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Experimental Study of Pyrite Oxidation at  
pH 6-9 and 30°C

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Abstract

Experimental studies of pyrite oxidation over the pH range 6-9 were carried out at 30°C in 0.1 M KCl under conditions of fixed pH and  $p_{O_2}$ . Rate of addition of base necessary to maintain a fixed pH was monitored. Samples were withdrawn periodically and analyzed for total sulfur in solution, thiosulfate, polythionates, and sulfide. The results demonstrate an increase in rate of hydrogen-ion production with increase in pH. Metastable sulfur oxyanions were detected as intermediates in the sulfur oxidation pathway. For short-term (less than 2 day) runs, the proportion of these sulfur oxyanions was less sensitive to the length of a run than to the pH of the run. At the lower pH values (6-7), tetrathionate and sulfate were the major observed species. As pH is increased, these ions diminish with respect to thiosulfate and sulfite. The short-term data are consistent with a rate-controlling step involving the pH-dependent oxygenation of the ferrous-iron component of the pyrite and subsequent rapid oxidation of the sulfur component to an intermediate oxidation state dictated by pH-dependent reactions. Ultimately, all sulfur is oxidized to sulfate.

## Introduction

Modern genetic models for the origin of the Wyoming and Texas roll-type uranium deposits place considerable emphasis on the relationships between sulfur geochemistry and ore deposition. This paper focuses on one of the processes related to ore genesis--pyrite oxidation. The function of pyrite oxidation in ore deposition has been discussed in terms of two contrasting models. One has been described as the biogenic or geochemical cell model (Rackley, 1972). In this formulation, sulfur is redistributed via bacterially catalyzed oxidation of iron-disulfide minerals producing sulfate ions that are carried with uranium-bearing ground water into reduced (iron sulfide and (or) organic carbon-bearing) rock. There, the sulfate is rereduced to aqueous sulfide which in part acts as a reductant for precipitating uranium as reduced (U(IV)) oxides or silicates, and in part reacts with available nonsulfide iron to form ore-stage iron-disulfide minerals. An alternative hypothesis (Granger and Warren, 1969) can be described as the nonbiogenic model. They proposed that inorganic pyrite oxidation might not go all the way to completion; that is, to the highest oxidation states attainable in the presence of excess dissolved oxygen. Rather, they suggested that aqueous sulfur species of intermediate oxidation state (for example, thiosulfate,  $S_2O_3^{2-}$ ) are generated. Subsequent reactions of these species would be analogous in many ways to bacterially derived sulfide (uranium reduction and reaction with iron to produce ore-stage sulfides).

Understanding the mechanism of pyrite oxidation would clearly help place important constraints on genetic concepts for this type of deposit. In fact, pyrite oxidation has been studied extensively in connection with its importance in producing the serious environmental problem of acid mine drainage. The literature is voluminous (see Nordstrom, 1981, for a recent

comprehensive review). There is a general consensus as to the overall mechanism under acidic (pH less than 4) conditions. The initial step consists of a simple dissolution leading to ferrous iron and disulfide ion ( $S_2^{2-}$ ) in solution (or perhaps a rapid sequence of oxidations subsequent to dissolution that ultimately produces aqueous ferrous iron and sulfate). The ferrous iron reacts with oxygen in a slow step to produce aqueous ferric iron, which in turn rapidly oxidizes pyrite to sulfate and ferrous iron. The reoxidation of this ferrous iron thus propagates the cycle. Bacteria of the thiobacillus-ferrobacillus group intervene in the propagation step by catalyzing the oxidation of ferrous iron. The pathway just outlined occurs at a rate that is independent of pH (for example, McKay and Halpern, 1958; Smith and Shumate, 1970). Sulfur of intermediate oxidation state is not typically reported, although elemental sulfur has been detected in a few studies (Bergholm, 1955; McKay and Halpern, 1958). This lack of observed intermediates does not imply that such intermediates do not occur in the pathway. As stressed by Nordstrom (1981) oxidation steps must occur by one or at most two electron transfers per reaction and there is a seven-electron difference in oxidation state between sulfur in pyrite and that in sulfate. Therefore, these sulfur oxidation steps must be rapid compared to the time scale of presently available measurements at low pH.

Despite the fact that the pathway just outlined is well established for acid pH's, several lines of evidence suggest that it may be inappropriate for the ground-water regime associated with roll-type uranium deposits. It must first be noted that the solubility of a major pyrite oxidant, ferric iron, "drops dramatically as pH is increased above 4, whereas studies of modern ground-water systems containing a redox (oxygen-sulfide) boundary do not report pH values below 6.5 (Edmunds, 1973; Lisitsyn and Kuznetsova, 1967; Dahl

and Hagmaier, 1974). Ground-water systems contain a range of sinks for hydrogen ion such as carbonates, clay minerals, and feldspars that are not present in the same relative abundance in the acid mine-drainage environment. Furthermore, polished sections from sedimentary uranium deposits show pseudomorphic textures in which iron oxides formed by oxidation of pyrite closely mimic the morphology of precursor sulfides (Reynolds and Goldhaber, 1978). These textures suggest that iron dissolution was at best incomplete, and thus the process differs fundamentally from that under acidic conditions. Also notable is the fact that sulfur intermediates in the pathway are reported during sulfide oxidation at higher pH's in contrast to what has been observed at low pH (Forward and Mackiw, 1955; Makhija and Hitchen, 1978). Although such intermediates have been noted, there has been no systematic laboratory study of the conditions of production of such intermediates that can be related to uranium deposition.

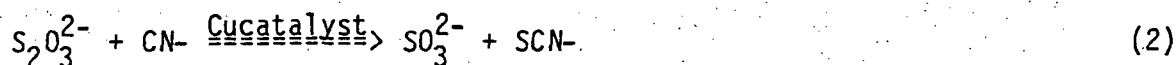
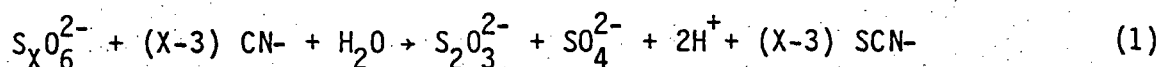
#### Experimental Procedures

Pyrite oxidation was carried out under conditions of constant pH,  $pO_2$  and temperature in a thermostatted glass reaction vessel, with a magnetic stirrer suspended from the cap and with two side ports. The two side ports were equipped with a gas-inlet tube plus inlet tube for NaOH titrant and combination pH electrode, respectively. pH control was realized via a pH stat similar to that described by Morse (1974). For experiments described below, the pH was held to within  $\pm 0.03$  of the reported value by addition of  $CO_2$ -free NaOH (0.1 M). The concentration of dissolved oxygen was fixed by bubbling water-saturated high purity oxygen or a prepared mixture of oxygen plus nitrogen through the sample solution. The gas was scrubbed free of  $CO_2$  prior to entering the cell. In all runs, the total gas-flow rate was fixed at



275 cm<sup>3</sup> per minute. The pyrite used was from the Climax Molybdenum Mine. No phases other than pyrite were observed in polished section or detected by X-ray diffraction. Observations of the starting material in polished section revealed <2 percent impurities, dominantly silicates and iron-titanium oxides. This pyrite was ground and sized by sieving at 44-62 micrometer and less than 44 micrometer and washed under a nitrogen atmosphere in a glove bag with dilute hydrochloric acid, followed by deoxygenated water, and finally acetone. Between experiments, the pyrite was stored in a vacuum desiccator. A large batch of the fine-grained pyrite was prepared initially and the majority of experimental data, except where specifically noted, was obtained with this same batch. The stirring rate in all experiments was the same. This rate was sufficient to suspend most of the finer grained fraction but not the coarser material greater than 44 micrometer. Consequently, most runs were done with less than 44-micrometer pyrite.

At the start of a run, 5 grams of pyrite was added to 1200 mL of 0.1 M KCl solution that had previously been thermally equilibrated to 30°C and pre-saturated with the appropriate gas mixture. The amount of sodium hydroxide added to maintain pH was noted as a function of time. In addition, 20-mL sample aliquots were periodically removed, immediately filtered through 0.45-micrometer membrane filters, and analyzed for a range of aqueous sulfur constituents. Polythionates and thiosulfate were determined by cyanolysis, followed by spectrophotometric determination of resulting thiocyanate (Nor and Tabatabai, 1976). These reactions proceed as follows:



At room temperature, reaction (1) only occurs with polythionates of  $M \geq 4$ . In the presence of a copper catalyst, two moles of thiocyanate are formed from tetrathionate, three from pentathionate, and four from hexathionate. In the absence of the copper catalyst, the thiocyanate equivalents formed from tetra-, penta-, and hexathionate are one, two, and three, respectively. Nor and Tabatabai (1976) assumed that all polythionate was present as tetrathionate, and determined an empirical factor of 1.75 to estimate the amount of tetrathionate in samples that also contained thiosulfate. In the present work, the same factor, 1.75, has been used. If higher polythionates than tetrathionate are present, this would result in an underestimate of polythionates relative to thiosulfate. This point is addressed further below. Sulfite was determined by the colorimetric procedure of West and Gaeke (1956). In the presence of thiosulfate, an elemental sulfur precipitate had been removed by membrane filtration prior to color development. Total sulfur in all forms was estimated by reduction to  $H_2S$  and determination of  $H_2S$  by methylene-blue colorimetry (Johnson and Nishita, 1952). This technique gave generally reasonable agreement ( $\pm 10$  percent), with values obtained at the end of selected runs by oxidizing the supernatant solution to sulfate with nitric acid and gravimetric determination of sulfate as  $BaSO_4$ . However, obviously erratic values were, for unknown reasons, occasionally obtained by the Johnson and Nishita procedure. Therefore, in certain instances when this occurred, the total sulfur data were interpolated from the remaining values.

