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Removing Sulfur Dioxide From Flue Gases

Regeneration Rates for Alkalized Alumina

UNITED STATES DEPARTMENT OF THE INTERIOR

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REMOVING SULFUR DIOXIDE FROM FLUE GASES

Regeneration Rates for Alkalized Alumina

by

J. W. Town,[1] J. H. Russell,[2] and H. J. Kelly[3]

ABSTRACT

The Bureau of Mines studied the effects of reducing gas composition, temperature, and superficial gas velocity on the regeneration rate of alkalized alumina. Regeneration was assumed to follow the simple first order reaction for removal of sorbed SO_2: $d\mu/dt = -K\mu$. An Arrhenius relationship can be plotted, which shows an activation energy of about 75 kcal/mole for simulated reformed propane. The general effects of the individual gases can be described as follows: (1) CO and H_2 produced rates proportional to their concentrations, up to about 5 percent for each; (2) addition of CO_2 had no effects on the regeneration rate by CO; (3) the regeneration rate by H_2 was lowered by the addition of H_2O while the regeneration rate by CO was increased by H_2O addition; (4) H_2S showed a positive effect up to concentration levels of about 2 percent and then produced a rapid negative effect; (5) carbonyl sulfate (COS) increased the sulfur content; and (6) propane was as effective in regenerating the loaded pellets as was simulated reformed propane.

INTRODUCTION

During the past decade, air pollution has become a national problem of increasing concern. The increase in air pollution, caused by a growing population and industrial expansion, has prompted air pollution research by private industry and by local, State, and Federal agencies. Several projected processes have been developed for the removal of sulfur dioxide from fossil-fuel powerplant gases. These include the dry alkalized alumina process for operation at elevated temperatures developed by the Bureau of Mines and patented by Bienstock and Field (2).[4]

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[4] Underlined numbers in parentheses refer to items in the list of references preceding the appendix.

Research on alkalized alumina as a solid sorbent for sulfur dioxide removal from flue gases was initiated by the Bureau in 1957 (1). Pilot plant studies (4) conducted on sorbent material prepared by the Davison Chemical Division of W. R. Grace and Co.[5] identified several problems in preparing a suitably active and physically stable sorbent.

Activation, sorption, and regeneration equations for alkalized alumina, along with attritioning and batch sorption studies, have been reported by Town and coworkers (5). The activated alkalized alumina (sodium aluminate) sorbs sulfur dioxide according to the following equations:

$$2NaAlO_2 + SO_2 \longrightarrow Na_2SO_3 + Al_2O_3\text{, below 230° C;}$$

and

$$2NaAlO_2 + SO_2 + 1/2\ O_2 \longrightarrow Na_2SO_4 + Al_2O_3\text{, above 230° C.}$$

In the presence of nitrogen oxides the second reaction occurs at temperatures above 100° C. The relationship of the Al_2O_3 and Na_2SO_4 in the sulfur-loaded sorbent is not completely understood. Regeneration with hydrogen or other reducing gases at 600° to 750° C reforms the $NaAlO_2$ according to the following equations:

$$Na_2SO_3 + Al_2O_3 + 3H_2 \longrightarrow 2NaAlO_2 + 2H_2O + H_2S,$$

and

$$Na_2SO_4 + Al_2O_3 + 4H_2 \longrightarrow 2NaAlO_2 + 3H_2O + H_2S.$$

The regenerated sorbent is then in its active form and ready for recycling. Studies by W. R. Grace (3) have shown that metallic elements, such as iron, copper, and nickel, accelerate the regeneration.

Under sponsorship of the National Air Pollution Control Administration (NAPCA), the Albany Metallurgy Research Center of the Bureau of Mines conducted differential thin-bed regeneration studies to determine the regeneration kinetics of loaded and partially loaded sorbent. Studies included evaluating the effects on regeneration rates of reducing gas (including independent effects of H_2, CO, CO_2, H_2O, H_2S, and COS), temperature, and superficial gas velocity. The evaluation was made on alkalized alumina which has been designated as Grace No. 1.

This report describes the procedures used in determining regeneration rates, the effects of different gases and temperatures upon the rates, and the mathematical evaluation of the results. Uncertainty estimates of the measured values of regeneration rates were about 20 percent.

EQUIPMENT AND EXPERIMENTAL PROCEDURE

To determine the regeneration rate of alkalized alumina with respect to sulfur load, temperature, gas composition, and gas velocity, a batch thin-bed regenerator test unit was built similar to that reported by Town and

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[5] Reference to company names is made for identification only and does not imply endorsement by the Bureau of Mines.

coworkers (5) for the study of sulfur dioxide sorption onto alkalized alumina. Since the sorption studies on alkalized alumina had been made on Grace No. 1 pelletized sorbent, this material was selected for the initial regeneration studies. The activated Grace No. 1 material in pellet form has a bulk density of 0.80 g/cu cm, a surface area of about 40 m^2/g, and a porosity of about 60 percent. Three samples were prepared, with sulfur loads of 2.3, 5.9, and 8.8 percent.

In the thin-bed test unit a synthetic reducing gas with water vapor added was used to regenerate the sulfur-loaded pellets. A schematic drawing of the regeneration system is shown in figure 1. Four gases--N_2, CO, H_2, and CO_2--were measured by separate flowmeters. The gas temperature was then raised to over 100° C, and H_2O was added through a flowmeter to obtain the desired moisture content. A 25-ft coil of 1/4-inch stainless steel tubing was used to preheat the regeneration gas. To prevent the regeneration gas from surging and to allow for continuous gas flow, a three-way valve was used to bypass the gas when it was not contacting the pellets. The pellet charge was held in a sample holder, which consisted of a 12-inch length of 3/4-inch-diameter stainless steel pipe threaded to 3 inches of heavy wall pipe. The inside of the heavy wall pipe was threaded about 1 inch above the lower end so that a retaining ring could be screwed in to support the 80-mesh stainless steel

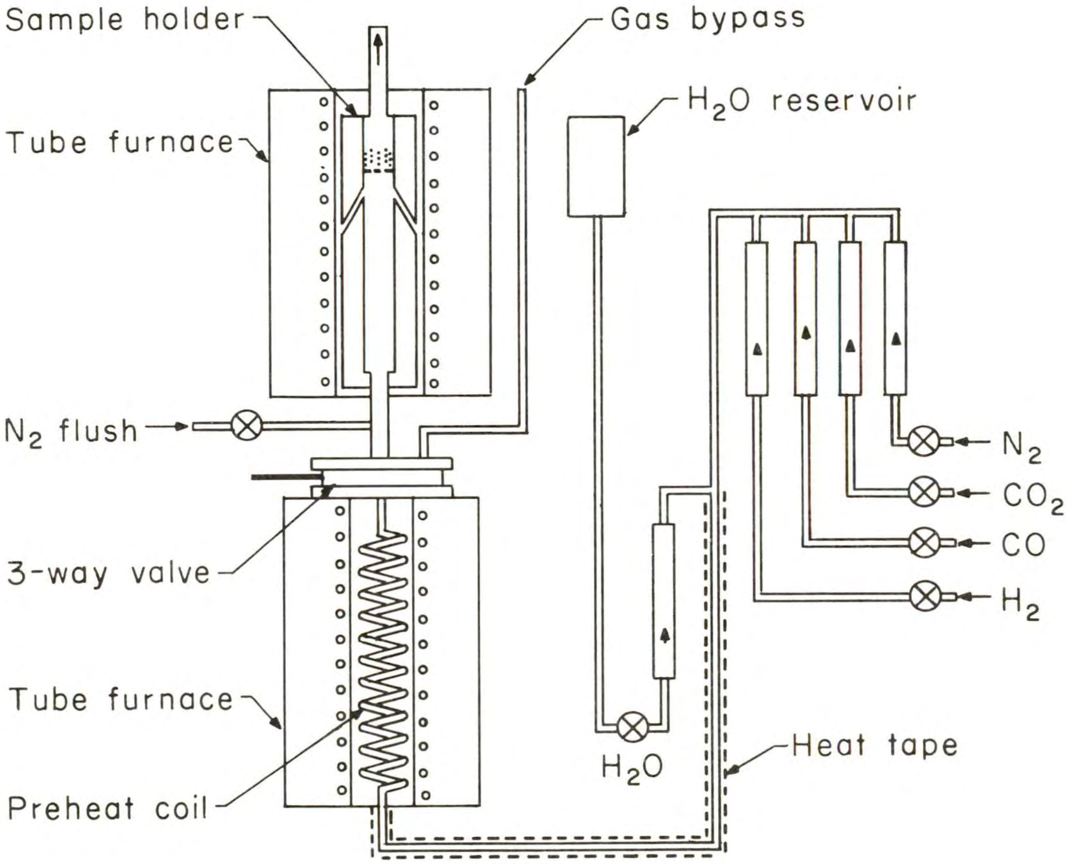

FIGURE 1. - Regeneration System.

screen used to retain the pellets. The bottom of the sample holder was machined to form an inverted cone that slip-fit onto a matching piece of heavy wall pipe. The heavy wall pipe was used as a heat sink to assist in maintaining the test temperature.

After the sample was poured into the holder, it was placed in the furnace and preheated for 15 minutes before the regeneration gas was allowed to contact the pellets. The three-way valve was then opened to allow the regeneration gas to pass up through the pellets for a predetermined time. The valve was then closed and the sample holder column was flushed with nitrogen. The sample holder was then removed from the furnace and inverted to remove the pellets. The pellets were then weighed to determine weight loss and prepared for sulfur analysis.

To determine the regeneration rate with gases of different composition, a 1.000-gram sample of sulfur-loaded pellets was used. The small sample formed an incomplete single layer in the holder and required only a small amount of reductant to remove the sorbed sulfur. Therefore, the regeneration gas composition above and below the sorbent was assumed to be essentially the same. This provided an opportunity to measure the amount of regeneration by a gas of fixed composition. Individual samples of loaded pellets were contacted with the regeneration gas for predetermined times (0, 4, 8, 16, 30, 60, and 120 minutes) and analyzed for sulfur. The amount of sulfur removed was determined in grams of sulfur per gram of untreated pellet (gS/gp) for each contact time. A plot of these data was then used to determine the regeneration rate. A standard method of calculation, shown in table 1, was used to determine the amount of sulfur removed from the 1.000-gram charge.

