

EPA 600/D-85/183
NTIS PB 85 238541

P-352

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18th ANNUAL OIL SHALE SYMPOSIUM
AIRPORT HILTON HOTEL
GRAND JUNCTION, COLORADO

APRIL 22-24, 1985

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This work was sponsored by the U.S. Environmental Protection Agency and was performed under subcontract to Metcalf & Eddy, Inc., Boston, Massachusetts, under EPA Contract No. 68-03-3166. It has been subject to the Agency's peer and administrative review, and it has been approved for publication as an EPA document. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

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ABSTRACT

The EPA's mobile wet scrubber was used on a 200 ACFM slipstream of the Geokinetics retort offgas to investigate the H₂S removal efficiency and selectivity (percent H₂S removal/percent CO₂ removal) as a function of liquid/gas contact time, alkaline solution OH⁻ concentration, and the specific scrubbing chemical. A venturi and a tray tower were used to produce contact times of approximately 0.003 and 0.2 second, respectively. Three alkaline solutions, NaOH, KOH, and NH₄OH were employed on each contactor at various concentrations for a total of 22 runs. To analyze these results and provide design criteria for future alkaline scrubbers a sophisticated computer model employing the penetration theory for liquid-phase mass transfer was developed.

INTRODUCTION

Oil shale facilities proposed for Colorado and Utah will produce substantial quantities of H₂S and other sulfur gases which could impact Class I airsheds such as the Flattops wilderness area. The Clean Air Act requires stringent control of such emissions through the use of best available control technology under PSD permits. This report provides data characterizing in-situ oil shale offgases from the Geokinetics (Seep Ridge) plant in eastern Utah and assessing the effectiveness of alkaline scrubbing processes in controlling the emission of H₂S and other sulfur compounds. The results should assist developers and

permit writers in selecting appropriate controls for the treatment of oil shale offgases.

The offgas from the horizontal in-situ retort at Geokinetics, in eastern Utah, contains approximately 0.15 percent (1500 ppmv) of H₂S, 22 percent CO₂, and 0.10 percent NH₃ in addition to N₂ (60 percent), H₂ (9 percent), CO (5 percent), CH₄ (1.5 percent), and other (2.25 percent). While these percentages are presented on a dry basis, the offgas is actually saturated with moisture. Also present, at levels of 0 to 10 ppmv each, are organic sulfur species such as carbonyl sulfide, mercaptans, thiophenes, and carbon disulfide. Lovell, et al. (1982) and Desai, et al. (1983) evaluated various sulfur-control processes and concluded that caustic (NaOH) scrubbing could be a candidate process if the selectivity of the scrubbing process were sufficiently high. Selectivity here is defined as the percent removal of H₂S (and the organic sulfur) divided by the percent removal of the CO₂. Both H₂S and CO₂ are acid gases and CO₂ is present in a concentration 150 times greater than that of H₂S. Therefore, any caustic or other alkaline scrubbing must take advantage of relative solubilities and reaction rates to achieve a high selectivity of H₂S relative to CO₂.

The full sulfur removal scheme for employing an alkaline scrubber is shown in Figure 1. The retort offgas enters the alkaline scrubber and gives up H₂S and CO₂ to the scrubber liquid. The scrubber liquid is cycled through a regenerator or stripper where the H₂S

