

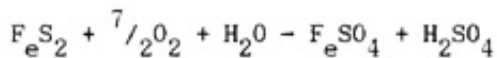
THE RELATIONSHIP BETWEEN PHYSICAL PARAMETERS AND THE REACTION RATE OF PYRITE IN MINE WASTE ROCK

BY

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Acid mine drainage (AMD) began when the first deeply buried rocks were exposed to the weathering environment as a result of mining. Iron sulfide minerals, namely pyrite, a mineral component in these rocks reacted with oxygen and water to produce soluble salts and sulfuric acid according to



These compounds are leached from the rock surfaces by rain water and enter the environment. The resulting streams have very low pH's and high iron and sulfate ions concentrations. They are rendered useless for human, industrial, and recreational purposes. The estimated cost for this pollution in 1978 for the Appalachian region was 13 billion dollars.¹

The AMD problem is a major concern to the mining community, since they are responsible for any water damage caused by their operation. Considerable effort was expended to develop a procedure to predict the potential acid production on a site before mining. The answer to that challenge was the acid base accounting procedure which is a simple stoichiometric balance test.² In this procedure the concentration of lime or limestone required to neutralize the amount of acid which would be produced if all the pyrite in a sample were oxidized is determined. If that amount of limestone is already present the rock material is believed not to produce acid; however if the amount of limestone is not present the rock is believed to produce acid. Common practice is to add the needed limestone in the belief that the addition would make the mixture neutral.

It was our belief that the amount of acid produced was less significant than the rate at which the acid is produced. So far the past several years we studied acid production rates of various mine rocks. We developed a procedure of simulated weathering followed by Soxhlet extraction to determine how fast acid is produced from mine rocks.³ The analytical results from these

leachates were used to successfully calculate observed reaction rate constants for the eight lithic units encountered during mining. Field experiments verified the accuracy of this procedure. The procedure is explained in details in other previous publications.^{4,5}

Through the course of these experiments the chemical process by which the pyrite reacted was never analyzed. Some very intriguing facts were observed: (1) The rate of acid production did not depend upon the amount of pyrite present. (2) Through the analysis of several samples of each of the different lithic units seemed to have its own reaction rate constant. (3) The reaction rate constant for a specific sample of rock did not vary significantly with particle sizes from 100 mesh to 24 mesh. It did dramatically increase when the particle size was less than 200 mesh. (4) All the reactions from any rock seemed to follow the first order rate law. (5) When mixtures of rock were evaluated, each rock contributed to the mixture as a separate entity. That is, the acid quantity and rate from each rock did not effect the acid quantity and rate from any other rock. Their contributions can be added together separately to give an accurate picture of the mixture.

The above observations caused us to theorize as to just how the reaction proceeded. We hypothesized that the reaction was not chemically controlled but diffusionally controlled. This means that the speed at which AMD is produced does not depend upon how fast the chemicals exchange electrons but rather upon how fast the reactant chemicals can get together. Since this reaction takes place on the exposed pyritic faces which are on the rock surface and within the cracks and crevices of a rock the reaction rate would greatly depend upon how fast the diffusion of the oxidizing agent and water proceed through the pore structure of the rock to those faces. The reaction rate would further depend upon how the products of chemical reaction would change the diffusion rate as the reaction proceeded. [For many people this is a radical departure from the traditional approach. When most people consider diffusion, the bulk porosity of the medium is considered; however the chemical reaction sites are on the order of microns therefore the porosity which must be considered here is that which is of the same order as the reactant site. In other words people normally focus on the macro environment but here the micro environment is also important]

The hypothesis above can be validated through two basic tests. (1) if the reaction is limited by diffusion then all rock materials would have the same reaction rate constant if all inhibitions to diffusion were removed. This could be accomplished if all the rocks were ground to a size such that the pyritic faces of measured the dimension of the pyrite which is about 20 micron, the reaction rate constant for all rock samples ground to -200 mesh (particle size -70 m) should all be the same. This experiment was run and our suspicions were verified. (see figure 1, 2 and 3)

(2) Chemical reactions are particularly sensitive to temperature, but diffusion controlled reactions are not. The temperature sensitivity of the rate could be tested by running the rate determining procedure for samples of the various lithic units at different temperatures. The standard procedure for comparison is to construct an Arrhenius plot which plots the log of the rate constant against the reciprocal of the temperature in degrees Kelvin. The result should be a straight line. The slope of that line is the activation energy divided by the gas constant. Experiments described above were run on samples from various lithic units and Arrhenius plots made of the data. Experiments were also run on the finely ground sample where diffusion is not limiting. The data are below for comparison. It can easily be seen that

for the nonground samples the temperature dependence is slight while for the ground samples the temperature dependence is large. (see figure 4 Arrhenius plot and figure 5 nonground)

The only conclusion is that in the rock samples the reaction is diffusion controlled. The only difference between the reaction rate for pyrite oxidation in rocks is the differences in diffusion due to physical properties of the rocks. A mathematical model can be derived to calculate the acid production rate of any rock based purely on the physical properties of the rock if the above hypothesis is correct.

DERIVATION OF THE MODEL

A simple figure which illustrates the model and from which the equations are derived is seen in figure 6 (model). The first drawing in the figure essentially shows that we expect the system to be constructed as a packed bed composed of a spherically shaped particles. The matrix of these particles does not change during the course of the reaction so the particle's shape and dimension are fixed. The second drawing in the figure shows that each particle, which composes the assemblage, is composed of spherically shaped clusters of reactant and (grains). In addition, it shows that the reactant grains on the surface are more easily oxidized than those near the center. Access to the central reactant grains for the oxidizing materials can only be obtained through the pore structure of the parent grain. Therefore, the bulk porosity and pore size-distribution are going to be the reaction limiting constraints. It is important to recognize that the ash, in this case ferrous sulfate, which coats the reactive faces will also impede the access of the oxidizing agent to the reaction sites. This effect will be more dramatic as the reaction proceeds.

