KINETICS OF RECOVERING SULFUR FROM THE SPENT SEED IN AN MHD POWER PLANT

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ABSTRACT

The open-cycle magnetohydrodynamic power plant offers a unique means of profitably recovering sulfur from its effluent gases. This is due to the high affinity the potassium or cesium seeding materials have for sulfur and their ease of regeneration. These compounds are added to make the gas electrically conductive and, because of their cost, must be recovered and recycled to the MHD generator. A process which removes the sulfur with hydrogen as hydrogen sulfide from the seed-slag mixture before the seed-slag mixture is recycled to the MHD generator is described and experimentally confirmed. As a result of this process the seed maintains its capacity to remove sulfur from the combustion products and a sulfur-free effluent gas is produced. A kinetic interpretation of the experimental data is presented. This data is used to specify the design and operating conditions for a sulfur recovery reactor for a 1000 MWe MHD power station.

The kinetic model is shown to apply also to the regeneration of the absorbent in the alkalized alumina process presently under development for removing sulfur dioxide from power plant stack gases.

INTRODUCTION

The basic nature of the operation of an MHD-topped power plant offers a means not available in a conventional power plant of recovering sulfur from the combustion products.

In an MHD-topped power plant, the combustion products are seeded with a potassium or cesium seed to make them electrically conductive. The condensed seed and whatever slag contaminants it contains are then recovered and recycled to the MHD generator. For economical operation of the MHD-topped power plant this recovery of seed must be essentially complete. Experimental and theoretical studies (1-3) indicate that if there is any sulfur in the combustion products, the potassium or cesium seed will condense as the sulfate and that this reaction can be stoichiometric.

We propose taking advantage of the chemistry and nature of the MHD-topped power plant operation to eliminate air pollution from sulfur oxides as well as to provide an economically attractive means of recovering the sulfur in coal. To achieve these goals it is necessary to remove the sulfur from the seed-slag mixture before recycling the mixture to the generator. To be most desirable, this process should remove the sulfur from the seed-slag mixture in a form that can be readily converted to a salable product.

This paper describes our experimental and kinetic analyses of a process to convert the sulfur in the seed-slag mixture to hydrogen sulfide with a hydrogen feed gas. The hydrogen sulfide can then be separated from the hydrogen by stripping with an ethanolamine solution and converted to elemental sulfur via the conventional Claus oxidation process.

$$2H_2S + 3O_2 \rightarrow 2SO_2 + 2H_2O$$

$$2H_2S + SO_2 \rightarrow 3S + 2H_2O$$

The kinetic model developed in this study is also applied to the regeneration of alkalized alumina with hydrogen.

EXPERIMENTAL PROCEDURE

Preparation of Simulated Seed-Slag Mixture

To simulate a seed-slag mixture such as would be recovered from an MHD plant (4), a 4.6/1 mole ratio of SiO_2/K_2SO_4 was mixed by ball milling and then fused at 2,100°F (the approximate dew point of K_2SO_4 in combustion products of sulfur-containing fuels) for 48 hours. The fused mixture was again ball milled and then formed into 1/8 x 1/4 cylindrical pellets. These pellets constituted the feed for the experiments.

Operation

Except where otherwise noted 55 g of sample were charged to the reactor, which was for most of the tests a "Vycor" tube 15/16 inches I.D. The reactor was heated under nitrogen pressure to the desired temperature and hydrogen was then admitted thru a quick opening valve. Hydrogen flow rates were maintained at 0.2 g mole/min for all the tests as this was found to approximate differential operation and, at the same time, to give measurable (0.1 to 2 mole percent) hydrogen sulfide concentrations. Except where otherwise noted by data points, gas samples were taken every two minutes over the first thirty minutes and every 10 minutes thereafter. The system was designed to minimize backmixing effects and the gas analyses indicate that these effects were negligible.

The sulfur removal rate was calculated from the data by the formula

$$r = Gy_{H_2S}/W_{SO}$$

where r is the H_2S formation rate in g-moles H_2S g-sample, min., G is the gas flow rate in g-moles/min, y_{H_2S} is the mole fraction of hydrogen sulfide, and W_{SO} is the initial weight of solid sample. The conversion to hydrogen sulfide as a function of solid residence time was obtained by graphically integrating r.

RESULTS AND DISCUSSION

The kinetic model is based primarily on the following experimental observations:

(1) The initial reaction rate is zero and increases over a time interval that depends on temperature to a maximum value, e.g. at 875°C, fig. 7, this time is one minute or less, at 800°C, fig. 6, it is approximately 6 minutes. Similar behavior is also shown in figs. 1 thru 5 for other temperatures.

(2) The maximum conversion level that can be achieved is also a function of temperature. For example, at 875°C only 4 percent of the sulfur can be converted before the reaction rate decays to zero, at 760° to 800°C roughly 50 percent of the sulfur can be converted to H_2S.