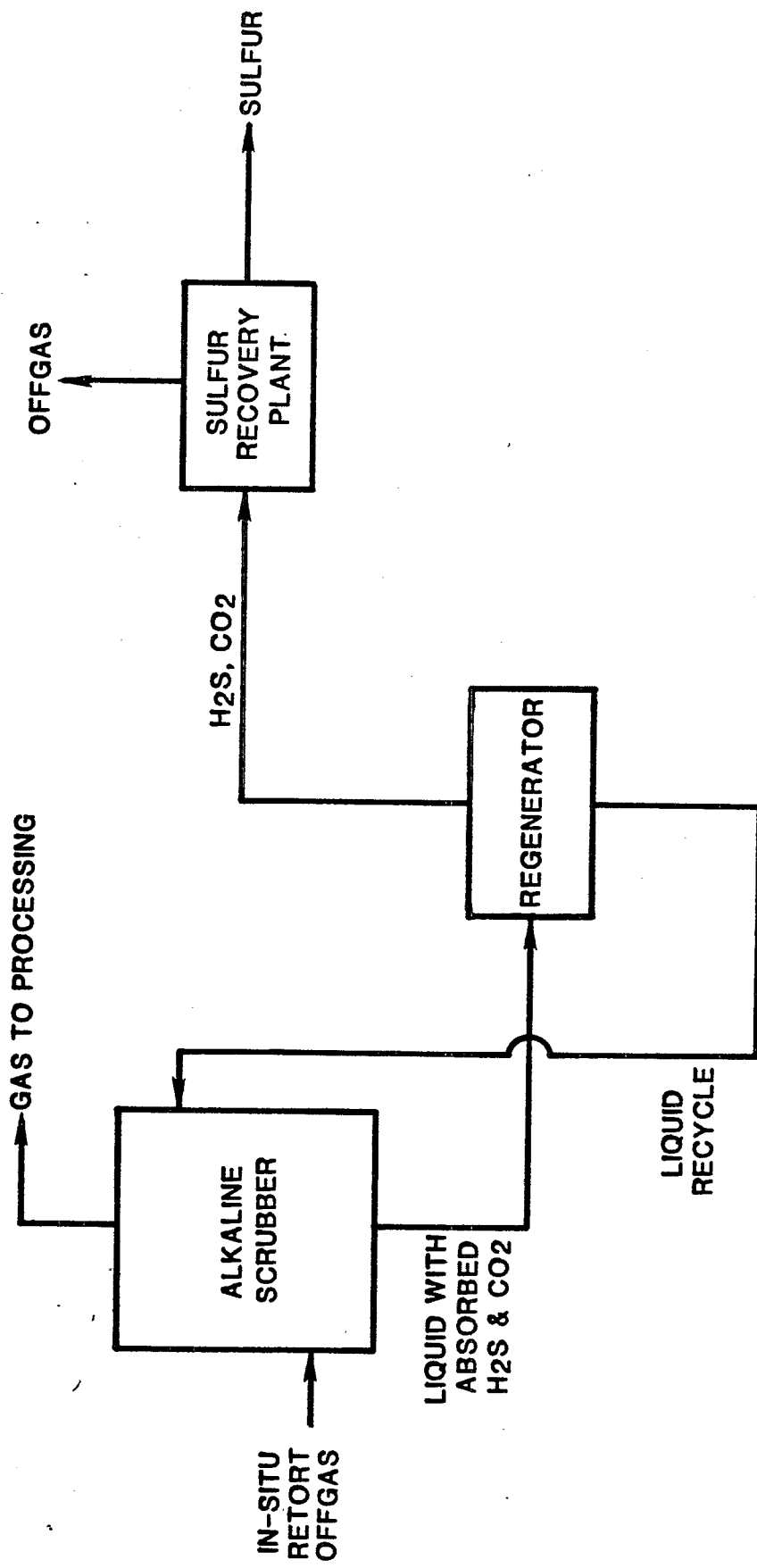


Figure 1. Alkaline Scrubbing Process Schematic for In-Situ Retort Offgas

and CO₂ are distilled off and sent to a sulfur recovery plant (such as Claus) where solid sulfur is produced and the CO₂ is released to the atmosphere. In this system an important parameter is the H₂S concentration in the feed gas to the Claus or other sulfur recovery plants. Desai, et al. (1983) indicated that the Claus process might work with a feed of 8 percent H₂S but at least 15 percent was needed for confidence and 25 percent or higher was desirable. The sulfur recovery plant inlet gas H₂S concentration is equal to the product of the H₂S/CO₂ ratio in the retort offgas times the selectivity factor for the alkaline scrubber. For an oil shale offgas such as that from Geokinetics, the selectivity required in the alkaline scrubbing process can be calculated from the ratio of H₂S to CO₂ in the retort offgas and the desired percentage of H₂S in the feed to the sulfur recovery plant. Some values are:

Sulfur Plant Inlet Gas H ₂ S Percentage Desired	Scrubber Selectivity Required
8	12
15	23
25	38

Thus, a scrubber selectivity of over 40 is desirable, 25 could be acceptable, and 10 is marginal for retort offgas similar to Geokinetics.

Selectivity, while important, is only one performance parameter determining H₂S removal. Unfortunately, many of the factors influencing scrubber performance have conflicting effects. Typical examples are that increasing the hydroxyl ion concentration ([OH⁻]) in the scrubbing solution and increasing the gas-to-liquid contact time may increase removal efficiency of H₂S while decreasing selectivity of H₂S relative to CO₂.

To investigate these effects the EPA sponsored a field testing program which is reported in detail by Taback, et al. (1985). This paper presents a summary of those results and conclusions.

EXPERIMENTAL APPROACH

The EPA's mobile wet scrubber was installed at the Geokinetics site to process a 220 ACFM slipstream of retort offgas. The objectives of these tests were to measure H₂S removal efficiency and selectivity as a function of (1) liquid/gas contact time, (2) scrubbing solution [OH⁻], and (3) specific scrubbing chemical. The mobile scrubber was equipped with both a venturi and a tray tower contactor which produced liquid/gas contact times of approximately 0.003 sec and 0.2 sec respectively. Alkaline solutions of NaOH, KOH, and NH₄OH were employed alternately on each of the contactors at various concentrations as summarized in Table 1. A run consisted of discharging the contents

of the 1-m³ mix tank once through the contactor for a period of approximately 40 minutes. This simulates the operation of the scrubber module in the system shown in Figure 1.