(A complete derivation with the entire mathematical basis for the model is not presented here. It is currently in press under the title "A Mathematical Model for Heterogeneous Reactions with a Moving Boundary" in the May issue of the American Institute of Chemical Engineers' Journal, Authored by K. Batarseh, G. Swaney, and A. Stiller. A general description of the procedure used in that derivation and a discussion of the results are included here)

The model is based on two phenomena. First oxygen and water must come into contact with the reactive pyrite surfaces through diffusion. When that occurs the reaction is infinitely fast by comparison to the diffusion rate. Therefore, the rate of oxygen to the surface from the outside environment and the rate of diffusion through any ash layer that forms immediately after the reaction starts. From this hypothesis we can write the first equation of the model as:

$$\frac{\partial}{\partial r} (r^2 N_A) - S_v r^2 N'_A \Big|_{r'=r_0} = 0$$

where

N_A is the flux of O_2 within the particle

$N'_A \Big|_{r'=r_0}$ is the flux of O_2 within the grain "ash layer"

Here $S_v = \frac{3\rho_b}{r_0 \rho_B} w$, the grain surface area per unit volume of particle, ρ_b is

the bulk density of the particles, ρ_B is the density of FeS_2 , w is the weight fraction of FeS_2 in the sample. Equation 2 is written as a partial differential equation because N_A and N'_A are functions of both radial

position and time.

The second step in the model development is that the matrix of the rock does not change during the reaction but an ash layer forms around the pyritic grains as they react. This ash layer inhibits diffusion as it must be penetrated by oxygen for the reaction to proceed. The fresh reacting grains essentially shrink as the reaction proceeds and the ash layer develops gradually while the rock matrix remains unchanged. The second step in the model development describes the restriction to diffusion of oxygen by this process using the shrinking core model. The equation is below.

$$\frac{\partial r_c(r,t)}{\partial t} = \frac{\bar{b}}{C_B} N'_A \Big|_{r'=r_c} = - \frac{\bar{b}}{C_B} C_F D'_e \left[\frac{\partial y'_A(r_c, r, t)}{\partial r'} \right] \Big|_{r'=r_c}$$

with initial condition

$$\text{at } t = 0: \quad r_c = r_0$$

Here, C_B and C_F are the molar densities of reactant FeS_2 and fluid H_2SO_4 respectively; \bar{b} is the stoichiometric ratio relating consumption of FeS_2 and O_2 , $\frac{2}{7} = \bar{b} = b/a$ and D'_e is the effective diffusivity of O_2 within the reacted shell.

The third step in the model development is essentially the combination of the equations in steps one and two. As mentioned above the details can be found elsewhere. The resulting equation with its boundary conditions is written as:

$$\frac{1}{r^2} \frac{\partial}{\partial r} \left[r^2 \frac{\partial y_A(r,t)}{\partial r} \right] = - \eta \frac{\partial r_c(r,t)}{\partial t} \cdot r_c^2$$

with the boundary conditions

$$\forall t > 0 \text{ at } r = R_0 \quad y_A = y_{Ax}$$

$$\forall t > 0 \text{ at } r = 0 \quad \frac{\partial y_A}{\partial r} = 0$$

where

$$\eta = \frac{S_V C_B}{b_D C_M r_o^2}$$

The final system of equations 12-16 now define a physically reasonable model describing the diffusion and the reaction of O_2 A within the particles.

Further refinements are required to relate easily measured physical parameters to the reaction rates of the pyrite within the rock material. When these are completed the final system of equations is determined and reads as:

$$\frac{1}{Z^2} \frac{\partial}{\partial Z} \left[Z^2 \left[Y^2(Z,t) - Y(Z,t) \right] \frac{\partial Y(Z,t)}{\partial Z} \right] = - \frac{\theta}{3} \left[Y^3(Z,t) - 1 \right]$$

Boundary conditions:

$$\begin{aligned} \forall t > 0 \text{ at } Z = 1 & \quad 1 + 2Y^{*3} - 3Y^{*2} = \beta t \\ \forall t > 0 \text{ at } Z = 0 & \quad \frac{\partial Y}{\partial Z} = 0 \end{aligned}$$

where

$$Z = \frac{r}{R_o}$$

$$Y = \frac{r_c}{r_o}$$

$$Y^* = Y(Z=1, t)$$

$$\theta = \eta \Omega r_o R_o^2 = \frac{3\rho_b^D R_o^2 C_F^W}{\rho_B^D r_o^2 C_M}$$

$$\beta = \frac{6\Omega}{r_o^2} y_{Ax} = \frac{6b_{y_{Ax}} C_F^{D'}}{r_o^2 C_B}$$

The solution of this system requires still further refinement and can not be done analytically. It can be accomplished numerically by standard procedures. (we used the fourth order Runga Kutta method)

TESTING THE SYSTEM EQUATION

The product of the mathematical model development is a computer program solution for the equation. The detailed program can be found in the masters thesis of Kareem Batarseh. It is hypothesized that when the appropriate physical data is put into the program, accurate predictions of the acid production rate from the described rock material can be calculated (the required data can be seen in Table 1) - This study would not be complete if we did not

test the ability of our model to predict the acid production rates of mine rock samples. We were very fortunate to have access to a completely analyzed suite of samples from the lithic units associated with coal in northern West Virginia. These are the same samples used in the pyrite morphology study of Laura Haines. The complete petrographic, analytical, and acid production rate data were available.

Essentially two additional types of data were required for us to test our hypothesis: (1) the pore radius, pore size distribution, and the bulk porosity; which are the physical rock parameters and (2) the dependence of porosity with time as the reaction progresses; this is due to the build up of ash layer. [Both of these measurements were made outside of our laboratory at a company called Quantachrome]. The first portion of the required data could be obtained by direct measurement of the rock samples to be used in the experiments by mercury and helium diffusion. This is a standard procedure. The second set of required data could be obtained only after the samples had partially reacted. This was accomplished by keeping the samples in the oven as per the Soxhlet exudation process for a set of increasing time intervals. The samples would be sent off for analysis after the completed time interval. A table of representative data are below (see tables 2 and 3).

To complete the comparison a new set of Soxhlet extraction runs were performed at three different temperatures, 25°, 45° and 60°, and the acid production rates were calculated. The physical data were put in the model computer program and the acid production rates were calculated for the three temperatures above. These values were compared to the Soxhlet values. The results can be seen in the following figures (see figures 7, 8 and 9).

Because the conversion of pyrite is very small in these runs, we decided to complete the model tests by running a sample to nearly total oxidation. Since the model is diffusion controlled a simple procedure to enhance conversion is to run the system at high pressure. This was done by placing 25 samples in separate Soxhlet thimbles in an autoclave reactor. The autoclave contained some water which was kept below the level of the thimbles and pressurized to 1400 lbs. with oxygen. Every other day a sample was removed and extracted to determine the extent of reaction. This procedure was continued until all the samples were analyzed. The physical data describing the rock was input into the program. The calculated data were compared to the experimental ones (see figure 10). The agreement is excellent.

