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**THE SOLUBILITY OF IRON SULFIDES AND
THEIR ROLE IN MASS TRANSPORT IN
GIRDLER-SULFIDE HEAVY WATER PLANTS**

by

P.H. TEWARI, G. WALLACE and A.B. CAMPBELL

**Whiteshell Nuclear Research Establishment
Pinawa, Manitoba**

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LA SOLUBILITE DES SULFURES DE FER ET LEUR ROLE
DANS LE TRANSPORT DE MASSE DANS LES USINES D'EAU LOURDE
UTILISANT LE PROCEDE GIRDLER AU SULFURE

par

P.H. Tewari, G. Wallace, et A.B. Campbell

RESUME

La solubilité de plusieurs sulfures de fer, la mackinawite FeS (1-x), la troilite FeS , la pyrrhotine $\text{Fe}_{(1-x)}\text{S}$ (monoclinique et hexagonale) et la pyrite FeS_2 , a été déterminée dans une solution aqueuse de H_2S à des pressions de 0.1 MPa et 1.8 MPa de H_2S , de 25° à 125°C. La dépendance de la solubilité du pH du milieu a été étudiée également.

En ce qui concerne la mackinawite, sa concentration en dissolution diminue de plus de 60 fois lorsqu'elle est chauffée de 25° à 125°C. Quant à la troilite et la pyrrhotine, leur solubilité ne diminue que d'un facteur approximatif de 2, entre 25° et 125°C. Pour la pyrite, sa solubilité est très faible, $<10^{-7}$ mol/kg, et les valeurs entre 25° et 125°C sont les mêmes dans les limites de l'incertitude expérimentale. La solubilité à 25°C et 1.8 MPa de pression de H_2S a le rapport de 6000:80:40:10:1 pour la mackinawite, la troilite, la pyrrhotine monoclinique, la pyrrhotine hexagonale et la pyrite respectivement.

Les taux de dissolution des sulfures à des acidités diverses ont également été déterminés. Pour la mackinawite et la troilite, le taux de dissolution et du premier ordre dans le H^+ , mais pour la pyrrhotine et la pyrite, il est essentiellement indépendant du H^+ (pH 0.9 à 4.0). Ces taux varient beaucoup. A 25°C et avec un pH de ≈ 3.5 , les taux de dissolution sont différents avec un rapport de $\approx 10^5:10^4:50:10:1$ pour la mackinawite, la troilite, la pyrrhotine hexagonale, la pyrrhotine monoclinique et la pyrite respectivement. Ces différences sont même plus grandes pour des acidités plus fortes.

L'addition de phosphate n'affecte ni le taux de dissolution ni la solubilité à l'état d'équilibre des sulfures de fer. Cependant l'addition d'une base diminue le taux de dissolution de la mackinawite et la troilite et réduit la solubilité à l'état d'équilibre de tous les sulfures de fer, surtout de la troilite et de la mackinawite.

Selon ces observations, la mackinawite est le sulfure de fer le plus soluble; il a le taux de dissolution le plus élevé et sa solubilité diminue le plus avec la température. Il faudra donc éviter sa formation prolongée pendant l'exploitation de l'usine afin de minimiser le transport de fer des zones de basse température à des zones de haute température dans les usines d'eau lourde utilisant le procédé Girdler au sulfure. On peut atteindre ce but en soumettant les surfaces en acier au carbone à un traitement préalable pour transformer la mackinawite en pyrrhotine et pyrite.

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ABSTRACT

The solubilities of several iron sulfides, mackinawite $\text{FeS}_{(1-x)}$, troilite FeS , pyrrhotite $\text{Fe}_{(1-x)}\text{S}$ (monoclinic and hexagonal), and pyrite FeS_2 have been determined in aqueous H_2S solution at 0.1 MPa and 1.8 MPa H_2S pressures between 25° and 125°C. The dependence of solubility on the pH of the medium has also been studied.

For mackinawite, dissolved iron concentrations decrease more than 60 times on heating from 25° to 125°C. For troilite and pyrrhotite, the decrease in solubility between 25° and 125°C is only about a factor of two. For pyrite, the solubility is very low, $< 10^{-7}$ mol/kg, and the values between 25° and 125°C are the same within experimental uncertainty. The solubilities at 25°C and 1.8 MPa H_2S pressure are in the ratio $\sim 6000:80:40:10:1$ for mackinawite, troilite, monoclinic pyrrhotite, hexagonal pyrrhotite and pyrite respectively.

The rates of dissolution of the sulfides at various acidities have also been determined. For mackinawite and troilite the rate of dissolution is first order in H^+ , but for pyrrhotite and pyrite it is essentially independent of H^+ (between pH 0.9 and 4.0). The rates vary widely. At 25°C and pH ~ 3.5 , the rates of dissolution differ by a ratio $\sim 10^5:10^4:50:10:1$ for mackinawite, troilite, hexagonal pyrrhotite, monoclinic pyrrhotite and pyrite respectively. These differences are even greater at stronger acidities.

Addition of phosphate does not change either the rate of dissolution or the equilibrium solubility of the iron sulfides. Addition of a base, however, lowers the rate of dissolution for mackinawite and troilite and decreases the equilibrium solubility of all the iron sulfides, but most markedly of troilite and mackinawite.

From these observations, it is concluded that since mackinawite is the most soluble of the iron sulfides, and has the highest dissolution rate and the steepest decline in solubility with temperature, its prolonged formation during plant operation should be avoided to minimize iron transport from lower to higher temperature areas in Girdler-Sulfide (G.S.) heavy water plants. This can be achieved by a preconditioning of carbon steel surfaces to convert mackinawite to pyrrhotite and pyrite.

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1. INTRODUCTION

Several different phases of iron sulfides form as a result of interaction between aqueous H_2S solutions and carbon steel⁽¹⁻⁴⁾. Many of these phases, listed below, have been identified in Girdler-Sulfide (G.S.) heavy water plant scales⁽⁵⁾, and on carbon steel coupons exposed to similar conditions⁽⁶⁾.

<u>PHASE</u>	<u>FORMULA</u>	<u>CRYSTAL STRUCTURE</u>
mackinawite	$FeS_{(1-x)}$ $Fe_{(1+x)}S$	tetragonal
cubic iron sulfide	FeS	cubic
troilite	FeS	hexagonal
pyrrhotite	$Fe_{(1-x)}S$	hexagonal and monoclinic
greigite	Fe_3S_4	cubic (spinel)
marcasite	FeS_2	orthorhombic
pyrite	FeS_2	cubic

The dissolution products of iron sulfides that form as corrosion products of carbon steel in G.S. plants are transported from lower to higher temperature zones of the heat exchangers and exchange towers, where a subsequent deposition in some critical areas results in a loss of production. Therefore, it seemed desirable to study the role of the solubility and dissolution rate of different iron sulfides in such transport.

There are only limited data on the solubility of iron sulfides in aqueous H_2S solutions. Kolthoff⁽⁷⁾ reviewed the early data on FeS solubility and the reported values differ widely, but in most cases the phases of the iron sulfides used are not well characterised. The majority of values for FeS solubility at $\sim 20^\circ C$ are in the range 10^{-5} - 10^{-4} mol/kg. Berner⁽⁸⁾ reported a solubility of 1.2×10^{-5} mol/kg for mackinawite at $25^\circ C$ and 0.1 MPa H_2S pressure. Data for the solubility of pyrrhotite and pyrite phases are scarce. Ol'shanskii and Ivaneko⁽⁹⁾ reported experimental values for the solubilities of Fe and Co sulfides that are several times larger than values calculated from thermodynamic data.

There have been several studies⁽¹⁰⁻¹³⁾ to determine the mechanism of the formation of sulfide ore deposits, which report data on the solubility of iron sulfides in the presence of electrolytes and complexing ligands. However, these data are not generally applicable to G.S. plant conditions, since, in many of the studies, solubilities less than 1 mg/kg were not considered significant⁽¹⁴⁾. Ol'shanskii et al.⁽¹⁵⁾ suggest that the solubility data of ore-forming sulfides reported in the geological literature are too low. There are some early reports giving calculated solubilities of different sulfides and these have been revised periodically⁽¹⁶⁻¹⁸⁾ on the basis of improved thermodynamic constants. In 1962 Pohl⁽¹⁹⁾ analysed the available thermodynamic data to calculate the solubilities of some iron sulfides under G.S. plant conditions, but his calculations are also subject to change because of more recent data⁽²⁰⁻²²⁾ for some of the constants for the dissociation of H_2S . Therefore, there is a need for an experimental evaluation of the solubility data for different iron sulfides, specially under G.S. plant conditions.

Data for mackinawite, troilite, pyrrhotite and pyrite are reported here because these are the phases most often seen in G.S. plants. Also, these phases can be prepared in the pure form and studied at the temperatures of interest with minimum conversion to other phases.