The retort offgas was sampled upstream and downstream of the scrubber and analyzed for specific sulfur compounds and total reduced sulfur. The sampling and the analytical procedures that were used for the specific reduced sulfur compounds are essentially those specified in EPA Methods 15 and 16 (40 CFR 60, Appendix A, July 1, 1982). This 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 at a known rate, scrubbed to remove SO₂ and diluted with clean dry air. An aliquot of the diluted sample is then analyzed for the following sulfur compounds: hydrogen sulfide (H₂S), carbonyl sulfide (COS), carbon disulfide (CS₂), methyl mercaptan (MeSH), and thiophene. In addition, continuous real-time analyses of total reduced sulfur (TRS) in the retort offgas were made by first removing SO₂, oxidizing the sample gas stream in a tube furnace, and then reading the total sulfur as SO₂ using a TECO continuous SO₂ monitor. This technique was derived from EPA Method 15A (40 CFR 60, Appendix A, July, 1982) and was used to provide a real-time display of removal efficiency during the test runs.

EXPERIMENTAL RESULTS

The test results are summarized in Table 2 and Figure 2. Three different solution concentrations were used for each alkali except for the last four runs (No. 19-22) where only the tower was used to make two high concentration runs for both NaOH and KOH.

As expected, it was found that the highest selectivity (percent removal of H₂S divided by percent removal of CO₂) was obtained at the lowest solution concentrations and at the shorter liquid/gas contact times (i.e., with the venturi contactor). Conversely, the highest H₂S removal efficiencies were obtained at the higher solution concentrations and the longer contact times (i.e., with the tray tower contactor). Figures 3 and 4 show the variation of H₂S removal efficiency with [OH⁻]. A limit of 94 percent removal efficiency was reached at an [OH⁻] 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 2). At the low [OH⁻] of 0.012 gram mole/liter the selectivity with the venturi reached as high as 79 with a removal efficiency of just over 50 percent.

The effect of [OH⁻] on selectivity for the venturi and the tower is plotted in Figure 5. Note that the venturi selectivity is more sensitive to [OH⁻] than that of the tower.

TABLE 1. SCRUBBING TESTS CONDUCTED

Run No.	Alkali	Conc. gmoles/liter	Contactors
1	Ammonia	2.0	tower
2	"	"	venturi
3	"	0.05	tower
4	"	"	venturi
5	"	0.3	tower
6	"	"	venturi
7	NaOH	0.05	tower
8	"	"	venturi
9	"	0.012	tower
10	"	"	venturi
11	"	0.023	tower
12	"	"	venturi
13	KOH	0.05	tower
14	"	"	venturi
15	"	0.012	tower
16	"	"	venturi
17	"	0.023	tower
18	"	"	venturi
19	"	0.9	tower
20	"	1.8	tower
21	NaOH	1.25	tower
22	"	2.5	tower

Gas flow approximately $0.1 \text{ m}^3/\text{s}$ (220 ACFM)

Liquid flow approximately 0.38 l/s (6 gpm)

Pressure differential across contactor: Venturi: 34 mmHg (18" H₂O)
 Tray tower: 23 mmHg (12" H₂O)

TABLE 2. SUMMARY OF ALKALI SCRUBBING RESULTS

Contactator	Alkali	OH ⁻ Conc. gmole/liter	Removal Efficiency %	Measured Selectivity*	Run No.
Venturi	NaOH	0.012	52	79	10
Venturi	KOH	0.012	53	71	16
Venturi	NaOH	0.023	48	60	12
Venturi	KOH	0.023	48	51	18
Venturi	NaOH	0.045	70	[84]†	8
Venturi	KOH	0.046	71	21	14
Venturi	NH ₄ OH	0.049	60	71	4
Venturi	NH ₄ OH	0.29	62	56	6
Venturi	NH ₄ OH	2.0	67	11	2
Tower	NaOH	0.012	52	52	9
Tower	KOH	0.012	54	43	15
Tower	NaOH	0.023	54	41	11
Tower	KOH	0.023	59	49	17
Tower	NaOH	0.045	83	36	7
Tower	KOH	0.046	88	41	13
Tower	NH ₄ OH	0.049	64	29	3
Tower	NH ₄ OH	0.29	91	29	5
Tower	NH ₄ OH	2.0	93	9	1
Tower	KOH	0.89	94	N/A	19
Tower	NaOH	1.25	93	N/A	21
Tower	KOH	1.79	92	N/A	20
Tower	NaOH	2.5	94	N/A	22

* Selectivity - A measure of the preferential removal of H₂S over CO₂ taking into account the relative difference in concentration between the two gases. In this paper, selectivity is the ratio of percent removal of H₂S to percent removal of CO₂.