One interpretation of the above experimental results is that initially the sulfur is in a state which will not react to form hydrogen sulfide. However, upon exposure to the reaction conditions the original inactive sulfur compound transforms to an active intermediate which reacts to form hydrogen sulfide. Thus, the hydrogen sulfide production rate reflects the concentration of active intermediate which starts at zero, rises to a maximum, and then decays with increasing time.

The decay of the hydrogen sulfide production rate to zero before sulfur conversion is complete can be accounted for by assuming that concurrent with the formation of an active intermediate, which reacts with hydrogen to form hydrogen sulfide, is the formation of a sulfur compound which is refractory to hydrogen. With these assumptions about the chemistry several equally plausible reaction models can be proposed. However, the rate equations corresponding to these different models are all of the same form making it impossible to distinguish between them on kinetic grounds.

Also, although attempts by x-ray analysis have been made, chemical identification of the actual species present has not yet been achieved. Thus, we chose to use the simplest physically feasible reaction scheme to derive the rate equations with which to analyze the data.

In detail, what we assume in our model is that the sulfur is in an initial state I which, under reaction conditions, is transformed into an active sulfur containing species A as well as a sulfur species R refractory to hydrogen. The chemical reactions occurring in the system are

$$I \xrightarrow{k_1} A, \tag{1}$$

$$A + H_2 \xrightarrow{k_2} H_2S, \tag{2}$$

$$I \xrightarrow{k_3} R, \tag{3}$$

where k_1, k_2 and k_3 are reaction rate constants. We take all of the above reactions to be first order with respect to the concentration of solid reactants.

Since the hydrogen partial pressure in this series of experiments is maintained constant, k_1, k_2, and k_3 are completely determined by the temperature although in general they are also dependent upon hydrogen partial pressure.

The reaction of primary interest is (2) since it is this reaction which removes sulfur from the solid sample and produces the hydrogen sulfide which can be converted to the desired elemental sulfur. At constant hydrogen partial pressure the rate of hydrogen sulfide production is taken to be

$$r = k_2(A).^{*/} \tag{4}$$

The concentration of A as a function of time can be found by solving the following differential equation

$$\frac{d(A)}{dt} = k_1(I) - k_2(A) \tag{5}$$

which describes A's net formation where the concentration of I is obtained by solving the differential equation,

*/ Quantities in parentheses are concentrations of solid reactants measured in g-moles/g-solid.

$$-\frac{d(I)}{dt} = (k_1+k_3)(I), \qquad (6)$$

describing I's disappearance. From (6) we have $(I) = (I_o)e^{-(k_1+k_3)t}$ where (I_o) is the initial concentration of sulfur in the solid. Substituting this value for (I) in (5) gives

$$\frac{d(A)}{dt} = k_1(I_o)e^{-(k_1+k_3)t} - k_2(A)$$

whose solution is

$$(A) = \frac{k_1(I_o)}{k_2-k_1-k_3}\left[e^{-(k_1+k_3)t} - e^{-k_2t}\right].$$

Thus, in view of (4), we see that the rate of hydrogen sulfide production is given by

$$r = \frac{k_1k_2(I_o)}{k_2-k_1-k_3}\left[e^{-(k_1+k_3)t} - e^{-k_2t}\right]. \qquad (7)$$

For the regeneration of fused K_2SO_4-SiO_2 mixtures our data indicate that in the neighborhood of 800°C k_1+k_3 is approximately equal to k_2.

Since

$$\lim_{k_1+k_3 \to k_2}\left(\frac{1}{k_2-k_1-k_3}\left[e^{-(k_1+k_3)t} - e^{-k_2t}\right]\right) = \frac{\partial}{\partial k_2}\left(e^{-k_2t}\right) = t\,e^{-k_2t},$$

we use the formula

$$r = k_1k_2(I_o)t\,e^{-k_2t} \qquad (8)$$

for the rate of hydrogen sulfide production when $k_1+k_3 = k_2$.

Equation (7) or (8) if appropriate, is used to correlate the directly measured rate data. Integration of (7) or (8) enables us to compare predicted conversion to hydrogen sulfide with experimentally determined conversion obtained by graphical integration of the measured rate data. Values for the coefficient $\frac{k_1k_2(I_o)}{k_2-k_1-k_2}$ or $k_1k_2(I_o)$ and the exponents (k_1+k_3) and k_2 are selected on the basis of the best least squares fit of (7) or (8) to the rate data.

