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ALKALINE AND STRETFORD SCRUBBING TESTS FOR H2S REMOVAL FROM IN-SITU

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Prepared for

EPA Region 8

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ALKALINE AND STRETFORD SCRUBBING TESTS FOR H_2S REMOVAL FROM IN-SITU OIL SHALE RETORT OFFGAS

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ABSTRACT

These tests were conducted to evaluate the performance of two mobile pilot-plant scrubbers for removing H_2S and other reduced sulfur compounds from the offgas of an in-situ shale oil retort in Utah.

A trailer-mounted scrubber system equipped with both a tray tower and a venturi contactor was used to investigate each of three alkaline solutions; sodium, potassium and ammonium hydroxide. The objective of this first test of the alkaline scrubber was to shakedown the equipment, and investigate the effects of scrubbing chemical, chemical concentration and liquid to gas contact time on removal efficiency and H_2S selectivity.

A skid-mounted Stretford scrubber system was also evaluated using a scrubbing mixture of sodium carbonate, sodium vanadate, anthraquinone disulfonic acid and water. A venturi scrubber was used through most of the test as the sole contactor. Near the end of the test, a field-fabricated packed tower was added in series downstream of the venturi in order to improve the removal efficiency. Since this was the fourth test of the Stretford unit, the test objectives were to obtain and maintain the highest removal efficiency possible and to attempt to explain some lower removal efficiencies observed during prior tests.

The retort offgas volumetric percent composition (dry) was approximately 59 N_2, 23 CO_2, 9 H_2, 5 CO, 2 O_2 2 CH_4 plus 0.15 (1500 ppmv) H_2S and other reduced sulfur species. The gas was saturated with water and contained a light mist of condensed water and oil particles.

The alkaline scrubber efficiencies varied directly with the OH^- concentration and gas/liquid contact time reaching 94 percent at the highest OH^- concentration used in the tray tower and 50 percent at the lowest concentration in the venturi. Conversely, it was found that the selectivity, the percent removal of H_2S divided by the percent removal of CO_2, was highest at the lowest OH^- concentrations and vice versa. It was found that selectivity also varied inversely with gas/liquid contact time, the venturi

contactor providing greater selectivity than the tray tower contactor. The selectivity varied from a low of 9 to a high of 79. At the lowest OH^- concentration where the venturi produced a selectivity of 79, the tray tower selectivity was only 22. The test results correlated well with a mathematical scrubber model based on the penetration theory.

The H_2S removal efficiency achieved for the Stretford plant was an average of 80 percent and a peak of 95 percent with the venturi contactor alone and an average of 93 percent and a peak of 99.4 percent with the venturi contactor followed by the packed-tower contactor.

Neither the alkaline scrubber nor the Stretford removed significant quantities of the organic sulfur compounds.

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SECTION 1.0

INTRODUCTION, SITE DESCRIPTION, FINDINGS, AND CONCLUSIONS

1.1 INTRODUCTION

1.1.1 Background

Removing hydrogen sulfide (H_2S) and other reduced sulfur compounds (carbonyl sulfide, carbon disulfide, mercaptans thiophenes, etc.) from shale oil retort offgas with a wet scrubber requires a process that will selectively react with the sulfur compounds and as little as possible with the carbon dioxide (CO_2) which is also present in much larger amounts than the H_2S. Typically the CO_2 concentration in retort gas is 20 percent while the H_2S concentration will range from 0.1 percent (1000 ppm) to 4 percent, depending on the particular retorting process used. This report covers the tests performed on a direct-fired, in-situ (under the ground), retort for which the lower H_2S concentration applies.

Since both H_2S and CO_2 are acid gases, it is the objective of any scrubbing system to selectively remove as much H_2S and other sulfur compounds as possible while minimizing the reaction with the accompanying CO_2. The reasons for this selectivity are to conserve the scrubbing chemicals and to concentrate the sulfur compounds so that they can be economically converted to a solid recoverable or a safely-disposable form.

Two liquid scrubbing concepts were evaluated on this test, alkaline and Stretford. The (Lovell et al, 1982 and Desai et al, 1983)* had identified these as potential processes for removing reduced sulfur compounds from shale oil retort offgas.

Field test data on retort offgas was limited especially for the alkaline scrubber. Monsanto Research Corporation (MRC) reported achieving up to 70 percent H_2S removal with aqueous ammonium in tests performed on retorts at DOE's Laramie Energy Technology Center.

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*All references are listed on Pages 140 and 141

The (Desai et al, 1983) primary concern with the alkaline process was that the selectivity might not be high enough to allow the removed sulfur to be recovered with a Claus process. Selectivity as used in this report is a measure of the reactivity of the scrubbing solution with H_2S compared to CO_2 and is precisely defined as the percent removal of H_2S from the gas stream divided by the percent removal of CO_2. The alkaline scrubber process envisioned by the EPA involved: (1) removing H_2S and the reduced sulfur compounds with the scrubbing solution; (2) stripping the sulfur gases from the scrubbing solution along with absorbed CO_2; and (3) processing the concentrated sulfur gases and CO_2 stream in the Claus unit to obtain elemental sulfur. The Claus process requires that the reduced sulfur (primarily H_2S) be at least eight percent of the feed gas with 15 percent or greater the desirable concentration. To obtain this, a minimum selectivity of 10 and preferably 30 or higher would be required. Because removal efficiency was known to vary inversely with selectivity, there was a question as to whether or not the selectivity could be achieved at an acceptable level of removal efficiency.

Therefore, in 1983, the EPA modified one of their existing trailer-mounted, wet-scrubber pilot plants to accommodate the potentially-combustible retort off-gas. Extensive modifications were made to the wiring, controls and power units in the EPA scrubber trailer and various safety devices were added to explosion-proof the unit and protect its operators from H_2S intrusion. Pressure, temperature and pH sensors were installed to monitor the process. Explosive gas and H_2S detectors with alarms were installed in the control room.

This was the first test of the modified pilot plant scrubber. A test plan was prepared with regard to chemicals to be used for scrubbing, addition rates, and solution pH levels to determine their effect on selectivity and removal efficiency. Time was allowed for system shakedown at the site since there was no feasible way to completely check out the system before taking it to the field. The field crew included personnel with technical skills to rework the system as needed. The Geokinetics, Inc. (GKI) facility at the test site was well equipped to support any modification activity with welding, crane and electrical services.

For the Stretford process this was the fourth test of the EPA's pilot plant which had been constructed as a transportable, skid-mounted unit. The first field test of the Stretford pilot plant was made at Occidental Oil Shale, Inc.'s (OXY) Logan Wash oil shale development mine near De Beque, Colorado in June and July 1982. This mine site is where OXY has conducted all of its oil shale research activities toward the development and commercialization of the vertical modified in situ (VMIS) recovery process.

The second field test of the Stretford plant was made in September and October 1982 at the GKI facility in Utah, the same site as this fourth test.

The third test in November 1982 represented a new application of the Stretford pilot plant--coal gasification. The test site was the U.S. Bureau of Mines (BOM)/Twin Cities Research Center (TCRC). The TCRC facility, which is located in Minneapolis, Minnesota, contains a pilot-scale, low Btu, coal gasifier.

For the Stretford process, the issue of selectivity per se is unimportant because the process is inherently selective. Therefore, the primary concern is removal efficiency. The performance of the Stretford pilot plant with respect to H_2S removal efficiency was improved significantly during each of these three test programs. At each of the test sites, gas conditions and composition were similar, which permitted comparisons and performance trend analysis. Removal efficiencies of H_2S improved from a low of 20 percent at OXY, to 80 percent at GKI, and a maximum of 99+ percent at TCRC. These incremental improvements in performance were obtained by various systematic modifications to the pilot plant's process design and operating parameters. It was desired to reproduce the 99+ percent removal efficiency on oil shale offgas and to gain some insight as to the cause of the lower efficiencies obtained in earler tests.

1.1.2 Objectives

The objectives for the GKI tests were as follows:

1. For the Alkali Scrubber Pilot Plant

    - Shakedown the equipment

- Investigate the influence of operating parameters pH, gas/liquid contact time, scrubbing agent, etc. on the selectivity and removal efficiency associated with scrubbing reduced sulfur compounds in the presence of high CO_2 concentration.

2. For the Stretford Pilot Plant

   - Duplicate on retort offgas the 99+ percent removal efficiency attained in the TCRC coal gasifier tests.

   - (Upon achieving that), attempt to explain the low removal efficiency on the 1982 test at GKI by deliberately introducing upsetting changes to the plant chemistry and then returning to the 99+ performance.

1.2 SITE AND PROCESS DESCRIPTION

The site of these sulfur scrubbing tests was the in-situ shale oil pilot test facility of Geokinetics, Inc. (GKI) in eastern Utah, 70 miles south of Vernal, Utah. This section describes the in-situ retorting process used by GKI, the properties of the gas emitted by that process and the installation of the two EPA pilot plants at the GKI site.

1.2.1 Shale Oil Production

Since early 1973, GKI has been developing a shale oil extraction process designed for areas where oil shale beds are relatively thin and close to the surface. Deposits with these characteristics have been found in areas of Brazil, Morocco, Australia, the United States, and elsewhere throughout the world.

In the southern Uintah Basin in the State of Utah, shallow oil shale deposits in the Mahogany Zone exceed two billion barrels in place. Major developers have generally ignored these deposits, and it was here that GKI was able to acquire its lease holdings, which total 30,000 acres containing oil shale seams averaging 30 feet in thickness and having an oil content of 22 gallons per ton.

In cooperation with the DOE, GKI is engaged in developing a true in-situ extraction process for use on shallow oil shale deposits. Because the process does not require the construction of a mine, surface retort, or associated rock-moving equipment, the front-end capital cost of a commercial operation is greatly reduced. GKI refers to their process as LOFRECO (low front end cost) covered by U.S. Patent 4037657.

In the GKI horizontal in-situ retorting process, a specific pattern of blast holes is drilled from the cleared surface through any overburden and into the oil shale bed. Explosives are placed in these holes and detonated by use of a carefully timed and planned blast system. The blast yields a well-fragmented mass of shale with high permeability and also produces a slightly sloping (approximately 4°) bottom surface that allows the produced oil to drain into a sump for collection. The fragmented zone constitutes the in-situ retort. The void space in the fragmented zone comes from lifting the overburden, producing a small uplift of the surface as shown in Figure 1(a) and Figure 2. Submerged-type oil well pumps are used to lift the recovered oil to surface storage tanks (see Figure 2).

Burning charcoal is introduced into drilled holes at the upper end of the rubblized zone to ignite the retort. Air inlet piping is also installed at this end of the retort. The burn front, consisting of a vertical wall approximately 30-ft high, travels toward the deep or low end of the retort. The objective is to retort the shale from one end to the other in a plug-flow fashion by maintaining a burn front that occupies the entire cross section of the bed. Typically the front travels at a speed of one foot per day. At normal production with two retorts operating, the GKI plant produced approximately 400 barrels/day of shale oil.

1.2.2 Retort Gas Properties and GKI Gas Processing

The GKI retort off-gas is brought to the surface for processing where it is treated in four steps, shown schematically in Figure 3 and photographically in Figure 1, before it is discharged to the atmosphere. First, the gas passes through a condenser/demister located upstream of the two blowers. The next treatment steps are the ammonia absorption, sulfur recovery, and incineration. The latter three operations are performed in series, with the treatment units arranged so that the desired treatment configuration can be obtained by bypassing one or more process steps. Expected operations during the scrubber test were to bypass the ammonia absorber and treat the gas in the sulfur recovery unit and the incinerator. A maximum of

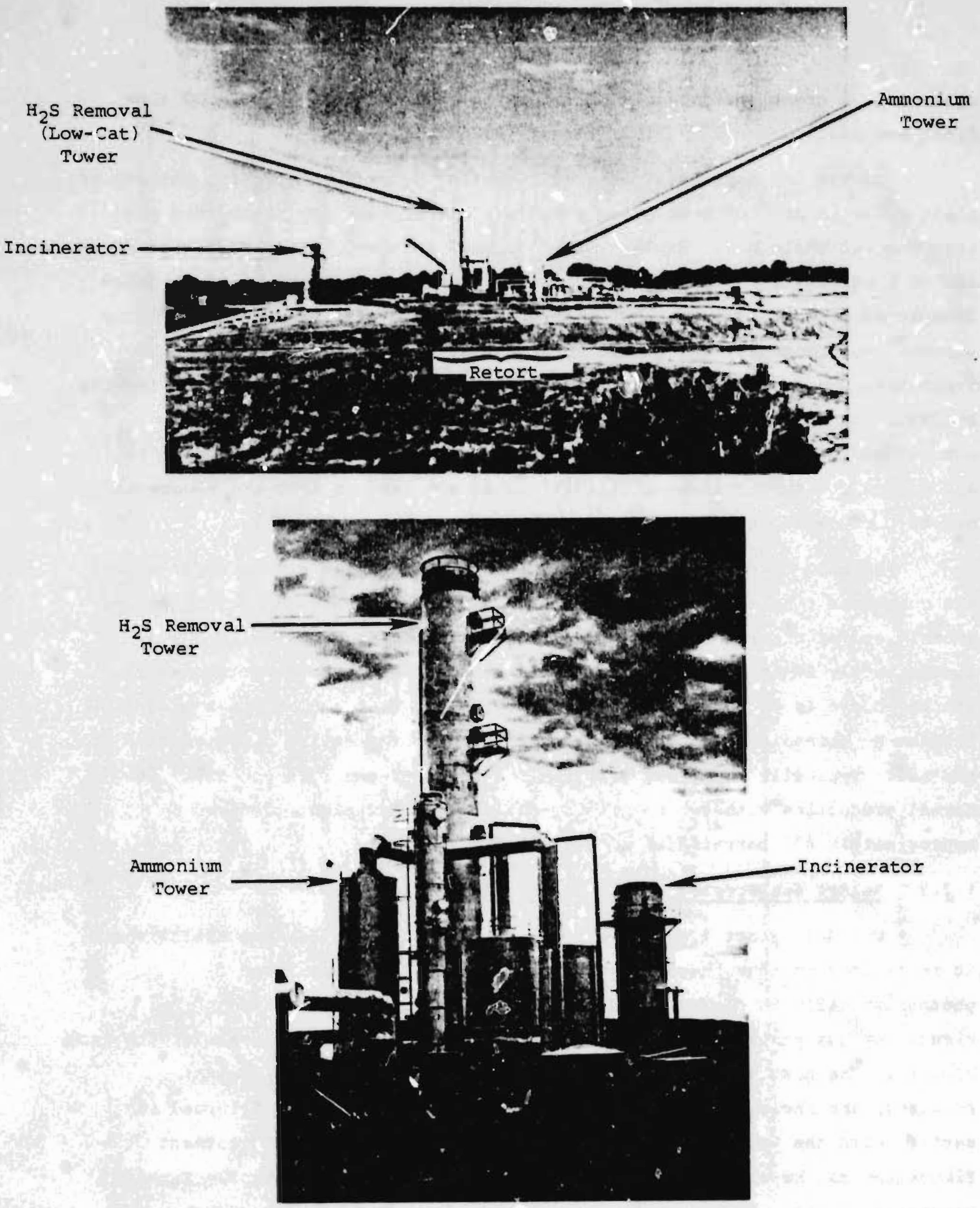

Figure 1. Equipment at the GKI Facility

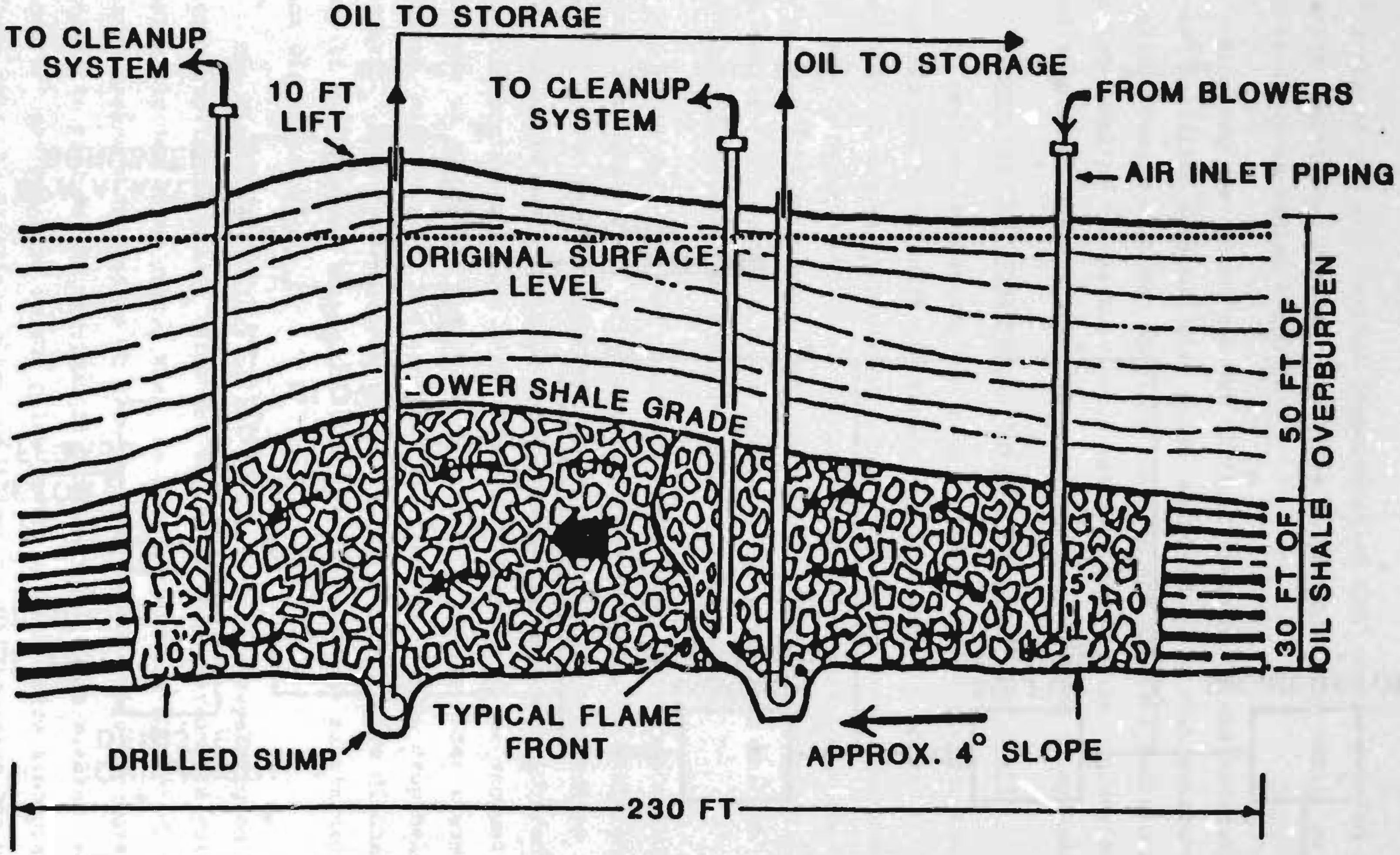

Figure 2. An example of a Geokinetics Horizontal In-Situ Retort

Source: Lekas, J. M., "The Geokinetics Horizontal In-Situ Retorting Process."

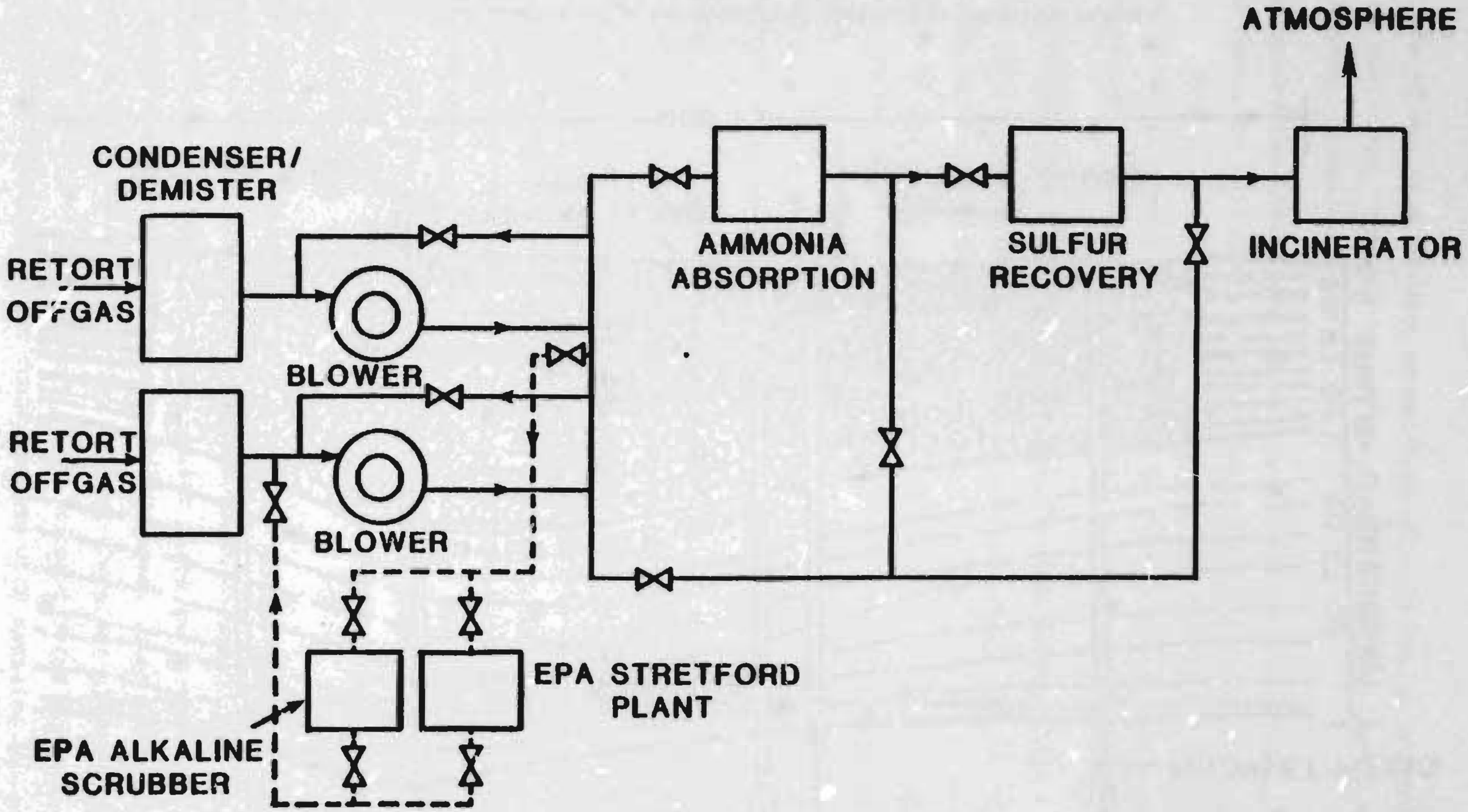

Figure 3. Schematic of Pilot Plant Installation in the Geokinetics Process

10 Sm^3/S cfm of gas at a maximum temperature of 82°C can be treated in the gas processing operation. Typical retort gas composition (dry basis) as provided by GKI is shown in Tables 1 and 2.

Sampling the retort gas was difficult because it was saturated with water and contained some oil mist which condensed along with moisture on the pipe walls. Over a week was spent by sampling and analysis technicians in developing sampling trains that would not be fouled by the condensing shale oil and moisture. The gas sampling apparatus is discussed in Appendix A.

1.2.3 Connecting the Scrubbers to the GKI Gas Processing Plant

As originally planned, the slip stream of retort gas for the two EPA pilot plants was to be extracted from a six-inch sampling valve on the main by-pass line of the gas processing plant. The outlet gases from the pilot plants were to be returned to another six-inch valve just downstream of the inlet valve. With this arrangement the inlet and outlet gas pressure would be the same and the pressure for circulating the retort gas through the pilot plants would be provided by their respective blowers.

Because GKI generates their own electricity, they have a limited capacity. To save power, it was agreed to use the pressure differential across the GKI blowers to drive the gas through the pilot plants as shown in Figure 3. GKI reported their blower discharge pressure as +140 g/cm^2 psig and the suction pressure as -280 g/cm^2 psig (i.e., 280 g/cm^2 psi vacuum). There was concern as to whether the pilot plants could operate under these conditions, especially if the internal gas pressure were to drop below atmospheric. However, by proper throttling at the respective discharge valves, it was believed that a positive pressure could be maintained upstream of that discharge valve.

The discharge pressure on the GKI plant varies depending on the pressure drop in the plant. With the sulfur plant on stream the pressure is approximately 140 g/cm^2 gage. When the sulfur plant was by-passed, the discharge pressure dropped to 70 g/cm^2 gage or lower. This pressure was still sufficient to produce the required flow through the pilot plants. However, the internal gas pressure in the pilot plants dropped below atmospheric. It was found that the Stretford plant could operate with negative gas pressure

TABLE 1. GEOKINETICS ESTIMATED RETORT OFF-GAS COMPOSITION*

Constituent	Mean Gas Analysis, Volume %
Nitrogen	59
Carbon Dioxide	22
Hydrogen	9.3
Carbon Monoxide	5.3
Oxygen	2
Methane	1.44
Ethane	0.26
Ethene	0.16
Propane	0.20
Hydrogen Sulfide	0.15
Ammonia	0.10
Propene	0.10
1-Butene	0.038
Butane	0.037
Isobutane	0.014
2-Methylbutane	0.026
1-Petene	0.015
Trans-Butene-2	0.007
Cis-Butene-2	0.004
1,3-Butadiene	0.003
Iso-Hexane	0.004
Hexane	0.010
Carbonyl Sulfide	0.008
1-Hexene	0.001
Methyl Mercaptan	0.001
Carbon Disulfide	<0.001
Thiophene	<0.001

*Lekas, 1984

TABLE 2. TYPICAL CHANGES IN OFF-GAS AMMONIA AND HYDROGEN SULFIDE LEVELS DURING BURN OF A GEOKINETICS RETORT (PPM)*

	H_2S	NH_3
Mean	1,382	958
Standard Dev.	599	530
Ten-Day Means		
1-10	61	16
11-20	125	13
21-30	220	69
31-40	479	444
41-50	947	862
51-60	1,506	824
61-70	1,431	1,013
71-80	1,586	1,061
81-90	2,048	1,207
91-100	1,754	595
101-110	1,990	1,142
111-120	1,734	914
121-130	1,186	1,053
131-140	1,493	7234
141-150	1,801	699
151-160	1,960	1,024
161-170	1,606	1,092
171-180	1,852	869
181-190	1,569	961
191-200	1,589	1,355
201-210	1,674	1,201
211-220	1,181	1,963
221-230	1,353	1,936
231-240	2,012	1,961

*Personal communication with James Lekas, Geokinetics.

downstream of the venturi contactor. The alkali scrubber however could not. The tray tower does not have a discharge pump and depends on gravity drainage. Therefore, a negative pressure in the tray tower defeats the automatic drain which opens when the liquid reaches a high level point.

To allow the pilot plant to operate, the main blower from the scrubber trailer was relocated from its position at the gas outlet inside the trailer to a position outside the trailer where it served as a forced draft fan to raise the inlet pressure. A four-inch diameter by-pass line and manual valve was installed across the blower. To achieve a desired flow through the scrubber it was necessary to manually trim the blower by-pass valve and adjust the electric flow control valve in the trailer. The system was sensitive to GKI's discharge pressure changes which at times caused mid-run adjustments and even several aborted runs.

The scrubber blower was first installed with a four-inch line direct from the GKI process. As mentioned earlier, the gas entering the scrubber and the Stretford had significant water and oil mist. The blower soon became flooded with this condensing liquid and a knockout tank (approximately 50 gallons) was installed. Photographs of the final installation are presented as Figure 4. After a day of operation, the knockout tank filled with oily water. A continuous drain was installed in the tank and the system functioned well enough to complete the runs. The knockouts merely collected liquid material running along the pipe walls. The suspended mist was carried into the two processes. The scrubber trailer discharges had an oil slick on the solution surface. The Stretford system had a foaming problem in their tanks which may have been caused by the suspended oil as discussed in Section 3.0.

In future tests of the scrubber it would be prudent to send some sampling crews to the site at least a few weeks before the equipment is shipped to characterize the exhaust gases regarding condensed phases which can clog sampling lines as well as the entire gas handling system. This will provide time to fabricate and install the proper knockout devices before the field test crew arrives on the site.

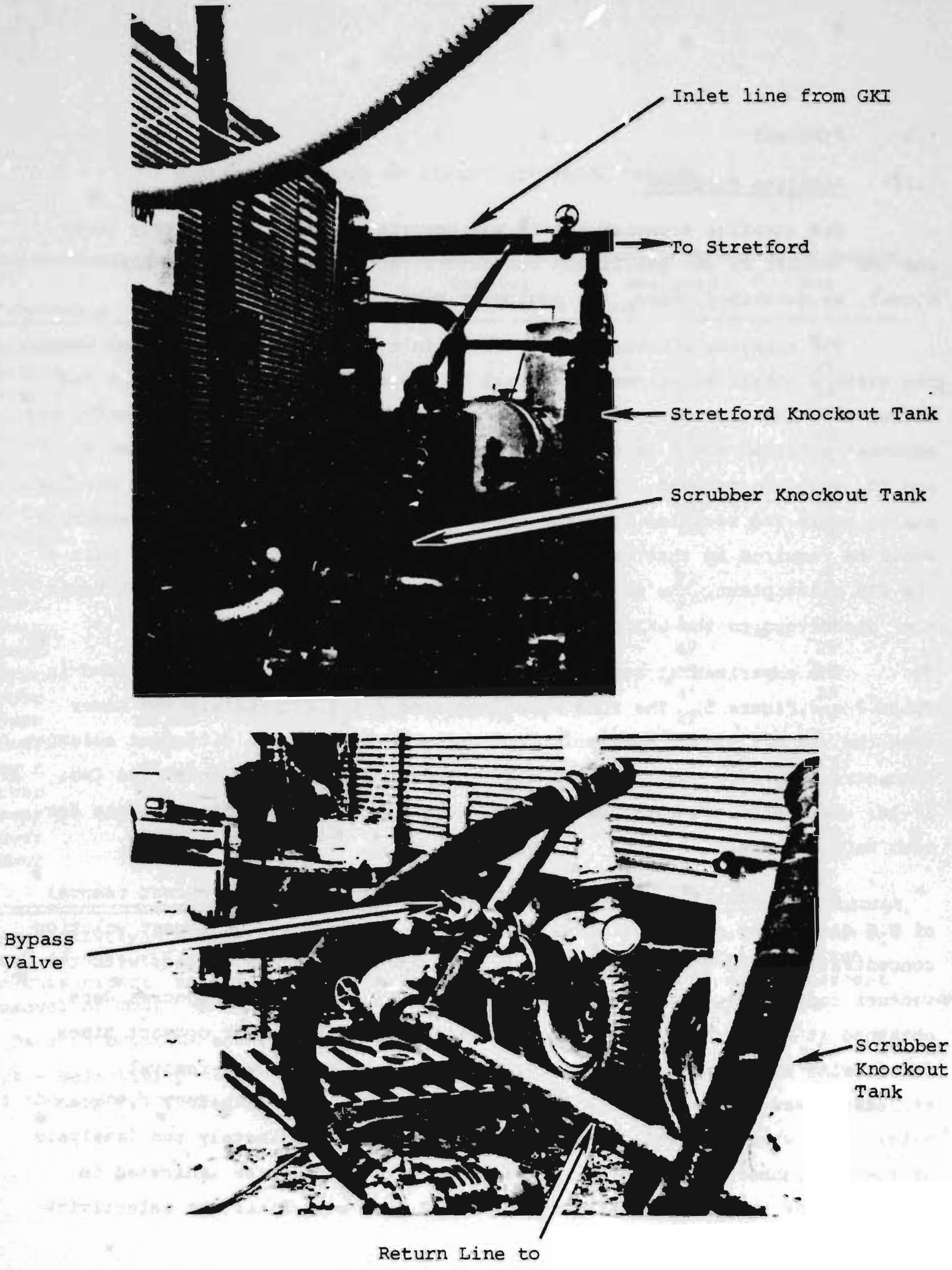

Figure 4. Photographs of the scrubber trailer inlet and outlet plumbing.

1.3 FINDINGS

1.3.1 Alkaline Scrubber

The alkaline scrubber system was operated using both the tray tower and the venturi as the gas/liquid contactor. After relocating the main blower, as described above, the equipment performed satisfactorily.

The alkaline scrubber was operated in a simple blowdown process where the various alkali solutions were mixed to a specific concentration and fed either into the tray tower or venturi contactors. In a real process unit, the scrubber solution would be cycled through a stripper where the absorbed H_2S and CO_2 would be removed. Then the solution would be returned to the original mixing tanks and recycled into the contactor. No significant alkali addition would be required in that case. Since a stripper was not included as part of the EPA pilot plant, the scrubbing solution was used on a once-through basis then discharged to the GKI pond.

The experimental results for the alkaline scrubber are summarized in Table 3 and Figure 5. The runs were conducted using alternately the tower then the venturi at the same solution concentration. Three different solution concentrations were used for each alkali except for the last four runs (No. 31-34) where only the tower was used to make two high concentration runs for both NaOH and KOH.

It was generally found that the highest selectivity (percent removal of H_2S divided by percent removal of CO_2) was obtained at the lowest solution concentrations and at the shorter solution/gas contact times (i.e., with the venturi contactor). Conversely, the highest H_2S removal efficiencies were obtained at the higher solution concentrations and the longer contact times (i.e., with the tray tower contactor). A limit of 94 percent removal efficiency was reached at an alkali concentration of approximately 0.9 gram moles/liter where the selectivity is estimated at approximately ten (analysis of spent scrubber solution was not performed on that test as indicated in Table 3). At the low concentration of 0.012 gram mole/liter the selectivity reached as high as 79.

All three of the alkaline solutions performed similarly. The plot of removal efficiency vs. selectivity in Figure 5 indicates the specific chemical

TABLE 3. SUMMARY OF ALKALI SCRUBBING RESULTS

Contactor	Alkali	OH^- Conc. gmole/liter	Removal Efficiency %	Measured Selectivity*	Run No.
Venturi	NaOH	0.012	52	79	21
Venturi	KOH	0.012	53	71	28
Venturi	NaOH	0.023	48	60	24
Venturi	KOH	0.023	48	51	30
Venturi	NaOH	0.045	70	(84)†	19
Venturi	KOH	0.046	71	21	26
Venturi	NH_4OH	0.049	60	71	15
Venturi	NH_4OH	0.29	62	56	17
Venturi	NH_4OH	2.0	67	11	13
Tower	NaOH	0.012	52	52	20
Tower	KOH	0.012	54	43	27
Tower	NaOH	0.023	54	41	22
Tower	KOH	0.023	59	49	29
Tower	NaOH	0.045	83	36	18
Tower	KOH	0.046	88	41	25
Tower	NH_4OH	0.049	64	29	14
Tower	NH_4OH	0.29	91	29	16
Tower	NH_4OH	2.0	93	9	12
Tower	KOH	0.89	94	N/A	31
Tower	NaOH	1.25	93	N/A	33
Tower	KOH	1.79	92	N/A	32
Tower	NaOH	2.5	94	N/A	34

* Selectivity - A measure of the preferential removal of H_2S over CO_2 taking into account the relative difference in concentration between the two gases. In this report, selectivity is the ratio of percent removal of H_2S to percent removal of CO_2.

† Data in brackets are suspected to be erroneous.

N/A - Selectivity values for these runs were not available because an analysis of the spent scrubbing solution was not performed.

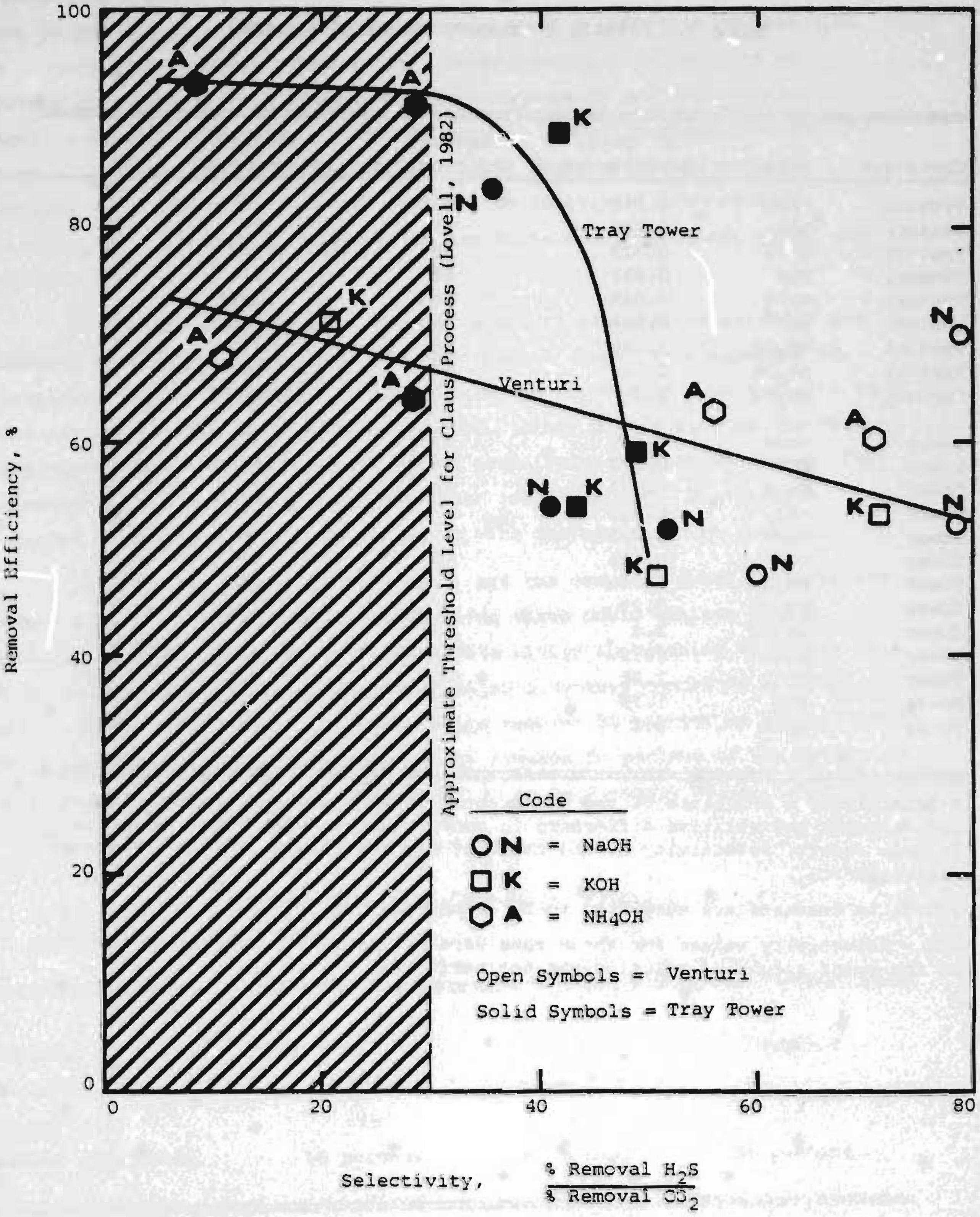

Figure 5. Removal Efficiency vs. Selectivity for Alkaline Scrubber

at each data point. All three solutions can produce removal efficiencies above 90 percent at a selectivity to be considered a candidate for use with the Claus sulfur recovery process. All three show high selectivity at recovery efficiencies high enough that with the use of multiple venturi stages, a removal efficiency of over 95 percent should be obtainable for the system. Since the system envisioned for using these chemicals involves recycling the alkali, the relative cost of the individual chemicals is insignificant. What may be significant are factors of corrosion, safety and availability.

To analyze these data, a computer model of an alkaline scrubber was developed employing the comprehensive penetration theory (See Appendix B). Penetration theory (Danckwertz, 1970) treats the gas/liquid mass transfer to allow contact time to be significant factor. Other models such as the two-plane theory have implicit assumptions of equilibrium and cannot account for the contact time difference between a tower and a venturi. The results predicted by the penetration theory agree with the experimental results.

Based on the experimental results and the computer model, an alkaline scrubbing system design concept is suggested which could achieve an H_2S removal efficiency of 95 percent with a selectivity approaching 40. This is a two stage scrubber with the first stage being a venturi contactor and the second stage a tray tower. The first stage removes 50 percent of the H_2S in a highly selective manner. The second stage removes 90 percent of the remaining H_2S at a lower selectivity. A summary of these performance values is as follows:

TWO-STAGE ALKALINE SCRUBBER - CONCEPT I

Stage No	I	II	Combined
Contactor	Venturi	Tray Tower	
Selectivity	110	40	37
Removal Efficiency	50 percent	90 percent	95 percent

Another concept employing a two-stage tray tower scrubber which results in a higher removal efficiency but a lower selectivity is summarized as follows:

TWO-STAGE ALKALINE TOWER SCRUBBER - CONCEPT II

Stage No	I	II	Combined
Contactor	Tray Tower	Tray Tower	
Selectivity	40	40	22
Removal Efficiency	90 percent	90 percent	99 percent

This "two-stage" tray tower scrubber can be combined into a single tower of double length.

The alkaline scrubber showed little removal of the organic sulfur compounds. This is similar to previous results reported in the literature. In reviewing the literature it was found that a commercial alkaline scrubber process exists, which has been successfully employed on the exhaust gases from black liquor boilers in the pulp and paper industry, to remove organic sulfur compounds as well as H_2S. The primary difference is that the scrubbing solution contains activated charcoal and a hypochlorite compound in addition to the NaOH. The small amount of activated charcoal (less than 0.1 weight percent) also aids in oxidizing HS^- to S_2O_3 and produces a saleable by-product of sodium thiosulfate. Prohocs, 1983 present the details of this system.

1.3.2 Stretford Plant

The Stretford operated for over 200 hours. For 140 hours, the plant operated with a venturi contactor. The venturi had been modified from that used in previous tests in that the throat area could be adjusted to handle variable gas flow rates. In this test the throat was adjusted to the smallest throat area, 18 cm, and held constant during most of the testing.

The maximum H_2S removal efficiency measured while using the venturi alone was 95 percent which was maintained only briefly. Over the period of operation with this contactor alone the removal efficiency averaged 80 percent. The short increase to 95 percent was not explained.

A brief attempt was made to experiment with increasing the venturi throat area. When no effect on removal efficiency was observed, the throat area experiment was discontinued.

Because of the failure of the plant to achieve the 99+ percent removal efficiency objective observed in the TCRC coal gasifier tests, the plant was equipped with a field-fabricated, packed-column contactor placed in series with and downstream of the venturi. This device increased the removal efficiency to the 99+ percent range during its period of operation. Because of the make-shift nature of this field modification, there was no instrumentation to measure the flow rate of the scrubber liquid through the tower. Thus, it was not possible to optimize the liquid distribution between the venturi and the tower.

1.4 CONCLUSIONS AND RECOMMENDATIONS

1.4.1 Conclusions

Based on the findings reported herein, the following conclusions were reached:

1. For shale oil retort offgas similar in composition to that from the GKI process, the alkaline scrubber, in combination with a stripper and a Claus plant, could be a viable means of H_2S removal. This overall conclusion is based on other conclusions as enumerated below.

2. For GKI-type process offgas and based on these tests, the performance of an alkaline scrubber with a tray tower contactor similar to that in the EPA pilot plant can achieve an H_2S removal efficiency of at least 90 percent with a selectivity of approximately 30. Under the same conditions a single venturi contactor in place of the tray tower would remove only 50 to 60 percent H_2S but with a selectivity of 70 to 80.

3. Based on the computer model developed to analyze these test results, the removal efficiencies and selectivity above are applicable to offgas with lower H_2S concentrations than found at GKI. This suggests a concept of multiple scrubbing actions to increase the H_2S removal. Because this increased removal efficiency is accompanied by a reduced selectivity which could present a problem for the Claus plant, the cost effectiveness of this concept requires a design study.

4. Based on a three gas component (H_2S, NH_3 and CO_2) analysis by the computer program, the principal reactant for the H_2S in the retort offgas is the NH_3 in that same offgas. In that NH_3 is present in the GKI offgas in similar molar quantities to that of the H_2S, the scrubber performance observed on these tests may not be applicable to retort offgas with little or no NH_3. This also suggests that the water and the NH_3 in the offgas would be an effective scrubbing agent without any alkali addition to the water. Scrubbing in this manner would certainly improve the selectivity but the H_2S removal efficiency obtainable is uncertain.

5. The alkaline scrubber removal efficiency and selectivity seemed to have little dependency on the alkali used. This is consistent with the above concept that it is the NH_3 in the offgas itself that is reacting the H_2S. Since the NH_3 and H_2S concentrations are variable, it is likely that some of the H_2S is reacted by the alkali. Therefore, it is likely some alkali will always be needed. However, the choice of scrubbing alkali may be made on such factors as cost, maintenance, safety, availability, crew comfort, etc. rather than performance.

6. The absorption of H_2S and CO_2 in the alkaline solution appears to be fully reversible by distillation. The sulfur in the scrubber solution is primarily in the form of sulfide. The sulfate or sulfite level determined in the scrubbing solution was equal to that in the water supply. The sulfide will distill off as H_2S (along with CO_2) while the sulfate will not. It had been suggested (Desai et al, 1983) that the H_2S would not be recoverable from the alkaline solution (presumably because it would be oxidized by the O_2 in the offgas). This does not seem to be the case based on this test.

7. With an adequate contactor, the Stretford process can obtain removal efficiencies of 99 percent. These tests suggest that if adequate H_2S removal cannot be achieved with a venturi, then a packed tower is a workable option for improving performance.

8. To insure continued satisfactory performance of a Stretford plant in processing retort offgas, it is important to provide effective removal of hydrocarbon mist and other particulate matter from the gas before it enters the plant.

1.4.2 Recommendations

The following recommendations are made regarding continued investigation of reduced sulfur compound removal from shale oil retort offgas:

A. It is recommended that a preliminary design study be conducted to determine the effect of removal efficiency and selectivity on the design of a sulfur removal system based on an alkaline scrubber and a Claus plant. The objective of this study would be to provide cost tradeoff data necessary to optimize a sulfur removal plant for any future installations.

B. To continue the research and development of the alkaline scrubber, it is recommended that the EPA mobile scrubber pilot plant be deployed for a further series of tests. The objective of these tests would be as follows:

1. Explore the effect of OH^- concentration on removal efficiency and selectivity. These tests would cover the concentration range from 0.0 to 0.012 gram moles/liter and from 0.05 to 1.0 gram moles/liter using both the venturi and tray tower.

2. Investigate the combined venturi and tray tower concept postulated in this report to see if the 95 percent removal efficiency and 37 selectivity is achievable. The operating parameters for this test would be selected after the field results from the concentration tests (above) are known.

3. Investigate the use of hypochlorite solution and charcoal in the NaOH scrubbing solution to improve the organic sulfur removal. Since neither the alkaline scrubber nor the Stretford plant was effective in removing organic sulfur compounds from the offgas, this test will determine whether or not this process will be as effective on shale oil retort offgas as it has been in the paper industry.

SECTION 2.0

SCRUBBER PILOT PLANT

This section describes the facilities, theory of operation and results of the scrubber pilot plant tests. It concludes with a concept design for a potentially viable alkaline scrubber for H_2S in a high-CO_2-concentration gas.

2.1 BACKGROUND (REVIEW OF H_2S REMOVAL PROCESSES)

Under EPA sponsorship, two studies of various H_2S removal processes as were conducted (Lovell, et al 1982 and Desai, et al 1983). These processes were evaluated with regard to removal efficiency, waste disposal requirements, safety requirements, overall treatment costs, state of development, licensing requirements and compatibility with EPA's concept of mobile pilot plant scrubbers. The six processes that were deemed to have applications to shale oil retort offgas were:

Lo-Cat (TM)
NaOH Scrubbing
Amine Scrubbing
Aqueous Ammonia Scrubbing
Stretford
Unisulf

The Stretford process will be discussed in Section 3.0. This discussion is concerned only with the caustic and aqueous ammonia scrubbing. In this report, caustic has been extended to include KOH as well as NaOH. NH_4OH, NaOH and KOH are referred to collectively in this report as alkali or alkaline material.

The caustic or ammonia scrubbing process (i.e., alkaline scrubbing process) consists of: (1) a scrubber to selectively remove H_2S from the retort gas, (2) a regenerator (distillation unit) to release the absorbed H_2S gas as well as the co-absorbed CO_2 gas and permit the recycling of the scrubbing liquid, and (3) a Claus plant to recover sulfur from the H_2S rich gas. The process schematic is shown in Figure 6.

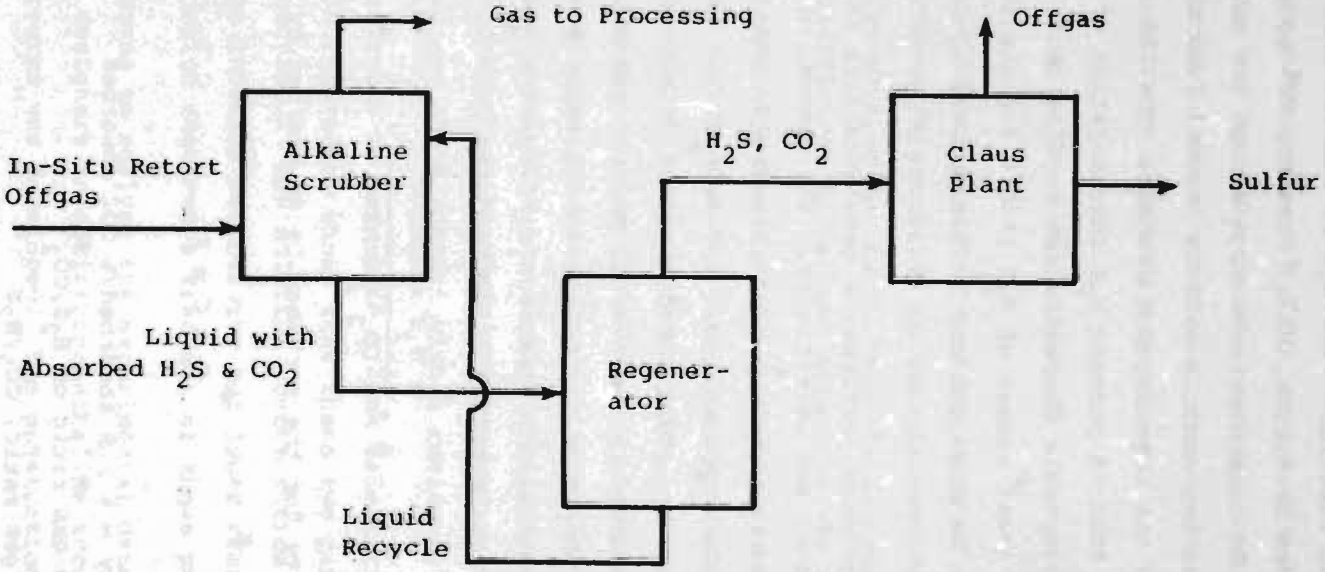

Figure 6. Alkaline Scrubbing Process Schematic In-Situ Retort Offgas.

The alkaline scrubbing process removes H_2S from the retort gas by absorption with chemical reaction. The H_2S is removed from the gas by reaction with OH^- to form bisulfide, HS^-. When the HS^- solution is heated, the H_2S is regenerated in concentrations high enough for sulfur recovery in a Claus process. Any absorbed ammonia will be removed from the scrubber liquid and can be recovered in the regeneration process. The Claus process is most effective with greater than 15 percent H_2S concentration of the feed gas although the minimum acceptable concentration is 8 percent. As the retort offgas contains CO_2 in great excess of H_2S (150:1 for the in-situ retort), the CO_2 absorption rate can be high and can be the primary limitation to the process.

There are two primary performance considerations in the scrubber design, removal efficiency and selectivity. The removal efficiency desired is at least 95 percent based on the expected allowable sulfur emission rates for regulating future oil shale processing. The selectivity is critical because of the need to obtain an acceptable concentration of H_2S in the Claus feed gas. The removal efficiency is the overall percent reduction in reduced sulfur while the selectivity is the relative preference given to absorption of H_2S over that of CO_2 considering the great difference in their concentration level. For this report selectivity is defined as:

$$S = \frac{\%\ H_2S\ \text{absorbed}}{\%\ CO_2\ \text{absorbed}}$$

The required selectivity for the scrubber is determined by the equation:

$$S = C \times R$$

where: S = selectivity = % H_2S absorbed/% CO_2 absorbed

C = Claus feed gas ratio of H_2S/CO_2

R = Retort offgas ratio, CO_2/H_2S

For a Claus feed gas ratio of (H_2S/CO_2) 0.08 and retort offgas CO_2/H_2S ratio of 150, the selectivity required is

$$S = 0.08 \times 150 = 12$$

The minimum criteria is to achieve an H_2S/CO_2 ratio of 0.08. However, the higher the selectivity, the less CO_2 absorbed and the lower the steam requirement to re-vaporize in the regeneration stage. To achieve the moderate H_2S/CO_2 ratio of 0.25 requires a selectivity of

$$S = 0.25 \times 150 = 38$$

Lovell, et al, 1982 has reported a selectivity of 29 as a maximum for the Japanese Diamox process (essentially an ammonia scrubbing process) and did not select alkaline scrubbing on the basis that the maximum selectivity of approximately 30 is insufficient for a cost effective system.

One of the primary objectives of this project was to examine the potential for achieving higher selectivities by maximizing the effect of the different reaction rates for H_2S and CO_2 absorption. Essentially, the H_2S absorption reaction is instantaneous while the CO_2 absorption rate is finite (6000 liters/gmole-sec). This suggests that limiting the reaction time and controlling the relative gas/liquid mass transfer coefficient should result in higher selectivities. Consequently, these tests were run with a tray tower at a residence time of 0.2 sec and a venturi with a residence time of 0.003 sec.

While it is desirable to have both a high selectivity and a high removal efficiency, the literature shows that these two parameters usually change in opposite directions. Low solution concentration and short gas/liquid contact time increase selectivity but lower removal efficiency. The optimum scrubber design requires a tradeoff of these parameters.

To provide a means to analyze the experimental data obtained in this program and to assist designers in optimizing alkaline scrubber performance an analytical computer program was developed. The penetration theory (Danckwertz, 1970) was used for modeling mass transfer in this program and the gas/liquid contactors assumed were venturis since these are discrete short interval contactors and have the most controllable operating parameters.

2.2 DESCRIPTION OF FACILITIES

The equipment used for the alkaline scrubbing test was contained in the EPA's Mobile Wet Scrubber Pilot Plant shown in Figure 7. A schematic diagram of the equipment inside the scrubber trailer is shown in Figure 8. The gas treatment equipment consists of a spray tower, venturi/cyclone combination, sieve tray tower, and a demister. The system can be operated in series with none, one or more treatment units excluded from operation. Peripheral equipment consists of a Roots blower, a sump tank, fabric filter/holding tank combination, a pump/mix tank, an air cooler, feed and recycle pumps, liquid control valves, gas temperature and flow/monitoring devices, gas pressure monitoring devices, and liquid flow and pH and monitoring instruments.

In these tests only the sieve tray tower or venturi/cyclone unit was used for gas treatment. The spray tower was not included in the gas train. As discussed in Section 3.3 the Roots blower was relocated upstream of the trailer inlet for the GKI tests to boost the inlet pressure.

2.2.1 Sieve Tray Tower

The sieve tray tower consists of four trays within an 46-cm-dia. pyrex glass column. Three sets of trays are available for this tower with varying hole diameter and spacing. The open area is the same for all trays. The sieve tray perforation size used for these tests was 0.32 cm. The sieve tray characteristic curves are shown in Figure 9.

2.2.2 Venturi/Cyclone

The Venturi scrubber consists of three interchangeable venturi throat sections (3.5, 6.0, 8.5 cm dia) which allow operation over a wide range of pressure drops and liquid-to-gas (l/g) ratios. Each venturi throat has a length of 30.5 cm and two radial inlet water nozzles 5.1 cm below the throat entrance. After leaving the venturi the scrubbed gas enters the cylone separator. The venturi throat used for these tests was the 3.5 centimeter diameter and the characteristic curve for the venturi scrubber is shown in Figure 10. The reader is referred to the "EPA Scrubber Trailer Operation Procedure," (Ctvrtnicek, 1984) for additional information regarding the details of the scrubber trailer and specific equipment contained within.

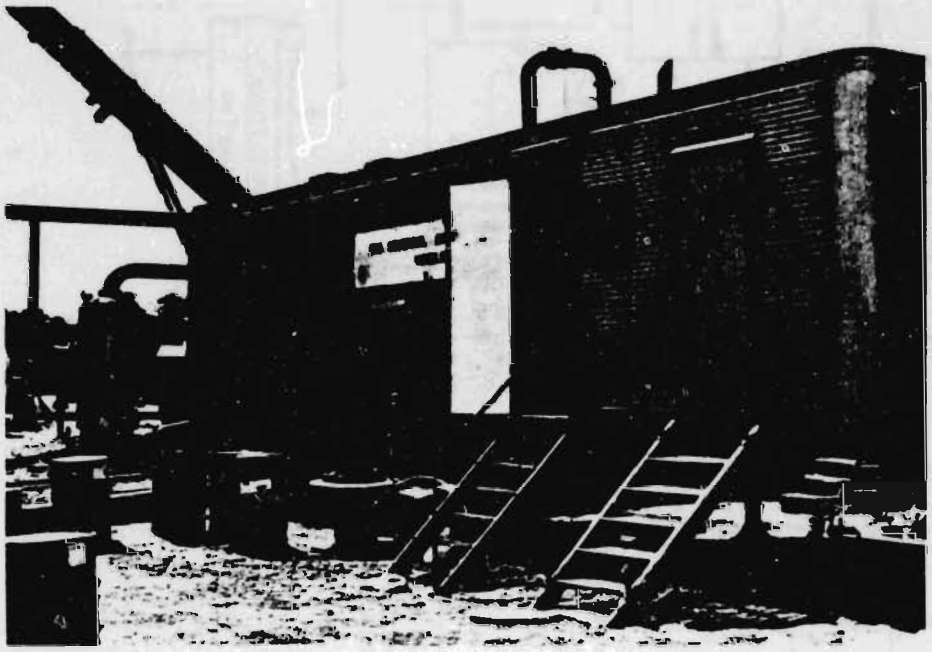

Figure 7. EPA's mobile wet scrubber trailer.