† Data in brackets are suspected to be erroneous.

N/A - Not available. Selectivity values for these runs were not available because the spent scrubbing solution was not analyzed.

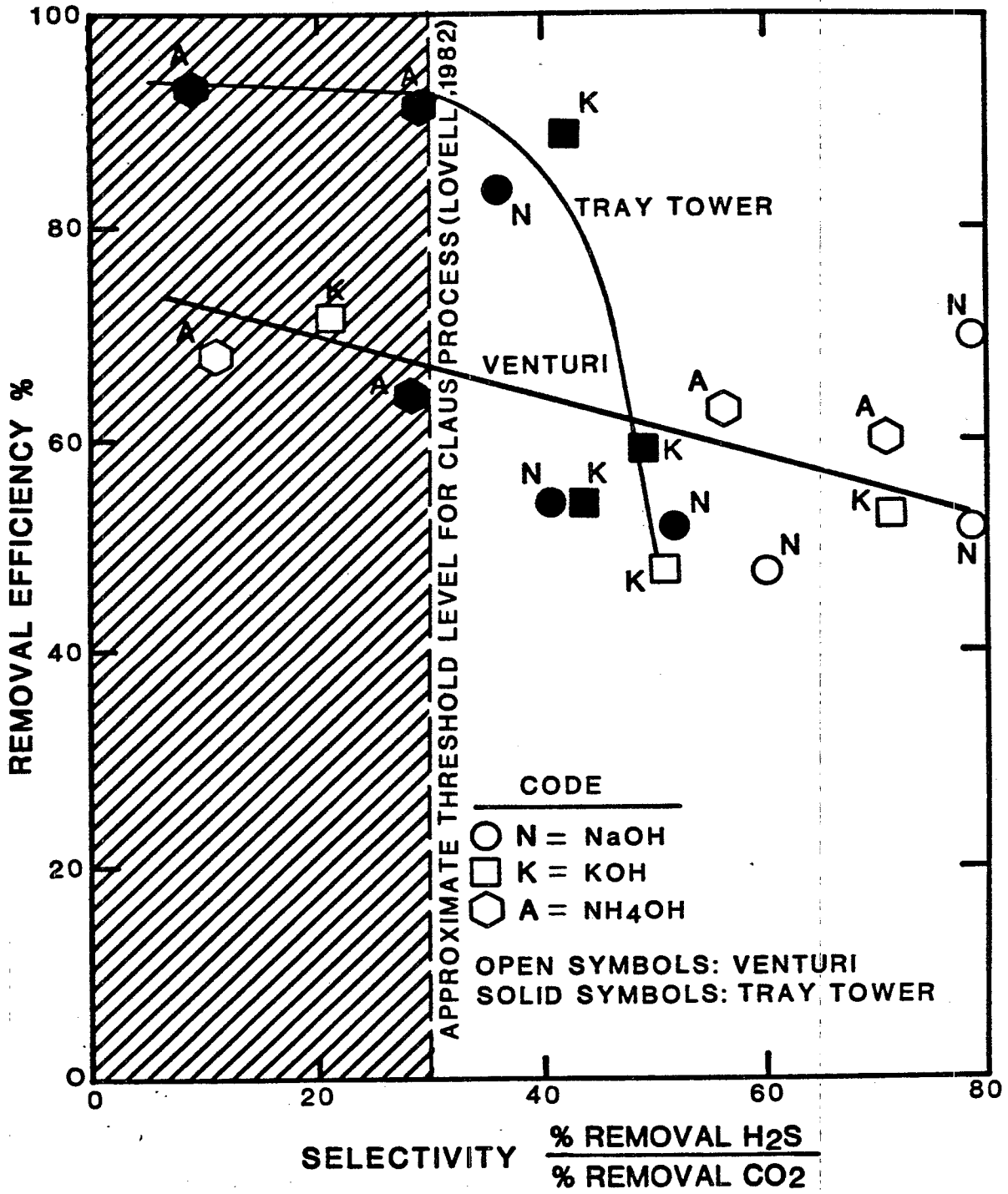


