

## HYDROGEN SULFIDE AND SULFUR DIOXIDE ADSORPTION ON SHALE PRODUCED IN A DIRECT HEATED RETORT

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### ABSTRACT

The adsorption of hydrogen sulfide and sulfur dioxide on retorted oil shale is investigated for two different grades of oil shale that were retorted in a combustion retort. The adsorption studies were carried out in a packed bed arrangement at three different temperatures and consisted of six different concentrations of either hydrogen sulfide or sulfur dioxide in pure nitrogen. Equilibrium data were fitted to the Langmuir and Freundlich equations and a generalized three parameter equation proposed by Radke and Prausnitz. The isosteric heat of adsorption were calculated and compared to the heat of condensation for each of the adsorbates separately.

### INTRODUCTION

In situ retorting of oil shale offers a solution to a number of ecological and engineering problems that face the oil shale industry. In this approach, oil is extracted from the shale by heating the underground formation which eliminates the mining of the raw shale and the pollution problem that accompanies the disposal of the spent shale.

Retorting of oil shale by an in situ process is carried out by initiating combustion or introducing heat into the formation which results in the decomposition of the organic material to oil, residual carbon, hydrocarbon gases and combustion products. Under these conditions, the complex mineral structure of the shale oil undergoes a number of changes depending on such factors as shale porosity, oil content, and the rate of air injection. Information regarding these changes may answer several fundamental questions. Two of these questions are the adsorptive properties of spent shale and the transfer rates of gases through the formation.

Recently it was noted that less sulfur dioxide than was expected was given off from the controlled state retort at Laramie, Wyoming and this was attributed to the uptake of  $\text{SO}_2$  by the oil shale. In other investigations, Hasanain et al. (1977) and Pedram et al. (1979), the adsorptive properties of oil shale that had been retorted in an inert atmosphere were determined for sulfur dioxide and hydrogen sulfide. This study investigates the adsorption of hydrogen sulfide and sulfur dioxide on two grades of oil shale that were retorted in a combustion retort. The effect of the oil content of the shale and the adsorption temperatures were both considered.

### EXPERIMENTAL

The two oil shale samples studied in this work were obtained from two different locations of the Green River formation with oil contents of 32.4 and 21.0 gal/ton respectively as determined by Fischer assay analysis. Large quantities of raw shale from each of the two locations were collected, ground and mixed several times to ensure that a homogeneous sample of each shale was used in the retorting. The samples were sieved and the shale which passed a one-fourth inch screen but was collected on a one-eighth inch screen was selected and retorted to provide the spent shale material for this study.

The retorting was done in a five foot long stainless steel retort with an inside diameter of five inches. The retort could be sealed with threaded caps that had been tapped at each end to allow for the introduction of either pure nitrogen or air and the removal of the oil and

combustion gases. A thermocouple well was placed in the center of the retort so that the retorting temperature could be monitored. To obtain the spent shale samples, the retort was packed with one of the oil shales and thermocouples were then inserted into the well to provide temperature measurements at five different zones in the retort. After sealing the retort, it was placed in a furnace that was divided into five different zones, each of which was provided with a thermocouple positioned at exactly the same location as the one inside the retort. Each section of the furnace was controlled to provide the quantity of heat necessary to simulate adiabatic in situ retorting. The process was started by passing pure nitrogen through the top zone of the furnace. The nitrogen supply was disconnected when the temperature reached 450<sup>o</sup>F and the supply of air was then started. The temperature of all sections of the furnace and the retort were continuously monitored and recorded. As the temperature of the last zone of the retort dropped off, combustion stopped and the furnace was then turned off. Following retorting, the shale was subsequently cooled to ambient temperature while air continued to flow through the retort. The spent shale samples were analyzed for residual carbon, hydrogen, nitrogen and sulfur. In addition to determining the surface area of each sample, an x-ray diffraction analysis was conducted to relate the effects of mineral content, surface area, and oil content to the adsorptive capacity of the spent shale.

