

**THE INFLUENCE OF WATER CHEMISTRY ON H₂ PRODUCTION
AND UPTAKE DURING ANAEROBIC IRON CORROSION**

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ABSTRACT

Iron corrosion is the most important economic and aesthetic problem facing utilities. In the water distribution system, problems caused by iron corrosion include “red water”, scale buildup, and pipe failures. It is necessary to improve our mechanistic understanding of anaerobic iron corrosion in order to better address these concerns.

Experiments were conducted to investigate the effect of soluble constituents (Fe²⁺, PO₄³⁻, and NH₄⁺) on H₂ evolution during anaerobic iron corrosion. At pH 7.0 when sulfide was absent, variable Fe²⁺ did not have much influence on H₂ release rates, whereas PO₄³⁻ and NH₄⁺ promoted H₂ evolution. If present, soluble sulfide controlled H₂ release rates in the solutions with Fe²⁺ or PO₄³⁻; however, NH₄⁺ and S²⁻ combined to inhibit H₂ release. A simplistic empirical model was developed that fit data on corrosion rates from previous researchers studying effects of sulfate-reducing bacteria (SRB) on iron corrosion. As a whole, the experimental data and the model results support the notion that water quality controls iron corrosion rates in the presence of SRB. The practical relevance of previous research is somewhat in doubt given the atypical levels of nutrients used in relation to those actually present in water and wastewater.

A second phase of research was aimed at exploring the equilibrium and kinetic aspects of iron corrosion in the presence of phosphate. The hypothesis that anaerobic iron corrosion is influenced by low pressure H₂ (<1 atm) buildup was examined. At pH 2.75 and pH 7.0 in the presence of 100 mg/L P-PO₄³⁻, variations in H₂ release were measured under different circumstances. Addition of PO₄³⁻ formed a protective film, possibly vivianite Fe₃(PO₄)₂, on the iron surface that eventually stopped H₂ release. However, results were consistent with the idea that corrosion is an irreversible process that is relatively insensitive to low level H₂ (<1 atm). Possible alternative explanations were provided to reconcile the past research data that purportedly demonstrated that removal of H₂ increased corrosion rates. A reaction that caused “decay” of H₂ in the presence of high phosphate was discovered that can not be readily explained.

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AUTHOR'S PREFACE

This work is presented in the Virginia Tech manuscript format. Each chapter is a separate manuscript formatted for journal submission.

Chapter I, "The Influence of Water Chemistry on H₂ Evolution during Anaerobic Iron Corrosion," evaluates possible relationships between water quality and corrosion rates. Chapter II, "Equilibrium and Kinetic Aspects of Anaerobic Iron Corrosion in the Presence of Phosphate," attempts to re-evaluate the equilibrium versus kinetics argument in anaerobic iron corrosion theory.

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CHAPTER 1

The Influence of Water Chemistry on H₂ Evolution During Anaerobic Iron Corrosion

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ABSTRACT

Experiments investigated the effect of various media constituents (Fe²⁺, PO₄³⁻, and NH₄⁺) on H₂ evolution during anaerobic iron corrosion. At pH 7.0 when sulfide was absent, Fe²⁺ did not have much influence on H₂ release rates, whereas higher PO₄³⁻ and NH₄⁺ promoted H₂ evolution. If present, soluble sulfide controlled H₂ release rates in the solutions with Fe²⁺ or PO₄³⁻. However, if both soluble sulfide and NH₄⁺ were present at high concentrations, very low rates of H₂ release were observed. A simplistic empirical model was developed to fit data on corrosion rates from previous research with sulfate-reducing bacteria (SRB). The best fit empirical coefficients were consistent with trends noted in this work and provided a good fit to previous research data, supporting the idea that water chemistry is more important to previous results obtained in the presence of SRB than is commonly realized. The practical relevance of previous studies is in doubt given the atypical levels of nutrients in media used.

INTRODUCTION

Several workers have noted that rapid anaerobic iron corrosion occurs when higher levels of soluble ferrous are present in water (1-5). The conventional wisdom is that in the presence of sulfate-reducing bacteria (SRB), sulfide produced by bacterial activity will normally react with the iron metal to form a protective film of FeS. However, if sufficient ferrous ion is present to maintain a residual level of soluble Fe²⁺, the protective film will not form on the metal surface due to precipitation of the soluble sulfide by the ferrous ion in solution.

There are three main sources of experimental data supporting the hypothesis that high levels of soluble ferrous ion is the key. The first is the experimental data of King et al. (2) who observed that an increase in ferrous ion concentration in the growth media also increased corrosion rates. King et al. (1) also discovered a roughly linear relationship between the iron corrosion rate and the total ferrous concentration on a log-log graph using data from other researchers (Figure 1-1).

Finally, Lee et al. noted that in continuous culture a step increase in ferrous concentration in the feed precipitated biogenic sulfide and led to increased corrosion rates (6).

Closer scrutiny of the earlier experimental data reveals that factors other than the ferrous concentration in the bacteria growth media were varying over a wide range (Table 1-1). For example, PO_4^{3-} salts were added into the medium as a nutrient source for the bacteria growth or as a buffer, resulting in concentrations of P- PO_4^{3-} from 2.50 mM to 7.36 mM. In addition, NH_4^+ came from two sources; one was directly from the addition of NH_4Cl and the other was from addition of ferrous as $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2$. The total amount of NH_4^+ in the biotic tests varied from 10 mM to 139.2 mM.

Preparation of the media recipes listed in Table 1-1 leads to formation of a noticeable solid as would be expected based on the high degree of oversaturation with vivianite [$\text{Fe}_3(\text{PO}_4)_2$]. It is instructive to confirm that vivianite precipitation impacts the concentration of soluble Fe^{2+} and PO_4^{3-} in the growth media via formation of $\text{Fe}_3(\text{PO}_4)_2$ solid. To this end, several solutions of King's "Modified Medium C" (KH_2PO_4 0.5 g/L, NH_4Cl 1.0 g/L, Na_2SO_4 2.6 g/L, $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ 0.1 g/L, $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ 2.0 g/L) were created by adding various doses of ferrous from 0 to 3 g/L, pH was adjusted to 7.0 \pm 0.2 as per King's experimental protocol, and samples were passed through a 0.45 μm pore size filter 24 hours later and analyzed for soluble Fe and P. Results were then compared to modeling prediction considering aquatic chemical equilibrium. There is a very good agreement between the model prediction and actual data on soluble Fe^{2+} , vivianite (particulate Fe) and soluble P in the media (Figure 1-2). Thus, it can be expected that concentrations of soluble phosphate and soluble Fe^{2+} were probably impacted by $\text{Fe}_3(\text{PO}_4)_2$ formation in experiments of other researchers as well.

To consider the effects of this, predicted or actual concentrations of various media constituents were correlated to iron corrosion rate data in King's compilation and data from other studies since that time (7) (Figure 1-3). Interestingly, the relationship between corrosion rate and total ferrous ion was quite poor. The best correlation was between log corrosion rate and log [NH_4^+], which is surprising because there is currently no data in the literature supporting a contribution to SRB corrosion from ammonia although it is briefly mentioned as a factor in a few other

corrosion investigations (8, 9). This suggests that ferrous may be less important to previous experimental results than believed and that ammonium may be more important.

The goal of this work is to re-examine King's hypothesis from the perspective of solution impacts on hydrogen evolution from pure iron under abiotic conditions. Hydrogen evolution was selected to track corrosion because if it is the only reduction reaction, and if the hydrogen entry into the metal can be ignored, total hydrogen evolution is proportional to the total amount of iron corrosion (i.e. $\text{Fe} + 2\text{H}^+ = \text{Fe}^{2+} + \text{H}_2$). Hydrogen evolved from the iron metal might also have supported microbial growth in previous work, since utilization of hydrogen from corroded iron by sulfate-reducing bacteria has been reported in earlier studies (10-13), so H_2 levels are also of direct importance to microbial growth under some circumstances. Finally, it is believed that the level of H_2 in water influenced the rate of iron corrosion in some previous investigations (11).

MATERIALS AND METHODS

To test the effect of different media constituents on hydrogen evolution in anaerobic iron corrosion, experiments were conducted in an anaerobic glove box. Specimens were cut from 1 mm diameter pure iron wire (99.99% Fe) into 1 cm lengths and weighed before each test. In addition to various doses of FeCl_2 , NaH_2PO_4 , and NH_4Cl , all solutions contained 0.001 M NaCl. The initial pH was adjusted to 7.0 ± 0.2 using 0.1 M NaOH or HCl and 40 mL glass vials were used as a reactor. The experimental approach was to fill 40 ml glass vials with approximately 20 ml solution, and then purge the solution with 99.998% N_2 for 30 minutes. Pre-weighed iron wire was placed in each sample vial and then the vial was sealed using a Mininert Valve. In general, samples were run in triplicate or duplicate unless stated in text.

Throughout the experiment, the headspace of the vials was sampled for hydrogen production with time. Hydrogen gas in the headspace was measured by RGA5 Process Gas Analyzer after sampling with a gas syringe. At the end of the experimental, the iron wire weight loss and concentration of total/soluble iron were measured. The sampling protocol was as follows: the concentration of total/soluble iron was measured with a JY 2000 Inductive Coupled Plasma-Emission Spectroscopy (ICP-ES) after the vials were opened in the glove box, soluble Fe^{2+} was

measured with a HACH Kit colorimetric test after samples were passed through a 0.45 μm pore size filter. pH was measured with a Corning pH meter and probe. The iron wires were rubbed with soft cloth to remove most corrosion products, rinsed with pure water for a few seconds, and then weighed on a balance.

The following procedure was used to screen out leaking sampling valves before tests. 1 ml pentane was added to a vial, which was then sealed, and the weight change of the vial was measured after 1 week. If weight loss from leakage exceeded 0.007 g the valve was discarded. Valves that passed this test leaked less than 15% of H_2 from the headspace over 15 days.

RESULTS

Results are organized into three sections examining the effect of Fe^{2+} , PO_4^{3-} and NH_4^+ on H_2 evolution. For each constituent, tests were conducted in the presence and absence of added S^{2-} . Thereafter, results are synthesized in a discussion section.

Effect of variable Fe^{2+} on H_2 evolution

Different doses of FeCl_2 were added to a 0.001 M NaCl solution (Base Solution) to produce total ferrous concentrations of 0, 1, 2, 10, 100 and 500 mg/L Fe^{2+} . Initial pH was adjusted to 7.0 ± 0.2 . To compare the effect of Fe^{2+} on H_2 evolution in the presence of sulfide, NaHS was dosed at 100 mg/L as S^{2-} in one set of samples and another set of samples was tested without sulfide. Assuming quantitative precipitation of the S^{2-} with Fe^{2+} as FeS (solid), the soluble sulfide would have been non-detectable and 40 mg/L in the sample at 500 mg/L Fe^{2+} and 100 mg/L Fe^{2+} , respectively (Table 1-2).

In the absence of sulfide, H_2 evolved was typically less than 1 μMole after 300 hours (Figure 1-4). The final pH in the 100 mg/L and 500 mg/L Fe^{2+} solution was 5.91 and 5.10 respectively. This is lower than the pH of 6.30 to 8.55 observed at the other levels of Fe^{2+} (Table 1-2), and is a likely reason why slightly higher H_2 evolution was observed in the 100 and 500 mg/L Fe^{2+} solution, although the significantly higher Cl^- at iron doses above 100 mg/L Fe^{2+} may also have been influential. This experiment was conducted in triplicate, and although samples for H_2 were

not collected at the exact same time in each experiment (so error bars cannot be generated) there was no significant difference in H_2 release between samples at 0, 1, 2, and 10 mg/L Fe^{2+} as determined using a paired t-test at 95% confidence. However, there was significant higher H_2 release if Fe^{2+} dose was above 100 mg/L, but this is likely a pH effect as mentioned earlier (14).

With the addition of 100 mg/L S^{2-} , there was an inverse relation between hydrogen evolution and ferrous ion added (Figure 1-5). In the solution containing 0, 1, 2, 10 mg/L Fe^{2+} , hydrogen release rates were almost the same, regardless of the initial Fe^{2+} concentration. However, the hydrogen release rate in solution containing 100 mg/L Fe^{2+} was lower, while in 500 mg/L Fe^{2+} solution it was almost zero. At the end of experiment, pH was measured and found to vary over a wide range (Table 1-2) that was not consistent with increased Fe^{2+} .

There are two possible explanations for the lower H_2 release above 100 mg/L Fe^{2+} . First, soluble sulfide seemed to control release of H_2 , as there is an approximate linear relationship between the H_2 release rate and the predicted soluble sulfide concentration (Figure 1-6). To further examine this issue, another experiment was conducted with iron wires exposed to the 0.001 M NaCl solution with 275 mg/L FeS solid or 275 mg/L FeS solid plus 100 mg/L S^{2-} . 275 mg/L FeS solid is the concentration of FeS estimated to form in the earlier test with 500 mg/L Fe^{2+} plus 100 mg/L S^{2-} solution. Very little H_2 was evolved in the presence of FeS alone, yet the system with FeS plus 100 mg/L S^{2-} released about as much H_2 as the test with S^{2-} alone (FeS test data in Figure 1-6). This directly confirms the importance of soluble S^{2-} in controlling H_2 release. In addition, the iron wire sample from the earlier experiment using 500 mg/L Fe^{2+} plus 100 mg/L S^{2-} was placed into the solution containing only 100 mg/L S^{2-} . While the initial H_2 release was low in the 100 mg/L S^{2-} solution with this old iron wire, 3 days later the H_2 release increased to about the same rate as in the test with new wire and 100 mg/L S^{2-} . In other words, experimental results under a wide range of conditions are consistent with soluble S^{2-} controlling the rate of H_2 release (Figure 1-7).

Another reaction that could be important in the solution with high Fe^{2+} and S^{2-} was the possible adsorption of H_2 by FeS, which would result in low detectable hydrogen release even if the corrosion rate was high. It is well established that hydrogen evolved from corroded iron can be

adsorbed in iron sulfide defects (15-18). In previous research, the iron sulfide increased the corrosion rate as measured by weight loss, and the corrosion rate was also dependent on the type of FeS solid formed. Given an iron corrosion rate of 10 mg iron/mMole FeS as noted by King (17), which is supposedly due to H₂ adsorption by FeS, it is predicted that 275 mg/L FeS in our tests could have adsorbed 11.2 μMole H₂. Our work showed no detectable H₂ when 275 mg/L FeS initially formed in the solution while 7.2 μMole H₂ was released without initial FeS present, so it is possible that the FeS could have adsorbed all of the H₂ when it was present. To further test this idea, 0.3% H₂ was spiked into the solution with 500 mg/L Fe²⁺ plus 100 mg/L S²⁻. There was less than 10% loss of total H₂ after one and half month, demonstrating the FeS itself does not adsorb H₂. It is believed that atomic hydrogen on the metal surface might be adsorbed by the FeS solid (16), consistent with this experimental result. Unfortunately, due to the small weight loss during our short term experiments, it could not be determined if FeS was accelerating corrosion rates.

Short term effect of PO₄³⁻ on H₂ evolution

NaH₂PO₄ was added to sub-samples of 0.001 M NaCl solution, producing concentrations of P-PO₄³⁻ of 0, 0.03, 0.1, 0.3, 1, 10, 20 and 100 mg/L at pH 7.0±0.2. In the absence of sulfide, if P-PO₄³⁻ was 1 mg/L or less, a steady slow increase in H₂ release was observed. However, if the P-PO₄³⁻ concentration was 10 mg/L or higher, a very high H₂ release occurred within a few days. The highest H₂ release rate was 0.83 μMole/cm²/day, which translates to a corrosion rate of 4.65 mg/dm²/day if H₂ evolution is proportional to corrosion rate. There is a roughly linear relationship between the H₂ release rate and the initial soluble P concentration (Figure 1-8). This result is consistent with previous findings where higher PO₄³⁻ in the media promoted H₂ release in the absence of bacteria (19, 20) and in the presence of SRB (7). However, if the experiment was repeated in the presence of 100 mg/L sulfide, phosphate concentration had almost no effect on the H₂ release rate (Figure 1-8).

As mentioned earlier, vivianite solid was likely to be present in the growth medium containing Fe²⁺ and PO₄³⁻, therefore it was desirable to test the effect of this solid on H₂ evolution under several different circumstances (Table 1-3). In the absence of sulfide, vivianite tended to increase the rate of H₂ evolution noted for a given soluble concentration of PO₄³⁻. A very high

H₂ release rate was observed in vivianite plus 100 mg/L P-PO₄³⁻ solution, which is 3.10 μMole H₂/cm²/day, about three times higher than previous results at a similar level of soluble PO₄³⁻ (Figure 1-8). However, in the presence of sulfide, even though the initial soluble P-PO₄³⁻ in solution was high, lower H₂ release rate was found compared to the vivianite tests or S²⁻ tests.