2. EXPERIMENTAL

2.1 MATERIALS

Single crystals of FeS troilite, pyrrhotite (monoclinic) and pyrite (obtained from the Mines Branch Ottawa, and the Geological Survey of the United States of America) were used for the solubility and rate of dissolution studies. The use of single crystals minimized any complicating contribution in determinations of dissolved Fe^{++} from fines and from surface impurities contained in powder materials. Single crystals of mackinawite and hexagonal pyrrhotite were not available; therefore these compounds were prepared in powder form in the laboratory.

Mackinawite ($\text{FeS}_{(1-x)}$)

Mackinawite was prepared electrochemically using a carbon steel anode and platinum cathode⁽²³⁾. A solution of 0.1 mol/kg NaOH, contained in an all-glass cell equipped for evacuating air, was purged with nitrogen for one hour before the passage of H_2S through the solution. A current of ≈ 20 mA was passed through the solution while H_2S was bubbled continuously through the cell for three days. Air occlusion was avoided during the reaction. The mackinawite powder formed during the process was washed with deoxygenated water under a nitrogen atmosphere and vacuum dried in a desiccator.

Troilite (FeS)

Some experiments with troilite powders prepared in the laboratory were also performed to compare with the single crystal results. Samples were prepared as follows:

Pure (99.995%) iron powder was first reduced in an H_2 atmosphere to remove surface oxides and then was reacted with the stoichiometric amount of sulfur in a sealed quartz tube. The tube was heated in stages at 200°, 300°, 400° and 450°C until there was no evidence of unreacted sulfur. The temperature was then raised to 800°C for three days, after which the sample was cooled and recovered from the quartz tube, ground under acetone and dried in a desiccator. The dried powder was transferred to another tube, which was evacuated and sealed, and kept at 120°C for 7 days. The capsule was quenched in ice-water, and then opened and the product ground. The ground powder was stored in a vacuum desiccator.

Hexagonal Pyrrhotite ($FeS_{(1.07)}$)

The required amounts of deoxygenated iron powder and sulfur were reacted in a quartz tube in stages as described for troilite until the sulfur was fully reacted. The temperature was raised to 800°C and maintained for three days. Finally, the reacted powder was crushed under acetone, dried under vacuum and stored in a desiccator.

Triple-distilled water containing less than 5×10^{-8} mol/kg iron was used in all solubility and rate of dissolution experiments. Analytical grade reagents were used throughout. H_2SO_4 was used to make up acidic solutions. High purity H_2S , N_2 and H_2 gases were used. NaOH solutions were CO_2 -free.

2.2 METHODS

All samples were analysed by X-ray powder diffraction before and after the dissolution experiments to observe changes of phase, if any, during the experiments. Troilite and pyrrhotite were not heated beyond 125°C during the solubility studies to avoid conversion to higher sulfide phases. High temperature solubility data were obtained in all-

titanium autoclaves with titanium valves. No stainless steel or iron-bearing material was exposed to the aqueous medium. A titanium frit was used in the exit sampling line to eliminate particles in the samples. The samples were taken at temperature through a high pressure filter jacket with 0.02 μm millipore filters which were inspected for rupture or particles after each filtration.

Iron analyses were done by atomic absorption spectroscopy (detection limit $\sim 6 \times 10^{-7}$ mol/kg) for samples containing more than 1 $\mu\text{g/g}$, and by colorimetry (Technicon Analyzer) for samples containing less than 1 $\mu\text{g/g}$. In the latter (detection limit 2×10^{-8} mol/kg), iron is reduced to Fe^{++} by hydroxylamine hydrochloride in a buffered solution of pH 5.4 before a colorimetric determination by 2,4,6 tri-2-pyridyl-S triazine (TPTZ) reagent. The precision of Fe^{++} determination was $\pm 12\%$ (2σ) in the concentration range less than 1 $\mu\text{g/g}$, and $\pm 5\%$ for concentrations $> 1 \mu\text{g/g}$.

Rate of dissolution studies were conducted in glass systems equipped to allow purging by, and maintaining of, an inert atmosphere, and the rates were measured without addition of H_2S unless specified otherwise. The apparatus was connected to a Technicon Analyzer, and periodic samples were fed directly into the analyser from the flask via a stop cock without exposing the solution to the outside atmosphere. Hence, the rate data for the single crystals were essentially free from sampling errors as no filtering or external sampling was involved. With mackinawite and hexagonal pyrrhotite, precautions were taken to minimize fines going to the analyser.

3. RESULTS

3.1 SOLUBILITY

3.1.1 Troilite

The data reported were obtained with single crystals (supplied by Mines Branch Ottawa), but the results for synthesized powder material were identical. The concentrations of dissolved Fe^{++} at 0.1 MPa and 1.8 MPa total H_2S pressure at different temperatures are given in Figure 1. The two curves are very similar, within the experimental uncertainty.

3.1.2 Pyrrhotite (monoclinic)

Whereas the equilibrium solubility of troilite was achieved within hours, for pyrrhotite it took at least seven days of vigorous agitation. All room temperature data reported are for runs carried out for a week or more. The solubility of pyrrhotite at 0.1 MPa H_2S pressure, as a function of temperature, is given in Figure 2. The corresponding values at an H_2S pressure of 1.8 MPa are also given. As with troilite, the concentration of dissolved Fe^{++} is affected only slightly by H_2S pressure, the difference being barely $\pm 10\%$ of the value at 0.1 MPa. Also, the solubility decreases at higher temperatures, but the difference between the value at 25°C and that at 120°C is only a factor of two (4.0×10^{-6} and 2.0×10^{-6} mol/kg respectively). The solubility of monoclinic pyrrhotite is lower than that of troilite by about a factor of two at the corresponding temperatures.

3.1.3 Pyrrhotite (hexagonal)

The solubility of hexagonal pyrrhotite, prepared by direct reaction of a mixture of iron and sulfur was $(1.5 \pm 1.0) \times 10^{-6}$ mol/kg at

25°C and 1.8 MPa H₂S pressure. Values within this range were obtained after 16, 72 and 100 hours of equilibration. When the temperature was raised to 120°C, the Fe⁺⁺ concentration did not change significantly (Figure 2). However, when the temperature was lowered back to 25°C, the dissolved iron concentration decreased, and decreased further on subsequent heating. The explanation for these observations may be the conversion of hexagonal pyrrhotite to the pyrite phase during heating. X-ray diffraction analysis showed that after the experiment the sample comprised mainly hexagonal pyrrhotite, but small amounts of pyrite were also present. These results are consistent with the conclusion that (hexagonal) pyrrhotite converts to pyrite to give lower solubilities.

Experiments also indicated that the surface conversion of hexagonal pyrrhotite to pyrite can take place even at room temperature in an aqueous H₂S medium. This hypothesis is supported by the observation that, in many experiments, we obtained solubility values at 25°C in the range (3-5)×10⁻⁷ mol/kg, and which did not change significantly with increasing temperature. These values are very close to the values measured for pyrite (~ 1×10⁻⁷ mol/kg), which also do not change significantly with temperature. Furthermore, as discussed later, dissolution rate data also indicate that the surface conversion of hexagonal pyrrhotite to pyrite can take place even at room temperature.

3.1.4 Pyrite

Pyrite single crystals obtained from the Geological Survey of the United States Department of the Interior were analysed for impurities by emission spectrography. The analysis was as follows: µg/g Mg 10, Pb 10, Cr 2, Si 75, Al 25, Cu 8, Ti 5, Ca 5, suggesting that the samples were of high purity. The X-ray powder diffraction pattern of the crystals indicated the presence of only pyrite (detection limit ~ 2%).

The solubility of pyrite was very low and at the limit of capability of our Fe^{++} detection. Since the iron content of the triple-distilled deionized water used in these experiments was about 6×10^{-8} mol/kg, and the iron values from pyrite were only slightly higher than the background, the reported values of iron are only approximate. Also, no noticeable change was observed in the dissolved iron concentration values at 1.8 MPa and 0.1 MPa H_2S pressures.

The solubility values at different temperatures (Figure 2) were almost constant within our experimental uncertainty. However, if we assume that the observed Fe^{++} values at 25°C are possibly due to a background impurity in the water itself, the values can be assumed to be the upper limit of dissolved Fe^{++} from FeS_2 . Thus, the solubility of FeS_2 is very much lower than that of the other iron sulfides studied.

3.1.5 Mackinawite

Though precautions were taken to avoid air exposure for all iron sulfides, this was specially critical for mackinawite. Therefore, mackinawite was always handled under nitrogen to prevent oxidation and its subsequent transformation to other sulfides. However, at 25°C and 0.1 MPa H_2S pressure, only in three runs out of 24, all with fresh batches of mackinawite with no detectable impurities, did the samples remain unchanged after the dissolution experiments. The others contained various amounts of other sulfides such as marcasite, greigite (Fe_3S_4) and pyrite.