The solid products of two of the runs were examined petrographically in polished grain mounts under reflected light. In addition, a separate experiment was conducted to observe petrographically, results of larger term oxidation. This was accomplished by maintaining a 140-milligram sulfide

concentrate consisting of intergrown pyrite and marcasite from the Benavides uranium deposit, south Texas, at saturation with air and at elevated pH by addition of sodium carbonate. The initial pH of the solution was 8.3; after 2 weeks the pH rose to about 10 and stayed approximately constant for the remaining 6 weeks of the experiment. A parallel experiment was run in which sodium carbonate was not added. The pH of this run started at 5.2 and was 4.4 after 2 weeks.

### Results

Results of this study clearly indicate that soluble metastable sulfur oxyanions are produced as intermediates during inorganic pyrite oxidation in the pH range 6-9. As an illustration of the point, first consider an experiment conducted at pH 9 utilizing pyrite in the <44-micrometer size range. Oxygen was held at saturation, corresponding to a concentration of 0.44 mM O<sub>2</sub> under the conditions of the experiment. The presence of metastable sulfur intermediates is indicated by the data points representing thiosulfate sulfur, sulfur, polythionate sulfur, and sulfite sulfur (fig. 1, table 6). The lines drawn through the data points deviate from a straight line. Nonlinearity is seen also in the plot of NaOH addition with time (fig. 2). In view of linear rates observed by other workers using more carefully sized material (see below) this behavior likely is caused by the large spectrum of particle sizes present in the starting material, as documented in the case of feldspar dissolution (Holdren and Berner, 1979). However, petrographic data (see below) demonstrate that oxide reaction-product coatings can develop over time such that the nonlinear rates may in fact be real. At present, the data are not sufficient to resolve this point.

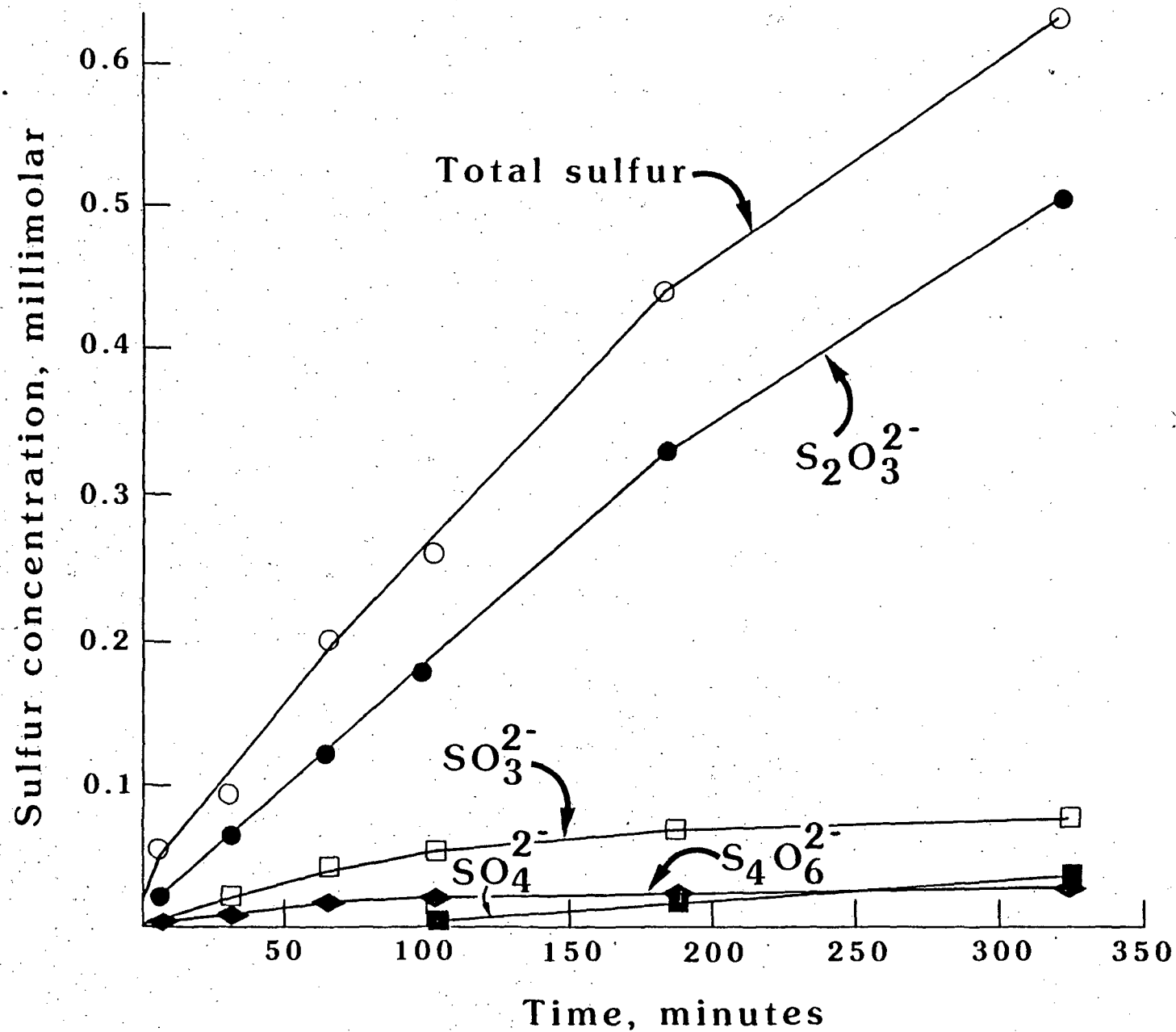


Figure 1. - Plot of sulfur species in solution produced during pyrite oxidation at pH 9 versus time. Oxygen held at saturation.

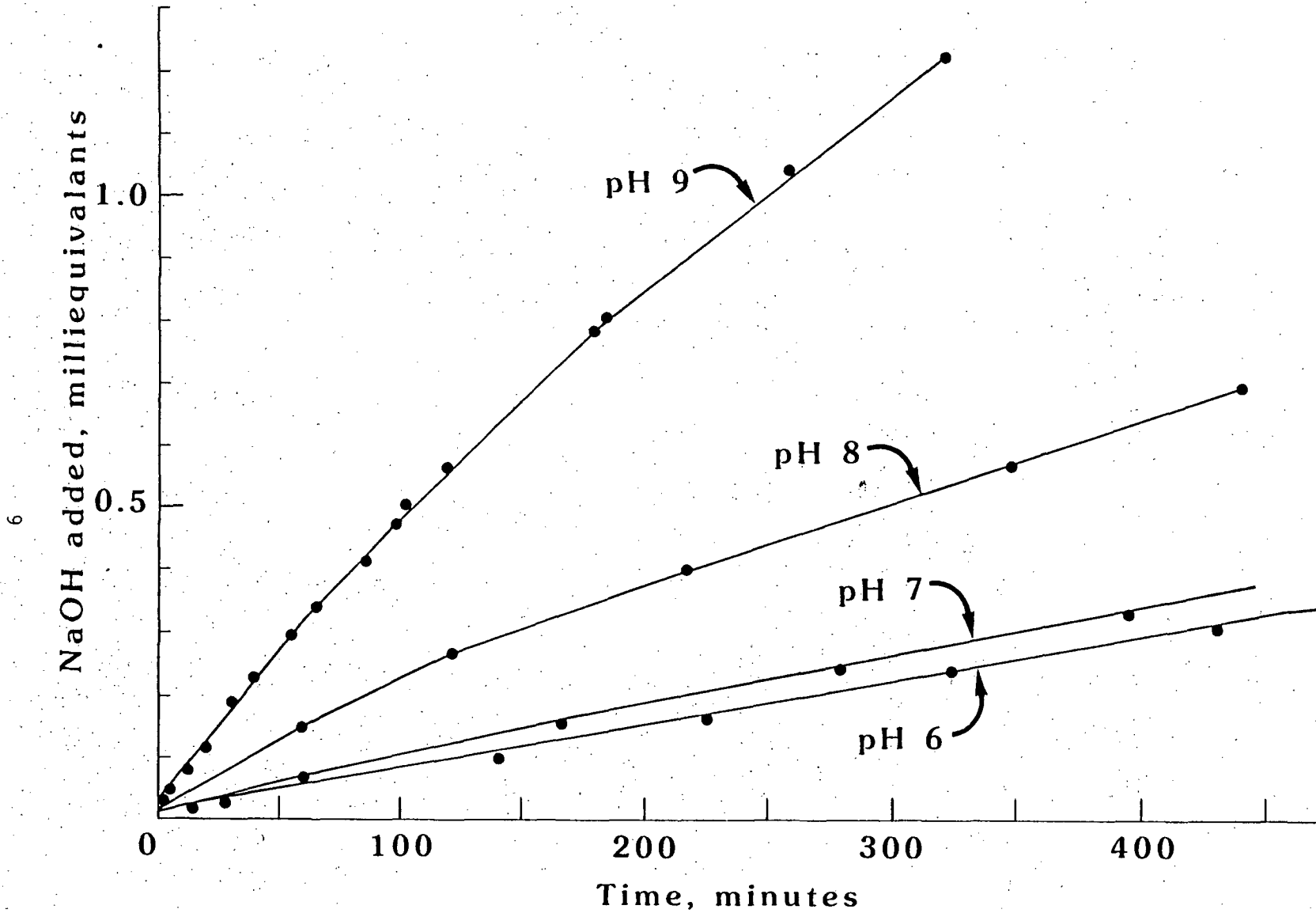


Figure 2. - Plot of milliequivalents of NaOH added to maintain pH constant versus time for pyrite oxidation experiments conducted at pH 6, 7, 8, and 9.