Short-term effect of NH₄⁺ on H₂ evolution

NH₄Cl was added to the NaCl base solution to produce concentrations of NH₄⁺ at 0, 0.0025 M and 0.139 M, a range consistent with media used in previous corrosion studies. The initial pH was adjusted to 7.0±0.2. In the absence of sulfide, higher NH₄⁺ increased the rate of H₂ release. The initial H₂ release rate in the solution containing 0.139 M NH₄⁺ was 2.04 μMole/cm²/day, while that in 0.0025 M NH₄⁺ solution was 0.61 μMole/cm²/day (Figure 1-9). However, with addition of 100 mg/L S²⁻, it was surprising to find almost no H₂ was evolved compared to the other conditions, and the initial H₂ release rate was only 0.10 μMole/cm²/day. This is ten times lower than in the solution of 100 mg/L S²⁻ alone and 15 times lower than in the system with NH₄⁺ alone. This result is consistent with a previous statement that ammonia and organic nitrogen-containing compounds are highly effective inhibitors for sulfide-induced corrosion (21, 22). A black coating was observed on the iron wire surface in this solution. At the end of the experiment, it was easy to remove this black coating with a soft cloth and uncover a shiny wire surface. Weight loss was not significant.

To investigate the effect of NH₄⁺ on H₂ evolution in the presence of PO₄³⁻, 100 mg/L P-PO₄³⁻ was added to four solutions of NH₄⁺ at 0, 0.0025 M, 0.010 M, 0.139 M. A synergistic effect of NH₄⁺ on H₂ release was observed in the presence of PO₄³⁻. The highest H₂ release rate observed in this work, which was 12.2 μMole/cm²/day, occurred in the 0.139 M NH₄⁺ plus 100 mg/L P-PO₄³⁻ solution (Figure 1-9). This converts to a corrosion rate of 67.9 mg/dm²/day. Again, in the presence of sulfide, almost no H₂ release was observed.

DISCUSSION

A schematic was developed to summarize these results and to serve as a basis for re-examining previous research results (Figure 1-10). In anaerobic solution at pH 7 and in the absence of

sulfide, Fe^{2+} in the media solution did not have much influence on H_2 evolution rates, while PO_4^{3-} and NH_4^+ promoted H_2 evolution. Soluble sulfide was linearly related to the H_2 release rate, but a combination of NH_4^+ and sulfide led to much lower rate of H_2 release than had been observed in the presence of each species alone. The impacts of PO_4^{3-} and NH_4^+ could be an important contributor to results in previous research.

There is some support in the literature for these trends. Recent work on anaerobic iron corrosion found that soluble PO_4^{3-} could increase H_2 release from metal in short term experiments (19, 20). With 8 mM P- PO_4^{3-} and 24.3 mM NH_4^+ at pH 7.0, in the absence of bacteria there was 16.1 μMole H_2 released over 210 min. This H_2 release rate was equivalent to the corrosion rate of 618.5 $\text{mg}/\text{dm}^2/\text{day}$, assuming H_2 evolution was proportional to the corrosion rate. The adverse effect of soluble sulfide and iron sulfide on iron corrosion has been reported elsewhere (16). However, all the earlier tests were conducted from the perspective of corrosion rate in terms of weight loss and their effect on H_2 evolution was not examined. In experiments with anaerobic culture, overall H_2 evolution would serve as an energy source for bacterial growth, and therefore the rate of H_2 release as measured in the headspace would not be proportional to corrosion rate even though it is fundamental to propagating the corrosive attack.

To indirectly test our hypothesis regarding the importance of media chemistry, we formulate a simplistic empirical model to fit reported corrosion rate data based only on solution composition:

$$I_{\text{corr}} = a [\text{soluble P-PO}_4^{3-}] + b [\text{soluble Fe}^{2+}] + c [\text{NH}_4^+] + d [\text{Vivianite}] + e [\text{Cl}^-] + f [\text{Na}^+] + g [\text{SO}_4^{2-}] + h [\text{H}^+] + \text{Constant}$$

Where []—Concentration of various media constituents initially in the growth media in μM ;

Using the data from Table 1-1, Microsoft Excel Solver program was run and coefficients that were unimportant were dropped, giving a final result:

$$I_{\text{corr}} = 0.01574 [\text{soluble P-PO}_4^{3-}] + 0.000274 [\text{NH}_4^+] + 0.03262 [\text{Vivianite}] - 0.001524 [\text{Na}^+] + 729.88 [\text{H}^+]$$

This overly simplistic model provided a good fit to previous research data (Figure 1-11). It is surprising that this model could explain 90% of the observed variation in corrosion rate reported in previous SRB work without considering experimental methods, bacteria strains, and type of metal used. Obviously, there are some experimental conditions that would not fit this model even though they are apparent in the literature review, but this exercise does reinforce the idea that inorganic water chemistry is important. We further note that the sign of each coefficient in the model is consistent with experimental observations obtained when sulfide was absent in our short term abiotic experiments. For example, soluble P, vivianite, NH_4^+ , and H^+ all increased corrosion rates.

Interestingly, the role of Fe^{2+} in our experiments and in the above equation was insignificant. While Fe^{2+} itself did not have a direct influence on H_2 release, it did have very important indirect impacts due to a variety of mechanisms. First, Fe^{2+} was added to the media as $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2$, increasing the concentration of NH_4^+ in the media which promotes H_2 release. Second, since S^{2-} prevented attack of NH_4^+ and PO_4^{3-} on iron, removal of soluble sulfide by addition of Fe^{2+} to the media is expected to increase the rate of corrosion. Additionally, iron sulfide itself is corrosive as has been reported in the literature. These effects appear to outweigh the benefit of Fe^{2+} in decreasing soluble PO_4^{3-} , a change that would tend to lower corrosion rate, although the resulting formation of vivianite solid is also detrimental.

To further test the controversial hypothesis that Fe^{2+} was acting indirectly the following experiment was conducted. Iron wire was placed into the solution containing 100 mg/L P- PO_4^{3-} , 0.139 M NH_4^+ , and 100 mg/L S^{2-} . The initial H_2 release was quite low as would be expected (Figure 1-12). After 23 days, Fe^{2+} was dosed to precipitate all S^{2-} present in the solution, and a rapid increase in H_2 release was noted. The result directly illustrates how Fe^{2+} increases corrosion rate by removing the S^{2-} that was preventing PO_4^{3-} and NH_4^+ attack, as was observed in previous research in continuous cultures with SRB (6). It also provides an alternative explanation for an unusual phenomena observed in Iverson's work (23), in that he reported a corrosion rate of only 2.5 mg/dm²/day in the presence of SRB with medium containing 178 mg/L P- PO_4^{3-} and 9.3 mM NH_4^+ ; however, the addition of Fe^{2+} as $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2$ to precipitate

soluble sulfide and removal of both bacteria cells and sulfide by filtration increased corrosion rate dramatically by 460 times (1152 mg/dm²/day).

This work makes some clear steps towards understanding previous research results. One question raised by this work is whether previous research has faithfully replicated the true problem of SRB attack in iron corrosion. That is, while it demonstrates that the concentrations of NH₄⁺ and PO₄³⁻ in the media can exert a controlling influence on corrosion, it is clear that the concentrations present are much higher than would be encountered in virtually any reasonable circumstance in water or municipal wastewater (Table 1-4). Additional work is necessary under more realistic conditions to better understand the mechanisms of SRB attack and possible remedial approaches.

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LITERATURE CITED

1. King R.A.; Miller J.D.A.; Wakerley D.S. *Br. Corros. J.* **1973**, *8*, 89.
2. King R.A.; Dittmer C.K.; Miller J.D.A. *Br. Corros. J.* **1976**, *11*, 105.
3. Booth G.H.; Copper P.M.; Wakerley D.S. *Br. Corros. J.* **1966**, *1*, 345.
4. Booth G.H.; Copper A.W.; Copper P.M. *Chemistry and Industry* **1967**, Dec. 2084.
5. Adams M.E.; Farrer T.W. *J. Appl. Chem.* **1953**, *3*, 117.
6. Lee W.; Lewandowski Z.; Nielsen P.H.; Hamilton W.A. *Biofouling* **1995**, *8*, 165.
7. Weimer P.J.; Van Kavelaar M.J.; Michel C.B.; Ng T.K. *Applied and Environmental Microbiology* **1988**, *54*, 386.
8. Sanctis O.; Gomez L.; Pellegrini N.; Duran A. *Surface and Coating Technology* **1995**, *70*, 251.
9. A laboratory Study on Metal Corrosion Ammonia Gas.
10. Hardy J.A. *Br. Corros. J.* **1983**, *18*, 190.
11. Rajagopal B.S.; LeGall J. *Appl. Microbiol. Biotechnol.* **1989**, *31*, 406.

12. Cord-Ruwisch R.; Widdel F. *Appl. Microbiol. Biotechnol.* **1986**, 25, 169.
13. Deckena S.; Blotevogel K.H. *Biotechnology Letters* **1990**, 12, 615.
14. *Internal Corrosion of Water Distribution Systems*, 2nd ed; AWWARF American Water Works Association: Denver, **1996**, p57.
15. King R.A.; Miller J.D.A.; Smith J.S. *Br. Corros. J.* **1973**, 8, 137.
16. Smith J.S.; Miller J.D.A. *Br. Corros. J.* **1975**, 10, 136.
17. King R.A.; Wakerley D.S. *Br. Corros. J.* **1973**, 8, 41.
18. Mara D.D.; Williams D.J.A. *Proceedings of Biodegradation of Materials* **1972**, 2, 103.
19. Bryant R.D.; Laishley E.J. *Can. J. Microbiol.* **1990**, 36, 259.
20. Bryant R.D.; Laishley E.J. *Appl. Microbiol. Biotechnol.* **1993**, 38, 824.
21. Rozenfeld I.L. *Corrosion Inhibitors*, McGraw-Hill Inc, **1981**, p281.
22. Oriani R.A.; Hirth J.P.; Smialowski M. *Hydrogen Degradation of Ferrous Alloys*, Noyes Publications: Park Ridge, **1985**, p244.
23. Iverson W.P. In *Underground Corrosion, ASTM STP 741*, E.Escalante (ed.); American Society for Testing and Materials: Philadelphia, **1981**, p33.
24. *Water Treatment Principle and Design*, James M.Montgomery, Consulting Engineers, Inc, **1985**, p12.
25. Davis M.L.; Cornwell D.A. *Introduction to Environmental Engineering*, 2nd ed; McGraw-Hill, Inc: New York, **1991**, p325.
26. Reynold T.D.; Richards P.A. *Unit Operation and Processes in Environmental Engineering*, 2nd ed; PWS Publishing Company: Boston, **1996**, p103.

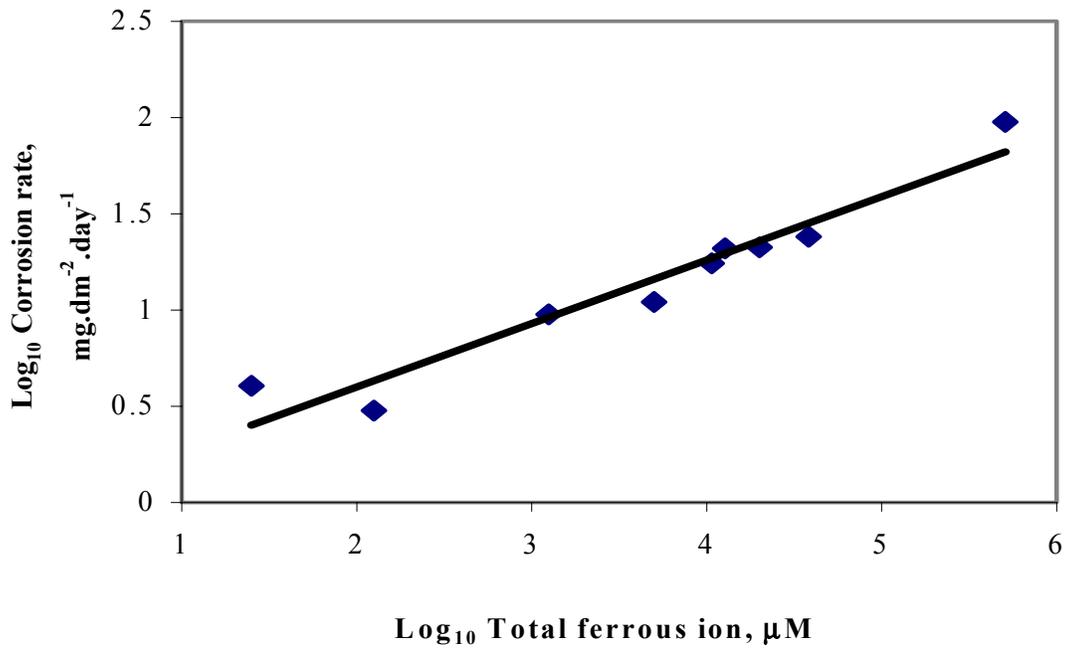


Figure 1-1. Effect of ferrous concentration on the corrosion rate of mild steel in cultures of sulphate-reducing bacteria. After King (1) et al.

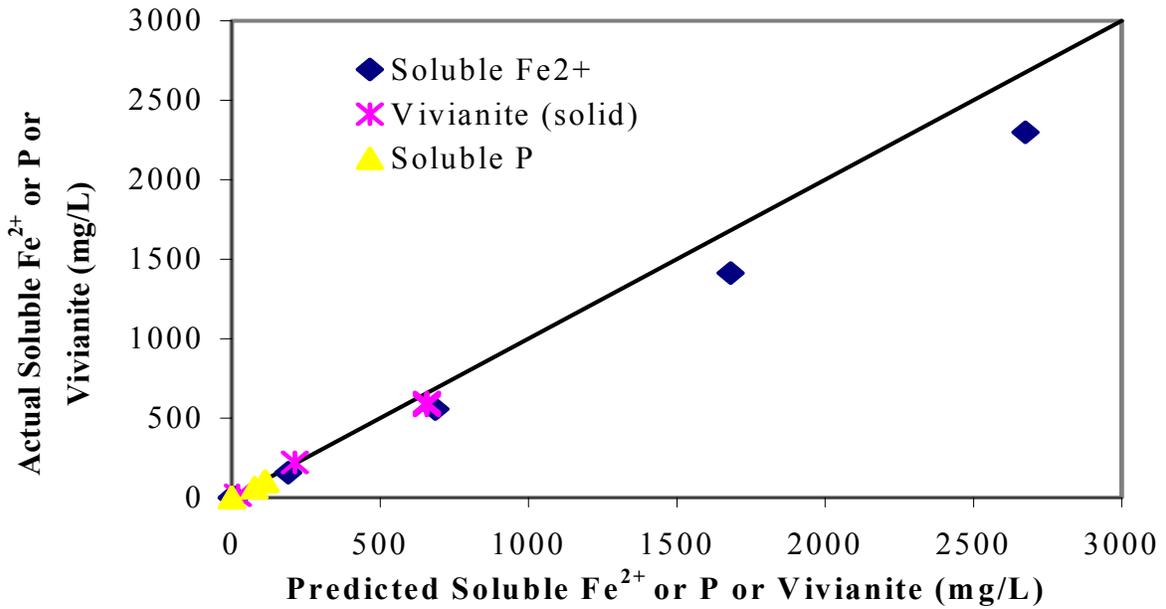


Figure 1-2. Comparison of modeling and experimental results for vivianite formation in test media.

Table 1-1. Different constituents in media used for previous anaerobic iron corrosion studies with sulphate-reducing bacteria.
The last three references come after King's 1976 study.

