DESULFURIZATION OF COAL-DERIVED PYRITE USING
SOLUTIONS CONTAINING DISSOLVED OXYGEN

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M. S. Thesis Submitted to Iowa State University

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Date Transmitted: July 1979

PREPARED FOR THE U.S. DEPARTMENT OF ENERGY
UNDER CONTRACT NO. W-7405-eng-82

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15-7-16

Desulfurization of coal-derived pyrite using
solutions containing dissolved oxygen

by

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A Thesis Submitted to the
Graduate Faculty in Partial Fulfillment of
The Requirements for the Degree of
MASTER OF SCIENCE

Department: Chemical Engineering and Nuclear Engineering
Major: Chemical Engineering

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1978

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NOMENCLATURE

b	stoichiometric constant, 4/15 for this chemical leaching process.
C_{Al}	concentration of oxygen in solutions, g. mole/cm ³ .
D_e	effective diffusivity, sq. cm./sec.
E_{diff}	activation energy for diffusion, Kcal./mole.
K_g	mass transfer coefficient between fluid and particle, cm./sec.
K_s	reaction rate constant, cm./sec.
L	length of the hypodermic tubing, cm.
N	molarity of barium perchlorate.
n_i	group size of i th group.
Δp	pressure drop across the hypodermic tubing, dyne/sq. cm.
Q	oxygen flow rate, cu. cm./sec.
R	the radius of pyrite particle, cm.
R_c	1.987 cal./degree mole.
R_h	inside radius of the hypodermic tubing, cm.
r_c	the radius of the unreacted core, cm.
S^2	variance.
T	absolute temperature, °K.
t	reaction time, sec.
t_a	actual leaching time, sec.
V	titrant volume, ml.
v	sample volume, ml.
x_B	fractional sulfur conversion of pyrite, %.
μ	viscosity of oxygen, g./cm. sec.
τ	the time for complete reaction of a pyrite particle, sec.
ρ_B	molar density of pyrite used, g. mole/cu. cm.

ABSTRACT

The effect of alkaline solutions containing dissolved oxygen on coal-derived pyrite was investigated in a tubular reactor. The rate of total sulfur conversion seems to be affected by oxygen partial pressure, oxygen flow rate, particle size, pyrite charge size and system temperature.

A shrinking core model was chosen to represent this chemical leaching process. From the results obtained, it seems that ash or product-layer diffusion is the rate-limiting step for leaching with the alkaline solution/oxygen system. The effective diffusivity is about 10^{-5} sq. cm./sec. The apparent activation energy for this process is 7.97 kcal/mole in the temperature range from 121° to 175°C.

For the tubular reactor system used, the rate of sulfur extraction appears to be proportional to the oxygen partial pressure. The rate of conversion increases as the oxygen flow rate decreases to a limit of 3 ml./sec. The rate also increases as the pyrite charge size decreases. The leaching solution flow rate has a negligible effect on the total sulfur conversion.

INTRODUCTION

Coal is one of the important energy resources. In the near future, the demand for coal will increase greatly. However, burning sulfur bearing coal produces a high level of sulfur dioxide emissions. Therefore preparation of clean fuel from coal is an important technical problem to be solved. There have been numerous efforts to develop processes to remove sulfur from coal to meet governmental regulations for atmosphere emissions in coal combustion flue gases.

Traditionally coal has been cleaned by washing and density separation which can prepare only a small portion of U.S. coal resources to meet environmental and air pollution requirements. Therefore other methods have been considered for preparing cleaner coal for use. The federal government is funding the development of promising coal conversion processes. But the economic penalty is still too high to meet commercial requirements. Stack gas clean-up methods are also being developed and used for removing sulfur compounds after coal combustion. However, as for coal gasification and liquefaction, the cost of stack gas clean-up is high. Now chemical coal cleaning processes are being considered as an alternative, since they are more effective than conventional physical cleaning methods and less costly than coal conversion processes.

Sulfur in coal exists both in discrete mineral particles and chemically bound to the organic material as so-called organic sulfur. Organic sulfur is believed to occur as mercaptans (RSH), sulfides (RSR'), disulfides (RS-SR') or thiophenes (16). The inorganic sulfur appears

as sulfates and pyrites (FeS_2). The sulfate content of coal is usually small and does not cause much of a problem. Some of the pyrite can be removed either by hand-picking or conventional washing processes. But small pyrite crystals retained in the coal matrix, as well as the organic sulfur, cannot be removed by simple physical methods. Most western United States coals are low in sulfur and can be burned to meet the federal standard for sulfur dioxide emissions (1.2 lb. SO_2 /million Btu) with only physical cleaning. But the sulfur content in most of the eastern state coals is too high to burn without further cleaning.

Chemical cleaning processes have the potential for removing both mineral and organic sulfur. Table 1 lists the characteristics of several proposed chemical cleaning processes which can remove more than 90% of the pyritic sulfur and, except for the Magnex and TRW processes, some of the organic sulfur. Among these processes, the TRW or Meyers process is close to commercial development. An 8 m. ton/day pilot plant went on stream in 1977. The Battelle process has been under development since 1960, but its development has been carried only through the pre-pilot plant stage. The Magnex process has been investigated on a bench scale and currently is under further study with a 1 ton/day process development unit. The other processes are still at a bench-scale level. The KVB process is the least developed of all the six processes. The reason why none of these processes are in commercial use is that there are still problems to be overcome. It is claimed that the Battelle process substantially reduces both the mineral and organic sulfur with a modest carbon loss due to removal of

Table 1. Comparison of chemical coal cleaning processes (25)

Process	Magnex	KVB	Battelle	TRW	Ledgemont	BCM/ERDA
Method	Dry chemical pretreatment plus magnetic separation	Dry oxidation plus caustic wash	Caustic leach	Acid leach	Oxygen/water leach	Air/water leach
Reagent	Fe(CO) ₅	O ₂ , N ₂ , NO, H ₂ O, NaOH	NaOH, Ca(OH) ₂ , H ₂ O, CO ₂	Fe ₂ (SO ₄) ₃ , H ₂ O, O ₂ , naphtha	O ₂ , H ₂ O, lime	Air, H ₂ O, lime
Pressure (psia)	Atmospheric	15-300	350-2500	15-80	0-1000	500-1500
Temp. (°F)	300-400	100-500	430-660	190-270	50-450	300-400
Retention (hr)	1/10-1	1	1/4-1/2	1/2-10	1/4-24	0-1
Removal % ash	0-40	—	—	—	—	—
Pyritic S	0-90+	0-90+	0-90+	0-90+	0-90+	0-90+
Organic S	0	0-40	0-70	0	0-10	0-40
Sulfur product	Dry sulfurous mineral matter	Gypsum	H ₂ S, elemental sulfur	Iron sulfates, elemental sulfur	Gypsum	Gypsum

organic acids from the coal. But operating costs for the Battelle process are high because of caustic regeneration requirements and because of a large consumption of fuel to supply heat for the calcining operation. The TRW process has a high capital cost because of the complexity of sulfate and elemental sulfur removal. The TRW process will have difficulty in competing with less expensive, advanced physical cleaning methods since it removes only inorganic sulfur. Capital and operating costs for the Magnex process are low because it is an all dry process. But like the TRW process, the Magnex process is restricted to the removal of mineral sulfur only. Furthermore, it processes finely pulverized coals. But there are no commercial magnetic separators available today for processing dry, finely pulverized material. The KVB process involves dry oxidation of pulverized coals. It may not be practical because of the possibility of explosion. The Ledgemont and BOM/ERDA processes are similar except that the BOM/ERDA process removes larger amounts of organic sulfur. Both processes have high capital costs because of reaction conditions. Corrosion problems are severe because both processes involve dilute sulfuric acid at elevated temperature.

Besides the Ledgemont and BOM/ERDA processes, there are other chemical coal cleaning processes under development which use solutions containing dissolved oxygen. One of these processes uses a basic solution of aqua ammonia (27). The basic solution seems to help the removal of organic sulfur.

Another chemical desulfurization process has been conceived at Iowa State University. This process involves leaching fine-size coal

with hot alkaline solutions containing dissolved oxygen. Two experimental systems have been used to investigate this process, a tubular reactor and a stirred autoclave. The work described here was carried out with the tubular reactor. Coal-derived pyrite was used to investigate the kinetics of this chemical desulfurization process since pyrite has a simpler structure than coal. Furthermore, the tubular reactor was too small (0.7 cm. I.D., 15.3 cm. length) to hold enough coal to be chemically analyzed with acceptable accuracy. Some runs with coal were made, but serious problems were encountered with foaming and plugging.

Other workers at Iowa State University have tested various alkalis to see which one might give the best results for extracting sulfur when oxygen is present to react with the pyrite. Among the alkalis tested $[\text{Na}_2\text{CO}_3, \text{NaOH}, \text{Na}_3\text{PO}_4, (\text{NH}_4)_2\text{CO}_3]$, sodium carbonate gave the best results. In addition, sodium carbonate has the advantages of being low in cost and relatively noncorrosive in aqueous solutions towards steel and other materials of reactor construction (31, 32). Thus, most of the runs conducted here were carried out with a sodium carbonate solution. Evidence will be presented which indicates that the following reaction occurred:

Sulfuric acid produced by the preceding reaction was neutralized immediately as shown below:

The rate of extracting sulfur from pyrite was investigated under various conditions to determine the effects of different system parameters such as particle size, oxygen partial pressure, temperature, solution concentration, oxygen flow rate, solution flow rate, and particle charge size. Different size fractions of pyrite were used including -60/+80, -80/+100 and -120/+140 mesh under oxygen partial pressures of 48, 98 and 198 lb./sq. in. (absolute). The effect of temperature was investigated in the range of 121° to 175°C. The effects of oxygen flow rate in the range of 0.003 to 0.04 cu. ft./min., liquid flow rate in the range of 1.5 to 3.0 ml./sec., and charge size in the range of 2.5 to 15 g. were also investigated. Furthermore, the effects of sodium carbonate concentrations from 0.5 to 6 wt. % and sodium bicarbonate concentrations from 1 to 4 wt. % were studied.

Several kinetic models were investigated to see whether any of them would adequately represent the reaction system. These models included the shrinking core particle model described by Levenspiel (18) for the case where the overall rate of reaction is controlled by film diffusion, ash or product-layer diffusion, or chemical reaction, respectively. The equations representing these models were fitted to the experimental results to determine whether any one of the models would provide an adequate representation of the data.

LITERATURE REVIEW

A general review of coal desulfurization methods has been published recently by Meyers (22) and reports of recent research on both physical and chemical methods of removing sulfur from coal have been compiled and edited by Wheelock (35). Meyers' book on coal desulfurization provides a thorough review of methods for removing sulfur from coal by chemical means. The book edited by Wheelock is based partly on a symposium held at the 173rd American Chemical Society Meeting. This book includes reports of basic and applied research and development on physical separation methods and on chemical processes.

Numerous processes for chemical extraction of sulfur from coal or sulfide minerals have been proposed. This survey of previous work reviews chemical leaching processes which use solutions containing dissolved oxygen to extract sulfur from pyrite as well as other relevant sulfide minerals and coal.