The thiosulfate was calculated, as discussed above, by assuming that the polythionate fraction is composed exclusively of tetrathionate. This calculation requires only a minor correction to the thiosulfate data in the experiment under consideration. "Sulfate", the difference between total S and the sum of the analyzed constituents, is present as an appreciable percentage of the total sulfur only for the first measurement taken at 7 minutes elapsed time. The sulfate result for this time interval is most likely an experimental artifact, because sulfate once formed would not disappear from solution as required by the data in table 1. "Sulfate" in the first time interval may, therefore, be taken to indicate the transient presence of a sulfur species not considered in the analytical scheme. One possibility is colloidal elemental sulfur finer than  $0.45 \mu\text{m}$  that passes through the membrane filter. Anomalous "sulfate" concentrations of this type were found during the first few minutes in a number of other experiments as well. These concentrations seem to reflect an initial "pre-oxidation" that occurs during handling of the pyrite. In support of this hypothesis, the intensity of this initial anomalous behavior was noted to increase markedly when the pyrite was not carefully cleaned and stored.

Disregarding, therefore, the initial data point at 7 minutes elapsed time the following results stand out: (1) Thiosulfate is the major component of total S in solution (66-79 percent of total S). (2) Sulfate constitutes only a small fraction of total S (1-6 percent), as does tetrathionate (4-11 percent). (3) Sulfite is relatively abundant (12-22 percent). (4) Systematic trends in the data indicate some minor tendency towards an increasing proportion of sulfate and thiosulfate and a decrease in relative amounts of tetrathionate and sulfite with time.

Table 1.--Results of pyrite oxidation at pH 6 and O<sub>2</sub> at saturation  
[mM, millimolar; leaders (---) indicate not detected]

Elapsed time (minutes)	Total sulfur (mM)	S <sub>4</sub> O <sub>6</sub> <sup>2-</sup> - sulfur (mM)	S <sub>2</sub> O <sub>3</sub> <sup>2-</sup> - sulfur (mM)	SO <sub>2</sub> <sup>2-</sup> - sulfur (mM)	"SO <sub>4</sub> <sup>2-</sup> " - sulfur (mM)	NaOH added (milliequivalents)
30	Trace	Trace	---	---	---	0.025
140	0.06	0.022	0.009	---	.029	.10
225	<sup>1</sup> 0.09	.045	---	---	.045	.17
325	.14	.080	---	---	.073	.24
430	.16	.093	---	---	.075	.31
600	.23	.12	---	---	.12	.39

<sup>1</sup>Interpolated value.

Results for a pH 6 run ( $O_2$  at saturation, less the 44-micrometer pyrite) are given in table 1 and plotted on figure 3. These data differ significantly from those at pH 9. Note first that the rate of production of total sulfur is much lower at pH 6 than at pH 9. Only 0.23 mM total sulfur was produced in 600 minutes, whereas at pH 9, 0.64 mM was detected at 325 minutes. The rate of NaOH consumption is likewise lower at pH 6 (fig. 2). The distribution of aqueous sulfur species is also markedly different. Sulfite was not detected above the blank at pH 6. Sulfate and tetrathionate sulfur are found in subequal concentrations, and both represent a higher percentage of total sulfur at pH 6 compared to pH 9.

Because of the importance of polythionates at the lower pH's studied, a separate experiment was conducted to examine the assumption that tetrathionate is the dominant species. This was done using the anion-exchange chromatographic technique of Pollard and others (1964), in which the polythionates were eluted with successively more concentrated HCl. Ions that eluted off the column were detected using ultraviolet spectroscopy. The separation procedure was checked using synthetic tetrathionate prepared and purified by the procedure of Stamm and others (1942). Figure 4 presents results from the supernatant of an experiment conducted at pH 6.5 ( $O_2$  at saturation, <44-micrometer pyrite). The integrated ultraviolet absorbances of the polythionates occur in the ratio 1: 11.1: 30 for  $S_3O_6^{2-}$  :  $S_4O_6^{2-}$  :  $S_5O_6^{2-}$ . Assuming that the molar extinction coefficients of the polythionate ions are comparable, these ratios would also correspond to their concentration ratios, or recalculated as percentage of total polythionate sulfur; 4.8, 71.2 and 24 percent, respectively. These data, although obviously extremely limited, serve to indicate the error that is incurred in assuming that tetrathionate is the dominant polythionate.



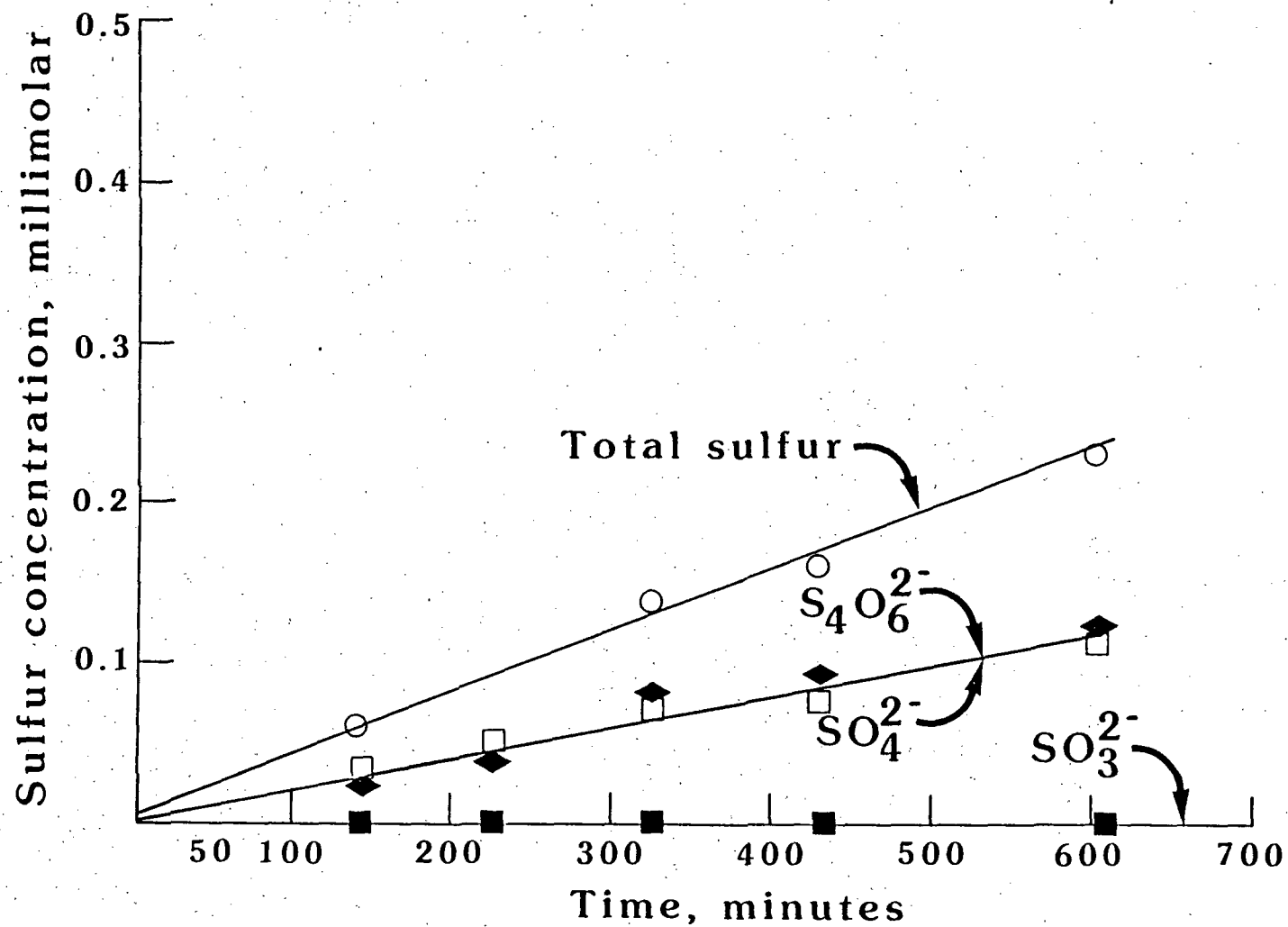


Figure 3. - Plot of sulfur species in solution (as S) produced during pyrite oxidation at pH 6 versus time. Oxygen at saturation.