Reference	pH	Fe ²⁺ mM	PO ₄ ³⁻ mM	NH ₄ ⁺ mM	Na ⁺ mM	SO ₄ ²⁻ mM	Type of Specimens	Corrosion Rate mg/dm ² /day
King et al 1976	7.20	0.025; 0.125; 0.525; 1.025	2.50	10	50	25.3	Iron (99.985% Fe)	0.58+/-0.14 0.72+/-0.12 0.80+/-0.08 0.83+/-0.09
King et al 1973	7.25	0.014	3.68	18.7	74.1	18	Mild Steel (99.267% Fe)	5.92+/-1.69
Adams et al 1953	7.30	1.27	2.87	21.25	31.2	18	Cast Iron (91.93% Fe)	16.6+/-3.52
Booth et al 1966	7.25	12.7	3.68	44.1	74.1	43.7	Mild Steel (99.267% Fe)	20.5+/-1.9
King et al 1973	7.25	38.3	3.68	95.3	74.1	94.9	Mild Steel (99.267% Fe)	18.3+/-1.8
Booth et al 1967	6.80	50.9	7.36	139.2	71.9	132.1	Mild Steel	156.3+/-47.7
Weimer et al 1988	6.60	0	0.01; 0.05; 0.30; 1.80; 4.00; 10.0	40.0	53.5	40.8	Mild Steel	84.7 152.5 67.8 141.2 242.9 254.1
Bryant et al 1993	7.00	0 0	8 4	24.3 9.3	5.13 10.3	0 0	Mild Steel, abiotic system, no H ₂ S	618.5* 19.4*
Bryant et al 1990	7.00	0	100	0	0	0	Mild Steel, abiotic system, no H ₂ S	645.12*

* Calculated assuming H₂ evolution is proportional to corrosion rate

◆ King et al ✕ Others ▲ Weimer et al

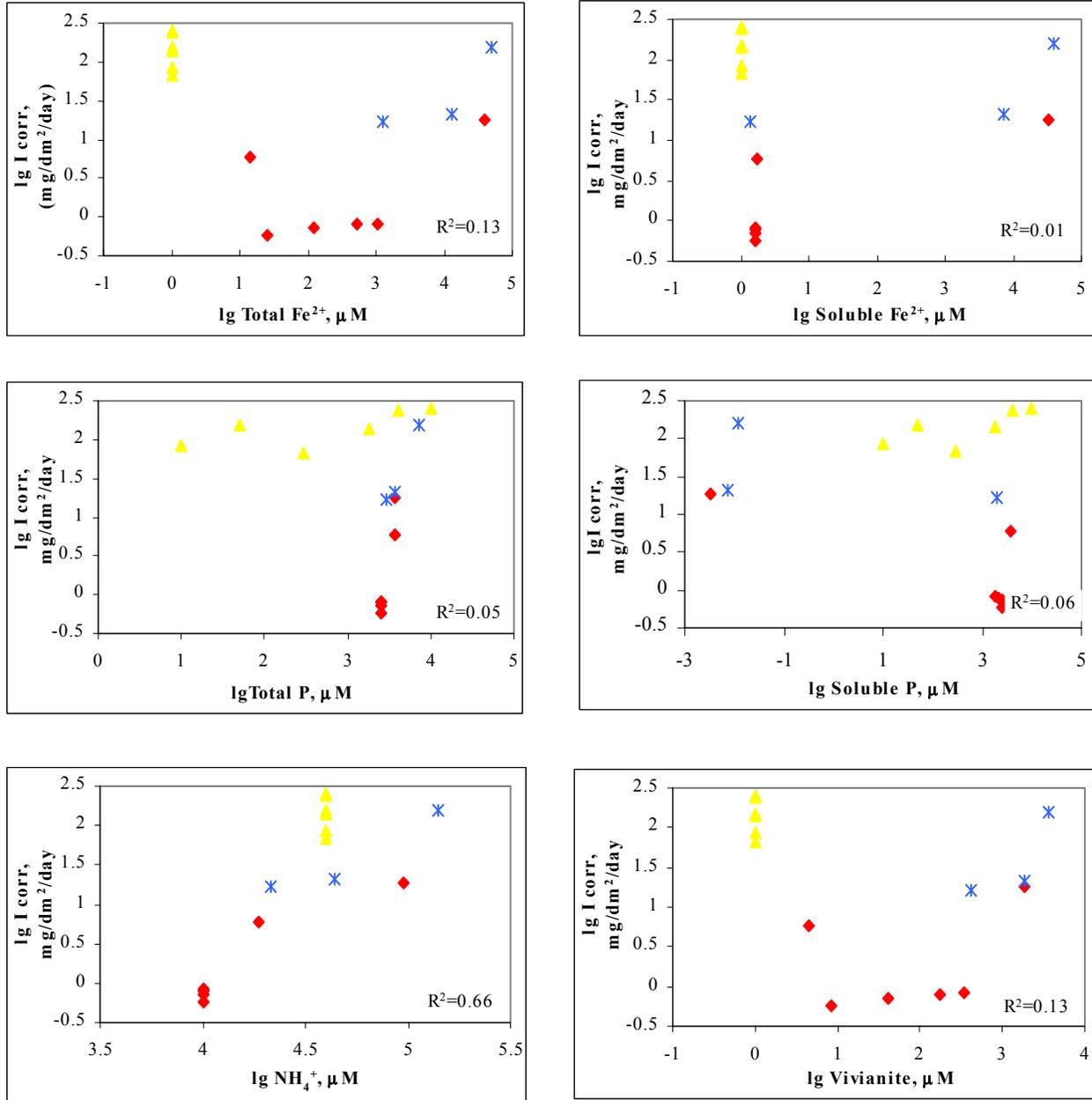


Figure 1-3. The relationship between different medium constituents and the anaerobic iron corrosion rate in previous research; Since Weimer et al (7) did not add any Fe²⁺ to the growth medium, corrosion rate data is plotted at 1 μM Fe (i.e. lg 1 μM=0) for purposes of this graph.

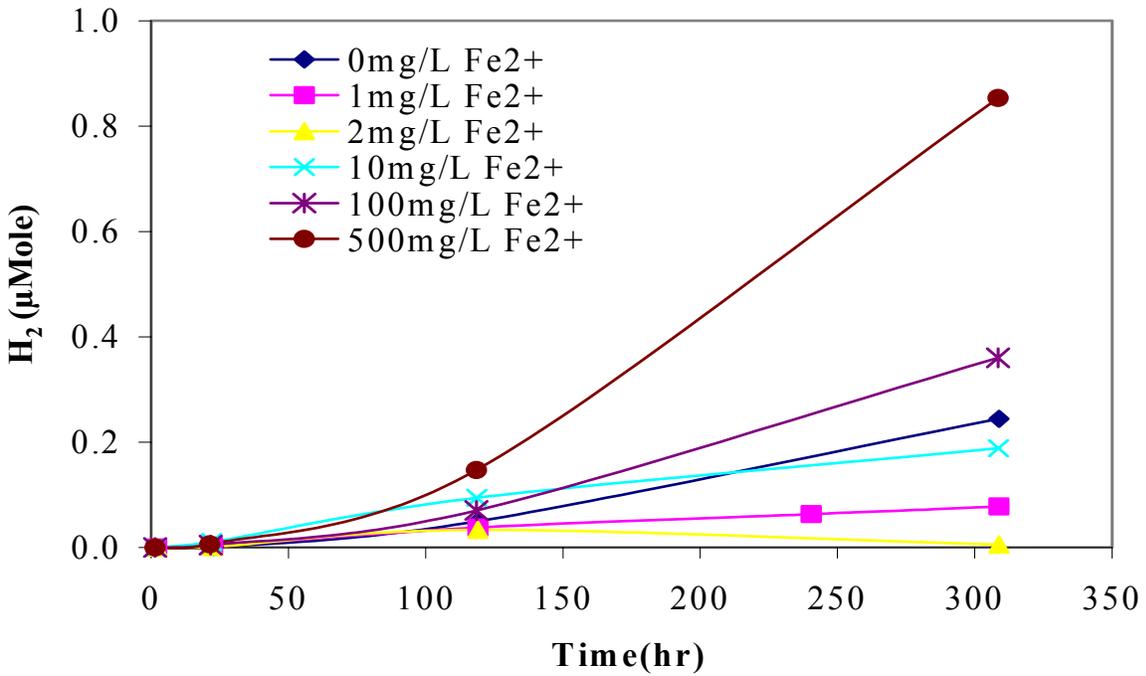


Figure 1-4. Typical effect of variable ferrous on H₂ evolution.

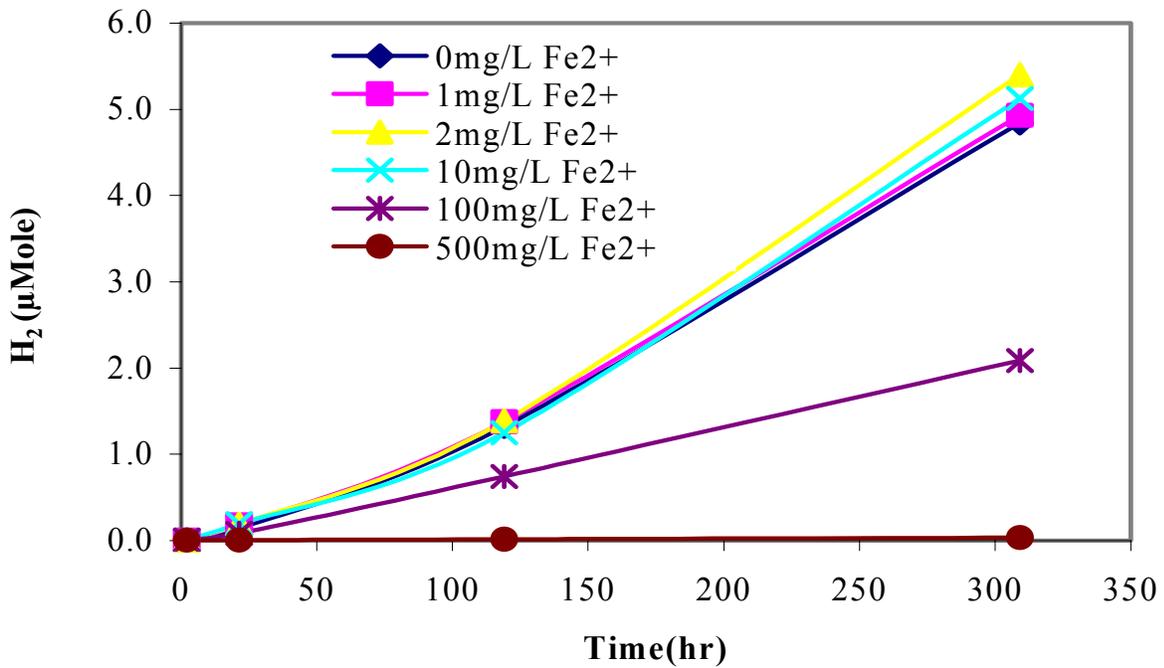
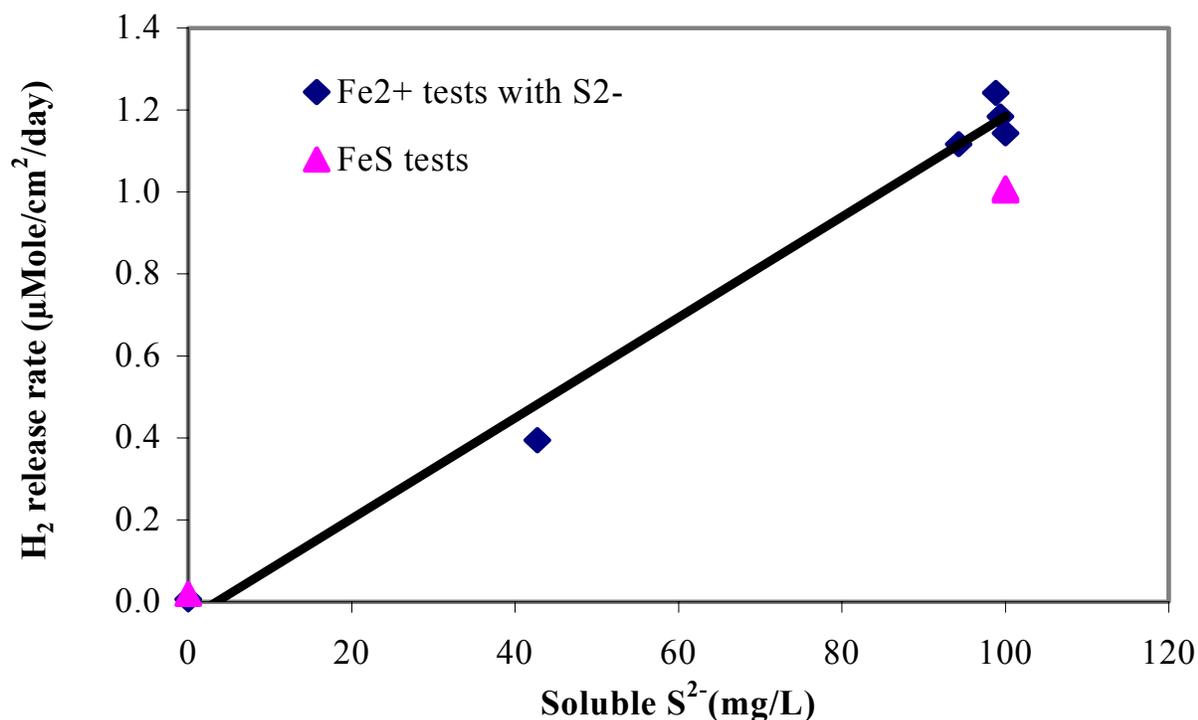


Figure 1-5. Effect of variable ferrous on H₂ evolution in the presence of sulfide.

Table 1-2. Predicted initial soluble S²⁻ concentration after formation of FeS and final pH in the reactor based on measurement after 2 months reaction time.

Test Solution	with S ²⁻ (mg/L)		Final pH	
	Initial Fe ²⁺	Initial soluble S ²⁻	with S ²⁻	without S ²⁻
BS*	0	100	8.37	8.56
BS+1 mg/L Fe ²⁺	0	99.4	8.21	7.44
BS+2 mg/L Fe ²⁺	0	98.8	8.16	6.72
BS+10 mg/L Fe ²⁺	0	94.3	8.05	6.29
BS+100 mg/L Fe ²⁺	0	42.6	9.45	5.91
BS+500 mg/L Fe ²⁺	325.6	0	6.94	5.1

*BS refers to a base solution containing 0.001 M NaCl.



**Figure 1-6. Relation between H₂ release and soluble S²⁻;
Rate calculated between t=0 to t=300 hrs.**

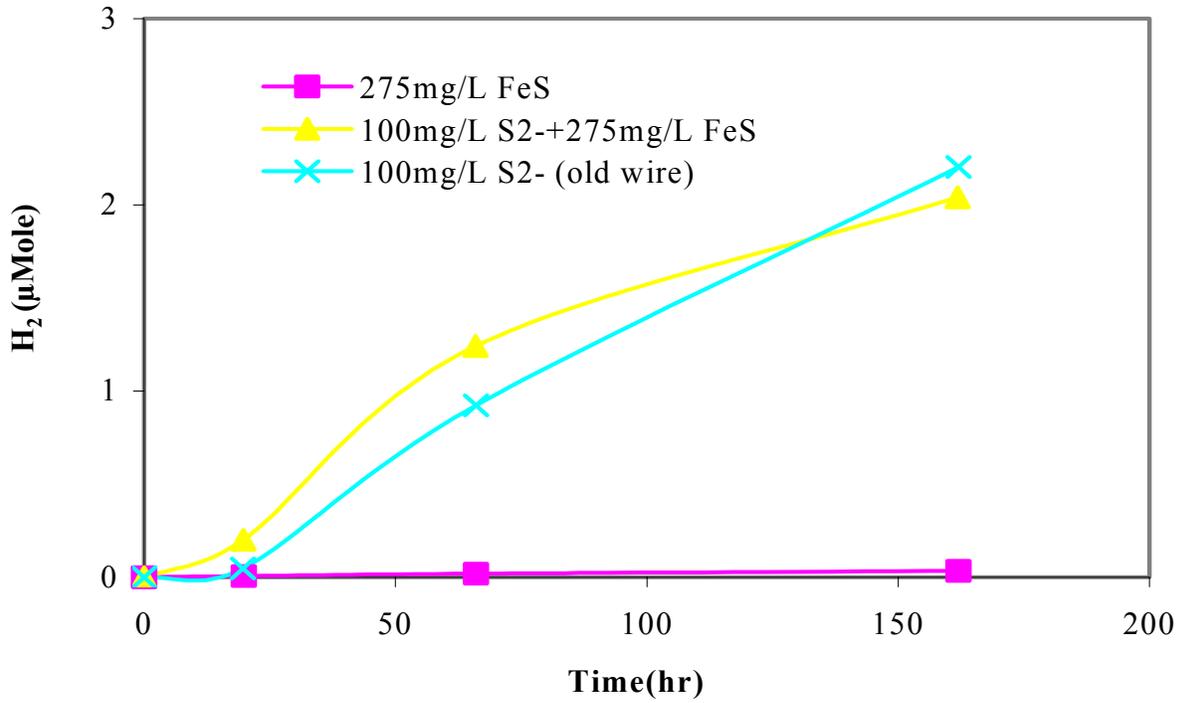


Figure 1-7. Effect of FeS solid on H₂ evolution under various circumstances.