As a result of this work, we can make several important conclusions (1) the oxidation reaction of pyrite in rock material is diffusion controlled (2) that process can be successfully modeled as a fixed matrix shrinking grain core model with a moving boundary (3) the result of the numerical solution of that model is a computer program which requires only some physical parameters describing the rock material of interest to calculate the acid production rate (4) that program has been validated by two different tests done in our laboratory. The important limitation of the model is that it was developed to understand the differences which occurred in Soxhlet tests. In essence there is no vertical oxygen gradient. In the actual field measurements such a gradient was described. This effect can be added to the current model through as a further parameter development but it is not included here.

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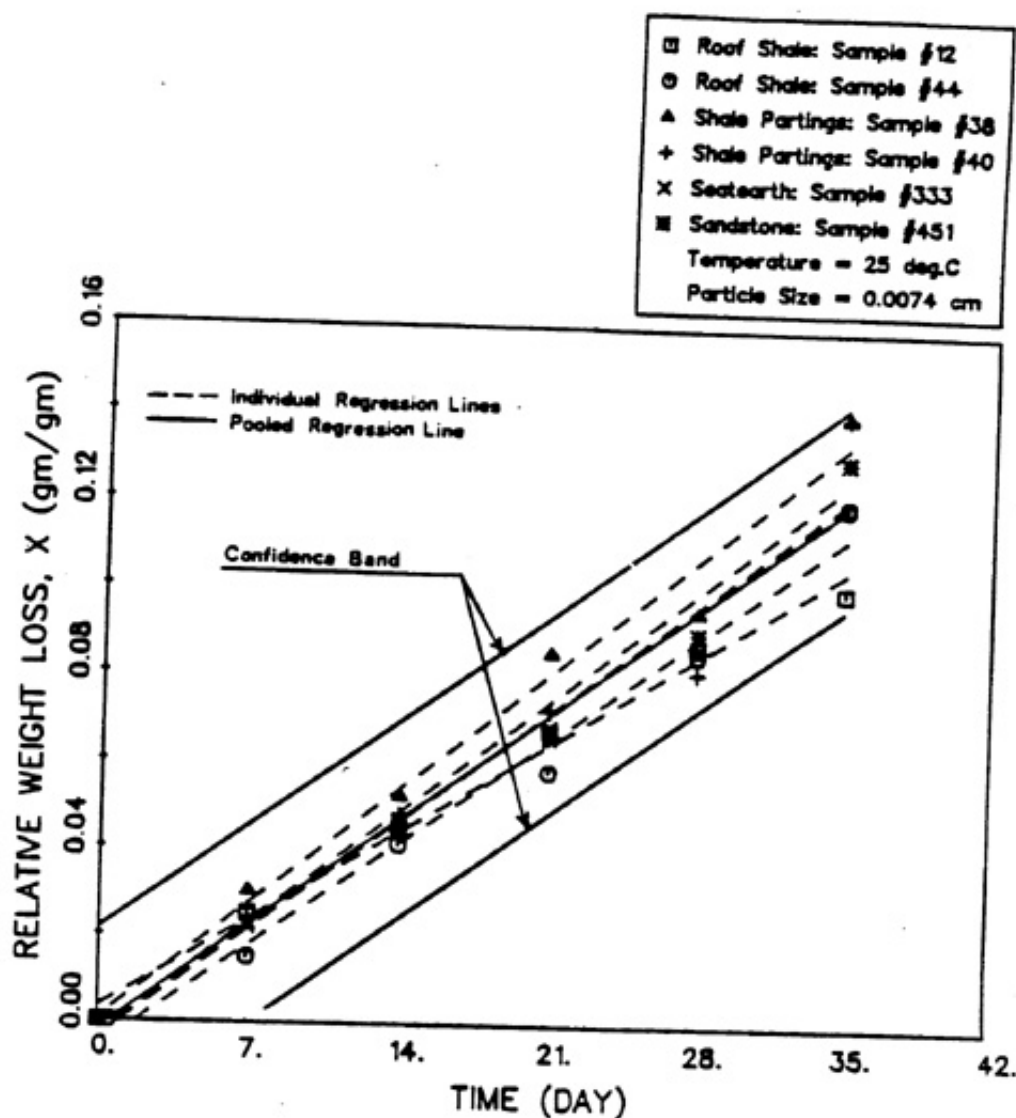


Figure-1 Statistical Analysis of Weight Changes of FeS_2 Powder at 25°C .

