2, while the transient effluent history from the three charged reactors using an equivalent run time axis is shown in Figure 4.2. Prior to breakthrough in all runs, no detectable H_2S (<0.1 ppm) was found. This was also found for the run using 110 ppm H_2S in N_2 carrier gas. This was encouraging in view of the very high levels of H_2S (~275 ppm) and very short bed residence times of ~2 or 4 seconds (calculated using 40% as the bed void fraction).

Calculated bed H_2S capacities to breakthrough of 5.7, 6.9, and 8.6 wt % of carbon were found. These results appeared high, especially the 8.6% level. It is also possible that the other metal oxides present (2.7% Cr, 0.32% Fe, as metals) may also tie up some sulfur. Regarding the chromate specifically (often speculated as performing a catalytic role in conversion of some organic sulfur to H_2S), there does exist some data which may indicate that under some conditions it may serve as an oxidation source for the partial in-situ regeneration of CuS back to CuO , thus increasing the capacity of FCA for H_2S via formation of some elemental sulfur (9). Finally, analysis of the spent carbon from reactors 2 and 4 indicated, after deduction of initial sulfur, levels of 6.1 and 5.0% sulfur, respectively. Little of this would be expected to be due to physically adsorbed H_2S which should have been largely desorbed. In view of all of the above, the general finding of H_2S capacity levels above 4%, under the run conditions followed, appeared reasonable.

TABLE 4.2

REMOVAL OF H₂S IN DRY SIMULATED SYNTHESIS GAS USING METAL-IMPREGNATED ACTIVATED CARBON (RUN 2, 4231-24)

Carbon: Katalco 7-2 (12-30 mesh); 0.53 g/ml
 Impregnants (as metals) = 8.0% Cu; 2.7% Cr

Feed Gas: ~275 ppm H₂S¹ in Dry Simulated Synthesis Gas
 (H₂ = 45%; CO = 15%; CH₄ = 35%; CO₂ = 1%;
 C₂H₆ = 1%, N₂ = 3%)

Pressure: 6.9 MPa (1000 psig)

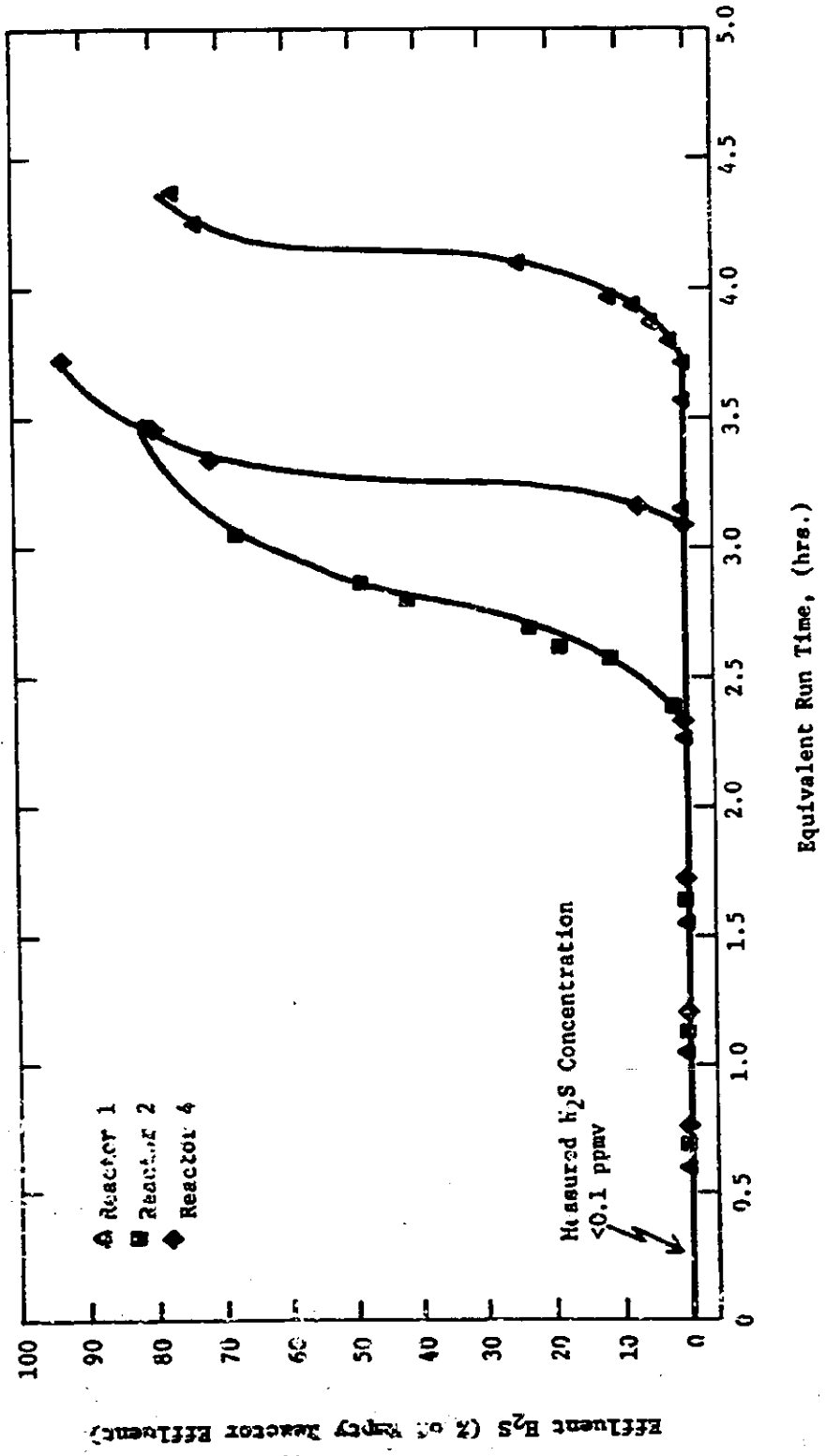
Temperature: 32°C

Bed Diameter = 0.775 cm

	<u>Reactor 1</u>	<u>Reactor 2</u>	<u>Reactor 4</u>
Carbon charged (gas)	1.59	1.59	3.18
Bed Depth (cm)	6.35	6.35	12.70
Vol. Feed Rate (std. ml/sec)	20.4	40.7	40.7
Superficial Velocity, actual (cm/sec)	0.66	1.33	1.33
Space Velocity, STP (hrs ⁻¹)	24,400	48,900	24,400
Time to Breakthrough (hrs) ²	3.72	2.33	3.08
Effluent H ₂ S before Breakthrough (ppm)	< .1	< .1	< .1
H ₂ S Capacity @ Breakthrough (wt %)	6.9	8.6	5.7
Approx. Max. H ₂ S Capacity (wt %) ³	7.7	10.6	6.0
Vol. Gas (STP)/Vol. Carbon @ Breakthrough	91,000	114,000	75,000
Approx. Max. Vol. Gas (STP)/Vol. Carbon ³	101,000	140,000	80,000

