

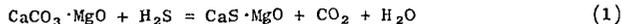
REACTION OF H₂S WITH HALF-CALCINED DOLOMITE IN A REGENERABLE PROCESS

G. P. Curran, B. Pasek, M. Pell, and E. Gorin

Research Division
Conoco Coal Development Company
Library, Pennsylvania 15129

Introduction

The Conoco hot desulfurization process makes use of the reaction of half-calcined dolomite with H₂S,



to remove H₂S from a fuel gas and also to regenerate sorbent dolomite. The Conoco gasification process yields a gas fairly high in H₂O, about 13%. This necessitates a high desulfurization temperature if a goal of 95% desulfurization is to be met. The conditions called for in the current design are as follows:

Desulfurization: 914°C; 13% H₂O, 8% CO₂ inlet; 0.02% H₂S exit
Regeneration: 704°C; 35% H₂O, 64% CO₂ inlet; 3.6% H₂S exit

The entire process runs at 15 atmospheres. Desulfurization operates at the equilibrium H₂S concentration, and regeneration is assumed to operate at about 90% approach to equilibrium. The above conditions provided the base case point about which experimental work was conducted. However, equipment limitations required the desulfurization temperature to be reduced to 871°C for most of our work.

Continuous Cycling Runs

Experiments were carried out in a three-inch diameter gas desulfurizer and a two-inch diameter regenerator. Both vessels contained fluidized beds and were continuously fed with both gas and solids. Details of the experimental technique have been given elsewhere.^(1,2) Dolomite was cycled through the vessels for numerous cycles so that the nature of the decline in activity could be studied. Detailed data on the conditions of these cyclic runs are presented in Tables 1 and 2.

It was found that the desulfurization reaction proceeded rapidly, and that a low concentration of H₂S was maintained until the supply of CaCO₃ was essentially exhausted. However, the regeneration reaction was incomplete, typically yielding but a fraction of the original CaCO₃ in an hour's residence time.

The regeneration activity, defined as mols CaCO₃ produced/100 mols CaS fed, declined as the stone was cycled. The activity decline is pictured in Figure 1. It can be seen that the decline is logarithmic in character. Thus, although a severe decline occurs in cycles 1 to 10, the stone contains modest residual activity even out to 100 cycles. This means that a regenerable process is feasible. The data presented in Figure 1 are for Canaan dolomite, our base case stone. Similar data were obtained for other dolomites.

Figure 2 presents deactivation data for three regeneration temperatures. The data lines are roughly parallel, but this is believed to be fortuitous and unlikely to hold for all conditions. The data indicate that at 593°C, the fractional regeneration is quite low, amounting to less than 10% within only 7 cycles. Only at low regeneration temperatures is the equilibrium H₂S concentration high enough for processing by a conventional Claus process. The Conoco process, however, uses a liquid-phase Claus reaction which is uniquely suited to handling low H₂S concentrations. Our interest therefore centered around the 704°C temperature where stone utilization is higher.

TABLE I

Conditions and Results for Gas Regalizer with Canaan Dolomite Feed

System Pressure: 15 atm (206 psig)
System Temperature: 871°C (1600°F)

Run Number	A7	A13	A15	A20A	A21	A22A	A36A
Canaan Dolomite Batch Number	1	35	48	2	2	20 x 28	2120
Acceptor Size Consist, Tyler Mesh	28 x 35	3040	1500	1810	35 x 48	1892	42
Feed Rate, gm/hr (half-calculated basis)	33	32	65	52	51	50	42
Nominal Solids Residence Time, min							
Inlet, SCFH ⁽¹⁾	175	178	178	148	148	148	310
Recycle to Bed							
H ₂ O	33	33	33	21	21	21	90
H ₂	40	40	40	25	25	25	90
CO	33	33	33	23	23	23	55
CO ₂	21	21	21	8.3	8.3	8.3	52
N ₂	96	96	96	66	66	66	22
H ₂ S	3.5	3.5	1.8	1.6	1.6	1.6	152
Purges (CO ₂) to Bed				5			1.8
Purges (N ₂) above Bed				15			
Recycle Acceptor Lift Gas, above Bed				71			110
Output in Cycle No.	2	6	1	23	18	8	4
Exit Gas Rate, SCFH (dry basis)	215	213	215	143	144	144	338
Composition, Mol %							
H ₂	17	17.5	18.2	16.5	16.6	16.6	17.5
CO	18	17.9	18.0	17.0	16.8	16.1	17.0
CO ₂	12	9.9	9.7	9.8	9.9	10.3	9.4
N ₂	53	54.4	54.0	56.6	56.3	57.0	56.0
H ₂ S	0.05	0.207 ⁽²⁾	0.048	0.03	0.03	0.03	0.04
Outlet Gas, Top of Bed							
Composition, Mol %							
H ₂ O	9.7	10.0	9.5	8.1	8.0	8.5	8.3
H ₂	15.4	16.4	17.1	16.0	16.1	16.0	16.5
CO	15.9	16.8	16.9	16.3	16.3	15.5	16.0
CO ₂	11.2	9.3	9.2	9.5	9.6	10.0	8.9
N ₂	47.7	47.3	47.3	49.9	49.6	50.0	50.3
H ₂ S	0.046	0.194	0.045	0.029	0.029	0.029	0.038
Flow Rate, SCFH, Top of Bed	416	418	418	300	301	303	690
Fluidizing Velocity, ft/sec	0.33	0.33	0.33	0.43	0.43	0.43	0.89 ⁽³⁾
Attrition % of Feed Rate	0.7	0.77	0.89	0.68	0.7	0.7	1.4
Duration of Circulation with H ₂ S Feed, hr	25.2	35.1	42.7	11.7	14.5	8.9	71
Removal of Feed Plus Recycle Sulfur, %	95.3	79	90	94.6	94.5	94.5	86.7
% H ₂ S in Outlet/Equilibrium % H ₂ S	1.4	6.8	1.7	1.3	1.3	1.1	1.7
Conversion of Acceptor/Pass, Mol % of Total Cs	19	16	18	13.8	13.6	13.2	12.6

(1) Inlet is given after shift reaction and hydrolysis of CS₂ have taken place.
(2) Gas sample taken after breakthrough had occurred.
(3) Includes 20-30% +100 mesh particles.