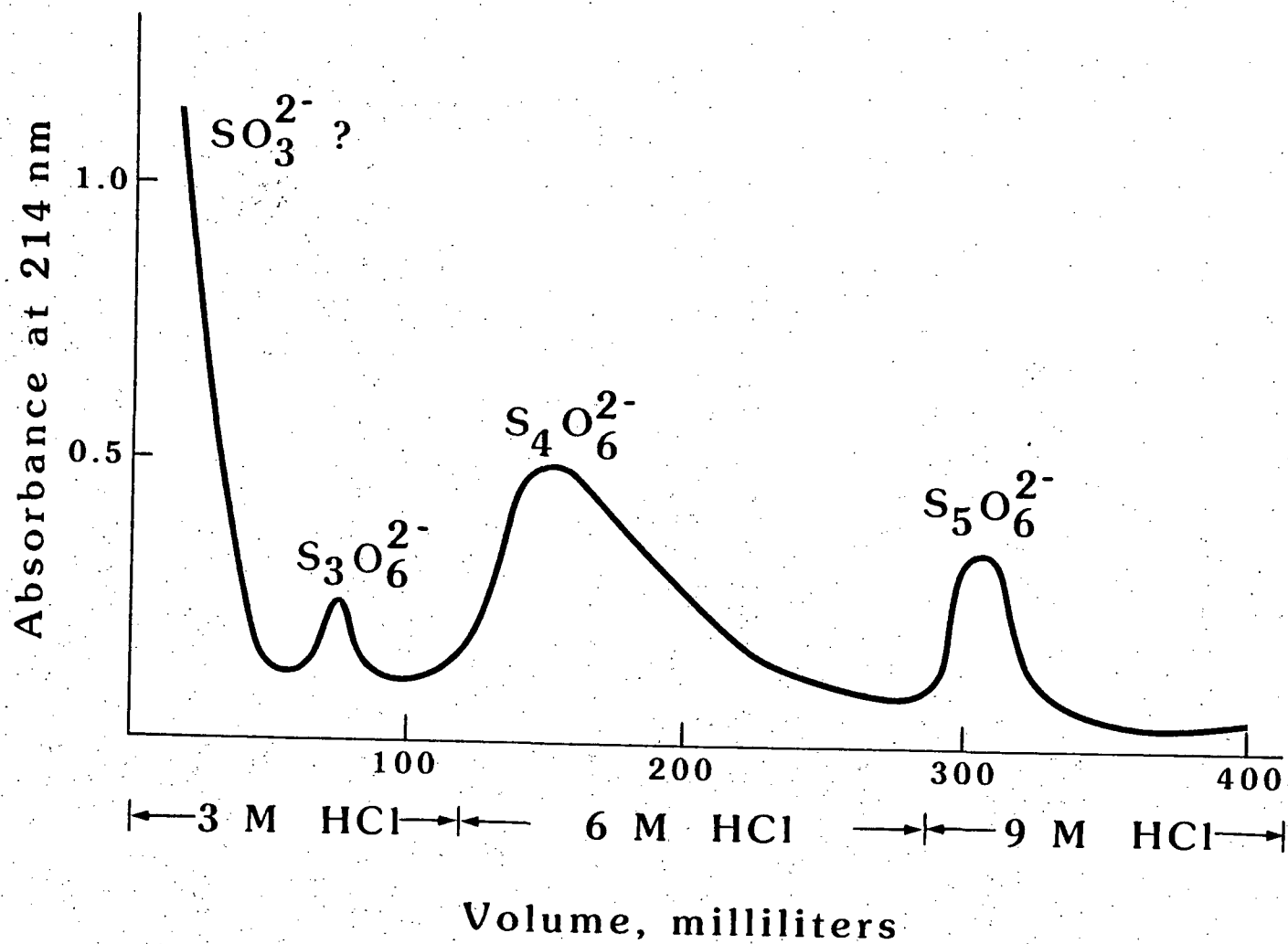


Figure 4. - Plot of absorbance at 214 nm versus volume of acid passed thru anion-exchange column showing resolution of polythionate anions.

In addition to the pyrite oxidation results for pH 6 and pH 9 discussed above, additional runs using fine-grained pyrite (less than 44 micrometer) and with  $O_2$  held at saturation were made at pH's of 6.5, 7, 7.5, and 8. Data for these experiments are given in tables 2-5, respectively. The runs at pH 6.5 and 7.5 were done using a separate batch of pyrite, and so the rate data are not directly comparable. Some limited work was also done at pH 8 with  $O_2$  at 50 and 20 percent of saturation. These experiments will not be discussed in detail except to note that the results suggest a linear relationship between NaOH consumption rate and oxygen concentration at constant pH.

The relative abundance of aqueous sulfur species produced during short-term pyrite oxidation experiments is clearly pH-dependent. This dependency is illustrated in figure 5 in which the percentage distribution of sulfur oxyanions produced during pyrite oxidation is plotted against the pH of the experiment. The range in this percentage value during the course of the run is indicated by a vertical bar. The initial experimental point in each run was not considered for reasons discussed previously. Figure 5 shows that, for the time interval studied, variations between runs at different pH's are more significant than changes in the proportion of sulfur constituents with time at a given pH. A notable exception to this behavior occurred at pH 7.5 (see below). As discussed previously, thiosulfate is dominant at pH 9, with subordinate sulfite and minor sulfate. As pH decreases, thiosulfate and sulfite diminish in relative importance compared to tetrathionate and sulfate. The results obtained at pH 7.5 differ somewhat from those at other pH's in that there is a more pronounced variability with time in the relative proportions of sulfur oxyanions. Initially, thiosulfate and tetrathionate sulfur are produced in approximately equal proportions (fig. 6). As the experiment progressed, however, thiosulfate declined relative to other forms

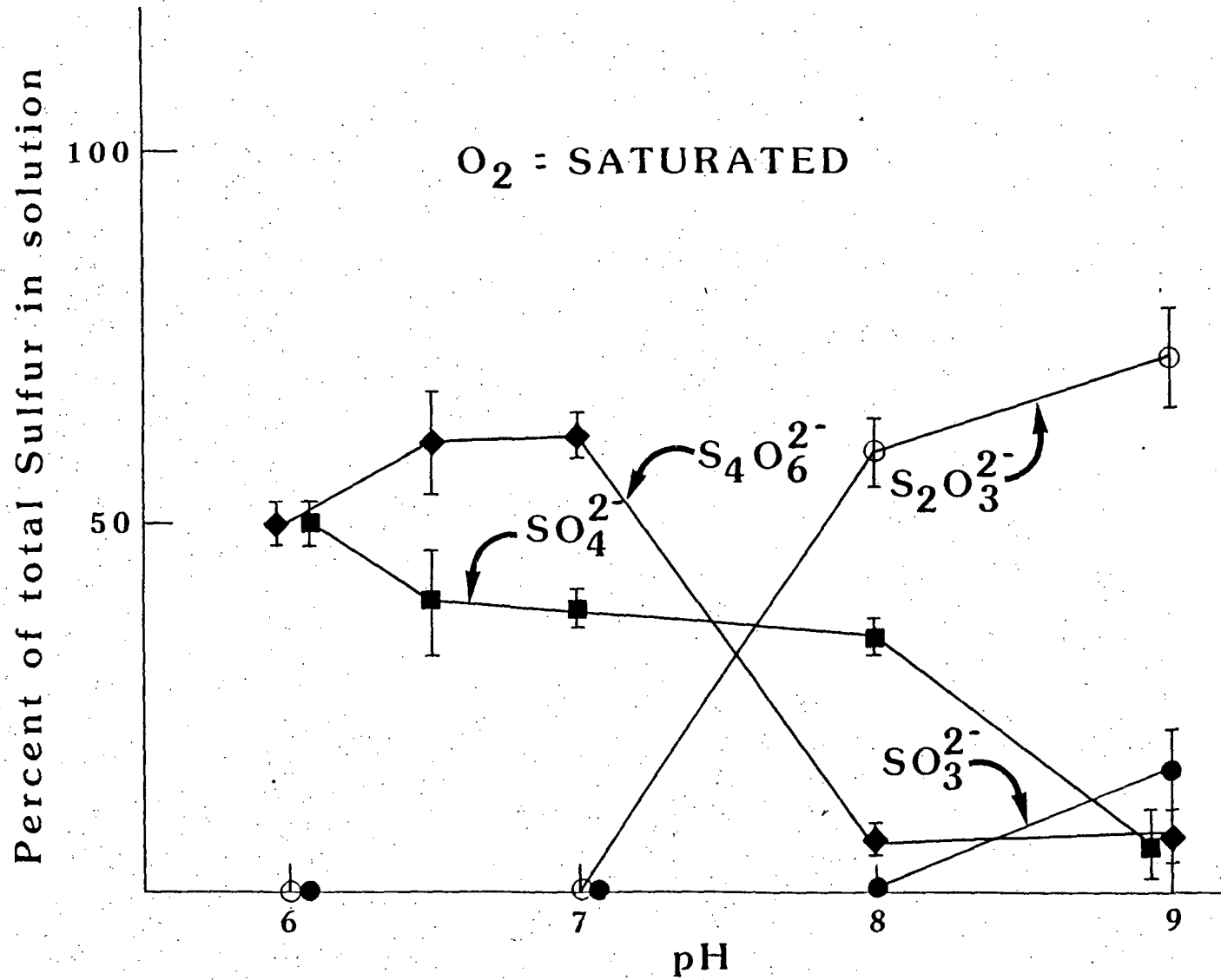


Figure 5. - Relative abundance of aqueous sulfur species (as S) produced during short-term pyrite oxidation experiments as a function of pH.