Adsorption studies were conducted in a packed bed that was designed to utilize an ultraviolet detector to measure and record gas concentrations. Spent shale samples obtained from the retorting process were crushed and sieved through a 16 U.S. mesh screen. The shale that collected on the 20 mesh screen was then packed into the column and the packing density was determined. The adsorption column was a 1/2 inch O.D. stainless steel tube 7.5 inches in length. It was furnished with union reducers at both ends so that one end could be connected to the heating coil and the other end to a Beckman model 25 ultraviolet detector. Each end of the column contained a 1.4 inch section of pyrex

glass wool to prevent small particles of spent shale from being carried into the gas flow. Thermocouples were attached to both ends of the column to monitor any changes in the gas stream temperature that might occur during the adsorption run. The gas flow rate was continuously monitored with a rotameter which has been calibrated to experimental conditions. The flow rates were checked periodically with a soap bubble meter to ensure steady flow. The column and the heating coils were immersed in a refrigeration-heating cycle water bath which was used to maintain the desired temperature for each adsorption run.

The adsorption process was started by passing pure nitrogen gas through the bed to flush any impurities from the shale and to establish a base line. After the spent shale reached thermal equilibrium with the bath, a gas mixture of either hydrogen sulfide in nitrogen or sulfur dioxide in nitrogen was then started. The effluent gas concentration was continuously monitored until it became equal to the inlet concentration of the gas mixture. The resulting breakthrough curves were analyzed for the shale uptake at equilibrium

## RESULTS AND DISCUSSION

### Properties of Retorted Shale

Retorting of the oil shale samples was carried out at the same operating conditions to minimize the effect of retorting conditions on the adsorptive properties of the spent shale. The chemical analyses of the spent shale samples are shown in Table I. A comparison of the values given shows that more mineral carbon and less residual organic carbon is present in the lower grade shale. The total residual carbon, which is the sum of the mineral and the organic carbon, is greater in the lower grade shale.

A BET surface area analysis was performed on the two spent shale samples. The rich shale has a surface area of 4.0 m<sup>2</sup>/g whereas

the low grade shale had an area of 3.6 m<sup>2</sup>/g. These values are very close to the surface areas measured by Slettevold, Biermann, and Burhnam (1978) for shale samples that had been decharred. Raw shale samples used in their study had oil contents ranging from 22 to 37.5 gallons per ton. In a study carried out by Pedram et al. (1979) on shale retorted in an inert atmosphere, it was noted that the surface area increased from 0.4 m<sup>2</sup>/g for shale retorted at 350°C to a maximum value of 8.8 m<sup>2</sup>/g for shale retorted at 750°C. The shale used in their study was the same 32.4 gal/ton shale used in this work. A comparison of the values shown in Table with the other studies indicates that the amount of surface area is strongly related to the quantity of residual organic carbon present on the spent shale.

#### Breakthrough Curves and Isotherms

Experimental breakthrough curves were obtained at 10, 25, and 40°C for gas concentrations of 2000, 3000, 5000, 7000, and 10,000 ppm hydrogen sulfide and sulfur dioxide in dry nitrogen. Each spent shale sample was ground to a size ranging from 16 to 20 U. S. mesh and packed into a column 7 inches long. Typical experimental breakthrough curves are shown in Figures 1 and 2 for the adsorption of sulfur dioxide and hydrogen sulfide on the 32.4 gal/ton spent shale. For each run the area under the breakthrough curve was determined and the concentration of adsorbate gas on the spent shale was calculated. The equilibrium isotherm data are shown Tables 2 and 3 for both gases.

A comparison of Table 1 with Tables 2 and 3 shows that the amount of gas adsorbed on each spent shale sample is strongly influenced by its total residual carbon content. In the presence of water vapor at the retorting temperature, the residual carbon is activated and becomes a good adsorbent for both SO<sub>2</sub> and H<sub>2</sub>S. The equilibrium data were correlated with three models: Radke-Prausnitz (1972), Langmuir (1918) and Freundlich. The Radke-Prausnitz equation is represented as

$$\frac{1}{q} = \frac{1}{aC} + \frac{1}{bC^\beta} \quad (1)$$

where q is the uptake of the solute by the solid, g adsorbate/g solid, C is the solute concentration in the gas, g/cm<sup>3</sup>, and β is constrained to be less than 1. The data can be fitted to the model by using the parameters given in Tables 4 and 5. The Radke-Prausnitz model is compared to the adsorption data for shale sample 1 in Figures 3 and 4 and to the data for sample 2 in Figure 5 and 6. The adequacy of the fit is also checked by calculating the coefficient of determination; this is also shown in Tables 4 and 5.