Extraction of Sulfur from Pyrite and Other Sulfur Minerals

Burke and Downs (7) investigated several variables to determine their influence on the rate of oxidation of pyrite by an aqueous solution. They used 1.0 N. hydrochloric acid, 28°C, and oxygen which was circulated through the system at atmosphere pressure for 2 hr. as "standard reference conditions." The effect of each variable was determined by changing one of the standard reference conditions at a time. They claimed that when water was used instead of 1.0 N. hydrochloric acid, a film of ferrous hydroxide formed on the surface of the pyrite.

Therefore, it is probable that the effect of hydrogen-ion concentration is simply to prevent the inhibition of the reaction caused by the formation of hydroxide films. They also observed that the rate of reaction was greatly reduced when experiments were conducted in the absence of oxygen. The rate was determined by the chemical reactivity of the pyrite sulfur and not by the physical conditions controlling the supply of the reacting materials.

Stenhouse and Armstrong (30) investigated the oxidation of pyrite in sodium hydroxide solutions under oxygen pressure. The effects of average particle size, oxygen partial pressure, system temperature and concentration of the caustic solution on oxygen consumption were investigated in a rocking-type autoclave. They concluded that the rate of oxidation is inversely proportional to the square of the average particle size. They also observed that the rate of oxidation of iron is proportional to the square root of the oxygen partial pressure. The rate of oxidation of pyrite was also studied in the range of caustic concentration from 1 to 2 molar. The rate of oxidation increased as the caustic concentration increased. From the effect of temperature on the rate of reaction, a very low apparent activation energy of the 4 Kcal./mole was obtained. Furthermore, a model for this process was proposed. In this model, sulfur diffuses through an iron oxide layer to the surface of the particle and reacts with oxygen. Both Fe_2O_3 and Fe_3O_4 were identified in the solid residue.

Andersen et al. (2) investigated the kinetics of the oxidation of galena (PbS) in sodium hydroxide solutions under oxygen pressure. The effects of temperature, oxygen pressure, and sodium hydroxide

concentration on the oxidation rate were determined. They observed that the rate of oxidation of galena was proportional to the square root of the oxygen partial pressure at 123°C in 0.5 N. sodium hydroxide solution. They also claimed that the reaction rate decreased as the caustic concentration increased from 0.5 to 6.0 N. The effect of temperature on the rate of reaction was investigated in the range from 93° to 175°C using a 0.5 N. sodium hydroxide solution and an oxygen partial pressure of 5.64 atm. An apparent activation energy of 6.3 Kcal./mole was determined. They also proposed that "the rate controlling step of the reaction is a heterogeneous process occurring at the galena surface and not a homogeneous reaction in solution."

Forward and Halpern (11) described a new process for extracting uranium from ores containing sulfidic minerals. This method comprised treating an aqueous pulp of the ore with air or oxygen at elevated temperatures and pressures. The acid required to extract the uranium is generated during leaching by oxidation of the sulfides. Several possible chemical reactions which might occur during leaching of pyrite with aqueous media under oxygen pressure were proposed and are shown below.

Gray (17) conducted a similar investigation of "the extraction of uranium from a pyritic ore by acid pressure leaching." He claimed that initially the iron and sulfur in the mineral are oxidized according to Equation 4. The ferrous sulfate is further oxidized to ferric sulfate as shown below.

Finally the ferric sulfate hydrolyzes to give insoluble basic ferric hydroxide and sulfuric acid:

Dresher et al. (10) made a kinetic study of the leaching of molybdenite (MoS_2) and evaluated the effects of temperature, oxygen pressure and potassium hydroxide concentration on the rate of leaching. Measurements were made in the temperature range of 100° to 175°C and in the oxygen pressure range of 0 to 700 lb./sq. in. (absolute). Under these conditions, both oxygen pressure and potassium hydroxide concentration were found to control the rate of leaching. The reaction rate was a function of the potassium hydroxide concentration and the maximum rate of reaction occurred when a 1 mole/liter potassium hydroxide solution was used. One of the possible explanations for the effect of alkali concentration is that the concentration of oxygen dissolved in the solution varied with the potassium hydroxide concentration. They also declared that the rate of leaching in sodium carbonate solutions was much slower than in potassium hydroxide solutions because of the buffering action of sodium carbonate and the resulting lower hydroxyl

ion concentration. They explained the kinetics by means of a steady-state analysis involving adsorption of oxygen at the surface followed by a configurational rearrangement of the oxygen on the surface. The oxidation product is then removed from the surface by a reaction with hydroxyl ions.

Another study of the pressure leaching of pyrite was made by Warren (34). He considered the following factors which might affect the rate of leaching: temperature, oxygen partial pressure, source and particle size of pyrite, and pH of the reaction medium. The effect of temperature on the rate of leaching was investigated on the range of 130°-210°C at 25 lb./sq. in. (absolute) oxygen partial pressure. The activation energy was found to be 20 Kcal./mole in this range. He also observed that the rate of oxidation of pyrite is proportional to the square root of the oxygen partial pressure from 25 to 200 lb./sq. in. (absolute). No relation between the reaction rate and the particle size was given. But he also buffered the reaction solution by using calcium carbonate and aluminum powder to investigate the effect of pH on the rate of reaction and found that the rate of reaction decreased as the pH increased from 0.5 to 6.5. Therefore he also claimed that the function of the acid is to prevent formation of an iron oxide film on the pyrite surface. Finally, he declared "the step controlling the rate of oxidation would appear to be a heterogeneous process at the pyrite surface, the oxygen participating in this process being in a dissociated rather than a molecular state; which is indicated by the dependence of the rate of oxidation on the square root of the oxygen partial pressure."

Forward and Halpern (12) reviewed hydrometallurgical processes involving pyrite as well as other metal compounds. They claimed that most of the heterogeneous reactions involved in hydrometallurgical processes consisted of the following steps:

- "(1) absorption of gaseous reactants (if any) by the solution;
- (2) transport of dissolved reactants from the main body of the solution to the solid-solution interface;
- (3) reaction on the surface (including adsorption and desorption steps);
- (4) transport of the soluble desorbed products into the main body of the solution."

They also found that when using gaseous oxygen under pressure in neutral or acidic solutions, the rate of oxidation was usually slower than in alkaline solutions. At temperatures ranging from 100° to 125°C with a solution pH below 1.5, and with a high oxygen partial pressure, pyrite was oxidized to sulfate almost exclusively in an autoclave.

A kinetic study of the oxidation of pyrite in acidic aqueous suspensions by molecular oxygen, at temperatures ranging from 100° to 130°C, was made with an autoclave by McKay and Halpern (21). They reported that the total rate of oxidation was directly proportional to the total surface area of the pyrite. The rate of oxidation was independent of the composition of the acidic solutions. But low acidities with high temperatures favored the formation of sulfuric acid while high acidities with low temperatures favored the formation of elemental sulfur. Furthermore, the total rate of oxidation of pyrite was directly proportional to the oxygen partial pressure, which is contrary to the findings of Warren (34). The apparent activation energy was 13.3 Kcal/

mole in the temperature range from 100° to 130°C. The rate-determining step proposed by McKay and Halpern for the oxidation of pyrite was "a heterogeneous process on the pyrite surface which involves only an oxygen molecule. This is supported by the observation that the rate is first order in oxygen and independent of the solution composition."

Cornelius and Woodcock (9) reported on the effects of several important variables which affect the oxidation rate of pyrite with oxygen in an aqueous suspension. They measured the ferrous ion and sulfate ion concentrations during the conduct of the investigation. The observed rate of ferrous ion production was approximately proportional to the square root of the oxygen partial pressure at 165°C. Also, the observed rate of ferrous ion production was directly proportional to the surface area of the pyrite. In addition an increase in the temperature gave an increase in the observed rate of ferrous ion production at temperatures ranging from 130° to 165°C. The residue was examined and found to be principally iron oxide.

Burkin and Edwards (8) conducted experiments involving oxygen pressure leaching of pyrite with alkaline solutions in a 2.5 l. stainless steel autoclave. The standard experimental conditions included temperatures in the range of 60° to 150°C and 2% W/V sodium hydroxide. The main reason for carrying out these experiments was to examine the iron oxide coatings formed during the experiments. They also reported that "evidence obtained more recently by X-ray powder diffraction and by electron diffraction has shown that the final oxidation product we obtained on leaching pyrite was, under most conditions, maghemite ($\gamma\text{Fe}_2\text{O}_3$)."

In addition, some other interesting results were observed.

No reaction occurred in the absence of oxygen even when a higher caustic concentration (10% W/V) was used at 150°C for 4 hr. With an oxygen partial pressure higher than 40 lb./sq. in. (absolute), the rate of decomposition of pyrite increased with oxygen partial pressure. When 200 lb./sq. in. (absolute) air was used, the rate of decomposition of pyrite increased as the concentration of sodium hydroxide increased up to 2% W/V. Above this concentration, in the temperature range studied, a slight lowering of the rate was observed as the alkali concentration increased. A possible explanation for the lowering of the rate is the lower solubility of oxygen in more concentrated solutions. They also observed that perfect crystals were attacked by alkali and oxygen less rapidly than particles made up of several crystals. They suggested that the latter were attacked more rapidly because of greater effective surface area. The proposed stoichiometry of the reaction is as follows.

The mechanism for the oxidation of pyrite was not discussed in this paper. The apparent activation energy of the initial reaction was found to be 9 Kcal./mole.

Morth and Smith (23) investigated the kinetics of the sulfide-to-sulfate reaction by conducting experiments involving oxidation of pyrite by water and oxygen in the temperature range of 20° to 50°C. Four important experimental results were obtained: 1) flow rates of the recirculated fluid had no effect on oxygen absorption rates, 2) rates were constant throughout the test period (one to two weeks),

removal of iron from solution did not affect rates, and 4) the activation energy determined from an Arrhenius plot was 14 Kcal./mole. It seemed evident that the reaction rate in the recirculating-type equipment was not influenced by diffusion resistances or by the desorption of oxidation products. Morth and Smith also claimed that water is involved in this system as a reaction medium rather than as a reactant. The basic function of water is probably to provide a medium for dissolving and removing the oxidation products from the pyrite surface. They proposed a possible mechanism which involves the dissociation of oxygen when adsorbed on "reactive sites" of pyrite. The proposed rate-limiting step for this mechanism is the decomposition of the activated complex formed by dissociated oxygen.

Majima and Peters (20) investigated the oxidation rates of pyrite and other sulfide minerals at 120°C, using aqueous phosphate solutions buffered to pH = 2.7, 7.1 and 11.2 as well as in a 1.0 N. sodium hydroxide solution and in ammonia-containing solutions. They found that in basic solutions elemental sulfur was never formed while in acid solutions the oxidation of many sulfide minerals led to the formation of elemental sulfur. They also observed that the mineral pyrite showed a higher oxidation rate in a 1.0 N. caustic solution than in neutral or acidic solutions.