Figure 2. Removal Efficiency vs. Selectivity for Alkaline Scrubber

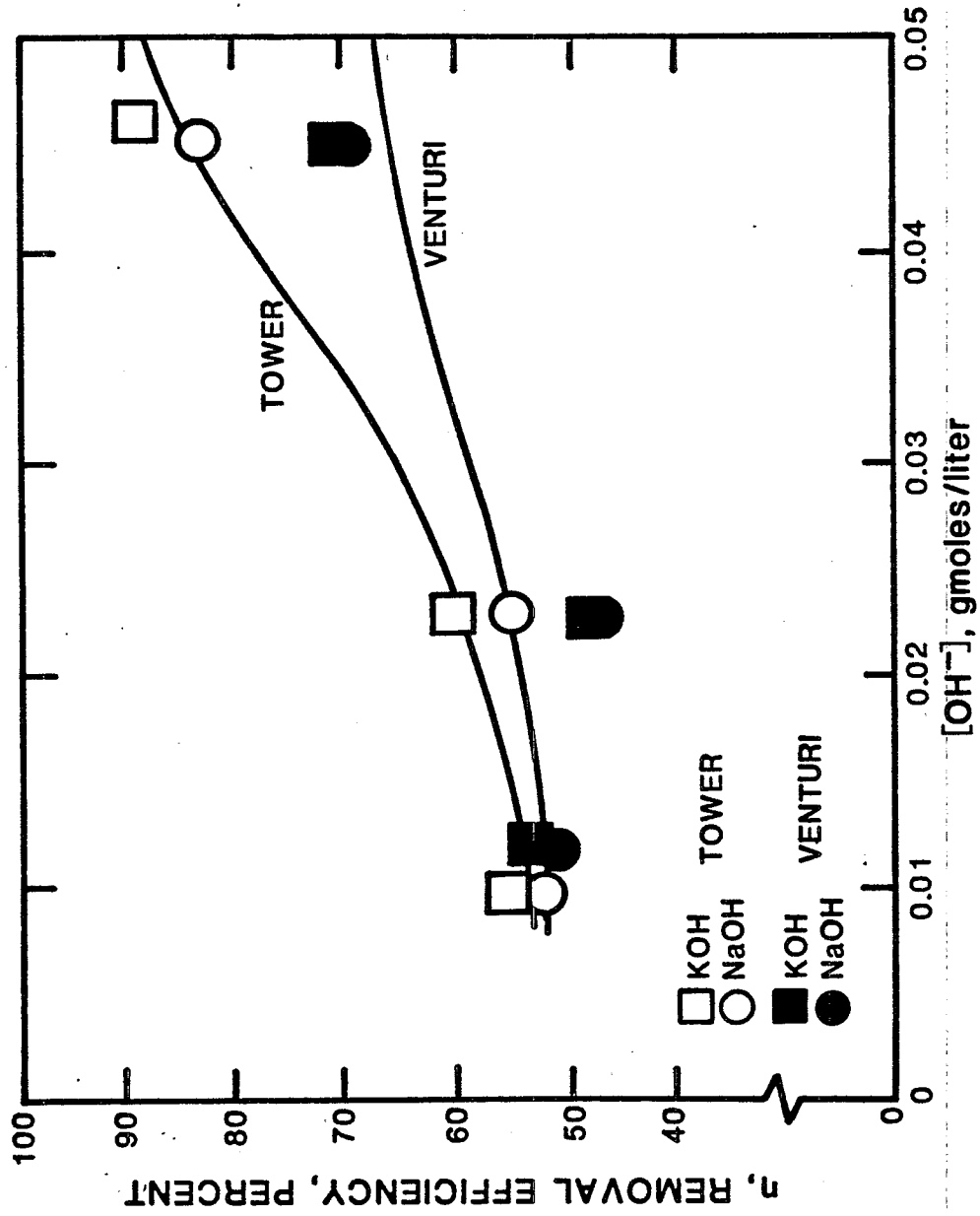


Figure 3. Removal Efficiency for Tower and Venturi at $[OH^-] < 0.05$ gmoles/liter