1. Represents effluent concentration (+ 25 ppm) from empty reactor during most meaningful period of run (see discussion in text).
2. Based on 275 ppm average feed level, and cumulative total H₂S feed to each reactor to breakthrough point.
3. Calculated by assuming idealized stoichiometric front (vertical breakthrough curve) occurs at 50% of feed concentration.

FIGURE 4.2
REMOVAL OF H₂S IN DRY SIMULATED SYNTHESIS GAS
VIA METAL-IMPREGNATED ACTIVATED CARBON
Run 2, 4231-24 (See Table 4.2 for Run Details)



An estimate of the natural variability in these types of adsorption measurements can be made by examining the results shown in Table 4.2. For example, comparing reactor 1 and 2 results, where the bed depth remained constant, a doubling of superficial velocity resulted in a 25% increase in capacity. This could be explainable if the system were mass transfer limited, but capacity in reactor 4 at the same high superficial velocity as reactor 2, displayed a drop in capacity. Similarly, comparing the capacity results of reactor 2 and 4, where superficial velocities were the same, but the bed depth in reactor 4 was doubled, showed a 17% drop in capacity for the deeper bed.

4.2.3 Carbonyl Sulfide in Synthesis Gas

Experimentation using impregnated (Cu and Cr oxides) carbon was conducted with COS representing the sulfur compound feed. Based on the literature, it was considered likely that COS represented the most difficult of the five sulfur compounds (H_2S , COS, CS_2 , CH_3SH , and thiophene) for the metal-impregnated carbon to remove.

The sulfur pump was used as the means of sulfur compound introduction, during this set of experiments.

Initial experimentation consisted of three beds, two of which contained 1.59 g each of metal-impregnated carbon (Katalco 7-2, equivalent to Pittsburgh FCA) while the third contained 1.59 g of unimpregnated carbon (Katalco 7-1, equivalent to Pittsburgh BPL). Bed depths of 6.5, 6.5, and 7.6 cm, respectively, and superficial velocities of 1.3, 2.6, and 1.3 cm/sec, respectively, were used. Very high COS levels (~300-400 ppm) were fed. In all cases, breakthrough of COS occurred prior to taking the first effluent samples (ca one-half hour after initiating COS feed). Thus, the possibility of containment of COS by the two varieties of carbon at the superficial velocities used could not be established. Furthermore, with the exception of the reactor containing the metal-impregnated carbon at a 1.3 cm/sec superficial velocity, breakthrough of the other two reactors was essentially complete, with the initially measured effluent levels comparable to feed levels. Regarding the other reactor, effluent levels remained in the 20-50 ppm range for approximately an additional half-hour, and then rapidly climbed to concentrations comparable to the others.

It was obvious that deeper beds and, in general, less severe conditions would be required to gain useful information regarding COS removal. One useful and interesting observation did apparently manifest itself from this run, however. This was the observation that at comparable conditions, the metal-impregnated carbon was apparently superior to the unimpregnated material with respect to COS containment and removal.

Additional experimentation was next conducted using deeper beds, at a superficial velocity of 1.36 cm/sec (comparable to the SYNTHANE 72 TPD pilot plant design value of 1.38), and with metal-impregnated carbon, exclusively. One of the reactors was left uncharged, while the others contained beds of 12, 24, and 49 cm depth. Simulated synthesis gas, approximately saturated with H_2O , was used as the carrier gas.

Sulfur-pump performance problems associated with fluctuating levels in feed were present. However, an approximate average empty reactor effluent concentration of 150 ppm COS characterized much of the run during which time the large majority of sulfur was fed to the charged reactors. Using 150 ppm COS as an equivalent feed concentration, and coupling this with the actual values of total COS fed to each reactor (determined by using actual COS effluent levels from the empty reactor) up to their breakthrough points, an equivalent time to breakthrough for each reactor was calculated in order to put the entire run on a comparative basis. Breakthrough curves themselves were determined by direct comparison of the effluent levels from each charged reactor to the actual effluent values from the empty reactor measured during breakthroughs.

Run conditions and results are summarized in Table 4.3, while the transient effluent concentration from each reactor (calculated as % of effluent from the empty reactor) using an equivalent run time axis is shown in Figures 4.3 and 4.4. (An expanded ordinate for reactors 2 and 4 data is also presented in order to better quantify the initial phases of their respective breakthroughs.) Actual breakthrough points for reactors 2 and 4 were selected as midway between the respective two points of sulfur non-detectability and detectability. For reactor 1, such a large increase in concentration occurred between these two points that the last (and only) point of non-detectability was selected as the breakthrough point.

Prior to breakthrough in all reactors, no detectable (<0.1-0.2 ppm) COS was found, although this period was very brief for both the 12 and 24 cm beds. Indicative of this are the calculated bed capacities at breakthrough of ~0.55 wt % of carbon for both of these cases, compared to the 1.75% calculated for the 49 cm bed. Such a dramatic increase beyond a certain bed length is common for adsorbents where the adsorbate is not strongly adsorbed. The considerable length of time required for a breakthrough curve to develop relative to the time for breakthrough to occur, as shown in Figures 4.3 and 4.4, is also characteristic of such systems.