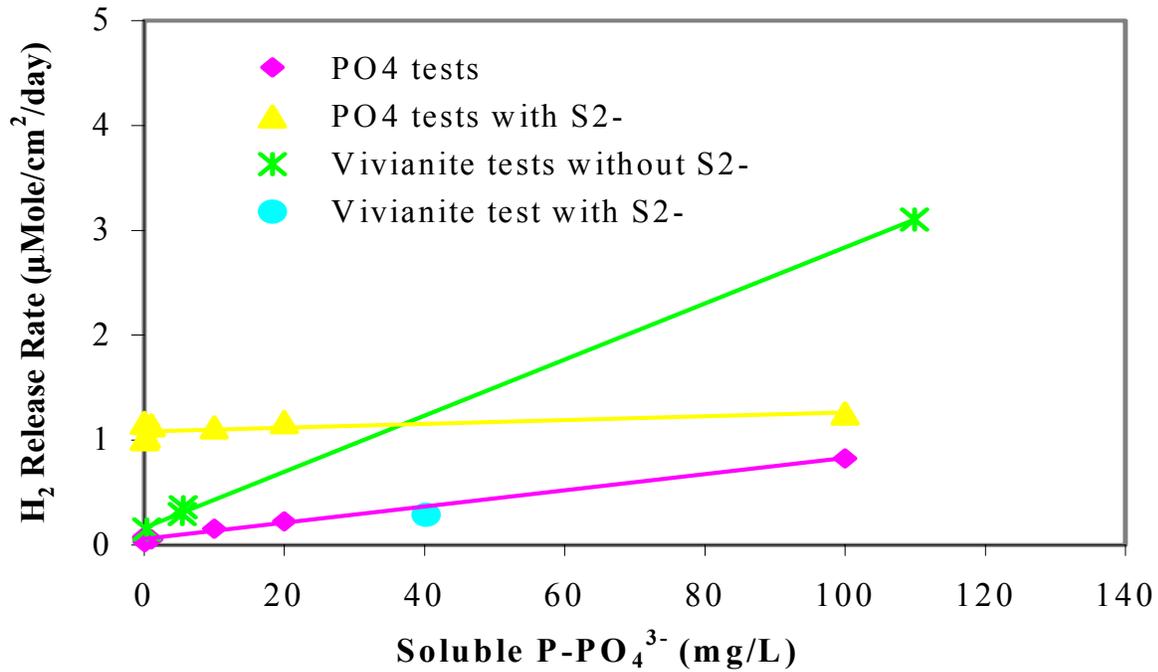


Figure 1-8. Relation between H₂ release rate and soluble P-PO₄³⁻.

Table 1-3. Description of sample preparation in experiment with vivianite.

Test solution	Sample Preparation	Initial pH	Initial soluble Fe mg/L	Initial soluble P mg/L
A: Vivianite	Mix 100 mg/L Fe ²⁺ and 37 mg/L P-PO ₄ ³⁻ to precipitate vivianite, get 100 mL sub-sample	7.06	5.82	5.52
B: Filtrate of vivianite solution	Pass 100 mL solution A through 0.45 μM pore size filter	7.02	4.96	5.41
C: Vivianite +100mg/L S ²⁻	Add 100 mg/L S ²⁻ into 100 mL solution A	7.07	19.41	40.23
D: Vivianite+100mg/L Fe ²⁺	Add 100 mg/L Fe ²⁺ into 100 mL solution A	7.04	91.7	0.38
E: Vivianite +100mg/L P-PO ₄ ³⁻	Add 100 mg/L P-PO ₄ ³⁻ into 100 mL solution A	7.08	1.73	109.87

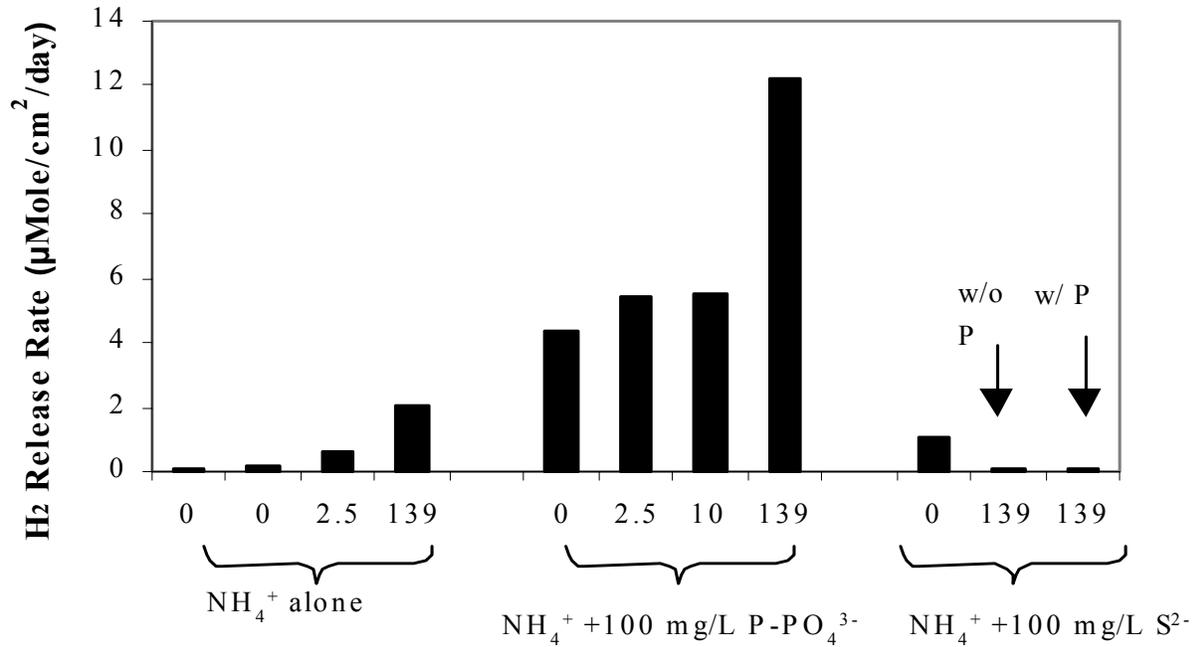


Figure 1-9. H₂ release in tests with NH₄⁺ and other constituents.

Rate calculated between t=0 to t=70hrs. X-axis label denotes NH₄⁺ concentration in mM.

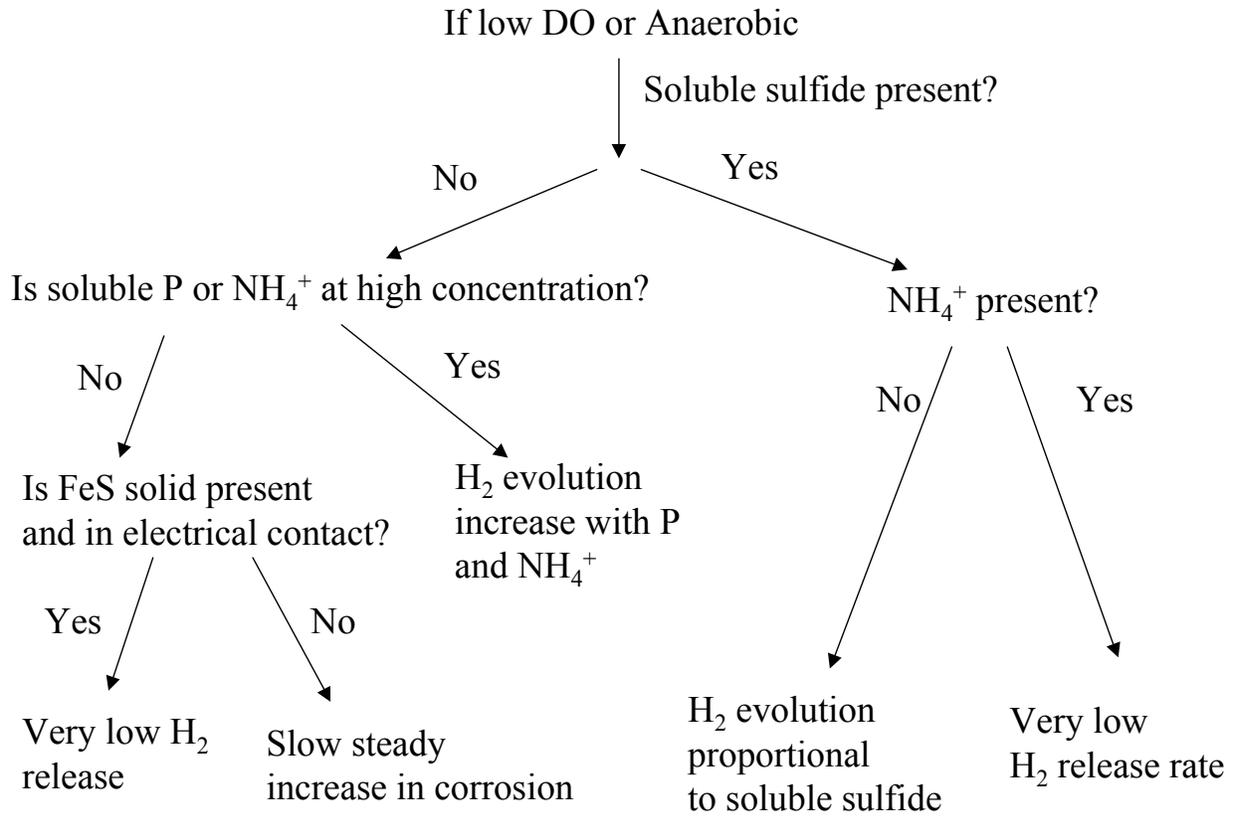


Figure 1-10. Decision tree describing phenomena in experiment.

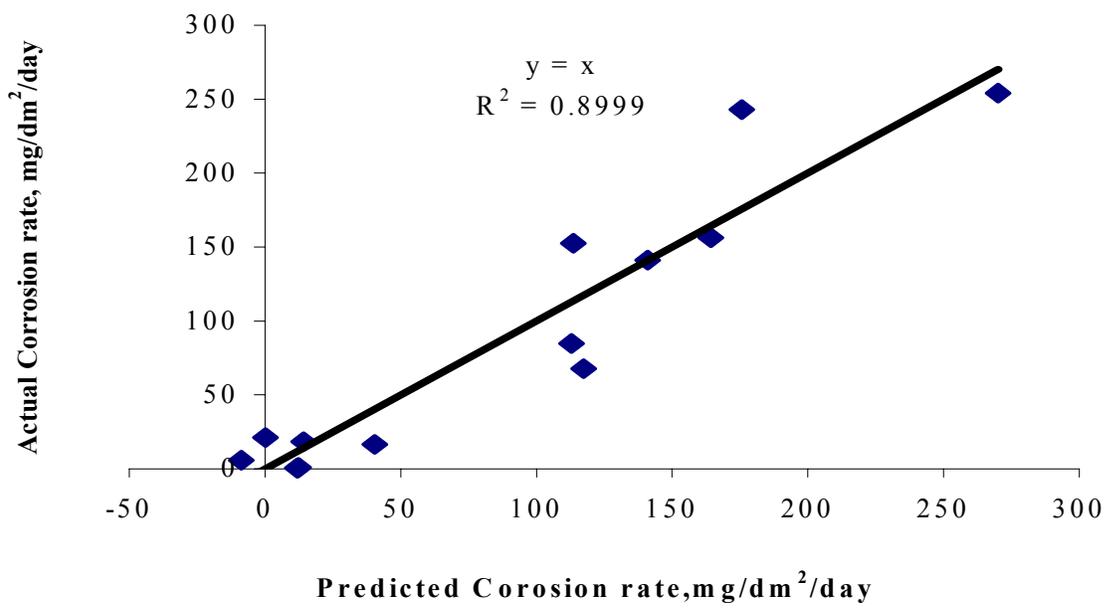


Figure 1-11. Comparison of predicted and experimental results in previous corrosion studies with SRB.

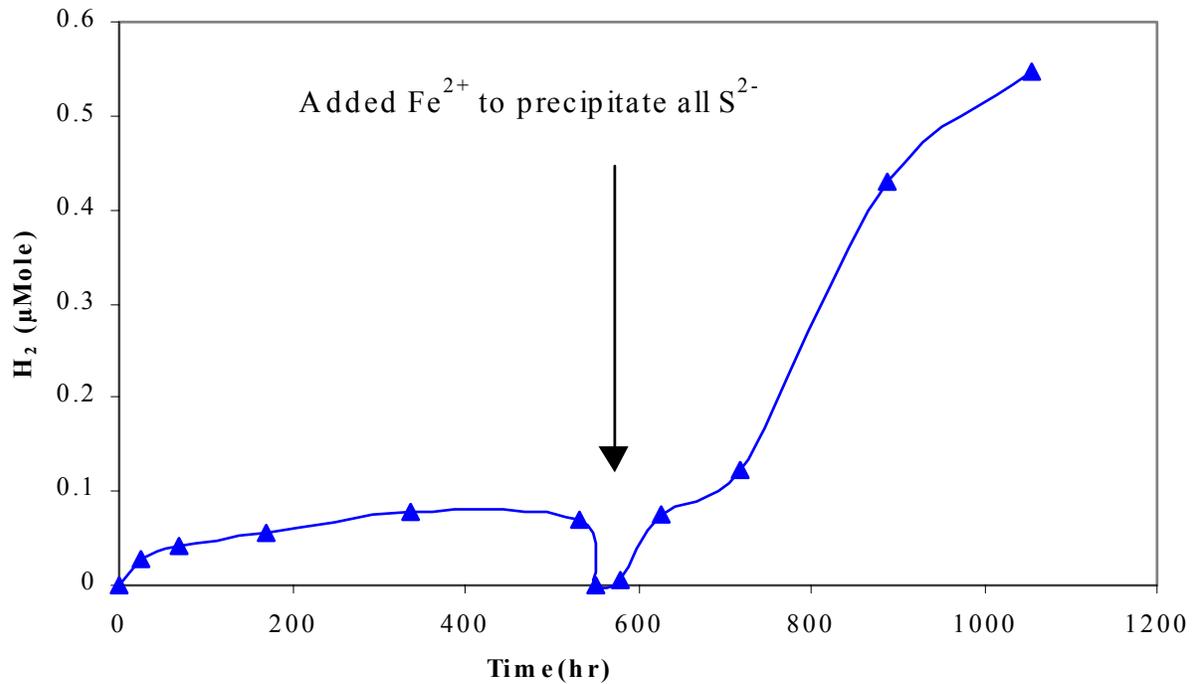


Figure 1-12. H₂ release in a system combined with NH₄⁺, PO₄³⁻, and S²⁻; At t=23 days, Fe²⁺ was added to the system to precipitate all present S²⁻.

Table 1-4. Comparison of water quality and media solution (24-26).

	High conc. in drinking water	High conc. in wastewater	Previous experiment with SRB
Fe ²⁺	< 2 mg/L	-	1.4 ~ 2850 mg/L
P-PO ₄ ³⁻	3 mg/L	20 mg/L as P	77 ~ 228 mg/L
NH ₄ ⁺	10 mg/L	35 mg/L as N	180 ~ 2506 mg/L
SO ₄ ²⁻	1000 mg/L	1000 mg/L	1728 ~ 12682 mg/L

CHAPTER 2

Equilibrium and Kinetic Aspects of Anaerobic Iron Corrosion in the Presence of Phosphate

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ABSTRACT

The hypothesis that anaerobic iron corrosion is influenced by low pressure H_2 (<1 atm) was examined. At pH 2.75 and pH 7.0 in the presence of 100 mg/L P- PO_4^{3-} , variations in H_2 gas evolution were measured under different circumstances. Addition of PO_4^{3-} eventually formed a protective film (Vivianite, $Fe_3(PO_4)_2$) on the iron surface that completely stopped H_2 release. Nearly all data were consistent with the idea that corrosion is an essentially irreversible process that is relatively insensitive to low level H_2 pressure (<1 atm). Possible alternative explanations were provided to reconcile the past research supporting the idea that H_2 buildup was an impediment to corrosion and that removal of H_2 increased corrosion rates. Current understanding can not readily explain an unusual H_2 “decay” observed in the presence of high phosphate.

INTRODUCTION

For over 60 years it has been suspected that sulfate-reducing bacteria (SRB) are a key contributor to anaerobic iron corrosion. SRB are present in every water distribution system and corrosion scale from drinking water pipe often contains 3~26 % S by weight (1,2), possibly due to sulfide in scale. Under anaerobic conditions, iron corrosion can proceed with H_2 evolution: $Fe+2H_2O = Fe^{2+}+H_2+2OH^-$. Even in the presence of O_2 and well mixed conditions, it has been noted that iron corrosion by H_2O reduction can account for a significant percentage of total corrosion. For instance, in ordinary neutral tap water, Speller reported that about 3~5% of the total corrosion proceeded by this pathway (3). More recently, Rushing et al. reported that 0.1~1.5% of the iron corrosion in a well aerated constantly stirred tap water occurred anaerobically (4). Moreover, Rushing argued this is a lower bound to the actual anaerobic corrosion because H_2 would have been consumed through a variety of reactions in aerobic and anaerobic systems (Figure 2-1). Recent studies of abiotic iron corrosion demonstrated that water quality exerts an important control on iron corrosion rates, in that extremely high levels of NH_4^+ and PO_4^{3-} tend to increase

rates in the absence of sulfide, while NH_4^+ tends to inhibit attack in the presence of sulfide. However, little is understood mechanistically about the effect of H_2 itself in controlling anaerobic corrosion rates.