Among all the iron sulfides studied (Figure 2), the solubility of mackinawite is highest. There is a large scatter in the data for dissolved Fe^{++} concentration even in the runs where the major phase of the product, after dissolution, remained mackinawite. This variation is possibly due to phase changes on the surface of the mackinawite that could not be detected by X-ray diffraction analysis. At 25°C and 0.1

MPa H_2S pressure, the observed values range from 0.2×10^{-3} to 1.0×10^{-3} mol/kg. The true value may be even higher than 1.0×10^{-3} mol/kg, since the unconverted phase (mackinawite) must have a higher solubility than the products of conversion.

The solubility of mackinawite at $T > 25^\circ C$ could not be accurately determined due to its rapid transformation to other sulfides at higher temperatures. Although the extremely poor reproducibility at $T > 25^\circ C$ precluded the possibility of obtaining accurate solubility data, it was concluded that mackinawite has a negative temperature coefficient of solubility. All the values measured at $T = 120^\circ C$ were in the range of $10^{-5} - 10^{-6}$ mol/kg, obviously lower than those measured at $25^\circ C$.

3.2 EFFECT OF pH AND PHOSPHATE ON SOLUBILITY

3.2.1 Effect of added acid or base

The equilibrium solubilities of different iron sulfides at $25^\circ C$ and 0.1 MPa H_2S pressure as a function of pH are given in Figure 3. The dissolved Fe^{++} concentrations differ significantly with pH. There is a large scatter in the data for mackinawite due to conversion of mackinawite to different phases as observed from X-ray diffraction data after the dissolution experiments. This will be discussed later.

The solubilities of iron sulfides decrease with increasing pH (Figure 3). Troilite has the sharpest decrease with increasing pH, followed by mackinawite and pyrrhotite. For example, an increase of pH from 3.5 to 4.0 reduces the dissolved iron concentration by a factor of ≈ 10 for troilite, ≈ 5 for mackinawite and $\approx 2-3$ for pyrrhotite respectively, at $25^\circ C$ and 0.1 MPa H_2S pressure (Table 1).

TABLE 1

Change of equilibrium solubility for a shift of pH
from 3.5 to 4.0 at 25°C and 0.1 MPa H₂S pressure

Solubility in $\mu\text{mol/kg}$

pH	Troilite	Mackinawite	Pyrrhotite (Monoclinic)	Pyrrhotite (Hexagonal)
3.5	66	2700	9 \pm 0.5	0.66 \pm 0.05
4.0	6.0 \pm 0.5	560	2.5 \pm 0.5	0.25 \pm 0.05

For pyrite, the observed effect of pH is least. There are two possible explanations: first, that the solubility of pyrite does not change with pH, or second, that the solubility is below the detection limit and the result is merely an artifact given by the background Fe⁺⁺ content in the water used.

The solubility of troilite at 1.8 MPa H₂S pressure with added NaOH (1.0×10^{-4} mol/kg) is given in Figure 1. The dissolved iron concentration decreases at all temperatures.

3.2.2 Effect of added phosphate

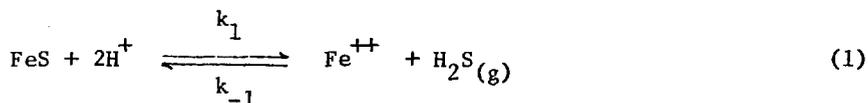
At 0.1 MPa H₂S pressure with 10 $\mu\text{g/g}$ phosphate added to the system, the dissolved iron concentrations from pyrrhotite and pyrite do not change as compared with the values when no phosphate is present. There was a slight decrease in the solubility of troilite (< 10%), but this decrease is accounted for by the slight rise in the pH (< 0.1 pH) of the system with the added phosphate. Therefore, addition of a phosphate does not affect the solubility of iron sulfides under conditions similar to those in G.S. Plants. This will be discussed further in connection with rates of dissolution of iron sulfides.

3.3 RATES OF DISSOLUTION OF IRON SULFIDES

Calculations from thermodynamic data give equilibrium solubilities. There is no way to calculate, a priori, the rates of such reactions from thermodynamic data. However, rates of dissolution may be very important in many industrial systems where fluids flow in a once-through process. This is also true for some sections of heavy water plants. Hence, the kinetics of dissolution were studied to understand the dynamics of the process.

3.3.1 Troilite

We have shown that the equilibrium solubility of troilite is achieved within hours. We also showed⁽²⁴⁾ experimentally that the rate of dissolution, R, for the reaction



is given by

$$R = k_1[\text{H}^+] - k_{-1}[\text{Fe}^{++}]^{1/2} (\text{p}_{\text{H}_2\text{S}})^{1/2} \quad (2)$$

where k_1 = rate constant of the forward reaction, k_{-1} = rate constant of the reverse reaction, $[\text{Fe}^{++}]$ = Fe^{++} concentration in mol/kg and $\text{p}_{\text{H}_2\text{S}}$ = H_2S pressure (kPa).

The rate of dissolution of troilite is first order with respect to H^+ , i.e. the higher the acidity, the higher the rate of dissolution. At 25°C, the rate constant k_1 obtained from the initial rate of dissolution of troilite at different acidities, ranging from pH 2.0 to 5.32, was $2.7 \pm 0.2 \mu\text{m/s}$.

The value of k_{-1} , the rate constant for the reverse reaction (precipitation by H_2S) was derived from the equilibrium constant⁽²⁴⁾, $K = [Fe^{++}] p_{H_2S} / [H^+]^2$ ($= 560 \pm 40$) and k_1 , the rate constant for dissolution of FeS , using the relationship $K = k_1/k_{-1}$. Van Lier, de Bruyn and Overbeek⁽²⁵⁾ have used a similar calculation to obtain the rate constant for crystallization of quartz from the rate of dissolution data. Our rate constant, thus derived, is much smaller (4.7×10^{-3} $\mu m/s$) than k_1 , suggesting that the rate of precipitation of FeS by Fe^{++} and $H_2S(g)$ is lower than that of dissolution.

We have shown⁽²⁴⁾ that the precipitation of troilite results from reaction of $Fe^{++} + HS^-$ and not by $Fe^{++} + H_2S$. We also evaluated the rate constant at 25°C for this precipitation reaction, k_b , from the equilibrium constant of the reaction



and the dissolution rate of FeS ($2.7 \mu m/s$) as was done by van Lier, de Bruyn and Overbeek⁽²⁵⁾. This was done using K_3 , the equilibrium constant for reaction (3) as follows:

$$K_3 = \frac{[Fe^{++}](p_{H_2S})K_1}{[H^+]^2} = 560xK_1$$

$$K_1 = \frac{[H^+][HS^-]}{(H_2S)} = 1x10^{-7}$$

$$\text{and } k_b = \frac{k_f}{K_3} = \frac{2.7x10^{-6}}{5.6x10^{-5}} = 0.05 \text{ m/s} .$$

The value obtained, 0.05 m/s, shows that the rate of precipitation of FeS is fairly fast compared with that of the dissolution process ($\mu m/s$), and also faster than the rate of precipitation by $Fe^{++} + H_2S$ (nm/s).

Effect of temperature

The energy of activation of troilite dissolution (60 ± 7 kJ/mol) was evaluated from the slope of a plot of $\log k$ vs. $1/T$ where k = rate constants at different temperatures (Table 2).

TABLE 2

Rate constants for dissolution of troilite
at different temperatures

<u>Temperature (°C)</u>	<u>Rate constants (m/s)</u>
25	2.7×10^{-6}
35	6.7×10^{-6}
45	15.0×10^{-6}
80	150×10^{-6}

It is evident that the rate of dissolution increases markedly at temperatures around 70 - 80°C.

3.3.2 Monoclinic Pyrrhotite

At 25°C and 0.1 MPa or 1.8 MPa H_2S pressure, the equilibrium solubility of pyrrhotite was achieved only after almost seven days. The rates of dissolution were determined from initial rates for dissolution of pyrrhotite single crystals at different acidities.

One very noticeable difference between the rates of monoclinic pyrrhotite and troilite dissolution is the dependence of the initial rate on solution pH. Whereas the initial rate of troilite dissolution is first order dependent on H^+ , the rate of dissolution of monoclinic pyrrhotite is almost independent of H^+ . The rate of dissolution of the

latter (Figure 4) between pH 0.90 and 3.98 was constant within the experimental variation $[(1.7 \pm 0.3) \times 10^{-9} \text{ mol/m}^2 \cdot \text{s}]$. Thus at pH 3.5, the rate of dissolution of monoclinic pyrrhotite was only $1.7 \times 10^{-9} \text{ mol/m}^2 \cdot \text{s}$ whereas for troilite it was $8.6 \times 10^{-7} \text{ mol/m}^2 \cdot \text{s}$ (~ 500 times higher). This difference between the rates of dissolution is greater at stronger acidities.