It logically follows that considerable unused bed capacity exists for the three cases run. An approximation of the maximum COS capacity obtainable in very long beds was made by assuming an idealized vertical breakthrough occurs at the point where effluent concentration equals 50% of the feed concentration following the method of Lukchis (14). When such an approximate technique was used for the current data, maximum adsorptive capacities ranging from 2.5-4.0 wt %, as listed in Table 4.3, resulted. It is interesting to note that this essentially equilibrium capacity range is similar to the equilibrium adsorption isotherm data for COS on BPL unimpregnated carbon (see Grant, *et al* (8)). For 150 ppm COS at 6.9 MPa (1000 psig), which is equivalent to a COS partial pressure of 1.0 kPa (0.15 psia), their results indicate a 3.5% equilibrium capacity. Such agreement may be fortuitous. If it is not, it may indicate that the presence of non-sulfur adsorbates present in the simulated synthesis gas, as well as total system pressure, have little influence on equilibrium COS adsorption. It is likely, however, that the presence of other sulfur compounds that are more strongly adsorbed than COS and more apt to be competing for the same adsorptive sites, would reduce COS adsorptive capacity considerably. Such determinations are discussed later when

TABLE 4.3
REMOVAL OF COS IN SIMULATED SYNTHESIS GAS USING
METAL-IMPREGNATED ACTIVATED CARBON (RUN 5, 4231-64)

Carbon: Katalco 7-2 (12-30 mesh); 0.55 g/ml
 Impregnants (as metals) = 8.0% Cu; 2.7% Cr

Feed Gas: ~ 150 ppmv COS¹ in Simulated Synthesis Gas
 (H₂ = 45%; CO = 15%; CH₄ = 35%; CO₂ = 1%;
 C₂H₆ = 1%; N₂ = 3%; H₂O = 0.07%)

Pressure: 6.9 MPa (1000 psig)

Temperature: 33°C

Bed Diameter: 0.775 cm

	<u>Reactor 1</u>	<u>Reactor 2</u>	<u>Reactor 4</u>
Carbon Charged (gm)	3.18	6.36	12.72
Bed Depth (cm)	12.2	24.4	48.6
Vol. Feed Rate (std. ml/sec)	41.7	41.7	41.7
Superficial Velocity, actual (cm/sec)	1.36	1.36	1.36
Space Velocity, STP (hrs ⁻¹)	25,880	12,940	6,470
Time to Breakthrough (hrs) ²	0.30	0.59	3.84
Effluent COS Before Breakthrough (ppm)	<.1-.2	<.1-.2	<.1-.2
COS Capacity @ Breakthrough (wgt %)	0.55	0.54	1.75
Approx. Max. COS Capacity (wgt %) ³	3.6	2.5	4.0
Vol. Gas (STP)/Vol. Carbon @ Breakthrough	7,800	7,600	24,800
Approx. Max. Vol. Gas (STP)/Vol. Carbon ³	51,300	35,300	57,100

¹ Represents approximate average effluent concentration from empty reactor during majority of run time (see discussion in text).

² Based on 150 ppm average feed level, and cumulative total COS fed to each reactor up to breakthrough (see text for additional discussion).

³ Calculated by assuming idealized stoichiometric front (vertical breakthrough curve) occurs at point where effluent equals 50% of empty reactor effluent.

FIGURE 4.3

REMOVAL OF COS IN SIMULATED SYNTHESIS GAS
VIA METAL-IMPREGNATED ACTIVATED CARBON
Run 5,4231-64 (See Table 4.3 for Run Details)