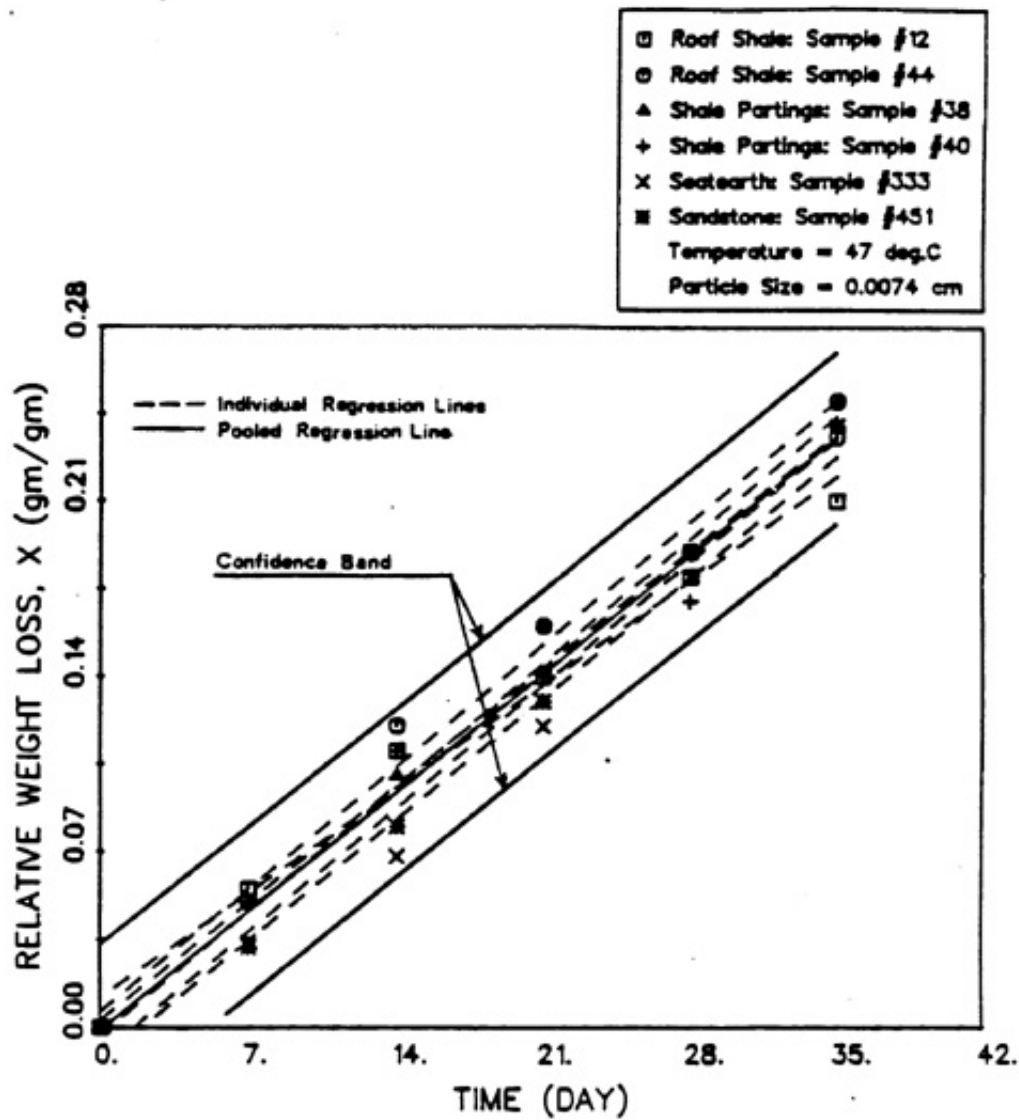


Figure-2 Statistical Analysis of Weight Changes of FeS_2 Powder at 47°C.

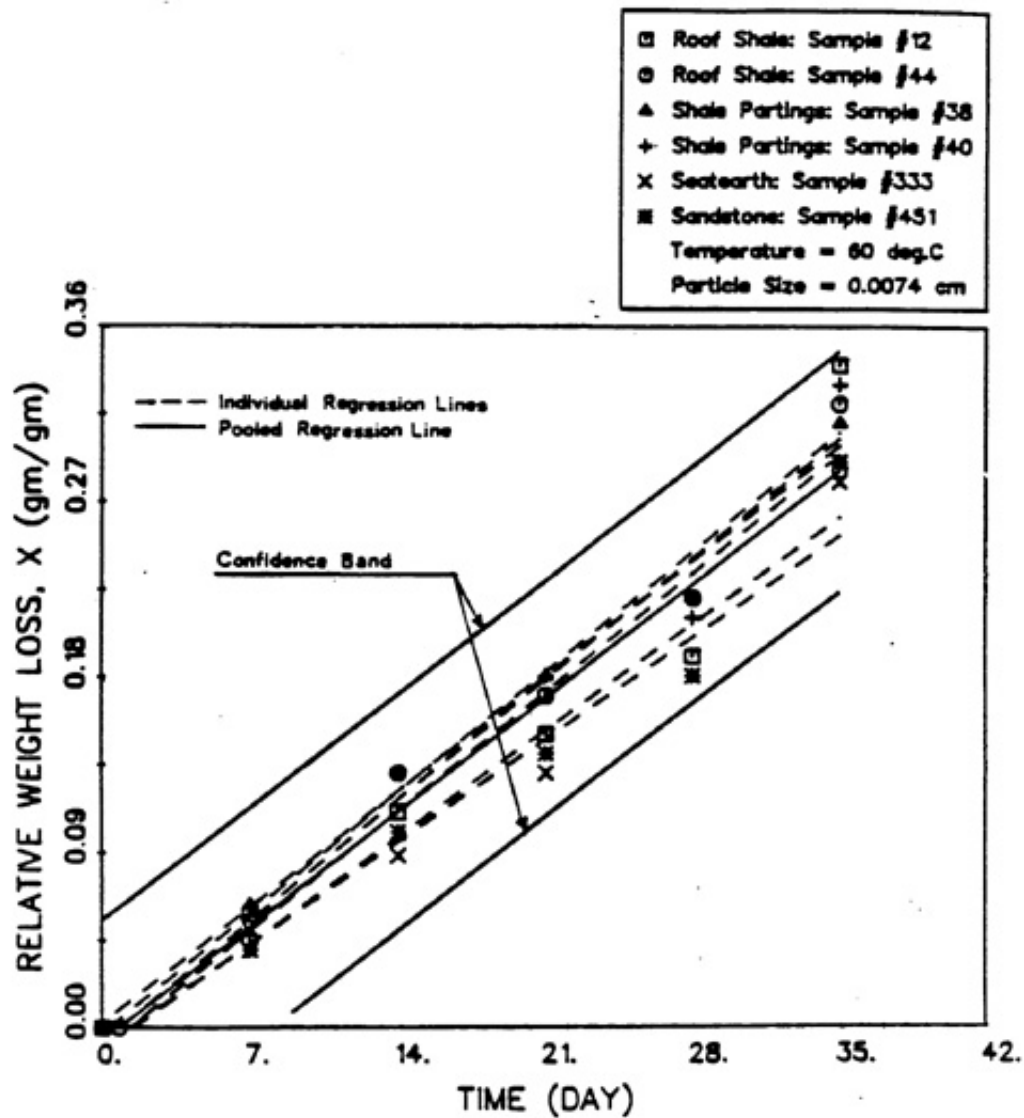


Figure-3 . . Statistical Analysis of Weight Changes of FeS₂ Powder at 60°C.