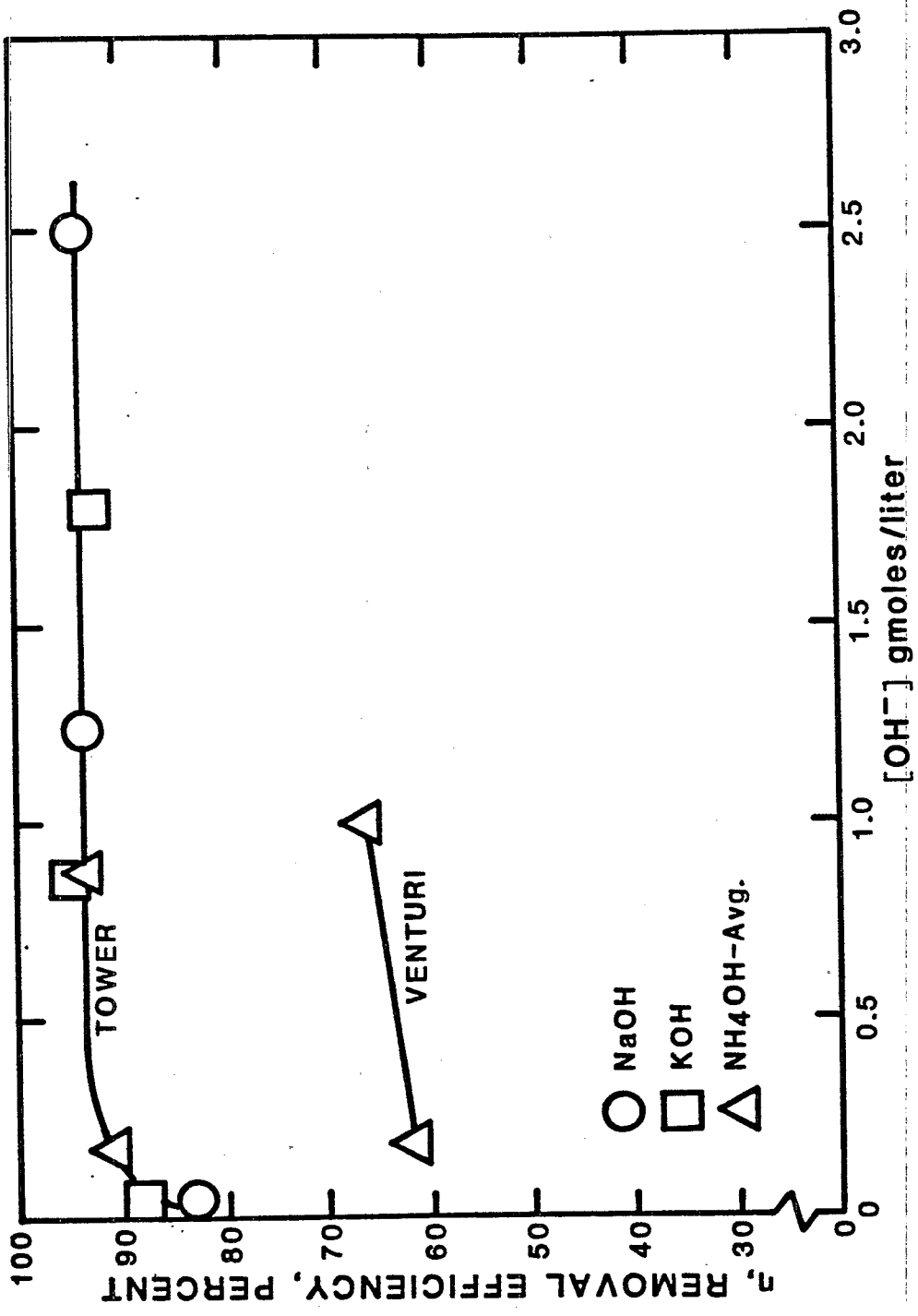


Figure 4. Removal Efficiency for Tower and Venturi at $[OH^-] > 0.05$ gmoles/liter

Discussion of Results

All three of the alkaline solutions performed similarly. The plot of removal efficiency vs. selectivity in Figure 2 indicates the specific chemical 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 Claus or other sulfur recovery processes. All three show high selectivity at recovery efficiencies high enough that, with the use of multiple venturi stages, a satisfactory H₂S removal efficiency (>95 percent) could be obtained for the system. Since the system envisioned for using these chemicals (Figure 1) involves recycling the alkali, the relative cost of the individual chemicals is insignificant. What may be significant are factors of corrosion, safety and availability as well as the cost of stripping the gases from the alkaline solution.

The test results indicate that the selectivity for the venturi is highly sensitive to the [OH⁻] with a rate of change, ds/d[OH⁻], of -1700 liter/gmole in the [OH⁻] 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 believed due to the presence of NH₃ 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 CO₂ enhancement. In other words, the short residence time means that the CO₂ has a limited time to react. However, as the H₂S absorption is controlled by the gas film, its absorption rate is independent of [OH⁻] at values less than 0.03 gmoles/liter.

Figure 5 shows that, at concentrations 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 NH₃. The higher gas film diffusion coefficient in the venturi essentially increases the availability of CO₂ 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 CO₂ absorption rate. In the tower, the gas film coefficient is lower which decreases the relative importance of the liquid film, and, therefore, decreases the dependence of the CO₂ absorption on [OH⁻]. Since the H₂S removal is determined solely by the gas film coefficient (due to the presence of NH₃ in the gas), the sensitivity of H₂S absorption to [OH⁻] in both tower and venturi is decreased.

These results indicate a clear choice of alternatives in deciding between a tower or venturi scrubber based on process requirements. If 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 combined removal efficiency and selectivity is greater than with the venturi.