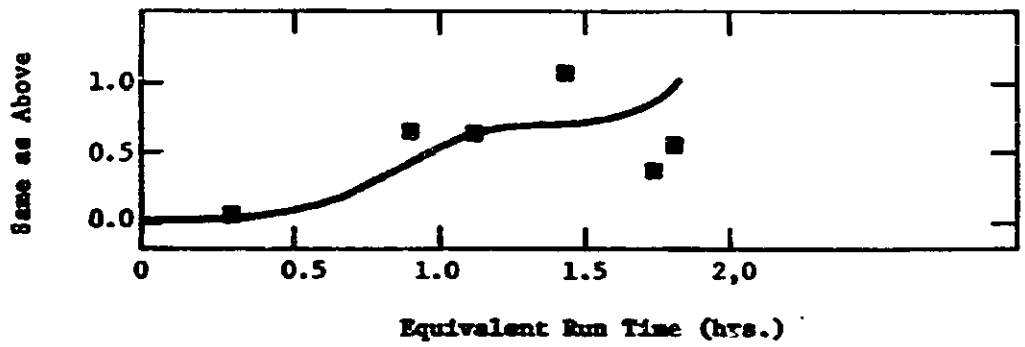
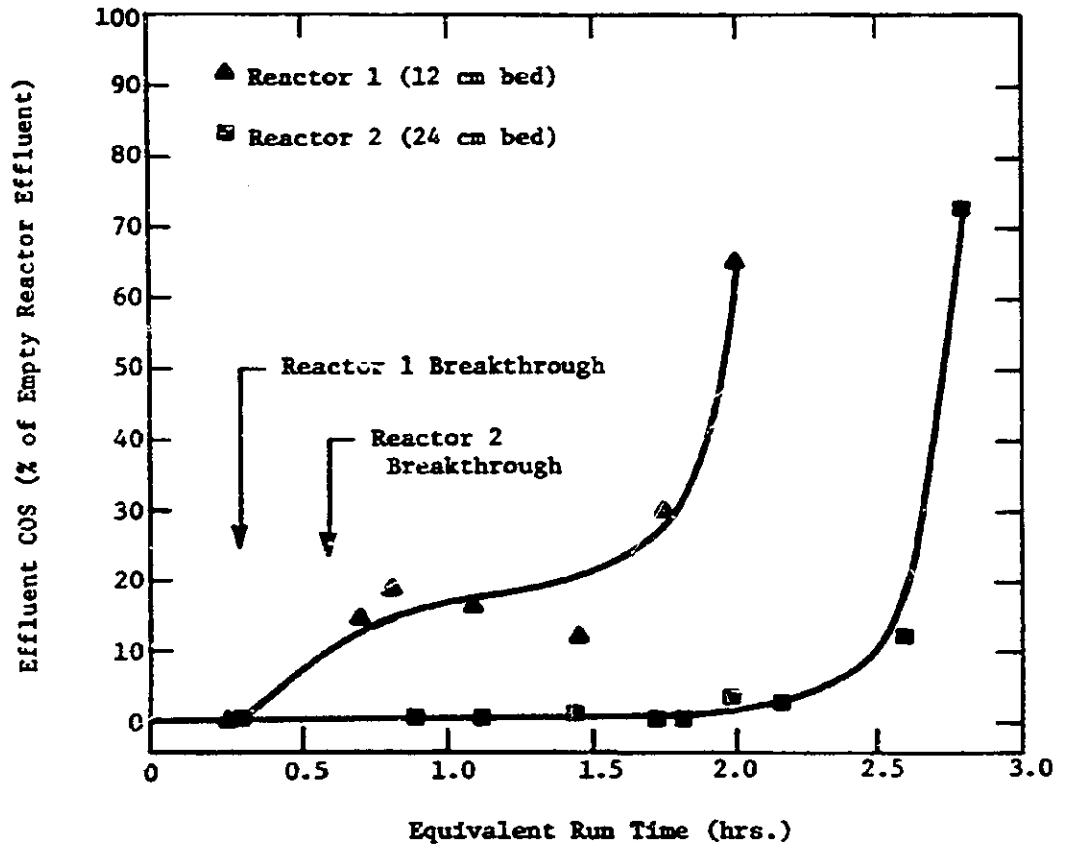
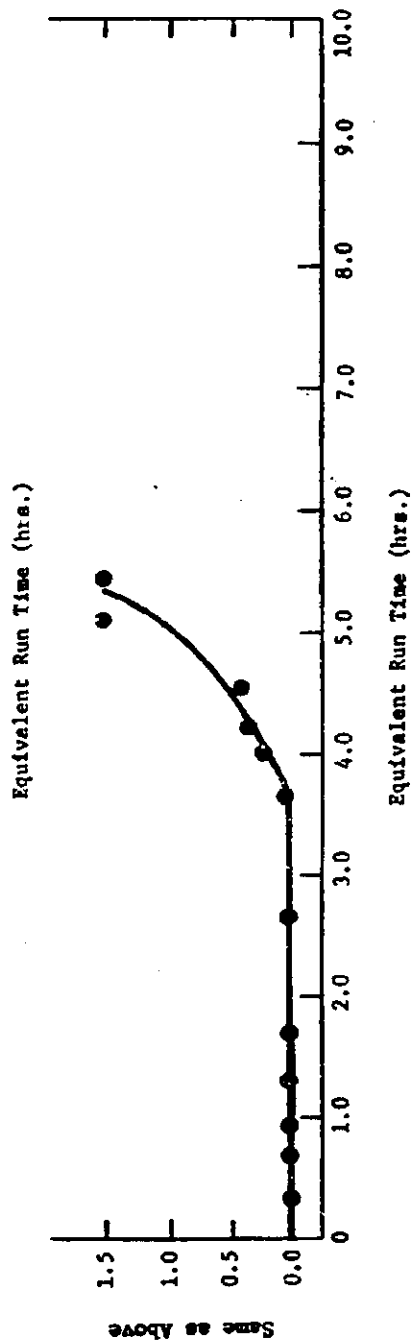
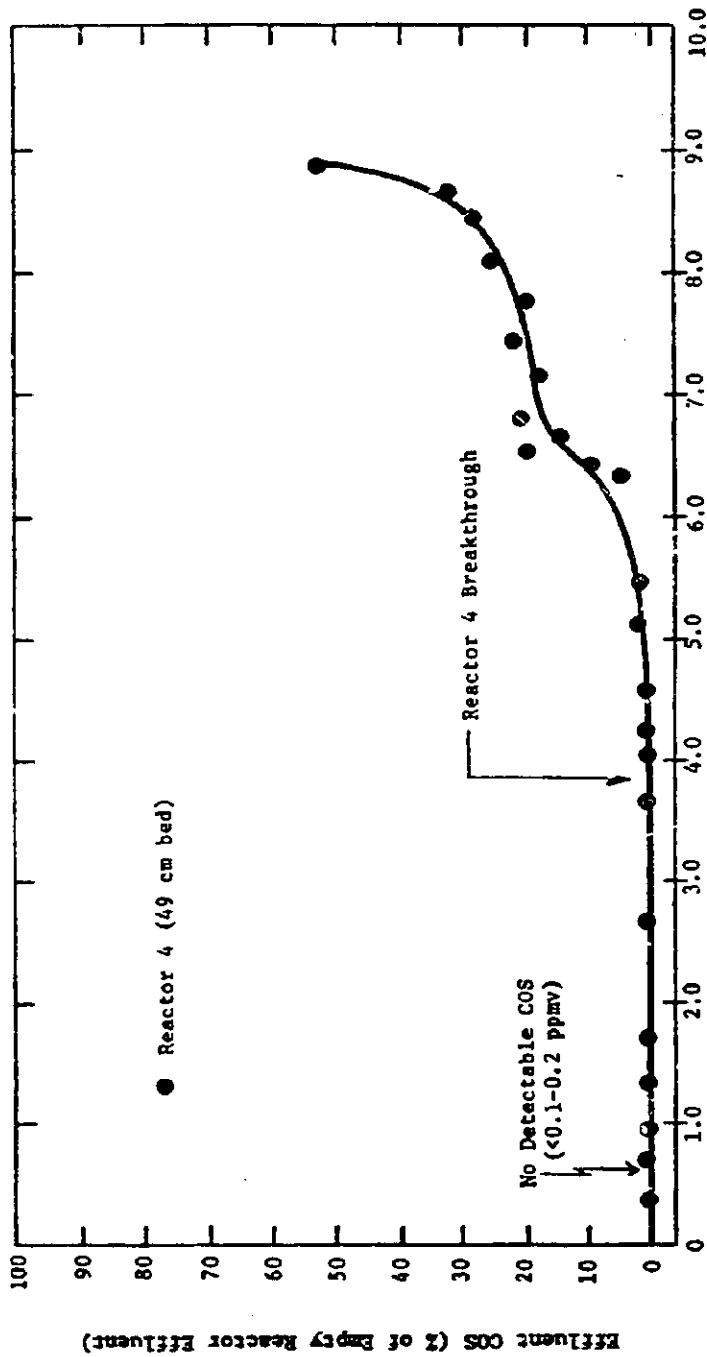


FIGURE 4.4
REMOVAL OF COS IN SIMULATED SYNTHESIS GAS VIA METAL-IMPREGNATED ACTIVATED CARBON
Run 5, 4231-64 (See Table 4.3 for Run Details)



multicomponent sulfur compound feeds are presented. However, the results obtained in this run indicated that the impregnated carbon is capable of removing COS down to target levels when it is present as the sole sulfur species in simulated synthesis gas processed at a superficial velocity and total system pressure comparable to that planned for the 72 TPD pilot plant.