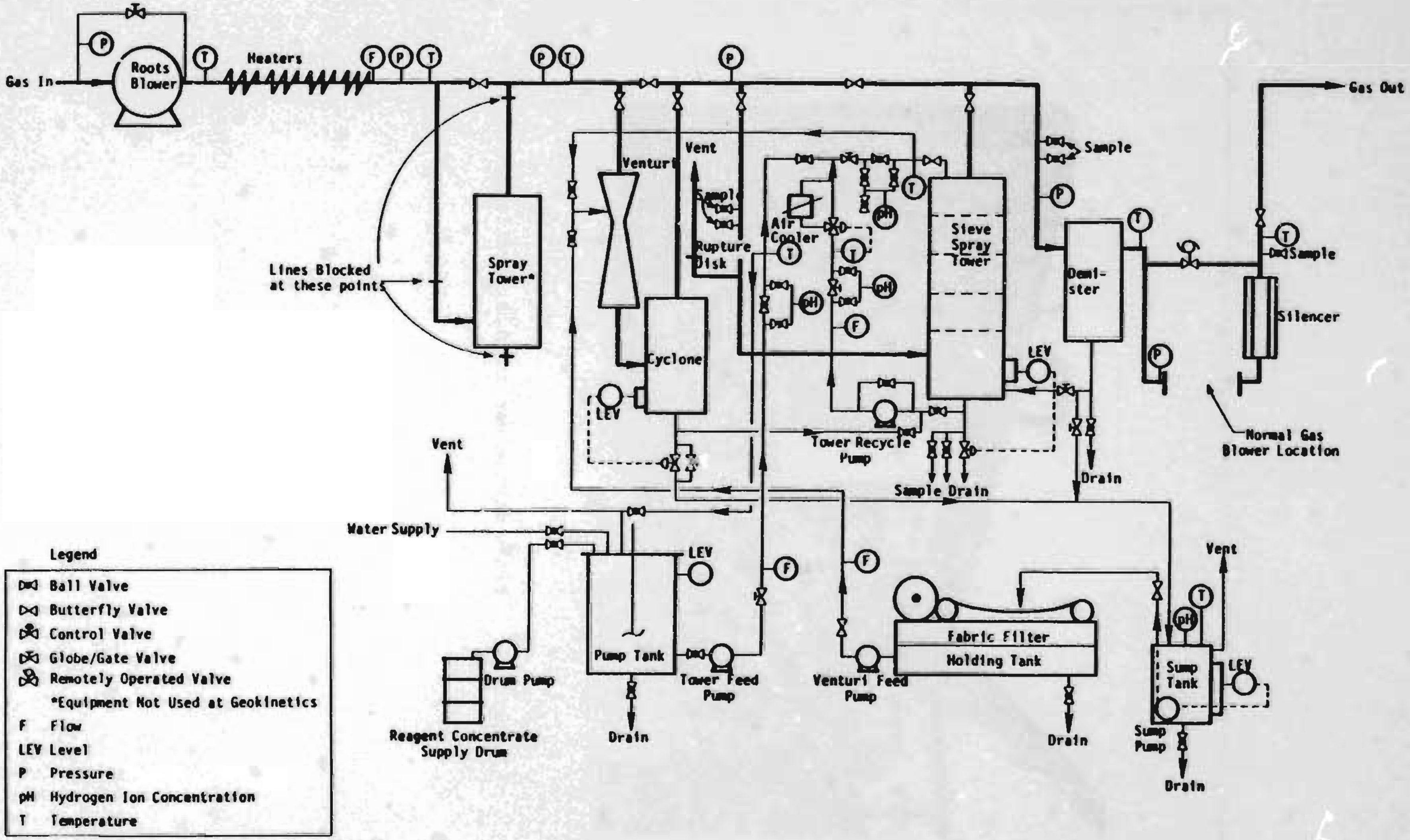

Figure 8. EPA scrubber trailer equipment and flow diagram (After Ctvrtnicek 1984).

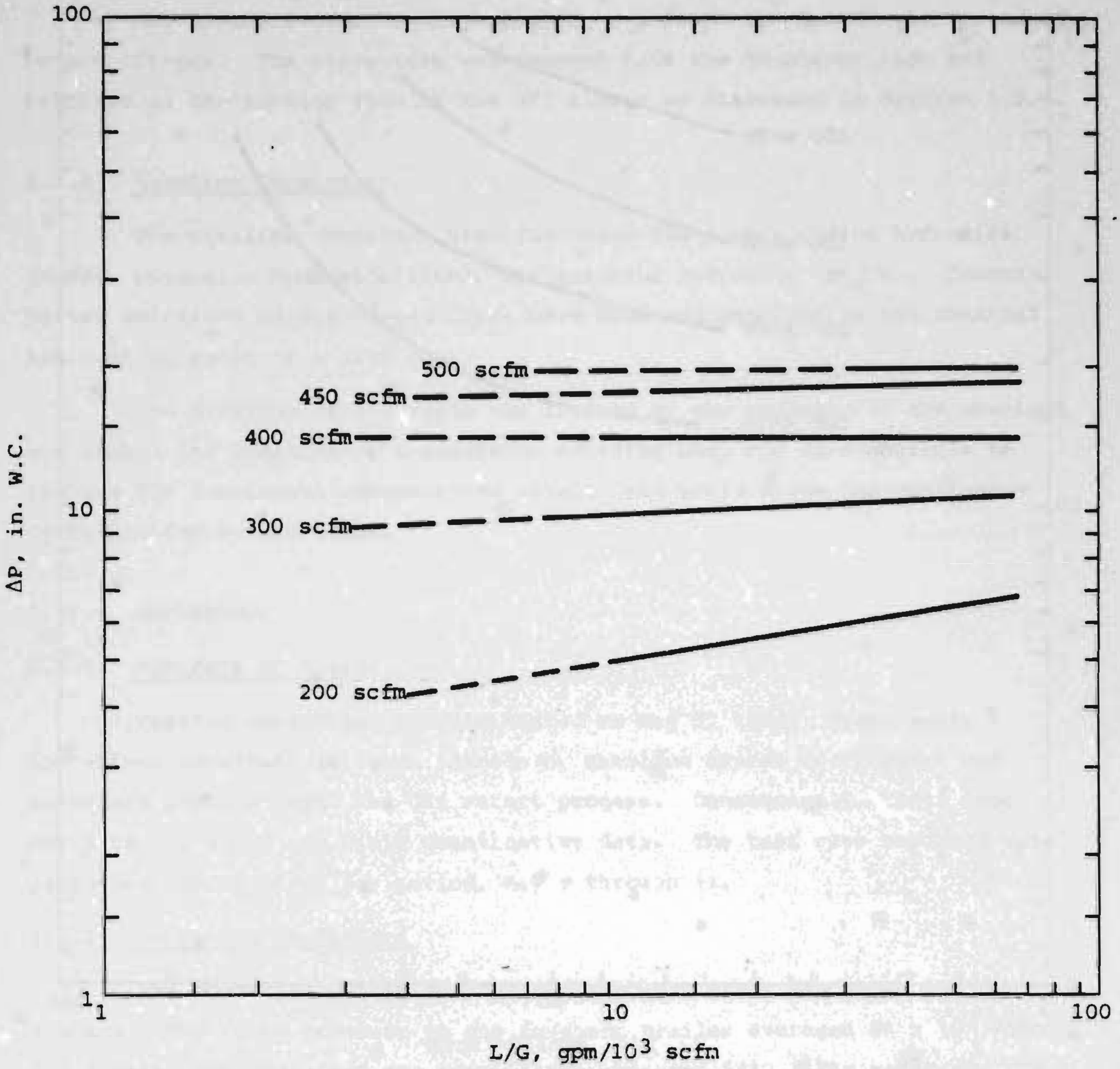

Figure 9. Sieve tray characteristic curve (Ctvrtnicek, 1984)

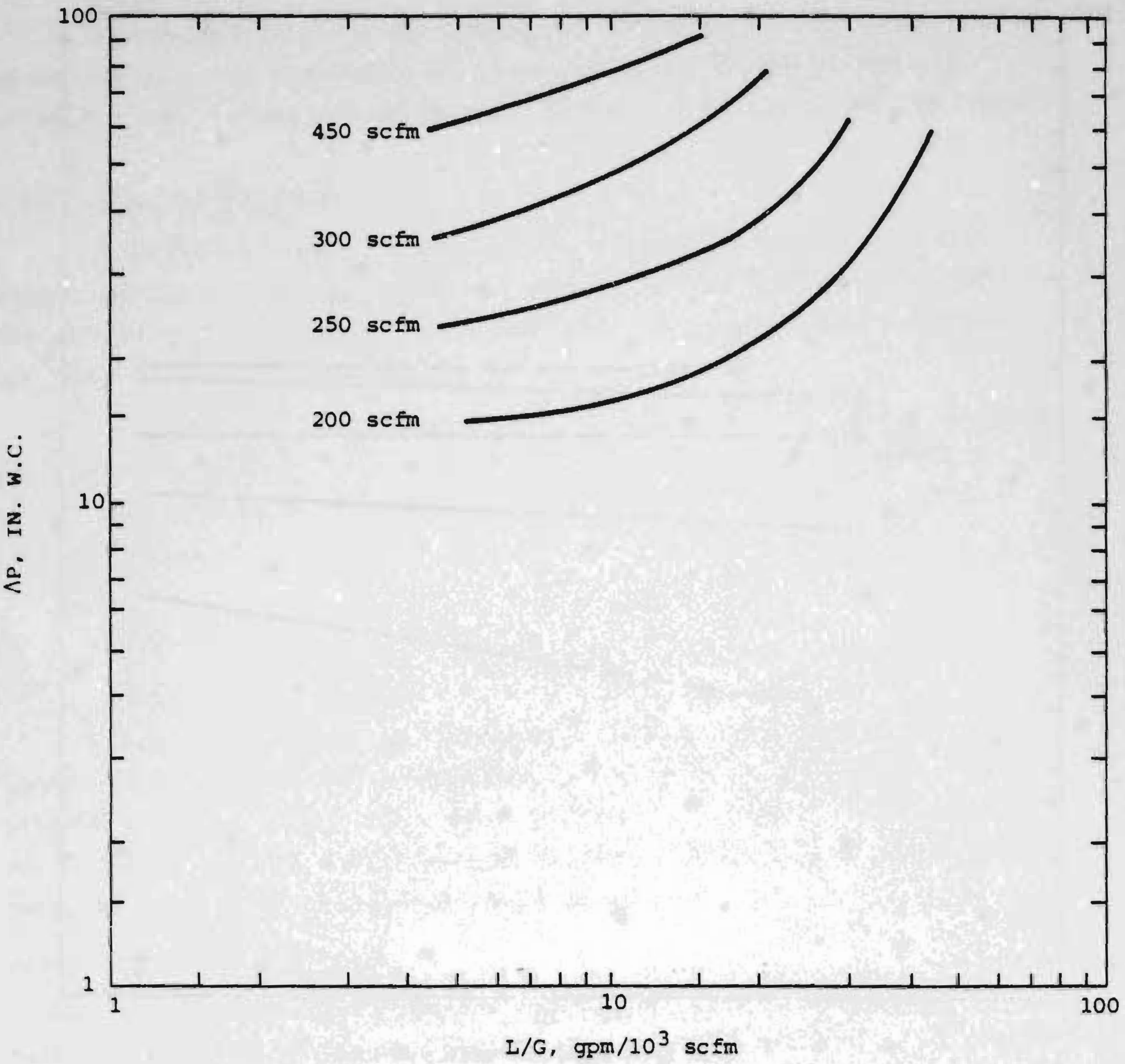

Figure 10. Characteristic curves for venturi with 3-cm-dia. throat. (Ctvrtnicek, 1984)

2.2.3 Retort Gas

The scrubber trailer was operated on a 0.094 Sm^3/S ACFM slipstream of retort off-gas. The slipstream was removed from the discharge side and returned to the suction side of the GKI blower as discussed in Section 1.2.3.

2.2.4 Alkaline Chemicals

The alkaline chemicals used for these tests were sodium hydroxide (NaOH), potassium hydroxide (KOH), and ammonium hydroxide (NH_4OH). Concentrated solutions in $0.21m^3$-gal drums were used and supplied to the chemical mix tank by means of a drum pump.

The duration of the tests was limited by the capacity of the chemical mix tank. The addition of a precision metering pump and flow controls to provide for continuous concentrated alkali feed would allow for continuous operation for future tests.

2.3 OPERATIONS

2.3.1 Schedule of Activities

Testing operations were initiated on May 5, 1984. These early operations involved equipment shakedown, sampling system development and interface problems with the GKI retort process. Consequently, tests from May 5 to May 8 did not yield quantitative data. The test runs reported were performed over a three day period, May 9 through 11.

2.3.2 Operating Conditions

The operating conditions for the scrubber tests are shown in Table 4. The inlet pressure to the scrubber trailer averaged 84 x 10^3 Pascal (12.2 psia) and the inlet gas temperature averaged 54°C. For reference the atmospheric pressure at Kamp Kerogen during the tests averaged 79 x 10^3 Pa (11.4 psia). The H_2S concentration of the inlet gas was fairly constant for most of the runs at 1,280 ppm. However, for runs 12-17 the H_2S was considerably higher with a level of 1780 ppm. The gas flow to the trailer

TABLE 4. OPERATING CONDITIONS FOR ALKALINE SCRUBBER TESTS

Run No.	Contactor	Gas							Water		
		Pressure, Pascal x 10^{-3}			Temperature, °C		H_2S, ppm	Flow Sm^3/S	Temperature, °C		Flow, l/s
		In	Out	ΔP	In	Out			In	Out	
12	Tower	80.7	77.9	2.8	50.1	35.0	1,780	0.099	22.9	41.6	0.379
13	Venturi	85.1	81.2	3.9	45.8	25.2	1,780	0.094	22.8	31.6	0.310
14	Tower	80.3	77.6	2.7	50.0	25.2	1,780	0.098	21.6	40.6	0.379
15	Venturi	84.3	79.8	4.5	46.6	32.3	1,780	0.097	21.4	31.6	0.303
16	Tower	83.8	81.4	2.4	50.5	31.5	1,780	0.100	22.9	41.6	0.379
17	Venturi	84.0	79.0	5.0	49.9	35.0	1,780	0.098	22.8	33.6	0.290
18	Tower	82.3	79.6	2.7	51.3	23.0	1,280	0.094	23.0	34.0	0.379
19	Venturi	83.9	78.5	5.4	52.2	35.0	1,280	0.109	22.0	34.0	0.335
20	Tower	80.4	77.4	3.0	52.2	26.0	1,280	0.109	22.0	34.6	0.379
21	Venturi	84.0	78.5	5.5	55.1	35.0	1,280	0.102	21.0	35.0	0.328
22	Tower	83.5	80.8	2.7	54.6	28.1	1,280	0.097	23.0	34.0	0.379
24	Venturi	84.1	78.7	5.4	54.0	35.6	1,280	0.098	21.0	36.0	0.347
25	Tower	88.5	85.9	2.6	58.0	29.0	1,280	0.088	24.1	30.4	0.379
26	Venturi	87.2	82.7	4.5	58.2	40.9	1,280	0.094	22.1	30.8	0.347
27	Tower	85.1	82.3	2.8	62.0	28.1	1,280	0.094	23.5	31.2	0.379
28	Venturi	91.2	87.4	3.8	64.2	38.3	1,280	0.090	22.2	33.8	0.316
29	Tower	83.0	80.4	2.6	58.1	30.7	1,280	0.104	22.0	34.2	0.379
30	Venturi	86.2	81.9	4.3	59.9	36.5	1,280	0.092	22.0	36.3	0.335
31	Tower	85.6	80.8	4.8	57.3	36.5	1280	0.104	22.3		0.379
32	Tower	84.2	80.2	4.0	52.1	35.7	1280	0.109	22.9		0.379
33	Tower	83.3	79.4	3.9	55.4	38.1	1280	0.099	22.7		0.379
34	Tower	84.7	81.4	3.3	51.2	40.0	1280	0.109	21.9		0.379
	Avg.	84.3			54.0			0.098	22.4		

averaged 1.00 Sm^3/s and was fairly constant during the runs. The inlet makeup water temperature averaged 22°C and showed little variation.

The liquid flows were maintained at 0.38 l/s for the sieve tray tower tests and approximately 0.32 l/s for the venturi tests. There was difficulty in controlling the liquid flow to the venturi and consequently the flow rates show considerable variation ranging from a low of 0.29 l/s to a maximum of 0.35 l/s.

2.3.3 Scrubber Operating Problems

A. Inlet Gas Pressure--

As discussed in Section 1.2.3, the inlet gas pressure from the GKI facility was insufficient to operate the scrubber train. The system requires a positive internal pressure. Therefore, it was necessary to relocate the Roots blower to the gas inlet to boost the pressure. A knock-out drum was also constructed and installed to prevent solids (stones in pipe line) and excessive slugs of water from entering the blower.

B. Liquid Flows--

Control of the liquid flow to the venturi at flow rates greater than 0.32 l/s was erratic and, therefore, it was decided to maintain a maximum flow rate of 0.32 l/s.

C. Gas Leak--

A gas leak developed at the flange on the inlet valve requiring shutdown and repair.

D. Liquid Level Control--

The liquid discharge from the tower sump was controlled by a high/low liquid level controller activating the drain valve. Initially the range was too small resulting in continuous on-off operation. Increasing the high/low range resolved the problem.

2.3.4 Test Plan

The test plan is shown in Table 5. The primary objectives of the test plan were to:

TABLE 5. TEST PLAN FOR ALKALINE SCRUBBER

Run No.	Alkali	Conc gmoles/liter	Contactor
12	Ammonia	2.0	tower
13	"	"	venturi
14	"	0.05	tower
15	"	"	venturi
16	"	0.3	tower
17	"	"	venturi
18	NaOH	0.05	tower
19	"	"	venturi
20	"	0.012	tower
21	"	"	venturi
22	"	0.023	tower
24	"	"	venturi
25	KOH	0.05	tower
26	"	"	venturi
27	"	0.012	tower
28	"	"	venturi
29	"	0.023	tower
30	"	"	venturi
31	"	0.9	tower
32	"	1.8	tower
33	NaOH	1.25	tower
34	"	2.5	tower

1. Evaluate the comparative scrubbing efficiency of ammonium hydroxide, sodium hydroxide, and potassium hydroxide.

2. Evaluate the effect of concentration on H_2S/CO_2 selectivity for these alkaline scrubbing chemicals.

3. Evaluate the performance of the tower and venturi with regard to both removal efficiency and H_2S/CO_2 selectivity.

The test plan was not designed to evaluate variations in the liquid to gas ratio or other variations in the tower or venturi characteristics (i.e., variation in venturi throat diameter, variation in sieve tray perforations).

2.3.5 Operating Procedure

Due to the problems with the GKI plant and the gas analysis, it was necessary to compress the individual test periods into a relatively short time. Eighteen tests were required in a 60 hour test period allowing only two hours per run. The following procedure proved to be effective in meeting this brisk schedule.

The mix tank was prepared with the proper solution strength in accordance with the test plan shown in Table 5. Gas flow was maintained during the down periods. Therefore, it was only necessary to initiate liquid flow to the contactor to begin the run.

There were two essential timing factors to consider. The first factor concerned the capacity of the mix tank. As the plant was running on a once-through basis with dilute alkaline make-up at a rate of 0.38 l/s gpm, there was only a 40 minute maximum run time.

The second aspect of the timing requirements was due to the gas sampling procedure. The gas analysis system was evaluating total reduced sulfur (TRS) alternating every ten minutes from the scrubber outlet to the Stretford outlet. Therefore, it was necessary to start the test run precisely at the beginning of the Stretford measurement cycle. This would give TRS readings for the scrubber outlet at 10-20 minutes and 30-40 minutes into the cycle. The 10-20 minute readings typically did not indicate the steady state condition which meant that the 30-40 minute readings were critical.

As it was necessary to refill the make-up tank after each run, the timing to prepare for the next run was also essential. This procedure proved to be effective once the timing sequence was fine-tuned.

2.4 THEORY OF H_2S/CO_2 SELECTIVITY

The following discussion is a review of the past research in the use of alkaline chemicals to scrub H_2S in the presence of large CO_2 concentrations. This discussion is presented at this time in order to provide the reader with a background to evaluate the test results. A reader familiar with the theory of selective absorption may go directly to Section 2.5 for a discussion of the test results. He may also care to refer to Appendix B for the mathematical derivation of the scrubber model.

To briefly summarize, the absorption of H_2S by alkaline scrubbing must occur with adequate removal efficiency while limiting the amount of CO_2 absorption. The key factors that affect the relative absorption rate of H_2S over CO_2 are liquid alkaline concentration, contact time and presence of NH_3 in the gas. The theoretical analysis for the H_2S selective absortion provides both a basis for data correlation and a predictive model for evaluation of this scrubbing process at varying conditions.

2.4.1 Mass Transfer Rate

Absorption of a species from a gas to a liquid occurs by mass transfer first through a gas film to an interface and then through the liquid film to the bulk liquid (Danckwertz, 1970).

The absorption rate is determined by the equation:

$$N = K_g A \left(C_g^{o} - C_g^{i}\right) = \beta K_l A \left(C_l^{i} - C_l^{o}\right) \qquad (1)$$

where N = mass transfer rate, gmoles/hr

K_g = gas side coefficient, gmoles/hr - m^2

K_l = liquid film coefficient, moles/hr - m^2

C = concentration, gmoles/liter

subscript (l) = liquid
subscript (g) = gas
superscript (i) = interface
superscript (o) = bulk fluid
β = chemical reaction enhancement factor, unitless
A = surface area for mass transfer, m^2

The gas film coefficient is determined by the physical characteristics of the system (type of contactor, flow rates, physical properties, etc.) and is not affected by the chemical type or concentration of the scrubbing solution.

The rate of mass transfer of any chemical species in the liquid film is a product of the concentration difference, the mass transfer coefficient and the chemical enhancement factor for that species (which is usually expressed as a multiplier of the liquid film coefficient).

A key element in optimizing selectivity is the relative importance of the gas and liquid film coefficients. The liquid phase reaction of H_2S is instantaneous while the CO_2 absorption reaction is finite. Therefore, the absorption of H_2S is limited by the gas film resistance while the CO_2 absorption is liquid film controlled. Consequently, maximizing the gas film coefficient while minimizing the liquid film coefficient can significantly increase selectivity. This discussion is continued in Section 2.4.3.

The gas bulk concentration of the species is determined by the process conditions. The H_2S concentration is approximately 0.15 percent and the CO_2 is approximately 23 percent. The liquid interface concentration is determined from the gas concentration by the solubility and volatility of the species. These properties are both affected by temperature, ionic strength (concentration of ionic species) and other dissolved components. The chemical enhancement is determined by the chemical type and composition of the scrubber liquid.

A. Gas Concentration--

As one of the purposes of this program is to evaluate the selectivity of the alkali scrubbing solution for H_2S over CO_2 it is useful to look at the initial parameters*. The rate of absorption of a species is directly related to its concentration. Therefore, the ratio of concentrations for H_2S and CO_2 indicates the nature of the problem. For the typical gas at GKI with 1500 ppm H_2S (0.15%) and 23% CO_2, the relative absorption rate or concentration ratio CO_2/H_2O is 23/0.15 = 150. This indicates that disregarding selectivity the absorption rate of H_2S will be less than one hundred and fiftieth that of CO_2.

B. Solubility--

The solubility of the species in the liquid determines the interface concentration.

There is a natural selectivity of this system for H_2S based on the relative solubility of CO_2 and H_2S. Essentially, the higher solubility of H_2S makes it easier to absorb than CO_2 and, therefore, increases the selectivity. This physical selectivity, δ, is defined as

$$\delta = \frac{\text{solubility } CO_2 \text{x gaseous concentration } CO_2}{\text{solubility } H_2S \text{ x gaseous concentration } H_2S} \quad (2)$$

At 25°C the solubility in water of $H_2S = 1.8 \times 10^{-3}$ mole fraction and $CO_2 = 0.6 \times 10^{-3}$ mole fraction. Therefore the physical selectivity is

$$\delta = (0.6 \times 23\%)\ CO_2/(1.8 \times 0.15\%)\ H_2S = 50$$

The physical selectivity (i.e., due to solubility) predicts a threefold increase in absorption of H_2S over that of CO_2 based only on the concentration conditions and results in a decrease from 150:1 to 50:1 for the CO_2/H_2S absorption ratio.

C. Chemical Enhancement--

When the gas species being absorbed reacts with the scrubbing solution, the absortion rate is increased due to the elimination of the species. The chemical enhancement factor is determined by: (1) the rate of reaction,

---

*If it were not for the selectivity of H_2S over CO_2 it would be impossible to use alkali solution to remove H_2S from the GKI retort gas.

(2) the concentration of the species, and (3) the diffusivity (ease at which the species dissolved in the gas moves through liquid) of the species. The chemical enhancement factor β, is defined as:

$$\beta = K_{xa} / K^*_{xa}$$

where K_{xa} = actual absorption coefficient
K^*_{xa} = absorption coefficient without reaction

The relative chemical enhancement, σ, is defined as the ratio of chemical enhancement for each species, i.e.

$$\sigma = \beta\ (H_2S)/\beta\ (CO_2)$$

Note: This term is sometimes referred to in the literature as selectivity. The terminology, relative enhancement, is used in this report to distinguish this item from the selectivity used in this report as defined in Section 2.1 (ratio of removal efficiencies H_2S to CO_2).

It is the relative liquid phase reaction rates and reaction mechanisms that account for the highly selective H_2S absorption required for the alkaline scrubbing process to be economically feasible. This chemistry is presented next.

2.4.2 Chemistry

A. General Kinetics--

For the absorption reaction of H_2S in alkali solution with no CO_2 present the initial reaction equation is:

$$H_2S + OH^- \rightarrow HS^- + H_2O \qquad (5)$$

and the reaction rate defined as:

$$r_{H_2S} = -k_{H_2S}\ [OH^-]\ [H_2S] \qquad (6)$$

where r = reaction rate
k = rate constant
$[OH^-]$ = hydroxyl ion concentration - bulk
$[H_2S]$ = H_2S concentration - interface

The system is also characterized by the chemical equilibrium constant

$$K_1 = \frac{[HS^-]}{[H_2S]\,[OH^-]} \tag{7}$$

Note: The second dissociation to S^{-2} ($HS^- + OH^- \rightarrow S^{-2} + H_2O$) is relatively small and can be neglected.

The concentration profile for this system is presented in Figure 11 which shows the reactant concentration variation in the liquid film.

This model assumes a single reaction plane where the reaction of H_2S with OH^- takes place.

The above rate and equilibrium equations can be combined to evaluate the relative rate of chemical absorption to that of physical absorption, i.e. chemical enhancement. The reader is referred to Astarita, 1964 and Danckwertz, 1970 for a complete description of this derivation. The resulting equation for chemical enhancement is:

$$\beta = 1 + \frac{[OH^-]}{[H_2S]} \tag{8}$$

where: $[OH^-]$ = hydroxyl ion concentraton in the bulk liquid, gmoles/liter
$[H_2S]$ = H_2S concentration at the interface, gmoles/liter

This approach is based on the single-reaction-plane concentration profile as shown in Figure 11. Experimental results reported in the literature for the alkaline scrubbing of CO_2 and H_2S are shown in Figure 12. The one-reaction-plane model represents the lower boundary for the data, i.e., predicting chemical enhancement lower than realized in the experimental investigation (Astarita, 1967).

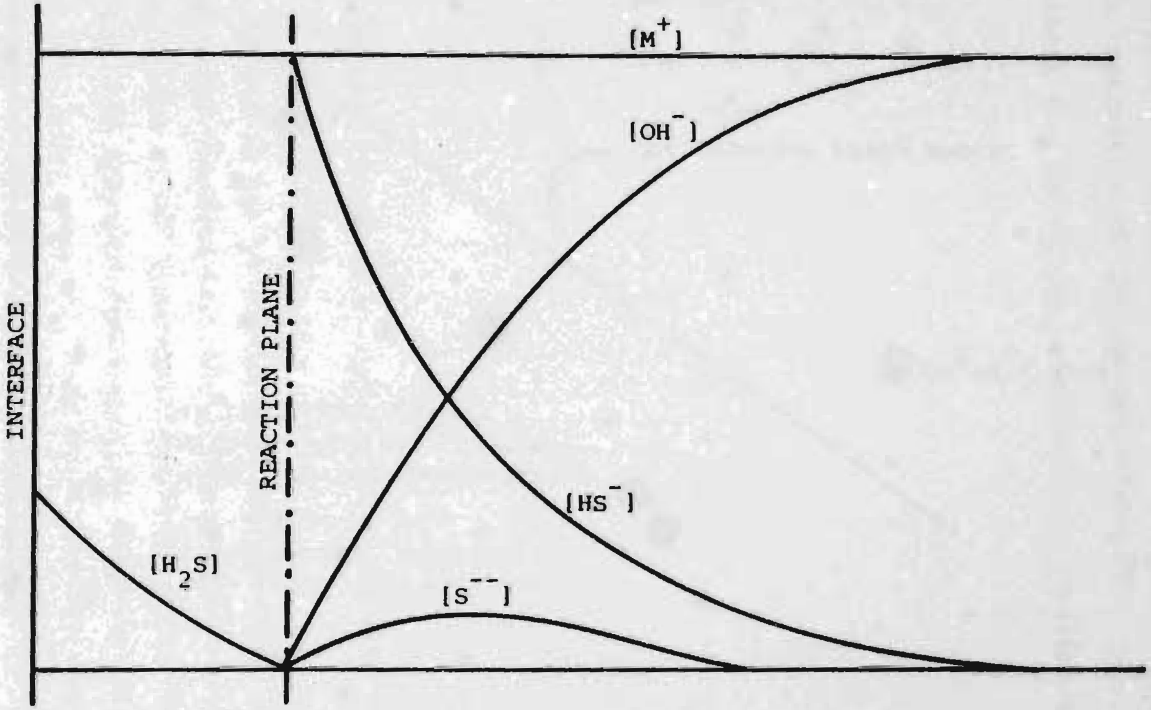

Figure 11. Single-reaction-plane concentration profile

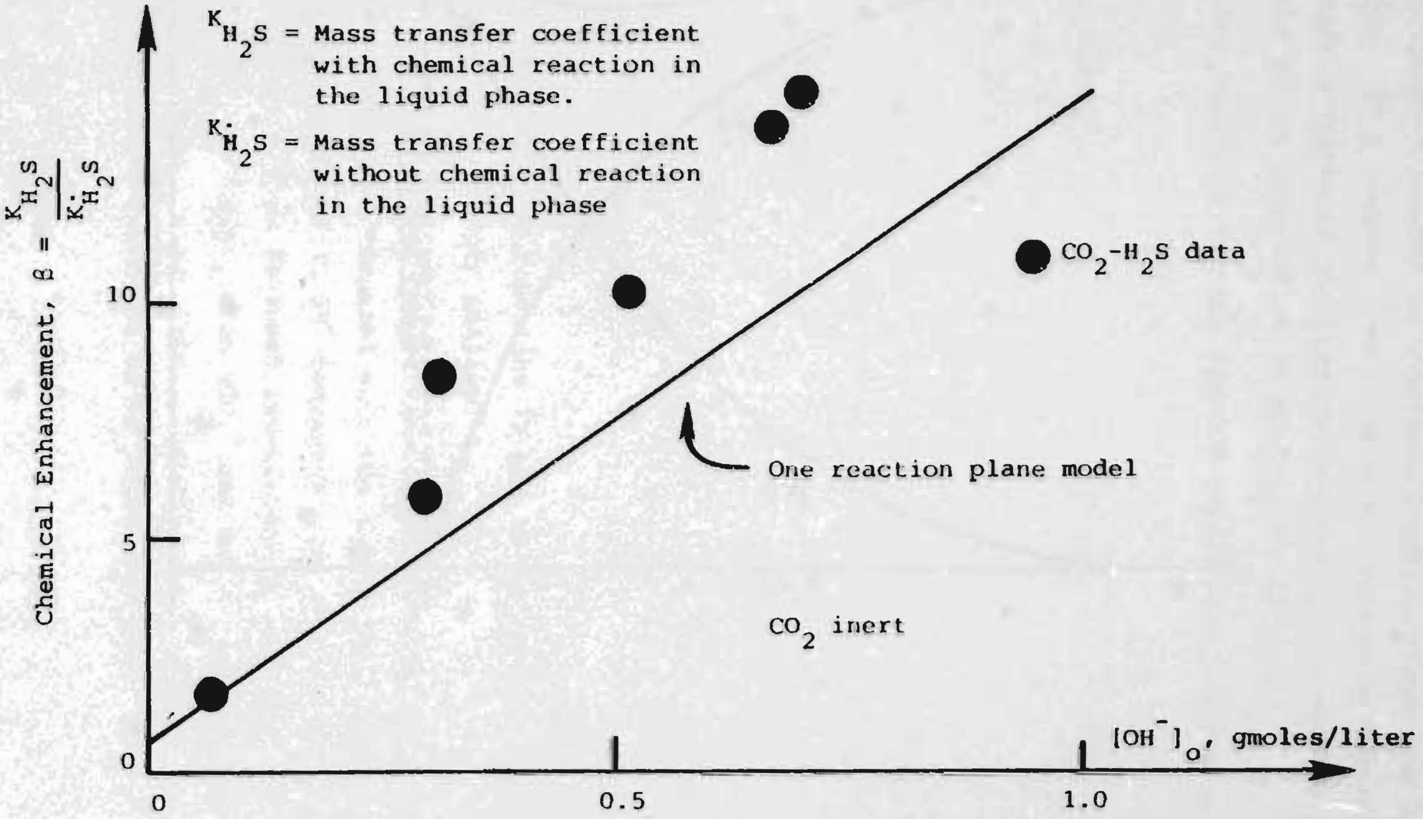

Figure 12. Chemical enhancement factor for H_2S single reaction plane. (Astarita, 1967)

B. Two Reaction Plane--

The above analysis assumed no interrelationship between the H_2S and other gases present. In a scrubber involving the simultaneous absorption of H_2S and CO_2 in aqueous hydroxide the prediction of chemical behavior is considered complicated by the interaction of the various reactants.

The complete chemistry for the H_2S-CO_2 absorption in alkaline solution is as follows:

$$CO_2 + OH^- \rightarrow HCO_3^- \tag{9}$$

$$H_2S + OH^- \rightarrow HS^- + H_2O \tag{10}$$

$$HCO_3^- + OH^- \rightarrow CO_3^{-2} + H_2O \tag{11}$$

$$HS^- + OH^- \rightarrow S^{-2} + H_2O \tag{12}$$

$$H_2S + CO_3^{-2} \rightarrow HS^- + HCO_3^- \tag{13}$$

$$HS^- + CO_3^{-2} \rightarrow S^{-2} + HCO_3^- \tag{14}$$

To simplify the analysis Reactions 12 and 14 can be neglected as the equilibrium values for S^{-2} are very small.

Reactions 9, 10, 11 and 12 can be considered instantaneous, regardless of reactant concentrations when compared with the diffusional process. Reaction 9 is only instantaneous at OH^- concentrations greater than 0.01 gmole/liter (where Reaction 9 is followed immediately by Reaction 11). When the OH^- concentration is low, i.e., when HCO_3^- and CO_3^{-2} coexist, Reaction 9 is too slow to affect the absorption rate. Therefore, Reactions 9 and 11 can be combined and the remaining reactions to be considered are:

$$CO_2 + 2OH^- \rightarrow CO_3^{-2} + H_2O \tag{15}$$

$$H_2S + OH^- \rightarrow HS^- + H_2O \tag{10}$$

$$H_2S + CO_3^{-2} \rightarrow HS^- + HO_3^- \qquad (13)$$

$$HCO_3^- + OH^- \rightarrow CO_3^{-2} + H_2O \qquad (11)$$

These reactions can all be considered as instantaneous and irreversible. Therefore, none of the couples of reactants involved may coexist in appreciable concentration levels at any point of the liquid.

The concentration profiles resulting from these reactions are shown in Figure 13. The primary reaction plane is the reaction interface for Reaction 9, the reaction of CO_2 with OH^-. Between the primary reaction plane and the interface the concentration of OH^- must approach zero.

The CO_3^{-2} ions are formed at the primary reaction plane. But since CO_3^{-2} can not coexist with H_2S, there can be no H_2S in the vicinity of the primary reaction plane. Therefore, a secondary reaction plane located between the interface and the primary reaction plane exists where the reaction of H_2S with CO_3^{-2} takes place.

The CO_2 is physically absorbed and diffuses from the surface to the primary reaction plane where it reacts with OH^-. The CO_3^{-2} ions formed diffuse toward the bulk of the liquid and towards the interface. The H_2S, physically adsorbed, diffuses to the secondary reaction plane where it reacts with the CO_3^{-2} to form HS^-.

The CO_3^{-2} and HCO_3^- ions loop back and forth in Zone II and Reaction 10 never actually takes place. However, the net results of Reaction 13 (which takes place at the secondary reaction plane) and Reaction 9 (which takes place at the primary reaction zone) is Reaction 10.

The reader is referred to Astarita, 1965 for a detailed description of the equations developed to calculate the plane depth and relative chemical enchancement factor.

Application of the penetration theory to the two reaction plane model has been investigated (Onda, 1972). Figures 14 and 15 show the chemical enhancement factors for H_2S and CO_2 as a function of OH^- concentration. The H_2S data shows good correlation with all three models, but a significantly better data fit with the unsteady-state penetration theory than the two film-

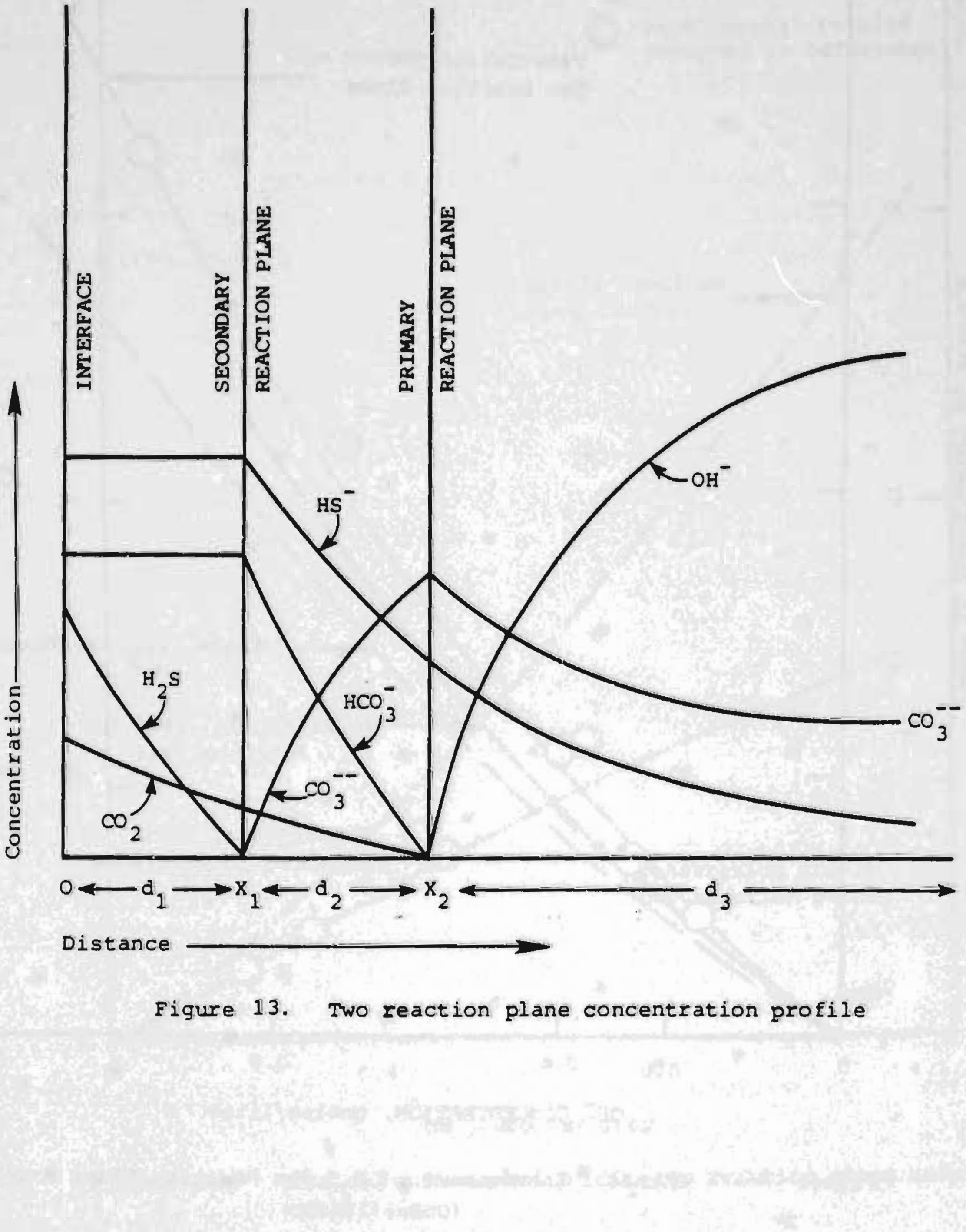

Figure 13. Two reaction plane concentration profile

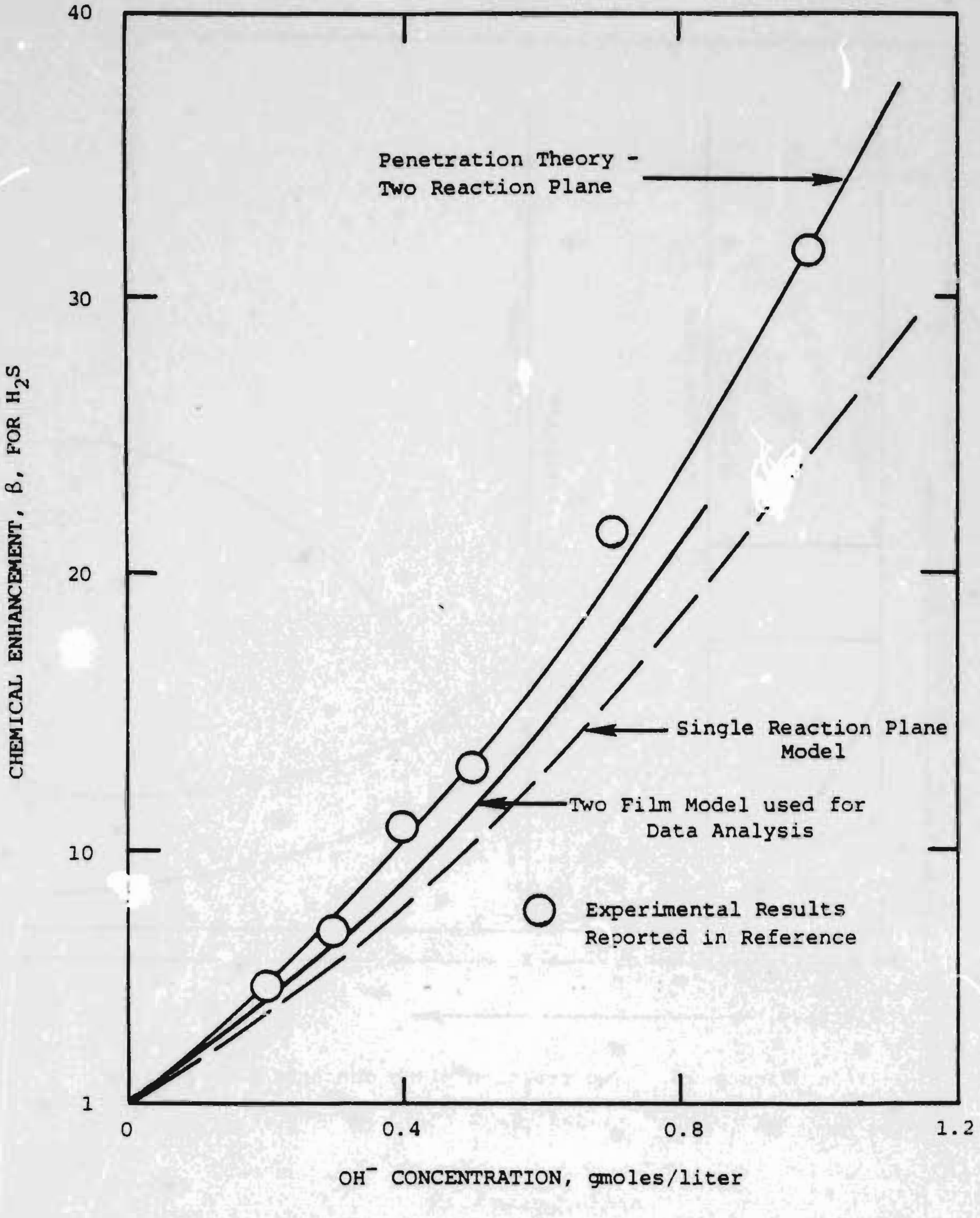

Figure 14. Chemical Enhancement of H_2S Two Reaction Plane Model (Onda, 1972)

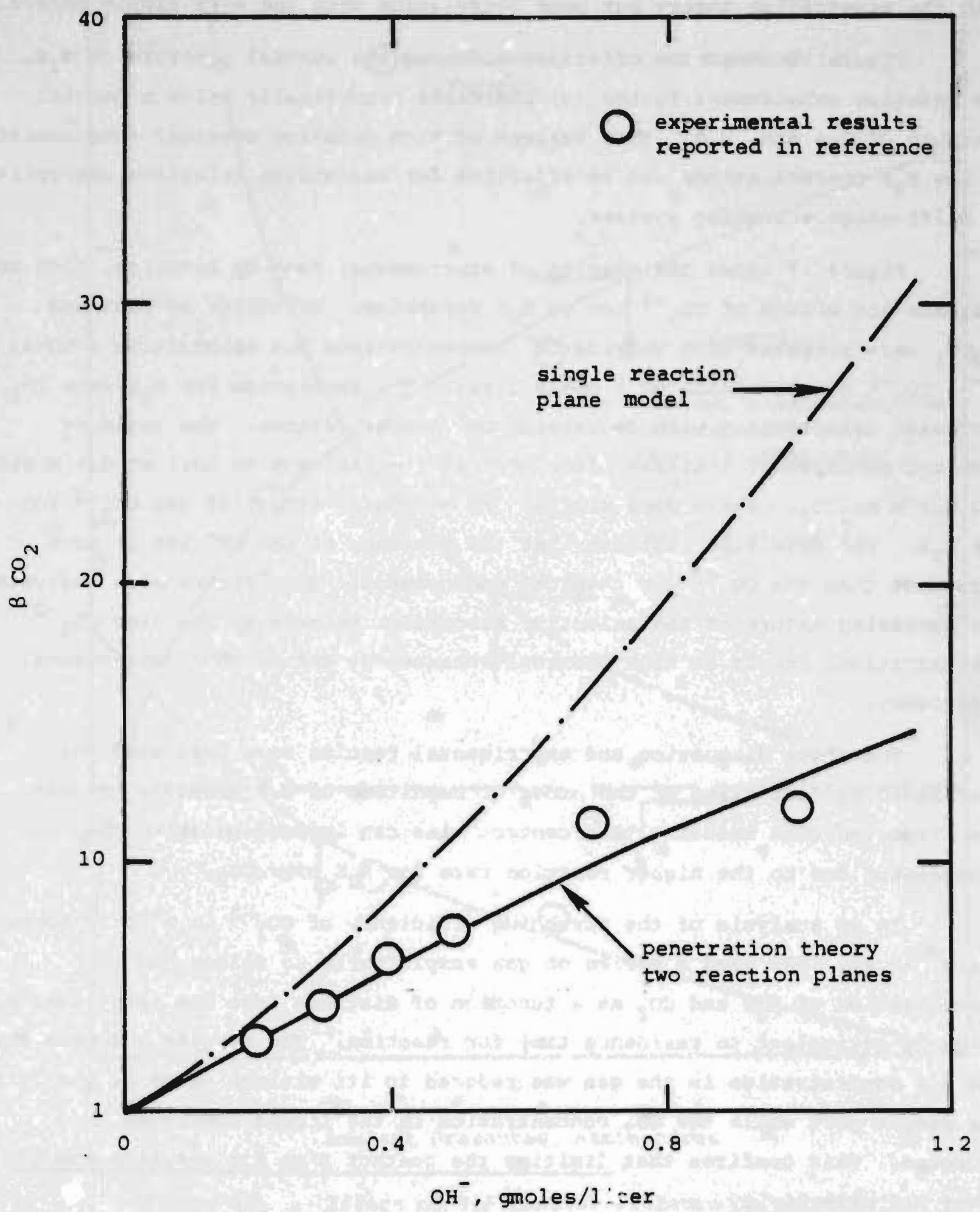

Figure 15. Chemical enhancement of CO_2 two reaction plane model (ONDA, 1972)

theory models. The data for the CO_2 enhancement factor shows good correlation with the penetration theory but poor correlation with the more simple models.

Figure 16 shows the effect of reducing the partial pressure of H_2S. The relative enhancement factor (σ) increases dramatically below a partial pressure of 0.4 atm. H_2S. This feature of high relative chemical enhancement at low H_2S concentrations can be effective for maximizing selective absorption in multi-stage scrubbing systems.

Figure 17 shows the results of experimental runs by Astarita, 1965 to evaluate the effect of CO_3^{-2} ion on H_2S scrubbing. Solutions of NaOH and Na_2CO_3 were prepared with varying OH^- concentrations but maintaining a total $OH^- + CO_3^{-2}$ concentration of 1 gmole/liter. The absorption for H_2S over CO_2 increases dramatically with decreasing OH^- concentrations. The ratio of chemical enhancement increases from 10:1 at 1 molar NaOH to 50:1 at 0.1 M NaOH and 0.9 M Na_2CO_3. These data confirm the scrubbing effect of the CO_3^{-2} ion for H_2S. The data also indicate that the presence of the OH^- ion is more important than the CO_3^{-2} for chemical enhancement. This figure also indicates the competing nature of the selective absorption process as the high CO_3^{-2} concentrations result in high chemical enhancement ratios but lower removal efficiency.

The above discussion and experimental results were evaluated for gas/liquid contact times of the order of magnitude of 0.1 seconds. It has been reported that reducing this contact time can improve relative chemical enhancement due to the higher reaction rate for H_2S over CO_2.

In an analysis of the scrubbing efficiency of CO_3^{-2} in a spray tower, Aiken, et al, 1983 used a series of gas sample ports to follow the concentration of H_2S and CO_2 as a function of distance from the spray nozzle, which is equivalent to residence time for reaction. The results indicate that the H_2S concentration in the gas was reduced to its minimum value at the first gas sample port while the CO_2 concentration in the liquid continued to increase. This confirms that limiting the contact time for reaction should favor H_2S selectivity.

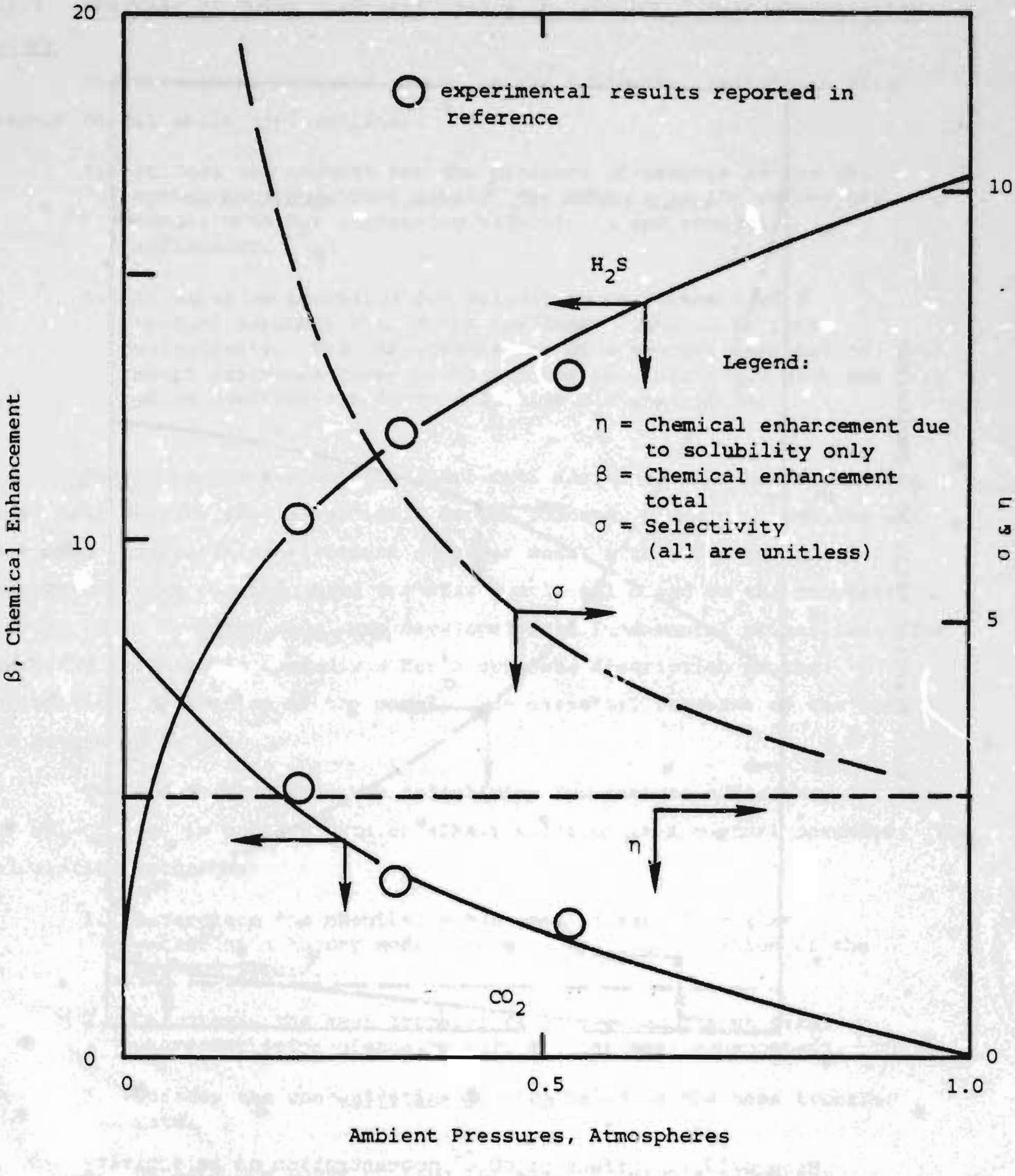

Figure 16. Effect of H_2S partial pressure on selectivity. (Onda, 1972)

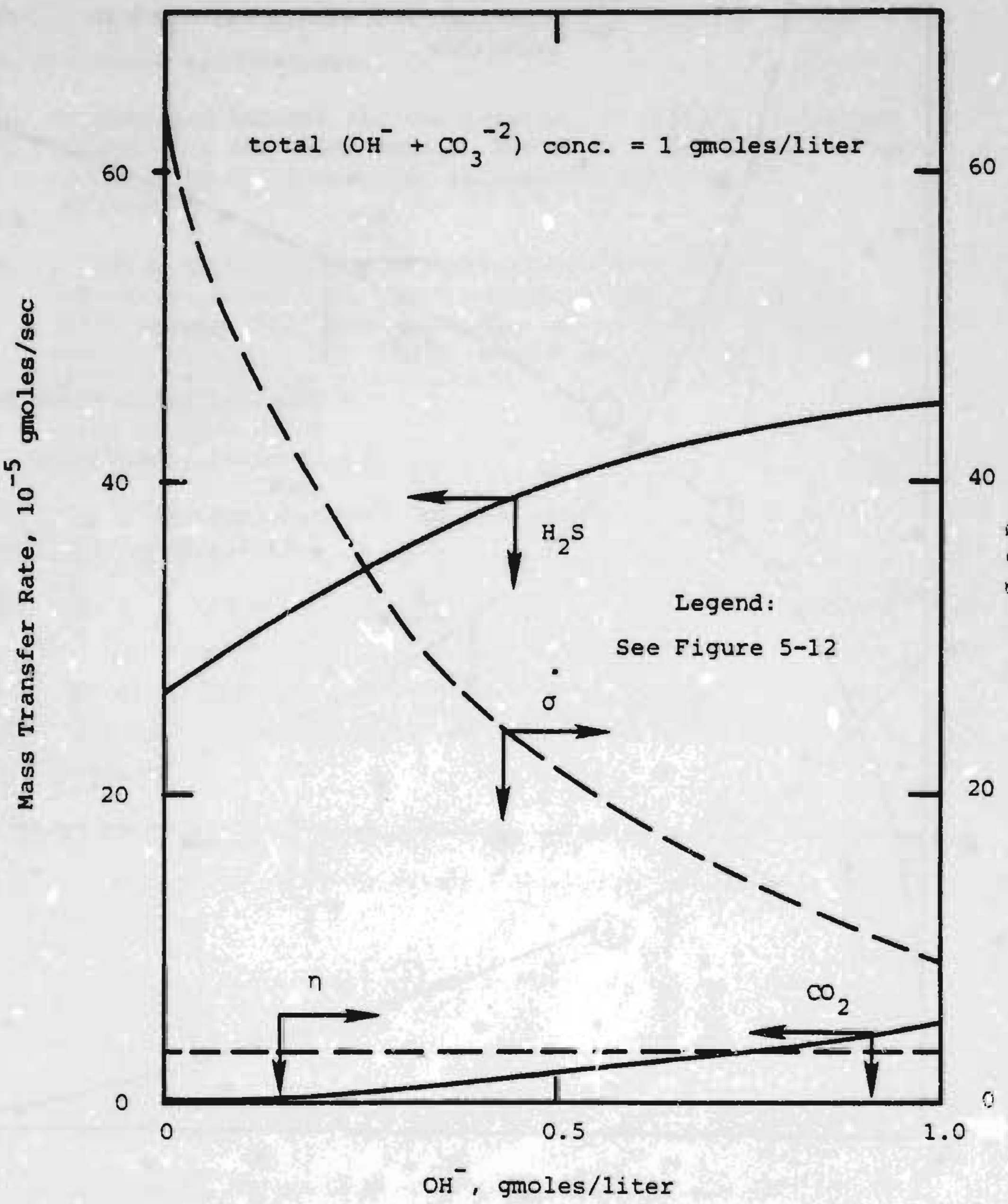

Figure 17. Effect of CO_3^{-2} concentration on selectivity (Onda, 1972)

2.4.3 Analysis of Three Component System (H_2S-NH_3-CO_2) Using Penetration Theory

The literature reviewed above has the following limitations with respect to oil shale applications:

1. It does not account for the presence of ammonia in the gas acting as a scrubbing agent. The ammonia in the retort gas reacts with H_2S increasing selectivity and removal efficiency.

2. It makes no provision for estimating performance of a venturi scrubber with short residence times to maximize selectivity. The characteristics of a venturi scrubber of short residence times 0.003 seconds and relatively high gas phase coefficients favor selective H_2S absorption.