The rate of dissolution determined for two sets of samples, one for a single crystal and the other for a synthesised powdered material, differed by a factor of more than two (2.4). This difference is possibly due to the uncertainty in the surface areas used to calculate these rates. The surface area for the single crystal was evaluated from the geometric area, and the actual area might be higher because of sample roughness and porosity. For the powder, the BET gas adsorption method was used, and since the surface area of the powder was only $\sim 2 \text{ m}^2/\text{g}$, its determination was not accurate in this range and may differ in magnitude by 100%. However, the actual rate determination was very reproducible and was accurate to $\pm 5\%$. If the effect of porosity in the single crystal is taken into account, the calculated rate of dissolution will be even lower. Hence the difference between the rate of troilite dissolution and that of monoclinic pyrrhotite may be greater than given here.

Dissolution rates of monoclinic pyrrhotite at pH 1.8 in the presence of H_2S (0.1 MPa), and without H_2S addition, did not differ appreciably ($4 \times 10^{-10} \text{ mol/m}^2 \cdot \text{s}$ and $1.7 \times 10^{-9} \text{ mol/m}^2 \cdot \text{s}$, respectively). This suggests that the precipitation of monoclinic pyrrhotite resulting from reaction of Fe^{2+} with H_2S is slow, since it is reasonable to assume that the equilibrium constants for the two conditions (with and without H_2S) are also not appreciably different. In fact, it can be shown that precipitation of monoclinic pyrrhotite is slow by considering the equilibrium constant, K , for the dissolution reaction, and the forward rate constant for dissolution, k_1 ($k_{-1} = K/k_1$). Since the free energy

of formation of monoclinic pyrrhotite, ΔG°_f , is approximately the same as that of troilite⁽²⁶⁾, it can be assumed that the equilibrium constant for the dissolution process of monoclinic pyrrhotite is also similar to that of troilite. Hence, by taking the value of K for troilite⁽²⁴⁾ (~ 560) and k_1 , the forward rate constant for the dissolution of monoclinic pyrrhotite ($\sim 10^{-8}$ m/s), the value of the reverse rate constant, k_{-1} , is calculated to be $\sim 10^{-10}$ m/s. This will obviously result in a very low precipitation rate for monoclinic pyrrhotite.

Effect of temperature

The rate of dissolution of monoclinic pyrrhotite increased with temperature, though not as much as for troilite. The activation energy for dissolution of pyrrhotite, obtained from a log k vs. 1/T plot between 6° and 50°C was 40 ± 10 kJ/mol, which is much lower than that for troilite.

Effect of phosphate and oxalic acid

The rate of dissolution of monoclinic pyrrhotite was not affected by addition of 10 $\mu\text{g/g}$ of phosphate or oxalic acid.

3.3.3 Hexagonal Pyrrhotite

The rate of dissolution of hexagonal pyrrhotite in an atmosphere of N_2 is low (5×10^{-9} mol/m².s) and is roughly comparable to that of monoclinic pyrrhotite (2×10^{-9} mol/m².s). The corresponding value for pyrite is $\sim 10^{-10}$ mol/m².s.

There is one aspect, however, in which hexagonal pyrrhotite differs markedly from monoclinic pyrrhotite. The latter dissolved very slowly in an H_2S medium and took almost a week to reach the equilibrium value. However, with hexagonal pyrrhotite, the equilibrium value was

achieved in approximately 3 - 6 hours. This rapid attainment of equilibrium was very similar to that observed for pyrite, which also attained equilibrium solubility in hours.

Why hexagonal pyrrhotite should behave differently from monoclinic pyrrhotite is not certain. It may be, as postulated above, that the surface of hexagonal pyrrhotite crystals readily converts to pyrite, resulting in a dissolution behaviour more like that of pyrite than monoclinic pyrrhotite. This conclusion is supported by the observation that the dissolution rate of hexagonal pyrrhotite is 1×10^{-8} mol/m².s in N₂, but 1×10^{-9} mol/m².s in air, closer to the rate of dissolution of pyrite (10^{-10} mol/m².s). A lower dissolution rate in air would be expected if, in fact, hexagonal pyrrhotite is converting to pyrite, since the conversion rate (an oxidation process) would be increased by the presence of air (O₂) in the solution.

3.3.4 Mackinawite

The rate of dissolution of mackinawite is proportional to acid concentration as shown in Figure 5. The actual rate of dissolution is complicated by the probable conversion of mackinawite to other phases as discussed earlier. The rate constant observed was 7 ± 3 μm/s. Thus, the rate of dissolution of mackinawite is higher than that of troilite by a factor of ~ 4, and higher by 1000 than that of pyrrhotite, depending on the acidity.

Effect of temperature

The temperature coefficient or the energy of activation for dissolution of mackinawite is more uncertain because of its fast conversion at higher temperature. But to a first approximation, the temperature dependence is similar to that of troilite.

Effect of phosphate

No significant change was noticed in the rate of dissolution of mackinawite with 10 µg/g of phosphate added to the system.

3.3.5 Pyrite

The rate of dissolution of single crystal pyrite was determined in sulfuric acid solutions. At 25°C in solutions without added H₂S at pH 1.40, the rate was only $(8 \pm 4) \times 10^{-11}$ mol/m².s. Although the rate of change of Fe⁺⁺ concentration in the experiments could be determined quite accurately (within ? 5%), a variation in the numerical value of the rate data arose due to the uncertainty in the surface areas of the samples. Since the specific surface area was very small, BET gas adsorption determinations were inaccurate. Geometrical surface area was used, even though the value may be somewhat doubtful because of surface roughness and porosity in the samples. However, surface roughness and porosity, if present, will make the rate still lower than reported. The rate of dissolution was, indeed, very low and was also independent of the acid concentration used. Between pH 0.8 and 3.8, the rates were the same within the experimental variation.

Effect of phosphate, other additives and temperature

At 25°C, the rate of dissolution was unaffected by addition of 10 µg/g of phosphate (Figure 6) or oxalic acid. Results obtained with oxalic acid were identical to those obtained with phosphate addition, but are not shown in the figure for clarity. Also, at 25°C the presence of N₂ or H₂ at 0.1 MPa pressure did not change the rate of dissolution, even after 150 hours.

Oxygen had no appreciable effect on the rate of dissolution at 25°C, but, at higher temperatures, seemed to accelerate the rate of dissolution markedly. This increase was more than the effect of temperature alone. In the presence of oxygen, the rate increased from 1×10^{-10} mol/m².s at 25° to 1×10^{-8} mol/m².s at 90°C, giving an activation energy of 100 ± 20 kJ/mol for the overall process. On the other hand, in the presence of N₂ the rate increased from 1×10^{-10} mol/m².s at 25° to only 2×10^{-9} mol/m².s at 90°C, giving an activation energy for dissolution of ~ 40 kJ/mol. There was a large scatter in the rate data, probably due to the presence of different trace amounts of oxygen in the N₂ atmosphere. However, the rate of dissolution in O₂ was definitely much higher at 90°C than in the presence of N₂ at this same temperature.

Furthermore, in a more oxidizing acid, HClO₄, the rate of dissolution of pyrite at pH 1.4 and 25°C was almost identical to that in H₂SO₄. At higher temperatures, however, there was a marked increase in the rate of dissolution in the presence of HClO₄ (Figure 6). The rate of dissolution for the sample with HClO₄ at 80°C was higher than the rate observed in H₂SO₄ medium at 90°C. The higher rates of dissolution observed at higher temperatures, in oxidizing media O₂ and HClO₄, seem consistent with the observation of Majima and Peters⁽²⁷⁾ that the oxidation of pyrite is slow at lower temperatures, but quite marked above 120°C.

It was also observed that the equilibrium solubility for pyrite in an H₂S medium was achieved overnight, whereas for monoclinic pyrrhotite it took almost 7 days. The rates of dissolution for monoclinic pyrrhotite and pyrite were of the order of 10^{-9} and 10^{-10} mol/m².s respectively. Thus, even though the rates of dissolution differed by a factor of only 10, the back reaction rate was quite different. It is, therefore, reasonable to deduce that the rate of precipitation of pyrite is higher than that of monoclinic pyrrhotite. Similarly the rate of precipitation of monoclinic pyrrhotite is much lower than that of troilite.

4. DISCUSSION

The temperature coefficients of solubility of troilite, pyrrhotite and pyrite are negative. Between 25° and 120°C, the decrease in solubility is as small as a factor of 2 for troilite and pyrrhotite, and much less for pyrite (Figure 2). Mackinawite has the steepest decline of solubility between the same temperatures.

