

- Fraser, R. P., P. Eisenklam, N. Dombrowski, and D. Hasson, "Drop Formation for Rapidly Moving Liquid Sheets," *AIChE J.*, **8**, 672 (1962).
- Fukui, N., and T. Sato, "The Study of Liquid Atomization by the Impingement of Two Jets," *Bull. Jap. Soc. Mech. Eng.*, **15**, 83, 609 (1972).
- Hasson, D., D. Luss, and R. Peck, "Theoretical Analyses of Vapor Condensation on Laminar Liquid Jets," *Intern. J. Heat Mass Trans.*, **7**, 969 (1966).
- Hunter, J. A., E. N. Sieder, and P. G. Tomalin, "Deaerators for Desalination Plants," Office of Saline Water R. and D. Prog. Rept. No. 314 (1967).
- Ranz, W. E., "Some Experiments on the Dynamics of Liquid Films," *J. Appl. Phys.*, **30**, 1950 (1959).
- Rasquin, E. A., "Vacuum Desorption of Gases and Volatile Organic Liquids from Water in Packed Columns," M.S. thesis, Dept. of Chem. Eng., Univ. Calif., Berkeley (1977).
- , S. Lynn, and D. N. Hanson, "Vacuum Degassing of Carbon Dioxide and Oxygen from Water in Packed Columns," *Ind. Eng. Chem. Fundamentals*, (Feb., 1977).
- Simpson, S. G., "Vacuum Stripping of Sparingly Soluble Gases from Water," Ph.D. thesis, Univ. Calif., Berkeley (1975).
- Squire, H. B., "Investigation of the Instability of a Moving Liquid Film," *Brit. J. Appl. Phys.*, **4**, 167 (1953).
- Taylor, G. I., "The Dynamics of Thin Sheets of Fluids," *Proc. Royal Soc.*, **A253**, 389 (1959).
- Tham, M. J., K. K. Bhatia, and K. E. Gubbins, "Steady State Method for Studying Diffusion of Gases in Liquids," *Chem. Eng. Sci.*, **22**, 309 (1967).
- Vivian, J. E., and C. I. King, "Diffusivities of Slightly Soluble Gases in Water," *AIChE J.*, **10**, 220 (1964).
- Wilke, C. R., and P. Chang, "Correlation of Diffusion Coefficients in Dilute Solutions," *ibid.*, **1**, 265 (1955).
- Wise, D. L., and G. Houghton, "The Diffusion Coefficients of Ten Slightly Soluble Gases in Water at 10-66°C," *Chem. Eng. Sci.*, **21**, 999 (1966).
- Witherspoon, P. A., and L. Bonoli, "Correlation of Diffusion Coefficients for Paraffin Aromatic and Cycloparaffin Hydrocarbons in Water," *Ind. Eng. Chem. Fundamentals*, **8**, 589 (1969).

Manuscript received June 30, 1976; revision received June 2, and accepted June 22, 1977.

Pyrite Oxidation in Aqueous Ferric Chloride

W. E. KING, JR.

and

D. D. PERLMUTTER

Department of Chemical and Biochemical Engineering
University of Pennsylvania
Philadelphia, Pennsylvania 19174

The rate of pyrite oxidation in aqueous ferric chloride was determined for two distinct solid particle systems: industrial grade pyrite and coal particles containing pyrite. The oxidation rate for the pyrite particle system was found to increase significantly with increasing temperature (40° to 100°C), ferric chloride concentration (0.1 and 1.0 M), and pyrite loading (2 to 20 g/l); the rate decreased with increasing particle size (—325 to 140 mesh). Agitation did not have a significant effect, and a kinetic model was developed and fit to the experimental data.

For the coal particle system used in this study, the most important variable was particle size. The oxidation rate of pyrite in coal smaller than 325 mesh was much greater than in larger coal particles. The effect of temperature (80° to 100°C) on the oxidation of pyrite in coal was not significant, nor was the effect of pretreatment with 0.1N hydrochloric acid. Approximately half of the detected ferric iron reduction was attributable to pyrite oxidation; the balance arises from other coal reactions.

SCOPE

The chemical treatment of pulverized coal with aqueous solutions of iron salts is reported (Hamersma et al., 1973) to be capable of almost complete removal of inorganic sulfur (pyrite) in residence times of the order of hours. Detailed kinetic studies are needed to provide a basis for optimum reactor design.

In the study reported here, oxidation rates in aqueous solutions of ferric chloride were measured for two distinct solid particle systems: industrial grade pyrite and coal

particles containing pyrite. For the former, the effects of temperature, ferric chloride concentration, reactor agitation, particle size, and solid loading were investigated. For the coal particle system, the effects of temperature, particle size, and dilute acid pretreatment were examined.

All experiments were carried out isothermally in a well-stirred batch reactor. Samples were taken at selected time intervals and analyzed for ferric and ferrous iron. The kinetic data for the pyrite particle system were used to develop a kinetic rate model.