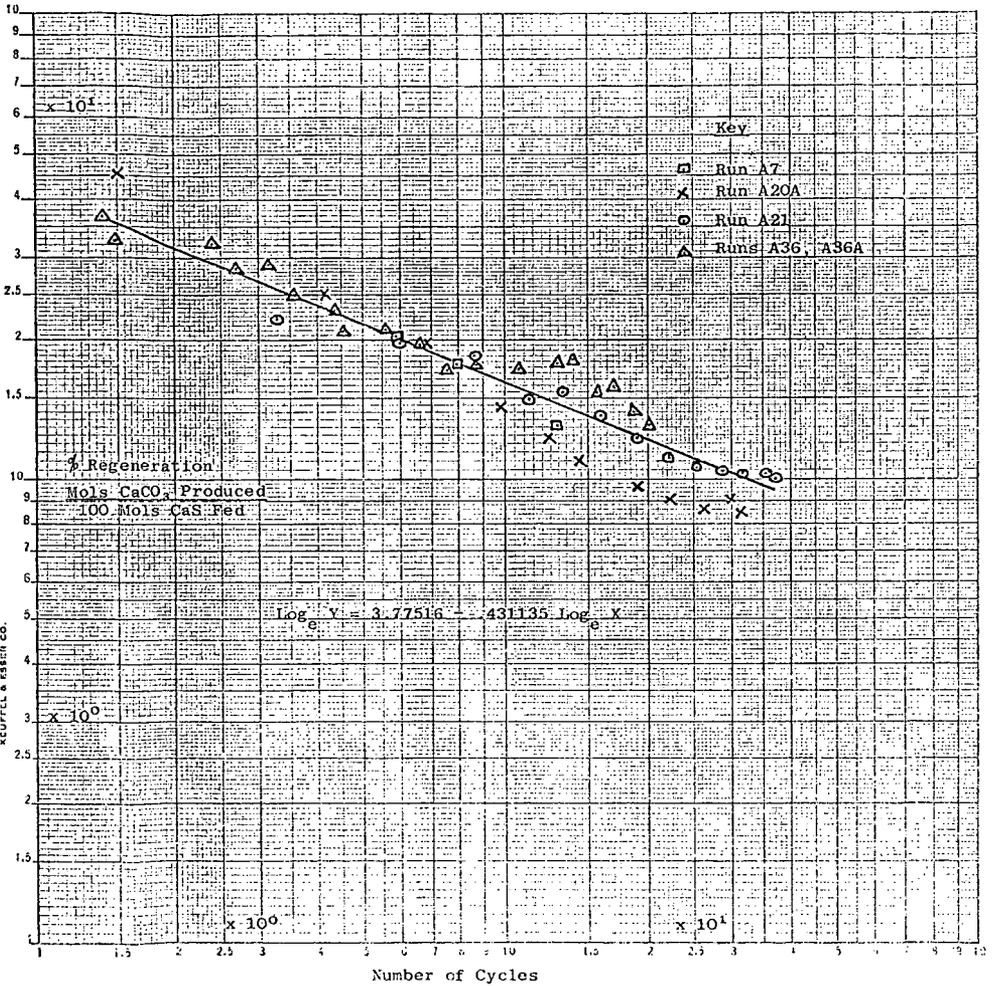
TABLE 2

Conditions and Results for Regenerator with Canmat Dolomite Feed
System Pressure: 45 atm (200 psig)

Run Number	A7	A15	A16	A20A	A21	A22A	A35A
	704 (1300)	593 (1100)	593 (1100)	704 (1300)	704 (1300)	760 (1400)	704 (1300)
	37	36	74	60	59	57	52
Temperature, °C (°F)							
Nominal Solids Residence Time, min.							
Innit. SCFH		0.0					
Recycle to Bed							
H ₂ O	110	100	109	53	102	0.0	0.0
H ₂	0.0	12	12	8.0	47	48	108
CO ₂	110	118	118	91	3.0	8.0	11
Purges (H ₂) to Bed	8	8	8	7	50	86	205
Purges (N ₂) above Bed	10	10	10	10	10	10	10
Purges (CO ₂) above Bed	5	5	5	4	0.0	10	0.0
					15	4.5	15
Output in Cycle No.	1	6	1	23	18	8	4
Exit Gas Rate, SCFH (dry basis)	133	194	152	120	33	116	236
Concentration, Mol %							
H ₂	ND	8.0	8.3	5.0	3.9	3.9	2.1
CO	ND	0.76	1.01	3.95	5.2	3.7	2.6
CO ₂	85.7	78.4	77.4	71.8	83.1	71.4	94.1
N ₂	13.5	11.4	12.8	18.3	5.2	19.4	0.6
H ₂ S	0.7	1.41	0.46	0.82	2.54	0.94	0.62
COS	ND	0.02	Trace	0.04	0.11	0.04	0.03
Outlet Gas, Top of Bed Composition, Mol %							
H ₂ O	46.3	41.6	44.1	32.9	29.0	32.9	33.5
H ₂	--	5.15	5.14	3.8	3.1	3.0	1.5
CO	--	0.49	0.63	3.0	4.1	2.8	1.8
CO ₂	47.8	48.5	46.0	52.0	57.5	51.8	62.4
N ₂	3.5	3.2	3.9	7.6	4.1	8.3	0.4
H ₂ S	0.4	0.91	0.28	0.82	2.03	0.72	0.44
COS	--	0.01	Trace	0.03	0.09	0.031	0.02
Flow Rate, SCFH Top of Bed	298	238	245	159	159	151	333
Fluidizing Velocity, ft/sec	0.63	0.60	0.61	0.44	0.47	0.44	0.92
% H ₂ S in Outlet/Equilibrium % H ₂ S	0.99	0.94	0.91	0.18	0.61	0.43	0.11
Regeneration of Acceptor/Pass, Mol % of Total Ca	5.1	11.5	7.5	8.8	7.4	9.3	11.0

ND - Not determined.