In the presence of SRB, the H_2 produced can be utilized as a microbial energy source to reduce sulfate to sulfide. Under such circumstance, the overall corrosion reaction can be expressed as: $4\text{Fe} + \text{SO}_4^{2-} + 8\text{H}^+ = 4\text{Fe}^{2+} + \text{S}^{2-} + 4\text{H}_2\text{O}$ (5). The classic theory of anaerobic corrosion is based on the premise that removal of H_2 by bacteria speeds up the overall corrosion rate. Data supporting this idea can be found even in very recent literature using a two bottle apparatus (6-9) (Table 2-1). The general approach of these experiments was to connect two bottles with glass tubing filled with N_2 atmosphere. Bottle A contains an iron or steel sample in a defined media solution, and bottle B contains either inoculated media solution or a cell extract solution containing hydrogenase. H_2 evolved from the iron by corrosion can transfer from bottle A to bottle B where it can be consumed by bacteria or hydrogenase. Any increase in the iron corrosion rate from H_2 removal is considered direct proof of the classic theory that H_2 buildup will impede corrosion.

For instance, the two bottle apparatus with SRB inoculated into bottle B demonstrated that consumption of H_2 by the bacteria increased overall corrosion of the remote iron sample (measured in H_2 release) by 300% (7). In another study using the two-bottle system, utilization of H_2 by hydrogenase increased Fe^{2+} release from iron metal by 19% over 50 min in the presence of 10 mM phosphate, confirming the idea that removal of H_2 promoted corrosion by upsetting equilibrium (8).

However, the idea that H_2 removal should speed up corrosion is perplexing based on Nernst equation and consideration of driving force. At equilibrium, $E_{\text{H}} = E_{\text{Fe}}$,

$$E_{\text{H}}^0 - E_{\text{Fe}}^0 = \frac{0.059}{2} \log \frac{P_{\text{H}_2} [\text{Fe}^{2+}]}{[\text{H}^+]^2}$$

and if $[\text{Fe}^{2+}] = 10^{-4}$ mol/L, the equilibrium hydrogen partial pressure would be 10^5 atmosphere at pH 7.0. From this perspective, removal of H_2 at <1 atm total pressure should have only insignificant impacts on the driving force and corrosion rate, and the only factor that should be relevant is possible reduction in corrosion rate by formation of a protective film. For instance, it

has been determined that solids formed on the metal surface during biocorrosion (vivianite, Fe_3C and FeCO_3) were protective and reduced the corrosion rate (10,11).

The hypothesis that H_2 influences corrosion by altering equilibrium or that corrosion is limited by a protective scale can be readily tested by experiments other than two bottle approach. Control of the corrosion rate by either scale formation or equilibrium might lead to a plateau in the H_2 release curve after a certain time (Figure 2-2). Mechanical removal of H_2 from water should increase the corrosion rate and addition of excess H_2 and Fe^{2+} should slow the corrosion reaction or even cause it to go backwards if equilibrium was controlling. Little effect should be observed during such tests if protective film formation was the key. Mechanical disruption of the protective film should allow rapid corrosion to proceed again if H_2 evolution stopped from formation of a protective layer, but no change in rate should occur if equilibrium was controlling.

It is also possible that both theories are valid but under different circumstances. One study on the role of hydrogen in H_2S corrosion produced data that we believe illustrate how this could occur (12). In that study, the equilibrium H_2 pressure is predicted to be about $10^{11.7}$ atm at 25°C when H_2S was present at 1 atm for the reaction $\text{Fe} + \text{H}_2\text{S} = \text{FeS} + \text{H}_2$, a prediction confirmed by experiment. However, after the iron was completely coated with sulfur, the equilibrium pressure of H_2 in solution is fixed by the reaction $\text{H}_2 + \text{S} = \text{H}_2\text{S}$ at only $10^{-6.1}$ atm, and any excess H_2 in solution would be removed by reaction with sulfur. Therefore, the coated metal was resistant to degradation from high pressure H_2 (Figure 2-3). Note that this mechanism does not involve equilibrium of the metal with H_2 in water, even though it would tend to maintain a specific H_2 controlled by equilibrium.

The goal of this work is to better understand whether abiotic iron corrosion is influenced by low pressure (<1 atm) H_2 buildup. Whenever possible, attempts are made to reconcile past research results.

MATERIALS AND METHODS

Experiments were conducted in an anaerobic glove box and followed a protocol described in detail elsewhere (Chapter 1). All solutions contained 0.001 M NaCl and chemical modifications described in text including addition of phosphate as NaH_2PO_4 . The initial pH after all modifications was adjusted to 7.0 ± 0.2 but was allowed to drift throughout the experiment. All solutions were then purged with N_2 . Briefly, specimens were 1 cm length 1 mm diameter pure iron wire (99.99% Fe), which were placed in a 40 mL glass vial reactors filled with 20 mL solution.

Throughout the experiment the headspace of the vials was sampled for hydrogen production with time. Hydrogen gas in the headspace was measured by RGA5 Process Gas Analyzer after sampling with a gas syringe. Amount of H_2 measured is proportional to the cumulative amount of iron corrosion and changes in H_2 over a certain time period are therefore proportional to the corrosion rate. QA/QC screened out valves that leaked more than 15% of the H_2 from the headspace over 15 days.

RESULTS AND DISCUSSION

Results are present in three sections including effect of PO_4^{3-} on H_2 release and protective scale formation, re-visiting the literature, and a novel uptake of H_2 observed in the presence of PO_4^{3-} and iron under anaerobic condition.

Effect of PO_4^{3-} on H_2 release and protective scale formation

In the absence of sulfide, high soluble PO_4^{3-} was roughly proportional to initial soluble P concentration. Two types of PO_4^{3-} were added to solutions in our experiment. One was derived directly from solution of NaH_2PO_4 and the other was from addition of solid vivianite at a concentration of 213.4 mg/L. If the soluble P- PO_4^{3-} was above 10 mg/L, H_2 in the headspace rapidly increased to a peak value, leveled off and eventually went to zero (Figure 2-4). An attempt was made to estimate the time of the peak by connecting H_2 release data with a smooth curve, and accuracy is limited by the number of data points collected. However, it is clear the time to peak H_2 and concentration of peak H_2 are dependent on the initial P in solutions (Figure 2-5), with higher initial P tending to shorten the time to the peak and a higher level of H_2 at the

peak. Final Fe^{2+} and pH were measured after 2 months and a variation in final pH was noted (Table 2-2). The likely impact of small changes in pH on peak time or highest H_2 was uncertain, although lower pH was associated with higher PO_4^{3-} .

There are two possibilities that could explain why H_2 level from the iron metal stopped increasing at the peak. The presence of PO_4^{3-} in the solution might have somehow created an equilibrium condition between iron corrosion and H_2 , or a protective scale might have formed on the metal surface which essentially stopped H_2 release. To test the hypothesis of protective scale formation, iron wire previously exposed to the PO_4^{3-} solutions (“Old Iron”) above 10 mg/L and for which H_2 release had stopped was placed into a fresh PO_4^{3-} solution. No additional H_2 release was observed. However, if new iron wire samples were put into the old PO_4^{3-} solution, the same trend as usual of H_2 release was found. Finally, if the “old iron” wire was polished with sandpaper and placed into fresh solution, H_2 release occurred although it was not quite as rapid as would be the case if there was complete removal of a protective coating (Figure 2-6). These results are all completely consistent with the idea that a protective film formed on the iron surface when PO_4^{3-} was in solution and inconsistent with equilibrium argument. To further investigate the nature of this protective film, passivated iron wire exposed to 100 mg/L PO_4^{3-} solution was put into a fresh PO_4^{3-} solution but with 100 mg/L S^{2-} . H_2 release increased to about the same rate as in the test with new wire and PO_4^{3-} plus 100 mg/L S^{2-} . Thus, this protective film broke down in the presence of sulfide (Figure 2-7).

It was reported in previous work that the removal of H_2 in a two bottle experiment increased Fe^{2+} release from iron metal in the presence of PO_4^{3-} , a fact attributed to the upset of the equilibrium of iron corrosion (8). To test this directly, solutions were made at 10 mM P- PO_4^{3-} at both pH 7.0 and pH 2.75 as per the original work (Table 2-3). 1% H_2 was injected in one set of samples to examine Fe^{2+} release in the presence of high H_2 and another set of samples was prepared without addition of H_2 . Fe^{2+} was measured with a colorimetric test after 1.5 hr (Table 2-3). This experiment was completed in triplicate. There was no significant difference between the two sets of samples at different H_2 as confirmed by a paired t-test at 95% confidence, contrary to the expectation based on Bryant’s experiment. Thus, assuming that Fe^{2+} measured is proportional to corrosion rate, removal of H_2 had no effect on corrosion.

To further examine the equilibrium issue, in the solution of 100 mg/L P-PO₄³⁻ at pH 7.0, the valve of test reactor was opened each day to remove the H₂ in the headspace. If equilibrium is influential, it is expected that this should lead to more H₂ release. However, this artificial removal of H₂ did not increase the net yield of H₂ release, but it eventually stopped as observed previously. Since each time the headspace was sampled for H₂ and the pressure dropped in the vial, total H₂ release was corrected for pressure changes (Appendix A). Compared with the control, the cumulative curve of H₂ released each day was within 10~30% of the control (Figure 2-8). Likewise, initial addition of H₂ into the system should slow H₂ release if equilibrium was controlling; however, initial addition of 0.3% H₂ did not slow H₂ evolution (Figure 2-9).

At pH 2.75 and 100 mg/L P-PO₄³⁻, the initial H₂ release rate (corrosion rate of 213.2 mg/dm²/day) was 8 times higher than at pH 7.0. Visually small bubbles formed on the wire surface right after iron wires were put into the solution. In this case it took a longer time for the H₂ release to a plateau. The peak H₂ release was 30 μMole (0.036 atm H₂) and the time to the peak was 400 hr. Two sets of samples were tested, one with the initial addition of 1% H₂ and the other without initial H₂ addition. Both sets have the similar trend of H₂ release (Figure 2-10). After the H₂ release leveled off, the old iron wire was put into fresh solution at the same pH. Within the first 3 hrs no bubbles were observed on the metal surface, and the initial H₂ release rate was low. However, if the old iron wire was polished with sandpaper before addition into a fresh solution, there was bubble formation on the iron wire immediately. Since bubbles covered only a small portion of iron wire surface, we do not think they significantly affected the overall corrosion rate. At pH 2.75 H₂ release increased gradually to a stable value as in the test with new wire and PO₄³⁻ (Figure 2-10). This result seems more consistent with the idea that equilibrium might be important.

In general, the above results support the idea that corrosion is irreversible and relatively insensitive to low level variations (<1 atm) in H₂ near neutral pH. When PO₄³⁻ is present in the solution, a protective film forms on the metal surface and thus stops H₂ release. However less extensive results at pH 2.75 suggest that H₂ buildup might be a controlling factor, although measurements of corrosion rate by release of Fe²⁺ could not support this.

Re-visiting the literature

Earlier studies on SRB attack supported the idea that removal of H₂ increased corrosion rates. Re-visiting of that literature is instructive. Some statements supporting the equilibrium hypothesis are simply erroneous. For example, a recent paper reported that ΔG^0 was greater than zero ($\Delta G^0=3.5$ kJ) for the reaction $\text{Fe}+2\text{H}^+=\text{Fe}^{2+}+\text{H}_2$ under standard condition and therefore iron corrosion would not proceed by H₂ evolution alone(9). This is obviously incorrect as a recalculation indicates a ΔG^0 of -84.9 kJ.

Much of the experimental data supporting this equilibrium idea came from the experiment using two bottle apparatus. This apparatus was selected to separate iron from SRB and avoid the interference with Fe²⁺ measurement due to the FeS precipitation, starting with the assumption that only H₂ transferred from bottle A to bottle B. However, the possible transport of gasses the other way also can be important. For instance, H₂S produced by SRB in bottle B could transfer back to bottle A, contacting iron and accelerating corrosion. This would be falsely interpreted as increased corrosion by removal of H₂. CO₂ used as flushing gas or produced by bacteria could also increase corrosion rates compared to the control (13). These possibilities are not considered.

In short, interpretation of two bottle results is subject to more impacts than just simple removal of H₂ gas, and there are some alternative explanations for the increased corrosion rates observed compared to controls (Table 2-1). We conclude there is relatively little direct support for the idea that equilibrium with H₂ influences corrosion at near neutral pH.

On the other hand, the results obtained at pH 2.75 in our work illustrated that equilibrium with H₂ might influence corrosion rates under at least some circumstances. Higher PO₄³⁻ was present in every medium used for corrosion studies with SRB. If pH dropped to a low level somehow by SRB activity and established a circumstance as indicated in this work, it might be possible that H₂ buildup was a key factor in previous findings.

A novel uptake of H₂ in the presence of PO₄³⁻

In the presence of PO_4^{3-} , headspace H_2 concentration increased initially, reached a plateau, and then unexpectedly went to zero. Even if 0.3% H_2 was spiked into the system where H_2 had already dropped to zero, the spiked H_2 was removed from the system again (Figure 2-6). Assuming that a protective scale had formed to reduce the rate of H_2 evolution, another reaction must have been operative that removed H_2 and caused the “decay” of total H_2 (Figure 2-4). There could be several possibilities for the decay of H_2 , for instance, leakage of H_2 from the vial, formation of FeH , H_2 entry into the iron metal, or reduction of phosphorus species with loss of H_2 . Each of these is discussed below.

The idea that H_2 might have leaked through sample valves is appealing; however, the H_2 decay was consistently observed only in the solutions with high PO_4^{3-} present and there is no reason to believe PO_4^{3-} in water would cause valve failure. Alternatively, H_2 might enter into the iron metal or form iron hydride FeH (Figure 2-1). A recent study focusing on anaerobic corrosion of granular iron found that 12% of total H_2 release went into the metal (14). Based on Sievert’s Law, the concentration of H_2 in the iron is proportional to the square root of hydrogen pressure (15). If the iron is at equilibrium with 3000 ppm H_2 , total H_2 uptake by iron wire is estimated to account for only 0.65% of the total H_2 that disappeared in our experiment. Iron hydride can also form at certain temperature and pressure by direct reaction between metal and gaseous hydrogen (16), and therefore its formation might cause the H_2 loss that was observed. Hydrogen in iron hydride and metal is expected to be released under normal atmosphere conditions (17). When iron wire from our tests was removed from solution and put in a dry environment to allow H_2 desorption, using wire samples from PO_4^{3-} test as well as those from earlier tests in the presence of Fe^{2+} and NH_4^+ described in Chapter 1, the H_2 released could explain less than 1% of the total H_2 loss during decay (Appendix B). As a result, it seems unlikely that H_2 decay came from uptake in the metal or formation of FeH .

Another possibility is that iron in the presence of PO_4^{3-} might catalyze the reaction $\text{H}_2 + \text{O}_2 = \text{H}_2\text{O}$, since traces of O_2 are likely present in the N_2 gas and in the glove box. Certain solid phases such as phosphide are known to catalyze this reaction on platinum (18). However, there was no significant difference in H_2 release between a sample purged with N_2 (99.998% pure) and N_2 which was further purified by passage through an oxygen trap (Supelco, model 2-2450-U).

It is possible that some reactions between H_2 and PO_4^{3-} might consume H_2 . In phosphoric acid fuel cell studies, reduced phosphorus species (i.e. PO_3^{3-}) are believed to be present as a contaminant in PO_4^{3-} solution or formed by the reaction of PO_4^{3-} and H_2 (19,20). Vogel suspected that H_3PO_4 reacted with H_2 to form phosphide or PH_3 on the platinum surface per the following equation: $2H_3PO_4+5H_2+2Pt=2P-Pt+8H_2O$ (20). If a similar reaction occurred in our system with iron (i.e. $2H_3PO_4+5H_2+2Fe=2P-Fe+8H_2O$), this could explain the H_2 decay. To test the hypothesis that a reduced phosphorus contaminant was influential, different NaH_2PO_4 and H_3PO_4 solutions at 100 mg/L P were ozonated for 0.5 hours to attempt to remove it as per tests of Sugishima with peroxide (19); however, the same trend of H_2 release was observed as usual (Figure 2-11). No PH_3 could be detected in the headspace. Furthermore, different amounts of PH_3 were added into headspace of sample vials with 100 mg/L P- PO_4^{3-} solution, and variable PH_3 did not impact H_2 release in the presence of PO_4^{3-} (Figure 2-12). These results do not completely rule out the idea that iron reduces phosphate, but it does suggest impacts of reduced phosphorus would be difficult to detect and results make it less likely that a reduced phosphorus contaminant was involved.