Calculated values of hydrogen sulfide generation rates using these constants are shown for the fused K_2SO_4-SiO_2 mixtures in figs. 1 thru 7 for temperatures of 700°, 725°, 760°, 775°, 800°, and 875°C. Examination of these results indicates considerable scatter in the rate data between 725° and 800°C. We attribute this scatter to the large variation in reaction rate with temperature which is clearly evident in figs. 1 thru 7. Not only does the shape of the reaction rate versus time curve change drastically in the temperature span from 700° to 875°C but there is also a pronounced variation in the magnitude of the reaction rates. This variability of reaction rate with temperature coupled with our inability to reduce temperature gradients in the sample much below 10° to 20°C make it impossible to exercise better control over reaction rate fluctuations. Running many duplicate determinations of rate versus time as is shown in fig. 6 at 800°C and using the average value for each time tends to smooth the rate data considerably.

Experimental levels of sulfur production gotten by integrating the rate data are compared in fig. 8 with those calculated by analytically integrating (7) and (8). The agreement between predicted conversion and measured conversion is well within the experimental error, especially when one considers that the errors in the integral data are cumulative and that relatively few data points past 31 or 41 minutes are taken. The scatter that does exist would have been further reduced if the least squares fit were based on this integral data rather than on the rate data. Thus, the derived rate equations can be used with good accuracy to predict the effect of reactor size on sulfur production over a wide range in shape of r(t,T) curves.

Effect of Temperature

In fitting (7) and (8) to the rate data, the groups involving the reaction velocity constants are evaluated rather than the constants k_1, k_2, and k_3 themselves. That is, if $k_2 \neq k_1+k_3$ then the coefficient $\frac{(I_o)k_1k_2}{k_2-k_1-k_3}$, and the exponents k_1+k_3 and k_2 are the terms determined by the least squares fit, whereas if $k_1+k_3 = k_2$ then the coefficient $k_1k_2(I_o)$ and the exponent k_2 are the quantities calculated.

The effect of temperature on k_1+k_3, k_2, and $\frac{(I_o)k_1k_2}{k_2-k_1-k_3}$ is shown in figs. 9 and 10, respectively. The reason for the hyperbolic behavior of the group $\frac{(I_o)k_1k_2}{k_2-k_1-k_3}$ becomes clear when one takes into account that for small values of k_1+k_3 relative to k_2 its essential behavior is that of $(I_o)k_1$ but as k_1+k_3 increases the dominating effect becomes the fact that $\underset{k_1+k_3 \to k_2}{\mathrm{LIM}} \left(\frac{(I_o)k_1k_2}{k_2-k_1-k_3}\right) = \infty$. Although (8) is strictly applicable only when $k_1+k_3 = k_2$, it does provide a satisfactory fit even to data well away from this constraint. Thus the problem of the inherent inaccuracy in the evaluation of large values of $\frac{(I_o)k_1k_2}{k_2-k_1-k_3}$ can be avoided by using (8) when k_1+k_3 is near k_2. For $k_1+k_3 > k_2$, $\frac{(I_o)k_1k_2}{k_2-k_1-k_3}$ is negative and for large values of k_1+k_3 relative to k_2 its essential behavior is that of $\frac{-(I_o)k_1k_2}{k_1+k_3}$. Thus for high temperatures (above 800°C in our study) the values of this group lie on a curve which is similar to the reflection of its graph generated at low temperatures (below 800°C) in the opposite quadrant. At temperatures above 725°C, k_2 is independent of temperature. This indicates the reaction for the production of hydrogen sulfide may be gas film or particle diffusion controlled above 725°C.

Knowing the initial concentration of sulfur, (I_o), allows the calculation of separate values for k_1 and k_3. Fig. 9 shows the dependence of these separate values on temperature. With this information the behavior of the system as a function of time and temperature can be explained.

For example, the experimental limitations of sulfur conversion to hydrogen sulfide are explained in terms of the formation of the solid sulfur compound R which will not react with hydrogen. The rate of formation of R is, according to our model, $d(R)/dt = k_3(I)$ and, as was seen from (6) $(I) = (I_o)e^{-(k_1+k_3)t}$. Thus the concentration of residual sulfur is

$$(R) = \frac{k_3(I_o)}{k_1+k_3}\left[1 - e^{-(k_1+k_3)t}\right].$$

The maximum conversion level to hydrogen sulfide is achieved when $t = \infty$ and is, at any given temperature, $\frac{(I_o)-(R)_{(t=\infty)}}{(I_o)} = 1 - \frac{k_3}{k_1+k_3}$. The maximum conversion level of sulfur to hydrogen sulfide, shown in fig. 11, is therefore a function of temperature only. This maximum is approximately 80 percent and should occur around 730°C. Unfortunately, our experiments at 700° and 725°C were terminated well before the maximum conversion was approached. However, at the other temperatures studied residence times were sufficiently long to enable close approach to maximum conversion. These data are compared with those predicted by the model in fig. 11.