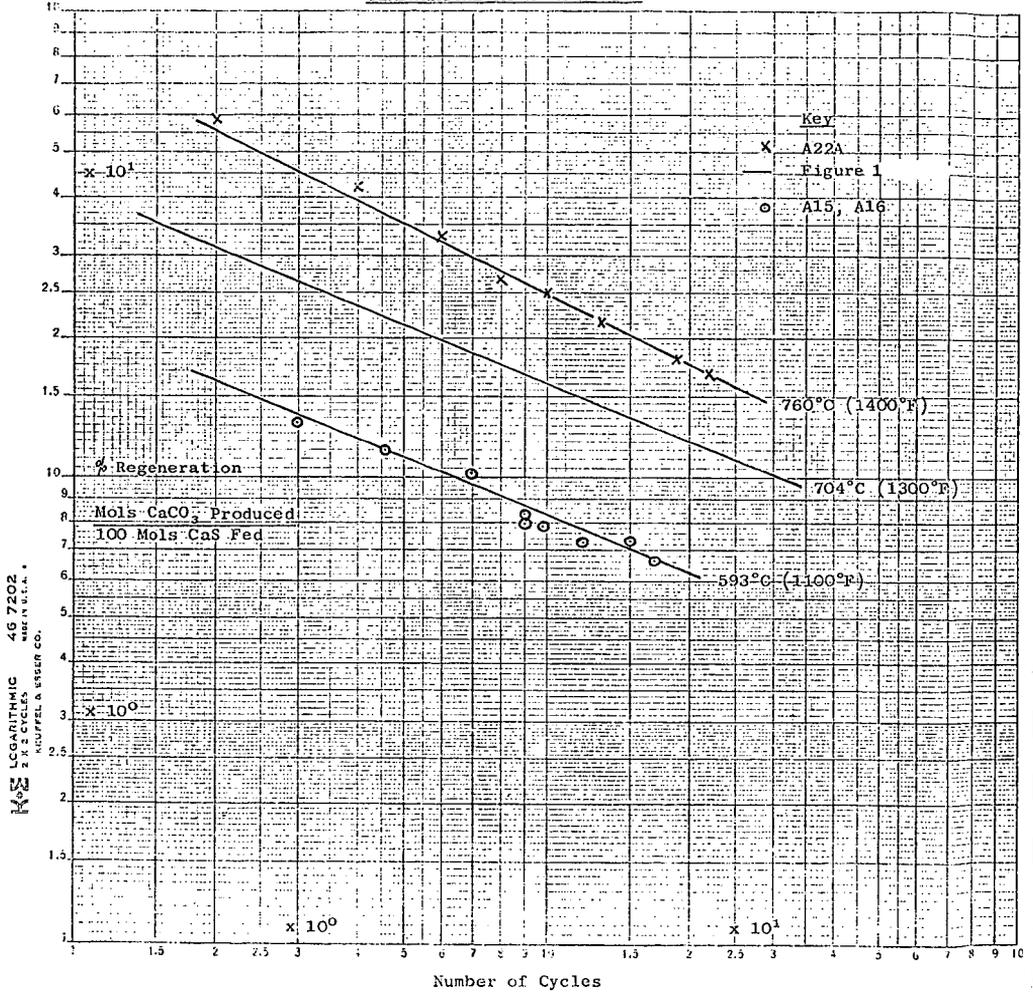
FIGURE 1
DEACTIVATION OF CaS IN CANAAN DOLOMITE
AT 704°C (1300°F)



46-7203
 LOG-ANTIC
 2 X 2 CYCLES
 KEUFFEL & ESSER CO.
 MADE IN U.S.A.

FIGURE 2

DEACTIVATION OF CaS WITH
TEMPERATURE AS A PARAMETER



Batch Regeneration

As a limiting step appeared to be regeneration, a batch regeneration program was set up to further explore the variables affecting the system. Results of these runs are given in Table 3. A statistical analysis of the data showed percent regeneration to increase with increasing temperature and decreasing age of stone. The effect of increasing temperature causing an increase in conversion was more pronounced for cycled stone than for fresh stone.

The effect of bed depth was unusual. It was expected that since the deeper bed ran at an H_2S outlet concentration closer to equilibrium, there would be less driving force for reaction and the regeneration conversion would be lower. In all six test pairs exactly the opposite was found. The runs with the deeper beds, i.e., higher H_2S outlet concentration, gave higher conversions. This is consistent with earlier conclusions that increasing the H_2S concentration does not adversely affect conversion in the regenerator.

In the course of running cyclic operations, the H_2S concentration in the outlet gas of the regenerator ranged from about 10% to 100% of the equilibrium value, and there was no detectable change in the rate of regeneration as the H_2S content approached equilibrium. It had been concluded that there would be no difficulty in running the regenerator close to the equilibrium H_2S concentration in the outlet gas.