TABLE 1. - Method and typical data used in calculating percent regeneration

Time, minutes	Temperature, ° C	Final weight, g		Analyses, percent sulfur		Units sulfur, gS/gp	Regeneration,[1] percent
Head......	-	1.000		7.86		0.0786	-
Dry head..	700	.971	X	8.80	=	.0854	-
4.........	700	.905	X	6.36	=	.0576	32.6
8.........	700	.823	X	4.49	=	.0370	56.7
16........	700	.835	X	2.37	=	.0198	76.8
30........	700	.793	X	1.29	=	.0102	88.1
60........	700	.759	X	.85	=	.0065	92.4
120.......	700	.758	X	.23	=	.0017	98.0

[1] Based on the grams sulfur remaining in sample and grams sulfur in dry head. The original sorbent contains about 0.0143 gram sulfur per gram pellet, so that 83.4 percent regeneration represents 100 percent removal of the sorbed sulfur.

In synthesizing a regeneration gas for testing, a composition similar to that of reformed propane was prepared, because in projected studies the fluidized-bed pilot plant would use reformed propane as a regenerating gas. The gas, flowing at about 3,000 cu cm/min, consisted of 50 percent nitrogen, 10 percent carbon dioxide, 15 percent carbon monoxide, 20 percent hydrogen, and 5 percent water. No increase in regeneration rate was noted when sample size was reduced to 0.500 gram or when gas velocity was increased. Tests were made at temperatures ranging from 600° to 730° C. Because pioneering work had shown that the regeneration rate of alkalized alumina was very temperature sensitive, a potentiometer-controlled resistance furnace was used to maintain the temperature of the sample within ±2° C at each temperature.

EXPERIMENTAL RESULTS

The results from the regeneration studies are listed under the following headings according to the gas compositions tested.

Regeneration by Simulated Reformed Propane

Simulated reformed propane was used to initiate the regeneration studies. The sulfur content for each sample, in gS/gp, for the designated times and temperatures is listed in table A-1 of the appendix. Results in figure 2 show that at 730° C all the sorbed sulfur is removed in about 10 minutes, while at 700° C about 30 minutes is required to remove the sulfur from the two samples with the higher loads. As the temperature is lowered, the regeneration rate continues to drop until at 600° C, virtually no sulfur is removed, even with contact times of 120 minutes. The horizontal line drawn in figure 2 at about 1.4 percent sulfur represents the residual sulfur level, or sulfur remaining on the sorbent as a result of the chemicals used in preparation of alkalized alumina.

Figure 3 shows the percent sulfur removed with respect to regeneration time and temperature. The plots clearly demonstrate that the higher temperatures are more effective in removing sorbed sulfur from the samples. The horizontal line across the figure represents the level at which all the sorbed sulfur has been removed. Because of the low sulfur level on the 2.3-percent sample, just over 40-percent regeneration represents 100-percent removal of sorbed sulfur; on the 5.9- and 8.8-percent samples, about 76- and 84-percent regeneration, respectively, represent 100-percent removal of sorbed sulfur.

In evaluating the regeneration tests by simulated reformed propane, there is one rate-limiting reaction of principal interest which has a relatively high activation energy. As shown in figure 2, a plot of the logarithm of the residual sulfur versus time can be resolved into two relatively straight lines. This kind of plot is typical of a system embracing two reactions, each having a kinetic equation of the form $d\mu/dt = -K\mu$. The first, more rapid, reaction is of principal interest because this represents the removal of sorbed sulfur. The second, slower reaction is of less interest both because it is slower and because it does not take place until essentially all the sorbed sulfur is removed. Thus, the second reaction represents the removal of residual sulfur.

The rate constants were calculated for each of the test runs, using only the data points for which the sulfur level was higher than the residual sulfur level. These rate constants are shown in the far right column of table A-1. An Arrhenius plot of log K versus 1/T is shown in figure 4. Except for some spread in the results, the data can be fitted to a straight line, with an

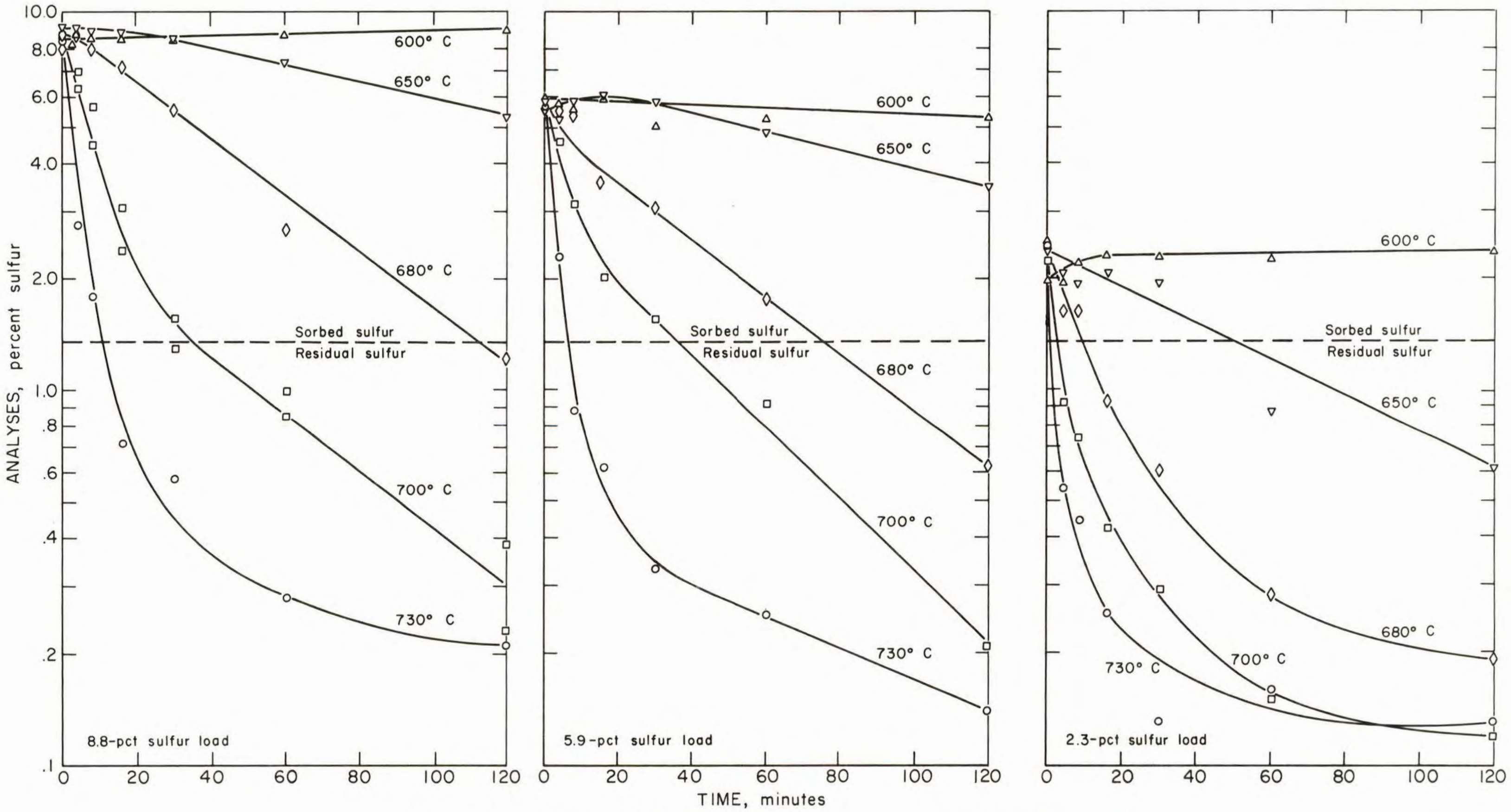

FIGURE 2. - Effect of Time and Temperature on Sulfur Removal.

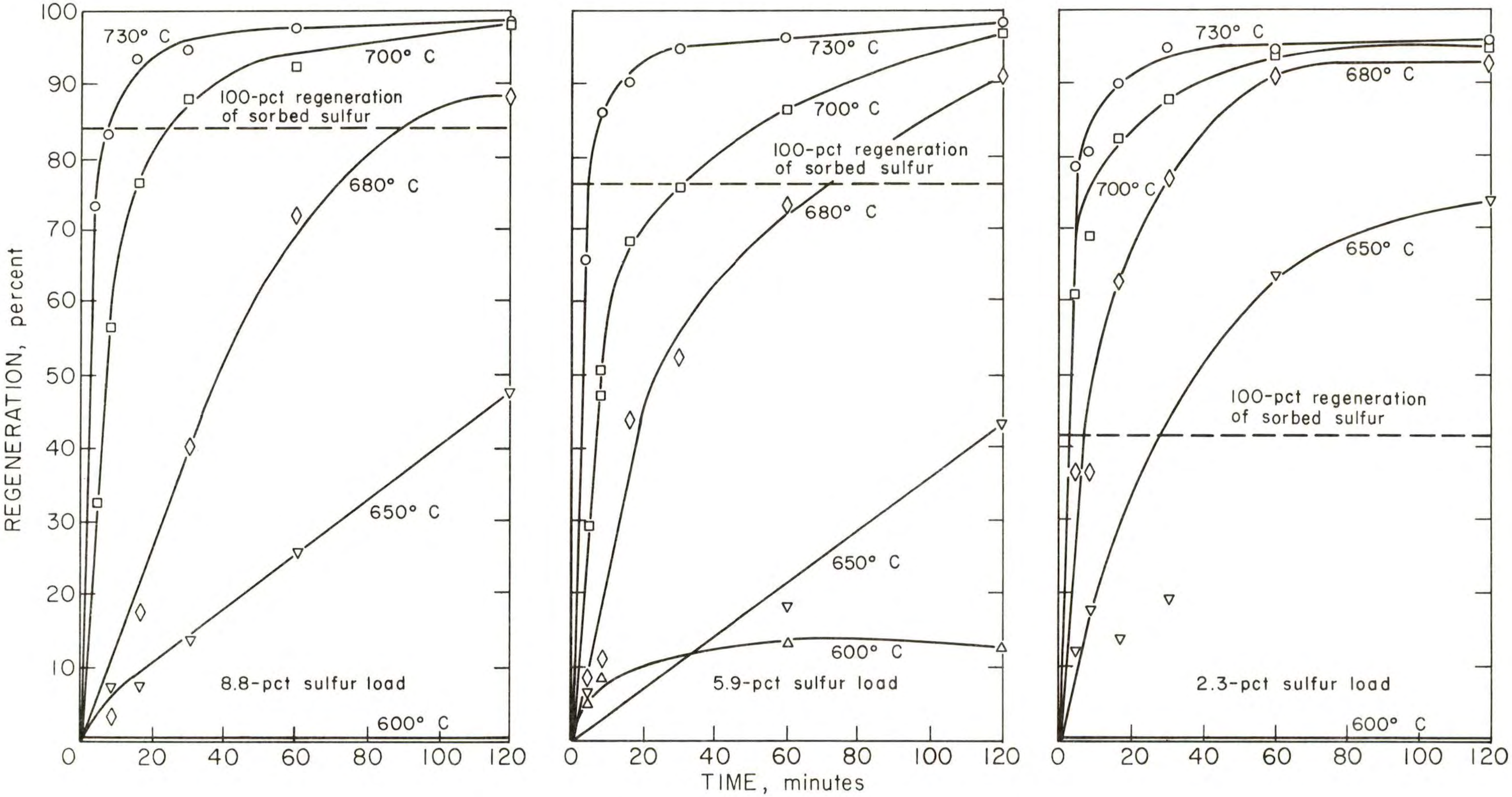

FIGURE 3. - Effect of Time and Temperature on Regeneration.