Both the maximum conversion data in fig. 11 and the reaction rate data in figs. 1 thru 7 indicate that operating at temperatures either above 800°C or below 725°C would not be practical. The optimum temperature depends on the sulfur level of the particular coal used and the effect of reactor size on the process economics.

Since the constancy of k_2 with respect to temperature indicates that the reaction rate to form hydrogen sulfide may be gas film or particle diffusion controlled, it is of interest to see what advantages may accrue by operating reactors at increased gas velocities or with finer particles in order to increase k_2. For values of k_2 much greater than k_1+k_3 and for $t > 0$ the reaction rate to form hydrogen sulfide is approximately given by $r_{max} = k_1(I_o)e^{-(k_1+k_3)t}$. Thus, increases in the specific gas flow rate above that used in our present experiments or operation with finer particles should at most allow conversion rates to increase to the values indicated by r_{max}. However, even with the higher values of k_2 the maximum conversion to hydrogen sulfide will remain fixed because it depends only on k_1 and k_3.

Application of the Model to the Regeneration of Alkalized Alumina

Hydrogen sulfide formation rates with hydrogen and sulfur-saturated alkalized alumina were measured at 680°C to see if the same kinetic model could be used to describe this apparently similar reaction system. The comparison, shown in fig. 12, of measured rates with rates calculated using the model verifies that the model also describes the kinetics of regenerating alkalized alumina. Comparison of the measured conversion level with that obtained by integration of the rate equation is shown in fig. 13. This similarity of regeneration kinetics indicates that techniques for regenerating alkalized alumina (5) can also be utilized to remove sulfur from seed-slag mixtures.

Economic Feasibility of Removing Sulfur from Recycling Seed-Slag Mixtures

While no detailed estimates have yet been made on the costs of removing sulfur from recycling seed-slag mixtures, it is possible to make a rough cost estimate using the data in this paper. For example, the sulfur production rate of a 1,000 MWe MHD-topped power plant having a thermal efficiency of 0.47 and using a 13,610 Btu/lb 3 wt-percent sulfur coal for fuel will be 383,000 lbs/day which, at a value of $40/2,240 lbs, is worth $6,830/day. Such a plant will be seeded with about 2 g-moles of K_2O/kg-coal. With this seeding level 47 percent of the sulfur content in the recycling seed-slag mixture will have to be converted to hydrogen sulfide each pass to ensure a sulfur-free power plant effluent gas. Using a fluid-bed seed-slag regeneration reactor (to avoid complication of varying hydrogen partial pressure in the reactor) operating at a pressure sufficient to maintain a

1 atm hydrogen partial pressure, we find from the data in fig. 8 the solids residence time needed to achieve the desired conversion level is 40 minutes at 775°C. This residence time requires a reactor volume of 145 m^3 for the bulk density of the material used in our experiments. The total reactor pressure which will be needed to maintain the 1 atm hydrogen partial pressure is approximately 1.2 atm for a hydrogen sulfide concentration in the product gas of 15 volume percent. A ball park estimate of the sulfur price necessary to realize a profit from its recovery in an MHD plant is given in table 1.

TABLE 1
Summary of unit cost/day which includes taxes and profit and is based on a 365 day year

Pelletizing	383	(3 times the cost of pelletizing iron ore)
Seed-slag sulfur removal reactor	639	(estimated from (6))
Hydrogen	1,820	@ $0.40/1,000 SCF
Claus unit for converting H_2S to S	2,300	(estimated from (7))
Selling price	$5,142	

Since the value of the sulfur produced will be $6,830/day and because the sulfur recovery system is so simple sulfur recovery will be part of any coal-fired MHD-topped power plant and high-sulfur coals will be considered a premium fuel.

CONCLUSIONS

Sulfur can be economically eliminated from the effluent gases of open-cycle MHD-topped power plants by recovering it from the recycling seed-slag mixture with hydrogen. The incorporation of this recovery step is a simple matter in the MHD power station because a potassium or cesium seeding material, which has a great affinity for sulfur, is added to make the combustion gas electrically conductive, and this seed must be recovered and recycled. Our kinetic model for the stripping of sulfur as hydrogen sulfide from seed-slag mixtures can be used to design reactors for this purpose. This model also describes the regeneration of the absorbent in the alkalized alumina process for removing sulfur dioxide from power plant stack gases.