Regeneration Kinetics

Regeneration kinetics were examined by recording the H_2S concentration in the exit gas as a function of time as the batch runs progressed. The total mols of H_2S produced were normalized to match the total mols of CaS reacted, and conversion as a function of time was then plotted. These results are presented in Figures 3 to 5 in the form of $(1 - X)$ versus time, where X is the fractional conversion of the CaS feed.

In all cases, the rate continuously decreased. It appeared that the reaction would eventually cease while there was still considerable CaS left. This is consistent with the notion that much of the CaS is simply unreactive. The initial reaction rate was faster for fresh stone than for cycled stone at all temperature levels. Additionally, the rate seemed to slow sooner for the cycled stone. The curves also show that the effect of bed depth is present even at the early stages of all reactions; the deeper beds had a higher reaction rate at all times.

While the reaction kinetics are complicated, they may be approximated by a simple first order rate constant for the short times (about an hour) of interest to the process. The reaction model would then be:

$$Kt = -\ln(1 - X)$$

where K = rate constant, hr^{-1} , whose function of gas concentration is yet to be determined.
 t = time, hours
and X = fractional conversion of the CaS fed.

The value of K was taken from the slope of the data from 5 to 50 minutes in Figures 3 to 5, and is tabulated in Table 4. The data of Table 4 are plotted in Figure 6. The activation energies for cycled and fresh stone are shown to be the same, about 19 kilocalories.

The kinetic mechanism proposed here allows one to calculate the effect of changing conditions of temperature or residence time upon fractional conversion of CaS (percent regeneration).

TABLE 3

Results of Regenerator Runs
All Runs 15 atm, 60% CO₂, 35% H₂O Inlet

Run No.	Dolomite	Bed Height, inches	Regeneration %	Equilibrium %	Maximum Approach to Equilibrium %	Run Time, hours	Maximum Dry Basis, % H ₂ O	Temperature, F (C)	Gas Residence Time, sec	10 ³ x Moles CaS Available Moles (CO ₂ + H ₂ O)/hr
A68	Sulfided	35.3	61.6	13.0	1.77	7.2	1200 (649)	4.9	20.6	
A69	Fresh	36.1	41	47.4	2.78	8.0	1300 (704)	4.7	24.8	
A70		36.3	80.8	93.7-102.6(1)	5.7	2.68-2.94(1)	1400 (760)	4.6	28.5	
A71		16.1	57.5	3.0	.41	8.4	1200 (649)	2.2	8.6	
A72		16.2	71.2	13.5	.79	8.0	1300 (704)	2.2	11.0	
A73		16.2	78.3	50.0	1.43	4.7	1400 (760)	2.0	11.4	
A74	Sulfided	37.9	14.5	2.8	.38	9.1	1200 (649)	5.3	5.39	
A75	Cycled	36.5	31.5	14.2	.83	8.1	1300 (704)	4.8	10.8	
A76		38.9	55.4	31.5	.90	10.0	1400 (760)	4.8	19.9	
A77		15.9	10.9	0.7	.09	3.7	1200 (649)	2.0	1.71	
A78		15.3	23.0	3.4	.20	7.8	1300 (704)	2.0	3.38	
A79		17.1	42.6	13.6	.39	8.0	1400 (760)	2.1	6.8	

(1) The high value is extrapolated where a portion of the chart was unreadable.