4.2.4 Thiophene in Synthesis Gas

Experimentation using metal-impregnated (Cu and Cr oxides) activated carbon continued with thiophene (C_4H_4S) in simulated synthesis gas representing the sulfur compound feed. Thiophene contained in CO-free simulated synthesis gas (CO balance made up with N_2) was introduced via the sulfur feed system into water saturated sulfur-free simulated synthesis gas at a blend ratio of $v_1/9$.

Three parallel beds were charged with impregnated carbon (Kataico 7-2 which is equivalent to Pittsburgh FCA) at levels of 0.8, 1.6, and 3.2 g, resulting in bed depths of 3.2, 6.4, and 12.8 cm, respectively. A superficial velocity of 1.37 cm/sec (equivalent to the current 72 TPD pilot plant design value) at 6.9 MPa (1000 psig) was maintained in all reactors. The remaining reactor was left uncharged to facilitate start-up and achievement of desired feed levels and occasionally monitor downstream thiophene levels during the run. After the desired feed concentration was reached, flow to the charged reactors was begun, while flow to the empty reactor was greatly reduced to conserve gas supplies. Run conditions and results are summarized in Table 4.4 while transient histories of thiophene effluent levels are shown in Figure 4.5.

Before discussing the results further, it is appropriate to point out that the run involving the deepest bed (reactor 4) was characterized by what is believed to be a "false breakthrough" in that detectable thiophene levels in the sampling line were noted before actual breakthrough occurred. Completion of experimentation with this particular reactor involved overnight shutdown of the unit. Prior to shutdown, no detectable (<0.1 ppm) thiophene in reactor 4 was noted. During the shutdown period, the reactor lost v_1 MPa in pressure and it is possible some minor desorption from the carbon bed occurred. When the reactor was brought back to pressure and feed gas at the desired thiophene concentration sent to the reactor, the first sample taken (at $v_6.5$ hours in Figure 4.5) contained $v_0.4$ ppm C_4H_4S . If the breakthrough had been real, subsequent increases in effluent levels would have been expected, but instead none was noted. Instead, levels in the $v_0.1-0.3$ ppm range were found during the next 3.5 hours, and were considered due to trace residual quantities which were not purged from lines leading from the reactor to the sampling port. Accordingly, breakthrough for reactor 4 was judged to take place when effluent levels first surpassed 0.4 ppm, which occurred after v_{10} hours of operation. Instrument lag time was too short to be considered a factor in the results.

With the exception of that mentioned above, no detectable thiophene (<0.1 ppm) was found in the effluent of any of the reactors prior to breakthrough. Thiophene capacity levels at breakthrough for the 3.2 cm and 12.8 cm beds were calculated to be 6.5 and 8.6 wt% of carbon charged. The higher level found for the deeper bed was expected as unused bed capacity, at the same superficial velocity, should represent a smaller fraction of the total bed than would be the case for the shallow bed. Surprisingly, the lowest breakthrough capacity level was found for the 6.4 cm bed. However, it was

TABLE 4.4

REMOVAL OF THIOPHENE IN SIMULATED SYNTHESIS GAS USING
KATALCO-IMPREGNATED ACTIVATED CARBON (RUN 7, 4231-82)

Carbon: Katalco 7-2 (12-30 mesh); 0.53 g/ml
Impregnants (as metals) = 8.0% Cu; 2.7% Cr

Feed Gas: ~ 53 ppmv C₄H₄S^① in Simulated Synthesis Gas
(H₂ ~ 45%; CO ~ 13.5%; CH₄ ~ 35%; CO₂ ~ 1%;
C₂H₆ ~ 1%; N₂ ~ 4.5%; H₂O ~ 0.08-0.09%)^②

Pressure: 6.9 MPa (1000 psig)