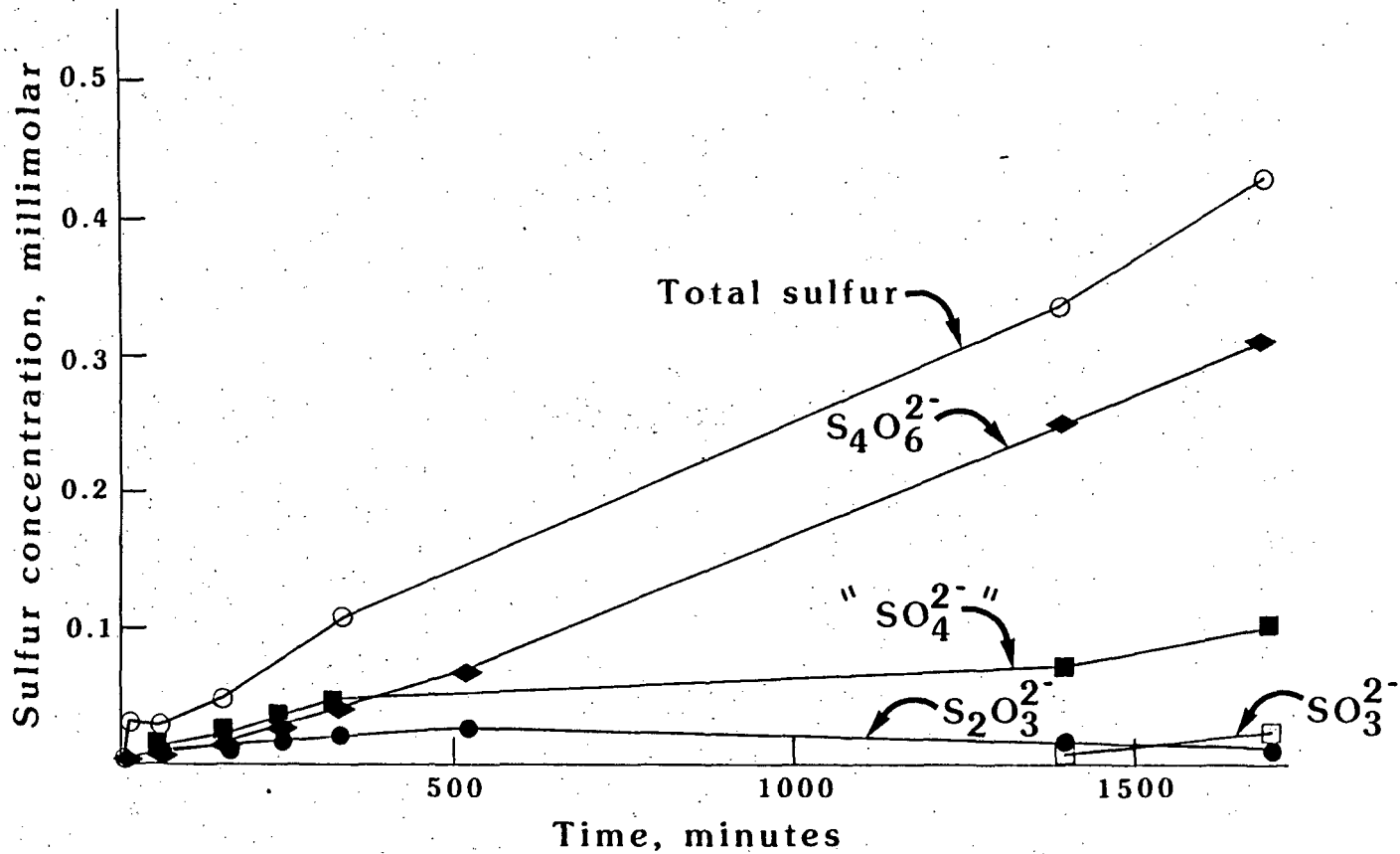


Figure 6. - Plot of sulfur species in solution (as S) produced during pyrite oxidation at pH 7.5 versus time. Oxygen at saturation.

of sulfur and in absolute concentration. Sulfite was detected only towards the end of the experiment. This pH is in the transitional region between products dominated by tetrathionate ( $\text{pH} \leq 7$ ) and thiosulfate ( $\text{pH} \geq 8$ ), and this transition is evidently reflected in the data from pH 7.5.

The relationships illustrated on figure 5 are representative of short time periods only. Eventually, all sulfur in solution will be oxidized to sulfate, which is the thermodynamically stable species in equilibrium with excess oxygen. Evidently this conversion to sulfate is subject to catalysis. This catalysis can be deduced from preliminary work on a more complex solution than the simple KCl matrix used in most of the study. A sterile bacterial medium (Stanier and others, 1963) was used in one experiment at pH 6.5 (Cathy Shepard, written commun., 1980). Although the dominant species are the same as those shown on figure 5, the abundance of tetrathionate sulfur relative to total sulfur in solution declined rapidly after 600 minutes in contrast to the results shown in table 2. This difference between the complex bacterial media and KCl solutions presumably indicates a catalytic effect in the complex media in which tetrathionate is converted to some other product--probably sulfate.

The data of figure 5 can be recast to show that the mean oxidation state of sulfur in solution increases with decreasing pH (fig. 7). This plot was constructed by combining the mean oxidation state of sulfur in each of the individual sulfur oxyanions in the proportions shown on figure 5. That the trend shown in figure 7 continues to lower and higher pH's can be inferred from the results of previous workers. At low pH, sulfate and, rarely, elemental sulfur are the sole sulfur-oxidation products, as noted in the introduction to this report. Results of low pH are indicated as a generalized point on figure 7. At highly alkaline pH, some sulfide (oxidation state -2) is produced (Stokes, 1907), possibly by an alkaline hydrolysis reaction.

Table 2.--Results of pyrite oxidation at pH 6.5 and O<sub>2</sub> at saturation

[mM, millimolar; leaders (---) indicate not detected]

Elapsed time (minutes)	Total sulfur (mM)	S <sub>4</sub> O <sub>6</sub> <sup>2-</sup> - sulfur (mM)	S <sub>2</sub> O <sub>3</sub> <sup>2-</sup> - sulfur (mM)	SO <sub>2</sub> <sup>2-</sup> - sulfur (mM)	"SO <sub>4</sub> <sup>2-</sup> " - sulfur (mM)	NaOH added (milliequivalents)
35	---	0.017	---	---	---	0.006
180	0.041	.038	---	---	.003	.063
360	.076	.052	---	---	.024	.14
1140	.28	.16	---	---	.12	.47
1440	<sup>1</sup> .32	.20	---	---	.12	.57
2040	<sup>1</sup> (.45)	.29	---	---	.16	.76
2640	.55	.32	---	---	.23	1.0
2940	.65	.35	---	---	.30	1.1

<sup>1</sup>Interpolated value.

Table 3.--Results of pyrite oxidation at pH 7 and O<sub>2</sub> at saturation

[mM, millimolar; leaders (---) indicate not detected]

Elapsed time (minutes)	Total sulfur (mM)	S <sub>4</sub> O <sub>6</sub> <sup>2-</sup> - sulfur (mM)	S <sub>2</sub> O <sub>3</sub> <sup>2-</sup> - sulfur (mM)	SO <sub>2</sub> <sup>2-</sup> - sulfur (mM)	"SO <sub>4</sub> <sup>2-</sup> " - sulfur (mM)	NaOH added (milliequivalents)
15	Not determined	Trace	---	---	Not detected	0.005
60	0.09	<sup>1</sup> (0.03)	---	---	0.06	.06
165	.11	.067	---	---	.039	.16
278	.17	.11	---	---	.07	.25
395	.23	.14	---	---	.09	.34

<sup>1</sup>Extrapolated value.



Table 4.--Results of pyrite oxidation at pH 7.5 and O<sub>2</sub> at saturation

[mM, millimolar; leaders (---) indicate not detected]

Elapsed time (minutes)	Total sulfur (mM)	S <sub>4</sub> O <sub>6</sub> <sup>2-</sup> - sulfur (mM)	S <sub>2</sub> O <sub>3</sub> <sup>2-</sup> - sulfur (mM)	SO <sub>2</sub> <sup>2-</sup> - sulfur (mM)	"SO <sub>4</sub> <sup>2-</sup> " - sulfur (mM)	NaOH added (milliequivalents)
12	0.34	0.003	0.004	---	0.024	0.012
65	.03	.008	.011	---	.011	.040
160	.048	.017	.014	---	.017	.074
243	<sup>1</sup> .075	.026	.017	---	(.032)	.11
328	.107	.042	.023	---	.042	.14
520	<sup>1</sup> .113	.067	.025	---	(.021)	.22
1398	.334	.25	.015	0.008	.069	.65
1693	.425	.31	.011	0.016	.104	.77

<sup>1</sup>Interpolated value.

Table 5.--Results of pyrite oxidation at pH 8 and O<sub>2</sub> at saturation

[mM, millimolar; leaders (---) indicate not detected]

Elapsed time (minutes)	Total sulfur (mM)	S <sub>4</sub> O <sub>6</sub> <sup>2-</sup> - sulfur (mM)	S <sub>2</sub> O <sub>3</sub> <sup>2-</sup> - sulfur (mM)	SO <sub>2</sub> <sup>2-</sup> - sulfur (mM)	"SO <sub>4</sub> <sup>2-</sup> " - sulfur (mM)	NaOH added (milliequivalents)
2	Not determined	---	---	---	---	0.01
16	0.037	<sup>1</sup> 0.007)	0.024	---	0.005	.05
58	.13	<sup>1</sup> (.010)	.074	---	.046	.15
122	.19	<sup>1</sup> (.015)	.12	---	.060	.27
217	.30	<sup>1</sup> (.020)	.17	---	.11	.40
346	.42	.026	.23	---	.14	.57

<sup>1</sup>Data are based upon a linear interpolation between an initial value of zero and the final value at 346.