The equilibrium data were also correlated with the Langmuir isotherm equation

$$q = \frac{a_1 C}{1 + a_2 C} \quad (2)$$

where a<sub>1</sub> is the first Langmuir constant with units of cm<sup>3</sup>-gas/g solid and a<sub>2</sub> is the second Langmuir constant with the units used in this

Table 1. Chemical Analysis of Retorted Oil Shale

RUN NO.	WEIGHT			PERCENT			
	CARBON	HYDROGEN	NITROGEN	SULFUR	CARBON DIOXIDE	MINERAL CARBON	ORGANIC CARBON
1	2.43	1.08	0.01	0.58	5.40	1.45	0.98
2	2.32	1.04	0.01	0.60	5.38	1.49	0.83
Ave	2.38	1.06	0.01	0.59	5.39	1.47	0.91
1	5.14	0.98	0.01	0.28	17.10	4.67	0.47
2	5.07	0.96	0.01	0.27	16.90	4.62	0.45
Ave	5.20	0.97	0.01	0.27	17.0	4.64	0.46

Table 2. Adsorption Isotherm Data of SO<sub>2</sub>

Gas Concentration (g SO <sub>2</sub> /cm <sup>3</sup> gas) 10 <sup>6</sup>	T, °K	SO <sub>2</sub> Loading, (g SO <sub>2</sub> /g SOLID) x 10 <sup>5</sup>	
		Spent Shale Sample No.1 (32.4 gal/ton)	Spent Shale Sample No.2 (21.0 gal/ton)
27.3934	283	55.93	80.38
20.3983		50.32	71.12
14.1088		44.05	58.89
8.4659		36.57	43.93
5.6430		31.06	34.20
2.8031		24.63	21.17
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26.0145	298	43.55	52.94
19.3715		39.08	45.98
13.3987		34.02	36.82
8.0397		- -	25.62
5.3589		21.97	19.02
2.6620		14.39	11.35
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24.7678	313	28.19	27.77
18.4432		26.40	25.01
12.7566		23.16	22.10
7.6544		19.02	17.14
5.1021		15.70	12.13
2.5345		10.86	8.39

Table 3. Adsorption Isotherm Data of H<sub>2</sub>S

Gas Concentration (g SO <sub>2</sub> /g/cm <sup>3</sup> gas) 10 <sup>6</sup>	T, °K	H <sub>2</sub> S Loading, (g H <sub>2</sub> O/g SOLID) x 10 <sup>5</sup>	
		Spent Shale Sample No.1 (32.4 gal/ton)	Spent Shale Sample No.2 (21.0 gal/ton)
14.8481	283	34.71	48.24
10.3937		30.29	40.08
7.4241		25.37	34.23
4.4544		18.64	30.32
2.9696		14.57	20.58
1.4848		9.78	12.87
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14.1007	298	25.08	27.69
9.8705		21.61	24.88
7.0504		18.22	20.76
4.2302		- -	14.49
2.8205		9.95	9.52
1.4101		6.05	5.53
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13.4250	313	15.27	15.80
9.3975		13.59	14.02
6.7125		12.20	11.63
4.0275		9.63	10.03
2.6850		7.37	7.72
1.3425		4.73	3.24