CONCLUSIONS AND SIGNIFICANCE

The oxidation rate for the pyrite particle system was found to increase significantly with temperature, ferric chloride concentration, and pyrite loading; the rate de-

creased with increasing particle size, while agitation did not have a significant effect. The experimental data for the pyrite particle system were empirically correlated over a wide range of operating conditions by the simple two-parameter kinetic model

W. E. King, Jr. is at the University of Maryland, College Park, Maryland 20742.

$$r = k \left[\frac{C_B}{C_{B_0}} \right]^{2/3} \left[\frac{C_A}{(C_A + KC_C)^2} \right]$$

For the coal particle system, the most important variable was particle size. The oxidation rate of pyrite in coal smaller than 325 mesh was much greater than in larger

coal particles. The effect of temperature change from 80° to 100°C was not significant, nor was the effect of pretreatment with 0.1N hydrochloric acid. For the coal used in this study, approximately half of the detected ferric iron reduction was attributable to pyrite oxidation, the balance arising from extraneous reactions.

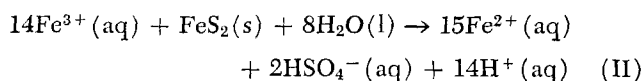
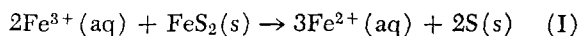
The treatment of coal particles with an aqueous solution of iron salts is one technique which has been proposed for the removal of sulfur from coal. The major part of this inorganic sulfur is in the form of iron disulfide (pyrite and/or marcasite), commonly referred to simply as pyrite (Walker and Hartner, 1965). It exists within the coal in both macroscopic and microscopic form; the latter is finely divided, primarily within the 20 to 50 μ range. As a result, it is not feasible to remove pyritic sulfur completely with physical cleaning techniques.

The first reported kinetic studies of pyrite oxidation in aqueous solutions involved the use of dissolved oxygen as the oxidizing agent (Warren, 1956; McKay and Halpern, 1958). Since then, investigators have studied pyrite oxidation in dilute (<0.02M) iron salt solutions (Garrels and Thompson, 1960; Sasmojo, 1969; Mathews and Robins, 1972). Meyers et al. (1975) were the first to examine pyrite oxidation in concentrated iron salt solutions (~1.0M). They have shown that a chemical treatment process using aqueous solutions of either ferric chloride or ferric sulfate can remove 98 to 100% of the pyritic sulfur from coal by oxidizing the pyrite to either elemental sulfur or sulfate ion.

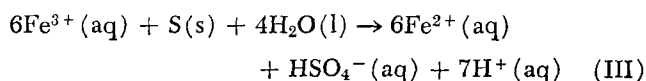
The study reported here extends the range of known behavior to include parameters of interest in practical design. The oxidation rates in aqueous solutions of ferric chloride were measured for two distinct solid particle systems: industrial grade pyrite and coal particles containing pyrite. For the former, the effects of temperature (maximum of 100°C), ferric chloride concentration, stirrer revolutions per minute, particle size, and solid loading were investigated. For the coal particle system, the effects of temperature, particle size, and dilute acid pretreatment were examined.

AQUEOUS REACTION CHEMISTRY

The inorganic chemistry of aqueous iron salt-pyrite systems involves numerous ionic species. Ferric ions from the dissociated iron salt react with FeS₂ to form ferrous ions and a sulfur product (elemental sulfur or sulfate ion), as reported in the literature (Hamersma et al., 1973; Garrels and Thompson, 1960; Sasmojo, 1969; Mathews and Robins, 1972):



Furthermore, it has been suggested (Sasmojo, 1969) that elemental sulfur can be oxidized by Fe³⁺ as follows



Whether reaction (I) or reaction (II) describes the stoichiometry of pyrite oxidation depends, therefore, on whether reaction (III) is relatively rapid or not. These reactions are all limited by kinetics and not thermodynamic

equilibrium (King, 1976). In addition, there are a number of chemical equilibria which exist among the many ions in solution (Sasmojo, 1969; Rabinowitch and Stockmayer, 1942) and shift with respect to one another as the pyrite oxidation reaction proceeds.

A significant simplification results if the kinetics of pyrite oxidation are studied in terms of total ferric and total ferrous concentrations (Fe^{III} and Fe^{II}) only. Since the aqueous solution does not contain any ferrous iron initially, the measurement of Fe^{II} as a function of time is a direct indication of the rate of reaction:

$$\Delta\text{Fe}^{\text{II}} = \Delta\text{Fe}^{2+} = b \Delta\text{FeS}_2 \quad (1)$$

When ferric ion is consumed by reaction, the numerous ferric complexes furnish new ferric ions virtually instantaneously. This bufferlike action provides the basis for the assumption used in the subsequent models to the effect that the reaction rate depends upon total ferric and ferrous concentrations.

EXPERIMENTAL PROCEDURES

An analytical procedure was developed for measuring the rate of pyrite oxidation in aqueous ferric chloride by determining the ferric and ferrous iron content of liquid samples via an emf measurement using platinum-calomel electrodes placed in the sample, and a light absorbance measurement using an atomic absorption spectrophotometer. The former measurement determines the ratio of ferric to ferrous iron in the sample, and the latter determines the total iron in solution. The emf data were found (King, 1976) to follow closely a Nernst-like equation of the form

$$E = A + B \ln R \quad (2)$$

where *R* is the ratio of ferric to ferrous iron concentrations, and this form was conveniently used to correlate the experimental measurements. Since the overall effective stoichiometry for pyrite oxidation lies between that of reactions (I) and (II), it was determined experimentally by interpolating the measured values between two calibration curves, each prepared to simulate the products from one of the two reactions. The total iron in solution was measured by atomic absorption spectroscopy using a Techtron AA120 absorption spectrophotometer. The relatively concentrated solutions used in this study (0.1 and 1.0M) had to be diluted for analysis.