Table 6.--Results of pyrite oxidation at pH 9 and O<sub>2</sub> at saturation

[mM, millimolar; leaders (---) indicate not detected]

Elapsed time (minutes)	Total sulfur (mM)	S <sub>4</sub> O <sub>6</sub> <sup>2-</sup> - sulfur (mM)	S <sub>2</sub> O <sub>3</sub> <sup>2-</sup> - sulfur (mM)	SO <sub>2</sub> <sup>2-</sup> - sulfur (mM)	"SO <sub>4</sub> <sup>2-</sup> " - sulfur (mM)	NaOH added (milliequivalents)
7	0.056	Trace	0.021	---	.035	
33	.095	0.008	.063	.021	.003	
68	<sup>1</sup> (.20)	.021	.12	.041	(.021)	
106	.26	.21	.18	.053	.002	
189	.44	.024	.33	.069	.021	
327	.64	.027	.50	.075	.035	

<sup>1</sup>Interpolated value.

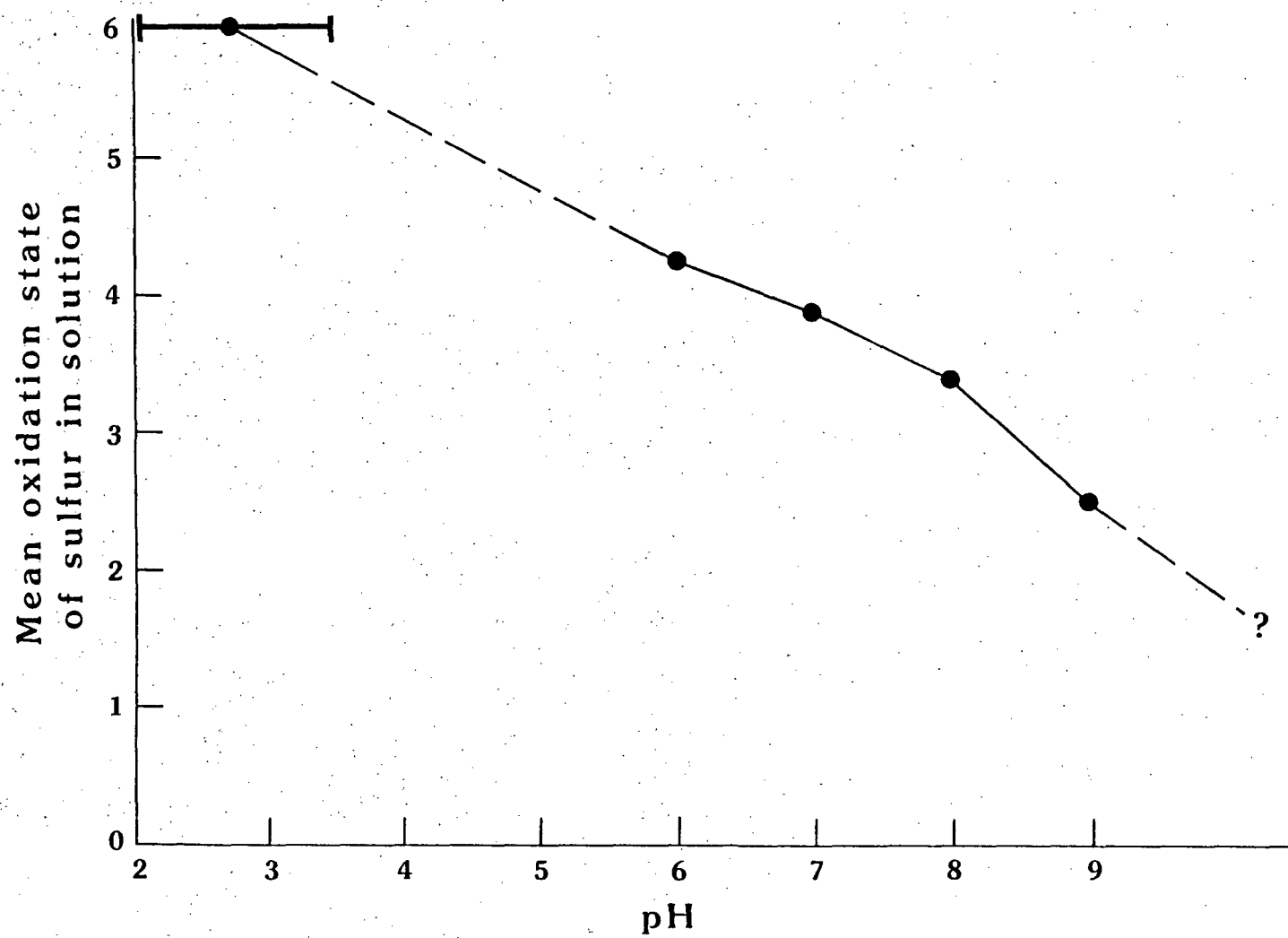
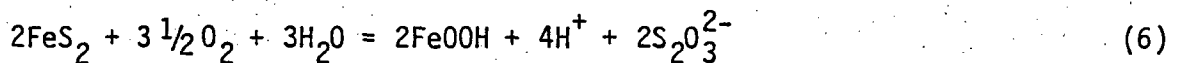
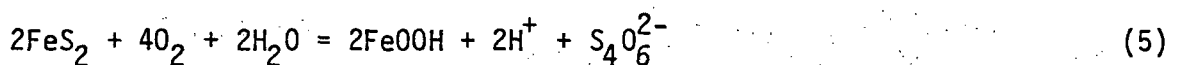
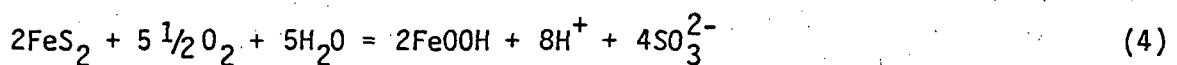
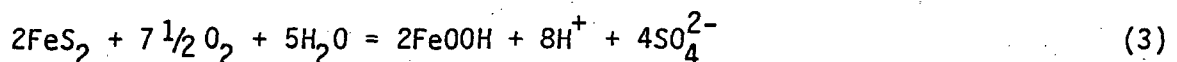


Figure 7. - Mean-oxidation state of sulfur in solution as a function of pH.

Figure 8 summarizes results of rate of addition of NaOH as a function of pH. This rate is the slope of the NaOH versus time curves in figure 2. For those plots that are nonlinear, the initial part of the experiment was neglected in this calculation on the assumption that this behavior is related to a more rapid reaction of the finest particles, as mentioned above. The plot demonstrates an increase in NaOH addition rate with increasing pH. This increase is particularly marked between pH 8 and 9. A similar result was noted by previous workers (Smith and Shumate, 1970).

At first glance, figure 8 suggests that rate of "pyrite oxidation" (which in this context is defined as the rate of oxidation of ferrous iron in pyrite to ferric iron in iron oxide) increases at pH 9 relative to pH 6. However, the relationship between hydrogen ion production (NaOH consumption) and rate of pyrite oxidation is dependent upon the particular sulfur oxidation product produced as illustrated by the following equations that are written so as to produce a constant amount of goethite (FeO.OH);



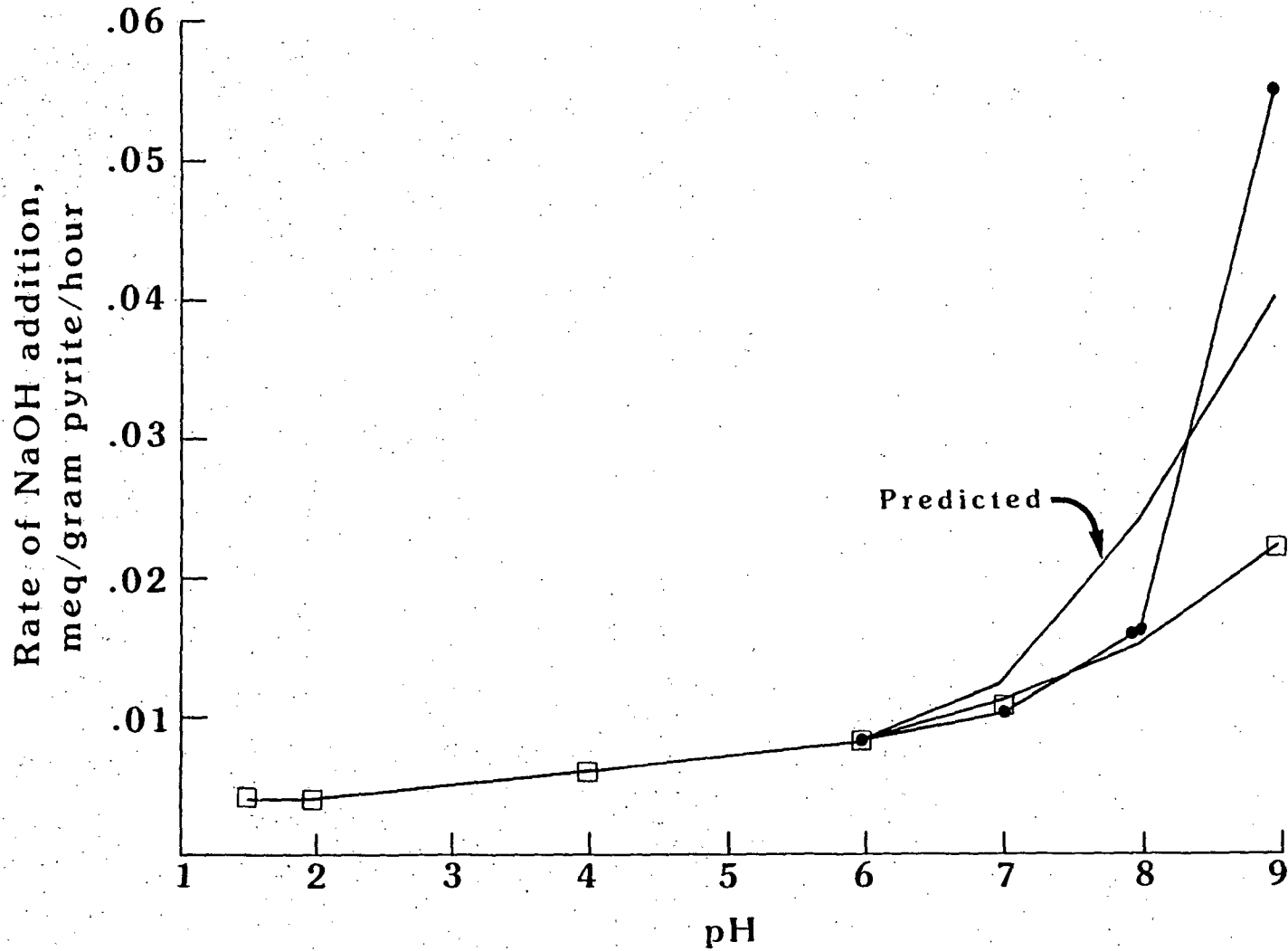


Figure 8. - Rate of NaOH addition in milliequivalents per gram pyrite per hour during pyrite oxidation as a function of pH.