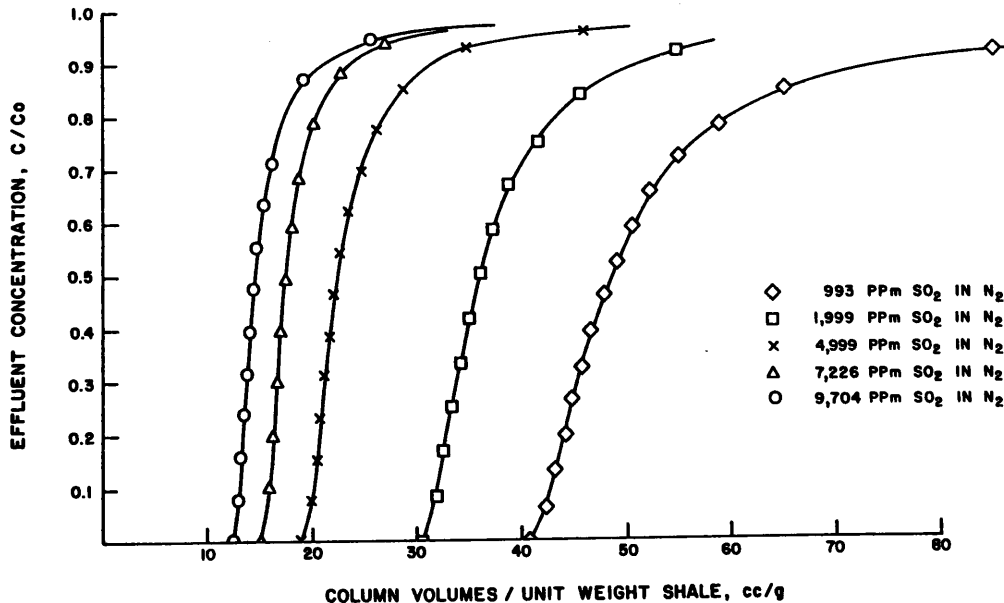


Figure 1. Comparison of Experimental Breakthrough Curves for Concentration of 993, 1999, 4999, 7226, 9704, PPM SO<sub>2</sub> in Nitrogen at 25°C. Spent Shale Sample No. 1 (32.4 gal/ton)

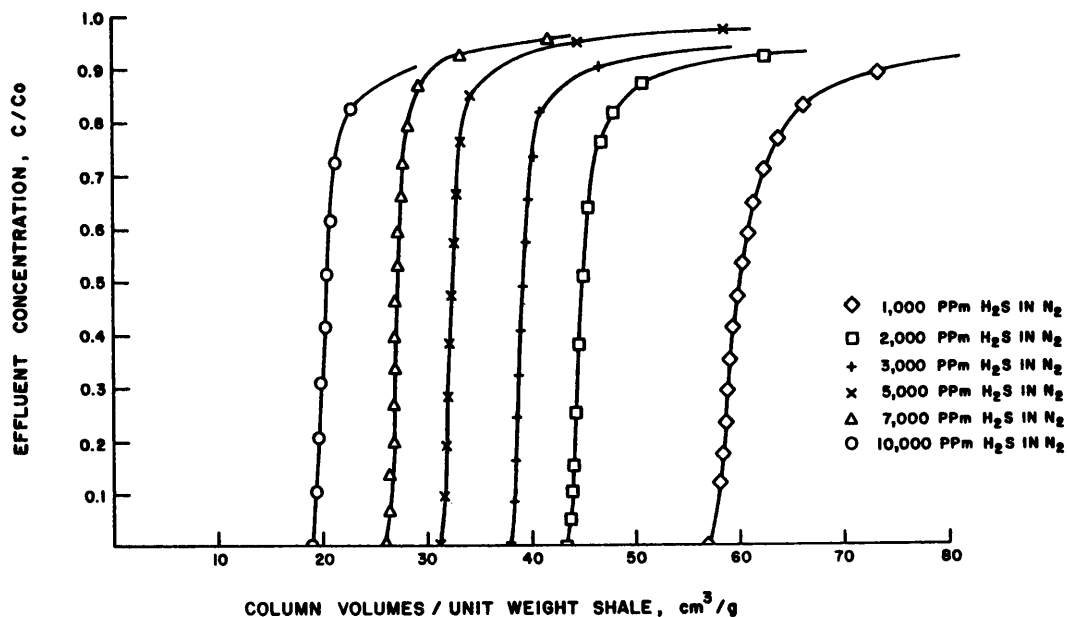


Figure 2. Comparison of Experimental Breakthrough Curves for Concentrations of 1000,2000, 3000, 5000, 7000, 10,000 PPM H<sub>2</sub>S in Nitrogen at 10°C. Spent Shale Sample No. 1 (32.4 gal/ton)

Table 4. Parameters of Equation 1 for SO<sub>2</sub>

ADSORBENT	T, °K	a x 10 <sup>-6</sup>	b x 10 <sup>-3</sup>	β	COEFFICIENT OF DETERMINATION
Spent Shale	283	169.08	2.2374	0.350	0.99998
Sample No. 1	298	9.5186	0.4361	0.200	0.99997
(32.4 gal/ton)	313	7.3446	0.1263	0.125	0.99963
Spent Shale	283	11.1573	1.2948	0.235	0.99967
Sample No. 2	298	5.3848	1.0868	0.240	0.99706
(21.0 gal/ton)	313	4.1634	0.0751	0.064	0.99359