The pyrite reactions were run in well-stirred, baffled cylindrical vessels made of Plexiglas or Pyrex, depending on reaction temperature; the former was used for all runs at temperatures of 80°C or less. Openings were provided for a teflon coated stirrer, for a thermometer, and for loading the solid particles. Reactor temperature was maintained to within $\pm 1^\circ\text{C}$ by control of an oil or water bath. Detailed schematics of the reactors are presented elsewhere (King, 1976).

The iron disulfide supplied by C-E Minerals, a division of Combustion Engineering, Inc., was in the marcasite form and has a reported analysis on a weight basis of

Fe	43.9%
S	49.8
SiO ₂	3.5
Impurities	2.8

This corresponds to an industrial grade solid material approximately 94% pyrite.

TABLE 1. SULFUR CONTENTS OF VARIOUS COAL FRACTIONS

Particle size fraction	Wt % pyritic	Wt % sulfate
14-18 mesh	1.1	0.1
18-30	1.1	0.2
30-50	1.1	0.1
50-100	1.2	0.2
100-200	1.4	0.3
200-325	1.4	0.3
-325	0.6	0.6

TABLE 2. REACTION WEIGHTS AND EFFECTIVE STOICHIOMETRIC COEFFICIENTS

Temperature, °C	X_I	X_{II}	a	c	c/a
40	0.8	0.2	4.5	5.5	1.2
50	0.6	0.4	6.6	7.6	1.2
60	0.4	0.6	8.8	9.8	1.1
70	0.4	0.6	9.0	10.0	1.1
80	0.5	0.5	7.7	8.7	1.1
100*	0.4	0.6	9.2	10.2	1.1

* Data from Hamersma et al. (1973).

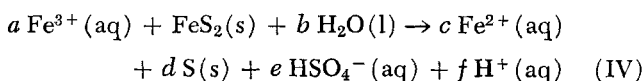
The coal used in this study was supplied by the Philadelphia Electric Company in two batches, containing coal before and after pulverization, respectively. The coal is a typical eastern coal from West Virginia. Further crushing and sieving produced the particle size fractions shown in Table 1. The corresponding pyritic and sulfate contents were established by a series of acid leaching experiments, following the detailed procedure presented by Mott (1950). The sulfate content of the coal samples was considerably higher than that of freshly mined coal, indicating that the coal had weathered somewhat; the pyritic sulfur contents are typical of many eastern coals.

RESULTS AND DISCUSSION

Stoichiometric Coefficients

Because the oxidation of pyrite is governed by a combination of reactions (I) and (III), it is necessary to determine an overall effective stoichiometry by experiment. This stoichiometry can in addition vary with temperature, since reactions (I) and (III) may have different activation energies.

The stoichiometry of the pyrite oxidation reaction can be expressed in a most general form to include all components that have been reported experimentally as



The ratio of the coefficients for the ferrous and ferric species are related to the experimental data by

$$\frac{c}{a} = \frac{\Delta \text{Fe}^{2+}}{\Delta \text{Fe}^{3+}} = \frac{\Delta \text{Fe}^{\text{II}}}{\Delta \text{Fe}^{\text{III}}} \quad (3)$$

where Δ refers to the difference in the concentrations between the first and last sample. The first sample is chosen rather than the initial condition because there may be an iron oxide film removed from the solid particles during the first few minutes of reaction.

A set of weights may be used to express the relative importance of reactions (I) and (II) in governing the stoichiometry; these weights are related by

$$2X_I + 14X_{II} = a \quad (4)$$

and

$$3X_I + 15X_{II} = c \quad (5)$$

$$X_I + X_{II} = 1.0 \quad (6)$$

where a and c are the effective stoichiometric coefficients described by reaction (IV). The reaction weights and effective stoichiometric coefficients a and c may be calculated from the simultaneous solution of Equations (4) to (6).

Table 2 presents a summary of these parameters found over the range of temperatures investigated in this study based on the 0.1M ferric chloride runs. Also included in Table 2 are results at 100°C based on the data of Hamersma et al. (1973). These results show that the contributions of reactions (I) and (II) approach reaction weights of approximately 0.4 and 0.6 as temperature increases. The atomic absorption spectroscopy technique is not sensitive enough to pick up small changes in the total iron concentration at the 1.0M ferric chloride level.

Kinetic Model Parameter Estimation

For practical reactor design, it is convenient to fit experimental data to an analytic form. To this end the parameter estimation techniques of Chandler et al. (1972) were used to evaluate four reaction rate models:

1. A pseudo-homogeneous model

$$r = k(C_B/C_{B0})^{2/3} C_A^n \quad (7)$$

2. A Langmuir-Hinshelwood form

$$r = k(C_B/C_{B0})^{2/3} \frac{C_A}{(C_A + KC_C)} \quad (8)$$

3. An empirical rate expression developed by Hamersma (1973) for pyrite removal from a coal particle system

$$r = k \left[\frac{C_A C_B}{C_A + KC_C} \right]^2 \quad (9)$$

4. An approximation of a theoretical model proposed by Sasmojo (1969)

$$r = k(C_B/C_{B0})^{2/3} \frac{C_A}{(C_A + KC_C)^2} \quad (10)$$

These four equations are each two parameter models, having therefore the same number of degrees of freedom for curve fitting. Except for Equation (9), each model accounts in the same way for surface area changes by assuming that the solid particles dissolve uniformly upon reaction, giving

$$a_s = a_{s0} (C_B/C_{B0})^{2/3} \quad (11)$$

Model Equation (10) gave the best fit of the experimental data in a least-squares sense. The results are summarized in Table 3 in the form of the best parameter estimates at various temperatures and concentration levels. Each entry in the table is accompanied by its standard error. The function $F(\alpha)$ is a least-squares sum defined as

$$F(\alpha) = \sum_{i=1}^N \left[\frac{f(x_i, \alpha) - y_i}{\sigma_i} \right]^2 \quad (12)$$