Therefore, to evaluate the test data and to be able to extrapolate these test results into a realistic design concept, a computer program was developed incorporating a venturi scrubber model with three component absorption, with reaction mass transfer model, all based on the penetration theory. This computer model was developed from fundamental principles. The reader is referred to Appendix B for a complete description of the mathematical derivation of the model. The essential features of the system are presented below.

The model calculates the selectivity and removal efficiency for the H_2S NH_3-CO_2 gas in contact with an alkali solution in a venturi scrubber. The calculation technique:

1. Determines the chemical enhancement factor from the penetration theory model based on the concentration of the gas and liquid.

2. Calculates the mass transfer rate based on the physical characteristics of the venturi and chemical enhancement.

3. Updates the concentration profile based on the mass transfer rate.

4. Repeats the above routine for small intervals along the length of the venturi.

A. Penetration theory for mass transfer and reaction of H_2S-CO_2-NH_3--

The presence of NH_3 in the retort gas significantly affects removal efficiency and selectivity for H_2S.

The gas reaction is:

$$H_2S + NH_3 \rightarrow HS^- + NH_4^+ \qquad (16)$$

Three cases must be considered depending on the initial concentrations of NH_3 and H_2S

I. $NH_3 > H_2S$

II. $NH_3 = H_2S$

III. $NH_3 < H_2S$

The species which is in lesser amount (NH_3 or H_2S) will be consumed at the interface (Reaction 16) and will not exist inside the liquid film. Its absorption rate will be entirely controlled by the gas film; liquid film resistance to mass transfer will be effectively zero. Its interfacial concentration can be set to zero for computing the rate of transfer across the gas film. The species in excess will diffuse into the liquid phase and react. Carbon dioxide, which is unaffected by the presence of NH_3, diffuses into the liquid and reacts according to the equation:

$$CO_2 + 2OH^- \rightarrow CO_3^{-2} + H_2O \qquad (13)$$

This reaction is also instantaneous and irreversible. There will be a reaction plane at which CO_2 and OH^- are consumed instantaneously.

<u>Case I. $[NH_3]_i > [H_2S]_i$</u>

H_2S reacts at the interface; the excess NH_3 (dissolved) is consumed by the instantaneous and irreversible reaction,

$$NH_3 + H^+ \rightarrow NH_4^+ \qquad (17)$$

The species to be considered are NH_4^+, HS^-, CO_2, CO_3^{-2}, and OH^-. The two species which react instantaneously and irreversibly at a plane are CO_2 and OH^- according to Reaction 13) above.

Reaction between CO_2 and ammonia (or NH_4^+) can be neglected because of unfavorable equilibrium constants ($K_{eq} \sim 10^{-4}$). All the other species undergo physical diffusion only. The enhancement factor for H_2S and NH_3 in the liquid film is infinite, i.e., absorption of H_2S and NH_3 is entirely controlled by gas film resistance. The interfacial concentration of both H_2S and NH_3 can be set equal to zero to calculate the rate of absorption across the gas film.

Solving the partial differential equations for diffusion to determine the chemical enhancement for CO_2 results

$$E_A \equiv \text{instantaneous enhancement factor} = \frac{1}{\text{erf}^* \left\{\frac{\alpha}{D_A}\right\}^{1/2}}$$

where D is the diffusion coefficient (cm/sec^2), α is determined by the equation

$$1 - \text{erf} \left\{\frac{\alpha}{D_C}\right\}^{1/2} = \frac{Co}{A_i} \sqrt{\frac{D_c}{D_A}} \; \text{erf} \left\{\frac{\alpha}{D_A}\right\}^{1/2} \; \exp \left\{\frac{\alpha}{D_A} - \frac{\alpha}{D_C}\right\}$$

and subscripts $A = CO_2$ and $C = OH^-$

These equations are shown here merely to illustrate the form of the solution. In this form, it is not possible to obtain a physical sense of the process. Only by a parametric study using these relationships can the process be understood. By comparing results predicted by this model with experimental measurements, such as performed in this test program, the validity of these abstract relationships can be evaluated.

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* erf = error function, a standard mathematical function

Case II $[NH_3]_i = [H_2S]_i$

This case is very similar to Case I. Both H_2S and NH_3 are consumed at the interface by the Reaction 12.

$$H_2S + NH_3 \rightarrow HS^- + NH_4^+ \tag{16}$$

Reaction 14 does not occur since there is no excess NH_3. Reaction 13 does occur, however. The concentration profile and enhancement factor for CO_2 remain the same as in Case I except that

$$[NH_4^+]_i = [HS^-]_i$$

Case III. $[H_2S]_i > [NH_3]_i$

This is the most complex and challenging case mathematically. NH_3 is converted to NH_4^+ at the interface by the reaction

$$H_2S + NH_3 \rightarrow HS^- + NH_4^+ \tag{16}$$

The excess H_2S along with CO_2 diffuses into the liquid and reacts with OH^-. The mathematical modeling expressions for this case are presented in Appendix B and as stated earlier are abstract and difficult to relate directly to physical phenomena. Basically, the approach taken is to use the two reaction plane theory discussed in Section 2.4.2.B and add penetration theory expressions which provide for a time variation of the concentration of each of the chemical species. This model can account for a process where the gas/liquid contact time is of the order of milliseconds such as in a venturi. It can also treat dimensional aspects of the system such as venturi geometry and liquid droplet size which can assist a designer in optimizing the venturi contactor.

B. Venturi Scrubber for Multicomponent Mass Transfer with Reaction--

Once the chemical enhancement factors have been determined for a specific concentration profile, the mass transfer rate must be determined by a mass balance.

The mass balance equations provide for the relationship between liquid and gas phase concentrations as material is transferred from the gas to the liquid phase. The rate of mass transfer is determined from the characteristics of the contactor. The gas-side mass transfer coefficient, k_G, is computed with consideration to the droplet size and varying relative velocity. The liquid-side mass transfer coefficient for physical absorption is taken from the penetration theory.

C. General Results--

The following discussion presents the results of a typical analysis. The application of the model to the test data is presented in Section 2-5.

Figure 18 shows the removal efficiency of H_2S and NH_3 versus distance down venturi throat; Figure 19 shows selectivity, S, defined as

$$S = \frac{\%\ \text{removal}\ H_2S}{\%\ \text{removal}\ CO_2}$$

versus length of venturi. Figure 18 indicates that 60 percent of the H_2S and 70 percent of the NH_3 is removed in a single pass through the venturi. Only two percent of the CO_2 is removed (not shown on the figure). Most H_2S removal occurs early in the throat. The corresponding selectivity shown in Figure 19 indicates that a maximum in the selectivity is likely at some intermediate venturi length. This agrees with the results of Hsieh and Aiken (1984) and can be explained by the notion that up to and including the region of the peak, H_2S is gas film controlled while CO_2 is liquid film controlled. The gas film coefficient is high for short contact time but decreases as the contact time increases. This is because the liquid droplets accelerate and the relative velocity between the gas and the droplets decreases while the liquid film coefficient does not decrease as rapidly.

Figure 20 shows the dependency of the selectivity on reactant concentration. The selectivity is seen to decrease substantially with increase in OH^- concentration. The CO_2 reaction is aided more by increased OH^- concentration than the H_2S reaction.

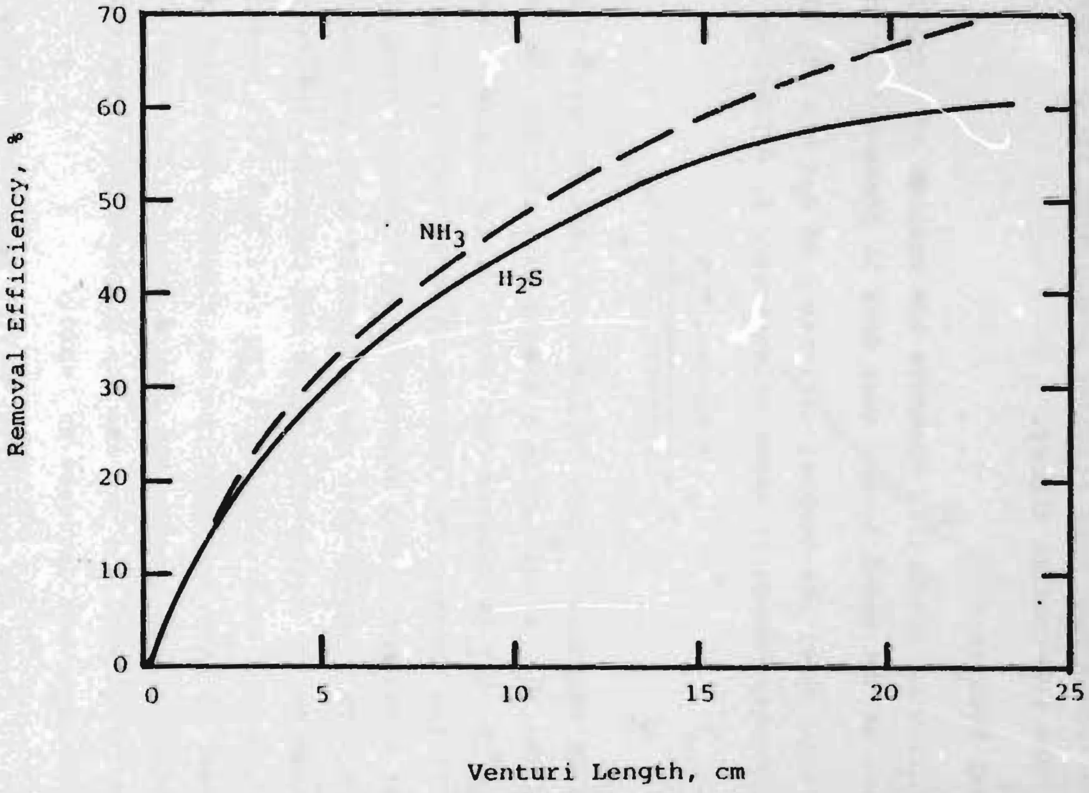

Figure 18. Variation of H_2S and NH_3 Removal Efficiency with Venturi Length[2] (Appendix B)

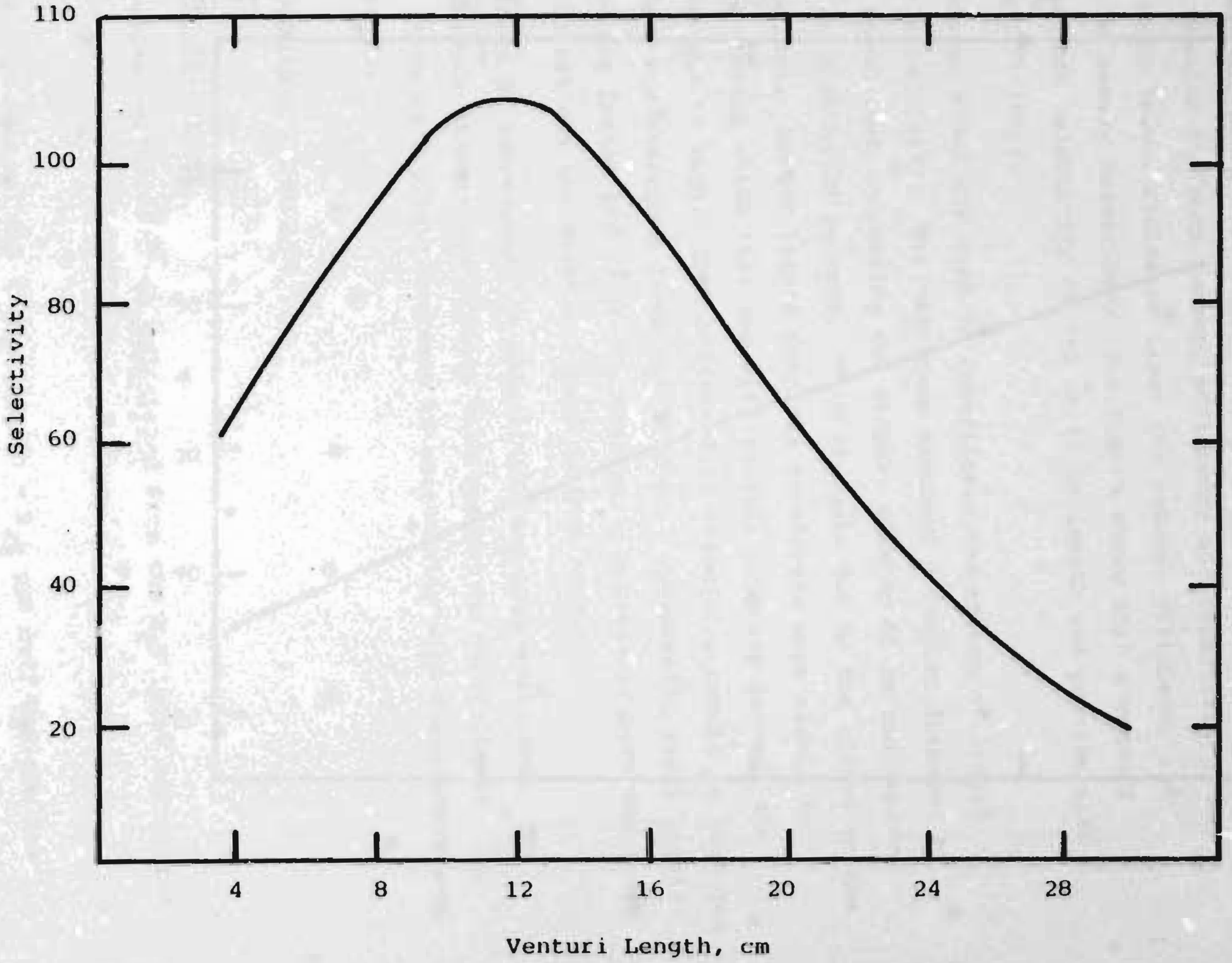

Figure 19. Selectivity as a function of residence time or venturi length (Appendix B)

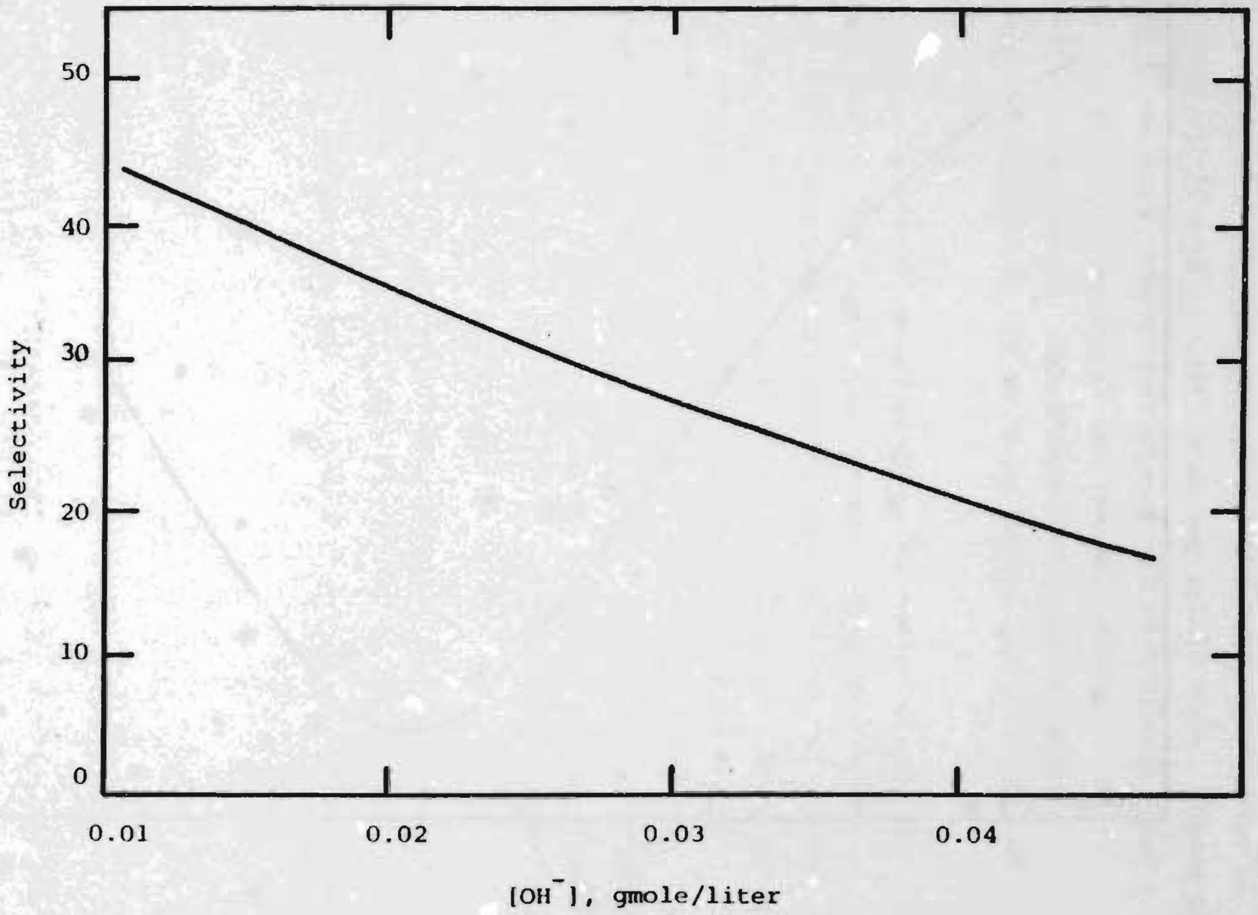

Figure 20. Effect of initial hydroxide concentration on selectivity. (Appendix B)

As discussed above, the required design for the venturi scrubber is based on the trade off between removal efficiency and selectivity. Figure 21 shows the model results for both removal efficiency and selectivity. For a given venturi length (i.e., residence time) the removal efficiency and selectivity can be easily determined. The figure shows that a venturi designed for the peak selectivity of 110 at 12 cm length can provide a 50 percent removal efficiency.

The computer model was used to investigate the effect of liquid droplet size on selectivity. The base case assessed a droplet diameter of 30 μm. It was found that increasing the droplet size to 60 μm can improve selectivity by as much as 20 percent. This is again due to the effect on the gas film coefficient. Larger liquid droplets accelerate more slowly to maximum velocity during which time the differential velocity between the droplets and the gas is high. High differential velocities result in high gas film coefficients and therefore favor H_2S removal. Conversely, small liquid droplets accelerate faster and favor CO_2 absorption because of both the lower gas film coefficient and the greater liquid surface area.

The effect of temperature on selectivity was also evaluated. The model only considers temperature effects with respect to vapor-liquid equilibrium. There is a slight increase in selectivity with temperature as shown in Figure 22.

2.5 DATA ANALYSIS TECHNIQUES

2.5.1 Removal Efficiency

The removal efficiency was calculated from the H_2S inlet and outlet concentrations as

$$\eta\ (H_2S) = \%\ \text{removal}\ H_2S = (H_2S\ \text{ppm in} - H_2S\ \text{ppm out})/H_2S\ \text{ppm in}$$

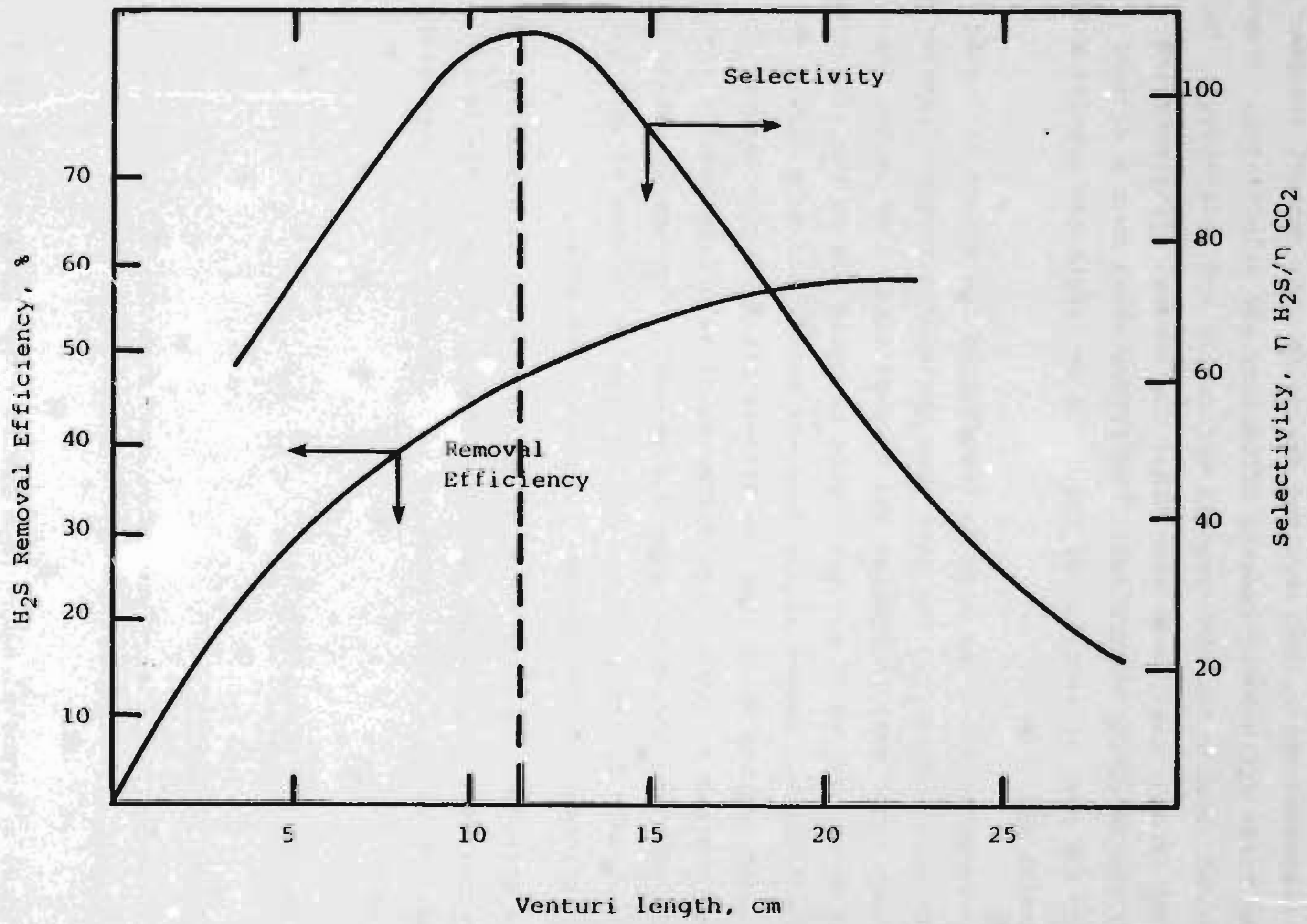

Figure 21. Removal Efficiency and Selectivity Variation with Venturi Length (Appendix B)

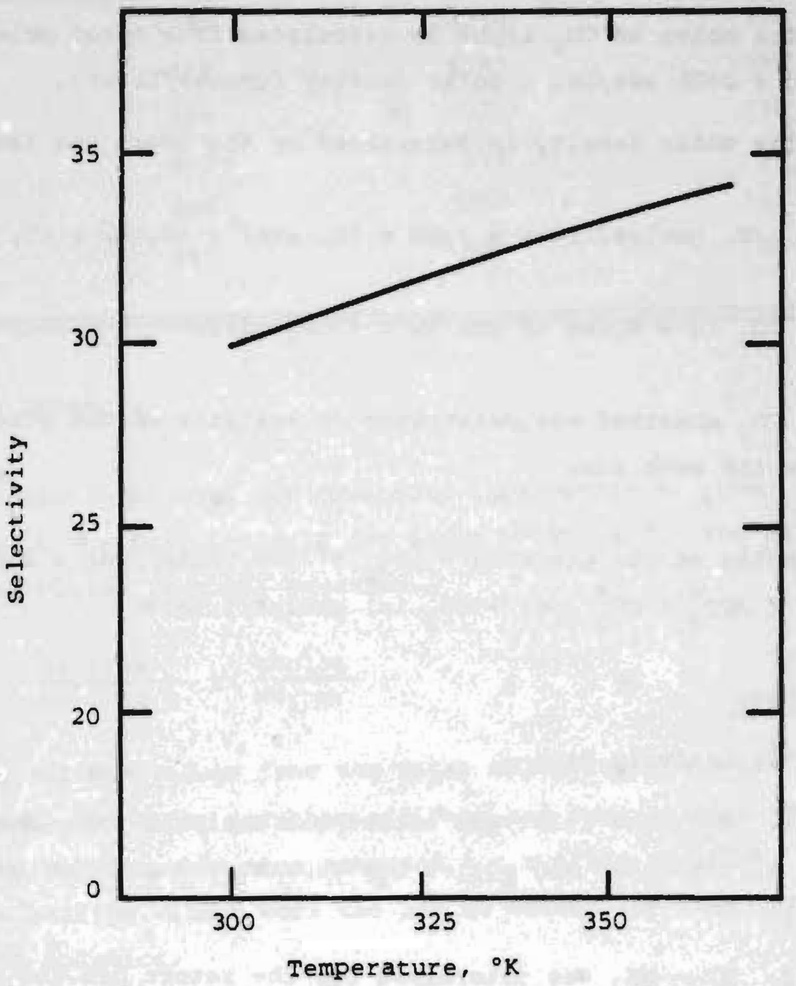

Figure 22. Effect of temperature on selectivity. (Appendix B)

2.5.2 Selectivity

Selectivity is defined as $S = \eta\ (H_2S)/\eta\ (CO_2)$ and $\eta\ (CO_2)$ = % removal CO_2 = moles of CO_2 absorbed/moles of CO_2 in the retort gas.

The moles of CO_2 input is calculated from total moles in = flow, liter/sec x 3600 sec/hr. x molar density (gmoles/liter).

The molar density is determined by the ideal gas law,

$$n/V, \text{ gmoles/liter} = P/RT = (P, \text{atm}) / (0.082 \times (T, °C + 273).$$

Moles of CO_2 in = moles of gas in x % CO_2 (0.23)

Moles of CO_2 absorbed was determined by analysis of the scrubber water discharge for each run.

$$\text{Moles of } CO_2 \text{ absorbed} = \text{liquid flow, liter/sec} \times 3600 \text{ sec/hr} \times [(HCO_3^- + CO_3^= \text{ out} - CO_3^= \text{ in}) \text{ gmoles/liter}]$$

2.5.3 Data

A. Gas Analysis Data--

1. H_2S--The inlet and outlet gas analysis technique is described in Appendix A. The inlet and outlet H_2S concentrations were used for the data analysis.

2. NH_3--NH_3 was determined for the retort gas and scrubber gas effluent. The results are shown in Table 6. The tests with high NH_4OH concentration showed considerable removal of the NH_3 resulting in large increases in the exit gas composition. At the low NH_4OH concentration, the NH_3 stripping was significantly less with the exit gas concentration increasing by 30-120 percent.

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TABLE 6. NH_3 CONCENTRATION IN GAS STREAM

Run	NH_4OH gmoles/liter	Inlet NH_3 ppm	Outlet NH_3 ppm	Increase, % NH_3
12	2	1190	24256	1938
13	2	414	6787	1539
14	0.049	611	1332	118
15	0.049	442	575	30
16	0.29	464	3007	548
17	0.29	461	947	105

B. Water Analysis Data--

The water analysis techniques are described in Appendix A. The pertinent results used in the data analysis are shown in Table 7. The molar concentrations were calculated from the equation.

$$\text{gmoles/liter} = \frac{\text{mg/liter}}{1000\ \text{mg/g}} \times \frac{\text{gmoles}}{\text{MW, g}}$$

Table 7 also shows the sulfate values from the water analysis. No appreciable sulfate was found and, in fact, the scrubber effluent had less sulfate than the make-up water. The samples were also measured for sulfite concentration. However, the sulfite values were too low to offset the interference from the sulfide ion in solution.

2.6 RESULTS

2.6.1 Removal Efficiency

The removal efficiency results from the test program are presented in Table 8 and Figures 23, 24, and 25. There is some question as to the correct $[OH^-]$ concentration to use when evaluating the data for ammonia. Ammonia is a weak base with the following reaction

$$NH_3 + H_2O \rightleftarrows NH_4 + OH^-$$

TABLE 7. WATER ANALYSIS DATA

Run No.	Sulfide Mg/l	Ammonia Mg/l	Carbonate mg/l*	Bicarbonate mg/l*	Hydroxide mg/l	Sulfate mg/l
12	670	20,000	19,000	<1	11,000	160
13	800	1,200	14,000	<1	10,000	33
14	400	1,800	4,100	<1	34	61
15	400	1,200	2,200	<1	200	53
16	490	7,300	6,200	<1	1,700	66
17	520	4,300	2,900	<1	1,600	38
18	400	250	1,100	3,200	<1	63
19	420	180	1,800	370	<1	75
20	280	340	600	1,600	<1	100
21	310	260	840	850	<1	110
22	290	260	600	2,000	<1	110
24	310	230	840	980	<1	120
25	660	280	1,300	2,600	<1	110
26	290	1,700	3,000	4,000	<1	100
27	250	370	960	1,500	<1	110
28	190	250	840	980	<1	110
29	300	290	960	1,600	<1	100
30	310	220	1,600	490	<1	110
Water	<1	1	26	250		230

* As $CaCO_3$, MW = 100

TABLE 8. H_2S REMOVAL EFFICIENCY (E) FOR SCRUBBER TESTS

Run No.	H_2S, ppm in	H_2S, ppm out	ΔH_2S, ppm	E, %	Alkali	Contactor	OH^- Concentration gmoles/liter
12	1780	128	1657	93	NH_4OH	tower	2.0
13	"	595	1185	67		venturi	2.0
14	"	645	1135	64		tower	0.049
15	"	704	1076	60		venturi	0.049
16	"	167	1613	91		tower	0.29
17	"	683	1097	62		venturi	0.29
18	1280	218	1062	83	NaOH	tower	0.045
19	"	384	896	70		venturi	0.045
20	"	614	666	53		tower	0.012
21	"	609	671	52		venturi	0.012
22	"	588	612	54		tower	0.023
24	"	666	614	48		venturi	0.023
25	1280	154	1126	88	KOH	tower	0.046
26	"	372	908	71		venturi	0.046
27	"	583	697	54		tower	0.012
28	"	596	697	53		venturi	0.012
29	"	519	761	59		tower	0.023
30	"	660	620	48		venturi	0.023
31	998	60	938	94	KOH	tower	0.89
32	1048	83	965	92	KOH	tower	1.79
33	1065	75	990	93	NaOH	tower	1.25
34	1003	62	941	94	NaOH	tower	2.49

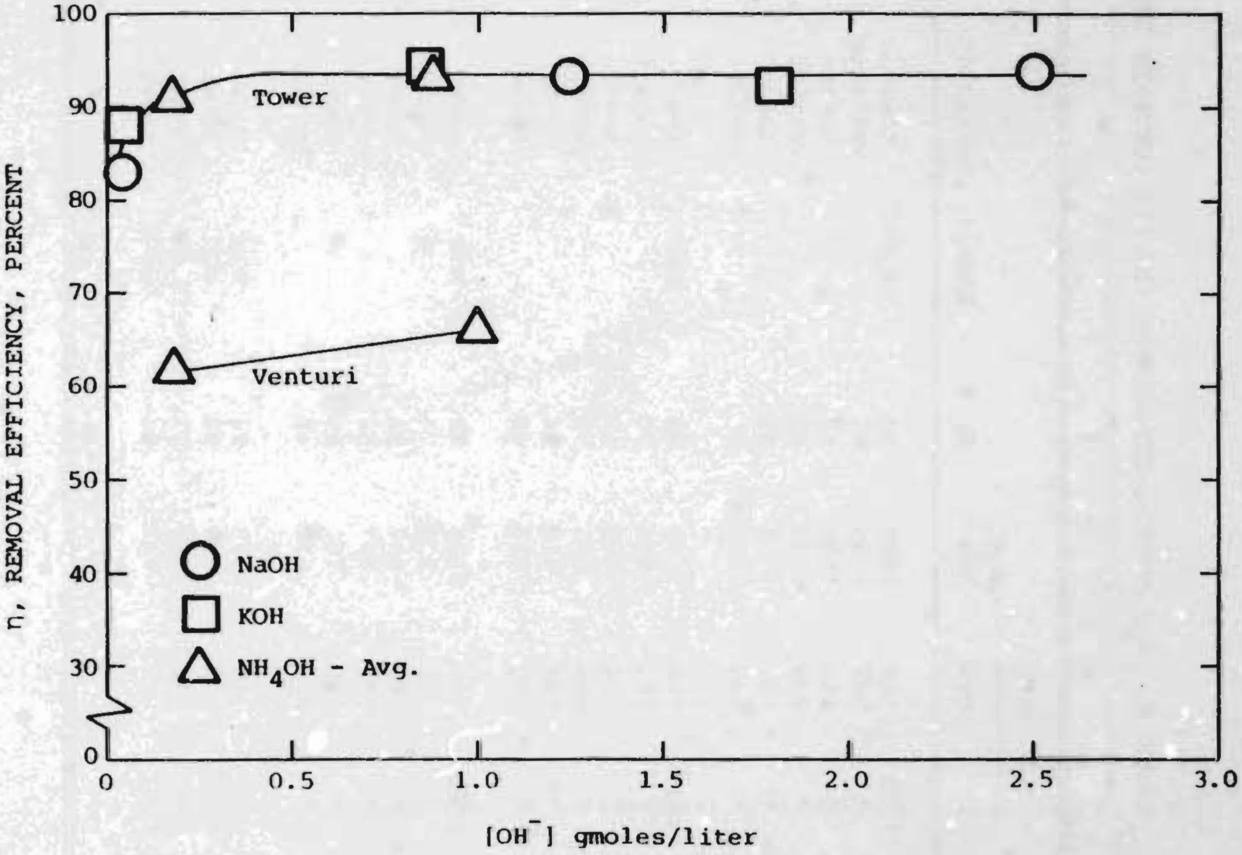

Figure 23. Removal Efficiency for Tower and Venturi at [OH^-] > 0.05 gmoles/liter

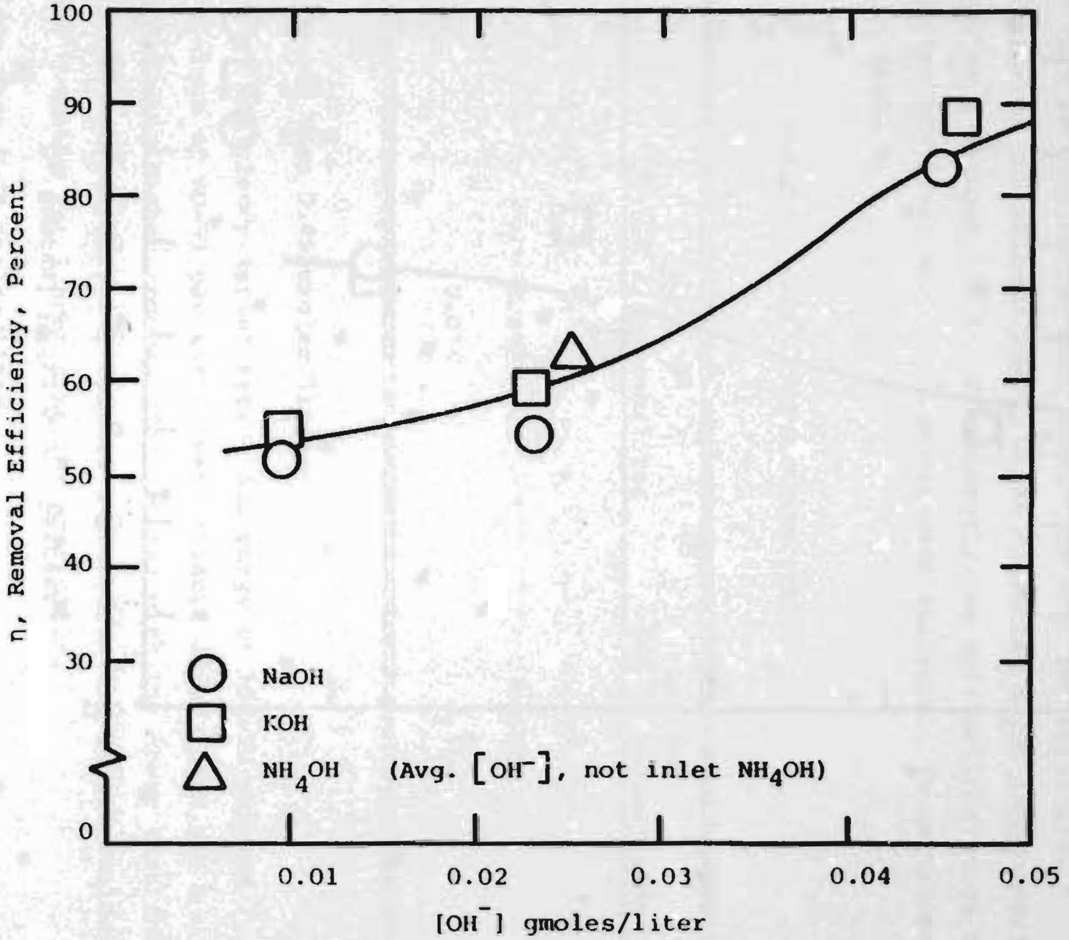

Figure 24. Removal Efficiency Results for Tower at [OH$^-$] < 0.05 gmoles/liter

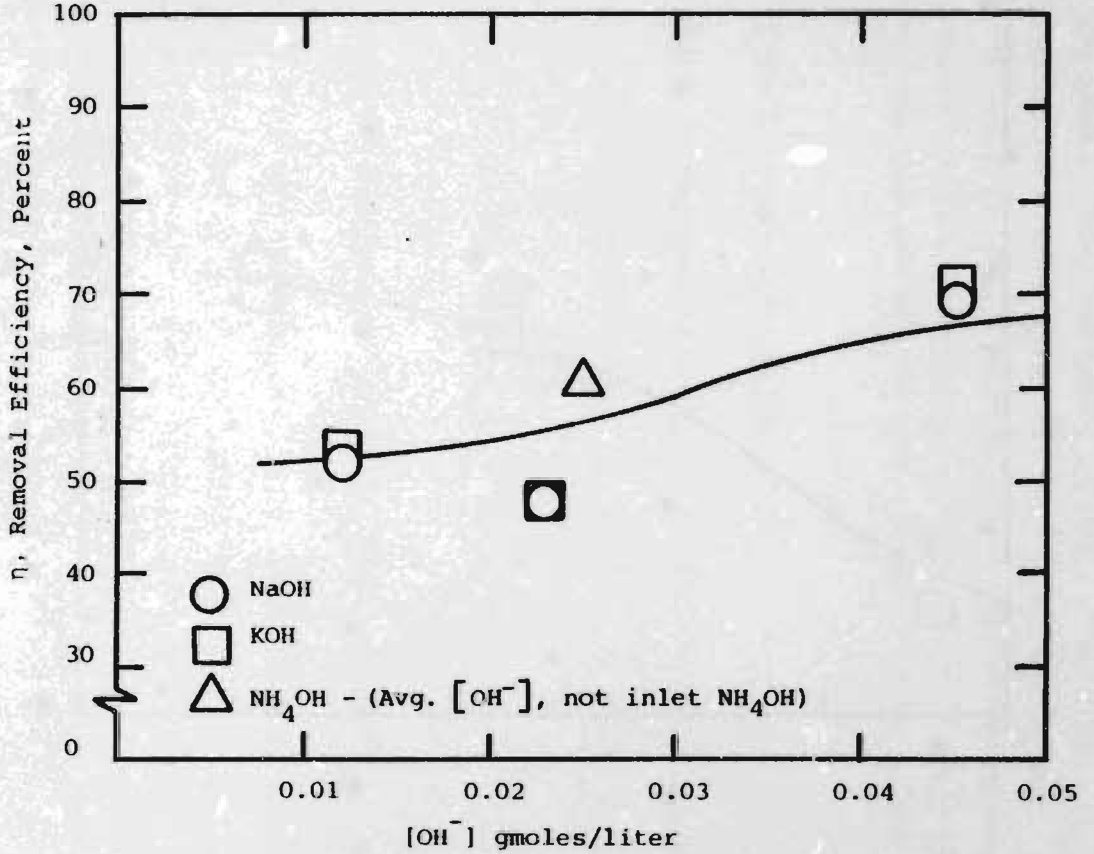

Figure 25. Removal Efficiency for Venturi at $[OH^-] < 0.05$ gmoles/liter

$$\text{and } K_D = \frac{[NH_4^+][OH^-]}{NH_3} = 1.75 \times 10^{-5} \text{ at } 25^0C$$

However, since the [OH⁻] is a product that is consumed, the dissociation reaction is driven to the right. Thus, continuous renewal of [OH⁻] is provided rather than an equilibrium condition. The exit scrubbing liquid [OH⁻] can be considered the minimum [OH⁻], while the inlet NH_4OH concentration can be considered as a maximum [OH⁻]. Consequently, an arithmetic average of the inlet and outlet [OH⁻] was used for ammonia data analysis. These values are summarized in Table 9.

TABLE 9. [OH⁻] FOR AMMONIA TESTS

Inlet NH_4OH Conc., gmoles/liter	Exit [OH⁻], gmoles/liter	Average [OH⁻], gmoles/liter
2.0	0.1	1.0
0.29	0.002	0.025
0.049	0.016	0.154

A. [OH⁻] Greater Than 0.05 gmoles/liter--

The removal efficiency varied from a low range of ~55-70 percent (venturi) to a maximum of 80-93 percent (tower) (Figure 23). There was a consistent trend showing higher removal efficiencies with the tower than the venturi at equal OH⁻ concentrations. This is expected as the longer residence time in the tower provides for longer time for absorption.

B. [OH⁻] Less Than 0.05 gmoles/liter--

1. Tower--The removal efficiency for the tower runs at [OH⁻] <.05 gmoles/liter is shown in Figure 24. The removal efficiency varied from 55 percent at the lower [OH⁻] of ~0.012 gmoles/liter to 86 percent at ~0.05 gmoles/liter of OH⁻. Two distinct trends are apparent. At [OH⁻] greater than

0.025 gmoles/liter, there is a significant improvement in removal efficiency with higher [OH^-]. This is to be expected on the [OH^-] determines the relative chemical enhancement. However, at [OH^-] less than 0.025 gmoles/liter, and greater than 0.01 gmoles/liter, the removal efficiency is relatively independent of [OH^-]. This result is due to the NH_3 present in the retort gas. As the H_2S is removed by its reaction with NH_3 (Reaction 12), the minimal (if any) dependence of H_2S removal with [OH^-] is consistent with the theoretical model discussed in Section 2.5.

It should be noted that this NH_3-H_2S reaction will occur at [OH^-] approaching zero which indicates removal of H_2S with a water scrubber without alkaline feed. This will affect the process and plant design for the in-situ plant analysis.

In a concept design for an in-situ shale oil retort offgas processing plant (Denver Research, 1983), the retort gas is first treated in an absorber-cooler, which "condenses light oils and ammonia containing water." The material balances given in this report indicate that with a 3:1 ratio of NH_3 to H_2S in the retort gas, only 1.4 percent of the H_2S is absorbed while 92.3 percent of the NH_3 is absorbed. This material balance is not consistent with either the theoretical or experimental results. Both the H_2S and NH_3 will be removed in the absorber and this fact will affect the process and plant design downstream. Qualitative observation of actual H_2S removal during the plant startup tests with water recirculation through the venturi showed a 10 to 15 percent H_2S removal efficiency. Similar conditions for the tower were not run but it would be expected that the longer residence times in the tower would result in greater H_2S removal.

There was no significant difference in the performance with any of the scrubbing chemicals at equivalent OH^- concentrations.

2. Venturi--The effect of [OH^-] on removal efficiency for the venturi runs at [OH^-] less than 0.05 gmoles/liter is shown in Figure 25. The removal efficiency ranged from 48 percent to 70 percent and showed a minimal dependence on OH^- concentration. These results also indicate the same "leveling off" of the dependence of removal efficiency with [OH^-] below OH^- concentrations of 0.025 gmoles/liter. At OH^- greater than 0.025 gmoles/liter,

there is a slight increase in removal efficiency with [OH^-] from 55 percent to 65 percent. These results are consistent with the discussion in the previous section on the scrubbing effect of NH_3 in the retort gas.

There was no significant difference in performance for any of the scrubbing chemicals at equivalent [OH^-].

3. Summary-Figure 26 shows the combined results for the tower and venturi runs.

The two contactors show similar performance at the low [OH^-] with the tower performance improving more rapidly than the venturi at [OH^-] between 0.02 and 0.05 gmoles/liter. For both contactors, the performance at 0.05 gmoles/liter [OH^-] approaches their maximum values of 93 percent and 66 percent for the tower and venturi respectively. It appears that the effect of the NH_3 in the retort gas which results in the lack of dependence at low [OH^-] becomes less important at [OH^-] greater than 0.25 gmoles/liter for both contactors.

2.6.2 Selectivity

The results for the selectivity analysis are presented in Table 10 and Figure 27.

A. Tower--

The selectivity for the tower runs ranged from a low of 9 for the high OH^- concentrations to a high of 52 at the low OH^- concentrations. This trend, increasing selectivity with decreasing OH^- concentration is consistent with the previous theoretical development. The ammonia test results using the average NH_4OH concentration do not correlate well showing lower selectivities than NaOH and KOH at equal [OH^-]. This is inconsistent with theoretical analysis and is most likely due to the emperical approach using the average concentration.

B. Venturi--

The selectivity for the venturi runs is also shown in Figure 27 and ranged from 11 at the high [OH^-] to 79 at the low [OH^-]. The high selectivity in the venturi is due to the short gas/liquid contact time of approximately

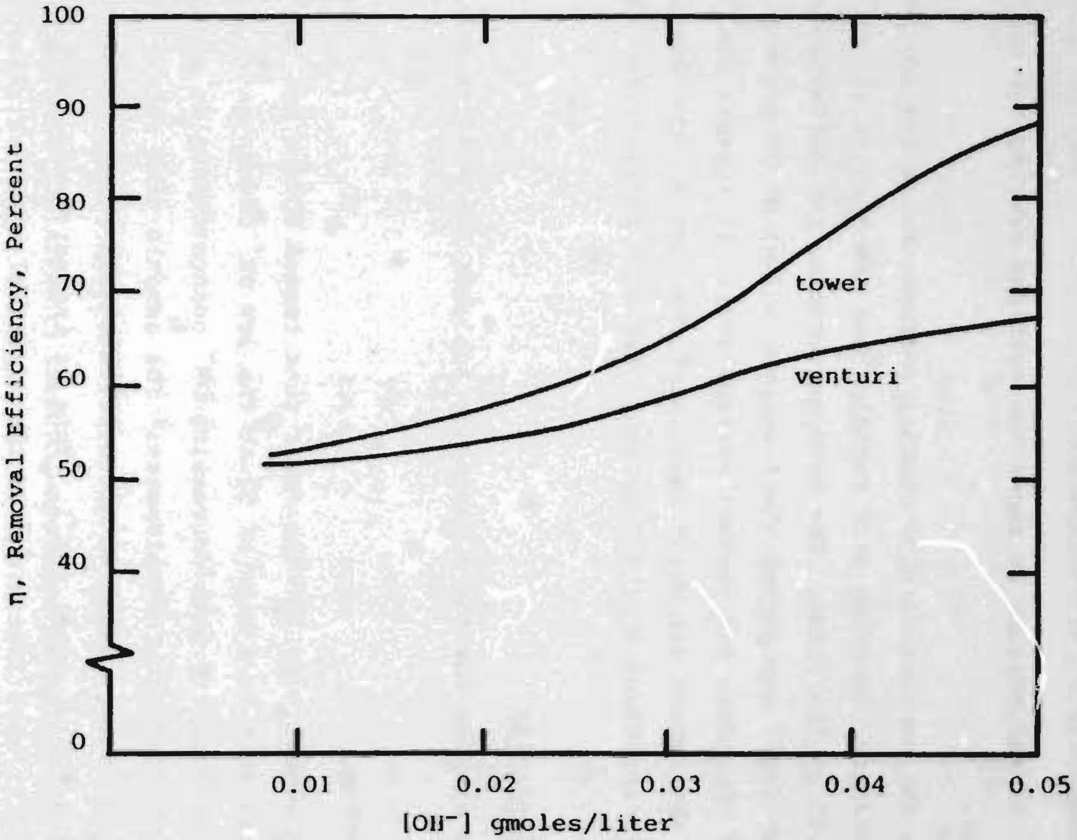

Figure 26. **Removal Efficiency for Tower and Venturi at $[OH^-] < 0.05$ gmoles/liter**

TABLE 10. TEST SELECTIVITY FOR THE ALKALINE SCRUBBER

			Removal Efficiency		
Run	Chemical	OH^- gmole/liter	H_2S, %	CO_2, %	Selectivity
Tower					
20	NaOH	0.012	52.0	1.0	52
27	KOH	0.012	54.5	1.27	43
22	NaOH	0.023	54.1	1.32	41
29	KOH	0.023	59.5	1.22	49
18	NaOH	0.045	83.0	2.32	36
25	KOH	0.046	88.0	2.14	41
14	NH_4OH	0.049	63.8	2.18	29
16	NH_4OH	0.29	90.6	3.15	29
12	NH_4OH	2.0	92.8	10.38	9
Venturi					
21	NaOH	0.012	52.4	0.66	79
28	KOH	0.012	53.4	0.75	71
24	NaOH	0.023	48.0	0.79	60
30	KOH	0.023	48.4	0.94	51
19	NaOH	0.045	70.0	0.84	84*
26	KOH	0.046	70.9	3.42	21
15	NH_4OH	0.049	60.5	0.85	72
17	NH_4OH	0.29	61.6	1.10	56
13	NH_4OH	2.0	66.6	6.11	11

*suspect water data

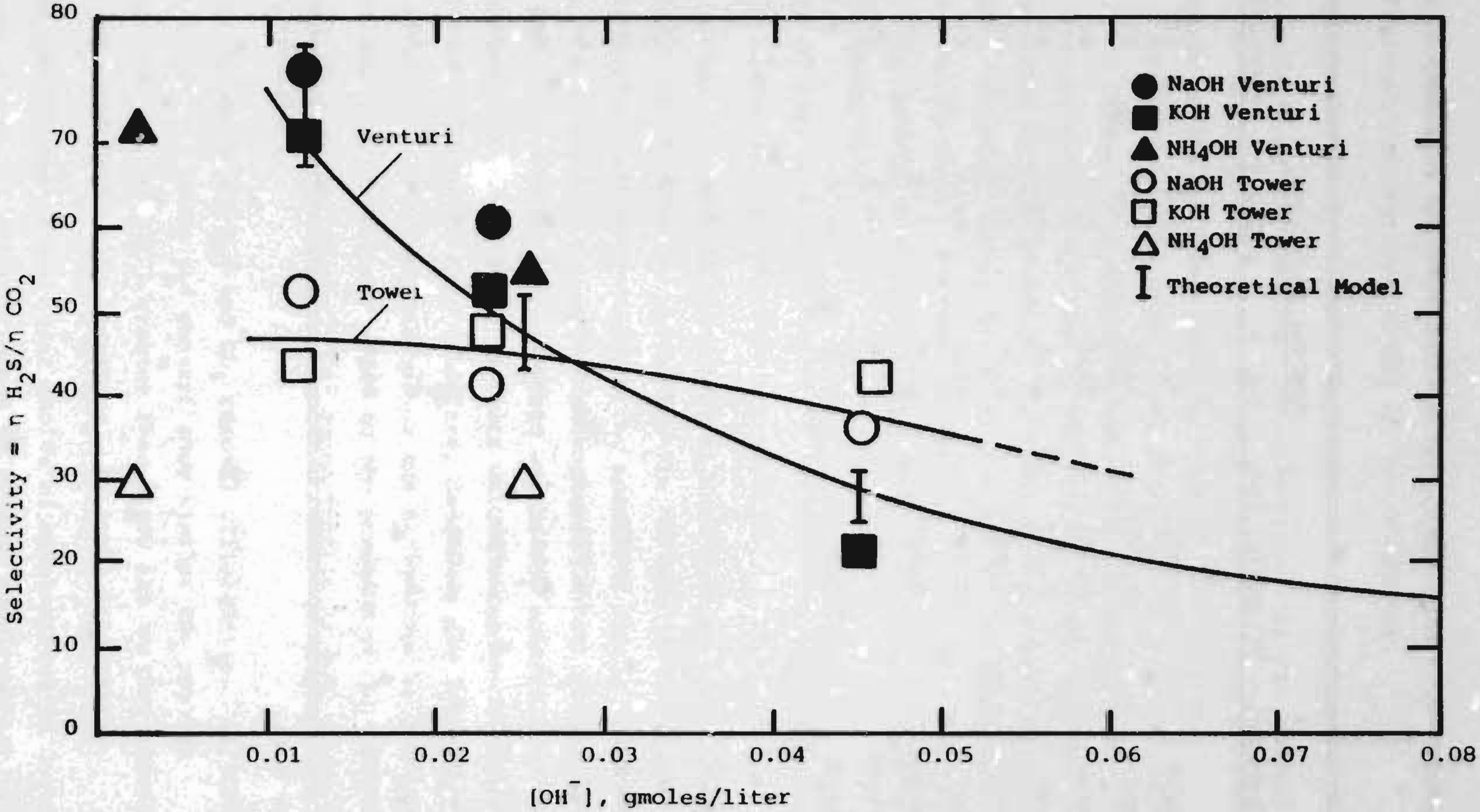

Figure 27. Selectivity at $[OH^-] < 0.05$ gmoles/liter.

0.003 seconds compared to approximately 0.2 sec. for the tray tower the high gas film coefficient and presence of NH_3 in the retort gas.

C. Comparison between Tower and Venturi--

The test results indicate that the selectivity for the venturi is highly sensitive to the OH^- concentration with a rate of change, dS/dOH^-, of -1700 liter/gmole in the OH^- concentration range of 0.01 to 0.04 gmole/liter. The tower results show a rate of change of only -300 liter/gmole in the same $[OH^-]$ range. This effect is due to the presence of NH_3 in the retort gas. The short residence time in the venturi (0.003 seconds) results in a high dependence of selectivity on $[OH^-]$ due to the direct dependence of CO_2 enhancement. In other words, the short residence time means that the CO_2 has a limited time to react. However, as the H_2S absorption is controlled by the gas/film, its absorption site is independent of the $[OH^-]$ at $[OH^-]$ values less than 0.03 gmole/liter.

Figure 27 also shows that, at $[OH^-]$ greater than 0.03 gmoles/liter the tower provides higher selectivity than the venturi.

This is due to the combined effect of the gas film coefficient and the presence of NH_3. The higher gas coefficient in the venturi essentially increases the availability of the CO_2 at the scrubbing liquid interface. Consequently, the liquid phase chemical enhancement factor, which is a direct function of $[OH^-]$, has a substantial effect on the CO_2 absorption rate. In the tower, the gas film coefficient is lower which decreases the relative importance of the liquid film and, therefore, decreases the dependency of the CO_2 absorption on OH^- concentration. Since the H_2S removal is determined solely by the gas film coefficient - due to the presence of NH_3 in the gas, the sensitivity of H_2S absorption to OH^- concentration in both tower and venturi is decreased.

Figure 28 shows the H_2S and CO_2 removal efficiencies. At $[OH^-]$ below 0.035 gmoles/liter, the tower and venturi show similar CO_2 removal efficiencies. However, at $[OH^-]$ greater than 0.035 the venturi removes CO_2 more readily than the tower and, therefore, has lower selectivity.

These results indicate a clear choice of alternatives in deciding between a tower or venturi scrubber based on process requirements. If

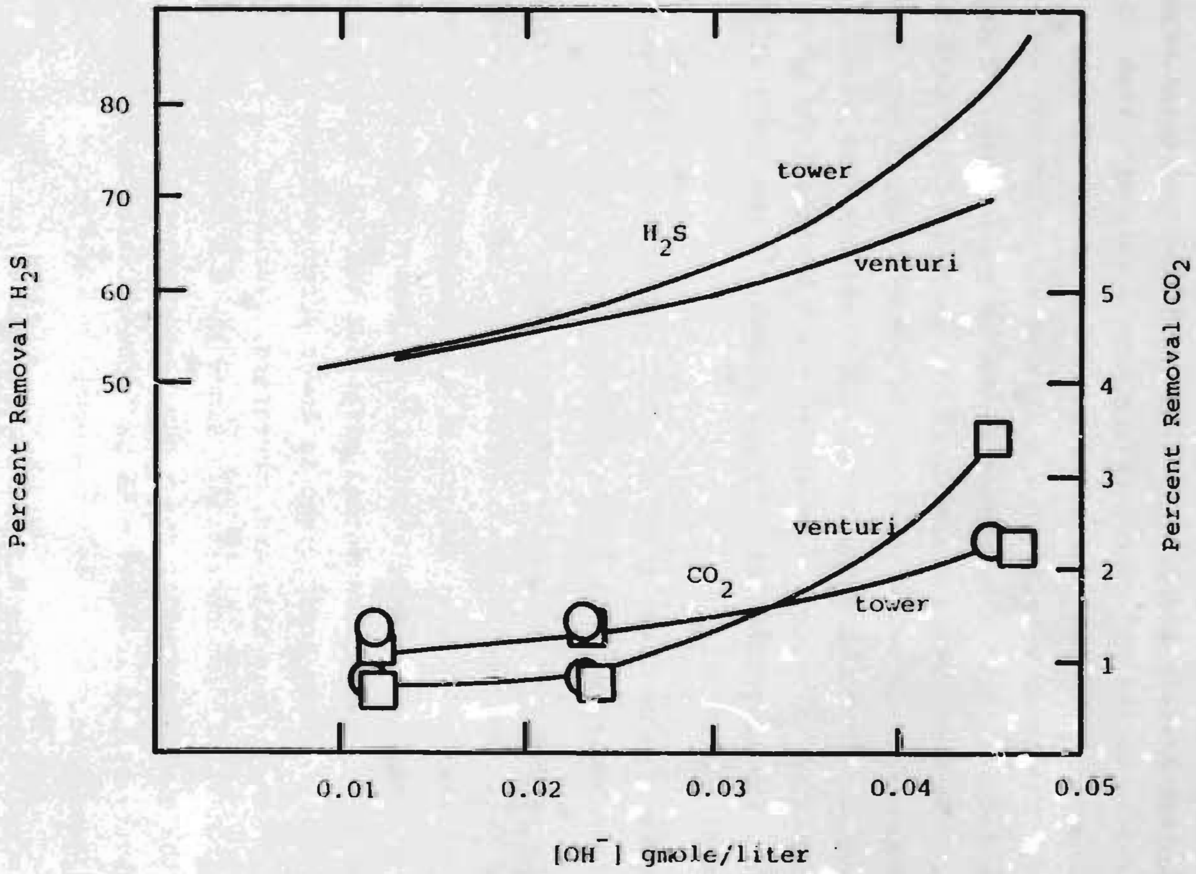

Figure 28. H_2S and CO_2 Removal Efficiency

selectivities greater than 50 are needed, the venturi is required to take advantage of the high selectivity at the short contact time. However, the venturi scrubber will only provide 50 to 60 percent removal efficiency per stage. If a selectivity less than 50 is acceptable, the tower is more effective in that both removal efficiency and selectivity is greater than with the venturi.