Pohl's⁽¹⁹⁾ calculated results show that the solubility of troilite decreases \sim 45 times between 25° and 120°C (3.2×10^{-4} mol/kg at 25° and 6.7×10^{-6} mol/kg at 120°C) and that the dissolved Fe⁺⁺ concentration is dependent on H₂S pressure. However, our calculated results⁽²⁸⁾, wherein lower values for K₂, the second dissociation constant for H₂S, and a smaller temperature dependence for K₂, were used*, give Fe⁺⁺ concentrations which are almost independent of H₂S pressure between 0.1 MPa and 1.8 MPa (Figure 1). Our experimental values for dissolved Fe⁺⁺ at these pressures are consistent with the latter calculations. Also, our calculated values of dissolved Fe⁺⁺ decrease less with temperature than was suggested by Pohl, and this also is confirmed by our experimental values. However, our experimental values fall between the two calculated curves (Figure 1), suggesting that choosing a slightly higher value of K₂ for the calculations may provide better agreement with the experiment.

Solubility values for mackinawite, troilite and pyrrhotite calculated by Macdonald⁽²⁹⁾ from thermodynamic data, have negative temperature coefficients, as is also observed here experimentally. However, his calculated values are much higher than those measured

* New values⁽²⁰⁻²²⁾ of K₂ \sim 10⁻¹⁸ - 10⁻¹⁶ instead of 10⁻¹³ - 10⁻⁹ at 120°C respectively and new ΔH for K₂ \sim 30 kJ/mol instead of 100 kJ/mol used by Pohl

experimentally (15 times higher for mackinawite, \sim 25 times higher for troilite and 5 times higher for pyrrhotite). The correspondence between the calculated and experimental values for mackinawite and pyrrhotite is reasonable in view of the uncertainties in both the experimental results and the thermodynamic constants used in the calculations, and especially since Macdonald's pyrrhotite phase, $\text{Fe}_{0.875}\text{S}$, was not specified as being either monoclinic or hexagonal. However, a difference of \sim 25 times between the calculated and the experimental values for troilite is beyond the expected uncertainty, especially since the experimental values are lower than the calculated ones. (The reverse is usually observed, and is generally attributed to fines or particulates from the dissolving material. We have used single crystals for the dissolution experiments, however, minimizing any contribution from fines.) The measured values for the dissolved iron are in the range where the accuracy of the analytical procedures is good. Hence we prefer the experimental values to those obtained by calculation.

Macdonald⁽²⁹⁾ predicts a positive temperature coefficient of solubility for pyrite, but our results show no increase in dissolved iron on heating from 25° to 125°C. Levels of dissolved iron are very low, and the iron content in the water used for dissolution was of the order of $\sim 10^{-8}$ mol/kg. Macdonald's calculated value at 25°C is of the order of only 10^{-11} mol/kg, much below the background level of Fe^{++} in the water used. Hence, we can conclude only that the solubility of pyrite is very low and is possibly below our detection limit.

Thus, the solubility of mackinawite is the highest among the iron sulfides studied, the order being mackinawite > troilite > pyrrhotite > pyrite. The differences between the solubility of mackinawite, troilite, pyrrhotite (monoclinic and hexagonal) and pyrite at 25°C and similar H_2S pressure (1.8 MPa) are in the order 6000:80:40:10:1 respectively.

The rates of dissolution of different phases of iron sulfides vary widely, as shown in Table 3.

TABLE 3

Rates of dissolution of iron sulfides at 25°C and pH 3.5

<u>Substance</u>	<u>Rate mol/m²s</u>
mackinawite	$> 2 \times 10^{-6}$
troilite	$(8 \pm 1) \times 10^{-7}$
hexagonal pyrrhotite	$(5 \pm 5) \times 10^{-9} *$
monoclinic pyrrhotite	$(1 \pm 1) \times 10^{-9} *$
pyrite	$(8 \pm 4) \times 10^{-11} *$

* The variation in the rates is due primarily to the uncertainty in the specific surface area of the sulfide samples. The rate data themselves are precise to $\pm 5\%$.

At 25°C and pH ≈ 3.5 , the rates of dissolution differ by a ratio $\approx 10^5:10^4:50:10:1$ for mackinawite, troilite, hexagonal pyrrhotite, monoclinic pyrrhotite and pyrite respectively. These differences are even greater at higher acidities, since the rates of dissolution for mackinawite and troilite depend on H^+ concentration, whereas the rates for pyrrhotite and pyrite are almost independent of H^+ .

Implications of solubility and dissolution rates of iron sulfides in corrosion of carbon steel in heavy water plants

Among the iron sulfides observed in G.S. plants, pyrite is the least likely to contribute to iron transport because it has the lowest

solubility, and because its solubility does not decrease with temperature. Supporting the above conclusion, much reduced release rates for carbon steel have been observed by Taylor⁽³⁰⁾ in loop tests with coupons having pyrite surfaces.

Based on kinetics of dissolution, the pyrrhotite phase is also not a likely major contributor to iron transport because hexagonal pyrrhotite has the second lowest solubility, and it converts easily to pyrite. Moreover, monoclinic pyrrhotite attains equilibrium solubility slowly over a week, and hence will not contribute much to iron transport. Thus, mackinawite and troilite are most likely the phases causing iron transport, and of the two mackinawite, is the more important.

For different iron sulfide phases, the rate of iron transport, R, can be calculated by

$$R = k[H^+] A (c_s - c)$$

where

- k = rate constant for the dissolution of the iron sulfide, m/s,
- $[H^+]$ = hydrogen ion concentration, mol/m³,
- A = surface area, m²,
- c_s = saturation solubility of the iron sulfide, mol/m³,
- c = concentration of dissolved Fe⁺⁺ in water at any time, mol/m³.

The calculated rates for iron transport resulting from dissolution of different iron sulfides (with c values from Figure 2 and k[H] values from Table 3 at $H^+ = 0.32$ mol/m³) are given in Table 4. Since the value of c is insignificant in comparison with those of c_s for the more soluble iron sulfides, it has been excluded from the release rate calculation.

TABLE 4

Release rate of iron from iron sulfides, having different rates of dissolution, and saturation solubilities, at pH 3.5 and 25°C

<u>Iron sulfide</u>	$K[H^+]$ (mol/m ² .s)	c_{s3} (mol/m ³)	Release rate (μg/m ² .d)
mackinawite	2×10^{-6}	1.0	1×10^7
troilite	8×10^{-7}	7×10^{-3}	3×10^4
pyrrhotite monoclinic or hexagonal	5×10^{-9}	1×10^{-3}	~ 20
pyrite	8×10^{-11}	1×10^{-4}	~ 4×10^{-2}

The release rate data clearly show that pyrite and pyrrhotite phases are not the major contributors to the iron release. For example, taking an area of 600 m² for the colder section of one unit of a G.S. plant (tower walls ~ 350 m², feed loop ~ 125 m², dehumid loop ~ 125 m²), a transport rate of 6 kg/d for mackinawite, ~ 20 g/d for troilite, less than 1 g/d for pyrrhotite and a negligible amount for pyrite is obtained, supporting the argument that a pyrrhotite surface also does not contribute significantly to iron transport. It may be noted that deposit rates of 5 kg/d have been observed in E₁ unit of Bruce Heavy Water Plant, suggesting mackinawite as the source of the iron transport.

The temperature coefficients of the dissolution rates of mackinawite and troilite are larger than those of pyrrhotite and pyrite. This is especially true of troilite for which the solubility decreases only slightly between 25° and 80°C (Figure 2), but the rate of dissolution increases by a factor of 55 (Table 2). It is therefore reasonable to expect for kinetic reasons a greater loss of iron by dissolution at

about 70° - 80°C. Beyond this temperature, the decreased solubility and the accompanying saturation levels of Fe^{+2} in solution will govern the dissolution rate. For example, at 80°C, the release rate of iron (calculated similarly as in Table 4) from troilite is $1.4 \text{ g/m}^2 \cdot \text{d}$ as compared with $0.03 \text{ g/m}^2 \cdot \text{d}$ at 25°C, an increase of almost 50 times.

It was shown that pyrrhotite (monoclinic) attains its equilibrium solubility more slowly than does troilite (days vs. hours), because the rate of dissolution of the former is lower than that of troilite by a factor of at least 1000. Therefore, since the equilibrium solubilities of troilite and monoclinic pyrrhotite are not very different, it can be assumed that the rate of precipitation of pyrrhotite, at equilibrium, is also very much lower. This may explain why troilite appears first on corroding carbon steel surfaces in spite of its higher solubility and thermodynamic instability with respect to pyrrhotite.

The rates of dissolution of both pyrrhotite and pyrite seem to be independent of acid concentration. This is quite significant for possible chemical decontamination of deposited pyrite since higher concentrations of acid will not aid removal of the deposited pyrite.