The standard deviations of the measured ferric iron concentration were calculated from the results of duplicate runs. For the 0.1M ferric chloride runs, four runs at 40°C and two runs at 60°C were performed. Values of σ_i at 80°C are based on three runs which were not repeated identically but varied only in the value of revolutions per minute. Values of σ_i at 50° and 70°C were obtained by interpolation. For the 1.0M ferric chloride runs, σ_i values at 80°C were obtained from two repeated runs and from

TABLE 3. PARAMETER ESTIMATES FOR MODEL EQUATION (10)

	Temperature at 1.0M FeCl ₃ concentration level				
	60°C	70°C	80°C	90°C	100°C
$k \times 10^2$	1.21 ± 0.75	0.58 ± 0.16	1.17 ± 0.34	0.99 ± 0.18	2.52 ± 0.67
K	29.2 ± 11.4	10.2 ± 2.2	11.4 ± 2.4	6.7 ± 0.9	11.7 ± 2.0
$F(\alpha)$	0.386	1.1	4.64	6.84	3.50

	Temperature at 0.1M FeCl ₃ concentration level				
	40°C	50°C	60°C	70°C	80°C
$k \times 10^2$	0.0184 ± 0.0107	0.0399 ± 0.0160	0.0386 ± 0.0099	0.0963 ± 0.0183	0.211 ± 0.052
K	12.0 ± 4.6	5.72 ± 1.58	3.45 ± 0.64	2.70 ± 0.39	2.43 ± 0.45
$F(\alpha)$	0.309	0.408	0.149	0.484	0.487

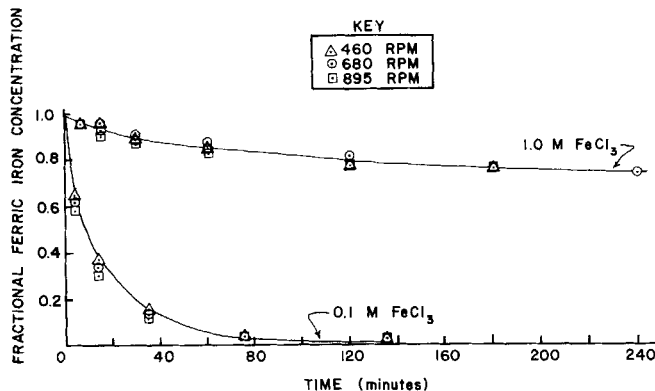
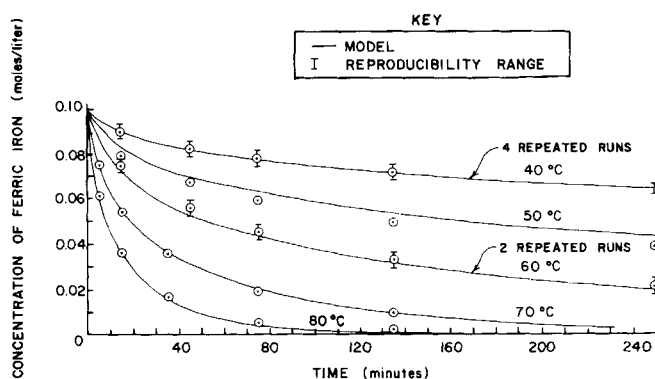
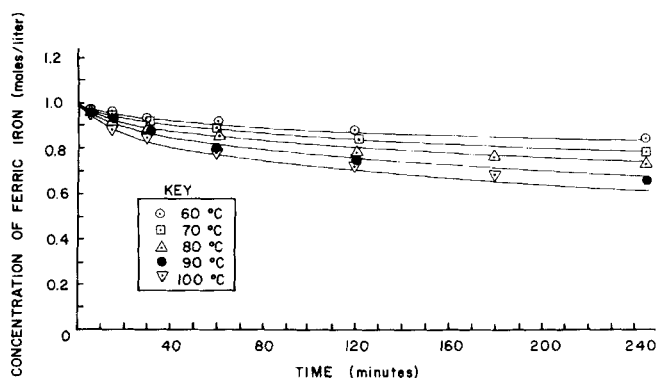


Fig. 1. Effect of agitation on reaction rate. Loading: 20 g/l, temperature: 80°C, pyrite particles: —325 mesh.

Fig. 2. Effect of temperature on reaction rate at 0.1M FeCl₃ concentration level. Loading: 20 g/l, pyrite particles: —325 mesh, stirrer speed: 680 rev/min.Fig. 3. Effect of temperature on reaction rate at 1.0M FeCl₃ concentration level. Loading: 20 g/l, pyrite particles: —325 mesh, stirrer speed: 680 rev/min.

two runs which varied only in value of revolutions per minute. This value of σ_i is used for all data interpretation at the 1.0M concentration level.