D. Comparison with Theoretical Model--

The theoretical model described in Appendix B was used to evaluate the correlation with the test results. The model results were evaluated at distances of 20.5 and 24 cm from the point of liquid injection. This range was used due to the fact that the effective scrubbing in the first 5 cm is questionable since it takes approximately 5 cm to achieve complete atomization. The resulting selectivities are shown in Table 11.

TABLE 11. COMPARISON THEORETICAL AND EXPERIMENTAL SELECTIVITIES

OH^-, gmoles/liter	Theoretical 24 cm*	20.5 cm*	Average	Experi- mental	Difference, %
0.045	25	31	28	21	25
0.023	43	53	48	55	14.6
0.012	66	82	74	75	1.4
				Avg.	13.7

*Distance along venturi throat that fluid is injected.

The theoretical selectivities are in good agreement with the test results with respect to both trend and absolute values. There is excellent agreement at the low concentration range (1.4 percent) while the higher concentration (0.045 gmoles/liter) has a 25 percent deviation. This information is also shown in Figure 27 as a range of predicted values for each concentration. The agreement of the theoretical model with the test results, particularly at the lower concentrations which are of primary interest when evaluating a venturi scrubber, indicate the model can be used for predictive studies of multi-stage performance.

2.7 FINDINGS

The following summarizes the pertinent alkaline scrubber results obtained from the test program:

1. All three alkaline solutions provided similar results at equal [OH^-] for both scrubbing efficiency and selectivity. Correlation of the ammonia results were complicated by incomplete dissociation of the weak base.

2. Removal efficiencies of 85-90 percent with a selectivity of 30 can be achieved in a tray tower with as low as 0.045 gmoles/liter OH^- concentration.

3. Selectivity in the tower was only slightly dependent on [OH^-] ranging from 45-50 at 0.012 gmoles/liter [OH^-] to 25-30 at 0.045, gmoles/liter [OH^-].

4. Removal efficiencies of 55-65 percent can be achieved in the venturi with nominal dependence on OH^- concentration.

5. Selectivity of 70-80 can be realized in a venturi at low (0.012 gmoles/liter) OH^- concentrations.

6. At [OH^-] less than 0.03 gmoles/liter, the venturi had higher selectivity than the tower, while at [OH^-] greater than 0.03 gmoles/liter, the tower exhibited higher selectivity than the venturi. This occurs because of the effect of the NH_3 in the retort gas which provides for H_2S removal based solely on the gas film coefficient. Therefore, at low [OH^-] the venturi scrubber is effective for H_2S removal with nominal CO_2 absorption. However, at high [OH^-], the CO_2 absorption increases more rapidly in the venturi than the tower due to the higher gas film coefficient in the venturi.

The following summarizes the alkaline scrubber results from the theoretical model analysis for the venturi:

7. The NH_3 in the retort gas reacts with the H_2S at the gas-liquid interface. Therefore, the removal efficiency is only marginally dependent on the [OH^-].

8. Removal efficiencies for NH_3 and H_2S are similar.

9. The selectivity is significantly affected by contract time with a maximum selectivity of 110 occuring at approximately 0.0015 seconds contact time.

10. The agreement between the theoretical model and field test results is excellent at low OH^- concentrations (0.012 to 0.025 gmoles/liter) which is the primary range of interest for the venturi.

11. Variations in temperature and liquid droplet size can have a significant effect on selectivity.

2.8 TWO STAGE SYSTEM

The above findings suggest two alternative alkaline scrubber design concepts for further consideration and evaluation. One system combines the high selectivity of the venturi with the high removal efficiency of the tower. The other design concept uses a tower for maximum H_2S removal and isolated liquid input to maximize selectivity for use with a Claus plant.

2.8.1 Venturi-Tower

The design objective for this concept is to obtain a minimum removal efficiency of 95 percent with selectivity greater than 30 which cannot be obtained with either the venturi or the tower in a single stage. The venturi can have the high selectivity but the low removal efficiency requires too many stages for the H_2S removal requirements. The tower can approach the 95 percent removal efficiency but selectivity drops below 30 at removal efficiencies greater than approximately 85 percent.

A two stage system that will exploit the specific design features for each unit can provide a system (shown in Figure 29) that will meet the above process requirements.

The first stage is a venturi designed for peak selectivity based on contact time and OH^- concentration. (See Figure 19). The theoretical model indicates a maximum selectivity of 110 will result in a 50 percent removal efficiency. The CO_2 removal efficiency is 0.4 percent.

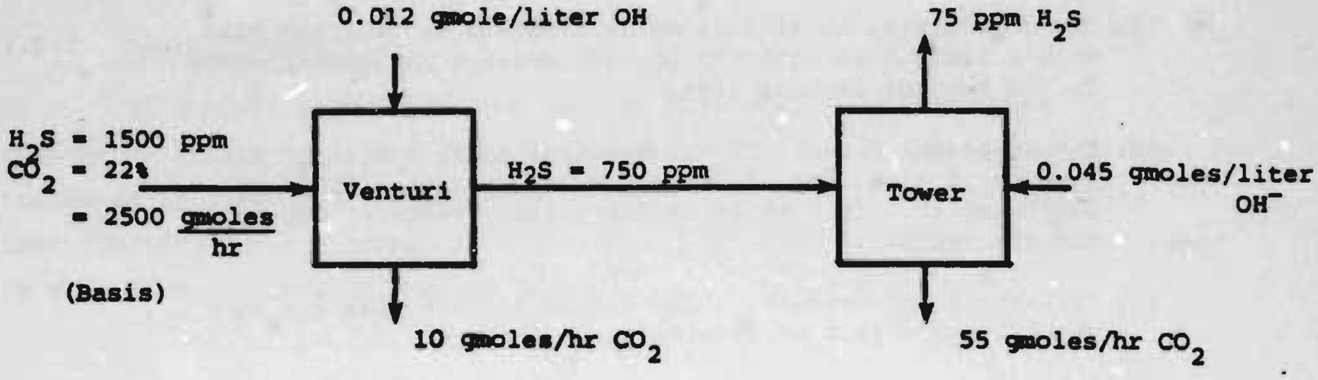

Figure 29. Two-Stage Process

The second stage, a tray tower, is designed for approximately 85-90 percent H_2S removal efficiency with a stage selectivity of 40 using an OH^- concentration of 0.045 gmoles/liter. The CO_2 removal efficiency is 2.2 percent.

The net result from this design is a 95 percent removal efficiency with a selectivity of 37. These results are shown in Table 12.

TABLE 12. TWO STAGE DESIGN CONDITIONS

Position	H_2S, ppm	CO_2, %	gmoles CO_2		OH^-, gmoles/liter
		Gas	Liquid		
Inlet	1500	22	2500		
Stage 1-Venturi	750	21.9	2490	10	0.012
Stage2-Tower	75	21.4	2435	55	0.045
			65		

$$H_2S \text{ removal Efficiency} = \frac{1500 - 75}{1500} = 95\%$$

$$CO_2 \text{ Removal Efficiency} = \frac{2500 - 2435}{2500} = 2.6\%$$

Selectivity = 37

2.8.2 Tower - Tower

If a lower selectivity can be tolerated and a higher removal efficiency is required, a multi-stage tower can be used. Selectivity can be increased by providing isolated stages with respect to scrubbing liquid to take advantage of the higher selectivity at low H_2S concentrations illustrated in Figure 16. Figure 30 shows a schematic for this tower design.

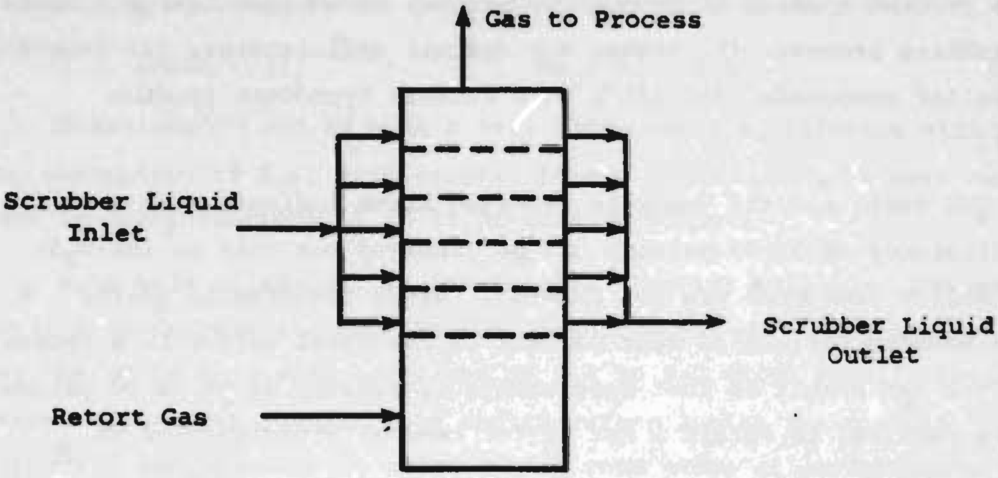

Figure 30. Tray Tower with Isolated Liquid Inlet

The H_2S concentration to each stage is reduced by approximately 50 percent per stage.

By using fresh scrubber solution for each tray, the removal efficiency/tray is maintained but selectivity should increase because of the lower inlet H_2S concentration to each stage. The performance of this concept is summarized as follows:

	Inlet (Assumed)	Stage 1 Exit	Scrubber Exit
H_2S Conc., ppm	1500	150	15
CO_2 Conc., %	22	21.5	21.0

$$H_2 \text{ removal eff.} = \frac{1500-15}{1500} = 99\%$$

$$CO_2 \text{ removal eff.} = \frac{22-21}{22} = 4.5\%$$

$$\text{Selectivity} = \frac{99}{4.5} = 22$$

2.9 ACTIVATED CARBON PROCESS

A variation of the caustic scrubbing process using activated carbon as a catalyst has been developed by the Pulp and Paper Research Institute of Canada (Prohocs, 1983) for the purpose of controlling H_2S emissions from black liquor recovery furnaces. The flue gas concentrations from these furnaces are similar to the retort gas concentration from in-situ retorts.

This process appears to have three process advantages over the basic alkaline scrubbing process: (1) higher H_2S removal efficiencies, (2) removal of organic sulfur compounds, and (3) a more salable byproduct (sodium thiosulfate).

The GKI tests and the analysis reported above indicate that a scrubbing efficiency of 93-95 percent can be achieved but only on the H_2S. The organic sulfur compounds are not removed. Since the organic sulfur compound can account for one to four percent of the total sulfur in a typical retort gas, the net result is that a scrubbing efficiency of 96 to 99 percent on the H_2S is required to obtain a net sulfur removal efficiency of 95 percent.

Scrubbing the offgas from a black liquor recovery furnace containing H_2S in the presence of large amounts of CO_2 was accomplished using as little as 0.03 weight percent of activated carbon in suspension. The principal reaction steps are:

1. $H_2S + CO_3^{-2} \rightarrow HCO_3^- + HS^-$
2. Partial adsorption of HS^- on the surface of the activated carbon
3. Oxidation of HS^- to $S_2O_3^{-2}$

The reactions are:

Absorption of CO_2:

$$2NaOH + CO_2 \rightarrow Na_2CO_3 + H_2O \qquad (17)$$

$$Na_2CO_3 + CO_2 + H_2O \rightarrow 2NaHCO_3 \qquad (18)$$

Absorption of H_2S:

$$Na_2CO_3 + H_2S \rightarrow NaHCO_3 + NaHS \qquad (19)$$

$$NaHCO_3 + H_2S \rightarrow NaHS + CO_2 + H_2O \qquad (20)$$

Reactions 17 and 18 govern the (initial) chemical composition and, more importantly, the pH of the scrubbing solution.

Reactions 19 and 20 have unfavorable equilibrium coefficient absorption of H_2S. Removing this limitation of H_2S absorption due to the unfavorable equilibrium is the purpose of the oxidation reaction --

$$2NaHS + 2O_2 \xrightarrow{\text{act. carbon}} Na_2S_2O_3 + H_2O \qquad (21)$$

Reactions 19 and 20 have a very unfavorable equilibrium with respect to the absorption of H_2S, particularly in the presence of the more acidic CO_2, present in concentrations of 10-16 percent by volume.

With NaOH or Na_2CO_3, in the initial alkaline solution, the absorbed CO_2 will also depress the pH. At 70°C (the typical scrubbing temperature range) the pH is depressed to values of 8.5 to 9.0 which significantly decreases the H_2S absorption rate and therefore limits the removal efficiency. But Reaction 21 under normal conditions of scrubbing, proceeds very rapidly to the right, thus allowing more H_2S to be absorbed by Reactions 19 and 20. A significant amount of the $Na_2S_2O_3$ is further oxidized to Na_2SO_4. H_2S removal efficiencies of 99 to 99.9 percent were readily achieved at H_2S inlet concentrations of <1100 ppm.

Reaction 21 requires 2-3 percent oxygen in the flue gas. At H_2S concentrations over 100-120 ppm, a separate aeration step was required. The aeration step occurs prior to the recycle of the scrubbing fluid. The aeration residence time and rate requirements are a function of H_2S load and the required exit gas concentration.

Removal of organic sulfur compounds can be enhanced by adding chlorine gas to the alkaline scrubbing solution or using hypochlorite solution. The absorption/adsorption and possible oxidation mechanisms of the organic sulfur compunds were not determined. However, early laboratory tests indicated that removal efficiency of the organic sulfur compunds may be improved by addition of activated carbon. In addition, laboratory tests with dilute sodium hypochlorite (500-700 ppm) resulted in an exit concentration of less than one ppmv of organic sulfur compounds regardless of the inlet concentration. This process is more expensive than the basic alkaline scrubbing process and could result in trace emissions of chlorinated organics.

SECTION 3.0

STRETFORD PILOT PLANT

3.1 PROCESS DESCRIPTION

The Stretford is a regenerative process that converts H_2S in the retort off-gas to elemental sulfur. It uses air oxidation to regenerate the chemicals reduced during the offgas treatment. The original Stretford process was developed in the early 1950's by the North Western Gas Board and the Clayton Aniline Company. The original pilot plant was operated on town gas at the Stretford Road Gas Works in the village of Stretford, England. The North Western Gas Board later became part of the British Gas Corporation (BGC), which currently licenses the process worldwide to engineering and construction companies.

The Stretford process has been in use for more than 25 years, and more than 90 commercial Stretford plants are currently in service worldwide for the following specific gas-treating applications:

- Coal gasification
- Coke oven gas
- Refinery fuel gas
- SNG (petroleum) plant gas
- Natural and associated gases
- Claus tail gas
- Geothermal power generation
- Carbon disulfide manufacture
- Ore roasting
- Sewage sludge digester gas

The most common application of this technology is for sulfur recovery (as part of the Beavon process for treating Claus plant tail gas). The commercial use of Stretford technology directly on synthetic fuel process gas streams has not been practiced. In the United States, a number of demonstration plants have been installed on coal gasification process gas streams; however, a variety of operating problems have limited the performance of these plants.

3.1.1 Process Chemistry

The process chemistry of the Stretford technology is based on the absorption of H_2S and subsequent liquid-phase oxidation of the captured H_2S to elemental sulfur in an alkaline solution of sodium, vanadium, and anthraquinone disulfonic acid salts.

The Stretford liquor is a dilute solution of sodium carbonate (Na_2CO_3), sodium metavanadate ($NaVO_3$), and sodium salts of the 2:6 and 2:7 isomers of anthraquinone disulfonic acid (ADA). The solution is maintained at a pH of 8.5 to 9.5 and a temperature of approximately 43°C.

Removing the H_2S from the gas stream and converting it to elemental sulfur is basically a five-step chemical process, as shown in the following simplified chemical reactions:

1. The H_2S reacts with the sodium carbonate to form sodium hydrosulfide and sodium bicarbonate:

   $$H_2S + Na_2CO_3 \rightarrow NaHS + NaHCO_3 \qquad (3\text{-}1)$$

2. The hydrosulfide then reacts with sodium metavanadate to form elemental sulfur, a quadravalent vanadium salt, and sodium hydroxide:

   $$2NaHS + 4NaVO_3 + H_2O \rightarrow Na_2V_4O_9 + 2S + 4NaOH \qquad (3\text{-}2)$$

3. The quadravalent vanadium salt then reacts with ADA* to regenerate the sodium metavanadate:

   $$Na_2V_4O_9 + 2NaOH + H_2O + 2ADA \rightarrow 4NaVO_3 + 2ADA \cdot 2H \qquad (3\text{-}3)$$

4. The sodium hydroxide and sodium bicarbonate reaction products further react to form sodium carbonate:

   $$NaOH + NaHCO_3 \rightarrow Na_2CO_3 + H_2O \qquad (3\text{-}4)$$

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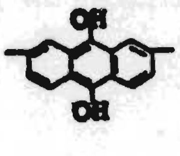
*The chemical formula for 2:7 ADA is: $NaSO_3$  $NaSO_3$

5. The reduced ADA** reacts with oxygen to regenerate the ADA:

$$2ADA \cdot 2H + O_2 \rightarrow 2ADA + 2H_2O \qquad (3\text{-}5)$$

The overall process reaction can be written as the oxidation of H_2S to elemental sulfur:

$$2H_2S + O_2 \rightarrow 2S + 2H_2O \qquad (3\text{-}6)$$

Several side reactions that form nonregenerable compounds are possible in the Stretford process. If sodium hydrosulfide contacts absorbed oxygen in either the absorber or the oxidation tank (which can occur if the system lacks adequate vanadium levels or is removing H_2S at levels above design), sodium thiosulfate forms according to the following reaction:

$$2NaHS + O_2 \rightarrow Na_2S_2O_3 + H_2O \qquad (3\text{-}7)$$

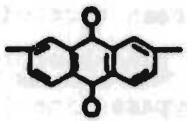
The amount of dissolved oxygen in the process liquor is pH-dependent. The rate of Reaction 3-7 is also dependent upon pH and will decrease as pH increases. The rate of H_2S absorption (Reaction 3-1) is also pH-dependent, which in turn is strongly influenced by the carbon dioxide content of the gas. High carbon dioxide concentrations, such as found in the gases from a shale oil retort, can cause the process to operate at lower pH levels, which reduces the overall removal efficiency.

Any SO_2 present in the feed gas is also absorbed and ultimately oxidized to form sodium sulfate according to the following reaction:

$$2SO_2 + O_2 + 2Na_2CO_3 \rightarrow 2Na_2SO_4 + 2CO_2 \qquad (3\text{-}8)$$

Any hydrogen cyanide present in the feed gas forms sodium thiocyanate according to the following reaction:

$$2HCN + 2NaHS + O_2 \rightarrow 2NaCNS + 2H_2O \qquad (3\text{-}9)$$

**The chemical formula for reduced 2:7 ADA is: $NaSO_3$  $NaSO_3$.

The nonregenerable compounds will build up in the system and eventually impede the performance of the Stretford process by interfering with the principal chemical reactions. These compounds must be removed from the process either by purging them from the system or by recovering them in a regeneration system.

3.1.2 Plant Design Description

The transportable pilot plant is mounted on three skids. It requires gas inlet/outlet connections, a condensate collection connection, and an electrical service connection with the host site facility. The plant's design configuration reflects the simplicity required to achieve the necessary mobility for assorted host sites and yet contains all the necessary elements to provide a workable, commercially representative Stretford process. An overall view of the Stretford plant is shown in Figure 31.

Table 13 provides a summary of the plant's design conditions with respect to gas characteristics and composition. Additional operating flexibility was incorporated into the pilot plant to withstand any anticipated gas conditions for processing oil shale retort offgas. This includes a maximum H_2S concentration of 3,000 ppmv and operating pressure from atmospheric to five psig.

Figure 32 presents a simplified process flow diagram of the pilot plant. This diagram depicts the basic design configuration of the plant, including a variable throat venturi scrubber gas/liquor contactor, reaction tank, oxidizer, pump tank, and slurry tank.

Before the retort offgas stream entered the Stretford, it was preconditioned in upstream equipment (vacuum blowers and mist eliminators) operated by GKI to remove any residual product oil. Thus, the gas stream was pre-cleaned and saturated prior to entering the Stretford. Normally, the gas stream would then enter the Stretford at the blower skid, which contains a compressor suction drum and booster fan assembly. (The compressor suction drum, "knock-out drum," served to remove any slugs of condensate that might have been carried over from the upstream product collection equipment. The booster fan assembly includes the booster fan, two silencers, and an emergency bypass line.) However, during this test program, the saturated gas

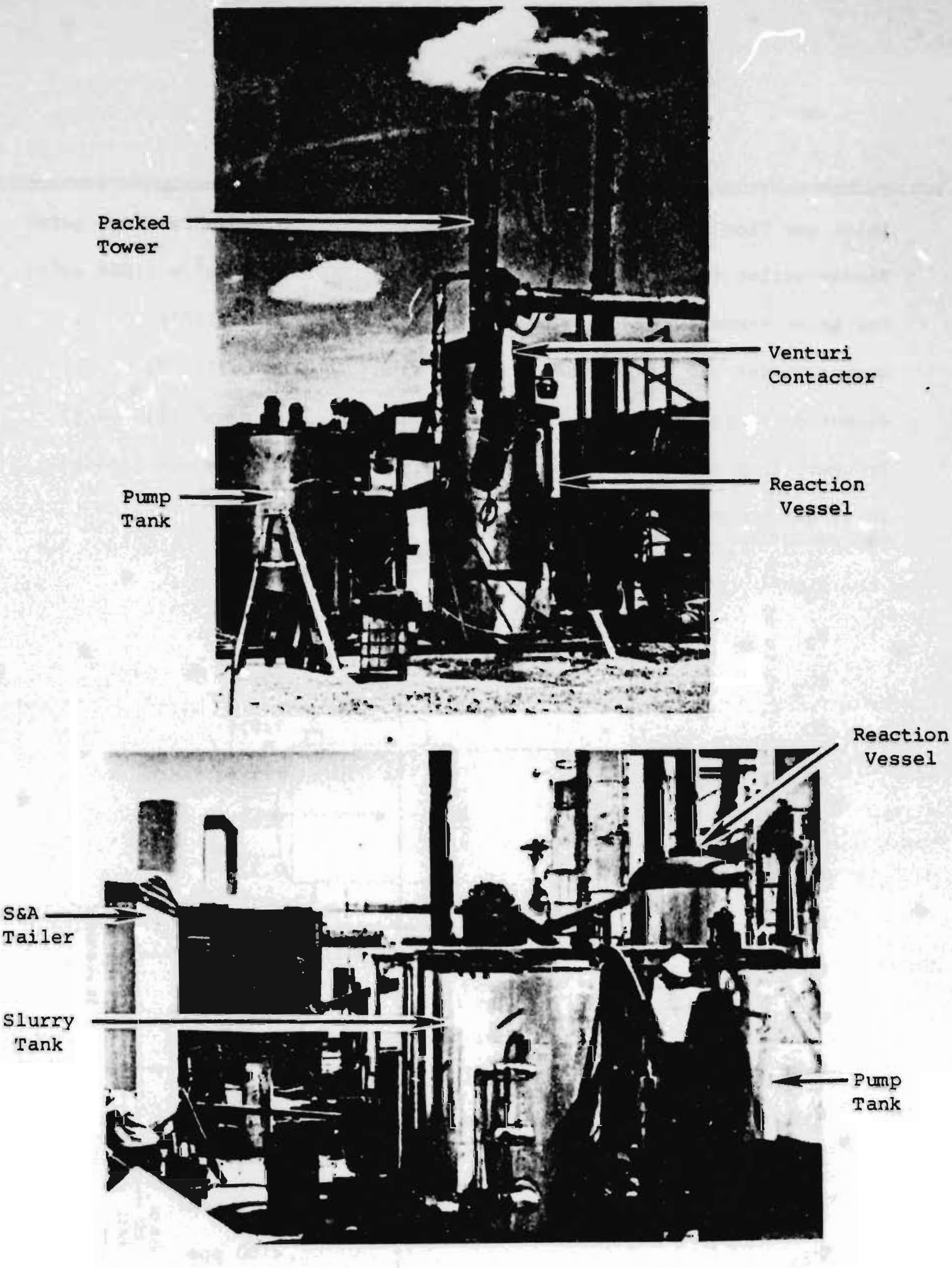


Figure 31. Overall View of Stretford Plant Installed at GKI

TABLE 13. KEY DESIGN PARAMETERS OF THE STRETFORD PILOT PLANT

Inlet gas flow rate	0.77 am^3/s (1640 acfm)
Blower outlet flow rate	0.74 am^3/s (1560 acfm)
Gas inlet temperature	38°C (100°F)
Blower outlet gas temperature	46°C (115°F)
Blower discharge pressure	70 g/cm^2 (1.0 psig)
Pressure drop across venturi	35 g/cm^2 (0.5 psig)
Inlet gas composition, concentration (volume)	
H_2O	6%
N_2	53%
CO_2	30.7%
CO	1.51%
CH_4	1.51%
H_2	5.85%
NH_3	0.22%
H_2S	0.13%
C_2H_6	0.33%
C_2H_4	0.22%
C_3H_8	0.17%
C_3H_6	0.17%
C_4 +	0.22%
COS	<110 ppm
CS_2	<100 ppm
RSH	<100 ppm

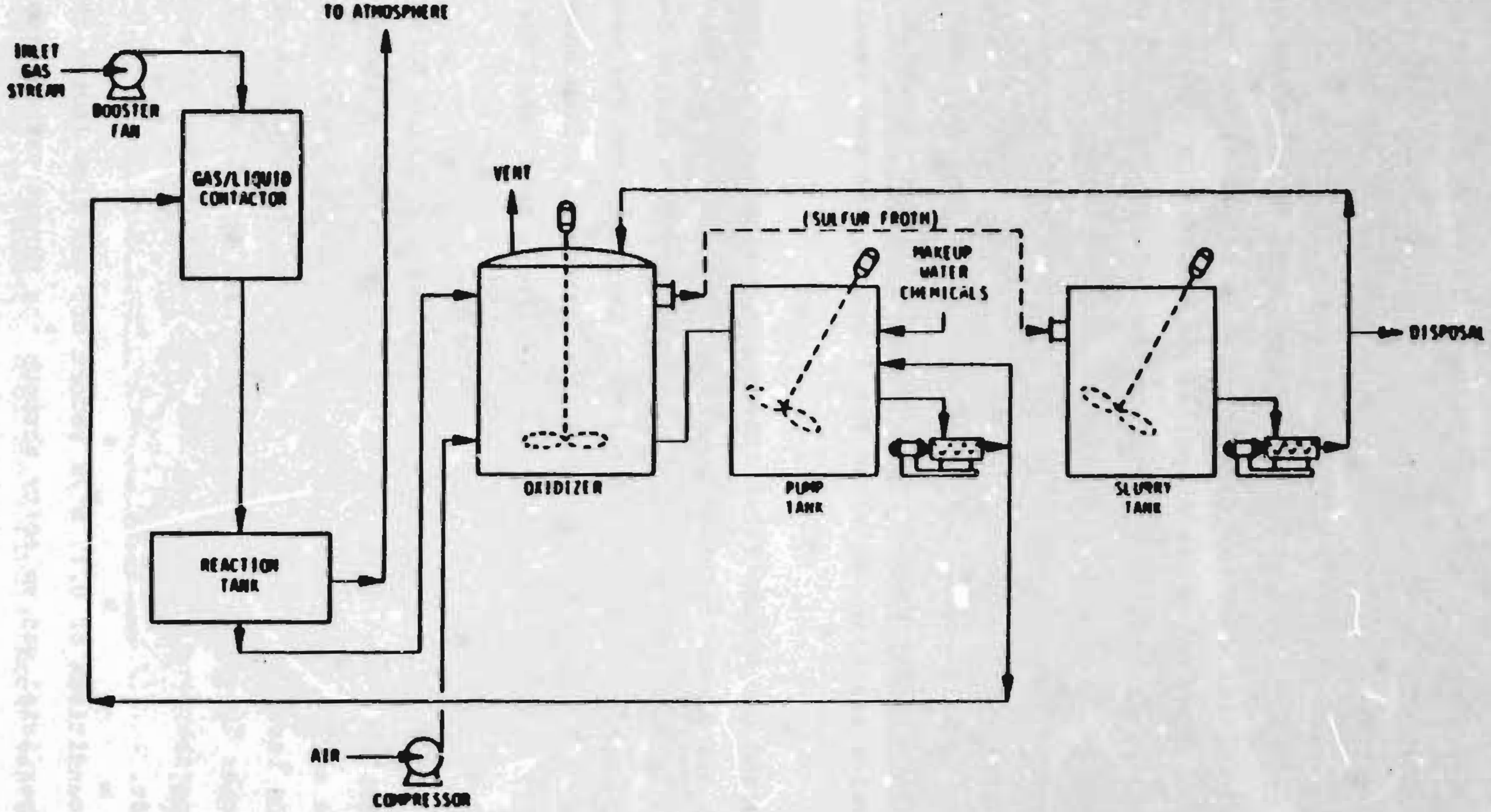


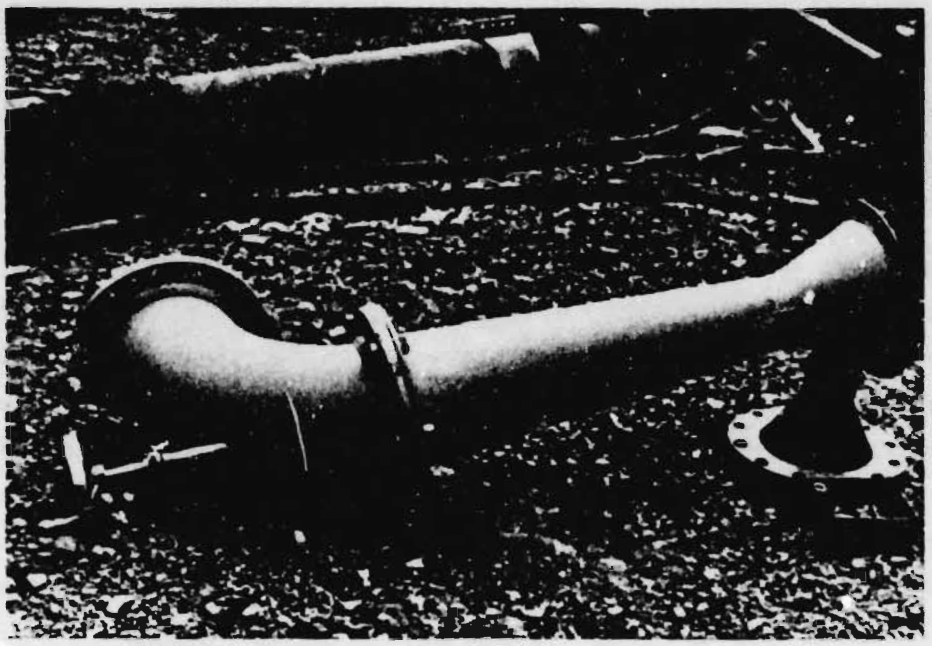
Figure 32. Simplified flow diagram of the Stretford pilot plant

stream entered the Stretford process at the venturi inlet by completely bypassing the blower skid. The blower was not necessary for this test program, because an adequate differential pressure existed across the GKI blower, thus allowing the retort gas to be easily introduced to the Stretford system from the discharge side of the GKI blower and to be exhausted to the inlet side of the GKI blower. Any initial concern regarding the Stretford discharge being upstream from the Stretford inlet was dispelled by considering the small volumetric flow of the Stretford plant compared to that of the GKI plant which is 0.33 Sm^3/S scfm compared to 10.4 Sm^3/S. Because the gas passes through the GKI compressor between the outlet and inlet the uniformity of composition at the Stretford inlet was considered to be good. The small amount of dilution caused by this plumbing arrangement had no effect on the program results. The experiment is to determine the removal efficiency from inlet to outlet. As long as the inlet value was measured after the dilution, the test results are valid.

The pressurized gas stream first enters the variable throat venturi scrubber, where the gas stream comes in contact with the Stretford solution. The solution is delivered to the top of the venturi through a single feed line with a spray nozzle. The Stretford solution injected into the venturi scrubber consists of a dilute solution of sodium carbonate, sodium ammonium vanadate, and the 2:7 isomer of anthraquinone disulfonic acid (ADA) for the removal of hydrogen sulfide.

A variable throat venturi designed by PEI was used during this test program. The venturi is shown in Figure 33. The top photograph shows an overall view of the entire venturi with the elbow joint connector. The lower photograph shows the inside of the variable-area throat. The throat of the venturi was six inches long, and had a diameter of six inches when fully open. Fully closing the venturi gave an area equivalent to that of a three inch diameter throat.

At design conditions of 0.71 m^3/s retort off gas flow (twice that for this test), the superficial gas velocity through the throat varied from 40 m/s to 155 m/s, depending upon the venturi position. This was equivalent to gas residence times from 0.004 to 0.001 seconds.



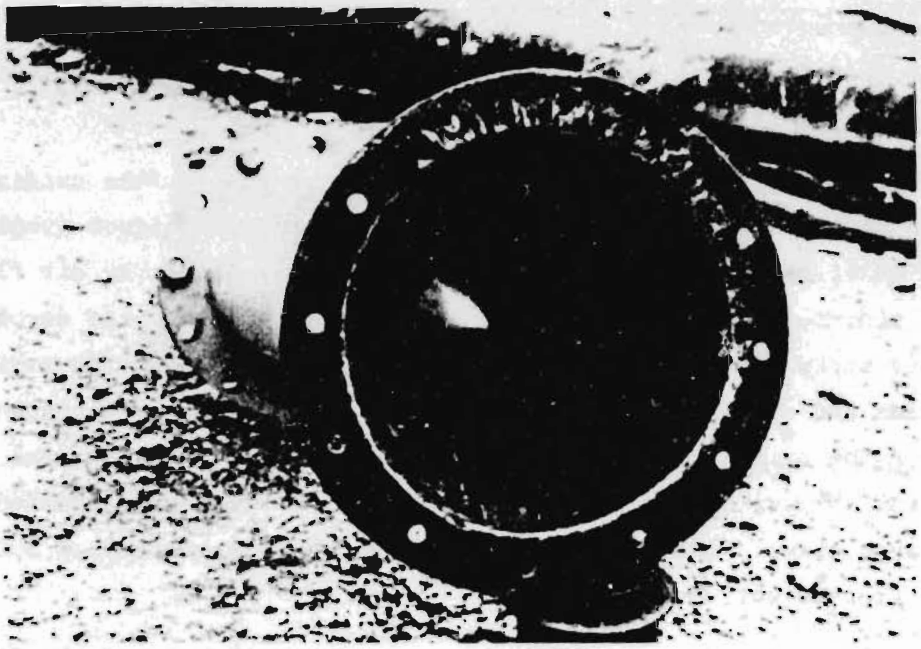


Figure 33. Photographs of the variable-throat venturi used on the Stretford plant.

An elbow joint connects the venturi contactor to the reactor. The reactor serves as a gas-liquid separator, collects the spent process liquor from the venturi, and provides holdup for completion of chemical reactions. The reactor has a liquid inventory of approximately 1060 liters.

The retort off-gas exited from the top of the reactor into the GKI blower suction line. The reactor discharge gas line was initially fitted with a baffle-type mist eliminator to minimize solution carryover. Near the end of the test program, a packed tower was fitted to the reactor outlet. The purpose of the packed tower was to increase the gas-liquid contact time, thereby increasing the H_2S removal efficiency. The packed tower was constructed of a three-meter long, 30-cm dia., steel pipe packed with 2.5-cm dia. Raschig rings. The process solution was injected countercurrent to the gas flow through the packed tower.

The packed tower is shown in Figure 34, and is the tall column located on top of the reaction vessel (on the left side of the photograph). The tube entering the packed tower near the top is the solution injection line. The variable throat venturi in the inlet line can be seen at the bottom of the photograph at the left hand edge.

The reduced process liquor flows from the reactor to the oxidizer. The function of the oxidizer is to reoxidize the Stretford liquor (replenish the reduced ADA), separate the sulfur product from the liquor by air flotation, strip bicarbonate formed in the process from the liquor (as carbon dioxide), and strip any ammonia absorbed from the gas stream. The stripped carbon dioxide and ammonia are removed from the process via an atmospheric vent stack in the oxidizer. Oxidation air is introduced into the base of the oxidation tank through a dispersion ring. The air is further dispersed into the liquid by a mixer. The oxidizer tank has a liquor inventory of 5,000 liters/hour (to the weir overflow).

The sulfur product is generated as a froth at the top of the oxidizer. This froth contains approximately seven percent (by weight) sulfur. The froth overflows a slurry weir into the slurry tank at a rate of approximately 38 liters (at design conditions). The slurry tank functions both as a slurry

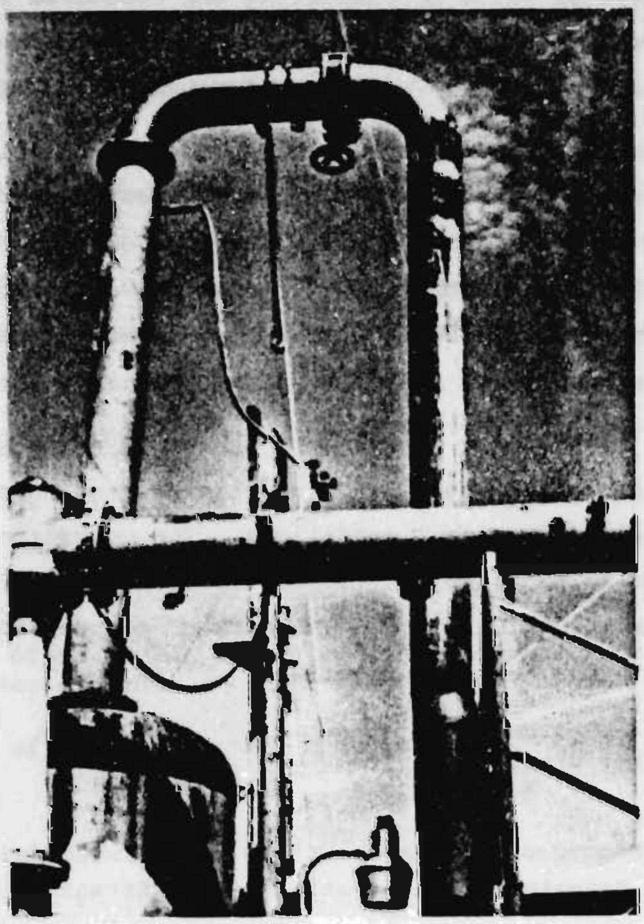


Figure 34. Packed tower installed at reaction vessel exit.

receiver and a decanting tank. The slurry tank is agitated and has a maximum liquid inventory of approximately 3400 liters.

The plant is also equipped with a pump tank that provides liquid surge capacity within the system while accommodating the recovered process liquor and the addition of makeup chemicals and makeup water. The pump tank is agitated and has a maximum liquid inventory of approximately 4,500 liters.

The pump tank is served by the solution feed pump, which delivers process liquor to the gas contactor. The liquor is routed through an electric coil solution heater before it enters the gas contactor. The solution heater allows the process liquor to contact the incoming gas at approximately the same temperature. This feature benefits the performance of the process with respect to chemical consumption, nonregenerative byproduct formation, and removal efficiency.

A modification was made to inject additional heat into the system, because of anticipated cold weather conditions. The compressed oxidizer air was originally cooled to near ambient temperatures in an aftercooler. This aftercooler was bypassed, which allowed the heat of compression to be added to the oxidizer, where the heat is essential.

3.2 STRETFORD PLANT OPERATIONS

3.2.1 Introduction

This section describes the operation of the Stretford pilot plant at the GKI site in Kamp Kerogen. In order to gain a complete understanding of the mechanics of H_2S removal by the Stretford process, a knowledge of the operating parameters and their effect on plant performance is required. This knowledge is also necessary for the development of full-scale designs based on the pilot plant experience. This section presents both the proposed and actual schedules of events, and summarizes the parameters maintained during the test program. These process parameter values and their influence on operations are discussed in detail in Section 3.3. Finally, operating problems are outlined, along with field-implemented corrective actions and some suggested alternatives.

3.2.2 Activities Schedule

Table 14 presents the comparison of projected and actual schedules. From the table, it is apparent that all activities did not proceed as planned. The most significant deviation was that the testing did not occur as a continuous series. GKI equipment failures, power outages, and sampling and analysis equipment malfunctions were the most frequent causes of delay during this test program.

Table 14 further shows that the planned unit upset was never performed. This step was eliminated due to the problems encountered in obtaining the desired H_2S removal efficiences. These equipment problems caused the expenditure of additional sampling crew man-hours that were not originally planned.

3.2.3 Summary of Operations

Startup of the Stretford pilot plant was achieved with a minimum of difficulty. From a mechanical standpoint, the unit worked well except for a few minor problems. These problems included the following:

- Failure of the solution heater due to corrosion of two of the heater elements.
- Failure of the slurry tank mixer motor.

Actual operations with oil shale off-gas being processed through the Stretford unit amounted to 204 hours. The test series time period totalled 255 hours. The total system operating time divided by total time available to operate was 80 percent. Of the total down time of 50 hours, 14 hours were due to system operating problems. The remaining 36 down time hours were due to GKI shut-downs. Excluding these 36 hours, the plant availability was 94 percent. The Stretford pilot plant run time for this program is summarized in Table 15 on a daily basis.

The test equipment malfunctions hindered the program's original goals, as discussed in Section 3.2.2. In spite of this, deliberate changes were made to the plant operating conditions, so that the effect of these changes could be documented. The aim of the work was to gather information on how different

TABLE 14. GEOKINETICS PROJECT SCHEDULE (1983/4)

Activity	Projected	Actual	No. of Personnel
Delivery of pilot plant	11/7/83	11/7/83	4
Assembly of pilot plant	11/8-11/83	11/8-11/83, 4/24-27/84	4
Connection of plumbing and electrical lines by GKI	11/8-11/83	4/24-27/84	4
Delivery of sampling equipment	4/30/84	4/30/84	7*
Plant startup/stabilization	5/1-2/84	5/3-4/84	7*
Continuous testing	5/3-7/84	5/5-11/84	7*
Deliberate system upset	5/8/84	--[†]	7*
Install and test packed tower	--	5/11-14/84	7*
Complete testing - evaluate recovery from system upset	5/9-13/84	--[§]	7*
Disassembly of pilot plant	5/14-16/84	5/14-16/84	5

* Includes three sampling and analysis technicians.

[†] System upset not conducted due to low initial H_2S removal efficiences

[§] Tests not run

TABLE 15. SUMMARY OF GKI ACCUMULATED RUN TIME

Date 1984	Hours Avail. for Operation		Hours of Operation		Downtime: Due to System		Downtime: Due to GKI		Comments
	Daily	Cum.	Daily	Cum.	Daily	Cum.	Daily	Cum.	
5/3	6	6	2	2	0	0	4	4	Plant stabilized. Begin shake down procedures. GKI shutdown.
5/4	24	30	8.5	10.5	0	0	15.5	19.5	Start up after maintenance on exhaust line.
5/5	24	54	24.0	34.5	0	0	0	19.5	Normal operation
5/6	24	78	24.0	58.5	0	0	0	19.5	Normal operation
5/7	24	102	16.75	75.25	0	0	7.25	26.75	GKI shutdown
5/8	24	126	18.25	93.5	0	0	5.75	32.50	GKI power failure due to system overpressure. High pressure drained solution in reaction vessel.
5/9	24	150	15.50	109.0	7.75	7.75	.75	33.25	Solution heater repair. GKI shutdown.
5/10	24	174	21.25	130.25	0	7.75	2.75	36.0	GKI shutdown
5/11	24	198	17.50	147.75	6.5	14.25	0	36.0	Installed packed column to improve gas/liquid contact.
5/12	24	222	24.0	171.75	0	14.25	0	36.0	Normal operation
5/13	24	246	24.0	195.75	0	14.25	0	36.0	Normal operation
5/14	8.75	254.75	8.75	204.5	0	14.25	0	36.0	GKI Power Failure. Final shutdown of Stretford testing.

operating parameters affected H_2S removal by the Stretford plant. The operating conditions maintained during this test program are discussed in detail in Section 3.3.2.

3.2.4 Unit Operating Conditions

This section gives a brief overview of the Stretford pilot plant operating conditions. A more complete discussion of these operating conditions is presented in Section 3.3.2.

A. Inlet Gas Conditions--

The inlet gas flow to the Stretford was initially measured by the use of a U-tube manometer in conjunction with an Accutube probe placed vertically in the inlet gas duct upstream of the gas/liquid contactor. The Accutube probe has two sets of four openings at various distances from the pipe centerline; one set faces upstream and the other faces downstream. The openings measure a velocity profile by comparing the high and low pressures observed by the upstream and downstream openings. The differential pressure, in inches of water, is displayed on the Capsuhelic gauge. Given this differential pressure, the gas flow is calculated by using the pressure reading, barometric pressure, gas temperature, internal pipe diameter, gas specific gravity, and an orifice constant.

During the final portion of the program, an S-type pitot tube was installed in place of the Accutube. The pitot tube was used in conjunction with both a U-tube manometer and a Capsuhelic differential pressure gauge. The switch from the Accutube to the pitot tube was required because of the failure of the Accutube.

The gas conditions encountered at GKI were similar to what was originally expected with the exception of lower H_2S levels. The originally planned H_2S concentrations of approximately 2000 ppm were not encountered during this program. The H_2S concentrations varied between 718 ppm and 2175 ppm, and averaged 1233 ppm during this program. The inlet gas temperatures remained within the expected range.

B. Plant Process Stream Conditions--

The two process streams of concern in the Stretford process are the liquor stream and the oxidizer air stream. The flow rates of both streams were measured by making use of in-line orifice plates to establish a differential pressure between the upstream and downstream faces. The differential pressure measured was sensed by a Meriam bellows-type indicator calibrated with the orifice constant of the plate used. Temperature and pressure are measured with in-line thermometers and pressure gauges.

The liquor stream characteristics are very important in operating and diagnosing the performance levels of the system. The solution flow rate varied from a minimum of 0.5 liter/sec to a maximum of 2.9 liter/sec. The solution temperature set point was approximately 43°C. This solution temperature provides a good balance between reaction kinetics and unwanted byproduct formation (with a corresponding chemical loss).

C. Chemical Concentrations and Additive Rates--

The three primary chemical ingredients required in a Stretford solution are a carbonate source, a vanadium source, and the 2:7 isomer of ADA. Sodium carbonate was used as the carbonate source, a 6.3 volume percent sodium metavanadate solution (ELVAN K) was used as the vanadium source, and ELVADA was used as the source of the 2:7 isomer of ADA. In addition to these ingredients, optional chemicals can be added to improve some aspect of plant performance. These optional chemicals included an antifoaming agent to control the foaming tendency of Stretford solution and a combination flotation aid/biocide (ELVAFORM). The purpose of the ELAFORM is to control the microbiological activity in the Stretford solution and to assist in sulfur froth formation. All of these chemicals were included in the Stretford solution used at GKI.

PEI's proposed concentrations of the primary chemicals in the Stretford solution for this test series were Na_2CO_3 - 25.0 g/liter, ADA - 9.6 g/liter, and $NaVO_3$ - 3.12 g/liter (as vanadium). These concentrations varied daily as make-up water and chemicals were added. In order to maintain the desired concentrations of the primary chemicals in the Stretford solution, a series of chemical analyses were performed on a regular basis. A summary of the chemical analysis test results is presented in Table 16. These results are discussed in detail in Section 3.3.2.

The pH of the Stretford solution was kept high to increase the vanadium solubility and H_2S removal. The pH level fluctuated during this test series, due to the daily addition of sodium carbonate. The pH value ranged between 12.3 and 7.4 during the GKI test program. This compares to a system start-up pH of 9.0.

The oxidizer air stream in the oxidizer tank is used to regenerate the reduced Stretford solution and to float the elemental sulfur into the slurry tank as a froth. The air also strips the bicarbonate and ammonia from the solution. The compressor was originally set up to route the air though an aftercooler to remove the heat of compression. The aftercooler was bypassed during this test series in order to help maintain the Stretford solution temperature at the desired level of 43°C. This was thought to be necessary due to the expected low ambient temperatures.

The oxidizer air flow was varied between 0.017 and 0.042 Sm^3/s during the course of the testing. Previous tests showed that flows over 0.038 Sm^3/s scfm were excessive, while flows in the range 0.021-0.038 Sm^3/s were acceptable for oxidation purposes.

When foaming occurred in the oxidizer task (attributed to condensed oil in the scrubbing solution), the air flow was reduced to correct the problem. Excessive foaming ultimately caused the recirculation of a solution that was not totally reoxidized, which also reduced the H_2S removal efficiency.

D. Consumption of Utilities--

1. Electric--The motor control center of the pilot plant was equipped with a 480-V, 300-amp main breaker indicating a power demand of 144 kW. Actual consumption, even at full loads, was less than this. Table 17 presents a breakdown of the current drawn by the various electrical components of the system during operation. Actual demand was equal to 85.4 kW. Based on the hours available for operating (205 hours), the total electrical consumption was 17,500 kWh.

TABLE 16. SUMMARY OF PRIMARY CHEMICAL ANALYSES

Test	High Value	Low Value	Number of Tests
Specific carbonate, g/liter	49.3	10.6	10
Vanadium, g/liter	3.5	2.1	5
ADA, g/liter	11.0	4.6	7
pH	12.3	7.4	49
Oxidation, rel. mv	+90	-87	49
Thiosulfate, g/liter	1.05	1.05	1

TABLE 17. ELECTRICAL REQUIREMENT FOR STRETFORD EQUIPMENT
(Amperes)

Equipment	Current Overload Rating*	Current Demand When Operating†	Current Demand-This Program	Current Breaker Rating
Gas blower	60.1	85.0	0	100
Solution heater	§	51.0	43.0 **	60
Solution pump	9.9	7.1	7.1	20
Condensate pump	0.7	1.7	0	15
Pump tank agitator	2.1	3.1	3.1	15
Slurry pump	1.4	2.4	2.4	15
Oxidizer agitator	9.9	13.6	13.6	20
Slurry tank agitator	1.7	2.4	0	15
Air compressor	60.1	85.0	85.0	100
Control transformer	15.0#	14.0	14.0	15
Heat trace	15.0#	10.0	0	15
Totals		275.3	163.3	390

* Per line -- multiply by 1.7 for total three-phase current demand

† 480 V

§ Variable with manually adjusted limit switch

\# Ratings given for circuit breaker

** Time weighted average

Electricity was produced on-site by diesel engine powered generators. Several power failures were experienced during the test.

2. Water--Water was added to the Stretford solution to replenish liquid levels lost because of evaporation and carryover in the outlet gas. The sulfur slurry (25 percent solids) purge which is usually a source of water loss was required only once during these tests. After the initial charge of 9,500 liters, nine water additions were necessary. Total water usage was about 17,000 liters.

E. Sulfur Production--

The pilot plant was designed to recover an average of 2.6 kg. of elemental sulfur per hour, or 65 kg per day. The sulfur was collected in the slurry tank, where it settled to the bottom. The clear liquid layer was recycled back into the process, and a portion of the slurry was drained into 210 liter drums once during the course of the test program. Precise measurements of the solids contents were not made. Slurry samples were taken in a graduated cylinder and the solids were allowed to settle. The solids content was then estimated by the ratio of the volume of solids in the cylinder to the total sample volume.

The exact amount of elemental sulfur produced is unknown; however, it is estimated that approximately 300 kg. of sulfur were recovered during the test program. The average values for gas flow rates (in standard cubic feet per minute) and the amount of H_2S removed (in parts per million by volume) were determined for each day for which H_2S concentration data were available. The data used to calculate the elemental sulfur production are contained in Table 18. Based on these numbers and their corresponding durations, the total amount of H_2S removed was calculated. The weight of H_2S removed was calculated and multiplied by the ratio of the molecular weight of sulfur to the molecular weight of H_2S to find the amount of elemental sulfur produced. This equated to a production rate of approximately 1.72 kg/hr or 41 kg/day (based on a 24-hour day). Thus the estimated sulfur production was only 66 percent of the design value. If the program average gas flow rate had been at the design level of 0.70 Sm^3/s instead of an actual rate of 0.28 Sm^3/s, the design sulfur removal rates may have been met. Lower than expected incoming

TABLE 18. DETERMINATION OF ELEMENTAL SULFUR PRODUCTION

Date 1984	Average H_2S Concentration, ppmV			Gas Flow gm^3/s	ΔH_2S Flow Sm^3/s	ΔH_2S Flow kg/hr	Hours On Line	ΔH_2S kg	Sulfur Produced kg
	Inlet	Outlet	Δ						
5/4	N/A*	N/A	--	0.344	--	--	8.5	--	--
5/5	1584	447	1137	0.253	0.0003	1.49	24	35.6	33.5
5/6	1719	261	1458	0.235	0.0003	1.77	24	42.4	39.9
5/7	N/A	N/A	--	0.221	--	--	16.75	--	--
5/8	1377	244	1133	0.476	0.0005	2.76	18.25	50.8	47.8
5/9	1638	278	1390	0.320	0.0004	2.31	15.5	35.5	33.5
5/10	1314	248	1066	0.246	0.0003	1.36	21.25	28.8	27.0
5/11	1144	228	916	0.281	0.0003	1.31	17.5	23.2	21.9
5/12	1141	10	1131	0.266†	0.0003	1.54	24	37.2	35.0
5/13	981	131	850	0.251	0.0002	1.09	24	26.4	24.9
5/14	1121	92	1029	0.209	0.0002	1.13	8.75	9.7	9.1
Total	--	--	--	--	--	--	177.25§	--	273.0

* N/A - data not available

† Average of 5/11 and 5/13 data - 5/12 data not available

§ Total of hours when H_2S concentration data were available.

H_2S concentrations also contributed to the lower than expected elemental sulfur production rates.

During this test program, the slurry tank was drained once during the test 417 liters removed) and again after the test. The sulfur content of the drained solution was not determined as part of this test program.

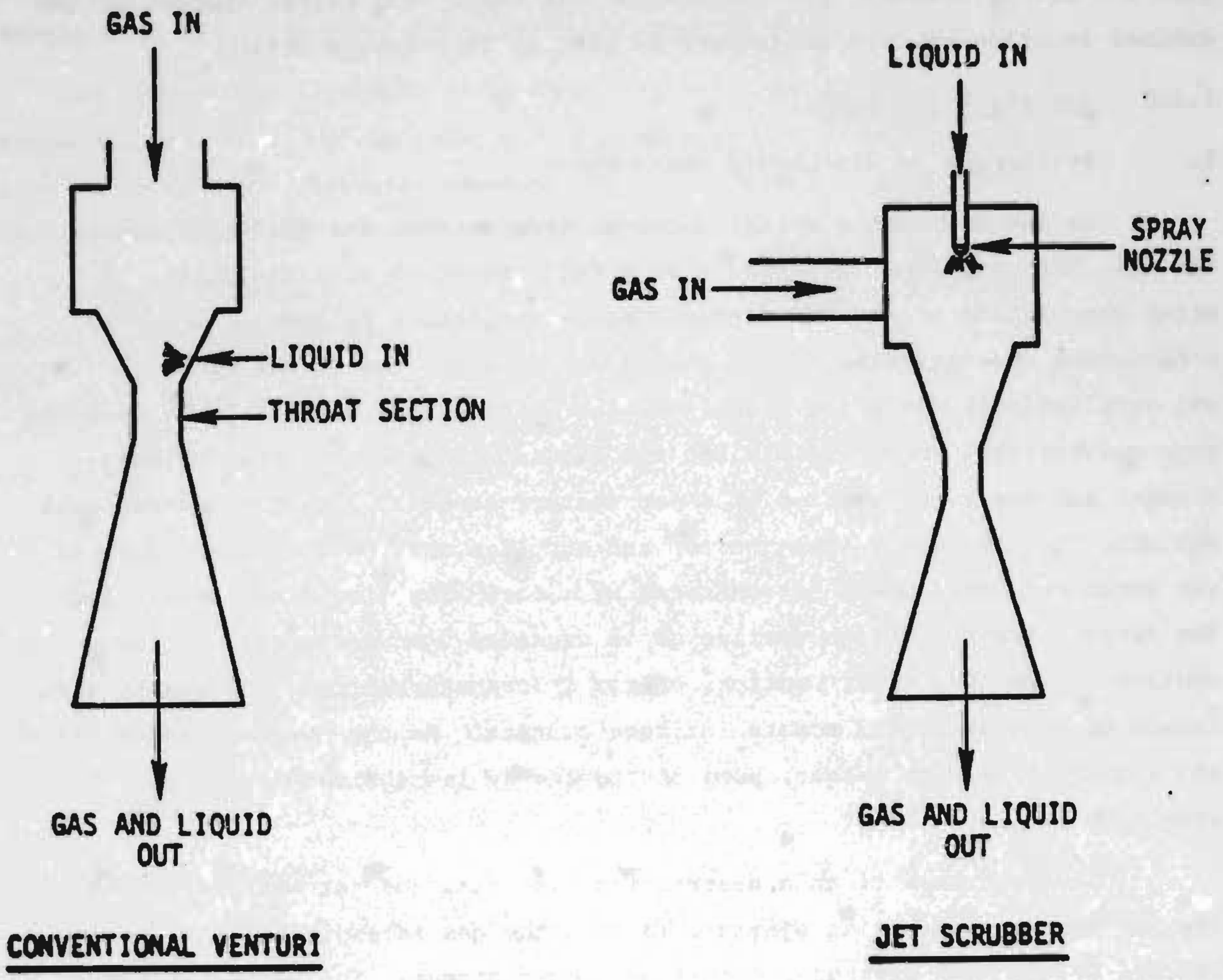
3.2.5 Operating Problems

A. Performace of Gas-Liquid Contactor--

On the GKI test a variable throat area venturi was used as a contactor. This replaced the venturi originally supplied with the plant. A brief description of the two venturi design variations follows in order to enhance the understanding of the design and intended use of the contactor that was supplied with the pilot plant. Figure 35 shows the difference between the more conventional venturi (in which the liquid is dispersed into the gas stream) and the configuration of a jet venturi scrubber. In the conventional venturi, the gas enters from the top and supplies most of the power input to the scrubber. This power is generated by a fan. The liquid is pumped into the venturi throat through nozzles or is cascaded down the inside of the contactor. In the throat section, energy is transferred from the gas to the liquid to atomize it and create intimate contact. As the combination of gas and liquid leaves the throat, some of the energy is regained by the gas stream.