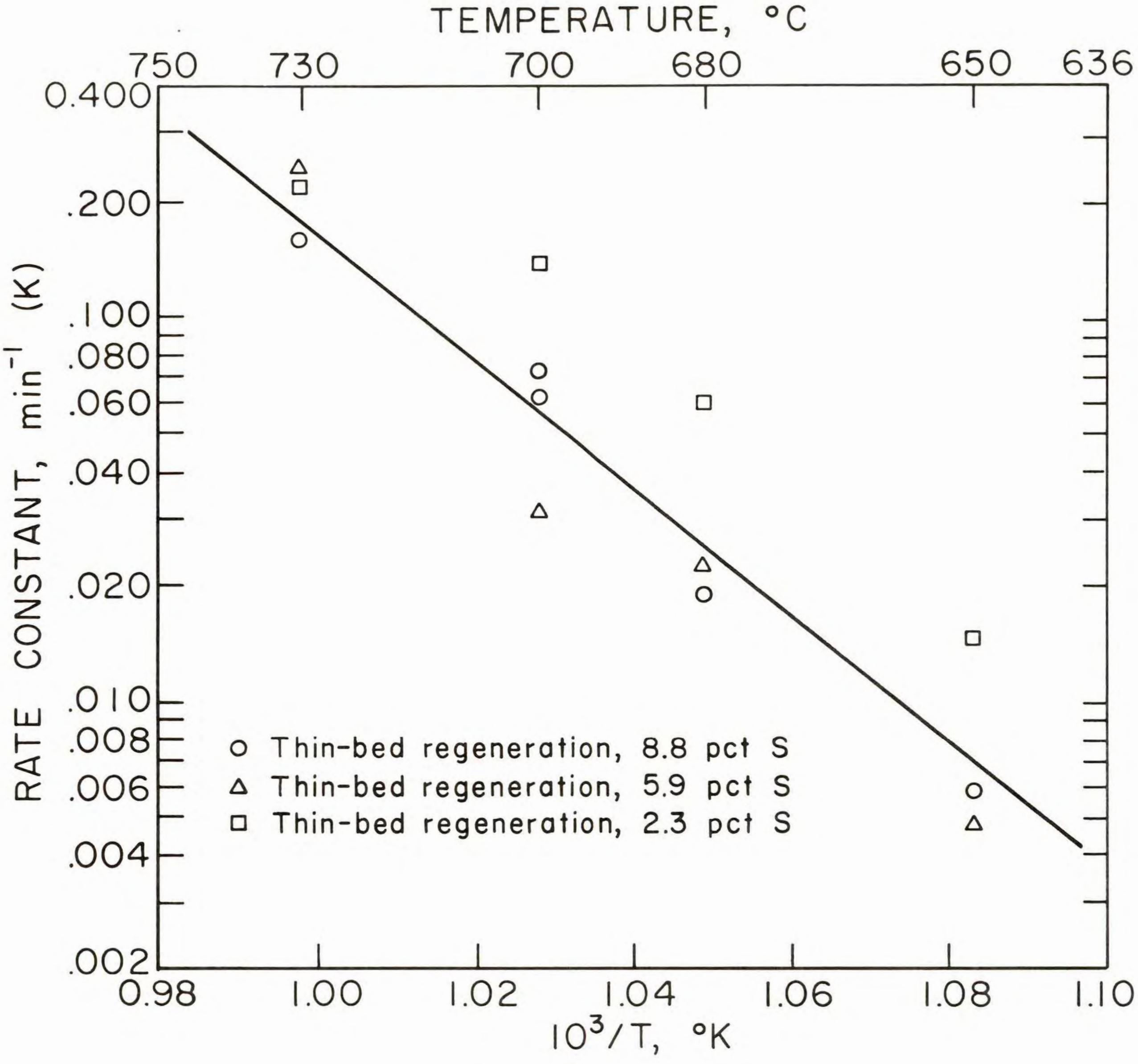

FIGURE 4. - Arrhenius Plot of Regeneration Rate Constants.

apparent activation energy of about 75±9 kcal/mole. The rather rapid change in the rate constant with temperature shows that careful control of temperature during testing is necessary if meaningful results are to be obtained.

Hydrogen Regeneration Studies

To study the effect of hydrogen concentration on regeneration rate with respect to temperature, gas velocity, water vapor, and hydrogen sulfide, four test series were made. The initial test series consisted of nine runs of six samples each to determine the effect of gas velocity using a regeneration gas of 5 percent hydrogen at 700° C. This test series was made so that on all

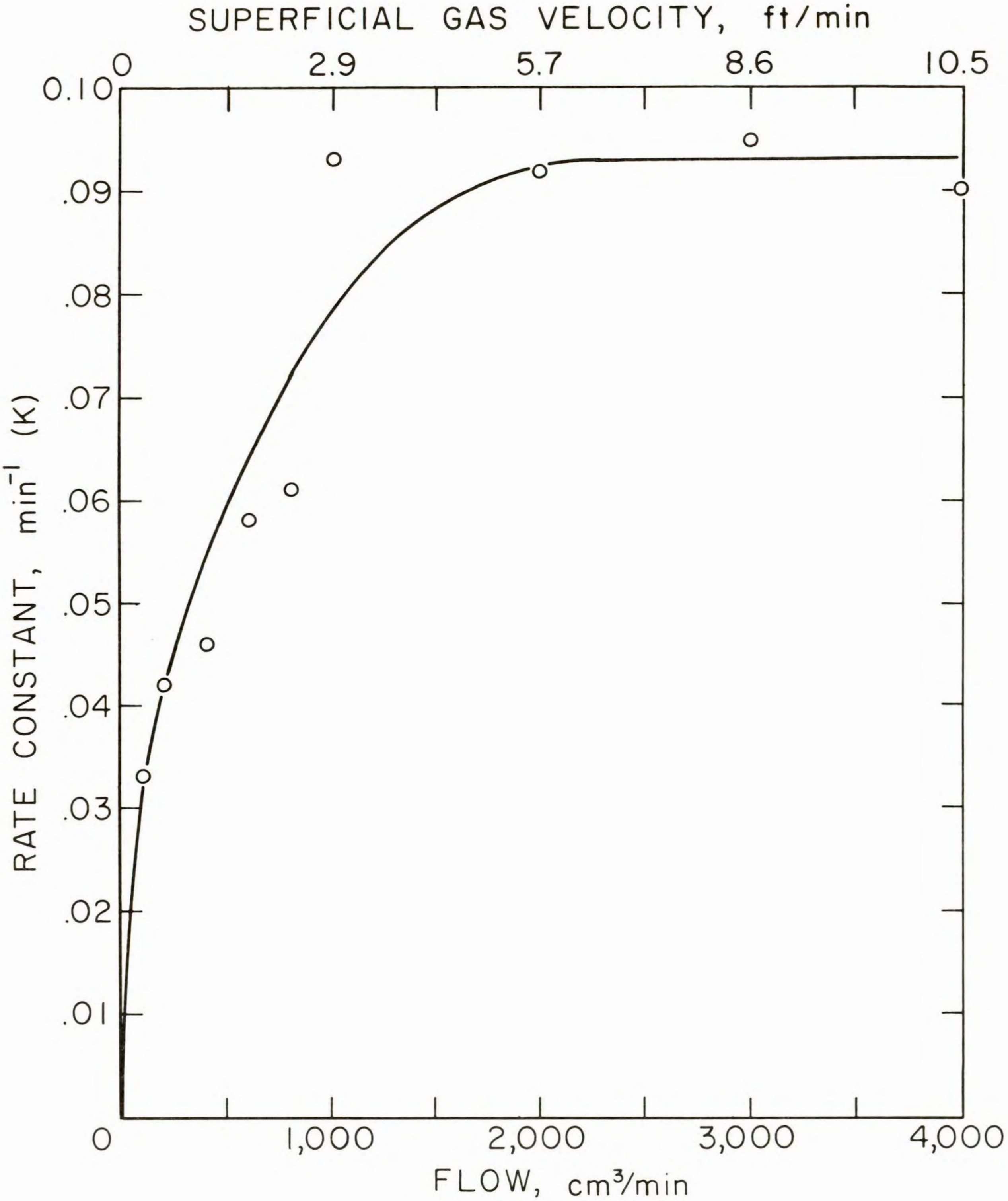

FIGURE 5. - Effect of Superficial Gas Velocity on Regeneration at 700° C.

future runs sufficient gas velocity would be used to insure maximum reaction rates for the test conditions being used. Figure 5 shows that as the flow rate was increased from 100 to 1,000 cu cm/min, the reaction rate increased from about 0.03 to 0.09 min^{-1}. No change in regeneration rate was observed as the gas flow was increased further from 1,000 to 4,000 cu cm/min. The test data for the curve shown in figure 5 are tabulated in table A-2. To insure sufficient gas flow, all the remaining tests were made at a flow rate of 3,000 cu cm/min.