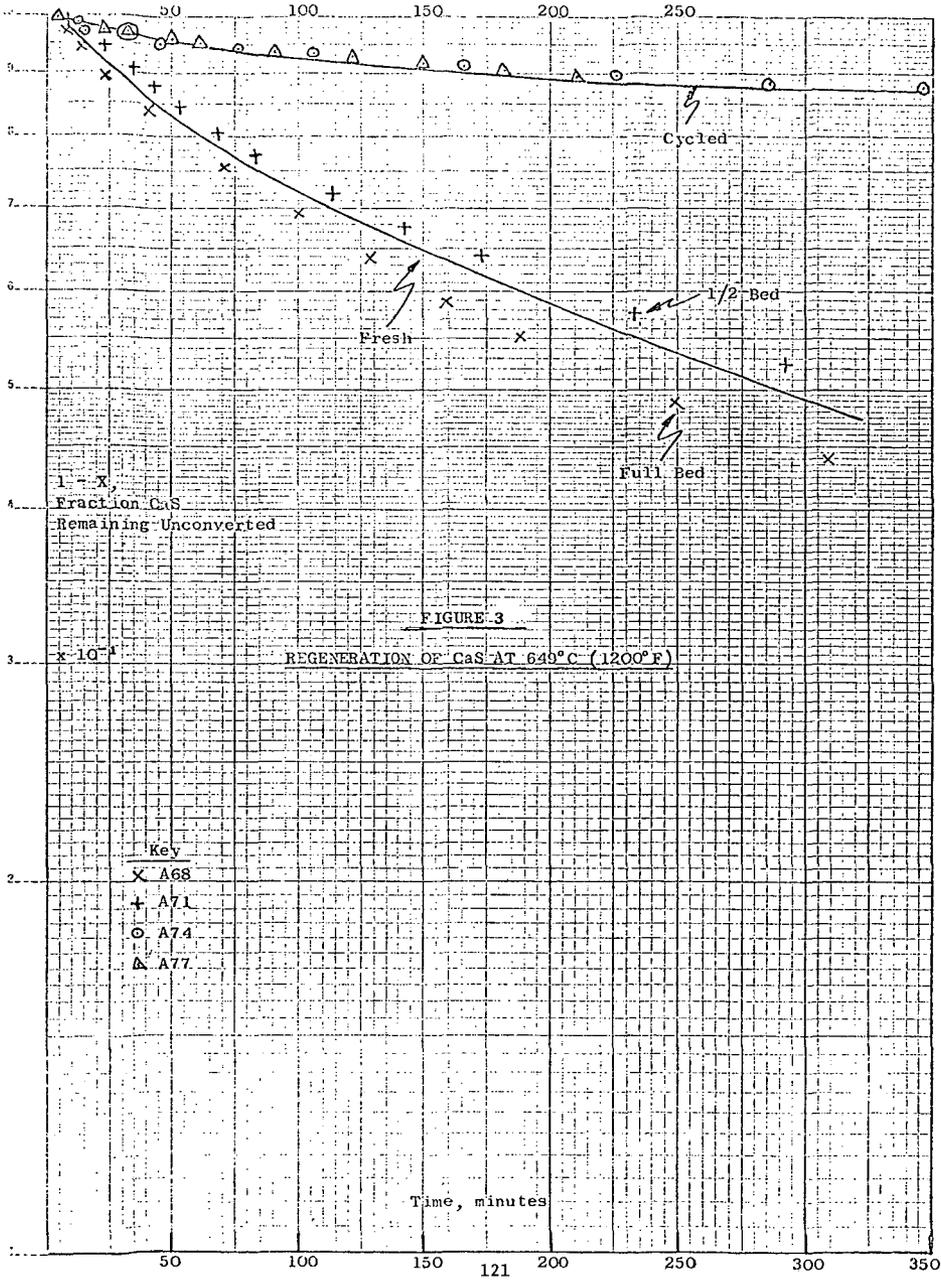


FIGURE 3

REGENERATION OF CaS AT 649°C (1200°F)

- Key
- × A68
 - + A71
 - A74
 - △ A77

Time, minutes

RESEARCH TRIANGLE CORPORATION - 45-1053
 1000 W. W. RIVERSIDE, DURHAM, N. C. 27709
 REPRODUCED BY PERMITS OF THE NATIONAL BUREAU OF STANDARDS

SEMI-COARTHMIC 46 4653
 1 CYCLE X 70 DIVISIONS
 HOFFMANN & DESSER CO.

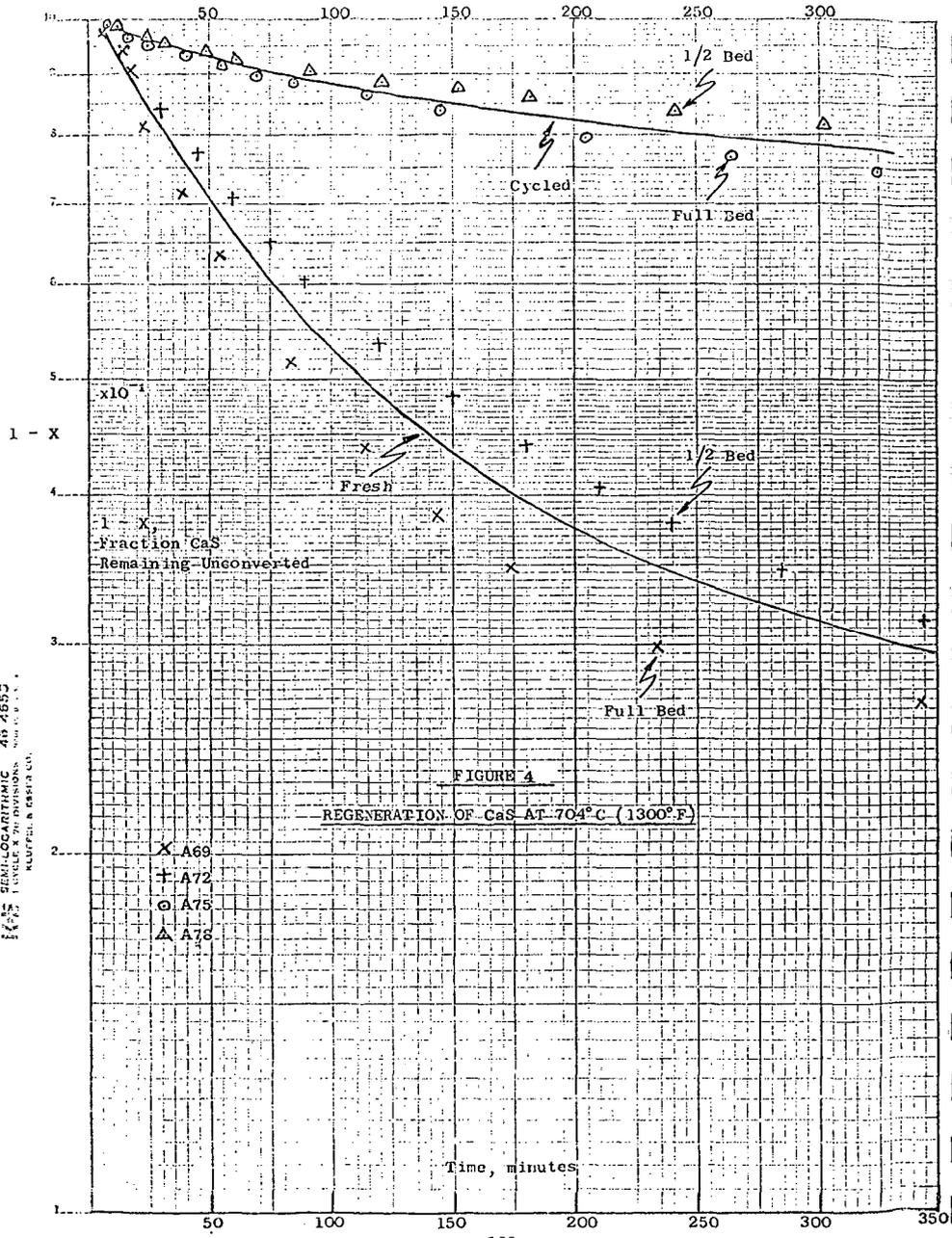


FIGURE 4
 REGENERATION OF CaS AT 704°C (1300°F)