A theoretical computer model was developed by Aiken (1985) using the penetration theory to correlate the venturi test results obtained in this program at

TABLE 3. COMPARISON OF THEORETICAL AND EXPERIMENTAL SELECTIVITIES

[OH ⁻] gmole/liter	Selectivity (Unitless)*			Experi- mental	Difference, Percent
	Theoretical				
	24 cm†	20.5 cm	Average		
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

*Selectivity is the percent H₂S removal/percent CO₂ removal

†Distance along venturi where liquid is injected

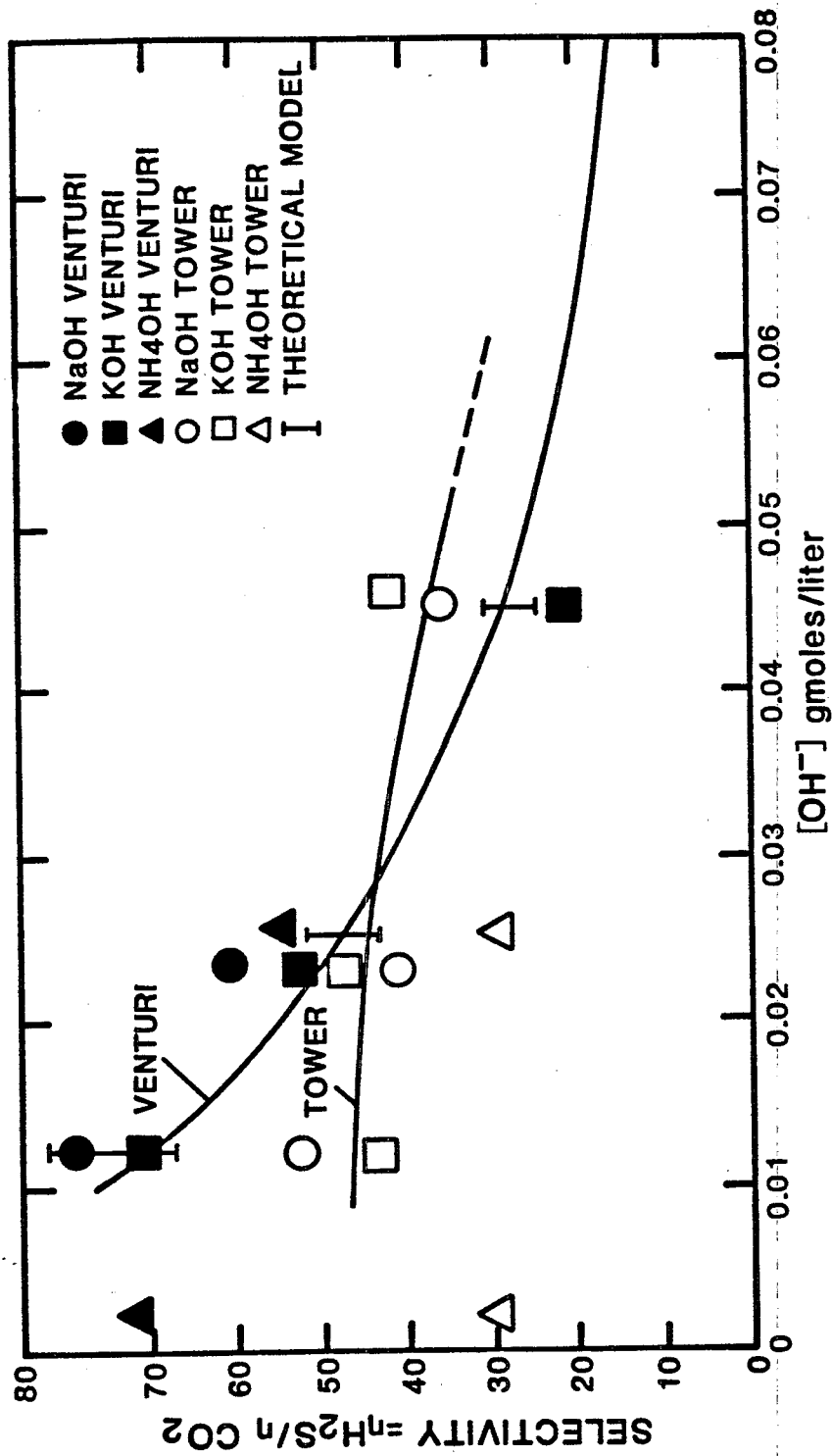


Figure 5. Selectivity at $[OH^-] < 0.05$ gmoles/liter

Geokinetics with the test conditions and provide a basis for detailed design of future alkaline scrubbers. One of the sensitive parameters in the analysis was the point of injection of the scrubber fluid into the gas stream. The actual injection point is 20.5 cm from the beginning of the venturi contactor. However, the injected liquid requires a few centimeters to atomize. Therefore, computer runs were made for distances of 20.5 and 24 cm. The computed selectivities are shown in Table 3 compared to the test results. Best agreement is between the test results and the numerical average of the computed results at 20.5 and 24 cm.