Sasmojo (29) investigated the oxidation of pyrite in aqueous media under two different environments at a constant temperature of 25°C. In one case oxygen was excluded from the reaction system and ferric ion was the oxidant. In the other case oxygen was the oxidizing agent. The oxidation by oxygen was conducted at pH of 2.2. The

effect of iron in the solution was investigated. The results showed that in aqueous media the oxidation rate of pyrite by oxygen is not controlled by the rate of oxidation of ferrous ions to ferric ions in the solution. Sasmojo also observed that the oxidation of pyrite by oxygen does not require the intermediate action of ferric ions in the solution.

Bunn (5) investigated the effect of aqueous sodium hydroxide solutions on pyrites in a tubular reactor. He also made three runs using a sodium carbonate solution containing dissolved oxygen to compare the results with those obtained with sodium hydroxide solutions without oxygen. He claimed that "since there were problems with the method of feeding oxygen and the oxygen flow rate could not be measured, the results presented here are considered preliminary and perhaps not typical of what might be expected from this system." But he did point out that the rate of pyrite leaching using the sodium carbonate/oxygen system was comparable or superior to the rate using the sodium hydroxide system.

Desulfurization of Coal

Burghardt's work (6) showed that the pyritic sulfur in coal could be oxidized by oxygen in aqueous solution. In 1926, Li and Parr (19) found that 15-24% total sulfur in Illinois coals (-80 mesh) could be oxidized at 100°C by oxygen saturated with moisture over six weeks while only 3-20% total sulfur in Illinois coals could be oxidized at 25°C. The oxidation rates of pyrite and marcasite (-325 mesh) were

also investigated under the conditions cited above. It was observed, for pyrite or marcasite, that the rate of oxidation is directly proportional to the temperature and inversely proportional to the diameter of the particles. It was concluded that moisture is important for the oxidation of pyrite. Dry air or oxygen does not react readily with pyrites.

In 1933, Nelson et al. (24) investigated a possible method of oxidizing and leaching pyritic sulfur in bituminous coal. The basic experiments were conducted in a batch system. Water was placed with coal in the reaction system and heated to the desired temperature while air was passed through the apparatus at a rate measured by means of a calibrated flow meter. Approximately 79% pyritic sulfur was removed from 25 g. pulverized coal suspended in 4.5 liter water at 90°C for 7 days. The air flow rate was kept as at 4 cu. ft./min. The rate of oxidation of pyritic sulfur increased as the temperature increased. The oxidation rate of pyritic sulfur in fine-size coal was found to be faster than that in coarse coal. The rate was inversely proportional to the average diameter of the coal particles. In this system, the air flow rate was not important for the process. When ferric sulfate was added to the system, in the temperature range from 22° to 70°C, the conversion of pyritic sulfur increased. When a small amount of chlorine gas was added to the air stream, a larger amount of pyritic sulfur was oxidized than when pure air was used. But no organic sulfur was removed during any of the experiments.

Agarwal et al. (1) estimated that approximately 10 to 15% of U.S. coal reserves have a low enough organic sulfur content that present

laws could be met with pyrite removal. An estimated additional 20 to 30% of U.S. coal could be used under the present law if up to 60% of the organic sulfur were removed from pyrite-free coal. So they suggested that the law would have to be changed in order to permit utilization of most of the U.S. coal reserves. In addition investment costs for pipeline gas, coal liquefaction, coal gasification, stack gas clean-up, and pyrite removal by the Ledge-mont process were compared. The costs were compared on an annual ton basis, which is the total investment divided by the plant capacity (ton of coal/year). The resultant rates were \$76 per annual ton for pipeline gas, \$60 per annual ton for coal liquefaction, \$70 per annual ton for low Btu gasification, \$55 per annual ton for stack gas clean-up and \$35 per annual ton for the Ledge-mont process which can remove more than 90% pyritic sulfur. Notice that the best conventional coal cleaning plant cost is \$4 per annual ton, but it can only remove up to 60% of the pyritic sulfur. Since the cost for the Ledge-mont process is comparatively low for an efficient pyrite removal process, it may be a possible alternative to physical coal cleaning. Agarwal et al. also described the Ledge-mont process. This process involves using oxygen and water to oxidize the pyritic sulfur in coal. The coal is subjected to physical cleaning first. The coal slurry is then pumped into a leaching reactor under suitable conditions of temperature, oxygen pressure and slurry density. The pyritic sulfur is converted to sulfate only. This process has several advantages: no elemental sulfur is formed; no regeneration of the leach solution is required; less washing of the product is required; and the reaction time is shorter than for ferric sulfate leaching. The

investigators claimed that 100% of the pyritic sulfur is removed under the conditions of 130°C, 300 lb./sq. in. (absolute) oxygen pressure, slurry density of 9%, and retention time of 2 hr.

Sareen et al. (28) conducted further studies of the Ledge-mont Oxygen Leaching (LOL) process, i.e., the use of oxygen/water for removal of sulfur from coal. They investigated the effect of temperature at 130°C, 100°C, and 80°C at 300 psi oxygen pressure. An activation energy of 14 Kcal./mole was found for the reaction of oxygen with pyrite, and this value compared favorably with that determined by previous investigations. But coal oxidation was even more temperature sensitive, with an activation energy of 17.64 Kcal./mole. Although pyrite oxidation would increase with temperature, an economic penalty would occur because of Btu losses and increased oxygen consumption. The effect of oxygen pressure was also investigated. They found that the rate of sulfur removal was proportional to the square root of the oxygen partial pressure. Finally, through an investigation of the oxygen requirement, they found that "the oxygen uptake by the coals appears to be pH dependent. This uptake may be minimized by operating the process at a high enough pH by considering the use of buffering agents." No organic sulfur removal was reported.

Work on another process has also been conducted at Kennecott Copper Corporation. Sareen (27) reported the process utilizes an ammonia/oxygen system to remove the pyritic sulfur and some of the organic sulfur from coal. Experiments were conducted with an autoclave at 130°C and 300 lb./sq. in. oxygen pressure. This system removed almost all of the pyritic sulfur and up to 25% of the organic sulfur

in 2.0 hr. It was found that increasing the reaction time and the ammonia concentration (from 0.5 molar to 5 molar) improved the extent of the organic sulfur removal. But changing the ammonia concentration had no effect on the pyritic sulfur removal. The carbon losses for this system were somewhat higher than for the LOL process because of the formation of coal acids.

Friedman et al. (13) has proposed a method which could remove more than 90% of the pyritic sulfur and up to 40% of the organic sulfur from coal as sulfuric acid. This process operates under conditions where the partial pressure of oxygen in air is approximately equal to the pressure of pure oxygen employed in the LOL process and at temperatures high enough to remove the organic sulfur. Air pressure up to 1,000 lb./sq. in. and temperatures from 140° to 200°C were used in the investigation. Friedman et al. hypothesized the removal of organic sulfur from coal involves two steps: first, the oxidation of organic sulfur to sulfone; and second, the elimination of sulfur dioxide by a base. The coal losses for this process are usually less than 10%. The cost for this method would be between the less costly but less completely physical coal cleaning methods and the more costly but more complete coal conversion techniques. In another paper, Friedman and Warzinski (14) also made comparisons of the costs and fuel value losses among different coal cleaning methods.

Tai et al. (32, 33) investigated the desulfurization of coal by oxidation in alkaline solutions. They used coal as well as pyrite to conduct the leaching experiments, using a stirred pressure reactor in both cases. For the pyrite runs, -200/+230 mesh pyrite particles were

leached for 1.0 hr. at 150°C under an oxygen partial pressure of 3.3 atm. The best results were obtained with a sodium carbonate solution concentration ranging from 1-3 wt. %. Almost all of the sulfur was extracted from the pyrite. Sodium hydroxide, sodium phosphate and ammonia carbonate solutions were used as well. The ammonium carbonate solution was not as effective as the others because it was less basic. Under the same conditions, the results of the sodium carbonate runs showed the sulfur conversion increased almost exponentially as the particle size was reduced. Increasing the temperature or oxygen partial pressure increased the sulfur conversion. For the coal runs, among various alkalies tested [Na_2CO_3 , NaOH , Na_3PO_4 , CaCO_3 , $\text{Ca}(\text{OH})_2$, and $(\text{NH}_4)_2\text{CO}_3$], sodium carbonate gave the best results also. When leaching conditions of 150°C, 3.3 atm. oxygen partial pressure, coal finer than 200 mesh, and a reaction time of 2 hr. were employed, two-thirds of the pyritic sulfur and almost all of the sulfate sulfur were removed. Further experiments were carried out by combining physical and chemical cleaning processes. The inorganic sulfur content for three different coals was reduced 93-95%.

EXPERIMENTAL METHOD

Apparatus

The experimental apparatus for investigation of the chemical desulfurization process was divided into three portions:

1. Liquid feed system
2. Tubular reactor system
3. Oxygen supply and control system.

These three portions were connected by a T-joint. The overall flow diagram is shown in Figure 1.

Liquid feed system

Liquid could be fed from two sources, either from a 50 gal. stainless steel deionized water tank or a 4 liter reagent flask. Selection of the feed source was controlled by two electric solenoid valves operated by a switch on the control panel.

The liquid feed was pumped by a positive displacement variable stroke pump ($3/4$ h.p., McCannatrol P/DI pump by Hills-McCanna Company). This pump could deliver from 1 to 5 ml./sec.

A pneumatic accumulator was used as a pulsation dampener to provide a smoother flow of liquid. It consisted of a 24 in. length of $1/2$ in. stainless steel pipe and was attached directly to the discharge of the pump. The other end of the accumulator was connected to a nitrogen cylinder. The volume of gas in the accumulator was controlled by feeding nitrogen to drive out a measured amount of water at a known system pressure.

Figure 1. Apparatus for investigating chemical desulfurization.

The pressure of the system was measured with two bourdon tube gauges. The pressure gauge upstream from the reactor had a range of 0 to 1000 lb./sq. in. and the pressure gauge downstream from the reactor had a range of 0 to 5000 lb./sq. in. The two gauges were calibrated by a "dead weight tester." All gauge lines were 1/8 in. stainless steel tubing.

Tubular reactor system

A fluidized sand bath was provided for heating the reaction system. The fluidized bed of sand was 12 in. in diameter and 4 ft. deep. Silica sand was used in the sand bath. The bed was insulated with 9 in. of Fiberfrax bulk fiber which was enclosed in an aluminum jacket.

Heating of the bed was by two Chromolox 0.457 in. diameter TRID-160 Incoloy sheathed resistance heating elements. Electrical power to the heaters was supplied and controlled by a 208 V. A.C. variable transformer. The temperature of the sand bath was measured by a potentiometer connected to a chromel-alumel thermocouple in a 1/8 in. O.D. Inconel thermowell.

The sand bath was fluidized with air measured by a rotameter manufactured by Brooks Rotameter Company. The flow rate of air was set at 15 cu. ft./min. which was controlled by a valve. The air passed through a gas distributor plate which was a 12 in. diameter disc of Dynapore porous stainless steel.