Table 5. Parameters of Equation 1 for H<sub>2</sub>S

ADSORBENT	T, °K	a x 10 <sup>-6</sup>	b x 10 <sup>-3</sup>	β	COEFFICIENT OF DETERMINATION
Spent Shale	283	11.2190	1.3186	0.305	0.99692
Sample No. 1	298	5.2572	0.1163	0.100	0.99910
(32.4 gal/ton)	313	4.6411	0.0289	0.032	0.99937
Spent Shale	283	12.8720	0.4235	0.171	0.98419
Sample No. 2	298	4.8472	0.2456	0.142	0.9557
(21.0 gal/ton)	313	3.8822	0.0912	0.121	0.93308

Table 6. Parameters of Equation 2 for SO<sub>2</sub>

ADSORBENT	T, °K	a <sub>1</sub> × 10 <sup>-6</sup>	a <sub>2</sub> × 10 <sup>-5</sup>	COEFFICIENT OF DETERMINATION
Spent Shale	283	10.8379	1.6414	0.99065
Sample No. 1	298	6.7972	1.2009	0.99730
(32.4 gal/ton)	313	5.7005	1.6290	0.99849
Spent Shale	283	8.5441	0.7102	0.99558
Sample No. 2	298	4.5528	0.4798	0.99293
(21.0 gal/ton)	313	3.8906	1.0012	0.99331

Table 7. Parameters of Equation 2 for H<sub>2</sub>S

ADSORBENT	T, °K	a <sub>1</sub> × 10 <sup>-6</sup>	a <sub>2</sub> × 10 <sup>-5</sup>	COEFFICIENT OF DETERMINATION
Spent Shale	283	7.1675	1.4155	0.98950
Sample No. 2	298	4.8860	1.2462	0.99836
(32.4 gal/ton)	313	4.4681	2.1923	0.99926
Spent Shale	283	10.4865	1.5599	0.98158
Sample No. 2	298	4.4944	0.8580	0.96807
(21.0 gal/ton)	313	3.5053	1.4446	0.94310

Table 8. Parameters of Equation 3 for SO<sub>2</sub>

ADSORBENT	T, °K	K × 10 <sup>5</sup>	n	COEFFICIENT OF DETERMINATION
Spent Shale	283	.0246	2.7742	0.99931
Sample No. 1	298	.0751	2.0645	0.99252
(32.4 gal/ton)	313	.0257	2.3794	0.98619
Spent Shale	283	.4016	1.7039	0.99427
Sample No. 2	298	.7661	1.4610	0.99646
(21.0 gal/ton)	313	.0903	1.8545	0.98261

Table 9. Parameters of Equation 3 for H<sub>2</sub>S

ADSORBENT	T, °K	K × 10 <sup>5</sup>	n	COEFFICIENT OF DETERMINATION
Spent Shale	283	0.1891	1.7769	0.99667
Sample No. 1	298	0.2940	1.5940	0.99371
(32.4 gal/ton)	313	0.0508	1.9573	0.97893
Spent Shale	283	0.2555	1.7861	0.96919
Sample No. 2	298	1.0363	1.3785	0.97966
(21.0 gal/ton)	313	0.2536	1.5479	0.94310