A short test series was then made to determine the effect of hydrogen concentration on regeneration rate with or without water vapor. Fourteen runs of seven samples each were made, eight runs without water vapor, and six runs with 4.8 percent H_2O. The results for dry hydrogen in figure 6 show a maximum rate constant of about 0.091 min^{-1}, which compares favorably with the results reported in figure 5, wherein a maximum rate constant of about 0.093 min^{-1} was obtained. With 4.8 percent H_2O in the regeneration gas, the maximum rate did not exceed 0.05 min^{-1}, even with 10 percent hydrogen. The results are shown in table A-3.

Because of the negative effect of water vapor on regeneration rate by hydrogen at 700° C, a larger test series was set up to evaluate the effects of hydrogen concentration, temperature, and water vapor, each at three levels. Hydrogen levels of 1.0, 2.2, and 5.0 percent and water vapor levels of 0, 2.4, and 4.8 percent were tested at 673°, 700°, and 730° C. The tabulated results are shown in table A-4. When these individual data points were plotted, the spread or random error resulted in a very inaccurate curve fit. Therefore, for each level of hydrogen or water vapor tested at a given temperature, an average of the three runs was made. Using this method of averaging to reduce the spread in results, the graphs in figure 7 were prepared to show the effects of both increased hydrogen and increased water vapor concentration. The plots on the left side of figure 7 show the negative effect of water vapor at the three temperatures with an average hydrogen concentration of 2.7 percent. The regeneration rate constant decreased from a high of 0.062 min^{-1} with zero percent water vapor at 730° C to 0.044 min^{-1} with 4.8 percent H_2O. At 700° C the effect of water vapor was about the same as for 730° C, while at 673° C the negative effect was not as pronounced. In the right half of figure 7, the increase in regeneration rate with hydrogen concentration is shown at the average water vapor level of 2.4 percent. The slope of the line nearly doubles with a 30° C rise in temperature. It appears that addition of water vapor to the hydrogen reduces the rate constant approximately in proportion to the water vapor concentration. This reduction can be interpreted as a masking by water of some of the reaction sites, thus making them unavailable for the hydrogen reaction.

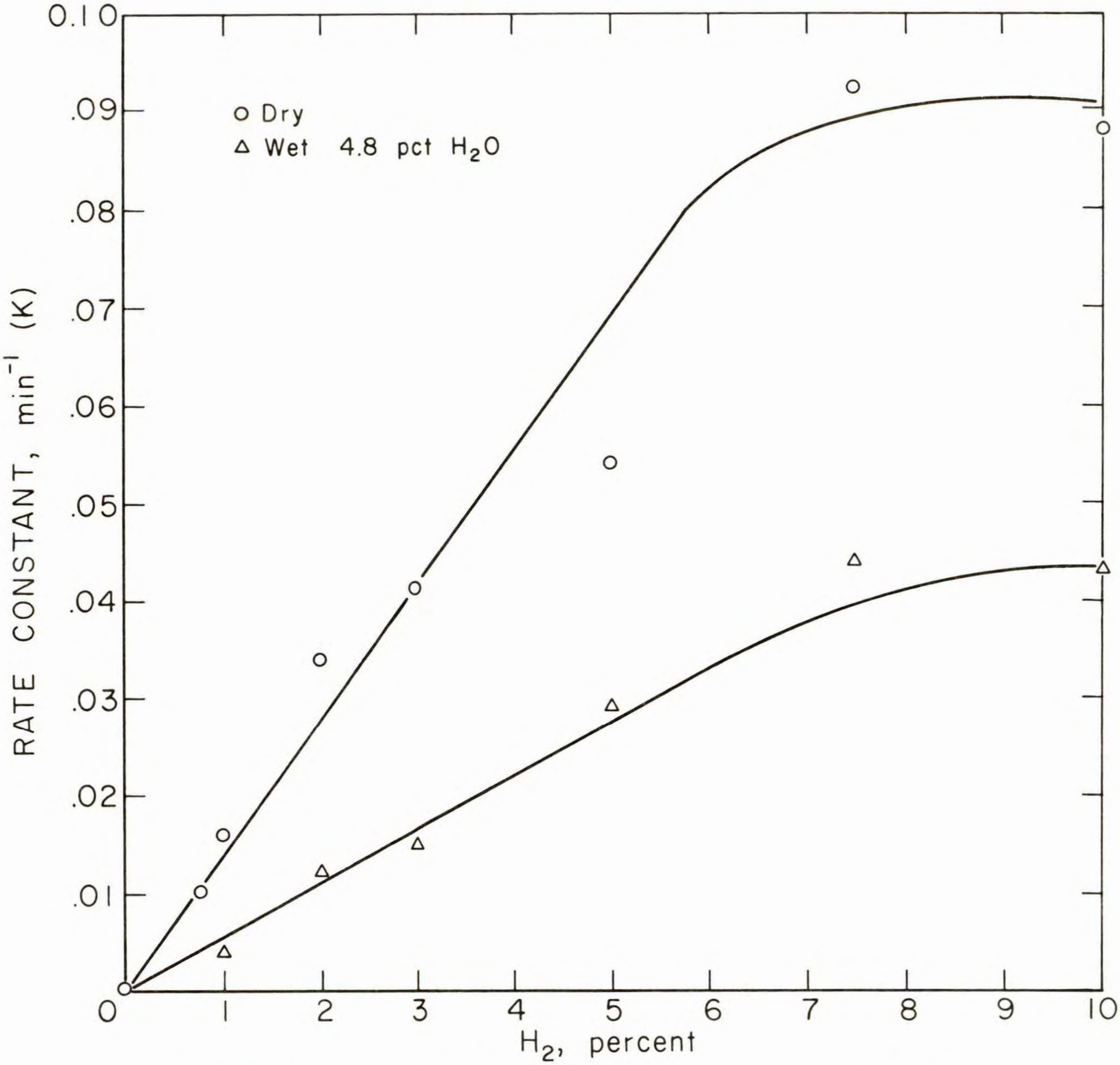

FIGURE 6. - Regeneration Rates by Dry and Wet Hydrogen at 700° C.

Therefore data in table A-4 have been fitted to the following rate equation:

$$K = a[1-b(H_2O)](H_2).$$

When the gas concentration is expressed in volume-percent, constant a has a value of 0.0046±0.0007 at 673° C, 0.013±0.001 at 700° C, and 0.024±0.002 at 730° C. From these values for a, it appears that the activation energy for the regeneration reaction with hydrogen is about 55±7 kcal/mole. Constant b has essentially the same value for all three temperatures, 0.089±0.042. As

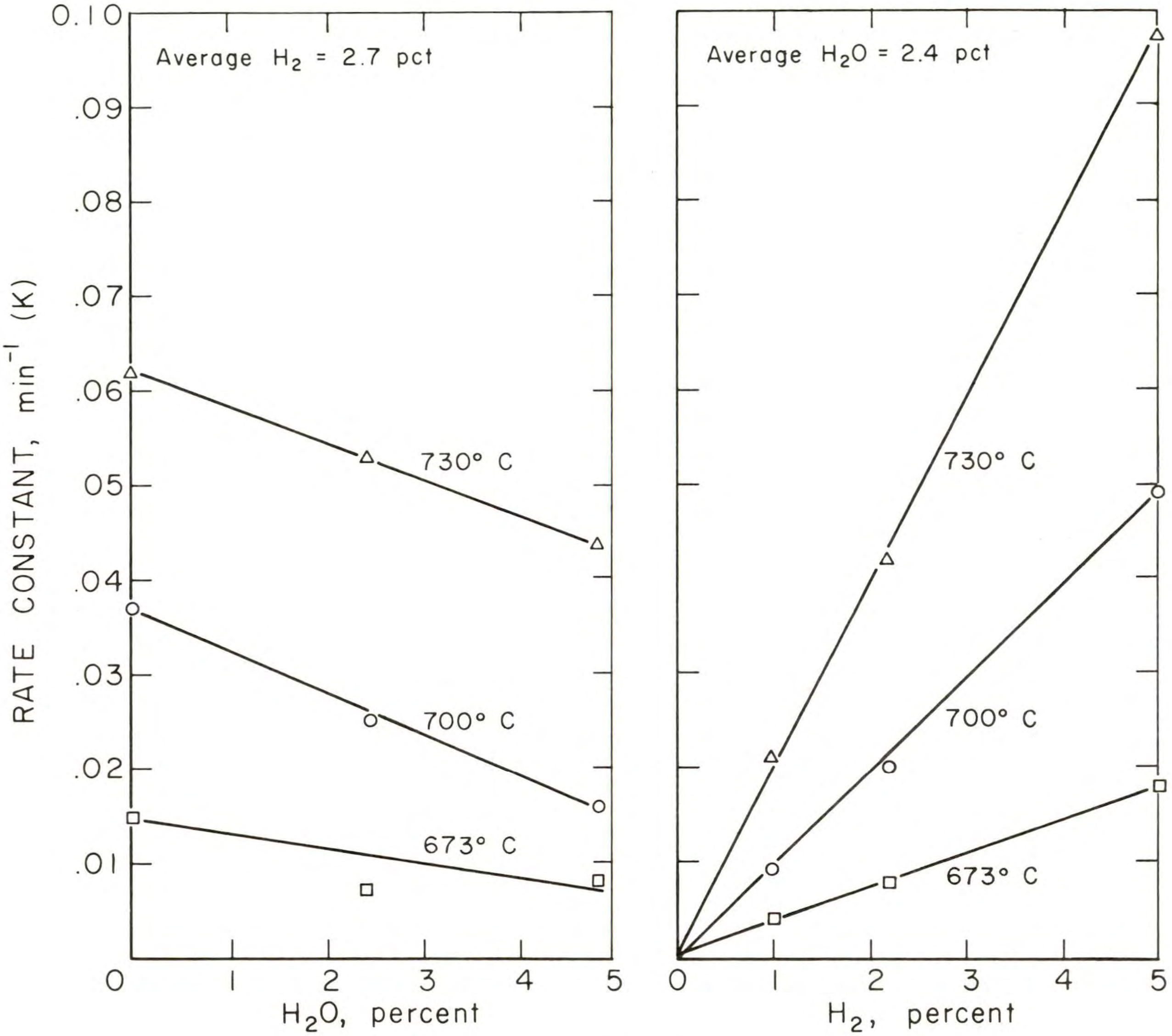

FIGURE 7. - Effect of H_2O and H_2 on Regeneration Rate.

reported previously, the rate constant is directly proportional to the hydrogen concentration up to 5 percent H_2, and is constant thereafter. This effect suggests that above 5 percent H_2, all the available reaction sites are saturated.