The process liquid was heated to reaction temperature in a coil made of 15 ft. of Inconel tubing which was immersed in the fluidized bed. The heated liquid then passed through the packed bed reactor. The reactor was a 15.3 cm. long piece of 0.7 cm. I.D. x 1.4 cm. O.D.

Inconel 600 tubing (Figure 2). The packed section was about 5 cm. long when the reactor was charged with 5 g. pyrite (shaded area in Figure 2). After leaving the reactor, the liquid was cooled at process pressure in a 20 ft. long, single-pass, counter-flow, double-pipe heat exchanger. The heat exchanger was made of standard tube fittings (1/4 in. tubing inserted into 1/2 in. tubing).

System pressure was controlled by means of a 0.047 in. orifice metering valve. Samples of liquid effluent were collected in a 250 ml. separatory funnel and then transferred to flasks to await chemical analysis. The size of the PYREX flasks depended on the liquid flow rate. For example, 500 ml. flasks were used for a 1.5 ml./sec. liquid flow rate and 1000 ml. flasks were used for a 3.0 ml./sec. liquid flow rate, respectively.

Oxygen supply and control system

Oxygen was fed from an oxygen cylinder equipped with a pressure reducer and regulator. A needle valve controlled the oxygen flow. The oxygen system pressure was measured with a pressure gauge (0 to 1500 lb./sq. in.) following the needle valve.

A piece of 0.013 in. inside diameter by 24 in. long hypodermic tubing was used as a flow resistance element. The pressure drop provided by the hypodermic tubing was measured with a differential pressure gauge. The gauge was manufactured by Merian Instrument Company and had a range of 0 to 50 in. water column. A bypass valve was used to protect the differential pressure gauge. A backpressure regulator

Figure 2. The tubular reactor.

was used to regulate the oxygen system pressure. The whole oxygen supply and control system is shown as Figure 3.

From the differential pressure measurement, the oxygen flow rate was given by (3)

$$Q = \frac{\pi(\Delta p)R_h^4}{8\mu L} \quad (11)$$

A check valve following the backpressure regulator was used as a safety measure to prevent back flow of alkali solution.

Oxygen passed through the tubular reactor and the separatory funnel. The total volume of oxygen was measured by a wet test meter manufactured by Precision Scientific Company.

Experimental Procedure

For each run, the liquid feed system was filled with deionized water before the reactor was inserted in the system. A small, measured quantity of ground and sized pyrite was placed in the tubular reactor. The loaded reactor was placed in the preheated fluidized sand bath and connected to the rest of the system (Figure 1).

The liquid feed system and the tubular reactor system were then pressurized with nitrogen and the feed pump started (this was time = 0). At first deionized water was pumped through the systems to wash out the water soluble sulfate. The nitrogen flow was stopped as soon as the systems were pressurized.

Stream pressure built up in the tubular reactor and increased the total system pressure (read from the upstream pressure gauge) to the

Figure 3. Oxygen supply and control system.

desired value. By adjusting the pressure reducing valve at the outlet end of the tubular reactor system, a constant system pressure could be maintained.

After rinsing the system for about 6 min., the feed solution was switched to a dilute alkaline solution. Almost concurrently a metered flow of oxygen was started. The oxygen flow rate was adjusted to the desired value by the needle valve ahead of the hypodermic tubing resistance element. The flow rate was measured by the differential pressure gauge which was calibrated with the wet test meter. No special effort was made to measure the oxygen partial pressure. It was taken to be the difference between the total system pressure and the vapor pressure of water at the system temperature. Again the pressure reducing valve located downstream from the reactor was adjusted to provide the desired system pressure. The run was continued while maintaining constant conditions of temperature, pressure, and liquid and gaseous flow rates.

During a run, the liquid effluent was collected in a series of measured portions which were analyzed later for sulfur using the method provided by Fritz and Yamamura (15). The detailed analysis procedure is described in Appendix B. Before analysis, the liquid samples were treated with hydrogen peroxide to assure that all of the soluble sulfur compounds were completely converted to sulfates.

After a run was completed, the oxygen flow was interrupted, the feed pump was stopped, and the reaction system was purged with nitrogen gas to drive out all the liquid. The tubular reactor was disconnected, emptied, and the solid residue was dried and weighed. The residue

was analyzed for total sulfur and iron by the Analytical Services Group of the Ames Laboratory.

Pyrite Samples

The pyrite used for this series of experiments was found in the strata just above and next to the lower coal seam of the ISU Demonstration Mine No. 1. The pyrite was recovered by hand-picking. It was cleaned, crushed, ground and screened to the desired size.

The composition of the pyrite is shown in Table 2. Since pure pyrites have about 53% sulfur, it is obvious that the pyrite used here was far from being pure. Also since the atomic ratio of sulfur to iron was not 2.0 as required for pure pyrite, not all of the iron was present in the form of FeS_2 .

Table 2. Pyrite analysis

Sample control No.	U.S. mesh size	Total sulfur, wt. %	Total iron, wt. %
2370	-120/+140	39.82	41.94
2658	-80/+100	41.43	42.80
2653	-60/+80	39.64	42.22

RESULTS AND DISCUSSION

Introduction

The experimental conditions employed during the series of runs and the results for each run are shown in Appendix A. The particle size, total system pressure, pyrite charge, temperature, concentration and type of alkali, and liquid and gaseous feed rates were varied among runs.

The results of a typical run will be presented first. The concentration of sulfur in the reactor effluent and the corresponding conversion as a function of time will be presented and discussed.

The principles of the shrinking core model will also be described. By means of this model the kinetics of the chemical leaching process will be analyzed.

After summarizing the kinetic data, the effects of different experimental conditions will be shown and discussed to aid in optimizing the process.

Concentration-Time Data

Typical experimental results are shown in Figures 4 and 5 for runs 62 and 35, respectively. In these diagrams the sulfur concentration of the reactor effluent is plotted versus terminal sampling time measured from the time when the feed pump was turned on. A total pressure of 100 lb./sq. in. (gauge) was employed in run 62 and 250 lb./sq. in. (gauge) in run 35 while other conditions were the same. All of the runs with sodium carbonate/oxygen followed the same trend. The

Figure 4. Sample concentration versus terminal sample time for run 62.

Figure 5. Sample concentration versus terminal sample time for run 35.

sulfur concentrations reported here are based on an analysis of the liquid effluent. Average values are given for each time interval.

Point A in Figure 4 indicates the time of appearance of the air bubble which was trapped in the reactor assembly before it was inserted in the sand bath. The peak after A is probably due to rapid leaching of water soluble sulfate. Point B corresponds to the time of switching to the solution of sodium carbonate and starting to feed oxygen. Point C indicates the time of appearance of the first oxygen bubble. The sodium carbonate solution and oxygen appeared in the separatory funnel almost simultaneously. The peak after C is the first sample taken after the pyrite was attacked by oxygen and the sodium carbonate solution. The sulfur concentration then decreased to an almost constant value.

The maximum sulfur concentration for run 35 was much higher than that for run 62. The much more rapid change in sulfur concentration for run 35 was probably due to a higher concentration of oxygen in solution because of the higher oxygen partial pressure.

For run 35, the sulfur concentration decreased much faster after the peak concentration than it did following the peak concentration in run 62. Consequently after a reaction time of 40 min., the concentration in run 35 was lower than in run 62.

Conversion-Time Data

The total sulfur conversion was based on the actual total sulfur content of the raw pyrite (e.g., from Table 2, the total sulfur content

is 39.8% for -120/+140 mesh pyrite). The total sulfur extracted from the solids divided by the total sulfur content of the raw pyrite gave the total sulfur conversion. The detailed method of calculation is shown in Appendix B.

Figures 6 and 7 are conversion versus time curves for typical runs. The slope of these curves is the rate of extraction. All the runs for the sodium carbonate/oxygen system showed a tendency for the reaction rate to decrease as the reaction proceeded.

In general, the sulfur conversion based on liquid effluent analysis was lower than that based on solid residue analysis. The differences were in the range of 0 to 20%. The reason for these differences is uncertain. One of the possibilities is the sulfur in the liquid effluent was not converted completely to sulfate which is the only form determined by the method of analysis. In run 35 (Figure 7), the conversion approached a maximum of 93% based on the liquid analysis or 98% based on the solids analysis. In run 62 (Figure 6), the total sulfur conversion after leaching for an hour was only 61.3% based on the liquid analysis but 73.1% based on the solids analysis.

Modeling

Model description

Some of the leached particles as well as the unleached particles were examined with a scanning electron microscope by Professor R. T. Greer (Figures 8 and 9). Individual pyrite particles seemed to be formed of aggregates of small grains. Professor Greer's analysis

Figure 6. Total sulfur conversion versus terminal sample time for run 62.

Figure 7. Total sulfur conversion versus terminal sample time for run 35.

LEACHED PYRITE

Figure 8. Photomicrographs of leached particles.

UNLEACHED PYRITE

LEACHED PYRITE

2 μ

Figure 9. The grain structure of leached particles was much finer than that of unleached particles.

showed that the pyrite grains were converted to hematite grains which were smaller in size. But the overall size and shape of the leached particles were similar to those of the unleached particles.

A shrinking core model described by Levenspiel (18) was investigated to see if it could represent the kinetics of the pyrite reaction with oxygen in an alkaline medium. Similar reactions may be represented by the equation

The shrinking core model assumes that the reaction occurs first at the surface of the particle. The reaction zone then moves inward and leaves behind a shell of completely reacted material. This material is referred to as "ash." The unreacted core of the particle shrinks in size during the reaction. A representation of the shrinking core model is shown in Figure 10.

This model was first developed by Yagi and Kunii (36), who proposed the following reaction steps:

- Step 1. Diffusion of reactant A through the fluid film surrounding the particle to the surface of the solid.
- Step 2. Diffusion of reactant A through the ash layer to the surface of the unreacted core.
- Step 3. Reaction of reactant A with solid at the reaction surface.
- Step 4. Diffusion of gaseous or liquid products through the ash layer to the surface of the solid.
- Step 5. Diffusion of gaseous or liquid products through the fluid film back into the main body of the fluid.

Figure 10. Representation of shrinking core model for single particle.

The relative positions of the fluid film, the reacted shell and the unreacted core are also shown in Figure 10. One of the above steps may be the rate-limiting step. Furthermore, if the reaction is irreversible and no liquid or gaseous products are formed, steps 4 and 5 will not be rate-controlling steps.

Levenspiel (18) analyzed the shrinking core model for the three cases corresponding to the rate of reaction controlled by steps 1, 2 or 3 above. This analysis gave the following equations:

(1) Diffusion through fluid film controls

$$\frac{t}{\tau} = 1 - \left(\frac{r_c}{R}\right)^3 = x_B \quad (13)$$

$$\tau = \frac{\rho_B R}{3b_k C_{A1}} \quad (14)$$

(2) Diffusion through ash layer controls

$$\frac{t}{\tau} = 1 - 3(1 - x_B)^{2/3} + 2(1 - x_B) = p(x_B) \quad (15)$$

$$\tau = \frac{\rho_B R^2}{6b_D C_{A1}} \quad (16)$$

(3) Chemical reaction controls

$$\frac{t}{\tau} = 1 - (1 - x_B)^{1/3} = g(x_B) \quad (17)$$

$$\tau = \frac{\rho_B R}{bK_s C_{A1}} \quad (18)$$

For the proposed conditions of chemical leaching of pyrite with the sodium carbonate/oxygen system, one of the products was found to be hematite (Fe_2O_3). The reactions appear to be as follows:

The primary reaction involves reacting pyrite with oxygen dissolved in water. The secondary reaction involves neutralizing sulfuric acid produced by the primary reaction. In this system, iron pyrite is solid B and dissolved oxygen is reactant A.