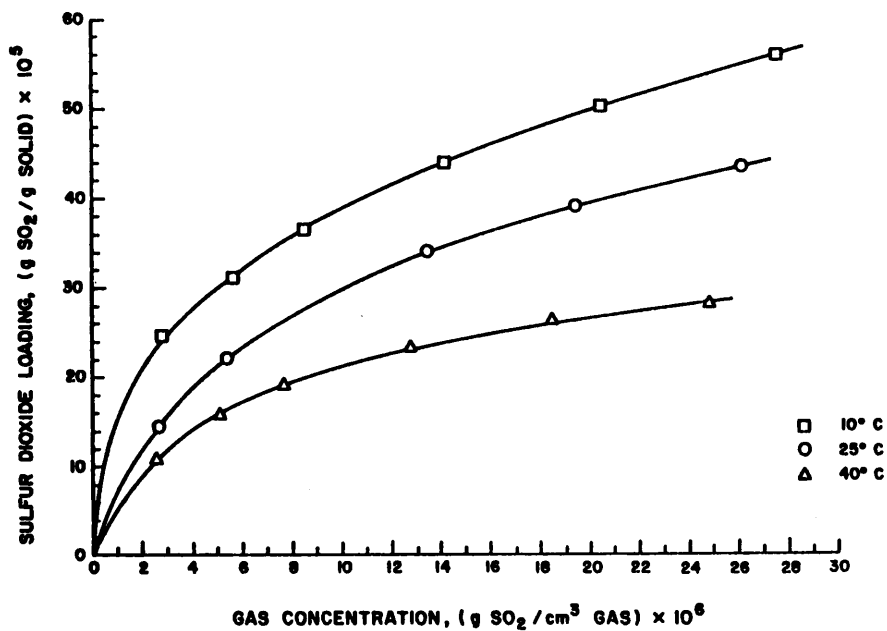


Figure 3. Equilibrium Isotherm for Adsorption of  $\text{SO}_2$  on Spent Shale Sample No. 1 at  $10^\circ\text{C}$ ,  $25^\circ\text{C}$ , and  $40^\circ\text{C}$  Fit to the Generalized Three Parameter Equation.

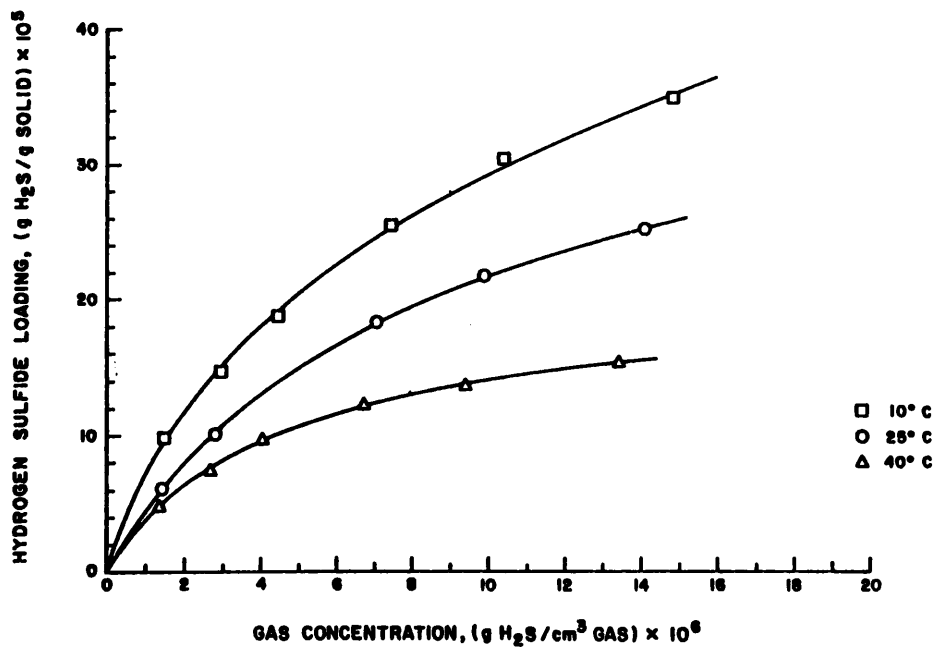


Figure 4. Equilibrium Isotherm for Adsorption of  $\text{H}_2\text{S}$  on Spent Shale Sample No. 1 at  $10^\circ\text{C}$ ,  $25^\circ\text{C}$ , and  $40^\circ\text{C}$  Fit to the Generalized Three Parameter Equation.