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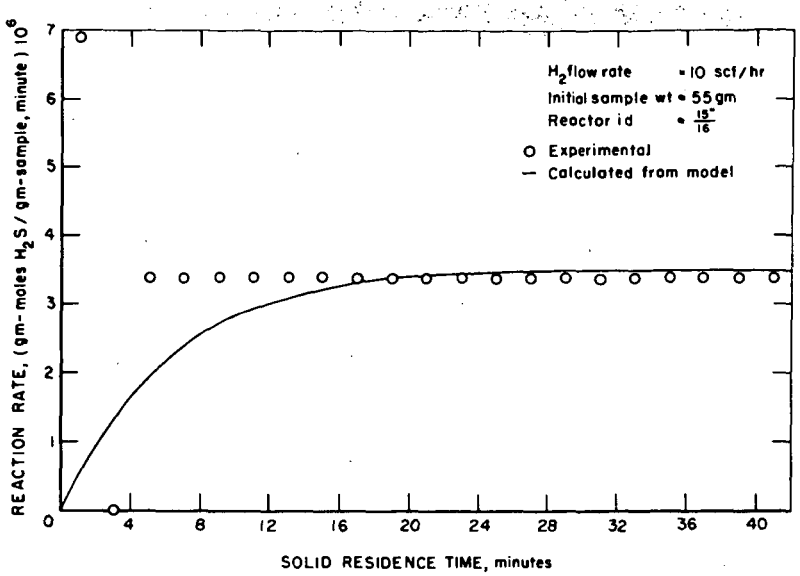

Figure 1.- Differential H_2S formation rate for the reaction of fused $K_2SO_4 - SiO_2$ with H_2: temperature = 700°C, H_2 partial pressure = 1 atm.

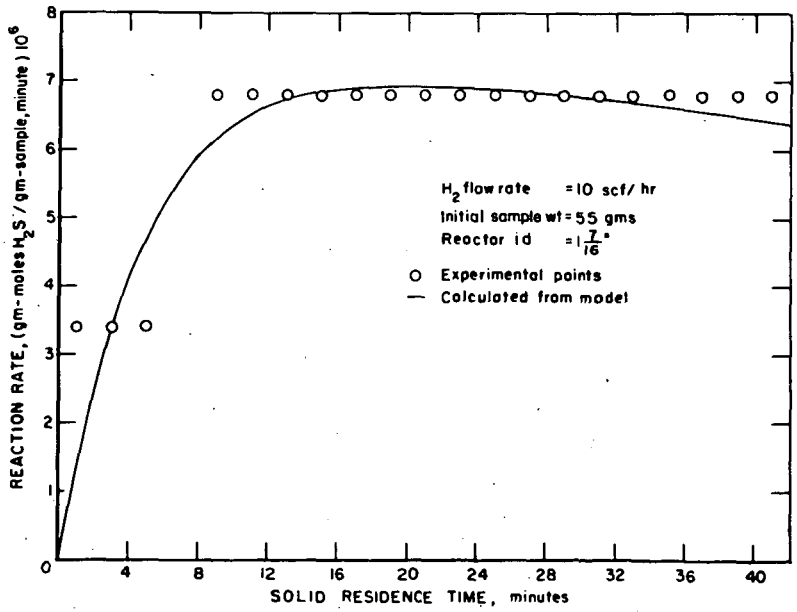

Figure 2.- Differential H_2S formation rate for the reaction of fused $K_2SO_4 - SiO_2$ with H_2: temperature = 725°C, H_2 partial pressure = 1 atm.

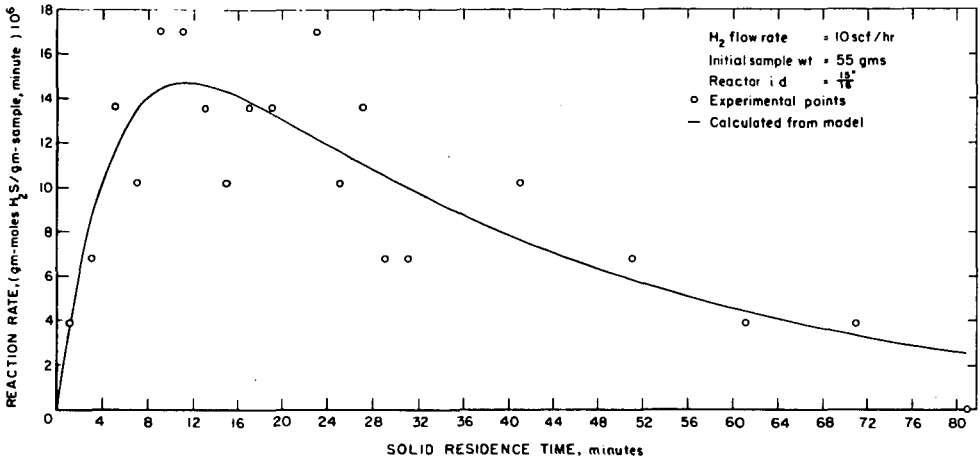

Figure 3.– Differential H_2S formation rate for the reaction of fused K_2SO_4 - SiO_2 with H_2: temperature = 760°C, H_2 partial pressure = 1atm.