Role of phosphate and alkali

It has been suggested⁽³¹⁾ that phosphate forms a complex of the type $[\text{FePO}_4]^-$ with dissolved iron, and that at higher temperatures 95% of dissolved Fe^{++} can be complexed as $[\text{FePO}_4]^-$, thereby preventing precipitation of FeS in hot towers. Our results show that addition of phosphate changes neither the rate of dissolution nor the equilibrium solubility of the iron sulfides studied. The rate of dissolution does not change in the presence of phosphate even at 90°C as shown in Figure 6. Therefore, addition of phosphate will not provide a solution to iron transport. However, addition of NaOH lowers the rate of dissolution of mackinawite and troilite, the two sulfides most likely causing major

transport. Their equilibrium solubility also decreases markedly with increased pH. Furthermore, we have observed that less soluble sulfides like pyrrhotite and pyrite are more easily formed at lower temperatures if the pH is higher i.e. in the presence of added alkali. This has also been noted from observations of coupons in loop experiments⁽³²⁾. Thus, addition of alkali will minimize iron transport.

5. CONCLUSIONS AND RECOMMENDATIONS

The solubilities of iron sulfides at 25°C and 1.8 MPa pressure are in the ratio $\approx 6000:80:40:10:1$ for mackinawite, troilite, monoclinic pyrrhotite, hexagonal pyrrhotite and pyrite respectively. At 25°C and pH 3.5, the rates of dissolution differ by a ratio $\approx 10^5:10^4:50:10:1$ for mackinawite, troilite, hexagonal pyrrhotite, monoclinic pyrrhotite and pyrite respectively. These differences are even greater at stronger acidities.

Compared with other iron sulfides, the initial corrosion product, mackinawite, is the most soluble, has the highest dissolution rate and the steepest decline of solubility with temperature. Consequently, its continued formation during plant operation should be avoided to minimize iron transport. Also, since mackinawite transforms easily to other phases, preconditioning of carbon steel surfaces to convert mackinawite to less soluble forms like pyrrhotite and pyrite is recommended. Since pyrite has the lowest solubility and dissolution rate, and since its solubility does not decrease with temperature, converting the carbon steel surface layers to pyrite will give minimum iron transport. However, preconditioning the plant to allow formation of a pyrrhotite layer should also effectively reduce iron transport, since the rate of pyrrhotite dissolution is very low and its solubility is appreciably lower than that of mackinawite and troilite. Moreover, it

is easier to form a pyrrhotite layer than a pyrite layer because pyrrhotite can be formed at much lower temperatures, especially by alkaline additions.

Based on our observation of both the rate of dissolution and the equilibrium solubility of iron sulfides, addition of phosphate will not reduce iron transport. Hence, its addition in plant trials does not seem justified. On the contrary, addition of alkali will reduce markedly both the rate of dissolution and the equilibrium solubility of mackinawite and troilite.

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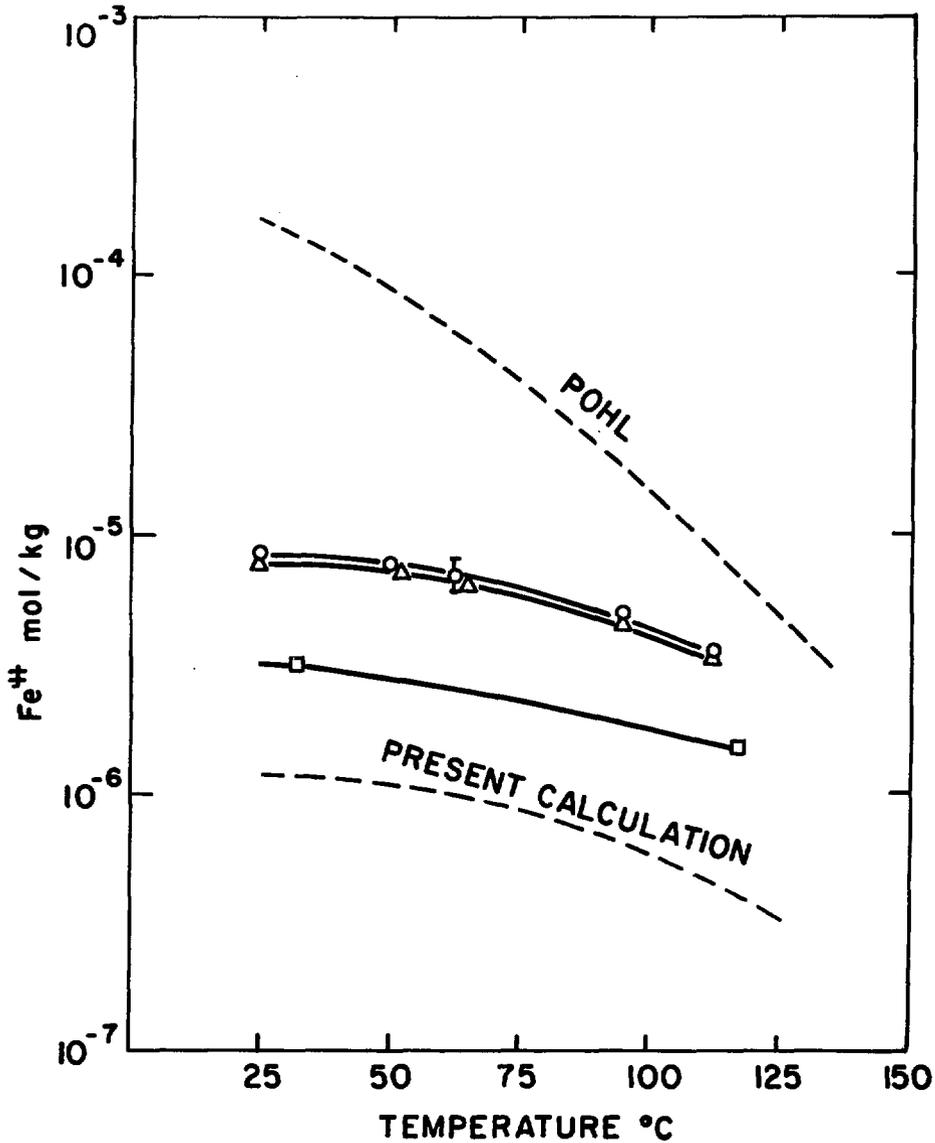


FIGURE 1 Solubility of FeS troilite at different temperatures.
Top dashed line calculated by Pohl⁽¹⁹⁾, 1.8 MPa H₂S
Bottom dashed line, present calculation 1.8 MPa H₂S
○ measured solubility at 0.1 MPa H₂S pressure
△ measured solubility at 1.8 MPa H₂S pressure
□ measured solubility with 1x10⁻⁴ mol/kg added NaOH

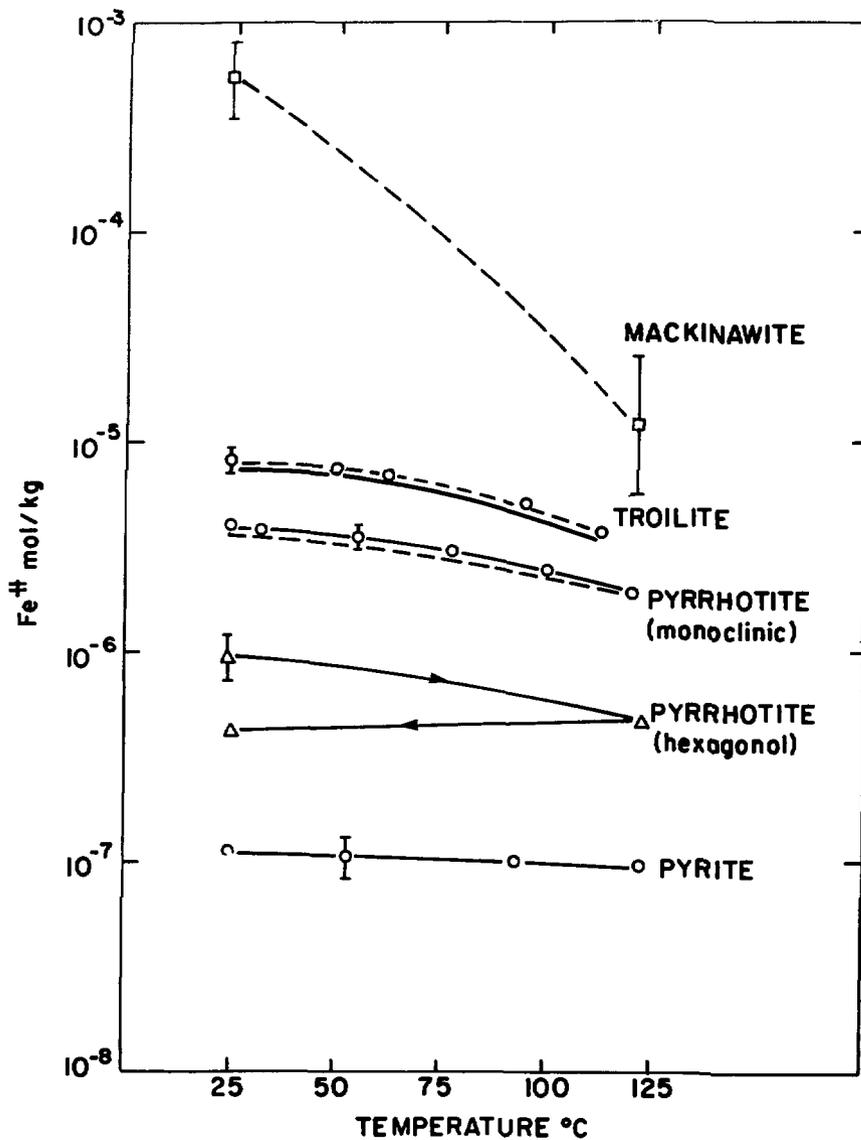


FIGURE 2 Solubility of iron sulfides at 1.8 MPa H₂S pressure. The adjacent curves for troilite and pyrrhotite represent 0.1 MPa (top) and 1.8 MPa (bottom) H₂S pressure. The arrows on pyrrhotite (hexagonal) curves show direction of temperature change.