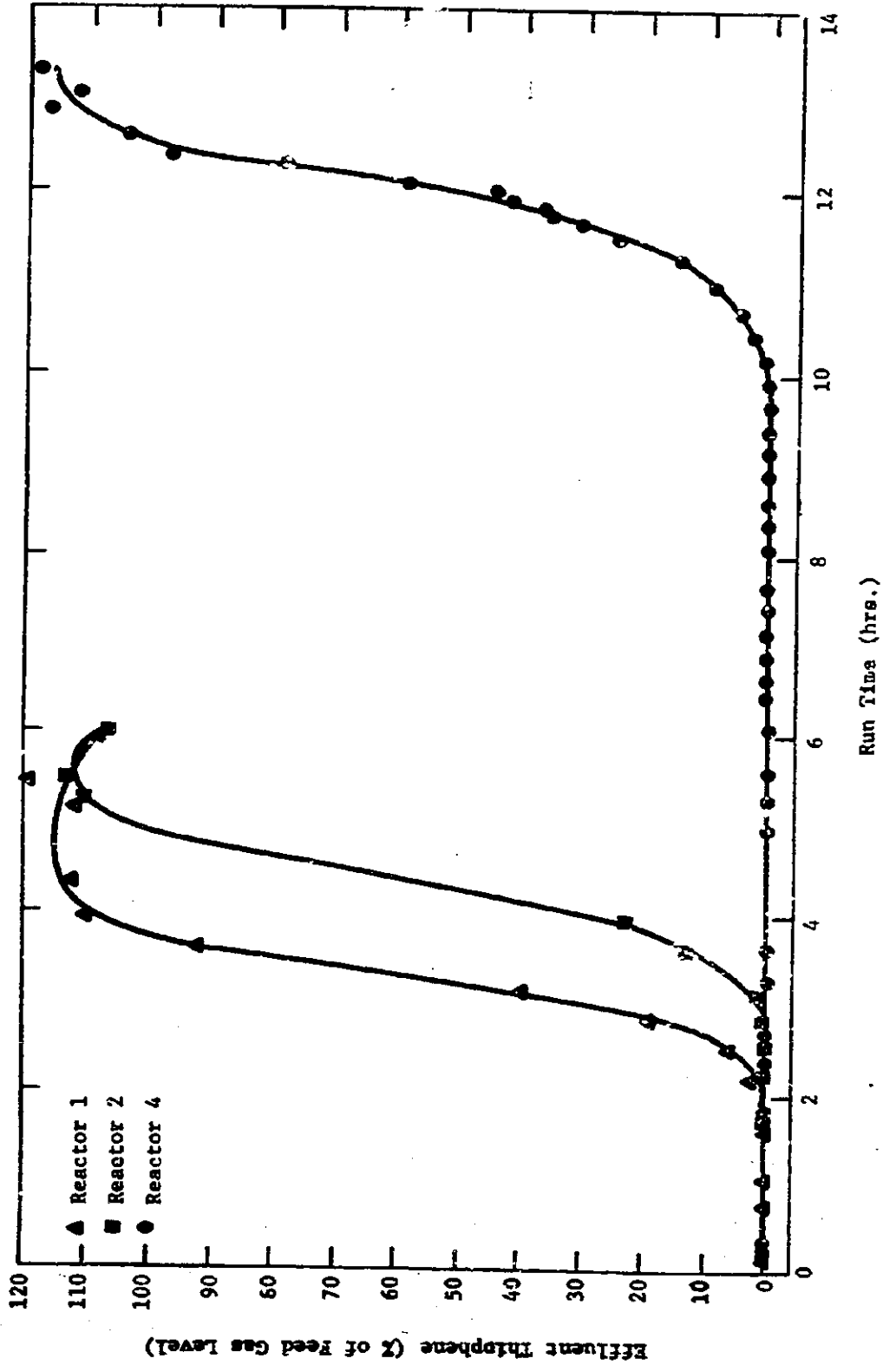
Temperature: 32.7 ± 0.5°C

Bed Diameter: 0.775 cm

	Reactor 1	Reactor 2	Reactor 4 ^③
Carbon Charged (g)	0.80	1.60	3.20
Bed Recovered (g)	0.91	1.58	3.79
Bed Depth (cm)	3.2	6.4	12.8
Vol. Feed Rate (std. ml/sec)	41.7	41.7	41.7
Superficial Velocity, actual (cm/sec)	1.36	1.36	1.36
Space Velocity, STP (hrs ⁻¹)	99,400	49,700	24,900
Time to Breakthrough (hrs)	1.63	2.88	9.93
Effluent C ₄ H ₄ S Before Breakthrough (ppm)	<0.1	<0.1	<0.1
C ₄ H ₄ S Capacity @ Breakthrough (wgt % of Carbon)	6.50	5.18	8.65
Approx. Max. C ₄ H ₄ S Capacity (wgt % of Carbon) ^④	11.4	7.8	10.4
Vol. Gas (STP)/Vol. Carbon @ Break- through	182,000	143,000	247,000
Approx. Max. Vol. Gas (STP)/Vol. Carbon ^④	319,000	212,000	298,000

1. Represents time-averaged feed concentration prior to breakthrough. Individual averaged feed levels for reactors 1, 2 and 4 were 53.2, 53.9, and 52.2 ppmv, respectively.
2. CO and N₂ levels are slightly lower and higher (1.5% absolute), respectively, than usual synthesis gas levels due to dilution by CO-free (N₂ supplemented) thiophene carrier gas.
3. Results ignore "false breakthrough" as discussed in text.
4. Calculated by assuming idealized stoichiometric front (vertical breakthrough curve) occurs at point where thiophene effluent equals 50% of feed concentration. Factor applied to breakthrough results is ratio of run time to 50% point/run time to breakthrough.

FIGURE 4.5
REMOVAL OF THIOPHENE IN SIMULTANEOUS SYNTHESIS GAS VIA METAL-IMPREGNATED ACTIVATED CARBON
Run 7,4231-82 (See Table 4.4 for Run Details)



that while the weight of recovered bed from reactors 1 and 4 ranged 10-20 wt % higher than that charged, that from reactor 2 was actually only less than its original charge. It is possible that a weighing error may have occurred in charging reactor 2 or a loss of material took place during the run.

Bed capacities were put on a common basis by estimating the equilibrium capacity of a fully saturated bed by using the technique which involves adjusting the breakthrough capacity by the ratio of the total time for effluent to reach 50% of feed level to the time to reach maximum. When this idealized approximate technique was used, maximum theoretical capacities (in theory, approachable in long beds) of 11.4% and 4% were calculated for the beds used in reactors 1 and 4, respectively, given in Table 4.4

Regarding the breakthrough curves, as shown in Figure 4.5, two additional comments are in order. First of all, with regard to reactor 2, when a desired number of data points was obtained during the development of the curve. This was due to the fact that a gas chromatograph problem occurred during this period which lasted approximately 50 minutes during which time no valid data were obtained. When the problem was corrected, breakthrough for reactor 2 was essentially complete. Another phenomenon, for all three curves, was the fact that effluent breakthrough levels reached a point where they exceeded levels of thiophene in the synthesis gas. For the two reactors (1 and 2) which were monitored past their breakthrough maxima, the trend back to equal feed and effluent levels was observed. Such a phenomenon is not unusual, however, when multiple adsorbates are present in a feed. Accordingly, the observation probably can be explained in terms of some displacement of a small portion of adsorbed thiophene by other species in the synthesis gas mix. Some system transient effects, related to location of sampling ports and fluctuations in feed concentration may also be involved.

In general, the experimental results indicate that the impregnated carbon is capable of removing expected maximum thiophene concentrations down to target levels when it is present as the only sulfur species in simulated synthesis gas processed at a pressure and superficial velocity equal to that used for the 72 TPD pilot plant. Furthermore, adsorption capacity is reasonably high relative to COS.

4.2.5 Hydrogen Sulfide (Low Concentrations) in Synthesis Gas

Experimentation using impregnated (Cu and Cr oxides) activated carbon for removal of low concentrations of H₂S in simulated synthesis gas was carried out. The gas blending sulfur delivery system was used for this work.