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 at the higher concentration (0.045 gmoles/liter) there is a 25 percent deviation. This information is also shown in Figure 5 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) indicates that the model can be used for predictive studies of multi-stage performance.

Some other interesting results derived from the modeling study, which included the chemical reaction of CO₂, H₂S, and NH₃ in the retort offgas with the alkaline solution in a venturi contactor are:

1. The NH₃ in the retort offgas reacts with the H₂S at the gas/liquid interface. Since the NH₃ present in the offgas is at approximately the same concentration as the H₂S, the removal efficiency is only marginally dependent upon the [OH⁻].
2. The removal efficiencies for NH₃ and H₂S are similar.
3. The H₂S selectivity is significantly affected by contact time with a maximum selectivity of 110 occurring at approximately 0.0015 sec contact time.
4. Variations in temperature and liquid droplet size can have a significant effect on selectivity.

Scrubber Concept Designs

These experimental and theoretical results suggest two alternative alkaline scrubber design concepts for future consideration. One system combines the high selectivity of the venturi with the high removal efficiency of the tower. The other uses a tray tower for maximum H₂S removal and isolated liquid scrubbing

stages to maximize the selectivity for use with a sulfur recovery plant.

For the first concept, the first stage is a venturi designed for peak selectivity based on contact time and [OH⁻]. The theoretical model indicates that a maximum selectivity of 110 will result in a 50 percent removal efficiency. The CO₂ removal efficiency is 0.40 percent.

The second stage is a tray tower designed for 90 percent H₂S removal efficiency with a stage selectivity of 40 using an [OH⁻] of 0.045 gmoles/liter. These values are based on the experimental results obtained in this program as shown in Figure 2. The CO₂ removal efficiency is 2.2 percent.

The overall performance for this design is a 95 percent H₂S removal efficiency with a selectivity of 37. These values are calculated as follows:

	Inlet (Assumed)	Stage 1 Venturi Exit	Stage 2 Tower Exit
H ₂ S conc., ppm	1500	750	75
CO ₂ conc., %	22	21.9	21.4
H ₂ S removal eff.	$= \frac{1500-75}{1500} = 95\%$		
CO ₂ removal eff.	$= \frac{22-21.4}{22} = 2.7\%$		
Selectivity	$= \frac{95}{2.7} = 37$		

The second concept is essentially two towers in series; but, in fact, the two tower stages could be combined into one partitioned vessel. Each stage has 90 percent H₂S removal efficiency and a selectivity of 40. The overall performance of the scrubber is 99 percent removal efficiency with a selectivity of 22. These values are calculated as follows:

	Inlet (Assumed)	Stage 1 Exit	Scrubber Exit
H ₂ S conc., ppm	1500	150	15
CO ₂ conc., %	22	21.5	21.0
H ₂ S removal eff.	$= \frac{1500-15}{1500} = 99\%$		
CO ₂ removal eff.	$= \frac{22-21}{22} = 4.5\%$		
Selectivity	$= \frac{99}{4.5} = 22$		

CONCLUSIONS

The findings reported above lead to the following conclusions:

1. For shale oil retort offgas similar in composition to that from the Geokinetics process, the alkaline scrubber, in combination with a stripper and a Claus plant, could be a technically viable means of H₂S removal. A design/cost study for such a system would determine its economic viability.
2. For Geokinetics-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 H₂S 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 H₂S 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 H₂S concentrations than found at Geokinetics. This suggests a concept of multiple scrubbing stages to increase the H₂S removal. Because this increased removal efficiency is accompanied by a reduced selectivity (which could present a problem by lowering the H₂S concentration in the feed gas to the sulfur recovery plant), the cost effectiveness of this concept requires a design study.
4. Based on a theoretical analysis of the three-gas component system (H₂S, NH₃, and CO₂), the principal reactant for the H₂S in the retort offgas is the NH₃ in that same offgas. In that NH₃ is present in the Geokinetics offgas in similar mole quantities to that of the H₂S, the scrubber performance observed on these tests may not be applicable to retort offgas with little or no NH₃. This suggests that the water and the NH₃ in the offgas would be an effective scrubbing agent without any alkali additive to the water. Scrubbing in this manner would certainly improve the selectivity, but the effect on removal efficiency obtainable is uncertain.
5. The alkaline scrubber removal efficiency and selectivity seemed to have little dependence on the alkali used. This is consistent with the above concept that it is the NH₃ in the

offgas itself that is reacting the H₂S. Since the NH₃ and H₂S concentrations are variable, it is likely that some of the H₂S 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, and crew comfort.

6. The absorption of H₂S and CO₂ in the alkaline solution occurs in reactions which should 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 H₂S (along with CO₂) while the sulfate and sulfite will not.

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