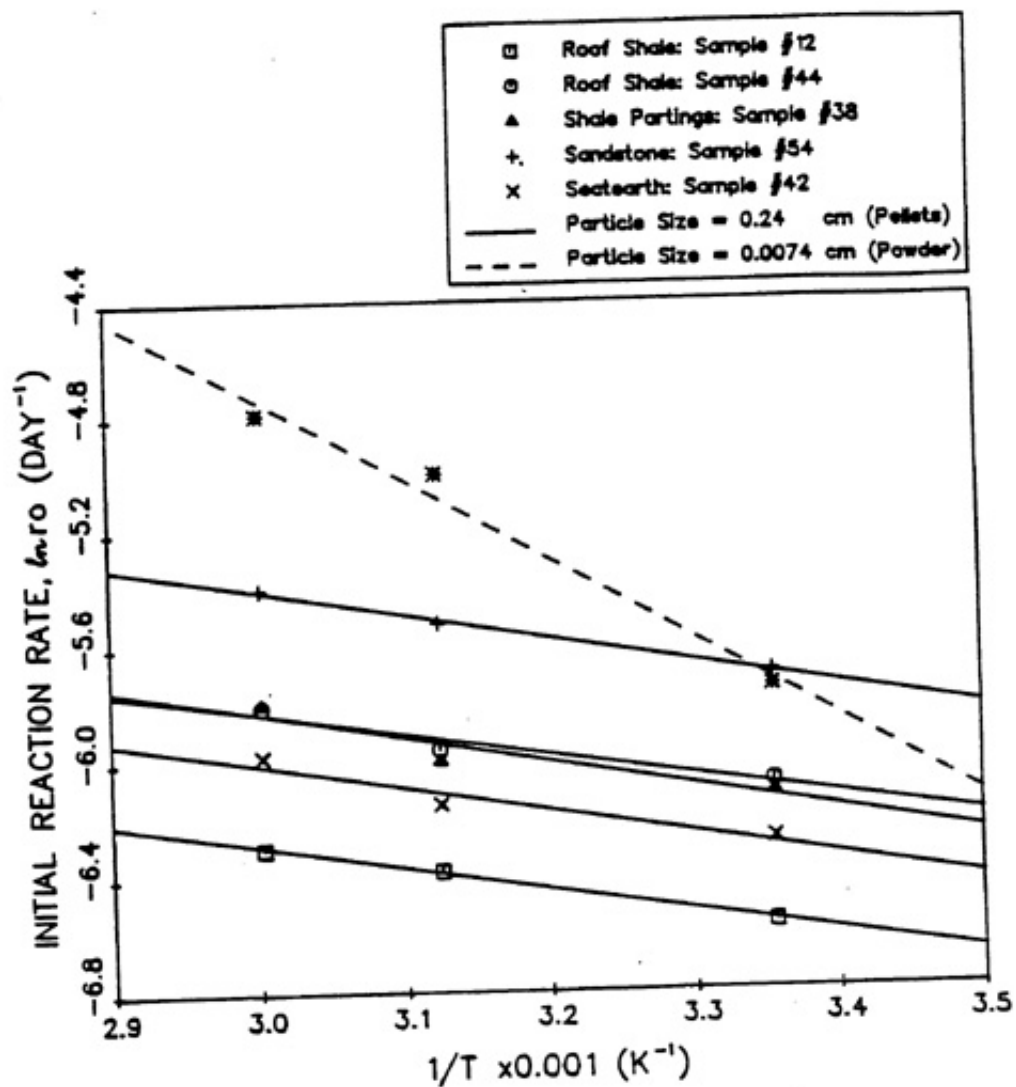


Figure-4 Arrhenius Plots of the Initial Reaction Rate for the Oxidation of FeS₂ by (O₂ + H₂O).

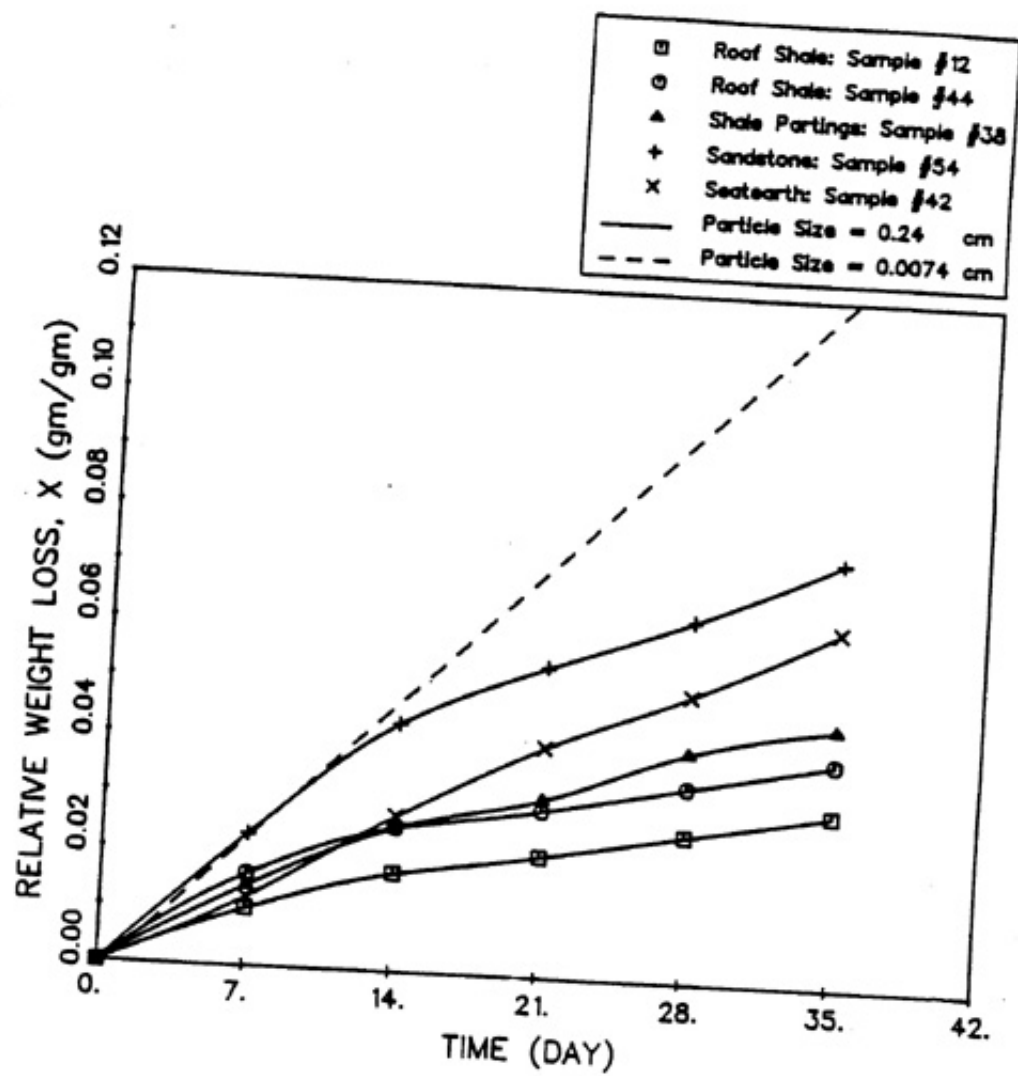


Figure-5 Effect of Particle Size on the Weight Loss of FeS_2 During Oxidation.