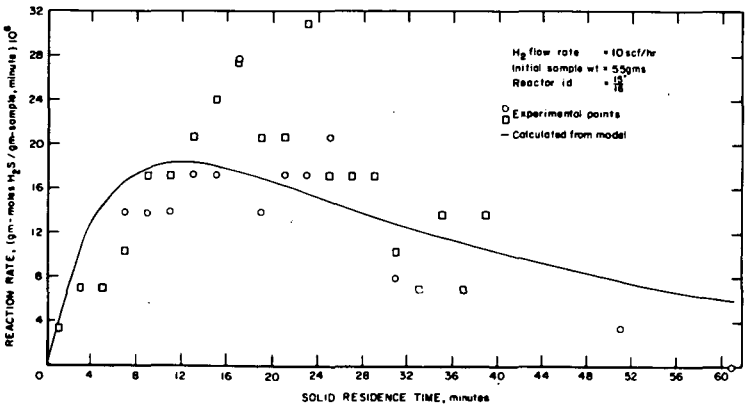

Figure4 – Differential H_2S formation rate for the reaction of fused K_2SO_4 – SiO_2 with H_2. temperature = 775°C, H_2 partial pressure = 1atm

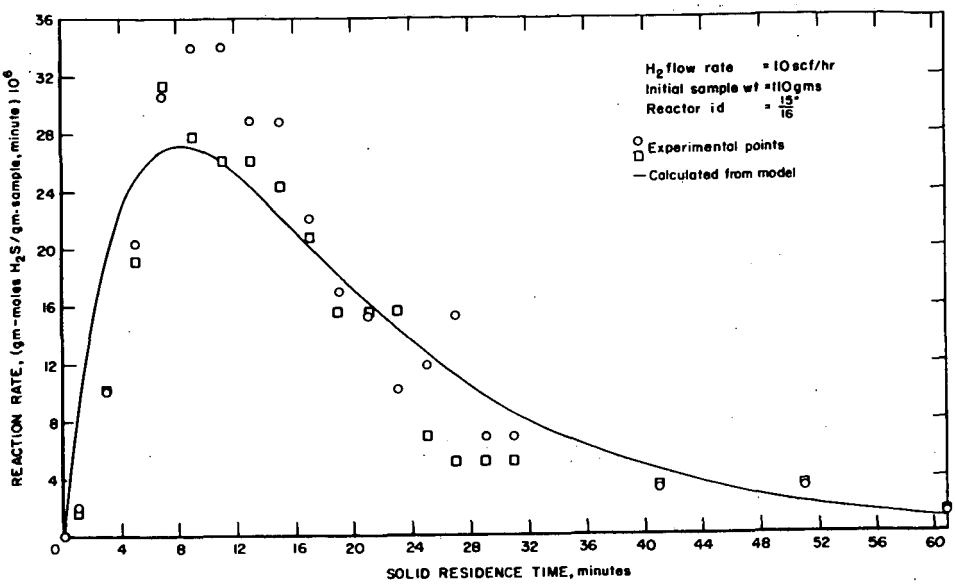

Figure 5 – Differential H_2S formation rate for the reaction of fused $K_2SO_4-SiO_2$ with H_2: temperature = 775°C, H_2 partial pressure = 1 atm.

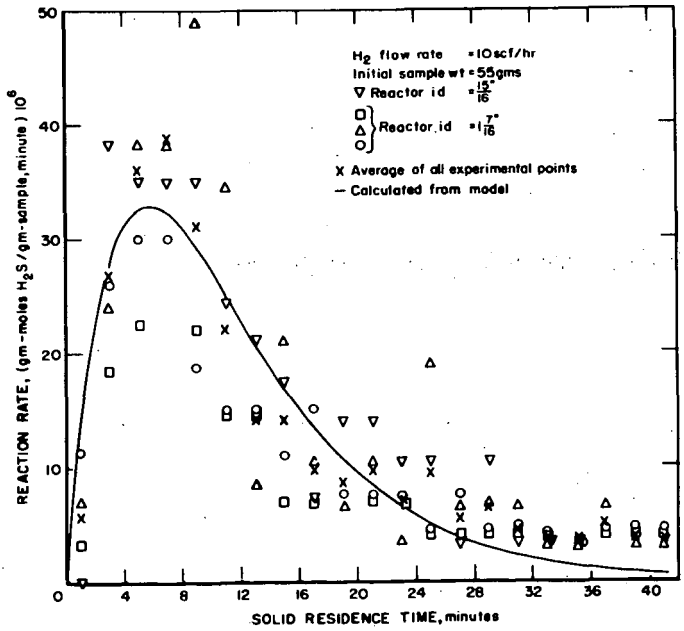

Figure 6 – Differential H_2S formation rate for the reaction of fused $K_2SO_4-SiO_2$ with H_2: temperature = 800°C, H_2 partial pressure = 1 atm.