Effect of Agitation

In several runs, only the stirrer revolutions per minute was varied to determine whether mass transfer resistance due to a liquid boundary layer surrounding the solid particles was significant. The results in Figure 1 reveal that there is no significant agitation effect. The data points lie within the reproducibility range of the experimental procedure at either of the two concentration levels tested. These findings are consistent with the calculated mass transfer rates estimated from literature correlations following the procedure of Furusawa and Smith (1973). The calculated mass transfer rates are on the order of 1,000 times faster than the maximum chemical reaction rate.

Effect of Temperature and Ferric Concentration

The effect of temperature on pyrite oxidation is shown in Figures 2 and 3 at two different concentration levels. Arrhenius and van't Hoff correlations are presented in Figures 4 and 5 for the parameters estimated for model Equation (10). The activation energies and adsorption enthalpies were estimated (from a least-squares fit) over the range of temperatures investigated and are shown in Table 4, together with the corresponding standard errors. Such large standard errors are common in parameter estimation studies of heterogeneous kinetic models. Application of the slopes test (Volk, 1969) reveals that there is no statistically significant difference between the activation energy and adsorption enthalpy estimates at the two ferric chloride concentration levels tested. The solid lines in Figures 2 and 3 show the fit to Equation (10) obtained using the Arrhenius and van't Hoff correlations shown in Figures 4 and 5, respectively.

Effect of Particle Size

Several runs were performed where only the particle size differed. Figure 6 shows response curves at 80°C for pyrite particles with the indicated size distributions. A significant increase in rate may be seen for particles smaller than 325 mesh.

Varying the particle size distribution at the same solid loading has the effect of varying the initial surface area a_{s0} . This parameter, which increases rapidly with decreasing particle size, may be estimated from the total area of all the particles divided by the weight of the sample (specific surface). Since the specific surface of the particles in the —325 mesh range was not measured, the average particle diameter for this range was adjusted until the model fit agreed with the experimental data for all the particle size ranges investigated. For particle size distributions other than —325 mesh, the median was used as an average particle diameter. If an average particle diameter of 10 μ is

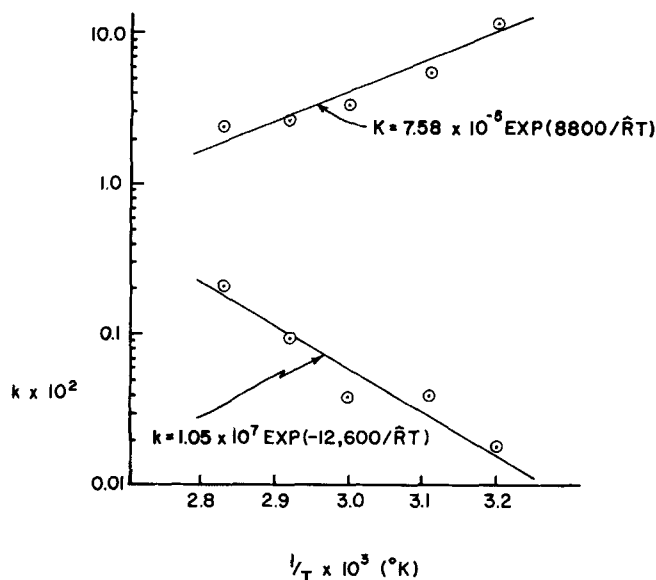


Fig. 4. Arrhenius and van't Hoff correlations for the constants of model Equation (18) at 0.1M FeCl_3 concentration level.

TABLE 4. ACTIVATION ENERGY AND ADSORPTION ENTHALPY ESTIMATES

Parameter	Concentration level	
	0.1M FeCl_3	1.0M FeCl_3
E (kcal/mole)	12.6 ± 2.1	4.8 ± 3.9
ΔH (kcal/mole)	8.8 ± 1.5	5.8 ± 3.6

used for the -325 mesh particles, Equation (18) accurately predicts the oxidation rates for both the 200 to 325 mesh and 140 to 200 mesh particles. This comparison is shown in Figure 6.

Effect of Solid Loading

Figure 7 shows the effect of the pyrite loading at 80°C. Variation of the pyrite loading is taken into account in the model by varying C_{B0} and a_{so} accordingly. The deviations of the model prediction are small in comparison with the experimental scatter. Figure 7 reveals that a loss of approximately 1 to 1.5 g/l would bring the experimental data into agreement with the model prediction. Such losses were observed in these experiments when solid particles climbed the stirrer rod and the walls of the reactor as the slurry was stirred. As the solid loading is decreased, this loss becomes relatively more important. It may be noted in this connection that ferric iron is the limiting reactant, since the pyrite loading corresponds to a stoichiometric excess in all the experiments of this series.

Aqueous Ferric Chloride-Coal Reaction

The oxidation of pyrite contained in a coal particle system was also measured in 1.0M ferric chloride solutions at temperatures in the 80° to 100°C range. Figure 8 shows results of three repeated runs as well as a fourth run on coal which was pretreated with 0.1N hydrochloric acid to remove iron sulfate. This fourth result was not significantly different from the other three, evidently, because a relatively small quantity of iron sulfate enters the solution compared with both the dissolution of pyrite and the reduction of ferric iron via interaction with the coal matrix. As further support, Figure 9 shows that 87 to 89% of the total iron sulfate present is removed in 2 hr for each of two samples. (A is 40 g of 100 to 200 mesh particles; B is 100 g of -325 mesh.) Titration of the filtrates from the hydrochloric acid leaching experiments showed the iron to be in the ferrous form. The high sulfate content in the coal