- X A69
- + A72
- o A75
- Δ A78

1455 SEMI-LOGARITHMIC AS 4850
 1 1/2" x 1 1/2" x 1 1/2" ZINCHROME, 500 P.P.M.
 NAUFEL & BROSIG CO.

1 - X

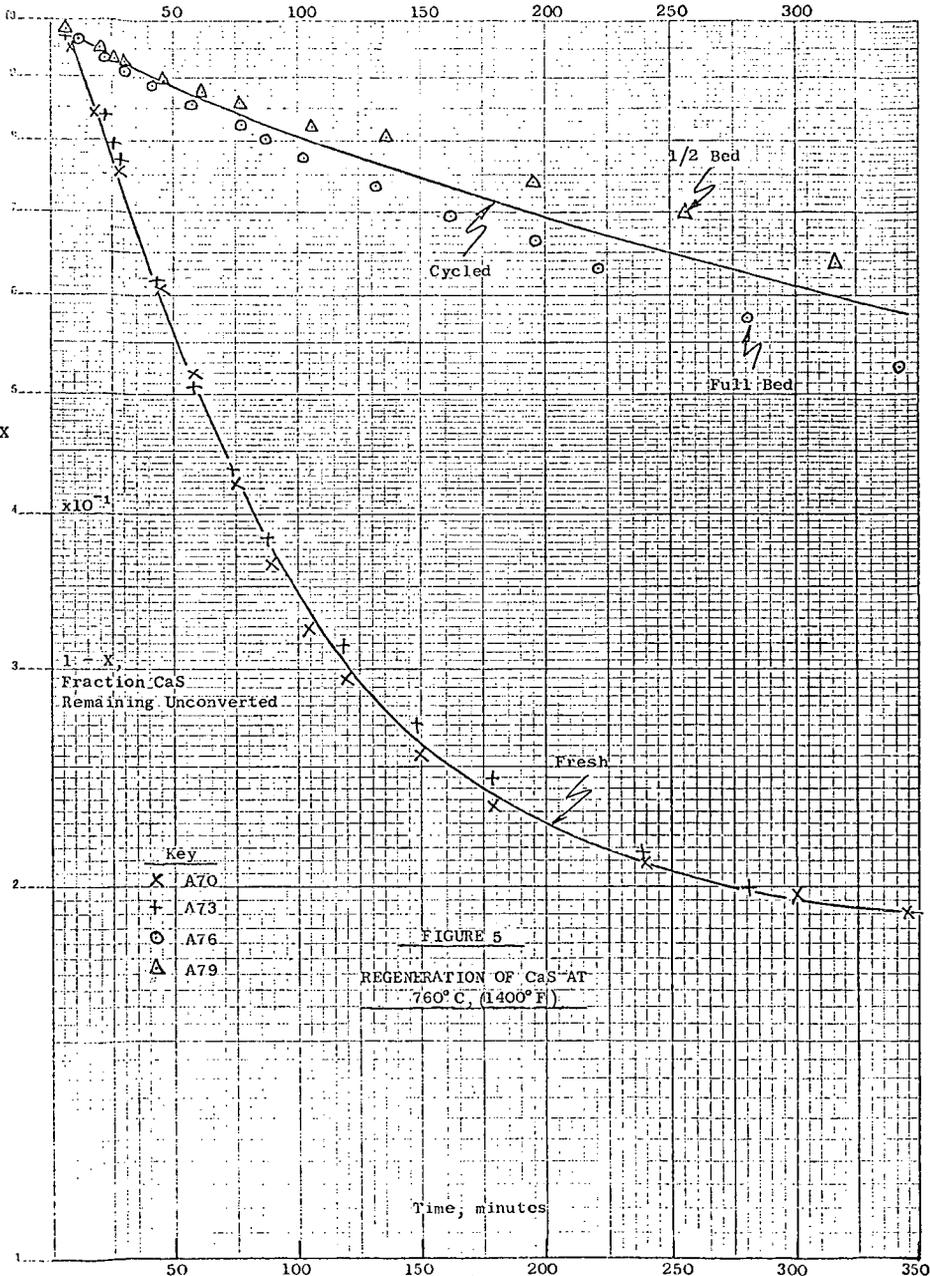


TABLE 4

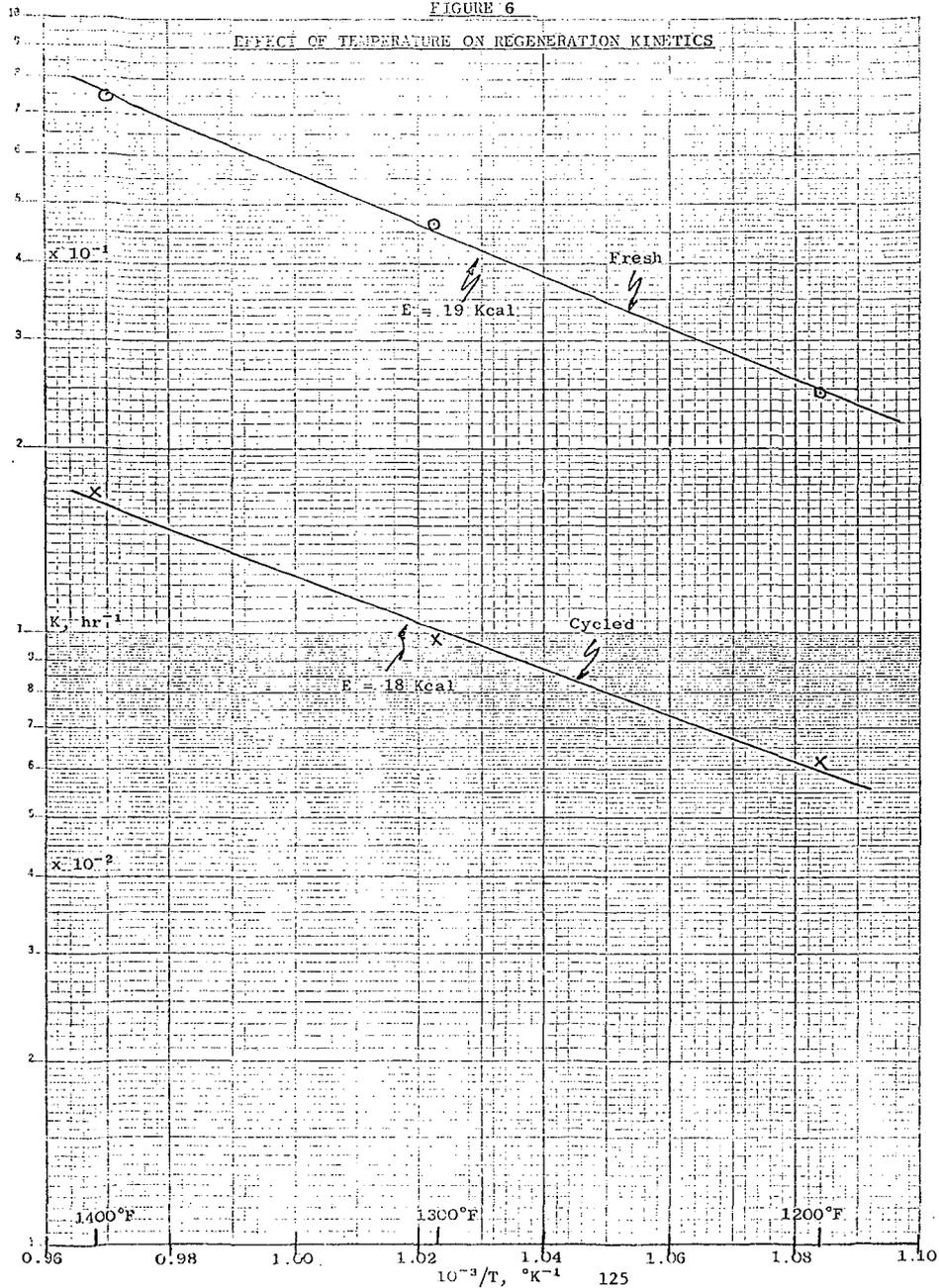
Initial Rate Constants for Regeneration Kinetics

System Pressure: 15 atm
Feed: 35% H₂O, 60% CO₂, 5% H₂

Temperature, °C (°F)	k, hr ⁻¹	
	Cycled	Fresh
649 (1200)	.063	.247
704 (1300)	.098	.468
760 (1400)	.170	.747

FIGURE 6

EFFECT OF TEMPERATURE ON REGENERATION KINETICS



Cycling with Varying Residence Times

Four batch cycling runs were made employing the possible combinations of 20 or 60 minutes residence time for sulfur absorption and regeneration. Results are presented in Figure 7. Tymochee 11 dolomite was the feedstock, and each run lasted for 11 cycles.

The effect of reducing residence time in the gas desulfurizer was striking. At 10 cycles, going from 60 to 20 minutes in the gas desulfurizer increased regeneration activity from 15 to 40% at 60 minutes regenerator time and from 15 to 23% at 20 minutes regenerator time. Conversely, going from 60 to 20 minutes regenerator time had no effect at the 60 minute desulfurizer level. Another effect observed was that attrition rates were highest at the short gas desulfurizer residence time, 2.3% average for 20 minutes versus 0.8% for 60 minutes.

It is believed that deactivation of stone takes place primarily in the gas desulfurizer due to crystal growth and particle sintering. This would explain the dramatic effect of time on activity. The results of the above runs are highly significant since they indicate the potential for greatly increasing the stone's capacity for sulfur absorption.

Scanning Electron Microscope Data

Selected samples of cycled stone were examined under an electron microscope equipped for energy dispersive X-ray analysis. It was found that cycled stone contained very large grains of CaS. The CaCO_3 which was present tended to be concentrated in smaller sizes. Both of the calcium species were larger than the MgO crystals or grains. It is believed that the larger CaS grains are unreactive in the regeneration step of the process.

Model for the Deactivation Process

The regeneration reaction suffers from deactivation of the CaS even from cycle 1. The model postulated below fits the behavior of the system so far. The part dealing with regenerator variables was developed jointly with A. M. Squires of The City College Clean Fuels Institute.