( ) data of this study.

( ) data of Smith and Shumate, (1970). Normalized to correspond at pH 6 to the results of this study.

The predicted curve is discussed in the text.

Of particular interest is the fact that pyrite oxidation leading exclusively to elemental sulfur ( $S^0$ , equation 7) produces no hydrogen ions. Therefore, the possibility exists that at low pH, where low rates of hydrogen-ion production (NaOH consumption) are observed, the oxidation of iron may nevertheless be proceeding at a rapid rate with an associated buildup of sizeable quantities of elemental sulfur in the solid phase. This possibility was examined in two ways. In one procedure, an attempt was made to measure ferric iron in oxidized pyrite and to compare this measured value to one predicted from the NaOH consumption data. Oxidized iron was determined by leaching pyrite previously oxidized in the pH-stadt in boiling 6 N HCl for 10 minutes. Pyrite is insoluble under these conditions, whereas iron oxides are soluble (Berner, 1970). Iron was determined on the supernatant by colorimetry utilizing the ferrozine technique (Stookey, 1970). A blank consisting of unreacted pyrite was run for comparison. The predicted values were calculated as follows: (1) The ratio of moles of iron oxidized to moles of hydrogen ion produced was calculated by combining equations 3-6 in the proportion dictated by the observed proportions of analytically detected aqueous sulfur species. (2) This ratio was then multiplied by the actual amount of hydrogen ions produced, as determined by the volume of NaOH consumed times its known concentration. The results of this calculation, as well as the observed values, are compared in table 7. The agreement between the two estimates is considered reasonable considering that the leaching procedure is rather crude. In particular, the results for the pyrite oxidized at pH 6 show no buildup of oxidized iron over that predicted from the analytically determined sulfur species.

In a second set of experiments, elemental sulfur was determined directly on the same previously oxidized pyrite samples as shown in table 7. A

Table 7.--Comparison of iron oxide iron predicted to have formed during pyrite oxidation experiments with that leached by HCl

	Predicted (mg)	Observed (mg)
pH6	5	3
pH8 (O <sub>2</sub> =50 percent)	4	4
pH8 (long term)*	84	101
pH9	28	18

\*This was a sample oxidized for longer (4700 minutes) than in other experiments (typically less than 450 minutes) to allow more extensive buildup of oxidation products.



separate aliquot of each of these samples was refluxed in acetone, as was a standard consisting of flowers of sulfur. Sulfur dissolved in the acetone was then determined by the procedure of Bartlett and Skoog (1954). All values determined were extremely low, and none were significantly above the values of the blank determined from unreacted pyrite. The two experiments together indicate that solid elemental sulfur was not a significant product in these experiments.

The data for  $H^+$  production as a function of pH is compared (fig. 8) to the oxygen-consumption results of Smith and Shumate (1970). The oxygen consumption data were normalized to correspond to the  $H^+$  production results at pH 6. Comparison of the two plots shows close correspondence at pH 7 and 8, but the  $H^+$  production shows a large relative increase at pH 9. In a general sense, the two measures of pyrite-oxidation rate should shift with respect to each other as a function of pH. Inspection of equations 3-7 shows that the relationship of  $O_2$  consumed to  $H^+$  produced is a function of the particular sulfur species produced as shown on figure 8 by the "predicted" curve in which the rate of  $H^+$  production is calculated relative to oxygen consumption based upon the observed distribution of sulfur oxyanions at each pH (fig. 5). Viewed in this way, there is rather poor agreement between the two data sets at pH 8 and 9. Although the origin of the discrepancy is not presently known, it may indicate a sensitivity of the distribution of sulfur products to the particular experimental design.

Observations on solid reaction products were consistent with the chemical data in that elevated pH led to much more rapid oxidation effects. Essentially no discernible differences were seen between unreacted pyrite and that oxidized at pH 6. Likewise, the sulfide concentrate from the Benavides deposit oxidized for 2 weeks between pH 5.2 and 4.4 was not detectably

affected. In comparison, pyrite oxidized at pH 9 had a distinctive surface tarnish but no discrete reaction rim was resolvable using the petrographic microscope. The sulfide concentrate, however, showed marked effects of oxidation after both 2 and 6 weeks. After 2 weeks, most grains had developed at least a discontinuous iron-oxide rim, presumably by replacement of iron disulfide. On some grains, these rims were continuous and crudely uniform in thickness; the rims were typically 1 micrometer thick. In many grains, the oxide rim had pulled away from the sulfide substrate, leaving a 1-3 micrometer gap between the two phases. This gap may have occurred either during reaction or perhaps as an artifact of desiccation during sample preparation. Marcasite oxidized more rapidly than pyrite, as evidenced by grains containing both phases in which the pyrite was significantly less replaced by oxide than was marcasite. Along one such grain perimeter, an oxide rim was 2 micrometers thick against marcasite and 1 micrometer thick against pyrite. In a large number of grains, there was extensive embayment of sulfides rather than uniform rimming, suggesting preferential attack along fractures or other zones of weakness.

After 6 weeks, the types of features observed were essentially similar to those at 2 weeks, although oxidation was more advanced in that a higher proportion of grains bore a continuous oxide rim and oxide rims were as much as 3 or 4 micrometers thick. Residual unreacted pyrite was occasionally contained within the oxide rim. In a few grains the outer margin of the oxide rim seemed to be pseudomorphic after the original grain boundary, but in most grains this relationship could not be established. Oxide rims on marcasite grains were as much as 11 micrometers thick; in some grains this rim had the definite appearance of a pseudomorphic replacement.

## Discussion

### Mechanism of pyrite oxidation

The results of this study demonstrate that metastable sulfur oxyanions accumulate as intermediates in the pathway of pyrite oxidation over the pH range 6-9. These species show a systemic pH dependence with a more oxidized assemblage detected at lower pH. A review of the literature on the chemistry of sulfur oxyanions suggests that the broad outlines of the observed distribution can be rationalized on the basis of well-established kinetic behavior of these ions.

Under weakly acidic conditions, thiosulfate is readily oxidized to tetrathionate by weak oxidizing agents (Lyons and Nickless, 1968) equation 8.



Alternatively, under strongly acid conditions, thiosulfate may disproportionate to elemental sulfur and sulfite.

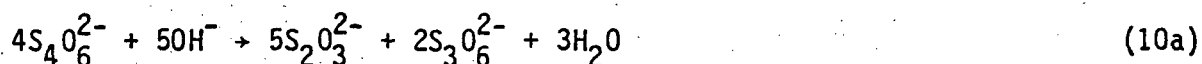


Thiosulfate is known to persist, however, under alkaline conditions (Dowson and Jones, 1974). This is clearly a kinetic phenomenon. Calculations on the position of the tetrathionate-thiosulfate equilibrium (equation 8), based upon the free-energy data in Garrels and Christ (1965) show that tetrathionate ought to predominate at the  $p\text{O}_2$  and pH of the experiments.

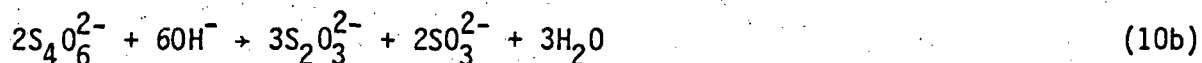
Sulfite is also relatively inert under alkaline conditions (Dowson and Jones, 1974) but is rapidly oxidized to sulfate under acidic conditions. Rand and Gale (1967) have determined that sulfite oxidation rate is proportional to

hydrogen-ion concentration to the 1.6 power over the pH range 6.5 to 7.7 and to hydrogen ion to the first power at lower pH's. The oxidation rate, with other variables held constant, decreases by three orders of magnitude between pH's of approximately 4 and 7.7. The mechanism of this oxidation is not straightforward, as indicated by fractional dependence of the rate on both hydrogen-ion and sulfite concentration.