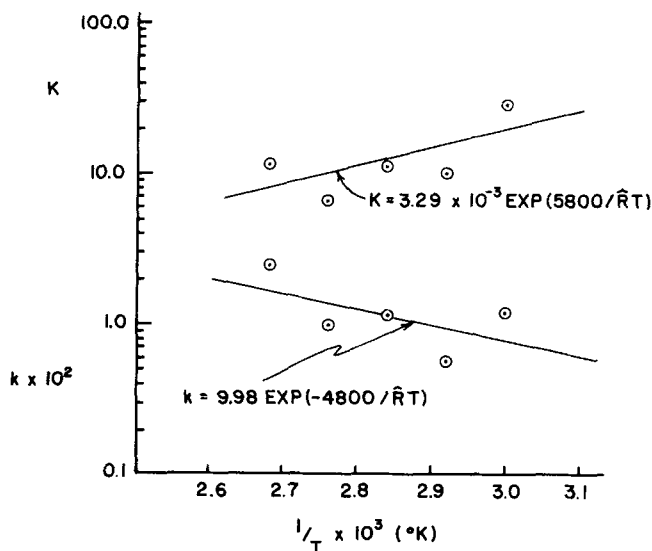


Fig. 5. Arrhenius and van't Hoff correlations for the constants of model Equation (18) at 1.0M FeCl_3 concentration level.

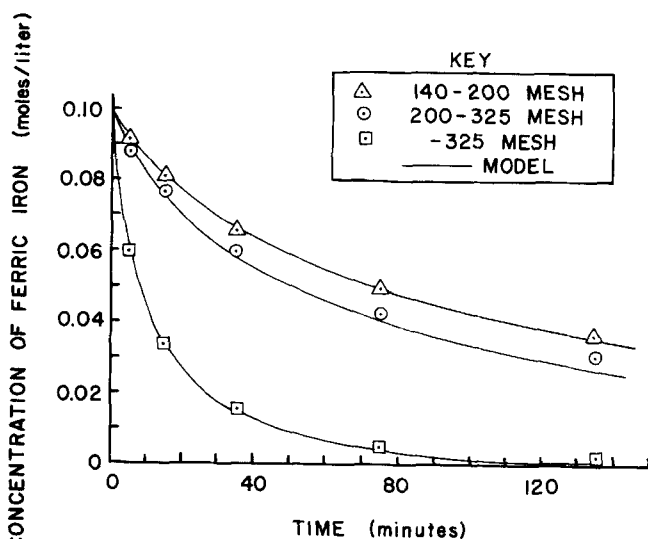


Fig. 6. Effect of particle size on reaction rate; FeCl_3 concentration level: 0.1M; stirrer speed: 680 rev/min; temperature: 80°C.

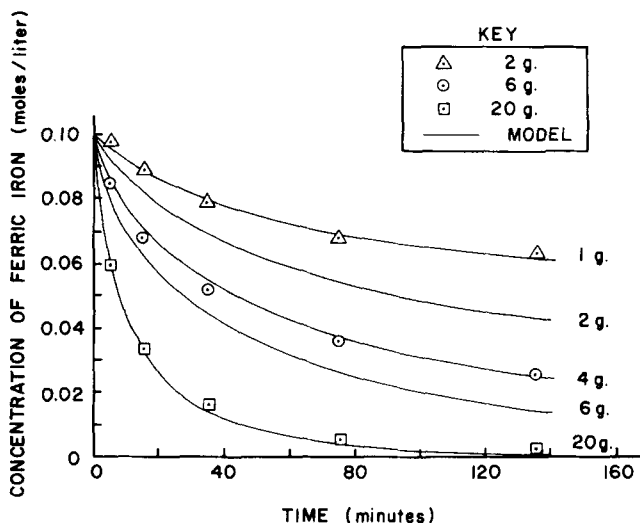


Fig. 7. Effect of pyrite loading on reaction rate; FeCl_3 concentration level: 0.1M; temperature: 80°C; stirrer speed: 680 rev/min; particle size: -325 mesh.

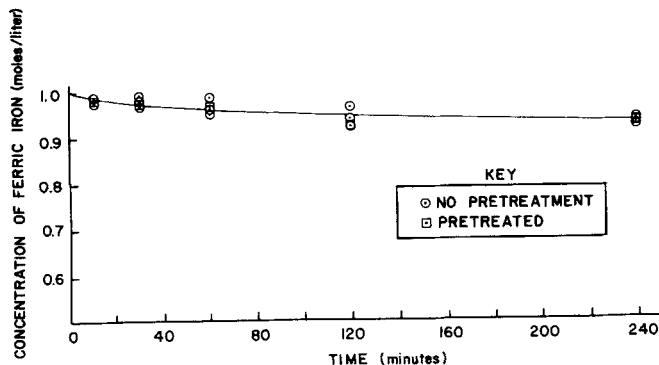


Fig. 8. Reproducibility and effect of dilute acid pretreatment on reaction rate at 1.0M FeCl_3 concentration level; loading 60.4 g/l; temperature: 80°C; coal particles: 100-200 mesh; stirrer speed: 680 rev/min.