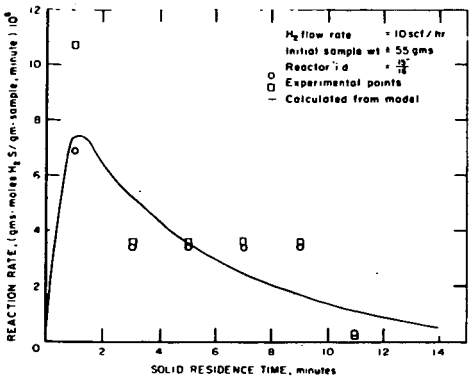

Figure 7. – Differential H_2S formation rate for the reaction of fused K_2SO_4 – SiO_2 with H_2 : temperature = 875°C, H_2 partial pressure = 1 atm.

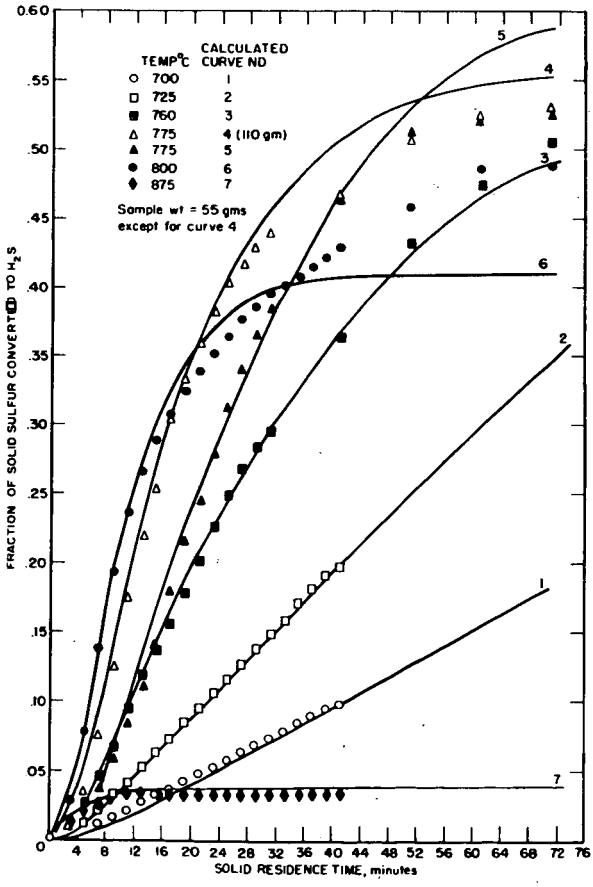

Figure8 – Effect of temperature and solid residence time on sulfur conversion to H_2S : H_2 partial pressure = 1 atm.

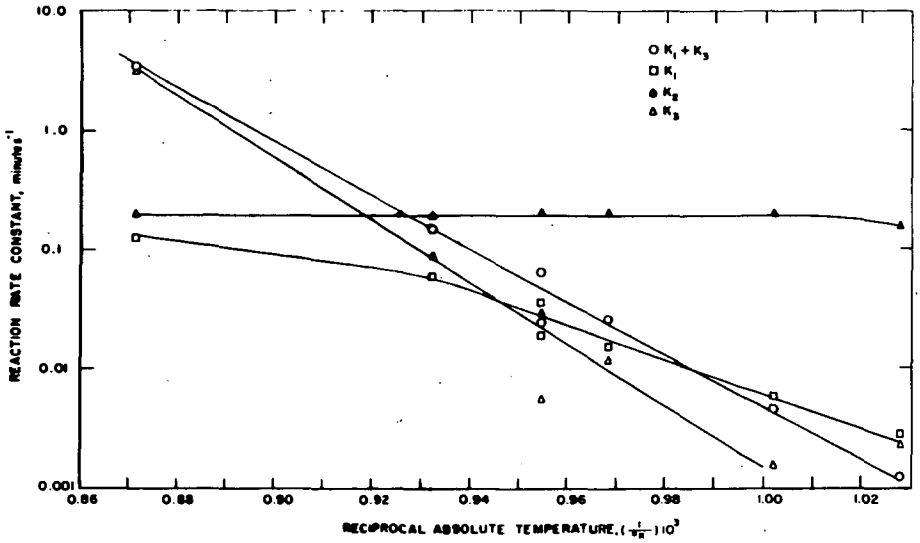

Figure 9 – Effect of temperature on reaction rate constants for the reaction : fused $(K_2SO_4 - SiO_2) + H_2 \rightarrow H_2S$.