Finally, it is possible that the unique H_2 decay observed in the PO_4^{3-} system may be controlled by the complete coating idea mentioned earlier. In the solution with high PO_4^{3-} , we speculate that Fe^{2+} released from iron corrosion might react with PO_4^{3-} to form a vivianite $Fe_3(PO_4)_2$ solid that completely covers the metal surface. H_2 evolves until coverage is complete. If this coating somehow reacted with H_2 , consuming H_2 as per the following example reaction: $3Fe^{2+}+Fe_3(PO_4)_2+11H_2+6OH^-=2Fe_3P+14H_2O$ (Figure 2-13), the decay could be explained. Complexes and solids containing Fe^{2+} have more reducing power than soluble Fe^{2+} species in the solution (21), and therefore would increase the likelihood of such reactions. This idea is also consistent with results noted in our work. For instance, initial higher PO_4^{3-} shortened the time to the peak H_2 , possibly due to the vivianite coating forming more quickly, and spiked H_2 was removed from the solution where it is believed that a vivianite coating had formed on the iron wire.

Nevertheless, at present this is speculation and there is no ready explanation for the observed H₂ decay phenomena when PO₄³⁻ was present during anaerobic iron corrosion. It is certainly important enough to warrant additional research.

CONCLUSIONS

- (1) At pH 7.0, initial H₂ evolution is promoted by the presence of high PO₄³⁻. A roughly linear relation is noted between initial H₂ release rate and initial soluble PO₄³⁻ concentration in the solution.
- (2) When high PO₄³⁻ is present, a protective film forms on the iron metal surface that stops H₂ evolution. However, the protective film breaks down in the presence of sulfide.
- (3) With high PO₄³⁻ present in the solution at pH 7.0, a reaction occurs that somehow consumes H₂ and removes it from solution.

ACKNOWLEDGEMENTS

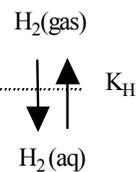
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LITERATURE CITED

1. Sarin P.; Snoeyink V.L.; Bebee J.; Kriven W.M.; Clement J.A. *Wat. Res.* **2001**, *35*, 2961.
2. Tuovinen O.H.; Button K.S.; Vuorinen A.; Carlson L.; Mair D.M.; Yut L.A. *JAWWA* **1980**, *72*, 626.
3. Speller F. N. *Corrosion Causes and Prevention*, 3rd ed; McGraw-Hill: New York and London, **1951**, p.39.
4. Rushing J.; McNeill L.; Edwards M. *Proceedings of AWWA Annual Conference* **2001**, Washington DC, June 14-17.
5. von Wolzogen Kuhr; van der Vlugt *Water* **1934**, *16*, 147.

6. Bryant R.D.; Laishley E.J. *Can. J. Microbiol.* **1990**, 36, 259.
7. Rajagopal B.S.; LeGall J. *Appl. Microbiol. Biotechnol.* **1989**, 31, 406.
8. Bryant R.D.; Laishley E.J. *Appl. Microbiol. Biotechnol.* **1993**, 38, 82.
9. Daniels L.; Belay N.; Rajagopal B. S.; Weimer P. J. *Science* **1987**, 237, 509.
10. Booth G.H.; Tiller A.K.; Wormwell F. *Corrosion Science* **1962**, 2,197.
11. Crolet J.L.; Thevenot N.; Nesic S. *Corrosion* **1998**, 54, 194.
12. Alekseev V.I.; Kiselev O.A.; Levshina I.V. *Sov. Mater. Sci.* **1990**, 26, 149.
13. *Internal Corrosion of Water Distribution Systems*, 2nd ed; AWWARF American Water Works Association: Denver, **1996**, p57.
14. Reardon E. J. *Environ. Sci. Technol.* **1995**, 29, 2936.
15. Kumnick A.J.; Johnson H.H. *Acta Metall.* **1980**, 28, 33.
16. Mackay K.M. *Hydrogen Compounds of the Metallic Elements*, 1st ed; E. & F. N. Spon: London, **1966**, p.25.
17. Zakroczmiski T.; Szklarska-smialowska Z.; Smialowski M. *Corrosion* **1983**, 39, 207.
18. U.S. Patent No. 3,449,169.
19. Sugishima N.; Hinatsu J. T.; Foulkes F. R. *J. Electrochem. Soc.* **1994**, 141, 3325.
20. Vogel W.M.; Baris J.M. *Electrochim. Acta* **1978**, 23, 463.
21. Stumm W.; Morgan J.J. *Aquatic Chemistry*, 3rd ed; John Wiley & Sons: New York, **1996**, p.491.

Gaseous Phase



Aqueous Phase

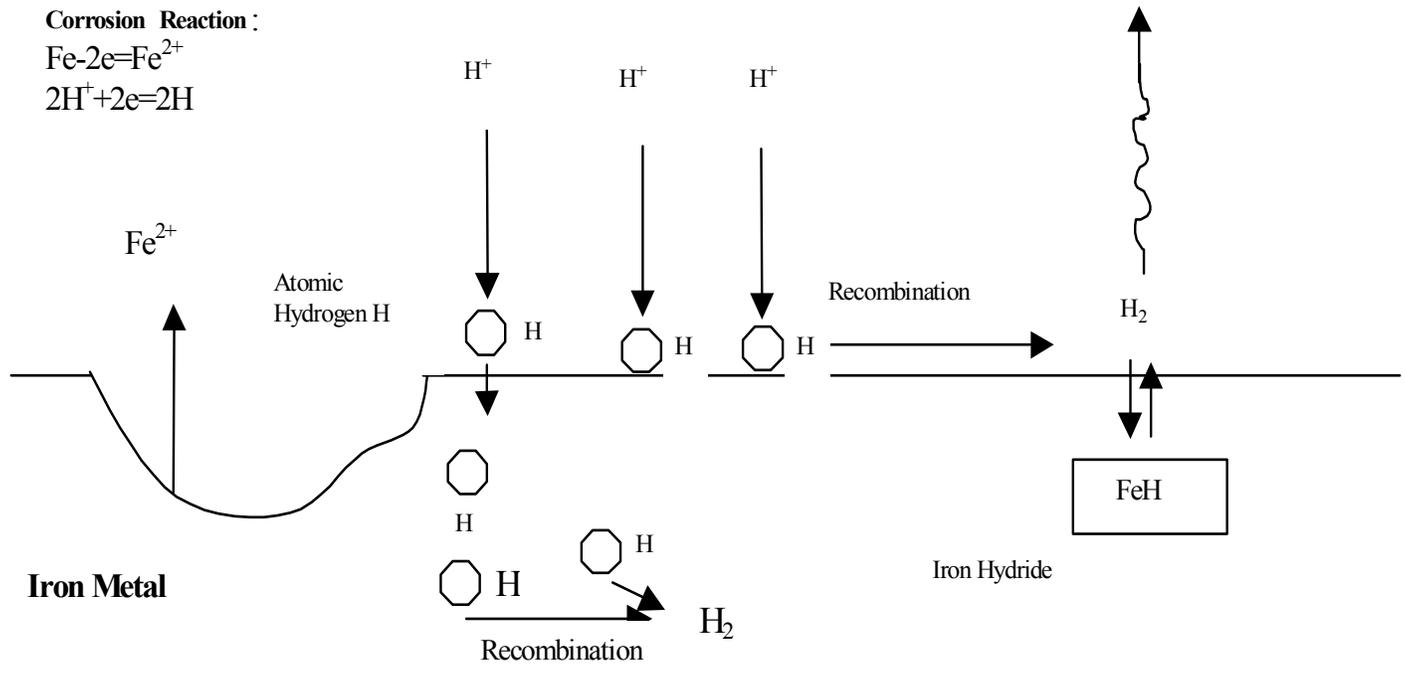
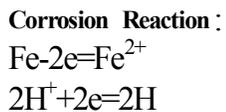


Figure 2-1. Important hydrogen phenomena during anaerobic iron corrosion.

Table 2-1. Key experiments supporting idea that H₂ removal increased iron corrosion rate.

Reference	Experiment condition	Key conclusion	Possible alternative explanation
Bryant et al 1993	Three mild steel rods immersed in 10 mM H ₃ PO ₄ at pH 2.75 in bottle A, cell-free extract containing hydrogenase placed in bottle B	In the presence of hydrogenase, Fe ²⁺ release increased by 19% due to the removal of H ₂ by hydrogenase	19% actually is not a big difference; low pH and higher PO ₄ ³⁻
Bryant et al 1990	Three mild steel rods in 100 mM KH ₂ PO ₄ at pH 7.0, cell-free extract containing hydrogenase added during the test to determine the of hydrogenase on H ₂ release	The addition of hydrogenase increased H ₂ release rate from 0.08 to 1 μM/cm ² /min	High PO ₄ ³⁻ in the solution can have been influential
Rajagopal et al 1989	Iron metal in 4 mM PO ₄ ³⁻ solution at pH 7.0, after 8 days the system was inoculated with SRB strains or flushed with N ₂ -CO ₂	Removal of H ₂ by flushing with N ₂ -CO ₂ increased by 100%; while removal of H ₂ by SRB increased total release by 300%	H ₂ S produced could transfer back to bottle A; CO ₂ as a flushing gas could increase corrosion
Daniels et al 1987	Iron powder was used for methanogens growth from CO ₂	Significant iron corrosion occurred with H ₂ consumption by the methanogens	Erroneous thermodynamic calculation; CO ₂ itself has adverse impact on corrosion

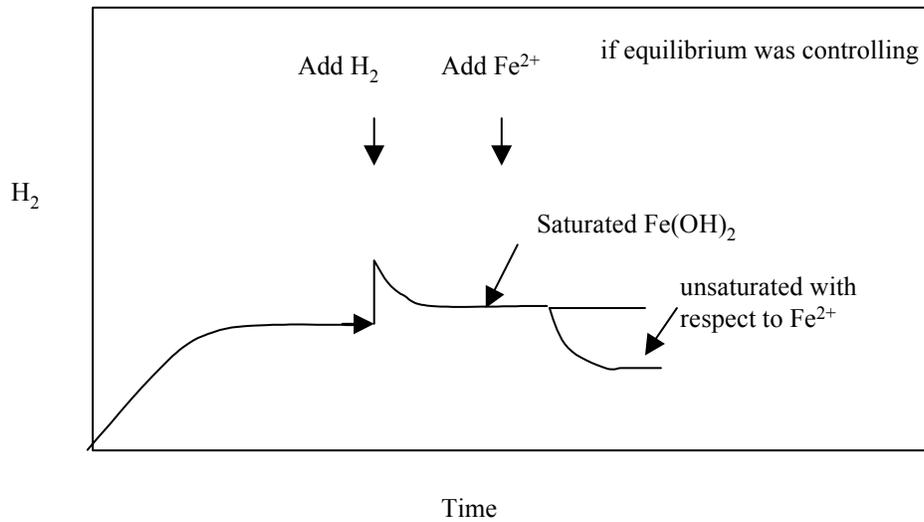
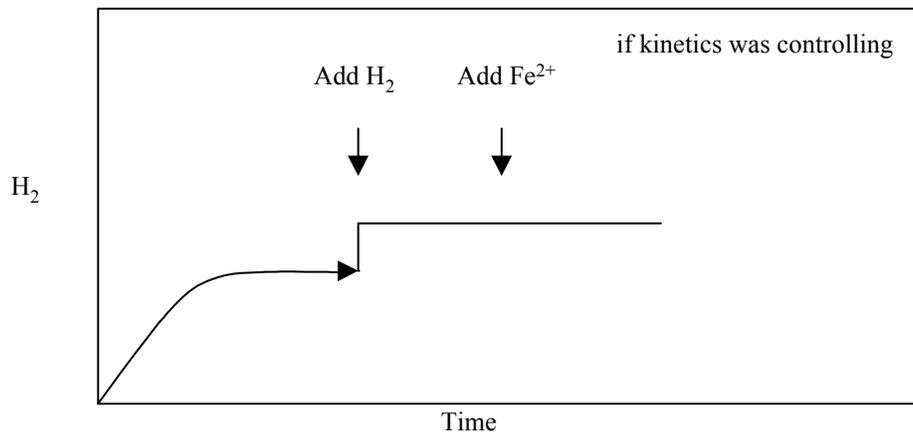
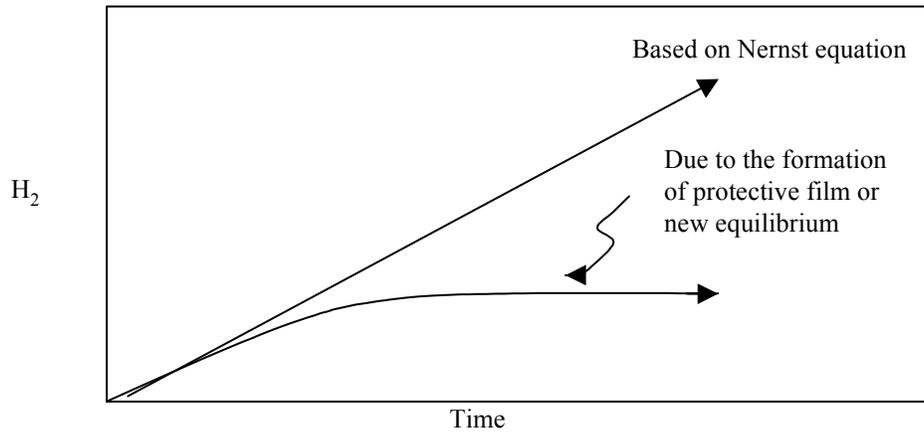
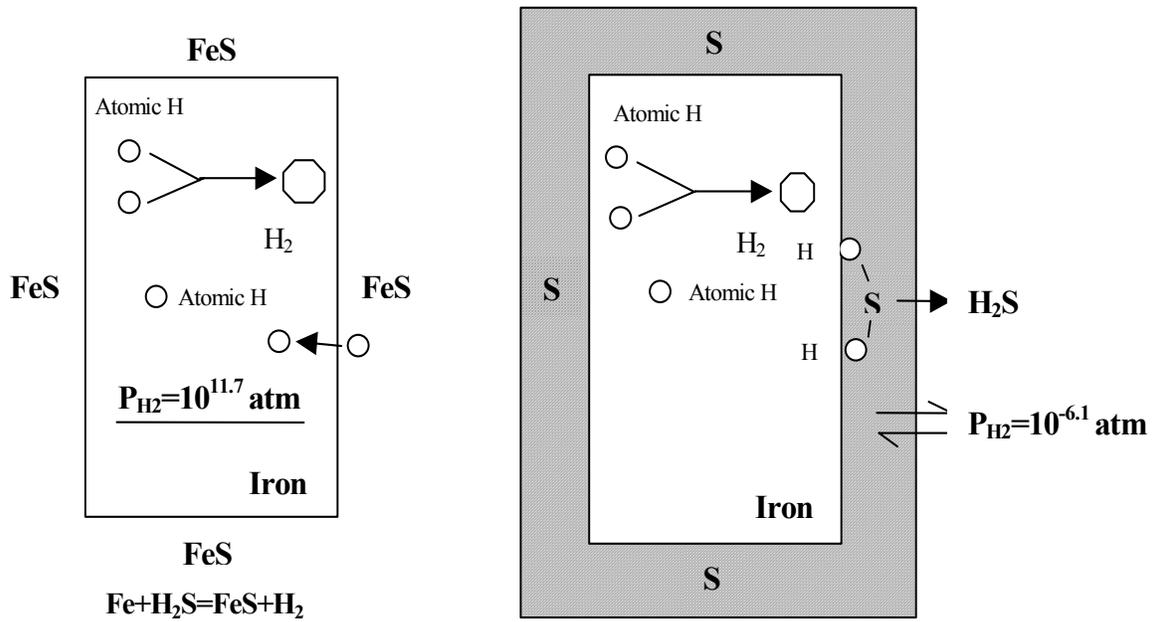


Figure 2-2. Expected variation in H_2 gas measurements if corrosion is controlled by equilibrium vs. kinetics.



(a) Iron exposed to H₂S.

(b) Sulfur-coated iron exposed to H₂S.

Figure 2-3. Conceptual schematic illustrating effect of different coatings on iron and equilibrium H₂ pressure.