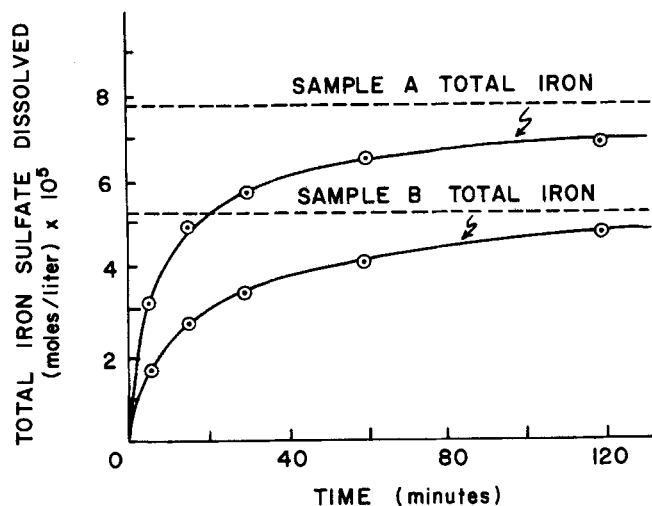


Fig. 9. Effect of treatment of coal with 0.1M HCl; temperature: 80°C; stirrer speed: 680 rev/min.

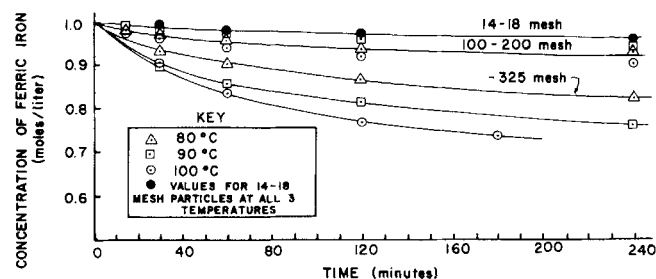


Fig. 10. Effect of coal particle size and temperature on reaction rate; concentration level: 1.0M FeCl_3 ; agitation: 680 rev/min; constant ratio of FeCl_3 to FeS_2 .

is probably a result of weathering, the conversion of which was originally pyritic sulfur to iron sulfate by exposure to moisture and air.

Figure 10 presents data for three particle size distributions in the 80° to 100°C temperature range. The results for the 14 to 18 mesh coal and the 100 to 200 mesh coal show no significant temperature effect considering reproducibility limits; however, the effect of temperature is clear for the -325 mesh coal. The anomaly at 30 min is due to the difficulty in wetting the very fine powder -325 mesh particles. Neither the other particle size coals nor the pyrite particles demonstrated this behavior. This difference in the pyrite particle and coal particle systems is at least in part attributable to the difference in the specific gravity of the two solids (5.0 and 1.25 g/cm³).

Since temperature change has an insignificant effect on the oxidation of pyrite in coal down to the 200 mesh level,

the rate is probably intraparticle diffusion limited. For the -325 mesh coal, temperature does appear to have a significant effect, indicating at least partial influence of chemical kinetics. It should be noted, however, that a significant fraction of the reacted ferric iron is reduced by coal constituents other than the pyrite.

Acid Leaching of Coal

In order to distinguish between the two forms of inorganic sulfur, the pyritic and sulfate contents of all the coal samples were measured before and after treatment. The results for total inorganic sulfur removal, that is, for both the sulfate and the pyritic forms, are presented in Table 5. Since over 85% of the sulfate is removed by a 2 hr treatment with 0.1N hydrochloric acid, the Table 5 results include complete sulfate removal as well as removal of a portion of the pyritic sulfur. The data show that the effect of particle size overshadows any effect of temperature, since even for the -325 mesh particles there is no significant difference in the inorganic sulfur removed with increasing temperature. Duplicate runs fell within a range of $\pm 4\%$, but some of the results for the largest particles show somewhat larger scatter. Table 6 shows the corresponding pyritic sulfur removed, repeated runs yielding values which lie within a 20% range.

The combination of data from Tables 5 and 6 enables one to calculate selectivities for the ferric chloride-pyrite reaction in coal. Hamersma et al. (1973) defined selectivity for such a system as the ratio of ferrous iron in the final batch liquid to the ferrous iron expected from the quantity of pyrite oxidized. By this index a selectivity of unity indicates that the ferrous iron is a result of only pyrite oxidation, whereas selectivities greater than unity indicate ferric reduction by interaction with the coal matrix. The selectivities shown in Table 7 are based on a reported SO_4/S ratio of 1.3 for coal from the Pittsburgh seam (Hamersma et al., 1973). There is on the average just as much reduction of ferric iron by interaction with the coal

TABLE 5. INORGANIC SULFUR REMOVED FROM COAL WITH 1.0M FeCl_3

	Temperature, °C		
	80	90	100
14-18 mesh	42%	39%	23%
100-200 mesh	38	34	42
-325 mesh	73	73	69
Reaction time, hr	4	4	3

TABLE 6. PYRITIC SULFUR REMOVED FROM COAL WITH 1.0M FeCl_3

	Temperature, °C		
	80	90	100
14-18 mesh	36%	36%	14%
100-200 mesh	26	14	24
-325 mesh	40	40	31
Reaction time, hr	4	4	3

TABLE 7. SELECTIVITY OF FERRIC CHLORIDE-PYRITE REACTION IN COAL

	Temperature, °C		
	80	90	100
14-18 mesh	1.0	1.1	2.0
100-200 mesh	2.0	1.9	2.4
-325 mesh	1.5	2.0	2.3
Reaction time, hr	4	4	3

matrix as by oxidation of pyrite. It should be noted further that stirring a coal slurry for several hours causes appreciable attrition of particles, especially of larger particles, and that this process contributes to the pyrite removal process. When a treated coal in the 14 to 18 mesh size range was examined after a reaction time of 4 hr, approximately 74% of the particles remained in the 14 to 18 mesh size range, but 21% dropped to the next smaller size range of 18 to 30 mesh. Some of the very fine particles agglomerated into +14 mesh particles during the filtration and drying processes.