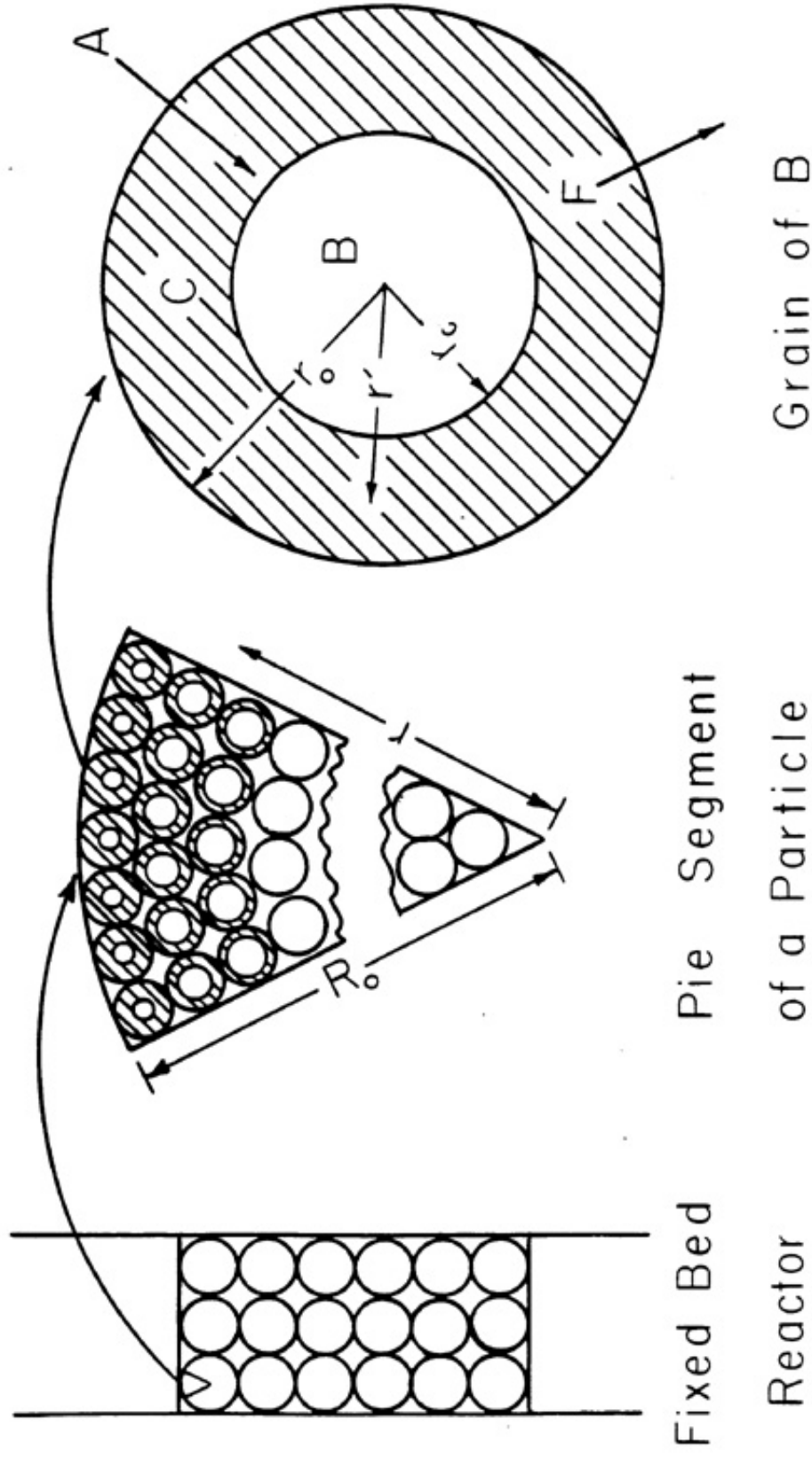


Figure-6 Schematic Representation of the Model.

Table-1

Program Input and Output

Input	Output
1. Stoichiometric ratio, b	Conversion profile, $X(Z,t)$
2. Molar density of FeS_2 , C_B	Total conversion, $X(1,t)$
3. Molar density of H_2SO_4 , C_F	
4. Molar density of H_2O , C_W	
5. Henry's constant of O_2 , H_A	
6. Molecular weight of H_2SO_4 , M_F	
7. Molecular weight of H_2O , M_W	
8. Partial pressure of O_2 , P_A	
9. Radius of the grains, r_0	
10. Radius of the particles, R_0	
11. Absolute temperature, T	
12. Molar volume of O_2 , V_A	
13. Weight fraction of FeS_2 , w	
14. Porosity of the particle, ϵ	
15. Porosity of the ash layer, ϵ'	
16. Viscosity of H_2SO_4 , μ_F	
17. Viscosity of H_2O , μ_W	
18. Tortuosity of the ash layer, τ'	
19. Association parameter of H_2SO_4 , ϕ_F	
20. Association parameter of H_2O , ϕ_W	

Table-2

Average Pore Radius of the Pellet Samples

Sample Number	Average Pore Radius (\AA)
12	1288
44	492
38	1327
54	1780
42	550

Table-3

Independence of the Porosity from Time for the Pellet Samples

Time (days)	Sample Number, ϵ (dimensionless)				
	12	44	38	54	42
0.0	0.104	0.098	0.0456	0.08	0.04
3.0	0.13	0.096	0.05	0.096	0.05
6.0	0.11	0.12	0.04	0.098	0.04