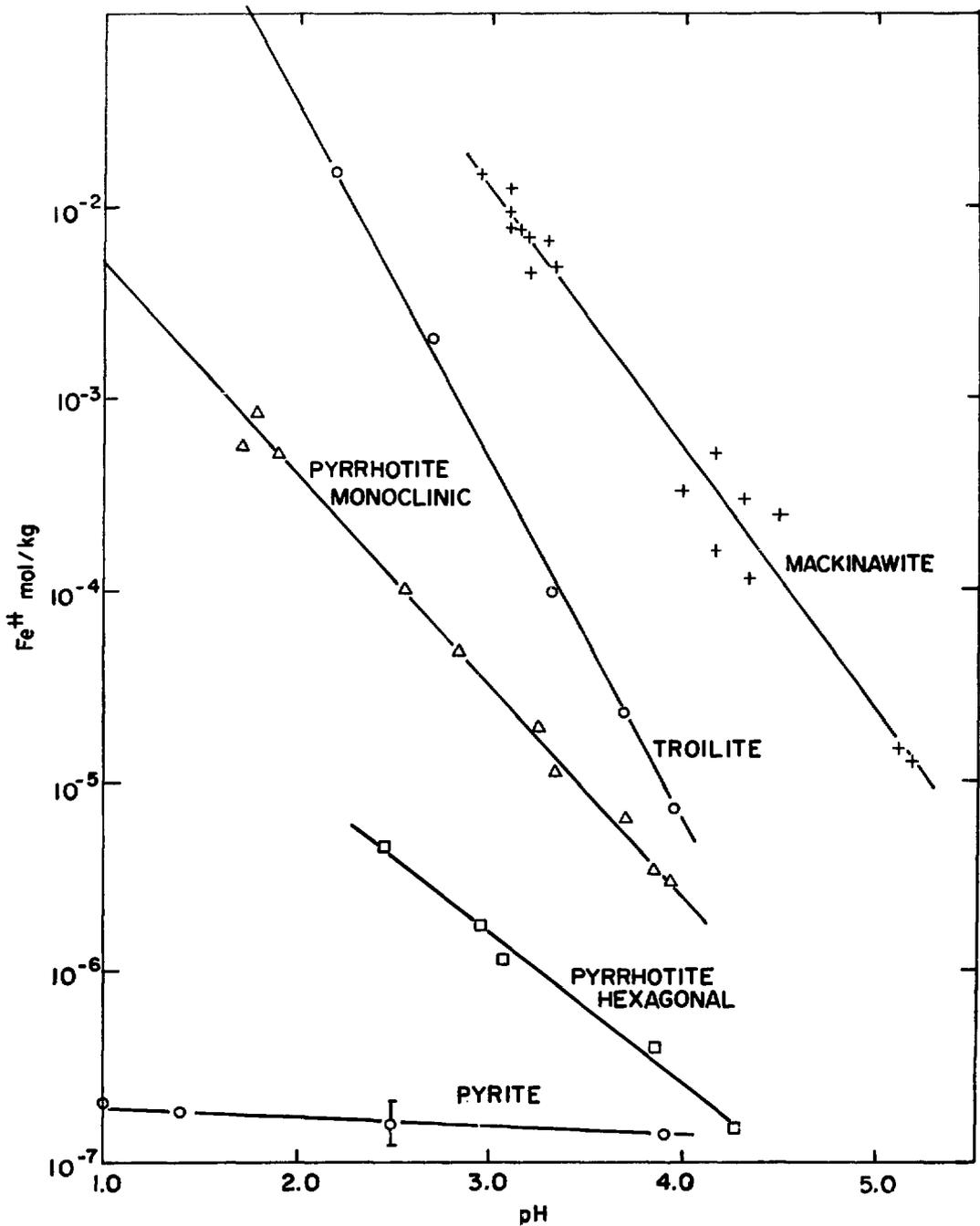


FIGURE 3 Dependence of dissolved Fe^{++} on pH at 25°C and 0.1 MPa H_2S pressure.

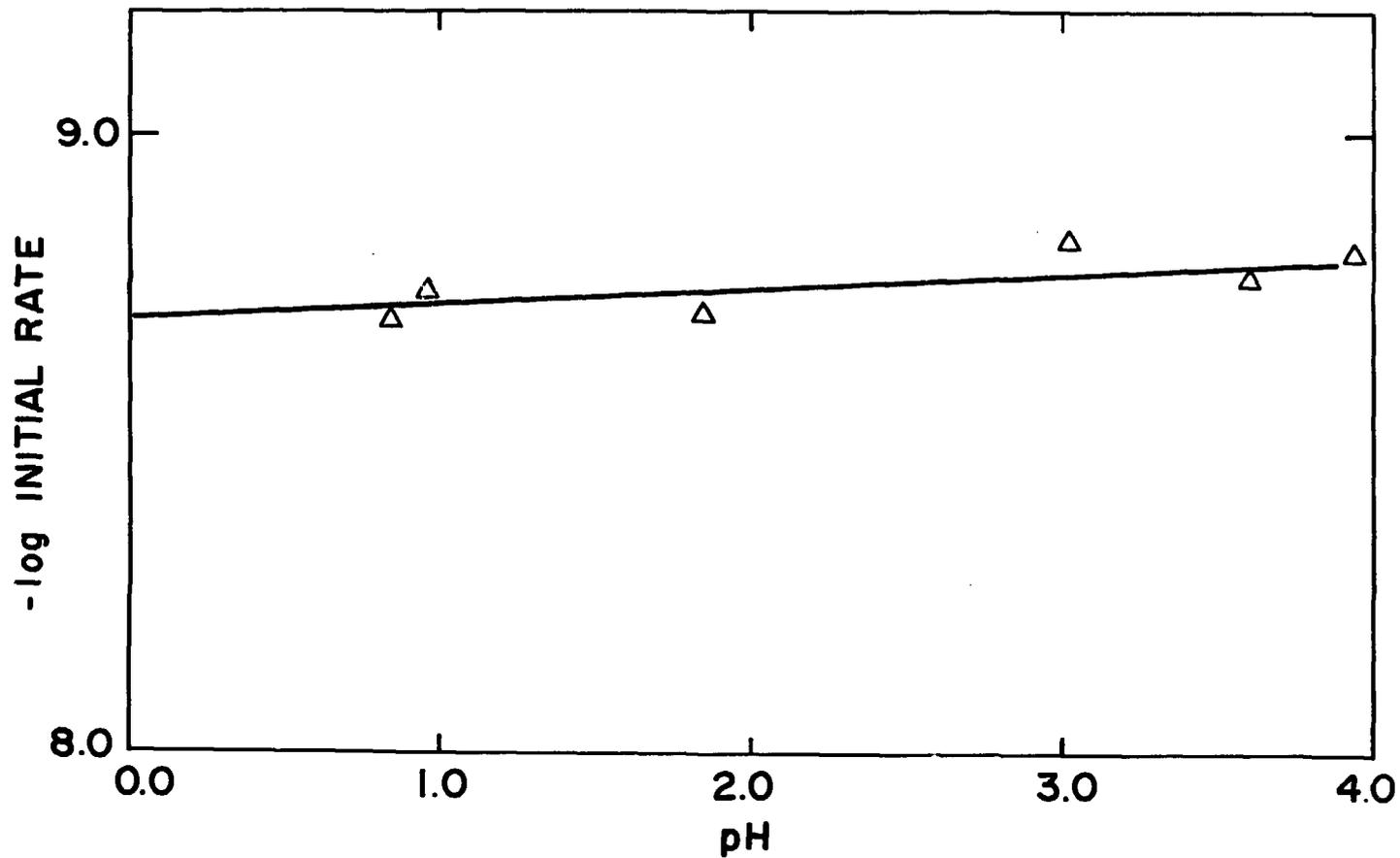


FIGURE 4 Dependence of rate of dissolution of monoclinic pyrrhotite on pH at 25°C.