To study the effect of hydrogen sulfide on the regeneration rate in a reducing gas composed of hydrogen and water vapor, 20 runs of six samples each were made at 700° C. The concentration of hydrogen sulfide was increased in about 1-percent increments from 0 to 5 percent at two levels each of hydrogen and water vapor. Hydrogen concentrations of 2.2 and 5.0 percent were used with water vapor levels of 2.4 and 4.8 percent. Results given in table A-5 were initially plotted individually; however, the spread in the data points was so great that little reliable information was developed. Therefore, the

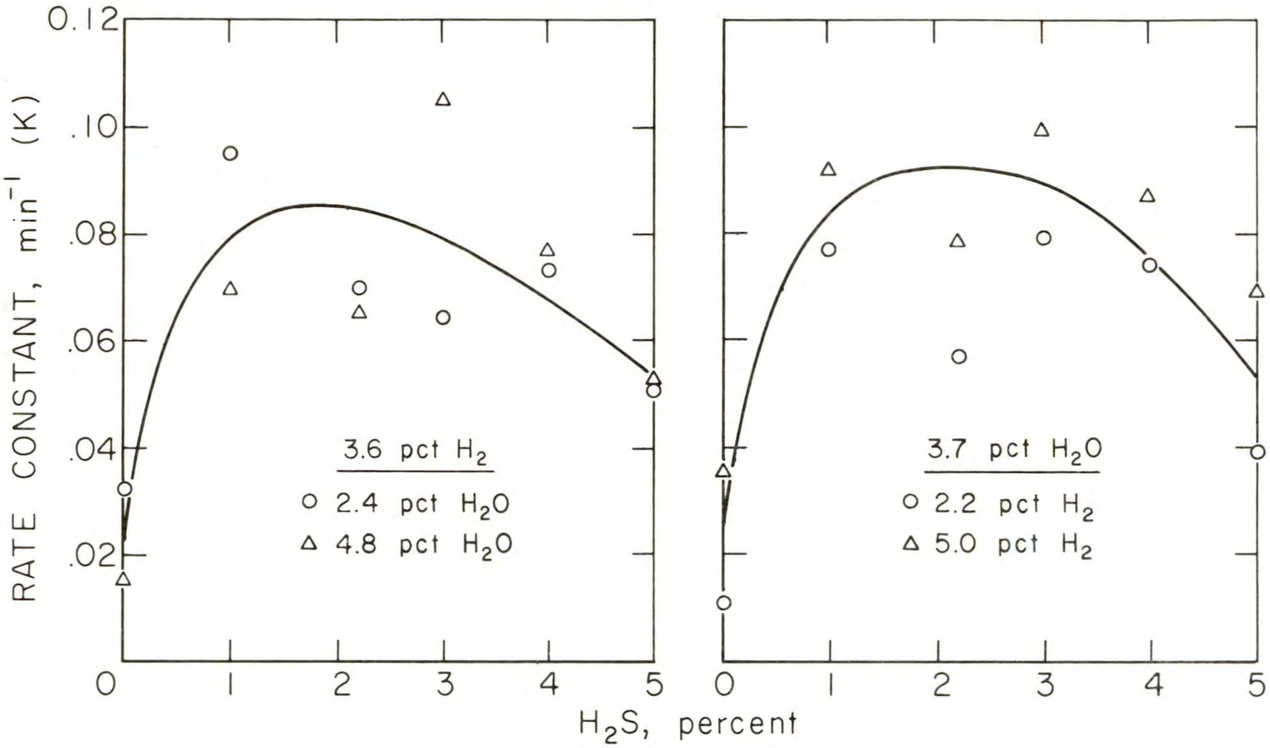

FIGURE 8. - Regeneration Rates as Affected by H_2S at 700° C.

results of the two tests of equal hydrogen or water vapor concentration were averaged, and the values were plotted in figure 8. The results still show considerable scatter; however, in every case the rate constant is low at zero percent H_2S, rises significantly at 1 to 2.2 percent H_2S, and then drops, so that the rate at 5 percent H_2S is about half the maximum rate. The maximum in the relationship between the rate constants and hydrogen sulfide concentration appears to be real. No model has been developed to explain the results, but the information is reported to show the unexpected effect of one of the reaction products on the regeneration rate constant.

Carbon Monoxide Studies

In studying the effect of carbon monoxide, either wet or dry, on the regeneration rate of alkalized alumina, one short test series was made at 700° C. The results in figure 9 show that dry carbon monoxide reaches a rate constant of about 0.06 min^{-1} at the 5-percent level and then does not increase. The results in table A-6 also show that dry carbon monoxide will not reduce the sulfur level below about 2 percent. When water vapor is added to the carbon monoxide-nitrogen gas mixture, the regeneration rate continues to increase until a rate constant of about 0.12 min^{-1} is reached at the 10-percent CO level. This rate compares favorably to the dry hydrogen rate and is probably due to the reaction of CO and H_2O at 700° C, which produces H_2 and CO_2. The wet carbon monoxide reduces the sulfur levels on the pellets to well below 1 percent. The equilibrium of the reaction

$$CO + H_2O \rightarrow H_2 + CO_2$$

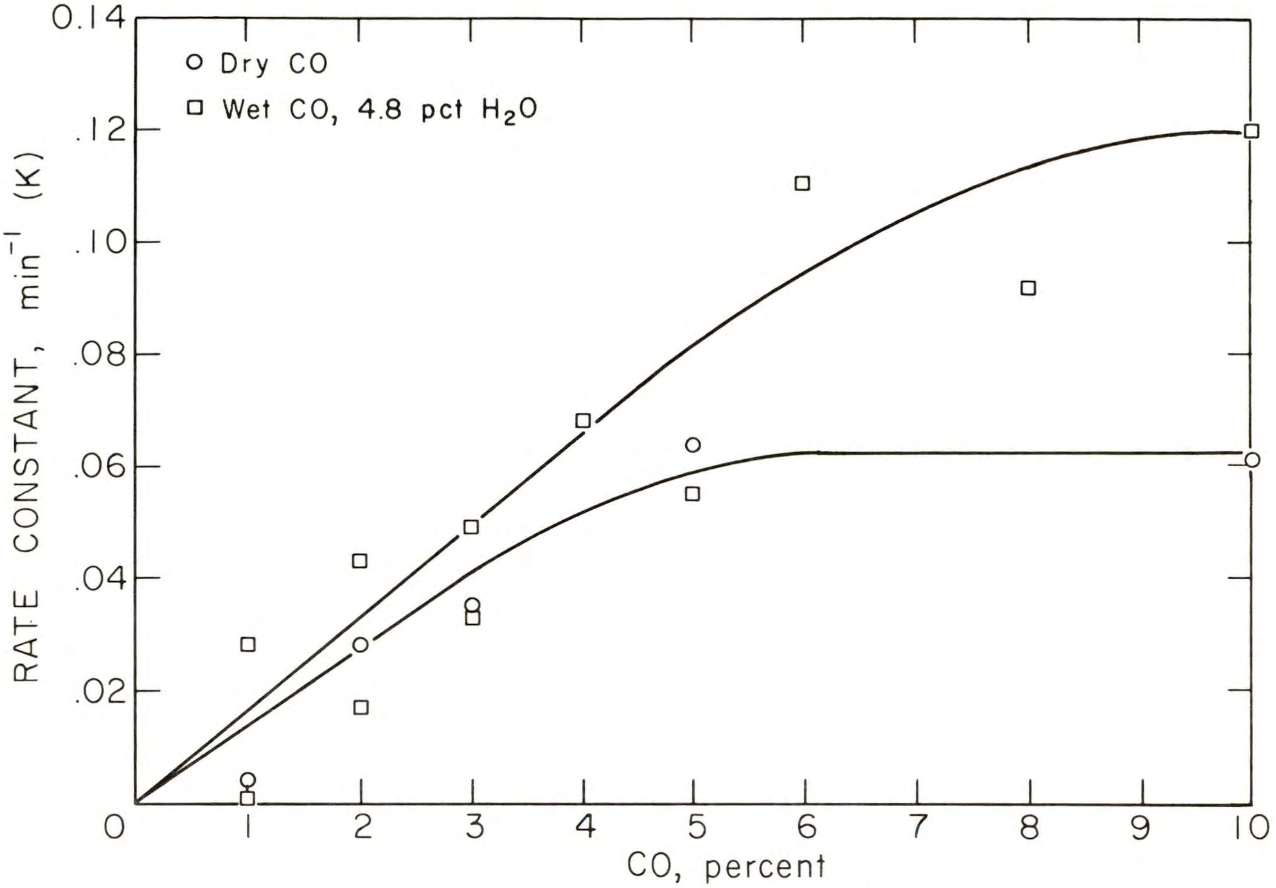

FIGURE 9. - Regeneration Rates by CO and H_2O at 700° C.

at 700° C was not pursued because the effect of carbon monoxide and hydrogen could be obtained much more easily and at known composition by mixing hydrogen and carbon monoxide from individual flowmeters.

To determine the combined effect of carbon monoxide and hydrogen on the regeneration rate, 27 runs were made at 673°, 700°, and 730° C, at three levels each of hydrogen and carbon monoxide. Both hydrogen and carbon monoxide were tested at levels of 0, 2.2, and 5.0 percent. The results in figure 10 and table A-7 show a linear increase in rate for both gases as their concentration is increased from 0 to 5 percent. Assuming that CO can mask the H_2 reaction sites and that H_2 can mask the CO reaction sites, the rate constant can be calculated from the equation:

$$K = a_1[1-b_1(CO)](H_2) + a_2[1-b_2(H_2)](CO)$$

$$= a_1(H_2) + a_2(CO) - (a_1b_1 + a_2b_2)(H_2)(CO),$$

where the concentrations are expressed in volume-percent. The tabulated results listed below show that a_1 and a_2 increase rapidly from 673° to 700° C and then show little increase as the temperature is increased to 730° C.