Curve fitting

The functions x_B , $p(x_B)$ and $g(x_B)$ were plotted versus t for each run to see whether a linear plot would result with any of the functions. If one of these functions should yield a straight line, this would be an indication that the corresponding step controls the reaction rate. For all of the sodium carbonate and sodium bicarbonate runs, a plot of $p(x_B)$ versus t gave the best fit to a straight line indicating that the diffusion of oxygen through the ash layer controls the rate of reaction. Among these runs, run 67 was selected at random to present as an example. Figure 11 shows that x_B versus t is not a straight line. The time when leaching started was determined by extrapolating the conversion versus time curve to the t -axis. Figure 12 shows $p(x_B)$ and $g(x_B)$ versus actual leaching time (t_a). From Figure 12, $g(x_B)$ versus t_a is not a straight line but $p(x_B)$ versus t_a falls nearly on a straight line.

Linear regression and correlation coefficient analysis was used to make a quantitative comparison of the fit of the three functions x_B , $g(x_B)$ and $p(x_B)$ to the data. A description of the method of

Figure 11. Total sulfur conversion versus terminal sample time for run 67.

Figure 12. $g(x_B)$ and $p(x_B)$ versus actual leaching time for run 67.

analysis is given in Appendix C. Values of the correlation coefficient for the typical case (run 67) and worst case (run 35) are shown in Table 3. The correlation coefficients for the $p(x_B)$ versus t_a curve of all the sodium carbonate and sodium bicarbonate runs except for run 35 are 0.99 or higher. For run 67, the correlation coefficient of $p(x_B)$ versus t_a curve is 0.9995 which is close to the value of 1.0000 for a straight line. Run 35 was unusual since it was made at a much higher oxygen partial pressure [198 lb./sq. in. (absolute)]. The sulfur extraction was almost complete after leaching for 40 min. But all runs were analyzed over 60 min. The largest deviation from a straight line for $p(x_B)$ versus t_a for run 35 occurred after leaching for about 40 min. (Figure 13). But the $p(x_B)$ function still fitted the data for run 35 better than either the x_B or $g(x_B)$ functions according to Table 3.

Table 3. Correlation coefficients for runs 67 and 35

	Correlation coefficient		
	x_B	$g(x_B)$	$p(x_B)$
Run 67	0.9707	0.9876	0.9995
Run 35	0.8718	0.9535	0.9672

From this analysis of the correlation coefficient, the $p(x_B)$ function is more likely to yield a straight line than either the x_B or $p(x_B)$ functions for the reaction system in question. Therefore the results provide a strong indication that the rate of reaction is controlled by ash or product layer diffusion.

Figure 13. $p(x_B)$ versus actual leaching time for run 35.

Calculating effective diffusivity

The calculation of the effective diffusivity (D_e) involves two steps:

(1) determining the slope of the $p(x_B)$ versus t_a curve which is equal to $1/\tau$

(2) calculating D_e by means of equation 16

$$D_e = \frac{\rho_B R^2}{6bC_{A1}\tau} \quad (21)$$

An example calculation of D_e for run 67 is given below. From a plot of $p(x_B)$ versus t_a the value of τ is found.

$$\tau = \frac{t}{p(x_B)} = \frac{\Delta t}{\Delta p(x_B)} = \frac{3600 - 150}{0.217} = 15,899 \text{ sec.}$$

The pyrite was hand-picked from the Iowa State University coal mine. The density of this pyrite was somewhat lower than for pure pyrite. It was measured by means of a pycnometer and found to be 4.33 g./cu. cm.

$$\rho_B = \frac{39.82 \text{ g.s.} \times 4.33 \text{ g. solids/cu. cm. solids}}{100 \text{ g. solids} \times 64.12 \text{ g.s./mole FeS}_2}$$

$$\rho_B = 0.0267 \text{ mole FeS}_2/\text{cu. cm. solids}$$

The pyrite particles were assumed to be spherical in shape. For -120/+140 mesh pyrite, the average diameter of the particles is 0.115 mm.

$$R = \frac{0.0115 \text{ cm.}}{2} = 0.00575 \text{ cm.}$$

The partial pressure of oxygen in run 67 was 48 lb./sq. in. (absolute).

Figure 2 in the paper by Pray et al. (26) was used to estimate the concentration

of oxygen in water. At 150°C, the solubility of oxygen in water is 0.07 ml. O₂/g. H₂O.

$$C_{Al} = \frac{0.07}{22400} = 3.125 \times 10^{-6} \text{ mole/cu. cm.}$$

This value is only an estimate because of the lack of data for the solubility of oxygen in sodium carbonate solutions. Figure 4 in the paper by Drescher et al. (10) can be used to estimate the concentration of oxygen in potassium hydroxide solutions. The result is about 3.89×10^{-6} mole/ml. for 48 lb./sq. in. (absolute) oxygen partial pressure at 150°C.

Using the above data in Equation 21, the effective diffusivity is calculated as

$$D_e = \frac{0.0269 \times (0.00575)^2 \times 15}{6 \times 4 \times 3.125 \times 10^{-6} \times 15899} = 1.12 \times 10^{-5} \text{ sq. cm./sec.}$$

It seems likely that the ash or product layer has a porous capillary structure which is filled with solution during the reaction. The oxygen dissolved in the solution has to diffuse through the solution to reach the solid reaction sites. Therefore the effective diffusivity should correspond to the diffusion coefficient for the oxygen in water system. The International Critical Tables (4) list the molecular diffusivity of oxygen in water at 18°C as determined by various investigators. The values range from 1.1×10^{-5} to 1.98×10^{-5} sq. cm./sec. The value of the diffusion coefficient increases only slightly with temperature (12).

There is other evidence to support the ash-layer diffusion control model for the reaction. For example, the effects of oxygen partial

pressure and leaching solution flow rate also support this model. This evidence will be presented below.

Effect of Oxygen Partial Pressure

The rate of reaction was found to be a function of oxygen partial pressure with the rate increasing as the oxygen partial pressure increases (Figure 14). Table 4 shows the effect of pressure on effective diffusivity.

Table 4. Effect of pressure on effective diffusivity (-120/+140 mesh, 150°C, 13.2 ml./sec. O₂ flow rate)

Run No.	Total pressure, lb./sq. in. (gauge)	O ₂ partial pressure, lb./sq. in. (absolute)	D _e x 10 ⁵ , sq. cm./sec.
12	100	48	1.01
62	100	48	1.08
70	100	48	1.37
14	150	98	1.18
24	150	98	1.10
35	250	198	1.13

A statistical analysis of this data showed that oxygen partial pressure has no significant effect on the effective diffusivity for -120/+140 mesh pyrite (Appendix D). Thus the effect of oxygen on the kinetics is accounted for completely by Equation 16 through the dissolved oxygen concentration term.

Figure 14. Effect of oxygen partial pressure on sulfur conversion.

From the paper reporting the solubility of oxygen in water (26) it can be seen that the solubility is a linear function of the oxygen partial pressure. Therefore the rate of total sulfur conversion is also a linear function of oxygen partial pressure.

Effect of Particle Size

In Figures 15 and 16 the conversion of pyrite is presented as a function of time for different particle sizes at two different pressures. In all cases, the total sulfur conversion decreased as the particle size increased. But the effect of particle size cannot be accounted for under all conditions by the R^2 term in Equation 16. Figure 17 shows a plot of τ versus R^2 for two different pressures. Obviously the data for 150 lb./sq. in. (gauge) does not fall on a straight line. On the other hand, the data for 100 lb./sq. in. (gauge) does appear to fall on a straight line. Therefore it seems that the effective diffusivity is probably independent of particle size for 100 lb./sq. in. (gauge) but not for 150 lb./sq. in. (gauge). Table 5 shows the effect of particle size on the effective diffusivity.

The statistical analysis presented in Appendix D shows that at 100 lb./sq. in. (gauge) the effect of particle size on the effective diffusivity is not significant at the 25 to 50% level. However, at 150 lb./sq. in. (gauge) the effect of particle size on the effective diffusivity is significant at the 99.5% level. Therefore it appears that the proposed kinetic model seems to represent the reaction mechanism more closely at lower pressures than at higher pressures because the

Figure 15. Effect of particle size on sulfur conversion at 150 psig.

Figure 16. Effect of particle size on sulfur conversion at 100 psig.

Figure 17. Time for complete reaction of a pyrite (τ) versus square of the particle size (R^2).

diffusivity should not be a function of pressure. Further experiments with different particle sizes should be conducted at different pressures in order to clarify the change in effective diffusivity.

Table 5. Effect of particle size on the effective diffusivity (150°C, 13.2 ml./sec. O₂ flow rate)

Run No.	Particle size, mesh	Total pressure, lb./sq. in. (gauge)	$D_e \times 10^5$, sq. cm./sec.
45	-60/+80	100	0.92
43	-60/+80	150	2.13
65	-60/+80	150	1.70
46	-80/+100	100	1.10
44	-80/+100	150	1.45
12	-120/+140	100	1.01
62	-120/+140	100	1.08
70	-120/+140	100	1.37
14	-120/+140	150	1.18
24	-120/+140	150	1.10

Effect of Temperature

Different runs were made at temperatures ranging from 121° to 175°C. For the runs shown in Table 6 the oxygen partial pressure, particle size, and other important system parameters were kept constant. The results presented in Table 6 show the effect of temperature on the effective diffusivity.

Table 6. Effect of temperature on diffusivity

Run No.	Temp., °C	1000/T, 1/°K	$D_e \times 10^5$, sq. cm./sec.
81	121	2.54	0.53
82	135	2.45	0.71
62	150	2.36	1.08
83	160	2.31	1.48
80	175	2.23	1.84

When the logarithm of the effective diffusivity was plotted against reciprocal temperature, a straight line was obtained (Figure 18). This line could be represented by a form of the Arrhenius equation shown below.

$$D_e = D_{e0} e^{-E_{\text{diff}}/R_c T} \quad (22)$$

$$\ln D_e = \ln D_{e0} - E_{\text{diff}}/R_c T \quad (23)$$

Since the slope of the line in Figure 18 is equal to E_{diff}/R , the activation energy is as follows:

$$\begin{aligned} E_{\text{diff}} &= 1.987 \times 4.01 \times 10^3 \text{ cal./mole} \\ &= 7.97 \text{ Kcal./mole} \end{aligned}$$

This value is higher than the activation energy of 2.4 Kcal./mole reported by Tai (31) for the same reaction system but Tai used an autoclave instead of a tubular reactor. The apparent activation energy of 7.97 Kcal./mole is somewhat high for a simple diffusion-controlled

Figure 18. Arrhenius plot for the temperature effect.

system. Therefore further study of the temperature effect should be made.