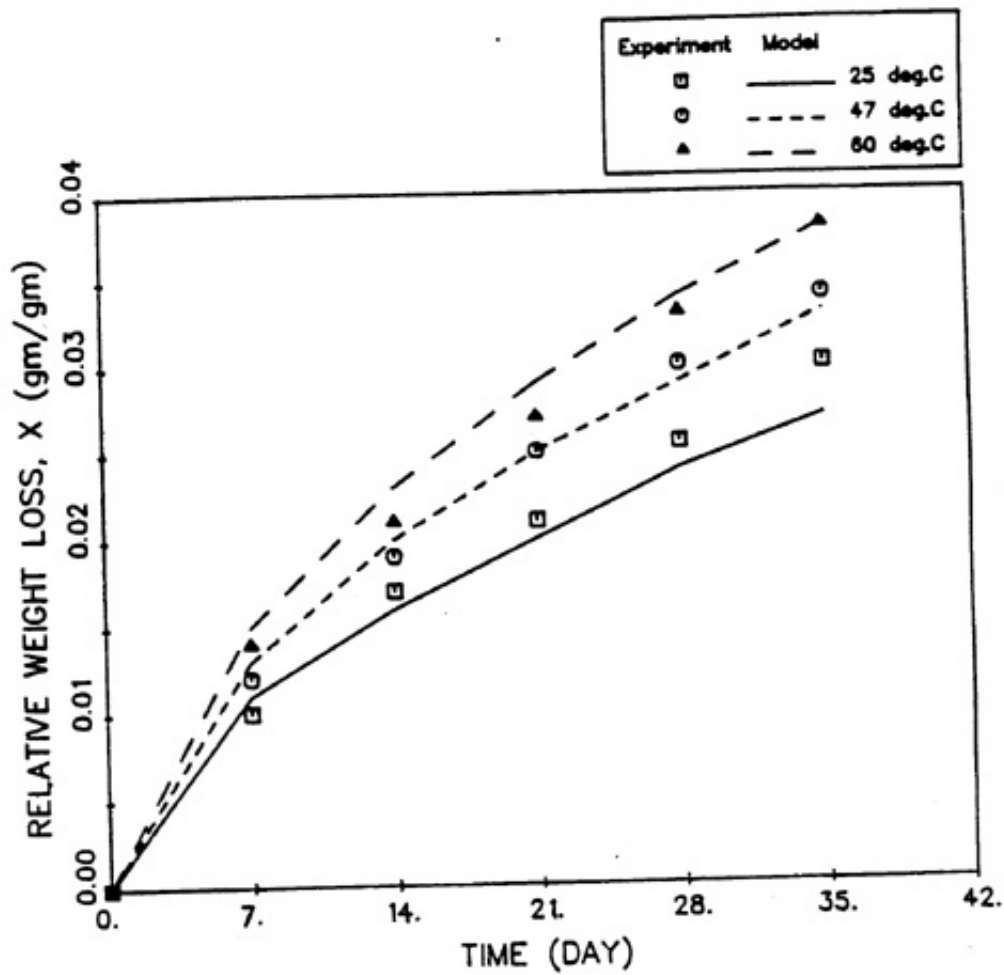


Figure-7 Comparison of Experimental Data with the Model Prediction for Sample Number 12.

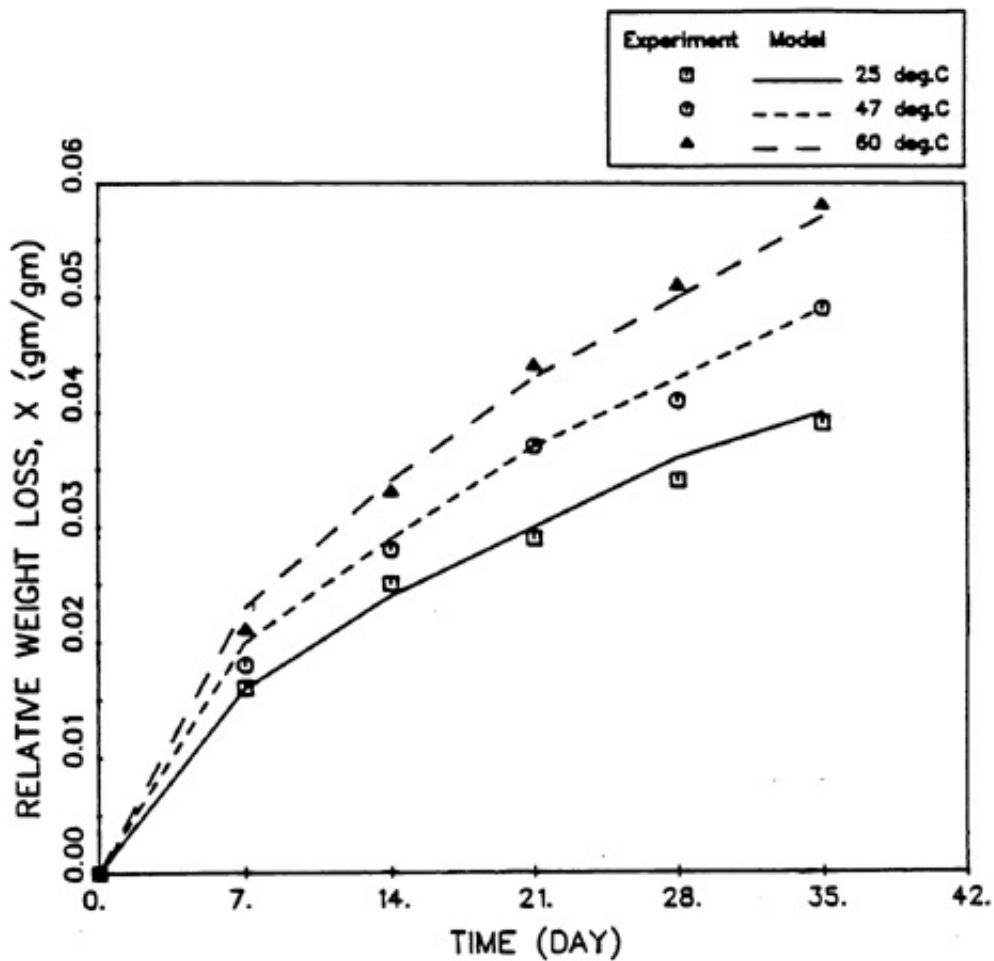


Figure-8 Comparison of Experimental Data with the Model Prediction for Sample Number 44.