ACKNOWLEDGMENT

This research was supported in part by a grant from the Pennsylvania Science and Engineering Foundation of the Commonwealth of Pennsylvania.

NOTATION

a, b, c, d, e, f = stoichiometric coefficients
 a_s = pyrite reaction surface area, cm^2
 a_{so} = initial pyrite reaction surface area, cm^2
 A, B = calibration constants
 C_A = concentration of liquid reactant A (ferric iron) in batch liquid, moles/l
 C_B = concentration of solid reactant B (pyrite), moles/l
 C_{Bo} = value of C_B initially, moles/l
 C_C = concentration of liquid product C (ferrous iron) in batch liquid, moles/l
 E = electrode potential, mv
 $F(\alpha)$ = weighted sum of squares defined by Equation (12)
 k = reaction velocity constant
 K = adsorption equilibrium parameter
 n = reaction order for a given component
 R = ratio of ferric iron concentration to ferrous iron concentration, $\text{Fe}^{III}/\text{Fe}^{II}$
 r = reaction rate of liquid reactant A (ferric iron)
 t = time, min
 T = temperature, $^{\circ}\text{C}$

X_I, X_{II} = reaction weights defined by Equations (4) to (6)

σ_i = standard deviation, moles/l

LITERATURE CITED

- Chandler, J. P., D. E. Hill, and H. O. Spivey, "A Program for Efficient Integration of Rate Equations and Least-Squares Fitting of Chemical Reaction Data," *Computers Biomed. Res.*, **5**, 515 (1972).
 Furusawa, T., and J. M. Smith, "Fluid-Particle and Intraparticle Mass Transport Rates in Slurries," *Ind. Eng. Chem. Fundamentals*, **12**, 197 (1973).
 Garrels, R. M., and M. E. Thompson, "Oxidation of Pyrite by Iron Sulfate Solutions," *Am. J. Sci.*, **258-A**, 57 (1960).
 Hamersma, J., E. Koutsoukos, M. Kraft, R. Meyers, G. Ogle, and L. Van Nice, "Chemical Desulfurization of Coal: Report of Bench Scale Development," Vol. 1, EPA Report No. EPA-R2-73-173a (1973).
 King, W. E., "Pyrite Oxidation in Aqueous Ferric Chloride: Rate Studies and Reactor Design," Ph.D. thesis, Univ Pa., Philadelphia (1976).
 Mathews, C. T., and R. G. Robins, "The Oxidation of Iron Disulfide by Ferric Sulfate," *Australian Chem. Eng.*, **21** (Aug., 1972).
 McKay, D. R., and J. Halpern, "A Kinetic Study of the Oxidation of Pyrite in Aqueous Suspension," *Trans. Met. Soc. AIME*, **301** (June, 1958).
 Meyers, R. A., "Desulfurize Coal Chemically," *Hydrocarbon Processing*, **93** (June, 1975).
 Mott, R. A., "Determination of Pyritic and Sulfate Sulfur in Coal," *Fuel*, **29**, 53 (1950).
 Rabinowitch, E., and W. H. Stoukmayr, "Association of Ferric Ions with Chloride, Bromide, and Hydroxyl Ions (A Spectroscopic Study)," *J. Am. Chem. Soc.*, **64**, 335 (1942).
 Sasmojo, S., "Oxidation Kinetics of Pyritic Materials in Aqueous Media," Ph.D. thesis, Ohio State Univ. (1969).
 Volk, W., *Applied Statistics for Engineers*, pp. 278ff McGraw-Hill, New York (1969).
 Walker F. E., and F. E. Hartner, "Forms of Sulfur in U.S. Coals," Pittsburgh Coal Research Center, Technical Report (Oct., 1965).
 Warren, I. H., "The Generation of Sulfuric Acid from Pyrite by Pressure Leaching," *Australian J. Appl. Sci.*, **7**, 346 (1956).

Manuscript received December 9, 1976; revision received May 16, and accepted May 27, 1977.

An Improved Corresponding States Method for Polar Fluids: Correlation of Second Virial Coefficients

An improved four-parameter corresponding states method that includes polar fluids has been developed. The four parameters are the critical temperature, the critical pressure, the radius of gyration, and a newly developed polarity factor based on the second virial coefficient. These parameters have been used to empirically correlate pure and interaction second virial coefficients of a variety of fluids.

RAMANATHAN R. TARAKAD

and

RONALD P. DANNER

Department of Chemical Engineering
 The Pennsylvania State University
 University Park, Pennsylvania 16802

SCOPE

Reliable physical and thermodynamic data on chemical compounds and their mixtures are needed for efficient design and operation of chemical processing plants.

Because experimental determination of all required data is a formidable proposition, it is usual practice to predict these data by the use of suitable correlations. Of the many correlational approaches that have been proposed, the corresponding states principle (CSP) has proved to be the most powerful framework.

Correspondence concerning this paper should be addressed to R. P. Danner. R. R. Tarakad is with Pullman Kellogg, 1300 Three Greenway Plaza East, Houston, Texas, 77046.