Effect of Leaching Solution Flow Rate

The effect of leaching solution flow rate was investigated for similar reaction conditions. For the chosen experimental conditions the liquid flow rate had a negligible effect on the rate of conversion (Figure 19).

The possible effect of flow rate on the effective diffusivity was also investigated (Table 7). A statistical analysis of the data showed there is no effect of flow rate on the effective diffusivity at 150 lb./sq. in. (gauge) when using -120/+140 mesh pyrite (Appendix D). This is further evidence in support of the ash layer diffusion model. Thus if film diffusion were rate controlling, the rate of reaction would depend on the liquid flow rate.

Table 7. The liquid flow rate had a negligible effect on the effective diffusivity (150°C, 150 lb./sq. in. (gauge), -120/+140 mesh)

Run No.	Liquid flow rate, ml./sec.	$D_e \times 10^5$, sq. cm./sec.
14	1.5	1.18
24	1.5	1.10
20	2.25	1.16
17	3.0	1.05

Figure 19. Liquid flow rate had little effect on the rate of conversion.

Effect of Oxygen Flow Rate

The oxygen flow rate had a large effect on the rate of sulfur extraction (Figures 20 and 21). A series of runs were made to investigate the optimum oxygen flow rate (Figure 22). From this study, it appears that the optimum oxygen flow rate is approximately 0.004 cu. ft./min., i.e., 3 ml./sec., because at this point the amount of sulfur extracted is a maximum.

Beyond the optimum flow rate, the rate of sulfur conversion decreased as the oxygen flow rate increased. It appears that an excessive gas flow rate may cause a contact problem between the liquid and solids. The surface of the solids may not have been totally wetted, so the reaction was not complete.

Below the optimum point, the rate of sulfur conversion decreased as the oxygen flow rate decreased. The decline may have been caused by insufficient oxygen to oxidize the pyritic sulfur.

Effect of Leaching Solution Concentration

Sodium carbonate

The data in Figure 23 show the effect of sodium carbonate concentration on the total sulfur conversion. For concentrations ranging from 0.25 to 6 wt. % sodium carbonate, the conversion did not change very much with concentration. However, a maximum conversion was achieved with 2 wt. % sodium carbonate. Similar results were observed by Tai et al. (33). It is noteworthy that with no sodium carbonate present the conversion was very low.

Figure 20. Increasing gas flow rate had an adverse effect on the rate of conversion.

Figure 21. Increasing gas flow rate had an adverse effect on the rate of conversion.

Figure 22. Effect of oxygen flow rate on sulfur conversion.

Figure 23. Effect of leaching solution concentration on sulfur conversion.

One of the roles of sodium carbonate is to neutralize sulfuric acid produced by the reaction shown below.

Therefore pH value should play an important part for the sodium carbonate/oxygen system. For sodium carbonate concentrations between 0.25 and 6%, the pH ranged from 11.12 to 11.55. The small change in pH may explain why there was not much difference in the rate of sulfur extraction for different concentrations.

Sodium bicarbonate

Sodium bicarbonate was tested as well as sodium carbonate. The neutralization process

yields sodium bicarbonate. The question arises as to whether the neutralizing ability of the sodium bicarbonate can also be utilized in the leaching process.

The data in Figure 23 also show the effect of sodium bicarbonate concentration on the total sulfur conversion for concentrations ranging from 1 to 4 wt. %. For 1 wt. % the total sulfur conversion was only a little lower than that for the sodium carbonate solution. However, between 2 and 3 wt. % sodium bicarbonate, the total sulfur conversion declined considerably. The reason for this decline can not be explained with certainty. A similar decline was observed by Burkin and Edwards (8) when they used a caustic solution to leach pyrite. They claimed the

decline was due to the lower solubility of oxygen at higher concentrations of caustic.

Water

Run 22 was made to investigate the effect of not using any alkali on leaching of pyrite at 150°C and 48 lb./sq. in. (absolute) oxygen partial pressure. The total sulfur conversion was only 12.8% (remember that the LOL process utilizes much higher oxygen partial pressures to obtain high total sulfur conversions).

Effect of Particle Charge Size

The effect of charge size on the total sulfur conversion appeared to be significant (Figures 24 and 25). The total sulfur conversion decreased as the charge size increased. Run 76 was made to investigate the sulfur conversion in different sections of the packed bed (Figure 26). After the run the pyrite residue was taken out in three different sections. The average total sulfur content of each section was determined separately by the standard ASTM method. The bar diagram (Figure 26) shows that the total sulfur conversion decreased in the flow direction. The x-axis corresponds to the longitudinal dimension of the bed. Although there are several possible explanations for the decline in sulfur conversion between the inlet and outlet, the actual explanation cannot be offered.

One possible explanation is the retention of some insoluble but mobile reaction products with the greater the charge size, the greater the retention problem. An example would be a gelatinous iron hydroxide

Figure 24. Increasing the pyrite charge had an adverse effect on the rate of conversion.

Figure 25. Effect of charge size on sulfur conversion.

Figure 26. Total sulfur conversion is a function of the longitudinal dimension of the packed bed.

precipitate. Since such a product would tend to be held back more by a bed of fine particles than by a bed of coarse particles, there would be a greater decline in conversion in the case of the fine particles than in the case of the coarse particles which is what was observed (Figure 25).

Another possible explanation is that the finer particles become compacted which causes poor flow distribution and channeling. Some compaction of the residue was noted when the solids were removed from the reactor after a run with fine size pyrite. Less compaction of the residue was noted in the case of coarser particles. Therefore the charge size would have less effect on the flow pattern in the case of coarser particles than in the case of finer particles.

Another possibility for the decline in rate with charge size is due to depletion of dissolved oxygen. In other words, the oxygen is removed from solution by the pyrite more rapidly than it can dissolve. This could be investigated by conducting an experiment similar to run 76 except using a higher oxygen partial pressure to provide higher dissolved oxygen concentration. Higher liquid flow rates should also be tried in combination with higher oxygen partial pressures because this would also provide more dissolved oxygen for the pyrite near the reactor outlet.

A further possibility is that the rate of reaction may be reduced by the presence of small concentrations of some soluble reaction product. In order to investigate this possibility a series of runs was made in which small amounts of possible reaction products were introduced in the liquid feed. Sodium sulfate (Na_2SO_4), sodium sulfite (Na_2SO_3), and

sodium thiosulfate ($\text{Na}_2\text{S}_2\text{O}_3$) were added to the feed solutions (Runs 26, 27, 28, 29). The results were not as expected, i.e., the rate of reaction was not reduced when the possible solution reaction products were introduced in the liquid feed.

CONCLUSIONS

1. A shrinking core model with the rate of reaction controlled by ash or product layer diffusion seems to represent the kinetics of the chemical leaching process for pyrite by hot alkaline solutions containing dissolved oxygen.
2. The experimental effective diffusivity of this process is about 10^{-5} sq. cm./sec. which corresponds to the molecular diffusivity for oxygen in water.
3. The model indicates that the rate of reaction is proportional to the dissolved oxygen concentration. This has been verified experimentally.
4. The model does not completely account for the effect of particle size since the effective diffusivity seems to be a function of particle size at higher pressures.
5. The apparent activation energy for this process is 7.97 Kcal./mole in the temperature range of 121° to 175°C.
6. Since the leaching solution flow rate does not have much effect on the rate of reaction in the experimental reactor, the process is not controlled by film diffusion.
7. The optimum oxygen flow rate in the experimental tubular reactor system is about 3 ml./sec.
8. Although the rate of reaction is not affected very much by the sodium carbonate concentration, the optimum concentration is about 2 wt. %.

9. Sodium bicarbonate was found to give nearly as good results as sodium carbonate when used in 1 wt. % concentration.

10. The total sulfur conversion decreased as the pyrite charge size increased. Some possible reasons for this effect have been given.

RECOMMENDATIONS

1. The effect of temperature was investigated over the range of 121° to 175°C. This effect should be investigated over a wider range of temperature.
2. The effect of pyrite charge size should be investigated in conjunction with high oxygen partial pressures and higher liquid flow rates to see whether the decline in conversion within the bed of pyrite is due to oxygen depletion of the solution.
3. Further experiments should be conducted to determine more accurately and more fully the effect of particle size on the rate of reaction and/or effective diffusivity.

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ACKNOWLEDGMENTS

The author would like to express his sincere appreciation to Dr. T. D. Wheelock who provided valuable guidance and suggestions throughout the project.

Appreciation is also expressed to Dr. A. H. Pulsifer for his timely advice.

A special note of appreciation is expressed to Dr. H. T. David and his group for their helpful assistance in the statistical analysis.

The Energy Research and Development Administration is also gratefully acknowledged for its financial support of this investigation.

Finally, the author expresses his sincere gratitude to his mother, Mrs. Shao Wong Chen; his sister, Theresa; and his wife, Li Hwa for their constant encouragement.

APPENDIX A. EXPERIMENTAL CONDITIONS AND RESULTS OBTAINED

Table A.1. Experimental conditions and results obtained

Run No.	Pyrite charge		Temp., °C	Alkali conc., wt. %	Liquid rate, ml./sec.	O ₂ rate, ml./sec.
	wt. g.	Size, mesh				
12	5	-120/+140	150	2% Na ₂ CO ₃	1.5	13.2
13	10	-120/+140	150	2% Na ₂ CO ₃	1.5	13.2
14	5	-120/+140	150	2% Na ₂ CO ₃	1.5	13.2
15	10	-120/+140	150	2% Na ₂ CO ₃	1.5	13.2
16	5	-120/+140	150	2% Na ₂ CO ₃	2.25	9.9
17	5	-120/+140	150	2% Na ₂ CO ₃	3.0	13.2
18	5	-120/+140	150	2% Na ₂ CO ₃	1.5	6.6
19	5	-120/+140	150	2% Na ₂ CO ₃	1.5	22.0
20	5	-120/+140	150	2% Na ₂ CO ₃	2.25	13.2
21	5	-120/+140	150	2% Na ₂ CO ₃	1.5	19.8
22	5	-120/+140	150	Water	1.5	13.2
23	10	-120/+140	150	2% Na ₂ CO ₃	1.5	13.2
24	5	-120/+140	150	2% Na ₂ CO ₃	1.5	13.2
25	5	-120/+140	150	2% Na ₂ CO ₃ 1% Na ₂ SO ₄	1.5	13.2
26	5	-120/+140	150	2% Na ₂ CO ₃ 0.05 % Na ₂ SO ₄	1.5	13.2
27	5	-120/+140	150	2% Na ₂ CO ₃ 0.1% Na ₂ SO ₄	1.5	13.2
28	5	-120/+140	150	2% Na ₂ CO ₃ 0.1% Na ₂ SO ₃	1.5	13.2
29	5	-120/+140	150	2% Na ₂ CO ₃ 0.1% Na ₂ S ₂ O ₃	1.5	13.2