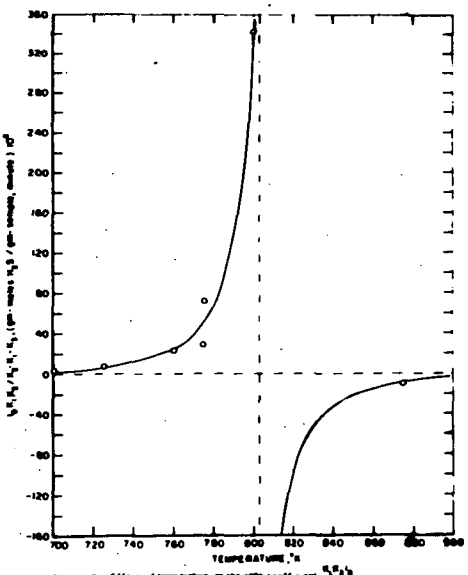

Figure 10 – Effect of temperature on the rate constant $\frac{K_1 K_2 K_3}{K_2 K_1 - K_3}$

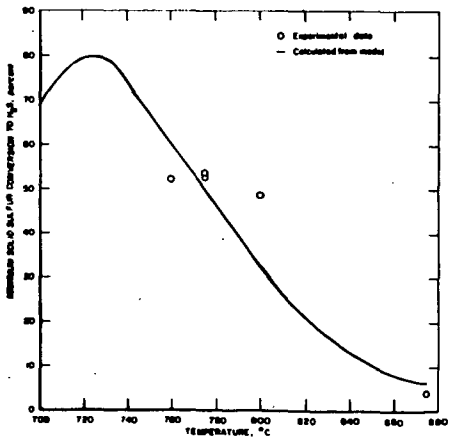

Figure – Variation of maximum sulfur conversion to H_2S with reactor temperature; H_2 feed, K_2SO_4-SiO_2 fused mixture

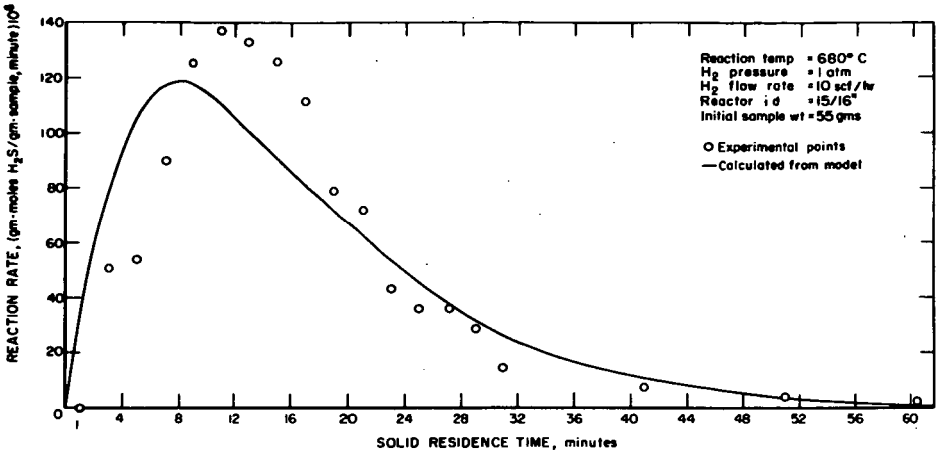

Figure 12.—Comparison of measured differential H_2S generation rates with that predicted by kinetic model for regeneration of spent alkalized alumina with H_2.

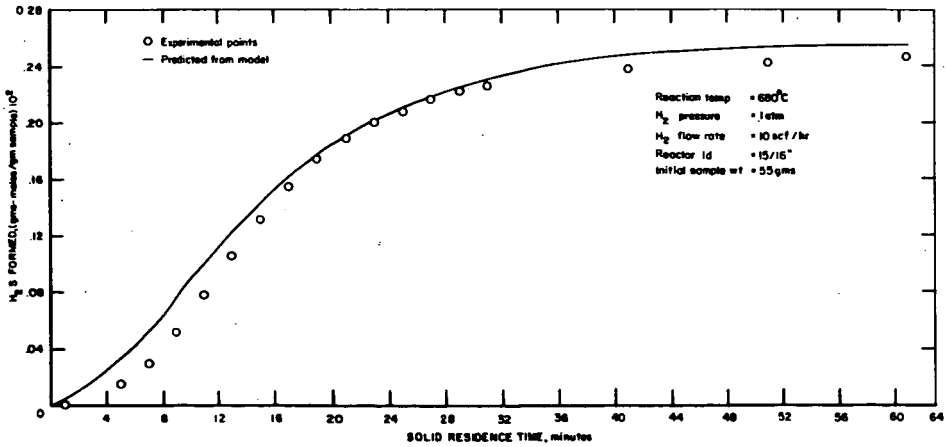

Figure 13.— Comparison of measured H_2S conversion with that predicted by kinetic model for the regeneration of spent alkalized alumina with H_2.