Temperature, ° C	a_1	a_2	$(a_1 b_1 + a_2 b_2)$
673.................	0.0053±0.0008	0.0045±0.0008	0.0007±0.0003
700.................	.0156± .0020	.0090± .0020	.0029± .0008
730.................	.0165± .0016	.010 ± .0016	.0023± .0006

A series also was made to determine whether or not carbon dioxide would affect the reaction rate of carbon monoxide by occupying similar reaction sites on the alkalized alumina. Results shown in figure 11 and table A-8 indicate an increase in the regeneration rate by CO when CO_2 is added. However, the regeneration rates without CO_2 in this series are not consistent with the results of the previous series shown in figure 9. The inconsistency has not been explained; however the carbon monoxide-carbon dioxide gas mixture did not reduce the sulfur level on the pellets below 2 percent and the mixture is therefore of little interest as a reducing gas in this process.

Effect of Various Gases in the Presence of Carbonyl Sulfide

During regeneration, carbonyl sulfide (COS) may be produced by the following reaction:

$$2H_2 + CO + SO_2 \rightarrow COS + 2H_2O.$$

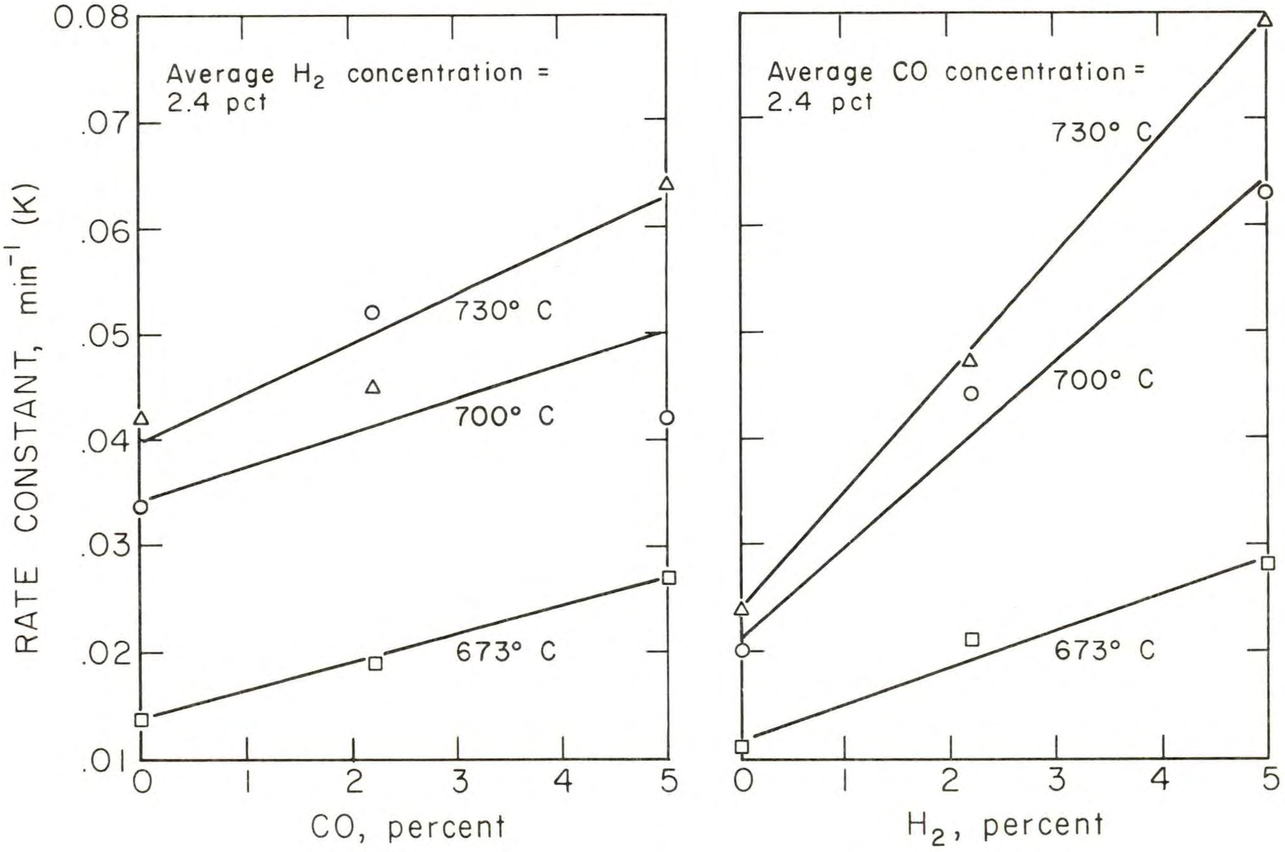

FIGURE 10. - Regeneration Rates by Dry CO and H_2.

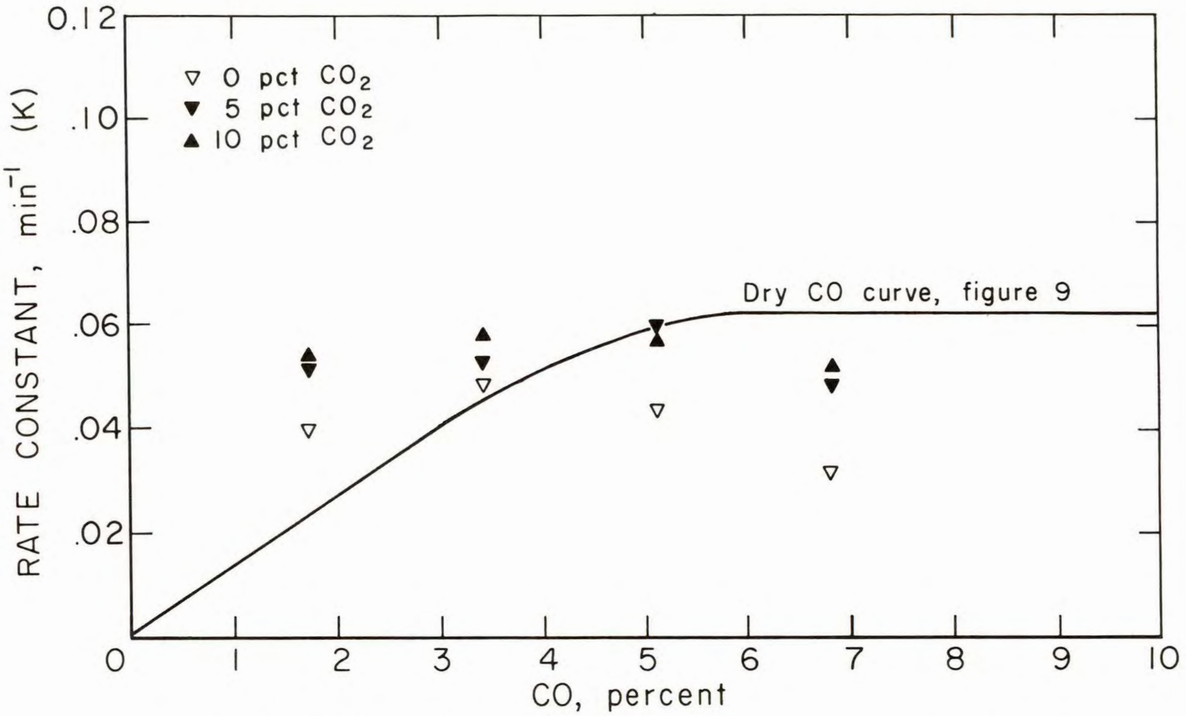

FIGURE 11. - Effect of CO and CO_2 on Regeneration Rates at 700° C.

Therefore, to determine its effect on the reaction rates, tests were made with different reducing gases in combination with 5 percent COS. The results in table 2 show that in all cases the sulfur content on the pellets increased. The presence of water vapor in the regeneration gas appears to inhibit the sorption of carbonyl sulfide, but the presence of hydrogen or carbon monoxide has no effect. The high sulfur content of the zero-time samples, which were heated in the regeneration unit for 15 minutes and then removed without being exposed to the regeneration gases, suggests that significant amounts of carbonyl sulfide are sorbed onto the walls of the sample holder and later released and sorbed onto the test samples. The effect of carbonyl sulfide is of only passing interest to a thin-bed or fluidized-bed reactor, wherein gas contact times are short; however, carbonyl sulfide could cause problems in a slow-moving, deep-bed reactor wherein the products of regeneration pass up through unreacted pellets.

TABLE 2. - Effect of various gases on regeneration in the presence of COS

Material tested	Gas composition, percent						Sulfur load, percent						
	H_2	H_2O	CO_2	CO	COS	N_2	0 min	6 min	12 min	24 min	30 min	60 min	120 min
Loaded......	5	0	0	5	5	85	9.71	7.87	10.2	13.2	6.95	19.6	18.3
Do........	0	4.8	0	5	5	85.2	9.77	4.06	4.20	3.41	13.6	4.19	2.86
Do........	0	0	5	5	5	85	9.28	8.25	9.22	11.8	9.33	13.8	15.9
Do........	0	0	0	5	5	90	6.92	9.86	11.6	16.8	15.5	17.1	17.3
Unloaded[1]...	0	0	0	5	5	90	5.93	8.35	9.80	17.6	10.2	18.1	17.4

[1] The unloaded material was Grace No. 1, which had only been activated and which had a residual sulfur load of about 1.46 percent.

Regeneration by Nonreformed Propane

It had been reported that alkalized alumina could be regenerated by propane (5). Since this might be a more convenient reductant than either hydrogen or carbon monoxide, the rate of regeneration by propane was measured at 600°, 673°, 700°, and 730° C. Propane levels of 5, 10, and 15 percent were investigated. The results are shown in table A-9. It was shown that regeneration by propane is just as effective as by simulated reformed propane. In fact, the propane is less sensitive to temperature variations than is reformed propane. An Arrhenius plot of log K versus 1/T is shown in figure 12, and except for some spread in the results at 600° C, the data can be fitted to a straight line. The apparent activation energy is about 46±2 kcal/mole.