O₂ pr
lb./s
(abs)

O ₂ press., lb./sq. in. (absolute)	Total press., lb./sq. in. (gauge)	Rx. time, min.	Total sulfur conversion, %		D _e x 10 ⁵ , sq. cm./sec.
			Based on liquid	Based on solids	
48	100	58	61.2	68	1.01
73	125	59	64.6	76.5	1.15
98	150	56	75	88	1.18
98	150	56	69	81	0.80
98	150	60	78.3	91.2	1.13
98	150	44	68.1	75.9	1.05
48	100	57	67.9	79.1	1.30
48	100	57	42.7	53.7	0.39
98	150	53	75.6	86.8	1.16
98	150	56	61.5	70.9	0.59
48	100	57	12.8	22.2	—
98	150	58	73.8	83.5	0.98
98	150	58	76.5	83.4	1.10
98	150	58	—	—	—
98	150	59	74.4	79.9	1.15
98	150	56	75.0	87.6	1.16
98	150	60	75.3	88.7	1.18
98	150	58	71.2	87.9	1.10

Table A.1. (continued)

Run No.	Pyrite charge		Temp., °C	Alkali conc., wt. %	Liquid rate, ml./sec.	O ₂ rate, ml./sec.
	wt. g.	Size, mesh				
30	2.5	-120/+140	150	2% Na ₂ CO ₃	1.5	13.2
31	1.5	-120/+140	150	2% Na ₂ CO ₃	1.5	13.2
32	5	-120/+140	150	1M NaHCO ₂	1.5	13.2
33	5	-120/+140	150	1% Na ₂ CO ₃ 0.1M NaHCO ₂	1.5	13.2
34	5	-120/+140	150	0.2M NaHCO ₂	1.5	13.2
35	5	-120/+140	150	2% Na ₂ CO ₃	1.5	13.2
36-42 ^a						
43	5	-60/+80	150	2% Na ₂ CO ₃	1.5	13.2
44	5	-80/+100	150	2% Na ₂ CO ₃	1.5	13.2
45	5	-60/+80	150	2% Na ₂ CO ₃	1.5	13.2
46	5	-80/+100	150	2% Na ₂ CO ₃	1.5	13.2
47	5	-120/+140	150	2% Na ₂ CO ₃	1.5	7.9
48	5	-120/+140	150	2% Na ₂ CO ₃	1.5	4.4
49	5	-120/+140	150	2% Na ₂ CO ₃	1.5	3.04
50	10	-60/+80	150	2% Na ₂ CO ₃	1.5	13.2
51	2.5	-60/+80	150	2% Na ₂ CO ₃	1.5	13.2
52	10	-80/+100	150	2% Na ₂ CO ₃	1.5	13.2
53	2.5	-80/+100	150	2% Na ₂ CO ₃	1.5	13.2

^aRuns 36-42 used coal as the packed sample. All of them failed because of the plugging and foaming problems.

O ₂ press., lb./sq. in. (absolute)	Total press., lb./sq. in. (gauge)	Rx. time, min.	Total sulfur conversion, %		D _e x 10 ⁵ , sq. cm./sec.
			Based on liquid	Based on solids	
98	150	58	82.4	90	1.30
98	150	59	77.3	—	1.10
98	150	59	—	—	—
98	150	59	80.3	—	1.34
98	150	59	—	—	—
198	250	61	93.2	98.2	1.13
98	150	60	61.9	61.3	2.13
98	150	60	65.1	71.9	1.45
48	100	60	35.8	52.6	0.92
48	100	59	48.6	66.2	1.10
48	100	58	65.6	73.1	1.17
48	100	58	69.9	75.5	1.38
48	100	60	72.4	74.5	1.52
98	150	59	56.5	59.8	1.70
98	150	59	57.0	58.9	1.79
98	150	59	67.9	71	1.59
98	150	60	72.6	75.3	1.97

Table A.1. (continued)

Run No.	Pyrite charge		Temp., °C	Alkali conc., wt. %	Liquid rate, ml./sec.	O ₂ rate, ml./sec.
	wt. g.	Size, mesh				
54	5	-120/+140	150	2% Na ₂ CO ₃	1.5	2.0
55	5	-120/+140	150	1.75% Na ₂ CO ₃	1.5	13.2
56	5	-120/+140	150	1.5% Na ₂ CO ₃	1.5	13.2
57	5	-120/+140	150	1.25% Na ₂ CO ₃	1.5	13.2
58	5	-120/+140	150	1% Na ₂ CO ₃	1.5	13.2
59	5	-120/+140	150	0.75% Na ₂ CO ₃	1.5	13.2
60	5	-120/+140	150	0.5% Na ₂ CO ₃	1.5	13.2
61	5	-120/+140	150	4% Na ₂ CO ₃	1.5	13.2
62	5	-120/+140	150	2% Na ₂ CO ₃	1.5	13.2
63	5	-120/+140	150	6% Na ₂ CO ₃	1.5	13.2
64	2.5	-60/+80	150	2% Na ₂ CO ₃	1.5	13.2
65	5	-60/+80	150	2% Na ₂ CO ₃	1.5	13.2
66	10	-60/+80	150	2% Na ₂ CO ₃	1.5	13.2
67	5	-120/+140	150	1% Na ₂ CO ₃	1.5	13.2
68	5	-120/+140	150	0.75% Na ₂ CO ₃	1.5	13.2
69	5	-120/+140	150	0.25% Na ₂ CO ₃	1.5	13.2
70	5	-120/+140	150	2% Na ₂ CO ₃	1.5	13.2
71	5	-120/+140	150	1.75% Na ₂ CO ₃	1.5	13.2
72	5	-120/+140	150	3% Na ₂ CO ₃	1.5	13.2
73	5	-60/+80	150	2% Na ₂ CO ₃	1.5	7.9

O ₂ press., lb./sq. in. (absolute)	Total press., lb./sq. in. (gauge)	Rx. time, min.	Total sulfur conversion, %		D _e x 10 ⁵ , sq. cm./sec.
			Based on liquid	Based on solids	
48	100	60	65.9	70.7	1.24
48	100	59	67.7	79	1.21
48	100	60	65.3	82.2	1.07
48	100	60	64.8	75.5	1.09
48	100	59	56.2	67.8	0.80
48	100	58	63.5	73.7	1.01
48	100	59	61.5	73.3	0.95
48	100	59	63.3	78	0.98
48	100	60	61.3	73.1	1.08
48	100	59	62.2	79.9	0.98
98	150	60	57.3	68.8	1.86
98	150	60	56.0	70.8	1.70
98	150	60	53.5	63.5	1.45
48	100	59	65.3	74.4	1.12
48	100	59	67.3	78.2	1.17
48	100	59	62.6	72	1.01
48	100	59	70.2	80.2	1.37
48	100	59	68.1	80.0	1.22
48	100	59	66.7	80.3	1.21
98	150	59	58.2	65.6	1.97

Table A.1. (continued)

Run No.	Pyrite charge		Temp., °C	Alkali conc., wt. %	Liquid rate, ml./sec.	O ₂ rate, ml./sec.
	wt. g.	Size, mesh				
74	5	-60/+80	150	2% Na ₂ CO ₃	1.5	3.04
75	5	-120/+140	125	2% Na ₂ CO ₃	1.5	13.2
76	16	-120/+140	150	2% Na ₂ CO ₃	1.5	13.2
77	5	-120/+140	175	2% Na ₂ CO ₃	1.5	13.2
78	5	-120/+140	150	2.5% Na ₂ CO ₃	1.5	13.2
79	5	-120/+140	200	2% Na ₂ CO ₃	1.5	13.2
80	5	-120/+140	175	2% Na ₂ CO ₃	1.5	13.2
81	5	-120/+140	121	2% Na ₂ CO ₃	1.5	13.2
82	5	-120/+140	135	2% Na ₂ CO ₃	1.5	13.2
83	5	-120/+140	160	2% Na ₂ CO ₃	1.5	13.2
84	5	-120/+140	150	1% NaHCO ₃	1.5	13.2
85	5	-120/+140	150	2% NaHCO ₃	1.5	13.2
86	5	-120/+140	150	3% NaHCO ₃	1.5	13.2
87	5	-120/+140	150	4% NaHCO ₃	1.5	13.2

O ₂ press., lb./sq. in. (absolute)	Total press., lb./sq. in. (gauge)	Rx. time, min.	Total sulfur conversion, %		D _e x 10 ⁵ , sq. cm./sec.
			Based on liquid	Based on solids	
98	150	60	44.0	49.4	0.78
48	100	59	65.8	75.4	1.14
58	110	60	64.2	69.9	1.12
48	100	60	55.4	62.4	0.97
48	100	60	69.1	80.3	1.25
—	150	60	57.5	67.5	—
48	161	60	75.7	91.1	1.84
48	69	59	50.0	53.7	0.53
48	80	59	52.0	56.6	0.71
48	123	59	72.4	79.6	1.48
48	100	60	58.8	66.1	0.76
48	100	60	57.0	67.8	0.76
48	100	60	53.2	63.3	0.745
48	100	60	42.4	—	0.48

APPENDIX B.

DETERMINATION OF SULFUR IN LIQUID SAMPLES

Procedure

After each run, the liquid samples were treated as follows:

1. A 100 ml. aliquot of the solution was taken from each sample collected during the leaching process. To this aliquot, 10 ml. of hydrogen peroxide was added to convert all sulfur compounds to sulfate. The solution was allowed to stand overnight.

2. The solution was treated with DOWEX 50 x 8 resin to reduce the pH to the range of 2.5 to 4.0. The resin was added until no red color appeared on the surface of the resin.

3. A 1 to 20 ml. portion of the solution was taken for titration. This volume was in the safe range for microtitration of sulfate. To this portion was added four times as much 2-propanol and 1 to 3 drops of thorin indicator to get a sharp and rapid end point.

4. The small portion was titrated with 0.005M barium perchlorate. The first permanent color change from yellow or yellow-orange to pink was taken as the end point. The bulk of the titrant was added rapidly, but 2 to 3 sec. was allowed between each of the last few increments.

Calculation Method

The above procedure provided a measure of the sample volume (v), and the titrant volume (V). The molarity of barium perchlorate (N) was determined by titrating it with sulfuric acid. The sulfur concentration of the

solution issuing from the reactor was calculated by using the following equation:

$$\text{Sulfur, mg./liter} = V \times \frac{32 \times N \times 1000}{v} \times 1.1 \quad (\text{B-1})$$

Sample Calculation of Sulfur Content

Barium perchlorate solution for titrating the samples from run 67 was prepared. A 20 ml. aliquot of sulfuric acid (0.005M) was titrated with 21 ml. of barium perchlorate to reach the end point with thorin as the indicator. Therefore the molarity of barium perchlorate was determined as follows:

$$\text{M Barium Perchlorate} = \frac{20 \times 0.005}{21} = 0.00476$$

The sulfur concentration of the first sample from run 67 was then determined.

$$\begin{aligned} \text{Sulfur, mg./liter} &= 4.9 \times \frac{32 \times 0.00476 \times 1000}{5} \times 1.1 \\ &= 164 \text{ mg./liter} \end{aligned}$$

The total volume of the first sample from run 67 was 350.8 ml. which was determined from the weight of the liquid sample divided by the density of the 2% sodium carbonate solution. The density was assumed to be 1.02 g./ml.