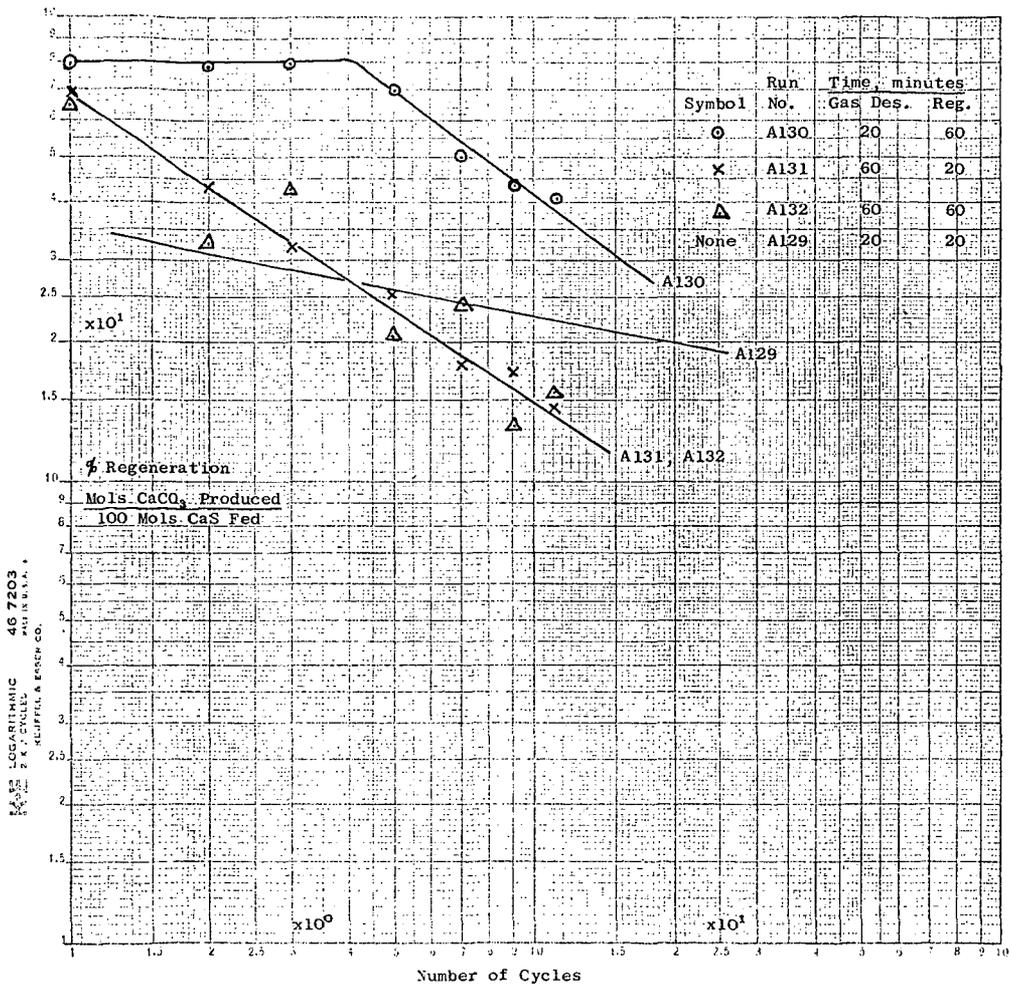
Deactivation of the dolomite occurs mainly in the gas desulfurizer due to the elevated temperature. Two mechanisms are operating. Crystal growth of CaCO_3 and CaS segregates the calcium crystals from the MgO and produces a material tending toward a limestone rather than a dolomite. Simple sintering and densification take place as well, and this both hardens the stone and tends to reduce porosity.

In the regenerator, densification does not occur. However, the reaction starts rapidly and then tails off to an insignificant rate. Using the same feed, it can be shown that the conversion at which reaction essentially ceases is a strong function of temperature, the lower temperature producing the lower conversion. It has further been observed that introducing product H_2S does not retard the rate of reaction, but conversely increases the ultimate level of conversion attainable.

The phenomenon of the products of reaction increasing the conversion of calcium in the sulfur-calcium system is not new. Peil⁽³⁾ found that H_2O increased the conversion of CaO to CaS in the reaction of H_2S with calcined dolomite, and Ruth⁽⁴⁾ showed that either CO_2 or H_2O could increase the conversion of CaCO_3 to CaS in the reaction of H_2S with half-calcined dolomite. Furthermore, both studies demonstrated the effect of the reaction flagging at lower and lower conversion levels as the reaction temperature decreased. Ruth⁽⁵⁾ proposed the following mechanism after examination of electron microscope results on various samples. "High levels of CO_2 . . . may promote the formation of large numbers of fine

FIGURE 7

Runs A129 to A132 - Deactivation of
CaS at 704°C (1300°F)



46 7203
LOGARITHMIC
SCALE
RELIEF & ENGER CO.
PAID IN U.S.A.

crystallites of CaS that do not protect the underlying CaCO₃. . . . On the other hand, at low levels of CO₂ a smaller number of large CaS crystals formed and grow together to close off the surface, thereby protecting the remaining CaCO₃ from further reaction."

Ruth's careful analysis of his data showed that in the presence of reaction products, the reaction was indeed slower initially. However, within a short time the conversion associated with the product-rich environment soon surpassed that in the product-poor environment.

It is postulated that a similar model fits the regeneration reaction. At low levels of H₂S, the CaCO₃ formed grows in large crystals shutting off the interior of the grain from further reaction. At high levels of H₂S, the reaction nucleates at many sites to produce many small crystals which leave the interior of the grain open to further reaction. Via such a mechanism, the presence of H₂S would enhance conversion in the regenerator. This is in full concordance with our experimental results.

Acknowledgment

Appreciation is expressed to the Environmental Protection Agency for financial support of the work presented in this paper and for permission to publish the results given.

References

1. Curran, G.P., Clancey, J.T., Pasek, B., Pell, M., Rutledge, G.D., and Gorin, E., "Production of Clean Fuel Gas from Bituminous Coals," (1973), EPA No. EPA-650/2-73-049, NTIS No. PB 232-695/AS.
2. Curran, G.P., Koch, B.J., Pasek, B., Pell, M., and Gorin, E., "High Temperature Desulfurization of Fuel Gas," Report to EPA under Contract No. 68-02-1333, in preparation.
3. Pell, M., "Reaction of Hydrogen Sulfide with Fully Calcined Dolomite," Ph.D. Thesis, The City University of New York (1971).
4. Ruth, L.A., Squires, A.M., and Graff, R.A., "Desulfurization of Fuels with Half-Calcined Dolomite: First Kinetic Data," Env. Science & Tech., 6, 1009-1014, 1972.
5. Ruth, L.A., "Reaction of Hydrogen Sulfide with Half-Calcined Dolomite," Ph.D. Thesis, The City University of New York (1972).