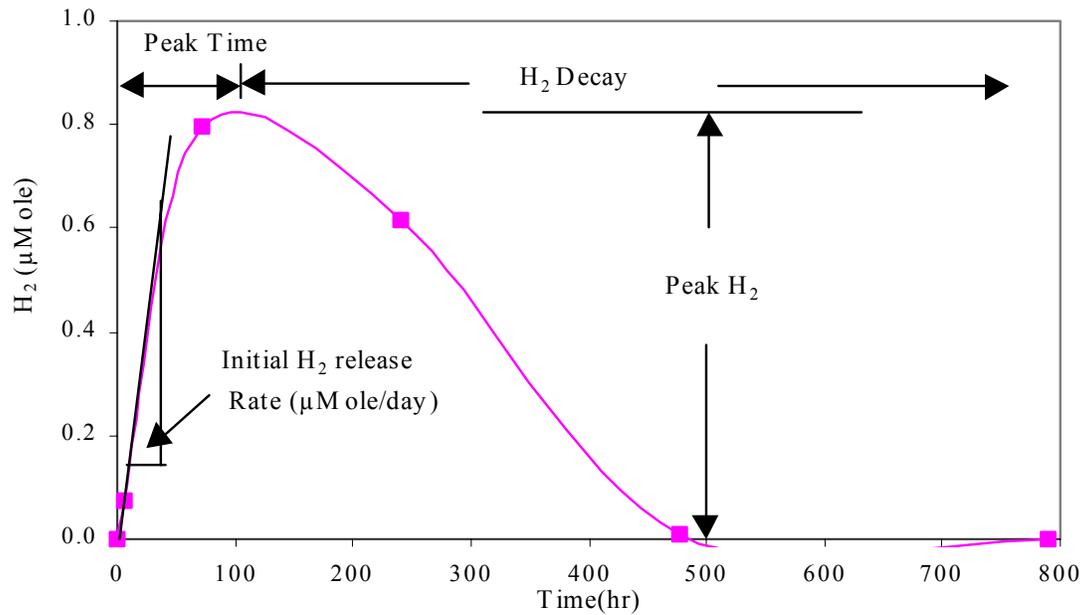


Figure 2-4. Typical H₂ release curve in the presence of high P-PO₄³⁻.

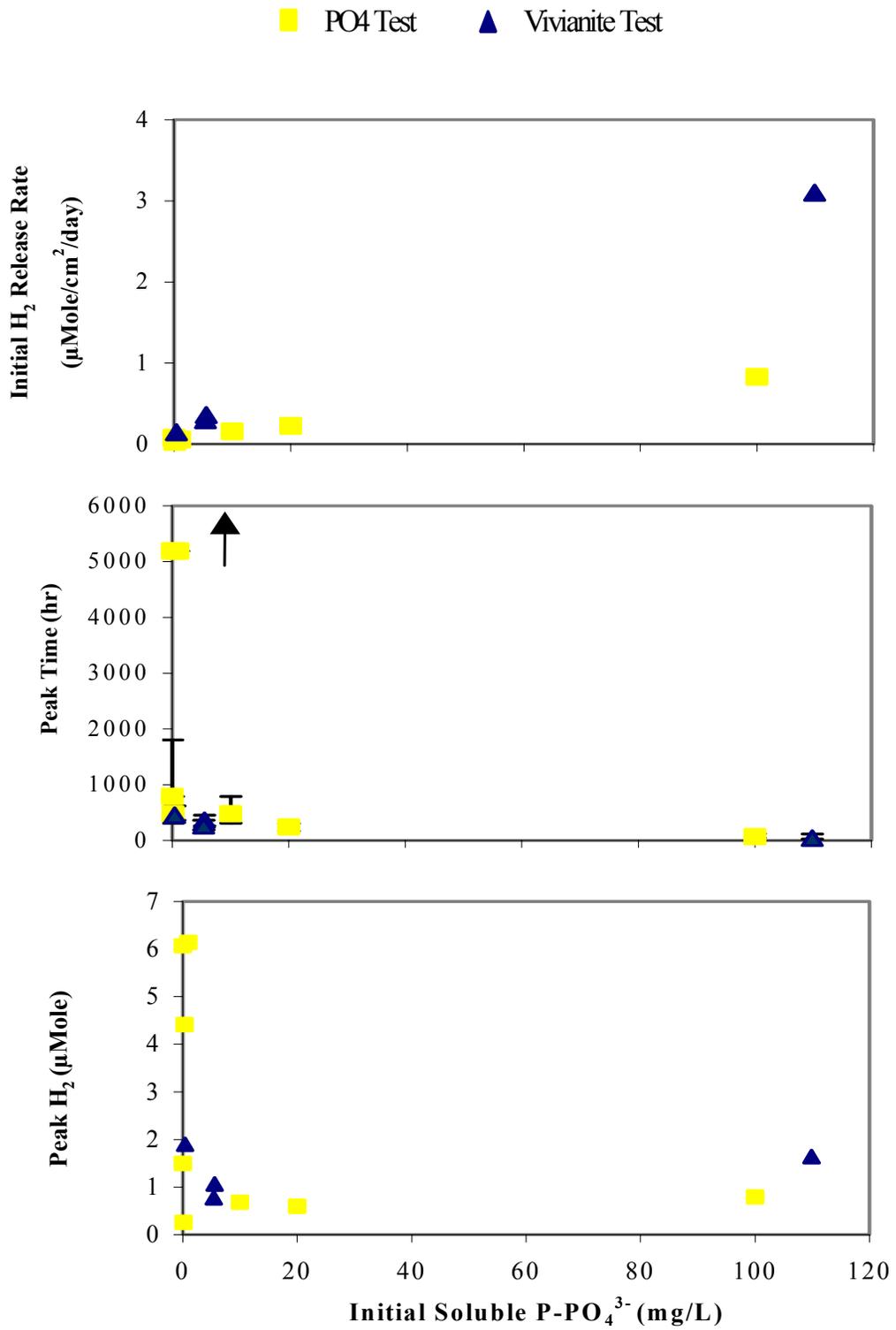
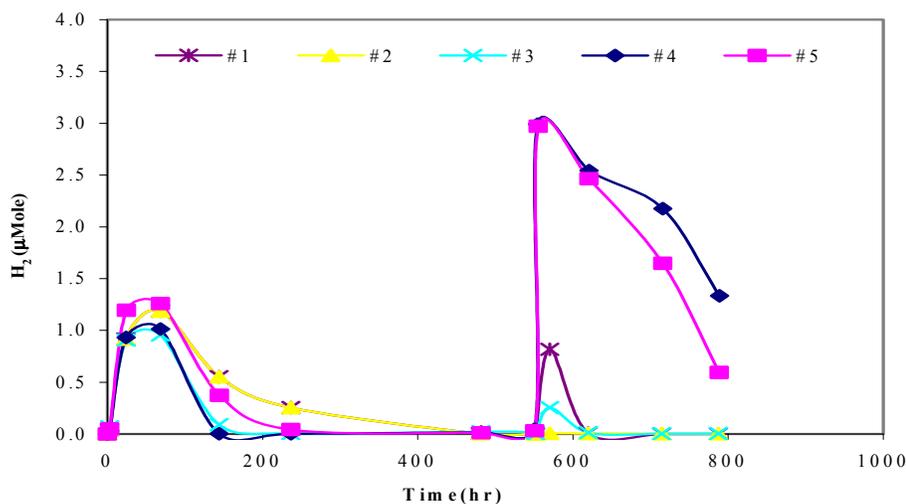


Figure 2-5. Relation between initial H₂ release rate, peak time, peak H₂ and initial soluble P-PO₄³⁻ concentration.

Table 2-2. Fe²⁺ release and final pH after exposure of wire to PO₄³⁻ and vivianite.

Test Solution	Initial pH	Final pH	Fe ²⁺ (mg/L)	Weight Loss (g)
BS	7.10	8.39	0.02	0.0002
BS+0.03 mg/L P-PO ₄ ³⁻	7.14	8.68	0.00	0.0004
BS+0.1 mg/L P-PO ₄ ³⁻	7.13	8.70	0.00	0.0002
BS+0.3 mg/L P-PO ₄ ³⁻	7.12	8.80	N/A	0.0003
BS+1 mg/L P-PO ₄ ³⁻	7.18	8.96	N/A	0.0002
BS+10 mg/L P-PO ₄ ³⁻	7.01	8.66	0.10	0.0003
BS+20 mg/L P-PO ₄ ³⁻	7.05	7.69	0.08	0.0000
BS+100 mg/L P-PO ₄ ³⁻	7.02	7.17	0.08	0.0000
Vivianite (100 mg/L Fe ²⁺ +37 mg/L P-PO ₄ ³⁻)	7.06	7.02	0.40	0.0000
Filtrate of vivianite	7.02	7.17	0.25	0.0002
Vivianite+100 mg/L Fe ²⁺	7.04	5.95	84.00	0.0003
Vivianite+100 mg/L P-PO ₄ ³⁻	7.08	7.24	0.12	0.0000



Note:

at t = 550 hr

#1 -- Put new iron wire into the old BS+100 mg/L P-PO₄³⁻

#2 -- Put old wire into fresh BS+100 mg/L P-PO₄³⁻

#3 -- Polish old wire with sand paper then put into fresh solution

#4 -- Spike 0.3% H₂ into BS+100 mg/L P-PO₄³⁻

#5 -- Spike 0.3% H₂ and 25 mg/L Fe²⁺ into BS+100 mg/L P-PO₄³⁻

Figure 2-6. H₂ release in 100 mg/L P-PO₄³⁻ solution under various conditions.

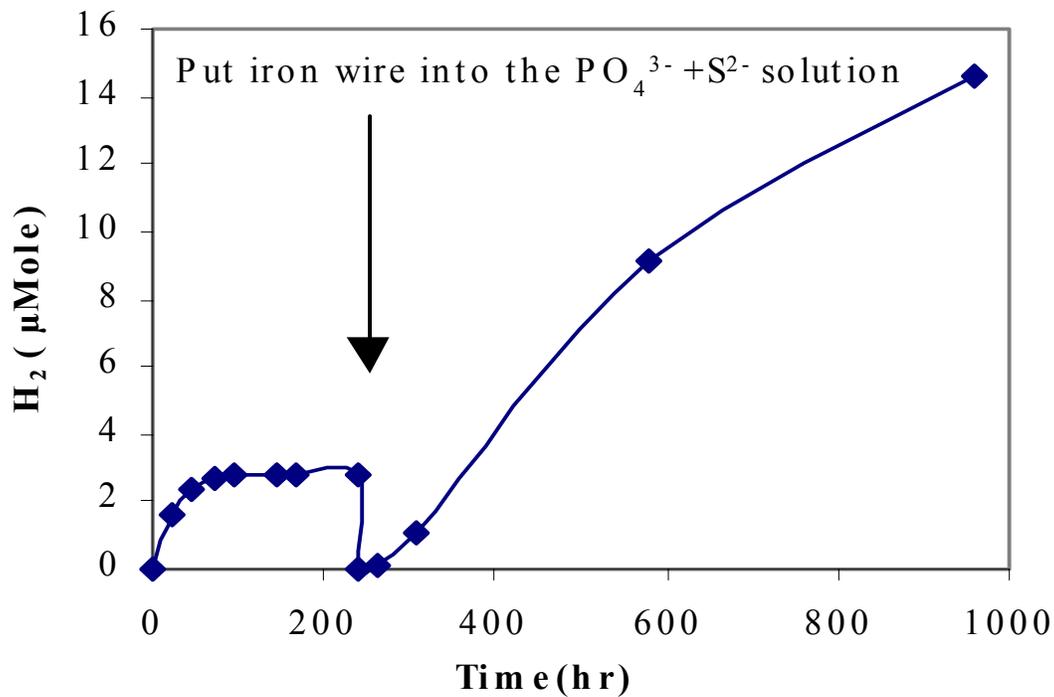


Figure 2-7. H₂ release in 100 mg/L P-PO₄³⁻ solution, at t=10 days, the passivated iron wire was put into 100 mg/L P-PO₄³⁻ +100 mg/L S²⁻ solution.

Table 2-3. Fe²⁺ and pH under various circumstances, based on measurement after 1.5 hr.

Sample		Total Fe ²⁺ mg/L	pH	
			Initial	Final
BS+309.7mg/L P-PO ₄ ³⁻	#1	0.10	6.90	6.92
	#2	0.08	6.90	6.92
	#3	0.10	6.90	6.93
BS+309.7mg/L P-PO ₄ ³⁻ +1% H ₂	#1	0.06	6.90	6.92
	#2	0.10	6.90	6.92
	#3	0.08	6.90	6.92
BS+309.7mg/L P-PO ₄ ³⁻	#1	3.08	2.33	2.34
	#2	3.48	2.33	2.33
	#3	3.56	2.33	2.33
BS+309.7mg/L P-PO ₄ ³⁻ +1% H ₂	#1	2.94	2.33	2.33
	#2	3.48	2.33	2.33
	#3	4.26	2.33	2.33

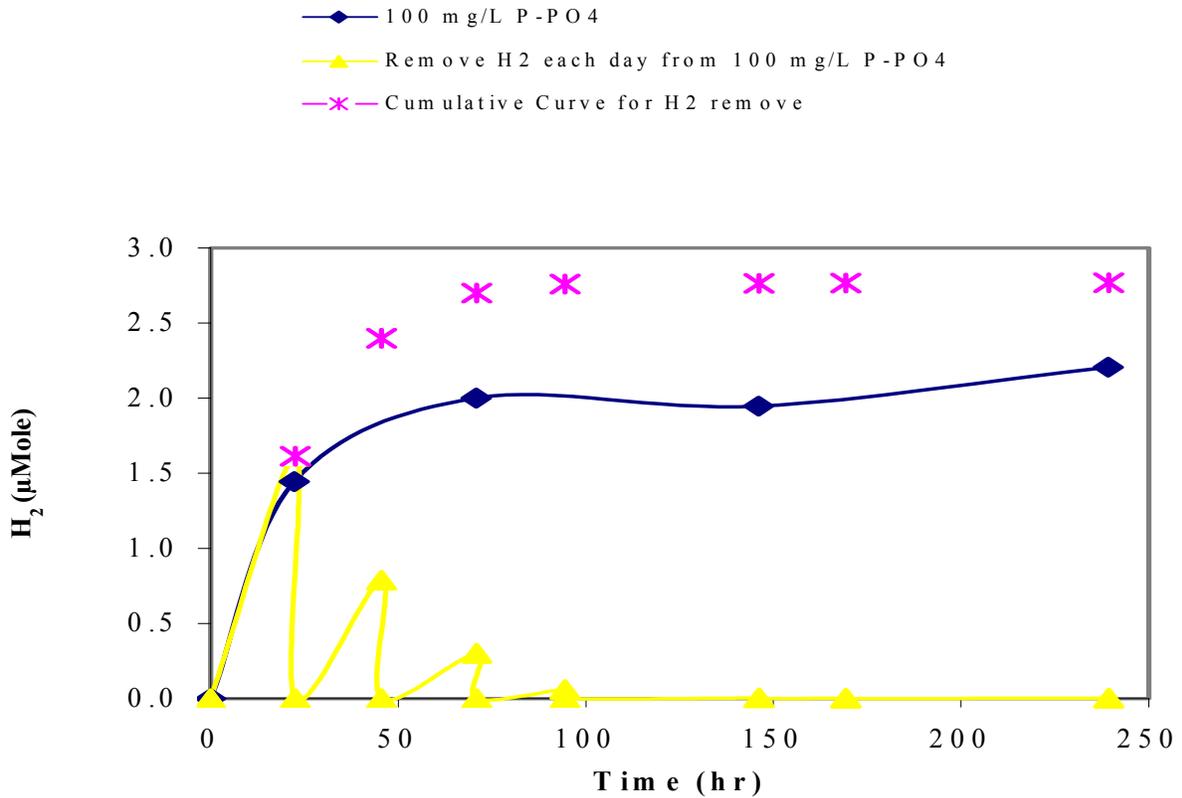


Figure 2-9. Release H₂ from sample vial headspace each day.

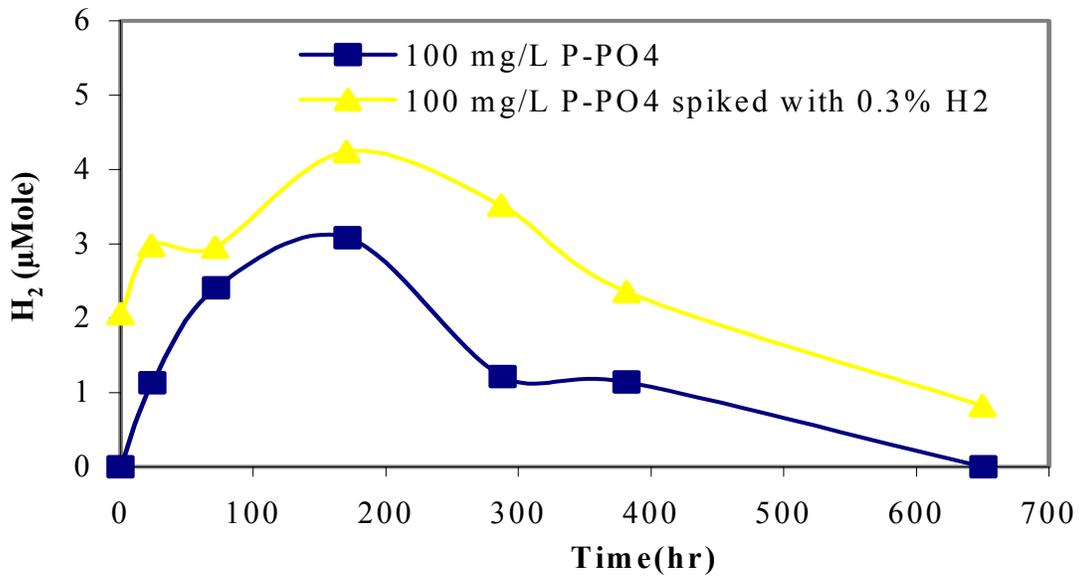


Figure 2-10. H₂ release in the solution initially spiked with 0.3 % H₂.