The total sulfur content of the first sample was

$$\text{Sulfur} = \frac{350.8 \times 164}{1000} = 57.5 \text{ mg.}$$

The weight of pyrite charged was 5.0007 g., so the sulfur content of the raw pyrite was

$$5.0007 \times 39.82\% \times 1000 = 1991.28 \text{ mg.}$$

The total sulfur conversion corresponding to the first sample was

$$\frac{57.5 \text{ mg.}}{1991.28 \text{ mg.}} = 0.029 \text{ or } 2.9\%$$

which is plotted at $t = 350$ sec. in Figure 11.

Subsequent samples from run 67 were treated the same way. The cumulative total sulfur conversion was plotted in Figure 11 at each terminal collection time.

APPENDIX C.

LINEAR REGRESSION AND CORRELATION COEFFICIENT

The analytical method for the linear regression and correlation coefficient is based on an HP9100A program. This program calculates the equation of the straight line for the best fit of a set of data points. The best fit is determined by minimizing the sum of squares of the deviations of the data points from the line.

The program calculates m and b for the equation

$$Y = mx + b \quad (C-1)$$

The program also calculates a correlation coefficient γ , an indication of goodness of fit. Note that γ lies between -1 and $+1$ where the sign corresponds to the slope m . If $\gamma = 0$, there is no correlation; and if $\gamma = \pm 1$, there is perfect correlation or a perfect fit.

The defining equations are

$$m = \frac{\sum_{i=1}^n (x_i - \bar{x})(y_i - \bar{y})}{\sum_{i=1}^n (x_i - \bar{x})^2} \quad (C-2)$$

$$b = \bar{y} - m\bar{x} \quad (C-3)$$

$$\text{where } \bar{y} = \frac{\sum_{i=1}^n y_i}{n} \quad (C-4)$$

$$\text{and } \bar{x} = \frac{\sum_{i=1}^n x_i}{n} \quad (C-5)$$

$$\gamma = \frac{\sum_{i=1}^n (x_i - \bar{x})(Y_i - \bar{Y})}{\sqrt{\sum_{i=1}^n (x_i - \bar{x})^2 \sum_{i=1}^n (Y_i - \bar{Y})^2}}$$

(C-6)

APPENDIX D.

STATISTICAL ANALYSIS

Certain experimental errors existed during the runs. These errors were observed for runs using the same experimental conditions. Nine groups of runs having the same experimental conditions within each group are listed in Table D-1. From this data, the variance of the experimental error (S_e^2) with 10 degrees of freedom is calculated as

$$S_e^2 \times 10^{10} = \frac{\text{total variance for 9 groups}}{\text{total degree of freedom}} = \frac{0.2825}{10} = 0.02825 \text{ (D-1)}$$

Based on the variance calculated from the experimental error, the possible significance of various parameters was investigated by using an F test.

Effect of Oxygen Partial Pressure

Table D-2 shows statistical data for the effect of oxygen partial pressure. The variance (S_o^2) was calculated as

$$S_o^2 \times 10^{10} = \frac{\sum_{n_i=1}^3 n_i (\bar{D}_{ei} - \bar{D}_e)^2}{\text{degree of freedom}} \quad (\text{D-2})$$

$$S_o^2 \times 10^{10} = [3 \times (1.145 - 1.153)^2 + 2 \times (1.145 - 1.14)^2 + (1.145 - 1.13)^2] / 2 = 0.00023$$

A testing hypothesis was set up as follows:

Table D-1. Statistical analysis for experimental error

Groups	Run No.	Effective diffusivity, $D_e \times 10^5$, sq. cm./sec.	Average $\bar{D}_e \times 10^5$	Degree of freedom	Variance, $S^2 \times 10^{10}$
1	12	1.01	1.153	2	0.0729
	62	1.08			
	70	1.37			
2	14	1.18	1.14	1	0.0032
	24	1.10			
3	15	0.80	0.89	1	0.0162
	23	0.98			
4	43	2.13	1.915	1	0.09245
	65	1.70			
5	50	1.70	1.575	1	0.03125
	66	1.45			
6	51	1.79	1.825	1	0.00245
	64	1.86			
7	55	1.21	1.215	1	0.00005
	71	1.22			
8	59	1.01	1.09	1	0.0128
	68	1.17			
9	58	0.80	0.96	1	0.0512
	67	1.12			
Σ				10	0.2825

Table D-2. Statistical analysis for the effect of oxygen partial pressure

Groups	Run No.	Oxygen partial pressure, lb./sq. in. (absolute)	Effective diffusivity, $D_e \times 10^5$ sq. cm./sec.	Average, $\bar{D}_e \times 10^5$	Total average, $\bar{D}_{ei} \times 10^5$	Degree of freedom
1	12	48	1.01	1.153	1.145	2
	62	48	1.08			
	70	48	1.37			
2	14	98	1.18	1.14	1.145	2
	24	98	1.10			
3	35	198	1.13	1.13		

Null hypothesis (H_0): oxygen partial pressure has no effect on the effective diffusivity for oxygen partial pressures of 48, 98 and 198 lb./sq. in. (absolute).

Alternative hypothesis (H_A): oxygen partial pressure has a certain effect on the effective diffusivity for conditions described in H_0 .

$$\text{Test Statistic: } F = \frac{s_o^2}{s_e^2} = \frac{0.00023}{0.02825} = 0.0081$$

This value was compared with the values under $F_p(2,10)$, where p is the probability of rejecting the null hypothesis when the null hypothesis is true. F values can be found in any book for statistical analysis.

$F_p(2, 10)$ was found in an F distribution table.

$$F_{0.995}(2,10) = 0.0050$$

$$F_{0.99}(2,10) = 0.010$$

Thus the probability of getting a value of this size (0.0074) or larger under the null hypothesis is between 0.99 and 0.995, and for reasonable significance levels we would fail to reject the null hypothesis. Indeed, the F-ratio is "significant" on the low-side, suggesting the possibility that the values of this particular analysis might not be reproducible.

Effect of Pyrite Particle Size

Table D-3 shows statistical data for the effect of pyrite particle size at 100 lb./sq. in. (gauge) total system pressure.

Table D-3. Statistical analysis for the effect of particle size at 100 lb./sq. in. (gauge) total system pressure

Groups	Run No.	Particle size, mesh	Effective diffusivity, $D_e \times 10^5$ sq. cm./sec.	Average, $\bar{D}_e \times 10^5$	Total average, $\bar{D}_{ei} \times 10^5$	Degree of freedom
1	45	-60/+80	0.92	0.92		
2	46	-80/+100	1.10	1.10		
					1.096	2
3	12	-120/+140	1.01			
	62	-120/+140	1.08	1.153		
	70	-120/+140	1.37			

The variance (S_{p1}^2) was calculated as in Equation D-2

$$S_{p1}^2 \times 10^{10} = [(1.096 - 0.92)^2 + (1.096 - 1.10)^2 + 3 \times (1.096 - 1.153)^2] / 2 = 0.02037$$

Null hypothesis (H_0): Particle size has no effect on the effective diffusivity at 100 lb./sq. in. (gauge) total system pressure.

Alternative hypothesis (H_A): Particle size has a certain effect on the effective diffusivity at 100 lb./sq. in. (gauge)

Test Statistic: $F = \frac{0.02037}{0.02825} = 0.721$

$F_{0.75}(2,10) = 0.296$

$F_{0.50}(2,10) = 0.743$

There is no strong evidence to reject the null hypothesis since the probability of getting a value of 0.721 or larger under the null hypothesis is between 0.50 and 0.75.

Table D-4 shows the statistical data for the effect of pyrite particle size at 150 lb./sq. in. (gauge) total system pressure.

Table D-4. Statistical analysis for the effect of particle size at 150 lb./sq. in. (gauge) total system pressure

Groups	Run No.	Particle size, mesh	Effective diffusivity, $D_e \times 10^5$ sq. cm./sec.	Average, $\bar{D}_e \times 10^5$	Total average, $\bar{D}_{ei} \times 10^5$	Degree of freedom
1	43	-60/+80	2.13	1.915		
	65	-60/+80	1.70			
2	44	-80/+100	1.45	1.45	1.512	2
3	14	-120/+140	1.18	1.14		
	24	-120/+140	1.10			

The variance (S_{p2}^2) was calculated as in Equation D-2

$$S_{p2}^2 \times 10^{10} = [2 \times (1.512 - 1.915)^2 + (1.512 - 1.45)^2 + 2 \times (1.512 - 1.14)^2] / 2 = 0.3027$$

Null hypothesis (H_0): Particle size has no effect on the effective diffusivity at 150 lb./sq. in. (gauge) total system pressure.

Alternative hypothesis (H_A): Particle size has a certain effect on the effective diffusivity at 150 lb./sq. in. (gauge).

Test Statistic: $F = \frac{0.3027}{0.02825} = 10.715$

But $F_{0.005}(2,10) = 9.43$

Thus for a significance level of 0.995 we would reject the null hypothesis, i.e., we could not accept the hypothesis that particle size has no effect on the effective diffusivity at 150 lb./sq. in. (gauge) total system pressure.

Effect of Leaching Solution Flow Rate

Table D-5 shows the statistical data for the effect of leaching solution flow rate.

Table D-5. Statistic analysis for the effect of leaching solution flow rate at 150 lb./sq. in. (gauge) total system pressure

Groups	Run No.	Liquid flow rate, ml./sec.	Effective diffusivity, $D_e \times 10^5$ sq. cm./sec.	Average, $\bar{D}_e \times 10^5$	Total average, $\bar{D}_{ei} \times 10^5$	Degree of freedom
1	14	1.5	1.18	1.14	1.1225	2
	24	1.5	1.10			
2	20	2.25	1.16	1.16		
3	17	3.0	1.05	1.05		

The variance (S_1^2) was calculated as in Equation D-2

$$S_1^2 \times 10^{10} = [2 \times (1.1225 - 1.14)^2 + (1.1225 - 1.16)^2 + (1.1225 - 1.05)^2] / 2 = 0.0036$$

Null hypothesis (H_0): The leaching solution flow rate has no effect on the effective diffusivity at 150 lb./sq. in. (gauge) total system pressure.

Alternative hypothesis (H_A): The leaching solution flow rate has a certain effect on the effective diffusivity at 150 lb./sq. in. (gauge) total system pressure.

Test Statistic: $F = \frac{0.0036}{0.02825} = 0.127$

and $F_{0.90}(2,10) = 0.106$

$F_{0.75}(2,10) = 0.196$

So the probability of getting a value of this size (0.127) or larger under the null hypothesis is between 0.75 and 0.90, and we would fail to reject the null hypothesis for reasonable significance levels.