Polythionates, in contrast to thiosulfate and sulfite, are unstable in alkaline solution, being converted dominantly to thiosulfate (Lyons and Nickless, 1968; Dowson and Jones, 1974), but are relatively stable under acidic conditions.



or



Therefore, the observed buildup of sulfite and thiosulfate at pH 8-9 can be postulated as due to the fact that these ions are intermediates in the sulfur-oxidation pathway, along which further oxidation is to some extent arrested in this pH range. The antipathetical relationship between thiosulfate sulfur and tetrathionate sulfur (figure 5) suggests the possibility that thiosulfate is likewise an intermediate at pH less than 8 which is converted to tetrathionate (equation 8) at a rapid rate compared to production from its precursor in the pathway. Furthermore, the sum of

sulfite-plus-sulfate sulfur at pH 9 is roughly similar to the proportion of sulfate to total sulfur at pH less than 9. This similarity suggests that sulfite oxidation provides a sizeable component of the observed sulfate. These observations imply, but do not prove, that the sequence of sulfur-oxidation steps is less sensitive to pH than is the relative rates of these steps.

A useful comparison is that between sulfur-oxidation products observed during oxygenation of aqueous  $\text{HS}^-/\text{H}_2\text{S}$  and those found during pyrite oxidation. Although a number of studies of the  $\text{HS}^-/\text{H}_2\text{S}$  pathway have been conducted, the most comprehensive work to date is that of Chen and Morris (1970, 1972). They noted an induction period prior to the initiation of sulfide removal and a pH-dependence of the nature of sulfur intermediates. At pH's greater than neutral, thiosulfate and sulfite were predominant. The ratio of thiosulfate sulfur to all other sulfur-oxidation products increased (at similar time of reaction) with increasing pH from about 52 percent to 75 percent over the pH range 7.9 to 8.8. The comparable figures from the present study are 54 percent and 70 percent, respectively (fig. 5). At pH less than seven, Chen and Morris detected polysulfide ions ( $\text{S}_X^{2-}$ ,  $X = 2-6$ ). Visible precipitation of elemental sulfur occurred at pH 6.7 and below. Polysulfides are stabilized by reaction of elemental sulfur with aqueous bisulfide (equation 12):

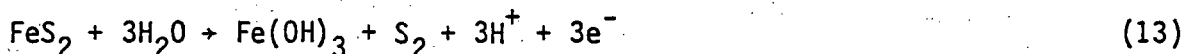


and therefore are not expected as persistent species in the pyrite-oxidation pathway. Polythionates, however, which are produced in the pyrite-oxidation pathway, have a linear structure as do polysulfides, and their S-S bonds react

chemically in a fashion similar to those of polysulfides. The polythionates may represent the oxidation products of polysulfides produced in the absence of aqueous sulfide.

Chen and Morris (1970, 1972) concluded that  $\text{HS}^-/\text{H}_2\text{S}$  oxidation in the neutral pH range operates by production of elemental sulfur via a chain mechanism (hence the induction period), and further reaction of this sulfur to form polysulfides that are much more rapidly oxidized than is  $\text{HS}^-$  or  $\text{H}_2\text{S}$ . Under alkaline conditions, elemental sulfur is still an important intermediate but polysulfide ions do not build up, owing to removal of zero-valent sulfur by a mechanism such as the reverse of equation 9.

The similarity in product species between  $\text{HS}^-/\text{H}_2\text{S}$  and pyrite oxidation probably indicates a similar pathway involving an intermediate that is some form of zero-valent sulfur. Sato (1960) tentatively proposed, on the basis of electrochemical measurements, that the initial step in pyrite oxidation at neutral to basic pH's (equation 13):



produces diatomic sulfur, a result that supports this interpretation. The absence of an induction period for pyrite oxidation (see for example, figure 1) likewise fits this hypothesis.

Although the generalized observations just presented serve to partially rationalize observed sulfur-species distributions, they do not completely explain the oxidation of the pyrite itself, in that the iron component is not specifically considered. In order to deal with this aspect, it is necessary to draw upon results of other studies.

Comparison of this study with those conducted at low pH suggests that there exist two pH regimes for pyrite oxidation that differ mechanistically. At pH less than about 4, ferrous iron is released to solution and only slowly is converted to ferric iron that can serve as an oxidant, sulfur appears in solution as sulfate, and the overall rate of oxidation is independent of pH. This pathway contrasts with results at pH greater than 4 in which ferric iron (as a hydrated(?) oxide) is rapidly produced, sulfur is not as fully oxidized as at lower pH's, and the reaction rate is pH-dependent. Review of the available literature on sulfur speciation and sulfur-oxidation kinetics reveals no obvious relationship of sulfur chemistry to the transitions from pH-independent kinetics to pH-dependent kinetics.

The pH of this transition, however, corresponds approximately to a change in the rate constant of homogeneous oxygenation of aqueous ferrous iron (Singer and Stumm, 1968). Above pH 4, this constant is dependent upon hydroxide concentration to the second power and below pH 4 is independent of pH. This observation must be carefully tempered by the fact that heterogeneous oxidation of ferrous iron in pyrite is being compared to homogeneous oxidation in aqueous solution, and by the fact that the rate dependence on hydroxide concentration is stronger for the aqueous system. Still, the observed behavior of iron during pyrite oxidation fits quite well with the postulate that pH control of this process resides in the increased rate of ferrous-iron oxidation that begins to manifest itself in the vicinity of pH 4 and above.

Although the evidence supports a mechanistic difference in pyrite oxidation above and below pH 4, two observations tend to be true for the entire pH range--the linear (0<sup>th</sup> order) overall reaction rate and a first-order dependence on oxygen concentration or partial pressure up to some limiting value.

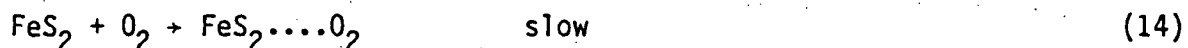
Linear rates of pyrite oxidation have been reported in strongly acid solutions at 100-130°C (McKay and Halpern, 1958) and 25-30°C (Smith and Shumate, 1970) and in mild to strong alkaline solutions at 60-120°C (Burkin, 1969). These constant rates hold over an extent of reaction of greater than 30 percent of the starting pyrite in some of the cited studies. Drescher and others (1956) found similar behavior for molybdenite ( $\text{MoS}_2$ ) oxidation under alkaline conditions at 110-200°C, indicating that the phenomenon is not unique to iron disulfide.

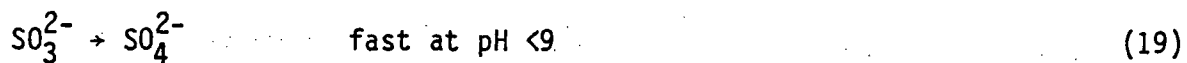
Several exceptions to the linear-rate behavior have been noted and these can be related to buildup of products on the pyrite surface. This non-linearity was observed under acidic conditions by Bergholm (1955) and was related to a diffusion barrier arising from a buildup of elemental sulfur. Burkin (1969) noted that when impure pyrite ore containing pyrite is oxidized at alkaline pH, the iron-oxide product is mechanically retained around the pyrite surface, causing a diffusional barrier and a decrease in rate with time. In pure pyrite, this oxide layer was observed to spall off, exposing fresh surface except where cracks penetrating into the grain mechanically retained the iron oxide. The petrographic observations of the present study indicate that for pyrite oxidation at alkaline pH's and at room temperature, an oxide diffusion barrier may indeed form. The discrepancy between this result and the observations of Burkin (1969) are perhaps relatable to the differing temperature regimes of the two studies. At the higher temperatures, differential stress between the oxide and sulfide layers may be greater, owing to a temperature-dependence or to the crystal structure of the oxide produced. The transition from a chemically controlled (linear) rate-determining step to a physically (diffusion) controlled one may, therefore, be related to second-order effects resulting from conditions of oxidation such as differing temperatures.



The approximate first-order dependence of oxidation rate on  $O_2$  has been found for  $O_2 \leq 1$  atmosphere partial pressure in several studies (Stenhouse and Armstrong, 1952; McKay and Halpern, 1958; Smith and Shumate, 1970; Bergholm, 1955; this study). An interesting similarity is evident in comparing the data of Stenhouse and Armstrong (1952) and the  $MoS_2$  study of Drescher and others (1956). Both studies found linear dependence of rate on  $O_2$  partial pressure up to 13.6 atmosphere  $O_2$ , with a flattening out of the rate curve at greater  $pO_2$ . A possible implication is that adsorption of  $O_2$  by the sulfide surface is more closely related to the  $-S_2$  group than to the nature of the metal. This conclusion needs to be tempered by the data of Smith and Shumate (1970) and of Clark (1966) who reported a similar form to the rate versus  $pO_2$  curve but a lower limiting  $pO_2$ . The general form of the rate versus  $pO_2$  curve is consistent with a mechanism involving surface adsorption on active sites on the pyrite surface.

Despite the fact that the preceding discussion does not uniquely define the mechanism of pyrite oxidation at pH's of 6-9, it does allow some generalizations to be drawn. These can be summarized in the following reaction scheme:





This sequence incorporates the information that the rate of oxidation is probably controlled in this pH range by iron chemistry (equation 14-16) and is sensitive to both  $O_2$  and  $OH^-$  concentrations. The fate of the sulfur component is extremely complex and cannot as yet be completely defined.

#### Implications for Ore Genesis

The results of this study indicate that metastable sulfur oxyanions can be produced during nonbiogenic oxidation of iron-disulfide minerals. This observation thus confirms in part the hypothesis of Granger and Warren (1969), as discussed in the introduction to the present paper. However, some caveats must be placed upon applying the present results to ore-depositing systems. This study was conducted in extremely simple solutions. Oxidation of sulfur oxyanions is clearly subject to both bacterial and inorganic catalysis (Chen and Morris, 1970; Shepard, written commun., 1980), and the influence of such catalysis must be evaluated to determine if metastable sulfur oxyanions can persist long enough as intermediates in pyrite oxidation to function as sulfur carriers in ore-forming systems.

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