Although much of this description also fits the jet venturi scrubber, the jet venturi acts as an ejector, in that the gas is aspirated into the venturi by the high-pressure, high-flow liquid stream. The liquid pressures in jet venturi applications are usually 7000 to 17,500 g/cm^2.

The design of the contactor that was supplied with this pilot plant more closely resembles the jet scrubber design. The liquid enters through a nozzle at the top, and the gas enters from the side. The gas was designed to supply the motivating force, with an inlet pressure of one to five psi from a booster blower. The liquid is supplied from a pump with a maximum delivery pressure of 3500 g/cm^2. This pressure distribution is not a representative one for H_2S removal by a jet venturi scrubber.



CONVENTIONAL VENTURI

JET SCRUBBER

Figure 35. Conventional venturi versus jet scrubber venturi.

As mentioned previously, the gas-liquid contactor used during this program was a variable throat venturi. When the throat plug was lowered completely, the venturi throat was free of obstruction. The venturi throat diameter was 15 cm at this condition. When the throat plug was fully raised, the throat area was reduced so that the equivalent diameter was 7.5 cm.

The venturi was designed to operate at a gas flow of up to approximately 0.42 m^3/s and to receive a gas pressurized to between 105 and 140 g/cm^2. Lower than expected pressures may have inhibited gas/liquid contact causing lower removal efficiencies than previously achieved.

As mentioned previously, a packed tower was added to the reactor vessel gas outlet near the end of the program. This tower was installed to enhance the system H_2S removal efficiency, which had peaked at about 95 percent while using only the venturi scrubber. This modification gave H_2S removal rates in excess of 99 percent.

B. Loss of Solution Heat--

The design of this pilot plant included a trim heater for system startup and temperature maintenance. A continuous heater was deemed unnecessary because of the high inlet gas temperature (60°C) and saturated conditions. Even though these conditions were approached at GKI, the evening ambient temperatures and moisture conditions were such that significant quantities of moisture evaporated from the system solution tanks. A cover was fitted to the pump tank, while the slurry tank remained uncovered. During the initial portion of the testing, the solution loss averaged about 30 liters per hour.

The failure of one of the heater elements during the test program required that the element be bypassed. This reduced the heating capacity by one-third and resulted in a corresponding increase in the time necessary to bring the system temperature back to the desired level following the addition of water to the system.

This shortcoming became apparent following the installation of the packed tower. When installing the packed tower, the mist eliminator was inadvertently left out of the system. The lack of the mist eliminator, combined with the installation of the packed tower, resulted in a system solution loss of about 155 liters per hour. The required amounts of cold water makeup resulted in low solution temperatures during much of the testing with the spray tower.

To maintain the solution temperature, on future tests the solution heater should be replaced with a larger capacity heater to reduce the system recovery time.

C. Sulfur Flotation--

One of the major problems encountered at GKI was the lack of sulfur flotation in the oxidizer tank. The system showed good sulfur flotation from its startup on May 4, 1984 through May 10, 1984. At that time, a major system upset occurred when the oxidizer began foaming out of control. The foaming was brought under control by the addition of an antifoaming agent. Once the foaming was under control, a flotation aid was added to the system. This did not, however, solve the problem. Various additions of the flotation aid were tried throughout the remainder of the program, along with varying the oxidizer air flow rates. None of these changes resulted in improved sulfur flotation.

D. Solution Foaming--

As mentioned above, one of the major problems encountered at GKI was excessive foaming in the oxidizer. During the May 10 upset, the antifoam agent was added at frequent intervals until the foaming was brought under control. During this time, the oxidizer air flow was reduced in an effort to reduce the foaming. In order to keep up with the flow of foam, a larger pulley was fitted to the slurry pump. This increased the slurry flow rate to the oxidizer tank from 8 liters/min to 40 liters/min and was necessary to prevent the slurry tank from overflowing.

The procedures outlined above are not solutions to the problem of excessive foaming, but rather are only a temporary treatment.

The cause of excessive foaming is not known; however, it is possible that hydrocarbon (oil mist) carryover in the retort off-gas may have been responsible. It is believed that oil mist carryover may have occured when the knock-out drum on the blower skid was completely filled. During that period, all of the oil normally collected in the knock-out drum would have been carried over to the Stretford plant. (Referring to Figure 4(a), the horizontal inlet line continues to the Stretford process while a vertical pipe is 'T'ed off the inlet line and runs vertically down to the knockout tank. There is no gas flow in the vertical line or through the knockout tank. If the knockout tank and vertical drain line fill up with condensed liquid, the remaining condensed liquid will drain into the Stretford process.) This would explain the sudden nature of the upset. The rate of liquid accumulation in the knock-out drum was much faster than anticipated. The use of a prequench or saturation chamber upstream of the gas/liquid contactor(s) might control this problem by scrubbing out the condensed hydrocarbon before the gas reaches the venturi contactor.

3.3 ANALYSIS OF PERFORMANCE

The process streams of the Stretford pilot plant were tested for selected species to evaluate removal efficiencies and interferences with process chemistry. Additionally, the influent and effluent emissions were characterized. This section details the characterization of the gaseous and liquid components and summarizes the program test results.

3.3.1 Program Test Results

The Stretford pilot plant process streams were tested for selected species in order to measure removal efficiences, evaluate interference with process chemistry, compute material balances, and characterize pollutants in the influent and effluent. The two process streams of primary concern for this Stretford test program were the retort off-gas and the Stretford solution. This section discusses the results of the analyses performed on both of the process streams. The results of the gas analyses are discussed in the first part of this section, while the second part contains the results of the Stretford solution analyses.

Table 19 summarizes the operating conditions maintained during this test program. This table contains the results of both the gas analyses and the solution analyses. These gas and solution test results are discussed in detail in the remainder of this section. Some of the test results presented

TABLE 19. STRETFORD OPERATING CONDITIONS MAINTAINED DURING GEOKINETIC TEST PROGRAM

Date 1984	Time	Gas Contct Device *	Gas Flow Rate Sm^3/s	Gas Out Temp °C	Gas Inlt Pres mm Hg	Inlt H_2S Conc ppmV	Out H_2S Conc ppmV	Removal Eff %	Sol Flow Rate SL/S	Sol Htr T in °C	Sol Htr T out °C	Oxidizer Air Flow Sm^3/s	Oxidizer Motor Curr amps	ADA Conc kg/m^3	Van. Conc kg/m^3	Carb. Conc kg/m^3	Thio-sul. Conc kg/m^3	pH	Oxidation Potential mv	Comments
5/3	17:00	V	-	38	1.27	OOS	OOS	--	1.29	43	45	0.023	7.4	9.6	3.1	24.4	0	--	--	Initial chemical charge
	18:15	V		38	34.2	OOS	OOS	--	1.42	43	45	0.022	7.5	9.5	3.1	24.2	0	--	--	Gas flow starts
	18:35	V	0.214	43	34.2	OOS	OOS	--	1.48	43	46	0.023	7.5	9.5	3.1	24.1	0	--	--	Close venturi
5/4	14:35	V	0	43	0.0	OOS	OOS	--	1.14	47	51	0.021	-	7.8	2.5	20.4	0	--	--	
	15:50	V	0.338	43	34.2	OOS	OOS	--	1.36	48	44	0.023	7.8	7.7	2.4	20.2	0.1	--	--	
	16:15	V	0.338	43	32.9	OOS	OOS	--	1.37	48	45	0.027	7.8	7.7	2.4	20.1	0.1	--	--	
	17:30	V	0.666	44	51.9	OOS	OOS	--	1.43	48	44	0.027	7.7	7.6	2.4	19.9	0.1	--	--	
	17:45	V	-	43	55.7	OOS	OOS	--	-	-	-	0.026	7.6	7.6	2.4	19.8	0.1	--	--	
	17:55	V	0.319	43	36.7	OOS	OOS	--	1.47	47	44	0.027	7.6	7.6	2.3	19.8	0.1	--	--	
	18:23	V	0.301	41	35.4	OOS	OOS	--	1.42	46	42	0.026	7.5	7.5	2.3	19.7	0.1	—	—	
	19:05	V	0.302	41	35.4	OOS	OOS	--	1.42	46	41	0.027	7.5	7.5	2.3	19.6	0.1	—	—	
	20:50	V	0.271	38	35.4	OOS	OOS	--	1.36	38	36	0.026	7.5	9.2	2.3	19.3	0.1	—	—	
	22:30	V	0.279	41	35.4	OOS	OOS	--	1.34	41	42	0.025	7.4	9.0	2.8	23.7	0.1	—	—	
	23:30	V	0.269	42	35.4	OOS	OOS	--	1.52	42	43	0.025	7.4	8.9	2.8	23.6	0.1	—	—	
5/5	00:30	V	0.269	42	35.4	OOS	OOS	--	1.45	43	44	0.029	7.4	8.9	2.8	23.4	0.1	9.9	-81	
	01:30	V	0.234	43	35.4	OOS	OOS	--	1.46	44	44	0.029	7.4	8.8	2.8	23.2	0.1	9.9	-57	
	02:25	V	0.254	44	32.9	OOS	OOS	--	1.46	45	46	0.029	7.4	8.7	2.7	23.0	0.1	10.0	-32	
	03:40	V	0.241	40	30.4	OOS	OOS	--	1.48	44	40	0.036	7.5	8.6	2.7	22.8	0.1	10.0	-8	
	04:30	V	0.201	-	35.4	OOS	OOS	--	1.48	44	46	0.037	7.4	8.5	2.7	22.5	0.1	9.9	+15	
	05:40	V	0.190	42	34.5	OOS	OOS	--	1.48	44	44	0.037	7.4	8.4	2.6	22.0	0.1	9.8	+38	
	06:30	V	0.208	43	34.5	OOS	OOS	--	1.48	45	45	0.036	7.4	8.4	2.6	21.6	0.1	9.7	+60	
	07:10	V	0.190	42	35.4	OOS	OOS	--	1.48	45	45	0.036	7.4	8.3	2.6	21.3	0.2	9.6	+83	
	07:55	V	0.191	42	35.4	OOS	OOS	--	1.55	45	44	0.036	7.4	8.3	2.6	21.0	0.2	9.6	+73	
	08:20	V	0.312	44	32.9	OOS	OOS	--	1.43	45	46	0.028	7.4	8.2	2.5	20.9	0.2	9.5	+62	
	09:00	V	0.327	46	29.9	OOS	OOS	--	1.42	46	47	0.025	7.4	8.2	2.5	20.6	0.2	9.5	+52	
	09:40	V	0.333	46	30.4	OOS	OOS	--	1.53	47	48	0.028	7.4	8.1	2.5	20.3	0.2	9.5	+41	
	10:14	V	0.327	48	30.4	OOS	OOS	--	1.64	47	48	0.031	7.4	8.1	2.5	20.1	0.2	9.4	+31	
	10:55	V	0.300	43	30.9	OOS	OOS	--	1.64	47	44	0.032	7.4	8.0	2.5	19.8	0.2	9.4	+20	
	12:30	V	0.300	43	31.1	OOS	OOS	--	1.58	47	43	0.033	7.4	7.9	2.4	19.1	0.2	9.4	+10	
	14:30	V	0.300	42	30.4	1608	--	--	1.61	44	42	0.033	7.5	7.7	2.4	18.3	0.2	9.3	-1	
	15:45	V	0.282	42	31.1	1588	488		1.81	45	42	0.035	7.5	7.6	2.3	17.8	0.2	9.3	-13	
	16:30	V	0.301	41	30.9	OOS	OOS	--	1.82	44	42	0.036	7.4	7.6	2.3	17.4	0.2	9.6	-1	
	16:50	V	0.231	41	17.7	OOS	OOS	--	1.91	44	41	0.036	7.5	7.6	2.3	17.3	0.2	9.9	+9	
	17:05	V	0.188	41	15.2	OOS	OOS	--	1.92	44	40	0.036	7.5	7.6	2.3	17.2	0.2	10.2	+18	
	17:35	V	0.188	40	15.2	OOS	385	--	1.93	43	41	0.036	7.5	7.5	2.3	17.0	0.2	10.5	+28	
	18:05	V	0.190	40	27.8	1617	401	75.2	1.93	43	40	0.036	7.5	7.5	2.3	16.8	0.2	10.8	+38	
	18:55	V	0.255	41	30.4	1579	400	74.7	1.91	43	43	0.035	7.3	7.5	2.2	16.4	0.2	10.5	+19	
	20:30	V	0.233	43	30.4	1633	429	73.7	1.79	44	44	0.029	7.4	7.5	2.2	15.8	0.2	10.2	0	
	21:45	V	0.256	40	30.4	1571	595	62.1	1.77	43	43	0.029	7.4	8.7	2.5	15.3	0.2	9.9	-21	
	22:35	V	0.269	43	30.4	1322	639	51.7	1.86	46	44	0.026	7.3	8.7	2.4	14.9	0.2	9.9	-15	
	23:30	V	0.269	44	32.9	1618	626	61.3	1.54	47	47	0.026	7.3	8.7	2.4	14.5	0.2	9.9	-8	

(continued)

OOS = out of service
DNA = data not available
Cal = calibration

V = venturi
V&T = venturi plus packed tower

TABLE 19. (Continued)

Date 1984	Time	Gas Contct Device *	Gas Flow Rate Sm³/s	Gas Out Temp °C	Gas Inlt Pres mm Hg	Inlt H_2S Conc ppmV	Out H_2S Conc ppmV	Removal Eff %	Sol Flow Rate SL/S	Sol Htr T in °C	Sol Htr T out °C	Oxidizer Air Flow Sm³/s	Oxidizer Motor Curr amps	ADA Conc kg/m³	Van. Conc kg/m³	Carb. Conc kg/m³	Thio-sul. Conc kg/m³	pH	Oxidation Potential mv	Comments
5/6	00:30	V	0.272	44	29.3	1623	443	72.7	1.60	47	47	0.026	7.3	8.7	2.4	14.1	0.2	9.8	-2	
	01:30	V	0.192	38	29.9	2169	444	79.5	1.48	47	41	0.026	7.4	8.6	2.4	13.7	0.2	9.8	+5	
	02:30	V	0.327	44	24.3	2018	195	90.3	1.48	46	46	0.025	7.4	8.6	2.3	13.3	0.2	9.1	+4	
	03:30	V	0.254	45	30.4	1886	125	93.4	1.51	46	46	0.024	7.3	8.6	2.3	12.9	0.2	8.4	+2	
	04:25	V	0.189	46	30.4	1741	100	94.3	1.48	47	47	0.024	7.3	8.5	2.3	12.5	0.3	7.7	+1	
	05:30	V	0.189	47	30.9	1590	101	93.7	1.50	48	47	0.026	7.3	8.5	2.2	12.0	0.3	7.0	0	
	06:30	V	0.198	47	30.9	OOS	OOS	--	1.49	48	46	0.026	7.3	8.5	2.2	11.6	0.3	7.4	-4	
	07:10	V	0.231	46	29.6	OOS	OOS	--	1.50	48	47	0.026	7.4	8.5	2.2	11.6	0.3	7.7	-9	
	07:58	V	0.240	42	29.3	Cal	Cal	--	1.57	47	42	0.026	7.5	8.4	2.2	11.7	0.3	8.1	-13	
	08:29	V	0.241	41	30.6	Cal	Cal	--	1.58	47	41	0.026	7.6	8.4	2.2	11.7	0.3	8.4	-18	
	09:03	V	0.241	43	31.6	Cal	Cal	--	1.71	46	44	0.021	7.4	8.4	2.1	11.7	0.3	8.8	-22	
	09:27	V	0.252	41	30.1	Cal	Cal	--	1.74	46	44	0.029	7.3	8.4	2.1	11.7	0.3	9.1	-27	
	10:32	V	0.317	44	30.6	Cal	Cal	--	1.45	44	46	0.027	7.3	8.4	2.1	11.8	0.3	9.5	-31	
	11:52	V	0.346	41	31.6	Cal	Cal	--	1.48	44	42	0.027	7.3	8.3	2.1	11.8	0.3	9.5	-29	
	12:31	V	0.248	41	30.1	Cal	Cal	--	1.50	44	47	0.027	7.2	8.3	2.1	11.8	0.3	9.5	-28	
	13:05	V	0.270	41	30.9	Cal	Cal	--	1.48	44	41	0.030	7.3	8.3	2.1	11.9	0.3	9.4	-26	
	13:31	V	0.242	43	37.4	Cal	Cal	--	1.50	44	46	0.031	7.2	8.3	2.1	11.9	0.3	9.4	-25	
	14:02	V	0.297	39	36.9	Cal	Cal	--	1.55	43	39	0.032	7.3	8.3	2.1	11.9	0.3	9.5	-10	
	14:34	V	0.296	42	37.2	Cal	Cal	--	1.58	43	44	0.034	7.3	8.3	2.1	11.9	0.3	9.5	+4	
	15:56	V	0.201	42	39.0	OOS	OOS	--	1.59	43	43	0.034	7.3	8.2	2.1	12.0	0.3	9.6	+19	Problems w/sample
						OOS	OOS													dilution system
	17:30	V	0.189	41	17.7	OOS	OOS	--	1.29	43	46	0.028	7.3	8.2	2.9	14.5	0.3	9.6	+33	Chemical addition
	17:50	V	0.191	41	30.4	OOS	OOS	--	1.29	44	46	0.029	7.3	8.2	2.9	14.5	0.3	9.7	+48	Problem w/sample
						OOS	OOS								2.9		0.3			dilution system
	18:30	V	0.190	42	30.4	OOS	OOS	--	1.26	44	46	0.027	7.3	8.1	2.9	14.5	0.3	10.0	+32	
	19:12	V	0.191	41	30.4	OOS	OOS	--	1.26	44	46	0.026	7.3	8.1	2.9	14.6	0.3	10.2	+16	
	20:05	V	0.191	41	31.6	OOS	OOS	--	1.26	44	46	0.026	7.3	8.1	2.9	14.6	0.3	10.5	0	
	21:05	V	0.209	41	27.8	OOS	OOS	--	1.26	44	46	0.026	7.2	8.1	2.9	14.7	0.3	10.7	-16	
	22:02	V	0.199	43	29.1	1367	307	78.0	1.26	46	46	0.026	7.2	8.0	2.9	14.7	0.3	10.4	-13	Inlet H_2S reading
															2.9		0.3			invalid
	23:06	V	0.190	43	27.8	OOS	OOS	--	1.51	46	46	0.026	7.3	8.0	2.9	14.7	0.3	10.1	-9	
5/7	00:21	V	0.201	43	32.9	OOS	OOS	--	1.53	47	46	0.026	7.3	8.0	2.9	14.8	0.3	9.9	-6	
	01:20	V	0.171	43	30.9	OOS	OOS	--	1.55	43	46	0.025	7.3	8.0	2.9	14.9	0.4	9.6	-2	
	02:30	V	0.200	43	30.4	OOS	OOS	--	1.55	47	46	0.025	7.2	7.9	2.9	14.9	0.4	9.3	+1	
	03:30	V	0.191	43	30.4	OOS	OOS	--	1.55	47	46	0.025	7.2	7.9	2.9	15.0	0.4	9.3	-1	
	04:30	V	0.191	43	30.4	OOS	OOS	--	1.59	47	46	0.026	7.2	7.9	2.9	15.0	0.4	9.3	-3	
	05:30	V	0.190	44	29.3	OOS	OOS	--	1.58	47	46	0.026	7.2	7.8	2.9	15.1	0.4	9.3	-5	
	06:30	V	0.170	44	29.9	OOS	OOS	--	1.58	47	46	0.026	7.2	7.8	2.9	15.2	0.4	9.4	-8	
	07:12	V	0.191	44	29.3	OOS	OOS	--	1.58	47	46	0.026	7.3	7.8	2.9	15.1	0.4	9.4	-11	
	07:39	V	0.181	44	29.3	OOS	OOS	--	1.57	47	47	0.026	7.3	7.8	2.9	15.0	0.4	9.5	-14	
	08:10	V	--	44	29.6	OOS	OOS	--	1.58	47	46	0.028	7.3	7.8	2.9	14.9	0.4	9.5	-17	
	16:18	V	0.274	38	32.9	Cal	Cal	--	1.55	38	36	0.031	7.4	6.8	2.9	13.5	0.4	9.5	-21	Calibration still in progress

(Continued)

TABLE 19. (Continued)

												Oxidizer								
Date 1984	Time	Gas Contct Device *	Gas Flow Rate Sm^3/s	Gas Out Temp °C	Gas Inlt Pres mm H_g	Inlt H_2S Conc ppmV	Out H_2S Conc ppmV	Removal Eff %	Sol Flow Rate SL/S	Sol Htr T in °C	Sol Htr T out °C	Air Flow Sm^3/s	Motor Curr amps	ADA Conc kg/m^3	Van. Conc kg/m^3	Carb. Conc kg/m^3	Thio-sul. Conc kg/m^3	pH	Oxidation Potential mv	Comments
5/7	17:00	V	0.306	41	40.5	Cal	Cal	--	1.52	38	40	0.031	7.4	10.5	3.3	16.8	0.4	9.5	-25	Calibration complete
	18:31	V	0.194	42	45.5	OOS	OOS	--	1.42	39	42	0.032	7.4	10.3	3.3	16.5	0.4	9.6	-28	Sample problems
	19:27	V	0.261	43	48.1	OOS	504	--	1.57	42	44	0.027	7.4	10.2	3.3	16.4	0.4	9.6	-32	Sample problems
	20:20	V	0.276	43	53.6	OOS	652	--	1.52	43	44	0.029	7.4	10.1	3.3	16.2	0.4	9.8	-41	Sample problems
	21:21	V	0.276	46	60.1	763	282	63.0	1.67	46	46	0.039	7.5	10.0	3.3	16.0	0.5	10.0	-50	Sample system ok
	22:02	V	0.206	43	65.8	1157	343	70.4	1.64	47	46	0.038	7.4	9.9	3.3	15.9	0.5	9.9	-37	
	22:50	V	0.219	36	68.3	1140	OOS	--	1.64	47	46	0.038	7.4	9.8	3.3	15.8	0.5	9.8	-24	No outlet data available
	23:20	V	0.286	30	70.8	1015	OOS	--	1.64	47	46	0.037	7.4	9.7	3.3	15.7	0.5	9.8	-12	No outlet data available
5/8	00:30	V	0.398	43	79.9	DNA	DNA	--	26.4	47	46	0.037	7.3	9.6	3.3	15.5	0.5	9.7	+1	Data not available
	01:30	V	0.455	45	89.1	DNA	DNA	--	1.64	46	46	0.037	7.3	9.5	3.3	15.3	0.5	9.6	+14	Data not available
	06:30	V	0.478	44	91.1	DNA	DNA	--	1.64	47	45	0.037	7.3	9.3	3.3	15.1	0.5	9.5	+27	Data not available
	03:30	V	0.569	44	110.8	DNA	DNA	--	1.62	47	45	0.037	7.3	9.2	3.3	14.9	0.5	9.5	+12	Data not available
	04:30	V	0.588	44	101.2	DNA	DNA	--	1.63	47	45	0.037	7.3	9.1	3.3	14.8	0.5	9.5	-3	Data not available
	05:30	V	0.641	43	106.3	DNA	DNA	--	1.47	46	44	0.033	7.4	9.0	3.3	14.6	0.5	9.5	-17	Data not available
	06:30	V	0.733	42	108.3	DNA	DNA	--	1.48	46	44	0.034	7.3	8.8	3.3	14.4	0.5	9.5	-32	Data not available
	07:05	V	0.761	43	109.0	DNA	DNA	--	1.48	46	44	0.034	7.3	8.8	3.3	14.5	0.5	9.5	-26	Data not available
	07:31	V	0.789	43	111.3	DNA	DNA	--	1.49	46	46	0.034	7.4	8.7	3.3	14.5	0.5	9.5	-20	Data not available
	08:00	V	0.641	44	233.0	DNA	DNA	--	1.42	46	46	0.034	7.2	8.6	3.3	14.6	0.5	9.5	-14	Data not available
	13:00	V	--	40	31.4	Cal	Cal	--	--	--	--	0.033	7.2	8.9	3.3	29.5	0.5	9.2	-18	Calibration
	13:05	V	0.360	41	31.1	Cal	Cal	--	1.60	43	43	0.033	7.2	8.9	3.3	29.5	0.5	9.0	-22	Calibration
	13:45	V	0.419	41	23.5	Cal	Cal	--	1.60	42	42	0.034	7.2	8.8	3.3	29.6	0.5	8.7	-26	Calibration
	14:05	V	0.273	36	24.0	Cal	Cal	--	1.60	42	42	0.034	7.3	8.8	3.3	29.6	0.5	8.5	-30	Calibration
	15:10	V	0.240	41	51.4	Cal	Cal	--	1.60	41	41	0.033	7.2	8.6	3.3	29.7	0.5	8.2	-33	Calibration
	15:40	V	--	41	122.2	Cal	Cal	--	1.52	42	41	0.033	7.1	8.6	3.3	2918	0.5	7.9	-37	Calibration
	16:28	V	0.211	43	101.2	Cal	Cal	--	1.52	42	40	0.035	7.5	8.5	3.3	29.8	0.5	7.7	-41	Calibration
	17:37	V	0.274	42	45.5	OOS	283	--	1.78	43	41	0.037	7.4	8.3	3.3	30.0	0.5	7.4	-45	System in service
	18:23	V	0.280	42	43.0	1369	212	84.5	1.80	43	41	0.034	7.5	8.2	3.3	30.0	0.6	7.4	-39	Unit down
	20:00	V	--	--	--	1372	75	94.5	--	--	--	--	--	8.0	3.3	30.2	0.6	7.4	-33	Unit restarted
	22:05	V	--	--	--	1378	320	76.8	--	--	--	--	--	7.7	3.3	30.4	0.6	7.4	-27	
	22:17	V	0.483	37	53.1	1392	263	81.1	1.74	39	36	0.030	7.4	7.6	3.3	30.4	0.6	7.4	-21	
	23:12	V	0.489	37	70.8	1395	276	80.2	1.71	39	34	0.034	7.4	7.5	3.3	30.5	0.6	7.8	-21	
	23:45	V	0.443	37	60.7	1398	269	80.8	1.73	39	34	0.034	7.4	7.4	3.3	30.6	0.6	8.2	-21	
5/9	00:45	V	0.443	36	65.8	1399	260	81.4	1.72	39	35	0.034	7.3	7.3	3.3	30.7	0.6	8.9	-21	
	01:30	V	0.487	36	68.3	1395	--	--	1.79	38	34	0.035	7.3	7.2	3.3	30.8	0.6	9.3	-21	
	02:30	V	0.490	36	78.4	DNA	DNA	--	1.80	38	34	0.034	7.3	7.1	3.3	30.9	0.6	9.7	-21	Data not available
	03:25	V	0.492	36	83.5	DNA	DNA	--	1.80	38	34	0.035	7.3	7.0	3.3	31.0	0.6	9.7	-15	Data not available
	04:25	V	0.430	36	96.1	DNA	DNA	--	1.81	38	34	0.036	7.3	6.8	3.3	31.1	0.6	9.7	-8	Data not available
	05:30	V	0.540	37	106.3	DNA	DNA	--	1.84	38	34	0.036	7.3	6.7	3.3	31.2	0.6	9.6	-2	Data not available
	06:30	V	--	37	86.0	DNA	DNA	--	1.84	39	36	0.036	7.3	6.6	3.3	31.3	0.6	9.6	+4	Data not available
	07:06	V	0.286	37	89.1	Cal	Cal	--	1.84	40	36	0.036	7.3	6.5	3.2	31.2	0.6	9.6	-9	Data not available
	07:35	V	0.287	37	93.1	Cal	Cal	--	1.84	40	36	0.036	7.4	6.4	3.2	31.2	0.6	9.5	-22	Data not available

(continued)

TABLE 19. (Continued)

Date 1984	Time	Gas Contct Device *	Gas Flow Rate Sm^3/s	Gas Out Temp °C	Gas Inlt Pres mm Hg	Inlt H_2S Conc ppmV	Out H_2S Conc ppmV	Removal Eff %	Sol Flow Rate SL/S	Sol Htr T in °C	Sol Htr T out °C	Oxidizer		ADA Conc kg/m^3	Van. Conc kg/m^3	Carb. Conc kg/m^3	Thio-sul. Conc kg/m^3	pH	Oxidation Potential mv	Comments
												Air Flow Sm^3/s	Motor Curr amps							
	08:32	V	0.353	37	102.7	Cal	Cal	--	1.84	39	37	0.037	7.4	6.3	3.2	31.1	0.6	9.5	-34	System calibration
	09:35	V	0.371	37	102.7	Cal	Cal	--	1.84	39	37	0.037	7.4	6.2	3.2	30.9	0.6	9.4	-47	Unit down
	15:09	V	0.255	42	144.7	Cal	Cal	--	1.79	42	43	0.038	7.4	4.6	3.2	30.2	0.7	9.4	-60	Restart
	16:10	V	0.208	42	140.2	1689	243	85.6	1.81	43	43	0.039	7.3	4.6	3.2	30.1	0.7	9.1	-69	
	16:30	V	0.218	42	146.7	1700	293	82.8	1.82	43	43	0.038	7.3	4.6	3.2	30.1	0.7	8.9	-78	
	18:02	V	0.215	42	126.5	1818	253	86.1	1.82	43	43	0.038	7.4	4.6	3.2	29.9	0.7	8.6	-87	
	19:02	V	0.203	43	120.2	OOS	OOS	--	1.82	44	44	0.039	7.4	4.6	3.2	29.8	0.7	9.3	-81	
	20:20	V	0.205	42	126.5	1768	306	82.7	1.90	43	43	0.038	7.4	4.6	3.2	29.6	0.7	9.9	-75	
	21:42	V	0.205	41	126.5	DNA	266	--	1.93	44	42	0.034	7.4	5.5	3.5	31.8	0.7	9.9	-67	
	22:13	V	0.192	39	35.4	DNA	295	--	1.96	44	41	0.034	7.5	5.5	3.5	31.7	0.7	9.8	-58	
	23:20	V	0.202	40	35.4	DNA	298	--	1.96	44	40	0.031	7.5	5.5	3.5	31.7	0.7	9.8	-50	
5/10	00:30	V	--	39	32.9	1761	301	82.9	1.93	43	39	0.030	7.4	5.5	3.5	31.5	0.7	9.7	-42	
	01:30	V	0.207	39	136.6	DNA	DNA	--	1.90	42	39	0.035	7.4	5.4	3.5	31.4	0.7	9.7	-33	Data not available
	02:35	V	0.324	39	124.0	DNA	DNA	--	1.58	42	42	0.030	7.5	5.4	3.5	31.3	0.7	9.6	-25	Data not available
	03:30	V	0.325	41	131.6	DNA	DNA	--	1.52	43	41	0.030	7.5	5.4	3.5	31.1	0.7	9.6	-20	Data not available
	04:30	V	0.146	42	141.7	DNA	DNA	--	2.24	44	42	0.033	7.5	5.4	3.5	31.0	0.7	9.5	-15	Data not available
	05:30	V	0.207	42	146.7	DNA	DNA	--	2.22	45	43	0.033	7.5	5.4	3.5	30.9	0.7	9.5	-10	Data not available
	06:35	V	0.210	42	167.0	DNA	DNA	--	2.24	45	41	0.033	7.5	5.4	3.5	30.6	0.7	9.5	-16	Data not available
	07:03	V	0.234	41	187.2	DNA	DNA	--	2.25	45	42	0.033	7.5	5.4	3.5	30.5	0.7	9.4	-22	Data not available
	07:30	V	0.234	41	187.2	Cal	Cal	--	2.26	46	41	0.033	7.6	5.4	3.5	30.3	0.7	9.4	-28	System Cal
	08:36	V	0.211	43	172.0	Cal	Cal	--	1.86	46	42	0.034	7.6	5.4	3.5	30.0	0.7	9.4	-34	System Cal
	09:27	V	0.343	43	217.6	Cal	Cal	--	1.85	46	43	0.035	7.5	5.3	3.5	29.8	0.7	9.4	-40	System Cal
	10:33	V	0.248	42	225.2	Cal	Cal	--	1.84	46	43	0.033	7.6	5.3	3.5	29.5	0.7	9.3	-46	System Cal
	11:30	V	0.270	43	245.4	Cal	Cal	--	1.83	46	44	0.033	7.6	5.2	3.5	29.2	0.7	9.3	-52	System Cal
	12:30	V	0.438	44	278.3	Cal	Cal	--	1.81	46	44	0.033	7.4	10.3	3.5	31.4	0.7	9.3	-59	System Cal
	13:45	V	0.378	43	225.2	Cal	Cal	--	1.84	46	43	0.034	7.3	10.2	3.4	31.1	0.8	9.2	-66	System Cal
	14:45	V	0	--	--	Cal	Cal	--	--	--	--	--	--	--	3.4	--	0.8	9.3	-60	GKI down
	17:16	V	0.189	38	15.2	1362	263	80.7	1.36	41	39	0.025	7.7	9.9	3.4	30.1	0.8	9.4	-54	S&A on line
	17:48	V	0.247	38	15.2	1330	255	80.8	1.36	41	39	0.024	7.7	9.9	3.4	29.9	0.8	9.4	-48	
	18:27	V	0.190	37	15.2	1305	249	80.9	1.36	40	39	0.024	7.7	9.8	3.4	29.8	0.8	9.5	-42	
	19:30	V	0.267	40	15.2	1283	243	81.1	1.35	41	42	0.024	7.7	9.7	3.4	29.5	0.8	9.5	-46	
	20:15	V	0.298	40	15.2	1270	240	81.1	1.36	41	42	0.020	7.7	9.7	3.3	29.3	0.8	9.4	-51	
	21:28	V	0.189	40	15.2	1259	240	80.9	1.36	42	42	0.019	7.7	9.6	3.3	28.9	0.8	9.4	-55	
	22:15	V	0.220	41	17.7	1255	235	81.3	1.36	43	43	0.019	7.8	9.5	3.3	28.7	0.8	9.5	-51	
	23:21	V	0.189	42	17.7	1250	237	81.0	1.38	44	44	0.019	7.7	9.5	3.3	28.4	0.8	9.7	-48	
5/11	00:30	V	DNA	42	12.7	1248	235	81.2	1.36	43	44	0.024	7.7	9.4	3.3	28.1	0.8	9.8	-44	Data not available
	01:30	V	DNA	39	12.7	1134	230	79.7	1.36	43	41	0.019	7.7	9.3	3.3	27.8	0.8	10.0	-41	Data not available
	02:30	V	DNA	39	12.7	1250	241	80.7	1.36	43	41	0.027	7.7	9.2	3.3	27.5	0.8	10.1	-37	Data not available
	03:30	V	DNA	39	12.7	1232	239	80.6	1.38	43	41	0.017	7.7	9.1	3.3	27.3	0.8	9.9	-23	Data not available
	04:35	V	DNA	40	12.7	1242	226	81.8	1.67	42	42	0.017	7.7	9.1	3.2	27.0	0.8	9.6	-10	Data not available
	05:30	V	DNA	40	10.1	1240	232	81.3	1.53	42	41	0.021	7.7	9.0	3.2	26.7	0.8	9.4	+4	Data not available
	06:35	V	DNA	39	10.1	1236	194	84.3	2.12	43	41	0.021	7.7	8.9	3.2	26.7	0.8	9.4	0	Data not available

(continued)

TABLE 19. (Continued)

Date 1984	Time	Gas Contct Device *	Gas Flow Rate Sm^3/s	Gas Out Temp °C	Gas Inlt Pres mm H_g	Inlt H_2S Conc ppmV	Out H_2S Conc ppmV	Removal Eff %	Sol Flow Rate SL/S	Sol Htr T in °C	Sol Htr T out °C	Oxidizer Air Flow Sm^3/s	Oxidizer Motor Curr amps	ADA Conc kg/m^3	Van. Conc kg/m^3	Carb. Conc kg/m^3	Thio-sul. Conc kg/m^3	pH	Oxidation Potential mv	Comments
5/11	07:10	V	DNA	39	14.2	Cal	Cal	--	1.52	43	42	0.020	7.8	8.9	3.2	26.7	0.8	9.4	-4	S&A calibration
	07:40	V	DNA	40	15.2	Cal	Cal	--	1.29	43	42	0.022	7.8	8.8	3.2	26.7	0.8	9.4	-8	S&A calibration
	08:35	V	DNA	41	14.4	Cal	Cal	--	1.26	43	44	0.019	7.8	8.7	[illegible]	26.7	0.8	9.3	-11	S&A calibration
	10:00	V	DNA	41	15.7	Cal	Cal	--	1.31	43	45	0.019	7.8	8.6	3.2	26.7	0.9	9.3	-15	S&A calibration
	10:30	V	DNA	41	16.4	Cal	Cal	--	1.29	44	46	0.019	7.8	8.6	3.2	26.7	0.9	9.3	-19	S&A calibration
	11:30	V	DNA	43	18.2	Cal	Cal	--	1.31	44	47	0.021	7.8	8.5	3.2	26.7	0.9	9.5	-21	S&A calibration
	12:00	V	DNA	--	--	Cal	Cal	--	--	--	--	--	--	8.5	3.1	26.7	0.9	9.7	-23	Unit Shut down to add packed tower
		V	DNA			Cal	Cal													
	19:40	V&T	DNA	33	12.7	1019	DNA	--	1.90	38	39	0.023	7.8	8.6	3.4	32.5	0.9	9.9	-25	Unit on line
	20:07	V&T	0.261	33	12.7	1042	DNA	--	1.92	38	40	0.023	7.8	8.7	3.4	32.5	0.0	10.5	-31	S&A dedicated to MRC scrubber
	21:07	V&T	0.330	33	12.7	1060	DNA	--	1.86	40	40	0.024	7.8	8.7	3.4	32.5	0.9	11.0	-38	scrubber
	21:30	V&T	0.287	27	12.7	1065	DNA	--	1.86	40	40	0.025	7.8	8.6	3.4		0.9	11.6	-44	scrubber
	22:20	V&T	0.193	27	15.2	1064	DNA	--	1.90	41	40	0.024	7.8	8.6	3.4		0.9	12.1	-50	scrubber
	23:20	V&T	0.334	28	12.7	1003	DNA	--	1.90	40	40	0.024	7.8	8.5	3.4	32.5	0.9	11.5	-44	scrubber
5/12	00:30	V&T	DNA	35	17.7	DNA	DNA	--	1.44	40	41	0.020	7.9	8.4	3.4	32.6	0.9	10.8	-38	S&A data not available
	01:30	V&T	DNA	35	17.7	DNA	DNA	--	1.24	41	42	0.019	7.8	8.4	3.4		0.9	10.2	-32	S&A data not available
	02:30	V&T	DNA	38	17.7	DNA	DNA	--	1.33	40	41	0.025	7.8	8.3	3.4		0.9	9.5	-26	S&A data not available
	03:30	V&T	DNA	43	17.7	DNA	DNA	--	1.90	41	40	0.027	7.8	8.2	3.3		0.9	9.5	-19	S&A data not available
	04:30	V&T	DNA	41	17.7	DNA	DNA	--	1.91	41	41	0.027	7.8	8.2	3.3		0.9	9.4	-12	S&A data not available
	05:30	V&T	DNA	38	17.7	DNA	DNA	--	1.29	41	41	0.029	7.8	8.1	3.3		0.9	9.4	-4	S&A data not available
	06:30	V&T	DNA	38	17.7	DNA	DNA	--	1.29	41	41	0.029	7.8	8.0	3.3	32.6	0.9	9.4	+6	S&A data not available
	07:50	V&T	DNA	38	16.7	DNA	DNA	--	1.33	41	40	0.029	7.8	8.0	3.3	32.5	0.9	9.4	+16	S&A data not available
	07:30	V&T	DNA	38	17.0	DNA	DNA	--	1.33	42	41	0.025	7.9	8.0	3.3	32.4	0.9	9.4	+25	S&A data not available
	08:30	V&T	DNA	38	15.9	Cal	Cal	--	1.35	41	42	0.024	7.9	7.9	3.3	32.1	0.9	9.3	+35	Calibration
	09:30	V&T	DNA	41	17.7	Cal	Cal	--	1.34	41	43	0.025	8.0	7.8	3.2	31.9	0.9	9.3	+45	Calibration
	10:30	V&T	DNA	41	18.2	Cal	Cal	--	1.34	42	46	0.026	8.0	7.7	3.2	31.6	0.9	9.3	+55	Calibration
	11:45	V&T	DNA	38	17.2	Cal	Cal	--	1.37	42	44	0.026	7.8	7.7	3.1	31.3	0.9	9.3	+38	Calibration
	12:25	V&T	DNA	38	19.5	Cal	Cal	--	1.37	42	44	0.026	7.7	7.6	3.1	31.2	0.9	9.3	+20	Calibration
	13:30	V&T	DNA	38	19.5	1024	9	99.1	1.63	42	42	0.026	7.8	7.5	3.0	30.9	1.0	9.3	+2	Calibration
	14:30	V&T	DNA	41	19.5	1036	8	99.2	1.64	43	45	0.027	7.8	7.5	3.0	30.7	1.0	9.3	-15	
	15:30	V&T	DNA	38	18.2	985	9	99.1	1.60	42	42	0.029	7.7	7.4	2.9	30.4	1.0	10.1	-15	
	16:22	V&T	DNA	38	25.3	1001	12	98.8	1.59	42	43	0.029	7.5	7.3	2.9	30.2	1.0	10.8	-16	
	17:19	V&T	DNA	38	22.8	1138	15	98.7	1.61	42	42	0.029	7.7	7.3	2.9	30.0	1.0	11.6	-16	
	18:25	V&T	DNA	39	22.8	1199	14	98.8	1.62	42	43	0.027	7.7	7.2	2.8	29.7	1.0	12.3	-17	
	19:19	V&T	DNA	39	25.3	1171	11	99.1	1.69	42	43	0.031	7.7	7.1	2.8	29.5	1.0	11.5	-22	
	20:18	V&T	DNA	38	25.3	1218	12	99.0	1.70	42	42	0.031	7.7	7.1	2.7	29.3	1.0	10.7	-27	
	21:25	V&T	DNA	39	25.3	1237	9	99.3	1.86	42	42	0.033	7.6	7.0	2.7	29.0	1.0	9.9	-32	
	22:24	V&T	DNA	100	27.8	1232	8	99.4	1.96	43	41	0.035	7.5	6.9	2.6	28.7	1.0	9.8	-23	
	23:21	V&T	DNA	39	25.3	1228	7	99.4	2.05	42	41	0.035	7.6	6.8	2.6	28.5	1.0	9.6	-13	

(continued)

TABLE 19. (Continued)

Date 1984	Time	Gas Contct Device *	Gas Flow Rate Sm^3/s	Gas Out Temp °C	Gas Init Pres mm Hg	Init H_2S Conc ppmV	Out H_2S Conc ppmV	Removal Eff %	Sol Flow Rate SL/S	Sol Htr T in °C	Sol Htr T out °C	Oxidizer		ADA Conc kg/m^3	Van. Conc kg/m^3	Carb. Conc kg/m^3	Thio-sul. Conc kg/m^3	pH	Oxidation Potential mv	Comments
												Air Flow Sm^3/s	Motor Curr amps							
5/13	00:55	V&T	DNA	43	20.2	DNA	DNA	--	1.94	39	39	0.035	7.6	6.7	2.5	28.1	1.0	9.5	-4	S&A data not available
	02:00	V&T	DNA	38	20.2	DNA	DNA	--	1.90	38	38	0.035	7.6	8.0	2.7	32.7	1.0	9.3	+5	S&A data not available
	03:05	V&T	DNA	38	17.7	DNA	DNA	--	1.93	40	39	0.034	7.6	7.9	2.7	32.4	1.0	9.3	+4	S&A data not available
	04:10	V&T	DNA	38	20.2	DNA	DNA	--	1.93	41	39	0.034	7.6	7.8	2.6	32.1	1.0	9.3	+2	S&A data not available
	05:05	V&T	DNA	38	20.2	DNA	DNA	--	1.94	41	39	0.034	7.6	7.7	2.6	31.9	1.0	9.4	0	S&A data not available
	06:00	V&T	DNA	38	20.2	DNA	DNA	--	1.96	41	39	0.037	7.6	7.7	2.5	31.7	1.0	9.4	-1	S&A data not available
	07:00	V&T	DNA	38	19.0	DNA	DNA	--	1.98	41	40	0.037	7.6	7.6	2.5	--	1.0	9.4	-2	S&A data not available
	07:30	V&T	DNA	38	18.7	Cal	Cal	--	2.06	41	41	0.037	7.7	7.6	2.5	--	1.0	9.4	-3	Calibration
	08:35	V&T	DNA	41	19.2	Cal	Cal	--	2.02	42	43	0.038	7.7	7.6	2.4	--	1.0	9.3	-3	Calibration
	09:45	V&T	DNA	41	19.5	Cal	Cal	--	2.07	42	42	0.039	7.6	7.6	2.4	--	1.0	9.3	-4	Calibration
	10:35	V&T	DNA	41	20.2	Cal	Cal	--	1.91	42	43	0.041	7.6	7.6	2.3	--	1.1	9.3	-5	Calibration
	11:30	V&T	DNA	41	20.2	Cal	Cal	--	1.88	42	44	0.042	7.6	7.6	2.3	--	1.1	9.3	0	Calibration
	12:30	V&T	DNA	41	20.0	Cal	Cal	--	1.93	42	44	0.042	7.6	7.6	2.2	--	1.1	9.3	+5	Calibration
	13:40	V&T	DNA	38	19.5	Cal	Cal	--	1.88	41	42	0.042	7.6	7.6	2.2	--	1.1	9.3	+10	Calibration
	14:50	V&T	DNA	38	20.2	Cal	Cal	--	1.90	39	39	0.042	7.7	7.6	2.1	--	1.1	9.6	+1	
	15:30	V*	DNA	38	20.0	990	130	86.9	1.88	39	41	0.042	7.6	7.6	2.1	--	1.1	9.9	-9	
	16:12	V*	DNA	39	25.3	797	125	84.3	1.86	41	41	0.043	7.6	9.7	2.8	--	1.1	10.1	-19	
	17:17	V*	DNA	39	25.3	749	125	83.3	1.79	42	42	0.044	7.6	9.7	2.7	--	1.1	10.4	-28	
	18:57	V*	0.250	39	25.3	940	137	85.4	1.82	40	41	0.043	7.6	9.7	2.6	--	1.1	10.6	-23	
	19:32	V*	0.251	38	25.3	1001	138	86.2	1.86	40	42	0.039	7.7	11.0	3.0	--	1.1	10.7	-18	
	20:16	V*	0.251	38	25.3	1063	139	86.9	1.83	42	42	0.038	7.6		3.0	--	1.1	10.9	-13	
	21:13	V*	0.251	38	25.3	1094	139	87.3	1.83	43	43	0.037	7.6		3.0	--	1.1	--	--	
	22:18	V*	0.250	39	26.3	1113	140	87.4	1.87	43	43	0.036	7.6		2.9	--	1.1	--	--	
	23:25	V*	0.250	39	22.8	1119	139	87.6	1.82	44	43	0.036	7.6		2.9	--	1.1	--	--	
5/14	00:00	V*	0.250	38	22.8	1125	138	87.7	1.83	44	43	0.036	7.6	11.0	2.8	--	1.1	--	--	
	01:00	V*	0.211	36	22.8	1133	137	87.9	1.80	40	38	0.033	7.6	11.0	2.8	--	1.1	--	--	
	02:00	V*	0.210	36	22.8	1133	137	87.9	1.77	40	41	0.031	7.6	11.0	2.7	--	1.1	--	--	
	03:00	V*	0.210	36	22.8	1128	132	88.3	2.02	41	42	0.031	7.6	11.0	2.7	--	1.1	--	--	
	04:00	V&T	0.210	37	22.8	1116	55	95.1	2.08	41	42	0.028	7.6	11.0	3.1	--	1.1	--	--	
	05:00	V&T	0.210	36	22.8	1127	56	95.0	2.05	38	37	0.031	7.6	11.0	3.0	--	1.1	--	--	
	06:00	V&T	0.210	37	22.8	1115	61	94.5	2.05	40	39	0.033	--	11.0	3.0	--	1.1	--	--	
	07:00	V&T	0.192	37	22.0	1106	62	94.4	2.27	39	39	0.033	7.6	11.0	2.9	--	1.1	--	--	
	07:30	V&T	0.182	37	17.5	1101	30	97.3	2.26	39	39	0.034	7.7	--	--	--	1.1	--	--	
	08:15	V&T	0.182	--	17.5	1091	14	98.7	2.26	39	39	0.034	7.7	--	--	--	1.1			Test over-unit shut down

* On these test, the packed tower was in place but no solution was flowing to it.

in Table 19 represent averages or estimated data. This was necessary because the chemical analysis schedule used and the time required to take a complete set of gas data.

A. Program Test Results - Gaseous--

The inlet gas samples were collected in a horizontal section of duct work upstream of the venturi contactor. The outlet samples were taken in a vertical section of duct downstream of the Stretford's outlet butterfly valve.

The gaseous results are presented in Table 19. The gas flow was initially measured using an Accutube flow indication device and a U-tube manometer. When the Accutube failed, an "S" type pitot tube, used in conjunction with a Magnehelic gauge, was substituted. Table 20 shows that the daily average flow rates, expressed on a wet basis at standard conditions (20°C and 760 mm Hg), varied between 0.209 and 0.476 Nm^3/s. The program average gas flow rate was 0.284 Nm^3/s.

The gas exit temperature varied from 37 to 48°C and averaged 41°C. The system inlet static pressure varied between 588 and 876 mm Hg, and averaged 648 mm Hg. The static outlet pressure averaged 628 mm Hg; the pressure readings varied between 506 and 841 mm Hg.

The daily reduced sulfur emission data are summarized in Table 21. These data were collected according to the general procedures set forth in EPA Methods 15 and 16. These methods call for the use of an on-line, semicontinuous sample extraction system, a dynamic dilution system and a gas chromatograph with flame photometric detector (GC/FPD). The details of these test methods are presented in the appendix.

The major indicator of performance during this test series is the H_2S removal efficiency. The large increase in H_2S removal efficiency between May 11 and May 12 (Table 19) was due to the installation of the packed tower. Prior to the installation of the tower, the average recorded H_2S removal efficiency was 80 percent, while the maximum recorded H_2S removal efficiency was 95 percent. In comparison the recorded H_2S removal efficiency averaged 93 percent following the tower installation. The maximum H_2S removal efficiency measured during this time was greater than 99 percent.

TABLE 20. SUMMARY OF RETORT OFF-GAS CONDITIONS

Date 1984	Volumetric Flow Rate Nm^3/S*	Temperature °C†	Absolute Pressure mm Hg§
5/4	0.344	42	630
5/5	0.253	45	623
5/6	0.235	42	626
5/7	0.221	42	645
5/8	0.476	42	689
5/9	0.320	39	701
5/10	0.246	41	717
5/11	0.281	37	614
5/12	OOS	38	623
5/13	0.251	39	626
5/14	0.209	36	625
Overall Average	0.284	41	648

* Measured at Stretford inlet, reported at standard temperature (20°C) and pressure (760 mm Hg).

† Outlet temperature reading given, inlet temperature indicator OOS

§ Inlet pressure

TABLE 21. REDUCED SULFUR SPECIES EMITTED** (ppm)

	H_2S Concentration				COS Concentration		MeSH Concentration	
	Inlet		Outlet					
Date 1984	Avg	Range	Avg	Range	Inlet	Outlet	Inlet	Outlet
5/5	1584	1322-1730	447	385-693	45	59	N.D.*	N.D.
5/6	1719	776-2165	261	16-559	190	36	N.D.	7
5/7†	--	--	--	--	--	--	--	--
5/8	1377	1367-1898	244	75-395	N.D.	54	N.D.	5
5/9	1638	1398-1935	278	188-343	35	82	N.D.	4
5/10	1314	1245-1761	248	235-301	N.D.	53	N.D.	N.D.
5/11	1144	1015-1253	228	190-240	26	52	N.D.	N.D.
5/12	1141	953-1249	10	6-15	99	72	N.D.	14
5/13	981	718-1125	131	7-140	88	76	N.D.	18
5/14	1121	1091-1137	92	14-138	94	79	N.D.	18

* N.D. = none detected, minimum detectable level

† No data available for 5/7 due to sample system problems

** GC/FPD measurements

Table 19 shows two cases (May 6 and May 8) where H_2S removal efficiencies exceeded 90 percent before the installation of the packed tower. In both cases, the high H_2S removal efficiencies were maintained for only a short time. A review of both the unit log and operating data provided no explanation for the high H_2S removal efficiencies. Following the installation of the packed tower on May 11, Table 19 shows two sets of H_2S removal efficiency data. The first set of data, taken on May 12, shows about ten hours of operation with H_2S removal efficiencies in excess of 98 percent. These data, taken when operating with maximum solution flow to the packed tower and the venturi throat plug in the fully closed position (i.e., 46 cm^2 throat area), are believed representative of the H_2S removal efficiencies that can be sustained by the Stretford plant when operated with the venturi contactor and the packed tower. The second set of H_2S removal data, taken during May 13 an 14 using the same venturi throat area, show H_2S removal efficiences ranging between 83 percent and 98 percent. The first 13 data points were taken while operating with no solution flow to the packed tower. These data show that the H_2S removal efficiency reached an equilibrium value of about 88 percent for operation without the packed tower. The sudden increase in H_2S removal efficiency from 88 percent to 95 percent was caused when the solution flow to the packed tower was restarted. The gradual increase in characteristic removal efficiencies after this point were due to gradual increases in the solution flow rate to the packed tower.

The lower than expected H_2S removal efficiences measured prior to the installation of the packed tower were probably due to several factors. The primary factor was probably the low residence time that the solution was allowed in the reaction vessel. Previous data have shown that a residence time of approximately 15 minutes is necessary during the treatment of lean (300-500 ppm) H_2S streams. Attempts were made during the program to maintain a minimum solution residence time of 15 minutes by controlling the solution flow rate and reaction vessel level. Unfortunately, this was not always achieved.

The lack of solution residence time in the reaction vessel causes problems to occur with the reactions involving the formation of sulfur particles from the HS^- radical and the reduction of the vanadium to its valence of four. If the NaHS is not completely reacted before it is transferred to the oxidizer, the formation of thiosulfate (a stable unwanted byproduct) increases greatly and lessens the opportunity for the vanadate/ADA reaction to be completed. This incomplete reoxidation of the main chemicals before recycling back to the pump tank causes numerous problems. One of these is an attempt to oxidize the NaHS molecule with an already reduced vanadium molecule. This lowers the efficiency and increases the chance of thiosulfate formation. The unwanted cycle is self-perpetuating.

Another problem is that the final conversion to elemental sulfur can form elsewhere in the system (in the piping and pump tank), where it will become a suspended solid. This is known to have been a problem during this test program. While draining the system at the end of the program, considerable sulfur deposits were found at the bottom of the pump tanks in addition to deposits at the bottom of both the reaction vessel and the oxidizer tank.

Another limiting factor was in the contact between the retort off-gas and the Stretford liquid. This became obvious following the installation of the packed tower. As noted previously, a large gain in H_2S removal efficiency was noted following the installation of the tower. Since the tower serves only to increase gas/liquid contact time and area, it follows that the contact time and area were the limiting factors in H_2S removal efficiences.

The removal efficiences for both the carbonyl sulfide (COS) and methyl mercaptans (MeSH) were negligible during this program. The variation of a few parts per million at the measured levels of inlet concentrations can be explained by the limitations of the sampling and analysis procedures.

B. Program Test Results - Liquid--

The Stretford solution is a dilute solution of sodium carbonate (Na_2CO_3), sodium metavanadate ($NaVO_3$), and sodium salts of the 2:6 and 2:7 isomers of anthraquinone disulfonic acid (ADA). These chemicals are referred to as the primary chemicals. The Stretford solution is intended to be maintained at a temperature of 110°F and a pH of 8.5 to 9.5.

Due to daily solution loss resulting from evaporation and carryover with the retort gas, it was necessary to add water and primary chemicals on a daily basis. The daily makeup rate for the primary chemicals is summarized in

Table 22. The daily makeup rates were based on measured solution concentrations, the liquid inventory, and the design feed gas conditions. Table 22 also indicates the consumption of ELVAFORM (a combination biocide flotation aid) that was added to control aerobic microbial growth and to assist in sulfur flotation.

In order to maximize H_2S removal efficiencies, it was important to maintain the proper concentrations of the primary chemicals. A daily routine of chemical analyses was established in order to accomplish this. Table 23 presents the complete results of the chemical analyses performed during this test program. The analyses performed included the following:

- pH
- oxidation level
- sodium carbonate
- ADA
- vanadium
- thiosulfate

The results of the pH tests are plotted versus time in Figure 36. This figure shows both the individual pH data and the daily average pH. The individual pH data show large variations between consecutive tests in many instances. The daily averages show that the pH was only in the desired range of 8.5 to 9.5 during four of the nine test days. During the remaining five days, the average pH was above 9.5. As mentioned in Section 3.1.1, the rate of H_2S absorption is pH-dependent; as the pH level decreases below the design levels, the H_2S removal efficiency decreases. Thus, it appears that operation with the pH in excess of the desired range would have had no adverse effect on the H_2S removal efficiency.

In Figure 37, the primary chemical concentrations as determined by laboratory analysis are plotted versus time.

The purpose of the sodium carbonate (Na_2CO_3) in the Stretford solution is to react with the incoming H_2S to form sodium hydrosulfate (NaHS) and sodium bicarbonate ($NaHCO_3$). Thus, low levels of Na_2CO_3 would result in reduced H_2S removal efficiency. The carbonate concentration during this test

TABLE 22. SUMMARY OF CHEMICAL USAGE DURING STRETFORD TESTING

Date 1984	Na_2CO_3 kg	ADA kg	$NaVO_3$ (ELVAN K) kg	H_2O liter	ELVAFORM liter
5/3*	226	111	90	9,304	7.6
5/4	45	22	18	1,804	0.99
5/5	0	16	9	1,137	0.99
5/6	23	0	23	0	0.99
5/7	33	45	13	1,308	0.99
5/8	136	10	0	868	1.2
5/9	23	11	9	902	1.5
5/10	23	61	0	803	0.99
5/11	54	25	12	1,270	1.5
5/12	0	0	0	0	2.0
5/13	130	39	39	5,264	0.99
5/14	59	0	12	3,676	0.00
Total†	752	340	225	26,336	19.7

* Indicates initial start-up charge.

† Includes chemicals remaining in system at completion of program.

Note: antifoaming agent of less than one gallon was added during the test.