Initial charges consisted of three parallel beds of impregnated carbon (Katalco 7-2, equivalent to Pittsburgh FCA) containing 0.8, 1.59, and 1.59 g, respectively, of material. Respective superficial velocities (at operating conditions) through each were 1.37 (equivalent to the 72 TPD pilot plant design value), 1.37, and 2.74 cm/sec. The remaining reactor was left uncharged

to monitor downstream H₂S levels. Because H₂S, for introduction into simulated synthesis gas, was contained in a 55%/45% N₂/H₂ carrier gas and blending ratios were higher than planned, the ultimate composition of feed gas with respect to its other constituents varied somewhat from established target levels. With the exception of H₂, maintained at its ~45% desired level, the remaining gross components were reduced by ca 20% (relative) levels while an N₂ level of ca 10% (absolute) higher was calculated. The entire feed gas blend also contained water, introduced via the saturator, at levels close to saturation at the conditions run.

After running the three reactors for ~14 hours cumulative time over two days (with intermittent shutdown and system lock in) and having noted no detectable H₂S breakthrough, coupled with our limited supply of rapidly diminishing H₂S for maintaining necessary levels, it was decided to discontinue the feed to reactor 2 which would be expected to be the last to breakthrough. In addition, flow to the empty reactor was reduced to ~10% of its original level. (Previous experimentation using 275 ppm average H₂S levels in dry simulated synthesis gas had yielded H₂S capacity levels to breakthrough in the 7% range.) Since physical adsorption of H₂S on carbon should be minimal vs. the believed major removal mechanism of conversion of CuO to CuS, it was expected that roughly comparable levels would also be eventually found, assuming conversion approached stoichiometric levels. A rough estimate of H₂S fed to the 14-hour point indicated such a total feed level was near and the decision was made to insure sufficient supply of H₂S at target pressure levels to obtain breakthrough curves on the two remaining, charged reactors.

Surprisingly, after an additional 13 hours of cumulative run time (27 hours of total run time), still no breakthrough of either the 0.8 g (3.2 cm depth) bed operating at a superficial velocity of 1.37 cm/sec, or the 1.59 g bed running at 2.74 cm/sec was noted. It was then decided to discontinue feeding the deeper bed, as pressure in the H₂S cylinder had reached a point where maintenance of ~1000 psig in the reactor was no longer possible. It then became necessary to reduce reactor pressure in the one remaining charged reactor to continue the run until breakthrough was achieved (and beyond), which eventually did take place after a total cumulative run time of ~41 hours.

A summary of run conditions and results for this one reactor are given in Table 4.5, while the transient history of effluent levels (as % of feed), as well as pressure and superficial velocity maintained, is shown in Figure 4.6. As indicated in Table 4.5, H₂S capacity to breakthrough, calculated by summing total feed to reactor 1 during the entire period, amounted to 19.7 wt % of carbon charged. The run was continued for an additional ~24 hours (total run time of ~65 hours) to obtain information relative to breakthrough. Including the additional net H₂S removed during this period, the total H₂S removed up to termination amounted to 31.9 wt % of original carbon charged (equivalent to 22.1 wt % of bed recovered).

Such levels are many times higher than one would predict assuming the main H₂S removal mechanism is via irreversible conversion to CuS (H₂S physical adsorption assumed of very minor significance at the low partial pressure run) given the 8.0 wt % Cu level in the carbon used. Total sulfur

TABLE 4.5

REMOVAL OF H₂S IN SIMULATED SYNTHESIS GAS USING
METAL-IMPREGNATED ACTIVATED CARBON (RUN 6, 4231-76)

<u>Carbon:</u>	Katalco 7-2 (12-30 mesh); 0.53 g/ml Impregnants (as metals) = 8.0% Cu; 2.7% Cr
<u>Feed Gas:</u>	~21.7 ppm H ₂ S ¹ in Simulated Synthesis Gas (H ₂ ~ 45%; CO ~ 12%; CH ₄ ~ 28.1%; CO ₂ ~ 0.8%; C ₂ H ₆ ~ 0.8%; N ₂ ~ 13.3%; H ₂ O ~ 0.05-0.1%) ²
<u>Initial Pressure</u> ³ :	6.9 MPa (1000 psig)
<u>Temperature:</u>	32.5 ± 1°C
<u>Bed Diameter:</u>	0.775 cm

	<u>Reactor 1</u>
Carbon Charged (gm)	0.800
Bed Recovered (gm)	1.157
Bed Depth (cm)	3.2
Vol. Feed Rate (std. ml/sec)	41.7
Initial Superficial Velocity ³ , actual (cm/sec)	1.37
Space Velocity, STP (hrs ⁻¹)	99,400
Time to Breakthrough (hrs)	40.7
Total Run Time (hrs)	64.8
Effluent H ₂ S Before Breakthrough (ppm)	<0.1-0.2
H ₂ S Removed at Breakthrough (wgt % of C)	19.7
H ₂ S Removed at End of Run (wgt % of C)	31.9
Vol. Gas Fed (STP)/Vol. Carbon @ Breakthrough	4 × 10 ⁶