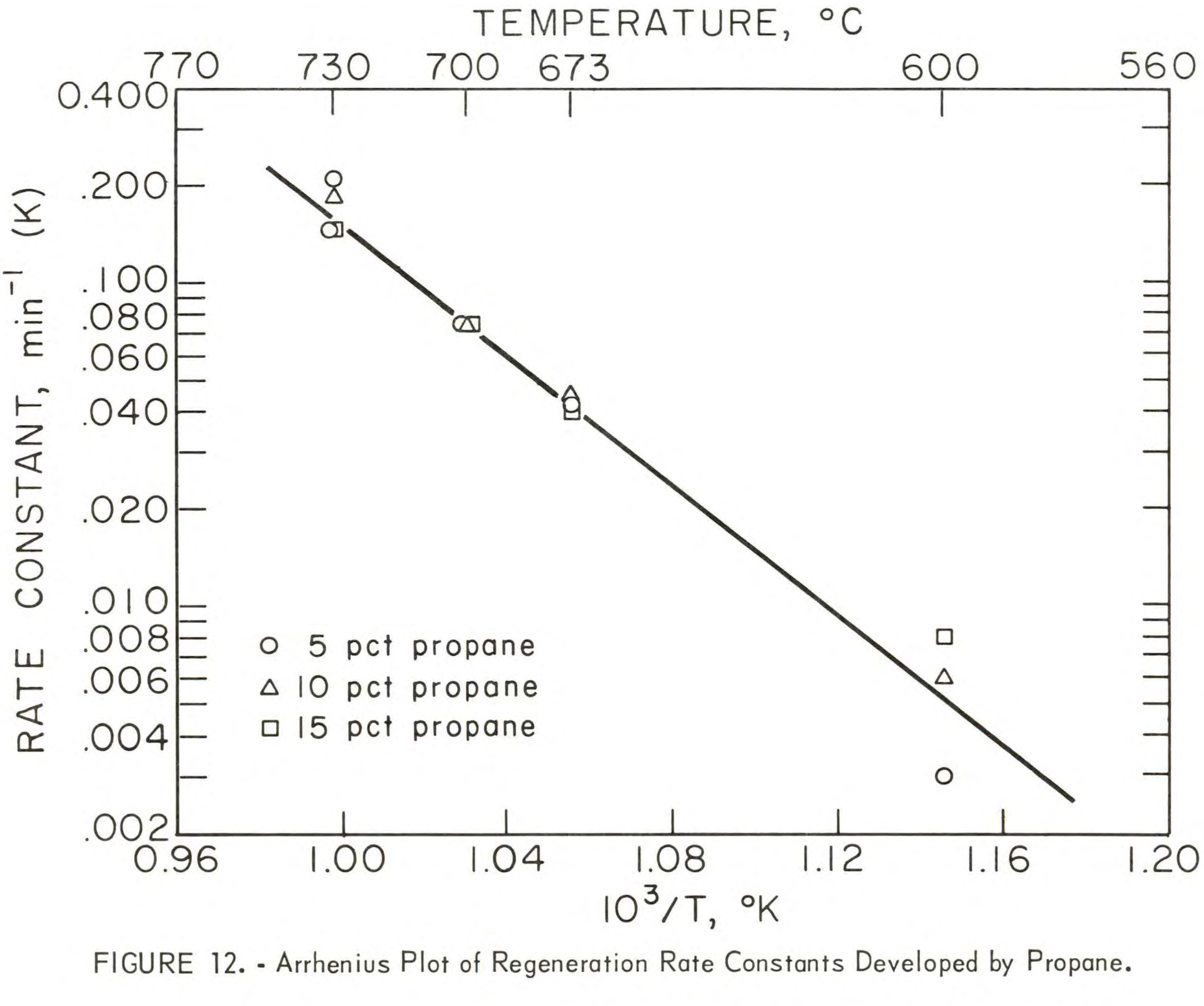

FIGURE 12. - Arrhenius Plot of Regeneration Rate Constants Developed by Propane.

SUMMARY

Regeneration rates of Grace No. 1 alkalized alumina were dependent on reducing gas concentration, regeneration temperature, and water vapor content. Although the data were somewhat scattered, a simple first order reaction rate equation, $d\mu/dt = -K\mu$, was used to calculate the removal rate of the sorbed sulfur. This equation fits the data for the removal of most of the sorbed sulfur.

Regeneration by simulated reform propane showed an Arrhenius relationship with an activation energy of about 75 kcal/mole. Nonreformed propane was nearly as effective as reformed propane and showed an activation energy of 46 kcal/mole.

The regeneration rates induced by the individual gases can be described as follows: (1) Rates from hydrogen and carbon monoxide both increased up to about 5-percent concentration, with hydrogen showing a maximum rate nearly 50 percent higher than that of carbon monoxide--0.09 min^{-1} and 0.06 min^{-1}, respectively; (2) water vapor reduced the regeneration rate from hydrogen by about 50 percent, while it increased the rate from carbon monoxide by 100 percent--0.045 min^{-1} and 0.12 min^{-1}, respectively; (3) carbon dioxide had no effect on the rate from carbon monoxide; (4) hydrogen sulfide had a significant positive effect with hydrogen to concentration levels up to about 2 percent and then produced a rapid negative effect; and (5) carbonyl sulfide produced an increase in sulfur.

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APPENDIX

Tables A-1 through A-9 contain the test results shown in figure 2 through figure 12. In calculating the rate constants, only the initial rapid sulfur removal was used. Therefore, an asterisk has been placed beside the last time-sample used in calculating the rate constants.

TABLE A-1. - Regeneration by simulated reformed propane

Temperature, ° C	Sulfur, gS/gp							Rate constant, min^{-1}
	0 min	4 min	8 min	16 min	30 min	60 min	120 min	
SAMPLE LOADED TO 8.8 PERCENT SULFUR								
600.........	0.111	0.112	0.108	0.107	0.107	0.112	0.116*	0.000
650.........	.122	.120	.115	.115	.109	.091	.061*	.006
680.........	.102	.114	.101	.088	.065	.029	.013*	.019
700.........	.114	.085	.067	.033	.016*	.010	.0039	.066
700.........	.113	.076	.051	.025	.013*	.0087	.0023	.072
730.........	.107	.030	.019	.0073*	.0059	.0028	.0021	.157
SAMPLE LOADED TO 5.9 PERCENT SULFUR								
600.........	0.070	0.067	0.063	0.069	0.057	0.060	0.061*	0.001
650.........	.065	.060	.068	.072	.068	.055	.038*	.005
680.........	.069	.063	.062	.039	.033	.018*	.0063	.023
700.........	.066	.051	.034	.021	.016*	.0093	.0021	.031
730.........	.066	.024	.0089	.0062*	.0033	.0025	.0014	.250
SAMPLE LOADED TO 2.3 PERCENT SULFUR								
600.........	0.020	0.020	0.023	0.024	0.024	0.024	0.025*	-0.001
650.........	.025	.022	.020	.021	.020	.0089*	.0063	.015
680.........	.026	.017	.017	.0094*	.0061	.0024	.0019	.060
700.........	.023	.0093	.0074	.0042*	.0029	.0015	.0012	.143
730.........	.026	.0055	.0044	.0025*	.0013	.0016	.0013	.223

TABLE A-2. - Effect of superficial gas velocity on regeneration rate at 700° C

Total flow, cu cm/min[1]	Sulfur, gS/gp						Rate constant, min^{-1}
	0 min	6 min	12 min	18 min	24 min	30 min	
4,000...............	0.053	0.045	0.018*	0.013	0.013	0.012	0.090
3,000...............	.047	.036	.015*	.012	.013	.012	.095
2,000...............	.063	.051	.029	.012*	.010	.009	.092
1,000...............	.057	.055	.018	.013*	.011	.010	.093
800...............	.059	.053	.049	.024	.014*	.017	.061
600...............	.056	.058	.036	.020	.017*	.017	.058
400...............	.054	.053	.048	.027	.019*	.023	.046
200...............	.061	.057	.047	.032	.023*	.0243	.042
100...............	.045	.049	.051	.039	.019*	.029	.033

[1] Gas composition was 5 percent H_2, 95 percent N_2.

TABLE A-3. - Effect of wet and dry hydrogen on regeneration rate at 700° C

Gas composition, percent[1]		Sulfur, gS/gp							Rate constant, min^{-1}
H_2	H_2O	0 min	4 min	8 min	16 min	30 min	60 min	120 min	
10	0	0.063	0.053	0.039	0.016*	0.012	0.0094	0.0063	0.088
7.5	0	.063	.052	.038	.015*	.011	.0068	.0052	.092
5	0	.074	.072	.071	.041	.016*	.016	.011	.054
3	0	.069	.066	.061	.030	.023*	.020	.015	.041
2	0	.061	.072	.063	.036	.026*	.019	.016	.034
1	0	.070	.070	.064	.065	.055	.027*	.013	.016
.67	0	.074	.071	.080	.075	.040	.051	.022*	.010
0	0	.066	.073	.067	.065	.062	.072	.069*	.000
10	4.8	.068	.059	.061	.027	.021*	.0065	.0014	.043
7.5	4.8	.079	.054	.057	.035	.020*	.0048	.0022	.044
5	4.8	.070	.071	.065	.040	.033*	.012	.0029	.029
3	4.8	.066	.064	.069	.056	.051	.028*	.010	.015
2	4.8	.069	.073	.066	.062	.051	.036*	.0092	.012
1	4.8	.076	.065	.063	.068	.064	.062	.043*	.004

[1] Balance N_2, total flow 3,000 cu cm/min.