TABLE 23. CHEMICAL ANALYSES RESULTS

Date 1984	pH	Oxidation Level rel MV	Sodium Carbonate g/liter	ADA g/liter	Vanadium g/liter	Thiosulfate g/liter
5/5	9.93	-81	22.8	7.6	--	--
	10.00	-6 to -10				
	9.61	+75 to +90				
	9.32	-10 to -11				
	10.84	+20 to +55				
	9.86	-21				
5/6	9.78	+5	11.6	--	2.1	--
	7.00	0				
	9.45	-31				
	9.38	-25				
	9.67	+46 to +50				
	10.70	-16				
5/7	9.30	+1	15.2	7.76	--	--
	9.30	0 to -10				
	9.49	-15.5 to -17.5				
	12.28	-57				
	9.60	-32				
	9.95	-50				
5/8	9.50	+27	14.4	--	3.3	--
	9.45	-32				
	9.51	-14				
	7.35	-45				
	7.40	-21				
5/9	9.66	-21	31.3	4.60	--	--
	9.60	+4				
	9.44	-60				
	8.60	-87				
	9.94	-75				

TABLE 23. (continued)

Date 1984	pH	Oxidation Level rel MV	Sodium Carbonate g/liter	ADA g/liter	Vanadium g/liter	Thiosulfate g/liter
5/10	9.63	-25	30.9	5.4	3.5	--
	9.53	-10				
	9.30	-52				
	9.22	-66				
	9.53	-42				
	9.43	-55				
5/11	10.12	-37	26.7	8.8	--	--
	9.44	+4				
	9.31	-19				
	9.93	-25				
	12.07	-50				
5/12	9.52	-26	32.6	--	3.3	--
	9.43	-4				
	9.34	+55				
	9.32	-15				
	12.30	-17				
	9.87	-32				
5/13	9.34	+5	31.7	7.6	--	1.1
	9.42	-1				
	9.33	-5				
	9.31	+10				
	10.43	-28				
	10.88	-13				
5/14	--	--		11.0	2.9	--

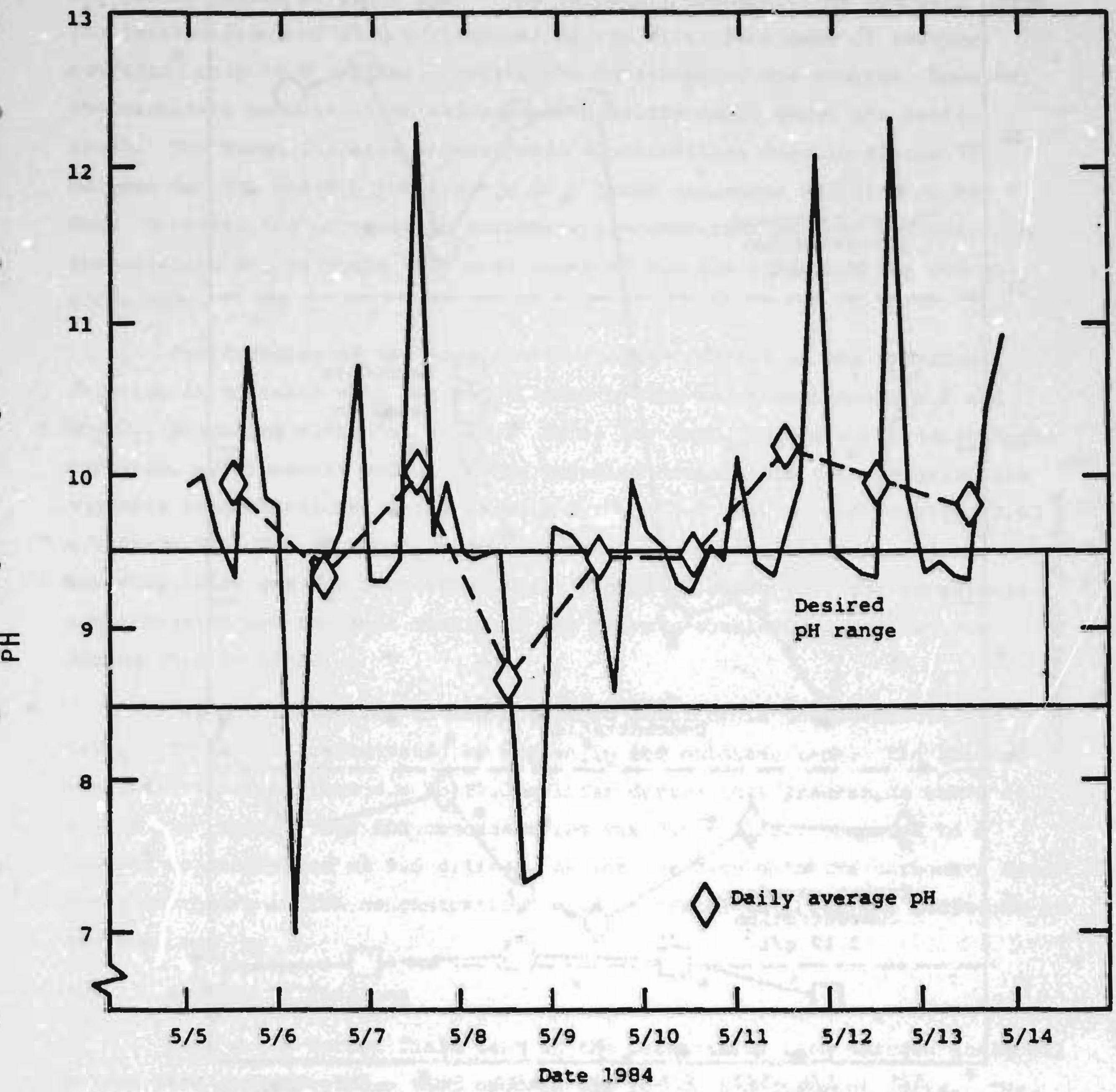


Figure 36. Stretford Solution pH vs. time

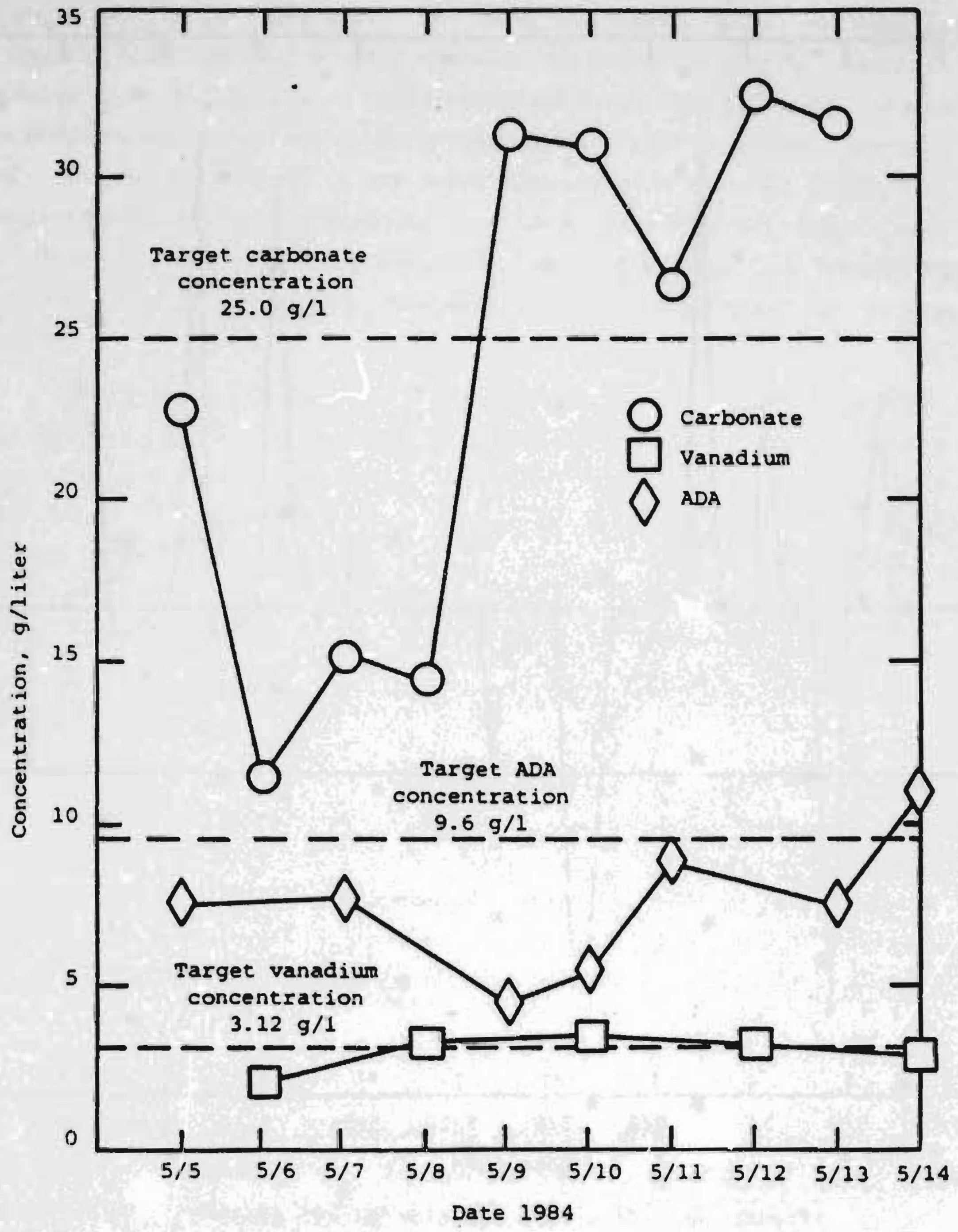


Figure 37. Primary Chemical Concentrations versus Time.

series varied from 11.6 to 32.6 g/liter and averaged 24.1 g/liter. In comparison, the design carbonate concentration was 25.0 g/liter based on an inlet H_2S concentration of 2,000 ppmV. The carbonate concentration was well below the desired level of 25.0 g/liter during the first four days of testing, averaging only 16.0 g/liter. During the remainder of the program, however, the carbonate concentration averaged 30.6 g/liter well above the design level. The large increase in carbonate concentration seen in Figure 37 between May 8th and 9th corresponds to a large carbonate addition on May 8th. However, the increase in carbonate concentration was not reflected in the solution pH, as would have been expected nor did it affect the removal efficiency.

The function of the sodium metavanadate ($NaVO_3$) in the Stretford solution is to react with the NaHS formed by the reaction between H_2S and Na_2CO_3, producing elemental sulfur. Thus, low $NaVO_3$ levels would inhibit the formation of elemental sulfur in the solution during this test program, the vanadium concentrations varied between 2.1 and 3.5 g/liter and averaged 3.02 g/liter. The desired vanadium concentration was 3.12 g/liter, based on expected inlet gas H_2S concentrations. Figure 37 shows that the vanadium concentration was the most stable of the primary chemical concentrations during this testing.

The ADA's function in the Stretford solution is to regenerate the $NaVO_3$. The ADA is regenerated by oxygen in the oxidizer tank. The ADA concentrations varied from 4.6 to 11.0 g/liter during this program as shown in Figure 37. The average ADA concentration was 7.5 g/liter, compared to a desired concentration of 9.6 g/liter. As was the case with the carbonate data, large increases in ADA concentration could be traced to large ADA additions on the previous day.

3.3.2 Summary of Findings

During its second field test at the Geokinetics Kamp Kerogen shale oil retort site, the Stretford test program was run in two distinct parts. The two program parts were as follows:

- Testing with only one gas-liquid contacting device (the variable-throat venturi scrubber)

- Testing with two gas-liquid contacting devices in series (the venturi scrubber and a packed tower)

The Stretford was operated for a total of 205 hours during a twelve day period between May 3, 1984 and May 14, 1984. Operation with the venturi scrubber accounted for 142 hours of operation. The remaining 63 hours of operation were with the venturi scrubber and the packed tower.

The H_2S removal efficiency averaged 80 percent during the initial portion of the testing. During this time, a maximum H_2S removal efficiency of 95 percent was achieved on two separate occasions, but documented H_2S removal efficiencies in excess of 90 percent were maintained for only 5 hours. For the remainder of this portion of the program, the H_2S removal efficiencies remained in the 80-90 percent range. Operating changes designed to increase the H_2S removal efficiency (i.e. decreasing the venturi area and increasing the solution residence time in the reaction vessel) did not seem to cause a significant increase in H_2S removal efficiency. The available data give no clue as to why the H_2S removal efficiencies peaked and dropped on two separate occasions; the lack of continuous H_2S removal data is the limiting factor in the ability to interpret the data.

During the second part of the program, when operating with the venturi scrubber and the packed tower, the H_2S removal efficiency averaged 93 percent. This number would have undoubtedly been considerably higher if the system had been operated continuously with the venturi area set at its minimum and maximum solution flow to the tower. When this was done (the latter half of May 12), the H_2S removal efficiency averaged 99 percent over a period of 10 hours. During the period between 4 pm on May 13 and the end of the program, the solution flow to the spray tower was deliberately shut down then restarted. This was done to allow the system to reach a steady-state condition while operating in its original configuration. Once this condition was achieved, and a steady-state H_2S removal efficiency of about 88 percent was achieved, the solution flow to the spray tower was restarted, increasing H_2S removal efficiency as the solution flow rate to the spray tower was increased.

The concentrations of the primary chemicals varied significantly during the course of the program. The carbonate and ADA concentrations varied the most, while the vanadium concentration remained relatively constant.

Four major problems were encountered during this test program, as listed below:

- inadequate venturi contactor performance
- lack of sulfur flotation
- excessive solution foaming (for a few hours)
- contamination of sampling and analysis system

The performance of the original gas-liquid contactor (the variable-throat venturi scrubber) was never up to the expected levels of 96-99 percent H_2S removal. It is believed that the reason for this was the low liquid pressures to the scrubber, which resulted in poor atomization of the Stretford solution. The installation of the packed tower dramatically increased H_2S removal efficiencies.

The system showed good sulfur flotation from startup on May 4, 1984 until May 10, 1984. At that time, a major system upset occured when the oxidizer began foaming out of control. Following the upset, the system showed poor sulfur flotation for the remainder of the program. While the cause of the foaming was not determined with any degree of confidence, it was most likely due to contamination of the Stretford solution by oil carried over in the retort off-gas.

Clogging of the sampling and analysis system resulted in large gaps in available H_2S removal efficiency data, as shown in Table 19. The clogging was caused by liquid and solid particulate matter in the offgas finding its way into the sample system. The most frequent points of clogging were the precision valves used to control the dilution air flow. These had to be disassembled and cleaned frequently until improved mist knockouts were developed.

Excessive solution foaming was a problem only during the above-mentioned upset. The problem was brought under control within a few hours using an antifoaming agent.

SECTION 4.0

QUALITY ASSURANCE

A formal quality assurance (QA) program was conducted for this test. Separate quality assurance project plans were prepared and approved by EPA and KVB project directors, project directors from PEI and MRC, and their respective QA officers. These QA plans defined the test objectives, sampling and analysis procedures, calibration procedures and frequency, sample custody procedures and management responsibility. This section presents certain data that will indicate the degree of error associated with the reported data.

4.1 GAS SAMPLING

Samples of retort offgas were taken at three locations, upstream from both the Stretford and the alkaline scrubber and downstream from each of those units. Daily calibration checks were performed. Each instrument was calibrated using certified gases of known concentration. Often three concentrations were used to establish a calibration curve. After the instrument calibration, recovery checks were made on the sampling lines by drawing calibration gas through the full system.

An example of one day's calibration of the gas chromatograph with a flame photmetric detector (GC/FPD) is presented as Table 24.

Each day after calibrating the GC/FPD and the continuous total reduced sulfur (TRS) monitor, recovery checks were made. First, the three trains were checked for leaks. Following the leak check, H_2S calibration gas was introduced to the sampling probe with excess flow; 1000 ppm H_2S was used for the inlet and 100 ppm H_2S was used for the outlets. The calibration gas was pumped through the entire sampling system and diluted. The dilution rate was measured with a bubble tube so a dilution factor could be established.

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ALKALINE AND STRETFORD SCRUBBING TESTS FOR H2S REMOVAL FROM IN-SITU

TABLE 24. REDUCED SULFUR CALIBRATION DATA

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COMPOUND		H_2S	COS	MeSH	CS_2	ANALYST	Greg Meiners
PERMEATION RATE (µl/min)/TUBE						DATE	5/3/84
RETENTION TIME (min)						LOCATION	GEO
LINEAR REGRESSION COEFFICIENTS	SLOPE, m	2.49792	1.861562	2.25279	1.954600	REGRESSION EQUATION FORM:	
	INTERCEPT, b	0.409991	1.15476	0.547620	1.281599	LOG (AREA) = m LOG (CONC.) + b	
	CORRELATION, r^2	0.99855	0.997691	0.999978	0.9999183		

TIME/ DATE	FLOW (liter/min)	CMPD	KNOWN[a] CONC. (ppm)	AREA 1	AREA 2	AREA 3	AREA AVG.	CALC.[b] CONC. (ppm)	NOTES/REMARKS
5/3 1430		H_2S	8.38	485.8	484.9	494.4	485	8.13 - 3.0%	Long Method
		COS	8.78	766.2	760.6	763.2	763	8.47 - 3.7%	Big Loop - approx. 1 ml
		MESH	8.59	453.1	447.0	435.7	445	8.56 - 0.3%	
		CS_2	8.08	1149.1	1145.9	1147.7	1147	8.04 - 0.5%	Start Cal 5/3/84
		Thiophene	8.23	425.5	424.0	418.1	422		@ 1432 hrs.
		H_2S	7.04	366.4	362.7	367.7	366	7.27 + 3.3%	End Cal 5/3/84
		COS	7.38	639.3	636.1	638.9	638	7.69 + 4.2%	
		MESH	7.22	309.1	300.9	307.9	306	7.25 + 0.4%	
		CS_2	6.79	847.5	832.0	840.1	840	6.85 + 0.9%	
		Thiophene	6.92	291.9	285.8	289.7	289		
		H_2S	2.86	35.3	34.4	35.2	35	2.84 0.7%	
		COS	3.00	108.9	106.6	110.1	109	2.98 0.7%	
		MESH	2.94	40.6	39.9	40.8	40	2.94 0.0%	
		CS_2	2.76	140.0	141.6	143.7	142	2.76 0.0%	
		Thiophene	2.81	51.3	54.4	54.1	53		

a, $\text{ppm} = \dfrac{\text{permeation rate (l/min)}}{\text{total cal gas flow (liter/min)}}$

b C, $\text{ppm} = \left[\dfrac{\text{Area}}{10^b}\right]^{1/m}$

After calculating the dilution factor the recovery gas was sampled by the GC/FCD and the continuous TRS monitor. The analytical response was applied to the respective calibration curve and translated to ppm at the instrument. The instrument ppm was multiplied by the dilution factor to obtain ppm at the stack. This calculated stack value should equal the calibration gas cylinder concentration for a 100 percent efficient recovery. Whenever the recovery check yielded a lower value than expected, the sampling train was checked for gas concentration at various points in the system. Due to the reactive nature of H_2S, degradation was a problem. Once the sampling system had been corrected and the gas flow had equilibrated, recovery checks ususally improved.

A recovery factor was calculated from the check and applied to the data for that day.

ppm analyzed x dilution factor x recovery factor = ppm stack

4.2 WATER DATA

A key element in the scrubber analysis was the carbonate, bicarbonate and hydroxide concentrations. To provide an indication of the accuracy of these laboratory values as well as the other water analysis, a series of control samples not identified to specific runs were submitted for analysis along with the primary samples. The results of these control samples are compared to those for the primary samples in Table 25.

The average differences between the sample and control values for carbonate, bicarbonate, and hydroxide are summarized below.

	Average Difference, %
carbonate	16.3
bicarbonate	27.6
hydroxide	21.1
Total Alkalinity	9.0

The carbonate and bicarbonate values have average differences of 16.3 percent and 27.6 percent respectively, based on the absolute value of the

TABLE 25. WATER ANALYSIS DATA QUALITY CONTROL

Run No.	Quality Control	Component	Sample	Control	Deviation S-C	%
14	J	Sulfide, mg/l	400	460	+60	15.0
30	O		310	330	20	6.5
18	D		400	400	0	0.0
						7.1
17	M	Sodium, mg/l	170	170	0	0.0
29	QQ		180	170	10	5.5
19	F		1,000	970	30	3.0
						2.8
15	A	Ammonia, mg/l	1,200	1,700	500	41.7
27	DD		370	540	170	45.9
25	AA		400	398	2	0.5
21	G		260	380	120	46.2
22	C		300	344	44	14.7
						29.8
15	A	Total Organic Carbon	280	230	50	18.0
27	DD		230	290	60	26.0
25	AA		260	280	20	7.7
21	G		250	330	80	32.2
22	C		160	160	0	0.0
						16.8
24	S	Alkalinity, mg/l as $CaCO_3$	2,200	2,100	100	4.5
16	H		20,300	19,000	1,300	6.4
12	P		96,000	120,000	24,000	25.0
28	TT		2,200	2,500	300	13.6
26	RR		8,300	7,500	800	9.6
20	U		2,300	2,200	100	4.3
13	SS		84,000	84,000	0	0.0
						9.0

(continued)

TABLE 25. (Continued)

Run No.	Quality Control	Component	Sample	Control	Deviation	
					S-C	%
24	S	Carbonate	840	960	-120	-14.3
16	H		6,200	6,700		-8.1
12	P		19,000	13,000	6,000	31.6
28	TT		840	800	40	4.8
26	RR		3,000	3,200	-200	-6.7
20	U		600	720	120	-20.0
13	SS		14,000	11,000	4,000	28.6
						16.31
24	S	Bicarbonate	980	610	370	37.8
16	H		<1	<1		
12	P		<1	<1		
28	TT		980	1,300	-320	-32.7
26	RR		4,000	3,400	600	15.0
20	U		1,600	1,200		25.0
13	SS		<1	<1		
						27.6
24	S	Hydroxide	<1	<1		
16	H		1,700	2,300	-600	35.3
12	P		11,000	13,000	-2000	-18.2
28	TT		<1	<1		
26	RR		<1	<1		
20	U		<1	<1		
13	SS		10,000	11,000	1,000	10.0
						21.1
24	S	Sulfate	120	110	10	8.3
16	H		66	98	32	48.5
12	P		160	120	40	25.0
28	TT		110	57	53	48.2
26	RR		100	98	2	2.0
20	U		100	81	19	19.0
13	SS		33	51	-18	54.5
						29.4

(continued)

TABLE 25. (Continued)

Run No.	Quality Control	Component	Sample	Control	Deviation S-C	%
24	S	Total Dissolved Solids	37,000	1,700		
16	H		80,000	690		
12	P		130,000	610		
28	TT		45,000	1,700	Error	
26	RR		32,000	3,500		
20	U		22,000	1,200		
13	SS		130,000	580		
24	S	Total Suspended Solids	120	70	50	41.7
16	H		150	66	84	56.0
12	P		150	35	115	76.7
28	TT		83	25	58	69.9
26	RR		74	18	56	75.7
20	U		57	8	49	86.0
13	SS		180	51	129	71.7
						68.2
24	S	Total Solids (mg/l)	37,000	1,800		
16	H		80,000	760		
12	P		130,000	650		
28	TT		45,000	1,700	Error	
26	RR		32,000	3,500		
20	U		22,000	1,200		
13	SS		130,000	630		

deviation. However, the total alkalinity average difference is only 9.0 percent. This is because the carbonate and bicarbonate are determined on the sample titration. A shift in the endpoint determination results in a higher carbonate value and a lower bicarbonate value or vice versa.

Evaluating the deviation for individual runs results in the following

Run	Quality Control	Carbonate % Deviation	Bicarbonate % Deviation	Total % Deviation
24	S	-14.3	37.8	23.5
28	TT	4.8	-32.7	-27.9
26	RR	-6.7	15.0	8.3
20	U	-20.0	25.0	5.0
				16.2

The average error for the total carbonate-bicarbonate is 16.2 percent.

To evaluate the effect on selectivity of these variations in carbonate-bicarbonate values, the selectivity for these runs was recalculated based on the control data concentrations. These results are shown in Table 26.

TABLE 26. COMPARISON OF SAMPLE & CONTROL WATER DATA
EFFECT ON SELECTIVITY

Run #	Contactor	Chemical	Sample % CO_2	Selectivity	Control % CO_2	Selectivity	Error
20	Tower	NaOH	1.0	51.8	.93	55.7	-3.9
18	Tower	NaOH	3.2	28.7	4.57	19.8	8.9
16	Tower	NH_4OH	10.4	8.9	7.06	13.1	-4.2
24	Venturi	NaOH	.79	60.4	.58	83.0	22.6
26	Venturi	KOH	3.42	20.8	3.43	20.7	.1
							7.9

With the exception of run No. 24, all of the error values are less than ten percent indicating reasonable agreement and accuracy for the calculated selectivty values.

The control samples for total Dissolved Solids is obviously in error.

As these values do not directly affect the results, this discrepancy was not investigated.

The control samples for the remaining components with the exception of Total Suspended Solids showed reasonable agreement with the original samples.

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APPENDIX A

SAMPLING AND ANALYSIS METHODOLOGY

A.1 GAS STREAMS

Two sampling and analysis (S&A) methods were used to determine the retort offgas composition during the test program run at GKI, instrumental and wet chemical. The majority of the tests were run using the electronic instruments described in Section A.1.1. The ammonia concentrations were determined using the wet chemical analysis method described in Section A.1.2.

A.1.1 Instrumental S&A

There were essentially three separate sampling and analysis systems used during this test program. One system was used to measure specific reduced sulfur compounds; this system is described in Subsection A. Another system provided a continuous, real time measurement of the total organic sulfur in the gas stream; this is described in Subsection B. The third system, used to measure the non-sulfur gas components, is described below in Subsection C.

A. Sampling and Analysis for Specific Reduced Sulfur Compounds--

The sampling and analytical procedures that were used for the reduced sulfur compounds are essentially those specified in EPA Methods 15 and 16 of the Federal Register.* The method employs a gas chromatograph (GC) with a flame photometric detector (FPD). In this procedure, a continuous gas sample is extracted from the emission source, scrubbed in a cold SO_2 scrubbing solution, and diluted with clean dry air. An aliquot of the diluted sample is then analyzed for the following sulfur compounds: hydrogen sulfide (H_2S), carbonyl sulfide (COS), carbon disulfide (CS_2), methyl mercaptan (MeSH), and thiophene.

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* 40 CFR 60, Appendix A, Reference Methods 15 and 16, July 1, 1982.

The sampling system, shown in Figure A-1, consisted of stainless steel probes, Telfon SO_2 scrubbing systems, utilizing a citrate buffer solution,* Telfon sample transfer lines, a dilution unit, GC-FPD, an integrator, and a calibration gas source. The samples were collected semicontinuously from three points; the combined inlet to both the Stretford and the alkaline scrubber and the respective outlet from each process.

The GC used was a Perkin-Elmer Model 990 with an FPD. This GC is equipped with a 10-port valve for automatic injection of the sample from the sample loop and for backflushing a precolumn that traps high-molecular-weight sulfur and hydrocarbon compounds. The sample loop for the GC is a 1/8-in OD Teflon tube, the length of which was adjusted to vary the amount of sample injected. The columns and conditions used in this analysis were as follows:

Precolumn	33 cm x 0.32-cm OD Teflon tubing with Carbopack BHT 100 40/60 mesh.
Analytical column	2.7 m x 0.32-cm OD Telfon tubing with 60/80 Carbopack B/1.5% x E60/1.0% H_3PO_4
Carrier gas	Helium at 50 cc/min
Oxidant	Air at 101 cc/min
Fuel	Hydrogen at 76 cc/min
Column temperature	60°C for 2 minutes; 25°C/min to 135° and hold for 7 minutes

The analysis procedure was as follows. The diluted sample was purged through the loop and injected into the precolumn. The H_2S, COS, MeSH, CS_2, and thiophene passed through the precolumn and were separated by the analytical column according to the above-mentioned temperature program. The DMOS and other high-molecular-weight sulfur and hydrocarbon compounds were removed by the precolumn, which was backflushed after each injection. The H_2S, COS, MeSH, and CS_2 concentrations were determined by comparison with calibration

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*Citrate buffer comprises 284 gram sodium citrate + 41 grams anhydrous citric acid in one liter of deionized water.

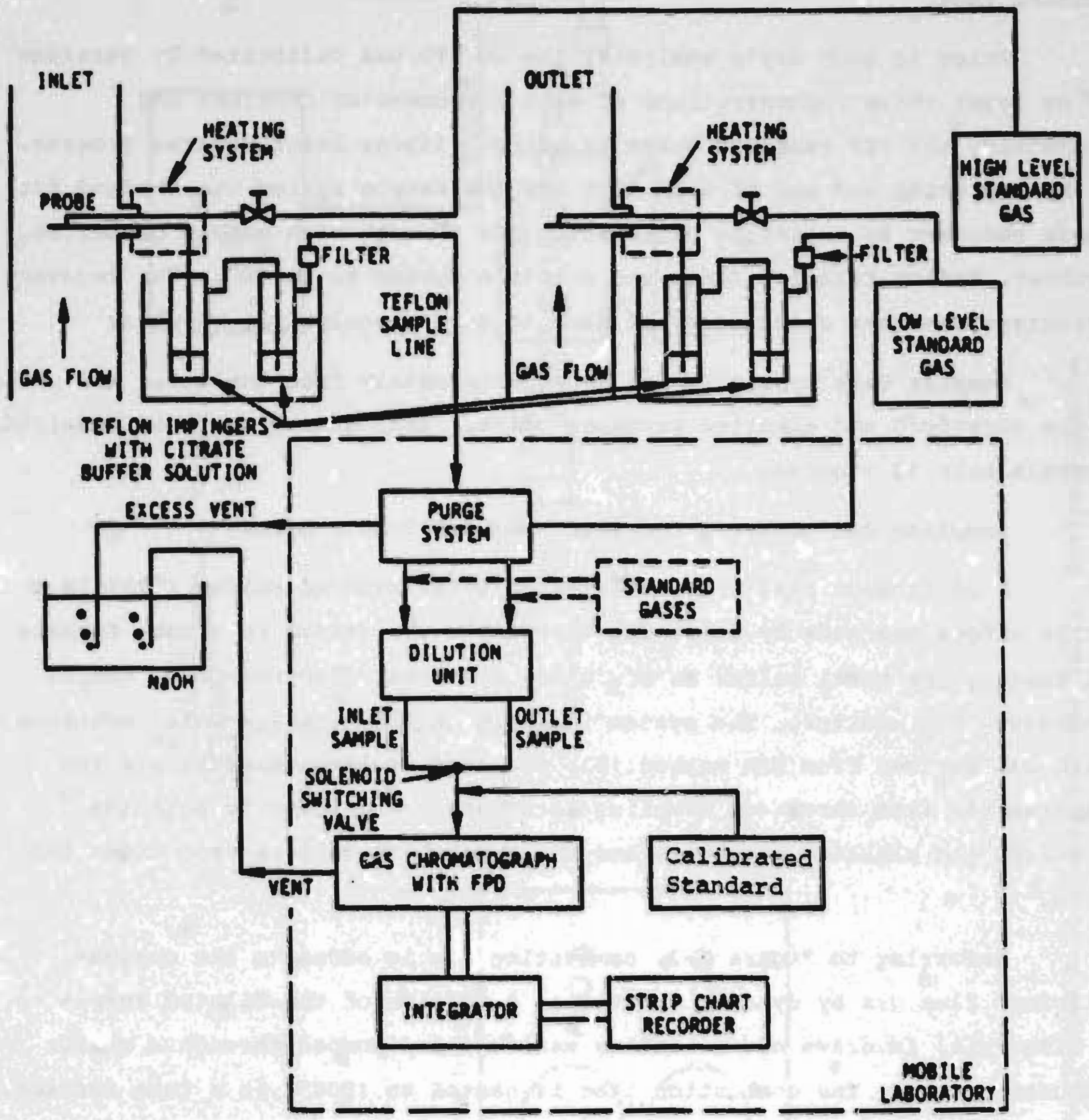

Figure A -1. Sampling and analytical system for reduced sulfur compounds.

gases generated with the permeation system. Thiophene was quantitated from a standard tank.

Prior to each day's analysis, the GC-FPD was calibrated by generating at least three concentrations of each component of interest and determining the FPD response curve by using a linear least-squares program. At the beginning and end of each test day the sample system was checked for sample recovery by injecting calibration gas through each sample probe, SO_2 scrubber, Teflon transfer line, and dilution system to the GC. The recovery percentage was then calculated and used to adjust analytical results.

Samples were typically collected alternately from the inlet and outlet of the Stretford and alkaline scrubber units. Each sample analysis required approximately 12 minutes.

B. Sampling and Analysis for Total Reduced Sulfur Gases--

A continuous real-time analyses of total reduced sulfur (TRS) in the retort offgas was made by oxidizing the sample gas stream in a tube furnace and reading the total sulfur as SO_2 using a Thermal Electron Corp. (TECO) continuous SO_2 monitor. The system is shown on Figure A-2. This technique, which was derived from EPA Method 15A, was used to provide alternate TRS measurements from three gas sampling locations: the inlet to both the Stretford and alkaline scrubbers and the respective outlets from those two units.

Referring to Figure A-2, combustion air is added to the oxygen-deficient flue gas by dynamic dilution. A portion of the diluted sample (2 liter/min) is drawn off a venting manifold and pumped through a quartz combustion tube. The combustion tube is heated to 1000°C in a tube furnace. The sample stream flows from the combustion tube to a second venting manifold. The TRS monitor takes its sample from this second manifold. The instrument response to the sample is recorded by a strip chart recorder.

The TRS monitor is calibrated at the zero to 100 ppm range with hydrogen sulfide (H_2S). The H_2S used for calibration is diluted and mixed in a porous plug dilution system. Each flow is measured with a bubble tube. The

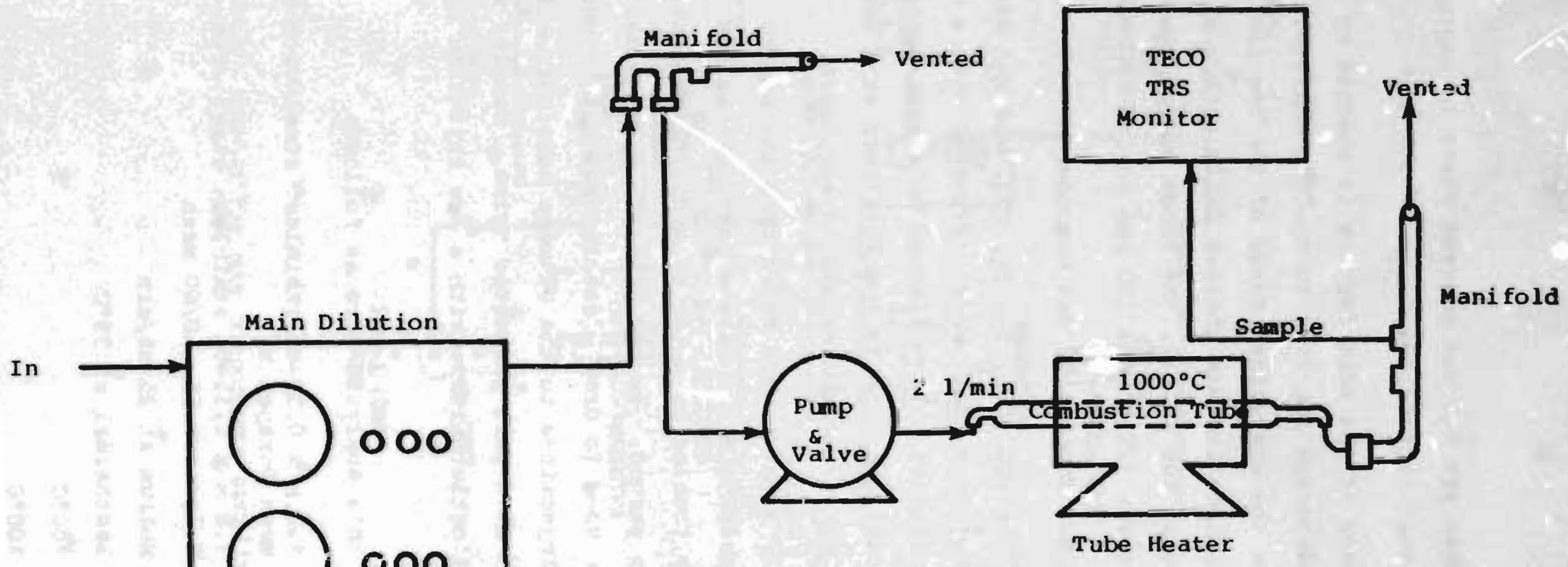

Figure A-2. Total Reduced Sulfur Analysis System calibration relationship between ppm H_2S and percent chart is expressed by the slope and intercept of its linear regression.

The oxidation efficiency of the tube furnace is checked by comparing the response of the gas chromatograph (GC/FPD) to the TRS monitor. The comparison is not direct since the analytical range of the two instruments is different. The TRS monitor calibration was checked daily with a mid-scale precision point. After the point was stable, the range was changed to the 500 ppm scale to verify the output was 1/5 of the 100 ppm scale.

C. Sampling and Analysis for Non-Sulfur Gas Components--

Sampling and analysis for (CO, CO_2, O_2, H_2, CH_4, and N_2) gases were conducted using a Baseline Industries, Inc. Model 1030-A GC with a thermal conductivity detector (TCD). Samples were collected on a semi-continuous basis from three sites, the inlet gas line to the Stretford unit and the alkaline scrubber and the outlets from the respective scrubbers.

As shown in Figure A-3, samples were drawn from the source through a coalescing filter and a condenser unit (to remove particulates and moisture) and conveyed to the laboratory trailer by means of a diaphragm pump. Both source lines were continuously purged. At the trailer, a valve manifold system and diaphragm pump were used to draw a sample from either purge line to fill the GC sample loop. Injections to the GC were made automatically from a 1.0-ml sample loop with a 10-port pneumatic valve. Samples were taken alternately from the inlet and outlet sites, with a new injection approximately every 15 minutes.

The GC conditions for this analysis were as follows:

Column 1	1.2 m x 0.32-cm stainless steel with 50/80 mesh Porapak N
Column 2	1.8 m x 0.32-cm stainless steel with Molesieve 5A, 40/60 mesh
Carrier gas	Helium at 25 ml/min
Column temperature	Isothermal at 75°C
Injection temperature	100°C
Detector temperature	100°C

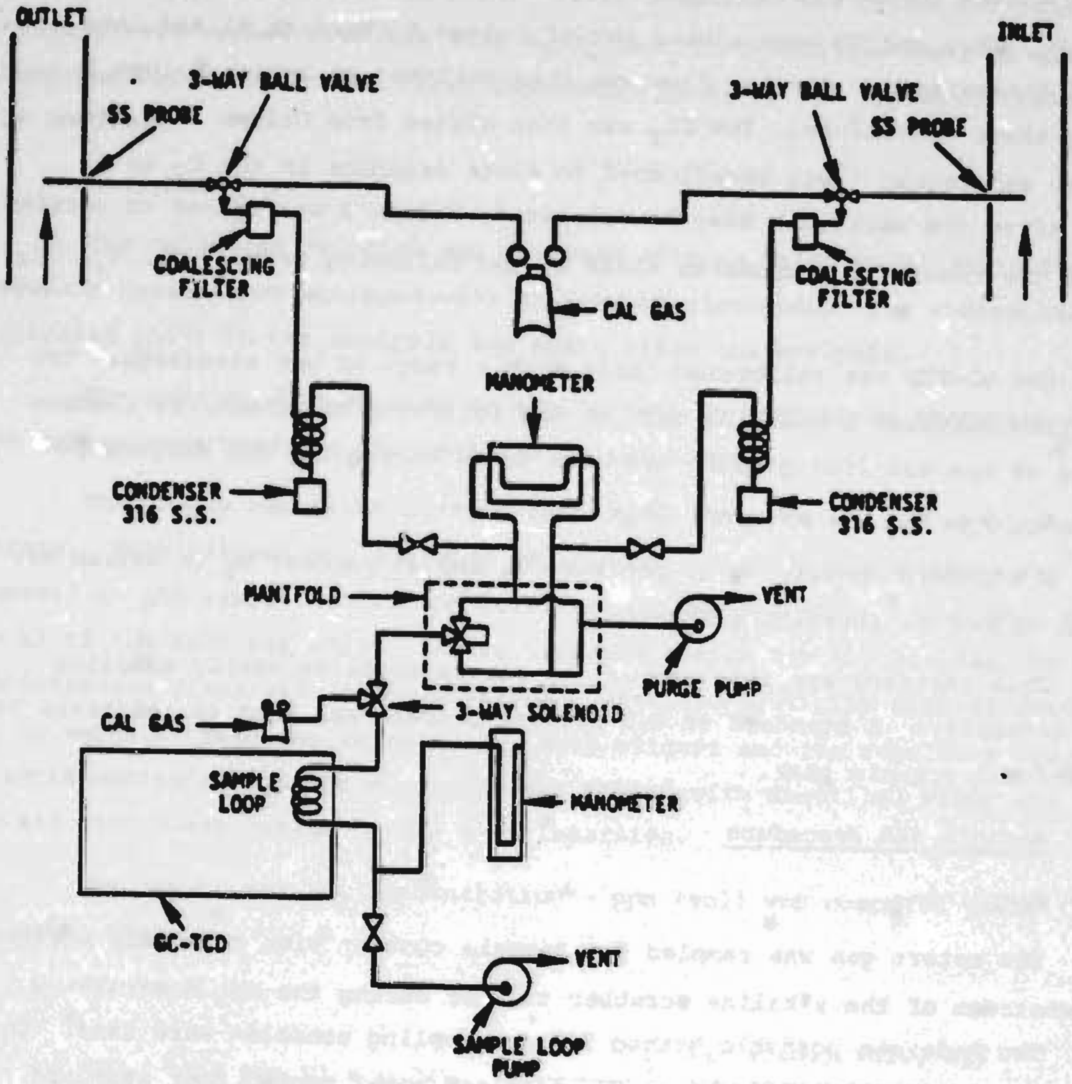

Figure A-3. Non-sulfur gas components sampling train schematic.

The analytical procedure was as follows. After its injection, the hydrogen elutes through both columns in less than one minute. At this point the O_2, N_2, CH_4, and CO have eluted out of Column 1 (Porapak N) and into Column 2 (molesieve). Carrier flow was then switched to bypass Column 2 trapping these components. The CO_2 was then eluted from Column 1 to the detector, and Column 1 was backflushed to elute organics in the C_2 to C_4 range. After the backflush step is completed, Column 2 was opened to carrier flow and the remaining components elute in the following order: O_2, N_2, CH_4, an CO.

The GC-TCD was calibrated daily with a range of gas standards. Two calibration mixtures containing each of the following components at concentrations of one and five percent are used to establish the low calibration scale: H_2, O_2, N_2, CO, CO_2, and CH_4.

A standard containing 30 percent CO_2 and 40 percent N_2 in helium was used for higher calibration standards.

This standard was injected at the sample probe to verify sampling system integrity. A standard of 0.5 percent propane was used to calibrate for the backflush organic peak.

A.1.2 Ammonia S&A Procedure

A. Sampling--

The retort gas was sampled for ammonia content simultaneously upstream and downstream of the alkaline scrubber trailer during the NH_3OH scrubbing tests. Two Andersen portable Method 5 type sampling consoles were used. The sampling train consisted of a 1-cm OD stainless steel probe, four standard impingers in an ice bath, a vacuum pump and dry gas meter. The first two impingers contained initially 1000 ml of a 0.02 N H_2SO_4 solution (0.55 ml/liter or 12 drops concentrated [37N] H_2SO_4/liter).

The third impinger was empty. The fourth impinger was filled with desicant. A glass wool plug was used inside the probe to capture particulates.

The sampling rate was maintained at between 0.00014 and 0.00019 am^3/s. 0.14 Sm^3 of gas was sampled. After sampling, the probe and connecting glassware were washed with the 0.2N H_2SO_4 absorbing solution and the washing liquid was collected in the first impinger. Finally, all impinger liquids were combined.

B. Analyses--

The collected solution was analyzed with an Orion Model 907 Microprocessor Ionanalyzer equipped with an ammonia electrode. The system was calibrated prior to the analysis and again after the analysis.

The samples were allowed to equilibrate to laboratory temperature (The same temperature used for the calibration solutions).

The sample was first divided into 90 ml aliquots in 250 ml plastic beakers. Each aliquot was analyzed as follows. The clean electrode was immersed in the sample. A teflon stirring bar was placed in the beaker and one ml of 10N NaOH was added. After stirring sample for two minutes the NH_3 concentration displayed on the instrument was recorded. The display read ppm NH_3 by weight. This was repeated for each aliquot and the results averaged. To avoid contamination the electrode was rinsed with distilled water and blotted with clean tissue before each immersion.

The retort gas NH_3 concentration - ppm (vol) was computed using the following equation:

$$NH_3 \text{ (dry ppm V)} = 0.049 \frac{\text{(ppm wt } NH_3 \text{ liq) (liq., vol., ml)}}{\text{DSCF } (16^0\text{C}) \text{ of sampled flue gas}}$$

A.2 LIQUID STREAMS

A.2.1 Scrubber

Liquid samples were taken from the scrubber effluent stream after approximately 20 minutes of test operation to assure steady state conditions. The samples were separated into seven containers and preserved in accordance with Table A-1.

TABLE A-1. ALKALI SCRUBBER WATER SAMPLES (Each Run)

(a) Preservation Methods

Pollutant	Container	Preservation
Sulfide	500-mL amber glass	Add zinc acetate (several crystals), Cool to 4°C
Ammonia/Ammonium	500-mL amber glass	Adjust to pH <2 w/H_2SO_4, Cool to 4°C
Alkalinity	500-mL amber glass	Cool to 4°C
Dissolved and Suspended Solids	500-mL amber glass	Cool to 4°C
Total Solids/ Sulfate/Sulfite	500-mL amber glass	Cool to 4°C
Total organic and inorganic carbon	500-mL amber glass	Adjust to pH <2 w/H_2SO_4, Cool to 4°C
Sodium	500-mL plastic	Adjust to pH <2 w/HNO_3, Cool to 4°C
pH		Analyze on site

(b) Analytical Methods

	Method No.*
Alkalinity ($CaCO_3$)	310.1
Bicarbonate (HCO_3)	310.1
Carbonate (CO_3)	310.1
Hydroxide (OH)	310.1
Residue, Filterable (TDS)	160.1
Residue, Non-filterable (TSS)	160.2
Residue, Total (TS)	160.3
Sulfate (SO_4)	375.2
Sulfide (S)	376.1
Sulfite (SO_3)	377.1

*EPA-600/4-79-020 "Methods for Chemical Analysis of Water and Wastes"

A.2.2 Stretford

A number of chemical analyses were conducted on the Stretford solution during this test program. These chemical analyses were performed in order to determine the following solution properties:

- pH
- oxidation level
- carbonate concentration
- anthraquinone disulfonic acid (ADA) concentration
- vanadium concentration
- thiosulfate concentration

The proposed test plan* specified that the chemical analyses be performed at fixed intervals. These intervals are shown in Table A-2, along with the method of analysis used and the desired levels. The samples for each of the required chemical analyses were taken from a sample line located at the bottom of the solution heater.

Each of the six chemical analysis methods are described below.

A. pH and Oxidation Level Analytical Procedure--

The pH and oxidation measurements were performed with an Orion Model 907 Microprocessor Ionanalyzer, pH probe and oxygen sensing probe respectively.

pH Procedure

1. Keep the Ionanalyzer plugged in at all times; switch to Standby when not in use. Suspend the pH electrode in deionized water or pH 7 buffer when not in use. Keep fill arm cap on when not in use.

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*Proposed Test Plan, Pilot Plant Testing of Stretford Technology on Oil Shale Retort Off-Gas at Geokinetic's Kamp Kerogen Facility. Second field test; Pedco Environmental, Inc., September 30, 1983, Appendix C.

TABLE A-2. PROPOSED CHEMICAL ANALYSIS SCHEDULE FOR STRETFORD PILOT PLANT

Analysis	Method	Schedule	Desired Level
pH	electro-chemical	6 per day	8.5-9.5
oxidation level	electro-chemical	6 per day	--
sodium carbonate	distillation/ titration	1 per day	25.0 g/liter
ADA	spectrophotometry	1 every 2 days	9.6 g/liter
Vanadium	titration	1 every 2 days	3.12 g/liter
Thiosulfate	titration	1 every 2 days	<20%

2. Make sure calibration buffers and samples are at room temperature. Calibrate the system daily as described here. Set the slope dial to 100 percent and the temperature dial to room temperature. Remove the rubber cap from the electrode fill arm. Immerse the electrode in pH 7 buffer, turn the mode switch to pH/0.01, and set the display to 7.00 by using the calibration knob. Switch beaker, and immerse it in pH 10 buffer. Switch to pH/0.01 and set the display to 10.00 with the "% slope" dial. Do not change the temperature setting. Switch to Standby and rinse as before.

3. Immerse the electrode in the sample, switch to pH/0.01, and record the sample pH. Switch and rinse between samples, as above.

4. Add electrode filling solution through fill arm as needed to keep the level within one inch of the arm.

Oxidation Level Procedure

The oxygen content of the Stretford solution was determined by substituting the oxygen sensing electrode into the Orio Ionanalyzer in place of the pH electrode. A calibration solution was not used.

B. Specific Carbonate Analytical Procedure--

Reagents:

1. Absorbing solution:* Dissolve 22 g NaOH and 1.0 g Na_2CO_3 in deionized water and dilute to one liter. Add a few crystals of thymolphthalein indicator.

2. Standard HCl, 0.5N: Dilute 42 ml concentrated HCl to one liter. Standardize against Na_2CO_3 solution carried through the entire procedure.

3. Barium chloride crystals.

4. Hydrogen peroxide, three percent: Dilute 100 ml of 30 percent H_2O_2 to one liter. Prepare every three days. Refrigerate.

5. Hydrochloric acid, 6N: Dilute 500 ml of concentrated HCl to one liter.

6. Sodium carbonate standard: Dissolve 15.8948 g of Na_2CO_3 in deionized water and dilute to one liter. (9.0 mg CO_3 per ml.)

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*EPA-600/4-79-020, "Methods for Chemical Analyses of Water and Waste Waters."

7. HCl, 2.4N: Dilute 200 ml concentrated HCl to one liter.

Procedure:

1. Assemble the apparatus as shown in Figure A-4. Pipette 15 ml of absorbing solution into the absorber. Put glass beads in the distilling flask.

2. Measure an aliquot of sample calculated to contain 100 to 150 mg of CO_3 into the distilling flask. Add water to cover the bottom of the thistle tube. Add ten ml three percent H_2O_2.

3. Turn on the vacuum so a gentle stream of bubbles is generated in the absorber. Add 20 ml of 6N H_2SO_4 through the thistle tube. Before the acid is completely drawn into the flask, attach the LiOH tube to the tube inlet. Adjust the vacuum as necessary during the distillation. Turn on the cooling water flow to the condenser.

4. Bring the solution to a gentle boil and hold for about two to three minutes. Turn off the flame and continue to draw air through the system for 15 minutes. If the absorbing solution does not remain blue, too much sample was used. Start again with less sample.

5. Remove the absorber and transfer the absorbing solution to a beaker. Rinse the absorber into beaker. Moisten a strip of lead acetate test paper with 2.4N HCl. With a stirring rod, transfer a drop of absorbing solution to the paper. If the paper turns black, H_2S has distilled over. Repeat the test, increasing the amount or strength of the H_2O_2 added, until no H_2S distills over.

6. When a sulfide-free distillate is obtained, add two to three g $BaCl_2$ while stirring. Lower the pH electrodes into the solution. Add rapidly but dropwise, enough 2.4N HCl to bring the pH to about 10. From that point, titrate the solution stepwise with 0.5N HCl, recording the number of milliters used and the pH after each addition. Titrate at least to pH 3.5. Make small additions near pH 8.3 and 4.5; larger ones can be used between these values.

7. Titrate 15 ml of absorbing solution in the same way each day.

Standardization:

1. Prepare the apparatus as described above. Pipette 15 ml of standard sodium carbonate into the distilling flask. Carry this solution through the entire distillation and titration procedure.

$$\underline{N}\ \text{HCl} = \frac{4.499}{\text{ml HCl}}$$

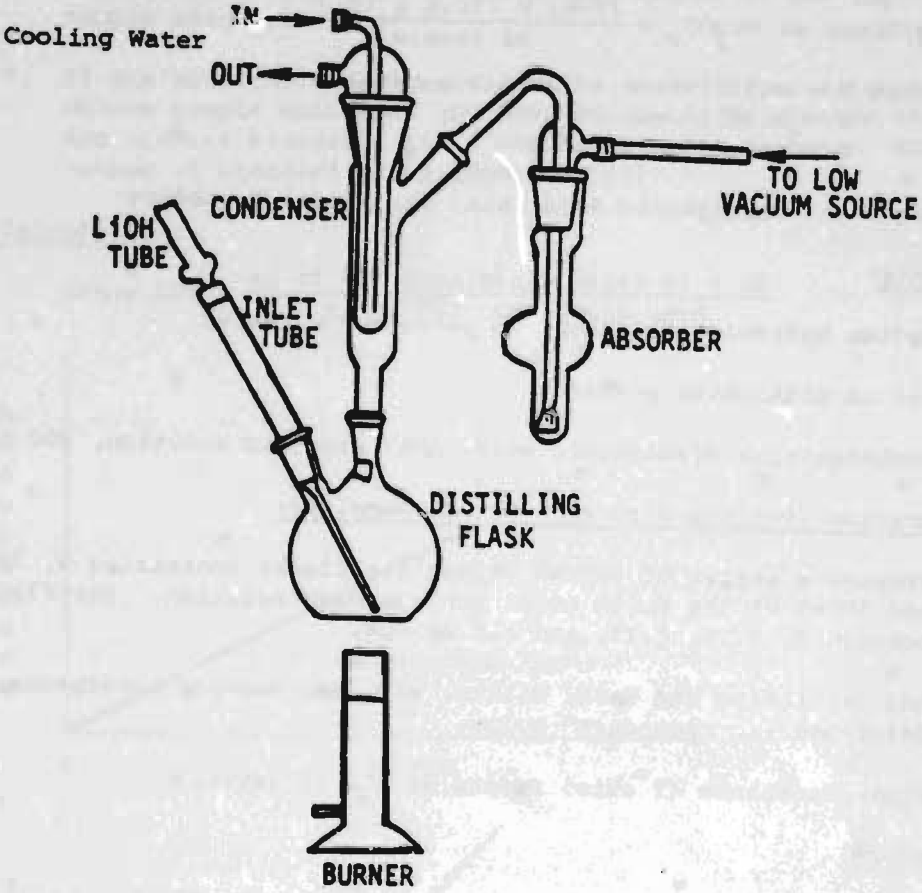


Figure A-4 Carbonate distillation apparatus.

Calculation:

1. Graph the results of the titration, milliliters versus pH. Connect the points with a smooth line. Determine the milliliters used between the two inflection points.

$$\text{g/liter of } Na_2CO_3 = \frac{(T-B)\ N\ (10.6 \times 10^5)}{\text{ml sample}}$$

where T = milliliters of acid for sample
B = milliliters of acid for blank
N = normality of acid

C. Anthraquinone Disulphonic Acid (ADA) Analytical Procedure

Reagents:

1. Sodium hydroxide solution, 30 percent W/W (NaOH)

2. Sodium dithionite powder

3. Anthraquinone disulphonic acid (ADA) standard solution, 250 mg.

Calibration (Perform with each set of samples):

1. Prepare a series of 100-ml volumetric flasks containing 0, 3, 5, and 10 ml of the 0.250 mg/ml ADA standard solution. The flasks contain 0, 0.75, 1.25, and 2.5 mg ADA.

2. Add dithionite and NaOH, dilute, mix, and measure absorbance as described in "Procedure" below.

3. Plot absorbance (Y axis) versus mg ADA (X axis).

Procedure:

1. Familiarize yourself with the operation of the Spectronic 70. Allow the instrument to warm up one hour before each use.

2. Pipette five ml of filtered Stretford solution into a 100 ml volumetric flask and dilute to volume with deionized water.

3. Pipette four aliquots of this solution (five ml each) into 100 ml volumetric flasks. To each flask add approximately 0.1g sodium dithionite powder and ten ml of 30 percent NaOH solution.

4. To three of the flasks pipette about 0.5 x, x and 1.5 x mg of ADA from the standard solution respectively, where x = the mg of ADA in the aliquot. Assuming the Stretford solution contains 6.2 g/l of ADA the volumes of standard to be added are 3, 5 and 10 ml or 0.75, 1.25, and 2.5 mg. Dilute each aliquot to volume.

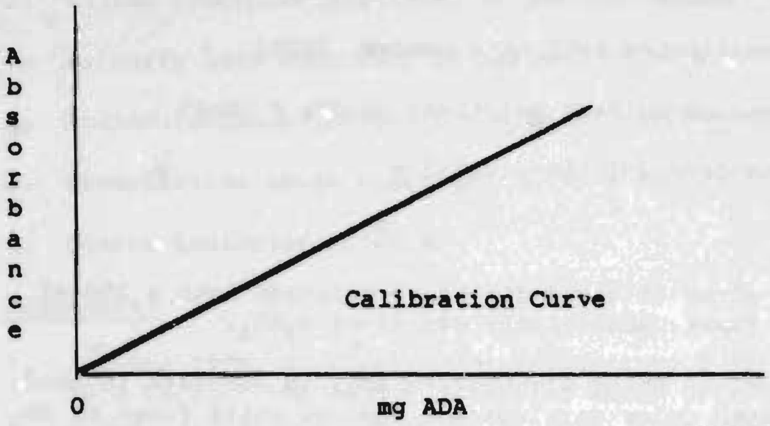
5. Measure the absorbance of each aliquot using the 0 mg ADA standard as zero, at 414 nμ. Determine the measured mg from the calibration curve.

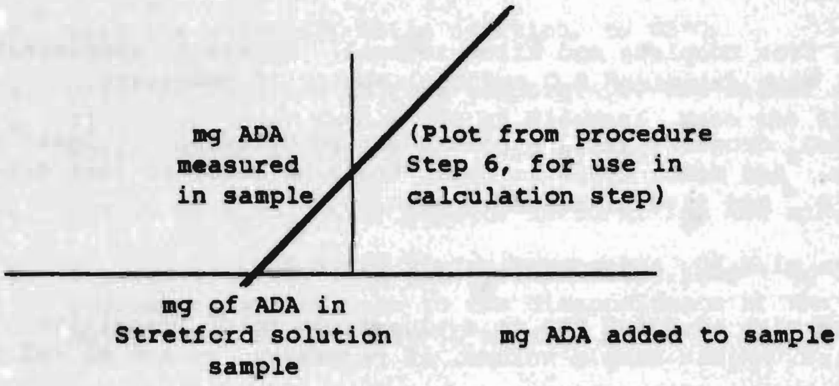
6. Plot the added mg on the X-axis versus the measured mg on the Y-axis. The x intercept is the actual amount of ADA (mg) in the sample aliquot.