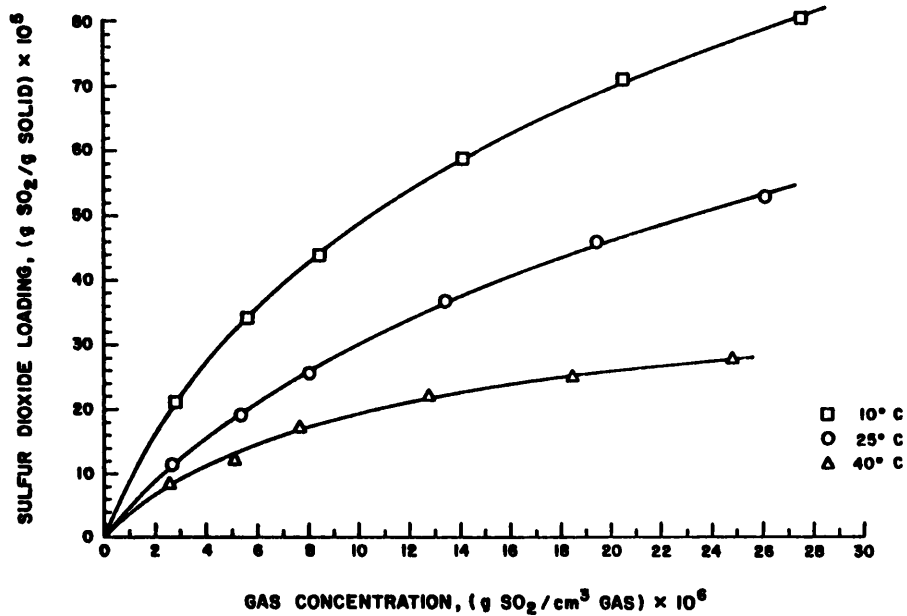


Figure 5. Equilibrium Isotherm for Adsorption of  $\text{SO}_2$  on Spent Shale Sample No. 2 at  $10^\circ\text{C}$ ,  $25^\circ\text{C}$ , and  $40^\circ\text{C}$  Fit to the Generalized Three Parameter Equation.

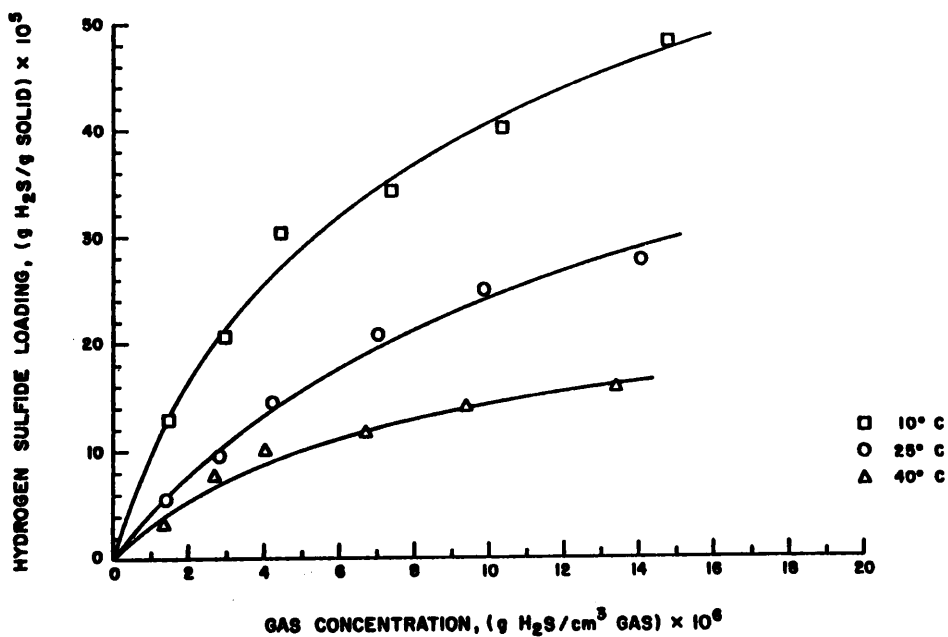


Figure 6. Equilibrium Isotherm for Adsorption of  $\text{H}_2\text{S}$  on Spent Shale Sample No. 2 at  $10^\circ\text{C}$ ,  $25^\circ\text{C}$ , and  $40^\circ\text{C}$  Fit to the Generalized Three Parameter Equation.



study of  $\text{cm}^3/\text{g}$ . The equation parameters along with the coefficient of determination for each temperature are given in Table 6 for  $\text{SO}_2$  and Table 7 for  $\text{H}_2\text{S}$ .

Finally, the equilibrium data were fitted with the Freundlich isotherm equation which is given as

$$q = KC^{1/n} \quad (3)$$

The parameters for the Freundlich model along with the coefficient of determination are given in Tables 8 and 9 for  $\text{SO}_2$  and  $\text{H}_2\text{S}$  respectively.

The equilibrium data for the adsorption of  $\text{SO}_2$  on both samples of spent shale were best fitted with the Radke-Prausnitz model as shown by the coefficient of determination. The adsorption of hydrogen sulfide on spent shale sample No. 1 (32.4 gal/ton) was also best fitted with the Radke-Prausnitz model but the Langmuir model provided a slightly better correlation than the other models for spent shale sample No. 2 (21.0 gal/ton).