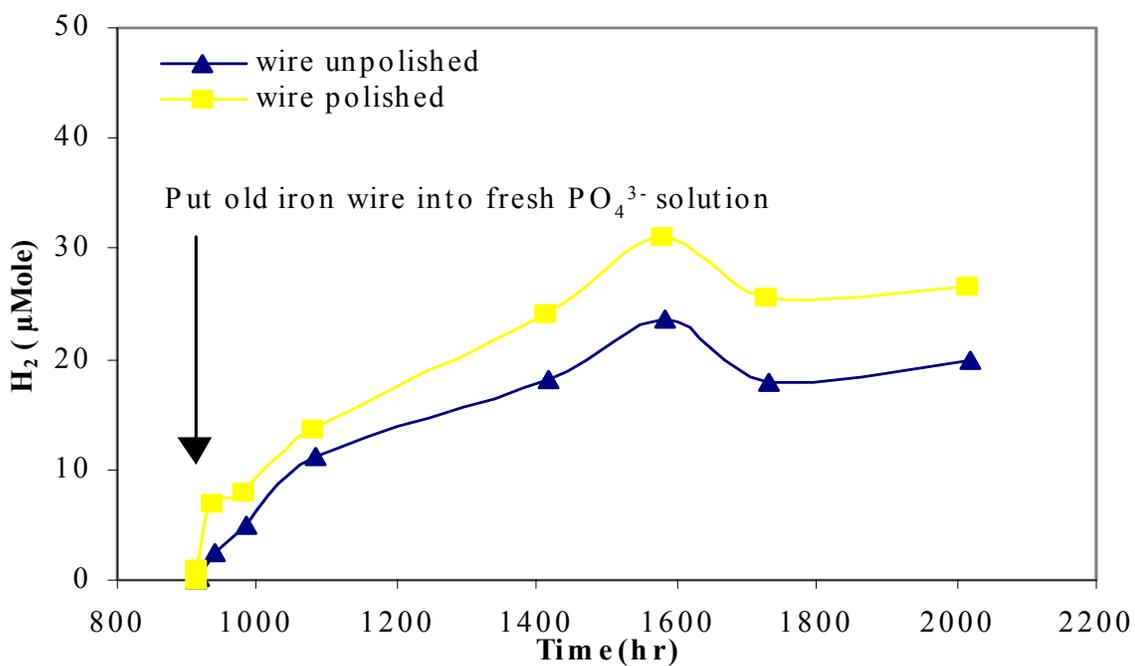
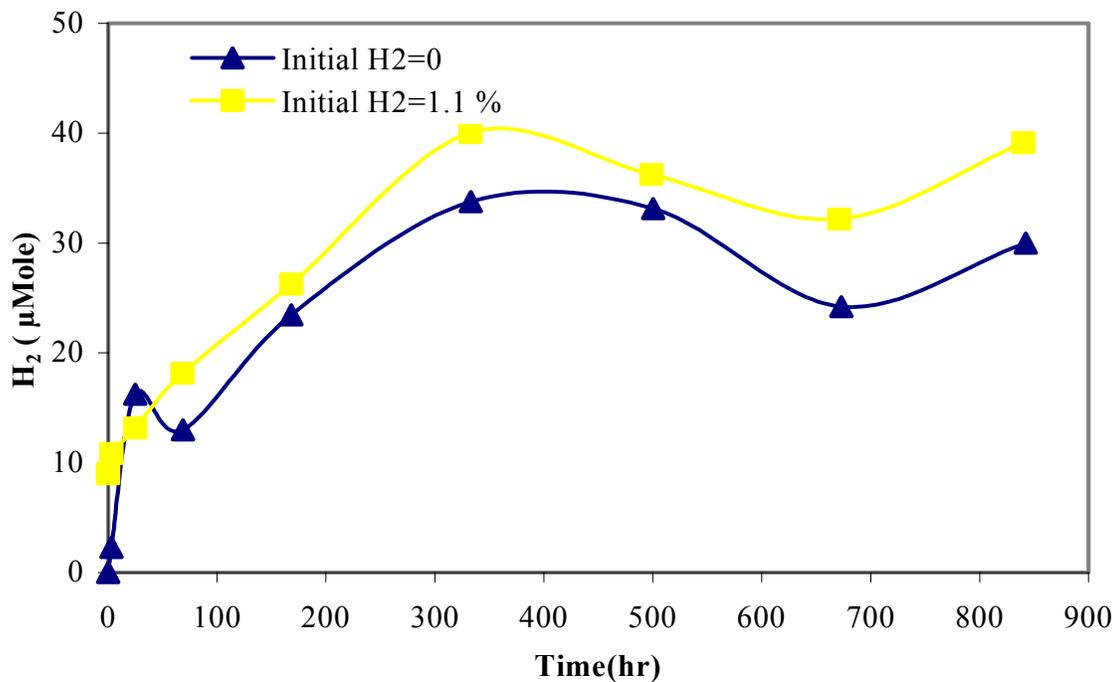


Figure 2-10. H₂ release in 100 mg/L P-PO₄³⁻ solution at pH=2.75, at t = 900 hrs, the iron wire was put into fresh 100 mg/L P-PO₄³⁻.

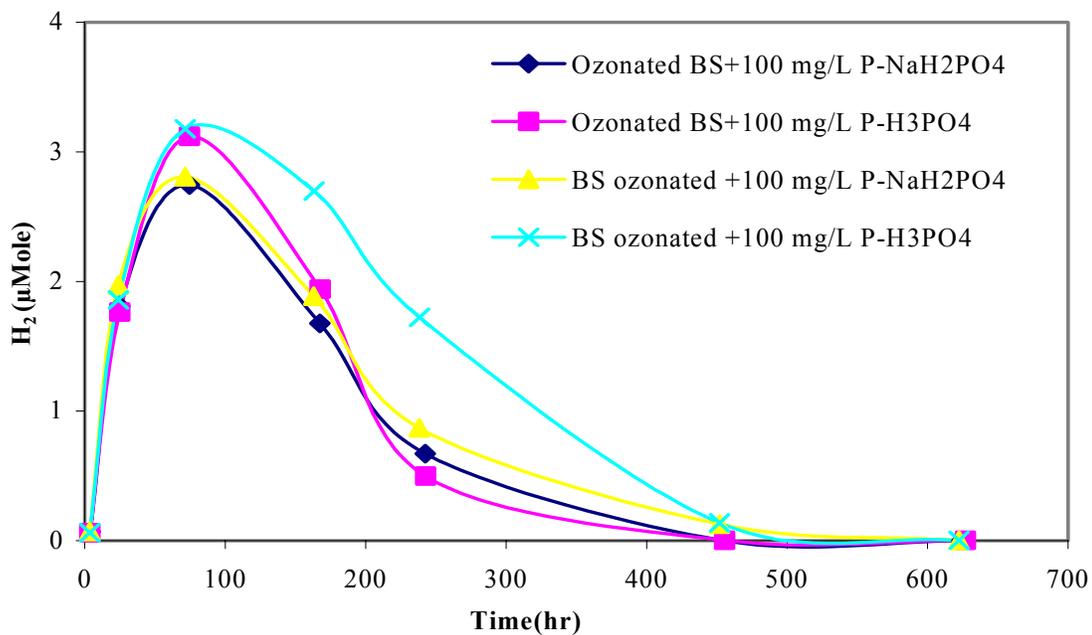


Figure 2-11. H₂ release in different ozonated 100 mg/L P solutions.

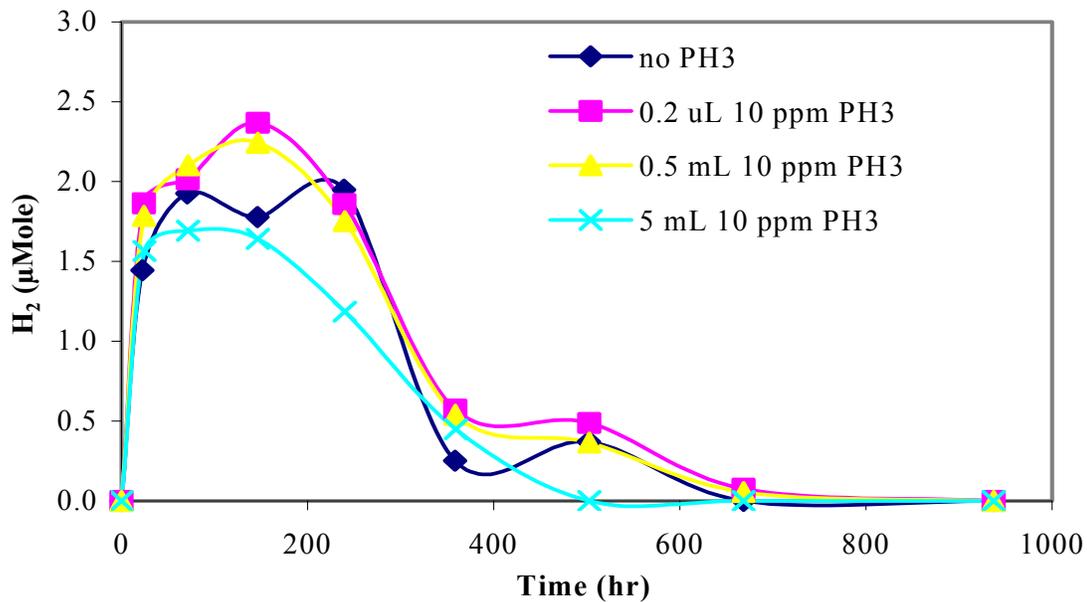
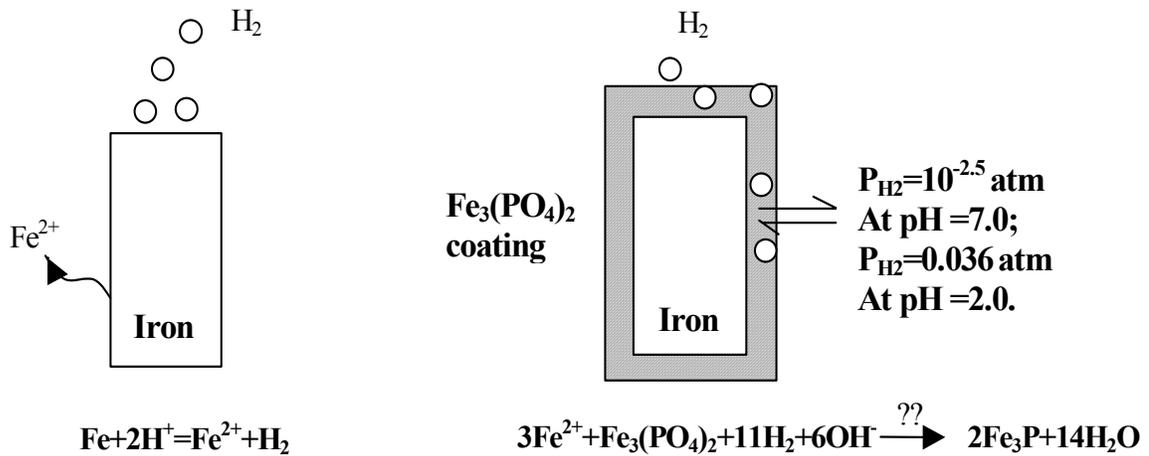


Figure 2-12. H₂ release in 100 mg/L P-PO₄³⁻ solution in the presence of variable PH₃.

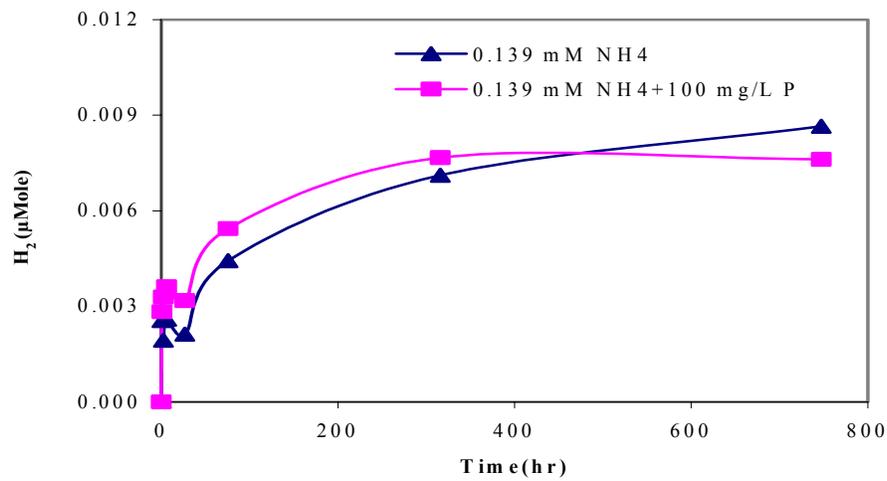
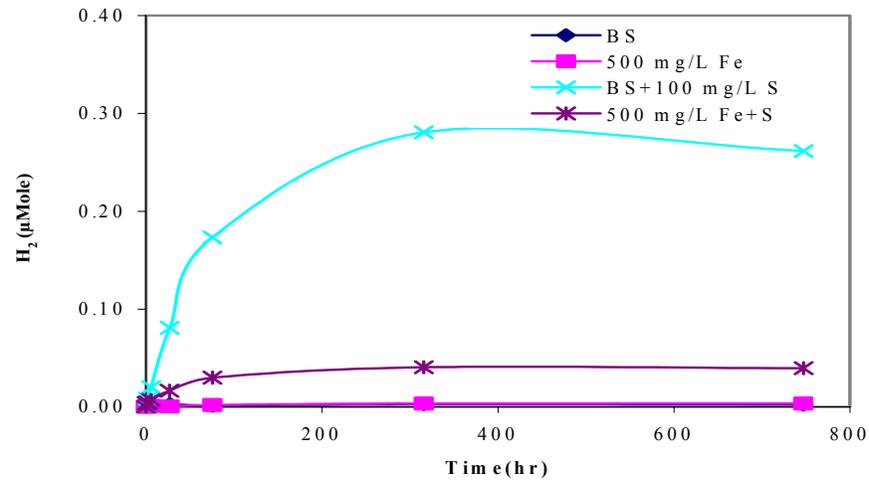
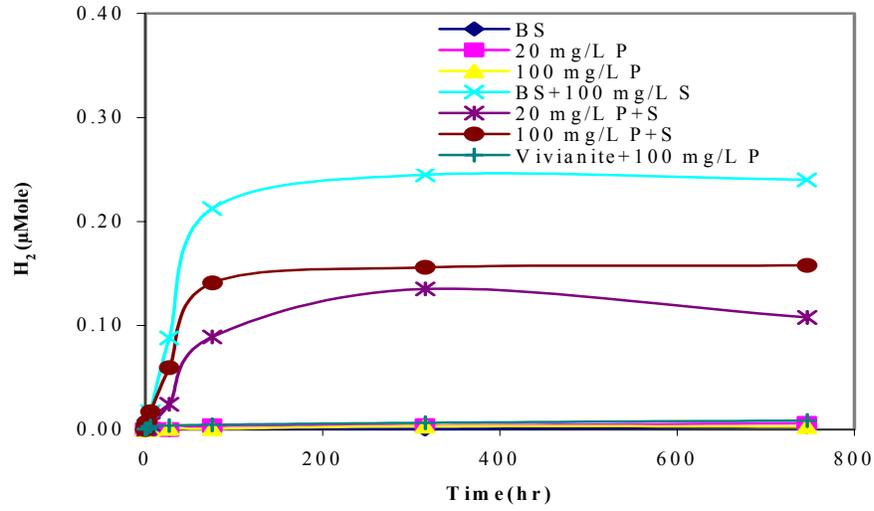


(a) Iron exposed to 100 mg/L PO_4^{3-} . (b) Vivianite-coated iron exposed to PO_4^{3-} .

Figure 2-13. Possible vivianite coating and reduction reaction with the loss of H_2 in the presence of high PO_4^{3-} .

Appendix A. H_2 release corrected for pressure change in headspace due to sampling.

Sampling time (hr)	H_2 (μMole)	Pressure Drop (atm)	H_2 corrected for pressure (μMole)
22.3	1.44	1.00	1.44
70.7	2.10	0.95	2.00
146.0	2.16	0.90	1.95
239.2	2.59	0.85	2.21



Appendix B. H₂ desorption from iron wires in a dry atmosphere after exposure to indicated solutions.

AUTHOR'S VITA

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Yue Sun was born on January 22, 1974 in Jiangxi Province in China. In addition to completing her Master's Degree in Environmental Engineering at Virginia Tech, Yue also holds a Bachelor of Science Degree and Master's Degree in Environmental Engineering from Tongji University, Shanghai, China.