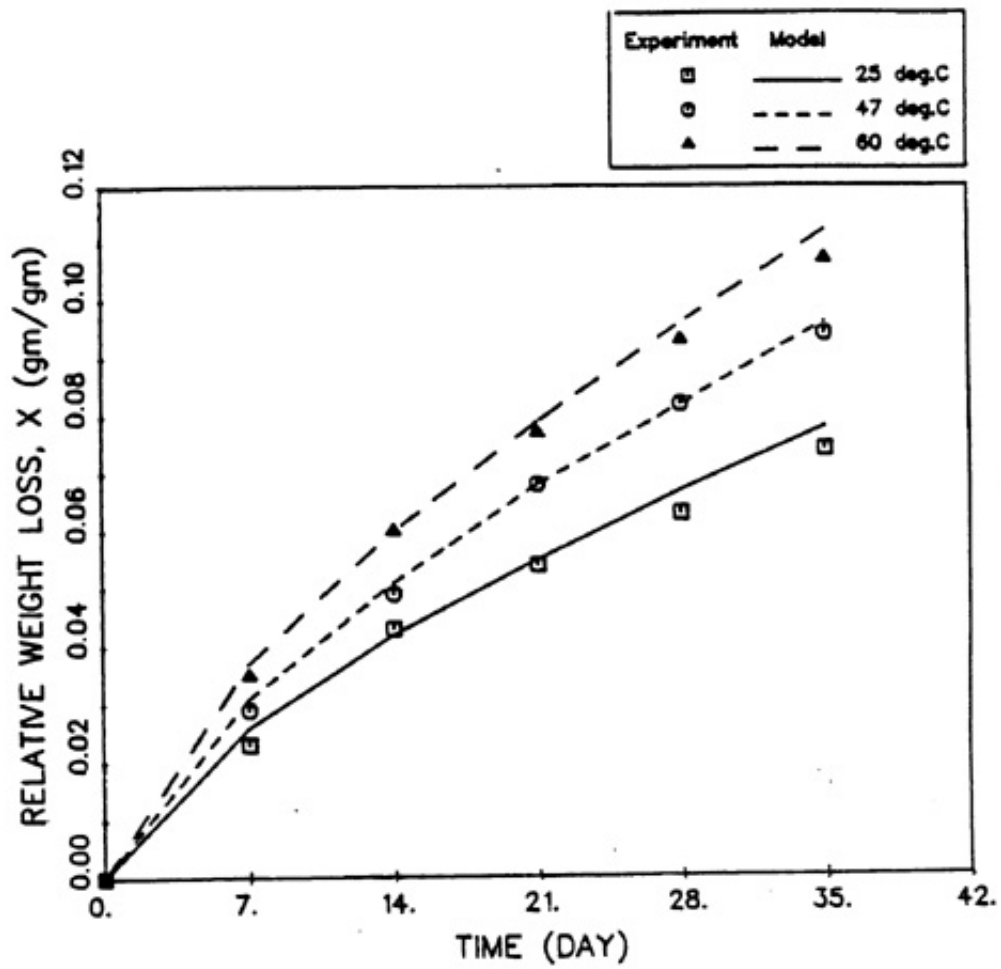


Figure-9 Comparison of Experimental Data with the Model Prediction for Sample Number 54.

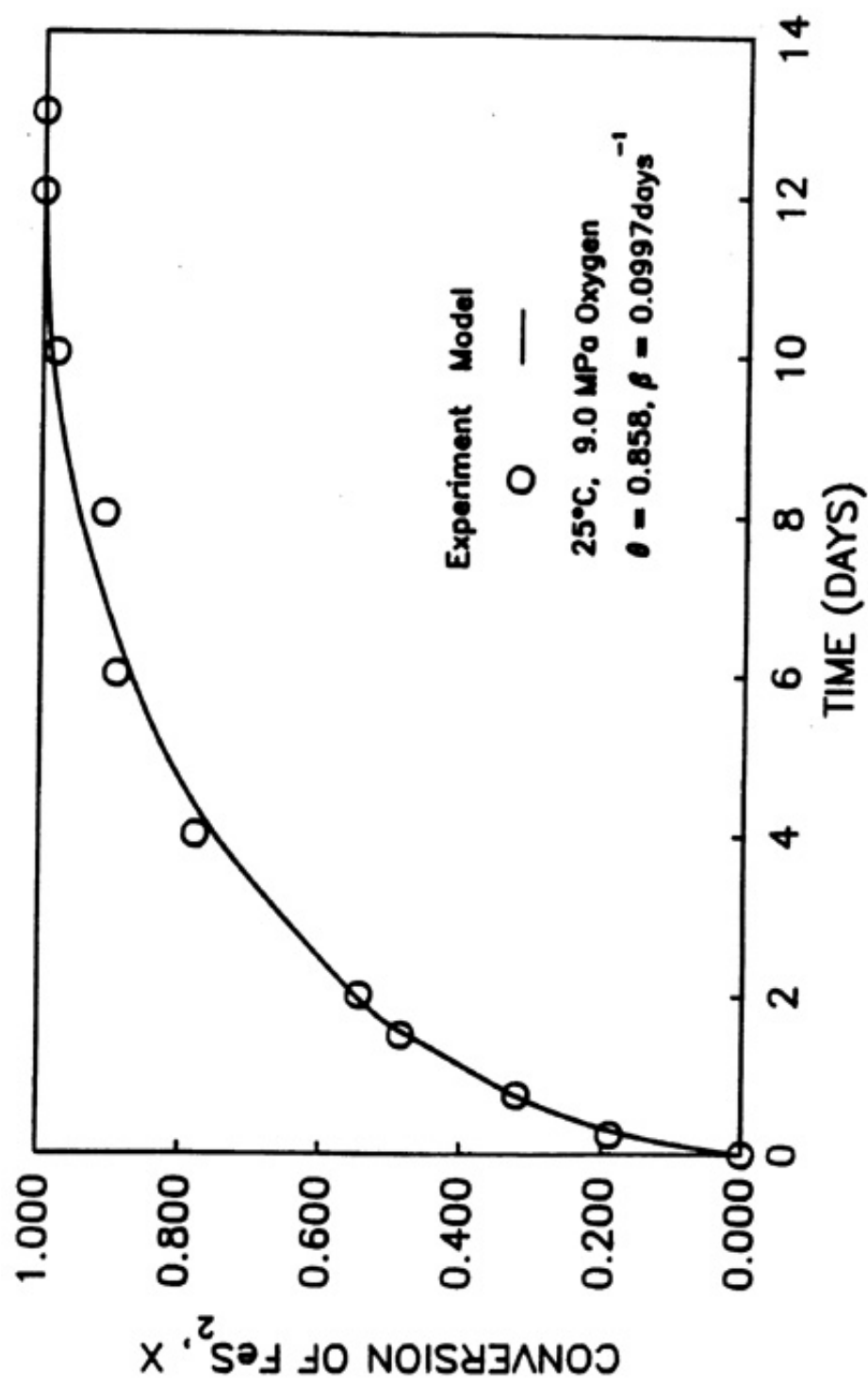


Figure-10 Comparison of High Pressure Oxidation Data
With the Model Prediction for Sample Number 54.