7. If the absorbance is less than 0.1, use a larger aliquot of the dilute sample solution. If the absorbance is greater than that of the highest standard, use a smaller aliquot. (Note: adjust the volume of standard added accordingly.)

Calculation:

$$\text{Grams ADA} = \frac{\text{mg of ADA from graph (step 6)} \times 20}{\text{ml of diluted sample used}}$$





Sample Absorbance Curve

D. Vanadium Analytical Procedure

This test <u>must</u> be performed in an exhaust hood. Highly toxic and corrosive sulfur trioxide gas is evolved during the procedure.

<u>Reagents</u>:

1. Sulfuric acid, 50 percent (H_2SO_4)
2. Concentrated nitric acid, 70 percent (HNO_3)
3. Potassium permanganate solution, 0.5 percent $KMnO_4$)
4. Sodium nitrite solution, 0.5 percent ($NaNO_2$)
5. Sulfamic acid solution, 10 percent
6. Concentrated phosphoric acid, 85 percent (H_3PO_4)
7. Sodium diphenylamine sulfonate powder, (SDS)
8. Ferrous ammonium sulfate solution, ~0.025 <u>N</u> (FAS)
9. Vanadium standard solution, 0.015 <u>N</u>

<u>Procedure</u>:

1. Pipette 25 ml of filtered Stretford solution into a 250-ml Erlenmeyer flask. Cautiously add 25 ml H_2SO_4.
2. Add 25 ml HNO_3. Bring solution to boil on hotplate in hood. Boil until greenish color develops and copious white fumes of SO_3 are evolved.
3. Remove from hotplate and allow to cool. Dilute to approximately 100 ml with deionized H_2O and cool again, if necessary.
4. Add $KMnO_4$ dropwise until a pink color persists for at least one minute. Add $NaNO_2$ dropwise until the pink color is just discharged. Add five ml sulfamic acid.
5. Add ten ml H_3PO_4 and approximately 0.1 g SDS.
6. Titrate with ~0.025 <u>N</u> FAS to a blue-green color transition endpoint. Adjust sample volume, if necessary, so ten ml <ml FAS <50 ml.
7. Standardize FAS by preparing and titrating 25 ml of 0.025 <u>N</u> vanadium standard solution as described above. You should use about 15 ml of FAS.

Calculations:

$$\underline{N} \text{ of FAS} = \frac{0.375}{\text{ml FAS}}$$

$$\text{Vanadium, g/liter} = \frac{\text{ml FAS} \times N \times 50.9}{\text{ml of sample}}$$

where N = normality of FAS

E. THIOSULFATE ANALYTICAL PROCEDURE

Reagents:

1. Calcium chloride crystals ($CaCl_2$)
2. Sodium hydroxide solution, 10 percent (NaOH)
3. Sulfuric acid solution, 25 percent (H_2SO_4)
4. Iodine/iodide solution, 0.1 $\underline{N}$ in I_2, 0.24 $\underline{N}$ in KI (I_2)
5. Phenylarsine oxide solution, 0.113 $\underline{N}$ (PAO)
6. Starch indicator solution

Procedure:

1. Pipette 25 ml of Stretford solution into a 250-ml beaker. Add 30 g $CaCl_2$. Add enough distilled water to allow the use of a pH probe, and adjust the pH to 10 to 11 with NaOH.
2. Heat the solution, while stirring, to 85°C.
3. Cool the solution to room temperature, and filter through Whatman 42 filter paper into a 250 ml Fleaker. Wash the filter cake with water, using a minimum of three rinses.
4. Add 25 ml H_2SO_4, mix, pipette in 50 ml I_2, and mix.
5. Titrate with PAO to a pale yellow color, add 1 to 2 ml starch indicator, and titrate to the disappearance of the blue color. Adjust sample volume so 10 ml $<$ ml PAO $<$ 50 ml.
6. Standardize the I_2 with each set of samples by pipetting 20 ml of it into a solution of 15 ml H_2SO_4 in about 50 ml water. Titrate with PAO as in step 5.

Calculations:

$$\underline{N} \text{ of } I_2 = \frac{2.26}{\text{ml } I_2}$$

$$\text{Sodium thiosulfate, g/l} = 158 \times \frac{(\text{ml } I_2 \times \underline{N}\ I_2) - (\text{ml PAO} \times .113)}{\text{ml of sample}}$$

APPENDIX B

SELECTIVE SCRUBBING OF H_2S FROM CO_2 IN SHALE OIL RETORT OFFGAS BASED ON THE PENETRATION THEORY

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PART 1

Penetration Theory for Mass Transfer and Reaction of H_2S-CO_2-NH_3

The simultaneous chemical absorption of CO_2, H_2S and NH_3 from exhaust gases by an alkaline scrubbing liquid is considered here. The following reactions are assumed to occur.

i) $$H_2S + NH_3 \rightarrow HS^- + NH_4^+$$

This reaction is instantaneous and irreversible. Since both components enter the liquid film from the gas phase, three cases have to be considered depending on the relative amounts of H_2S and NH_3 at the interface:

I. $[NH_3]_i > [H_2S]_i$;

II. $[NH_3]_i = [H_2S]_i$;

III. $[NH_3]_i < [H_2S]_i$.

The species which is in lesser amount will be consumed at the interface and will not exist inside the liquid film. Its absorption will be entirely controlled by the gas film; liquid film resistance to mass transfer will be effectively zero. Its interfacial concentration can be set to zero for computing the rate of transfer across the gas film. The species in excess will diffuse in and react. Carbon dioxide diffuses in and reacts according to

ii) $$CO_2 + 2OH^- = CO_3^{-2} + H_2O \quad .$$

This reaction is also instantaneous and irreversible. There will be a reaction plane at which CO_2 and OH^- are consumed instantaneously.

Case I. $[NH_3]_i > [H_2S]_i$

H_2S is annihilated at the interface; the excess NH_3 (dissolved) is consumed by the instantaneous and irreversible reaction

$$NH_3 + H^+ \rightarrow NH_4^+ \quad . \qquad \text{Ia}$$

The species to be considered are NH_4^+, HS^-, CO_2, CO_3^{-2} and OH^-. The two species which react instantaneously and irreversibly at a plane are CO_2 and OH^- according to ii) above.

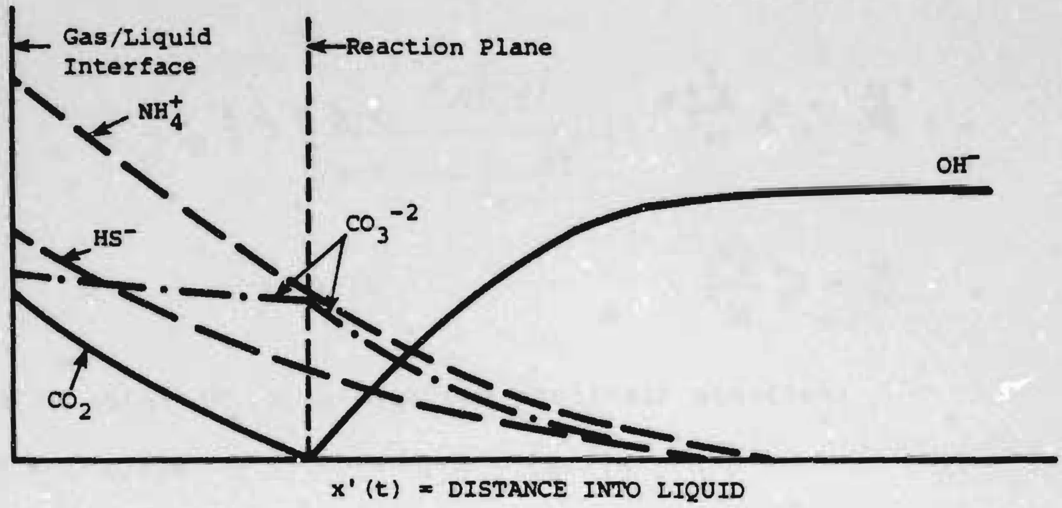
$$CO_2 + 2OH^- = CO_3^{-2} + H_2O. \qquad \text{Ib}$$

Reaction between CO_2 and ammonia (or NH_4^+) can be neglected because of unfavorable equilibrium constants ($K_{eq} \sim 10^{-4}$). All the other species undergo physical diffusion only. The enhancement factor for H_2S and NH_3 in the liquid film is infinite, i.e. absorption of H_2S and NH_3 is entirely controlled by gas film resistance. the interfacial concentration of both H_2S and NH_3 can be set equal to zero to calculate the rate of absorption across the gas film. At any time t, the concentration profile in the liquid film is shown in Figure B-1a.

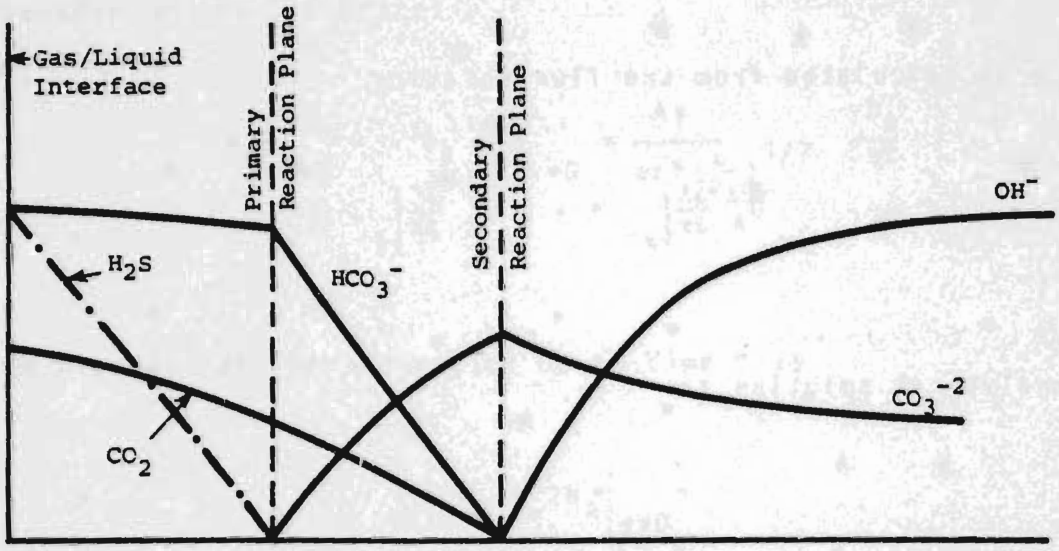
Let

$A \equiv CO_2$; $\qquad C \equiv OH^-$

x' = location of reaction plane



a. Case I - $[NH_3]i > [H_2S]i$



b. Case III - $[H_2S]i > [NH_3]i$

Figure B-1. Concentration Profiles

$$\frac{\partial A}{\partial t} = D_A \frac{\partial^2 A}{\partial x^2} ; \qquad 0 \leq x \leq x'$$

$$\frac{\partial c}{\partial t} = D_c \frac{\partial^2 C}{\partial x^2} , \qquad x' \leq x < x.$$

$A(0,x) = 0;$ $\quad A(t,0) = A_i;$ $\quad A(t,x') = 0;$

$C(0,x) = C_0);$ $\quad C(t,x') = 0;$ $\quad C(t,\infty) = C_0.$

Following the treatment by Bird, Stewart and Lightfoot (1960), we can write

$$x' = \sqrt{4\alpha t} ,$$

and α is calculated from the flux relation

$$D_A \left.\frac{\partial A}{\partial x}\right|_{x'} = - 2 D_c \left.\frac{\partial C}{\partial x}\right|_{x'}$$

The analytical solution is:

$$A = A_i \left[1 - \frac{\operatorname{erf}\left\{\frac{x}{\sqrt{4D_A t}}\right\}}{\operatorname{erf}\left\{\frac{\alpha}{D_A}\right\}^{1/2}}\right] , \qquad 0 \leq x \leq x'.$$

$$C = C_0 \left[1 - \frac{\operatorname{erfc} \left\{ \frac{x}{\sqrt{4 D_c t}} \right\}}{\operatorname{erfc} \left\{ \frac{\alpha}{D_c} \right\}^{1/2}} \right] , \qquad x' \leq x < \infty .$$

α is obtained by solving the nonlinear equation:

$$1 - \operatorname{erf} \left\{ \frac{\alpha}{D_c} \right\}^{1/2} = \frac{Co}{A_i} \sqrt{\frac{D_c}{D_A}} \quad \operatorname{erf} \left\{ \frac{\alpha}{D_A} \right\}^{1/2} \exp \left\{ \frac{\alpha}{D_A} - \frac{\alpha}{D_C} \right\} .$$

From the concentration profiles we can calculate the rate of mass transfer at the interface:

$$N_A \Big|_{x=0} = - D_A \frac{\partial A}{\partial x} \Big|_{x=0} = \frac{A_i}{\operatorname{erf} \left\{ \frac{\alpha}{D_A} \right\}^{1/2}} \sqrt{\frac{D_A}{\pi t}}$$

The average rate of absorption up to time t is

$$\bar{N}_A = 2 N_A \Big|_{z=0}$$

The enhancement factor is:

$$E_A \equiv \text{instantaneous enhancement factor} = \frac{1}{\operatorname{erf} \left\{ \frac{\alpha}{D_A} \right\}^{1/2}} ,$$

and $\bar{E}_A$ ≡ average enhancement factor up to time t = $2E_A$.

Case II. $[NH_3]_i = [H_2S]_i$

This case is very similar to Case I. Both H_2S and NH_3 are consumed at the interface by the reaction

$$H_2S + NH_3 \rightarrow HS^- + NH_4^+ .$$

Reaction Ia does not occur since there is no excess NH_3. Reaction Ib does occur, however. The concentration profiles and enhancement factory for CO_2 remain the same as in Case I except that

$$[NH_4^+]_i = [HS^-]_i .$$

Case III. $[H_2S]_i > [NH_3]_i$

This is the most complex and interesting case mathematically. NH_3 is converted to NH_4^+ at the interface by the reaction

$$H_2S + NH_3 = HS^- + NH_4^+ .$$

The excess H_2S along with CO_2 diffuses into the liquid and reacts with OH^-. This process can be modelled using the two-reaction plane approach of Astarita (1965). Alternatively, the penetration theory equations may be used and the enhancement factors for H_2S and CO_2 in the liquid film calculated, as by Onda et al. (1972).

Fixing the H_2S concentration at the interface is trickey. We can just set it equal to the difference in solubilities between H_2S and NH_3. The profile at any time t is shown in Figure B-1b.

The expressions for the concentration profiles and enhancement factors given by Onda et al. (1972) follow:

Let

$$A \equiv CO_2, \qquad B \equiv H_2S$$

$$A = A_i \left[1 - \frac{\mathrm{erf}\,\{\frac{x}{\sqrt{4D_A t}}\}}{\mathrm{erf}\,\{\frac{x_2}{\sqrt{4D_A t}}\}} \right] ,$$

$$B = B_i \left[1 - \frac{\mathrm{erf}\,\{\frac{x}{\sqrt{4D_B t}}\}}{\mathrm{erf}\,\{\frac{x_1}{\sqrt{4D_B t}}\}} \right] .$$

$$E_A = \frac{1}{\mathrm{erf}\,(\phi_2)} ,$$

$$E_B = \frac{1}{\mathrm{erf}\,(\phi_1 \sqrt{r_A})} ,$$

where

$$\phi_1 = \frac{x_1}{\sqrt{4D_A t}} , \qquad r_A = \frac{D_A}{D_B} ,$$

and

$$\phi_2 = \frac{x_2}{\sqrt{4D_A t}}$$

ϕ_1 and ϕ_2 are obtained by solving equations (31) and (32) in Onda et al.

Design of Venturi Scrubber for Multicomponent Mass Transfer with Reaction

Consider a differential segment of a venturi scrubber of length dz, in which several gaseous species (S species in total) are absorbing into a reactive liquid. For the nth component, a mass balance based on the liquid side gives:

$$N_n a dz = d(L_m X_n) = L_m dX_n + X_n dL_m$$

$$dL_m = N_t a dz, \quad N_t = \sum_{j=1}^{S} N_j$$

so

$$N_n a dz = L_m dX_n + X_n N_t a dz$$

or

$$dz = \frac{L_m dX_n}{N_n a - N_t a X_n} \quad \text{or} \quad \frac{dX_n}{dz} = \frac{N_n a}{L_m} - \frac{N_t a X_n}{L_m}$$

Define the overall coefficient K_{oL_n}:

$$N_n = K_{oL_n} \bar{\rho} (X_n^* - X_n), \quad \frac{1}{K_{oL_n}} = \frac{1}{k_L E_n} + \left(\frac{\bar{\rho}}{P M_m}\right) \frac{1}{kg} ,$$

$$\text{where } M_n = \frac{Y_n - Y_{ni}}{X_n^* - X_{ni}}$$

Mn is derived as follows:

The overall mass transfer coefficient, based on liquid side for multicomponent absorption with reaction, is defined from

$$N_n = k_g P(Y_n - Y_{ni}) = k_L \bar{\rho} (X_{ni} - X_n)$$

$$N_n = K_{oL_n} \bar{\rho} (X_n^* - X_n) ,$$

where X_n^* is the concentration of component n that would be in equilibrium with the bulk gas of mole fraction Y_n. Using these equations,

$$\frac{1}{K_{oL_n}} = \frac{1}{k_L E_n} + \frac{\bar{\rho}}{PM_n} \left(\frac{1}{kg}\right) ,$$

where

$$M = \frac{Y_n - Y_{ni}}{X_n^* - X_{ni}} ,$$ E_n is the enhancement factor for n.

Substitute for N_n:

$$\frac{dX_n}{dz} = \frac{K_{oL_n} a\bar{\rho}}{L_m} (X_n^* - X_n) - \frac{X_n}{L_m} [\sum_{j=1}^{s} K_{oL_j} a\bar{\rho} (X_j^* - X_j)]$$

Take $n = 1, 2, \ldots S$

$$\frac{1}{K_{oL_n} a} = \frac{1}{k_L a E_n} + \frac{\bar{\rho}}{P M_n} \left(\frac{1}{k_g a}\right)$$

Now derive the similar relation for mass transfer of component n based on the gas side:

$$N_n adz = -d(G_m Y_n) = - G_m dY_n - Y_n dG_m$$

$$dG_m = - N_t adz$$

$$N_n adz = - G_m dY_n + Y_n N_t adz$$

$$\frac{dY_n}{dz} = \frac{Y_n N_t a}{G_m} - \frac{N_n a}{G_m}$$

where

$$N_n = K_{oG_n} P(Y_n - Y_n^*)$$

$$\frac{1}{K_{oG_n}} = \frac{1}{k_g} + M \frac{P}{\bar{\rho}} \left(\frac{1}{k_L}\right), \quad M = \frac{Y_{n_i} - Y_n^*}{X_{n_i} - X_n}$$

$$N_t = \sum_{j=1}^{s} N_j$$

To relate the gas and liquid-side balances, consider:

$$-d(G_m Y_n) = d(L_m X_n),$$

$$-G_m dY_n - Y_n dG_m = L_m dX_n + X_n dL_m,$$

$$dG_m = -N_t a dz,$$

$$dL_m = N_t a dz,$$

so that

$$-G_m dY_n + Y_n (N_t a dz) = L_m dX_n + X_n (N_t a dz),$$

or

$$-G_m \frac{dY_n}{dz} + Y_n N_t a = L_m \frac{dX_n}{dz} + X_n N_t a.$$

Rearrange to:

$$\frac{dY_n}{dz} = \frac{N_t a}{G_m} (Y_n - X_n) - \frac{L_m}{G_m} \frac{dX_n}{dz}$$

$$\frac{dG_m}{dz} = - N_t a$$

$$\frac{dL_m}{dz} = N_t a$$

Assuming that the liquid atomizes instantly into the droplet form with a constant mean diameter at the point of entry to the gas stream, the force balance yields (Uchida and Wen, 1973):

$$\frac{dV_L}{dt} = g + \frac{3}{4} \frac{C_d}{d_p} \left(\frac{\rho_g}{\rho_L}\right) \frac{(V_G - V_L)|V_G - V_L|}{V_L}$$

where t is time (s) after gas contact in the throat section. The gas velocity is taken to be a constant in this region. For the drag coefficient, the relation of Ingebo (1956) is used:

$$C_d = 27/Re^{0.84} ,$$

where

$$Re = d_p |V_G - V_L| \rho_G / \mu_G .$$

Distance along the throat is obtained from

$$\frac{dz}{dt} = V_L .$$

The gas-side mass transfer coefficient, k_G, is computed with consideration to the droplet size and varying relative velocity. We use the correlation of Gupalo and Ryazantser (1972):

$$Sh = 0.991\ Pe^{1/3}(1+Re/4)^{0.27}$$

$$= \frac{k_G RT d_p}{D_G} ,$$

where

$$Pe = \frac{d_p |V_L - V_G|}{D_G} .$$

The liquid-side mass transfer coefficient for physical absorption is taken from the penetration theory as

$$k_L = 2 \sqrt{\frac{D_L}{\pi t}} ,$$

where D_L is diffusion rate into infinitely dilute solution.

The parameter a, surface area/volume of unit, is calculated from

$$a = 6(1-\varepsilon)/dp,$$

where

$$\varepsilon = 1-L_o/(V_L A) .$$

Vapor-liquid equilibria

Let n = 1 for H_2S, n = 2 for CO_2, and n = 3 for NH_3. We recognize for inlet partial pressures of H_2S and NH_3 of the same order of magnitude that the NH_3, being much more soluble than H_2S, will be present at the gas-liquid interface in larger concentrations than H_2S. Furthermore, as NH_3 and H_2S participate in a very fast reaction (usually, as here, considered instantaneous),

$$NH_3 + H_2S \rightleftarrows NH_4^+ + HS^- ,$$

to a first approximation we will assume that the interfacial concentration of H_2S is zero and the concentration at NH_3 is equal to its value for physical absorption, with gas film controlling, minus that for H_2S under physical absorption (no NH_3 present), also gas film controlling. This will be approximately true until NH_3 has been depleted in the gas phase enough that its single-solute physical absorption leads to a concentration equal to that of H_2S. After that point, further loss of NH_3 reverses the role of NH_3 and H_2S: the interfacial concentration of NH_3 is zero and that of H_2S is computed by subtracting the single-solute physical absorption concentration of NH_3 from H_2S (Van Krevelen and Hoftijzer 1949).

The use of physical absorption data for calculation of interfacial concentration is appropriate here since the liquid is assumed stagnant and reaction fronts are set up for the fast reaction involving OH^- and CO_3^{-2} that move away from the interface.

For equilibrium of H_2S take

$$X_1 = PY_1/H_1\bar{\rho} ,$$

where $\log H_1 = 102.325 - 4423.11\ T^{-1} - 36.6296 \log T + 0.013870T$ (Mason and Kao, 1979). Here the ionic strength was taken to be zero for this infinite dilution Henry's constant; T is in degrees Kelvin.

For NH_3, the equilibrium expression

$$X_3 = PY_3/H_3\bar{\rho} ,$$

where $\ln H_3 = - 157.552/T + 28.1\ \mathrm{lu}T - 0.049227T - 149.006$ as given by Edwards et al. (1978).

For physical absorption of CO_2

$$X_2 = Y_2/\bar{\rho}\, H_2 ,$$

where

$$\log H_2 = 3.822 - 7.8665 \times 10^{-4} \exp(T/100)$$

$$- 0.04145\ (T/100)^2 - 17.457(T/100)^{-2}$$

as given by Mason and Kao (1979).

Parameters used in this study

Physical and chemical parameters used in this study appear in Table B-1; operating parameters and their ranges in Table B-2. A standard case representing a most probable actual operating condition appears in Table B-3 (only shown are parameters given ranges in Table B-2).

Table B-1. Physical and Chemical Parameters

$$\mu_G = 8\times10^{-3} g/cm.s$$

$$\rho_G = 7.3 \times10^{-4} g/cm^3$$

$$\rho_L = 1g/cm^3$$

$$\bar{\rho} = 0.0562 gmol/cm^3$$

$$g = 980 cm/s^2$$

$$D_{H_2S} = 2.21 \times 10^{-5} cm^2/S$$

$$D_{CO_2} = 10^{-5} cm^2/s$$

$$D_{OH^-} \sim (1.7 - 2.7) D_{CO_2}$$

$$D_{H_2S} \text{ (gas phase)} = 0.424 cm^2/s$$

$CO_2 + OH^- \rightleftarrows HCO_3^-$ $k_f = 6000$ ℓ/gmol s $K_{eq} = 3.4 \times 10^7$

$H_2S + OH^- \rightleftarrows HS^- + H_2O$ $K_{eq} = 8.9 \times 10^8$

Table B-2. Operating Parameters

V_L (inlet) 200-5000 cm/s

dp = 10-70 μm

venturi throat diameter = 3.5 cm

venturi throat length = 25-40 cm

temperature: 30 degrees C

L_m = 1.7 gmol/s cm^2

G_m = 0.4 gmol/s cm^2

P = 1 atm

inlet OH^- concentration = 0.01 - 2 gmol/ℓ

inlet gas H_2S concentration = 50 - 2000 ppm

inlet gas NH_3 concentration = 10 - 2000 ppm

inlet CO_2 concentration 10 - 30% (vol)

Table B-3. Standard Case Operating Conditions

$V_L = 200$ cm/s

$d_p = 30$ µm

venturi throat length = 30.5 cm

inlet liquid $OH^- = 0.025$ gmol/ℓ

inlet gas $H_2S = 1400$ ppm

inlet gas $NH_3 = 950$ ppm

inlet gas $CO_2 = 22\%$ (vol)

RESULTS AND DISCUSSION

The venturi design equations and the penetration theory equations described in this report were coded in a computer program and run on a UNIVAC 1100/61 at the University of Utah Computer Center. A partial listing of this program appears in Part II, Page B-36 with output for the base case presented on Pages B-43 and B-44.

In addition to the listed program, subroutines on the UNIVAC library for stiff differential equation solution and simultaneous nonlinear algebraic equations were utilized.

Figure B-2 shows the percent removal of H_2S and CO_2 versus distance down venturi throat; Figure B-3 shows selectivity, S defined as

$$S = \frac{\%\ \text{removal}\ H_2S}{\%\ \text{removal}\ CO_2},$$

versus distance down the venturi throat. Figure B-2 indicates a substantial portion of H_2S (59%) is removed in a single pass through the venturi, while only a small fraction of CO_2 (1.8%) is removed (NH_3 is reduced 69%). Most H_2S removal occurs early in the throat. The corresponding selectivity shown in Figure B-3 indicates that a maximum in the selectivity is likely some intermediate distance down the throat. This agrees with the results of Hsieh and Aiken (1984) and is a result of the fact that up to and including the region of the peak H_2S is gas film controlled while CO_2 is liquid film controlled; the gas film coefficient is quite high for small contact time but decreases as the gas-liquid relative velocity decreases, while the liquid film coefficient does not decrease as fast.

Figure B-4 shows the dependency of the selectivity on reactant concentration. The selectivity is seen to decrease substantially with increase in OH^- concentration. CO_2 is apparently aided relatively more than H_2S by the reactant.

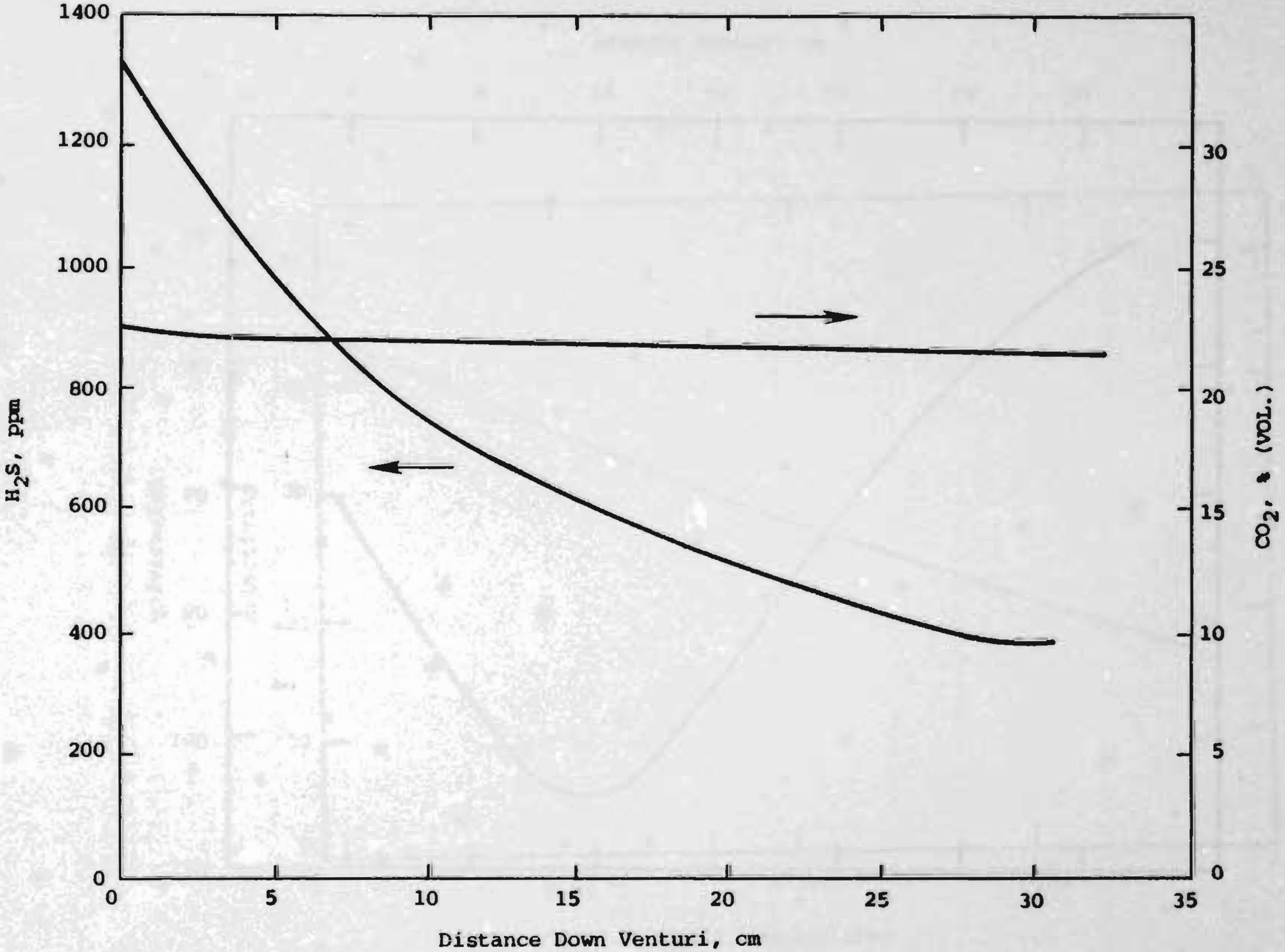


Figure B-2. Base case: removal of hydrogen sulfide and carbon dioxide as a function of distance down venturi throat.

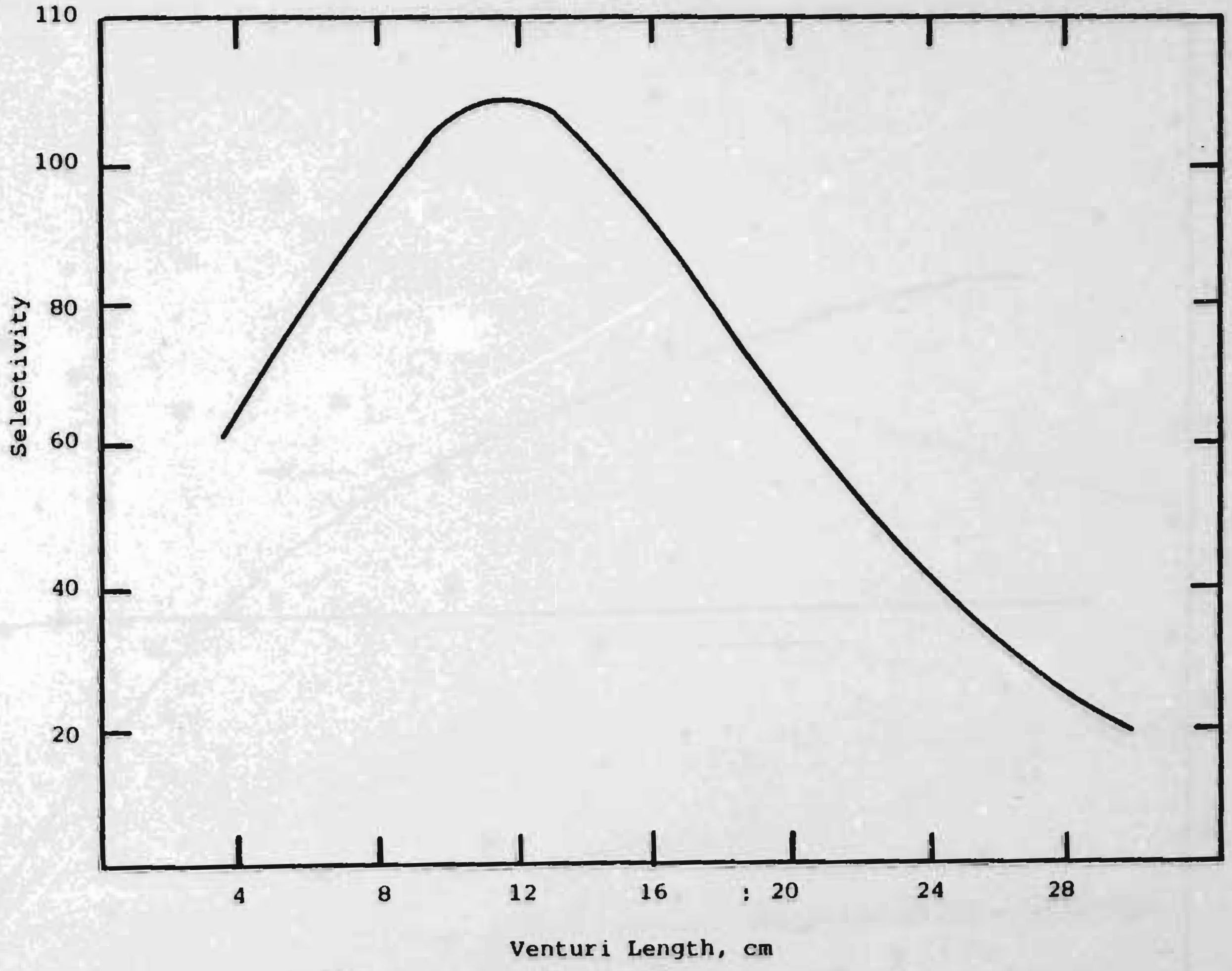


Figure B-3. Selectivity as a function of residence time or venturi length

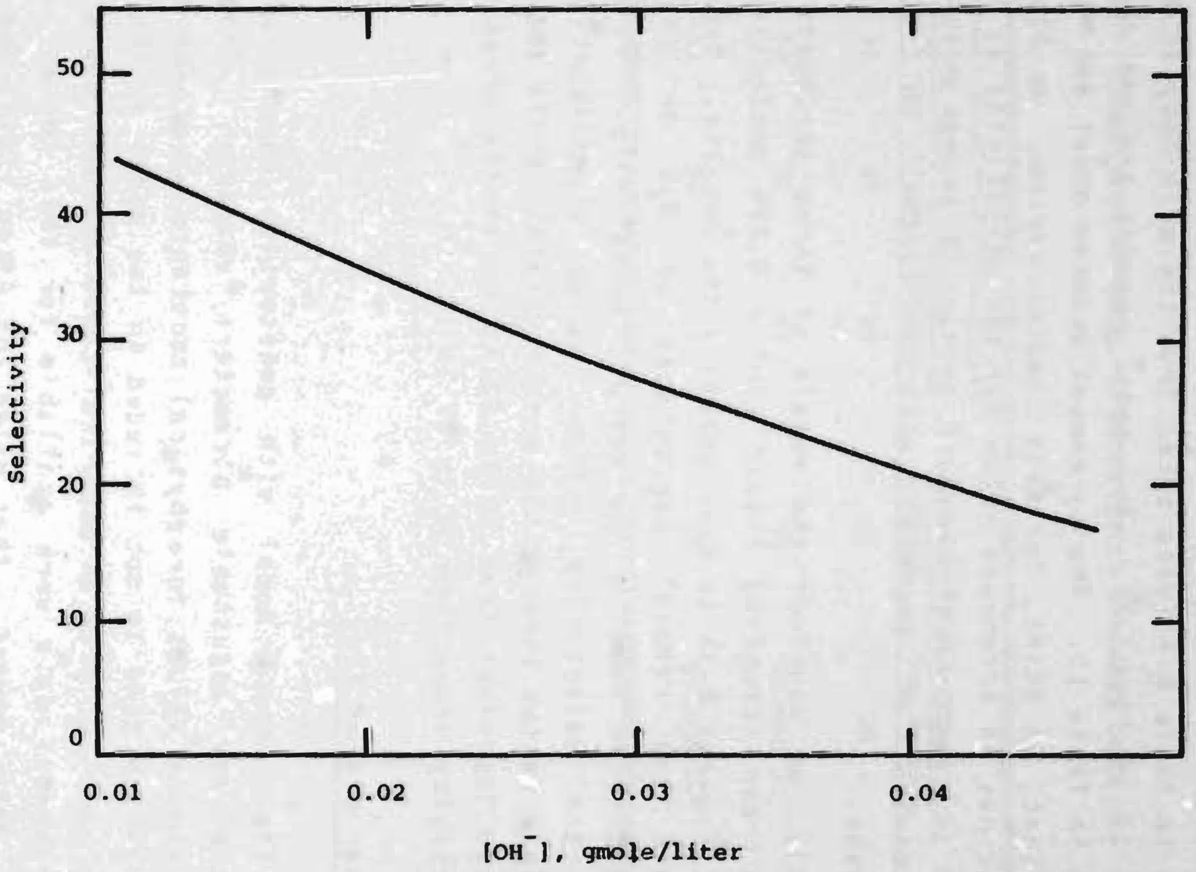


Figure B-4. Effect of initial hydroxide concentration on selectivity.

Comparison with the alkaline scrubber tests on gases from an oil shale in-situ retort of Geokinetics (Uintah County, Utah) is shown in Table B-4 (data taken from the main body of this report, Table 10 on Page 73). The model results are the same as tabulated in Table 10. The agreement between model and experiment is excellent, we think, for this complex system. We claim that Run No. 19 has an erroneous value for the selectivity as indicated in Table 10, page 73 of the main text. It is not possible for the selectivity to increase with a further OH^- concentration increase.

Finally, we consider the result of three scrubbers in series, with fresh scrubbing liquid (OH^- = 0.025 gmole/liter) in each pass; Figures B-5a to B-5c contains the results. Panels a and b contain the removal percentages of H_2S or NH_3 and CO_2, respectively: panel c the overall selectivity. It may be seen that the selectivity suffers quite significantly from the multiple passes through the venturi chain. While the percent H_2S removed increases from 70 to 82 to 93 in the three passes, the selectivity drops from 32 to 23 to 15.

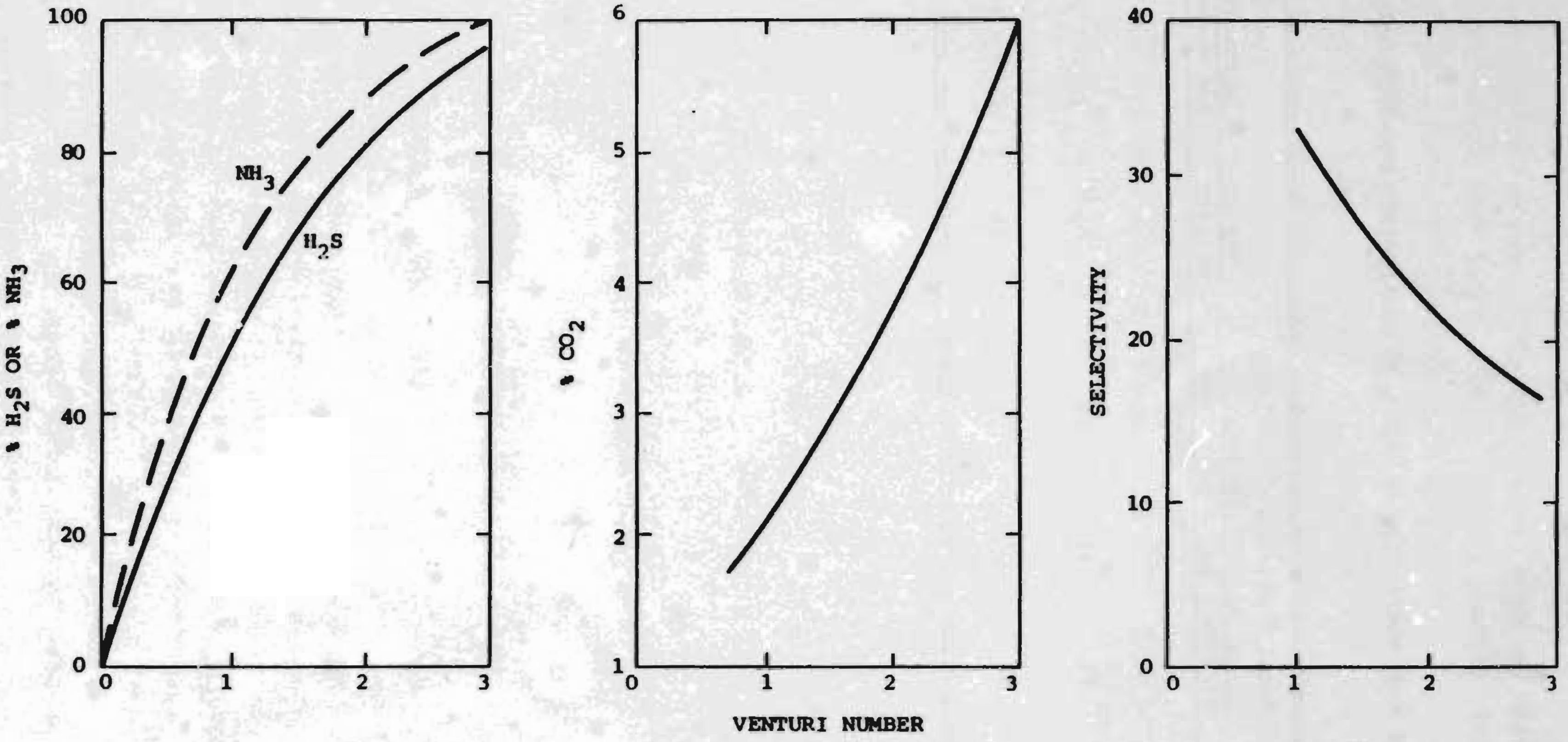
Further discussion

The venturi model with penetration theory does not now include any adjustable parameters whatever, although rather approximate values for physical constants have been chosen. The atomization zone is not included in the model as its physics are quite complex; only an empirical-based approach could be taken if experimental data were available for this region, which it is not. Note, however, that Hsieh and Aiken (1984) and Bendall and Aiken (1982) found experimentally quite unfavorable selectivity in the atomization region of a pressure nozzle and this is likely to be so for the venturi. The overall selectivity would thus decrease somewhat for the unit.

Our results would indicate that a low value reactant concentration, less than 0.01 gmole/liter, be used in a several-

TABLE B-4 COMPARISON OF MODEL TO GEOKINETICS SCRUBBER DATA

[OH$^-$] gmole/liter	Model Predicted Selectivity at Venturi Lengths 20.5 cm	24 cm	Average	Measured Selectivity Average	Run Numbers
0.045	31	25	28	21	26
0.023	53	43	48	55	24 and 30
0.012	82	66	74	75	21 and 28



(a)

(b)

(c)

Figure B-5. Effect of several venturis in series on percent removal of three gases and selectivity of the acid gases pass venturi serial chain. The residence time of each venturi should be optimized and quite likely significantly shorter than the 30.5 cm throat of the present configuration.

The smaller the droplets the better would be the selectivity and extent of H_2S removal since the gas film can limit transfer of H_2S but not CO_2 (not documented herein). Similarly, the higher the gas flow rate the better will be the selectivity (not documented herein); this is so because smaller droplets are produced as well as a large relative velocity, which also increases the gas film coefficient. Again, however, we must qualify these observations with the fact that no consideration is given in the model to the atomization process.

Extent of Removal vs. Selectivity

We seek a single measure of the performance of a mass transfer unit for the selective and extensive removal of hydrogen sulfide from carbon dioxide. The only parameter used up to this point has been defined as the selectivity on page B-19.

This does not consider at all how much hydrogen sulfide is removed. Thus a process may have excellent selectivity while transferring a negligible quantity of hydrogen sulfide! An alternative may be to weight more heavily the percent removal of hydrogen sulfide:

$$\frac{(\text{\% removal of hydrogen sulfide})^{\alpha}}{\text{\% removal of carbon dioxide}}$$

where α is greater than unity. The result of doing this is indicated in Figure B-6 as a function of distance down the venturi. Note on this figure $\alpha = 1$ corresponds to the curve of Figure B-2 but has a different character here. It was seen on the original that a maximum in selectivity occurred at about 12 cm down the throat; this resulted from a decreasing gas film mass transfer coefficient as the gas-liquid velocity decreased and in increasing liquid film coefficient for carbon dioxide as the atomization zone is neared due to liquid mixing. Because we cannot at this level of model development specify well such behavior, we have chosen to omit it here.

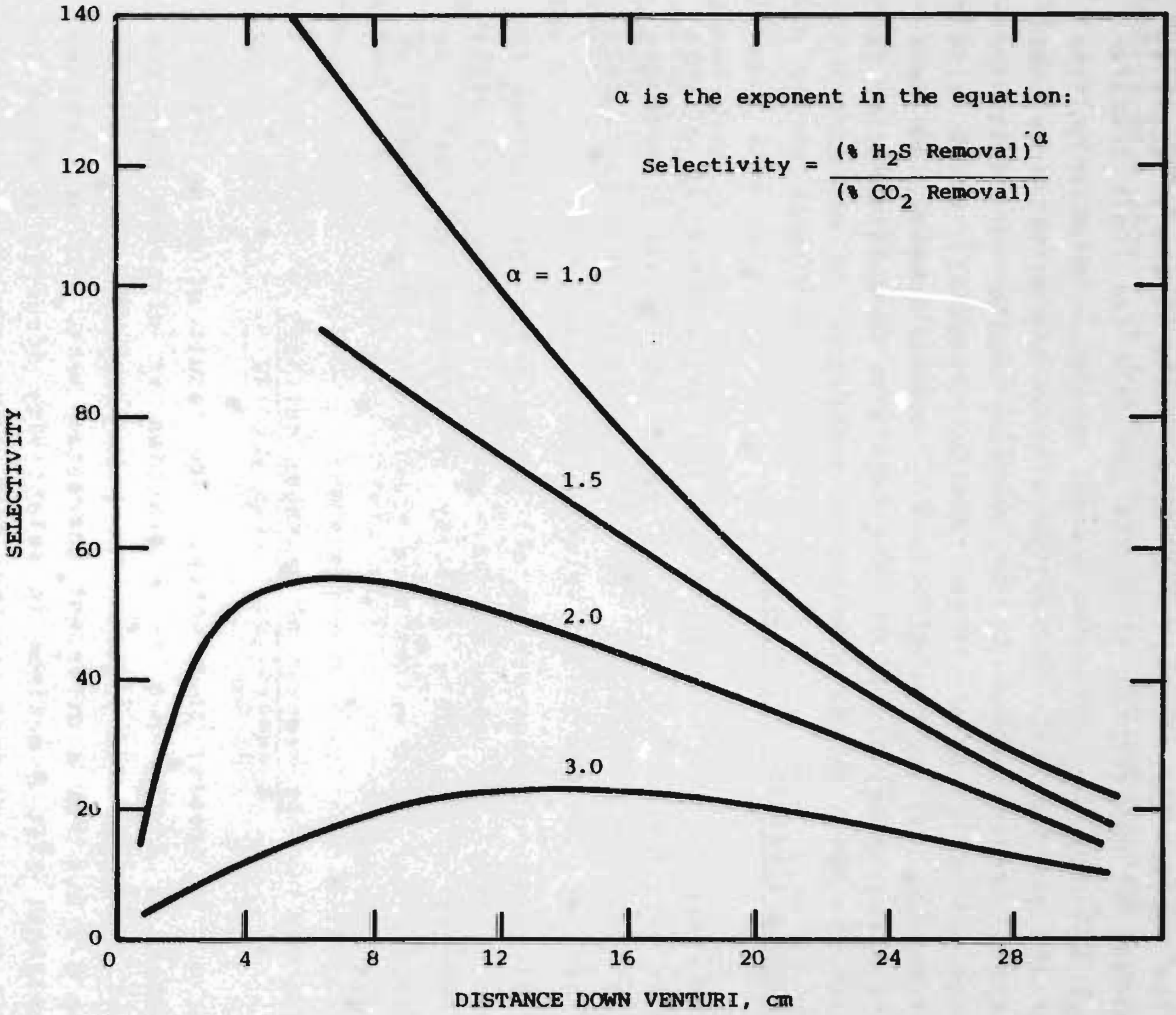
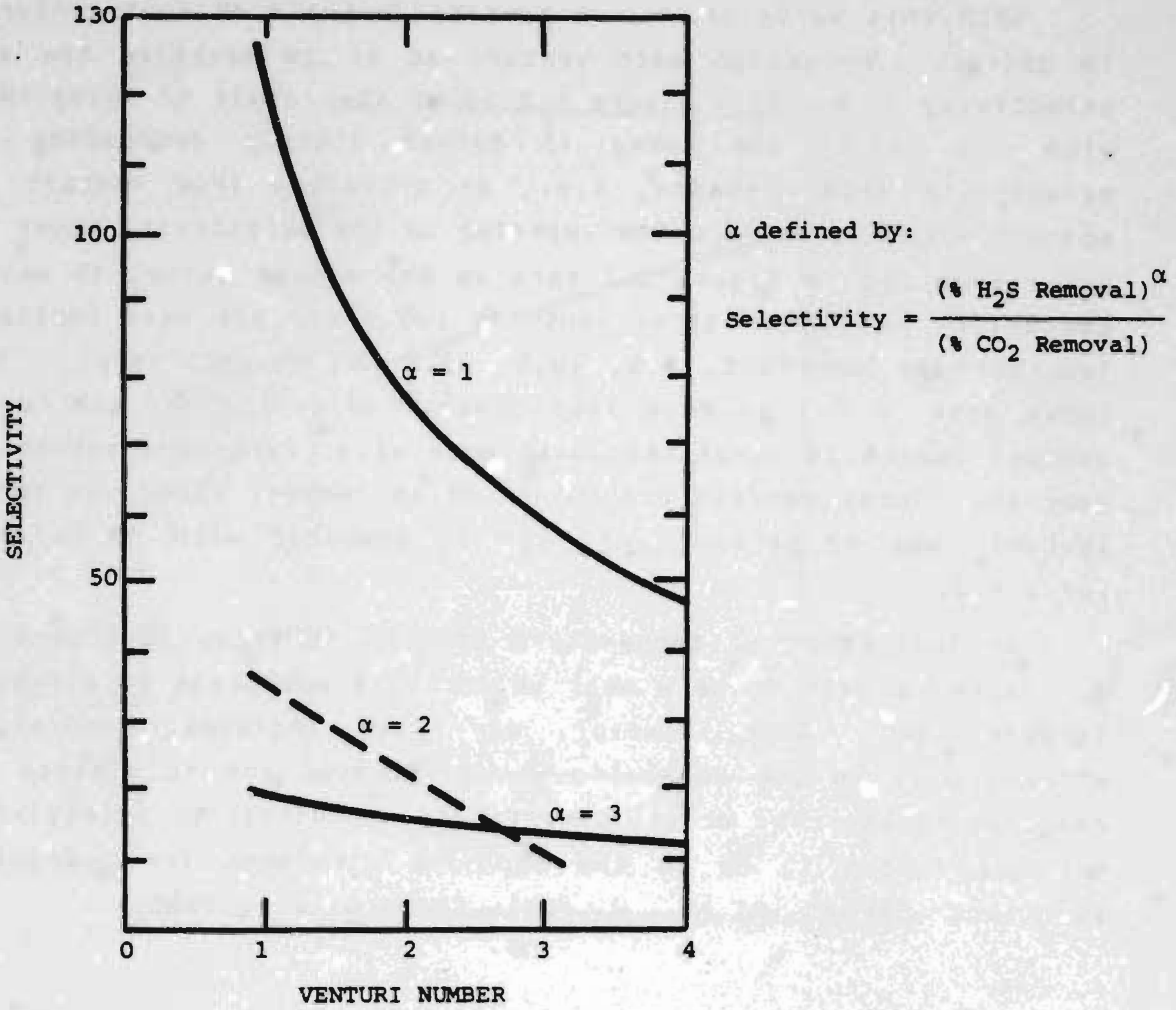


Figure B-6. Study of single optimization parameter in definition of selectivity

As α increases in Figure B-6, an optimum is reached in selectivity that occurs later in the throat as α becomes larger. This is quite reasonable, as more emphasis on extent of removal would favor higher residence times. Clearly a good choice of α should be greater than unity; we choose here $\alpha = 3$.

With this value of α, we consider a train of four venturis in series. We design each venturi so as to maximize the new selectivity ($\alpha = 3$). Figure B-6 shows the result of doing this with $\alpha = 1$; the curve is rather steeply decreasing in selectivity with distance, i.e., as traveling from venturi to venturi - but is still quite superior to the selectivity given in and reproduced in Figure B-7 here as the dashed curve, in which the entire length of three venturis (30.5 cm) was used (optimum lengths here were 9.5, 9.5, 10.5, 11.5 cm, respectively). The curve with $\alpha = 3$ is much less steep, indicating our choice of venturi length is consistent with good selectivity and extent of removal. Total percent hydrogen sulfide removal after the three venturis was 93 percent for $\alpha = 1$, compared with 90 percent for $\alpha = 3$. •

An indication of temperature effects is shown in Figure B-8. There is seen to be a weak selectivity advantage to elevated temperatures. Note, however, our model includes temperature effects only in the vapor-liquid equilibrium and no effects on reaction rates. The actual temperature dependence of selectivity has been shown to be in the opposite direction for hydroxide solutions (Garner, et al., J. Appl, Chem. 8, 325, 1958).



α defined by:

$$\text{Selectivity} = \frac{(\%\ H_2S\ \text{Removal})^{\alpha}}{(\%\ CO_2\ \text{Removal})}$$

Figure B-7. Selectivity vs. venturi pass; solid curves based on optimum selection of venturi length for two different definitions of selectivity. Also shown selectivity for full 30 cm venturi (dashed curve).

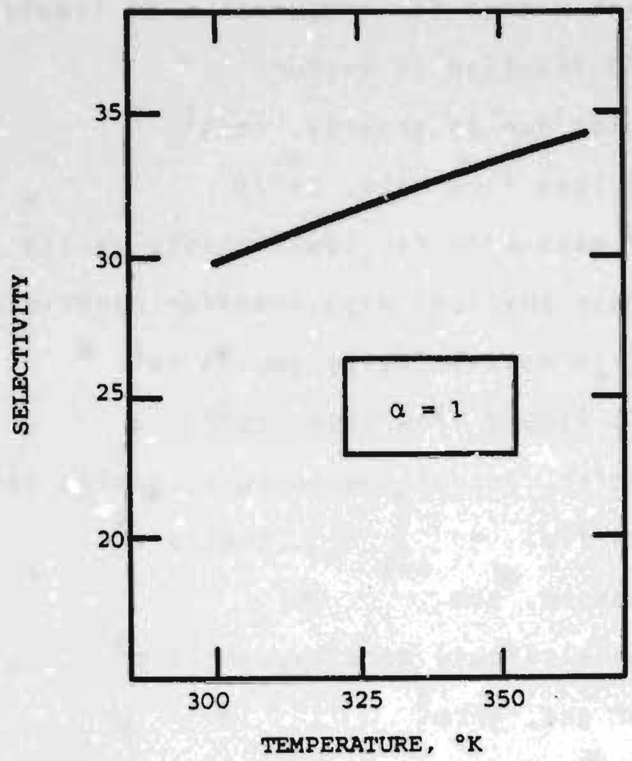


Figure B-8. Effect of Temperature on Selectivity

Nomenclature

A = local venturi cross sectional area, cm^2

C_d = drag coefficient

d_p = droplet diameter, cm

E_n = enhancement factor for component n in liquid.

ϵ = local void fraction in venturi

g = acceleration due to gravity, cm/s^2

G_o = volumetric gas flow rate, cm^3/s

k_g = gas phase mass-transfer coefficient, gmol/s cm^2 atm

k_L = liquid phase physical mass-transfer coefficient, cm/s

L_M = molar liquid mass velocity gmol/s cm^2

L_o = volumetric liquid flow rate, cm^3/s

N_n = mass transfer flux of component n, gmol/s cm^2

N_t = total mass flux $= (\sum_{n=1}^{S} N_n)$, gmol/s cm^2

P = total pressure, atm

$\bar{\rho}$ = average molal liquid density, $gmol/cm^3$

ρ_G = density of gas, g/cm^3

ρ_L = density of liquid, g/cm^3

S = number of species transferred from gas to liquid

t = contact time, s

V_g = gas velocity, cm/s

V_L = liquid velocity (droplet velocity), cm/s

X_n = mole fraction of n in the liquid (mixing cup)

X_{ni} = mole fraction of n in the liquid at the interface

X_n^* = liquid phase mole fraction of A that would be in equilibrium with gas of mole fraction Y_n.