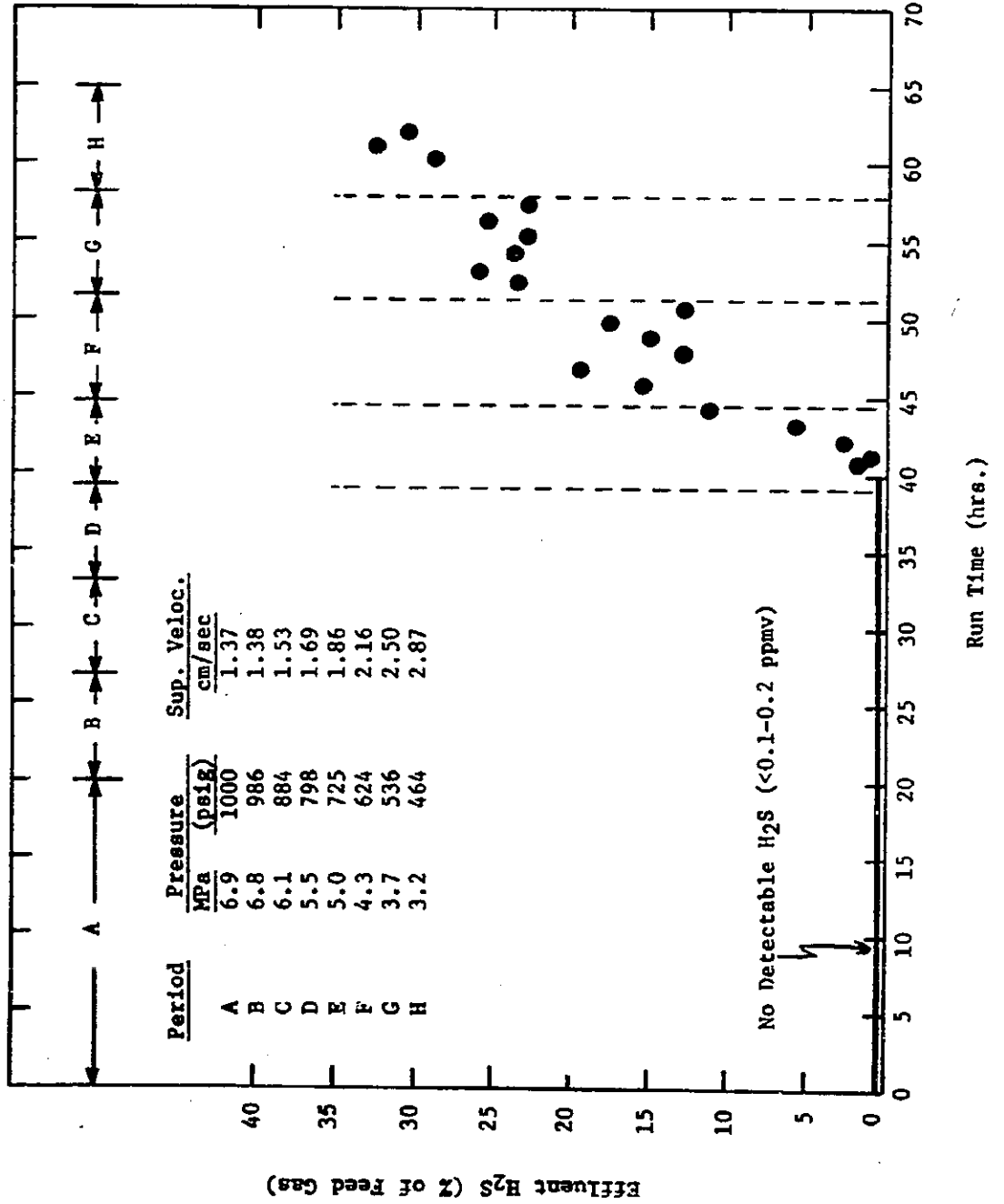
¹Represents time-averaged feed concentration during entire run. Average concentration before breakthrough was 17.7 ppm; during remainder of run it was 28.5 ppm.

²Synthesis gas composition differs in some respects to that used previously due to dilution by H₂/N₂ H₂S carrier gas.

³See Figure 4.6 and discussion in text for additional information.

FIGURE 4.6

REMOVAL OF H₂S IN SIMULATED SYNTHESIS GAS VIA METAL-IMPREGNATED ACTIVATED CARBON
 Run 6, 4231-76 (See Table 4.5 for Run Details)



analysis of the recovered bed was run to ascertain the validity of the high removal levels found. Initial testing, using a technique (Dieter analysis) considered valid for solids containing sulfur up to ~7%, indicated much higher levels were present. Parr bomb testing was then done and yielded a sulfur content of the sample of 29.2 wt %. After deducting for sulfur present in the original virgin impregnated carbon (0.69 %) and converting to an equivalent H₂S basis, the result was 30.5 wt % of bed recovered, compared to the 22.1 wt % figure cited in the previous paragraph. Despite some discrepancy in agreement, the result of the sulfur analysis offers substantial support that the high removal noted is valid.

Additional evidence of high removal involved the deeper carbon bed (1.59 g, 6.4 cm) which was on stream for a cumulative time of 27 hours at the higher superficial velocity of 2.74 cm/sec before premature run termination. Using the approximate H₂S feed gas levels over this period yielded an H₂S pickup of 11.8 wt % of original carbon charged (11.1 wt % of the 1.69 g of material recovered). Total sulfur analysis by Parr bomb indicated, after making corrections for original sulfur and converting to an equivalent H₂S basis, an H₂S pickup of 14.3 wt % of recovered material compared to the calculated 11.1% level.

The reason for such high apparent H₂S removal is not clear. It is possible that in situ regeneration of CuS back to CuO and elemental sulfur promoted by possible oxygen contamination in sulfur-free synthesis gas, or the presence of the chromium oxide impregnant may be involved. Regarding the former, O₂ levels in the various gases originally charged to the unlined synthesis gas cylinders are sufficiently low that levels of well below 50 ppm would be expected in originally filled cylinders. Furthermore, given the high reducing conditions, very high H₂ partial pressure, and metal surfaces, it would be reasonable to assume its existence as molecular oxygen (as opposed to conversion to H₂O) would be short-lived.

Regardless of the specific mechanism(s), the evidence to date supports the fact that under the conditions addressed in our experiments program, mechanisms more complex than purely physical adsorption or irreversible conversion of H₂S to CuS were taking place. It is possible that, given the complexity of the feed system, the nature of the metal-impregnated carbon involved, and the run conditions present, catalytic conversion reactions involving H₂S (possibly to elemental sulfur or some other highly sorbed sulfur species?) were occurring.

In addition, it was observed that the color of recovered bed from the long duration run was not the typical pure black coloration observed after earlier reported runs involving COS in wet simulated synthesis gas or H₂S (at feed concentrations greater than an order of magnitude above this run). In contrast, the particle surface had an original dark green contrast which has tended to become dark blue with time as it was contained in its sampling bottle. In addition, the material from the bed run for a 27-hour cumulative time also displayed particles with similar coloration, as well as some that had a rust brown appearance possibly indicative of elemental sulfur or copper formation.