#### Heat of Adsorption

The isosteric heat of adsorption at constant loading is given by the equation

$$\Delta H = -R \left[ \frac{\partial(\ln C)}{\partial(1/T)} \right]_q \quad (4)$$

Heats of adsorption were determined graphically from plots of  $\ln C$  vs  $1/T$ . The heat that is given off during the adsorption process is due to the

decrease of the free energy and the entropy of the system. The decreases in the amount of heat given off that accompanies the decreases in the amount of gas adsorbed are shown in Tables 10 and 11.

A comparison of the heat of adsorption for either  $\text{SO}_2$  or  $\text{H}_2\text{S}$  at the same loading for both samples of spent shale indicates that the less rich shale has a higher energetic surface than the rich shale; this is consistent with the adsorptive capacity of the shales for both gases. The calculated values for the heat of adsorption were found to be of the same order of magnitude as the heat of condensation. This suggests that the gas molecules are held on the surface of the shale primarily by physical forces. However, the complete removal of the  $\text{H}_2\text{S}$  and  $\text{SO}_2$  from the shale bed was only possible by heating to  $150^\circ\text{C}$  under a vacuum for four hours. This indicates that some chemisorption may have occurred. The increase in the heat of adsorption with increased surface loading is a further indication that some of the molecules are chemisorbed.

#### CONCLUSIONS

The adsorption of hydrogen sulfide and sulfur dioxide on two grades of spent shale was investigated and the equilibrium data for most of the runs were best fitted with the

Table 10. Isosteric Heat of Adsorption for  $\text{H}_2\text{S}$

Loading $\left(\frac{\text{g SO}_2}{\text{g solid}}\right) \times 10^5$	$\Delta H, \frac{\text{K cal}}{\text{g mole}}$	
	Spent shale Sample No. 1 (32.4 gal/ton)	Spent Shale Sample No. 2 (21.0 gal/ton)
14.0	7.84	9.98
10.0	5.62	8.81
6.0	4.55	7.21

Table 11. Isosteric Heat of Adsorption for  $\text{SO}_2$

Loading $\left(\frac{\text{g SO}_2}{\text{g solid}}\right) \times 10^5$	$\Delta H, \frac{\text{K cal}}{\text{g mole}}$	
	Spent Shale Sample No. 1 (32.4 gal/ton)	Spent Shale Sample No. 2 (21.0 gal/ton)
26.0	9.83	10.25
20.0	7.69	8.51
14.0	6.78	7.36

Radke-Prausnitz model. The increase in the heats of adsorption with increased loading indicates that some of the molecules were chemisorbed. The low heat of adsorption, however, is characteristic of physical adsorption.

The oil content of the shale influenced the surface area of the spent shale, but had little effect on its adsorptive capacity. However, the total residual carbon content of the spent shale had a great influence on its adsorptive properties.

Since spent shale has been shown to adsorb hydrogen sulfide and sulfur dioxide, the use of spent shale beds as a means of disposing of undesirable retort gases appears feasible. The extent to which these gases will ultimately be adsorbed depends on several factors including: the presence of other gases, the retorting atmosphere and the size of the shale in the retort. Thus, a prediction as to the effectiveness of the retort zone as a disposal site would be premature. Further adsorption studies of the retort product gases should be carried out on shale that has been wet with water. This will take advantage of the ion exchange capacity of the various minerals present in the spent shale. Ultimately, the overall uptake of the  $\text{SO}_2$  and  $\text{H}_2\text{S}$  should be increased.

#### ACKNOWLEDGEMENT

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#### NOMENCLATURE

- a = parameter in Radke-Prausnitz equation ( $\text{cm}^3/\text{gm-solid}$ )
- $a_1$  = first Langmuir constant ( $\text{CM}^3 \text{ gas}/\text{gm-solid}$ )
- $a_2$  = second Langmuir constant ( $\text{cm}^3/\text{g}$ )
- b = gas phase concentration, ( $\text{g}/\text{cm}^3$ )
- C = gas phase concentration, ( $\text{g}/\text{cm}^3$ )
- $C_0$  = inlet gas concentration ( $\text{g}/\text{cm}^3$ )
- $\Delta H$  = the isosteric heat of adsorption (K cal/g mole)
- K = constant in Freundlich equation
- n = constant in Freundlich equation
- q = equilibrium concentration of adsorbed gas ( $\text{g}/\text{cm}^3$ )
- R = gas constant
- T = temperature

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