Y_n = mole fraction of n in gas

Y_{ni} = mole fraction of n at the interface in the gas

Y_n^* = gas phase mole fraction of n in equilibrium with bulk concentration in liquid n

z = absorber length, cm

PART II

PENETRATION THEORY COMPUTER PROGRAM LISTING

```
L          IIII     SSSSS    TTTTTTTT    IIII   N      NN   GGGGG
L           II     SSSSSSS   TTTTTTTT     II    NN     NN  GGGGGGG
L           II    SSS    SS     TT        II    NN     NN GGG    GG
L           II    SS            TT        II    NNN    NN GG
L           II    SSS           TT        II    NNNN   NN GG
L           II    SSSSSSSS      TT        II    NN NN  NN GG
L           II     SSSSSSSS     TT        II    NN NNN NN GG     GGG
L           II          SSS     TT        II    NN  NN NN GG      GG
L           II           SS     TT        II    NN   NNNN GG      GG
L           II    SS    SSS     TT        II    NN    NNN GGG    GGG
LLLLLLLLL   II     SSSSSSS      TT        II    NN     NN  GGGGGGG
LLLLLLLLL  IIII     SSSSS       TT       IIII   NN      N   GGGGG
```

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* * * * UNIVERSITY OF UTAH COMPUTER CENTER - UNIVAC 1100 BATCH/TIME-SHARING EXEC LEV. 30R5MP/PROD5 SITE * U OF U * * * *
```

```
  OWNER: 352700  INPUT DEVICE: CRTC9  PART-NUMBER:  0  ACCOUNT-NUMBER: 352700      USER-ID: 352700        CREATOR: 352700
FILE-NAME ON$ITEPRINT$  OUTPUT DEVICE:  CC2    CREATED AT: 00:22:13 NOV 20,1984        PRINTED AT:  00:23:07 NOV 20,1984
```

```
@PRT HOPE
FURPUR F28R1   UC1E  E38 S74T11 11/20/84 00:22:25
```

```
AIKEN*EPA(1).HOPE
              PROGRAM MAIN
            . INTEGER N,NEQN,IFLAG
              REAL KL1,KL2,LMOLD,LMNEW,LENGTH,NH3I
              DIMENSION TIME(100),GK(100),AREA(100),STEP(100)
      C
      C       COMMON BLOCKS
      C
              COMMON /DIFFUS/ D1,D2,D4,D5,D6
              COMMON /GASPRP/ VG,DENSG,VISCG,DIFFG
              COMMON /DROP/ DP,DENSL,DENMOL
              COMMON /HENRY/ HCO2,HH2S,HNH3
              COMMON /CONDS/ TEMP,P,R
      C
      C       DATA ASSIGNMENT
      C
              DATA PI/3.1415927/
              DATA D1,D2,D4,D5,D6/ 2.21E-5,2.0E-5,2.17E-5,1.2E-5,1.2E-5/
              DATA VG,DENSG,VISCG,DIFFG/19000.0,7.3E-4,0.0E-3,0.424/
              DATA DP,DENSL,DENMOL/3.0E-3,1.0,0.0562/
              DATA TEMP,P,R/303.0,1.0,82.00/
      C
      C       ASSIGN PARAMETER VALUES
      C
              LENGTH = 30.5
      C
      C       SET INTEGRATION PARAMETERS
      C
              N = 51
              NEQN = N+1
      C
      C       CALCULATE HENRY'S CONSTANT FOR THE THREE COMPONENTS
      C
              CALL HENRYS(TEMP)
      C
      C       CALCULATE RESIDENCE TIME AND GAS PHASE COEFFICIENT IN EACH SEGMENT
      C
              CALL PARAM(N,NEQN,GK,TIME,AREA,STEP)
      C
      C       FIX THE INITIAL CONDITIONS FOR ALL ODEs
      C
              Y1OLD = 0.214E-3
              Y2OLD = 0.212
              Y3OLD = 0.915E-4
              CAOLD = 0.023E-3
              GMOLD = 3.031
              LMOLD = 1000.0/60.0
      C
      C       WRITE HEADING FOR OUTPUT
      C
              WRITE (6,41)
        41    FORMAT ('1',5X,'SECTION #',5X,'GAS FLOW',5X,'LIQ FLOW',5X,'YH2S'
            *,5X,'YCO2',5X,'COH-',5X,'YNH3'//)
      C
      C       BEGIN STEPPING ALONG THE THROAT OF THE VENTURI
      C
              DO 31 I = 2,NEQN
```

```
      J = I-1
      H = STEP(J)
C
C     CALCULATE INTERFACIAL CONCENTRATIONS
C
      H2SI = P*Y1OLD/HH2S
      CO2I = P*Y2OLD/HCO2
      NH3I = P*Y3OLD/HNH3
C
C     CHOOSE THE SET OF ODEs TO INTEGRATE
C
      IF (NH3I.GE.H2SI) THEN
         NH3I = NH3I-H2SI
         STOR = NH3I*HNH3/P
         IFLAG = 1
         IF (J.EQ.1) THEN
              CAOLD = CAOLD - H2SI
         END IF
         CALL SOLVE1( CAOLD,CO2I,E2,IERROR )
         IF (IERROR.EQ.1) THEN
              PRINT *, 'ROUT FINDER DOES NOT CONVERGE'
              STOP
         END IF
      ELSE
         IFLAG = 2
         H2SI = H2SI-NH3I
         CALL SOLVE2(CAOLD,CO2I,H2SI,E1,E2,IERROR)
         IF (IERROR.GT.129) THEN
              PRINT *, 'ROOT FINDER DOES NOT CONVERGE'
              PRINT *, IER
              STOP
         END IF
      END IF
C
C     BEGIN INTEGRATING APPROPRIATE ODE SET
C
      IF (IFLAG.EQ.1) THEN
         KL1 = 2.0*SQRT(D1/TIME(J)/PI)
         KL2 = 2.0*SQRT(D2/TIME(J)/PI)
         TERM = GK(J)*AREA(J)*P
         TERM1 = TERM*Y1OLD
         IF (I.LT.7) THEN
            TERM3 = 1.2*KL1*AREA(J)*NH3I
         ELSE
            TERM3 = 1.2*TERM*Y3OLD
         END IF
         TERM2 = KL2*E2*AREA(J)*Y2OLD*P/HCO2
         FLUX = TERM1+TERM3+TERM2
C
C     EULER'S METHOD
C
         Y1NEW = Y1OLD+STEP(J)*(Y1OLD*FLUX-TERM1)/GMOLD
 97      Y2NEW = Y2OLD+STEP(J)*(Y2OLD*FLUX-TERM2)/GMOLD
         Y3NEW = Y3OLD+STEP(J)*(Y3OLD*FLUX-TERM3)/GMOLD
         GMNEW = GMOLD - STEP(J)*FLUX
         LMNEW = LMOLD + STEP(J)*FLUX
         CANEW = CAOLD+STEP(J)*2.0*P*(Y2OLD*FLUX-TERM2)/(R*TEMP*
```

```
     *              GMOLD)
           ELSE
             KL1 = 2.0*SQRT(D1/(TIME(J)*PI))
             KL2 = 2.0*SQRT(D2/(TIME(J)*PI))
             TERM1 = KL1*E1*P*AREA(J)*Y1OLD/HH2S
             TERM2 = KL2*E2*P*AREA(J)*Y2OLD/HCO2
             TERM3 = GK(J)*AREA(J)*P*Y3OLD
             FLUX = TERM1+TERM2+TERM3
C
C     EULER'S METHOD
C
             Y1NEW = Y1OLD+STEP(J)*(Y1OLD*FLUX-TERM1)/GMOLD
             Y2NEW = Y2OLD+STEP(J)*(Y2OLD*FLUX-TERM2)/GMOLD
             Y3NEW = Y3OLD+STEP(J)*(Y3OLD*FLUX-TERM3)/GMOLD
             GMNEW = GMOLD - STEP(J)*FLUX
             LMNEW = LMOLD + STEP(J)*FLUX
             C4NEW = C4OLD+STEP(J)*P*(2.*(Y2OLD*FLUX-TERM2)+(Y1OLD-
     *              TERM1))/(R*TEMP*GMOLD)
           END IF
C
C     WRITE RESULTS AT THIS STEP
C
   99 WRITE (6,42) STEP(J),GMNEW,LMNEW,Y1NEW,Y2NEW,CANEW,Y3NEW
   42 FORMAT (' ',5X,F7.3,7X,E9.4,4X,E9.4,4(2X,E8.3))
C
C     UPDATE FUNCTION VALUEES FOR THE NEXT ITERATION
C
           Y1OLD = Y1NEW
           Y2OLD = Y2NEW
           Y3OLD = Y3NEW
           C4OLD = CANEW
           GMOLD = GMNEW
           LMOLD = LMNEW
C
   31 CONTINUE
C
      STOP
      END
C
C
      SUBROUTINE PARAM (N,NEQN,GK,TIME,AREA,STEP)
      INTEGER N,NEQN
      REAL VLBAR,GK(N),TIME(N),H,AREA(N),VL(1),WK(12),STEP(N)
      EXTERNAL FUNCN,FCNJ
C
      COMMON /GASPRP/ VG,DENSG,VISCG,DIFFG
      COMMON /DROP/ DP,DENSL,DENMOL
      COMMON /CONDS/ TEMP,P,R
      COMMON /LOCAL/ G,RAT
C
      DATA G,VLOLD/900.0,50.00/
C
      RATIO1 = DENSG*DP/VISCG
      RATIO2 = DENSG/DENSL/DP
      RAT = 0.75+27.0*RATIO2/RATIO1**0.84
      RATIO3 = DP/DIFFG
      RATIO4 = DIFFG/(R*TEMP*DP)
```

```
C
C     SET PARAMETERS FOR GEAR'S METHOD
C
      N = 1
      METH = 2
      MITER = 2
      INDEX = 1
      IWK = N
      H = 1.0E-7
      TOL = 1.0E-5
      Z = 0.0
      ZEND = 0.01
      VL(1) = VLOLD
C
C     CALCULATE FOR EACH SEGMENT OF THE THROAT THE AVERAGE
C     LIQUID VELOCITY, RESIDENCE TIME AND THE GAS PHASE MASS
C     TRANSFER COEFFICIENT
C
      WRITE (6,21)
 21   FORMAT ('1',5X,'SECTION #',5X,'AVG. LIQ. VEL',5X,'CONTCT. TIME',
     + 5X,'GAS M.T COEFF.',5X,'AREA'//)
C
      DO 10 I = 2,NEQN
          J = I-1
          STEP(J) = ZEND
          DIFF = ZEND-Z
          VL(1) = VLOLD
          CALL DGEAR(N,FUNXN,FCNJ,Z,H,VL,ZEND,TOL,METH,MITER,INDEX,
     *                    IWK,WK,IER)
          IF (IER.GE.132) THEN
             PRINT *, 'GEARS METHOD FAILS -- IER= ',IER
             STOP
          END IF
C
          Z = ZEND
          IF (I.LT.7) THEN
             ZEND = ZEND+0.01
             GO TO 69
          END IF
          IF (I.EQ.7) THEN
             ZEND = 0.1
             GO TO 69
          END IF
          IF (I.LT.12) THEN
             ZEND = ZEND+0.1
          ELSE IF (I.LT.22) THEN
             ZEND = ZEND+0.2
          ELSE IF (I.LT.26) THEN
             ZEND = ZEND+0.25
          ELSE
             ZEND = ZEND+1.0
          END IF
 69       VLNEW = VL(1)
          VLBAR = (VLNEW+VLOLD)*0.5
          VLOLD = VLNEW
          TIME(J) = DIFF/VLBAR
          PECLET = RATIO3*ABS(VLBAR-VG)
```

```
                PECLET = 0.991*PECLET**0.3333
                REYNLD = RATIO1*ABS(VG-VLBAR)
                GK(J) = RATIO4*PECLET*(1.0+0.25*REYNLD)**0.27
                VOIDAG = 1.0-315.0/(9.6*VLBAR)
                AREA(J) = 6.0*(1.0 - VOIDAG)/DP
                WRITE(6,22) STEP(J),VLBAR,TIME(J),GK(J),AREA(J)
   22           FORMAT (' ',5X,F7.3,10X,E9.4,10X,E9.4,8X,E9.4,5X,E9.4)
C
   10     CONTINUE
C
          RETURN
          END
C
C
          SUBROUTINE HENRYS(T)
C
          COMMON /HENRY/ HCO2,HH2S,HNH3
C
C         HENRY'S CONSTANT FOR H2S
C
          DUMP = 102.325-4423.11/T-36.6295*ALOG10(T)+0.01387*T
          HH2S = 10**DUMP
          HH2S = HH2S*1000.0
C
C         HENRY'S CONSTANT FOR CO2
C
          DUMP = 3.822-7.8665E-4*EXP(T/100.0)-0.04145*(T/100.0)**2
     *    -17.457/(T/100.0)**2
          HCO2 = 10**DUMP
          HCO2 = HCO2*1000.0
C
C         HENRY'S CONSTANT FOR NH3
C
          DUMP = -157.552/T+28.1*ALOG(T)-0.049227*T-149.006
          HNH3 = EXP(DUMP)
          HNH3 = HNH3*1000.0
C
          RETURN
          END
C
C
         SUBROUTINE SOLVE1(CAOLD,CO2I,E2,IERROR)
         INTEGER IERROR,ITMAX
         COMMON /DIFFUS/ D1,D2,D4,D5,D6
C
         DATA ITMAX,TOLL/25,1.0E-5/
C
C        INITIAL GUESSES FOR THE ROOT
C
         GUESS1 = 0.0
         GUESS2 = 1.0
C
C        BEGIN ITERATION FOR THE ROOT
C
         DO 61 I = 1,ITMAX
            IF (I.EQ.1) THEN
               AA = D4/D2
```

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ALKALINE AND STRETFORD SCRUBBING TESTS FOR H2S REMOVAL FROM IN-SITU

```
             CONST = (RA-1.0)/RA
             RA = SQRT(RA)
             Q = CAOLD/(2.0*CO2I)
          END IF
          F1=Q*RA*ERF(GUESS1)*EXP(CONST*GUESS1**2)+ERF(GUESS1/RA)-1.0
          F2=Q*RA*ERF(GUESS2)*EXP(CONST*GUESS2**2)+ERF(GUESS2/RA)-1.0
          HF = (GUESS2-GUESS1)*0.5D0
          AV = GUESS1+HF
          F=Q*RA*ERF(AV)*EXP(CONST*AV*AV)+ERF(AV/RA)-1.0
          IF (F.EQ.0.0D0. OR .HF.LT.TOLL) THEN
             ROOT = AV
             E2 = 1.0/ERF(ROOT)
             IERROR  = 0
             GO TO 75
          ELSEIF (F1*F .GT. 0.0D0) THEN
             GUESS1 = AV
          ELSE
             GUESS2 = AV
          END IF
 61   CONTINUE
      IERROR = 1
 75   RETURN
      END
C
C
      SUBROUTINE SOLVE2(CAOLD,CO2I,H2SI,E1,E2,IER)
      EXTERNAL FCN
      DIMENSION X(2),WK(42),PAR(2)
C
      N = 2
      NSIG = 4
      ITMAX = 50
      X(1) = 0.20
      X(2) = 0.20
      PAR(1) = CO2I/H2SI
      PAR(2) = CAOLD/H2SI
C
      CALL ZSCNT(FCN,NSIG,N,ITMAX,PAR,X,FNORM,WK,IER)
      IF (IER.GT.120) GO TO 99
C
C     CALCULATE ENHANCEMENT FACTORS
C
      E1 = 1.0/ERF(X(1))
      E2 = 1.0/ERF(X(2))
C
 99   RETURN
      END
C
C
      SUBROUTINE FCN(X,F,N,PAR)
      REAL X(N),F(N),PAR(2)
C
      TERM1 = EXP(-X(1)**2)/ERF(X(1))
      TERM2 = EXP(-X(2)**2)*PAR(1)/ERF(X(2))
      TERM3 = EXP(1.67*(X(1)**2-X(2)**2))
      TERM4 = ERF(1.67*X(1))
      TERM5 = ERF(1.67*X(2))
```

```
      TERM6 = EXP(-X(2)**2)*PAR(2)/(1.0-ERF(X(2)))
C
      F(1) = TERM1*TERM3+2.0*TERM2-TERM6
      F(2) = (TERM1*TERM3/(TERM5-1.0))*(TERM4-TERM5)-TERM2
C
      RETURN
      END
C
C
      SUBROUTINE FUNXN(M,Z,VL,VLPRIM)
      REAL VL(M),VLPRIM(M)
C
      COMMON /LOCAL/ G,RAT
      COMMON /GASPRP/ VG,DENSG,VISCG,DIFFG
C
      DO 1 I = 1,M
          VLPRIM(I) = (G+RAT*(VG-VL(I))*(ABS(VG-VL(I)))**0.16)/VL(I)
    1 CONTINUE
C
      RETURN
      END
C
C
      SUBROUTINE FCNJ(M,Z,VL,PD)
      REAL VL(M),PD(M,M)
      RETURN
      END
```

(**)

```
SECTION #    GAS FLOW    LIQ FLOW    YH2S      YCO2      COH-      YNH3

   ***      .3883+01  .1667+02  .128-002  224+00  .230-04  .960-03 - initial conditions
   .010      .3883+001   .1667+002 .127-002 .220+000 .229-004 .947-003
   .020      .3883+001   .1667+002 .127-002 .220+000 .229-004 .930-003
   .030      .3883+001   .1667+002 .127-002 .220+000 .229-004 .907-003
   .040      .3883+001   .1667+002 .126-002 .220+000 .229-004 .880-003
   .050      .3883+001   .1667+002 .125-002 .220+000 .229-004 .850-003
   .060      .3883+001   .1667+002 .125-002 .220+000 .229-004 .844-003
   .100      .3882+001   .1667+002 .124-002 .220+000 .229-054 .837-003
   .200      .3882+001   .1667+002 .123-002 .220+000 .229-004 .827-003
   .300      .3882+001   .1667+002 .121-002 .220+000 .229-004 .816-003
   .400      .3882+001   .1667+002 .120-002 .220+000 .229-004 .804-003
   .500      .3882+001   .1667+002 .118-002 .220+000 .229-004 .790-003
   .700      .3882+001   .1667+002 .116-002 .220+000 .229-004 .775-003
   .900      .3881+001   .1667+002 .114-002 .220+000 .229-004 .759-003
  1.100      .3881+001   .1667+002 .112-002 .220+000 .229-004 .741-003
  1.300      .3881+001   .1667+002 .110-002 .220+000 .229-004 .724-003
  1.500      .3880+001   .1667+002 .107-002 .220+000 .229-004 .706-003
  1.700      .3880+001   .1667+002 .105-002 .220+000 .229-004 .687-003
  1.900      .3880+001   .1667+002 .103-002 .220+000 .229-004 .669-003
  2.100      .3879+001   .1667+002 .100-002 .220+000 .229-004 .650-003
  2.300      .3879+001   .1667+002 .981-003 .220+000 .229-004 .632-003
  2.500      .3879+001   .1667+002 .958-003 .220+000 .229-004 .614-003
  2.750      .3878+001   .1667+002 .934-003 .220+000 .229-004 .596-003
  3.000      .3878+001   .1667+002 .911-003 .220+000 .229-004 .578-003
  3.250      .3877+001   .1667+002 .887-003 .220+000 .228-004 .560-003
  3.500      .3877+001   .1667+002 .865-003 .220+000 .228-004 .543-003
  4.500      .3876+001   .1667+002 .839-003 .220+000 .228-004 .524-003
  5.500      .3876+001   .1667+002 .815-003 .219+000 .228-004 .506-003
  6.500      .3876+001   .1667+002 .792-003 .219+000 .228-004 .489-003
  7.500      .3875+001   .1667+002 .771-003 .219+000 .228-004 .473-003
  8.500      .3875+001   .1668+002 .751-003 .219+000 .228-004 .458-003
  9.500      .3874+001   .1668+002 .731-003 .219+000 .228-004 .444-003
 10.500      .3874+001   .1668+002 .714-003 .219+000 .228-004 .431-003
 11.500      .3873+001   .1668+002 .697-003 .219+000 .228-004 .419-003
 12.500      .3872+001   .1668+002 .681-003 .219+000 .228-004 .407-003
 13.500      .3872+001   .1668+002 .666-003 .219+000 .228-004 .397-003
 14.500      .3871+001   .1668+002 .652-003 .219+000 .228-004 .387-003
 15.500      .3870+001   .1668+002 .639-003 .219+000 .228-004 .377-003
 16.500      .3869+001   .1668+002 .627-003 .218+000 .228-004 .369-003
 17.500      .3868+001   .1668+002 .616-003 .218+000 .227-004 .361-003
 18.500      .3868+001   .1668+002 .605-003 .218+000 .227-004 .353-003
 19.500      .3867+001   .1668+002 .595-003 .218+000 .227-004 .346-003
 20.500      .3866+001   .1668+002 .586-003 .218+000 .227-004 .340-003
 21.500      .3865+001   .1669+002 .578-003 .218+000 .227-004 .334-003
 22.500      .3864+001   .1669+002 .572-003 .217+000 .227-004 .330-003
 23.500      .3863+001   .1669+002 .567-003 .217+000 .227-004 .326-003
 24.500      .3861+001   .1669+002 .563-003 .217+000 .226-004 .324-003
 25.500      .3860+001   .1669+002 .556-003 .217+000 .226-004 .319-003
 26.500      .3859+001   .1669+002 .549-003 .216+000 .226-004 .314-003
 27.500      .3858+001   .1669+002 .542-003 .216+000 .226-004 .309-003
 28.500      .3857+001   .1669+002 .533-003 .216+000 .226-004 .303-003
 29.500      .3855+001   .1669+002 .525-003 .216+000 .225-004 .298-003
```

@PRT HOPE

```
    SECTION #     AVG. LIQ. VEL     CONTCT. TIME     GAS M.T COEFF.     AREA

      .000         .50+02              ---                ---            ---        initial conditions
*** WARNING WITH FIX ERROR  (IER =  66) FROM IMSL ROUTINE DGEAR
       .010        .1429+004         .6998-005         .3481-001     .4593+002
       .020        .3339+004         .2995-005         .3296-001     .1965+002
       .030        .4260+004         .2348-005         .3203-001     .1541+002
       .040        .4964+004         .2015-005         .3130-001     .1322+002
       .050        .5548+004         .1802-005         .3069-001     .1183+002
       .060        .6052+004         .1652-005         .3016-001     .1084+002
       .100        .7027+004         .5693-005         .2910-001     .9339+001
       .200        .8942+004         .1118-004         .2691-001     .7339+001
       .300        .1088+005         .9193-005         .2451-001     .6033+001
       .400        .1219+005         .8203-005         .2274-001     .5384+001
       .500        .1317+005         .7592-005         .2132-001     .4983+001
       .700        .1422+005         .1406-004         .1967-001     .4614+001
       .900        .1528+005         .1309-004         .1782-001     .4294+001
      1.100        .1604+005         .1247-004         .1633-001     .4091+001
      1.300        .1660+005         .1205-004         .1509-001     .3953+001
      1.500        .1703+005         .1174-004         .1403-001     .3853+001
      1.700        .1737+005         .1152-004         .1311-001     .3779+001
      1.900        .1763+005         .1134-004         .1230-001     .3721+001
      2.100        .1785+005         .1121-004         .1158-001     .3677+001
      2.300        .1802+005         .1110-004         .1092-001     .3641+001
      2.500        .1817+005         .1101-004         .1033-001     .3612+001
      2.750        .1830+005         .1366-004         .9738-002     .3586+001
      3.000        .1842+005         .1357-004         .9134-002     .3563+001
      3.250        .1851+005         .1350-004         .8589-002     .3545+001
      3.500        .1859+005         .1345-004         .8095-002     .3530+001
      4.500        .1871+005         .5344-004         .7171-002     .3507+001
      5.500        .1884+005         .5306-004         .5832-002     .3482+001
      6.500        .1891+005         .5288-004         .4841-002     .3470+001
      7.500        .1895+005         .5278-004         .4084-002     .3464+001
      8.500        .1897+005         .5272-004         .3490-002     .3460+001
      9.500        .1898+005         .5269-004         .3016-002     .3458+001
     10.500        .1899+005         .5267-004         .2629-002     .3457+001
     11.500        .1899+005         .5266-004         .2312-002     .3456+001
     12.500        .1899+005         .5265-004         .2046-002     .3455+001
     13.500        .1900+005         .5264-004         .1819-002     .3455+001
     14.500        .1900+005         .5264-004         .1623-002     .3455+001
     15.500        .1900+005         .5264-004         .1454-002     .3454+001
     16.500        .1900+005         .5264-004         .1309-002     .3454+001
     17.500        .1900+005         .5264-004         .1181-002     .3454+001
     18.500        .1900+005         .5263-004         .1065-002     .3454+001
     19.500        .1900+005         .5263-004         .9520-003     .3454+001
     20.500        .1900+005         .5263-004         .8414-003     .3454+001
     21.500        .1900+005         .5263-004         .7225-003     .3454+001
     22.500        .1900+005         .5263-004         .5815-003     .3454+001
     23.500        .1900+005         .5263-004         .3970-003     .3454+001
     24.500        .1900+005         .5263-004         .3538-003     .3454+001
     25.500        .1900+005         .5263-004         .4956-003     .3454+001
     26.500        .1900+005         .5263-004         .5570-003     .3454+001
     27.500        .1900+005         .5263-004         .5899-003     .3454+001
     28.500        .1900+005         .5263-004         .6047-003     .3454+001
     29.500        .1900+005         .5263-004         .6136-003     .3454+001
```

PART III

COMPUTATIONAL STUDIES
OF THE SIMULTANEOUS CHEMICAL ABSORPTION
OF THREE GASEOUS COMPONENTS
INTO A REACTIVE LIQUID

The situation considered here is the simultaneous absorption of three gases into a liquid containing a nonvolatile solute with which two of the gases react; the third gas reacts with both the absorbed gases in the liquid phase, but not in the gas phase. Such a situation occurs in the absorption of a gas containing CO_2, H_2S and NH_3 in an alkaline solution. CO_2 and H_2S react with the alkali and the dissolved NH_3 reacts with the dissolved CO_2 and H_2S.

Let $A = CO_2$

$B = H_2S$

$C = OH^-$

$E = NH_3$

The reaction scheme considered is:

$$\begin{aligned}
A + n_1C &\rightarrow P_1, &\quad \text{rate} &= k_1AC \\
B + n_2C &\rightarrow P_2, &\quad \text{rate} &= k_2BC \\
A + n_3E &\rightarrow P_3, &\quad \text{rate} &= k_3AE \\
B + n_4E &\rightarrow P_4, &\quad \text{rate} &= k_4BE
\end{aligned}$$

A material balance over a differential element of liquid results in the unsteady state diffusion equations with reaction terms.

$$\frac{\partial A}{\partial t} = D_A \frac{\partial^2 A}{\partial x^2} - k_1AC - k_3AE ,$$

$$\frac{\partial B}{\partial t} = D_B \frac{\partial^2 B}{\partial x^2} - k_2 BC - k_4 BE \ ,$$

$$\frac{\partial C}{\partial t} = D_C \frac{\partial^2 C}{\partial x^2} - n_1 k_1 AC - n_2 k_2 BC \ ,$$

$$\frac{\partial E}{\partial t} = D_E \frac{\partial^2 E}{\partial x^2} - n_3 k_3 AE - n_4 k_4 BE \ .$$

The boundary conditions are:

$a(x,0) = 0$; $A(0,t) = A_i$; $A(\infty,t) = 0$;

$B(x,0) = 0$; $B(0,t) = B_i$; $B(\infty,t) = 0$;

$C(x,0) = C_o$; $\frac{\partial C}{\partial x}(0,t) = 0$; $C(\infty,t) = C_0$;

$E(x,0) = 0$; $E(0,t) = E_i$: $E(\infty,t) = 0$.

The following dimensionless variables are introduced:

$\eta = \left(\frac{k_2 C_0}{D_B}\right)^{1/2} x$, $\theta = k_2 C_0 t$,

$a = \frac{A}{A_i}$ $b = \frac{B}{B_i}$, $c = \frac{C}{C_0}$, $e = \frac{E}{E_i}$,

$p_1 = k_1/k_2$, $p_3 = k_3/k_2$, $p_4 = k_4/k_2$,

$r_A = D_A/D_B$ $r_c = D_c/D_B$, $r_E = D_E/D_B$

$m_A = \frac{n_i A_i}{C_0}$, $m_B = n_2 B_i/C_0$, $m_E = \frac{E_i}{C_0}$,

$q_3 = \frac{n_3}{n_1}$, $q_4 = \frac{n_4}{n_2}$.

The terms in equation 1 become:

$$\frac{\partial A}{\partial t} = A_i \frac{\partial a}{\partial \theta} = k_2 C_0 A_i \frac{\partial a}{\partial \theta} ;$$

$$\frac{\partial^2 A}{\partial x^2} = A_2 \frac{\partial^2 a}{\partial n^2} \left(\frac{\partial n}{\partial x}\right)^2 = \frac{k_2 C_0 A_i}{D_B} \frac{\partial^2 a}{\partial n^2} ;$$

$$k_1 AC = k_1 C_0 A_i ac; \quad k_3 AE = k_3 A_i E_i ae ;$$

$$\frac{\partial B}{\partial t} = B_i \frac{\partial b}{\partial \theta} \frac{\partial \theta}{\partial t} = k_2 C_0 B_i \frac{\partial b}{\partial \theta} ;$$

$$\frac{\partial^2 B}{\partial x^2} = B_i \frac{\partial^2 b}{\partial n^2} \left(\frac{\partial n}{\partial x}\right)^2 = \frac{k_2 C_0 B_i}{D_B} \frac{\partial^2 b}{\partial n^2} ;$$

$$k_2 BC = k_2 C_0 B_i\, bc \; ; \qquad k_4 BE = k_4 E_i B_i be \; ;$$

$$\frac{\partial C}{\partial t} = C_0 \frac{\partial c}{\partial \theta} \frac{\partial \theta}{\partial t} = k_2 C_0^2 \frac{\partial c}{\partial \theta} \; ;$$

$$\frac{\partial^2 C}{\partial x^2} = C_0 \frac{\partial^2 c}{\partial n^2} \left(\frac{\partial n}{\partial x}\right)^2 = \frac{k_2 C_0^2}{D_B} \frac{\partial^2 c}{\partial x^2} \; ;$$

$$m_1 k_1 AC + n_2 k_2 BC = n_1 k_1 A_i C_0\, ac + n_2 k_2 B_i C_0 bc \; .$$

***

Substituting these relations into Equation 1, we get the dimensionless form of the model equations:

***

$$\frac{\partial E}{\partial t} = E_i \frac{\partial e}{\partial \theta} \frac{\partial \theta}{\partial t} = k_2 C_0 E_i \frac{\partial e}{\partial \theta} \; ;$$

$$\frac{\partial^2 E}{\partial x^2} = E_i \frac{\partial^2 e}{\partial y^2} \left(\frac{\partial n}{\partial x}\right)^2 = \frac{k_2 C_0 E_i}{D_B} \frac{\partial^2 e}{\partial n^2} \; ;$$

$$n_3 k_3 AE = n_3 k_3 A_i E_i\, ae \; ; \qquad n_4 k_4 BE = n_4 k_4 B_0 E_i\, be \; ;$$

$$\frac{\partial a}{\partial \theta} = r_A \frac{\partial^2 a}{\partial \eta^2} - p_1 ac - p_3 m_E ae$$

$$\frac{\partial b}{\partial \theta} = \frac{\partial^2 b}{\partial \eta^2} - bc - b_4 m_E \; be$$

$$\frac{\partial c}{\partial \theta} = r_C \frac{\partial^2 c}{\partial \eta^2} - b_1 m_A ac - m_B bc \;,$$

$$\frac{\partial e}{\partial \theta} = r_E \frac{\partial^2 e}{\partial \eta^2} - b_3 q_3 m_A ae - p_4 q_4 m_B be$$

$a(\eta, 0) = 0$; $b(0, \theta) = 1$; $a(\infty, \theta) = 0$;

$b(\eta, 0) = 0$; $b(0, \theta) = 1$; $b(\infty, \theta) = 0$;

$c(\eta, 0) = 1$; $\frac{\partial c}{\partial \eta}(0, \theta) = 0$; $c(\infty, \theta) = 1$.

$e(\eta, 0) = 0$; $e(0, \theta) = 1$; $e(\infty, \theta) = 0$

These nonlinear coupled PDEs must be solved numerically to give concentration profiles as function of θ and other parameters; however, before they can be solved numerically, the boundary condition at $\eta \rightarrow \infty$ has to be eliminated by an additional variable transformation. Let

$$\xi = \frac{1}{1+\eta} ;$$

$$\frac{\partial \xi}{\partial \eta} = \frac{-1}{(1+\eta)^2} = -\xi^2 ,$$

$$\frac{\partial^2 \xi}{\partial y^2} = \frac{2}{(1+\eta)^3} = 2\xi^3 ,$$

and

$$\frac{\partial^2}{\partial y^2} = \left(\frac{\partial \xi}{\partial y}\right)^2 \frac{\partial^2}{\partial \xi^2} + \frac{\partial^2 \xi}{\partial y^2} \frac{\partial}{\partial \xi}$$

with this transformation, equation 2 now becomes:

$$\frac{\partial a}{\partial \theta} = r_A \xi^A \frac{\partial^2 a}{\partial \xi^2} + 2 r_A \xi^3 \frac{\partial a}{\partial \xi} - p_1 ac - p_3 m_E ae$$

$$\frac{\partial b}{\partial \theta} = \xi^4 \frac{\partial^2 b}{\partial \xi^2} + 2\xi^3 \frac{\partial b}{\partial \xi} - bc - p_4 m_E be$$

$$\frac{\partial c}{\partial \theta} = r_c \xi^4 \frac{\partial^2 c}{\partial \xi^2} + 2 r_c \xi^3 \frac{\partial c}{\partial \xi} - p_1 m_A ac - m_B bc,$$

$$\frac{\partial e}{\partial \theta} = r_E \xi^4 \frac{\partial^2 e}{\partial \xi^2} + 2 Y_E \xi^3 \frac{\partial e}{\partial \xi} - p_3 q_3 m_A ae - p_4 q_4 m_B be ,$$

$a(\eta,0) = 0;$ $a(0,\theta) = 0 ;$ $a(1,\theta) = 1;$

$c(\eta,0) = 1 ;$ $c(0,\theta) = 1 ;$ $\frac{\partial c}{\partial \xi}(1,\theta) = 0 ;$

$e(\eta,0) = 0 ;$ $e(0,\theta) = 0 ;$ $e(1,\theta) = 1 .$

Parameter values for which I is to be solved:

i) $r_A = r_c = r_E = 1 \rightarrow D_A = D_B = D_C = D_E = 2.0 \times 10^{-5}$ cm^2/s ;

ii) $\eta_1 = 1$; $\eta_2 = 2$; $\eta_3 = 1$; $\eta_4 = 2$;

iii) $A_i = .02$ m/lt, $B_i = .002$ m/lt, $E_i = .0016$ m/lt; $C_0 = .2$ m/lt;

iv) $k_1 = 1.0 \times 10^3$ lt/m s ;

v) vary t, p_1, p_3, p_4 suitably

MASS TRANSPORT PARAMETERS:

The instantaneous rate of absorption of A and B is:

$$N_A = - D_A \left.\frac{\partial A}{\partial x}\right|_{x=0} = \left(\frac{r_A k_1 D_A C_0}{p_1}\right)^{1/2} \quad A_i \left.\frac{\partial a}{\partial \xi}\right|_{\xi=1} ,$$

and

$$N_B = - D_B \left.\frac{\partial B}{\partial x}\right|_{x=0} = (k_2 D_B C_0)^{1/2} \quad B_i \left.\frac{\partial b}{\partial \xi}\right|_{\xi=1}$$

$$N_E = - D_E \left.\frac{\partial E}{\partial x}\right|_{x=0} = (k_2 D_E C_0 Y_E)^{1/2} \quad E_i \left.\frac{\partial e}{\partial \xi}\right|_{\xi=1}$$

$$S = \frac{(N_B/B_i)}{(N_A/A_i)} = \frac{1}{r_A} \left[\frac{\partial b/\partial \xi}{\partial a/\partial \xi}\right]_{\xi=1}$$

i) For a given parameter set, look at S vs t; is there an optimum contact time?

ii) For a given contact time, other parameters remaining constant, look at S vs. p; does the effect of one reaction being much faster 'level off'?

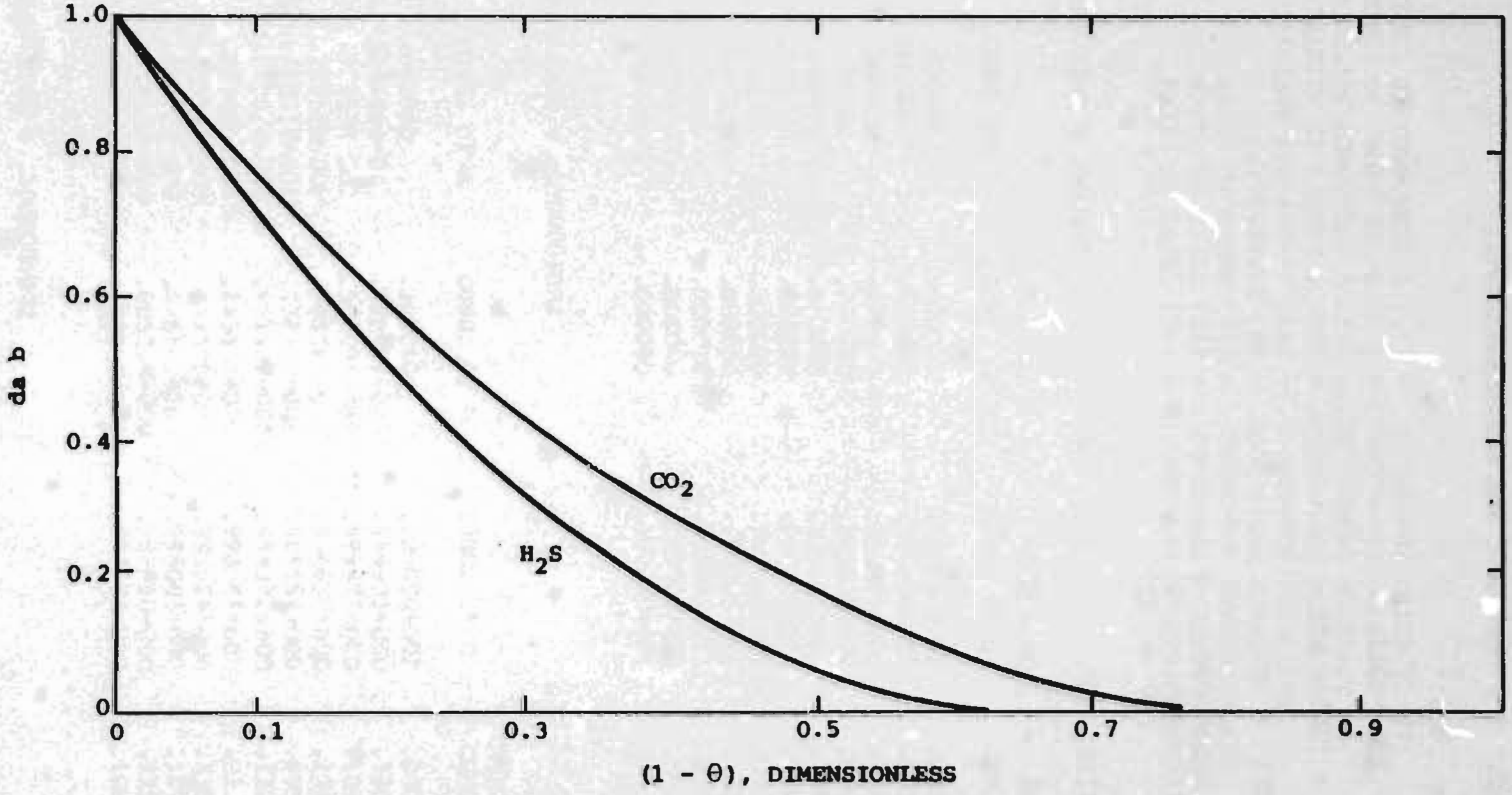

Figure B-5. Profile of hydrogen sulfide and carbon dioxide with distance from interface at time of approximately 0.01 seconds

```
LSODE, RUN NO.  1 - TEST CASE FOR NEW APPROACH

INITIAL T  =  .000

FINAL T  =  .200 + 003

INTERVAL T  = .200 + 002

NUMBER OF ODES  =  44

INTEGRATION ALGORITHM  =  2
  1 - NONSTIFF  (MF  =  10)
  2 - STIFF     (MF  =  22)

ERROR CRITERION - REL

MAXIMUM ERROR  =  .100 - 006
```

INPUT PARAMETERS ARE

```
 INTERFACIAL CONC. OF COMPONENT A (AI) = .200000-001 MOLES/LT CO2
 INTERFACIAL CONC. OF COMPONENT B (BI) = .200000-002 MOLES/LT H2S
 INTERFACIAL CONC. OF COMPONENT E (EI) = .160000-002 MOLES/LT NH3
 INITIAL CONCNTRATION OF LIQUID C (CO) = .200000+000 MOLES/LT OH-
REACTION RATE CONSTANT FOR A+C--P (KA) = .100000+004 LT/MOLE*S
                       DIFFUSIVITY (D) = .200000-004 CM**2/S
                 RATIO OF KA/KB (P1) = .100000-001 DIMENSIONLESS
                 RATIO OF K3/K2 (P3) = .100000-001 DIMENSIONLESS
                 RATIO OF K4/K2 (P4) = .100000+001 DIMENSIONLESS

AT DIMENSIONLESS TIME = .000000

 POSITION      CONC. OF A     CONC. OF B     CONC. OF C     CONC. OF D

.000000        .000000        .000000        .100000+001    .000000
.100000+000    .000000        .000000        .100000+001    .000000
.200000+000    .000000        .000000        .100000+001    .000000
.300000+000    .000000        .000000        .100000+001    .000000
.400000+000    .000000        .000000        .100000+001    .000000
.500000+000    .000000        .000000        .100000+001    .000000
.600000+000    .000000        .000000        .100000+001    .000000
.700000+000    .000000        .000000        .100000+001    .000000
.800000+000    .000000        .000000        .100000+001    .000000
.900000+000    .000000        .000000        .100000+001    .000000
.100000+001    .000000        .000000        .100000+001    .000000

AT DIMENSIONLESS TIME = .200000+002

 POSITION      CONC. OF A     CONC. OF B     CONC. OF C     CONC. OF D

.000000        .000000        .000000        .100000+001    .000000
.100000+000    .294016-003    .878867-005    .999993+000    .320827-003
.200000+000    .573658-002    .507091-003    .999837+000    .609640-002
.300000+000    .229578-001    .508065-002    .999637+000    .236652-001
.400000+000    .598230-001    .238339-001    .999254+000    .608238-001
.500000+000    .119076+000    .663402-001    .998972+000    .120241+000
.600000+000    .211053+000    .145651+000    .998557+000    .212272+000
.700000+000    .336968+000    .267508+000    .998324+000    .338080+000
.800000+000    .508210+000    .446546+000    .998005+000    .509087+000
.900000+000    .725232+000    .685229+000    .997918+000    .725723+000
.100000+001    .100000+001    .100000+001    .997784+000    .100000+001

AT DIMENSIONLESS TIME = .400000+002
```

```
 POSITION        CONC. OF A      CONC. OF B      CONC. OF C      CONC. OF D

.000000         .000000         .000000         .100000+001      .000000
.100000+000     .381004-003     .878720-005     .999991+000      .435383-003
.200000+000     .631849-002     .507203-003     .999766+000      .686030-002
.300000+000     .233125-001     .508038-002     .999626+000      .241300-001
.400000+000     .603422-001     .238355-001     .999178+000      .615044-001
.500000+000     .119459+000     .663400-001     .998959+000      .120743+000
.600000+000     .211469+000     .145654+000     .998480+000      .212818+000
.700000+000     .337276+000     .267509+000     .998310+000      .338483+000
.800000+000     .508463+000     .446549+000     .997928+000      .509418+000
.900000+000     .725367+000     .635230+000     .997904+000      .725899+000
.100000+001     .100000+001     .100000+001     .997707+000      .100000+001

AT DIMENSIONLES TIME = .600000+002

 POSITION        CONC. OF A      CONC. OF B      CONC. OF C      CONC. OF D

.000000         .000000         .000000         .100000+001      .000000
.100000+000     .411941-003     .878584-005     .999995+000      .485275-003
.200000+000     .642041-002     .507283-003     .999726+000      .702366-002
.300000+000     .233804-001     .508009-002     .999631+000      .242392-001
.400000+000     .604340-001     .238366-001     .999136+000      .616516-001
.500000+000     .119529+000     .663395-001     .998965+000      .120856+000
.600000+000     .211544+000     .145656+000     .998437+000      .212937+000
.700000+000     .337332+000     .267509+000     .998316+000      .338573+000
.800000+000     .508508+000     .446551+000     .997885+000      .509490+000
.900000+000     .725391+000     .685230+000     .997909+000      .725938+000
.100000+001     .100000+001     .100000+001     .997664+000      .100000+001

AT DIMENSIONLESS TIME = .800000+002

 POSITION        CONC. OF A      CONC. OF B      CONC. OF C      CONC. OF D

.000000         .000000         .000000         .100000+001      .000000
.100000+000     .427272-003     .878485-005     .100000+001      .515536-003
.200000+000     .644276-002     .507335-003     .999704+000      .706740-002
.300000+000     .234000-001     .507987-002     .999640+000      .242778-001
.400000+000     .604555-001     .238372-001     .999112+000      .616935-001
.500000+000     .119548+000     .663391-001     .998973+000      .120893+000
.600000+000     .211561+000     .145657+000     .998413+000      .212971+000
.700000+000     .337346+000     .267509+000     .998325+000      .338601+000
.800000+000     .508519+000     .446552+000     .997861+000      .509512+000
.900000+000     .725397+000     .685230+000     .997918+000      .725950+000
.100000+001     .100000+001     .100000+001     .997640+000      .100000+001

AT DIMENSIONLESS TIME = .1000000+003
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 POSITION         CONC. OF A        CONC. OF B        CONC. OF C        CONC. OF D

.000000          .000000           .000000           .100000+001       .000000
.100000+000      .436048-003       .678412-005       .100001+001       .536724-003
.200000+000      .645007-002       .507368-003       .999691+000       .708486-002
.300000+000      .234085-001       .507971-002       .999648+000       .242982-001
.400000+000      .604631-001       .238376-001       .999098+000       .617116-001
.500000+000      .119556+000       .663366-001       .998982+000       .120911+000
.600000+000      .211568+000       .145658+000       .998399+000       .212987+000
.700000+000      .337352+000       .267508+000       .998334+000       .338615+000
.800000+000      .508523+000       .446552+000       .997847+000       .509522+000
.900000+000      .725399+000       .685230+000       .997927+000       .725956+000
.100000+001      .100000+001       .100000+001       .997626+000       .100000+001

AT DIMENSIONLESS TIME = .120000+003

 POSITION         CONC. OF A        CONC. OF B        CONC. OF C        CONC. OF D

.000000          .000000           .000000           .100000+001       .000000
.100000+000      .441300-003       .878357-005       .100001+001       .552230-003
.200000+000      .645351-002       .507391-003       .999684+000       .709493-002
.300000+000      .234131-001       .507958-002       .999657+000       .243119-001
.400000+000      .604668-001       .238379-001       .999090+000       .617226-001
.500000+000      .119560+000       .663383-001       .998990+000       .120923+000
.600000+000      .211571+000       .145658+000       .998391+000       .212997+000
.700000+000      .337355+000       .267508+000       .998342+000       .338623+000
.800000+000      .508525+000       .446553+000       .997839+000       .509528+000
.900000+000      .725401+000       .685230+000       .997935+000       .725959+000
.100000+001      .100000+001       .100000+001       .997618+000       .100000+001

AT DIMENSIONLESS TIME = .140000+003

 POSITION         CONC. OF A        CONC. OF B        CONC. OF C        CONC. OF D

.000000          .000000           .000000           .100000+001       .000000
.100000+000      .444482-003       .878314-005       .100002+001       .563719-003
.200000+000      .645546-002       .507407-003       .999679+000       .710186-002
.300000+000      .234159-001       .507948-002       .999664+000       .243217-001
.400000+000      .604689-001       .238381-001       .999086+000       .617302-001
.500000+000      .119562+000       .663380-001       .998997+000       .120931+000
.600000+000      .211573+000       .145659+000       .998386+000       .213003+000
.700000+000      .337356+000       .267508+000       .998349+000       .338629+000
.800000+000      .508527+000       .446553+000       .997834+000       .509532+000
.900000+000      .725401+000       .685230+000       .997942+000       .725962+000
.100000+001      .100000+001       .100000+001       .997613+000       .100000+001
AT DIMENSIONLESS TIME = .160000+003
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 POSITION       CONC. OF A      CONC. OF B      CONC. OF C      CONC. OF D

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.100000+000    .446416-003     .878280-005     .100003+001     .572258-003
.200000+000    .645661-002     .507420-003     .999676+000     .710690-002
.300000+000    .234175-001     .507940-002     .999670+000     .243290-001
.400000+000    .604702-001     .238382-001     .999083+000     .617358-001
.500000+000    .119563+000     .663378-001     .999004+000     .120937+000
.600000+000    .211574+000     .145659+000     .998383+000     .213008+000
.700000+000    .337357+000     .267508+000     .998355+000     .338634+000
.800000+000    .508527+000     .446553+000     .997831+000     .509535+000
.900000+000    .725402+000     .685230+000     .997949+000     .725963+000
.100000+001    .100000+001     .100000+001     .997610+000     .100000+001

AT DIMENSIONLESS TIME = .180000+003

 POSITION       CONC. OF A      CONC. OF B      CONC. OF C      CONC. OF D

.000000        .000000         .000000         .100000+001     .000000
.100000+000    .447592-003     .878252-005     .100003+001     .578610-003
.200000+000    .645732-002     .507429-003     .999674+000     .711063-002
.300000+000    .234185-001     .507934-002     .999676+000     .243343-001
.400000+000    .604710-001     .238383-001     .999081+000     .617399-001
.500000+000    .119564+000     .663376-001     .999009+000     .120942+000
.600000+000    .211575+000     .145659+000     .998381+000     .213012+000
.700000+000    .337358+000     .267507+000     .998361+000     .338637+000
.800000+000    .508528+000     .446553+000     .997829+000     .509538+000
.900000+000    .725402+000     .685230+000     .997954+000     .725965+000
.100000+001    .100000+001     .100000+001     .997608+000     .100000+001

AT DIMENSIONLESS TIME = .200000+003

 POSITION       CONC. OF A      CONC. OF B      CONC. OF C      CONC. OF D

.000000        .000000         .000000         .100000+001     .000000
.100000+000    .448307-003     .878229-005     .100004+001     .583336-003
.200000+000    .645775-002     .507436-003     .999673+000     .711341-002
.300000+000    .234191-001     .507928-002     .999680+000     .243384-001
.400000+000    .604715-001     .238384-001     .999079+000     .617430-001
.500000+000    .119565+000     .663374-001     .999014+000     .120945+000
.600000+000    .211575+000     .145659+000     .998380+000     .213015+000
.700000+000    .337358+000     .267507+000     .998366+000     .338640+000
.800000+000    .508528+000     .446553+000     .997828+000     .509539+000
.900000+000    .725402+000     .685230+000     .997959+000     .725966+000
.100000+001    .100000+001     .100000+001     .997606+000     .100000+001
```

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UNIVERSITY OF UTAH COMPUTER CENTER 1100/61-H2 1100/OS:38R5MP/PROD514-74  BUILD-1

       RUNID:  SRINI      ACCOUNT 581000              EXEC-ID:  38R5MP/PROD5
   PROJECT:  SELECTIVITY OPTS:  CPTN    USER-ID:  352700        P/S:  S/CR1
       EST. TIME:  02:00:00    EST. PAGES:    50     EST. CARDS:      0

*PROGRAM:  SUBMIT
*INITIATION TIME:  02:29:02   NOV 20, 1984
*I/O TIME:  00:00:00.086           ER TIME:    00:00:00.751
*CPU TIME:  00:00:00.012      AVE-MEM-SIZE:              16K
*TOT UNITS:  00:00:00.849   CONDITION WORD:  0000,0000,0000
*TERMINATION TIME:  02:29:03  NOV 20, 1984

*PROGRAM:  SUBMIT/CURRENT
*INITIATION TIME:  02:29:03   NOV 20, 1984
*I/O TIME:  00:00:00.305           ER TIME:    00:00:02.560
*CPU TIME:  00:00:00.011      AVE-MEM-SIZE:              45K
*TOT UNITS:  00:00:00.876   CONDITION WORD:  0000,0000,0000
*TERMINATION TIME:  02:29:05  NOV 20, 1984

*PROGRAM:  CONNECT
*INITIATION TIME:  02:29:05   NOV 20, 1984
*I/O TIME:  00:00:00.040           ER TIME:    00:00:00.035
*CPU TIME:  00:00:00.003      AVE-MEM-SIZE:               9K
*TOT UNITS:  00:00:00.078   CONDITION WORD:  0000,0000,0000
*TERMINATION TIME:  02:29:06  NOV 20, 1984

*PROGRAM:  CONNECT
*INITIATION TIME:  02:29:07   NOV 20, 1984
*I/O TIME:  00:00:00.071           ER TIME:    00:00:00.209
*CPU TIME:  00:00:00.003      AVE-MEM-SIZE:               9K
*TOT UNITS:  00:00:00.284   CONDITION WORD:  0000,0000,0000
*TERMINATION TIME:  02:29:08  NOV 20, 1984

*PROGRAM:  ILSODE/DOUBLE
*INITIATION TIME:  02:29:08   NOV 20, 1984
*I/O TIME:  00:00:00.360           ER TIME:    00:00:01.770
*CPU TIME:  00:01:13.633      AVE-MEM-SIZE:              44K
*TOT UNITS:  00:01:15.763   CONDITION WORD:  0000,0000,0000
*TERMINATION TIME:  02:34:48  NOV 20, 1984

#FILE:  352700*SUBMIT$PF(1)                   DELETED:  02:34:48  NOV 28, 1984

     SPINI  FIN

;I/O TIME:    00:00:01.113                          ER TIME:   00:00:09.378
;CPU TIME:    00:01:13.662                   AVE-MEM-SIZE:              41K
;TOT UNITS:   00:01:24.153                  KILO-MEM-SECS:         3493.212

BILLING INFORMATION 1100/61 UNITS:          83.017
TOTAL-RUNS B/D 114/019 AS OF  02:11:  NOV 20, 1984
CARDS-IN:    22,  OUT:       0     PAGES:    16  TAPEES - LIB/0C:00/00

*EST. COST:   $2.08 USED BY USR-ID:  $1673.80 USR-ID HAS LEFT:   $2026.20
ACCT-BAL   $1697.14 AT 09:06 NOV 19, 1984  EXPIRATION*23:59  DEC 31, 1986
```

Nomenclature

A = local verturi cross sectional area, cm^2

C_d = drag coefficient

d_p = droplet diameter, cm

E_n = enhancement factor for component n in liquid.

ε = local void fraction in venturi

g = acceleration due to gravity, cm/s^2

G_o = volumetric gas flow rate, cm^3/s

k_g = gas phase mass-transfer coefficient, gmol/s cm^2 atm

k_L = liquid phase physical mass-transfer coefficient, cm/s

L_M = molar liquid mass velocity gmol/s cm^2

L_o = volumetric liquid flow rate, cm^3/s

N_n = mass transfer flux of component n, gmol/s cm^2

N_t = total mass flux $= (\sum_{n=1}^{s} N_n)$, gmol/s cm^2

P = total pressure, atm

$\bar{\rho}$ = average molal liquid density, $gmol/cm^3$

ρ_G = density of gas, g/cm^3

ρ_L = density of liquid, g/cm^3

S = number of species transferred from gas to liquid

t = contact time, s

V_g = gas velocity, cm/s

V_L = liquid velocity (droplet velocity), cm/s

X_n = mole fraction of n in the liquid (mixing cup)

X_{ni} = mole fraction of n in the liquid at the interface

X_n^* = liquid phase mole fraction of A that would be in equilibrium with gas of mole fraction Y_n.

Y_n = mole fraction of n in gas

Y_{ni} = mole fraction of n at the interface in the gas

Y_n^* = gas phase mole fraction of n in equilibrium with bulk concentration in liquid n

z = absorber length, cm

TECHNICAL REPORT DATA

(Please read Instructions on the reverse before completing)

1. REPORT NO. EPA-600/7-85-029	2.	3. RECIPIENT'S ACCESSION NO.
4. TITLE AND SUBTITLE Alkaline and Stretford Scrubbing Tests for H_2S Removal from In-situ Oil Shale Retort Offgas		5. REPORT DATE June 1985 6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) H. J. Taback, G. C. Quartucy, and R. J. Goldstick		8. PERFORMING ORGANIZATION REPORT NO. KVB72 807430-1982
9. PERFORMING ORGANIZATION NAME AND ADDRESS KVB, Inc.* 18006 Skypark Boulevard Irvine, California 92714		10. PROGRAM ELEMENT NO. 11. CONTRACT/GRANT NO. 68-02-3166
12. SPONSORING AGENCY NAME AND ADDRESS EPA, Office of Research and Development Air and Energy Engineering Research Laboratory Research Triangle Park, NC 27711		13. TYPE OF REPORT AND PERIOD COVERED Final; 2/83 - 2/85 14. SPONSORING AGENCY CODE EPA/600/13

15. SUPPLEMENTARY NOTES AEERL project officer is Edward R. Bates (EPA, HWERL, Cincinnati, OH 45268, 513/684-7774).(*)Under subcontract to Metcalf and Eddy, Inc., Wakefield, MA 01880.

16. ABSTRACT The report gives results of an evaluation of two mobile pilot-plant scrubbers (one alkaline, the other Stretford) for removing reduced sulfur compounds from the offgas of an in-situ retort at Geokinetics. The alkaline scrubber had a tray tower and a venturi contactor used alternately with NaOH, KOH, and NH4OH to investigate the effects of scrubbing chemical, chemical concentration, and residence time on removal efficiency and H2S selectivity. The Stretford plant employed a venturi contactor (near the end of the test, a packed-tower contactor was added downstream of the venturi). The Stretford test objectives were to repeat a 99+% removal efficiency observed in the previous test and to explain some lower removal efficiencies observed prior to that. The alkaline scrubber efficiency varied inversely with selectivity: at high solution concentration in the tower, 94% removal was achieved at a selectivity of 9; and at low concentration in the venturi, the removal was 50% and the selectivity was 79. The Stretford achieved 99+% removal with the packed tower and 95% with the venturi. A computer model of the alkaline scrubber, based on the penetration theory, was developed and agrees well with the observed performance. Based on this model, it appears possible to design an alkaline scrubber system that can achieve 95% H2S removal at a selectivity of 37.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS		b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Pollution	Alkalinity	Pollution Control	13B
Oil Shale	Ammonia	Stationary Sources	08G
Retorts (Reactors)		Stretford Process	07A
Desulfurization		Caustic Scrubbing	07D
Hydrogen Sulfide			07B
Scrubbers			13I

18. DISTRIBUTION STATEMENT Release to Public	19. SECURITY CLASS *(This Report)* Unclassified	21. NO. OF PAGES 233
	20. SECURITY CLASS *(This page)* Unclassified	22. PRICE

EPA Form 2220-1 (9-73)

END OF

PAPER