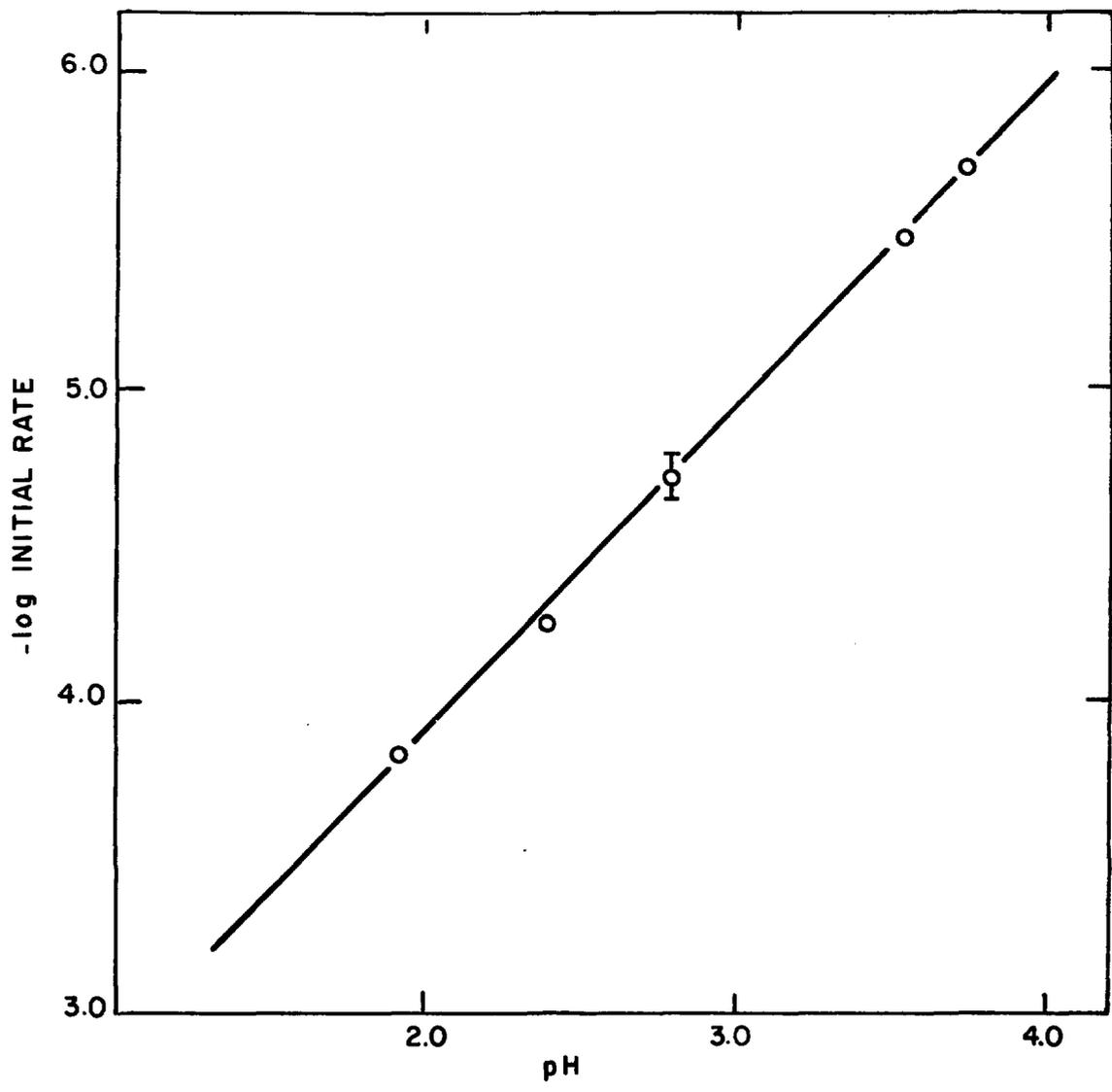


FIGURE 5 Dependence of rate of dissolution of mackinawite on pH at 25°C.

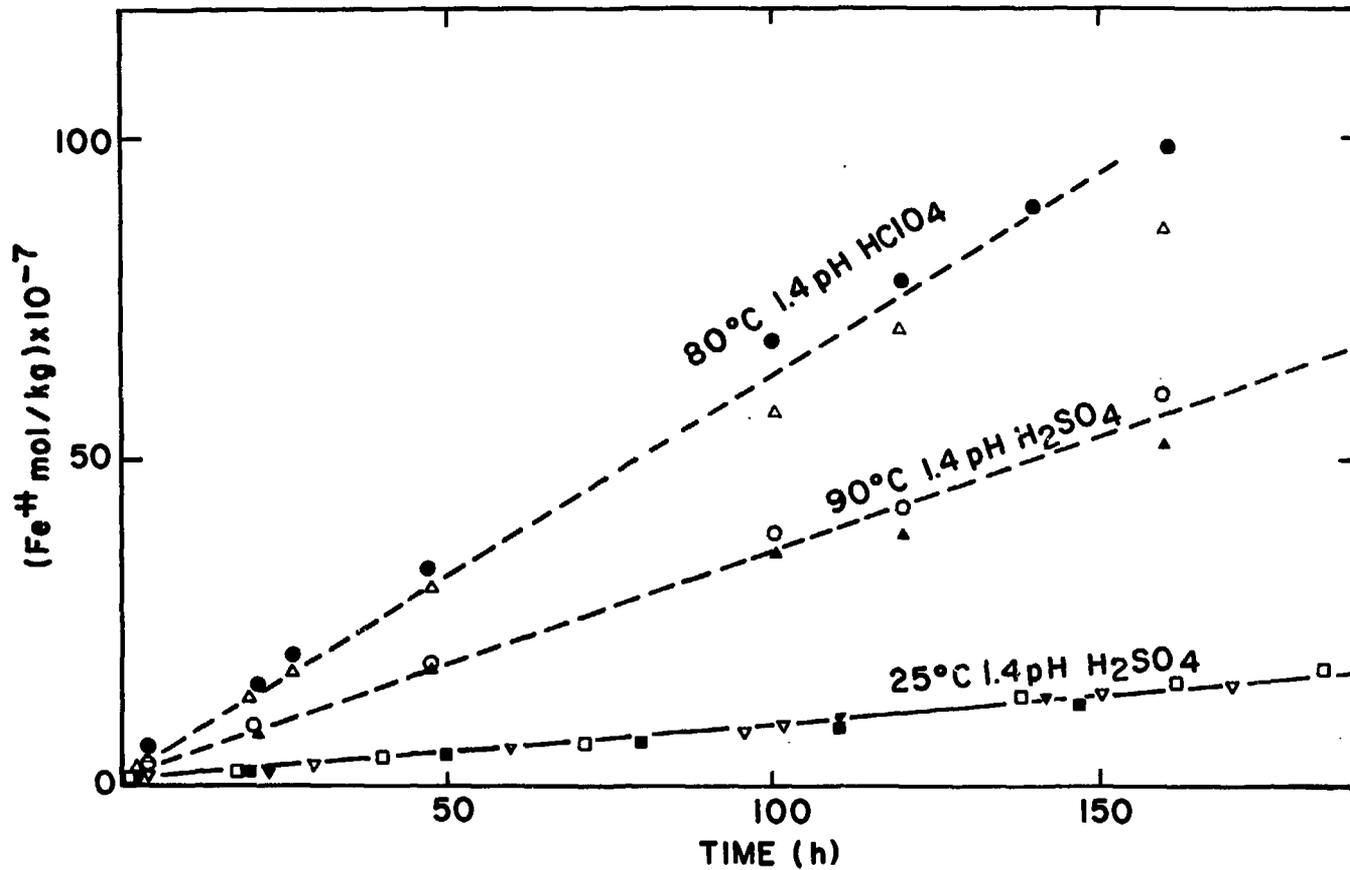


FIGURE 6 Rate of dissolution of pyrite in different media

Rate at 25°C in pH 1.4 H₂SO₄

□ pH 1.4 H₂SO₄ only

■ pH 1.4 H₂SO₄ + N₂

▽ pH 1.4 H₂SO₄ + phosphate (10 μg/g)

▼ pH 1.4 H₂SO₄ + H₂

Rate at 80°C

● pH 1.4 HClO₄ only

Δ pH 1.4 HClO₄ + phosphate
(10 μg/g)

Rate at 90°C

○ pH 1.4 H₂SO₄ only

▲ pH 1.4 H₂SO₄ + phosphate
(10 μg/g)

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