TABLE A-4. - Effect of wet and dry hydrogen on regeneration rate at 673°, 700°, and 730° C

Temperature, ° C	Gas composition, percent			Sulfur, gS/gp						Rate constant, min^{-1}
	H_2	H_2O	N_2	0 min	6 min	12 min	18 min	24 min	30 min	
673.........	1.0	0	99.0	0.067	0.067	0.070	0.069	0.059	0.061*	0.004
	1.0	2.4	96.6	.066	.063	.058	.061	.052	.062*	.004
	1.0	4.8	94.2	.059	.065	.058	.061	.060	.054*	.003
	2.2	0	97.8	.064	.061	.058	.052	.047	.046*	.012
	2.2	2.4	95.8	.077	.073	.068	.067	.067	.071*	.003
	2.2	4.8	93.0	.084	.072	.073	.060	.061	.063*	.010
	5.0	0	95.0	.068	.069	.062	.041	.032	.035*	.029
	5.0	2.4	92.6	.061	.060	.047	.046	.045	.042*	.013
	5.0	4.8	90.2	.072	.064	.052	.053	.054	.047*	.013
700.........	1.0	0	99.0	.063	.067	.063	.064	.056	.048*	.009
	1.0	2.4	96.6	.068	.067	.058	.061	.056	.047*	.011
	1.0	4.8	94.2	.067	.066	.058	.061	.055	.055*	.007
	2.2	0	97.8	.061	.056	.054	.047	.030	.025*	.031
	2.2	2.4	95.8	.069	.069	.065	.055	.054	.037*	.019
	2.2	4.8	93.0	.067	.062	.069	.071	.061	.059*	.009
	5.0	0	95.0	.068	.062	.032	.021	.014*	.012	.071
	5.0	2.4	92.6	.068	.053	.047	.033	.023*	.013	.044
	5.0	4.8	90.2	.060	.063	.053	.038	.036	.022*	.033
730.........	1.0	0	99.0	.067	.063	.054	.051	.040	.030*	.026
	1.0	2.4	96.6	.066	.062	.055	.054	.037	.030*	.026
	1.0	4.8	94.2	.070	.076	.077	.069	.060	.057*	.011
	2.2	0	97.8	.067	.055	.057	.035	.022	.018*	.047
	2.2	2.4	95.8	.067	.070	.059	.044	.034	.031*	.043
	2.2	4.8	93.0	.055	.054	.047	.037	.025	.022*	.034
	5.0	0	95.0	.066	.044	.017*	.014	.013	.012	.113
	5.0	2.4	92.6	.081	.068	.048	.015*	.011	.010	.091
	5.0	4.8	90.2	.065	.054	.023*	.008	.006	.006	.087

TABLE A-5. - Regeneration rates by different levels of H_2S at 700° C

Gas composition, percent[1]			Sulfur, gS/gp						Rate constant, min^{-1}
H_2	H_2O	H_2S	0 min	6 min	12 min	18 min	24 min	30 min	
2.2	2.4	0	0.069	0.069	0.065	0.055	0.054	0.037*	0.019
2.2	2.4	1	.084	.073	.054	.015	.013*	.012	.089
2.2	2.4	2.2	.071	.080	.068	.040	.026*	.022	.047
2.2	2.4	3	.057	.056	.035	.022	.018*	.019	.054
2.2	2.4	4	.081	.071	.051	.026	.022*	.017	.060
2.2	2.4	5	.088	.087	.066	.046	.038	.034*	.036
2.2	4.8	0	.067	.062	.069	.071	.061	.059*	.003
2.2	4.8	1	.062	.064	.040	.023	.016*	.011	.064
2.2	4.8	2.2	.098	.091	.065	.036	.021*	.019	.067
2.2	4.8	3	.093	.083	.056	.023	.014*	.015	.084
2.2	4.8	4	.067	.055	.032	.023	.020*	.016	.067
2.2	4.8	5	.088	.073	.060	.044	.032*	.028	.042
5.0	2.4	0	.068	.053	.047	.033	.023*	.013	.044
5.0	2.4	1	.060	.039	.018	.011*	.010	.010	.098
5.0	2.4	2.2	.109	.087	.055	.020*	.017	.016	.092
5.0	2.4	3	.058	.058	.021	.019*	.017	.017	.073
5.0	2.4	4	.063	.062	.022	.016*	.016	.015	.086
5.0	2.4	5	.097	.092	.054	.031	.023*	.025	.066
5.0	4.8	0	.060	.063	.053	.038*	.036	.022	.026
5.0	4.8	1	.055	.039	.014	.014*	.011	.011	.086
5.0	4.8	2.2	.091	.096	.063	.030*	.017	.016	.063
5.0	4.8	3	.113	.072	.026	.013*	.011	.010	.125
5.0	4.8	4	.067	.048	.017	.015*	.013	.013	.087
5.0	4.8	5	.105	.079	.050	.029*	.019	.021	.072

[1] Balance N_2.

TABLE A-6. - Effect of CO and H_2O on regeneration rates at 700° C

Gas composition, percent[1]		Sulfur, gS/gp							Rate constant, min^{-1}
CO	H_2O	0 min	4 min	8 min	16 min	30 min	60 min	120 min	
10	0	0.076	0.068	0.062	0.029*	0.031	0.030	0.023	0.061
5	0	.074	.071	.054	.028*	.030	.029	.030	.064
3	0	.067	.059	.070	.037*	.036	.028	.022	.035
2	0	.071	.071	.074	.046*	.048	.028	.020	.028
1	0	.065	.063	.074	.068	.072	.051	.044*	.004
5	4.8	.059	.059	.057	.025*	.009	.005	.003	.055
3	4.8	.076	.061	.068	.044	.028*	.010	.002	.033
2	4.8	.065	.065	.062	.047	.049	.023*	.003	.017
1	4.8	.065	.065	.055	.053	.056	.044	.055*	.001
		0 min	6 min	12 min	18 min	24 min	30 min		
10	4.8	0.094	0.081	0.042	0.012*	0.008	0.008	-	0.120
8	4.8	.087	.085	.055	.016*	.013	.010	-	.092
6	4.8	.095	.075	.036	.013*	.004	.007	-	.111
[2]4	4.8	.046	.035	.026	.013*	.012	.012	-	.068
[2]3	4.8	.043	.040	.031	.020	.014*	.019	-	.049
[2]2	4.8	.047	.038	.033	.021	.017*	.014	-	.043
[2]1	4.8	.060	.048	.044	.035	.030*	.033	-	.028

[1] Balance N_2.

[2] New sample with lower head.

TABLE A-7. - Combined effect of hydrogen and carbon monoxide on regeneration rate at 673°, 700°, and 730° C

Temperature, ° C	Gas composition, percent			Sulfur, gS/gp						Rate constant, min^{-1}
	H$_2$	CO	N$_2$	0 min	6 min	12 min	18 min	24 min	30 min	
673........	0	0	100	-	-	-	-	-	-	0.000
	0	2.2	97.8	0.074	0.081	0.073	0.063	0.053	0.053*	.015
	0	5.0	95.0	.074	.064	.071	.055	.049	.044*	.017
	2.2	0	97.8	.064	.061	.058	.052	.047	.046*	.012
	2.2	2.2	95.6	.067	.064	.063	.048	.041	.041*	.019
	2.2	5.0	92.8	.082	.064	.061	.044	.036	.032*	.032
	5.0	0	95.0	.068	.069	.062	.041	.032	.035*	.029
	5.0	2.2	92.8	.083	.077	.068	.051	.043	.045*	.024
	5.0	5.0	90.0	.082	.067	.064	.046	.037	.033*	.032
700........	0	0	100	-	-	-	-	-	-	.000
	0	2.2	97.8	.086	.077	.060	.048	.038	.035*	.033
	0	5.0	95.0	.072	.067	.051	.038	.034	.036*	.028
	2.2	0	97.8	.061	.056	.054	.047	.030	.025*	.031
	2.2	2.2	95.6	.061	.058	.046	.021*	.022	.022	.042
	2.2	5.0	92.8	.104	.071	.036	.020*	.020	.019	.060
	5.0	0	95.0	.068	.062	.032	.021*	.014	.012	.070
	5.0	2.2	92.8	.093	.058	.045	.020*	.019	.015	.081
	5.0	5.0	90.0	.066	.060	.037	.025*	.024	.025	.037
730........	0	0	100	-	-	-	-	-	-	.000
	0	2.2	97.8	.071	.062	.048	.043*	.035	.033	.029
	0	5.0	95.0	.073	.051	.033	.035*	.034	.036	.044
	2.2	0	97.8	.067	.055	.057	.035*	.022	.018	.032
	2.2	2.2	95.6	.073	.069	.064	.035*	.022	.021	.038
	2.2	5.0	92.8	.089	.070	.042	.026*	.022	.021	.070
	5.0	0	95.0	.066	.044	.017	.014*	.013	.012	.093
	5.0	2.2	92.8	.074	.074	.047	.022*	.018	.018	.068
	5.0	5.0	90.0	.084	.064	.040	.021*	.018	.016	.077

TABLE A-8. - Effect of CO$_2$ on regeneration rate by CO at 700° C

Gas composition, percent			Sulfur, gS/gp						Rate constant, min^{-1}
CO	CO$_2$	N$_2$	0 min	6 min	12 min	18 min	24 min	30 min	
1.7	0	98.3	0.058	0.048	0.026	0.026	0.023*	0.022	0.041
1.7	5	93.3	.066	.055	.038	.026	.020*	.019	.052
1.7	10	88.3	.066	.066	.039	.027	.021*	.020	.053
3.4	0	96.6	.070	.053	.025	.024	.024*	.024	.049
3.4	5	91.6	.070	.043	.026	.022	.020*	.020	.053
3.4	10	86.6	.069	.049	.029	.022	.018*	.016	.058
5.1	0	94.9	.066	.050	.027	.025	.025*	.022	.044
5.1	5	89.9	.071	.073	.028	.025	.020*	.021	.060
5.1	10	84.9	.065	.046	.026	.019	.018*	.016	.058
6.8	0	93.2	.064	.046	.021	.025	.023*	.022	.032
6.8	5	88.2	.061	.030	.023	.021	.017*	.016	.049
6.8	10	83.2	.055	.041	.036	.019	.017*	.015	.052

TABLE A-9. - Regeneration by propane

Propane, percent[1]	Sulfur, gS/gp								Rate constant, min^{-1}
	0 min	4 min	8 min	15 min	30 min	60 min	120 min		
600° C:									
5.........	0.065	0.065	0.066	0.063	0.062	0.066	0.042*		0.003
10.........	.072	.071	.066	.069	.060	.049	.037*		.006
15.........	.071	.073	.067	.075	.067	.046	.029*		.008
	0 min	1 min	3 min	6 min	12 min	18 min	24 min	30 min	
673° C:									
5.........	0.066	-	-	0.059	0.057	0.033	0.024	0.022*	.042
10.........	.065	-	-	.053	.039	.026	.022	.019*	.044
15.........	.067	-	-	.057	.037	.027	.023	.021*	.040
700° C:									
5.........	.065	-	-	.060	.021	.021*	.019	.015	.074
10.........	.069	-	-	.042	.025	.016*	.016	.013	.076
15.........	.064	-	-	.039	.023	.017*	.015	.017	.075
730° C:									
5.........	.063	-	-	.026*	.016	.017	.016	.012	.148
5.........	.068	0.062	0.029	.021*	.017	.016	-	-	.208
10.........	.066	.056	.028	.023*	.019	.017	-	-	.184
15.........	.048	.057	.037	.022*	.017	.015	-	-	.148

[1] Balance N_2.